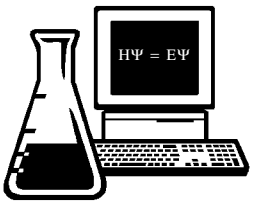
AMPAC 5.0

with Graphical User Interface

User's Manual

A Product of:



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* *AMPAC is the product of many people's efforts spanning many years. We have included these workers to the extent possible above. The vast majority of the initial method and code development was carried out by Professor Michael J.S. Dewar and researchers working under his direction at the University of Texas at Austin. Since its introduction in 1985, other individuals and research groups have developed algorithms and computer codes that interface with and enhance the capabilities of AMPAC, and many of these have kindly contributed to AMPAC as it now stands. Their contributions are also listed. We intend to update and expand this section of the manual as appropriate. A bibliography listing literature references is included in Chapter 13.*

CITATION

When the results of a calculation using AMPAC 5.0 is published or referred to, the following citation should be used:

AMPAC 5.0, ©1994 Semichem, 7128 Summit, Shawnee, KS 66216.

References for the various models and methods in AMPAC are included in Chapter 13. The version of the program will change over time and the citation should be adjusted accordingly, and this information is included at the top of the archive and output files resulting from an AMPAC calculation.

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PREFACE to AMPAC 4.0 Manual

Dear Colleagues,

This version of AMPAC represents the beginning of a new era. I have decided to retire at the end of this year, and Professor Andrew Holder, a former member of my research group, now at the University of Missouri – Kansas City, has agreed to take over the AMPAC project and also the development and promotion of new theoretical procedures. Several other former members of my group have already agreed to assist Andy in the development and support of AMPAC.

One other change concerns the distribution of AMPAC. Andy Holder is intending, at my suggestion and with my full approval, to publish AMPAC 4.0 and any future programs on a commercial basis. There are three good reasons for this change:

> **FIRST**, to prevent proliferation for the sake of proliferation. My only concern is that other programs should not cause confusion by calling themselves versions of AMPAC. Fortunately, I possess legal rights to the term "AMPAC," which I have, of course, passed to Andy.
>
> **SECOND,** to provide secure funding for the further development of semiempirical methods.
>
> **THIRD**, because it seems only fair that the chemical industry should contribute to a project which has proved of great value to them and is likely to be of even more value in the future.

Since this will be the last version of the AMPAC program with which I am directly associated, I would like to make three closing comments:

> **1.** The term "quantum chemistry" should imply the area of science concerned directly with the use of quantum theory as an aid in solving chemical problems, and work in this area should be judged solely by its value to chemistry.
>
> **2.** The basic idea behind the semiempirical approach is that the practical effectiveness of any procedure can be upgraded to an incredible extent by introducing parameters whose values are adjusted to fit experiment. If one is concerned with *results*, this is the way to get them at minimum cost.
>
> **3.** AM1 is by no means the end of the road concerning "semiempirical" SCF MO treatments. On the contrary, the conventional semiempirical approach seems likely to remain for many years the best practical way to use quantum theory as a chemical tool. Far better procedures are being developed, and in fact we have pioneered a "fourth generation" successor to AM1, the Semiempirical *ab initio* Method, Version 1 (SAM1).

Andy has my best wishes for success, and I know that he will carry on the development and expansion of the semiempirical methods that I invented and have for so many years promoted.

Yours sincerely,

Michael J.S. Dewar

PREFACE to AMPAC 5.0 Manual

Dear Colleagues,

With this version of AMPAC, we introduce a truly significant scientific advance: SAM1 parameters for iron. This represents the first time that any of the Dewar-style semiempirical methods have been extended to treat transition metals with incomplete sets of *d*-electrons.

All of Semichem's staff is now sited in Kansas City and we are working very hard to develop SAM1 parameters for transition metals and the heavy main group elements. We are also constantly upgrading and expanding the program both as we see areas for improvement and in response to your requests. Thank you for your support, and we look forward to more releases with yet more capabilities in the future.

Many thanks,

Andrew J. Holder
President
May 25, 1994

NEW IN AMPAC 5.0

New SAM1 Elements

- *Phosphorous (P) and Iron (Fe).*

Graphical User Interface

- *Display of partial charges by color.*
- *Input and output of Gaussian file formats.*
- *Improved set-up of AMPAC special options.*

New Algorithms

- *Improved treatment of solvated systems by AMSOL.*
- *Improved SCF procedures for treatment of transition metals.*

Improvements over Earlier Versions of AMPAC

- *Documentation – Updated, expanded, and including full references.*
- *Numerous "bug fixes."*

CHAPTER 1: INTRODUCTION

AMPAC 5.0 is the latest product of a continuing research effort spanning some three decades. It is a general purpose semiempirical package designed for an audience of both theoreticians and experimentalists. AMPAC offers some of the most advanced computational capabilities available in any computational chemistry software package, yet is simple enough in application that occasional users can obtain important information from these calculations.

1.1 Summary of AMPAC 5.0 Capabilities

1. SAM1, AM1, PM3, MNDO, MNDOC, and MINDO3 Hamiltonians
2. RHF and UHF methods
3. Extensive Configuration Interaction (C.I.)
   a. Selected configurations from a 10x10 manifold
   b. Spin states up to 20 unpaired electrons
   c. Excited states
   d. Geometry optimization, etc., on specified states
4. Single SCF calculation
5. Geometry optimization
6. Gradient minimization
7. Transition state location
8. Reaction path calculation
9. Intrinsic Reaction Coordinate calculation
10. Annealing for multiple minima searches
11. Force constants and vibrational frequency analysis
12. Normal mode analysis
13. Solvated molecular properties (AMSOL)
14. Thermodynamic properties
15. Localized orbitals
16. Covalent bond orders and charge distributions (Mulliken, ESP, NBO, Coulson)
17. Unpaired spin densities

1.2 Computational Chemistry in Context

Computational chemistry is one of today's most rapidly expanding and exciting areas of scientific endeavor. New computer technologies have made the purchase and maintenance of computational resources less expensive than most other major chemical instrumentation, and a trained researcher can usually perform an extensive computational study in much less time than is required for the complete experimental counterpart. Given the rising cost of maintaining laboratories and trained personnel, computational chemistry often becomes a cost-effective alternative and companion to traditional bench chemistry. As with any other scientific method, the results from computational chemistry require careful interpretation. The limitations and results of each type of technique must be considered in the broader context of all the information available for a particular system.

Computational chemistry finds one of its most important applications in the support of experimental efforts. As noted in the Table below, many types of data that are directly measured experimentally can be computed as well. An example of one of the most useful of these is vibrational spectra (IR and Raman). Detailed descriptions of vibrational motions and fairly accurate frequency predictions are sometimes critical for explaining spectra that are the result of complicated experimental situations, such as a mixture of conformers. Extensive calculations can be performed on the specific conformers of a particular compound, yielding such information as a particular conformer's dipole moment, its relative energy as compared to other conformers, and its unique spectra without the interference of the other conformers. Band assignment can be facilitated by the ability to subtract calculated spectra from experimental and to assign, based on the computational description, particular motions to spectral bands.

As well as supporting experimental studies, electronic structure methods can also produce data that is not generally available from experiment. Electron densities on specific atoms is one of the most important examples of this type of data. Although recent advances[1] indicate that more regular determinations of experimental charge densities may be on the horizon, these techniques are not routine. Information about charge densities can be used to predict relative reactivities of different substrates as well as sites of reaction. Also available from these methods are electronic bond orders. The bond orders are measures of the net bonding between pairs of atoms. Many qualitative assessments of a species' bonding patterns can be made using bond orders. Such information can also be correlated with other observables like bond lengths, vibrational frequencies, and NMR coupling constants.[2]

Electronic structure methods can also be used to study reaction mechanisms. This is particularly true for the semiempirical techniques. Because of their fast computational speed, they can be used to extensively examine reaction potential surfaces. Indeed, an impressive arsenal is available for the virtually automated location and characterization of transition states. These calculations can then rapidly differentiate between a set of mechanisms postulated from the available experimental data. In short, the application of computational methods is only limited to the investigator's ability to define a problem into a proper set of questions. Indeed, a recent study[3] on hexuloses has shown that such a nebulous property as sweetness can be predicted computationally!

1.3 Models and Results

So, then, what sort of results are expected from computational methods and how are they useful to the experimental chemist? Some of the information obtained from different types of methods is listed in the Table below. One group of popular computational methods is based on the approximation of the various interactions present in molecular systems in terms of a force field. These procedures fall in the general category of Molecular Mechanics (MM) and

---

1 Coppens, P. J. Phys. Chem. 1989 , 93, 7979.

2 a. Facelli, J. C.; Biekofsky, R. R.; Pomilio, A. B.; Contreras, R. H.; Orendt, A. M. J. Phys. Chem. 1990 , 94, 7418; b. Sternhell, S.; Gready, J. E.; Hambley, T. W.; Kakiuchi, K.; Kobiro, K.; Tansey, C. W.; Tobe, Y. J. Am. Chem. Soc. 1990 , 112, 7537.

3 Szarek, W. A.; Smith, V. H.; Woods, R. J. J. Am. Chem. Soc. 1990 , 112, 4732.

Molecular Dynamics (MD). They are parameterized to fit a large body of experimental data by defining bond force constants along with angle and torsional stretching potentials for different chemical environments. (For example, there are different MM parameters for the C-N bond of an amine and the C-N bond of an amide.) Molecular Mechanics techniques do not, however, treat electrons, limiting the relevance of the MM/MD model in many situations. MM/MD finds its greatest utility in the prediction of conformational energies and structures, and is often applied in the study of biological systems due to their large size and MM/MD's computational speed. Calculations using MM models are the fastest of the computational chemistry approaches.

Two other types of procedures, the semiempirical and ab initio molecular orbital approaches, are examples of Electronic Structure methods applying quantum mechanics. They implicitly consider the electron distribution in chemical systems as a function of nuclear position. Electronic structure theories vary greatly in complexity and accuracy. Some models are essentially conceptual, requiring no computations and are best suited to paper and pencil. Others only become usable when supercomputers are applied to their solution. At present, the best and most flexible chemical models are derived from quantum mechanics and are based on the Schrödinger Equation. The Schrödinger Equation relates the properties of electrons to those of waves and permits a mathematical description of atomic, and by extension, molecular characteristics. The standard form of the Schrödinger Equation can be solved exactly, however, for only the simplest case, the hydrogen atom. Significant approximations are required to apply the Schrödinger wave function approach to problems of interest. A commonly used and essentially standard set of approximations and assumptions has come to be known as Hartree-Fock (HF) Theory and is the basis for the majority of work done in electronic structure chemistry at present.

Table Information Available from Computational Methods.

Data Item	*Molecular Mechanics*	*Semiempirical*	*ab Initio*
Heat of Formation	•	•	•
Entropy of " "	•	•	•
Free Energy " "	•	•	•
Heat of Activation		•	•
Entropy of " "		•	•
Free Energy " "		•	•
Heat of Reaction	•	•	•
Entropy of " "	•	•	•
Free Energy " "	•	•	•
Strain Energy	•	†	†
Vibrational Spectra		•	•
Dipole Moments		•	•
Optimized Geometries	•	•	•
Electronic Bond Order		•	•
Electronic Distribution		•	•
Mulliken Pop. Analysis		•	•
Transition State Location		•	•

• *Property Predicted*
† *Indirectly Available*

A rigorous execution of Hartree-Fock Theory is called an ab initio ("from first principles") approach. These calculations involve a near complete mathematical treatment of the theoretical model underlying Hartree-Fock Theory. Comprehensive calculations of this type result in a potentially enormous number of integrations and differentiations of complex algebraic formulae. The sheer number of separate computations can easily become so vast that only a supercomputer has the requisite speed, memory, and disk storage space for even moderately sized systems (i.e., <10 non-hydrogen atoms). Ab initio methods, by virtue of being derived from the Hartree-Fock assumptions and approximations, have theoretical inaccuracies that cause difficulties in certain cases. Perhaps the most important of these is the neglect of the dynamic electron correlation effects in the motion of electrons within the self-consistent field used in the iterative solution process. Ab initio corrections are available for correlation, (e.g. Møller-Plesset (MP) Perturbation Theory, configuration interaction (CI), or multi-configuration-SCF (MCSCF)), but are very expensive in terms of computing time and disk space. It should be emphasized that in the great majority of cases where ab initio methods have been rigorously applied, the results have been very good. However, the constraints listed above strictly limit the size and complexity of the systems feasible for a full ab initio treatment.

A computational method which is similar to, yet still separate from, other HF molecular orbital techniques is density functional theory (DFT).[4] *The basic principle behind DFT is that the electron density is a fundamental quantity that can be used to develop a rigorous many-body theory, applicable to any atomic, molecular, or solid state system. In the mid-1960's, Kohn, Hohenberg, and Sham derived a formal proof of this principle as well as a set of equations, the Kohn-Sham equations, which are very close in nature to the Hartree-Fock equations of molecular orbital theory. This formalism is such that electron correlation is inherently included in the method at no extra cost in computational efficiency. The basic difference between HF theory and DFT can be summarized in the following way: for a given set of atomic positions, HF theory expresses the total energy of the system of nuclei and electrons as a function of the total wave function, whereas DFT expresses this total energy as a functional of the total electron density. Current DFT methods contain no empirical or adjustable parameters and are, thus, acknowledged to be "ab initio" approaches.*

Acceptance of DFT methods by chemists is growing now that general purpose computational packages exist containing them. This acceptance is also based on literature reports of systematic comparisons of DFT methods with experiment as well as with HF and post-HF methods. Chemists are also quickly learning that DFT methods are computationally more efficient than ab initio HF methods. HF calculations formally scale as N^4 *for N basis functions but, in reality, scale* $N^{2.5} - N^3$*, depending on the size of the molecular system. Post-HF methods, which include electron correlation in some manner, scale as* N^m *where* $m > 4$*. DFT methods, however, scale as* $N^2 - N^3$*, including some electron correlation. Therefore, DFT calculations are practical for molecular systems which may be too large and/or troublesome for ab initio HF techniques. For example, DFT methods have been particularly successful in predicting the*

---

[4] *These two paragraphs have been distilled from : a. Johnson, B. G.; Gill, P. M. W.; Pople, J. A. J. Chem. Phys. 1993 , 98, 5612; b. Wimmer, E. in Labanowski, J. K. Andzelm, J. W.; Springer-Verlag, New York, 1991; pp 7; c. Zeigler, T. Chem. Rev. 1991 , 91, 651.*

properties of transition metal systems which have been notoriously difficult for HF and post-HF techniques.

Semiempirical quantum mechanical methods are also based on Hartree-Fock Theory. Semiempirical calculations ignore some of the less important aspects of HF theory that full ab initio treatments explicitly compute, so that fewer actual operations are performed. Also, the semiempirical approach uses empirically determined parameters and parameterized functions to replace some sections of a more complete HF treatment. The approximations in semiempirical theory result in much more rapid single energy calculations than in either HF or DFT ab initio methodologies. The advantage gained in the energy calculations leads to semiempirical methods being some 100-1000 times faster overall than ab initio HF or DFT methods of comparable predictive quality. The most popular of the semiempirical methods are those developed by or derived from work by Michael J. S. Dewar.[5] They include MINDO3,[6] MNDO,[7] PM3,[8] AM1,[9] and SAM1.[10] Some older semiempirical programs and methods are still used successfully for specific purposes (e.g. HAM3 for spectroscopic calculations or ZINDO for metallic systems). In summary, semiempirical methods offer chemical accuracy as well as computational efficiency. As computational power increases, so will the size of systems to which semiempirical methods are applied.

---

5 *Most of this work was accomplished at the University of Texas at Austin.*

6 *Dewar, M. J. S.; Bingham, R. C.; Lo, D. H. J. Am. Chem. Soc. 1975 , 97, 1285.*

7 *Dewar, M. J. S.; Thiel, W. J. Am. Chem. Soc. 1977 , 99, 4907.*

8 *a. Stewart, J. J. P. J. Comput. Chem. 1989 , 10, 209; b. Stewart, J. J. P. J. Comput. Chem. 1989 , 10, 221.*

9 *Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. J. Am. Chem. Soc. 1985 , 107, 3902.*

10 *Dewar, M. J. S.; Jie, C.; Yu, G.; Ruiz, J. M. R.; Healy, E. F. Tet. 1992 , in press.*

CHAPTER 2: PRESENTING INPUT TO THE PROGRAM

The structure and components of an AMPAC data file will be discussed in this section. The AMPAC input file is simple in structure and has several required sections along with a number of optional sections for specialized tasks. All data are passed to the program via the data file (jobname.DAT) and the results are returned in several other files (jobname.OUT, jobname.ARC, etc.). The general structure of the data files is given below:

* ***Section 1:*** Keywords (up to three lines)

Section 2: Comments (two lines REQUIRED)

Section 3: Geometry Specification

One blank line or all zeros to terminate section.

** ***Section 4:*** Symmetry Definitions

One blank line or all zeros to terminate section.

Section 5: Reaction Path Coordinates

One blank line or all zeros to terminate section.

Section 6: TV Weights

Section 7: Transition Vector Information

Section 8: CHAIN Left Minimum

One blank line or all zeros to terminate section.

Section 8a: CHAIN Right Minimum

One blank line or all zeros to terminate section.

Section 9: ANNEALing Dedicated Data

Section 10: RECLAS Permutation of MOs Before CI

* These sections are required and MUST be present in every data file.

** These sections are optional and will be present depending on the keyword line (Section1).

2.1 Keywords

Keywords are the communication link between the user and AMPAC. The type and method of calculation is defined by selecting the proper set of keywords (see Chapter 3 for a full description of each keyword). Keywords may be arranged in any order, may be upper or lower case (or mixed), but MUST be separated from one another by at least one blank space. Note that some keywords require additional data to be added at the bottom of the input file (Sections 4, 6-10).

Unlike previous versions of AMPAC, AMPAC 5.0 can accept up to three 80-character lines of keywords. The program looks for additional keyword lines if the last characters on the line are a blank and a plus sign: " +". The following is an example of a multiple-line keyword definition:

```
AM1 PRECISE GRAD bonds t=3595 nointer noXYZ +
C.I.=4   PROTO=1 MECI +
ESP NBO VECTORS
"Comments line 1 of 2"
"Comments line 2 of 2"
```

Some keywords should be present in almost every AMPAC input deck. We recommend the following:

```
AMl  PRECISE  GRAD  BONDS  T=3595
```

The first keyword (AM1) specifies the particular semiempirical method to be used. For purposes of clarity and consistency, this should always be the first item on any keyword line. If no method is specified, AMPAC defaults to the MNDO method. As noted above, the MINDO3, MNDO, PM3, MNDOC, SAM1, and AM1 methods are available in AMPAC, but for general purpose use we favor the highly successful and extensively tested AM1 procedure. The next keyword, PRECISE, is also recommended for most calculations. It has the effect of increasing the convergence criteria at all stages of the calculation by 10 times and requiring that certain parts of the calculation use more accurate, albeit slower, algorithms. The keyword GRAD forces reporting of the final normalized gradient ("gnorm") and the components of the gnorm corresponding to each optimizable geometric parameter resulting from the geometry optimization. It also provides a listing of each geometric parameter's contribution to the gnorm. At an optimized geometry, the overall gnorm should be close to zero, as should the value for each component. Generally, a gnorm value of less than 1.00 indicates a successful geometry search. In the cases of very large molecules, however, this number may be larger than 1.00 due to the sheer number of contributors. See Section 5.13 for a discussion of computation of the gnorm. The BONDS keyword requests calculation of the two-center bond order matrix. This matrix should directly correspond to the valence bond picture of the molecule. T=3595 tells AMPAC how many seconds of CPU time it may use before writing the restart files. One hour (3600 seconds) is the default, but it is best to explicitly define this value.

2.2 Title and Comments

Even if the user does not wish to place comments in the file, two blank lines must be added as the program expects there to be text in this position. A recommended form has come into use in which the first comment line contains

the name and chemical formula of the compound and the second comment line contains information about the person performing the calculation, date, and other relevant items. However, any information may be placed on either line, as they are simply text fields.

2.3 Geometry Specification

The spatial arrangement of the nuclei of a molecule can be specified either by Cartesian or internal coordinates. Internal coordinates are convenient in that they represent chemically intuitive items that can usually be estimated a priori and have meaning a posteriori. Cartesian coordinates are available from many sources and also define an absolute orientation for the molecule. The initial coordinates for each atom are used as the starting geometry for further calculation. It must be emphasized at this point, that whichever method is chosen to enter the geometry, atomic positions are all that is being provided to the program. Information about bond connectivity, such as would be found in a molecular mechanics input file, is not required in AMPAC. Based on the results of the electronic structure calculation, bonding is determined instead from the wavefunction.

Internal Coordinates *Three internal coordinates for each atom are required (except for atoms 1, 2, and 3, see below). These are arranged in standard z-matrix fashion.*[11] *The three internal coordinates for the atoms are the bond length, bond angle, and dihedral angle. Each of these items is referenced to other atoms that have already been defined. In some cases, care must be exercised as to the order of atomic definition. AMPAC geometry input lines are "free-format", that is the items do not need to be in specific columns to be read properly. The items must, however, be presented in the correct order. The standard form for a line of an internal coordinate z-matrix is listed below:*

Symbol Bond Length BL Bond Angle BA Dihedral Angle DA N_A N_B N_C Spec

The symbol of an element can be defined by either letters (referencing specific elements on the periodic table) or atomic numbers. Differences between lower case and upper case characters are ignored. In both Cartesian and internal coordinate geometry definitions, isotopic masses may also be given for particular atoms. This is most useful for the purposes of kinetic isotope effect or vibrational frequency calculational studies. The mass to use for the atom is placed directly after the atomic symbol, with no spaces. Thus for carbon-13:

```
C13.00  1.54  1  109.50  1  180.00  1    3  2  1
```

The optimization flags (BL, BA, and DA) are listed for the preceding geometric variable. If a flag is set to zero, the variable is not optimized in the course of the calculation. If the value is set to one, the parameter is allowed to vary. Definitions of reaction coordinates and grid search patterns can also be specified by way of the optimization flags (see keywords STEPx=n.nn and Section

---

[11] *The actual form of the matrix with AMPAC is an x-matrix. That is, the first atom is located at the origin and the first bond is along the x-axis of an orthogonal Cartesian coordinate system. Historically, the first bond was defined to be along the z axis, hence z-matrix. The term z-matrix, while strictly incorrect for AMPAC, has become common usage and will be retained here.*

4.4). N_A, N_B, and N_C are the numbers of previously defined atoms to which the geometric parameters of the present atom are referenced.

Optimization Flag	Effect
0	Parameter IS NOT optimized
1	Parameter IS optimized
-1	Parameter is a reaction or grid coordinate

The bond length of an atom is with reference to one other atom, and is the distance from that atom in Angstroms, (Å). The value for a bond length must be greater than zero. In the case of the AMPAC input line, the bond length is referenced to atom N_A. While the term "bond length"[12] is used, a better descriptor might be "interatomic distance". For purposes of geometry definition, the atoms are not required to be chemically bonded either at the beginning or end of the calculation. The structure of a molecule is usually defined, however, by the bonding framework. This is easier to conceptualize and standard values for bond lengths are available in tabular form from a number of convenient sources.[13] If atoms are defined via the bonding network, this also makes the interpretation of the output easier as these chemically important values are direct results of the calculation. Note that the first atom in a z-matrix does not have a bond length, as there is no preceding atom from which to reference the bond length. The second and all succeeding atoms have bond length values.

The bond angle[14] of an atom is with reference to two other atoms and is simply the angle formed by the three atoms (See Figure 3.1). The values for bonds angles must be positive. In the protocol of AMPAC, this is the angle XN_AN_B (where X is the present atom). Note again that it is not required that the atoms used to define a bond angle be chemically connected to one another. It is not possible to define a bond angle until atom number three is listed. Thus atom 3 and all subsequent atoms have bond angles. AMPAC requires all bond angles to be positive.

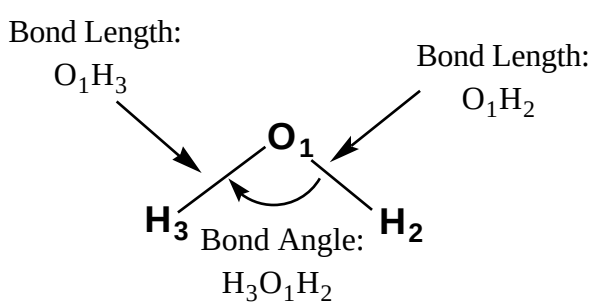


Figure 2.1 Bond Lengths and Bond Angle for Water

---

12 All length measurements in AMPAC are in angstroms (Å), whether Cartesian or internal coordinates are used.

13 Gordon, A. J.; Ford, R. A. The Chemist's Companion; John Wiley & Sons: New York, 1972.

14 All angular measurements in AMPAC are in terms of degrees, whether for bond angles or dihedral angles.

The dihedral angle (also referred to as the torsional or tortional angle in some cases) is defined by reference to three previously defined atoms. The dihedral is defined as the angle of rotation about the $N_A N_B$ axis (viewed in this manner) that is required to bring the atom under consideration (X) into alignment with atom N_C. (See Figure 3.2) Dihedrals may either be positive or negative. The possible range is –360° to +360°, although AMPAC will translate all dihedrals to –180° to +180°. (Thus an input dihedral value of 240° will be output as –120°.) It is required that the three atoms to which the dihedral of a fourth atom is referenced do not assume a straight line arrangement either as a part of the definition or as a result of the geometry optimization. The program checks for this condition at the beginning of the input and also at each step in the geometry optimization. This difficulty (e.g. encountered in the definition of alkynes) can be circumvented by the use of dummy atoms (see below).

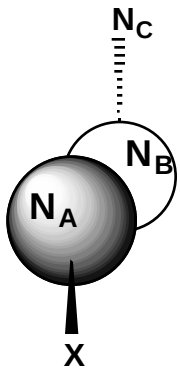


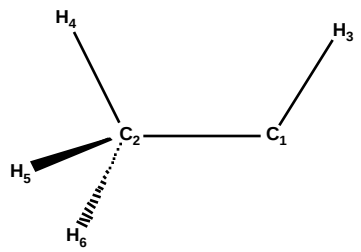
Figure 2.2. Newman Projection Showing Dihedral Angle Definition

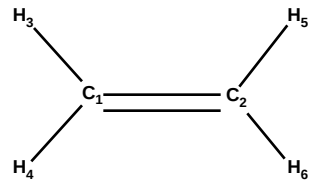
$$X\ N_A\ N_B\ N_C = 180^\circ$$

The sign convention for defining dihedral angles in AMPAC is as follows:

When looking down the N_A–N_B axis, the dihedral angle is <u>positive</u> if X can be rotated into congruence with N_C by moving clockwise less that 180°. Conversely, the dihedral angle is <u>negative</u> if X can be rotated into congruence with N_C by moving counterclockwise less that 180°.

Some examples of dihedral angle definitions are shown below. A dihedral angle cannot be specified until atom number four. All subsequent atoms have dihedrals.






```
C   0.00  0    0.00  0    0.00  0  0  0  0
C   1.54  1    0.00  0    0.00  0  1  0  0
H   1.00  1  109.50  1    0.00  0  1  2  0
H   1.00  1  109.50  1    0.00  1  2  1  3
H   1.00  1  109.50  1  120.00  1  2  1  4
H   1.00  1  109.50  1 -120.00  1  2  1  4
```

```
C   0.00  0    0.00  0    0.00  0  0  0  0
C   1.30  1    0.00  0    0.00  0  1  0  0
H   1.00  1  120.00  1    0.00  0  1  2  0
H   1.00  1  120.00  1  180.00  1  1  2  3
H   1.00  1  120.00  1    0.00  1  2  1  3
H   1.00  1  120.00  1  180.00  1  2  1  5
```

The above examples illustrate some important principles for defining z-matrices and especially dihedral angles. First, there are several possible schemes that would properly define the geometry of either of these molecules. One advantage the scheme used possesses is that all components of the geometry specification correspond to actual internal coordinates of the molecule: bond lengths define actual bonds and so forth. While it is not always possible to implement this pattern, it is usually simplest.

Another advantage is the "modularity" of the hydrogen atom definitions. In both cases, some of the hydrogen atom dihedral angles are defined with respect to previously defined hydrogens. This allows easy rotation of both species about interatomic axes. For instance in the first example, the entire methyl group could be rotated by simply changing the dihedral of the first hydrogen. The other two hydrogens will "follow" as this one is rotated. Similarly, twist-ethylene could be produced in the second case by changing the dihedral angle of hydrogen 5 to 90° rather than 0°. This type of organization is quite useful when a conformational search is being performed or a methyl rotation is interfering with location of a transition state. It is also generally useful to keep functional groups such as phenyls modularized. This allows relatively easy replacement for studies of substituent effects

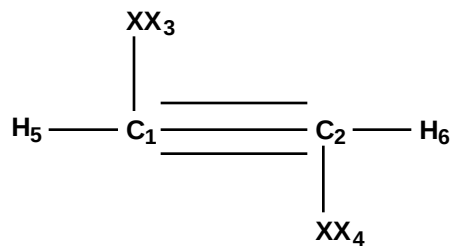
Dummy Atoms *As noted above, it is not always possible to use "natural" bond patterns to define a molecule. A classic example is acetylene, C_2H_2. The first three atoms are easily defined:*

```
C  0.00  0    0.00  0     0.00  0    0  0  0
C  1.20  1    0.00  0     0.00  0    1  0  0
H  1.10  1  180.00  1     0.00  0    1  2  0
```

There is some difficulty in defining the dihedral of the fourth atom. This atom may not be referenced to the previous three atoms because they fall on a straight line. This will cause the dihedral of the fourth hydrogen to become undefined and the program will generate an error message and halt computation.

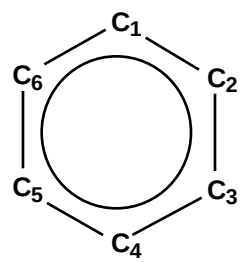
The solution to this problem lies in adding "dummy atoms." These atoms are place holders that have no chemical significance. They simply provide a point in space to which other atoms may be referred, and are commonly applied in the case of linear molecules as noted above. The AMPAC symbol for dummy atoms is "XX" or "Xx", or they may be specified by the atomic number "99".

Continuing with the example of acetylene, the geometry is redefined below using two dummy atoms. (Note that the dummy atom geometric parameters are not optimized, as they have no chemical significance in this case.)



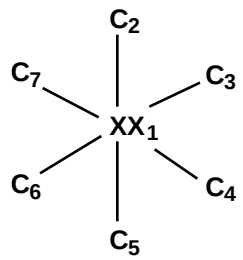

```
C   0.00  0    0.00  0     0.00  0    0  0  0
C   1.20  1    0.00  0     0.00  0    1  0  0
XX  1.00  0   90.00  0     0.00  0    1  2  0
XX  1.00  0   90.00  0   180.00  0    2  1  3
H   1.10  1   90.00  1   180.00  1    1  3  2
H   1.10  1   90.00  1   180.00  1    2  4  1
```

Another use of dummy atoms is for the definition of molecules with particular difficulties. A convenient example is a cyclic ring system such as benzene. (The AMPAC optimization routines handle the case of benzene with no difficulty, but it can be used to illustrate the point for other systems of similar types.) If the carbon skeleton of benzene or some other cyclic system is defined before the hydrogens, a C-C bond is left undefined (i.e. "dangling"):




```
C  0.00  0    0.00  0     0.00  0    0  0  0
C  1.40  1    0.00  0     0.00  0    1  0  0
C  1.40  1  120.00  1     0.00  0    1  2  0
C  1.40  1  120.00  1     0.00  1    3  2  1
C  1.40  1  120.00  1     0.00  1    4  3  2
C  1.40  1  120.00  1     0.00  1    5  4  3
```

Notice that the C_1-C_6 bond is not specifically defined in this z-matrix. In those cases where an optimization might fail, the problem usually arises when the first geometry optimization step causes a widening of the ring angles because there is no optimizable parameter "closing" the ring. Dummy atoms can be used to solve this case by "spinning" the atoms out from a central position like the spokes on a wheel. This eliminates all explicit bond specifications and the optimization will be more likely to proceed smoothly. Below is an example of the carbon skeleton of benzene defined using a central dummy atom:




```
XX   0.00  0    0.00  0     0.00  0    0  0  0
C    1.40  1    0.00  0     0.00  0    1  0  0
C    1.40  1    0.00  0     0.00  0    1  2  0
C    1.40  1   60.00  1   180.00  1    1  3  2
C    1.40  1   60.00  1   180.00  1    1  4  3
C    1.40  1   60.00  1   180.00  1    1  5  4
C    1.40  1   60.00  1   180.00  1    1  6  5
```

Some care should be used in employing dummy atoms. In the examples above, the coordinates of the dummy atoms are not optimized. This insures that only the 3N-6 independent internal coordinates (N is the number of atoms) of the molecules are correctly described. If more than 3N-6 parameters are allowed to vary, dependencies will be present during the geometry optimizations which can produce spurious results. For this reason, optimization of dummy atom parameters should not be carried out except in special circumstances. As a general rule, dummy atoms can cause unexpected difficulties in the geometry optimization procedures and should be avoided when possible.

The "Spec" item is used presently for entering atom types for SM1A calculations, partial charges for sparkles (see below), and/or special information for use in an SM2.1 calculation.

Cartesian Coordinates *As well as internal coordinates, Cartesian coordinates (x, y, z) may be used for specification of geometries for AMPAC. This option allows easy interface with other modeling or graphics packages that provide or require the coordinates of atoms in Cartesian space. Each atom is defined by distances along three orthogonal axes and no connectivity list is provided. Following each coordinate is an optimization flag for the preceding coordinate. Note immediately that this type of geometry results in six more parameters to be optimized during the geometry search than an equivalent internal coordinate definition. Although generally of little consequence, this type of definition does require more calculational time than a z-matrix definition scheme. When reading a geometry from an input file, AMPAC will search for a connectivity list at the end of each line. If one is not located, AMPAC will assume that the geometry is in Cartesian coordinates and proceed with input on that basis.*

There are several special rules that apply when input is provided in Cartesian coordinates. Unlike previous versions of AMPAC, users may now define optimization options for Cartesian coordinates. Also, the user should be aware that only internal coordinates are used for triatomic systems. (On input, AMPAC assumes a connectivity pattern for the first three atoms, and thus will not allow Cartesian coordinate to be utilized.) The keyword XYZ is not required to define a Cartesian geometry. Its use causes the entire calculation to be performed in Cartesian space, regardless of the initial geometry definition (internal or Cartesian space). (See the discussion of the XYZ keyword.) This is useful in eliminating possible problems with undefined dihedrals during optimizations or

searches for transition states, such as might be the case with CHAIN. It is not necessary to use dummy atoms with Cartesian coordinate definitions.

Defined Parameters:

The following table shows which atom pairs are parameterized within the MINDO3 semiempirical model. An dot (•) indicates that calculations may be performed on an atom pair of the type shown.

MINDO3 Atom Pair Parameters

	H	**B**	**C**	**N**	**O**	**F**	**Si**	**P**	**S**	**Cl**
H	•	•	•	•	•	•	•	•	•	•
B	•	•	•	•	•	•				
C	•	•	•	•	•	•	•	•	•	•
N	•	•	•	•	•	•			•	•
O	•	•	•	•	•	•			•	•
F	•	•	•	•	•	•			•	
Si	•		•				•			
P	•		•					•		•
S	•		•	•	•	•			•	•
Cl	•		•	•	•			•	•	•

AMPAC now includes a filter for testing for allowed MINDO3 atom pairs upon input. Note that even a non-bonded atom pair for which there are no parameters is not permitted by this check. The reason for this is that there is no adequate rule for determining a distance cutoff in this context. For most situations (except perhaps cations) one of the NDDO methods such as AM1 or SAM1 is preferable to MINDO3.

The following table lists the elements parameterized within the MNDO, PM3, AM1, MNDOC, and SAM1 semiempirical methods. Again a dot (•) indicates that the element has been parameterized.

MNDO, PM3, AM1, MNDOC, SAM1, and SAM1D Elemental Parameter Sets

Element	MNDO	PM3	AM1	MNDOC	SAM1	SAM1D	Element
H	•	•	•	•	•	*	H
Li	•						Li
Be	•						Be
B	•		•				B
C	•	•	•	•	•	*	C
N	•	•	•	•	•	*	N
O	•	•	•	•	•	*	O
F	•	•	•		•	*	F
Na							Na
Mg	•						Mg
Al	•	•	•				Al
Si	•	•	•		•	*	Si
P	•	•	•		•	*	P
S	•	•	•		•	*	S
Cl	•	•	•		•	•	Cl
Ca							Ca
Fe					•	*	Fe
Cu					•		Cu
Zn	•	•	•				Zn
Ga	•	•					Ga
Ge	•	•	•				Ge
As		•	•				As
Se		•	•				Se
Br	•	•	•		•	•	Br
Cd	•	•					Cd
In		•					In
Sn	•	•	•				Sn
Sb		•	•				Sb
Te		•	•				Te
I	•	•	•		•	*	I
Hg	•	•	•				Hg
Tl		•					Tl
Pb	•	•					Pb
Bi		•					Bi
Po		•					Po
At		•					At

** The SAM1D keyword calls for use of d-orbitals on the elements Cl and Br. The remainder of the parameters for SAM1D are exactly the same as those for SAM1.*

Sparkles Four extra "elements" are included in AMPAC. These items represent pure ionic charges, roughly equivalent to the following chemical entities:

Symbol	At. #	Equivalent to:
+	104	Tetramethyl ammonium radical, K atom or Cs atom.
++	103	Ba atom.
–	106	Borohydride radical, Halogen, or Nitrate radical.
––	105	Sulfate, oxalate.

For the purposes of discussion these entities are called "sparkles". They all have an ionic radius of 0.7 Å, so that any two sparkles of opposite sign will form an ion pair with an interatomic separation of 1.4 Å. They have a zero heat of atomization, no orbitals, and no ionization potential. They do not contribute to the orbital count, and cannot accept or donate electrons. Since they appear as uncharged species which immediately ionize, attention should be given to the charge on the whole system (see the CHARGE= keyword). For example: the alkaline metal salt of formic acid would have the formula HCOO+, where + is the unipositive sparkle. The charge on the system would then be zero. A water molecule polarized by a positive sparkle would have the formula H_2O+, and the charge on the system would be +1. A sparkle is best conceptualized as a sphere of diameter 1.4 Å, with the charge delocalized over its surface. Computationally, a sparkle is an integer charge at the center of a repulsion sphere of form $e^{-\alpha r}$. The hardness of the sphere defined by this function is such that other atoms or sparkles can approach within about 2 Å quite easily, but only with great difficulty come closer than 1.4 Å.

Sparkles find utility in several situations. They can be used as counterions, e.g. for acid anions or for cations. They can also operate as polarization functions (see the keyword POLAR). A controlled, shaped electric field can be produced by combining one or more sparkles.

Sparkles may also now be specified with partial charges. This allows the user to construct electrostatic environments of any shape with exactly specified charges at precise locations. This approach may be useful in studying the interaction of a molecule with a simlulated active site or receptor region. The partial charges for each sparkle are specified by using one of the four symbols given above and adding a field at the end of the line in the input file. (The field is labelled "Spec" above). The number in this field becomes the sparkle's new charge. Note that charge accounting within AMPAC still relies on the actual symbols, not the assigned partial charge values. Sparkles may be assigned partial charge values from -20 to +20.

Sparkles can also be used in frequency calculations, but a mass must be provided in the form noted at the beginning of this section for isotopic mass specification (i.e. the symbol followed by the mass with no space between).

2.4 Symmetry Definition

[Only active if SYMMETRY is on the keyword line.] "Symmetry" as used in AMPAC is different than what most chemists think of as symmetry. In the case of geometry definitions for AMPAC, symmetry is used to set certain geometric parameters equal to one another during the course of a geometry optimization.

This accomplishes two major objectives. First, the number of variables is decreased and the optimization proceeds more rapidly. Second, AMPAC's symmetry option allows the user to impose specific constraints on the molecule in keeping with that molecule's point group or some item of chemical interest. However, caution must be exercised in that imposition of symmetry is a chemical presupposition that may or may not be correct in the context of the problem. If a molecule should be symmetric (is a member of a particular point group), use of the proper symmetry will usually lead to a slightly lower energy than a full optimization where all independent coordinates are varied.

The symmetry utilities are invoked by using the keyword SYMMETRY and then providing a list of functions and relationships in the appropriate place in the input file. AMPAC presently accepts 20 different symmetry functions (see the SYMMETRY keyword description). These functions allow the internal (or Cartesian) coordinates of a molecule to be equated to one another, and in the case of dihedral angles can be defined as the negative of one another, or varied as sums and differences with respect to a reference angle. The method of symmetry definition is a series of lines at the end of the geometry specification section that is interpreted by the program if the SYMMETRY keyword is used. Each line of symmetry information has the following format:

<u>Reference Atom</u> separator <u>Symmetry Function</u> separator <u>Dependent Atom(s)</u>

In this arrangement, the Reference Atom is the atom who's geometric parameter is used as the beginning value and will be adjusted in the course of the calculation. Symmetry Function is the AMPAC defined symmetry function relating the reference and dependent atoms. The Dependent Atom(s) is one or more atoms to which the indicated symmetry function is applied. The separator can be either a blank space, a tab, or a comma.

The full list of available symmetry relations is as follows:

SYMMETRY FUNCTIONS

1	BOND LENGTH	is set equal to the reference bond length
2	BOND ANGLE	is set equal to the reference bond angle
3	DIHEDRAL ANGLE	is set equal to the reference dihedral angle
4	DIHEDRAL ANGLE	varies as 90 degrees minus reference dihedral
5	DIHEDRAL ANGLE	varies as 90 degrees plus reference dihedral
6	DIHEDRAL ANGLE	varies as 120 degrees minus reference dihedral
7	DIHEDRAL ANGLE	varies as 120 degrees plus reference dihedral
8	DIHEDRAL ANGLE	varies as 180 degrees minus reference dihedral
9	DIHEDRAL ANGLE	varies as 180 degrees plus reference dihedral
10	DIHEDRAL ANGLE	varies as 240 degrees minus reference dihedral
11	DIHEDRAL ANGLE	varies as 240 degrees plus reference dihedral
12	DIHEDRAL ANGLE	varies as 270 degrees minus reference dihedral
13	DIHEDRAL ANGLE	varies as 270 degrees plus reference dihedral
14	DIHEDRAL ANGLE	varies as the negative of the reference dihedral
15	BOND LENGTH	varies as half the reference bond length
16	BOND ANGLE	varies as half the reference bond angle
17	BOND ANGLE	varies as 180 degrees minus reference bond angle
18	NO LONGER USED	
19	CARTESIAN x	is set equal to the negative of the reference atom's x
20	CARTESIAN y	is set equal to the negative of the reference atom's y

21 CARTESIAN z is set equal to the negative of the reference atom's z

An example of a symmetry definition is the case of methane, where all four C-H bonds and all bond angles are treated as equivalent and the dihedral of atom 5 is defined as the negative of the dihedral of atom 4:

```
AM1 PRECISE GRAD T=295 BONDS SYMMETRY
Methane in Td symmetry
AJH   4/6/92
C  0.00  0    0.00  0     0.00  0   0  0  0
H  1.10  1    0.00  0     0.00  0   1  0  0
H  1.10  0  109.50  1     0.00  0   1  2  0
H  1.10  0  109.50  0   120.00  1   1  2  0
H  1.10  0  109.50  0  -120.00  0   1  2  4
0  0.00  0    0.00  0     0.00  0   0  0  0
2, 1,  3, 4, 5
3, 2,  4, 5
4, 14, 5
```

2.5 Reaction Coordinate Values

[Only active if ONE of the geometric parameters is marked with a "–1" for the optimization flag.] One of the optimizable geometric parameters may be designated as the "reaction coordinate". This is typically done in order to locate the position of an approximate transition state along a proposed reaction pathway. The definition is accomplished by marking that item with a –1 as its optimization flag. The values supplied in this section of the input file are then substituted one after another (the first value used is that in the geometry itself) and the requested properties computed at each value. See Section 4.4 for a more complete description of the use of the reaction coordinate.

2.6 Transition Vector Weights

[Only active if the keyword WEIGHT is present along with PATH and T.V.] This section is used to provide weights to particular components of the oriented transition vector supplied for PATH. See Section 4.7 for an example of the use of WEIGHT.

2.7 Transition Vector Information

[Only active if the keyword T.V. has been specified with either PATH or IRC.] This section is used to list the components of the oriented transition vector for the PATH (in internal coordinates) or IRC (in Cartesian coordinates) method to follow. See Sections 4.7 and 4.8 for an example of its application.

2.8 CHAIN Minima

[Only active if CHAIN has been specified on the keyword line.] The left and right minima (respectively) must be provided if the CHAIN algorithm is to be used. The first geometry in Section 3 of the input file is the "guess" geometry for the transition state used to define the reaction path. The two minima must be separated by a blank line or a line of zeros. See Section 4.6 for an example of the CHAIN method.

2.9 Data for ANNEALing and MANNEALing

[Only active if ANNEAL or MANNEAL has been specified along with LIMIT.] This section is used to provide upper and lower bounds for each optimizable geometric parameter in the annealing procedure. The lower bound for each parameter is given first (in free format, up to 80 characters per line, in order of appearance on the z-matrix) and next the upper bound for each parameter in the same order and fashion as the lower bound). See Chapter 9 for a detailed explanation on the use of ANNEAL and MANNEAL.

2.10 PERTU MOs for CI

[Only active if C.I. is specified and PERTU is also used.] This section gives the perturbation of MOs for use in the CI procedure. See Chapter 6 for a discussion of the use of PERTU.

CHAPTER 3: KEYWORDS

3.1 Specification of Keywords

Keywords are used to define the type of calculation to be carried out. They are specified on the first line (may be extended up to 240 characters (three lines)) of the input file. If more than one line of keywords is used, the first and/or second line must be terminated with a " +". Keywords may be abbreviated and the acceptable abbreviations are found in the description of each keyword that follows.

Note that if a keyword is misspelled or a keyword is used that AMPAC does not recognize, AMPAC will ignore it and no error message will be generated. The top of the output file should be checked if there is any doubt about which keywords were recognized by AMPAC, as they are echoed here. Keywords specific to specialized modules are listed in the Chapters describing those modules. The "lead-in" keywords to these modules are found in this section. The "[XXX]" format after the short descriptions below indicates that these keywords are dependent upon the concurrent use of XXX.

3.2 Summary of Major Keywords Used in AMPAC

0SCF	- read in data, then stop
1SCF	- do 1 SCF calculation and then stop
AM1	- the AM1 Hamiltonian will be used
ALLVEC	- all atomic orbital contributions to the MOs will be printed
ANNEAL	- simulated annealing search for geometric minima
BIRADICAL	- system has two unpaired electrons
BONDS	- final two–center bond order matrix will be printed
C.I.(n,m)	- a multi-electron configuration interaction specified
C.I.=n	- include n orbitals around the HOMO in the CI manifold
CHAIN	- transition state will be located
CHARGE=n	- charge on system = n (e.g. NH_4^+, CHARGE=1)
CYCLES=nn	- maximum number of cycles is nn
DENMAT	- density matrix written to disk in ASCII format
DENOUT	- density matrix written to disk in binary format
DENSITY	- final density matrix will be printed
DERINU	- derivatives will be computed numerically
DFP	- use Davidon-Fletcher-Powell rather than BFGS in geom. opt.
DOUBLET	- RHF doublet state required
EF	- use the eigenvector following method to locate a minima
ENPART	- energy will be partitioned into components
ESR	- unpaired spin density on atoms will be calculated
ESP	- invokes the electrostatic potential method for charge calculation
EXCITED	- first excited singlet state will be optimized
FILL	- requires filling of initial prototype MOs
FILL=n	- requires filling of the nth MO
FILL=(n1,...)	- requires filling of the specified MOs

FORCE	- force calculation for a Cartesian frequency analysis requested
GEO-OK	- override interatomic distance check
GNORM=n.n	- exit geometry optimizations when gradient norm falls below n.n
GRADIENTS	- all gradient components and the gnorm will be printed
GRAPH	- generate a file for molecular orbital plotting
IRC=n.n	- follow the intrinsic reaction coordinate
ISOTOPE	- final force matrix written to disk (channel 9)
ITRY=nn	- set limit of number of SCF iterations to nn
KPOLAR	- use Kurtz's method for computing nonlinear optical properties
LET	- do not reduce gradients in FORCE [FORCE]
LICENSE	- output information on your AMPAC license
LOCALIZE	- localized orbitals will be printed
LTRD	- minimize gradient using full Newton algorithm
MANNEAL	- simulated annealing search for minima within an energy range
MECI	- print information about CI microstates and transitions [C.I.]
MINDO3	- the MINDO3 Hamiltonian will be used
MNDO	- the MNDO Hamiltonian will be used (default)
MNDOC	- the MNDOC Hamiltonian will be used
MPG	- find molecular point groups and list tolerances
MPGCRT=n.n	- use n.n as tolerance to compute molecular point group
MULLIK	- performs a pseudo-Mulliken population analysis
NBO	- invoke the Natural Bond Orbital analysis package
NEWTON	- minimize energy using full Newton algorithm
NLLSQ	- minimize gradients using NLLSQ
NOINTER	- interatomic distances will not be printed
NOREF	- elemental parameter set references will not be printed
NOTHALWEG	- modifies the manner in which IRC follows the TV [IRC]
NOXYZ	- Cartesian coordinates will not be printed
OLDENS	- initial density matrix read from binary file
OLDMAT	- initial density matrix read from ASCII file
PATH	- follow the descending reaction path
PI	- resolve density matrix into sigma and pi bonds
PM3	- the PM3 Hamiltonian will be used
POLAR	- compute polarizability volume
POWELL	- minimize gradient using Powell method
PRECISE	- all termination criteria increased, numerical derivatives
PRINT=n	- printout level = n
PULAY	- Pulay's method will be used in SCF convergence
QUARTET	- RHF quartet state required
QUINTET	- RHF quintet state required
RESTART	- calculation will be restarted using results from disk
ROT=n	- defines rotational symmetry [FORCE, LTRD, IRC, NEWTON]
SAM1	- the new SAM1 Hamiltonian will be used
SAM1D	- the new SAM1 Hamiltonian, with d's on I and Cl will be used
SCFCRT=n.n	- SCF termination criteria computed based on the value supplied
SEXTET	- RHF sextet state required
SHIFT=n.n	- virtual MOs are increased in energy to damp oscillations
SIGMA	- gradients will be minimized using SIGMA
SINGLET	- RHF singlet state required
SM1	- invokes the AM1-SM1 AMSOL model [AM1]
SM1A	- invokes the AM1-SM1a AMSOL model [AM1]
SM2	- invokes the AM1-SM2 AMSOL model [AM1]
SM2.1	- invokes the AM1-SM2.1 AMSOL model [AM1]
SM3	- invokes the PM3-SM3 AMSOL model [PM3]

SPIN	*- final UHF spin matrix will be printed [UHF]*
STEPx=n.nnn	*- step size for coordinates in grid calculation*
SYMMETRY	*- symmetry conditions will be imposed*
T=nnn	*- a time of nnn seconds requested*
T.V.	*- a transition vector is provided for IRC or PATH [PATH, IRC]*
THERMO( )	*- thermodynamics calculation is done [FORCE, LTRD, IRC, NEWTON]*
TRANS=n	*- deletes the n lowest vibrations in a THERMO calculation [THERMO]*
TRIPLET	*- triplet state required*
TS	*- use the eigenvector following method to locate a transition state*
UHF	*- spin-unrestricted Hartree-Fock calculation*
VECTORS	*- selected atomic orbital contributions to the MOs will be printed*
WEIGHT	*- weights for T.V. components will be provided for PATH [PATH]*
XYZ	*- optimization to proceed in Cartesian space*

3.3 Definitions of Keywords

0SCF

The data is read and printed in the output file, but no actual calculation is performed. 0SCF is useful for checking data files. Abbreviation: None

1SCF

This keyword instructs AMPAC to perform a single SCF energy calculation at the geometry specified in the input file. AMPAC normally performs a number of SCF calculations in geometry optimizations. 1SCF is useful for calculating properties of a previously optimized geometry. Abbreviation: None

ALLVEC

The full set of eigenvectors (both occupied and virtual) listing the LCAO-MO solution to the wavefunction will be printed in the .OUT file. If UHF was specified, then both alpha and beta eigenvectors will be printed. The eigenvectors are normalized to unity, such that the sum of the squares of the coefficients is required to be exactly one. See the keyword VECTORS for an abbreviated set of eigenvectors. Abbreviation: None

AM1

The AM1 method will be used for calculation. AM1 is the recommended method for general utility. MNDO is taken as the default if no other Hamiltonian is specified. (See MINDO3, MNDO, MNDOC, PM3, and SAM1.) Abbreviation: None

ANNEAL

The ANNEAL method locates a set of minima on a potential energy surface by a procedure employing a mixture of non-local simulated annealing and gradient minimization. See Chapter 9 for discussion of the use of this method as well as an explanation of the dedicated keywords used in the annealing procedure. The energy (Heat of Formation) is minimized and is the criterion of search for ANNE. NEWTON mat also be specified as the default algorithm for geometry location in the quenching step. (See MANNEAL.) Abbreviation: ANNE

BIRADICAL

This keyword or UHF should be specified when attempting to calculate properties of molecules which have biradicaloid character. If BIRADICAL is used, a Half Electron RHF SCF (HE-RHF) calculation is done first to generate the reference wavefunction. The microstates of the reference wavefunction noted below are then mixed in a post-SCF CI calculation. (Note that this is significantly different

from a more direct CI approach, in that the reference wavefunction arises from an HE-RHF treatment rather than a pure RHF calculation.)

	Microstate 1					Microstate 2		Microstate 3	
	Alpha	Beta	Alpha	Beta		Alpha	Beta	Alpha	Beta
LUMO	+	—	—	+		—	—	+	+
					+				
HOMO	—	+	+	—		+	+	—	—

The effect of the keyword BIRADICAL may be duplicated by using the CI keywords "OPEN(2,2) SINGLET."

The result of any CI calculation is usually a net stabilization due to "double-counting" of the correlation energy (CI plus the implicit inclusion in the parameters). However, if the first singlet excited state is much higher in energy than the closed shell ground state, BIRADICAL may lead to an overall destabilization. It is recommended that more precise CI keywords be used in place of BIRADICAL to insure that the desired calculation is being carried out. Abbreviation: BIRAD.

BONDS

The bond order between all pairs of atoms is printed. In this context a bond is defined as the sum of the squares of the density matrix elements connecting any two atoms. For ethane, ethylene, and acetylene the carbon-carbon bond orders are roughly 1.00, 2.00, and 3.00 respectively. The diagonal terms are the valences calculated from the atomic terms only and are defined as the sum of the bonds the atom makes with other atoms. This type of analysis is carried out by the Coulson method (see Chapter 13 for references). In UHF wavefunctions (alpha and beta density matrices) the calculated valence will be somewhat incorrect. (See NBO for an alternative bonding analysis.) Abbreviation: None

C.I.(n,m)

(Caution: Note the periods in the keyword. The program will not recognize this keyword without them.) This keyword explicitly invokes AMPAC's extensive configuration interaction (CI) module. CI is useful, and indeed necessary, in a variety of contexts. CI allows the mixing of various electronic states (microstates) to generate a multiple-determinant wavefunction. The user has control over which microstates are mixed, allowing almost any valence-shell CI arrangement to be calculated. Configuration interaction may also be summoned automatically if any of the keywords implying a CI calculation are used. In AMPAC 5.0, CI is implied if an open shell situation is encountered or if an electron becomes unpaired. (This is the case with such keywords as BIRADICAL, TRIPLET, QUARTET, etc. Note that ROOT=n does NOT imply a CI calculation; ROOT=n is only used when a C.I. calculation is done.). Since "implied" CIs involve the minimum number of configurations, users may want to define a larger than minimum CI in those cases where required, in which case the keyword C.I.(n,m)

or C.I.=n must be included. When C.I.(n,m) is specified, MOs n through m (whether virtual or occupied) are included in the CI active space. Users should be aware of the rapid increase in the size of the CI with increasing numbers of MOs. The number of microstates implied by use of the keyword C.I.(n, m) is defined by a permutation of the n through m manifold of MOs. This figure is (m – n +1)! and can become enormous with only very limited CI inclusion. If a spin multiplicity keyword (SINGLET, DOUBLET, etc.) is specified, the CI module optimizes to the lowest eigenstate of that multiplicity. If no multiplicity keyword is used, AMPAC will report the spin states in order of increasing energy. See Chapter 6 for a more complete discussion of AMPAC's CI capability. Abbreviation: None

C.I.=n

(Caution: Note the periods in the keyword. The program will not recognize this keyword without them.) When C.I.=n is specified, the n MOs "bracketing" the occupied-virtual energy levels will be used. Thus C.I.=2 will include both the HOMO and the LUMO. C.I.=3 will include HOMO-1, HOMO, and LUMO. C.I.=1 (automatically implied for odd electron systems) will only include the HOMO. This has no effect for a closed shell system and leads to Dewar's Half-Electron correction for odd electron systems. If a spin multiplicity keyword (SINGLET, DOUBLET, etc.) is specified, the CI module optimizes to the lowest eigenstate of that multiplicity. If no multiplicity keyword is used, AMPAC will report the spin states in order of increasing energy. See Chapter 6 for a more complete discussion of CI. Abbreviation: None

CHAIN

A transition state lying between the two provided minima on the path of transformation suggested by the guess transition state will be located by the chain method. This algorithm is very successful at finding the highest transition state in a multi-step mechanism. Three separate geometries must be given: the first geometry is an approximate transition state, the second and third geometries are the left and right minima, respectively. It is important to use the same format and connectivity for all three geometries.

Advanced use of CHAIN: Some of the variables that govern CHAIN's performance are adjustable by the user based on output from the program when a calculation is performed. The form of keyword specification becomes: CHAIN(d_{max},costet,trusq). In this format, d_{max} is the length of each CHAIN segment (default of 0.3 Å), costet is the discrimination angle between links (default value of 30°), trusq is the confidence radius of Hessian elements computed in the CHAIN search (default value of 0.3 Å). Any of the three items may be left out (default values will be used), but the correct number of commas is required. These items should only be adjusted away from their default values with caution. (See Section 4.6 for an example of CHAIN's application.) Abbreviation: None

CHARGE=n

The charge on a system can be defined using CHARGE=n. Note that if a sparkle is used, the charge keyword must be invoked to account for the charge on the sparkle. Example: phosphate, $(PO_4)^{3-}$, CHARGE=-3. Abbreviation: None

CYCLES=n

The number of cycles in most processes can be increased by explicitly specifying CYCLES=n, where n is the maximum number of cycles. For most calculations, the default values are sufficient, but if this message occurs carefully examine your input to insure that the proper type of calculation has been requested. Abbreviation: None

DENMAT

The density matrix at the end of the calculation is printed as a formatted ASCII text file (jobname.DMT). Rather than generating an initial guess density matrix, the output density matrix can be used as input for a subsequent calculation using the keyword OLDMAT. This allows the user to manually alter a density matrix and start a new calculation with this altered matrix as the initial guess for the SCF procedure. Caution: Manual alteration of the density matrix may cause unpredictable results. (See OLDMAT.) Abbreviation: None

DENOUT

The density matrix at the end of the calculation is dumped in binary form (jobname.DEN) suitable for input to begin another job. If a calculation stops because the AMPAC time limit is exceeded, DENOUT is invoked automatically. (See RESTART and OLDENS.) Abbreviation: None

DENSITY

At the end of a job, the final density matrix is printed in the output file. For RHF the normal density matrix is printed, for UHF both alpha and beta density matrices are printed. If DENSITY is not requested, then the diagonal of the final density matrix (i.e., the electron density on atomic orbitals) is printed and labeled "Atomic Orbital Electron Populations." Abbreviation: DENS

DERINU

The effect of this keyword is to force all energy derivatives (gradients and second derivatives) to be computed using numerical methods. This keyword is useful when the derivatives or gradients are suspected of being in error. It should be noted that the majority of these computations in AMPAC are performed analytically and use of this keyword will drastically increase the computation time of most procedures. Abbreviation: None

DFP

This keyword requires use of the Davidon-Fletcher-Powell (DFP) algorithm in energy minimization. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) modification to DFP is the AMPAC default and is marginally more efficient in most cases. It should be noted that this pair of algorithms may fail when the initial geometry has been placed very close to a saddle point. See Section 5.15 for a more complete description of this difficulty. Abbreviation: None

DOUBLET

Defines the DOUBLET spin state (one unpaired electron spin) for use in the calculation. Note that while almost every odd electron system will have a doublet ground state, DOUBLET should still be specified if the desired state for examination must be a doublet. (See CI and SINGLET.) Abbreviation: DOUB

EF

The eigenvector following (EF) routine contributed by Frank Jensen is used to locate a minimum on the potential energy surface. See Chapter 11 for a more complete discussion and specialized keywords. Abbreviation: None

ENPART

The total energy (in eV) obtained by the addition of the electronic and nuclear terms is partitioned into discrete mono- and bicentric contributions. These contributions are further divided into nuclear, one-, and two-electron terms. Abbreviation: ENPA

ESP

This keyword activates access to the Electrostatic Potential (ESP) charge calculation algorithm contributed by K.D. Merz and B.H. Besler. See Chapter 7 for a more complete description of the ESP methods and the dedicated keywords that it uses. Abbreviation: None

ESR

The unpaired spin density on atoms arising from an ODD ELECTRON system can be calculated for both RHF and UHF wavefunctions. In UHF calculations, the alpha and beta MOs have different spatial forms, so the user should be aware that unpaired spin density can be present on in-plane hydrogen atoms such as those in the phenoxy radical. In the RHF formalism a MECI calculation is performed and the unpaired spin density is then calculated from the state function. The results of this calculation may be compared to electron spin resonance experiments. Abbreviation: None

EXCITED

The energy and properties of the first excited state will be computed. This state normally corresponds to the one resulting from a one electron excitation from the HOMO to the LUMO. If the lowest singlet state is a biradical, the EXCITED state will be a closed shell and will be calculated from a BIRADICAL calculation in which the second root of the CI matrix is selected. It is recommended that more precise CI keywords be used in place of EXCITED to insure that the desired calculation is being carried out. See Chapter 6 for a discussion of CI. Abbreviation: EXCI.

FILL

In the course of a reaction or geometry optimization, the molecular orbital description may change substantially. This keyword and the two following are intended to give the user some control over this situation. Use of the FILL keyword requires the computation to be carried out using a prototype set of MOs. After the first iteration (not after the first SCF calculation, but after the first iteration within the first SCF procedure), the set of resultant molecular orbitals are defined as the prototypes for the remainder of the calculation. These MOs will be required to remain filled for both SCF convergence and geometry optimization. This keyword is functional only with RHF calculations, whether open-shell or closed-shell. (See FILL=n and FILL=(n1,n2,...).) Abbreviation: None

FILL=n

When FILL=n is specified, the nth MO is constrained to be occupied throughout the calculation. As above, the prototype MOs are defined after the first SCF interation and MO n is stored. If it is occupied at the end of the SCF procedure, no further action is taken. If unoccupied, then the HOMO and the nth MO are swapped, so that the nth MO is now filled. On all subsequent iterations the MO nearest in character to the stored MO is forced to be filled, and the stored MO replaced by that MO. This keyword is functional only with RHF calculations, whether open-shell or closed-shell. (See FILL and FILL=(n1,n2,...).) Abbreviation: None

FILL=(n1,n2,...)

When this keyword is used, it requires filling of the n1, n2, ... MOs. Its function is quite similar to FILL=n above. The order of the MOs on the argument list is important in open-shell systems, in that those specified last are the partially filled MOs. This keyword is functional only with RHF calculations, whether open-shell or closed-shell. (See FILL and FILL=n.) Abbreviation: None

FORCE

A frequency analysis in Cartesian coordinates is performed on the system. This is accomplished by computing the Hessian, (that is the matrix in millidynes per Angstrom of second derivatives of the energy with respect to displacement of all

pairs of atoms in x, y, and z). When the Hessian is diagonalized, the force constants for the molecule are generated and a force matrix, appropriately weighted for isotopic masses, is calculated. The force matrix is then used to calculate the vibrational frequencies. Before a FORCE calculation is performed, the gradient norm (gnorm) is computed for the input geometry, and if this value is larger than 3.00, the computation is halted. (See Section 4.2 for an example of the use of FORCE and Sections 5.4 and 5.5 on the characterization of stationary points.) It is possible to override the GNORM test by specifying the keyword LET. (See THERMO, LET, LTRD, TRANS, or ISOTOPE.) Abbreviation: FORC

GEO-OK

AMPAC will halt execution and generate a warning message if any two atoms are within 0.8 Å of one another. GEO-OK will override the termination sequence and allow the calculation to proceed. In most cases, this warning message indicates a serious error condition and is the result of a flaw in the geometry specification. A common exception to this warning is the hydrogen molecule, which has an H-H bond at 0.74 Å. Abbreviation: None

GNORM=n.n

This keyword allows manual replacement of gradient norm termination criteria (n.n) for a geometry optimization. The keyword GNORM=5.0 allows the geometry optimization to be concluded when the computed GNORM value falls below 5.0. The AMPAC default value is 1.00, and this is sufficient for most cases. However, some geometries require more extensive refinement and a smaller value such as GNORM=0.1 could be used. Also, in the case of very large molecules, a larger value than 1.00 may be required to allow reasonable termination. (See Section 5.13 for an explanation of how the GNORM is computed.) There are three situations to be aware of when redefining the GNORM termination criteria. First, the optimization may halt if the calculation passes other tests but has not yet attained the proper gradient norm. Second, use of the keyword PRECISE automatically decreases the GNORM termination criteria to one tenth of its standard value. This is overridden by use of GNORM=n.n. Third, a very small value of n.n can cause the calculation not terminate in a reasonable period of time. Abbreviation: None

GRADIENTS

When the GRADIENTS keyword is used, two additional items are printed. The first is the gradient norm (in the .ARC file) and the second are the gradient components of each optimizable geometric parameter (in the .OUT file). These gradient components are used to compute the GNORM (see Section 5.13). It is recommended that GRAD be used routinely. Abbreviation: GRAD.

GRAPH

This keyword causes the information used by several popular orbital plotting programs to produce electron density contour maps to be written to a file with the extension jobname.GPT. GRAPH also requires specification of the keyword MULLIK. Abbreviation: GRAP

IRC=n.n

An IRC calculation follows the reaction vector in much the same manner as PATH. (See Section 4.8 for an example of the application of IRC and Sections 5.10 and 5.11 for a more detailed description of the IRC algorithm.) Abbreviation: None

ISOTOPE

The keyword ISOTOPE causes the force constant matrix (also called the Hessian or second derivative matrix) to be output to disk in a form (jobname.RES)readable for subsequent calculations, whether or not the calculation has been completed. This is especially useful for kinetic isotope effect (KIE) studies where the force constants do not change, only the reduced masses of the atoms. Full diagonalization of this matrix of second derivatives of energy with respect to nuclear position is very CPU intensive and ISOTOPE may be used with RESTART for lengthy frequency calculations. If RESTART and ISOTOPE are specified in the same file, the force constants are read from disk. Abbreviation: ISOT

ITRY=nn

This keyword changes the default number of iterations in the SCF procedure. The current AMPAC default is 100 cycles initially. If further difficulty is experienced in the SCF procedure and other convergers are called into play (see Section 5.1), an additional 200 cycles are allowed. The default combination of cycles and methods should be sufficient for most cases. Manually altering ITRY should only be used as a last resort to obtain SCF convergence. Abbreviation: None

KPOLAR=n.nnn

This keyword activates the polarizability (non-linear optical properties) calculation method contributed by Henry Kurtz.. See Section 5.8 for a discussion of the application of this theoretical method. (See also POLAR). The value n.nnn is the finite field strength and should only be adjusted by experienced users. The default value for n.nnn is 0.001. Abbreviation: None

LET

In cases where the force constant matrix is computed by invocation of FORCE, AMPAC will calculate the gradients of the input geometry and halt execution if the gradient norm is not less than 3.0 to ensure that the computation is carried out on a fully minimized geometry. The LET keyword allows the calculation to be completed without regard to this test. It should be emphasized that force constants at any place other than a fully optimized stationary point are UNDEFINED. LET should be used with extreme care. (See Sections 5.4 and 5.5 for a discussion of stationary point characterization.) Dependent On: FORCE; Abbreviation: None

LICENSE

This keyword enables printing of information in the .OUT file about the status of your AMPAC license. Such items as expiration date, licensee's name and address, and contact information for Semichem is listed. Abbreviation: None

LOCALIZE

When LOCALIZE is used on the keyword line, the occupied molecular orbitals are transformed into a set of orbitals whose atomic orbital components are more like those expected from an intuitive valence-bond picture of the system. See Section 5.9 for a more complete description of this method. Abbreviation: LOCAL.

LTRD

When LTRD is used, the gradient norm will be minimized using the full Newton algorithm. Additionally, a full Hessian is computed at each step making LTRD the most reliable (and expensive) method for gradient minimization. LTRD can also be used with CYCLES=O to build and diagonalize a Hessian matrix in a given subset of internal coordinates. Thermodynamic quantities may also be computed from the results of an LTRD calculation. Abbreviation: None

MANNEAL

The MANNEAL method locates a set of stationary points on a potential energy surface by a procedure employing a mixture of non-local simulated annealing and gradient minimization MANNEAL differs from ANNEAL in that it searches only within a specified energy range (the "crenel") and uses gradient minimizations rather than energy minimizations. This allows location of transition states as well as minima. See Chapter 9 for discussion of the use of this method as well as an explanation of the dedicated keywords used in the annealing procedure. The gradient norm is minimized and is the search criterion for MANN. LTRD may be used with MANN in the search for gradient minima. (See ANNEAL) Abbreviation: MANN

MECI

MECI is recommended for all CI calculations. See Chapter 6 for a more complete discussion of AMPAC 's CI capabilities. MECI enables the output of important information:

- *the number of microstates at each stage of the selection procedure*
- *AO coefficients of the CI-active MOs*
- *energies, spin multiplicities, and coefficients of the best microstates (states 1 to about L+18)*

– *wavelengths and transition dipoles/oscillator strengths (UV/Visible spectral bands) for transitions between state L and other states with the same spin multiplicities*

– *when DEBUG is also specified, AMPAC prints (at each call to CI routines) the full list of selected MSs, the CI matrix, its eigenvalues and eigenvectors, the* S^2 *and* S_z *components of each state, and transitions from L to the whole set of states.*

Dependent On: C.I.; Abbreviation: None

MINDO3

The MINDO3 method will be used for calculation. MNDO is taken as the default if no other Hamiltonian is specified. (See AM1, MNDO, MNDOC, PM3, and SAM1.) Abbreviation: MINDO or MINDO3

MNDO

The MNDO method will be used for calculation. MNDO is taken as the default if no other Hamiltonian is specified. (See AM1, MINDO3, MNDOC, PM3, and SAM1.) Abbreviation: None

MNDOC

The MNDOC method will be used for calculation. MNDOC is only available for Li, C, H, O, and N and is usually invoked along with extensive CI. MNDO is taken as the default if no other Hamiltonian is specified. (See AM1, MINDO3, MNDO, PM3, and SAM1.) Abbreviation: None

MPG

The application of the MPG keyword will compute the molecular point group symmetry (method contributed by David Danovich.) of the optimized geometry at a number of tolerances and list these in the file. This allows the user to input the tolerance required to produce the correct point group using the MPGCRT keyword below. Abbreviation: None

MPGCRT=x.xxxxx

Specification of the proper tolerance using this keyword will allow the user some control over the final molecular point group used to compute the irreducible representations of the molecular orbitals. See MPG above. Abbreviation: None

MULLIK

A full Mulliken-type Population analysis is done on the final RHF wavefunction. This involves the following steps:

(1) The eigenvector matrix is divided by the square root of the overlap matrix, S

(2) The Coulson type density matrix, P, is formed from the modified eigenvector matrix;

(3) The overlap population is formed from $P_{ij} * S_{ij}$;

(4) Half the off-diagonal terms are summed into the diagonal terms.

NBO

This keyword calls the Natural Bond Orbital population analysis method contributed by F. Weinhold, A.E. Reed, E.D. Glendening, J.E. Carpenter, T.K. Brunck, J.P. Foster, A.B. Rives, and R.B. Weinstock. See Chapter 8 for a more detailed discussion of the use and theory of NBO. NBO may not be applied when the SAM1 Hamiltonian is used. Abbreviation: None

NEWTON

A geometry optimization to minimize the energy is performed using the full Newton algorithm. Abbreviation: NEWT

NLLSQ

A geometry optimization to minimize the gradient is performed using Bartel's method (a Non-Linear Least Squares gradient minimization routine). Abbreviation: None

NOINTER

The use of this keyword suppresses the printing of the interatomic distance matrices in the .OUT file. Abbreviation: NOIN

NOREF

The use of this keyword suppresses the printing of the elemental parameter references in the .OUT file. These citations should be referenced in all publications using the models in AMPAC. See Chapter 13 for a complete listing of references. Abbreviation: None

NOTHALWEG

(Used exclusively with IRC.) If an IRC calculation is begun from a point on the PES with a gradient very near zero, the optimization proceeds along the indicated transition vector (TV) until a point with a significant gradient is located. From that point, an energy minimization is performed in the space transverse to the TV, allowing quick location of the valley ("thalweg") corresponding to the reaction's PES. The use of the NOTHALWEG keyword in conjunction with an IRC calculation, will suppress the requirement of the optimizer to reach an energy minima. This modification to IRC is useful when following unstable eigenmodes that may lie transverse to the actual reaction path. This may be the case when the user is attempting to eliminate spurious negative eigenvalues in the refinement of a transition state. Dependent On: IRC; Abbreviation: None

NOXYZ

The use of this keyword suppresses the printing of Cartesian coordinates for the atoms in the .OUT file. Abbreviation: NOXY

OLDENS

A density matrix (written in packed binary form) produced by an earlier run of AMPAC using the keyword DENOUT is used as the SCF guess for the current calculation. The file to be used will have an extension of jobname.DEN and must share a root name with the jobname.DAT file. Abbreviation: None

OLDMAT

A density matrix (written in ASCII form) produced by an earlier run of AMPAC using the keyword DENMAT is used as the SCF guess for the current calculation. The file to be used will have an extension of jobname.DMT and must share a root name with the jobname.DAT file. Abbreviation: None

PATH

This option allows following a weighted steepest descent path. The most common application is to begin at a transition state geometry and move in the direction of the transition vector. (See T.V. and WEIGHT and Section 4.7.) Abbreviation: None

PI

PI analyzes the density matrix resulting from the SCF procedure to output the composition of each atom-atom interaction in terms of sigma and pi bonds. The resulting description is composed of the following basis functions: s-sigma, p-sigma, p-pi, d-sigma, d-pi, d-dell. The diagonal terms give the hybridization state, so that an sp^2 hybridized system would be represented as s-sigma 1.0, p-sigma 2.0, p-pi 1.0. Abbreviation: None

PM3

The PM3 method will be used for calculation. MNDO is taken as the default if no other Hamiltonian is specified. (See AM1, MINDO3, MNDO, MNDOC, and SAM1) Abbreviation: None

POLAR

Calculates the polarization volume of the molecule by applying an electric field produced by a specific arrangement of sparkles. See Section 5.7 for a description of AMPAC's polarizability method. (See also KPOLAR). Abbreviation: None

POWELL

A geometry optimization to minimize the gradient norm is performed using the Powell algorithm. The search direction is chosen as the steepest descent, the full Newton quadratic direction, or a hybrid of the two. POWELL provides the index of the Hessian at the starting point, an estimate of the index at the final point, and a statistical estimate of the accuracy of the final geometry. This method is probably the best choice for refining the approximate geometry of a transition state. Abbreviation: POWE

PRECISE

The criteria for terminating all optimizations (both electronic and geometric) will be increased by a factor of 10. This keyword should be used in most cases and only left out if the calculation is encountering difficulty converging in either geometry or SCF. If the results are going to be used in a FORCE, LTRD, or IRC calculation, where the geometry needs to be known to a high degree of accuracy, then specification of PRECISE is very strongly recommended. As well as increasing convergence criteria, PRECISE also requires more accurate determination of all numerical derivatives by use of a central finite difference rather than a forward finite difference algorithm. Abbreviation: PREC

PRINT=n

This keyword controls the level of detail printed by the optimization methods at each iteration. The level of printout ranges from 0 to 5, zero being minimal printout. Error messages and final results are always printed. Abbreviation: None

PULAY

By adding this keyword to the input file, the default converger in the SCF calculation will be replaced by Pulay's procedure of density matrix projection as soon as the density matrix is sufficiently stable. A considerable improvement in speed can be achieved by use of PULAY in some cases where convergence is typically difficult Abbreviation: PULA

QUARTET

Defines the QUARTET spin state (three unpaired electron spins) for use in the calculation. (See CI and SINGLET.) Abbreviation: QUAR

QUINTET

Defines the QUINTET spin state (four unpaired electron spins) for use in the calculation. (See CI and SINGLET.) Abbreviation: QUIN

RESTART

The use of this keyword tells AMPAC to read information from jobname.RES and jobname.DEN files with the same root name to continue a calculation that has previously been halted. When a job is stopped by the program and the program has created a restart file, the calculation can be continued by specifying RESTART. The most common cause of a job stopping prematurely is exceeding the AMPAC defined time limit (see T=). If the CPU time limit for a particular job is exceeded before the AMPAC time limit, no files usable for RESTART will be produced. When RESTARTing a calculation, it is not necessary to change the geometric data in the input file to reflect the new geometry. The geometry printed at the start of a restarted job will be that of the original data, not that of the restart file. NOTE: RESTART is intended for use in geometry optimizations. It's use in other circumstances (frequency calculations, CI procedures, etc.) may lead to unpredictable results. Warning: The jobname.RES files can grow to very large size on disk. Abbreviation: REST

ROT=n

In calculation of rotational contributions to thermodynamic quantities, the rotational symmetry number of the molecule can be supplied by using this keyword. This requires the calculation to properly account for rotational symmetry, leading to a more accurate result. The symmetry number of a point group is the number of equivalent positions attainable by pure rotations. No reflections or improper rotations are allowed. This number is assumed by default to be 1. The proper value may be affected by subtle modifications to the molecule, such as isotopic substitution. A list of the most important symmetry numbers as they relate to the point groups follows. Dependent On: FORCE, LTRD, IRC or NEWTON; Abbreviation: None

---- *TABLE OF SYMMETRY NUMBERS* ----

C_1	C_i	C_s	1	D_2	D_{2d}	D_{2h}	4	$C_{\infty v}$	1
C_2	C_{2v}	C_{2h}	2	D_3	D_{3d}	D_{3h}	6	$D_{\infty h}$	2
C_3	C_{3v}	C_{3h}	3	D_4	D_{4d}	D_{4h}	8	T T_d	12
C_4	C_{4v}	C_{4h}	4	D_6	D_{6d}	D_{6h}	12	O_h	24
C_6	C_{6v}	C_{6h}	6	S_6			3		

SAM1

M.J.S. Dewar's new SAM1 (Semi-ab initio method, Version 1) method will be used for calculation. See Section 5.18 for a discussion of the theoretical basis of SAM1. MNDO is taken as the default if no other Hamiltonian is specified. (See AM1, MINDO3, MNDO, MNDOC, and PM3). Abbreviation: None

SAM1D

A special version of M.J.S. Dewar's new SAM1 (Semi-ab initio method, Version 1) method will be used for calculation. This is identical to SAM1 above, except that it contains explicit d-functions on Cl and Br. It is somewhat slower than a regular SAM1 calculation when these elements are involved. MNDO is taken as the default if no other Hamiltonian is specified. (See SAM1, AM1, MINDO3, MNDO, MNDOC, and PM3) Abbreviation: None

SCFCRT=n.nnn

The default SCF convergence criterion (in eV) will be derived from the value given for n.nnn. The SCFCRT can be varied between 0.1 and 1 x 10^{-11}. Use SCFCRT=0 for the highest possible criteria in SCF convergence. See Section 5.1 for a discussion of how SCFCRT relates to wavefunction convergence. Abbreviation: None

SEXTET

Defines the SEXTET spin state (five unpaired electron spins) for use in the calculation. This is the highest number of unpaired spins allowed in AMPAC. (See CI and SINGLET.) Abbreviation: SEXT

SHIFT=n.n

SHIFT is useful in obtaining an SCF in situations where oscillations (sometimes attributed to autoregenerative charge fluctuations) are hindering or preventing convergence of the wavefunction. This is accomplished by raising the virtual (unoccupied) and singly occupied MOs in energy relative to the occupied set, thus decreasing the polarizability of the occupied MOs. The value specified as n.n is the energy offset in eV. Note that a dynamic shift algorithm has been added to the "emergency" covergence suite (see Section 5.1). As the SCF approaches convergence, the SHIFT is gradually decreased. As some virtual MOs are used in non-variationally optimized calculations, SHIFT is automatically annulled at the end of the SCF in these circumstances. All effects of SHIFT are removed before results are printed. Caution: Use of the SHIFT method may cause slower SCF convergence. Abbreviation: None

SIGMA

SIGMA uses the McIver-Komornicki gradient norm minimization methods to optimize the geometry. These routines do not converge to a stationary point for all species, but if the gradient norm is low (less than 5.0), SIGMA will probably

work, and execute more rapidly than the other gradient minimization methods (see POWELL, LTRD, and NLLSQ). POWELL is recommended in general for this task. Abbreviation: SIGM

SINGLET

Defines the SINGLET electronic spin state (no unpaired electrons) for the calculation. When used with a configuration interaction calculation, all spin states are calculated simultaneously, either for z-component of spin = 0 (even-electron system) or 1/2 (odd-electron system). When only singlet states are of interest, then SINGLET can be specified, and all other spin states, while calculated, are ignored in the choice of the root. Note that while almost every even-electron system will have a singlet ground state, SINGLET should still be specified if the desired state must be a singlet. SINGLET has no meaning in a UHF calculation. (See also DOUBLET, TRIPLET, QUARTET, QUINTET, SEXTET, UHF, C.I.) Abbreviation: SING

SM1

This keyword activates one of the AMSOL models contributed by D.G. Truhlar, C.J. Cramer, and G.C. Lynch. See Chapter 10 for a more complete description of the AMSOL methods and additional dedicated keywords. By using both SM1 and AM1, the user requests a calculation in aqueous solution by the AM1-SM1 method. The actual quantities reported are the gaseous heat of formation as predicted by AM1, the aqueous free energy of solvation, and the electronic energy plus the aqueous free energy of solvation. In SM1 the accessible-surface-area parameters are independent of chemical environment and there is thus, a unique value of each surface tension for each atom type. Other than including the SM1 keyword, no modifications need be made to the standard AMPAC input file. Dependent On: AM1; Abbreviation: None

SM1A

This keyword activates one of the AMSOL models contributed by D.G. Truhlar, C.J. Cramer, and G.C. Lynch. (See Chapter 10 for a more complete description of the AMSOL methods and additional dedicated keywords.) The keyword SM1A together with AM1 requests a calculation in aqueous solution by the AM1-SM1a method. The keyword SM1A functions analogously to SM1 with respect to energetics and output, with the exception that the accessible-surface-area terms are dependent not only on atomic number but also on chemical environment. When SM1A is specified the atom types must be provided to the program in the input file. They follow the connectivity information (in the field labeled "Spec" in Section 2.3) at the end of each atomic specification. No atom type entry need be made for dummy atoms as the program will not try to assign an atom type for them. While AM1-SM1a is more successful than AM1-SM1 in reproducing experimental free energies of solvation for neutral solutes, it suffers from the necessity of assigning explicit chemical environments. For cases where that is ambiguous, the user is left to his own intuition or else the AM1-SM2 or PM3-SM3 solvation models should be used. These models are very successful, nearly approaching the accuracy of AM1-SM1a, and they are applicable to ions and unusual bonding situations, whereas AM1-SM1a is not. Dependent On: AM1; Abbreviation: None

The allowed atom types in Version 4.1 of AMSOL are as follows:

1. *any carbon atom or attached hydrogen atom*
2. *hydrogen atom attached to a nitrogen atom*
3. *hydrogen atom attached to an oxygen atom*
4. *hydrogen atom attached to a sulfur atom*
5. *sp^3 or amide nitrogen atom*
6. *sp, sp^2, or aromatic nitrogen atom*
7. *sp^3 oxygen atom*
8. *sp^2 oxygen atom (e.g., ketone, aldehyde, sulfoxide, nitro, etc.)*
9. *fluorine atom*
10. *sulfur atom*
11. *chlorine atom*
12. *bromine atom*
13. *iodine atom*
14. *phosphorus atom or attached hydrogen*

The output file will echo back the atom types it has assigned along with the geometric information, etc. If an atom is defined to have any number between the current highest defined type and 100, a factor of 0.00 will be employed for the surface area calculation.

SM2

This keyword activates one of the AMSOL models contributed by D.G. Truhlar, C.J. Cramer, and G.C. Lynch. (See Chapter 10 for a more complete description of the AMSOL methods and additional dedicated keywords.) By using both the SM2 and AM1 keywords, the user requests a calculation in aqueous solution by the AM1-SM2 method. While analogous to the SM1 method in its generality, the SM2 model recognizes the importance of classifying hydrogen atoms based on the heavy atom to which they are attached and derives that information from the bond order matrix. As a result, it is considerably more accurate and consistent than the SM1 approach. The output from such a calculation will include the final bond order matrix together with the contributions to surface-area-dependent terms from both heavy-atom surface tensions and attached hydrogen atoms (which do not block the solvent-accessible-surface-area of the heavy atoms to which they are attached). In SM2 all accessible-surface-area parameters are independent of chemical environment; thus there is a unique value for all surface tension parameters for each atom type. Other than including the SM2 keyword, no modifications need be made to the standard AMPAC input file. Dependent On: AM1; Abbreviation: None

SM2.1

This keyword activates the SM2.1 AMSOL solvation model and the force trapezoid radial quadrature scheme contributed by C. J. Cramer, G. D. Hawkins, G. C. Lynch, D. G. Truhlar, and D. A. Liotard. (See Chapter 10 for a more complete description of the AMSOL methods and additional dedicated keywords. All other SMx models use the force rectangle scheme for radial quadratures, resulting in slightly less accurate evaluations of these quantities and slower speed.) The keyword SM2.1

together with the AM1 keyword requests a calculation in aqueous solution by the AM1-SM2.1 method. This is completely analogous to the SM2 method except that it was parameterized using essentially converged radial quadratures in the dielectric screening algorithm, as calculated by the force trapezoid rule, whereas in SM2 the parameters were obtained using unconverged quadratures carried out by the force rectangle rule. The force trapezoid rule is more efficient and more stable than the force rectangle rule, and it is recommended for that reason. Except for small changes in the parameters and the use of a different radial quadrature scheme, the SM2.1 model is the same as SM2, and the results are generally very similar. The force trapezoid quadrature scheme, however, allows use of the TEXPN, TONE, and EXTM options, which are unavailable in SM1, SM1a, SM2, and SM3. Greater computational efficiency of the force trapezoid rule and/or the use of one or more of the TEXPN, TONE, and EXTM keywords are the main reasons why the SM2.1 option would be chosen over one of the previous models. Dependent On: AM1; Abbreviation: None

SM3

This keyword activates one of the AMSOL models contributed by D.G. Truhlar, C.J. Cramer, and G.C. Lynch. (See Chapter 10 for a more complete description of the AMSOL methods and additional dedicated keywords.) By using both SM3 and PM3, the user requests a calculation in aqueous solution by the PM3-SM3 method. This is completely analogous to the SM2 method except that the underlying gas-phase Hamiltonian is the PM3 model and the solvation model parameters are based upon that approach rather than AM1. The most desirable feature of the PM3 model is that it appears to more accurately predict the properties of hydrogen bonds in terms of their linearity, distance, and energy than does AM1. A significant drawback in comparison to AM1 is that the PM3 nitrogen charges are usually much too positive and the SM3 model is thus reduced in its effectiveness when employed for amines, nitriles, and nitro compounds. In SM3 all accessible-surface-area parameters are independent of chemical environment, thus there is a unique value for all surface tension parameters for each atom type. PM3-SM3 is less accurate than AM1-SM2 (although more accurate than AM1-SM1) and may be used at the investigators discretion to compare AM1 and PM3 results or for cases where it is expected that PM3 treats the solute more accurately than AM1. Other than including the SM3 keyword, no modifications need be made to the standard AMPAC input file. Dependent On: PM3; Abbreviation: None

SPIN

The spin matrix, defined as the difference between the alpha and beta density matrices in a UHF SCF procedure, will be printed. If the system has a closed shell ground state (e.g. methane with UHF) the spin matrix will be null. If SPIN is not requested in a UHF calculation, then the diagonal of the spin matrix, that is the spin density on the atomic orbitals, will be printed. Dependent On: UHF; Abbreviation: None

STEP1=n.n, STEP2=n.n

In a two dimensional grid calculation, the step size (in degrees or Angstroms) for the first and second parameters are given by n.nnn and m.mmm, respectively.

These parameters are defined in the input file by a "-1" as the optimization flags (see Section 2.3). Eleven steps along each parameter are defined, giving a total of 121 points on the grid. The origin is in the center at position (6,6). Abbreviation: None

SYMMETRY

This tells AMPAC that symmetry data defining the constraints on related bond lengths, angles and dihedrals has been defined by the user. The additional data is supplied after the geometry. If there are any other data, such as values for the reaction coordinates, or additional geometries (CHAIN), they follow the symmetry data (see Section 2.4 for a more complete discussion symmetry in the data file structure and the symmetry functions themselves). Symmetry data are terminated by one blank line. It is now possible to utilize symmetry constraints with Cartesian coordinates as well as internal geometry definition systems.

For non-variationally optimized systems, symmetry constraints can save significant time by reducing the number of derivatives that must be calculated. At the same time, there is a risk that adding these assumptions (biases) to the calculation will lead to an incorrect result. In the case of the methane radical cation, if it is defined as being tetrahedral, no indication is given that the result is faulty until a frequency analysis calculation (see Section 5.5) reveals a non-zero number of negative eigenvalues in the Hessian matrix. (This system undergoes spontaneous Jahn-Teller distortion.)

In some cases, a lower heat of formation can be obtained when SYMMETRY is specified, if the molecule actually possesses the defined symmetry elements. To see why, consider the geometry of benzene. If no assumptions are made regarding the geometry, then all the C-C bond lengths will be very slightly different, and the angles will be almost, but not exactly 120 degrees. Fixing all angles at 120 degrees, dihedrals at 180 or 0 degrees, and only optimizing one C-C and one C-H bond length will result in a 2-D optimization, and exact D_{6h} *symmetry. Any deformation from this symmetry must involve error, so by imposing symmetry the error is removed, and the heat of formation slightly decreased. Abbreviation: SYMM.*

T=nnn

This option allows the program to shut down in an orderly manner after a period of time has been used by the process. This is usually important when the calculation is being run on a batch queue system. The total CPU time allowed for the current job is limited to nnn seconds. If the next cycle of the calculation cannot be completed without exceeding the assigned time, the calculation will write restart files and stop. (The safety margin is 100 percent, so enough time to do at least two full cycles must remain.) By default, nnn = 3600 seconds. Abbreviation: None

T.V.

The oriented transition vector at the starting point of a PATH (internal coordinates) or IRC (Cartesian coordinates) calculation will be given in the data file (see Sections 4.7 and 4.8). The components of the transition vector are entered in the same order as the optimized coordinates, in free format, after the weights (if any, see the keyword WEIGHT). If no transition vector is provided, PATH will start in the direction of the vanishing driving force encountered. Dependent On: PATH or IRC; Abbreviation: None

THERMO

This keyword calls for the thermodynamic values of internal energy, heat capacity, partition function, and entropy to be calculated for translational, rotational, and vibrational degrees of freedom. Special situations such as linear systems and transition states are automatically accommodated. The TRANS= keyword may be used in conjunction with THERMO to correct for additional rotational modes that are present in some molecules. A Hessian matrix must be computed prior to application of the approximations in THERMO, and this can be accomplished by the simultaneous use of FORCE, IRC, NEWTON, or LTRD.

If THERMO alone is specified, the default values of the temperature range are assumed (200K to 400K in steps of 10 degrees). Three options exist for overriding the default temperature range, and they are given below. (Caution: The approximations used in the THERMO calculation are invalid below 100K.) Dependent On: FORCE, LTRD, IRC or NEWTON; Abbreviation: THER

THERMO(nnn)

The thermodynamic quantities for a 200 degree range of temperatures, starting at nnn Kelvin in steps of 10 degrees, will be calculated. Dependent On: FORCE, LTRD, IRC or NEWTON; Abbreviation: None

THERMO(nnn,mmm)

The thermodynamic quantities for the temperature range limited by a lower bound of nnn Kelvin and an upper bound of mmm Kelvin will be calculated. The step size is calculated to give approximately 20 points, and a reasonable value for the step. The size of the step will be 1, 2, or 5, times a power of 10. Dependent On: FORCE, LTRD, IRC or NEWTON; Abbreviation: None

THERMO(nnn,mmm,ooo)

The thermodynamic quantities for the temperature range limited by a lower bound of nnn Kelvin and an upper bound of mmm Kelvin will be calculated. The step size is given by ooo Kelvin and cannot be less than 1K. Dependent On: FORCE, LTRD, IRC or NEWTON; Abbreviation: None

TRANS=n

This keyword is used in conjunction with THERMO. TRANS=n will remove the n lowest vibrations whether real or imaginary. The imaginary frequency due to the reaction vector in a thermodynamics calculation on a transition state is automatically deleted from consideration. TRANS=n can be used with THERMO to allow proper definition of systems with internal rotations. For example, TRANS=2 would be suitable for Xylene. Dependent On: FORCE; Abbreviation: None

TRIPLET

Defines the TRIPLET spin state (two unpaired electron spins) for use in the calculation. In the case of RHF/TRIPLET, an RHF MECI calculation is performed to calculate the triplet state. If no other CI keywords are used, then only this one state is calculated by default. (See CI and SINGLET.) Abbreviation: TRIP

TS

The eigenvector following (EF) routine contributed by Frank Jensen is used to locate a transition state on the potential energy surface. See Chapter 11 for a more complete discussion and specialized keywords. Abbreviation: None

UHF

The spin-unrestricted Hartree-Fock method will be used. This requires that each electron is treated separately rather than as a spin-matched pair. UHF should be used for open-shell systems. For closed-shell systems, the UHF solution will collapse to the RHF solution if the RHF description is of sufficient flexibility. Caution should be exercised in the use of UHF as it will generally require more computational effort than RHF for those systems to which RHF is suited. Abbreviation: None

VECTORS

Selected eigenvectors (for the top six occupied MOs) listing the LCAO-MO solution to the wavefunction will be printed in the .OUT file. If UHF was specified, then both alpha and beta eigenvectors will be printed. The eigenvectors are normalized to unity, such that the sum of the squares of the coefficients is required to be exactly one. See the keyword ALLVEC for a full set of eigenvectors. Abbreviation: VECT

WEIGHT

The weights for a PATH calculation will be given in the data file. Weight data should be entered after the geometry and symmetry data (if any) in the same order as the optimized coordinates, in free format (data separated by a space, a comma or a semicolon, up to 80 characters per line). If no weights are provided then all the weighting factors are set to 1. This is analogous to following the path

of steepest descent in the coordinate system used. The keyword T.V. must also be used to activate WEIGHT. Dependent On: TV and PATH; Abbreviation: WEIG

XYZ

This keyword requires that AMPAC runs the geometry optimization in Cartesian coordinates rather than the default internal coordinate system. If the geometry is provided to AMPAC in Cartesian coordinates, a full 3N coordinate optimization is executed in Cartesian space. If a geometry is provided to AMPAC in internal coordinates, the keyword XYZ causes it to be converted to Cartesian coordinates, retaining the optimization flags, except for the first six which are set to zero, leading to a 3N-6 Cartesian geometry optimization. This allows an optimization to be run in a subset of the Cartesian coordinates. Abbreviation: None

CHAPTER 4: TECHNIQUES AND EXAMPLES

This chapter of the manual gives examples of some of the specialized computational tasks that AMPAC can perform. It contains information on both the construction of data files and the interpretation of output files. Discussions of the theoretical underpinnings and fine points of the procedures will generally be reserved for the next chapter. Your copy of AMPAC includes an extensive set of data files for testing and validating most of the program's functions. These files will be used here for reference and illustration.

4.1 A General Calculation

The first example listed is the geometry optimization of a distorted benzene ring using AMPAC's default optimizer, the BFGS modification to DFP. Further examples in this chapter will refer to and explain items NOT FOUND in this example. All users should therefore familiarize themselves with the following example regardless of their intended used of the program.

Input File (TEST01.DAT) :

```
 AM1 PRECISE GRAD GEO-OK                                                    Note 1
 C6H6, benzene
 AJH 10/6/92
C   0.000000   0    0.000000   0    0.000000   0  0   0   0
C   1.500000   1    0.000000   0    0.000000   0  1   0   0
C   1.200000   1  110.000000   1    0.000000   0  2   1   0
C   1.500000   1  130.000000   1   20.000000   1  3   2   1
C   1.200000   1  105.000000   1  -20.000000   1  4   3   2
C   1.500000   1  130.000000   1   25.000000   1  5   4   3
H   0.800000   1  109.500000   1  145.000000   1  1   2   3
H   1.200000   1  130.000000   1 -135.000000   1  2   3   4
H   1.200000   1  109.500000   1  140.000000   1  3   4   5
H   0.800000   1  130.000000   1 -135.000000   1  4   5   6
H   1.200000   1  120.000000   1 -135.000000   1  5   6   1
H   0.800000   1  120.000000   1  145.000000   1  6   1   2
0   0          0    0          0    0          0  0   0   0                  Note 2
```

NOTE 1: The keyword line specifies that the AM1 Hamiltonian will be used. The geometry provided is very distorted, so GEO-OK is needed to allow the calculation to proceed.

NOTE 2: The geometry specification section is terminated by a line of zeros. A blank line would also serve this purpose. No further data is required by the keywords, so this is the last line of the file.

Archive File (TEST01.ARC) :

```
                SUMMARY OF   AM1   CALCULATION                                Note 1
                                                  6-MAY-94
                    AMPAC Version  5.00                                       Note 2
                       Presented by:
```

```
                    Semichem, Inc.
                    7128 Summit
                    Shawnee, KS  66216
                    (913) 268-3271
                    (913) 268-3445 (fax)

C 6 H 6                                                                          Note 3
 C6H6, benzene
 AJH 10/6/92

        HEAT OF FORMATION       =    22.022357 KCAL                              Note 4
        ELECTRONIC ENERGY       = -3253.386466 EV
        CORE-CORE REPULSION     =  2403.050149 EV
        GRADIENT NORM           =     0.102078                                   Note 5
        DIPOLE                  =     0.00011 DEBYE                              Note 6
        NO. OF FILLED LEVELS    =    15                                          Note 7
        IONISATION POTENTIAL    =     9.652639 EV                                Note 8
        MOLECULAR WEIGHT        =    78.113                                      Note 9
        COMPUTATION TIME        =   118.32 SECONDS                               Note 10

        FINAL GEOMETRY OBTAINED   Note 10                CHARGE                   Note 12
AM1 PRECISE GRAD GEO-OK                                                          Note 13
 C6H6, benzene
 AJH 10/6/92
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0   -0.1301            Note 14
 C     1.395017  1    0.000000  0    0.000000  0   1  0  0   -0.1301
 C     1.395007  1  119.999934  1    0.000000  0   2  1  0   -0.1301
 C     1.395026  1  120.000611  1    0.005965  1   3  2  1   -0.1301
 C     1.395057  1  120.000420  1   -0.001872  1   4  3  2   -0.1301
 C     1.395033  1  119.998577  1   -0.003664  1   5  4  3   -0.1301
 H     1.099635  1  119.997336  1  179.992799  1   1  2  3    0.1301
 H     1.099623  1  119.995871  1 -179.988209  1   2  3  4    0.1301
 H     1.099639  1  120.005190  1  179.990442  1   3  4  5    0.1301
 H     1.099650  1  120.000013  1  179.997965  1   4  5  6    0.1301
 H     1.099656  1  119.998513  1 -179.986902  1   5  6  1    0.1301
 H     1.099672  1  119.998346  1  180.002787  1   6  1  2    0.1301
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0
```

Note 1: The banner indicates which Hamiltonian (here AM1) was used to obtain the results.

Note 2: This line gives information about which version of AMPAC (in this case 5.0) was used in this calculation. This data must be referenced when publishing results.

Note 3: The molecular formula of the species is printed.

Note 4: The Heat of Formation (ΔH_f) begins the summary section in the .ARC file. This value is computed from the ELECTRONIC ENERGY and the CORE-CORE REPULSION ENERGY. See Section 5.14 for details.

Note 5: The gradient norm (gnorm) value indicates how well the geometry has been refined. A value of less than 1.0 is acceptable for most purposes. See discussion of the GNORM= keyword for additional information.

Note 6: The dipole moment (in Debyes) is reported. As expected with benzene, this value is essentially zero.

Note 7: For even electron systems, the number of doubly-occupied valence shell orbitals is noted in the summary section. Other information is presented if the calculation involved an open shell species or configuration interaction.

Note 8: The ionization potential (as predicted by Koopman's Theorem as the negative of the energy of the HOMO) is listed in electron volts (eVs).

Note 9: The molecular weight as calculated from the molecular formula is given. Note that the atomic masses used in AMPAC are the isotopically averaged ones found on the Periodic Table of the Elements.

Note 10: The total time for the calculation is listed here. If extensive post-SCF calculations are performed, see the bottom of the .OUT file for a more exact estimate of the CPU time actually used. This time will vary widely depending on the speed of the system used to do the calculation.

Note 11: This phrase is presented at the end of most successful AMPAC runs where the calculation has been completed as requested.

Note 12: A summary of the atomic charges as predicted by AMPAC's analysis of the MOs is listed in the archive file.

Note 13: The keyword line and comments are echoed back to allow the user to identify the results and interpret the calculation.

Note 14: The final optimized geometry as predicted by the program is listed in internal coordinates in the order that the atoms were entered. If the geometry was in initially provided in internal coordinates, the connectivity remains the same as defined. If the geometry was provided as Cartesians coordinates, AMPAC will assign a connectivity pattern.

Output File (TEST01.OUT):

```
******************************************************************************
                           AM1 CALCULATION RESULTS                                  Note 1
******************************************************************************
*                            AMPAC Version  5.00                                    Note 2
*                               Presented by:
*
*                           Semichem, Inc.
*                           7128 Summit
*                           Shawnee, KS  66216
*                           (913) 268-3271
*                           (913) 268-3445 (fax)
*                                                                                   Note 3
*           - MINIMIZE ENERGY USING B-F-G-S  METHOD
*  GEO-OK   - OVERRIDE INTERATOMIC DISTANCE CHECK
*  PRECISE  - OPTIMIZATION CRITERIA TO BE INCREASED BY 10 TIMES,
*           -     S.C.F.   CRITERIA BY 100 TIMES,
*           - AND USE ACCURATE FINITE DIFFERENCE FORMULA IN HESSIAN
*  GRADIENTS- ALL GRADIENTS TO BE PRINTED
*  AM1      - THE AM1 HAMILTONIAN TO BE USED
******************************************************************************
AM1 PRECISE GRAD GEO-OK                                                            Note 4
 C6H6, benzene
 AJH 10/6/92
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE                     Note 5
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C
     2     C          1.50000 *                                  1
     3     C          1.20000 *      110.00000 *                 2  1
     4     C          1.50000 *      130.00000 *    20.00000 *   3  2  1
```

```
    5     C          1.20000 *      105.00000 *   -20.00000 *   4  3  2
    6     C          1.50000 *      130.00000 *    25.00000 *   5  4  3
    7     H          0.80000 *      109.50000 *   145.00000 *   1  2  3
    8     H          1.20000 *      130.00000 *  -135.00000 *   2  3  4
    9     H          1.20000 *      109.50000 *   140.00000 *   3  4  5
   10     H          0.80000 *      130.00000 *  -135.00000 *   4  5  6
   11     H          1.20000 *      120.00000 *  -135.00000 *   5  6  1
   12     H          0.80000 *      120.00000 *   145.00000 *   6  1  2

        CARTESIAN COORDINATES                                                  Note 6
  NO.       ATOM         X         Y         Z
   1         6        0.0000    0.0000    0.0000
   2         6        1.5000    0.0000    0.0000
   3         6        1.9104    1.1276    0.0000
   4         6        1.2255    2.4030    0.3930
   5         6        0.0527    2.1544    0.3413
   6         6       -0.6612    0.8415    0.4706
   7         1       -0.2670   -0.6177   -0.4325
   8         1        2.0191   -1.0098    0.3885
   9         1        2.8508    1.3779   -0.7022
  10         1        1.6106    2.9885    0.7789
  11         1        0.1001    2.9061    1.2754
  12         1       -1.3555    1.0432    0.1281

        SINGLET STATE CALCULATION                                              Note 7
        RHF CALCULATION, No. OF DOUBLY OCCUPIED LEVELS = 15

 H  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)          Note 8
 C  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)

          INTERATOMIC DISTANCES                                                Note 9
             C   1      C   2      C   3      C   4      C   5      C   6
-----------------------------------------------------------------------------
   C   1   0.000000
   C   2   1.500000   0.000000
   C   3   2.218394   1.200000   0.000000
   C   4   2.725924   2.450313   1.500000   0.000000
   C   5   2.181868   2.617709   2.149825   1.200000   0.000000
   C   6   1.169103   2.366528   2.629954   2.450313   1.500000   0.000000
   H   7   0.800000   1.921233   2.823962   3.469003   2.895791   1.760798
   H   8   2.290677   1.200000   2.175139   3.503785   3.725658   3.258514
   H   9   3.243253   2.053361   1.200000   2.211720   3.085624   3.741306
   H  10   3.483077   3.090333   2.039482   0.800000   1.820481   3.140969
   H  11   3.175270   3.468733   2.840274   1.516092   1.200000   2.343075
   H  12   1.715250   3.042784   3.269508   2.929290   1.806401   0.800000
             H   7      H   8      H   9      H  10      H  11      H  12
-----------------------------------------------------------------------------
   H   7   0.000000
   H   8   2.460509   0.000000
   H   9   3.711625   2.753592   0.000000
   H  10   4.242406   4.038033   2.515129   0.000000
   H  11   3.933138   4.450111   3.716587   1.592148   0.000000
   H  12   2.063451   3.958565   4.300487   3.606251   2.627815   0.000000

USE 2-POINT FORMULA IN INTEGRAL DERIVATIVES WITH STEP  0.00002000              Note 10
STANDARD DEVIATION ON ENERGY   (KCAL)        0.000001494
STANDARD DEVIATION ON GRADIENT (KCAL/A,RD,RD)  0.0000664 0.0001275 0.0001094

AM1 PRECISE GRAD GEO-OK                                                        Note 11
  Distorted Benzene for geom. opt. tests
  BFGS

    GRADIENT (COMPONENT) TEST WAS SATISFIED IN BFGS OR DFP                     Note 12
    SCF FIELD WAS ACHIEVED                                                     Note 13

                              AM1    CALCULATION                               Note 14
                                                        VERSION  5.00

        FINAL HEAT OF FORMATION =    22.022357 KCAL
        ELECTRONIC ENERGY       = -3253.386466 EV
```

```
CORE-CORE REPULSION     =  2403.050149 EV
GRADIENT NORM           =     0.102078
IONISATION POTENTIAL    =     9.652639 EV
NO. OF FILLED LEVELS    =    15
MOLECULAR WEIGHT        =    78.113
SCF CALCULATIONS        =   72
COMPUTATION TIME=       118.32 SECONDS
                                          6-MAY-94
```

Note 15

FINAL POINT AND DERIVATIVES

PARAMETER	ATOM	TYPE	VALUE	GRADIENT	
1	2 C	BOND	1.395017	-0.035506	KCAL/ANGSTROM
2	3 C	BOND	1.395007	-0.059262	KCAL/ANGSTROM
3	3 C	ANGLE	119.999934	-0.000844	KCAL/RADIAN
4	4 C	BOND	1.395026	0.002277	KCAL/ANGSTROM
5	4 C	ANGLE	120.000611	0.029685	KCAL/RADIAN
6	4 C	DIHEDRAL	0.005965	0.001698	KCAL/RADIAN
7	5 C	BOND	1.395057	0.037494	KCAL/ANGSTROM
8	5 C	ANGLE	120.000420	0.032695	KCAL/RADIAN
9	5 C	DIHEDRAL	-0.001872	0.011557	KCAL/RADIAN
10	6 C	BOND	1.395033	0.000240	KCAL/ANGSTROM
11	6 C	ANGLE	119.998577	0.012136	KCAL/RADIAN
12	6 C	DIHEDRAL	-0.003664	0.003354	KCAL/RADIAN
13	7 H	BOND	1.099635	-0.012369	KCAL/ANGSTROM
14	7 H	ANGLE	119.997336	-0.007121	KCAL/RADIAN
15	7 H	DIHEDRAL	179.992799	-0.003534	KCAL/RADIAN
16	8 H	BOND	1.099623	-0.022853	KCAL/ANGSTROM
17	8 H	ANGLE	119.995871	-0.011709	KCAL/RADIAN
18	8 H	DIHEDRAL	-179.988209	0.007623	KCAL/RADIAN
19	9 H	BOND	1.099639	-0.010152	KCAL/ANGSTROM
20	9 H	ANGLE	120.005190	0.016011	KCAL/RADIAN
21	9 H	DIHEDRAL	179.990442	-0.008704	KCAL/RADIAN
22	10 H	BOND	1.099650	0.001159	KCAL/ANGSTROM
23	10 H	ANGLE	120.000013	0.002344	KCAL/RADIAN
24	10 H	DIHEDRAL	-180.002035	0.001206	KCAL/RADIAN
25	11 H	BOND	1.099656	0.008130	KCAL/ANGSTROM
26	11 H	ANGLE	119.998513	-0.007207	KCAL/RADIAN
27	11 H	DIHEDRAL	-179.986902	0.008153	KCAL/RADIAN
28	12 H	BOND	1.099672	0.020238	KCAL/ANGSTROM
29	12 H	ANGLE	119.998346	-0.004047	KCAL/RADIAN
30	12 H	DIHEDRAL	180.002787	0.001647	KCAL/RADIAN

Note 16

ATOM NUMBER (I)	CHEMICAL SYMBOL	BOND LENGTH (ANGSTROMS) NA:I	BOND ANGLE (DEGREES) NB:NA:I	TWIST ANGLE (DEGREES) NC:NB:NA:I	NA	NB	NC
1	C						
2	C	1.39502 *			1		
3	C	1.39501 *	119.99993 *		2	1	
4	C	1.39503 *	120.00061 *	0.00596 *	3	2	1
5	C	1.39506 *	120.00042 *	-0.00187 *	4	3	2
6	C	1.39503 *	119.99858 *	-0.00366 *	5	4	3
7	H	1.09964 *	119.99734 *	179.99280 *	1	2	3
8	H	1.09962 *	119.99587 *	-179.98821 *	2	3	4
9	H	1.09964 *	120.00519 *	179.99044 *	3	4	5
10	H	1.09965 *	120.00001 *	-180.00203 *	4	5	6
11	H	1.09966 *	119.99851 *	-179.98690 *	5	6	1
12	H	1.09967 *	119.99835 *	180.00279 *	6	1	2

Note 17

INTERATOMIC DISTANCES

	C 1	C 2	C 3	C 4	C 5	C 6
C 1	0.000000					
C 2	1.395017	0.000000				
C 3	2.416231	1.395007	0.000000			
C 4	2.790040	2.416247	1.395026	0.000000		
C 5	2.416271	2.790080	2.416288	1.395057	0.000000	
C 6	1.395045	2.416278	2.790066	2.416272	1.395033	0.000000
H 7	1.099635	2.165446	3.413101	3.889676	3.413170	2.165516
H 8	2.165510	1.099623	2.165412	3.413095	3.889703	3.413182
H 9	3.413085	2.165407	1.099639	2.165542	3.413215	3.889705
H 10	3.889690	3.413142	2.165490	1.099650	2.165523	3.413176

```
   H  11   3.413171   3.889736   3.413211   2.165559   1.099656   2.165491
   H  12   2.165513   3.413183   3.889738   3.413217   2.165545   1.099672
              H   7      H   8      H   9      H  10      H  11      H  12
-------------------------------------------------------------------------------
   H   7   0.000000
   H   8   2.494672   0.000000
   H   9   4.320778   2.494474   0.000000
   H  10   4.989326   4.320824   2.494750   0.000000
   H  11   4.320920   4.989359   4.321007   2.494759   0.000000
   H  12   2.494697   4.320938   4.989377   4.320977   2.494711   0.000000

                EIGENVALUES                                                    Note 18
-39.14709 -31.36865 -31.36823 -23.06058 -23.06025 -17.85617 -16.12310 -15.40014
-14.16087 -14.16071 -13.38098 -11.88763 -11.88750  -9.65278  -9.65264   0.55465
  0.55473   2.97778   4.03642   4.03650   4.04733   4.19236   4.59851   4.59864
  5.12324   5.12326   5.61160   5.61169   5.72916   6.13275

         NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS                           Note 19
        ATOM NO.   TYPE          CHARGE        ATOM  ELECTRON DENSITY
          1         C           -0.1301          4.1301
          2         C           -0.1301          4.1301
          3         C           -0.1301          4.1301
          4         C           -0.1301          4.1301
          5         C           -0.1301          4.1301
          6         C           -0.1301          4.1301
          7         H            0.1301          0.8699
          8         H            0.1301          0.8699
          9         H            0.1301          0.8699
         10         H            0.1301          0.8699
         11         H            0.1301          0.8699
         12         H            0.1301          0.8699
DIPOLE (DEBYE)   X          Y          Z       TOTAL
POINT-CHG.     0.000      0.000      0.000     0.000
HYBRID         0.000      0.000      0.000     0.000
SUM            0.000      0.000      0.000     0.000

         CARTESIAN COORDINATES                                                 Note 20
   NO.       ATOM               X         Y         Z
    1        C                   0.0000    0.0000    0.0000
    2        C                   1.3950    0.0000    0.0000
    3        C                   2.0925    1.2081    0.0000
    4        C                   1.3950    2.4162    0.0001
    5        C                   0.0000    2.4163    0.0002
    6        C                  -0.6975    1.2081    0.0001
    7        H                  -0.5498   -0.9523   -0.0001
    8        H                   1.9449   -0.9523    0.0001
    9        H                   3.1922    1.2080   -0.0002
   10        H                   1.9449    3.3686    0.0002
   11        H                  -0.5499    3.3686    0.0005
   12        H                  -1.7972    1.2081    0.0001

         ATOMIC ORBITAL ELECTRON POPULATIONS                                   Note 21
  1.21857   0.93887   0.97267   1.00000   1.21857   0.93888   0.97267   1.00000
  1.21857   0.98956   0.92199   1.00000   1.21858   0.93887   0.97266   1.00000
  1.21858   0.93887   0.97266   1.00000   1.21859   0.98956   0.92198   1.00000
  0.86989   0.86989   0.86989   0.86988   0.86988   0.86988
FULL COMPUTATION TIME :   118.430 SECONDS                                      Note 22
```

Note 1: The banner indicates which Hamiltonian (here AM1) was used to obtain the results. Recall that MNDO is the default if no other Hamiltonian is specified.

Note 2: As in the archive file, this line gives information about which version of AMPAC (in this case 5.0) was used in this calculation. This data must be referenced when publishing results.

Note 3: The keywords that AMPAC recognized from the input file are printed here and short summaries of their implications are provided. If an expected keyword is not present in this group, check the input file for spelling or omission.

Note 4: The keyword line and informational comment lines are echoed to the output file to help the user identify the calculation.

Note 5: The internal coordinates of the initial geometry (whether provided to the program as internals or Cartesians) are listed. Only those geometric parameters with asterisks (*) beside them will be optimized.

Note 6: The Cartesian coordinates of the initial geometry (again whether provided to the program as internals or Cartesians) are listed. This output may be suppressed by use of the NOXYZ keyword.

Note 7: This short section defines the calculation that AMPAC expects to perform. In this case a singlet spin state is assumed (default if no spin multiplicity keywords are used), and there are 15 doubly occupied MOs in the occupied valence manifold. Open shell calculations (UHF) will show the electrons divided between alpha and beta electron spin states.

Note 8: References to the parameters for the particular Hamiltonian chosen are listed. These citations should be used in papers. A complete bibliography may be found in Chapter 13.

Note 9: This section contains a lower diagonal matrix of the interatomic distances of the input geometry in the molecule. The user can use this to verify that the geometry has been properly read by AMPAC. This output may be suppressed by use of the NOINTER keyword. At this stage, a test is applied to ensure that no interatomic distances fall below the threshold (may be overridden by GEO-OK as in the present case).

Note 10: A summary of the geometry optimization methods and criteria is presented in this section. More information, including results for each step, may be obtained by using the PRINT=n keyword.

Note 11: Again, the keyword line and informational comment lines are echoed to the output file.

Note 12: This message is one of the several that AMPAC can provide to inform the user that the geometry has been properly optimized (see Section 5.3 for a list and description of the possible messages). Always check this line for possible failure of the geometry optimization or SCF procedure.

Note 13: This message informs the user that SCF convergence was attained at the geometry that the optimization halted on. The results following are for the final wavefunction and geometry.

Note 14: This summary section is almost an exact copy of that found in the archive file. See above for an explanation of its components.

Note 15: The gradient components that are used to compute the gnorm are listed here for each optimizable parameter. This report is a result of using the keyword

GRAD. The gnorm should have a low value as should each component. In the event that a geometry optimization is not converging, an examination of these components may suggest a method of redefining the geometry so that a particularly troublesome component with a high gradient value is eliminated.

Note 16: The internal coordinates of the fully optimized geometry are printed here. Again, only those components notated with an asterisk have been optimized.

Note 17: A lower-diagonal interatomic distance matrix of the final optimized geometry is printed. This output may be suppressed by use of the NOINTER keyword.

Note 18: The energy values (in eV) of the final molecular orbitals (both occupied and virtual) are listed here. In benzene, there are 15 occupied MOs, with the highest being a degenerate pair corresponding to part of the π bonding picture. Generally, occupied MOs have energies < 0.0 eV and virtuals have energies > 0.0 eV.

Note 19: The partial charges on each atom are tabulated. This quantity is obtained by subtracting the sum of the number of core electrons and the valence electrons present on that atom as predicted by AMPAC from the atomic number (number of protons). These figures are used to compute the net dipole moment of the species.

Note 20: The Cartesian coordinates of the final geometry are printed. This output may be suppressed by use of the NOXYZ keyword.

Note 21: The valence orbital electron populations (the diagonal of the final density matrix) are listed for reference.

Note 22: The total time for the calculation, including any time expended in post-SCF procedures is listed.

4.2 Cartesian Frequencies and Thermodynamics (FORCE)

This example illustrates a FORCE calculation and the generation of thermodynamic data for the conrotary cyclization transition state of cis-1,3-butadiene -> cyclobutene. Recall that only those items different from or not present in the above example will be described here.

Input File (TEST15.DAT):

```
 AM1 PRECISE FORCE +                                                    Note
 T=3595 GRAD +
 THERMO TRANS=1 ROT=2
 Conrotary cyclization TS
 FORCE on TS, preoptimized structure
C     0.000000  0    0.000000  0    0.000000  0   0  0  0
C     1.388681  1    0.000000  0    0.000000  0   1  0  0
C     1.427616  1  103.838361  1    0.000000  0   2  1  0
C     1.427758  1  103.826319  1  -18.665140  1   1  2  3
H     1.088191  1  129.204926  1  154.433803  1   1  2  3
H     1.088194  1  129.190066  1  154.437643  1   2  1  4
```

```
H     1.095941  1  121.105676  1  136.752600  1   4  1  2
H     1.095943  1  121.109463  1  136.761344  1   3  2  1
H     1.098242  1  120.317329  1  -65.107436  1   4  1  2
H     1.098255  1  120.313896  1  -65.097794  1   3  2  1
0     0.000000  0    0.000000  0    0.000000  0   0  0  0
```

Note: This file uses AMPAC's multi-line input capability. The last two characters of each line are " +". This indicates to AMPAC that further lines should be read as data, up to a total of 240 characters. The keywords call for a frequency calculation (in Cartesians) along with the generation of thermodynamic data. THERMO can only be requested if a keyword requiring computation of the Hessian (matrix of second derivatives) is used (see discussion of the THERMO keyword). In order to obtain correct results for the energy partition, the symmetry number for the point group must be given. The TS's point group is C_{2v} *, requiring ROT=2. The keyword TRANS is optional as the new AMPAC automatically accounts for the presence of a negative eigenvalue.*

Output File (TEST15.OUT):

```
*****************************************************************************
                              AM1 CALCULATION RESULTS
*****************************************************************************
*                              AMPAC Version 5.0
*                                 Presented by:
*
*                             Semichem, Inc.
*                             7128 Summit
*                             Shawnee, KS  66216
*                             (913) 268-3271
*                             (913) 268-3445 (fax)
*
*                   WARNING: YOUR LICENSE EXPIRES IN 22 DAYS!!
*
*  FORCE    - FORCE CALCULATION SPECIFIED
*  THERMO   - THERMODYNAMIC QUANTITIES TO BE CALCULATED
*  ROT      - SYMMETRY NUMBER OF  2 SPECIFIED
*  TRANS=   -  1 LOWEST VIBRATIONS TO BE DELETED FROM THERMO CALC.
*  PRECISE  - OPTIMIZATION CRITERIA TO BE INCREASED BY 10 TIMES,
*           -     S.C.F.   CRITERIA BY 100 TIMES,
*           - AND USE ACCURATE FINITE DIFFERENCE FORMULA  IN HESSIAN
*  GRADIENTS- ALL GRADIENTS TO BE PRINTED
*   T=      - A TIME OF  3595.0 SECONDS REQUESTED
*  AM1      - THE AM1 HAMILTONIAN TO BE USED
*****************************************************************************
AM1 PRECISE FORCE T=3595 GRAD THERMO TRANS=1 ROT=2
   Conrotary cyclization TS
   FORCE on TS, preoptimized structure, three input lines
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I   NA  NB  NC
     1     C
     2     C          1.38868 *                                   1
     3     C          1.42762 *      103.83836 *                  2   1
     4     C          1.42776 *      103.82632 *   -18.66514 *    1   2   3
     5     H          1.08819 *      129.20493 *   154.43380 *    1   2   3
     6     H          1.08819 *      129.19007 *   154.43764 *    2   1   4
     7     H          1.09594 *      121.10568 *   136.75260 *    4   1   2
     8     H          1.09594 *      121.10946 *   136.76134 *    3   2   1
     9     H          1.09824 *      120.31733 *   -65.10744 *    4   1   2
    10     H          1.09825 *      120.31390 *   -65.09779 *    3   2   1

         CARTESIAN COORDINATES
   NO.       ATOM         X         Y         Z
    1         6        0.0000    0.0000    0.0000
    2         6        1.3887    0.0000    0.0000
    3         6        1.7301    1.3862    0.0000
```

```
   4         6       -0.3412    1.3135    0.4437
   5         1       -0.6878   -0.7607   -0.3639
   6         1        2.0763   -0.8373    0.1013
   7         1       -1.1402    1.8853   -0.0417
   8         1        2.5293    1.7725    0.6428
   9         1       -0.0862    1.6386    1.4612
  10         1        1.4751    2.0199   -0.8599

 MOLECULAR POINT GROUP            SYMMETRY CRITERIA
          C2                          0.10000000


        RHF CALCULATION, No. OF DOUBLY OCCUPIED LEVELS = 11

      **  REFERENCES TO PARAMETERS  **

 H  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
 C  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)


          INTERATOMIC DISTANCES
             C   1      C   2      C   3      C   4      H   5      H   6
-----------------------------------------------------------------------------
   C   1   0.000000
   C   2   1.388681   0.000000
   C   3   2.216954   1.427616   0.000000
   C   4   1.427758   2.216885   2.119584   0.000000
   H   5   1.088191   2.241200   3.253922   2.252645   0.000000
   H   6   2.241067   1.088194   2.252547   3.253835   2.804064   0.000000
   H   7   2.203707   3.154606   2.913733   1.095941   2.703658   4.216542
   H   8   3.154732   2.203620   1.095943   2.913799   4.216680   2.703604
   H   9   2.197196   2.644904   2.344792   1.098242   3.074018   3.557532
   H  10   2.644892   2.197042   1.098255   2.344676   3.557522   3.073932
             H   7      H   8      H   9      H  10
-----------------------------------------------------
   H   7   0.000000
   H   8   3.734533   0.000000
   H   9   1.852230   2.743851   0.000000
   H  10   2.743619   1.852242   2.823292   0.000000
STANDARD DEVIATION ON ENERGY   (KCAL)       0.00000014506
STANDARD DEVIATION ON GRADIENT (KCAL/A,RD,RD)  0.00000890 0.00000000 0.00000000

HEAT OF FORMATION=   81.094373 KCAL/MOLE   (    0.31 SECONDS)
RMS GRADIENT NORM=    0.049226 KCAL/MOLE/A (    0.13 SECONDS)                    Note 1
ORIENTATION OF MOLECULE IN FORCE CALCULATION:                                          Note 2
 NO. ATOM     X         Y         Z       NO. ATOM     X         Y         Z
  1    6   -0.0833   -0.7155   -0.6894     2    6    0.0834   -0.7155    0.6893
  3    6   -0.0989    0.6524    1.0552     4    6    0.0989    0.6525   -1.0551
  5    1   -0.3999   -1.5251   -1.3439     6    1    0.3999   -1.5252    1.3437
  7    1   -0.5647    1.1381   -1.7797     8    1    0.5646    1.1379    1.7800
  9    1    1.0739    1.1384   -0.9162    10    1   -1.0739    1.1382    0.9162

VIBRATIONAL FREQUENCIES AND ERRORS (CM-1),
REDUCED FORCE CONSTANTS (MILLIDYNE/ANGSTROMS).
DIPOLE DERIVATIVES (DEBYE/ANGSTROMS)
FREQ  :    849.1     32.4     26.7     17.4     22.3     25.0     20.5    418.0      Note 3
ERROR :      0.4      0.0      0.0      0.0      0.0      0.0      0.0      1.4
F-CST : -0.21237  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.05146     Note 4
DIP(X):    0.000   -0.016    0.000    0.003   -0.002    0.012    0.002    0.000
DIP(Y):   -0.199   -0.002   -0.002   -0.002   -0.004    0.000   -0.002   -0.032
DIP(Z):    0.000    0.000   -0.014   -0.001   -0.004    0.000   -0.006    0.000
DIP TOT    0.199    0.017    0.014    0.003    0.006    0.012    0.007    0.032      Note 5

FREQ  :    661.4    710.5    756.3    872.8    891.5    986.1    997.2   1031.1
ERROR :      1.1      0.9      0.6      0.9      0.9      0.7      1.0      0.6
F-CST :  0.12889  0.14873  0.16853  0.22441  0.23415  0.28644  0.29293  0.31320
DIP(X):    0.033   -0.180    0.000    0.000   -0.205    0.000    0.506    0.000
DIP(Y):   -0.003   -0.002    0.065   -0.392   -0.001    0.516   -0.001   -0.368
DIP(Z):   -0.166   -0.285    0.000    0.000   -0.425    0.000   -0.049   -0.001
DIP TOT    0.169    0.337    0.065    0.392    0.472    0.516    0.509    0.368
```

```
FREQ  :   1047.5   1125.7   1192.1   1368.2   1390.5   1498.4   1535.7   1616.4
ERROR :      0.5      0.9      0.8      0.7      0.3      0.2      0.2      0.1
F-CST :  0.32326  0.37330  0.41865  0.55146  0.56962  0.66142  0.69477  0.76975
DIP(X):   -0.371    0.000   -0.260    0.001    0.124    0.001   -0.227    0.000
DIP(Y):   -0.002   -0.328   -0.002    0.878   -0.002   -0.468   -0.003   -0.237
DIP(Z):   -0.947    0.000   -0.059    0.000   -0.567    0.005   -0.803    0.000
DIP TOT    1.017    0.328    0.266    0.878    0.580    0.468    0.834    0.237

FREQ  :   3166.7   3167.8   3201.5   3202.7   3255.5   3264.0
ERROR :      0.2      0.5      0.4      0.4      0.3      0.3
F-CST :  2.95422  2.95630  3.01952  3.02172  3.12220  3.13853
DIP(X):   -0.402   -0.014    0.241    0.004   -0.002    0.001
DIP(Y):   -0.009    0.200   -0.003    0.034   -0.001    0.065
DIP(Z):   -0.325   -0.011   -0.528   -0.008    0.091    0.000
DIP TOT    0.517    0.201    0.580    0.035    0.091    0.065
```

DESCRIPTION OF NORMAL MODES IN TERM OF BONDED INTERATOMIC DISTANCES Note 6

```
VIB.  1    ATOMS  C  3  AND  C  4  SHIFT  0.39  ANGSTROMS   99.9%  RADIALLY
FREQ.     849.06  C  4       H  9         0.63               0.1%
                  C  3       H 10         0.63               0.1%

VIB.  2    ATOMS  C  1  AND  C  4  SHIFT  0.34  ANGSTROMS    0.0%  RADIALLY

VIB.  3    ATOMS  C  3  AND  C  4  SHIFT  0.40  ANGSTROMS    0.0%  RADIALLY

VIB.  5    ATOMS  C  3  AND  C  4  SHIFT  0.37  ANGSTROMS    0.0%  RADIALLY

VIB.  8    ATOMS  C  1  AND  H  5  SHIFT  0.33  ANGSTROMS    1.5%  RADIALLY
FREQ.     417.95  C  2       H  6         0.33               1.5%

VIB.  9    ATOMS  C  4  AND  H  7  SHIFT  0.55  ANGSTROMS    0.1%  RADIALLY
FREQ.     661.44  C  3       H  8         0.55               0.1%
                  C  4       H  9         0.42               2.1%
                  C  3       H 10         0.42               2.1%

VIB. 10    ATOMS  C  1  AND  H  5  SHIFT  0.46  ANGSTROMS    2.1%  RADIALLY
FREQ.     710.54  C  2       H  6         0.46               2.1%
                  C  4       H  7         0.32               4.0%
                  C  3       H  8         0.32               4.0%

VIB. 11    ATOMS  C  4  AND  H  9  SHIFT  0.56  ANGSTROMS    1.7%  RADIALLY
FREQ.     756.35  C  3       H 10         0.56               1.7%

VIB. 12    ATOMS  C  1  AND  H  5  SHIFT  0.66  ANGSTROMS    0.5%  RADIALLY
FREQ.     872.79  C  2       H  6         0.66               0.5%
                  C  4       H  7         0.35               3.3%
                  C  3       H  8         0.35               3.3%

VIB. 13    ATOMS  C  1  AND  H  5  SHIFT  0.65  ANGSTROMS    0.2%  RADIALLY
FREQ.     891.53  C  2       H  6         0.65               0.2%
                  C  4       H  9         0.38               0.4%
                  C  3       H 10         0.38               0.4%

VIB. 14    ATOMS  C  4  AND  H  7  SHIFT  0.74  ANGSTROMS    1.9%  RADIALLY
FREQ.     986.06  C  3       H  8         0.74               1.9%

VIB. 15    ATOMS  C  1  AND  H  5  SHIFT  0.36  ANGSTROMS    0.8%  RADIALLY
FREQ.     997.16  C  2       H  6         0.36               0.8%
                  C  4       H  7         0.49               2.3%
                  C  3       H  8         0.49               2.3%
                  C  4       H  9         0.56               3.7%
                  C  3       H 10         0.56               3.7%

VIB. 16    ATOMS  C  1  AND  H  5  SHIFT  0.45  ANGSTROMS    0.8%  RADIALLY
FREQ.    1031.09  C  2       H  6         0.45               0.8%
                  C  4       H  7         0.51               3.1%
                  C  3       H  8         0.51               3.1%
                  C  4       H  9         0.47               6.0%
                  C  3       H 10         0.47               6.0%
```

```
VIB. 17    ATOMS  C  4  AND  H  7  SHIFT  0.54  ANGSTROMS    3.0%  RADIALLY
FREQ.    1047.53  C  3       H  8         0.54               3.0%
                  C  4       H  9         0.46               3.2%
                  C  3       H 10         0.46               3.2%

VIB. 18    ATOMS  C  1  AND  H  5  SHIFT  0.68  ANGSTROMS    0.2%  RADIALLY
FREQ.    1125.68  C  2       H  6         0.68               0.2%

VIB. 19    ATOMS  C  1  AND  H  5  SHIFT  0.67  ANGSTROMS    0.3%  RADIALLY
FREQ.    1192.10  C  2       H  6         0.67               0.3%

VIB. 20    ATOMS  C  4  AND  H  7  SHIFT  0.43  ANGSTROMS    3.8%  RADIALLY
FREQ.    1368.18  C  3       H  8         0.43               3.8%
                  C  4       H  9         0.49               0.8%
                  C  3       H 10         0.49               0.8%

VIB. 21    ATOMS  C  4  AND  H  7  SHIFT  0.48  ANGSTROMS    3.1%  RADIALLY
FREQ.    1390.53  C  3       H  8         0.48               3.1%
                  C  4       H  9         0.51               1.2%
                  C  3       H 10         0.51               1.2%

VIB. 22    ATOMS  C  2  AND  C  3  SHIFT  0.49  ANGSTROMS   99.0%  RADIALLY
FREQ.    1498.39  C  1       C  4         0.49              99.0%
                  C  4       H  7         0.55               3.3%
                  C  3       H  8         0.54               3.3%
                  C  4       H  9         0.67               2.9%
                  C  3       H 10         0.66               2.9%

VIB. 23    ATOMS  C  1  AND  C  2  SHIFT  0.55  ANGSTROMS    0.1%  RADIALLY
FREQ.    1535.70  C  2       C  3         0.58              99.7%
                  C  1       C  4         0.58              99.7%
                  C  3       C  4         0.55               0.3%
                  C  1       H  5         0.53               2.6%
                  C  2       H  6         0.53               2.5%
                  C  4       H  7         0.52               3.1%
                  C  3       H  8         0.52               3.1%
                  C  4       H  9         0.57               2.0%
                  C  3       H 10         0.58               2.0%

VIB. 24    ATOMS  C  1  AND  C  2  SHIFT  0.95  ANGSTROMS  100.0%  RADIALLY
FREQ.    1616.44  C  2       C  3         0.50               3.7%
                  C  1       C  4         0.50               3.7%
                  C  1       H  5         0.53               4.5%
                  C  2       H  6         0.53               4.5%
                  C  4       H  7         0.33               8.8%
                  C  3       H  8         0.33               8.8%

VIB. 25    ATOMS  C  4  AND  H  7  SHIFT  0.43  ANGSTROMS   99.9%  RADIALLY
FREQ.    3166.71  C  3       H  8         0.46              99.9%
                  C  4       H  9         0.62             100.0%
                  C  3       H 10         0.66             100.0%

VIB. 26    ATOMS  C  4  AND  H  7  SHIFT  0.46  ANGSTROMS   99.9%  RADIALLY
FREQ.    3167.82  C  3       H  8         0.43              99.9%
                  C  4       H  9         0.66             100.0%
                  C  3       H 10         0.62             100.0%

VIB. 27    ATOMS  C  4  AND  H  7  SHIFT  0.60  ANGSTROMS   99.9%  RADIALLY
FREQ.    3201.52  C  3       H  8         0.62              99.9%
                  C  4       H  9         0.41              99.8%
                  C  3       H 10         0.42              99.8%

VIB. 28    ATOMS  C  4  AND  H  7  SHIFT  0.62  ANGSTROMS   99.9%  RADIALLY
FREQ.    3202.68  C  3       H  8         0.61              99.9%
                  C  4       H  9         0.42              99.8%
                  C  3       H 10         0.41              99.8%

VIB. 29    ATOMS  C  1  AND  H  5  SHIFT  0.76  ANGSTROMS  100.0%  RADIALLY
FREQ.    3255.49  C  2       H  6         0.76             100.0%

VIB. 30    ATOMS  C  1  AND  H  5  SHIFT  0.76  ANGSTROMS  100.0%  RADIALLY
```

```
FREQ.    3263.99  C  2       H  6         0.76             100.0%

ZERO POINT ENERGY:     54.83 KCAL/MOLE,   ERROR:  0.001                                    Note 7
MOLECULAR WEIGHT:      54.091400 AMU
MOMENTS OF INERTIA IN 10**(-40)GRAM-CM**2:  136.682771   88.953955   59.988774              Note 8
MOMENTS OF INERTIA (CM-1):                    0.204805    0.314694    0.466642
    SYSTEM IS A STABLE SPECIES
    "TRANS= 1" INVOKED, THUS  1 FREQUENCIES FINALLY EXCLUDED.                        Note 9
                  CALCULATED THERMODYNAMIC PROPERTIES
                  ASSUMING NO INTERNAL ROTATIONS.
THERE ARE 23 GENUINE VIBRATIONS IN THIS SYSTEM                                                Note 10
TEMP. (K)  PARTITION FUNCTION    ENTHALPY    HEAT CAPACITY    ENTROPY
                                  CAL/MOL       CAL/K/MOL      CAL/K/MOL
  200 VIB.   0.1080D+01         119.30275       2.61808        0.74882
      ROT.   0.8376D+04         596.17800       2.98089       20.93217
      INT.   0.9044D+04         715.48075       5.59897       21.68099
      TRA.   0.2115D+27         993.63000       4.96815       35.88643
      TOT.                     1709.11075      10.56712       57.56742
  220 VIB.   0.1117D+01         179.73190       3.44008        1.03618
      ROT.   0.9664D+04         655.79580       2.98089       21.21628
      INT.   0.1079D+05         835.52770       6.42097       22.25246
      TRA.   0.2440D+27        1092.99300       4.96815       36.35971
      TOT.                     1928.52070      11.38912       58.61217
  240 VIB.   0.1164D+01         257.45063       4.34377        1.37373
      ROT.   0.1101D+05         715.41360       2.98089       21.47565
      INT.   0.1281D+05         972.86423       7.32466       22.84938
      TRA.   0.2780D+27        1192.35600       4.96815       36.79179
      TOT.                     2165.22023      12.29281       59.64117
  260 VIB.   0.1222D+01         353.89507       5.30936        1.75920
      ROT.   0.1242D+05         775.03140       2.98089       21.71425
      INT.   0.1517D+05        1128.92647       8.29025       23.47344
      TRA.   0.3135D+27        1291.71900       4.96815       37.18926
      TOT.                     2420.64547      13.25840       60.66270
  280 VIB.   0.1293D+01         470.10982       6.31773        2.18936
      ROT.   0.1388D+05         834.64920       2.98089       21.93515
      INT.   0.1794D+05        1304.75902       9.29862       24.12451
      TRA.   0.3503D+27        1391.08200       4.96815       37.55726
      TOT.                     2695.84102      14.26677       61.68177
  300 VIB.   0.1378D+01         606.77357       7.35156        2.66039
      ROT.   0.1539D+05         894.26700       2.98089       22.14081
      INT.   0.2121D+05        1501.04057      10.33245       24.80120
      TRA.   0.3885D+27        1490.44500       4.96815       37.89986
      TOT.                     2991.48557      15.30060       62.70106
  320 VIB.   0.1481D+01         764.24131       8.39585        3.16816
      ROT.   0.1695D+05         953.88480       2.98089       22.33320
      INT.   0.2510D+05        1718.12611      11.37674       25.50136
      TRA.   0.4280D+27        1589.80800       4.96815       38.22034
      TOT.                     3307.93411      16.34489       63.72170
  340 VIB.   0.1602D+01         942.59364       9.43815        3.70847
      ROT.   0.1857D+05        1013.50260       2.98089       22.51391
      INT.   0.2974D+05        1956.09624      12.41904       26.22238
      TRA.   0.4688D+27        1689.17100       4.96815       38.52138
      TOT.                     3645.26724      17.38719       64.74377
  360 VIB.   0.1744D+01        1141.68741      10.46853        4.27718
      ROT.   0.2023D+05        1073.12040       2.98089       22.68430
      INT.   0.3529D+05        2214.80781      13.44942       26.96148
      TRA.   0.5107D+27        1788.53400       4.96815       38.80522
      TOT.                     4003.34181      18.41757       65.76669
  380 VIB.   0.1912D+01        1361.20361      11.47930        4.87037
      ROT.   0.2194D+05        1132.73820       2.98089       22.84546
      INT.   0.4195D+05        2493.94181      14.46019       27.71583
      TRA.   0.5539D+27        1887.89700       4.96815       39.07370
      TOT.                     4381.83881      19.42834       66.78953
  400 VIB.   0.2109D+01        1600.69054      12.46481        5.48436
      ROT.   0.2369D+05        1192.35600       2.98089       22.99836
      INT.   0.4996D+05        2793.04654      15.44570       28.48272
      TRA.   0.5982D+27        1987.26000       4.96815       39.32841
      TOT.                     4780.30654      20.41385       67.81113
FULL COMPUTATION TIME :    19.170 SECONDS
```

Note 1: The gnorm of the input geometry is immediately computed. If this value is greater that 3.0 that indicates that the geometry is not at a well-defined stationary point on the potential surface, and the calculation is halted. Frequencies computed at positions not corresponding to stationary points are MEANINGLESS. This test may be overridden by using the LET keyword. See Section 5.5 for an explanation of characterizing stationary points.

Note 2: The molecule is oriented in such a way that the center of mass is at the origin and the axes are the axes of inertia for the FORCE calculation. These Cartesian coordinates list the new orientation of the molecule.

Note 3: These are the predicted frequencies in cm^{-1} *or wavenumbers. Note that the first frequency is negative, indicating that this is a transition state linking two minima. Movement along the vibration described by the components of the imaginary frequency will lead to reactant or products. There are six (five in the linear case) trivial vibrations whose frequencies are essentially zero. Vibrations are then listed in increasing order of frequency. The error in the frequencies is also listed in this section. To reduce these errors, the wavefunction must be more carefully defined. This can be accomplished by defining SCFCRT (see keyword section) more stringently and repeating the calculation.*

Note 4: The force constant for this vibrational mode is listed.

Note 5: The intensity of infrared (IR) spectral bands is proportional to the square of the transition dipole listed here times the vibrational frequency.

Note 6: The vibrational modes are described through the bonding framework. These should be only an aid to assigning modes, as the description is crude. A translation with a large % radial component indicates rotation about the interatomic axis. A low % radial component describes a stretching motion.

Note 7: The zero point energy (ZPE) at 298 K is computed as:

$$ZPE = \tfrac{1}{2} \sum Vibrations(frequencies)$$

This quantity is defined as the amount of energy of content that the system possesses at 0K. All energetic quantities in AMPAC are referenced to 298 K.

Note 8: The principle moments of inertia lead to the microwave spectral bands for the molecule. They are computed very accurately by AMPAC.

Note 9: One negative eigenvalue (transition vector) as required by the TRANS=1 keyword and the six trivial vibrations were excluded from the thermodynamics calculation.

Note 10: The partition function is computed in terms of vibrational, rotational, internal (vibrational + rotational), and translational components. The thermodynamic quantities enthalpy, heat capacity, and entropy are then computed using these components and totaled. The entropy listed is NOT the ΔS_f*, which could be used for determination of* ΔG_f*, but is easily related to that quantity. In the example of methane,* CH_4*, the entropy value listed is the entropy of the reaction (*ΔS_{rxn}*):*

$$C_{(graph)} + 2\,H_{2\,(g)} \rightarrow CH_{4\,(g)}$$

The entropy of formation of CH_4 can then be computed by using standard molar elemental entropies:

$$\Delta S_{f(CH_4)} = \Delta S_{rxn} - \sum \Delta S_{elements}$$

4.3 Internal Coordinate Frequencies and Gradients (LTRD)

This example illustrates another method to complete a force calculation using again the conrotary cyclization transition state of cis-1,3-butadiene -> cyclobutene. The vibrations will be more intuitively interpretable because the eigenmodes are expressed in terms of the internal coordinates using LTRD.

Input File (TEST10.DAT):

```
AM1 PRECISE LTRD T=3595 GRAD BONDS
Conrotary cyclization TS
LTRD on TS
C    0.000000  0    0.000000  0    0.000000  0   0  0  0
C    1.368591  1    0.000000  0    0.000000  0   1  0  0
C    1.467760  1  101.846287  1    0.000000  0   2  1  0
C    1.467760  1  105.846287  1  -18.651781  1   1  2  3
H    1.088208  1  133.192008  1  157.464541  1   1  2  3
H    1.088208  1  125.192008  1  145.464541  1   2  1  4
H    1.096007  1  117.078638  1  133.669157  1   4  1  2
H    1.095904  1  124.139890  1  139.767746  1   3  2  1
H    1.098257  1  124.343753  1  -63.184369  1   4  1  2
H    1.098289  1  117.265822  1  -67.054326  1   3  2  1
0    0.000000  0    0.000000  0    0.000000  0   0  0  0
```

Archive File (TEST10.ARC):

```
                    SUMMARY OF   AM1   CALCULATION
                                                    6-MAY-94
                         AMPAC Version  5.00
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)

C 4 H 6
  Conrotary cyclization TS
  LTRD on TS

        HEAT OF FORMATION       =    81.094412 KCAL
        ELECTRONIC ENERGY       = -1951.487975 EV
        CORE-CORE REPULSION     =  1360.165495 EV
        GRADIENT NORM           =     0.029329                                    Note
        DIPOLE                  =     0.44625 DEBYE
        NO. OF FILLED LEVELS    =    11
        IONISATION POTENTIAL    =     9.073897 EV
        MOLECULAR WEIGHT        =    54.091

        FINAL GEOMETRY OBTAINED                                CHARGE
```

```
AM1 PRECISE LTRD T=3595 GRAD BONDS
  Conrotary cyclization TS
  LTRD on TS
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0      -0.1709
 C     1.388722  1    0.000000  0    0.000000  0   1  0  0      -0.1709
 C     1.427731  1  103.833264  1    0.000000  0   2  1  0      -0.1858
 C     1.427755  1  103.831264  1  -18.663733  1   1  2  3      -0.1858
 H     1.088199  1  129.195876  1  154.430653  1   1  2  3       0.1382
 H     1.088199  1  129.195115  1  154.433283  1   2  1  4       0.1382
 H     1.095943  1  121.107571  1  136.759682  1   4  1  2       0.0989
 H     1.095943  1  121.107477  1  136.760268  1   3  2  1       0.0989
 H     1.098247  1  120.314232  1  -65.095921  1   4  1  2       0.1195
 H     1.098248  1  120.314771  1  -65.093793  1   3  2  1       0.1195
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0
```

Note: The geometry has changed slightly and the gnorm is very low. The frequencies predicted by this procedure will likely be extremely accurate.

Output File (TEST10.OUT):

```
*****************************************************************************
                            AM1 CALCULATION RESULTS
*****************************************************************************
*                              AMPAC Version  5.00
*                                 Presented by:
*
*                           Semichem, Inc.
*                           7128 Summit
*                           Shawnee, KS  66216
*                           (913) 268-3271
*                           (913) 268-3445 (fax)
*
*  LTRD     - MINIMISE GRADIENT USING FULL-NEWTON
*  PRECISE  - OPTIMIZATION CRITERIA TO BE INCREASED BY 10 TIMES,
*           -     S.C.F.   CRITERIA BY 100 TIMES,
*           - AND USE ACCURATE FINITE DIFFERENCE FORMULA IN HESSIAN
*  BONDS    - FINAL BOND-ORDER MATRIX TO BE PRINTED
*  GRADIENTS- ALL GRADIENTS TO BE PRINTED
*   T=      - A TIME OF  3595.0 SECONDS REQUESTED
*  AM1      - THE AM1 HAMILTONIAN TO BE USED
*****************************************************************************
AM1 PRECISE LTRD T=3595 GRAD BONDS
  Conrotary cyclization TS
  LTRD on TS
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C
     2     C          1.36859 *                                   1
     3     C          1.46776 *      101.84629 *                  2  1
     4     C          1.46776 *      105.84629 *   -18.65178 *   1  2  3
     5     H          1.08821 *      133.19201 *   157.46454 *   1  2  3
     6     H          1.08821 *      125.19201 *   145.46454 *   2  1  4
     7     H          1.09601 *      117.07864 *   133.66916 *   4  1  2
     8     H          1.09590 *      124.13989 *   139.76775 *   3  2  1
     9     H          1.09826 *      124.34375 *   -63.18437 *   4  1  2
    10     H          1.09829 *      117.26582 *   -67.05433 *   3  2  1

         CARTESIAN COORDINATES
   NO.       ATOM         X         Y         Z
    1         6        0.0000    0.0000    0.0000
    2         6        1.3686    0.0000    0.0000
    3         6        1.6699    1.4365    0.0000
    4         6       -0.4008    1.3378    0.4516
    5         1       -0.7448   -0.7328   -0.3041
    6         1        1.9957   -0.8554    0.2434
    7         1       -1.1852    1.8440   -0.1226
    8         1        2.4739    1.8963    0.5859
    9         1       -0.1764    1.7496    1.4447
```

```
  10        1        1.4007    2.0071   -0.8990

        SINGLET STATE CALCULATION
        RHF CALCULATION, No. OF DOUBLY OCCUPIED LEVELS = 11

 H  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
 C  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)

          INTERATOMIC DISTANCES
             C   1      C   2      C   3      C   4      H   5      H   6
-------------------------------------------------------------------------------
   C   1   0.000000
   C   2   1.368591   0.000000
   C   3   2.202750   1.467760   0.000000
   C   4   1.467760   2.263709   2.121649   0.000000
   H   5   1.088208   2.257420   3.260240   2.230876   0.000000
   H   6   2.184919   1.088208   2.327663   3.255262   2.797396   0.000000
   H   7   2.195480   3.152361   2.886677   1.096007   2.620447   4.187969
   H   8   3.171625   2.271735   1.095904   2.931486   4.250180   2.813791
   H   9   2.275808   2.745048   2.365195   1.098257   3.089238   3.598221
   H  10   2.607389   2.199445   1.098289   2.348891   3.530441   3.138888
             H   7      H   8      H   9      H  10
-----------------------------------------------------
   H   7   0.000000
   H   8   3.727434   0.000000
   H   9   1.866269   2.789864   0.000000
   H  10   2.704901   1.835434   2.836659   0.000000

USE 2-POINT FORMULA IN INTEGRAL DERIVATIVES WITH STEP  0.00002000                    Note 1
STANDARD DEVIATION ON ENERGY   (KCAL)        0.000000031
STANDARD DEVIATION ON GRADIENT (KCAL/A,RD,RD)  0.0000037 0.0000053 0.0000049

QUADRATIC CRITICAL POINT RESEARCH IN 24 VARIABLES  ITE MAX:   8                      Note 2
HESSIAN MATRIX BY THE TWOSTEP METHOD  (ANAL-NUM)
REQUIRED CONVERGENCE ON RMS GRADIENT  1.0D-01
ERROR ON ENERGY     :  3.07D-08
      ON DERIVATIVES:  3.75D-06  5.26D-06  4.90D-06
LARGEST ALLOWED STEP:  0.012000  0.067500  0.091500
LOWEST  ALLOWED STEP:  0.001000  0.010000  0.010000
ITER   2     ELAPSED TIME :   79.26 SECONDS
ENERGY 8.10944122D+01     <G|G> 8.60171815D-04     RMS GRAD  5.98669D-03
GRAD  -2.6435D-04 -2.8578D-02  3.9437D-03 -3.1548D-03 -1.4140D-03 -1.7193D-03
      -8.9636D-05  3.1002D-04  1.1947D-04 -2.1357D-03  1.5487D-03  1.6400D-03
      -4.3156D-04  3.5356D-04  2.0180D-04 -9.9287D-04 -7.3937D-04 -3.4579D-04
      -4.6684D-04  3.0795D-04 -7.0486D-04 -4.8283D-04 -3.8359D-04  5.2880D-05
COORD  1.3887D+00  1.4277D+00  1.8122D+00  1.4278D+00  1.8122D+00 -3.2574D-01
       1.0882D+00  2.2549D+00  2.6953D+00  1.0882D+00  2.2549D+00  2.6954D+00
       1.0959D+00  2.1137D+00  2.3869D+00  1.0959D+00  2.1137D+00  2.3869D+00
       1.0982D+00  2.0999D+00 -1.1361D+00  1.0982D+00  2.0999D+00 -1.1361D+00
NUMBER OF NEGATIVE EIGENVALUES                1
FIRST EIGENVALUES : -3.20D+02  2.79D+01  3.00D+01  4.05D+01  4.33D+01  5.91D+01
 7.29D+01  7.57D+01  7.91D+01  1.01D+02  1.46D+02  1.78D+02  1.80D+02  3.13D+02
 3.77D+02  7.77D+02  7.80D+02  8.16D+02  8.32D+02  8.38D+02  8.48D+02  9.53D+02
 1.40D+03  1.86D+03
ROUND-OFF STD DEV.:  1.56D-03  1.49D-03  1.48D-03  1.38D-03  1.36D-03  1.50D-03
 1.51D-03  1.43D-03  1.41D-03  1.54D-03  1.54D-03  1.27D-03  1.27D-03  1.58D-03
 1.63D-03  1.33D-01  1.30D-01  1.42D-01  1.47D-01  1.42D-01  1.44D-01  1.44D-01
 1.49D-01  1.45D-01
USING FINITE DIFF.:  9.99D-03  1.00D-02  1.00D-02  1.00D-02  1.00D-02  1.00D-02
 1.00D-02  1.00D-02  1.00D-02  1.00D-02  1.00D-02  1.00D-02  1.00D-02  9.98D-03
 9.96D-03  1.00D-03  1.00D-03  1.01D-03  1.00D-03  1.00D-03  1.00D-03  1.02D-03
 1.02D-03  1.02D-03

MATRIX OF SECOND DERIVATIVES                                                          Note 3
        1          2          3          4          5          6
  1  1.301D+03
  2  3.563D+02  1.295D+03
  3 -2.302D+01  3.118D+02  2.223D+02
  4  3.562D+02 -5.526D+01  1.446D+02  1.295D+03
  5 -2.302D+01  1.448D+02 -9.715D+01  3.116D+02  2.223D+02
  6 -9.141D+01 -1.603D+01 -1.220D+02 -1.604D+01 -1.220D+02  2.169D+02
```

```
  7  4.696D+01  2.855D+00  3.544D+00  4.487D+01 -3.969D+01 -2.622D+00
  8  4.825D+01  2.507D+00  4.353D+00 -4.757D+01  6.169D+01  6.540D+00
  9  4.262D+01 -1.395D+01  2.331D+01 -1.501D+01  2.237D+01 -2.205D+01
 10  4.717D+01  4.474D+01 -3.940D+01  2.722D+00  3.828D+00 -2.598D+00
 11  4.824D+01 -4.758D+01  6.169D+01  2.510D+00  4.353D+00  6.539D+00
 12  4.262D+01 -1.504D+01  2.237D+01 -1.392D+01  2.332D+01 -2.206D+01
 13 -2.693D+00  1.361D+00 -2.241D+00  5.223D+01  4.245D+00  1.923D+00
 14  1.139D+01 -1.933D+00  4.770D+00  4.748D+01  1.311D+01 -3.594D+00
 15 -3.810D+01  9.062D+00 -2.492D+01  3.113D+01 -2.115D+01  1.594D+01
 16 -2.479D+00  5.212D+01  4.505D+00  1.225D+00 -1.969D+00  1.928D+00
 17  1.141D+01  4.746D+01  1.313D+01 -1.942D+00  4.799D+00 -3.594D+00
 18 -3.811D+01  3.116D+01 -2.114D+01  9.032D+00 -2.491D+01  1.594D+01
 19  2.253D+01  3.057D-01  2.819D+01  5.647D+01  3.703D+01 -1.471D+01
 20 -6.230D+00  7.292D+00 -2.033D+00  6.844D+01  2.474D+00 -6.633D+00
 21 -1.020D+02  2.250D+01 -9.699D+01  1.780D+01 -1.242D+02  4.133D+01
 22  2.254D+01  5.645D+01  3.703D+01  3.080D-01  2.818D+01 -1.471D+01
 23 -6.237D+00  6.845D+01  2.464D+00  7.287D+00 -2.046D+00 -6.634D+00
 24 -1.019D+02  1.785D+01 -1.242D+02  2.244D+01 -9.699D+01  4.133D+01
        7          8          9         10         11         12
  7  8.449D+02
  8  7.772D-01  1.236D+02
  9  3.260D+00 -4.752D+00  3.473D+01
 10  5.456D-01 -9.350D-02 -3.732D-01  8.449D+02
 11 -8.698D-02  5.485D-01 -8.712D-02  7.709D-01  1.236D+02
 12 -3.322D-01 -8.758D-02 -2.332D+00  3.222D+00 -4.752D+00  3.473D+01
 13  2.038D-01  1.995D-01  5.886D-01  2.448D-01  8.559D-01  1.056D+00
 14 -2.098D-01  2.602D-02 -1.309D-01  4.699D-01  1.312D+00  7.306D-01
 15 -5.681D-01  9.088D-02  9.026D-01  9.328D-01  3.199D-01  3.142D+00
 16  2.401D-01  8.500D-01  1.018D+00  2.219D-01  1.992D-01  5.503D-01
 17  4.771D-01  1.311D+00  7.266D-01 -2.171D-01  2.553D-02 -1.347D-01
 18  8.871D-01  3.191D-01  3.142D+00 -5.269D-01  8.945D-02  9.014D-01
 19  1.160D-01 -1.327D+00  9.631D-02  4.304D-03  2.834D-02 -1.128D+00
 20  1.386D+00 -4.393D+00  1.130D+00 -3.981D-01 -8.837D-02 -5.943D-01
 21  1.511D+00 -1.577D+00 -4.558D-01  4.064D-01  3.309D-01  5.575D+00
 22  1.143D-02  2.872D-02 -1.131D+00  1.156D-01 -1.329D+00  9.921D-02
 23 -4.135D-01 -8.719D-02 -5.926D-01  1.408D+00 -4.392D+00  1.132D+00
 24  3.343D-01  3.312D-01  5.573D+00  1.590D+00 -1.577D+00 -4.567D-01
       13         14         15         16         17         18
 13  8.113D+02
 14  7.964D+00  1.271D+02
 15 -6.688D+00  6.922D+00  4.611D+01
 16  3.375D-01  1.092D-01 -6.586D-01  8.113D+02
 17  1.183D-01  1.234D-01 -2.244D-02  7.964D+00  1.271D+02
 18 -6.951D-01 -2.661D-02  1.677D-01 -6.643D+00  6.926D+00  4.612D+01
 19  3.393D+01 -3.154D+01 -8.358D+00  3.421D-01 -1.065D-01  3.008D-01
 20 -3.183D+01  5.219D+01  1.028D+01  1.370D-01  3.435D-02 -8.312D-01
 21  1.054D+01 -1.253D+01 -2.121D+01 -6.173D-01  8.573D-01 -5.630D+00
 22  3.510D-01 -1.014D-01  2.992D-01  3.389D+01 -3.154D+01 -8.358D+00
 23  1.204D-01  3.308D-02 -8.342D-01 -3.181D+01  5.219D+01  1.028D+01
 24 -6.852D-01  8.490D-01 -5.630D+00  1.062D+01 -1.252D+01 -2.120D+01
       19         20         21         22         23         24
 19  8.059D+02
 20  1.288D+01  1.302D+02
 21 -1.828D+00 -2.227D+01  5.014D+01
 22  3.906D-01  1.408D-01  1.403D+00  8.059D+02
 23  1.443D-01  1.354D-03 -1.715D+00  1.288D+01  1.302D+02
 24  1.406D+00 -1.710D+00 -8.884D+00 -1.827D+00 -2.228D+01  5.014D+01

AND FIRST EIGENVECTORS
  1  1.79D-01 -2.05D-01  4.96D-01 -2.05D-01  4.96D-01  1.74D-01  1.66D-02
    -1.16D-01 -1.01D-01  1.62D-02 -1.16D-01 -1.01D-01  8.98D-03 -2.03D-03
     1.23D-01  8.61D-03 -2.11D-03  1.23D-01 -1.99D-02  5.66D-02  3.71D-01
    -1.99D-02  5.67D-02  3.71D-01
  2 -1.76D-02 -9.17D-03  9.19D-02 -9.18D-03  9.19D-02  2.84D-01  4.21D-03
    -4.21D-02  6.47D-01  4.21D-03 -4.21D-02  6.47D-01 -1.32D-03 -1.47D-02
    -1.66D-01 -1.31D-03 -1.47D-02 -1.66D-01 -3.38D-03  4.59D-02  1.95D-02
    -3.38D-03  4.59D-02  1.94D-02
  3 -8.60D-06  1.12D-02 -3.52D-02 -1.12D-02  3.51D-02 -6.47D-05  6.71D-04
     4.13D-03  4.44D-01 -6.70D-04 -4.09D-03 -4.44D-01 -1.31D-03  2.21D-02
     4.09D-01  1.31D-03 -2.21D-02 -4.09D-01  6.53D-03  1.45D-02  3.65D-01
    -6.52D-03 -1.45D-02 -3.65D-01
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Note 4

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 4  8.03D-06 -1.38D-02  3.38D-02  1.38D-02 -3.37D-02  8.86D-05 -5.37D-03
    5.55D-02  5.42D-01  5.37D-03 -5.56D-02 -5.42D-01 -9.61D-04  1.11D-02
   -3.96D-01  9.56D-04 -1.11D-02  3.96D-01 -5.93D-03 -2.08D-02 -2.12D-01
    5.92D-03  2.09D-02  2.12D-01
 5 -7.96D-03  2.85D-02 -1.04D-01  2.85D-02 -1.04D-01 -2.76D-01 -8.28D-03
    1.37D-01  2.38D-01 -8.24D-03  1.37D-01  2.37D-01 -1.68D-03  1.48D-02
    5.90D-01 -1.66D-03  1.48D-02  5.90D-01  1.05D-02 -7.52D-02  1.46D-01
    1.05D-02 -7.52D-02  1.46D-01
 6 -3.57D-06 -1.33D-02  7.73D-02  1.33D-02 -7.73D-02 -3.90D-05 -3.17D-03
    5.46D-02  6.56D-02  3.16D-03 -5.45D-02 -6.56D-02 -2.15D-03  7.39D-02
    3.91D-01  2.15D-03 -7.39D-02 -3.91D-01  1.01D-02 -2.69D-01 -5.05D-01
   -1.01D-02  2.69D-01  5.05D-01
 7  9.98D-03 -2.37D-02  8.12D-02 -2.37D-02  8.12D-02  2.42D-01  6.59D-03
   -2.21D-01 -3.54D-03  6.57D-03 -2.20D-01 -3.52D-03 -1.94D-02  3.97D-01
    1.11D-01 -1.94D-02  3.96D-01  1.11D-01  2.58D-02 -4.44D-01 -2.16D-01
    2.58D-02 -4.44D-01 -2.16D-01
 8  4.60D-06  3.14D-03 -2.89D-02 -3.15D-03  2.89D-02  9.01D-05  2.98D-03
   -5.99D-02 -4.30D-02 -2.98D-03  5.99D-02  4.30D-02 -2.91D-02  5.13D-01
   -1.31D-01  2.92D-02 -5.14D-01  1.31D-01  2.99D-02 -4.22D-01  1.82D-01
   -2.99D-02  4.22D-01 -1.83D-01
 9  2.67D-02 -3.82D-02  7.49D-02 -3.82D-02  7.49D-02  3.27D-01  6.43D-03
   -2.14D-01 -3.13D-02  6.37D-03 -2.14D-01 -3.14D-02  2.31D-02 -3.26D-01
    2.88D-01  2.30D-02 -3.26D-01  2.88D-01 -1.41D-02  1.90D-01 -4.08D-01
   -1.41D-02  1.89D-01 -4.08D-01
10 -4.65D-06 -5.35D-02  2.08D-01  5.35D-02 -2.08D-01  1.99D-05 -1.58D-02
    6.63D-01 -5.61D-02  1.58D-02 -6.63D-01  5.61D-02 -3.54D-03  4.87D-02
   -1.30D-02  3.55D-03 -4.87D-02  1.30D-02  2.31D-03  1.28D-03  9.40D-02
   -2.32D-03 -1.29D-03 -9.40D-02
11  1.58D-02  2.11D-02 -1.38D-01  2.10D-02 -1.38D-01 -4.37D-01 -1.13D-02
   -5.98D-01  5.97D-02 -1.12D-02 -5.98D-01  5.97D-02  3.86D-04 -5.75D-02
   -4.15D-02  4.81D-04 -5.76D-02 -4.15D-02 -3.17D-03  2.34D-02  1.34D-01
   -3.18D-03  2.35D-02  1.34D-01
12  1.78D-02 -4.20D-02 -5.68D-02 -4.21D-02 -5.68D-02  2.15D-02 -1.97D-03
   -4.37D-02 -2.49D-03 -1.96D-03 -4.37D-02 -2.50D-03  2.35D-02  4.80D-01
    7.71D-02  2.35D-02  4.79D-01  7.70D-02  2.29D-02  5.01D-01 -6.96D-02
    2.28D-02  5.01D-01 -6.95D-02
13  6.85D-06 -4.89D-02 -1.12D-02  4.88D-02  1.12D-02  3.21D-05 -1.88D-03
    1.34D-02 -8.87D-03  1.88D-03 -1.34D-02  8.86D-03 -2.55D-02 -4.75D-01
   -7.10D-02  2.55D-02  4.75D-01  7.10D-02 -1.72D-02 -4.96D-01  1.39D-01
    1.72D-02  4.96D-01 -1.39D-01
14 -4.04D-06  9.73D-02 -6.57D-01 -9.73D-02  6.57D-01 -6.17D-05  6.10D-02
    2.25D-01 -3.48D-03 -6.10D-02 -2.25D-01  3.50D-03  2.45D-03  3.57D-03
    4.27D-03 -2.46D-03 -3.57D-03 -4.29D-03 -7.43D-05 -1.25D-02 -6.92D-02
    9.30D-05  1.24D-02  6.91D-02
15 -2.03D-02 -1.62D-01  3.47D-01 -1.62D-01  3.46D-01 -6.69D-01  4.21D-02
    9.85D-02  9.36D-02  4.18D-02  9.86D-02  9.36D-02  3.01D-02  2.42D-02
   -6.99D-02  2.97D-02  2.43D-02 -6.98D-02 -5.46D-02 -5.68D-03 -3.16D-01
   -5.46D-02 -5.66D-03 -3.16D-01
16 -5.39D-04  1.09D-02  1.07D-03 -1.11D-02  2.64D-05 -3.81D-04  5.16D-03
    5.82D-05  1.39D-03 -3.67D-03 -4.76D-05 -1.42D-03 -4.72D-01 -2.96D-02
   -2.36D-03  4.65D-01  2.92D-02  2.38D-03  5.32D-01  3.06D-02 -1.00D-02
   -5.24D-01 -3.01D-02  9.76D-03
17 -2.08D-02 -3.83D-02  3.62D-02 -3.82D-02  3.62D-02 -4.48D-02  6.28D-02
    2.35D-03  2.17D-03  6.28D-02  2.35D-03  2.20D-03 -4.58D-01 -3.03D-02
   -4.60D-03 -4.65D-01 -3.07D-02 -4.64D-03  5.22D-01  2.73D-02 -1.91D-02
    5.30D-01  2.78D-02 -1.92D-02
18  3.06D-01 -2.19D-01 -8.93D-02 -2.20D-01 -8.96D-02 -1.67D-02 -2.49D-01
    2.67D-02  1.89D-02 -2.51D-01  2.67D-02  1.89D-02  4.20D-01 -2.80D-02
   -2.98D-02  4.18D-01 -2.78D-02 -2.97D-02  3.93D-01 -4.12D-02 -1.96D-02
    3.91D-01 -4.12D-02 -1.97D-02
19 -3.97D-06 -9.65D-02 -3.49D-02  9.56D-02  3.50D-02 -5.98D-05 -1.98D-01
   -3.03D-03 -1.39D-03  2.01D-01  3.08D-03  1.38D-03 -5.01D-01  2.35D-02
    1.27D-02  5.04D-01 -2.37D-02 -1.27D-02 -4.41D-01  2.51D-02 -8.83D-03
    4.44D-01 -2.53D-02  8.93D-03
20 -1.31D-01  6.54D-03 -2.19D-02  5.92D-03 -2.19D-02  2.08D-02  6.25D-01
   -1.03D-02 -6.13D-03  6.25D-01 -1.04D-02 -6.13D-03  2.71D-01 -7.44D-03
    3.21D-03  2.67D-01 -7.30D-03  3.29D-03  1.64D-01 -8.10D-03  2.92D-02
    1.61D-01 -7.90D-03  2.92D-02
21 -2.80D-04  6.58D-03  6.15D-02 -6.16D-03 -6.18D-02  8.76D-05  6.75D-01
   -3.34D-03  2.95D-03 -6.73D-01  3.25D-03 -2.96D-03 -1.50D-01  3.03D-03
    1.01D-03  1.50D-01 -2.98D-03 -9.87D-04 -1.40D-01  5.21D-03  1.44D-03
    1.39D-01 -5.19D-03 -1.33D-03
```

```
 22 -6.38D-01  3.61D-01  2.28D-01  3.61D-01  2.28D-01 -1.21D-02 -1.94D-01
   -3.89D-02 -2.92D-02 -1.95D-01 -3.89D-02 -2.92D-02  1.90D-01  1.25D-02
    2.71D-02  1.89D-01  1.25D-02  2.71D-02  1.88D-01  3.40D-02  3.11D-02
    1.87D-01  3.41D-02  3.11D-02
 23  5.24D-05 -6.89D-01 -1.06D-01  6.90D-01  1.05D-01 -7.16D-06  4.43D-02
   -2.26D-02 -3.48D-04 -4.42D-02  2.26D-02  3.76D-04  6.35D-02  2.77D-02
    1.13D-02 -6.35D-02 -2.77D-02 -1.13D-02  7.00D-02  3.43D-02 -5.06D-03
   -6.99D-02 -3.42D-02  5.01D-03
 24 -6.69D-01 -4.97D-01 -1.35D-01 -4.97D-01 -1.35D-01  7.09D-02 -4.98D-02
   -1.05D-02 -1.19D-02 -4.99D-02 -1.05D-02 -1.19D-02 -2.47D-02 -1.91D-02
    6.55D-03 -2.48D-02 -1.91D-02  6.55D-03 -5.10D-02 -2.08D-02  4.46D-02
   -5.10D-02 -2.08D-02  4.46D-02

VIBRATIONAL FREQUENCIES AND ERRORS (CM-1).
FREQ:  -849.6     0.0     0.0     0.0     0.0     0.0     0.0   418.0   661.6
ERROR     0.2     0.0     0.0     0.0     0.0     0.0     0.0     0.7     0.6

FREQ:   710.5   756.2   872.8   891.6   986.1   997.3  1031.1  1047.5  1125.6
ERROR     0.5     0.1     1.4     0.9     0.4     0.8     0.4     0.4     0.4

FREQ:  1192.1  1368.2  1390.5  1498.2  1535.5  1616.0  3166.7  3167.7  3201.5
ERROR     0.2     0.2     0.2     0.1     0.1     0.1     0.1     0.3     0.3

FREQ:  3202.5  3255.4  3263.8
ERROR     0.3     0.2     0.1

ZERO POINT ENERGY:     53.40 KCAL/MOLE,   ERROR:  0.001
AM1 PRECISE LTRD T=3595 GRAD BONDS
  Conrotary cyclization TS
  LTRD on TS

    GEOMETRY OPTIMISED : GRADIENT NORM MINIMISED
    SCF FIELD WAS ACHIEVED

                              AM1    CALCULATION
                                                          VERSION  5.00

         FINAL HEAT OF FORMATION =    81.094412 KCAL
         ELECTRONIC ENERGY       = -1951.487975 EV
         CORE-CORE REPULSION     =  1360.165495 EV
         GRADIENT NORM           =     0.029329
         IONISATION POTENTIAL    =     9.073897 EV
         NO. OF FILLED LEVELS    =    11
         MOLECULAR WEIGHT        =    54.091
         SCF CALCULATIONS        =  114
         COMPUTATION TIME=       138.78 SECONDS
                                                       6-MAY-94

      FINAL  POINT  AND  DERIVATIVES
  PARAMETER     ATOM    TYPE            VALUE       GRADIENT
     1          2 C     BOND            1.388722    -0.000264  KCAL/ANGSTROM
     2          3 C     BOND            1.427731    -0.028578  KCAL/ANGSTROM
     3          3 C     ANGLE         103.833264     0.003944  KCAL/RADIAN
     4          4 C     BOND            1.427755    -0.003155  KCAL/ANGSTROM
     5          4 C     ANGLE         103.831264    -0.001414  KCAL/RADIAN
     6          4 C     DIHEDRAL      -18.663733    -0.001719  KCAL/RADIAN
     7          5 H     BOND            1.088199    -0.000090  KCAL/ANGSTROM
     8          5 H     ANGLE         129.195876     0.000310  KCAL/RADIAN
     9          5 H     DIHEDRAL      154.430653     0.000119  KCAL/RADIAN
    10          6 H     BOND            1.088199    -0.002136  KCAL/ANGSTROM
    11          6 H     ANGLE         129.195115     0.001549  KCAL/RADIAN
    12          6 H     DIHEDRAL      154.433283     0.001640  KCAL/RADIAN
    13          7 H     BOND            1.095943    -0.000432  KCAL/ANGSTROM
    14          7 H     ANGLE         121.107571     0.000354  KCAL/RADIAN
    15          7 H     DIHEDRAL      136.759682     0.000202  KCAL/RADIAN
    16          8 H     BOND            1.095943    -0.000993  KCAL/ANGSTROM
    17          8 H     ANGLE         121.107477    -0.000739  KCAL/RADIAN
    18          8 H     DIHEDRAL      136.760268    -0.000346  KCAL/RADIAN
    19          9 H     BOND            1.098247    -0.000467  KCAL/ANGSTROM
    20          9 H     ANGLE         120.314232     0.000308  KCAL/RADIAN
    21          9 H     DIHEDRAL      -65.095921    -0.000705  KCAL/RADIAN
```

Note 5

```
   22         10 H     BOND            1.098248    -0.000483  KCAL/ANGSTROM
   23         10 H     ANGLE         120.314771    -0.000384  KCAL/RADIAN
   24         10 H     DIHEDRAL      -65.093793     0.000053  KCAL/RADIAN

  ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
 NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
  (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
    1     C
    2     C          1.38872 *                                  1
    3     C          1.42773 *      103.83326 *                 2  1
    4     C          1.42776 *      103.83126 *   -18.66373 *   1  2  3
    5     H          1.08820 *      129.19588 *   154.43065 *   1  2  3
    6     H          1.08820 *      129.19511 *   154.43328 *   2  1  4
    7     H          1.09594 *      121.10757 *   136.75968 *   4  1  2
    8     H          1.09594 *      121.10748 *   136.76027 *   3  2  1
    9     H          1.09825 *      120.31423 *   -65.09592 *   4  1  2
   10     H          1.09825 *      120.31477 *   -65.09379 *   3  2  1

        INTERATOMIC DISTANCES
             C   1      C   2      C   3      C   4      H   5      H   6
-------------------------------------------------------------------------------
   C   1   0.000000
   C   2   1.388722   0.000000
   C   3   2.217001   1.427731   0.000000
   C   4   1.427755   2.216990   2.119644   0.000000
   H   5   1.088199   2.241163   3.253946   2.252683   0.000000
   H   6   2.241156   1.088199   2.252652   3.253942   2.804078   0.000000
   H   7   2.203726   3.154751   2.913856   1.095943   2.703700   4.216690
   H   8   3.154763   2.203703   1.095943   2.913860   4.216697   2.703668
   H   9   2.197164   2.644890   2.344667   1.098247   3.074092   3.557509
   H  10   2.644898   2.197149   1.098248   2.344646   3.557505   3.074069
             H   7      H   8      H   9      H  10
-------------------------------------------------------
   H   7   0.000000
   H   8   3.734654   0.000000
   H   9   1.852260   2.743714   0.000000
   H  10   2.743686   1.852262   2.823098   0.000000

                EIGENVALUES
-37.23737 -27.67140 -24.68032 -19.24712 -16.24124 -14.92006 -14.37841 -12.74042
-12.64730  -9.47253  -9.07390   0.56125   1.21687   4.23791   4.48543   4.57449
  4.62444   4.94528   4.96787   5.29226   5.38588   6.04888

        NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS
       ATOM NO.   TYPE          CHARGE        ATOM  ELECTRON DENSITY
         1         C           -0.1709          4.1709
         2         C           -0.1709          4.1709
         3         C           -0.1858          4.1858
         4         C           -0.1858          4.1858
         5         H            0.1382          0.8618
         6         H            0.1382          0.8618
         7         H            0.0989          0.9011
         8         H            0.0989          0.9011
         9         H            0.1195          0.8805
        10         H            0.1195          0.8805
DIPOLE (DEBYE)   X         Y         Z       TOTAL
POINT-CHG.     0.000     0.368     0.060     0.373
HYBRID         0.000     0.072     0.012     0.073
SUM            0.000     0.440     0.072     0.446

        CARTESIAN COORDINATES
   NO.       ATOM               X         Y         Z
    1        C                   0.0000    0.0000    0.0000
    2        C                   1.3887    0.0000    0.0000
    3        C                   1.7301    1.3863    0.0000
    4        C                  -0.3413    1.3135    0.4437
    5        H                  -0.6877   -0.7607   -0.3640
    6        H                   2.0764   -0.8372    0.1014
    7        H                  -1.1404    1.8852   -0.0417
    8        H                   2.5292    1.7727    0.6428
    9        H                  -0.0862    1.6386    1.4611
   10        H                   1.4749    2.0200   -0.8599
```

```
        ATOMIC ORBITAL ELECTRON POPULATIONS
  1.23313   0.94831   0.95832   1.03112   1.23312   0.94831   0.95558   1.03386
  1.27053   0.96070   0.94439   1.01015   1.27054   0.96070   0.94388   1.01065
  0.86176   0.86176   0.90111   0.90111   0.88048   0.88048

                 BOND ORDERS AND VALENCIES

             C   1      C   2      C   3      C   4      H   5      H   6
-------------------------------------------------------------------------------
   C   1   3.925944
   C   2   1.582511   3.925948
   C   3   0.007699   1.336540   3.915893
   C   4   1.336533   0.007698   0.643000   3.915890
   H   5   0.941907   0.009239   0.015939   0.009510   0.980889
   H   6   0.009239   0.941908   0.009510   0.015939   0.000151   0.980890
   H   7   0.008220   0.011553   0.001860   0.957688   0.000018   0.001018
   H   8   0.011554   0.008219   0.957688   0.001860   0.001018   0.000018
   H   9   0.007984   0.020296   0.000196   0.943465   0.003098   0.000009
   H  10   0.020298   0.007984   0.943463   0.000196   0.000009   0.003098
             H   7      H   8      H   9      H  10
-----------------------------------------------------
   H   7   0.990220
   H   8   0.000056   0.990220
   H   9   0.009432   0.000376   0.985715
   H  10   0.000376   0.009431   0.000860   0.985715
FULL COMPUTATION TIME :   138.890 SECONDS
```

Note 1: These messages show some of the effects of specifying PRECISE. A more accurate numerical method than the default is used to determine the second derivatives.

Note 2: Information on the set-up and initial stages of the LTRD procedure are listed in this section.

Note 3: Listed here is the matrix of second derivatives as reported by LTRD.

Note 4: These are the internal coordinate components of the vibrations. The components are ordered in exactly the same manner as the optimizable geometric parameters in the input file. This portion of the output may be analyzed by finding the largest components and relating them to motions of the molecule defined by the internal coordinates. The largest components of the first eigenvector (the transition vector) are components #3, #5, #21, and #24. The first two components correspond to compression of the C=C–C angles. This is a required motion in moving from open 1,3-butadiene to closed cyclobutene. The other two components are twisting motions (dihedral movements) of the terminal hydrogens, also along the reaction pathway. In order to force a new optimization to proceed to products, one could decrease the C=C–C angles slightly and decrease the dihedrals of the last two hydrogens. A geometry optimization would then likely follow the path of steepest descent and move toward cyclobutene. Opposite alteration of these components followed by reoptimization should lead to reactants.

Note 5: As in the case with the FORCE calculation in the previous example, the frequencies in listed cm^{-1} *or wavenumbers. Note the close similarity in the predicted values by LTRD and FORCE.*

4.4 Reaction Pathway

This example illustartes the use of the reaction coordinate method for locating an approximate transition state for furter refinement. It involves computation of the rotational barrier of ethane using the MINDO3 Hamiltonian. The energies and reaction coordinates could be plotted to produce a potential map such as that shown in Section 5.4. It should be noted in this connection that a reaction path may fail to pass through a saddle point (be discontinuous). Also, the intermediate points generated along the reaction path are not defined in a strict mathematical sense because one of the degrees of freedom (the reaction coordinate) is not variable.

Input File (TEST09.DAT) :

```
MINDO3 PREC GRAD
Ethane rotational barrier
MINDO3, reaction coordinate
C    0.000000 0    0.000000 0    0.000000  0   0  0  0
C    1.544846 1    0.000000 0    0.000000  0   1  0  0
H    1.116935 1  110.665270 1    0.000000  0   2  1  0
H    1.116935 1  110.665213 1  120.000000  1   2  1  3
H    1.116935 1  110.665213 1 -120.000000  1   2  1  3
H    1.116935 1  110.665213 1   60.000000 -1   1  2  3                    Note 1
H    1.116935 1  110.665213 1  120.000000  1   1  2  6
H    1.116935 1  110.665213 1 -120.000000  1   1  2  6
0    0.000000 0    0.000000 0    0.000000  0   0  0  0
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60                                   Note 2
```

Note 1: The dihedral angle of this atom is marked with a "-1" for the optimization flag. This is the reaction coordinate. The hydrogens after the one defining the reaction coordinate have their dihedrals defined with respect to it. A change in the dihedral of this atom will rotate the entire methyl group beacuse of the way the geometry is defined. This is a common and useful way to define the geometries of methyl groups.

Note 2: The line of data at the bottom of the file gives the values which the reaction coordinate is to take on in the course of the study. The first calculation will use 60°, the second 50°, and so forth. All geometric parameters marked for optimization (except the reaction coordinate itself) will be optimized at each of these points. The archive file and output file will contain each of these results. There is considerable savings in computational effort in using the reaction coordinate method instead of a series of individual calculations, in that the density matrix from the last step in the reaction coordinate is used as the starting point for the next step. This approximation can also cause difficulties if the wavefunction becomes undefined or does not evolve rapidly enough in relation to the reaction coordinate.

Archive File (TEST09.ARC) :

This file is somewhat abbreviated to conserve space. The marker "=========" is used to show where some of the results were omitted. A complete copy of the file is found in the test suite results directory.

```
SUMMARY OF MINDO3 CALCULATION
                                    8-MAY-94
AMPAC Version  5.00
```

```
                         Presented by:

                      Semichem, Inc.
                      7128 Summit
                      Shawnee, KS  66216
                      (913) 268-3271
                      (913) 268-3445 (fax)

C 2 H 6
  Ethane rotational barrier
  MINDO3, reaction coordinate

         HEAT OF FORMATION       =   -19.856467 KCAL
         ELECTRONIC ENERGY       =  -918.454608 EV
         CORE-CORE REPULSION     =   575.247000 EV
         GRADIENT NORM           =     0.079710
         FOR REACTION COORDINATE =      60.0000 DEGREES                          Note 1
         REACTION GRADIENT       =     0.000003 KCAL/RADIAN                      Note 2
         DIPOLE                  =     0.00000 DEBYE
         NO. OF FILLED LEVELS    =     7
         IONISATION POTENTIAL    =    11.758547 EV
         MOLECULAR WEIGHT        =    30.069

         FINAL GEOMETRY OBTAINED                                CHARGE
MINDO3 PREC GRAD
  Ethane rotational barrier
  MINDO3, reaction coordinate
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0       0.0761
 C     1.477278  1    0.000000  0    0.000000  0   1  0  0       0.0761
 H     1.111359  1  113.134797  1    0.000000  0   2  1  0      -0.0254
 H     1.111359  1  113.134772  1  120.000426  1   2  1  3      -0.0254
 H     1.111359  1  113.134995  1 -119.999727  1   2  1  3      -0.0254
 H     1.111359  1  113.134875  1   60.000000 -1   1  2  3      -0.0254   Note 3
 H     1.111359  1  113.134949  1  119.999633  1   1  2  6      -0.0254
 H     1.111359  1  113.134743  1 -120.000309  1   1  2  6      -0.0254
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0

                    SUMMARY OF MINDO3 CALCULATION
                                                   8-MAY-94
                         AMPAC Version  5.00
                            Presented by:

                      Semichem, Inc.
                      7128 Summit
                      Shawnee, KS  66216
                      (913) 268-3271
                      (913) 268-3445 (fax)

C 2 H 6
  Ethane rotational barrier
  MINDO3, reaction coordinate

         HEAT OF FORMATION       =   -19.795291 KCAL
         ELECTRONIC ENERGY       =  -918.429592 EV
         CORE-CORE REPULSION     =   575.224637 EV
         GRADIENT NORM           =     0.095730
         FOR REACTION COORDINATE =      50.0000 DEGREES                          Note 4
         REACTION GRADIENT       =    -0.686435 KCAL/RADIAN
         DIPOLE                  =     0.00125 DEBYE
         NO. OF FILLED LEVELS    =     7
         IONISATION POTENTIAL    =    11.748868 EV
         MOLECULAR WEIGHT        =    30.069

         FINAL GEOMETRY OBTAINED                                CHARGE
MINDO3 PREC GRAD
  Ethane rotational barrier
  MINDO3, reaction coordinate
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0       0.0761
 C     1.477333  1    0.000000  0    0.000000  0   1  0  0       0.0761
 H     1.111371  1  113.148681  1    0.000000  0   2  1  0      -0.0253
 H     1.111220  1  113.275266  1  120.380213  1   2  1  3      -0.0249
```

```
 H     1.111533  1  113.055641  1 -119.621526  1   2  1  3      -0.0259
 H     1.111371  1  113.148581  1   50.000000 -1   1  2  3      -0.0253
 H     1.111220  1  113.274934  1  120.380021  1   1  2  6      -0.0249
 H     1.111533  1  113.056075  1 -119.622385  1   1  2  6      -0.0259
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0
```

Note 5

```
==========

                    SUMMARY OF MINDO3 CALCULATION
                                                    8-MAY-94
                         AMPAC Version  5.00
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)

C 2 H 6
  Ethane rotational barrier
  MINDO3, reaction coordinate

         HEAT OF FORMATION       =   -19.150642 KCAL
         ELECTRONIC ENERGY       =  -918.141001 EV
         CORE-CORE REPULSION     =   574.964000 EV
         GRADIENT NORM           =     0.057951
         FOR REACTION COORDINATE =      20.0000 DEGREES
         REACTION GRADIENT       =    -1.263954 KCAL/RADIAN
         DIPOLE                  =     0.00072 DEBYE
         NO. OF FILLED LEVELS    =     7
         IONISATION POTENTIAL    =    11.734457 EV
         MOLECULAR WEIGHT        =    30.069

         FINAL GEOMETRY OBTAINED                                CHARGE
MINDO3 PREC GRAD
  Ethane rotational barrier
  MINDO3, reaction coordinate
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0       0.0760
 C     1.478921  1    0.000000  0    0.000000  0   1  0  0       0.0760
 H     1.111300  1  113.376313  1    0.000000  0   2  1  0      -0.0252
 H     1.110958  1  113.543617  1  120.703866  1   2  1  3      -0.0244
 H     1.111727  1  113.186617  1 -119.318339  1   2  1  3      -0.0263
 H     1.111300  1  113.377094  1   20.000000 -1   1  2  3      -0.0252
 H     1.110959  1  113.540643  1  120.712703  1   1  2  6      -0.0244
 H     1.111726  1  113.188563  1 -119.310769  1   1  2  6      -0.0263
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0
```

Note 6

```
                    SUMMARY OF MINDO3 CALCULATION
                                                    8-MAY-94
                         AMPAC Version  5.00
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)

C 2 H 6
  Ethane rotational barrier
  MINDO3, reaction coordinate

         HEAT OF FORMATION       =   -18.970743 KCAL
         ELECTRONIC ENERGY       =  -918.067504 EV
         CORE-CORE REPULSION     =   574.898305 EV
         GRADIENT NORM           =     0.250952
         FOR REACTION COORDINATE =      10.0000 DEGREES
         REACTION GRADIENT       =    -0.743323 KCAL/RADIAN
         DIPOLE                  =     0.00033 DEBYE
```

```
         NO. OF FILLED LEVELS    =     7
         IONISATION POTENTIAL    =    11.735529 EV
         MOLECULAR WEIGHT        =    30.069

         FINAL GEOMETRY OBTAINED                                  CHARGE
MINDO3 PREC GRAD
  Ethane rotational barrier
  MINDO3, reaction coordinate
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0       0.0759
 C     1.479351  1    0.000000  0    0.000000  0   1  0  0       0.0759
 H     1.111318  1  113.415900  1    0.000000  0   2  1  0      -0.0253
 H     1.111124  1  113.513656  1  120.433575  1   2  1  3      -0.0248
 H     1.111518  1  113.326510  1 -119.560235  1   2  1  3      -0.0259
 H     1.111318  1  113.410842  1   10.000000 -1   1  2  3      -0.0253
 H     1.111123  1  113.518317  1  120.432218  1   1  2  6      -0.0248
 H     1.111519  1  113.327189  1 -119.564717  1   1  2  6      -0.0259
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0

                    SUMMARY OF MINDO3 CALCULATION
                                                      8-MAY-94
                         AMPAC Version  5.00
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)

C 2 H 6
  Ethane rotational barrier
  MINDO3, reaction coordinate

         HEAT OF FORMATION       =   -18.904110 KCAL
         ELECTRONIC ENERGY       =  -918.027781 EV
         CORE-CORE REPULSION     =   574.861471 EV
         GRADIENT NORM           =     0.113774
         FOR REACTION COORDINATE =       0.0000 DEGREES
         REACTION GRADIENT       =    -0.000659 KCAL/RADIAN
         DIPOLE                  =     0.00010 DEBYE
         NO. OF FILLED LEVELS    =     7
         IONISATION POTENTIAL    =    11.735751 EV
         MOLECULAR WEIGHT        =    30.069

         FINAL GEOMETRY OBTAINED                                  CHARGE
MINDO3 PREC GRAD
  Ethane rotational barrier
  MINDO3, reaction coordinate
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0       0.0759
 C     1.479555  1    0.000000  0    0.000000  0   1  0  0       0.0759
 H     1.111321  1  113.449678  1    0.000000  0   2  1  0      -0.0253
 H     1.111354  1  113.450902  1  119.998632  1   2  1  3      -0.0253
 H     1.111246  1  113.450431  1 -119.994599  1   2  1  3      -0.0253
 H     1.111321  1  113.450167  1    0.000000 -1   1  2  3      -0.0253
 H     1.111353  1  113.451500  1  119.993306  1   1  2  6      -0.0253
 H     1.111246  1  113.449229  1 -119.999919  1   1  2  6      -0.0253
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0

                    SUMMARY OF MINDO3 CALCULATION
                                                      8-MAY-94
                         AMPAC Version  5.00
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)

C 2 H 6
  Ethane rotational barrier
```

Note 7

```
  MINDO3, reaction coordinate

         HEAT OF FORMATION       =   -18.970765 KCAL
         ELECTRONIC ENERGY       =  -918.058952 EV
         CORE-CORE REPULSION     =   574.889751 EV
         GRADIENT NORM           =     0.173977
         FOR REACTION COORDINATE =     -10.0000 DEGREES
         REACTION GRADIENT       =     0.742158 KCAL/RADIAN                          Note 8
         DIPOLE                  =     0.00024 DEBYE
         NO. OF FILLED LEVELS    =     7
         IONISATION POTENTIAL    =    11.735502 EV
         MOLECULAR WEIGHT        =    30.069

         FINAL GEOMETRY OBTAINED                                  CHARGE
MINDO3 PREC GRAD
  Ethane rotational barrier
  MINDO3, reaction coordinate
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0       0.0760
 C     1.479327  1    0.000000  0    0.000000  0   1  0  0       0.0760
 H     1.111299  1  113.459443  1    0.000000  0   2  1  0      -0.0253
 H     1.111529  1  113.312142  1  119.597237  1   2  1  3      -0.0259
 H     1.111123  1  113.533378  1 -120.385914  1   2  1  3      -0.0248
 H     1.111302  1  113.436916  1  -10.000000 -1   1  2  3      -0.0253
 H     1.111525  1  113.326516  1  119.589563  1   1  2  6      -0.0259
 H     1.111124  1  113.541175  1 -120.418671  1   1  2  6      -0.0248
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0

==========

                    SUMMARY OF MINDO3 CALCULATION
                                                        8-MAY-94
                         AMPAC Version  5.00
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)

C 2 H 6
  Ethane rotational barrier
  MINDO3, reaction coordinate

         HEAT OF FORMATION       =   -19.856456 KCAL
         ELECTRONIC ENERGY       =  -918.446478 EV
         CORE-CORE REPULSION     =   575.238871 EV
         GRADIENT NORM           =     0.092204
         FOR REACTION COORDINATE =     -60.0000 DEGREES                              Note 9
         REACTION GRADIENT       =     0.001550 KCAL/RADIAN
         DIPOLE                  =     0.00004 DEBYE
         NO. OF FILLED LEVELS    =     7
         IONISATION POTENTIAL    =    11.758094 EV
         MOLECULAR WEIGHT        =    30.069

         FINAL GEOMETRY OBTAINED                                  CHARGE
MINDO3 PREC GRAD
  Ethane rotational barrier
  MINDO3, reaction coordinate
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0       0.0761
 C     1.477262  1    0.000000  0    0.000000  0   1  0  0       0.0761
 H     1.111393  1  113.127036  1    0.000000  0   2  1  0      -0.0254
 H     1.111413  1  113.134063  1  120.006364  1   2  1  3      -0.0254
 H     1.111377  1  113.149228  1 -119.988004  1   2  1  3      -0.0254
 H     1.111395  1  113.120510  1  -60.000000 -1   1  2  3      -0.0254
 H     1.111413  1  113.137625  1  120.009604  1   1  2  6      -0.0254
 H     1.111377  1  113.152019  1 -119.985949  1   1  2  6      -0.0254
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0
```

Note 1: The value used in the input file is the first position to which the reaction coordinate is set, in this case 60°.

Note 2: The reaction gradient is computed for each value of the reaction coordinate, and represents the slope of the energy profile along the reaction coordinate. The reaction gradient should approach zero and change sign when a transition state is crossed in the reaction coordinate. If a bond length is chosen as the reaction coordinate the units are in terms of kcal/Angstroms, otherwise they are in kcal/radian.

Note 3: While the other values in the geometry have been optimized, the reaction coordinate is not altered. Due to this constraint, this is not a valid stationary point. The gnorm value, though very low for this geometry, does not reflect any contribution from unoptimized parameters such as the reaction coordinate.

Notes 4 and 5: The reaction coordinate for the next step corresponds to the first item in the list following the blank line terminating the geometry definition.

Note 6: Several points have been omitted, but the calculation is now at a 20° torsional angle. The reaction gradient is now quite significant and is negative.

Note 7: The value of 0° for the reaction coordinate should theoretically be the very top in energy and correspond to the transition state for this process. The reaction gradient value is now almost zero, indicating that this point is very near the transition state. This is probably a good approximate geometry for the transition state, and the geometry here could now be gradient minimized using POWELL or another appropriate procedure.

Note 8: The reaction coordinate has passed over the transition state and we are now proceeding downhill. Note that the reaction gradient has changed sign. In the present case, one of the reaction coordinate values was close to the transition state and a very small value was obtained. In some cases, a sudden change from a large negative to a large positive value can be observed in a reaction gradient between two steps. An approximate transition state geometry can be interpolated from this information or a reaction coordinate with smaller intervals could be attempted.

Note 9: This is the final point of the reaction coordinate and the value corresponds to the last value in the list following the line of zeros terminating the geometry definition.

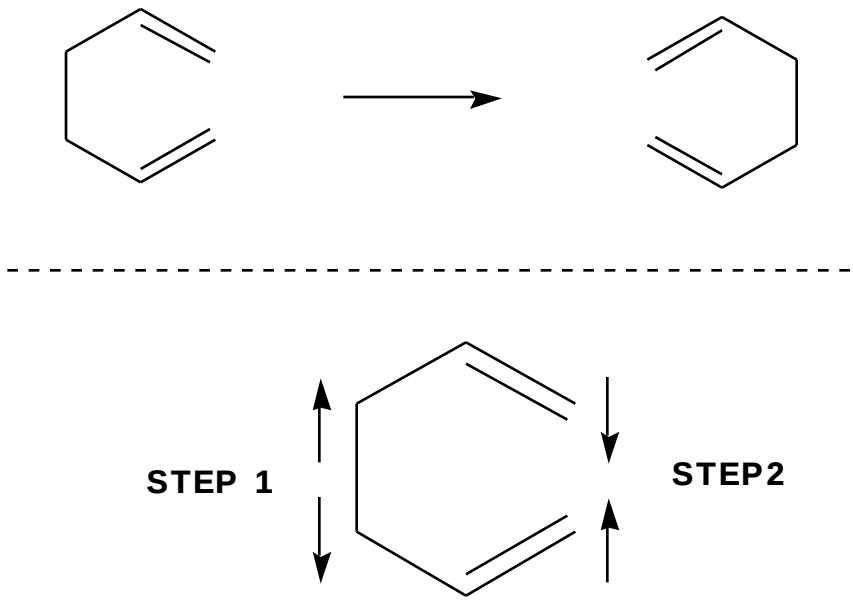
Output File (TEST09.OUT):

Due to its size, this file was not placed in the manual. It simply contains the full output as called for by the keywords in an .OUT file for each step in the reaction coordinate. A full copy may be found in the results directory of the test suite.

4.5 Two-Dimensional Grid Search

A two-dimensional grid search calculates the properties of geometries corresponding to a set of points in a grid of user-defined size in two dimensions.

In many ways, it is analogous to the reaction coordinate method described above, although two variables are changed and not as much information is provided. The final result is an 11x11 matrix of energies (121 in all) corresponding to sites on the grid. A grid search is called for if the keywords STEP1=n.n and STEP2=n.n are on the keyword line and two coordinates are marked with "-1" as the optimization flags. They are related to STEP1 and STEP2 in order of their definition. The reaction described in this file is part of the surface describing the inversion of 1,5-hexadiene:



Input File (TEST27.DAT) :

```
 AM1 PREC GRAD T=20000 STEP1=0.05 STEP2=0.05
 1,5-HEXADIENE INVERSION
 GRID
C   0.000000   0    0.000000   0    0.000000   0  0   0   0
C   1.300000   1    0.000000   0    0.000000   0  1   0   0
C   1.540000   1  130.000000   1    0.000000   0  2   1   0
C   1.540000  -1  120.000000   1    0.000000   1  3   2   1                    Note 1
C   1.540000   1  120.000000   1    0.000000   1  4   3   2
C   2.190000  -1  110.000000   1    0.000000   1  1   2   3                    Note 2
H   1.000000   1  120.000000   1   90.000000   1  1   2   3
H   1.000000   1  120.000000   1  180.000000   1  1   2   7
H   1.000000   1  120.000000   1 -180.000000   1  2   3   4
H   1.000000   1  109.500000   1  120.000000   1  3   4   5
H   1.000000   1  109.500000   1 -120.000000   1  3   4   5
H   1.000000   1  109.500000   1  120.000000   1  4   3   2
H   1.000000   1  109.500000   1 -120.000000   1  4   3   2
H   1.000000   1  120.000000   1  120.000000   1  5   4   3
H   1.000000   1  120.000000   1   90.000000   1  6   5   4
H   1.000000   1  120.000000   1  180.000000   1  6   5  15
0   0          0    0          0    0          0  0   0   0
```

Note 1: *This is the first reaction coordinate and will be incremented and decremented by the value in STEP1.*

Note 2: *This is the second reaction coordinate and will be incremented and decremented by the value in STEP2. These two items will be used to construct a grid of points and optimizations will be carried out at each point on the surface. The point given in the geometry definition is the center of the grid and five*

steps are taken in each direction from this center point. The following list shows the values that the first and second reaction coordinates will take on. The center point is indicated by ◊:

Step 1

		1.29	1.34	1.39	1.44	1.49	1.54	1.59	1.64	1.69	1.74	1.79
	1.94	•	•	•	•	•	•	•	•	•	•	•
	1.99	•	•	•	•	•	•	•	•	•	•	•
	2.04	•	•	•	•	•	•	•	•	•	•	•
S	2.09	•	•	•	•	•	•	•	•	•	•	•
t	2.14	•	•	•	•	•	•	•	•	•	•	•
e	2.19	•	•	•	•	•	◊	•	•	•	•	•
p	2.24	•	•	•	•	•	•	•	•	•	•	•
	2.29	•	•	•	•	•	•	•	•	•	•	•
2	2.34	•	•	•	•	•	•	•	•	•	•	•
	2.39	•	•	•	•	•	•	•	•	•	•	•
	2.44	•	•	•	•	•	•	•	•	•	•	•

Archive File :

No archive file is produced by grid searches.

Output File (TEST27.OUT) :

```
*******************************************************************************
                            AM1 CALCULATION RESULTS
*******************************************************************************
*                             AMPAC Version  5.00
*                                Presented by:
*
*                           Semichem, Inc.
*                           7128 Summit
*                           Shawnee, KS  66216
*                           (913) 268-3271
*                           (913) 268-3445 (fax)
*
*  STEP1    - 2-D GRID CALCULATION TO BE PERFORMED
*  PRECISE  - OPTIMIZATION CRITERIA TO BE INCREASED BY 10 TIMES,
*           -     S.C.F.   CRITERIA BY 100 TIMES,
*           - AND USE ACCURATE FINITE DIFFERENCE FORMULA IN HESSIAN
*  GRADIENTS- ALL GRADIENTS TO BE PRINTED
*   T=      - A TIME OF 20000.0 SECONDS REQUESTED
*  AM1      - THE AM1 HAMILTONIAN TO BE USED
*******************************************************************************
  AM1 PREC GRAD T=20000 STEP1=0.05 STEP2=0.05
  1,5-HEXADIENE INVERSION
  GRID
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C
     2     C          1.30000 *                                  1
     3     C          1.54000 *      130.00000 *                 2  1
     4     C          1.54000        120.00000 *     0.00000 *   3  2  1
     5     C          1.54000 *      120.00000 *     0.00000 *   4  3  2
     6     C          2.19000        110.00000 *     0.00000 *   1  2  3
     7     H          1.00000 *      120.00000 *    90.00000 *   1  2  3
     8     H          1.00000 *      120.00000 *   180.00000 *   1  2  7
     9     H          1.00000 *      120.00000 *  -180.00000 *   2  3  4
    10     H          1.00000 *      109.50000 *   120.00000 *   3  4  5
    11     H          1.00000 *      109.50000 *  -120.00000 *   3  4  5
    12     H          1.00000 *      109.50000 *   120.00000 *   4  3  2
```

```
   13     H          1.00000 *      109.50000 *  -120.00000 *   4  3  2
   14     H          1.00000 *      120.00000 *   120.00000 *   5  4  3
   15     H          1.00000 *      120.00000 *    90.00000 *   6  5  4
   16     H          1.00000 *      120.00000 *   180.00000 *   6  5 15

         CARTESIAN COORDINATES
  NO.       ATOM         X         Y         Z
   1         6        0.0000    0.0000    0.0000
   2         6        1.3000    0.0000    0.0000
   3         6        2.2899    1.1797    0.0000
   4         6        1.7632    2.6268    0.0000
   5         6        0.2466    2.8943    0.0000
   6         6       -0.7490    2.0579    0.0000
   7         1       -0.5000    0.0000   -0.8660
   8         1       -0.5000    0.0000    0.8660
   9         1        1.6420   -0.9397    0.0000
  10         1        2.8470    1.0272   -0.8164
  11         1        2.8470    1.0272    0.8164
  12         1        2.0919    3.1017    0.8164
  13         1        2.0919    3.1017   -0.8164
  14         1       -0.1706    3.4075    0.7500
  15         1       -1.1319    1.7363    0.8660
  16         1       -1.1319    1.7363   -0.8660
         SINGLET STATE CALCULATION
         RHF CALCULATION, No. OF DOUBLY OCCUPIED LEVELS = 17
 H  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
 C  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)

           INTERATOMIC DISTANCES
              C   1      C   2      C   3      C   4      C   5      C   6
-------------------------------------------------------------------------------
   C   1   0.000000
   C   2   1.300000   0.000000
   C   3   2.575912   1.540000   0.000000
   C   4   3.163712   2.667358   1.540000   0.000000
   C   5   2.904738   3.080000   2.667358   1.540000   0.000000
   C   6   2.190000   2.904060   3.163271   2.575817   1.300256   0.000000
   H   7   1.000000   1.997498   3.150431   3.573829   3.111926   2.246570
   H   8   1.000000   1.997498   3.150431   3.573829   3.111926   2.246570
   H   9   1.891891   1.000000   2.216213   3.568585   4.080000   3.834425
   H  10   3.134774   2.028477   1.000000   2.097552   3.303660   3.828818
   H  11   3.134774   2.028477   1.000000   2.097552   3.303660   3.828818
   H  12   3.829247   3.303660   2.097552   1.000000   2.028477   3.134776
   H  13   3.829247   3.303660   2.097552   1.000000   2.028477   3.134776
   H  14   3.493244   3.786344   3.402911   2.216213   1.000000   1.648761
   H  15   2.246322   3.111082   3.573276   3.150293   1.997729   1.000000
   H  16   2.246322   3.111082   3.573276   3.150293   1.997729   1.000000
              H   7      H   8      H   9      H  10      H  11      H  12
-------------------------------------------------------------------------------
   H   7   0.000000
   H   8   1.732051   0.000000
   H   9   2.494248   2.494248   0.000000
   H  10   3.501401   3.884293   2.446856   0.000000
   H  11   3.884293   3.501401   2.446856   1.632703   0.000000
   H  12   4.378242   4.042410   4.147503   2.745774   2.207614   0.000000
   H  13   4.042410   4.378242   4.147503   2.207614   2.745774   1.632703
   H  14   3.785651   3.425358   4.769319   4.150306   3.843955   2.284080
   H  15   2.532606   1.847726   3.950387   4.377705   4.041828   3.501360
   H  16   1.847726   2.532606   3.950387   4.041828   4.377705   3.884256
              H  13      H  14      H  15      H  16
-----------------------------------------------------
   H  13   0.000000
   H  14   2.768768   0.000000
   H  15   3.884256   1.931399   0.000000
   H  16   3.501360   2.515627   1.732051   0.000000
  FIRST VARIABLE   SECOND VARIABLE   FUNCTION
USE 2-POINT FORMULA IN INTEGRAL DERIVATIVES WITH STEP  0.00002000
STANDARD DEVIATION ON ENERGY   (KCAL)        0.000001494
STANDARD DEVIATION ON GRADIENT (KCAL/A,RD,RD)  0.0000598 0.0001244 0.0001109
:         1.29000         1.94000    87.313190                                  Note 1
:         1.29000         1.99000    84.029957
```

```
:        1.29000        2.04000    80.657898
:        1.29000        2.09000    77.334497
:        1.29000        2.14000    74.171138
:        1.29000        2.19000    71.248889
:        1.29000        2.24000    68.615763
:        1.29000        2.29000    66.291325
:        1.29000        2.34000    64.272173
:        1.29000        2.39000    62.539505
:        1.29000        2.44000    61.064178
:        1.34000        2.44000    46.437659
:        1.34000        2.39000    47.857351
:        1.34000        2.34000    49.530154
:        1.34000        2.29000    51.485933
:        1.34000        2.24000    53.744614
:        1.34000        2.19000    56.309941
:        1.34000        2.14000    59.162672
:        1.34000        2.09000    62.254261
:        1.34000        2.04000    65.504362
:        1.34000        1.99000    68.800249
:        1.34000        1.94000    72.003872
:        1.39000        1.94000    61.344627
:        1.39000        1.99000    58.229769
:        1.39000        2.04000    55.017238
:        1.39000        2.09000    51.846016
:        1.39000        2.14000    48.829965
:        1.39000        2.19000    46.050223
:        1.39000        2.24000    43.555065
:        1.39000        2.29000    41.364305
:        1.39000        2.34000    39.473163
:        1.39000        2.39000    37.861088
:        1.39000        2.44000    36.497953
:        1.44000        2.44000    30.389974
:        1.44000        2.39000    31.695547
:        1.44000        2.34000    33.245282
:        1.44000        2.29000    35.070027
:        1.44000        2.24000    37.190877
:        1.44000        2.19000    39.612521
:        1.44000        2.14000    42.315698
:        1.44000        2.09000    45.251376
:        1.44000        2.04000    48.337052
:        1.44000        1.99000    51.457655
:        1.44000        1.94000    54.472340
:        1.49000        1.94000    50.608477
:        1.49000        1.99000    47.707744
:        1.49000        2.04000    44.689844
:        1.49000        2.09000    41.697834
:        1.49000        2.14000    38.848807
:        1.49000        2.19000    36.226876
:        1.49000        2.24000    33.882061
:        1.49000        2.29000    31.833798
:        1.49000        2.34000    30.077449
:        1.49000        2.39000    28.591490
:        1.49000        2.44000    27.344714
:        1.54000        2.44000    26.678221
:        1.54000        2.39000    27.864615
:        1.54000        2.34000    29.284734
:        1.54000        2.29000    30.970111
:        1.54000        2.24000    32.942367
:        1.54000        2.19000    35.206105                                    Note 2
:        1.54000        2.14000    37.741093
:        1.54000        2.09000    40.495800
:        1.54000        2.04000    43.383968
:        1.54000        1.99000    46.285845
:        1.54000        1.94000    49.055120
:        1.59000        1.94000    49.194306
:        1.59000        1.99000    46.578648
:        1.59000        2.04000    43.809682
:        1.59000        2.09000    41.038015
:        1.59000        2.14000    38.387139
:        1.59000        2.19000    35.946359
:        1.59000        2.24000    33.769180
```

```
:         1.59000         2.29000    31.877049
:         1.59000         2.34000    30.265958
:         1.59000         2.39000    28.914286
:         1.59000         2.44000    27.790396
:         1.64000         2.44000    30.166135
:         1.64000         2.39000    31.224770
:         1.64000         2.34000    32.504684
:         1.64000         2.29000    34.037386
:         1.64000         2.24000    35.844102
:         1.64000         2.19000    37.927888
:         1.64000         2.14000    40.265431
:         1.64000         2.09000    42.800287
:         1.64000         2.04000    45.439413
:         1.64000         1.99000    48.053916
:         1.64000         1.94000    50.487296
:         1.69000         1.94000    52.473180
:         1.69000         1.99000    50.259308
:         1.69000         2.04000    47.827180
:         1.69000         2.09000    45.341474
:         1.69000         2.14000    42.937963
:         1.69000         2.19000    40.715177
:         1.69000         2.24000    38.733498
:         1.69000         2.29000    37.018841
:         1.69000         2.34000    35.569757
:         1.69000         2.39000    34.365879
:         1.69000         2.44000    33.375990
:         1.74000         2.44000    37.075603
:         1.74000         2.39000    37.992280
:         1.74000         2.34000    39.114817
:         1.74000         2.29000    40.473652
:         1.74000         2.24000    42.087804
:         1.74000         2.19000    43.956315
:         1.74000         2.14000    46.049573
:         1.74000         2.09000    48.301876
:         1.74000         2.04000    50.607201
:         1.74000         1.99000    52.820182
:         1.74000         1.94000    54.764860
:         1.79000         1.94000    57.041292
:         1.79000         1.99000    55.432796
:         1.79000         2.04000    53.488298
:         1.79000         2.09000    51.399058
:         1.79000         2.14000    49.323941
:         1.79000         2.19000    47.379237
:         1.79000         2.24000    45.638088
:         1.79000         2.29000    44.135234
:         1.79000         2.34000    42.874998
:         1.79000         2.39000    41.840455
:         1.79000         2.44000    41.002458

         HORIZONTAL: VARYING SECOND PARAMETER,
         VERTICAL:   VARYING FIRST PARAMETER
         WHOLE OF GRID, SUITABLE FOR PLOTTING

 87.31  72.00  61.34  54.47  50.61  49.06  49.19  50.49  52.47  54.76  57.04
 84.03  68.80  58.23  51.46  47.71  46.29  46.58  48.05  50.26  52.82  55.43
 80.66  65.50  55.02  48.34  44.69  43.38  43.81  45.44  47.83  50.61  53.49
 77.33  62.25  51.85  45.25  41.70  40.50  41.04  42.80  45.34  48.30  51.40
 74.17  59.16  48.83  42.32  38.85  37.74  38.39  40.27  42.94  46.05  49.32
 71.25  56.31  46.05  39.61  36.23  35.21  35.95  37.93  40.72  43.96  47.38
 68.62  53.74  43.56  37.19  33.88  32.94  33.77  35.84  38.73  42.09  45.64
 66.29  51.49  41.36  35.07  31.83  30.97  31.88  34.04  37.02  40.47  44.14
 64.27  49.53  39.47  33.25  30.08  29.28  30.27  32.50  35.57  39.11  42.87
 62.54  47.86  37.86  31.70  28.59  27.86  28.91  31.22  34.37  37.99  41.84
 61.06  46.44  36.50  30.39  27.34  26.68  27.79  30.17  33.38  37.08  41.00
FULL COMPUTATION TIME :  5628.990 SECONDS
```

Note 3

Note 1: This is a list of the AM1 energies of the optimized geometries at each pair of STEP1, STEP2 coordinates. Due to the size of the output, the geometries are not printed. This information may be obtained by increasing the print level (see

keyword PRINT=). A more efficient method may be to simply do a single calculation on the point of interest located on the grid.

Note 2: This is the center point of the grid.

Note 3: This is an 11x11 matrix of the energies at the points in the order described above. Future versions of the AMPAC GUI will present this data in graphical form.

4.6 CHAIN Calculation

Input File (TEST20.DAT) :

```
AM1 CHAIN CYCLES=1000 T=20000 PREC GRAD
ETHANE ROTATIONAL BARRIER
AM1 CHAIN
 C    0.000000 0    0.000000 0    0.000000  0   0  0  0                                    Note 1
 C    1.544846 1    0.000000 0    0.000000  0   1  0  0
 H    1.116935 1  110.665270 1    0.000000  0   2  1  0
 H    1.116935 1  110.665213 1  120.000000  1   2  1  3
 H    1.116935 1  110.665213 1 -120.000000  1   2  1  3
 H    1.116935 1  110.665213 1   10.000000  1   1  2  3
 H    1.116935 1  110.665213 1  120.000000  1   1  2  6
 H    1.116935 1  110.665213 1 -120.000000  1   1  2  6
 0    0.000000 0    0.000000 0    0.000000  0   0  0  0
 C    0.000000 0    0.000000 0    0.000000  0   0  0  0                                    Note 2
 C    1.544846 1    0.000000 0    0.000000  0   1  0  0
 H    1.116935 1  110.665270 1    0.000000  0   2  1  0
 H    1.116935 1  110.665213 1  120.000000  1   2  1  3
 H    1.116935 1  110.665213 1 -120.000000  1   2  1  3
 H    1.116935 1  110.665213 1   60.000000  1   1  2  3
 H    1.116935 1  110.665213 1  120.000000  1   1  2  6
 H    1.116935 1  110.665213 1 -120.000000  1   1  2  6
 0    0.000000 0    0.000000 0    0.000000  0   0  0  0
 C    0.000000 0    0.000000 0    0.000000  0   0  0  0                                    Note 3
 C    1.544846 1    0.000000 0    0.000000  0   1  0  0
 H    1.116935 1  110.665270 1    0.000000  0   2  1  0
 H    1.116935 1  110.665213 1  120.000000  1   2  1  3
 H    1.116935 1  110.665213 1 -120.000000  1   2  1  3
 H    1.116935 1  110.665213 1  -60.000000  1   1  2  3
 H    1.116935 1  110.665213 1  120.000000  1   1  2  6
 H    1.116935 1  110.665213 1 -120.000000  1   1  2  6
 0    0.000000 0    0.000000 0    0.000000  0   0  0  0
```

Note 1: This is the geometry of the approximate transition state. Note that the dihedral is set at 10° which is somewhat different than the expected 0°. The geometry of this transition state guess is not critical. It is provided in order to give CHAIN an idea as to the path to follow in transforming the left minima to the right minima. Different mechanisms for a reaction involving the same reactants and products may be studied by defining different paths for CHAIN to follow based on the mode of transformation. Note carefully that it is required that the three geometries share the same connectivity pattern. The dihedral angles of the three geometries must also remain coherent throughout the calculation. This means that all dihedrals must smoothly pass from the left to guess to right geometries without generating any ambiguity in the exact determination the geometry from the input. This is usually accomplished by carefully considering the values through which the dihedrals will pass in the cahin search and ensuring that there are no possible questions by using the proper sign conventions (see Section 2.3). Additional input required by other keywords such

as symmetry constraints and so forth are entered at the end of this section before the other two minima are defined.

Note 2: *The geometry specification of the left minima is provided.*

Note 3: *The geometry specification of the right minima is provided.*

Archive File (TEST20.ARC) :

```
                    SUMMARY OF AM1 CALCULATION
                                                        8-MAY-94
                         AMPAC Version  5.00
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)
C 2 H 6
 ETHANE ROTATIONAL BARRIER
 AM1 CHAIN

    GEOMETRY OPTIMISED : GRADIENT NORM MINIMISED
    SCF FIELD WAS ACHIEVED

         HEAT OF FORMATION       =   -16.166993 KCAL
         ELECTRONIC ENERGY       =  -929.926141 EV
         CORE-CORE REPULSION     =   590.838371 EV
         GRADIENT NORM           =     0.188401
         DIPOLE                  =     0.00004 DEBYE
         NO. OF FILLED LEVELS    =     7
         IONISATION POTENTIAL    =    11.729103 EV
         MOLECULAR WEIGHT        =     6.008
         SCF CALCULATIONS        =    86
         COMPUTATION TIME        =    20.86 SECONDS

         FINAL GEOMETRY OBTAINED                          CHARGE
 AM1 CHAIN CYCLES=1000 T=20000 PREC GRAD
 ETHANE ROTATIONAL BARRIER
 AM1 CHAIN
 C  0.000000  0    0.000000  0    0.000000  0   0  0  0   -0.2114                                Note
 C  1.503330  1    0.000000  0    0.000000  0   1  0  0   -0.2114
 H  1.116973  1  111.055362  1    0.000000  0   2  1  0    0.0705
 H  1.117022  1  111.045098  1  119.960606  1   2  1  3    0.0704
 H  1.116951  1  111.059647  1 -120.042842  1   2  1  3    0.0705
 H  1.116981  1  111.053318  1   -1.431509  1   1  2  3    0.0705
 H  1.117027  1  111.043390  1  119.946712  1   1  2  6    0.0704
 H  1.116935  1  111.063433  1 -120.052934  1   1  2  6    0.0705
 0  0.000000  0    0.000000  0    0.000000  0   0  0  0
```

Note: The geometry in the archive file is the geometry of the transition state located by CHAIN.

Output File (TEST20.OUT) :

```
*******************************************************************************
                            AM1 CALCULATION RESULTS
*******************************************************************************
*                             AMPAC Version  5.00
*                                Presented by:
*
*                           Semichem, Inc.
*                           7128 Summit
*                           Shawnee, KS  66216
*                           (913) 268-3271
```

```
*                          (913) 268-3445 (fax)
*
*  CHAIN    - TRANSITION STATE TO BE LOCATED
*  CYCLES=  - DO A MAXIMUM OF 1000 CYCLES IN OPTIMIZATION
*  PRECISE  - OPTIMIZATION CRITERIA TO BE INCREASED BY 10 TIMES,
*           -     S.C.F.   CRITERIA BY 100 TIMES,
*           - AND USE ACCURATE FINITE DIFFERENCE FORMULA IN HESSIAN
*  GRADIENTS- ALL GRADIENTS TO BE PRINTED
*   T=      - A TIME OF 20000.0 SECONDS REQUESTED
*  AM1      - THE AM1 HAMILTONIAN TO BE USED
*****************************************************************************
AM1 CHAIN CYCLES=1000 T=20000 PREC GRAD
 ETHANE ROTATIONAL BARRIER
 AM1 CHAIN
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C
     2     C          1.54485 *                                  1
     3     H          1.11694 *      110.66527 *                 2  1
     4     H          1.11694 *      110.66521 *   120.00000 *   2  1  3
     5     H          1.11694 *      110.66521 *  -120.00000 *   2  1  3
     6     H          1.11694 *      110.66521 *    10.00000 *   1  2  3
     7     H          1.11694 *      110.66521 *   120.00000 *   1  2  6
     8     H          1.11694 *      110.66521 *  -120.00000 *   1  2  6

         CARTESIAN COORDINATES
   NO.       ATOM         X         Y         Z
    1         6        0.0000    0.0000    0.0000
    2         6        1.5448    0.0000    0.0000
    3         1        1.9390    1.0451    0.0000
    4         1        1.9390   -0.5225    0.9051
    5         1        1.9390   -0.5225   -0.9051
    6         1       -0.3942    1.0292   -0.1815
    7         1       -0.3942   -0.6718   -0.8006
    8         1       -0.3942   -0.3574    0.9820
         SINGLET STATE CALCULATION
         RHF CALCULATION, No. OF DOUBLY OCCUPIED LEVELS =  7
 H  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
 C  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)

           INTERATOMIC DISTANCES
              C   1      C   2      H   3      H   4      H   5      H   6
-----------------------------------------------------------------------------
   C   1   0.000000
   C   2   1.544846   0.000000
   H   3   2.202719   1.116935   0.000000
   H   4   2.202719   1.116935   1.810113   0.000000
   H   5   2.202719   1.116935   1.810113   1.810114   0.000000
   H   6   1.116935   2.202719   2.340296   3.005362   2.893998   0.000000
   H   7   1.116935   2.202719   3.005363   2.893998   2.340295   1.810114
   H   8   1.116935   2.202719   2.893999   2.340295   3.005362   1.810114
              H   7      H   8
-----------------------------
   H   7   0.000000
   H   8   1.810114   0.000000
TIME ALLOWED FOR THIS RUN:  20000.00 SECONDS
SADDLE POINT RESEARCH ... CHAIN METHOD, VERSION 3.0 (1991)
        DISCRIMINATION ANGLE: 30.0 DEGREES       LINK SIZE: 0.292
        DIMENSION: 18     MAX. OF CYCLES:1000
        RMS-G CV THRESHOLD: 1.0D-01          PRINTOUT LEVEL:  0
COORDINATES OF MINIMA AND INTERMEDIATE POINT:
  N      LEFT MINI   INTERMEDIATE   RIGHT MINI

   1      1.544846      1.544846      1.544846                                    Note 1
   2      1.116935      1.116935      1.116935
   3      1.931473      1.931473      1.931473
   4      1.116935      1.116935      1.116935
   5      1.931472      1.931472      1.931472
   6      2.094395      2.094395      2.094395
   7      1.116935      1.116935      1.116935
```

```
   8      1.931472      1.931472      1.931472
   9     -2.094395     -2.094395     -2.094395
  10      1.116935      1.116935      1.116935
  11      1.931472      1.931472      1.931472
  12      1.047198      0.174533     -1.047198
  13      1.116935      1.116935      1.116935
  14      1.931472      1.931472      1.931472
  15      2.094395      2.094395      2.094395
  16      1.116935      1.116935      1.116935
  17      1.931472      1.931472      1.931472
  18     -2.094395     -2.094395     -2.094395

ENERGY   -1.6495D+01   -1.5502D+01   -1.6495D+01                                  Note 2

USE 2-POINT FORMULA IN INTEGRAL DERIVATIVES WITH STEP  0.00002000                  Note 3
STANDARD DEVIATION ON ENERGY   (KCAL)        0.000001493
STANDARD DEVIATION ON GRADIENT (KCAL/A,RD,RD)  0.0000415 0.0000295 0.0000397
THE HESSIAN BECOMES OF INDEX 1 AT CYCLE  17
CHAIN CONVERGED AFTER  83 CALLS TO ENERGY  37 OF WHICH WITH GRADIENT
CYCLE  18 HIGHEST POINT...ENERGY: -1.61669928D+01   RMS-G: 4.44D-02
<G|G>:  3.5495D-02   INDEX:   1   CHAIN LENGTH...  LEFT: 4 RIGHT: 5
VARIABLES:  1.5033  1.1170  1.9383  1.1170  1.9381  2.0937  1.1170  1.9384
           -2.0951  1.1170  1.9382 -0.0250  1.1170  1.9381  2.0935  1.1169
            1.9384 -2.0953
GRADIENT :   -0.09    0.02    0.02    0.03    0.02    0.02    0.02    0.02
              0.01    0.02    0.02    0.15    0.02    0.03    0.01    0.02
              0.02    0.01
EIGENVALUES AND EIGENVECTORS OF THE HESSIAN                                         Note 4
 1 -4.1610D+00: -0.0046  0.0006  0.0076 -0.0002  0.0113  0.0318  0.0022  0.0012
                 0.0304  0.0009  0.0066  0.9982  0.0000  0.0105  0.0255  0.0017
                 0.0030  0.0257
 2  4.8488D+01:  0.0004 -0.0056  0.0370 -0.0259  0.1757  0.6903  0.0337 -0.2103
                 0.6559  0.0002  0.0015 -0.0482 -0.0034  0.0151  0.0769  0.0033
                -0.0151  0.0786
 LEFT CHAIN, LENGTH:  4     ENERGY AND VARIABLES ...                                Note 5
-1.649465D+01 :  1.5448  1.1169  1.9315  1.1169  1.9315  2.0944  1.1169  1.9315
                -2.0944  1.1169  1.9315  1.0472  1.1169  1.9315  2.0944  1.1169
                 1.9315 -2.0944
-1.630683D+01 :  1.5448  1.1169  1.9315  1.1169  1.9315  2.0944  1.1169  1.9315
                -2.0944  1.1169  1.9315  0.7563  1.1169  1.9315  2.0944  1.1169
                 1.9315 -2.0944
-1.665409D+01 :  1.5032  1.1147  1.9296  1.1147  1.9296  2.0950  1.1147  1.9296
                -2.0938  1.1147  1.9296  0.4684  1.1147  1.9296  2.0950  1.1147
                 1.9296 -2.0938
-1.621037D+01 :  1.5052  1.1147  1.9301  1.1147  1.9301  2.0947  1.1147  1.9301
                -2.0941  1.1147  1.9301  0.1778  1.1147  1.9301  2.0947  1.1147
                 1.9301 -2.0941
RIGHT CHAIN, LENGTH:  5     ENERGY AND VARIABLES ...                                Note 6
-1.623592D+01 :  1.5038  1.1158  1.9341  1.1159  1.9340  2.0938  1.1158  1.9341
                -2.0950  1.1158  1.9341 -0.1712  1.1159  1.9340  2.0937  1.1158
                 1.9342 -2.0951
-1.638983D+01 :  1.5044  1.1147  1.9299  1.1147  1.9299  2.0939  1.1147  1.9299
                -2.0949  1.1147  1.9299 -0.3175  1.1147  1.9299  2.0939  1.1147
                 1.9299 -2.0949
-1.683499D+01 :  1.5038  1.1148  1.9295  1.1148  1.9295  2.0938  1.1148  1.9295
                -2.0950  1.1148  1.9295 -0.5620  1.1148  1.9295  2.0938  1.1148
                 1.9295 -2.0950
-1.635970D+01 :  1.5448  1.1169  1.9315  1.1169  1.9315  2.0944  1.1169  1.9315
                -2.0944  1.1169  1.9315 -0.8029  1.1169  1.9315  2.0944  1.1169
                 1.9315 -2.0944
-1.649465D+01 :  1.5448  1.1169  1.9315  1.1169  1.9315  2.0944  1.1169  1.9315
                -2.0944  1.1169  1.9315 -1.0472  1.1169  1.9315  2.0944  1.1169
                 1.9315 -2.0944
AM1 CHAIN CYCLES=1000 T=20000 PREC GRAD
 ETHANE ROTATIONAL BARRIER
 AM1 CHAIN

    GEOMETRY OPTIMISED : GRADIENT NORM MINIMISED
    SCF FIELD WAS ACHIEVED
```

```
                              AM1    CALCULATION
                                                          VERSION  5.00

        FINAL HEAT OF FORMATION =   -16.166993 KCAL
        ELECTRONIC ENERGY       =  -929.926141 EV
        CORE-CORE REPULSION     =   590.838371 EV
        GRADIENT NORM           =     0.188401
        IONISATION POTENTIAL    =    11.729103 EV
        NO. OF FILLED LEVELS    =     7
        MOLECULAR WEIGHT        =     6.008
        SCF CALCULATIONS        =   86
        COMPUTATION TIME=        26.50 SECONDS
                                                        8-MAY-94

     FINAL  POINT  AND  DERIVATIVES
  PARAMETER     ATOM    TYPE            VALUE       GRADIENT
     1          2 C     BOND            1.503330    -0.087283  KCAL/ANGSTROM
     2          3 H     BOND            1.116973     0.016795  KCAL/ANGSTROM
     3          3 H     ANGLE         111.055362     0.024860  KCAL/RADIAN
     4          4 H     BOND            1.117022     0.025001  KCAL/ANGSTROM
     5          4 H     ANGLE         111.045098     0.024492  KCAL/RADIAN
     6          4 H     DIHEDRAL      119.960606     0.019441  KCAL/RADIAN
     7          5 H     BOND            1.116951     0.020033  KCAL/ANGSTROM
     8          5 H     ANGLE         111.059647     0.018319  KCAL/RADIAN
     9          5 H     DIHEDRAL     -120.042842     0.013642  KCAL/RADIAN
    10          6 H     BOND            1.116981     0.019920  KCAL/ANGSTROM
    11          6 H     ANGLE         111.053318     0.022440  KCAL/RADIAN
    12          6 H     DIHEDRAL       -1.431509     0.146783  KCAL/RADIAN
    13          7 H     BOND            1.117027     0.023383  KCAL/ANGSTROM
    14          7 H     ANGLE         111.043390     0.025585  KCAL/RADIAN
    15          7 H     DIHEDRAL      119.946712     0.007378  KCAL/RADIAN
    16          8 H     BOND            1.116935     0.017006  KCAL/ANGSTROM
    17          8 H     ANGLE         111.063433     0.019801  KCAL/RADIAN
    18          8 H     DIHEDRAL     -120.052934     0.008242  KCAL/RADIAN
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C
     2     C          1.50333 *                                  1
     3     H          1.11697 *      111.05536 *                 2  1
     4     H          1.11702 *      111.04510 *   119.96061 *   2  1  3
     5     H          1.11695 *      111.05965 *  -120.04284 *   2  1  3
     6     H          1.11698 *      111.05332 *    -1.43151 *   1  2  3
     7     H          1.11703 *      111.04339 *   119.94671 *   1  2  6
     8     H          1.11694 *      111.06343 *  -120.05293 *   1  2  6

        INTERATOMIC DISTANCES
             C   1      C   2      H   3      H   4      H   5      H   6
-------------------------------------------------------------------------------
   C   1   0.000000
   C   2   1.503330   0.000000
   H   3   2.171218   1.116973   0.000000
   H   4   2.171125   1.117022   1.805227   0.000000
   H   5   2.171254   1.116951   1.805830   1.805510   0.000000
   H   6   1.116981   2.171198   2.306032   2.920250   2.936865   0.000000
   H   7   1.117027   2.171108   2.920172   2.936974   2.305958   1.805135
   H   8   1.116935   2.171290   2.936963   2.306050   2.920100   1.805905
             H   7      H   8
------------------------------
   H   7   0.000000
   H   8   1.805524   0.000000

                EIGENVALUES
-33.15930 -23.63347 -14.88288 -14.88246 -13.17992 -11.72953 -11.72910   4.07172
  4.07199   4.68899   4.93993   5.06654   5.06680   5.24652

        NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS
       ATOM NO.   TYPE          CHARGE        ATOM  ELECTRON DENSITY
         1         C           -0.2114          4.2114
         2         C           -0.2114          4.2114
         3         H            0.0705          0.9295
```

Note 7

```
          4         H            0.0704          0.9296
          5         H            0.0705          0.9295
          6         H            0.0705          0.9295
          7         H            0.0704          0.9296
          8         H            0.0705          0.9295
DIPOLE (DEBYE)   X         Y         Z       TOTAL
POINT-CHG.     0.000     0.000     0.000     0.000
HYBRID         0.000     0.000     0.000     0.000
SUM            0.000     0.000     0.000     0.000

         CARTESIAN COORDINATES
   NO.       ATOM               X         Y         Z
    1        C                   0.0000    0.0000    0.0000
    2        C                   1.5033    0.0000    0.0000
    3        H                   1.9046    1.0424    0.0000
    4        H                   1.9045   -0.5206    0.9032
    5        H                   1.9047   -0.5218   -0.9023
    6        H                  -0.4013    1.0421    0.0260
    7        H                  -0.4011   -0.4977   -0.9161
    8        H                  -0.4014   -0.5444    0.8889

         ATOMIC ORBITAL ELECTRON POPULATIONS
  1.22186   0.95745   1.01606   1.01607   1.22186   0.95745   1.01606   1.01607
  0.92951   0.92957   0.92947   0.92952   0.92958   0.92946
FULL COMPUTATION TIME :    26.550 SECONDS
```

NOTE 1: These are the geometries of the three molecules provided in the data file. They are ordered by the definition of the variables in the input file. Bond lengths are in Angstroms and angles are in radians.

NOTE 2: These are the initial energies in kcal/mol of the three geometries as predicted by AM1.

NOTE 3: This section of the output summarizes the numerical algorithms and convergence criteria used in the calculation. This will vary depending on whether or not PRECISE is used.

NOTE 4: These are final results on the located saddle point. At this point, the Hessian will usually possess one negative eigenvalue, and the eigenvector associated with it corresponds to a good estimate of the transition vector.

NOTE 5: This part of the output lists those points finally generated between the transition state and the left minima. These points define a continuous path between the transition state and the minima.

NOTE 6: This part of the output lists those points finally generated between the transition state and the right minima. These points define a continuous path between the transition state and the minima.

NOTE 7: The summary section deals with the located transition state.

4.7 PATH Calculation with Transition Vector

The PATH algorithm in AMPAC is designed to follow the steepest descent path from a point on the potential surface to its conclusion. It performs this numerical task by integrating the reaction path and following the force it is

supplied with or that it detects (see Section 5.10 for a discussion on the theory of integrating reaction pathways). The PATH technique is useful for several tasks:

1. *Following an identified T.V. to determine if the transition state that has been located corresponds to the reaction mechanism and products desired. This is also important in that the reverse of the T.V. should also be followed to reactants to ensure that it does correspond to a pathway between reactants and products.*

2. *Following other negative eigenvalues to refine a transition state by eliminating spurious vibrations. PATH is very efficient at this, one of the most difficult obstacles in the computational study of transition states and reaction mechanisms.*

3. *To computationally explore the results of selectively exciting a particular vibrational mode by some experimental technique.*

4. *To locate a weak intermediate between a transition state and a minima.*

The example that will be used to illustrate the use of PATH is the conrotary cyclization of 1,3-butadiene.

Input File (TEST38.DAT) :

```
  AM1 PRECISE PATH T=3595 GRAD T.V. WEIGHT
  Conrotary cyclization TS
  PATH, path oriented toward products
C     0.000000  0    0.000000  0    0.000000  0   0  0  0      -0.1709                 Note 1
C     1.388681  1    0.000000  0    0.000000  0   1  0  0      -0.1708
C     1.427616  1  103.838361  1    0.000000  0   2  1  0      -0.1858
C     1.427758  1  103.826319  1  -18.665140  1   1  2  3      -0.1858
H     1.088191  1  129.204926  1  154.433803  1   1  2  3       0.1383
H     1.088194  1  129.190066  1  154.437643  1   2  1  4       0.1382
H     1.095941  1  121.105676  1  136.752600  1   4  1  2       0.0989
H     1.095943  1  121.109463  1  136.761344  1   3  2  1       0.0989
H     1.098242  1  120.317329  1  -65.107436  1   4  1  2       0.1195
H     1.098255  1  120.313896  1  -65.097794  1   3  2  1       0.1195
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0
 1.0000  1.0000  3.0000  1.0000  3.0000  1.0000  1.0000  1.0000  1.0000                Note 2
 1.0000  1.0000  1.0000  1.0000  1.0000  1.0000  1.0000  1.0000  1.0000
 1.0000  1.0000  3.0000  1.0000  1.0000  3.0000
-0.1790  0.2050 -0.4960  0.2050 -0.4960 -0.1740 -0.0165  0.1160  0.1010        Note 3
-0.0166  0.1160  0.1000 -0.0083 -0.0021 -0.1230 -0.0084  0.0021 -0.1230
 0.0020 -0.0567 -0.3710  0.0200 -0.0567 -0.3710
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0
```

Note 1: *The geometry provided to PATH is the transition state geometry.*

Note 2: *These are the weights of the transition vector components, and are supplied because the keyword WEIGHT was specified. The weights are paired exactly with the components below. Note that four of the components have a weight value of 3.0000. These are the largest components of the T.V. and movement in this direction is emphasized by enhancing the weights in this manner.*

Note 3: *This is the oriented transition vector (T.V.) in internal coordinates as requested by the T.V. keyword. This information may be obtained from an LTRD calculation, such as was performed on this system in Section 4.3 (see Note 9*

on the output file). The first eigenvector in that list corresponds to the transition vector and has the following values:

```
  1  1.79D-01 -2.05D-01  4.96D-01 -2.05D-01  4.96D-01  1.74D-01  1.66D-02
    -1.16D-01 -1.01D-01  1.62D-02 -1.16D-01 -1.01D-01  8.98D-03 -2.03D-03
     1.23D-01  8.61D-03 -2.11D-03  1.23D-01 -1.99D-02  5.66D-02  3.71D-01
    -1.99D-02  5.67D-02  3.71D-01
```

In this input file, the "phase" of the T.V. has been reversed by reversing the signs of each component. As PATH follows this T.V., it will optimize to the products. If the output phase above is used, PATH will optimize to the reactants.

Archive File (TEST38.ARC) :

```
                    SUMMARY OF   AM1   CALCULATION
                                                    9-MAY-94
                         AMPAC Version  5.00
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)

C 4 H 6
   Conrotary cyclization TS
   PATH, path oriented toward products

    GEOMETRY OPTIMISED : GRADIENT NORM MINIMISED
    SCF FIELD WAS ACHIEVED

         HEAT OF FORMATION       =    45.832728 KCAL
         ELECTRONIC ENERGY       = -1985.331527 EV
         CORE-CORE REPULSION     =  1392.479986 EV
         GRADIENT NORM           =     1.780956
         DIPOLE                  =     0.16645 DEBYE
         NO. OF FILLED LEVELS    =    11
         IONISATION POTENTIAL    =     9.717794 EV
         MOLECULAR WEIGHT        =    54.091
         SCF CALCULATIONS        =    207
         COMPUTATION TIME        =   130.92 SECONDS

         FINAL GEOMETRY OBTAINED                                CHARGE
AM1 PRECISE PATH T=3595 GRAD T.V. WEIGHT
   Conrotary cyclization TS
   PATH, path oriented toward products
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0      -0.1829         Note
 C     1.354373  1    0.000000  0    0.000000  0   1  0  0      -0.1829
 C     1.521883  1   94.009881  1    0.000000  0   2  1  0      -0.1573
 C     1.521880  1   94.007619  1   -1.501455  1   1  2  3      -0.1573
 H     1.079883  1  136.266059  1  178.740239  1   1  2  3       0.1486
 H     1.079886  1  136.260824  1  178.739104  1   2  1  4       0.1486
 H     1.108124  1  115.258425  1  117.303755  1   4  1  2       0.0960
 H     1.108124  1  115.260320  1  117.303483  1   3  2  1       0.0960
 H     1.109606  1  114.486655  1 -112.717518  1   4  1  2       0.0956
 H     1.109605  1  114.485878  1 -112.716937  1   3  2  1       0.0956
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0
```

Note: The geometry in the archive file is that of the minimized result of following the PATH. Since the T.V. was oriented toward the products, this is the optimized geometry for cyclobutene.

Output File (TEST38.OUT) :

```
*****************************************************************************
                              AM1 CALCULATION RESULTS
*****************************************************************************
*                              AMPAC Version  5.00
*                                 Presented by:
*
*                             Semichem, Inc.
*                             7128 Summit
*                             Shawnee, KS  66216
*                             (913) 268-3271
*                             (913) 268-3445 (fax)
*
*  PATH      - FOLLOW THE STEEPEST DESCENT PATH
*  T.V.      - TRANSITION VECTOR TO BE PROVIDED FOR PATH
*  WEIGHT    - WEIGHT TO BE PROVIDED FOR PATH
*  PRECISE   - OPTIMIZATION CRITERIA TO BE INCREASED BY 10 TIMES,
*            -     S.C.F.   CRITERIA BY 100 TIMES,
*            - AND USE ACCURATE FINITE DIFFERENCE FORMULA IN HESSIAN
*  GRADIENTS- ALL GRADIENTS TO BE PRINTED
*   T=       - A TIME OF  3595.0 SECONDS REQUESTED
*  AM1       - THE AM1 HAMILTONIAN TO BE USED
*****************************************************************************
AM1 PRECISE PATH T=3595 GRAD T.V. WEIGHT
   Conrotary cyclization TS
   PATH, path oriented toward products
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C
     2     C          1.38868 *                                  1
     3     C          1.42762 *      103.83836 *                 2  1
     4     C          1.42776 *      103.82632 *   -18.66514 *   1  2  3
     5     H          1.08819 *      129.20493 *   154.43380 *   1  2  3
     6     H          1.08819 *      129.19007 *   154.43764 *   2  1  4
     7     H          1.09594 *      121.10568 *   136.75260 *   4  1  2
     8     H          1.09594 *      121.10946 *   136.76134 *   3  2  1
     9     H          1.09824 *      120.31733 *   -65.10744 *   4  1  2
    10     H          1.09826 *      120.31390 *   -65.09779 *   3  2  1
         CARTESIAN COORDINATES
   NO.       ATOM         X         Y         Z
    1         6        0.0000    0.0000    0.0000
    2         6        1.3887    0.0000    0.0000
    3         6        1.7301    1.3862    0.0000
    4         6       -0.3412    1.3135    0.4437
    5         1       -0.6878   -0.7607   -0.3639
    6         1        2.0763   -0.8373    0.1013
    7         1       -1.1402    1.8853   -0.0417
    8         1        2.5293    1.7725    0.6428
    9         1       -0.0862    1.6386    1.4612
   10         1        1.4751    2.0199   -0.8599
         SINGLET STATE CALCULATION
         RHF CALCULATION, No. OF DOUBLY OCCUPIED LEVELS = 11
 H  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
 C  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
          INTERATOMIC DISTANCES
             C   1      C   2      C   3      C   4      H   5      H   6
-----------------------------------------------------------------------------
   C   1   0.000000
   C   2   1.388681   0.000000
   C   3   2.216954   1.427616   0.000000
   C   4   1.427758   2.216885   2.119584   0.000000
   H   5   1.088191   2.241200   3.253922   2.252645   0.000000
   H   6   2.241067   1.088194   2.252547   3.253835   2.804064   0.000000
   H   7   2.203707   3.154606   2.913733   1.095941   2.703658   4.216542
   H   8   3.154732   2.203620   1.095943   2.913799   4.216680   2.703604
   H   9   2.197196   2.644904   2.344792   1.098242   3.074018   3.557532
   H  10   2.644892   2.197042   1.098255   2.344676   3.557522   3.073932
             H   7      H   8      H   9      H  10
-----------------------------------------------------
```

```
   H   7   0.000000
   H   8   3.734533   0.000000
   H   9   1.852230   2.743851   0.000000
   H  10   2.743619   1.852242   2.823292   0.000000
USE 2-POINT FORMULA IN INTEGRAL DERIVATIVES WITH STEP  0.00002000
STANDARD DEVIATION ON ENERGY   (KCAL)        0.000001493
STANDARD DEVIATION ON GRADIENT (KCAL/A,RD,RD)  0.0000467 0.0000645 0.0000604
REACTION PATH...MIN/MAX STEPS : 0.00200 0.20000 WITH REQUIRED ACCURACY :0.000800        Note 1
                MAX ITERATIONS=  500            PRINTOUT LEVEL =  0
                CONV. THRESHOLD ON RMS-G  =     4.0D-01
                STANDARD DEVIATION ON GRADIENT  4.7D-05  6.4D-05  6.0D-05
                STARTING POINT ENERGY= 8.109D+01, RMS-G = 4.138D-02
                <T.VCTOR|GRADIENT>= -6.7D-02
WEIGHTS   0.833   0.833   2.498   0.833   2.498   0.833   0.833   0.833   0.833                Note 2
          0.833   0.833   0.833   0.833   0.833   0.833   0.833   0.833   0.833
          0.833   0.833   2.498   0.833   0.833   2.498
T-VECTR -0.1791  0.2051 -0.4964  0.2051 -0.4964 -0.1741 -0.0165  0.1161  0.1011               Note 3
        -0.0166  0.1161  0.1001 -0.0083 -0.0021 -0.1231 -0.0084  0.0021 -0.1231
         0.0020 -0.0567 -0.3713  0.0200 -0.0567 -0.3713
START ALONG THE TRANSITION VECTOR
START EULER-CAUCHY  PREDICTOR-CORRECTOR AT ITERATION  1
WITH ENERGY=  8.1084D+01   RMS-G=  5.32D-01 AND LENGTH=    0.008000
START EXPONENTIAL PREDICTOR-CORRECTOR AT ITERATION  3
WITH ENERGY=  8.1080D+01   RMS-G=  6.32D-01 AND LENGTH=    0.009560
WHAO ... CONVERGENCE ACHIEVED
ITE   44  ENERGY=  4.5833D+01    RMS GRADIENT=  3.64D-01                                      Note 4
          INTEGRATED PATH LENGTH=  2.4178D+00    GRADIENT CALLS=  206
COORD=   1.35437   1.52188   1.64078   1.52188   1.64074  -0.02621   1.07988                  Note 5
         2.37829   3.11961   1.07989   2.37820   3.11959   1.10812   2.01164
         2.04734   1.10812   2.01167   2.04733   1.10961   1.99817  -1.96729
         1.10961   1.99816  -1.96728
GRAD.=      0.01      0.01      0.00     -0.01     -0.01     -0.24      0.00                  Note 6
            0.00     -0.20      0.00      0.00     -0.20     -0.01      0.07
            0.33     -0.01      0.07      0.33      0.01     -0.05      1.18
            0.01     -0.05      1.18
AM1 PRECISE PATH T=3595 GRAD T.V. WEIGHT
   Conrotary cyclization TS
   PATH, path oriented toward products
    GEOMETRY OPTIMISED : GRADIENT NORM MINIMISED
    SCF FIELD WAS ACHIEVED

                              AM1    CALCULATION
                                                          VERSION  5.00

         FINAL HEAT OF FORMATION =    45.832728 KCAL
         ELECTRONIC ENERGY       = -1985.331527 EV
         CORE-CORE REPULSION     =  1392.479986 EV
         GRADIENT NORM           =     1.780956
         IONISATION POTENTIAL    =     9.717794 EV
         NO. OF FILLED LEVELS    =    11
         MOLECULAR WEIGHT        =    54.091
         SCF CALCULATIONS        =  207
         COMPUTATION TIME=       130.89 SECONDS
                                                     9-MAY-94

      FINAL  POINT  AND  DERIVATIVES
  PARAMETER     ATOM    TYPE            VALUE       GRADIENT
     1          2 C     BOND            1.354373     0.014011  KCAL/ANGSTROM
     2          3 C     BOND            1.521883     0.007290  KCAL/ANGSTROM
     3          3 C     ANGLE          94.009881     0.003156  KCAL/RADIAN
     4          4 C     BOND            1.521880    -0.009840  KCAL/ANGSTROM
     5          4 C     ANGLE          94.007619    -0.009129  KCAL/RADIAN
     6          4 C     DIHEDRAL       -1.501455    -0.242476  KCAL/RADIAN
     7          5 H     BOND            1.079883    -0.000291  KCAL/ANGSTROM
     8          5 H     ANGLE         136.266059     0.003490  KCAL/RADIAN
     9          5 H     DIHEDRAL      178.740239    -0.200381  KCAL/RADIAN
    10          6 H     BOND            1.079886     0.000131  KCAL/ANGSTROM
    11          6 H     ANGLE         136.260824    -0.004472  KCAL/RADIAN
    12          6 H     DIHEDRAL      178.739104    -0.201088  KCAL/RADIAN
    13          7 H     BOND            1.108124    -0.007890  KCAL/ANGSTROM
```

```
   14          7 H     ANGLE         115.258425     0.067496  KCAL/RADIAN
   15          7 H     DIHEDRAL      117.303755     0.331429  KCAL/RADIAN
   16          8 H     BOND            1.108124    -0.006442  KCAL/ANGSTROM
   17          8 H     ANGLE         115.260320     0.070510  KCAL/RADIAN
   18          8 H     DIHEDRAL      117.303483     0.331723  KCAL/RADIAN
   19          9 H     BOND            1.109606     0.005988  KCAL/ANGSTROM
   20          9 H     ANGLE         114.486655    -0.052935  KCAL/RADIAN
   21          9 H     DIHEDRAL     -112.717518     1.182822  KCAL/RADIAN
   22         10 H     BOND            1.109605     0.005708  KCAL/ANGSTROM
   23         10 H     ANGLE         114.485878    -0.053797  KCAL/RADIAN
   24         10 H     DIHEDRAL     -112.716937     1.182202  KCAL/RADIAN
```

Note 7

```
  ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
 NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
  (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
    1     C
    2     C          1.35437 *                                  1
    3     C          1.52188 *       94.00988 *                 2  1
    4     C          1.52188 *       94.00762 *    -1.50145 *   1  2  3
    5     H          1.07988 *      136.26606 *   178.74024 *   1  2  3
    6     H          1.07989 *      136.26082 *   178.73910 *   2  1  4
    7     H          1.10812 *      115.25842 *   117.30375 *   4  1  2
    8     H          1.10812 *      115.26032 *   117.30348 *   3  2  1
    9     H          1.10961 *      114.48666 *  -112.71752 *   4  1  2
   10     H          1.10961 *      114.48588 *  -112.71694 *   3  2  1

        INTERATOMIC DISTANCES
             C   1      C   2      C   3      C   4      H   5      H   6
-----------------------------------------------------------------------------
   C   1   0.000000
   C   2   1.354373   0.000000
   C   3   2.106828   1.521883   0.000000
   C   4   1.521880   2.106788   1.567663   0.000000
   H   5   1.079883   2.261426   3.186015   2.362833   0.000000
   H   6   2.261388   1.079886   2.362866   3.185979   2.914893   0.000000
   H   7   2.232323   2.904720   2.270692   1.108124   2.853909   3.949926
   H   8   2.904771   2.232348   1.108124   2.270697   3.949971   2.853974
   H   9   2.224231   2.865391   2.254642   1.109606   2.862734   3.897842
   H  10   2.865418   2.224224   1.109605   2.254648   3.897869   2.862769
             H   7      H   8      H   9      H  10
-----------------------------------------------------
   H   7   0.000000
   H   8   3.081578   0.000000
   H   9   1.823368   2.481877   0.000000
   H  10   2.481878   1.823366   3.077103   0.000000

                EIGENVALUES
-38.63133 -26.37009 -25.59264 -18.81373 -16.48806 -15.68404 -13.76321 -12.33476
-11.92228 -11.54211  -9.71779   1.19460   3.78377   3.78556   4.21547   4.24027
  4.71705   4.85861   4.87729   5.06504   5.12649   6.14544

        NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS
       ATOM NO.   TYPE          CHARGE        ATOM  ELECTRON DENSITY
         1         C           -0.1829          4.1829
         2         C           -0.1829          4.1829
         3         C           -0.1573          4.1573
         4         C           -0.1573          4.1573
         5         H            0.1486          0.8514
         6         H            0.1486          0.8514
         7         H            0.0960          0.9040
         8         H            0.0960          0.9040
         9         H            0.0956          0.9044
        10         H            0.0956          0.9044
DIPOLE (DEBYE)   X          Y          Z       TOTAL
POINT-CHG.     0.000     0.236     0.003     0.236
HYBRID         0.000    -0.070    -0.001     0.070
SUM            0.000     0.166     0.002     0.166

        CARTESIAN COORDINATES
   NO.       ATOM               X         Y         Z
    1        C                   0.0000    0.0000    0.0000
```

```
    2        C                  1.3544    0.0000    0.0000
    3        C                  1.4608    1.5182    0.0000
    4        C                 -0.1064    1.5176    0.0398
    5        H                 -0.7803   -0.7464   -0.0164
    6        H                  2.1346   -0.7466   -0.0031
    7        H                 -0.5980    1.9804   -0.8389
    8        H                  1.9524    1.9577    0.8905
    9        H                 -0.5275    1.9246    0.9822
   10        H                  1.8820    1.9497   -0.9315

         ATOMIC ORBITAL ELECTRON POPULATIONS
  1.25612   0.95579   0.96367   1.00735   1.25612   0.95578   0.96360   1.00741
  1.23359   0.95880   0.94430   1.02058   1.23359   0.95880   0.94435   1.02053
  0.85140   0.85141   0.90398   0.90397   0.90442   0.90442
FULL COMPUTATION TIME :   130.930 SECONDS
```

Note 1: The information listed here describes the algorithms and criteria that will be used in the calculation.

Note 2: These are the normalized weighting factors for the components of the T.V. By weighting these components, it is possible to emphasize certain motions. Note that while the weights do not have the exact values supplied in the input file, the ratio between the weighting factors is correct. Changing the phase of the T.V. can be accomplished by changing the signs of the T.V. components, NOT by specifying negative scaling factors.

Note 3: This is the T.V. in internal coordinates. There are 21 items, corresponding to the 21 optimizable geometric parameters, both in number and order, in the molecule. The user should be certain that these correspond to the values entered.

Note 4: PATH has converged after 44 iterations.

Note 5: These are the optimizable coordinates at the final geometry, (bond lengths in Angstroms and angles in radians.)

Note 6: These are the gradients associated with each of the parameters above.

Note 7: The geometry is the same as that found in the archive file and is that of the result of following the T.V.

4.8 Intrinsic Reaction Coordinate (IRC) Calculation

The theory and rationale behind the Intrinsic Reaction Coordinate is discussed in detail in Section 5.11. It performs the same general function as PATH, but works in Cartesian coordinates and will compute the properties of points along the reaction pathway. Again, we have chosen the conrotary cyclization of 1,3-butadiene as our example.

Input file (TEST28.DAT) :

```
   AM1 PRECISE T=3595 GRAD T.V. IRC THERMO(298,298)
   Conrotary cyclization TS
   IRC
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0      -0.1709
 C     1.388681  1    0.000000  0    0.000000  0   1  0  0      -0.1708
```

```
 C     1.427616  1  103.838361  1    0.000000  0   2  1  0      -0.1858
 C     1.427758  1  103.826319  1  -18.665140  1   1  2  3      -0.1858
 H     1.088191  1  129.204926  1  154.433803  1   1  2  3       0.1383
 H     1.088194  1  129.190066  1  154.437643  1   2  1  4       0.1382
 H     1.095941  1  121.105676  1  136.752600  1   4  1  2       0.0989
 H     1.095943  1  121.109463  1  136.761344  1   3  2  1       0.0989
 H     1.098242  1  120.317329  1  -65.107436  1   4  1  2       0.1195
 H     1.098255  1  120.313896  1  -65.097794  1   3  2  1       0.1195
   0    0.000000  0    0.000000  0    0.000000  0   0  0  0
 -0.0358  0.0771 -0.0383  0.0358  0.0771  0.0383 -0.0097 -0.0848  0.1969
  0.0097 -0.0848 -0.1969 -0.2300  0.0503  0.0783  0.2300  0.0503 -0.0782
  0.1758 -0.1422 -0.3834 -0.1760 -0.1422  0.3835 -0.1993  0.1839  0.3347
  0.1994  0.1841 -0.3345
   0    0.000000  0    0.000000  0    0.000000  0   0  0  0
```

Note

Note: This is the oriented transition vector in Cartesian coordinates. These may be obtained for a particular vibration by performing a FORCE calculation with the PRINT=2 keyword. There are thirty components, corresponding to the 3 x (10 atoms) Cartesian values.

Archive File (TEST28.ARC) :

```
                    SUMMARY OF   AM1   CALCULATION
                                                    9-MAY-94
                         AMPAC Version  5.00
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)

C 4 H 6
   Conrotary cyclization TS
   IRC

    GEOMETRY OPTIMISED : GRADIENT NORM MINIMISED
    SCF FIELD WAS ACHIEVED

         HEAT OF FORMATION       =    45.773182 KCAL
         ELECTRONIC ENERGY       = -1985.290700 EV
         CORE-CORE REPULSION     =  1392.436576 EV
         GRADIENT NORM           =     1.215713
         DIPOLE                  =     0.16614 DEBYE
         NO. OF FILLED LEVELS    =    11
         IONISATION POTENTIAL    =     9.716801 EV
         MOLECULAR WEIGHT        =    54.091
         SCF CALCULATIONS        =    299
         COMPUTATION TIME        =   199.26 SECONDS

         FINAL GEOMETRY OBTAINED                                CHARGE
AM1 PRECISE T=3595 GRAD T.V. IRC THERMO(298,298)
   Conrotary cyclization TS
   IRC
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0      -0.1831
 C     1.354433  1    0.000000  0    0.000000  0   1  0  0      -0.1831
 C     1.522065  1   93.992803  1    0.000000  0   2  1  0      -0.1568
 C     1.522065  1   93.992802  1   -0.706850  1   1  2  3      -0.1568
 H     1.079839  1  136.273855  1  179.349961  1   1  2  3       0.1486
 H     1.079838  1  136.273909  1 -179.943193  1   2  1  3       0.1486
 H     1.108729  1  115.030638  1  116.093159  1   4  1  2       0.0956
 H     1.108729  1  115.030590  1  116.093169  1   3  2  1       0.0956
 H     1.109250  1  114.615617  1 -114.333449  1   4  1  2       0.0957
 H     1.109250  1  114.615588  1 -114.333429  1   3  2  1       0.0957
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0
```

Note

Note: Again, as was the case with PATH, the final optimized geometry is listed in the archive file. For this reaction and T.V., it is the product cyclobutene.

Output File (TEST28.OUT) :

```
*****************************************************************************
                          AM1 CALCULATION RESULTS
*****************************************************************************
*                            AMPAC Version  5.00
*                               Presented by:
*
*                          Semichem, Inc.
*                          7128 Summit
*                          Shawnee, KS  66216
*                          (913) 268-3271
*                          (913) 268-3445 (fax)
*
*   IRC     - FOLLOW IRC, COMPUTING TRANSVERSE HESSIAN
*  THERMO   - THERMODYNAMIC QUANTITIES TO BE CALCULATED
*  PRECISE  - OPTIMIZATION CRITERIA TO BE INCREASED BY 10 TIMES,
*           -     S.C.F.   CRITERIA BY 100 TIMES,
*           - AND USE ACCURATE FINITE DIFFERENCE FORMULA IN HESSIAN
*  GRADIENTS- ALL GRADIENTS TO BE PRINTED
*   T=      - A TIME OF  3595.0 SECONDS REQUESTED
*  AM1      - THE AM1 HAMILTONIAN TO BE USED
*****************************************************************************
AM1 PRECISE T=3595 GRAD T.V. IRC THERMO(298,298)
   Conrotary cyclization TS
   IRC
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C
     2     C          1.38868 *                                  1
     3     C          1.42762 *      103.83836 *                 2  1
     4     C          1.42776 *      103.82632 *   -18.66514 *   1  2  3
     5     H          1.08819 *      129.20493 *   154.43380 *   1  2  3
     6     H          1.08819 *      129.19007 *   154.43764 *   2  1  4
     7     H          1.09594 *      121.10568 *   136.75260 *   4  1  2
     8     H          1.09594 *      121.10946 *   136.76134 *   3  2  1
     9     H          1.09824 *      120.31733 *   -65.10744 *   4  1  2
    10     H          1.09826 *      120.31390 *   -65.09779 *   3  2  1

         CARTESIAN COORDINATES
   NO.       ATOM         X         Y         Z
    1         6        0.0000    0.0000    0.0000
    2         6        1.3887    0.0000    0.0000
    3         6        1.7301    1.3862    0.0000
    4         6       -0.3412    1.3135    0.4437
    5         1       -0.6878   -0.7607   -0.3639
    6         1        2.0763   -0.8373    0.1013
    7         1       -1.1402    1.8853   -0.0417
    8         1        2.5293    1.7725    0.6428
    9         1       -0.0862    1.6386    1.4612
   10         1        1.4751    2.0199   -0.8599
         SINGLET STATE CALCULATION
         RHF CALCULATION, No. OF DOUBLY OCCUPIED LEVELS = 11
 H  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
 C  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)

           INTERATOMIC DISTANCES
              C   1      C   2      C   3      C   4      H   5      H   6
-----------------------------------------------------------------------------
   C   1   0.000000
   C   2   1.388681   0.000000
   C   3   2.216954   1.427616   0.000000
   C   4   1.427758   2.216885   2.119584   0.000000
   H   5   1.088191   2.241200   3.253922   2.252645   0.000000
   H   6   2.241067   1.088194   2.252547   3.253835   2.804064   0.000000
   H   7   2.203707   3.154606   2.913733   1.095941   2.703658   4.216542
```

```
   H   8   3.154732   2.203620   1.095943   2.913799   4.216680   2.703604
   H   9   2.197196   2.644904   2.344792   1.098242   3.074018   3.557532
   H  10   2.644892   2.197042   1.098255   2.344676   3.557522   3.073932
              H   7      H   8      H   9      H  10
-----------------------------------------------------
   H   7   0.000000
   H   8   3.734533   0.000000
   H   9   1.852230   2.743851   0.000000
   H  10   2.743619   1.852242   2.823292   0.000000
USE 2-POINT FORMULA IN INTEGRAL DERIVATIVES WITH STEP  0.00002000                    Note 1
STANDARD DEVIATION ON ENERGY   (KCAL)        0.000000031
STANDARD DEVIATION ON GRADIENT (KCAL/A,RD,RD)  0.0000021 0.0000000 0.0000000
REACTION PATH...MIN/MAX STEPS : 0.00100 0.10000 WITH REQUIRED ACCURACY :0.000400
                MAX ITERATIONS=  500            PRINTOUT LEVEL =  0
                CONV. THRESHOLD ON RMS-G  =     4.0D-01
                STANDARD DEVIATION ON GRADIENT  2.1D-06  0.0D+00  0.0D+00
                STARTING POINT ENERGY= 8.109D+01, RMS-G = 4.926D-02
                <T.VCTOR|GRADIENT>=  3.3D-02
                SCREENING STEP FOR IRC =   0.411 ANGSTROMS
WEIGHTS   4.423   4.423   4.423   4.423   4.423   4.423   4.423   4.423   4.423   Note 2
          4.423   4.423   4.423   0.371   0.371   0.371   0.371   0.371   0.371
          0.371   0.371   0.371   0.371   0.371   0.371   0.371   0.371   0.371
          0.371   0.371   0.371
T-VECTR -0.0358  0.0771 -0.0383  0.0358  0.0771  0.0383 -0.0097 -0.0848  0.1969   Note 3
         0.0097 -0.0848 -0.1969 -0.2300  0.0503  0.0783  0.2300  0.0503 -0.0782
         0.1758 -0.1422 -0.3834 -0.1760 -0.1422  0.3835 -0.1993  0.1839  0.3347
         0.1994  0.1841 -0.3345
START ALONG THE TRANSITION VECTOR
IRC STARTING POINT, E=   81.0991 KCAL/MOL
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C          0.00000 *        0.00000 *     0.00000 *   0  0  0          Note 4
     2     C          1.38897 *        0.00000 *     0.00000 *   1  0  0
     3     C          1.42694 *      103.83749 *     0.00000 *   2  1  0
     4     C          1.42692 *      103.82302 *   -18.62868 *   1  2  3
     5     H          1.08860 *      129.24553 *   154.49797 *   1  2  3
     6     H          1.08872 *      129.22158 *   173.12220 *   2  1  3
     7     H          1.09567 *      121.08893 *   136.71708 *   4  1  2
     8     H          1.09582 *      121.10699 *   136.72172 *   3  2  1
     9     H          1.10034 *      120.35044 *   -65.16714 *   4  1  2
    10     H          1.10035 *      120.30252 *   -65.18211 *   3  2  1
START EULER-CAUCHY  PREDICTOR-CORRECTOR AT ITERATION  1
WITH ENERGY=  8.1099D+01   RMS-G=  7.72D-01 AND LENGTH=    0.000000
START EXPONENTIAL PREDICTOR-CORRECTOR AT ITERATION  2
WITH ENERGY=  8.1095D+01   RMS-G=  3.84D-01 AND LENGTH=    0.001833

IRC LENGTH=    0.0018 ANGSTROMS.  ENERGY=   81.0955 KCAL/MOLE.
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C          0.00000 *        0.00000 *     0.00000 *   0  0  0
     2     C          1.38890 *        0.00000 *     0.00000 *   1  0  0
     3     C          1.42720 *      103.83518 *     0.00000 *   2  1  0
     4     C          1.42718 *      103.82244 *   -18.63514 *   1  2  3
     5     H          1.08833 *      129.24138 *   154.48994 *   1  2  3
     6     H          1.08838 *      129.22076 *   173.12111 *   2  1  3
     7     H          1.09586 *      121.08291 *   136.71855 *   4  1  2
     8     H          1.09590 *      121.10013 *   136.72283 *   3  2  1
     9     H          1.09896 *      120.34640 *   -65.16140 *   4  1  2
    10     H          1.09898 *      120.30482 *   -65.17588 *   3  2  1
MOMENTS OF INERTIA (CM-1):    0.204848    0.314697    0.466837
===> BEFORE ANNIHILATION OF IRC:
FREQ:  -846.8     0.0     0.0     0.0     0.0     0.0     0.0   418.3   662.4
ERROR     0.1     0.0     0.0     0.0     0.0     0.0     0.0     0.3     0.3
FREQ:   710.9   757.2   873.2   892.4   986.3   996.8  1031.6  1047.7  1126.0
ERROR     0.2     0.2     0.1     0.2     0.2     0.2     0.1     0.2     0.2
FREQ:  1192.1  1368.7  1391.0  1500.0  1537.3  1615.6  3163.2  3164.3  3200.3
ERROR     0.2     0.1     0.1     0.0     0.0     0.0     0.1     0.1     0.1
FREQ:  3201.5  3254.3  3262.8
ERROR     0.1     0.1     0.1
```

```
ZERO POINT ENERGY:     53.40 KCAL/MOLE, ERROR:     0.000
PERCENT OF IRC IN NORMAL MODES:
 62% ( 3164.3) 15% ( 1500.0) 13% ( 3201.5)  3% ( 1368.7)  2% ( 3262.8)
===> AND AFTER ANNIHILATION OF IRC:
FREQ:  -824.2     0.0     0.0     0.0     0.0     0.0     0.0     0.0   420.7
ERROR     0.1     0.0     0.0     0.0     0.0     0.0     0.0     0.0     0.3
FREQ:   662.4   710.9   757.5   873.4   893.4   986.3   999.1  1037.5  1048.6
ERROR     0.3     0.2     0.1     0.2     0.1     0.2     0.4     0.1     0.1
FREQ:  1151.7  1192.1  1388.0  1395.1  1537.3  1609.1  1970.8  3163.2  3194.7
ERROR     0.2     0.1     0.1     0.1     0.0     0.0     0.0     0.0     0.1
FREQ:  3200.4  3254.2  3260.4
ERROR     0.1     0.1     0.1
ZERO POINT ENERGY:     49.62 KCAL/MOLE, ERROR:     0.000
NORMAL MODE (MASS-WEIGHTED CART.) WITH  FREQUENCY: -824.2 CM-1
-0.0805  0.1593 -0.0504  0.0860  0.1270  0.1013  0.4572 -0.1485 -0.1172 -0.4636
-0.1695  0.0592  0.0573  0.0489 -0.1697 -0.0513 -0.0044  0.1760 -0.2526 -0.1051
 0.1418  0.2487 -0.0602 -0.1680  0.2111  0.1375 -0.1594 -0.2100  0.0926  0.2037
NORMAL MODE (MASS-WEIGHTED CART.) WITH  FREQUENCY:    0.0 CM-1
 0.0837 -0.5473  0.1287 -0.0123 -0.3550  0.1049 -0.1867 -0.0013 -0.2253 -0.1616
-0.2565  0.0485  0.1248 -0.1605  0.0748 -0.0369  0.0023  0.0858 -0.1180 -0.1248
-0.0373 -0.0462  0.0578 -0.0764 -0.0991 -0.1549 -0.3419 -0.0309 -0.2669  0.1977

============================
```

Note 5

```
                  CALCULATED THERMODYNAMIC PROPERTIES
                  ASSUMING NO INTERNAL ROTATIONS.
THERE ARE 22 GENUINE VIBRATIONS IN THIS SYSTEM
TEMP. (K)  PARTITION FUNCTION    ENTHALPY    HEAT CAPACITY    ENTROPY
                                 CAL/MOL       CAL/K/MOL     CAL/K/MOL
  298 VIB.   0.1363D+01         584.33657       7.13288       2.57689
      ROT.   0.3046D+05         888.30522       2.98089      23.49771
      INT.   0.4153D+05        1472.64179      10.11377      26.07459
      TRA.   0.3847D+27        1480.50870       4.96815      37.86664
      TOT.                     2953.15049      15.08192      63.94123

IRC LENGTH=    0.4289 ANGSTROMS.  ENERGY=   51.2604 KCAL/MOLE.
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C          0.00000 *        0.00000 *     0.00000 *   0  0  0
     2     C          1.35668 *        0.00000 *     0.00000 *   1  0  0
     3     C          1.50286 *       95.55402 *     0.00000 *   2  1  0
     4     C          1.50286 *       95.55402 *   -10.30045 *   1  2  3
     5     H          1.08099 *      134.43811 *   168.88025 *   1  2  3
     6     H          1.08099 *      134.43811 *   179.18069 *   2  1  3
     7     H          1.10327 *      117.57670 *   127.08662 *   4  1  2
     8     H          1.10327 *      117.57670 *   127.08661 *   3  2  1
     9     H          1.10937 *      113.71062 *  -100.33501 *   4  1  2
    10     H          1.10937 *      113.71064 *  -100.33500 *   3  2  1
MOMENTS OF INERTIA (CM-1):    0.224492    0.401888    0.416941
===> BEFORE ANNIHILATION OF IRC:
FREQ:     0.0     0.0     0.0     0.0     0.0     0.0   363.8   694.0   750.3
ERROR     0.0     0.0     0.0     0.0     0.0     0.0     0.7     0.2     0.6
FREQ:   841.0   860.7   876.2  1023.4  1024.1  1054.1  1070.2  1081.3  1155.0
ERROR     0.3     0.2     0.3     0.4     0.7     0.3     0.4     0.2     0.5
FREQ:  1246.1  1295.8  1345.9  1414.1  1417.1  1735.3  3107.9  3119.1  3172.3
ERROR     0.3     0.1     0.2     0.2     0.3     0.0     0.1     0.2     0.1
FREQ:  3178.4  3298.4  3311.0
ERROR     0.1     0.1     0.2
ZERO POINT ENERGY:     54.95 KCAL/MOLE, ERROR:     0.000
PERCENT OF IRC IN NORMAL MODES:
 83% (  694.0) 16% (  363.8)
===> AND AFTER ANNIHILATION OF IRC:
FREQ:     0.0     0.0     0.0     0.0     0.0     0.0     0.0   435.6   750.3
ERROR     0.0     0.0     0.0     0.0     0.0     0.0     0.0     0.4     0.5
FREQ:   841.0   860.7   875.8  1022.2  1024.1  1054.1  1070.1  1080.7  1153.8
ERROR     0.4     0.3     0.6     0.2     0.2     0.3     0.4     0.2     0.3
FREQ:  1246.1  1295.7  1345.9  1414.1  1417.1  1735.3  3107.9  3119.1  3172.3
ERROR     0.2     0.2     0.2     0.6     0.2     0.0     0.1     0.1     0.1
FREQ:  3178.4  3298.4  3311.0
ERROR     0.1     0.1     0.1
```

Note 6

```
ZERO POINT ENERGY:     54.05 KCAL/MOLE, ERROR:     0.000
                   CALCULATED THERMODYNAMIC PROPERTIES
TEMP. (K)  PARTITION FUNCTION    ENTHALPY    HEAT CAPACITY    ENTROPY
                                 CAL/MOL       CAL/K/MOL     CAL/K/MOL
  298 VIB.   0.1283D+01         490.00997       6.35276       2.13919
      ROT.   0.2724D+05         888.30522       2.98089      23.27603
      INT.   0.3495D+05        1378.31519       9.33365      25.41522
      TRA.   0.3847D+27        1480.50870       4.96815      37.86664
      TOT.                     2858.82389      14.30180      63.28186
WHAO ... CONVERGENCE ACHIEVED
ITE   28  ENERGY=  4.5773D+01    RMS GRADIENT=  2.22D-01
          INTEGRATED PATH LENGTH=  6.5703D-01    GRADIENT CALLS=   84
COORD=  -0.66925  -0.79835  -0.02611   0.66920  -0.76474  -0.23084   0.77255
         0.73762  -0.00970  -0.77250   0.69575   0.24533  -1.44101  -1.55359
        -0.03300   1.44090  -1.48250  -0.46609  -1.37812   1.26509  -0.48840
         1.37821   1.04207   0.86766  -1.07275   0.95761   1.28057   1.07283
         1.31708  -0.90664
GRAD.=     -0.15      0.08     -0.68      0.15     -0.14      0.67     -0.06
            0.07     -0.40      0.06     -0.06      0.40     -0.01      0.04
           -0.17      0.01     -0.01      0.17     -0.06      0.08      0.13
            0.06      0.11     -0.09      0.08     -0.10      0.10     -0.08
           -0.06     -0.13

IRC LENGTH=    0.6570 ANGSTROMS.  ENERGY=   45.7732 KCAL/MOLE.
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C          0.00000 *        0.00000 *     0.00000 *   0  0  0
     2     C          1.35443 *        0.00000 *     0.00000 *   1  0  0
     3     C          1.52207 *       93.99280 *     0.00000 *   2  1  0
     4     C          1.52207 *       93.99280 *    -0.70685 *   1  2  3
     5     H          1.07984 *      136.27386 *   179.34996 *   1  2  3
     6     H          1.07984 *      136.27391 *  -179.94319 *   2  1  3
     7     H          1.10873 *      115.03064 *   116.09316 *   4  1  2
     8     H          1.10873 *      115.03059 *   116.09317 *   3  2  1
     9     H          1.10925 *      114.61562 *  -114.33345 *   4  1  2
    10     H          1.10925 *      114.61559 *  -114.33343 *   3  2  1
MOMENTS OF INERTIA (CM-1):    0.227154    0.408283    0.425566
===> BEFORE ANNIHILATION OF IRC:
FREQ:     0.0     0.0     0.0     0.0     0.0     0.0   358.6   762.0   849.4
ERROR     0.0     0.0     0.0     0.0     0.0     0.0     1.0     0.9     0.2
FREQ:   870.2   872.4   996.8  1023.2  1035.6  1037.5  1069.6  1104.1  1192.7
ERROR     0.6     0.8     0.2     0.6     0.3     0.4     0.4     0.4     0.3
FREQ:  1253.3  1283.1  1314.9  1411.0  1420.1  1741.1  3097.8  3116.4  3161.2
ERROR     0.4     0.1     0.3     0.6     0.4     0.0     0.1     0.1     0.1
FREQ:  3168.0  3304.4  3318.2
ERROR     0.2     0.1     0.2
ZERO POINT ENERGY:     55.41 KCAL/MOLE, ERROR:     0.001
PERCENT OF IRC IN NORMAL MODES:
 99% (  358.6)
===> AND AFTER ANNIHILATION OF IRC:
FREQ:     0.0     0.0     0.0     0.0     0.0     0.0     0.0   762.0   849.4
ERROR     0.0     0.0     0.0     0.0     0.0     0.0     0.0     0.7     0.1
FREQ:   870.2   872.4   996.8  1023.2  1035.6  1037.5  1069.6  1104.1  1192.7
ERROR     0.7     0.6     0.2     0.6     0.2     0.5     0.6     0.3     0.2
FREQ:  1253.3  1282.8  1314.9  1411.0  1420.1  1740.9  3097.8  3116.4  3152.8
ERROR     0.5     0.1     0.2     0.3     0.3     0.0     0.1     0.2     0.1
FREQ:  3168.0  3304.4  3310.4
ERROR     0.2     0.2     0.2
ZERO POINT ENERGY:     54.88 KCAL/MOLE, ERROR:     0.001
                   CALCULATED THERMODYNAMIC PROPERTIES
TEMP. (K)  PARTITION FUNCTION    ENTHALPY    HEAT CAPACITY    ENTROPY
                                 CAL/MOL       CAL/K/MOL     CAL/K/MOL
  298 VIB.   0.1131D+01         333.35849       5.26990       1.36389
      ROT.   0.2660D+05         888.30522       2.98089      23.22828
      INT.   0.3009D+05        1221.66371       8.25079      24.59218
      TRA.   0.3847D+27        1480.50870       4.96815      37.86664
      TOT.                     2702.17241      13.21894      62.45882
AM1 PRECISE T=3595 GRAD T.V. IRC THERMO(298,298)
   Conrotary cyclization TS
   IRC
```

Note 7

```
GEOMETRY OPTIMISED : GRADIENT NORM MINIMISED
SCF FIELD WAS ACHIEVED

                          AM1    CALCULATION
                                                    VERSION  5.00

     FINAL HEAT OF FORMATION =    45.773182 KCAL
     ELECTRONIC ENERGY       = -1985.290700 EV
     CORE-CORE REPULSION     =  1392.436576 EV
     GRADIENT NORM           =     1.215713
     IONISATION POTENTIAL    =     9.716801 EV
     NO. OF FILLED LEVELS    =    11
     MOLECULAR WEIGHT        =    54.091
     SCF CALCULATIONS        =  299
     COMPUTATION TIME=       199.21 SECONDS
                                          9-MAY-94

   FINAL  POINT  AND  DERIVATIVES
PARAMETER     ATOM    TYPE            VALUE       GRADIENT
   1          1 C                   -0.669253    -0.145831  KCAL/ANGSTROM
   2          1 C                   -0.798348     0.079450  KCAL/ANGSTROM
   3          1 C                   -0.026111    -0.680722  KCAL/ANGSTROM
   4          2 C                    0.669196     0.145970  KCAL/ANGSTROM
   5          2 C                   -0.764742    -0.142777  KCAL/ANGSTROM
   6          2 C                   -0.230839     0.670295  KCAL/ANGSTROM
   7          3 C                    0.772549    -0.064129  KCAL/ANGSTROM
   8          3 C                    0.737623     0.066283  KCAL/ANGSTROM
   9          3 C                   -0.009703    -0.395786  KCAL/ANGSTROM
  10          4 C                   -0.772497     0.064107  KCAL/ANGSTROM
  11          4 C                    0.695755    -0.063841  KCAL/ANGSTROM
  12          4 C                    0.245330     0.395949  KCAL/ANGSTROM
  13          5 H                   -1.441010    -0.009760  KCAL/ANGSTROM
  14          5 H                   -1.553593     0.043867  KCAL/ANGSTROM
  15          5 H                   -0.032997    -0.168665  KCAL/ANGSTROM
  16          6 H                    1.440900     0.009653  KCAL/ANGSTROM
  17          6 H                   -1.482501    -0.012197  KCAL/ANGSTROM
  18          6 H                   -0.466095     0.173889  KCAL/ANGSTROM
  19          7 H                   -1.378122    -0.056864  KCAL/ANGSTROM
  20          7 H                    1.265091     0.078814  KCAL/ANGSTROM
  21          7 H                   -0.488395     0.125910  KCAL/ANGSTROM
  22          8 H                    1.378206     0.056956  KCAL/ANGSTROM
  23          8 H                    1.042073     0.114898  KCAL/ANGSTROM
  24          8 H                    0.867662    -0.093919  KCAL/ANGSTROM
  25          9 H                   -1.072746     0.079378  KCAL/ANGSTROM
  26          9 H                    0.957612    -0.101331  KCAL/ANGSTROM
  27          9 H                    1.280568     0.103026  KCAL/ANGSTROM
  28         10 H                    1.072828    -0.079480  KCAL/ANGSTROM
  29         10 H                    1.317080    -0.063165  KCAL/ANGSTROM
  30         10 H                   -0.906640    -0.129978  KCAL/ANGSTROM

 ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
NUMBER   SYMBOL     (ANGSTROMS)    (DEGREES)     (DEGREES)
 (I)                   NA:I         NB:NA:I      NC:NB:NA:I  NA NB NC
   1     C          0.00000 *       0.00000 *     0.00000 *   0  0  0
   2     C          1.35443 *       0.00000 *     0.00000 *   1  0  0
   3     C          1.52207 *      93.99280 *     0.00000 *   2  1  0
   4     C          1.52207 *      93.99280 *    -0.70685 *   1  2  3
   5     H          1.07984 *     136.27386 *   179.34996 *   1  2  3
   6     H          1.07984 *     136.27391 *  -179.94319 *   2  1  3
   7     H          1.10873 *     115.03064 *   116.09316 *   4  1  2
   8     H          1.10873 *     115.03059 *   116.09317 *   3  2  1
   9     H          1.10925 *     114.61562 *  -114.33345 *   4  1  2
  10     H          1.10925 *     114.61559 *  -114.33343 *   3  2  1

     INTERATOMIC DISTANCES
          C   1      C   2      C   3      C   4      H   5      H   6
-----------------------------------------------------------------------
  C   1   0.000000
  C   2   1.354433   0.000000
  C   3   2.106719   1.522065   0.000000
```

Note 8

Note 9

```
   C   4   1.522065   2.106719   1.566512   0.000000
   H   5   1.079839   2.261504   3.185915   2.363037   0.000000
   H   6   2.261504   1.079838   2.363036   3.185915   2.915139   0.000000
   H   7   2.230243   2.894490   2.265558   1.108729   2.855928   3.936579
   H   8   2.894490   2.230242   1.108729   2.265558   3.936579   2.855926
   H   9   2.225671   2.878405   2.262367   1.109250   2.857835   3.914511
   H  10   2.878404   2.225670   1.109250   2.262367   3.914511   2.857834
               H   7      H   8      H   9      H  10
-----------------------------------------------------
   H   7   0.000000
   H   8   3.079931   0.000000
   H   9   1.821271   2.486924   0.000000
   H  10   2.486923   1.821272   3.084896   0.000000

                 EIGENVALUES
-38.63123 -26.37036 -25.59691 -18.81384 -16.49199 -15.67715 -13.76180 -12.32853
-11.93625 -11.53777  -9.71680   1.19508   3.78081   3.79449   4.21830   4.22905
  4.71725   4.86277   4.87906   5.06521   5.12350   6.14658

         NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS
        ATOM NO.   TYPE          CHARGE        ATOM  ELECTRON DENSITY
          1         C           -0.1831          4.1831
          2         C           -0.1831          4.1831
          3         C           -0.1568          4.1568
          4         C           -0.1568          4.1568
          5         H            0.1486          0.8514
          6         H            0.1486          0.8514
          7         H            0.0956          0.9044
          8         H            0.0956          0.9044
          9         H            0.0957          0.9043
         10         H            0.0957          0.9043
DIPOLE (DEBYE)   X         Y         Z       TOTAL
POINT-CHG.     0.000     0.233     0.038     0.236
HYBRID         0.000    -0.069    -0.011     0.070
SUM            0.000     0.164     0.027     0.166

         CARTESIAN COORDINATES
   NO.       ATOM               X         Y         Z
    1        C                 -0.6693   -0.7983   -0.0261
    2        C                  0.6692   -0.7647   -0.2308
    3        C                  0.7725    0.7376   -0.0097
    4        C                 -0.7725    0.6958    0.2453
    5        H                 -1.4410   -1.5536   -0.0330
    6        H                  1.4409   -1.4825   -0.4661
    7        H                 -1.3781    1.2651   -0.4884
    8        H                  1.3782    1.0421    0.8677
    9        H                 -1.0727    0.9576    1.2806
   10        H                  1.0728    1.3171   -0.9066

         ATOMIC ORBITAL ELECTRON POPULATIONS
  1.25621   0.95709   0.96576   1.00405   1.25621   0.95709   0.96385   1.00596
  1.23336   0.96005   0.94648   1.01695   1.23336   0.96004   0.94599   1.01744
  0.85140   0.85140   0.90441   0.90441   0.90425   0.90425
FULL COMPUTATION TIME :   199.270 SECONDS
```

Note 1: As in PATH, the information listed here describes the algorithms and criteria that will be used in the calculation.

Note 2: These are the weighting factors for the components of the T.V. It is not possible in IRC to define weights as it is in PATH. Changing the phase of the T.V. can be accomplished by changing the signs of the T.V. components. These weighting factors cannot be applied because IRC uses the square roots of the nuclear masses by definition. Isotopic studies may be carried out by explicitly defining the masses of particular atoms in the input file (see Section 2.3).

Note 3: This is the T.V. in Cartesian coordinates. There are 30 items, corresponding to the 30 Cartesian coordinates that a 10-atom molecule possesses. The user should be certain that these correspond to those input.

Note 4: This is the initial z-matrix. Note that all parameters are marked for optimization regardless of the specification in the input file. This is a default when IRC is used.

Note 5: The normal modes in terms of mass-weighted Cartesian coordinates are listed. Some have been removed to conserve space in the manual. A full listing is available in the results directory of the test suite.

Note 6: The use of the THERMO keyword requires that thermodynamic information be computed from the Hessian at each step. This is the first such listing.

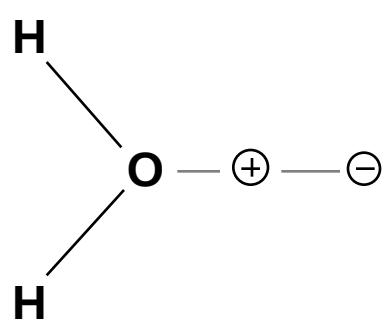
Note 7: This the thermodynamic data for the final point.

Note 6: These are the gradients associated with each of the Cartesian coordinates.

Note 7: The geometry is the same as that found in the archive file and is that of the result of following the T.V.

4.9 Use of Partial Charge Sparkles

As mentioned in Chapter 2, sparkles may be defined with partial charges to simulate the electrostatic interaction between the molecular system and some surrounding environment such as a solvent, counterion, or active site. To illustrate this concept, TEST40 consists of a water molecule polarized by two oppositely charges sparkles in the following arrangement:



Input file (TEST40.DAT) :

```
AM1 PREC CHARGE=2 SYMMETRY GRAD
WATER WITH TWO PARTIAL CHARGED SPARKLES
SPARKLES
O      0.00  0    0.00  0     0.00  0   0  0  0
+      1.00  0    0.00  0     0.00  0   1  0  0  0.5
H      1.00  1  128.30  1     0.00  0   1  2  0
H      1.00  1  128.30  1   180.00  0   1  2  3
+      2.00  0  128.30  0   180.00  0   1  3  4 -0.5
```

```
 0      0.00  0    0.00  0     0.00  0   0  0  0
 3, 1, 4,
 3, 2, 4, 5,
```

The results from the output file follow:

Output file (TEST40.OUT) :

```
*****************************************************************************
                            AM1 CALCULATION RESULTS
*****************************************************************************
*                             AMPAC Version 5.0
*                                Presented by:
*
*                           Semichem, Inc.
*                           7128 Summit
*                           Shawnee, KS  66216
*                           (913) 268-3271
*                           (913) 268-3445 (fax)
*
*                  WARNING: YOUR LICENSE EXPIRES IN 24 DAYS!!
*
*           - MINIMIZE ENERGY USING B-F-G-S  METHOD
*  PRECISE  - OPTIMIZATION CRITERIA TO BE INCREASED BY 10 TIMES,
*           -     S.C.F.   CRITERIA BY 100 TIMES,
*           - AND USE ACCURATE FINITE DIFFERENCE FORMULA  IN HESSIAN
*  SYMMETRY - SYMMETRY CONDITIONS TO BE IMPOSED
*  GRADIENTS- ALL GRADIENTS TO BE PRINTED
*  AM1      - THE AM1 HAMILTONIAN TO BE USED
*****************************************************************************
THE SPARKLE No   2 ACCOUNTS FOR  1 TO THE CHARGE ON THE SYSTEM
                   BUT HOLDS A CHARGE  0.50000
THE SPARKLE No   5 ACCOUNTS FOR -1 TO THE CHARGE ON THE SYSTEM
                   BUT HOLDS A CHARGE -0.50000

    PARAMETER DEPENDENCE DATA
       REFERENCE ATOM      FUNCTION NO.    DEPENDENT ATOM(S)
           3                  1             4
           3                  2             4  5

           DESCRIPTIONS OF THE FUNCTIONS USED
  1      BOND LENGTH    IS SET EQUAL TO THE REFERENCE BOND LENGTH
  2      BOND ANGLE     IS SET EQUAL TO THE REFERENCE BOND ANGLE
AM1 PREC SYMMETRY GRAD
  WATER WITH TWO PARTIAL CHARGED SPARKLES
  SPARKLES
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I   NA  NB  NC
     1     O
     2     +          1.00000                                    1
     3     H          1.00000 *      128.30000 *                 1   2
     4     H          1.00000 *      128.30000 *   180.00000     1   2   3
     5     -          2.00000        128.30000     180.00000     1   3   4

         CARTESIAN COORDINATES
   NO.       ATOM         X         Y         Z
    1         8        0.0000    0.0000    0.0000
    2       104        1.0000    0.0000    0.0000
    3         1       -0.6198    0.7848    0.0000
    4         1       -0.6198   -0.7848    0.0000
    5       106        2.0000    0.0000    0.0000

  MOLECULAR POINT GROUP            SYMMETRY CRITERIA
           C2V                         0.10000000


         RHF CALCULATION, No. OF DOUBLY OCCUPIED LEVELS =  4
```

Note 1

```
      **  REFERENCES TO PARAMETERS  **

 H  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
 O  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
 +  SPARKLE : ALL METHODS.
 -  SPARKLE : ALL METHODS.


          INTERATOMIC DISTANCES
             O   1      +   2      H   3      H   4      -   5
-----------------------------------------------------------------
   O   1   0.000000
   +   2   1.000000   0.000000
   H   3   1.000000   1.799877   0.000000
   H   4   1.000000   1.799877   1.569553   0.000000
   -   5   2.000000   1.000000   2.734797   2.734797   0.000000
STANDARD DEVIATION ON ENERGY   (KCAL)       0.00000745813
STANDARD DEVIATION ON GRADIENT (KCAL/A,RD,RD)  0.00010344 0.00010344 0.00000000
AM1 PREC SYMMETRY GRAD
  WATER WITH TWO PARTIAL CHARGED SPARKLES
  SPARKLES

    TEST ON RESIDUES SATISFIED IN BFGS OR DFP
    SCF FIELD WAS ACHIEVED

                              AM1    CALCULATION
                                                        VERSION 5.0

                                                    18-May-94

        FINAL HEAT OF FORMATION =     122.807311 KCAL                          Note 2
        ELECTRONIC ENERGY       =    -505.405279 EV
        CORE-CORE REPULSION     =     164.736933 EV
        GRADIENT NORM           =       0.342136
        IONISATION POTENTIAL    =      13.937186 EV
        MOLECULAR POINT GROUP   = C2V   0.100000
        NO. OF FILLED LEVELS    =       4
        MOLECULAR WEIGHT        =      18.015
        SCF CALCULATIONS        =      16
        COMPUTATION TIME        =       0.35 SECONDS

     FINAL  POINT  AND  DERIVATIVES
  PARAMETER     ATOM    TYPE            VALUE       GRADIENT
     1          3 H     BOND            0.975868     0.237545  KCAL/ANGSTROM
     2          3 H     ANGLE         129.212900     0.246231  KCAL/RADIAN
     3          4 H     BOND            1.000000     0.000000  KCAL/ANGSTROM
     4          4 H     ANGLE         128.300000     0.000000  KCAL/RADIAN
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE                  Note 3
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I   NA  NB  NC
     1     O
     2     +          1.00000                                    1
     3     H          0.97587 *      129.21255 *                 1   2
     4     H          0.97587 *      129.21255 *   180.00000     1   2   3
     5     -          2.00000        129.21255     180.00000     1   3   4

        INTERATOMIC DISTANCES
             O   1      +   2      H   3      H   4      -   5
-----------------------------------------------------------------
   O   1   0.000000
   +   2   1.000000   0.000000
   H   3   0.975867   1.784993   0.000000
   H   4   0.975867   1.784993   1.512215   0.000000
   -   5   2.000000   1.000000   2.723983   2.723983   0.000000

  MOLECULAR POINT GROUP            SYMMETRY CRITERIA
           C2V                         0.10000000
```

```
                EIGENVALUES
-37.65949 -19.26641 -16.84295 -13.93719   3.23378   4.80842

         NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS                    Note 4
        ATOM NO.   TYPE          CHARGE        ATOM  ELECTRON DENSITY
          1         O           -0.4642          6.4642
          2         +            0.5000          0.0000
          3         H            0.2321          0.7679
          4         H            0.2321          0.7679
          5         -           -0.5000          0.0000
DIPOLE (DEBYE)   X         Y         Z       TOTAL
POINT-CHG.    -3.777     0.000     0.000     3.777
HYBRID        -0.752     0.000     0.000     0.752
SUM           -4.529     0.000     0.000     4.529

         CARTESIAN COORDINATES
   NO.       ATOM               X         Y         Z
    1        O                   0.0000    0.0000    0.0000
    2        +                   1.0000    0.0000    0.0000
    3        H                  -0.6169    0.7561    0.0000
    4        H                  -0.6169   -0.7561    0.0000
    5        -                   2.0000    0.0000    0.0000

         ATOMIC ORBITAL ELECTRON POPULATIONS
  1.85977   1.37272   1.23169   2.00000   0.76791   0.76791
FULL COMPUTATION TIME :     0.380 SECONDS
```

Note 1: The contribution and charge information for the sparkles is presented here. Note that the total charge on the system is a function of the charge of the sparkles. Thus if two "+" sparkles (even a "+" sparkle could hold a negative partial charge) had been used instead, the total charge on the system would have been +2.

Note 2: There is a large increase in the system's energy due to the polarization by the sparkles. The normal AM1 heat of formation for water is -59.2 kcal/mol.

Note 3: The geometry has been distorted by the presence of the sparkles. The HOH angle has decreased by about 3° and the bonds are slightly longer than in regular water.

Note 4: The effect of the sparkles can also be seen in the electron distribution on the atoms. A comparison of the atomic charges with and without sparkles is listed below. The near proximity of the +0.500 sparkle has the effect of concentrating more negative charge on the oxygen atom as expected. The hydrogens are thus slightly more positive.

Method	*Charge on O*	*Charge on H*
Sparkles	*-0.4642*	*0.2321*
No Sparkles	*-0.3827*	*0.1914*

4.10 Polarizability Using the Kurtz Method

Henry Kurtz has contributed an excellent method for computing polarizabilities to AMPAC (see Section 5.8). TEST61 from the test suite gives an example of this computation carried out on a water molecule.

Input file (TEST61.DAT) :

```
AM1 PREC KPOLAR
```

```
   H2O
   KPOLAR
  O    0.000000  0    0.000000  0    0.000000  0   0  0  0
  H    0.961270  1    0.000000  0    0.000000  0   1  0  0
  H    0.961270  1  103.531481  1    0.000000  0   1  2  0
```

The results from the output file follow:

Output file (TEST61.OUT) :

```
*****************************************************************************
                              AM1 CALCULATION RESULTS
*****************************************************************************
*                              AMPAC Version 4.5
*                                 Presented by:
*
*                             Semichem, Inc.
*                             7128 Summit
*                             Shawnee, KS  66216
*                             (913) 268-3271
*                             (913) 268-3445 (fax)
*
*           - MINIMIZE ENERGY USING B-F-G-S  METHOD
*  PRECISE  - OPTIMIZATION CRITERIA TO BE INCREASED BY 10 TIMES,
*           -     S.C.F.   CRITERIA BY 100 TIMES,
*           - AND USE ACCURATE FINITE DIFFERENCE FORMULA  IN HESSIAN
*  KPOLAR   - CALCULATE HYPER-POLARIZATION TENSORS
*  AM1      - THE AM1 HAMILTONIAN TO BE USED
*****************************************************************************
AM1 PREC KPOLAR
    H2O
    KPOLAR
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I   NA  NB  NC
     1     O
     2     H          0.96127 *                                   1
     3     H          0.96127 *      103.53148 *                  1   2

         CARTESIAN COORDINATES
   NO.       ATOM         X         Y         Z
    1         8        0.0000    0.0000    0.0000
    2         1        0.9613    0.0000    0.0000
    3         1       -0.2249    0.9346    0.0000


  MOLECULAR POINT GROUP:  C2V

         RHF CALCULATION, No. OF DOUBLY OCCUPIED LEVELS =  4

       **  REFERENCES TO PARAMETERS  **

 H  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
 O  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)


           INTERATOMIC DISTANCES
              O   1      H   2      H   3
-----------------------------------------
   O   1   0.000000
   H   2   0.961270   0.000000
   H   3   0.961270   1.510130   0.000000
USE 2-POINT FORMULA IN INTEGRAL DERIVATIVES WITH STEP  0.00002000
STANDARD DEVIATION ON ENERGY   (KCAL)        0.000000058
STANDARD DEVIATION ON GRADIENT (KCAL/A,RD,RD)  0.0000029 0.0000028 0.0000000
AM1 PREC KPOLAR
    H2O
    KPOLAR
```

```
    GRADIENT (COMPONENT) TEST WAS SATISFIED IN BFGS OR DFP
    SCF FIELD WAS ACHIEVED

                              AM1    CALCULATION
                                                          VERSION 4.5

                                                     24-Jun-93

         FINAL HEAT OF FORMATION =     -59.240698 KCAL
         ELECTRONIC ENERGY       =    -493.269273 EV
         CORE-CORE REPULSION     =     144.706733 EV
         GRADIENT NORM           =       0.004102
         IONISATION POTENTIAL    =      12.464161 EV
         NO. OF FILLED LEVELS    =       4
         MOLECULAR WEIGHT        =      18.015
         SCF CALCULATIONS        =       1
         COMPUTATION TIME        =       0.14 SECONDS

   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I   NA  NB  NC
     1     O
     2     H          0.96127 *                                  1
     3     H          0.96127 *      103.53148 *                  1   2

         INTERATOMIC DISTANCES
              O   1      H   2      H   3
-----------------------------------------
   O   1   0.000000
   H   2   0.961270   0.000000
   H   3   0.961270   1.510130   0.000000


  MOLECULAR POINT GROUP:  C2V

                 EIGENVALUES
-36.42405 -18.19965 -14.95258 -12.46416   4.41827   6.19152

         NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS
        ATOM NO.   TYPE          CHARGE        ATOM  ELECTRON DENSITY
          1         O           -0.3827          6.3827
          2         H            0.1914          0.8086
          3         H            0.1914          0.8086
DIPOLE (DEBYE)   X         Y         Z       TOTAL
POINT-CHG.     0.677     0.859     0.000     1.094
HYBRID         0.475     0.602     0.000     0.767
SUM            1.151     1.461     0.000     1.860
NOTE: "TRANSLATION" DIPOLE TO BRING CENTER OF MASS TO THE ORIGIN HAS BEEN ADDED

         CARTESIAN COORDINATES
   NO.       ATOM               X         Y         Z
    1        O                   0.0000    0.0000    0.0000
    2        H                   0.9613    0.0000    0.0000
    3        H                  -0.2249    0.9346    0.0000

         ATOMIC ORBITAL ELECTRON POPULATIONS
  1.86274   1.24275   1.27722   2.00000   0.80865   0.80865

DIPOLE MOMENT, POLARIZABILITY, AND 1ST AND 2ND HYPERPOLARIZABILITY                    Note 1
-------------------------------------------------------------------
CENTER OF MASS AT ORIGIN,  PRINCIPLE AXES AS:
    X, MOMENT=    2.960478 10**(-40)GRAM-CM**2
    Y, MOMENT=    1.908372 10**(-40)GRAM-CM**2
    Z, MOMENT=    1.052107 10**(-40)GRAM-CM**2
CARTESIAN COORDINATES ARE (ANGSTROMS):
   NO.       ATOM               X         Y         Z
    1        O                0.0000   -0.0666    0.0000
    2        H                0.0000    0.5283    0.7551
    3        H                0.0000    0.5283   -0.7551

ZERO FIELD HEAT OF FORMATION (KCAL)=  -59.24069784019775
```

```
          PERMANENT DIPOLE (DEBYE)=     0.00000     1.86048     0.00000

STANDARD DEVIATION ON ENERGY: 5.0D-12 (Kcal/mol) AND DIPOLE: 4.1D-08 (Debye)
APPLIED ELECTRIC FIELD MAGNITUDE: 0.00200 (A.U.)  0.10285 (V/cm)
STANDARD DEVIATIONS "std" CALCULATED FROM THIS FIELD AND PREVIOUS STD DEVIATION,
ASSUMING TERMS OF ORDERS 5, 6 IN TAYLOR EXPANSION ACTUALLY NEGLIGIBLE.

****************************** DIPOLE ******************************

COMPONENT         E4       std          DIP       std
    X           0.000000 2.6D-12       0.000000 1.6D-08
    Y          -0.732074 2.6D-12      -0.732021 1.6D-08
    Z           0.000000 2.6D-12       0.000000 1.6D-08
MAGNITUDE:      0.732074 2.6D-12       0.732021 1.6D-08  (A.U.)
                1.860612               1.860477          (DEBYE)
```

Note 2

```
********************** POLARIZABILITY (ALPHA) *********************

 COMPONENT        E4       std          DIP       std       E4 + ATOMIC CORR.
   XX           0.256063 6.3D-09       0.256042 7.7D-06       0.256063
   YY           3.538602 6.3D-09       3.538373 7.7D-06       3.538602
   ZZ           6.339278 6.3D-09       6.338855 7.7D-06       6.339278
   XY           0.000000 1.3D-09       0.000000 7.7D-06       0.000000
   XZ           0.000000 1.3D-09       0.000000 7.7D-06       0.000000
   YZ           0.000000 1.3D-09       0.000000 7.7D-06       0.000000
AVERAGE:
         A.U.    3.377981 3.6D-09       3.377757 4.4D-06       3.377981
      ANG.**3    0.500565 5.4D-10       0.500531 6.6D-07       0.500565
 ESU (X10-24)    1.001071 1.1D-09       1.001005 1.3D-06       1.001071
```

Note 3

```
*************************** SECOND-ORDER (BETA) ***************************

COMPONENT         E4       std          DIP       std
  XXX           0.000001 1.6D-06       0.000000 2.7D-03
  XYY           0.000000 1.7D-06       0.000000 2.7D-03
  XZZ           0.000001 1.7D-06       0.000000 2.7D-03
  YYY           8.640311 1.6D-06       8.642210 2.7D-03
  YXX           0.142123 1.7D-06       0.141416 2.7D-03
  YZZ          13.191372 1.7D-06      13.190399 2.7D-03
  ZZZ           0.000002 1.6D-06       0.000022 2.7D-03
  ZXX           0.000002 1.7D-06       0.000000 2.7D-03
  ZYY           0.000002 1.7D-06       0.000000 2.7D-03
VECTOR COMPONENTS GIVEN BY: Bi=(3/5)*(Bi11+Bi22+Bi33)
   BX           0.000001 1.8D-06       0.000000 2.8D-03
   BY          13.184284 1.8D-06      13.184415 2.8D-03
   BZ           0.000003 1.8D-06       0.000013 2.8D-03
VALUE OF BETA ALONG THE DIPOLE MOMENT:
A.U.          -13.184284             -13.184415
ESU (X10-30)   -0.114138              -0.114139
```

Note 4

```
*********************** THIRD-ORDER (GAMMA) ***********************

COMPONENT         E4       std          DIP       std
 XXXX           1.850406 4.2D-03       1.850595 2.0D+00
 YYYY          20.291323 4.2D-03      19.224969 2.0D+00
 ZZZZ         -38.502151 4.2D-03     -37.627157 2.0D+00
 XXYY          -3.330223 3.0D-03      -2.489858 3.5D+00
 XXZZ          -4.414087 3.0D-03      -2.739779 3.5D+00
 YYZZ          -9.298408 3.0D-03      -8.501965 3.5D+00
AVERAGE GAMMA GIVEN BY:  (1/5)*(GXXX + GYYY + GZZZ + 2*(GXXYY + GXXZZ + GYYZZ))
   A.U.      -1.00892D+01 7.6D-03   -8.80296D+00 4.2D+00
ESU (X10-36) -5.09620D-03-3.8D-06   -4.44652D-03-2.1D-03
```

Note 5

```
NOTE: for more accurate "E4" results, double the field magnitude and
extrapolate linearly at zero field vs the square root of the field.
FULL COMPUTATION TIME :     1.320 SECONDS
```

Note 1: *The KPOLAR output section begins here.*

Note 2: This section presents values of the dipole moment in various units as computed by this module.

Note 3: This section of the output lists the polarizability (first order) or α *value of the computed structure, again in a variety of units.*

Note 4. The output here describes the second order polarizability or hyperpolarizability. This value is commonly referred to as β.

Note 5. This section of the output lists the third order polarizability or the second order hyperpolarizability. This value is commonly referred to as γ.

CHAPTER 5: BACKGROUND

This chapter provides a brief summary of some of the more important algorithms found in AMPAC. A full bibliography is provided in Chapter 13.

5.1 The Self Consistent Field Procedure

Criteria and Accuracy in SCF Convergence: As programs in high-level languages like FORTRAN are moved ("ported") from one system to another, slight discrepancies can arise in some of the calculated values due to different implementation of compilers and architecture. This is to be expected and the differences should be systematic (up to 0.05 kcal/mol on ΔH_f and 0.01 kcal/mol/Å on derivatives). On a given computer system these errors must be very small to allow the density matrix (and hence the energy gradients which are highly dependent on the density matrix) to converge. Second order properties such as polarizability and force constants are very sensitive to this lack of convergence and can take on incorrect values if the gradient and wavefunction convergence are not complete. The quality of the density matrix convergence is governed by the SCFCRT parameter. The following table lists the default values of SCFCRT in different situations.

Optimizer	SCFCRT	PRECISE
BFGS, DFP, NLLSQ, POWELL, SIGMA, PATH, CHAIN	1×10^{-5}	1×10^{-7}
FORCE, IRC, NEWTON, LTRD	1×10^{-8}	1×10^{-10}

As noted in Chapter 4, the user may specify convergence criteria by using the SCFCRT= keyword. The lower boundary allowed for this value in 1×10^{-11} and is used if SCFCRT=0 is placed on the keyword line.

Two criteria (SELCON and PLTEST) are used to test for SCF convergence, and both must be met before a self-consistent field is achieved.

SELCON: (SELCON is the value of SCFCRT re-expressed in kcal/mol. A lower bound is set on this value based on an internal estimate of the accuracy of the computer.) If the difference in electronic energy between any two consecutive iterations drops below SELCON, then the first test is satisfied.

PLTEST: This is the convergence threshold for the diagonal elements of the density matrix. This criterion is not a simple value, but is coupled with the SCFCRT via an empirical equation taking into account the roundoff level and the particular wavefunction in use for the calculation. By relating these two values one obtains smoother and more consistent behavior of the SCF response vs. the SCFCRT criterion used alone. This is required in the frequent cases where the energy appears to be stationary but the density matrix is still oscillating (e.g. molecules with heteroatoms involved in a donor-acceptor bond). With PLTEST,

one can obtain a comparable level of self-consistence for both the energy and the density matrix.

Convergence Techniques in the SCF Calculation: Three methods have been included in AMPAC to promote SCF convergence. Each of them is suitable for RHF, RHF/HE, or UHF calculations, with or without the SMx solvation models. Each convergence approach uses a different and exclusive method from the others, so only one may be invoked at a time. AMPAC will usually make decisions based on the progress of the SCF as to which is most advantageous for a particular problem and interchange them automatically as appropriate.

1. Two-point linear or geometric interpolation and extrapolation of molecular orbital subspace: This converger function is dominated by a steepest descent method in order to minimize the risk of convergence towards spurious SCF solutions.

2. Pulay's DIIS method: PULAY relies on the fact that the eigenvectors of the density and Fock matrices are identical at self-consistency. The extent to which this condition is not met is a measure of the deviance from self-consistency. Pulay's method uses this relationship to calculate a linear combination of Fock matrices, and this new Fock matrix is then used in the SCF calculation. This method competes in efficiency with quadratic techniques, rapidly converging toward the nearest stationary SCF solution, which may or may not be a minimum.

3. Energy level shift technique: The energy gaps between subsets of molecular orbitals with differing occupancies is increased when this approach is used. This has the effect of damping oscillations in occupancy between nearly degenerate virtual and filled MOs and biasing the procedure towards a steepest descent method. Intrinsically divergent equations can often be changed to intrinsically convergent forms by this technique. Note that AMPAC now uses a dynamic shift algorithm that decreases the separation as the SCF approaches convergence.

By default, AMPAC begins by using methods 1 and 2, but will switch to method 3 as soon as there is either no reasonable decrease in the computed energy (no SMx model in use) or no stabilization of charge (SMx model in use). If method 3 fails or the default value of 100 SCF cycles (150 with SMx) is exceeded, (see the discussion on the keyword ITRY), method 3 is re-entered with a large damping factor and the system is allowed a new set of cycles double the original in number. Virtually any wavefunction will be converged to a reasonable degree using the SHIFT method within 200 cycles and methods 1 and 2 may be re-entered safely. This switching of SCF convergence procedure and resetting of the SCF cycle counter is performed automatically by AMPAC.

The user may intervene in the SCF convergence procedure at the following points:

1. Change the default number of SCF cycles using the ITRY keyword.

2. Change the priority between convergence methods 1 and 2 by invoking the keyword PULAY.

3. Request the level shift algorithm to be implemented immediately by invoking the keyword SHIFT=n.nnn. If large enough values for ITRY and SHIFT are provided, progress toward an SCF solution is almost assured, though such progress will likely be computationally expensive.

4. Define prototype MOs to be followed throughout the SCF procedures using one or another of the FILL keywords (see Chapter 3).

5.2 LTRD and NEWTON

LTRD and NEWTON are quadratic optimization methods exclusive to AMPAC. They are very accurate and highly reliable, but are slow for larger systems since they calculate a full Hessian matrix at each step in the optimization. NEWTON minimizes the heat of formation (energy), and LTRD minimizes the gradient norm. The Hessian matrix is usually computed from an analytical-numerical method but a twice-numerical method is used if the keyword DERINU is specified. In both cases, simple forward finite difference or central finite difference (better) is used depending on whether the keyword PRECISE is specified. An estimated standard deviation value for each eigenvalue is printed. LTRD also computes the components of the vibrational frequencies in terms of the internal coordinates rather than Cartesian coordinates, as is the case with FORCE.

Both methods are usable with either internal coordinates or Cartesian coordinates (see keyword XYZ) and are insensitive to the redundancies that might arise in some geometry definition schemes (dummy atoms and/or translations-rotations). Although not exactly the same as a set of local normal modes, the eigenmodes (eigenvectors of the Hessian available at each iteration) provide a quantitative picture of the curvature of the potential energy surface in terms of the coordinates defined by the user through the geometry definition. A vibrational analysis is carried out at convergence, providing some or all of the following, depending on the value of PRINT=: the Hessian matrix, its eigenvalues and eigenvectors, the vibrational frequencies, ZPE (along with errors), the Jacobian matrix between the user-defined internal coordinates and the Cartesian coordinates, the force constant matrix (millidynes/Angstroms) in Cartesian coordinates, and the weighted force constant matrix (millidynes/Angstroms/amu).

Both methods make use of a mixed optimization strategy employing the steepest descent in the energy or in the gradient norm, the quadratic direction, or hybrid of the two. Also the space may be partitioned according to the signs of the eigenvalues. The inflection points on a potential surface may be local minima of the gradient norm, characterized by an extra zero in the eigenvalues of the Hessian. Such points are usually “attractors” of quadratic methods (NLLSQ, SIGMA, POWELL), but LTRD characterizes them accurately. In contrast, NEWTON avoids these points by biasing the search towards the steepest descent in energy.

5.3 Geometry Optimization

The default procedure for geometry optimization is the BFGS modification to the DFP algorithm (for references see Chapter 13). This method minimizes a real valued function (in this case the heat of formation, ΔH_f) evaluated for the

system after each SCF convergence. The following messages are produced when AMPAC achieves geometric convergence:

1. TEST ON RESIDUES SATISFIED

   (Formerly "Herbert's Test") The estimated distance from the current geometry to the minimum is less than EYEAD. The default value of EYEAD is 0.001, and when PRECISE is specified drops to 0.0001.

2. TEST ON RMS GRADIENT SATISFIED

   The RMS gradient norm is less than TOLERG. The default value is 1.0 kcal mol^{-1} $Å^{-1}$ (or kcal mol^{-1} rad^{-1}). With PRECISE, this is multiplied by a factor of 0.1. If the keyword GNORM is specified, then TOLERG is replaced by the value supplied.

3. TEST ON X SATISFIED

   The relative change in the geometry over any two successive iterations has dropped below TOLERX. The default value is 0.0001 Å. When PRECISE is specified, this value is lowered to 0.00001 Å.

4. HEAT OF FORMATION TEST SATISFIED

   The calculated values of the heat of formation on two successive cycles differ by less than TOLERF. Default value is 0.002 kcal mol^{-1}, becoming 0.0002 kcal mol^{-1} when PRECISE is specified.

5. GRADIENT COMPONENT TEST SATISFIED

   (Formerly "Peter's Test") In addition to the TOLERG, TOLERF and TOLERX tests, a second test in which no individual component of the gradient norm is larger than TOLERG must be satisfied. If on three (five with PRECISE) successive cycles this test fails, while all other criteria are met and the heat of formation has dropped by less than 0.3 kcal/mol, then the calculation is stopped after issuing the message:

```
        THERE HAVE BEEN 3 ATTEMPTS TO REDUCE THE GRADIENT
DURING THESE ATTEMPTS THE ENERGY DROPPED BY LESS THAN 0.3 KCAL/MOL
        FURTHER CALCULATION IS NOT JUSTIFIED AT THIS TIME
```

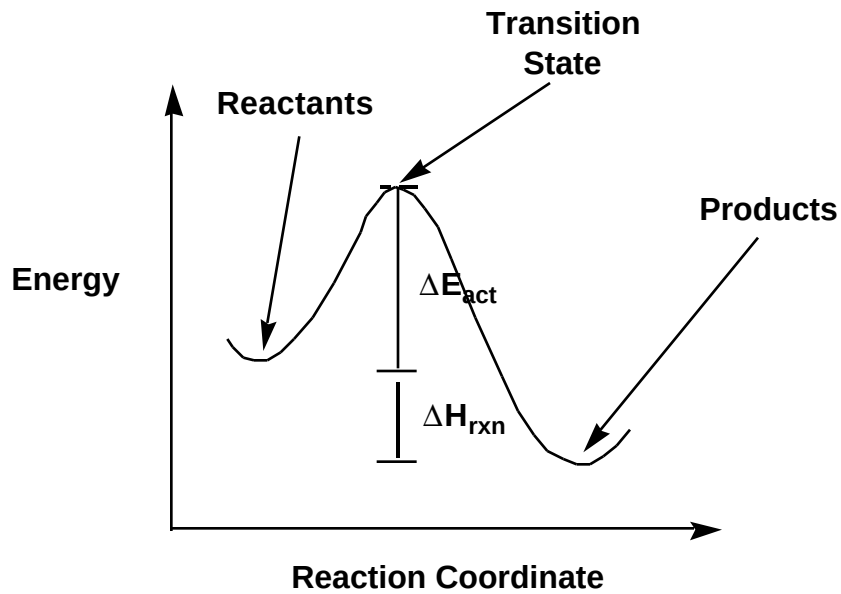
5.4 Potential Energy Surfaces (PES)

A stationary point on a potential energy surface (PES) is a point where the gradient vector (first derivative of energy with respect to atomic positions) approaches zero. Such a point is mathematically described most accurately as a critical point. The behavior of the PES in the vicinity of a critical point depends on the second order derivatives of the energy with respect to the atomic position, i.e. the Hessian matrix. The Hessian matrix, its eigenvalues and eigenvectors, are coordinate-dependent but the signs of the eigenvalues do not depend on a change of the coordinates (as long as the full space is spanned). Thus, it is the signs of the eigenvalues which characterize the nature of a critical point. Mathematically, critical points are classified by the number of strictly negative eigenvalues of the Hessian, called the index of the critical point.

At a critical point with index zero, the energy rises upon movement in any direction with respect to the energy value at the critical point. This set of conditions defines a minimum on the PES, a stable conformation of the system. If one or more eigenvalues of a stationary point are negative, there exist directions where the energy rises as above, and others where the energy decreases. This set of conditions defines a critical point that is no longer a minimum, but something else variously called a "col", a "hilltop", a "ridge", or a "super saddle point". Among these critical points of various indices, the ones of index 1 play a special role in chemistry as they correspond to the transition statesin the Theory of Rate Processes.

The mathematical description of the energy surface can be related to chemical processes. Reactions are often visualized in terms of an energy profile vs. some chemically important reaction coordinate. The components of this arrangement are shown on the simple (actual PESs may have many degrees of freedom and be multidimensional) figure below. The points labeled correspond to two minima (Reactants, Products) and a maxima (Transition State) and are collectively know as stationary points. Minima on the graph represent stable species on the PES, and are thus stationary points with index 0. The transition state (maxima) on the graph corresponds to a stationary point of index 1. It must be emphasized that these points are the only ones which have mathematically defined properties on the potential graph. Intermediate points on the surface require that some subset of the parameters be constrained, a condition inconsistent with the definition of a stationary point. It should be noted that the semiempirical parameters were derived from molecules at stationary points (minima in fact) and the properties produced by the models are thus only strictly meaningful at these points. However, it has been shown that the chemical model comprising the semiempirical methodologies is valid at positions away from the minima, such as transition states.

Some of the thermodynamic quantities that can be computed by AMPAC and their relationship to the axes of the graph are also presented on the figure. The relationship between kinetics and thermodynamics is well known and the ΔE_{act} (where E is either free energy (G) or enthalpy (H)) is the quantity usually related to kinetics.



5.5 Characterization and Refinement of Stationary Points

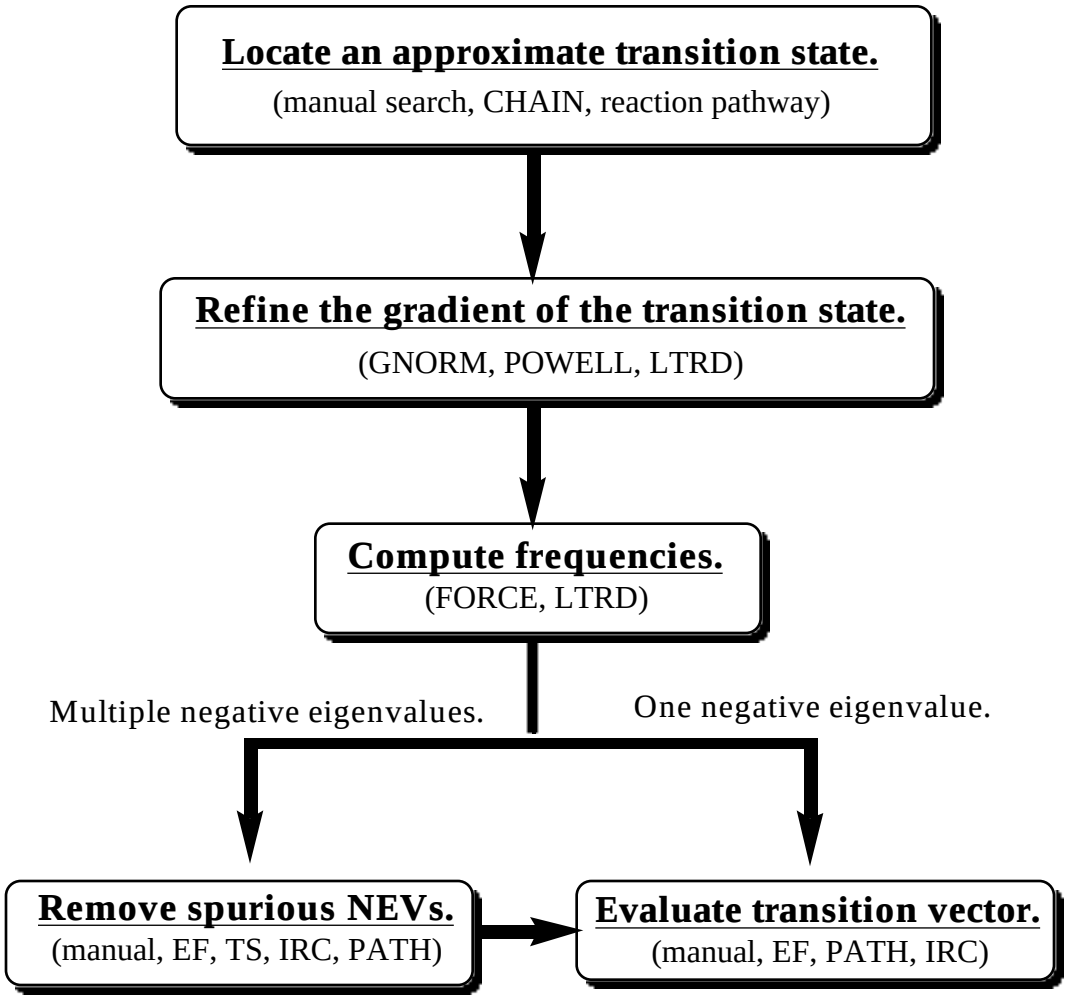
The final stage in any calculation is the proper characterization of all results as particular types stationary points. This requires a frequency analysis by FORCE or LTRD. (An exception is CHAIN, which locates a point of index 1.) Ample data exists in the literature showing the danger of not completing this final step in any computational study.[15] Section 4.2 describes this type of analysis using FORCE on the cyclization transition state of 1,3-butadiene and Section 4.3 shows the LTRD treatment of the same system. Further, the gradient must be refined to a very high degree (reduced in value) for a frequency analysis to be useful. This can be accomplished by the use of the keywords PRECISE and/or GNORM=. An unrefined gnorm or gradient component indicates that there are residual forces acting on the geometry of the system that must be eliminated before a stationary point is achieved. If FORCE is being used for the frequency computation, a gnorm test is applied and calculation is halted if the value is above 3.0 (see keyword LET). If LTRD is being used and the gnorm is too large, an optimization proceeds using the full Newton algorithm (see Section 5.2 for a discussion of LTRD's function).

As mentioned in the last section, if a system has more than one negative eigenvalue, then it is not a transition state, but a point termed variously a "col", a "hilltop", or a "ridge" or "super saddle point." In general, this type of point is near a transition state, and some method must be utilized to optimize to the true transition state. There are several automated techniques in AMPAC for following vibrational modes that aid in this procedure (PATH EF, TS, and IRC), but this problem can also be solved manually. The basic technique is to determine the atomic motions composing the vibration to be followed, increment the geometry a small amount along these coordinates, and reoptimize (gradient minimization).

---

15 Pople, J. A.; Raghavachari, K.; Whiteside, R. A.; Schleyer, P. v. R. J. Am. Chem. Soc. 1981 , 103, 5649. Incorrect indetification of points pointed out in: Dewar, M. J. S.; Healy, E. F.; Ruiz, J. M. J. Chem. Soc., Chem. Commun. 1987 , 943.

As well as refining the stationary point, it is important to verify that a located transition state does indeed lie along the pathway between reactants and products. This can be accomplished by incrementing the geometry of the transition state toward the reactants and requiring an energy minimization. The reactants should result. An analogous procedure can be employed for locating the products. The AMPAC GUI can be very helpful in analyzing vibrations and performing the needed geometry modifications. See Section 2.5 of the AMPAC Graphical User Interface Manual for an example of how this is done. The steps for proper refinement and confirmation of a transition state may be summarized as follows:



If any constraints (i.e. SYMMETRY or reaction coordinate) are imposed on the system in the course of the geometry optimization, the resulting geometry is NOT always a valid stationary point. The geometry will be a valid stationary point if and only if the constraints reflect correct point group symmetry for the system. In these cases the gnorm may be quite low, but it should be recognized that the gnorm does NOT include components from unoptimized parameters, which may be quite significant. Full characterization requires a geometry optimization resulting in a low gnorm after removal of all constraints as the starting point for a frequency analysis.

A common example of spurious negative eigenvalues is a methyl rotation. The rotation of a methyl group about a single bond is a low-energy process (usually a small negative frequency) and is very difficult to eliminate in some cases. In the case of a methyl rotation, the components will almost certainly be the dihedral angles of the hydrogen atoms, an easy case to solve.

5.6 SIGMA

SIGMA is another in AMPAC's arsenal of gradient minimization utilities. SIGMA first calculates an accurate Hessian matrix (a very slow step), then determines the direction of most rapid descent, and searches along that direction until the gradient norm is minimized. The Hessian is then partially updated in light of the new gradients, and a fresh search direction calculated. Clearly, if the Hessian changes markedly as a result of the line search, the update will be inaccurate, and the new search direction will be faulty. SIGMA is best at the final refinement of a geometry that is near its minima. If very far away from the proper point, the Hessian update error can cause it to converge very slowly.

5.7 Polarizability Calculations

Polarizability can be defined as the tendency of a molecule's electrons to be deformed by an applied electric field. At present, the polarizability volume is calculated by placing the molecule in a shaped electric field produced by four sparkles and calculating the deformation of the electrons. This polarizability method is activated by using the keyword POLAR.

5.8 H. Kurtz's Alternative Polarizability Method

Henry Kurtz has contributed to AMPAC a new polarizability method that differs in approach from that described above. Rather than using sparkles to create a shaped electric field to determine polarizability, Professor Kurtz's method works directly on the elements of Hamiltonian matrix. The perturbation of the energy operator can be expressed as follows:

$$\Delta H_f = \Delta H_f^o - V\, E_{charge} - \frac{dV}{dx}\, E_{dipole} - \frac{d^2V}{dx^2}\, E_{polarizability}$$

From this basic idea, the polarizability volume (in $Å^3$) may be computed. A similar perturbative approach (dipole moment with respect to electric field) can be used to obtain the first (β) and second hyperpolarizability (γ) values, useful in non-linear optical studies. See the references in Chapter 13 and Section 4.10 for a more detailed discussion and an example. This polarizability method is activated by using the keyword KPOLAR.

5.9 LOCALIZE

Chemists think of molecules in terms of the overlap and combination of atomic orbitals to form molecular orbitals. It is often difficult to analyze the final MOs from an AMPAC calculation based on the output eigenvectors, which are the coefficients of the atomic orbitals. Using LOCALIZE, the occupied eigenvectors

are transformed into a localized set of MOs by a series of 2 x 2 rotations which maximize $<\Psi^4>$. The value of $1/<\Psi^4>$ is a direct measure of the number of centers involved in the MO, thus for H_2 the value of $1/<\Psi^4>$ is 2.0, for a three-center bond it is 3.0, and for a lone pair it is 1.0. Higher degeneracies than allowed by point group theory are readily obtained. For example, benzene would give rise to a 6-fold degenerate C-H bond, a 6-fold degenerate C-C sigma bond and a three-fold degenerate C–C pi bond. In principle, there is no single step method to unambiguously obtain the most localized set of MOs in systems where several canonical structures are possible, just as no simple method exists for finding the most stable conformer of some large compound. However, the localized bonds generated from this procedure will usually be acceptable for routine applications and more closely follow the chemist's intuitive expectation.

5.10 Integration of a Reaction Path in PATH or IRC

<u>Differential Equations of a Path:</u> The concept of a "reaction path" suffers from the lack of a clear definition, in that it has no mathematical form and is coordinate dependent. A reaction path is probably best defined as a special case of a steepest descent path, i.e. a trajectory with the force vector corresponding to the reaction pathway as a tangent. With s (a parameter of integration) and E (the energy as a function of a set of coordinates, x), such a trajectory is defined by the first order system of differential equations:

$$\frac{\partial x_i}{\partial s} = -w_i \frac{\partial E}{\partial x_i} \quad (i = 1, n)$$

where w_i is defined as a positive weight, e.g. the inverse of the masses of the nuclei.

With s=O as a starting point, a unique trajectory is defined and will always end at a critical point (most of the time, a minimum) when s approaches infinity. The length l of the trajectory from s=O to s=t is given by the following integral along the path:

$$l(t) = \int_0^t \sqrt{\sum_i \left(\frac{dx_i}{ds} \right)^2} \, ds$$

A unifying definition for the reaction path has been proposed on the basis of dynamics in the limiting case of vanishing kinetic energy. This leads to an opposite-gradient trajectory (steepest descent path), but only within the mass-weighted Cartesian coordinate system. This trajectory defines the intrinsic reaction coordinate or IRC. This definition may also be useful in following steepest descent paths in other coordinate systems. These paths no longer correspond to the IRC, but will end at the same critical point, as the topology of the potential surface is not a function of connectivity.

The PATH method in AMPAC follows such general steepest descent trajectories. This method is often useful for locating weakly stable intermediates

along a reaction path or following a spurious eigenmode to refine a transition state. In contrast, the IRC method focuses on the reaction path and the physical properties along it.

<u>The Choice of a Numerical Integrator:</u> A variety of numerical integration algorithms are available in the literature and have been extensively tested in chemical kinetics using semi-classical trajectories. None of the standard methods (Runge-Kutta or Predictor-Corrector) are efficient enough for the integration of a reaction path when a valley (minimum energy reaction pathway, MERP) is followed.

Elsewhere, special integrators have been derived for systems with a large time constant and take the form:

$$\frac{\partial x_i}{\partial s} = -r x_i(s) + f_i(s)$$

with r a "large" positive number and $f_i(s)$ a slowly varying function of s. This is also the case (with $f_i(s) = O$) for a reaction path expressed in the normal modes of a quadratic potential. Anharmonic effects are taken into account by $f_i(s)$. Using these properties, a mixed strategy employing both a standard Predictor-Corrector when r is small or negative and an exponential integrator when r becomes large can be derived. This approach does not require that the Hessian matrix (needed for rotation onto the local normal mode basis) be explicitly computed. This condition saves a large amount of computational time and effort. The Hessian is updated using only the gradient evaluations along the path. Such a mixed integrator works much more efficiently than either single standard method when applied to a reaction path expressed in internal coordinates.

5.11 Intrinsic Reaction Coordinate (IRC)

(See Sections 4.8 and 5.11 for a description of the application and underlying theory of the IRC.) If physical properties are to be obtained along the reaction path, then IRC should be used. The IRC can be described as a "local normal mode", immediately related to statistical theories of reaction rates such as transition state theory, RRKM theory, or variational transition state theory. IRC was implemented in AMPAC 5.0 making extensive use of available materials such as the steepest descent integrator from PATH, the force constants matrix from LTRD, and thermodynamic methods from FORCE. While similar to PATH in many respects, the following differences should be noted:

- IRC uses mass weighted Cartesian coordinates even if the geometry is provided in terms of internal coordinates.

- IRC explicitly computes the HESSIAN along the path and is more accurate than PATH.

- The PATH keyword WEIGHT is inactive with IRC, but an oriented transition vector can be supplied via T.V.

- IRC can be used to study the properties of points along the reaction path. If n.n is specified, these properties are computed at each n.n Å

interval. "Transverse" thermodynamic properties are also computed if THERMO is invoked within IRC.

5.12 Transition State by the CHAIN Method

(See Section 4.6 for a description of the application of CHAIN.) The location of transition states and the calculation of their properties is the central question in studying reaction mechanisms using quantum mechanical procedures. Optimization and location of a transition state can fail for several reasons not applicable to a minima. There are several automated methods in AMPAC for locating transition states, but CHAIN is the premier technique in this application. CHAIN has significant advantages over the reaction coordinate method (see Section 4.4) in that the RC generates a series of relatively inexpensive intermediate optimizations, but also can fail to locate a saddle point when a non-continuous reaction path is followed. Transition states corresponding to the crossing of electronic states (an avoided crossing) are often responsible for such discontinuities in the reaction path. Also, the gradient norm minimization techniques are not selective and may locate any nearby critical point including local minima or other nearby critical points (inflection points) without regard to their relationship to the reaction path.

The primary task of a procedure designed to find a transition state lying between a given set of minima (respectively the reactants and the products of the chemical reaction under study) is to ensure that it moves smoothly toward a true transition state. A mathematical solution involves stepping along the gradient vector field of an arbitrary continuous path between the reactants and the products. This procedure leads to a limiting path where the highest energetic point is a saddle point. In the case of a multi-step reaction mechanism, the highest energy transition state will be located. The algorithm consists of replacing a chain of points C(n)=(R,...,p(i),...,P) running from reactants R to products P by a new chain C(n+1) at iteration n+l. In order to maintain the connectivity of the path, the distance between two successive points on the chain is required to not exceed a given length (0.3 Å in AMPAC). New points are inserted as soon as a link length becomes too long. An iteration roughly consists of skipping the current highest point of the chain along either a descending direction (thus insuring the energetic relaxation of the whole path) or an ascending direction (resulting in interpolation of a point along the path). Successive evaluations of the gradient are used to update a quadratic local estimate of the potential, which makes location of the transition easier and provides a good estimate of the transition vector.

5.13 Calculation of Gradient Norms

AMPAC uses geometric gradients extensively in determining when to terminate calculations and to find search directions. These gradients (first derivatives of energy with respect to atomic position) may be computed either analytically (by taking the derivative of an algebraic equation) or numerically (finite difference, must be requested by the keyword DERINU). Each optimizable geometric parameter is assigned a gradient component (g) and the square root of the sum of the squares of these components defines the gnorm:

$$gnorm = \sqrt{\sum_{i}^{N} g_i^2}$$

The RMS gradient norm is used in the geometry optimization methods and is defined:

$$gnorm_{rms} = \sqrt{\frac{\sum_{i}^{N} g_i^2}{N}}$$

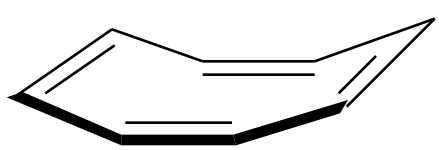
In both cases N is the number of optimizable geometric parameters.

5.14 Semiempirical Heats of Formation

The Heats of Formation resulting from AMPAC's semiempirical calculations are calculated using atomic Heats of Atomization stored in the program. The first step is to calculate the HF total energy of the system as predicted by AMPAC. This is the sum of the CORE-CORE REPULSION ENERGY and the ELECTRONIC ENERGY, both of which quantities are present in the output and archive files. The atomization energy is then computed by subtracting the total energies of the atoms (as predicted by the model being used) in their stoichiometric ratios. The Heat of Formation, ΔH_f, of the system can then be calculated using the enthalpies of atomization of the atoms and the atomization energy. While this is not a "true" ΔH_f, all of the semiempirical methods in AMPAC were parameterized to experimental ΔH_f at 298 K using this formalism.

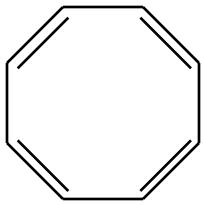
5.15 AMPAC Energy Minimizers Near Maxima

The standard suite of AMPAC energy minimizers (DFP/BFGS is the default) is usually sufficient to optimize a given geometry to a minimum on the PES. The performance of these minimizers can fail, however, when the initial geometry provided to the program is near a maxima. An example of this is cyclooctatetraene, which takes on a "bathtub" conformation when optimized in its minimum energy conformation:



However, if the initial geometry is provided as planar (see below), DFP/BFGS will predict the system to be planar. A frequency analysis (FORCE or LTRD) carried out at this point will show one negative eigenvalue, characterizing the geometry

as a transition state. In this case the TS corresponds to the process of inversion of the "tub".



This failure in the energy minimizers is due to the fact that DFP/BFGS treats the entire PES as a minimum, using a definite positive Hessian matrix to determine search direction. The region near a stationary point has a slowly changing gradient and is thus "flat" as far as the search algorithm is concerned. This (coupled with the definite positive Hessian approximation from above) makes this region appear to DFP/BFGS to be a very shallow minima with an extremely narrow peak corresponding to the actual critical point. Further, if the well is very symmetric, none of the points generated in the search will fall in the very small region of the peak and the search algorithm will not be informed of its existence. Only a full quadratic algorithm such as LTRD will explore the PES in sufficient detail to reveal a problem of this type, (at a large cost in computational effort, as many exact Hessians are computed). Care must be exercised in this region of the PES. The problem can be generally solved by simply introducing a slight degree of asymmetry to the molecule's definition, allowing it to naturally "roll down the hill".

5.16 The Computational Challenges of Transition Metal Systems

Calculations involving transition metal elements is one of most important areas of chemistry that has been excluded from routine treatment by computational modeling. This is largely because methods that allow standard programs to implement high quality semiempirical theoretical approaches to systems containing these elements are only now being developed and are becoming available to the chemical community at large. SAM1 is one of the most successful of these new approaches. It should be emphasized at the outset of this discussion that only a limited amount of our accumulated wisdom and experience with organic and main group elements will be transferable to work on iron and other transition metals. It is a virtually new area using the Dewar-style semiempirical methodology. Previous experience has largely been with closed-shell systems (singlet spin state) and much more "regular" chemistry. This is certainly not the case with transition metals.

We began the parameterization of transition metals using a simple closed-shell approach as a way of exploring the problems that will be encountered. In this light, our preliminary efforts were very instructive and valuable. A number of obstacles (both expected and unexpected) were identified and have been overcome. Some of these are listed below.

- *development of new and larger CI algorithms and approaches*
- *difficulty extrapolating initial values for the parameters from which to begin searches*
- *ordering of the atomic orbitals*
- *intelligent approach to CI for easier calculation and determination of the minimum level of CI required for a particular system*
- *lack of high quality experimental data on spin multiplicity*

The programmatic implementation of an "intelligent CI" is an important addition to AMPAC in working with certain transition metal systems. These include situations where the HOMO/LUMO MOs are degenerate to some degree, that should lead to unpaired electrons with potentially high spin multiplicities. In this case extreme caution must be exercised in choosing the correct OPEN pattern or the reference wave function will be a poor description and all subsequent calculations will be compromised. A segment of program code has been added that will determine the degeneracies of the MOs near the HOMO/LUMO boundary and suggest an OPEN pattern to use for this system to obtain a good reference wave function. (The user can obviously override these default values if the need arises.) The "natural" first guess orbitals from AMPAC are used to commence the SCF procedure and to analyze the MOs. In this approach, the RHF wavefunction from which the microstates are constructed for subsequent mixing is one where orbital occupancy and degeneracy patterns are largely defined by the values of the parameters. Any method that is developed ignoring this additional complication to more familiar semiempirical problems will not be accurate or chemically meaningful. See Section 4.11 for an example of how this procedure is applied.

5.17 NDDO Theory

MNDO, PM3, and AM1 are representatives of the NDDO (neglect of diatomic differential overlap) family of methods. As this model is applied to AM1 and PM3, there are seven basic parameters that must be considered for each atom. These are augmented with up to three (four in the special case of carbon) Gaussian corrections to adjust the core/core repulsion function (CRF). The two parameters with the largest effect are the one-center/one-electron energies, U_{ss} and U_{pp}. These represent the kinetic energy and core-electron attractive energy of single electrons in s- and p-orbitals. The next pair of parameters are adjustments to the two-center/one-electron resonance integral, $\beta_{\mu\upsilon}$, and are termed β_s and β_p. These parameters are responsible for bonding interactions between atoms. Another approximation within AM1 is the use of Slater functions to describe spatial features of the atomic orbitals. Slater functions are used because they require fewer parameters and are more easily parameterized. The exponents of the s- and p-orbitals on each atom become parameters and are abbreviated respectively, ζ_s and ζ_p. It should be noted that ζ_s and ζ_p also affect $\beta_{\mu\upsilon}$, as it is proportional to the overlap integral ($S_{\mu\upsilon}$), which is in turn calculated from the Slater exponents.

The CRF combines the Hamiltonian's nuclear terms with core-electron repulsive and attractive effects. The α parameter scales the entire CRF up and down, providing a radial dimension to the atom's core. The Gaussian correction functions added with AM1 operate on the CRF directly to correct it for specific defects. This type of correction can accommodate several chemical phenomena. One example is atoms that expand their octet when bonding, such as sulfur and phosphorous. Atoms with expanded octets are thought to use d-orbitals to allow back-donation of electrons for additional bonding. Although, AM1 has no explicit descriptions of d-orbitals, some of the effects d-orbitals have on bonding can be imitated by the Gaussian functions. Also, the single-ζ nature of the AM1 orbital basis set makes the method insensitive to some electronic factors and the Gaussians can mitigate these failures to some extent. For instance, semiempirical approximations tend to yield poor results for molecules where large charges are localized on atoms. The occupied orbitals of negatively charged species tend to expand in space due to electron repulsion. An analogous but opposite effect is noted for positively charged systems. These phenomena are accounted for in ab initio methods by using double- or triple-ζ basis sets or even additional special orbital functions (diffuse functions). This lack of flexibility in the AM1 orbital basis can be overcome to some degree by the Gaussian corrections. The use of Gaussians is an artificial correction made to the semiempirical treatment and should be avoided if possible. In some cases, however, Gaussians are beneficial and indeed necessary. Each Gaussian function consists of three parts: intensity (in eV), position (in Å) and width (in Å^{-2}).

MNDO differs from AM1 and PM3 in that, for the lighter elements near the top of the Periodic Table, the following assumptions were made to save time:

$$\zeta_s = \zeta_p$$

$$\beta_s = \beta_p$$

Also, the MNDO method includes no Gaussian functions.

5.18 General Theoretical Basis of SAM1

SAM1 is the next step in the development process that produced MNDO and AM1. It uses a new theoretical basis for the underlying model and gives better results than previous models. SAM1 will also eventually allow the study of new elements (those that require d-orbitals) while retaining the traditional computational efficiency of semiempirical methods. The need for a new theoretical approach to semiempirical calculations is evident for two primary reasons. First, the known deficiencies of AM1 and MNDO in certain cases are resistant to removal by parameterization within the present theoretical model. The problems are inherent to the theoretical treatment and the only reasonable solution is a new method. Second, the present formalism for computing bicentric two-electron repulsion integrals (TERIs) is very cumbersome and difficult when applied to d-orbitals. At present AM1 and MNDO use a modified multipole expansion for computation of TERIs:

$$\langle \mu\nu | \lambda\sigma \rangle = \sum_{l_1} \sum_{l_2} \sum_{m} \left[M^{A}_{l_1 m}, M^{B}_{l_2 m} \right]$$

where M values are multipoles. The TERI values are computed by determining the magnitude of the electrostatic repulsions between the multipoles as described by Dewar, Sabelli, Klopman, and Ohno (DSKO method). While this expansion yields only 22 unique repulsion integrals for s- and p-orbitals, the number of integrals when d-functions are included is enormous. As has also been pointed out, integrals of this form are not rotationally invariant in the case of d-functions and the ME fails to converge to the appropriate one-center integral boundaries at short distances. A number of approaches have been attempted to "patch" the problems with DSKO repulsion integrals, but they either failed due to poor performance or reduce the flexibility of the semiempirical approximation to unacceptable levels.

The mode of calculation of TERIs is extremely important in semiempirical methods of the MNDO/AM1 family as other quantities depend on their values, e.g. the CRF (the repulsive force between core electrons) is simulated by use of an <ss/ss> integral. As noted above, the major difference between AM1 and MNDO is an additional modification of this function using a linear combination of Gaussian terms to correct for the inadequacies of the model. The core-electron attraction integrals (CEA, the attractive force between core electrons on one atom and nuclei on another) are also based on the TERI/ME formalism. With this in mind, it becomes clear that an alternative method of computing TERIs is a functional definition of a new semiempirical methodology. This new method of computing TERIs is the primary difference between SAM1 and the earlier NDDO semiempirical methods.

The approach chosen in the case of SAM1 is to utilize ab initio integrals, scaled using adjustable parameters so as to retain the implicit treatment of correlation effects, characteristic of the semiempirical methods. The form of the TERIs used is:

$$\langle \mu\nu | \lambda\sigma \rangle = f(R_{AB}) \langle \mu\nu | \lambda\sigma \rangle^{CGF}$$

where $\langle \mu\nu | \lambda\sigma \rangle^{CGF}$ *are ab initio integrals evaluated from contracted Gaussian basis functions fit to Slater type orbitals (STO-3G) using standard methods. The function* $f(R_{AB})$ *is a scaling function that features adjustable parameters, altered systematically to reproduce experimental data.*

There are several significant advantages in the use of ab initio TERIs with a semiempirical procedure. First, the formulae are well defined and have been used for many years. Second, the gradients are easily computed from the Cartesian form of the Gaussian functions. This allows for the rapid and efficient construction of the Gaussians and their derivatives simultaneously. Third, formulae for d-orbitals already exist and these functions are bound by none of the limitations of the ME TERIs discussed earlier. It should be noted that the computation and manipulation of repulsion integrals is the most time-consuming (both CPU and I/O intensive) part of any ab initio calculation. The main reason for this is not the time required for a single integral calculation, but the large number of independent integrals which must be computed. In the SAM1 protocol, the NDDO approximation is still active, limiting the integrals which must be explicitly calculated to bicentric terms only, excluding three- and four-center terms from consideration. Because of the increased time spent on each integration, preliminary data shows that SAM1 is about two times slower than

AM1. This is still well within acceptable limits when compared to ab initio treatments of similar accuracy.

Further details of this method are in preparation for publication.

5.19 A General Philosophy for Semiempirical Parameterization

The parameterization process allows assignment of specific values to quantities not directly available from experiment and difficult to estimate a priori accurately. The parameters may be based on either experimental data or the results of more complete HF calculations. The methods in AMPAC have traditionally depended on developing parameters based on experiment. This has significant advantages, first, in that any theoretical inadequacies of higher level ab initio methods are circumvented. Second, relaxation of the parameters in such a way as to reproduce experiment handles in one step a multitude of chemical factors not directly includable in the model.

The semiempirical approach used by Dewar et. al. requires parameters to be derived for each type of atom in a molecule. Experimental data from a small group of representative molecules (which we refer to as the molecular basis set for parameterization, MBSP) is used to derive the parameter values. The items of data used are heats of formation (ΔH_f, kcal/mol), ionization potentials (IP, eV), dipole moments (μ, Debyes), and molecular geometries (bond lengths, bond angles, and dihedral angles), all gas phase. Extensive experience has shown that the parameterization algorithm will eventually generate a set of parameter values that is extendible beyond the limits of those molecules in the MBSP. The derivation of the parameters proceeds by computing gradients of the parameters with respect to the experimental data. This generates an error function, SSQ, which is a weighted least-squares index quantifying the difference between calculation and experiment. A line search along this direction yields the optimum step size, and this information is used to update the Hessian (second derivatives) matrix which guides the search of the parameter hypersurface. The algorithm used in this regard is a modification of the Davidon-Fletcher-Powell procedure. New results are then calculated and compared with experiment. This series of steps is repeated iteratively until threshold values of gradient and SSQ are attained. The parameters are then considered to be optimized and testing may begin to determine their suitability for further calculations.

Several points must be noted about the parameterization process itself. It requires a systematic and tenacious approach and a large commitment of computational resources. The mathematical methodology will find some local minimum for the differences between experimental and calculated values (SSQ). This may not, however, be a minimum corresponding to sensible chemistry. The parameterization process requires constant attention to insure that the search algorithm (which tends to take occasional "sidetrips") does not wander into an unprofitable region of the parameter hypersurface. Also, the minimum predicted by the program's search algorithm is strongly dependent on the beginning values of the parameters. While projections for initial values can be made on the basis of the periodicity of chemical quantities (including semiempirical parameters), a reliable parameterization process requires two dimensional grid searches in the area of physical viability for the parameters.

These searches help determine the best area of the parameter hypersurface from which to begin optimization. Grid searches are time-consuming and tedious, but necessary for proper refinement of the parameters. The molecules selected for the MBSP also have a great deal to do with the values that the parameters will finally assume. Every attempt is made to select species that represent important and useful chemistry without exceptionally biasing the results. In some cases, the MBSP must even be altered during the procedure to retain important aspects of the element's chemistry and remove extraneous effects. The concept of using a small group of representative molecules for development of parameters to extend well beyond the MBSP has been tested and proven many times over, as exemplified by the large number of successful semiempirical parameter sets for several different methods produced by Dewar et. al. over the past 30 years. It should also be noted that only non-radical (closed shell) and neutrally charged species are generally used in the MBSP. There are approximations within the method to specifically account for open shell species and parameters extendible to radicals and ions are reliably developed with this limitation.

Special considerations have been and will need to be made when dealing with transition metal systems and parameterization. First, the spin multiplicities and orbital mixing (CI) must be implemented and properly assigned as described above. Second, the data is limited in both quantity and quality. Both of these ideas lead to the idea that supporting calculations at the ab initio level will likely have to be done to support semiempirical calculations. They will likely fill "holes" in the data by providing correct spin multiplicities and geometries. Another point to note is the proper orbital description of the transition metal species will only be possible if parameterization is performed on molecules with the proper spin multiplicity pre-defined. This means that in addition to the traditional items used in parameterization (see above), spin multiplicity has been implicitly added to the list of data.

As pointed out both here and in the literature, the development of parameters is a difficult and tedious task. When done by the method here large amounts of computer time are required. This is especially true of the semi-ab initio protocol on which SAM1 is based. Parameterization requires a careful balance between acceptance of results from the search algorithm and intuition as to what is important and correct chemically: the HUMAN FACTOR.

CHAPTER 6: CONFIGURATION INTERACTION

6.1 Introduction

AMPAC 5.0 offers users a vastly improved and expanded configuration interaction (CI) capability when compared to other semiempirical programs. Given the special keywords and preselection techniques that have been implemented, AMPAC can now perform both extremely complex, yet efficient CI calculations. A CI calculation involves the interaction of microstates representing specific permutations of electrons within a defined set of MOs. The reference set of MOs (see Section 6.2 below) is obtained in various ways from an RHF or RHF/partial-electron calculation. All of the electrons are removed from the interacting MOs and the microstates are constructed by arranging the electrons in the MOs in various ways according to a specific set of rules. The energy of each configuration is evaluated, as is its energy of interaction with all previously defined configurations. The diagonalization of this matrix produces the eigenstates, which are linear combinations of some subset of the microstates constructed above. The microstates generated in CI will be eigenvectors of the S_z operator according to which of the spinstate keywords (SINGLET, ..., SEXTET) were used. If no spin state is specified, then the lowest energy spin states will be listed. See Section 6.4 for a description of the computation of spin states in CI.

The treatment in AMPAC is based on a CAS-CI formalism involving m electrons distributed among n CI-active MOs. The possible number of microstates representing the different distributions of electrons in the MOs can rapidly become computationally intractable. (If CAS-CI involving 10 electrons and 10 MOs is requested, this generates some 63,504 microstates!) For this reason, AMPAC 5.0 uses a preselection scheme to reduce the number of microstates that are retained for the actual configuration interaction matrix diagonalization.

In the semiempirical formalism, some of the non-specific correlation is absorbed by the parameterization and a crude large-scale CI is meaningless. However, for certain processes that can be modeled computationally (i.e. electronic spectroscopy on the lowest excited states of a system) an adapted CI is preferable. This approach features an explicit accounting for the re-polarization of MOs in excited states with respect to the ground state. For this to function as expected, a carefully chosen subset of the available microstates is needed. This set of microstates must have the capability of handling the specific correlation present in the system.

Caution should be employed with any CI procedure to insure that all members of degenerate sets of orbitals are included in the CI manifold. If this is not the case a warning message will be displayed. The user should be aware of this situation prior to requesting a CI calculation (see use of the keyword VECTORS).

6.2 The Reference Wave Function for a CI Calculation

In performing a CI calculation, the quality of the CI result and the ability of the calculation to converge to a proper SCF solution are almost completely dependent on the reference wave function used to construct the microstates,

which are then sorted as below. In AMPAC's CI module, there are a variety of paths to different solutions to use for this reference wave function. If a simple "C.I.=X" or "C.I.=(m, n)" is requested with no other options, AMPAC uses Dewar's half-electron (more properly "partial electron") method within the RHF protocol to construct the SCF. More control can be exercised on which MOs are partially filled by using the OPEN statement. This is especially important with transition metal systems (see Section 5.16).

Noted that if an error message is generated by AMPAC during a CI calculation stating that the program was unable to achieve SCF, this is likely not a CI error, but indicates that the program is probably unable to construct a reference wave function for further calculations. A good procedure to follow at this point is to perform a 1SCF calculation at the initial geometry and examine the wavefunction to ensure that the requested CI was of the proper size.

6.3 Microstate Selection Procedure

In any large-scale configuration interaction (CI) approach, only a subset of the eigenstates are of interest. This target group is usually composed of the ground eigenstate and a few of the lowest eigenstates. This set can further be characterized as having relatively large components in a small subset of microstates (MS) we will refer to as D, such that $D = D_0 + D_1 + D_2 + ... + D_n$. Within this notation, D_0 roughly corresponds to the ground state and D_1 ... D_n to the targeted excited states, selected based on symmetry and spectroscopy. Most of the information relevant to the targeted eigenstates are included in D, the "reference" set. However, a CI matrix constructed from D alone would suffer from two major deficiencies. First, there is a lack of specific correlation on the ground state or some set of important excited states. Second, the lowest excited states are unable to repolarize because a single-configuration SCF procedure such as that used in AMPAC is designed to describe the ground state most accurately. (Recall that CI uses this ground state wavefunction as the basis for constructing the microstates.)

The objective of the selection procedure is to extract from the enormous list of possible microstates excluded from D the ones which contribute most directly to specific correlation and repolarization. Perturbation theories are the most efficient tool to extract specific items (in the case at hand, an ordered list of MS interacting with D) from such a large list as that generated in the microstate construction step. The Epstein-Nesbet (EN) algorithm coupled with first order corrections on the eigenvectors was selected as the most successful approach from those tested.

At end of this process, the number of MSs still must not exceed $NMECI^2$ in AMPAC. If the CAS-CI list is larger than this, then a further sort is performed following two criteria:

i) Increasing order of the MS energies, i.e. diagonal elements of the CI matrix. This sort orders the MSs in the list from 1 to I, with $0 < I < M+1$. The variable M is defined as $NMECI^2$ (presently 10 in AMPAC) so M=100.

ii) Decreasing order of the EN corrections with respect to MS I_1 to I_2, with $0 < I_1 <= I_2 <= I$. This sort fills the MS list up to rank M. By default, I = 7, I_1 = 1, and I_2 = 7.

At each stage of the sorting procedure, the MS list is required to conform to the spin and/or space degeneracy elements present. This is achieved by inspection of the Møller-Plesset energies of the MSs at a threshold 1.0×10^{-4} eV. The Møller-Plesset energies are also used to extract from the CAS-CI list a medium-sized list of about 2000 MS on which sorts i) and ii) will actually operate.

Explicit handling of degeneracies is tedious and time-consuming work. AMPAC 5.0 automatically accounts for degenerate MOs remaining within the threshold value of 1.0×10^{-4} eV. As an example, the methane (T_d symmetry), with C.I.=8 produces the following CI output:

```
 4900 MICRO-STATES GENERATED VS  2278 ROOM AVAILABLE.
 1974 MICRO-STATES KEPT AFTER MOLLER-PLESSET SELECTION
SELECTION CRITERIA:1) FIRST 19 LOWEST MICRO-STATES
                   2) DECREASING 1-ORDER E.N. PERTURB. ON MICRO-STATES 1 TO 19
  855 MICRO-STATES KEPT FOR PERTURBATIVE SORT
   33 MICRO-STATES FINALLY SELECTED
```

In this example, CAS-CI generated 4900 MS, of which 1974 are kept within the medium-sized list. Note that the list is somewhat shorter than 2278 due to a quick sort by blocs. The MSs of reference are extended from the default (7) to 19, accounting for the degeneracy of single HOMO-LUMO excitation. MSs 856 to 1974 are degenerate and are eliminated as a whole (no room) before entering the EN sorting procedure. After this sort, MS 34 to >100 (degenerate) are also discarded because the list exceeds the limit of 100. At the end remain (from the CAS list) the closed shell ground state and the monoexcitations. Eigenstates resulting from diagonalization of the CI matrix (of size 33) are free from spin or spatial errors, even if accidental degeneracy between states with different multiplicities occurs.

6.4 Configuration Interaction Dedicated Keywords

CI-OK

In most cases, all of the members of a set of degenerated MOs must be taken into account in a CAS-CI procedure. AMPAC now performs a test of this requirement on the MOs, and if one or more of the selected orbitals are found to be degenerate with MOs not in the CI manifold, the program halts with an error message. The threshold for degeneracy is a difference in MO energies of less that 1×10^{-4} eV. To override this condition, specify CI-OK. Note that this adds the risk of biasing spin multiplicities and corrupting the geometric gradients. Abbreviation: None

OPEN(a, b)

The keyword OPEN(a,b) implies a CI calculation on b MOs with a electrons. This requires an occupancy of a/b electrons on the b highest occupied MOs when the reference wave function is being constructed. This "minimum" CI can also be

imbedded in a larger process by use of C.I.=c, implying c CI-active MOs. Abbreviation: None

PERTU(n,m)

This keyword overrides the default perturbative selection (See Section 6.2) of microstates in the CI procedure. This is accomplished by setting $I = n$ and $I_2 = m$. (Note that the values of I_1 and I_2 may be shifted upwards by using ROOT=r, which implies that I_1 = the greater of 1 or $r - \frac{m}{2}$, and $I_2 = I_1 + m$.) Abbreviation: None

Two limiting cases require consideration:

- PERTU(1,0) - focuses selection on the ground state only
- PERTU(101,m) - inhibits the perturbative sort because $n > M$, which is set at 100

PROTO=n

During the course of some optimizations, the canonical order of the MOs may evolve. MOs may cross, resulting in abrupt changes in energy due to discontinuities in the CI description. Such changes are automatically prevented in the course of gradient computation by the numerical method (using the keyword DERINU) or during a Hessian matrix evaluation, but not in the course of a normal optimization. When continuity is required, a set of "prototype" MOs can be defined for use in the remainder of the calculation. Such prototypes are used to select a subset of the full set of MOs which are the most similar to the prototype subspace. The criterion of proximity is the sum of the squares of the overlap between MOs and prototypes. The CI keyword PROTO=n is designed to accomplish this task. The value for n may be either 1 or 2, with the following consequences. If n = 1 (or simply PROTO), the first CI-active MOs will be prototypes for the entire calculation, without update. If n = 2, the calculation is begun as before, but selected CI-active MOs become prototypes for the next CI cycle. In this case, the prototype MOs evolve with the geometry.

For geometry optimization algorithms, (BFGS, POWELL, PATH, LTRD), PROTO=2 may be useful, but for CHAIN (which moves a path, not a point), or for a grid calculation or reaction coordinate calculation, PROTO=1 should be used, as the next step should not depend on the results of a previous calculation. Abbreviation: None

RECLAS(n,m)

When the user wishes to specify specific MOs to be used in a CI calculation or suitable MOs are not consecutive, this keyword indicates that canonically ordered MOs ranging from n to m will be reordered before entering CI. The explicit permutation order must be given at the end of the data in Section 10 of the input file. Making use of PROTO (see above) with RECLAS implies that the re-ordering is performed the first time CI is entered. Following this, CI uses previously generated prototypes and RECLAS becomes inactive. For example, with the

keyword RECLAS(2,7) and the data in Section 10 of the input file "5 4 2 3 7 6", the following permutation will occur in the canonically ordered MOs:

A E D B C G F H I J K L M N ...

Warning: The permutation must preserve the full set of MOs and must not reorder MOs between sets with different occupancies. This will cause the program to abort. Abbreviation: None

ROOT=n

The CI procedure generates many states, and the keyword ROOT allows just one of the states to be followed during the course of an optimization. If a keyword specifying the spin state is also present, e.g. SINGLET or TRIPLET, then the nth root of that state will be selected. Thus ROOT=3 and SINGLET will select the third singlet root. If ROOT=3 is used alone, then the third root will be used, regardless of spin state. Unusual care should be exercised when ROOT=n is specified. Note that ROOT=n does not imply a CI calculation; ROOT=n is only used when a CI calculation will be performed. Abbreviation: None

6.5 Calculation of Spin States

In order to calculate the spin state, the expectation value of S^2 *is calculated.*

Where N_{tot} = *No. of electrons in C.I.*

C_{ik} = *Coefficient of Microstate i in State k*

N_i^{α} = *Number of alpha electrons in Microstate i*

N_i^{β} = *Number of beta electrons in Microstate i*

n_{li}^{α} = *Occupancy of alpha MO l in Microstate i*

n_{li}^{β} = *Occupancy of beta MO l in Microstate i*

S^+ = *Spin shift up or step up operator*

S^- = *Spin shift down or step down operator*

$\delta_{C_{ik} S^+ S^- C_{jk}}$ *The Kroneker delta is 1 if the two terms are identical, zero otherwise.*

The spin state is calculated from $S = \frac{1}{2}\left(\sqrt{1 + 4S^2} - 1\right)$.

In practice, S is calculated to be exactly integer or half integer, thus there is insignificant error due to the approximations used. This does not imply that the method is accurate. The spin calculation is completely precise in the "group theory" sense, but the accuracy of the calculation is limited by the space-dependent Hamiltonian.

6.6 "Implied" Configuration Interaction

A number of practical situations or particular combinations of keywords will invoke AMPAC's CI module without explicit use of any of the C.I. keywords. These include BIRAD and EXCITED, the exact effects of which can be duplicated using more precise and directed keywords as shown below. It is recommended that actual CI keywords be used rather than these "combination" approaches in order to avoid unexpected results.

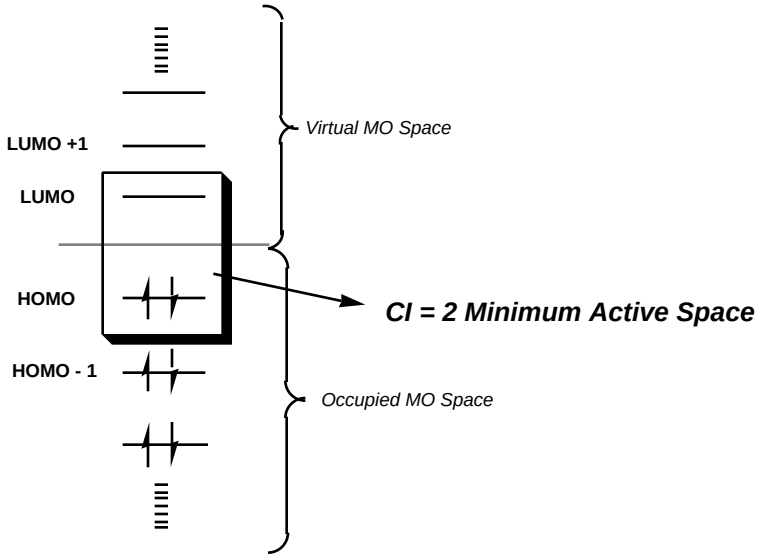
BIRAD :	OPEN(2,2) SINGLET
EXCITED :	OPEN(2,2) SINGLET ROOT=2

6.7 Configuration Interaction Example

Input File (TEST25.DAT) :

```
AM1 PREC GRAD T=3500 BONDS NOINT NOXYZ POWELL GNORM=0.10 SYMMETRY +          Note 1
C.I.=2 MECI
ETHYLENE
CI BY ANALYTIC GRADIENTS
C   0.00  0    0.00  0     0.00  0  0  0  0
C   1.30  1    0.00  0     0.00  0  1  0  0
H   1.00  1  120.00  1     0.00  0  1  2  0
H   1.00  0  120.00  1   180.00  0  1  2  3
H   1.00  0  120.00  1   180.00  0  2  1  3
H   1.00  0  120.00  1   180.00  0  2  1  5
0   0     0    0     0     0     0  0  0  0
3, 1, 4, 5, 6,                                                               Note 2
3, 2, 4, 5, 6,
```

Note 1: The keyword line requests C.I.=2. This means that the two MOs bracketing the occupied/virtual MO space are used:



The same effect could be achieved using the alternate keyword C.I.=6,7. This form of the C.I. keyword exactly specifies the range of MOs by number.

Note 2: These are the symmetry functions as required by the SYMMETRY keyword.

Archive File (TEST25.ARC) :

```
                    SUMMARY OF   AM1   CALCULATION
                                                    10-Feb-93
                         AMPAC Version 5.0
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)

C 2 H 4
  ETHYLENE
  CI BY ANALYTIC GRADIENTS

    GEOMETRY OPTIMISED : GRADIENT NORM MINIMISED
    SCF FIELD WAS ACHIEVED

         HEAT OF FORMATION       =       8.587131 KCAL                                    Note 1
         ELECTRONIC ENERGY       =    -733.475917 EV
         CORE-CORE REPULSION     =     422.773044 EV
         GRADIENT NORM           =       0.022125
         DIPOLE                  =       0.000000 DEBYE
         NO. OF FILLED LEVELS    =       6
         CONFIGURATION INTERACTION WAS USED                                               Note 2
         IONISATION POTENTIAL    =      10.368164 EV
         MOLECULAR WEIGHT        =      28.054
         COMPUTATION TIME        =      10.43 SECONDS

         FINAL GEOMETRY OBTAINED                                  CHARGE
AM1 PREC GRAD T=3500 BONDS NOINT NOXYZ POWELL GNORM=0.10 SYMMETRY C.I.=2 +
MECI
  ETHYLENE
  CI BY ANALYTIC GRADIENTS
 C     0.000000  0    0.000000  0    0.000000  0    0   0   0   -0.2216
 C     1.351712  1    0.000000  0    0.000000  0    1   0   0   -0.2216
 H     1.108025  1  122.518744  1    0.000000  0    1   2   0    0.1108
 H     1.108025  0  122.518744  1  180.000000  0    1   2   3    0.1108
 H     1.108025  0  122.518744  1  180.000000  0    2   1   3    0.1108
 H     1.108025  0  122.518744  1  180.000000  0    2   1   5    0.1108
 0     0.000000  0    0.000000  0    0.000000  0    0   0   0
  3,   1,   4,
  3,   1,   5,
  3,   1,   6,
  3,   2,   4,
  3,   2,   5,
  3,   2,   6,
```

Note 1: Note that the energy has decreased substantially (AM1 ΔH_f is ~14 kcal/mol) by the double-inclusion of correlation effects via CI.

Note 2: The summary section of the .ARC file tells the user that CI was utilized.

Output File (TEST25.OUT) :

```
*******************************************************************************
                              AM1 CALCULATION RESULTS
*******************************************************************************
```

```
*                            AMPAC Version 5.0
*                               Presented by:
*
*                           Semichem, Inc.
*                           7128 Summit
*                           Shawnee, KS  66216
*                           (913) 268-3271
*                           (913) 268-3445 (fax)
*
*  POWELL   - MINIMISE GRADIENT USING POWELL METHOD
*  GNORM=   - OPTIMIZATION EXIT WHEN GRADIENT NORM BELOW    0.100
*  PRECISE  - OPTIMIZATION CRITERIA TO BE INCREASED BY 10 TIMES,
*           -     S.C.F.   CRITERIA BY 100 TIMES,
*           - AND USE ACCURATE FINITE DIFFERENCE FORMULA  IN HESSIAN
*  SYMMETRY - SYMMETRY CONDITIONS TO BE IMPOSED
*  NOINTER  - INTERATOMIC DISTANCES NOT TO BE PRINTED
*  NOXYZ    - CARTESIAN COORDINATES NOT TO BE PRINTED
*  BONDS    - FINAL BOND-ORDER MATRIX TO BE PRINTED
*  GRADIENTS- ALL GRADIENTS TO BE PRINTED
*  MECI     - PRINT DETAILED RESULTS IN C.I.
*   T=      - A TIME OF  3500.0 SECONDS REQUESTED
*  C.I.=N   - 2 M.O.S TO BE USED IN C.I.
*  AM1      - THE AM1 HAMILTONIAN TO BE USED
*****************************************************************************

    PARAMETER DEPENDENCE DATA
       REFERENCE ATOM      FUNCTION NO.    DEPENDENT ATOM(S)
           3                  1             4  5  6
           3                  2             4  5  6

            DESCRIPTIONS OF THE FUNCTIONS USED
  1      BOND LENGTH    IS SET EQUAL TO THE REFERENCE BOND LENGTH
  2      BOND ANGLE     IS SET EQUAL TO THE REFERENCE BOND ANGLE
AM1 PREC GRAD T=3500 BONDS NOINT NOXYZ POWELL GNORM=0.10 SYMMETRY C.I.=2 +
MECI
  ETHYLENE
  CI BY ANALYTIC GRADIENTS
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I   NA  NB  NC
     1     C
     2     C          1.30000 *                                   1
     3     H          1.00000 *      120.00000 *                  1   2
     4     H          1.00000        120.00000 *   180.00000      1   2   3
     5     H          1.00000        120.00000 *   180.00000      2   1   3
     6     H          1.00000        120.00000 *   180.00000      2   1   5
         SINGLET STATE CALCULATION
         RHF CALCULATION, No. OF DOUBLY OCCUPIED LEVELS =  6

       **  REFERENCES TO PARAMETERS  **

 H  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
 C  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)

USE 2-POINT FORMULA IN INTEGRAL DERIVATIVES WITH STEP  0.00002000
STANDARD DEVIATION ON ENERGY   (KCAL)        0.000001492
STANDARD DEVIATION ON GRADIENT (KCAL/A,RD,RD)  0.0192072 0.0124205 0.0000000

STATIONARY POINT RESEARCH ... NUMBER OF VARIABLES  6
     MAXIMUM NUMBER OF GRADIENT CALLS    70
REQUIRED CONVERGENCE ON RMS GRADIENT  4.7D-02
ERROR ON DERIVATIVES:  1.92D-02      STEP FOR HESSIAN:  1.50D-02<   3.00D-01
TYPICAL TIME FOR ONE CYCLE OF 'POWELL'=    0.590
THE HESSIAN AT CYCLE    7 IS OF INDEX   3
FINAL SOLUTION CALCULATED BY POWELL:

ITE  17   ENERGY=  8.58713D+00  <G|G>= 4.89532607D-04  RMS GRAD= 9.03265010D-03
          CORRECTION OF  NEWTON  TYPE     PREDICTED STEP LENGTH:  1.500D-02
COORD    1.3517D+00  1.1080D+00  2.1384D+00  1.0634D+00  1.6815D+00  2.1906D+00

SQ.DEV. -1.2552D-05  3.7471D-06  2.8677D-06 -1.4087D-04 -2.5751D-04 -1.2400D-04
```

```
INDEX OF THE HESSIAN:  3 (ESTIMATE)
GRAD.    1.9776D-02 -9.8701D-03  1.0086D-03  0.0000D+00  0.0000D+00  0.0000D+00

AM1 PREC GRAD T=3500 BONDS NOINT NOXYZ POWELL GNORM=0.10 SYMMETRY C.I.=2 +
MECI
  ETHYLENE
  CI BY ANALYTIC GRADIENTS

    GEOMETRY OPTIMISED : GRADIENT NORM MINIMISED
    SCF FIELD WAS ACHIEVED

                              AM1    CALCULATION
                                                          VERSION 5.0

                                                     10-Feb-93

         FINAL HEAT OF FORMATION =       8.587131 KCAL
         ELECTRONIC ENERGY       =    -733.475917 EV
         CORE-CORE REPULSION     =     422.773044 EV
         GRADIENT NORM           =       0.022125
         IONISATION POTENTIAL    =      10.368164 EV
         NO. OF FILLED LEVELS    =       6
         MOLECULAR WEIGHT        =      28.054
         SCF CALCULATIONS        =      19
         COMPUTATION TIME        =      10.40 SECONDS

      FINAL  POINT  AND  DERIVATIVES
  PARAMETER     ATOM    TYPE            VALUE       GRADIENT
     1          2 C     BOND            1.351712     0.019776  KCAL/ANGSTROM
     2          3 H     BOND            1.108025    -0.009870  KCAL/ANGSTROM
     3          3 H     ANGLE         122.518744     0.001009  KCAL/RADIAN
     4          4 H     ANGLE          60.926096     0.000000  KCAL/RADIAN
     5          5 H     ANGLE          96.340809     0.000000  KCAL/RADIAN
     6          6 H     ANGLE         125.512795     0.000000  KCAL/RADIAN
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I   NA  NB  NC
     1     C
     2     C          1.35171 *                                   1
     3     H          1.10803 *      122.51874 *                  1   2
     4     H          1.10803        122.51874 *   180.00000      1   2   3
     5     H          1.10803        122.51874 *   180.00000      2   1   3
     6     H          1.10803        122.51874 *   180.00000      2   1   5

                EIGENVALUES
-32.67889 -21.83845 -15.63879 -14.20596 -11.86588 -10.36816   1.35321   4.02268
  4.30948   4.99548   5.51560   5.72978
        CONFIGURATION INTERACTION CALCULATION
    4 MICRO-STATES GENERATED VS  2278 ROOM AVAILABLE.

C.I-ACTIVE MOLECULAR ORBITALS                                                    Note 1

ROOT NO.    1        2
        -10.3682   1.3532
      1  0.00000  0.00000
      2  0.00000  0.00000
      3  0.00000  0.00000
      4 -0.70711 -0.70711
      5  0.00000  0.00000
      6  0.00000  0.00000
      7  0.00000  0.00000
      8 -0.70711  0.70711
      9  0.00000  0.00000
     10  0.00000  0.00000
     11  0.00000  0.00000
     12  0.00000  0.00000

ROW: MAIN MICRO-STATES OVER THE   4 SELECTED IN C.I.                              Note 2
COLUMN: EIGENSTATES FROM  1 TO  4

MO:  6  7 1:SINGLET 2:TRIPLET 3:SINGLET 4:SINGLET                                Note 3
```

```
      EV:   0.00000   2.86141   6.54891   9.41032
  1  1  0       96%        0%        0%        4%
     1  0 ( 0.9798) ( 0.0000) ( 0.0000) (-0.2000)
  2  1  0        0%       50%       50%        0%
     0  1 ( 0.0000) ( 0.7071) (-0.7071) ( 0.0000)
  3  0  1        0%       50%       50%        0%
     1  0 ( 0.0000) ( 0.7071) ( 0.7071) ( 0.0000)
  4  0  1        4%        0%        0%       96%
     0  1 (-0.2000) ( 0.0000) ( 0.0000) (-0.9798)

TRANSITION DIPOLE (A.U) AND OSC. STRENGTHS FROM STATE 1 TO OTHER SINGLET
STATE   NM      X       Y       Z   STRENGTH
  3   189.3   1.409   0.000   0.000  0.3184
  4   131.8   0.000   0.000   0.000  0.0000
       SUM OF OSCILLATOR STRENGTHS:  0.3184 OF  2.0000

         NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS
        ATOM NO.   TYPE          CHARGE        ATOM  ELECTRON DENSITY
          1         C           -0.2216          4.2216
          2         C           -0.2216          4.2216
          3         H            0.1108          0.8892
          4         H            0.1108          0.8892
          5         H            0.1108          0.8892
          6         H            0.1108          0.8892
DIPOLE (DEBYE)   X         Y         Z       TOTAL
POINT-CHG.     0.000     0.000     0.000     0.000
HYBRID         0.000     0.000     0.000     0.000
SUM            0.000     0.000     0.000     0.000

         ATOMIC ORBITAL ELECTRON POPULATIONS
  1.25463   0.95174   1.01526   1.00000   1.25463   0.95174   1.01526   1.00000
  0.88918   0.88918   0.88918   0.88918

                  BOND ORDERS AND VALENCIES

             C   1      C   2      H   3      H   4      H   5      H   6
------------------------------------------------------------------------------
   C   1   3.924801
   C   2   1.843445   3.924801
   H   3   0.956759   0.007143   0.987720
   H   4   0.956759   0.007143   0.009131   0.987720
   H   5   0.007143   0.956759   0.013159   0.001528   0.987720
   H   6   0.007143   0.956759   0.001528   0.013159   0.009131   0.987720
FULL COMPUTATION TIME :    10.440 SECONDS
```

Note 4

Note 1: The two MOs included in the CI mixing and from which the microstates are constructed are listed. Note that AMPAC has an automatic check for energetically degenerate orbitals (within 0.05 eV) near the CI active space. If these are located, the calculation is halted and the user is informed of the degeneracy. The user may bypass the test by specifying CI-OK. The MOs correspond to the π and π MOs in the system.*

Note 2: This note explains how the microstates and eigenstates are arranged below.

Note 3: The eigenstates, corresponding to minimized linear combination coefficients of the various microstates (rows), are listed by column. For example, Eigenstate 1 is labeled as a singlet and consists almost entirely (96%) of the ground state microstate. Some of the components of the printout will be identified below.

HOMO LUMO

Alpha Spin Electron

Beta Spin Electron

```
MO:  6  7 1:SINGLET 2:TRIPLET 3:SINGLET 4:SINGLET
 EV:   0.00000   2.86141   6.54891   9.41032
1  1  0       96%        0%        0%        4%
   1  0 ( 0.9798) ( 0.0000) ( 0.0000) (-0.2000)
2  1  0        0%       50%       50%        0%
   0  1 ( 0.0000) ( 0.7071) (-0.7071) ( 0.0000)
3  0  1        0%       50%       50%        0%
   1  0 ( 0.0000) ( 0.7071) ( 0.7071) ( 0.0000)
4  0  1        4%        0%        0%       96%
   0  1 (-0.2000) ( 0.0000) ( 0.0000) (-0.9798)
```

Spin reversal on promotion to retain singlet spin state indicated by negative coefficient.

Note 4: The CI transition data summarizes the predicted UV-visible spectral results. The only transition with measurable intensity corresponds to the $\pi \rightarrow \pi^*$ transition observed experimentally at 193 nm. The other transition, while allowed by spin, is symmetrically forbidden and also corresponds to a two-electron excitation. For these reasons, the intensity is essentially zero.

CHAPTER 7: ELECTROSTATIC POTENTIAL

(Note: This Chapter of the manual was adapted from the ESP Manual by B.H. Besler and K.D. Merz.)

7.1 Introduction

The ESP program module calculates the expectation values of the electrostatic potential of a molecule on a uniform distribution of points. The resultant ESP surface is then fit to atom centered charges that best reproduce the electron distribution in a least-squares sense. It offers the capability to accurately compute charges in situations where other methods may fail. The keyword ESP is required for all electrostatic potential calculations. It is also strongly recommended that the PRECISE keyword be used for all ESP calculations since the charge values are fairly sensitive to the convergence of the semiempirical density matrix.

7.2 Notes and Background

Surface Generation Routines The set of points defining the default surface is generated according to the algorithm of Connolly.[16] Williams' method[17] for generating surfaces may be used as an alternative to the default Connolly procedure. Van der Waals radii for the Williams method are included for hydrogen, boron, carbon, nitrogen, oxygen, fluorine, phosphorous, sulfur, chlorine, bromine, and iodine. Van der Waals radii for all elements through chlorine plus zinc are included for the Connolly surfaces.

ESP Integral Calculation ESP integrals are equivalent to nuclear attraction integrals. The formulae of Obara and Saika[18] are used in the ESP subroutines. The great majority of the computation time for a semiempirical ESP calculation is taken in the integral calculation. After the calculations for the integrals of single contracted function are complete, restart information is written to the file jobname.ESR. The information is in the form of the number of the contracted functions for which calculations were just completed followed by the array ES which contains the partially summed values of the potential for each probe point. If a restart calculation is being done, ESP will commence at the last stored point in jobname.ESR.

Accuracy and Number of Probe Points In general, the accuracy of an ESP charge calculation can be enhanced by increasing the number of probe points used for fitting on the Williams or Connolly surfaces. The number of probe points may be adjusted away from default values (determined to be generally adequate by experience) by utilizing the ESP dedicated keywords DEN and NSURF.

---

16 Connolly, M. L. J. Appl. Cryst. 1983 , 16, 548.

17 Williams, D. E. J. Comput. Chem. 1988 , 9, 745.

18 Obara, S.; Saika, A. J. Chem. Phys. 1986 , 84, 3693.

7.3 ESP Dedicated Keywords

CONNOLLY

Enables use of the Connolly surface for the ESP calculation. Four surfaces of a density of one point per angstrom based on multiples of 1.4, 1.6, 1.8, and 2.0 times the Van der Waal radii of the atoms are used. The CONNOLLY keyword is provided (although it is the default surface algorithm) to allow inputs and outputs to be marked as using this surface. (See DEN, NSURF, SCALE and SCINCR.) Abbreviation: None

DEN=n.n

This keyword specifies a different point density in points per Angstrom for the Connolly surface. The default value is 1.0. (See CONNOLLY.) Abbreviation: None

DIPOLE

Normally the only constraint imposed on the least squares fitted charges is that their sum be equal to the total charge of the molecule(s) on which that calculation is being performed. Use of DIPOLE will constrain the ESP charges to values that will produce the same dipole moment as predicted by AMPAC's Coulson analysis. The DIPOLE option is only available for systems with a total charge of zero due to the ambiguity in definition for the dipole moment of a charged system. Abbreviation: None

DIPX=n.n, DIPY=n.n, DIPZ=n.n

These keywords are similar to DIPOLE, but require fit only to the respective Cartesian component(s) of the dipole moment specified and the value given for n.n. Abbreviation: None

ESPRST

This keyword may be used to restart a stopped ESP calculation. Do not use it in the same keyword line as RESTART, as it has no connection with the RESTART keyword in AMPAC. It is necessary for the ESP module to have been entered for ESPRST to perform properly. If the program has generated the file jobname.ESR before the computer crashed, it will be safe to use ESPRST. This file is written at regular intervals, so only a few minutes of CPU time should be lost in the event the calculation times out. Abbreviation: None

NSURF=n

The NSURF keyword is used to change the number of surfaces used in the Connolly algorithm. The default value is four surfaces. (See CONNOLLY.) Abbreviation: None

POTWRT

The POTWRT keyword is provided to dump out the surface points and electrostatic potential values in atomic units (Hartrees for the potential and Bohrs for the coordinates) to UNIT 21 and will be named jobname.ESP. The file may be then used by plotting programs, etc. The first line of this file contains the number of probe points in I5 format. There is one line following for each probe point containing first the value of the electric potential in Hartrees, followed by the Cartesian coordinates of the probe point in Bohrs. Each line is written in the format (1X,4E16.7). Abbreviation: None

SCALE=n.n

The SCALE keyword changes the base scaling factor of the initial surface in the Connolly treatment, set to 1.4 by default. (See CONNOLLY.) Abbreviation: None

SCINCR=n.n

SCINCR is the increment between multipliers for the Connolly surface. The value is 0.2 by default. (See CONNOLLY.) Abbreviation: None

SLOPE=n.n

When an MNDO/ESP calculation is run, in addition to the fitted charges scaled values are also provided. As shown by the authors, MNDO charges when multiplied by a factor of 1.42 may be used in place of 6-31G electric potential derived charges. The keyword SLOPE is provided to change this scaling factor. Abbreviation: None*

SYMAVG

Both the Williams and Connolly surfaces possess a common drawback: in systems with symmetry elements, the generated set of surface points will not be perfectly symmetric. This is particularly evident in the example of benzene. To compensate for this problem an option is included in the program to average charges which should have the same value by symmetry. A simple but effective method for determining which ESP derived charges should be equivalent due to molecular symmetry is incorporated: The absolute values of the atomic charges computed by the standard AMPAC are compared and those which are within 10^{-5} charge units of each other are defined equivalent. To enable this option use the keyword SYMAVG. Abbreviation: None

STO3G, STO6G

Two different basis sets (STO-3G and STO-6G) may be used to "deorthogonalize" the semiempirical density matrix for additional flexibility. The STO-3G basis has received little testing, but is provided nonetheless since preliminary testing

shows it to give about the same charge and ESP values as the STO-6G and requires approximately 1/3 of the computer time. Abbreviation: None

WILLIAMS

The surface generation procedure of Donald Williams is included in the program as an alternative to the Connolly surface. The Williams procedure is limited in the types of atoms which can be present in the system compared to the Connolly procedure. Its use is enabled via the keyword WILLIAMS. Abbreviation: None

7.4 Differences in the AMPAC Implementation

The implementation of ESP in AMPAC 5.0 has been generalized to handle UHF and/or CI wavefunctions as well as the more regular RHF solutions. ESP will now also handle charged species. Also, rather than setting the maximum number of probe points available for fitting the surface as a constant (MESP), this value is computed dynamically at compile time based on the number of atoms according to the following equation:

$$MESP = 50xMAXAOP$$

where MAXAOP is the maximum number of atoms with p-orbitals allowed in the calculation.

7.5 Example Calculation

Formaldehyde using the MNDO model is computed with several ESP options on the common keyword line.

Input File (TEST53.DAT) :

```
  MNDO GEO-OK PREC ESP SYMAVG
  Formaldehyde
  ESP options
 H  0.00000 1   0.00000 0   0.00000 0 0 0 0
 C  1.09400 1   0.00000 1   0.00000 0 1 0 0
 O  1.42500 1 107.00000 1   0.00000 1 2 1 0
 H  0.94500 1 108.50000 1 180.00000 1 3 2 1
 H  1.094   1 107.0     1 -60.00000 1 2 3 4
 H  1.094   1 107.00000 1  60.00000 1 2 3 4
```

Archive File (TEST53.ARC) :

```
                    SUMMARY OF  MNDO   CALCULATION
                                                        9-MAY-94
                         AMPAC Version 5.0
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)
```

```
              WARNING: YOUR LICENSE EXPIRES IN 10 DAYS!!                                Note 1

C   H 4 O
  Formaldehyde
  ESP options

         HEAT OF FORMATION       =   -57.354124 KCAL
         ELECTRONIC ENERGY       = -1079.561969 EV
         CORE-CORE REPULSION     =   572.050424 EV
         DIPOLE                  =     1.47926 DEBYE
         NO. OF FILLED LEVELS    =     7
         IONISATION POTENTIAL    =    11.415235 EV
         MOLECULAR WEIGHT        =    32.042

         FINAL GEOMETRY OBTAINED                                  CHARGE
MNDO GEO-OK PREC ESP SYMAVG
  Formaldehyde
  ESP options
 H     0.000000  0    0.000000  0    0.000000  0   0  0  0       0.0161                Note 2
 C     1.114993  1    0.000000  0    0.000000  0   1  0  0       0.1927
 O     1.390708  1  108.080572  1    0.000000  0   2  1  0      -0.3291
 H     0.946586  1  111.578647  1  180.000000  1   3  2  1       0.1803
 H     1.119038  1  112.319004  1  -60.586310  1   2  3  4      -0.0300
 H     1.119038  1  112.319004  1   60.586310  1   2  3  4      -0.0300
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0
```

Note 1: This is a message generated by the key/timer in your program. AMPAC will cease functioning 10 days from the date of the calculation unless a new key/timer is obtained from Semichem.

Note 2: These are the Coulson charges from AMPAC, not the ESP values.

Output File (TEST53.OUT) :

```
*****************************************************************************
                            MNDO CALCULATION RESULTS
*****************************************************************************
*                              AMPAC Version 5.0
*                                 Presented by:
*
*                            Semichem, Inc.
*                            7128 Summit
*                            Shawnee, KS  66216
*                            (913) 268-3271
*                            (913) 268-3445 (fax)
*
*                  WARNING: YOUR LICENSE EXPIRES IN 10 DAYS!!
*
*           - MINIMIZE ENERGY USING B-F-G-S  METHOD
*  GEO-OK   - OVERRIDE INTERATOMIC DISTANCE CHECK
*  PRECISE  - OPTIMIZATION CRITERIA TO BE INCREASED BY 10 TIMES,
*           -     S.C.F.   CRITERIA BY 100 TIMES,
*           - AND USE ACCURATE FINITE DIFFERENCE FORMULA IN HESSIAN
*  SYMMETRY - SYMMETRY CONDITIONS TO BE IMPOSED
*  ESP      - ELECTROSTATIC POTENTIAL CALCULATION
*  SYMAVG   - AVERAGE SYMMETRY EQUIVALENT ESP CHARGES
*****************************************************************************

MNDO GEO-OK PREC ESP SYMAVG
  Formaldehyde
  ESP options
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     H
     2     C          1.09400 *                                  1
     3     O          1.42500 *      107.00000 *                 2  1
     4     H          0.94500 *      108.50000 *   180.00000 *   3  2  1
```

```
     5     H          1.09400 *      107.00000 *   -60.00000 *   2  3  4
     6     H          1.09400 *      107.00000 *    60.00000 *   2  3  4

         CARTESIAN COORDINATES
   NO.       ATOM         X         Y         Z
    1         1        0.0000    0.0000    0.0000
    2         6        1.0940    0.0000    0.0000
    3         8        1.5106    1.3627    0.0000
    4         1        2.4553    1.3875    0.0000
    5         1        1.5007   -0.4588   -0.9060
    6         1        1.5007   -0.4588    0.9060
         SINGLET STATE CALCULATION
         RHF CALCULATION, No. OF DOUBLY OCCUPIED LEVELS =  7
 H  (MNDO):  M.J.S. DEWAR, W. THIEL, J. AM. CHEM. SOC., 99, 4899, (1977)
 C  (MNDO):  M.J.S. DEWAR, W. THIEL, J. AM. CHEM. SOC., 99, 4899, (1977)
 O  (MNDO):  M.J.S. DEWAR, W. THIEL, J. AM. CHEM. SOC., 99, 4899, (1977)

           INTERATOMIC DISTANCES
              H   1      C   2      O   3      H   4      H   5      H   6
-------------------------------------------------------------------------------
   H   1   0.000000
   C   2   1.094000   0.000000
   O   3   2.034465   1.425000   0.000000
   H   4   2.820213   1.943767   0.945000   0.000000
   H   5   1.812067   1.094000   2.034465   2.267356   0.000000
   H   6   1.812067   1.094000   2.034465   2.267356   1.812067   0.000000
USE 2-POINT FORMULA IN INTEGRAL DERIVATIVES WITH STEP  0.00002000
STANDARD DEVIATION ON ENERGY   (KCAL)        0.000001493
STANDARD DEVIATION ON GRADIENT (KCAL/A,RD,RD)  0.0000471 0.0000526 0.0000397
MNDO GEO-OK PREC ESP SYMAVG
  Formaldehyde
  ESP options

    GRADIENT (COMPONENT) TEST WAS SATISFIED IN BFGS OR DFP
    SCF FIELD WAS ACHIEVED

                              MNDO    CALCULATION
                                                          VERSION  5.00

         FINAL HEAT OF FORMATION =   -57.354124 KCAL
         ELECTRONIC ENERGY       = -1079.561969 EV
         CORE-CORE REPULSION     =   572.050424 EV
         GRADIENT NORM           =     0.066902
         IONISATION POTENTIAL    =    11.415235 EV
         NO. OF FILLED LEVELS    =     7
         MOLECULAR WEIGHT        =    32.042
         SCF CALCULATIONS        =   18
         COMPUTATION TIME=         3.89 SECONDS
                                                      9-MAY-94
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     H
     2     C          1.11499 *                                  1
     3     O          1.39071 *      108.08057 *                 2  1
     4     H          0.94659 *      111.57865 *   180.00000 *   3  2  1
     5     H          1.11904 *      112.31900 *   -60.58631 *   2  3  4
     6     H          1.11904 *      112.31900 *    60.58631 *   2  3  4

         INTERATOMIC DISTANCES
              H   1      C   2      O   3      H   4      H   5      H   6
-------------------------------------------------------------------------------
   H   1   0.000000
   C   2   1.114993   0.000000
   O   3   2.034642   1.390708   0.000000
   H   4   2.847988   1.948948   0.946586   0.000000
   H   5   1.810825   1.119038   2.090055   2.373503   0.000000
   H   6   1.810825   1.119038   2.090055   2.373503   1.803525   0.000000

                 EIGENVALUES
-41.93271 -27.81245 -18.66497 -15.39915 -15.31456 -12.81856 -11.41523   3.78974
  3.93580   4.69930   5.00681   6.75464
```

```
        NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS
       ATOM NO.   TYPE          CHARGE        ATOM  ELECTRON DENSITY
         1         H           0.0161          0.9839
         2         C           0.1927          3.8073
         3         O          -0.3291          6.3291
         4         H           0.1803          0.8197
         5         H          -0.0300          1.0300
         6         H          -0.0300          1.0300
DIPOLE (DEBYE)   X         Y         Z       TOTAL
POINT-CHG.     0.323    -0.732     0.000     0.800
HYBRID         0.631    -0.399     0.000     0.746
SUM            0.953    -1.131     0.000     1.479

        CARTESIAN COORDINATES
   NO.       ATOM               X         Y         Z
    1        H                   0.0000    0.0000    0.0000
    2        C                   1.1150    0.0000    0.0000
    3        O                   1.5466    1.3220    0.0000
    4        H                   2.4914    1.3798    0.0000
    5        H                   1.4664   -0.5618   -0.9018
    6        H                   1.4664   -0.5618    0.9018

        ATOMIC ORBITAL ELECTRON POPULATIONS
  0.98393   1.22134   0.91614   0.78149   0.88829   1.81756   1.23471   1.31285
  1.96395   0.81968   1.03003   1.03003
```

Note 1

```
AICAS DUMPED:  16.67 PERCENT COMPLETE
AICAS DUMPED:  33.33 PERCENT COMPLETE
AICAS DUMPED:  50.00 PERCENT COMPLETE
AICAS DUMPED:  66.67 PERCENT COMPLETE
AICAS DUMPED:  83.33 PERCENT COMPLETE
AICAS DUMPED: 100.00 PERCENT COMPLETE

AICAP DUMPED:  10.00 PERCENT COMPLETE
AICAP DUMPED:  20.00 PERCENT COMPLETE
AICAP DUMPED:  30.00 PERCENT COMPLETE
AICAP DUMPED:  40.00 PERCENT COMPLETE
AICAP DUMPED:  50.00 PERCENT COMPLETE
AICAP DUMPED:  60.00 PERCENT COMPLETE
AICAP DUMPED:  70.00 PERCENT COMPLETE
AICAP DUMPED:  80.00 PERCENT COMPLETE
AICAP DUMPED:  90.00 PERCENT COMPLETE
AICAP DUMPED: 100.00 PERCENT COMPLETE
```

Note 2

```
          ELECTROSTATIC POTENTIAL CHARGES

      ATOM NO.    TYPE    CHARGE   SCALED CHARGE
         1         H      0.0243      0.0346
         2         C      0.2124      0.3021
         3         O     -0.4825     -0.6861
         4         H      0.3047      0.4332
         5         H     -0.0295     -0.0419
         6         H     -0.0295     -0.0419
```

Note 3

```
          THE NUMBER OF POINTS IS:       431
          THE RMS DEVIATION IS:       0.9192
          THE RRMS DEVIATION IS:      0.1349

    DIPOLE MOMENT EVALUATED FROM THE POINT CHARGES

           X        Y        Z       TOTAL
         0.7839  -0.8855   0.0000   1.1826
```

Note 4

```
   ELECTROSTATIC POTENTIAL CHARGES AVERAGED FOR
   SYMMETRY EQUIVALENT ATOMS

      ATOM NO.    TYPE    CHARGE   SCALED CHARGE
```

Note 5

```
        1         H      0.0243      0.0346
        2         C      0.2124      0.3021
        3         O     -0.4825     -0.6861
        4         H      0.3047      0.4332
        5         H     -0.0295     -0.0419
        6         H     -0.0295     -0.0419

       TIME TO CALCULATE ESP:   24.80 SECONDS                                    Note 6
FULL COMPUTATION TIME :    28.760 SECONDS
```

Note 1: *This table lists the Coulson charges predicted by AMPAC based on its analysis of the final density matrix.*

Note 2: *The series of informational items tell that the ESP procedure is calculating the integrals.*

Note 3: *This table presents the ESP charges. Note that since MNDO was used as the model, the charges were scaled by 1.42. This is the column labeled "SCALED CHARGE".*

Note 4: *This line is a count of the number of points on the Connolly surface used in this calculation.*

Note 5: *As called for by the SYMAVG keyword, the charges of symmetrically related atoms are averaged to account for the asymmetry of the surface.*

Note 6: *The user should be aware that an ESP calculation can be quite expensive computationally. In this case, virtually all of the CPU time required for the entire job was spent in the ESP routines.*

CHAPTER 8: NATURAL BOND ORBITAL POPULATION ANALYSIS

(Note: This Chapter of the manual was adapted from the NBO 3.0 Program Manual by F. Weinhold, A.E. Reed, E.D. Glendening, J.E. Carpenter, T.K. Brunck, J.P. Foster, A.B. Rives, and R.B. Weinstock This is a significantly abbreviated adaptation of that material. The NBO program is extensive and many of its options will not be described here. A full copy of the NBO Program Manual is available from Semichem on request.)

8.1 NBO Keylists and Interaction with AMPAC

The NBO keyword on the regular AMPAC 5.0 keyword invokes the NBO module. The NBO program options are controlled by keywords in a prescribed keylist format. Four distinct keylists are recognized ($NBO, $CORE, $CHOOSE, and $DEL in that order only). These keylists are located in an external file, named "jobname.NBO". If this file is not located in the same directory as the input file, AMPAC will use the default keylist (no specific keywords, DEFAULT.NBO) in the program directory. The four keylist types have common rules of syntax: Keylist delimiters are identified by a "$" prefix. Each keylist begins with the parent keylist name (e.g., "$NBO"), followed by any number of keywords, and terminated with the word "$END"; for example:

```
$NBO keywordl keyword2      . . . $END
```

8.2 The $NBO Keylist

The $NBO keylist is the principal means of specifying NBO job options and controlling output, and must precede any other keylist in your input file. The allowed keywords that can appear in a $NBO keylist are grouped as follows:

Job Control Keywords:

NPA	NBOSUM	NOBOND	SKIPBO
NBO	RESONANCE	3CBOND	NLMO

Job Threshold Keywords:

BEND(.ang,pct,occ)
E2PERT(=val)

Matrix Output Keywords:

NHONBO	NBONLMO	NLMOMO	AONHO
NAONBO	NHONLMO	NBOMO	AONBO
NHOMO	AONLMO	AOMO	DMAO
FAO	DMNHO	FNHO	DMNBO
FNBO	DMNLMO	FNLMO	

Other Output Control Keywords:

LFNPR	DETAIL	BNDIDX	AOINFO
PLOT	ARCHIVE	NBODAF	

Print Level Control:

PRINT=n

Some keywords of the $NBO keylist require (or allow) numerical values or other parameters to specify their exact function, via an "=".

Job Control Keywords

The keywords in this group activate or deactivate basic tasks to be performed by the NBO programs, or change the way the NBO search is conducted. Each keyword is described in terms of the option it activates (together with an indication of where the option is useful):

KEYWORD OPTION	DESCRIPTION
NPA	Request Natural Population Analysis and printing of NPA summary tables.
NBO	Request calculation of NBOs and printing of the main NBO table (default).
NBOSUM	Request printing of the NBO summary table. This combines elements of the NBO table and 2nd-order perturbation theory analysis table in a convenient form for recognizing the principal delocalization patterns.
RESONANCE	Request search for highly delocalized structures. The NBO search normally aborts when one or more Lewis NBOs has less than the default occupancy threshold of 1.90 electrons for a 'good' electron pair. When the RESONANCE keyword is activated, this threshold is successively lowered in 0.10 decrements to 1.50, and the NBO search repeated to find the best Lewis structure within each occupancy threshold. The program returns with the best overall Lewis structure (lowest total non-Lewis occupancy) found in these searches.
NOBOND	Request that no bonds (2-center NBOs) are to be formed in the NBO procedure. The resulting NBOs will then simply be l-center atomic hybrids.
3CBOND	Request search for 3-center bonds. The normal default is to search for only 1- and 2-center NBOs.
SKIPBO	Skip the computation of NBOs, i.e., only determine NAOs and perform natural population analysis. Note that the SKIPBO keyword has higher precedence than other keywords in this list, so that keywords with which it is implicitly in conflict (e.g., NBO, 3CBOND, NLMO) will be ignored if SKIPBO is included in the SNBO keylist.
NLMO	Compute and print out the summary table of Natural Localized Molecular Orbitals. NLMOs are similar to Boys or Edmiston-Ruedenberg LMOs, but more efficiently calculated. (Activated

automatically by all keywords that pertain to NLMOs (e.g., AONLMO, SPNLMO, DIPOLE).

Job Threshold Keywords

KEYWORD	parameter(s)	OPTION DESCRIPTION
BEND	ang, pct, occ	Request the NHO Directional Analysis table. The three parameters and [default values] have the following significance: ang [1.0] = threshold angular deviation for printing; pct [25] - threshold percentage p-character for printing; occ [0.1] - threshold NBO occupancy for printing
E2PERT	eval	Request the Perturbation Theory Energy Analysis table, where eval [0.5] = threshold energy (in kcal/mol) for printing

Matrix Output Keywords

The keywords in this group activate the printing of various matrices to the output file, or their writing to (or reading from) external disk files. The large number of keywords in this group provide great flexibility in printing out the details of the successive transformations

input AOs—(PNAOs)—NAOs—NHOs—NBOs—NLMOs—canonical MOs

of the matrices of various operators in the natural localized basis sets. This ordered sequence of transformations forms the basis for naming the keywords.

The keyword for printing the matrix for a particular basis transformation, IN — OUT, is constructed from the corresponding acronyms for the two sets in the generic form "INOUT". For example, the transformation AO—NBO is keyed as "AONBO", while that from NBOs to NLMOs is correspondingly "NBONLMO". The transformations are always specified in the ordered sequence shown above (i.e., "AONBO" is allowed, but "NBOAO" is an unrecognized 'backward' keyword). Keywords are recognized for all possible transformations from the input AOs to other sets (NAO, NHO, NBO, NLMO, MO, or the pre-orthogonal PNAO, PNHO, PNBO, PNLMO sets) in the overall sequence leading to canonical MOs, i.e.,

AO basis:	AONHO	AONBOAONLMO	AOMO

and from each of the orthonormal natural localized sets to sets lying to the right in the sequence, i.e.,

AO basis:	NAONBO		
NHO basis:	NHONBO	NHONLMO	NHOMO
NBO basis:	NBOMO		
NLMO basis:	NLMOMO		

Other Output Control Keywords

The keywords in this group also help to control the I/O produced by a specified set of job options, and thus supplement the keywords of the previous section. However, the keywords of this section 'steer' the flow of information that is routinely produced by the NBO program (or can be passed through AMPAC) without materially affecting the actual jobs performed by the NBO program. The options associated with each keyword are tabulated below:

KEYWORD	*OPTION DESCRIPTION*
BNDIDX	*Request print-out of the NAO-Wiberg Bond Index array and related valency indices. The elements of this array are the sums of squares of off-diagonal density matrix elements between pairs of atoms in the NAO basis, and are the NAO counterpart of the Wiberg bond index (K. Wiberg, Tetrahedron 24 1083 (1968)). This bond index is routinely used to 'screen' atom pairs for possible bonding in the NBO search, but the values are not printed unless the BNDIDX keyword is activated.*
PRINT=n	*This keyword requests more and more information to be output by the NBO modules. A value of "0" suppresses all output and the default value is "2".*

8.3 Example

This example includes the NBO output only from TEST51.OUT on N-methylamine.

```
*******************************************************************************
          N A T U R A L   A T O M I C   O R B I T A L   A N D
        N A T U R A L   B O N D   O R B I T A L   A N A L Y S I S
*******************************************************************************

Job title:   NBO

Storage needed:   625 in NPA,   634 in NBO ( 160000 available)


NATURAL POPULATIONS:  Natural atomic orbital occupancies                                Note 1

 NAO Atom #  lang   Type(AO)    Occupancy      Energy
-------------------------------------------------------
  1    C  1  s      Val( 2s)     1.22785     -16.17384
  2    C  1  px     Val( 2p)     0.88236      -4.69850
  3    C  1  py     Val( 2p)     0.99127      -4.66363
  4    C  1  pz     Val( 2p)     1.02724      -4.88727

  5    N  2  s      Val( 2s)     1.57839     -22.79724
  6    N  2  px     Val( 2p)     1.07810      -6.13343
  7    N  2  py     Val( 2p)     1.62073      -8.35977
  8    N  2  pz     Val( 2p)     1.07432      -5.86128

  9    H  3  s      Val( 1s)     0.96913      -5.63260

 10    H  4  s      Val( 1s)     0.91783      -5.15043

 11    H  5  s      Val( 1s)     0.91783      -5.15043
```

```
 12    H  6  s      Val( 1s)     0.85747      -5.25761

 13    H  7  s      Val( 1s)     0.85747      -5.25761

[  4 electrons found in the effective core potential]
```

Note 2

Summary of Natural Population Analysis:

Note 3

Atom #	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
C 1	-0.12873	2.00000	4.12873	0.00000	6.12873
N 2	-0.35153	2.00000	5.35153	0.00000	7.35153
H 3	0.03087	0.00000	0.96913	0.00000	0.96913
H 4	0.08217	0.00000	0.91783	0.00000	0.91783
H 5	0.08217	0.00000	0.91783	0.00000	0.91783
H 6	0.14253	0.00000	0.85747	0.00000	0.85747
H 7	0.14253	0.00000	0.85747	0.00000	0.85747
* Total *	0.00000	4.00000	14.00000	0.00000	18.00000

```
                              Natural Population
-------------------------------------------------------
  Effective Core             4.00000
  Valence                   14.00000 (100.0000% of  14)
  Natural Minimal Basis     18.00000 (100.0000% of  18)
  Natural Rydberg Basis      0.00000 (  0.0000% of  18)
-------------------------------------------------------
```

Note 4

```
   Atom #          Natural Electron Configuration
-------------------------------------------------------------------------
     C  1      [core]2s( 1.23)2p( 2.90)
     N  2      [core]2s( 1.58)2p( 3.77)
     H  3            1s( 0.97)
     H  4            1s( 0.92)
     H  5            1s( 0.92)
     H  6            1s( 0.86)
     H  7            1s( 0.86)
```

NATURAL BOND ORBITAL ANALYSIS:

Note 5

Cycle	Occ. Thresh.	Occupancies: Lewis	Non-Lewis	Lewis Structure: CR	BD	3C	LP	Low occ (L)	High occ (NL)	Dev
1(1)	1.90	17.90661	0.09339	0	6	0	1	0	0	0.03

Structure accepted: No low occupancy Lewis orbitals

```
-------------------------------------------------------
  Effective Core            4.00000
  Valence Lewis            13.90661 ( 99.333% of  14)
 ==================       ============================
  Total Lewis              17.90661 ( 99.481% of  18)
 -------------------------------------------------------
  Valence non-Lewis         0.09339 (  0.519% of  18)
  Rydberg non-Lewis         0.00000 (  0.000% of  18)
 ==================       ============================
  Total non-Lewis           0.09339 (  0.519% of  18)
-------------------------------------------------------
```

Note 6

```
    (Occupancy)   Bond orbital/ Coefficients/ Hybrids
-------------------------------------------------------------------------------
  1. (1.98975) BD ( 1) C 1- N 2
               ( 45.56%)   0.6750* C 1 s( 21.46%)p 3.66( 78.54%)
```

```
                                        0.4633  0.8841  0.0609  0.0000
              ( 54.44%)   0.7378* N 2 s( 18.06%)p 4.54( 81.94%)
                                        0.4250 -0.8963  0.1264  0.0000
  2. (1.99006) BD ( 1) C 1- H 3
              ( 52.11%)   0.7219* C 1 s( 25.64%)p 2.90( 74.36%)
                                        0.5064 -0.3205  0.8006  0.0000
              ( 47.89%)   0.6920* H 3 s(100.00%)
                                        1.0000
  3. (1.98696) BD ( 1) C 1- H 4
              ( 54.16%)   0.7359* C 1 s( 26.45%)p 2.78( 73.55%)
                                        0.5143 -0.2404 -0.4215 -0.7071
              ( 45.84%)   0.6771* H 4 s(100.00%)
                                        1.0000
  4. (1.98696) BD ( 1) C 1- H 5
              ( 54.16%)   0.7359* C 1 s( 26.45%)p 2.78( 73.55%)
                                        0.5143 -0.2404 -0.4215  0.7071
              ( 45.84%)   0.6771* H 5 s(100.00%)
                                        1.0000
  5. (1.98762) BD ( 1) N 2- H 6
              ( 57.22%)   0.7564* N 2 s( 19.13%)p 4.23( 80.87%)
                                        0.4374  0.2755  0.4825  0.7071
              ( 42.78%)   0.6541* H 6 s(100.00%)
                                        1.0000
  6. (1.98762) BD ( 1) N 2- H 7
              ( 57.22%)   0.7564* N 2 s( 19.13%)p 4.23( 80.87%)
                                        0.4374  0.2755  0.4825 -0.7071
              ( 42.78%)   0.6541* H 7 s(100.00%)
                                        1.0000
  7. (1.97763) LP ( 1) N 2             s( 43.67%)p 1.29( 56.33%)
                                        0.6609  0.2118 -0.7200  0.0000
  8. (0.01205) BD*( 1) C 1- N 2
              ( 54.44%)   0.7378* C 1 s( 21.46%)p 3.66( 78.54%)
                                        0.4633  0.8841  0.0609  0.0000
              ( 45.56%)  -0.6750* N 2 s( 18.06%)p 4.54( 81.94%)
                                        0.4250 -0.8963  0.1264  0.0000
  9. (0.03088) BD*( 1) C 1- H 3
              ( 47.89%)   0.6920* C 1 s( 25.64%)p 2.90( 74.36%)
                                       -0.5064  0.3205 -0.8006  0.0000
              ( 52.11%)  -0.7219* H 3 s(100.00%)
                                       -1.0000
 10. (0.01278) BD*( 1) C 1- H 4
              ( 45.84%)   0.6771* C 1 s( 26.45%)p 2.78( 73.55%)
                                       -0.5143  0.2404  0.4215  0.7071
              ( 54.16%)  -0.7359* H 4 s(100.00%)
                                       -1.0000
 11. (0.01278) BD*( 1) C 1- H 5
              ( 45.84%)   0.6771* C 1 s( 26.45%)p 2.78( 73.55%)
                                       -0.5143  0.2404  0.4215 -0.7071
              ( 54.16%)  -0.7359* H 5 s(100.00%)
                                       -1.0000
 12. (0.01245) BD*( 1) N 2- H 6
              ( 42.78%)   0.6541* N 2 s( 19.13%)p 4.23( 80.87%)
                                       -0.4374 -0.2755 -0.4825 -0.7071
              ( 57.22%)  -0.7564* H 6 s(100.00%)
                                       -1.0000
 13. (0.01245) BD*( 1) N 2- H 7
              ( 42.78%)   0.6541* N 2 s( 19.13%)p 4.23( 80.87%)
                                       -0.4374 -0.2755 -0.4825  0.7071
              ( 57.22%)  -0.7564* H 7 s(100.00%)
                                       -1.0000


NHO Directionality and "Bond Bending" (deviations from line of nuclear centers)
```

Note 7

```
        [Thresholds for printing:  angular deviation  >  1.0 degree]
                                   hybrid p-character > 25.0%
                                   orbital occupancy  >  0.10e

                     Line of Centers        Hybrid 1              Hybrid 2
                     ---------------  -------------------   ------------------
          NBO          Theta   Phi    Theta   Phi    Dev    Theta   Phi    Dev
```

1. BD (1) C 1- N 2	90.0	0.0	90.0	3.9	3.9	90.0	172.0	8.0
2. BD (1) C 1- H 3	90.0	114.3	90.0	111.8	2.5	--	--	--
3. BD (1) C 1- H 4	144.2	236.1	145.5	240.3	2.7	--	--	--
4. BD (1) C 1- H 5	35.8	236.1	34.5	240.3	2.7	--	--	--
5. BD (1) N 2- H 6	35.5	51.2	38.2	60.3	6.1	--	--	--
6. BD (1) N 2- H 7	144.5	51.2	141.8	60.3	6.1	--	--	--
7. LP (1) N 2	--	--	90.0	286.4	--	--	--	--

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis

Threshold for printing: 0.50 kcal/mol

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) e.V.	F(i,j) e.V.
within unit 1				
1. BD (1) C 1- N 2	/ 9. BD*(1) C 1- H 3	1.73	25.63	0.987
1. BD (1) C 1- N 2	/ 10. BD*(1) C 1- H 4	1.33	25.93	0.864
1. BD (1) C 1- N 2	/ 11. BD*(1) C 1- H 5	1.33	25.93	0.864
1. BD (1) C 1- N 2	/ 12. BD*(1) N 2- H 6	1.20	26.85	0.835
1. BD (1) C 1- N 2	/ 13. BD*(1) N 2- H 7	1.20	26.85	0.835
2. BD (1) C 1- H 3	/ 8. BD*(1) C 1- N 2	3.00	22.43	1.208
2. BD (1) C 1- H 3	/ 9. BD*(1) C 1- H 3	0.66	21.52	0.559
2. BD (1) C 1- H 3	/ 10. BD*(1) C 1- H 4	1.85	21.82	0.937
2. BD (1) C 1- H 3	/ 11. BD*(1) C 1- H 5	1.85	21.82	0.937
3. BD (1) C 1- H 4	/ 8. BD*(1) C 1- N 2	1.24	22.37	0.775
3. BD (1) C 1- H 4	/ 9. BD*(1) C 1- H 3	2.10	21.46	0.993
3. BD (1) C 1- H 4	/ 11. BD*(1) C 1- H 5	1.45	21.76	0.826
3. BD (1) C 1- H 4	/ 12. BD*(1) N 2- H 6	3.06	22.68	1.228
4. BD (1) C 1- H 5	/ 8. BD*(1) C 1- N 2	1.24	22.37	0.775
4. BD (1) C 1- H 5	/ 9. BD*(1) C 1- H 3	2.10	21.46	0.993
4. BD (1) C 1- H 5	/ 10. BD*(1) C 1- H 4	1.45	21.76	0.826
4. BD (1) C 1- H 5	/ 13. BD*(1) N 2- H 7	3.06	22.68	1.228
5. BD (1) N 2- H 6	/ 8. BD*(1) C 1- N 2	1.67	24.99	0.951
5. BD (1) N 2- H 6	/ 10. BD*(1) C 1- H 4	1.63	24.39	0.930
5. BD (1) N 2- H 6	/ 13. BD*(1) N 2- H 7	1.55	25.31	0.923
6. BD (1) N 2- H 7	/ 8. BD*(1) C 1- N 2	1.67	24.99	0.951
6. BD (1) N 2- H 7	/ 11. BD*(1) C 1- H 5	1.63	24.39	0.930
6. BD (1) N 2- H 7	/ 12. BD*(1) N 2- H 6	1.55	25.31	0.923
7. LP (1) N 2	/ 9. BD*(1) C 1- H 3	3.95	19.21	1.285
7. LP (1) N 2	/ 10. BD*(1) C 1- H 4	0.57	19.51	0.494
7. LP (1) N 2	/ 11. BD*(1) C 1- H 5	0.57	19.51	0.494

Natural Bond Orbitals (Summary): Note 8

NBO	Occupancy	Energy	Principal Delocalizations (geminal,vicinal,remote)
Molecular unit 1 (CH5N)			
1. BD (1) C 1- N 2	1.98975	-21.51839	9(g),10(g),11(g),12(g),13(g)
2. BD (1) C 1- H 3	1.99006	-17.40468	8(g),10(g),11(g),9(g)
3. BD (1) C 1- H 4	1.98696	-17.34854	12(v),9(g),11(g),8(g)
4. BD (1) C 1- H 5	1.98696	-17.34854	13(v),9(g),10(g),8(g)
5. BD (1) N 2- H 6	1.98762	-19.97224	8(g),10(v),13(g)
6. BD (1) N 2- H 7	1.98762	-19.97224	8(g),11(v),12(g)
7. LP (1) N 2	1.97763	-15.09155	9(v),10(v),11(v)
8. BD*(1) C 1- N 2	0.01205	5.02116	
9. BD*(1) C 1- H 3	0.03088	4.11417	
10. BD*(1) C 1- H 4	0.01278	4.41394	
11. BD*(1) C 1- H 5	0.01278	4.41394	
12. BD*(1) N 2- H 6	0.01245	5.33467	
13. BD*(1) N 2- H 7	0.01245	5.33467	
Total Lewis	17.90661	(99.4811%)	
Valence non-Lewis	0.09339	(0.5189%)	
Rydberg non-Lewis	0.00000	(0.0000%)	
Total unit 1	18.00000	(100.0000%)	

```
        Charge unit  1    0.00000

FULL COMPUTATION TIME :     4.700 SECONDS
```

Note 1: This table describes the electron populations of the atomic orbitals as defined by the final wavefunction.

Note 2: The semiempirical methods use the "valence-only" approximation. The NBO module handles this as if the core electrons were being treated with the ab initio effective core potential (ECP) approximation. Integer numbers of electrons are assigned to the core orbitals.

Note 3: This table lists the computed charges from NBO. The NBO method orthogonalizes orbital descriptions into "natural orbitals" for its analysis. The semiempirical wavefunction is already orthogonalized, so these charges are the same as those predicted by the AMPAC Coulson analysis.

Note 4: The ratios of electrons to atomic orbital populations here can be related to the electron configuration at the atom under examination.

Note 5: This line describes the search for Lewis structures in the valence orbitals. The occupancy threshold for a classical structure search is 1.9 electrons. Use of the NBO keyword RESONANCE will search for delocalized Lewis structures.

Note 6: This table describes in detail the AO components of the MO, the energies of these MOs, and an evaluation of the type of orbital: BD = bonding, BD = antibonding, and NB = non-bonding. For example, the first MO listing is as follows:*

```
  1. (1.98975) BD ( 1) C 1- N 2
               ( 45.56%)   0.6750* C 1 s( 21.46%)p 3.66( 78.54%)
                                    0.4633  0.8841  0.0609  0.0000
               ( 54.44%)   0.7378* N 2 s( 18.06%)p 4.54( 81.94%)
                                    0.4250 -0.8963  0.1264  0.0000
```

This output indicates that the MO is bonding (BD) between C1 and N2 and has an occupancy of 1.98975 electrons. The bond is divided into percentages on the atoms and further decomposed into AO components on each atom.

Note 7: This table describes the "off-center" component of the interatomic bonding components.

Note 8: Final NBO summary listing.

CHAPTER 9: SIMULATED ANNEALING

9.1 Introduction

One of the most difficult problems to solve in computational chemistry is the "multiple-minima" problem, or the location and characterization of geometric minima on a complex multidimensional potential energy surface. Since many chemical phenomena (especially in biological systems) depend on the structural arrangement of the molecule, determining the global minimum energy conformation is an important goal. For complex molecules, there can often be hundreds or thousands of reasonable candidate structures which are almost impossible to generate a priori and adequately explore.

Modern strategies to minimize a function in several unconstrained variables were defined in the 1970s. These methods fall into the general category of "pseudo-Newton" approaches and make extensive use of the gradient of the function, the only way to retain computational efficiency with large numbers of variables. The minimizers in AMPAC (DFP or BFGS for energy or POWELL, LTRD, or NEWTON for gradient) are local minimizers in that they converge toward the minimum that is in the most favorable position when related to the starting point. This may not be the global minimum, but only the one that is lowest in energy in a specific region of the potential energy surface. When multiple minima do exist on the potential surface, it is often difficult to locate them directly. A tedious process of trial and error is usually followed by defining a variety of starting points around the area of viability for the optimizable parameters (a grid search). Thus, an open problem in theoretical optimization, the location of the absolute minimum of a function in many unconstrained variables, has direct application to one of the most persistent and annoying problems in computational chemistry, the “multiple-minima” dilemma. In 1983, Kirkpatrick et al. suggested a heuristic answer to this problem, making use of a method of simulation in statistical mechanics coupled with Boltzmann's law at decreasing temperatures. "Simulated annealing" was the name given the procedure.

A reasonable question for computational chemistry is not necessarily finding the minimum solution of the energy/geometry function defining the molecule, but collecting a variety of possible solutions, i.e. local geometric minima. If properly structured and implemented, the simulated annealing process can be used to collect an entire set of minima. The simulated annealing procedure is very slow in refining the exact location of a minimum, and specialized local methods (much more rapid) are used for exact location. A mixed strategy can be derived in which the approximate locations of the minima are generated by the annealing procedure and the final refinement is carried out from each starting place by one of the local optimization protocols mentioned above.

The AMPAC keyword "ANNE" is dedicated to locating energetic minima on the potential surface (search criterion is minimizing energy). The keyword “MANN” is a generalization of ANNE in that it searches for minima of the gradient norm within prescribed lower and upper bounds of energy (search criterion is minimizing gradient norm). Thus, MANN locates not only minima but transition states and other critical points.

Most annealing algorithms and other multiple-minima search procedures are applied in the context of molecular mechanics (MM). This is because a large number of independent energy calculations usually need to be carried out and MM is the only chemical modeling method efficient enough to do this. To minimize the number of such calculations required using the higher quality, but much slower semiempirical methods, the researcher can apply certain additional constraints to the preliminary search (prior to the use of semiempirical energy calculations), based on his chemical understanding of the problem. These constraints are treated as penalty functions to the genuine search criterion (energy (ANNE) or gradient norm (MANN)). Enormous savings and enhanced efficiency can result. For example, in conformational problems involving aliphatic rings, up to 99% of the configurations generated correspond to geometries that are so poor that SCF convergence will be difficult. These conformations are discarded by the annealing procedure at a cost of only 1% of the computer time. The constraints presently implemented are

- Explicit boundaries on changing coordinates (Cartesian or internal, with or without symmetry constraints). Such a constraint is actually seen as a periodic condition, as recommended in the original Metropolis algorithm (see annealing keyword LIMIT).

- A severe penalty function is added if an interatomic distance drops below some threshold. This precludes atoms from collapsing onto one another (see annealing keyword PEN1).

- A bounded molecular system can be defined in which it is forbidden for any molecular configuration to have total inertia greater than some defined value (see annealing keyword PENA=n,m).

- Indestructible chemical bonds can be defined by adding a penalty function if a bond leaves a specific range (see annealing keywords PEN2 and TOL=n.n).

9.2 Strategies for Annealing Searches

The overall computational and algorithmic approach to a mixed strategy annealing search as implemented in AMPAC can be summarized in three distinct steps:

1. simulated annealing - The Markov chains resulting from the Metropolis walk on the PES at successive temperatures are used to generate "candidates" for quenching (refinement). Candidates are generated at each temperature until the average energy falls within a specific boundary. The temperature is then decreased and the process repeated.

2. filtering - (This process is also referred to as a “clustering sort”.) The Metropolis walk visits several minima in the course of its Markovian prospection at a given temperature, and since the walk concentrates on lower regions of the potential with decreasing temperature, some minima may be visited many times at various temperatures. All of the candidates are analyzed on

the basis of nearly equivalent conformations, accounting for translation/rotation/reflection and for permutations within a set of equivalent nuclei. A "distance" between conformations is calculated and candidates are clustered into closely related groups on this basis. Each cluster then generates a final candidate, the best of the members of the cluster with respect to the criterion. The distance between conformations is calculated from changes in the number of neighbors of atoms at various distances, making use of band-pass filters.

3. *quenching - Each candidate from Stage 2 then undergoes a local minimization for final refinement of the geometry. With ANNE, the minimization criterion is energy and AMPAC's standard implementation of BFGS or DFP is used. With MANN, the minimization criterion is the gradient norm and this is reduced using POWELL. The final output of the procedure provides the main characteristics of the minima collected through the process. Additional output can be obtained by using the PRINT= keyword. (Note that none of the annealing search penalty functions are active during quenching, with the exception of PENA=n,m)*

While the annealing procedure in AMPAC is designed to somewhat automate the search for minima (and other critical points using MANN) on a potential energy surface, it is not a "black box." The judicious use of geometry input and the various penalty functions can make the search both complete in the quantum mechanical potential energy space and efficient computationally. It is not chemically correct nor necessary to search ALL of the potential energy surface, when only a few geometric variables define all of the meaningful differences between minima and maxima. A few points to note:

1. *Divide the potential energy search into primary and secondary degrees of freedom as the degrees of freedom are expressed in the optimizable geometric parameters. The secondary degrees of freedom can then be stringently constrained using the LIMIT keyword and wide variance can be allowed the primary degrees of freedom.*

2. *The TEMP=XXX keyword can be used to allow the search to overcome larger energy barriers by increasing the value of XXX. TEMP is expressed in kcal/mol and should be at least twice the value of the energy barrier to be overcome. The default value is 50 (200 in MANN). The annealing process will take substantially longer if TEMP is increased.*

3. *The TLAW=XXX keyword allows a wider search of the PES by slowing the rate of temperature decay. A higher value for XXX results in a slower decay rate.*

4. *The thoroughness with which the PES is searched at each temperature can be increased by decreasing the value for SIGMA. This may cause the search to locate more remote minima on the PES, at each temperature. Note that a value of SIGMA that*

is too small will cause a limited search to require an inordinate amount of time.

5. A smaller value of FILTER can be used to retain configurations that are geometrically similar. Too small a value for FILTER will result in a large number of virtually equivalent conformers being passed to the quenching routines. This approach should be used where conformers are separated by slight differences in geometry.

6. As the Markov chains are generated, they get sectioned into pieces by the annealing algorithm. Each piece hopefully refers to a specific minima on the surface. The length of these sections is governed by the annealing keyword NCHECK. A smaller value of NCHECK allows a wider sampling of the Markov chain on the surface.

9.3 ANNE and MANN Dedicated Keywords

Some keywords apply both to annealing and quenching (DFP or POWELL). Others apply only to the quenching portion of the annealing procedure (CYCLES= and GNORM=).

FILTER=n.n

Threshold on number of neighbors to each atom that is used to determine the possible equivalency of configurations during the clustering sort. Making this value smaller will result in generating more conformers for quenching. This parameter should not generally be adjusted unless other methods have been attempted first. The default value is 1.4. (Default is 0.7 when MANN is specified.) Abbreviation: None

FREF=n.n

(Used only with MANN.) This is the central value of the energy range ("crenel") defined for the MANN search. See the discussion of the MANN keyword for more information. Abbreviation: None

LIMIT

This keyword causes periodic boundaries to be entered from a special section of the input file. When LIMIT is invoked, N lower bounds for the optimizable geometric parameters in order of their definition in the input file, followed by N upper bounds in the same fashion. The data is entered free format and may occupy more than one line. Use of the LIMIT keyword is strongly recommended for efficiency in searching the potential energy surface. Unit are angstroms and degrees. Abbreviation: None

LTRD

The use of the regular AMPAC keyword LTRD along with MANN causes the slower but more reliable LTRD algorithm to be used in the critical point searching procedure. Abbreviation: None

MARK

All points of the Markov chains are written to channel 8. A file is created named jobname.MRK. Abbreviation: None

NCHECK=n

When this keyword is used, a candidate for quenching is produced each NCHECK random moves at each temperature. It should be noted that thermalisation criteria can be bypassed by using very small value for NCHECK. Alternatively, large values of NCHECK improve thermalisation but reduce the number of candidates unless a small value for SIGMA is provided. This parameter should not generally be adjusted unless other methods have been attempted first. The default value for NCHECK is 30. Abbreviation: None

NEWTON

The use of the regular AMPAC keyword NEWTON along with ANNE causes the slower but more reliable NEWTON algorithm to be used in the geometry searches rather than the default DFP/BFGS. Abbreviation: NEWT

NMAX=n

*This variable defines the maximum value of calls to the criterion at a given temperature. With N the number of optimized variables, the default is 40*N, with the minimum value 150 and the maximum value 500. (This is tripled with PRECISE). Abbreviation: None*

NOQU

The calculation is halted after the annealing section, and no quenching is performed. Abbreviation: None

NRAND=n

This provides a negative integer value to "seed" the sequence of pseudo random numbers required for the annealing walk. Abbreviation: None

PENA=n.n

This keyword activates the penalty function which limits the inertial moment of the molecule to the value n.n Angstroms^2. Note that in the computation, each atomic mass is taken as unity and this penalty is also active in the course of quenching. Abbreviation: None

PEN1

Use of this keyword activates a penalty function that acts to eliminate conformations where two atoms are within a distance of 0.6 Angstroms. Abbreviation: None

PEN2

Use of this keyword activates a penalty function eliminating conformations where two atoms are too close together (within a distance which is specific to the pair of atoms) or where a bond length (of a bond existing in the initial geometry) is too large. Use of PEN2 should be sparing as the conditions it assesses are not common. (See TOL=n for specifying these distances.) Abbreviation: None

PREF=n.n

(Used only with MANN.) This is the penalty applied to the RMS gradient outside of the permitted range of energy for a MANN search. The default value is 80% of the highest temperature.. See the discussion of the MANN keyword for more information. Abbreviation: None

SIGMA=n.n

"Thermalisation" criterion on the relative expectation value of the energy ([E]) at each temperature. The default value is 0.1 (0.07 with PRECISE). (Default is 0.15 when MANN is specified.) Abbreviation: None

SREF=n.n

(Used only with MANN.) This variable specifies the width of the searched energy range defined for the MANN search. The default value is 30 kcal/mol. See the discussion of the MANN keyword for more information. Abbreviation: None

STEP=n.n

This is the maximum step size in the annealing search. The default value is 2.0 Angstroms or radians. This keyword also provides an estimate of the shortest distance between the various minima of the function (see keyword STEPCV). (Default is 1.00 when MANN is specified.) Abbreviation: None

STEPCV=n.n

The value defined for this keyword is the ratio of STEP defining a lower bound for the stepsize. The default value is STEP*$(2/NMAX)^{1/2}$. The current step size is updated internally and usually decreases with the temperature. The simulated annealing procedure halts when either the current step size drops below STEPCV or the random walk is trapped in some minimum on the previous 2 (3 with PRECISE) values of the temperature. Abbreviation: None

TEMP=n.n

Starting "temperature" (kcal/mol) for the annealing procedure. The default value is 50. (Default is 200 when MANN is specified.) Abbreviation: None

TLAW=n.n

TLAW is the decay constant in the temperature. The default value of n.n is 0.8 and 0.0 < n.n < 1.0. Abbreviation: None

TOL=n

Permitted relative variation of a bond length from its initial value (used with PEN2). The default value is 0.1. Abbreviation: None

9.4 Example I ("Floppy" system)

The cyclohexane molecule has been chosen as an example of a molecule with relatively low rotational barriers. There are four conformers of the molecule that can be identified (chair, boat (flexible), twist or skew boat, and half-chair) and all of these are located by AMPAC's annealing protocol, using relaxed constraints and limited penalty functions.

Input File (TEST22.DAT) :

```
   AM1 NOXY NOINT GNORM=0.1 T=50000 ANNE +
   FILTER=1.  PEN2 LIMIT NCHECK=10
   CYCLOHEXANE
   ANNEALING TEST
C          0.00000 0        0.00000 0     0.00000 0   0  0  0
C          1.52088 0        0.00000 0     0.00000 0   0  0  0
C          1.52088 0      112.70693 1     0.00000 0   0  0  0
C          1.52088 0      112.70693 1    -7.37672 1   3  2  1
C          1.52088 0      112.70693 1   -46.31002 1   1  2  3
C          1.52088 0      112.70693 1    50.81948 1   5  1  2
H          1.12120 0      112.38414 1    75.00687 1   1  2  3
H          1.12120 0      112.38414 1  -167.31305 1   1  2  3
H          1.12120 0      112.38414 1   121.01956 1   2  3  1
H          1.12120 0      112.38414 1  -121.14480 1   2  3  1
H          1.12120 0      112.38414 1   113.45520 1   3  2  1
H          1.12120 0      112.38414 1  -128.80283 1   3  2  1
H          1.12120 0      112.38414 1   177.86240 1   4  3  2
H          1.12120 0      112.38414 1   -63.80798 1   4  3  2
H          1.12120 0      112.38414 1    57.50585 1   5  4  3
H          1.12120 0      112.38414 1  -154.79728 1   5  4  3
H          1.12120 0      112.38414 1   121.56636 1   6  5  4
H          1.12120 0      112.38414 1  -122.04050 1   6  5  4
0          0.00000 0        0.00000 0     0.00000 0   0  0  0
100 100 -180 100 -180 100 -180 100 -180 100 -180 100 -180 100 -180 100 -180                    Note 1
    100 -180 100 -180 100 -180 100 -180 100 -180 100 -180 100 -180
130 130  180 130  180 130  180 130  180 130  180 130  180 130  180 130  180                    Note 2
    130  180 130  180 130  180 130  180 130  180 130  180 130  180
```

Note 1: These are the <u>lower</u> boundaries of the bond angles and dihedrals (in order as specified) as required for by the annealing keyword LIMIT. Note that no values for the bond lengths are included. This is because none of them are marked for optimization.

Note 2: These are the <u>upper</u> boundaries of the bond angles and dihedrals (in order as specified) as required for by the annealing keyword LIMIT.

Archive File (TEST22.ARC) :

```
                    SUMMARY OF   AM1   CALCULATION
                                                    9-MAY-94
```

```
                        AMPAC Version  5.00
                           Presented by:

                      Semichem, Inc.
                      7128 Summit
                      Shawnee, KS  66216
                      (913) 268-3271
                      (913) 268-3445 (fax)

C 6 H 12
   CYCLOHEXANE
   ANNEALING TEST

    GRADIENT (COMPONENT) TEST WAS SATISFIED IN BFGS OR DFP
    SCF FIELD WAS ACHIEVED

         HEAT OF FORMATION       =   -38.461501 KCAL
         ELECTRONIC ENERGY       = -4341.805474 EV
         CORE-CORE REPULSION     =  3407.048735 EV
         DIPOLE                  =     0.00943 DEBYE
         NO. OF FILLED LEVELS    =    18
         IONISATION POTENTIAL    =    10.674868 EV
         MOLECULAR WEIGHT        =    84.161
         SCF CALCULATIONS        =   3499
         COMPUTATION TIME        =  5286.24 SECONDS

         FINAL GEOMETRY OBTAINED                                CHARGE
AM1 NOXY NOINT GNORM=0.1 T=50000 ANNE
   CYCLOHEXANE
   ANNEALING TEST
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0      -0.1535
 C     1.520880  0    0.000000  0    0.000000  0   1  0  0      -0.1535
 C     1.520880  0  111.135222  1    0.000000  0   2  1  0      -0.1541
 C     1.520880  0  111.150389  1   55.480798  1   3  2  1      -0.1530
 C     1.520880  0  111.127787  1  -55.507382  1   1  2  3      -0.1541
 C     1.520880  0  111.146663  1   55.504872  1   5  1  2      -0.1531
 H     1.121200  0  109.419097  1   65.443947  1   1  2  3       0.0766
 H     1.121200  0  109.548606  1 -176.697366  1   1  2  3       0.0779
 H     1.121200  0  109.418244  1 -120.941612  1   2  3  1       0.0767
 H     1.121200  0  109.552764  1  121.198124  1   2  3  1       0.0780
 H     1.121200  0  109.543660  1  176.684362  1   3  2  1       0.0759
 H     1.121200  0  109.416371  1  -65.469034  1   3  2  1       0.0758
 H     1.121200  0  109.446598  1 -176.932285  1   4  3  2       0.0765
 H     1.121200  0  109.308311  1   65.479699  1   4  3  2       0.0778
 H     1.121200  0   93.039320  1  109.411277  1   5  4  3       0.0758
 H     1.121200  0  143.755648  1 -124.626421  1   5  4  3       0.0758
 H     1.121200  0  109.312181  1  121.083111  1   6  5  4       0.0779
 H     1.121200  0  109.449734  1 -121.317988  1   6  5  4       0.0765
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0

                    SUMMARY OF   AM1   CALCULATION
                                                   9-MAY-94
                        AMPAC Version  5.00
                           Presented by:

                      Semichem, Inc.
                      7128 Summit
                      Shawnee, KS  66216
                      (913) 268-3271
                      (913) 268-3445 (fax)

C 6 H 12
   CYCLOHEXANE
   ANNEALING TEST

    GRADIENT (COMPONENT) TEST WAS SATISFIED IN BFGS OR DFP
    SCF FIELD WAS ACHIEVED

         HEAT OF FORMATION       =   -35.290855 KCAL
         ELECTRONIC ENERGY       = -4341.805474 EV
         CORE-CORE REPULSION     =  3407.048735 EV
```

Note 1

```
         DIPOLE                  =     0.02560 DEBYE
         NO. OF FILLED LEVELS    =    18
         IONISATION POTENTIAL    =    10.674868 EV
         MOLECULAR WEIGHT        =    84.161
         SCF CALCULATIONS        =   3499
         COMPUTATION TIME        =  5286.28 SECONDS

         FINAL GEOMETRY OBTAINED                                CHARGE
AM1 NOXY NOINT GNORM=0.1 T=50000 ANNE
   CYCLOHEXANE
   ANNEALING TEST
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0      -0.1535
 C     1.520880  0    0.000000  0    0.000000  0   1  0  0      -0.1535
 C     1.520880  0  112.210880  1    0.000000  0   2  1  0      -0.1541
 C     1.520880  0  111.551438  1  -29.882971  1   3  2  1      -0.1530
 C     1.520880  0  111.546023  1  -30.218148  1   1  2  3      -0.1541
 C     1.520880  0  111.557413  1   62.790091  1   5  1  2      -0.1531
 H     1.121200  0  109.544065  1   90.515390  1   1  2  3       0.0766
 H     1.121200  0  109.605267  1 -151.786288  1   1  2  3       0.0779
 H     1.121200  0  109.697283  1  121.277958  1   2  3  1       0.0767
 H     1.121200  0  108.984507  1 -121.709981  1   2  3  1       0.0780
 H     1.121200  0  109.542321  1   90.860903  1   3  2  1       0.0759
 H     1.121200  0  109.624102  1 -151.450981  1   3  2  1       0.0758
 H     1.121200  0  109.527117  1 -175.434301  1   4  3  2       0.0765
 H     1.121200  0  108.881982  1  -58.279899  1   4  3  2       0.0778
 H     1.121200  0  106.603597  1   51.209129  1   5  4  3       0.0758
 H     1.121200  0  137.681749  1 -166.341503  1   5  4  3       0.0758
 H     1.121200  0  109.648214  1  121.393288  1   6  5  4       0.0779
 H     1.121200  0  108.896720  1 -121.788672  1   6  5  4       0.0765
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0

                    SUMMARY OF   AM1   CALCULATION
                                                        9-MAY-94
                         AMPAC Version  5.00
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)

C 6 H 12
   CYCLOHEXANE
   ANNEALING TEST

    GRADIENT (COMPONENT) TEST WAS SATISFIED IN BFGS OR DFP
    SCF FIELD WAS ACHIEVED

         HEAT OF FORMATION       =   -34.938318 KCAL
         ELECTRONIC ENERGY       = -4341.805474 EV
         CORE-CORE REPULSION     =  3407.048735 EV
         DIPOLE                  =     0.00391 DEBYE
         NO. OF FILLED LEVELS    =    18
         IONISATION POTENTIAL    =    10.674868 EV
         MOLECULAR WEIGHT        =    84.161
         SCF CALCULATIONS        =   3499
         COMPUTATION TIME        =  5286.33 SECONDS

         FINAL GEOMETRY OBTAINED                                CHARGE
AM1 NOXY NOINT GNORM=0.1 T=50000 ANNE
   CYCLOHEXANE
   ANNEALING TEST
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0      -0.1535
 C     1.520880  0    0.000000  0    0.000000  0   1  0  0      -0.1535
 C     1.520880  0  112.667758  1    0.000000  0   2  1  0      -0.1541
 C     1.520880  0  112.672072  1    0.236805  1   3  2  1      -0.1530
 C     1.520880  0  111.660726  1   51.646179  1   1  2  3      -0.1541
 C     1.520880  0  112.670814  1  -52.047191  1   5  1  2      -0.1531
 H     1.121200  0  109.315983  1  172.739426  1   1  2  3       0.0766
 H     1.121200  0  109.513691  1  -69.802504  1   1  2  3       0.0779
 H     1.121200  0  109.783226  1 -121.504978  1   2  3  1       0.0767
```

```
 H     1.121200  0  109.371819  1  121.292662  1   2  3  1       0.0780
 H     1.121200  0  109.776597  1  121.734505  1   3  2  1       0.0759
 H     1.121200  0  109.371609  1 -121.056684  1   3  2  1       0.0758
 H     1.121200  0  109.183978  1 -173.350057  1   4  3  2       0.0765
 H     1.121200  0  109.377266  1   69.523449  1   4  3  2       0.0778
 H     1.121200  0  123.015101  1  -58.522863  1   5  4  3       0.0758
 H     1.121200  0  123.778991  1  152.640292  1   5  4  3       0.0758
 H     1.121200  0  109.249556  1  121.450715  1   6  5  4       0.0779
 H     1.121200  0  109.666540  1 -121.634886  1   6  5  4       0.0765
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0

                    SUMMARY OF   AM1   CALCULATION
                                                        9-MAY-94
                         AMPAC Version  5.00
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)

C 6 H 12
   CYCLOHEXANE
   ANNEALING TEST

    GRADIENT (COMPONENT) TEST WAS SATISFIED IN BFGS OR DFP
    SCF FIELD WAS ACHIEVED

         HEAT OF FORMATION       =   -31.839914 KCAL
         ELECTRONIC ENERGY       = -4341.805474 EV
         CORE-CORE REPULSION     =  3407.048735 EV
         DIPOLE                  =     0.10662 DEBYE
         NO. OF FILLED LEVELS    =    18
         IONISATION POTENTIAL    =    10.674868 EV
         MOLECULAR WEIGHT        =    84.161
         SCF CALCULATIONS        =   3499
         COMPUTATION TIME        =  5286.36 SECONDS

         FINAL GEOMETRY OBTAINED                                CHARGE
AM1 NOXY NOINT GNORM=0.1 T=50000 ANNE
   CYCLOHEXANE
   ANNEALING TEST
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0      -0.1535
 C     1.520880  0    0.000000  0    0.000000  0   1  0  0      -0.1535
 C     1.520880  0  116.858320  1    0.000000  0   2  1  0      -0.1541
 C     1.520880  0  111.722355  1   29.123218  1   3  2  1      -0.1530
 C     1.520880  0  119.687006  1    4.866913  1   1  2  3      -0.1541
 C     1.520880  0  117.083060  1   -5.967953  1   5  1  2      -0.1531
 H     1.121200  0  107.775325  1  128.304783  1   1  2  3       0.0766
 H     1.121200  0  107.423268  1 -117.851380  1   1  2  3       0.0779
 H     1.121200  0  108.167718  1 -121.928633  1   2  3  1       0.0767
 H     1.121200  0  108.107799  1  123.136900  1   2  3  1       0.0780
 H     1.121200  0  109.242533  1  150.747601  1   3  2  1       0.0759
 H     1.121200  0  109.707571  1  -91.880808  1   3  2  1       0.0758
 H     1.121200  0  109.734799  1  176.657666  1   4  3  2       0.0765
 H     1.121200  0  109.897770  1   58.276305  1   4  3  2       0.0778
 H     1.121200  0  135.843727  1  -81.350590  1   5  4  3       0.0758
 H     1.121200  0  107.600852  1  139.797195  1   5  4  3       0.0758
 H     1.121200  0  109.471336  1  121.233786  1   6  5  4       0.0779
 H     1.121200  0  109.056065  1 -121.950072  1   6  5  4       0.0765
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0

                    SUMMARY OF   AM1   CALCULATION                                    Note 2
                                                        9-MAY-94
                         AMPAC Version  5.00
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
```

```
                    (913) 268-3271
                    (913) 268-3445 (fax)

C 6 H 12
   CYCLOHEXANE
   ANNEALING TEST


    SCF FIELD WAS ACHIEVED

         HEAT OF FORMATION       =   -38.461532 KCAL
         ELECTRONIC ENERGY       = -4336.114556 EV
         CORE-CORE REPULSION     =  3401.221024 EV
         DIPOLE                  =     0.00090 DEBYE
         NO. OF FILLED LEVELS    =    18
         IONISATION POTENTIAL    =    10.953938 EV
         MOLECULAR WEIGHT        =    84.161
         SCF CALCULATIONS        =   3500
         COMPUTATION TIME        =  5288.58 SECONDS

         FINAL GEOMETRY OBTAINED                                CHARGE
AM1 NOXY NOINT GNORM=0.1 T=50000 ANNE
   CYCLOHEXANE
   ANNEALING TEST
 C     0.000000  0    0.000000  0    0.000000  0   0  0  0      -0.1551
 C     1.520880  0    0.000000  0    0.000000  0   1  0  0      -0.1551
 C     1.520880  0  111.135222  1    0.000000  0   2  1  0      -0.1552
 C     1.520880  0  111.150389  1   55.480798  1   3  2  1      -0.1547
 C     1.520880  0  111.127787  1  -55.507382  1   1  2  3      -0.1552
 C     1.520880  0  111.146663  1   55.504872  1   5  1  2      -0.1547
 H     1.121200  0  109.419097  1   65.443947  1   1  2  3       0.0782
 H     1.121200  0  109.548606  1 -176.697366  1   1  2  3       0.0769
 H     1.121200  0  109.418244  1 -120.941612  1   2  3  1       0.0782
 H     1.121200  0  109.552764  1  121.198124  1   2  3  1       0.0769
 H     1.121200  0  109.543660  1  176.684362  1   3  2  1       0.0769
 H     1.121200  0  109.416371  1  -65.469034  1   3  2  1       0.0782
 H     1.121200  0  109.446598  1 -176.932285  1   4  3  2       0.0767
 H     1.121200  0  109.308311  1   65.479699  1   4  3  2       0.0781
 H     1.121200  0   93.039320  1  109.411277  1   5  4  3       0.0782
 H     1.121200  0  143.755648  1 -124.626421  1   5  4  3       0.0769
 H     1.121200  0  109.312181  1  121.083111  1   6  5  4       0.0781
 H     1.121200  0  109.449734  1 -121.317988  1   6  5  4       0.0767
  0    0.000000  0    0.000000  0    0.000000  0   0  0  0
```

Note 1: Each of the located and quenched minima is sequentially listed in the archive file.

Note 2: The last listing in the file is the most stable geometry in the set of located minima.

Output File (TEST22.OUT) :

```
*******************************************************************************
                            AM1 CALCULATION RESULTS
*******************************************************************************
*                             AMPAC Version  5.00
*                                Presented by:
*
*                           Semichem, Inc.
*                           7128 Summit
*                           Shawnee, KS  66216
*                           (913) 268-3271
*                           (913) 268-3445 (fax)
*
*  ANNE     - ANNEALING METHOD ON ENERGY TO BE USED
*  GNORM=   - OPTIMIZATION EXIT WHEN GRADIENT NORM BELOW    0.100
*  NOINTER  - INTERATOMIC DISTANCES NOT TO BE PRINTED
```

```
*  NOXYZ    - CARTESIAN COORDINATES NOT TO BE PRINTED
*   T=      - A TIME OF 50000.0 SECONDS REQUESTED
*  AM1      - THE AM1 HAMILTONIAN TO BE USED
*****************************************************************************
AM1 NOXY NOINT GNORM=0.1 T=50000 ANNE
   CYCLOHEXANE
   ANNEALING TEST
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C
     2     C          1.52088                                   1
     3     C          1.52088        112.70693 *                2  1
     4     C          1.52088        112.70693 *    -7.37672 *  3  2  1
     5     C          1.52088        112.70693 *   -46.31002 *  1  2  3
     6     C          1.52088        112.70693 *    50.81948 *  5  1  2
     7     H          1.12120        112.38414 *    75.00687 *  1  2  3
     8     H          1.12120        112.38414 *  -167.31305 *  1  2  3
     9     H          1.12120        112.38414 *   121.01956 *  2  3  1
    10     H          1.12120        112.38414 *  -121.14480 *  2  3  1
    11     H          1.12120        112.38414 *   113.45520 *  3  2  1
    12     H          1.12120        112.38414 *  -128.80283 *  3  2  1
    13     H          1.12120        112.38414 *   177.86240 *  4  3  2
    14     H          1.12120        112.38414 *   -63.80798 *  4  3  2
    15     H          1.12120        112.38414 *    57.50585 *  5  4  3
    16     H          1.12120        112.38414 *  -154.79728 *  5  4  3
    17     H          1.12120        112.38414 *   121.56636 *  6  5  4
    18     H          1.12120        112.38414 *  -122.04050 *  6  5  4
         SINGLET STATE CALCULATION
         RHF CALCULATION, No. OF DOUBLY OCCUPIED LEVELS = 18

        **  REFERENCES TO PARAMETERS  **

 H  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
 C  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)

*****************************************************************************
*  KEYWORDS OF THE ANNEALING SECTION
*
*  LIMIT    - USE PERIODIC CONDITIONS ON VARIABLES
*  CHECK=   - SET MARKOV CHAIN IN PIECES OF   10 LONG
*  FILTER=  - SET THRESHOLD OF DISTINGUISHED CONFIGURATION TO 1.000
*  PEN2     - PENALTY ON BOUNDS TO INTERATOMIC DISTANCES
*****************************************************************************

SIMULATED ANNEALING BY METROPOLIS SCHEME IN   31 VARIABLES
     VERSION 1  (JULY 1991)
    THERMALIZATION THRESHOLD ON CRITERION          0.100
    MAXIMUM STEP SIZE                            2.00000
    CONVERGENCE CRITERION ON STEP SIZE           0.12649

MAXIMUM NUMBER OF CALL AT EACH TEMPERATURE         500
    FIRST TEMPERATURE (HOT) SET TO               200.00
    TEMPERATURE EXPONENTIAL DECAY                  0.80
    LAST TEMPERATURE (COLD) SET TO                 2.00
RANDOM SEQUENCE INITIATOR                       -9876543
    MARKOV CHAIN STUDIED BY PIECES OF                 10
    No OF TEMPERATURES TO DETECT A FROZEN SYSTEM       2
EQUIVALENCE THRESHOLD IN CLUSTERING ANALYSIS        1.00
    BAND-PASS FILTER NO 1 CENTERED AT               2.30 ANGSTROMS
    HALF BAND-WIDTH                                13.50 %
PENALTIES ACTIVATED:
    ON CHEMICAL BONDS, THRESHOLD:        0.10
 PERIODIC BOUNDARY CONDITIONS (ANGSTROMS, DEGREES)
 LOWER BOUND  100.0000  100.0000 -180.0000  100.0000 -180.0000  100.0000
             -180.0000  100.0000 -180.0000  100.0000 -180.0000  100.0000
             -180.0000  100.0000 -180.0000  100.0000 -180.0000  100.0000
             -180.0000  100.0000 -180.0000  100.0000 -180.0000  100.0000
             -180.0000  100.0000 -180.0000  100.0000 -180.0000  100.0000
             -180.0000
 TRIAL COORD  112.7069  112.7069   -7.3767  112.7069  -46.3100  112.7069
```

Note 1

Note 2

Note 3

Note 4

```
              50.8195  112.3841   75.0069  112.3841 -167.3131  112.3841
             121.0196  112.3841 -121.1448  112.3841  113.4552  112.3841
            -128.8028  112.3841  177.8624  112.3841  -63.8080  112.3841
              57.5059  112.3841 -154.7973  112.3841  121.5664  112.3841
            -122.0405
 UPPER BOUND  130.0000  130.0000  180.0000  130.0000  180.0000  130.0000
              180.0000  130.0000  180.0000  130.0000  180.0000  130.0000
              180.0000  130.0000  180.0000  130.0000  180.0000  130.0000
              180.0000  130.0000  180.0000  130.0000  180.0000  130.0000
              180.0000  130.0000  180.0000  130.0000  180.0000  130.0000
              180.0000
 USE 1-POINT FORMULA IN INTEGRAL DERIVATIVES WITH STEP  0.00000015
STANDARD DEVIATION ON ENERGY   (KCAL)        0.000022406
STANDARD DEVIATION ON GRADIENT (KCAL/A,RD,RD)  0.0000000 0.0017949 0.0017900

CRITERION IS ENERGY (KCAL/MOLE)
PENALTY FUNCTION FOR LOCATION OF BONDS AND DETAILLED MINIMUM DISTANCE CHECK IS I
INITIALIZED WITH TOLERANCE 0.100
LOCATED BONDS BETWEEN THE FOLLOWING ATOMS:
  123456789012345678
 1 .*..*.**..........
 2 *.*.....**........
 3 .*.*......**......
 4 ..*..*......**....
 5 *....*........**..
 6 ...**..........**
 7 *................
 8 *................
 9 .*...............
 0 .*...............
 1 ..*..............
 2 ..*..............
 3 ...*.............
 4 ...*.............
 5 ....*............
 6 ....*............
 7 .....*...........
 8 .....*...........

SIMULATED ANNEALING SECTION
---------------------------

* * * SYSTEM LOOKS FROZEN AT TEMPERATURE   52.4288 KCAL
NORMAL END AFTER   956 CALLS TO CRITERION
LAST CONFORMATION GENERATED IN ANNEALING:
         HEAT OF FORMATION       =   309.688877 KCAL
CURRENT COORDINATES (ANGSTROMS, DEGREES)
 122.8645  109.4697   -0.1385  101.7734   35.4076  120.7542   -4.7775  106.0578
 132.6553  124.7628  -60.6607  115.4515  -89.7454  112.9152  134.5978  107.8259
 111.2445  120.3982 -133.7582  103.3739  125.1756  122.3924  -30.3674  127.8616
 -86.4672  111.5445  103.8057  104.4060  109.1693  108.2641 -151.0594
ELAPSED TIME IN ANNEALING   2313.28 SECONDS
TABLE OF NEARLY IDENTICAL CONFIGURATIONS AT THRESHOLD =  1.00 A
CRITERION  ,CONFIGURATIONS    (A "*" MEANS IDENTICAL)
             2 4 6 8 0 2 4 6 8 0 2 4 6 8 0 2 4 6 8 0 2 4 6 8 0 2 4 6 8 0
-25.9782   1*
169.4355   2.*
172.3481   3..*
173.8003   4...*
177.7012   5....*
183.3653   6.....*
187.3695   7......*
207.5741   8.......*
210.5442   9........*
215.7192  10.........*
228.2270  11..........*
229.4250  12...........*
240.0843  13............*
241.7630  14.............*
248.8990  15..............*
254.1291  16...............*
```

Note 5

Note 6

Note 7

```
259.4544  17...............*
267.7038  18................*
273.5529  19.................*
278.6025  20.................*
278.8421  21..................*
279.0007  22...................*
285.2877  23....................*
291.9699  24.....................*
296.2070  25......................*
296.9052  26.......................*
297.2189  27........................*
298.2857  28.........................*
299.4340  29..........................*
299.6169  30...........................*
299.8830  31............................*
305.2041  32.............................*
306.2753  33..............................*
306.3548  34...............................*
313.4561  35....................*...........*
325.4604  36................................*
333.6938  37.................................*
336.6588  38..................................*
339.5859  39...................................*
343.8418  40....................................*
347.3736  41.....................................*
353.7301  42......................................*
356.0777  43.......................................*
360.0392  44........................................*
365.8669  45.........................................*
368.0156  46..........................................*
371.5702  47...........................................*
373.3745  48............................................*
378.1391  49.............................................*
384.9393  50..............................................*
407.3956  51...............................................*
413.5496  52................................................*
420.6527  53.................................................*
430.3329  54..................................................*
454.3606  55...................................................*
468.0668  56....................................................*
469.6961  57.....................................................*
483.4926  58......................................................*
525.7859  59.......................................................*
532.1847  60........................................................*
```

```
NUMBER OF SELECTED CONFIGURATION 59
CRITERIA:  -25.9782  169.4355  172.3481  173.8003  177.7012  183.3653  187.3695
 207.5741  210.5442  215.7192  228.2270  229.4250  240.0843  241.7630  248.8990
 254.1291  259.4544  267.7038  273.5529  278.6025  278.8421  279.0007  285.2877
 291.9699  296.2070  296.9052  297.2189  298.2857  299.4340  299.6169  299.8830
 305.2041  306.2753  306.3548  325.4604  333.6938  336.6588  339.5859  343.8418
 347.3736  353.7301  356.0777  360.0392  365.8669  368.0156  371.5702  373.3745
 378.1391  384.9393  407.3956  413.5496  420.6527  430.3329  454.3606  468.0668
 469.6961  483.4926  525.7859  532.1847
```

Note 8

```
QUENCHING OF REMAINING POINTS AFTER CLUSTERING ANALYSIS
-------------------------------------------------------
DONE WITHOUT PERIODIC BOUNDARIES
DONE WITHOUT PENALTIES ON  INTERATOMIC DISTANCES
MINIMIZE ENERGY USING BFGS ALGORITHM


RESULTS OF QUENCHING No  1
.........................
         HEAT OF FORMATION       =   -35.290855 KCAL
CURRENT COORDINATES (ANGSTROMS, DEGREES)
 112.2109  111.5514  -29.8830  111.5460  -30.2181  111.5574   62.7901  109.5441
  90.5154  109.6053 -151.7863  109.6973  121.2780  108.9845 -121.7100  109.5423
  90.8609  109.6241 -151.4510  109.5271  184.5657  108.8820  -58.2799  106.6036
  51.2091  137.6817 -166.3415  109.6482  121.3933  108.8967 -121.7887
```

Note 9

```
RESULTS OF QUENCHING No  2
.........................
         HEAT OF FORMATION       =   -38.461501 KCAL
CURRENT COORDINATES (ANGSTROMS, DEGREES)
 111.1352  111.1504   55.4808  111.1278  -55.5074  111.1467   55.5049  109.4191
  65.4439  109.5486 -176.6974  109.4182 -120.9416  109.5528  121.1981  109.5437
 176.6844  109.4164  -65.4690  109.4466 -176.9323  109.3083   65.4797   93.0393
 109.4113  143.7556 -124.6264  109.3122  121.0831  109.4497 -121.3180

RESULTS OF QUENCHING No  3
.........................
         * * * QUENCHING INTERRUPTED: POINT PREVIOUSLY FOUND.

RESULTS OF QUENCHING No  4
.........................
         * * * QUENCHING INTERRUPTED: POINT PREVIOUSLY FOUND.

====================================

RESULTS OF QUENCHING No 11
.........................
         * * * QUENCHING INTERRUPTED: POINT PREVIOUSLY FOUND.

RESULTS OF QUENCHING No 12
.........................
         HEAT OF FORMATION       =   -34.938318 KCAL
CURRENT COORDINATES (ANGSTROMS, DEGREES)
 112.6678  112.6721    0.2368  111.6607   51.6462  112.6708  -52.0472  109.3160
 172.7394  109.5137  -69.8025  109.7832 -121.5050  109.3718  121.2927  109.7766
 121.7345  109.3716 -121.0567  109.1840  186.6499  109.3773   69.5234  123.0151
 -58.5229  123.7790  152.6403  109.2496  121.4507  109.6665 -121.6349

RESULTS OF QUENCHING No 13
.........................
         * * * QUENCHING INTERRUPTED: POINT PREVIOUSLY FOUND.

RESULTS OF QUENCHING No 14
.........................
         * * * CRITERION =   -35.307591 POINT PREVIOUSLY FOUND.

====================================

RESULTS OF QUENCHING No 37
.........................
         * * * QUENCHING INTERRUPTED: POINT PREVIOUSLY FOUND.

RESULTS OF QUENCHING No 38
.........................
         HEAT OF FORMATION       =   -31.839914 KCAL
CURRENT COORDINATES (ANGSTROMS, DEGREES)
 116.8583  111.7224   29.1232  119.6870    4.8669  117.0831   -5.9680  107.7753
-231.6952  107.4233 -117.8514  108.1677 -121.9286  108.1078  123.1369  109.2425
 150.7476  109.7076  268.1192  109.7348 -183.3423  109.8978   58.2763  135.8437
 -81.3506  107.6009  139.7972  109.4713  121.2338  109.0561 -121.9501

RESULTS OF QUENCHING No 39
.........................
         * * * QUENCHING INTERRUPTED: POINT PREVIOUSLY FOUND.

====================================

RESULTS OF QUENCHING No 58
.........................
         * * * QUENCHING INTERRUPTED: POINT PREVIOUSLY FOUND.

RESULTS OF QUENCHING No 59
.........................
         * * * CRITERION =   -35.306965 POINT PREVIOUSLY FOUND.
TABLE OF NEARLY IDENTICAL CONFIGURATIONS AT THRESHOLD =  1.10 A
CRITERION  ,CONFIGURATIONS    (A "*" MEANS IDENTICAL)
             2 4
-38.4615   1*
```

```
-35.2909   2.*
-34.9383   3..*
-31.8399   4...*

NUMBER OF SELECTED CONFIGURATION  4                                          Note 10
CRITERIA:  -38.4615  -35.2909  -34.9383  -31.8399

DETAILS ON NON EQUIVALENT STATIONARY POINTS FOUND                            Note 11
-------------------------------------------------

STATIONARY POINT No  1
......................
         HEAT OF FORMATION       =   -38.461501 KCAL
         RMS GRADIENT NORM       =     0.021791 KCAL/ANGSTROMS
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C
     2     C          1.52088                                    1
     3     C          1.52088        111.13522 *                 2  1
     4     C          1.52088        111.15039 *    55.48080 *   3  2  1
     5     C          1.52088        111.12779 *   -55.50738 *   1  2  3
     6     C          1.52088        111.14666 *    55.50487 *   5  1  2
     7     H          1.12120        109.41910 *    65.44395 *   1  2  3
     8     H          1.12120        109.54861 *  -176.69737 *   1  2  3
     9     H          1.12120        109.41824 *  -120.94161 *   2  3  1
    10     H          1.12120        109.55276 *   121.19812 *   2  3  1
    11     H          1.12120        109.54366 *   176.68436 *   3  2  1
    12     H          1.12120        109.41637 *   -65.46903 *   3  2  1
    13     H          1.12120        109.44660 *  -176.93228 *   4  3  2
    14     H          1.12120        109.30831 *    65.47970 *   4  3  2
    15     H          1.12120         93.03932 *   109.41128 *   5  4  3
    16     H          1.12120        143.75565 *  -124.62642 *   5  4  3
    17     H          1.12120        109.31218 *   121.08311 *   6  5  4
    18     H          1.12120        109.44973 *  -121.31799 *   6  5  4

    ORDERED CARTESIAN (INERTIA FRAME)  AND  INTERNAL COORDS (A, DEGREES)
   NO.    X         Y         Z              BOND     ANGLE   DIHEDRAL A  B  C
 1( 4)  -1.25447   0.72047   0.23088
 2( 6)  -1.25394  -0.72140  -0.23099        1.51404                    1
 3( 1)   1.25505  -0.72395  -0.23150        2.50900    90.08           2  1
 4( 2)   1.25458   0.72477   0.23138        1.52088    89.92    -0.04  3  2  1
 5( 3)  -0.00109   1.44775  -0.23085        1.52088   111.25    27.83  1  2  3
 6( 5)  -0.00009  -1.44765   0.23105        1.52088    34.43   129.71  3  2  1
 7(10)   2.15958   1.24831  -0.17356        1.12120   109.55  -148.94  4  3  2
 8( 8)   2.16040  -1.24689   0.17344        1.12120   143.89   124.42  3  2  1
 9(13)  -2.16002   1.24499  -0.17154        1.12120   109.65   149.04  1  2  3
10(18)  -2.15919  -1.24641   0.17147        1.12120   109.64   149.02  2  1  3
11(16)  -0.00123  -2.49303  -0.17426        1.12120   109.55   121.20  6  3  2
12(11)  -0.00289   2.49299   0.17481        1.12120   109.55  -176.80  5  1  2
13(14)  -1.31229   0.75539   1.35005        1.12120   109.52   -93.12  1  2  3
14(17)  -1.31161  -0.75647  -1.35016        1.12120   109.53   -93.14  2  1  3
15( 9)   1.31351   0.75849   1.35053        1.12120   109.42    93.21  4  3  2
16( 7)   1.31394  -0.75769  -1.35065        1.12120    93.02  -109.49  3  2  1
17(12)  -0.00099   1.51651  -1.34994        1.12120   109.42    65.35  5  1  2
18(15)   0.00026  -1.51605   1.35016        1.12120   109.41  -120.96  6  3  2

STATIONARY POINT No  2
......................
         HEAT OF FORMATION       =   -35.290855 KCAL
         RMS GRADIENT NORM       =     0.092765 KCAL/ANGSTROMS
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C
     2     C          1.52088                                    1
     3     C          1.52088        112.21088 *                 2  1
     4     C          1.52088        111.55144 *   -29.88297 *   3  2  1
     5     C          1.52088        111.54602 *   -30.21815 *   1  2  3
     6     C          1.52088        111.55741 *    62.79009 *   5  1  2
     7     H          1.12120        109.54407 *    90.51539 *   1  2  3
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     8     H          1.12120        109.60527 *  -151.78629 *   1  2  3
     9     H          1.12120        109.69728 *   121.27796 *   2  3  1
    10     H          1.12120        108.98451 *  -121.70998 *   2  3  1
    11     H          1.12120        109.54232 *    90.86090 *   3  2  1
    12     H          1.12120        109.62410 *  -151.45098 *   3  2  1
    13     H          1.12120        109.52712 *   184.56570 *   4  3  2
    14     H          1.12120        108.88198 *   -58.27990 *   4  3  2
    15     H          1.12120        106.60360 *    51.20913 *   5  4  3
    16     H          1.12120        137.68175 *  -166.34150 *   5  4  3
    17     H          1.12120        109.64821 *   121.39329 *   6  5  4
    18     H          1.12120        108.89672 *  -121.78867 *   6  5  4

    ORDERED CARTESIAN (INERTIA FRAME)  AND  INTERNAL COORDS (A, DEGREES)
   NO.    X          Y          Z              BOND     ANGLE   DIHEDRAL A  B  C
 1( 6)  -1.51025   0.00491  -0.00108
 2( 2)   1.51170  -0.00679  -0.00124        3.02198                     1
 3( 3)   0.65777  -1.21010  -0.36991        1.52088    56.06            2  1
 4( 4)  -0.67016  -1.20098   0.37143        1.51615    56.14    34.20   1  2  3
 5( 5)  -0.65842   1.20951  -0.37043        1.52088    56.15  -146.01   1  2  3
 6( 1)   0.66936   1.20351   0.37122        1.52088   111.56   -30.08   5  1  2
 7(17)  -2.17848   0.26569   0.86064        1.12120   126.65   123.67   1  2  3
 8( 9)   2.17823  -0.26666   0.86206        1.12120   126.54   -90.40   2  1  3
 9(18)  -2.17515  -0.24899  -0.86741        1.12120   126.31   -56.52   1  2  3
10(10)   2.17679   0.24757  -0.86729        1.12120   126.32    89.53   2  1  3
11(16)  -1.21684   2.15249  -0.13372        1.12120   109.63  -151.65   5  1  2
12(12)   1.21446  -2.15389  -0.13229        1.12120   109.62  -151.59   3  2  1
13( 8)   1.23547   2.14244   0.13664        1.12120   109.60  -175.64   6  5  1
14(13)  -1.23528  -2.14118   0.13957        1.12120   109.69  -151.71   4  1  2
15(14)  -0.46983  -1.19390   1.47456        1.12120   109.62    90.62   4  1  2
16(15)  -0.45928   1.20418  -1.47379        1.12120   109.55    90.64   5  1  2
17(11)   0.45935  -1.20523  -1.47340        1.12120   109.54    90.72   3  2  1
18( 7)   0.47052   1.19688   1.47462        1.12120   108.97   -58.28   6  5  1

STATIONARY POINT No  3
......................
         HEAT OF FORMATION       =   -34.938318 KCAL
         RMS GRADIENT NORM       =     0.023748 KCAL/ANGSTROMS
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C
     2     C          1.52088                                    1
     3     C          1.52088        112.66776 *                 2  1
     4     C          1.52088        112.67207 *     0.23681 *   3  2  1
     5     C          1.52088        111.66073 *    51.64618 *   1  2  3
     6     C          1.52088        112.67081 *   -52.04719 *   5  1  2
     7     H          1.12120        109.31598 *   172.73943 *   1  2  3
     8     H          1.12120        109.51369 *   -69.80250 *   1  2  3
     9     H          1.12120        109.78323 *  -121.50498 *   2  3  1
    10     H          1.12120        109.37182 *   121.29266 *   2  3  1
    11     H          1.12120        109.77660 *   121.73451 *   3  2  1
    12     H          1.12120        109.37161 *  -121.05668 *   3  2  1
    13     H          1.12120        109.18398 *   186.64994 *   4  3  2
    14     H          1.12120        109.37727 *    69.52345 *   4  3  2
    15     H          1.12120        123.01510 *   -58.52286 *   5  4  3
    16     H          1.12120        123.77899 *   152.64029 *   5  4  3
    17     H          1.12120        109.24956 *   121.45071 *   6  5  4
    18     H          1.12120        109.66654 *  -121.63489 *   6  5  4

    ORDERED CARTESIAN (INERTIA FRAME)  AND  INTERNAL COORDS (A, DEGREES)
   NO.    X          Y          Z              BOND     ANGLE   DIHEDRAL A  B  C
 1( 6)   1.27528   0.72950   0.20319
 2( 2)  -1.27886  -0.72805   0.20382        2.94077                     1
 3( 3)  -1.23675   0.79224   0.20698        1.52088    58.70            2  1
 4( 5)   1.23704  -0.79088   0.20882        1.52088    58.85   179.61   1  2  3
 5( 4)   0.03762   1.34469  -0.41261        1.51310    59.41   -28.37   1  2  3
 6( 1)  -0.03437  -1.34760  -0.41301        1.52088   112.67    26.29   4  1  2
 7(18)   2.17718   1.08218  -0.36187        1.12120   148.72  -104.13   1  2  3
 8( 9)  -2.17903  -1.08157  -0.36347        1.12120   148.59    76.37   2  1  3
 9(16)   2.12099  -1.19474  -0.35031        1.12120   109.78   147.79   4  1  2
10(11)  -2.11820   1.19734  -0.35519        1.12120   109.78   147.67   3  2  1
11( 7)  -0.06246  -2.45900  -0.26783        1.12120   109.32  -173.14   6  4  1
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12(13)   0.06395   2.45664  -0.27136        1.12120   109.43   147.05  5  1  2
13(17)   1.38340   1.10044   1.25572        1.12120   104.33    75.54  1  2  3
14(10)  -1.38641  -1.09930   1.25629        1.12120   104.34  -104.20  2  1  3
15(12)  -1.31936   1.16438   1.26139        1.12120   109.37   -95.12  3  2  1
16(15)   1.31788  -1.16129   1.26397        1.12120   109.39   -95.00  4  1  2
17(14)   0.02962   1.14910  -1.51659        1.12120   109.61   -95.54  5  1  2
18( 8)  -0.02712  -1.15308  -1.51719        1.12120   109.50    69.41  6  4  1

STATIONARY POINT No  4
......................
         HEAT OF FORMATION       =   -31.839914 KCAL
         RMS GRADIENT NORM       =     0.054964 KCAL/ANGSTROMS
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C
     2     C          1.52088                                    1
     3     C          1.52088        116.85832 *                 2  1
     4     C          1.52088        111.72236 *    29.12322 *   3  2  1
     5     C          1.52088        119.68701 *     4.86691 *   1  2  3
     6     C          1.52088        117.08306 *    -5.96795 *   5  1  2
     7     H          1.12120        107.77532 *  -231.69522 *   1  2  3
     8     H          1.12120        107.42327 *  -117.85138 *   1  2  3
     9     H          1.12120        108.16772 *  -121.92863 *   2  3  1
    10     H          1.12120        108.10780 *   123.13690 *   2  3  1
    11     H          1.12120        109.24253 *   150.74760 *   3  2  1
    12     H          1.12120        109.70757 *   268.11919 *   3  2  1
    13     H          1.12120        109.73480 *  -183.34233 *   4  3  2
    14     H          1.12120        109.89777 *    58.27631 *   4  3  2
    15     H          1.12120        135.84373 *   -81.35059 *   5  4  3
    16     H          1.12120        107.60085 *   139.79719 *   5  4  3
    17     H          1.12120        109.47134 *   121.23379 *   6  5  4
    18     H          1.12120        109.05607 *  -121.95007 *   6  5  4

    ORDERED CARTESIAN (INERTIA FRAME)  AND  INTERNAL COORDS (A, DEGREES)
   NO.    X         Y         Z              BOND     ANGLE   DIHEDRAL A  B  C
 1( 2)   1.36757  -0.62315  -0.02429
 2( 5)  -1.25507  -0.82031  -0.03666        2.63008                    1
 3( 6)  -1.28939   0.68721  -0.23484        1.52088    87.07           2  1
 4( 3)   1.17123   0.86822  -0.24867        1.52088    86.79    -0.97  1  2  3
 5( 1)   0.11130  -1.46466   0.13918        1.52088    30.16  -174.68  2  1  3
 6( 4)  -0.10660   1.37224   0.40416        1.50884   112.16   -30.32  3  2  1
 7(11)   2.05282   1.42343   0.16561        1.12120   109.24   153.19  4  1  2
 8(18)  -2.24249   1.09141   0.19563        1.12120   109.06  -152.27  3  2  1
 9(13)  -0.18732   2.48256   0.27092        1.12120   110.05  -177.85  6  3  2
10(16)  -1.87040  -1.06846   0.86716        1.12120   124.06  -110.03  2  1  3
11( 9)   1.99528  -0.75875   0.89478        1.12120   123.58   108.76  1  2  3
12( 7)   0.17884  -2.32351  -0.57838        1.12120   107.74  -123.46  5  2  1
13(10)   1.96624  -1.02863  -0.88119        1.12120   120.12  -110.08  1  2  3
14(15)  -1.76911  -1.29755  -0.91135        1.12120   119.52   109.12  2  1  3
15( 8)   0.14057  -1.91579   1.16520        1.12120   107.44   122.71  5  2  1
16(17)  -1.29939   0.91985  -1.33160        1.12120   109.47    90.91  3  2  1
17(12)   1.12866   1.08274  -1.34833        1.12120   109.71   -89.43  4  1  2
18(14)  -0.08223   1.15988   1.50479        1.12120   110.29   -59.04  6  3  2
ELAPSED TIME IN QUENCHING   2973.07 SECONDS
CALLS TO CRITERION IN QUENCHING: 2543
AM1 NOXY NOINT GNORM=0.1 T=50000 ANNE
   CYCLOHEXANE
   ANNEALING TEST


    SCF FIELD WAS ACHIEVED

                              AM1    CALCULATION                                Note 12
                                                        VERSION  5.00

         FINAL HEAT OF FORMATION =   -38.461532 KCAL
         ELECTRONIC ENERGY       = -4336.114556 EV
         CORE-CORE REPULSION     =  3401.221024 EV
         GRADIENT NORM           =     0.120150
         IONISATION POTENTIAL    =    10.953938 EV
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         NO. OF FILLED LEVELS    =    18
         MOLECULAR WEIGHT        =    84.161
         SCF CALCULATIONS        = 3500
         COMPUTATION TIME=      5288.56 SECONDS
                                                    9-MAY-94
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                    NA:I          NB:NA:I      NC:NB:NA:I  NA NB NC
     1     C
     2     C          1.52088                                    1
     3     C          1.52088        111.13522 *                 2  1
     4     C          1.52088        111.15039 *    55.48080 *   3  2  1
     5     C          1.52088        111.12779 *   -55.50738 *   1  2  3
     6     C          1.52088        111.14666 *    55.50487 *   5  1  2
     7     H          1.12120        109.41910 *    65.44395 *   1  2  3
     8     H          1.12120        109.54861 *  -176.69737 *   1  2  3
     9     H          1.12120        109.41824 *  -120.94161 *   2  3  1
    10     H          1.12120        109.55276 *   121.19812 *   2  3  1
    11     H          1.12120        109.54366 *   176.68436 *   3  2  1
    12     H          1.12120        109.41637 *   -65.46903 *   3  2  1
    13     H          1.12120        109.44660 *  -176.93228 *   4  3  2
    14     H          1.12120        109.30831 *    65.47970 *   4  3  2
    15     H          1.12120         93.03932 *   109.41128 *   5  4  3
    16     H          1.12120        143.75565 *  -124.62642 *   5  4  3
    17     H          1.12120        109.31218 *   121.08311 *   6  5  4
    18     H          1.12120        109.44973 *  -121.31799 *   6  5  4

                  EIGENVALUES
-38.74134 -31.46176 -31.41973 -23.23082 -23.21259 -20.00688 -16.47263 -15.03268
-14.89882 -14.87722 -13.50952 -13.06790 -13.02597 -11.85911 -11.85082 -11.07315
-10.99134 -10.95394   3.70337   3.89036   3.91230   4.28174   4.29289   4.51385
  4.58951   4.62173   4.66679   4.85487   5.00223   5.00927   5.10742   5.12900
  5.36536   5.41564   5.42775   5.49575

         NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS
        ATOM NO.   TYPE          CHARGE        ATOM  ELECTRON DENSITY
          1         C           -0.1551          4.1551
          2         C           -0.1551          4.1551
          3         C           -0.1552          4.1552
          4         C           -0.1547          4.1547
          5         C           -0.1552          4.1552
          6         C           -0.1547          4.1547
          7         H            0.0782          0.9218
          8         H            0.0769          0.9231
          9         H            0.0782          0.9218
         10         H            0.0769          0.9231
         11         H            0.0769          0.9231
         12         H            0.0782          0.9218
         13         H            0.0767          0.9233
         14         H            0.0781          0.9219
         15         H            0.0782          0.9218
         16         H            0.0769          0.9231
         17         H            0.0781          0.9219
         18         H            0.0767          0.9233
DIPOLE (DEBYE)   X         Y         Z       TOTAL
POINT-CHG.     0.000     0.001     0.001     0.001
HYBRID         0.000     0.000     0.000     0.000
SUM            0.000     0.001     0.000     0.001

         ATOMIC ORBITAL ELECTRON POPULATIONS
  1.21962   0.95354   0.99714   0.98483   1.21962   0.95354   0.96514   1.01682
  1.21965   0.99593   0.95474   0.98486   1.21827   0.95377   0.99752   0.98518
  1.21965   0.99594   0.95475   0.98481   1.21827   0.95377   0.96548   1.01721
  0.92176   0.92313   0.92178   0.92313   0.92313   0.92182   0.92325   0.92189
  0.92181   0.92315   0.92185   0.92325
FULL COMPUTATION TIME :  5288.600 SECONDS
```

Note 1: This section lists the dedicated annealing keywords found by the program.

Note 2: Information on the methods and criteria that annealing will use is listed in this section of the output.

Note 3: This section lists the active penalty functions defined by the annealing keywords.

Note 4: The lower bounds, beginning values, and upper bounds for the optimizable parameters are summarized in this table. The user should carefully examine this table to ensure that the proper limits have been defined.

Note 5: The located bonded atoms are noted in this table. This has implications for the penalty functions such as PEN2 used in annealing.

Note 6: These are the coordinates at the end of the annealing configuration search.

Note 7: This table describes the presorted configurations and eliminates identical members from consideration. In this case, out of the 60 candidates generated only one was filtered out, leaving 59 quenching steps. This low level of filtering was required by use of the FILTER=1.0 keyword (default=1.4). This approach minimizes the chance of missing a minima, but drastically increases the amount of time required in the quenching process.

Note 8: These are the ordered initial energies of the 59 selected configurations for quenching.

Note 9: This section describes the quenching of each state. If after some quenching, the configuration is determined to be equivalent to a previously located one, the optimization is halted and the configuration discarded. Some of these have been omitted to conserve space. A full listing of the file is in the directory section of the test suite.

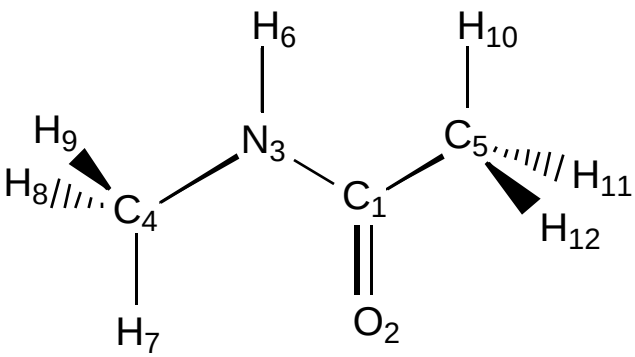
Note 10: This section begins the listing of the selected configurations, four of which were located.

Note 11: A more detailed description of each quenched geometry is listed.

Note 12: The lowest energy state is selected and a full set of results is presented at the end of the output file. In this case it is the chair form of cyclohexane.

9.5 Example II ("Rigid" System)

The following molecule (methyl-N-methyl-amide) has been selected for illustration of the annealing procedure in the case of a relatively rigid system:



As mentioned in section 9.3, the general strategy to use is to divide the conformational search problem into primary and secondary degrees of freedom. Then a connectivity may be defined which allows an explicit description of the primary degrees of freedom. In this case, three primary degrees of freedom may be identified as the rotation about bonds C_1–N_3^A, C_4–N_3^B, *and* C_5–C_1^C. *The following is a viable (but not necessarily unique) connectivity pattern for this system that produces explicit descriptions of the primary degrees of freedom. (Note that the superscripts A, B, and C above identify below which of the dihedrals are used to specify the rotations.)*

```
C      0.000000  0    0.000000  0    0.000000  0    0    0    0
O      1.243077  1    0.000000  0    0.000000  0    1    0    0
N      1.366966  1  121.946787  1    0.000000  0    1    2    0
C      1.520000  1  120.615770  1   -0.000067A 1    3    1    2
C      1.540000  1  123.093733  1 -179.998834  1    1    2    3
H      0.986177  1  121.170189  1  179.991444  1    3    1    4
H      1.004440  1  108.958790  1    0.000000B 1    4    3    1
H      1.004440  1  108.958790  1  120.000000  1    4    3    7
H      1.000000  1  109.885165  1 -120.000000  1    4    3    7
H      1.004440  1  108.958790  1  180.000000C 1    5    1    2
H      1.004440  1  108.958790  1  120.000000  1    5    1   10
H      1.000000  1  109.885165  1 -120.000000  1    5    1   10
```

As mentioned is Section 2.3, this modular designation of the hydrogen atoms of a methyl group allows easy manipulation of the orientation of the entire group by altering one dihedral angle. In this example, the master degrees of freedom are defined by the dihedrals of particular atoms: the dihedral on H_7 *for the* C_4 *methyl (*C_4–N_3 *rotation), the dihedral on* H_{10} *for the* C_5 *methyl (*C_5–C_1 *rotation), and the dihedral on* C_5 *for the* C_1–N_3 *rotation. The LIMIT keyword can now be used to define boundaries for the search of conformational space. The secondary variables are not important to the annealing procedure and should be limited to about ±10% of their original value. (Note that all annealing boundary conditions are ignored during the local quenching of the located minima.) The definition of the problem in these terms requires some chemical knowledge and intuition, but saves enormous computational effort. The final input and results files for the problem is listed below.*

Input File (TEST45.DAT) :

```
AM1 GNORM=0.1 PRECISE T=3500 NOINT NOXYZ +                    Note 1
```

```
ANNE LIMIT FILTER=1.2                                                          Note 2
METHYL-N-METHYL-AMIDE
ANNEALING, RIGID SYSTEM
C             0.000000  0    0.000000  0    0.000000  0    0    0    0
O             1.243077  1    0.000000  0    0.000000  0    1    0    0
N             1.366966  1  121.946787  1    0.000000  0    1    2    0
C             1.520000  1  120.615770  1   -0.000067  1    3    1    2          Note 3
C             1.540000  1  123.093733  1 -179.998834  1    1    2    3
H             0.986177  1  121.170189  1  179.991444  1    3    1    4
H             1.004440  1  108.958790  1  -60.000000  1    4    3    1          Note 3
H             1.004440  1  108.958790  1  120.000000  1    4    3    7
H             1.000000  1  109.885165  1 -120.000000  1    4    3    7
H             1.004440  1  108.958790  1  120.000000  1    5    1    2          Note 3
H             1.004440  1  108.958790  1  120.000000  1    5    1   10
H             1.000000  1  109.885165  1 -120.000000  1    5    1   10
0             0.000000  0    0.000000  0    0.000000  0    0    0    0
1.2   1.3 110   1.5 110 -180   1.5 100 -190   0.9 100 160   0.9 100 -180         Note 4
0.9 100  100    0.9 100 -140   0.9 100 -180   0.9 100 100   0.9 100 -140
1.3   1.4 130   1.6 130  180   1.6 140 -170   1.1 130 200   1.1 130  180         Note 5
1.1 130  140    1.1 130 -100   1.1 130  180   1.1 130 140   1.1 130 -100
```

Note 1: The keyword ANNE activates energy-based annealing. Note that the specific annealing keywords are segregated on one line. While this is certainly not required, it simplifies interpretation of the files.

Note 2: LIMIT is used to restrict the range the over which the geometry can vary. The FILTER keyword tightens the criteria (default =1.2) for elimination of a candidate geometry as already located. For situations such as distinguishing between methyl rotations this value should probably be raised to 1.4.

Note 3: The dihedrals on these lines comprise the three primary degrees of freedom.

Note 4: These are the lower limits each geometric parameter can assume. Note that most are very close to their initial values but items # 6, 15, and 24 have a lower limit of -180.00°.

Note 5: These are the upper limits each geometric parameter can assume. As before, most are very close to their initial values but items # 6, 15, and 24 now have an upper limit of 180.00°. The range -180° to +180° represent a full circle rotation about the required bonds.

Archive File (TEST45.ARC) :

```
SUMMARY OF   AM1   CALCULATION
                                        06-Mar-93
     AMPAC Version 5.0
        Presented by:

   Semichem, Inc.
   7128 Summit
   Shawnee, KS  66216
   (913) 268-3271
   (913) 268-3445 (fax)


C 3 H 7 N   O
 METHYL-N-METHYL-AMIDE
```

```
 ANNEALING, RIGID SYSTEM

    GRADIENT (COMPONENT) TEST WAS SATISFIED IN BFGS OR DFP
    SCF FIELD WAS ACHIEVED

         HEAT OF FORMATION       =     -47.270462 KCAL
         ELECTRONIC ENERGY       =   -3381.295462 EV
         CORE-CORE REPULSION     =    2372.993225 EV
         GRADIENT NORM           =       0.104198
         DIPOLE                  =       3.671274 DEBYE
         NO. OF FILLED LEVELS    =      15
         IONISATION POTENTIAL    =       9.967297 EV
         MOLECULAR WEIGHT        =      73.094
         COMPUTATION TIME        =     562.44 SECONDS

         FINAL GEOMETRY OBTAINED                                CHARGE
AM1 GNORM=0.1 PRECISE T=3500 NOINT NOXYZ ANNE LIMIT FILTER=1.2
 METHYL-N-METHYL-AMIDE
 ANNEALING, RIGID SYSTEM
 C     0.000000  0    0.000000  0    0.000000  0    0   0   0    0.2991
 O     1.247319  1    0.000000  0    0.000000  0    1   0   0   -0.3725
 N     1.381379  1  121.216881  1    0.000000  0    1   2   0   -0.3917
 C     1.426628  1  123.079250  1   -1.889177  1    3   1   2   -0.0690
 C     1.509707  1  121.528052  1  179.633990  1    1   2   3   -0.2367
 H     0.990147  1  119.024321  1 -176.078147  1    3   1   4    0.2334
 H     1.123257  1  110.106564  1    6.822027  1    4   3   1    0.0618
 H     1.123739  1  109.908609  1  120.134501  1    4   3   7    0.0763
 H     1.124167  1  110.445524  1 -120.189049  1    4   3   7    0.0856
 H     1.116468  1  110.384536  1  117.304525  1    5   1   2    0.1159
 H     1.116326  1  110.677867  1  120.954590  1    5   1  10    0.1015
 H     1.117332  1  108.683270  1 -119.426903  1    5   1  10    0.0962
 0     0.000000  0    0.000000  0    0.000000  0    0   0   0
```

Note 1

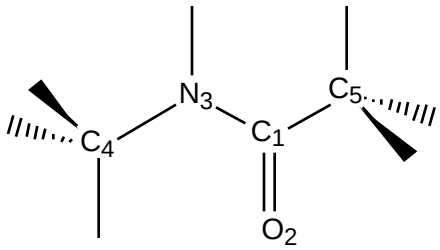
```
                    SUMMARY OF   AM1   CALCULATION
                                                  06-Mar-93
                         AMPAC Version 5.0
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)


C 3 H 7 N   O
 METHYL-N-METHYL-AMIDE
 ANNEALING, RIGID SYSTEM

    GRADIENT (COMPONENT) TEST WAS SATISFIED IN BFGS OR DFP
    SCF FIELD WAS ACHIEVED

         HEAT OF FORMATION       =     -47.128784 KCAL
         ELECTRONIC ENERGY       =   -3381.295462 EV
         CORE-CORE REPULSION     =    2372.993225 EV
         GRADIENT NORM           =       0.020873
         DIPOLE                  =       3.907491 DEBYE
         NO. OF FILLED LEVELS    =      15
         IONISATION POTENTIAL    =       9.967297 EV
         MOLECULAR WEIGHT        =      73.094
         COMPUTATION TIME        =     562.47 SECONDS

         FINAL GEOMETRY OBTAINED                                CHARGE
AM1 GNORM=0.1 PRECISE T=3500 NOINT NOXYZ ANNE LIMIT FILTER=1.2
 METHYL-N-METHYL-AMIDE
 ANNEALING, RIGID SYSTEM
 C     0.000000  0    0.000000  0    0.000000  0    0   0   0    0.2991
 O     1.247950  1    0.000000  0    0.000000  0    1   0   0   -0.3725
 N     1.382482  1  118.894980  1    0.000000  0    1   2   0   -0.3917
 C     1.424030  1  123.390181  1  174.686310  1    3   1   2   -0.0690
 C     1.505910  1  121.879204  1 -178.853431  1    1   2   3   -0.2367
```

Note 2

```
 H     0.993655  1  117.631354  1 -170.520754  1    3   1   4    0.2334
 H     1.123759  1  110.502783  1   48.298442  1    4   3   1    0.0618
 H     1.122174  1  109.499994  1  119.706182  1    4   3   7    0.0763
 H     1.125281  1  111.378768  1 -120.217975  1    4   3   7    0.0856
 H     1.116585  1  110.807507  1 -126.864144  1    5   1   2    0.1159
 H     1.117211  1  108.781662  1  120.061436  1    5   1  10    0.1015
 H     1.117078  1  110.016746  1 -120.612082  1    5   1  10    0.0962
 0     0.000000  0    0.000000  0    0.000000  0    0   0   0

                    SUMMARY OF   AM1   CALCULATION
                                                        06-Mar-93
                         AMPAC Version 5.0
                            Presented by:

                       Semichem, Inc.
                       7128 Summit
                       Shawnee, KS  66216
                       (913) 268-3271
                       (913) 268-3445 (fax)


C 3 H 7 N   O
 METHYL-N-METHYL-AMIDE
 ANNEALING, RIGID SYSTEM


    SCF FIELD WAS ACHIEVED

         HEAT OF FORMATION       =     -47.270461 KCAL
         ELECTRONIC ENERGY       =   -3372.708738 EV
         CORE-CORE REPULSION     =    2364.400358 EV
         GRADIENT NORM           =       0.322214
         DIPOLE                  =       3.512276 DEBYE
         NO. OF FILLED LEVELS    =      15
         IONISATION POTENTIAL    =       9.919666 EV
         MOLECULAR WEIGHT        =      73.094
         COMPUTATION TIME        =     563.43 SECONDS

         FINAL GEOMETRY OBTAINED                                CHARGE
AM1 GNORM=0.1 PRECISE T=3500 NOINT NOXYZ ANNE LIMIT FILTER=1.2
 METHYL-N-METHYL-AMIDE
 ANNEALING, RIGID SYSTEM
 C     0.000000  0    0.000000  0    0.000000  0    0   0   0    0.3002
 O     1.247319  1    0.000000  0    0.000000  0    1   0   0   -0.3705
 N     1.381379  1  121.216881  1    0.000000  0    1   2   0   -0.3917
 C     1.426628  1  123.079250  1   -1.889177  1    3   1   2   -0.0753
 C     1.509707  1  121.528052  1  179.633990  1    1   2   3   -0.2429
 H     0.990147  1  119.024321  1 -176.078147  1    3   1   4    0.2202
 H     1.123257  1  110.106564  1    6.822027  1    4   3   1    0.1178
 H     1.123739  1  109.908609  1  120.134501  1    4   3   7    0.0668
 H     1.124167  1  110.445524  1 -120.189049  1    4   3   7    0.0629
 H     1.116468  1  110.384536  1  117.304525  1    5   1   2    0.0976
 H     1.116326  1  110.677867  1  120.954590  1    5   1  10    0.0973
 H     1.117332  1  108.683270  1 -119.426903  1    5   1  10    0.1176
 0     0.000000  0    0.000000  0    0.000000  0    0   0   0
```

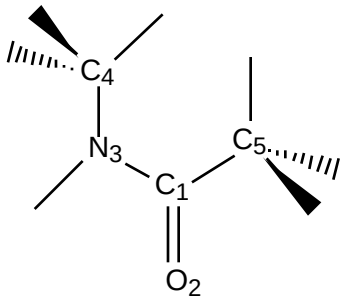
Note 3

Note 1: This is the data relating to the first minima located by annealing, and is a refined version of the input structure:



This structure happens to be the global minima on the PES and is referred to as the "trans-minima".

Note 2: This is the data relating to the second minima located by annealing. It is referred to as the "cis-minima".



Note 3: This data is a repeat of the most stable minima located, in this case the first or trans-minima.

Output File (TEST45.OUT):

```
*******************************************************************************
                              AM1 CALCULATION RESULTS
*******************************************************************************
*                               AMPAC Version 5.0
*                                  Presented by:
*
*                             Semichem, Inc.
*                             7128 Summit
*                             Shawnee, KS  66216
*                             (913) 268-3271
*                             (913) 268-3445 (fax)
*
*                   WARNING: YOUR LICENSE EXPIRES IN 19 DAYS!!
*
*  ANNE     - ANNEALING METHOD ON ENERGY TO BE USED
*  GNORM=   - OPTIMIZATION EXIT WHEN GRADIENT NORM BELOW    0.100
*  PRECISE  - OPTIMIZATION CRITERIA TO BE INCREASED BY 10 TIMES,
*           -     S.C.F.   CRITERIA BY 100 TIMES,
*           - AND USE ACCURATE FINITE DIFFERENCE FORMULA  IN HESSIAN
*  NOINTER  - INTERATOMIC DISTANCES NOT TO BE PRINTED
*  NOXYZ    - CARTESIAN COORDINATES NOT TO BE PRINTED
*   T=      - A TIME OF  3500.0 SECONDS REQUESTED
*  AM1      - THE AM1 HAMILTONIAN TO BE USED
*******************************************************************************
AM1 GNORM=0.1 PRECISE T=3500 NOINT NOXYZ ANNE LIMIT FILTER=1.2
 METHYL-N-METHYL-AMIDE
```

```
 ANNEALING, RIGID SYSTEM
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I   NA  NB  NC
     1     C
     2     O          1.24308 *                                   1
     3     N          1.36697 *      121.94679 *                  1   2
     4     C          1.52000 *      120.61577 *    -0.00007 *    3   1   2
     5     C          1.54000 *      123.09373 *  -179.99883 *    1   2   3
     6     H          0.98618 *      121.17019 *   179.99144 *    3   1   4
     7     H          1.00444 *      108.95879 *   -60.00000 *    4   3   1
     8     H          1.00444 *      108.95879 *   120.00000 *    4   3   7
     9     H          1.00000 *      109.88517 *  -120.00000 *    4   3   7
    10     H          1.00444 *      108.95879 *   120.00000 *    5   1   2
    11     H          1.00444 *      108.95879 *   120.00000 *    5   1  10
    12     H          1.00000 *      109.88517 *  -120.00000 *    5   1  10
         SINGLET STATE CALCULATION
         RHF CALCULATION, No. OF DOUBLY OCCUPIED LEVELS = 15

       **  REFERENCES TO PARAMETERS  **

 H  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
 C  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
 N  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)
 O  (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985)


*****************************************************************************
*  KEYWORDS OF THE ANNEALING SECTION
*
*  LIMIT    - USE PERIODIC CONDITIONS ON VARIABLES
*  FILTER=  - SET THRESHOLD OF DISTINGUISHED CONFIGURATION TO 1.200
*****************************************************************************

SIMULATED ANNEALING BY METROPOLIS SCHEME IN   30 VARIABLES
     VERSION 1  (JULY 1991)
    THERMALIZATION THRESHOLD ON CRITERION          0.080
    MAXIMUM STEP SIZE                            2.00000
    CONVERGENCE CRITERION ON STEP SIZE           0.08944

MAXIMUM NUMBER OF CALL AT EACH TEMPERATURE        1000
    FIRST TEMPERATURE (HOT) SET TO                 50.00
    TEMPERATURE EXPONENTIAL DECAY                   0.80
    LAST TEMPERATURE (COLD) SET TO                  0.50
RANDOM SEQUENCE INITIATOR                       -9876543
    MARKOV CHAIN STUDIED BY PIECES OF                 30
    No OF TEMPERATURES TO DETECT A FROZEN SYSTEM       3
EQUIVALENCE THRESHOLD IN CLUSTERING ANALYSIS        1.20
    BAND-PASS FILTER NO 1 CENTERED AT               2.30 ANGSTROMS
    HALF BAND-WIDTH                                13.50 %
PERIODIC BOUNDARY CONDITIONS (ANGSTROMS, DEGREES)
LOWER BOUND    1.2000    1.3000  110.0000    1.5000  110.0000 -180.0000
               1.5000  100.0000 -190.0000    0.9000  100.0000  160.0000
               0.9000  100.0000 -180.0000    0.9000  100.0000  100.0000
               0.9000  100.0000 -140.0000    0.9000  100.0000 -180.0000
               0.9000  100.0000  100.0000    0.9000  100.0000 -140.0000
TRIAL COORD    1.2431    1.3670  121.9468    1.5200  120.6158   -0.0001
               1.5400  123.0937 -179.9988    0.9862  121.1702  179.9914
               1.0044  108.9588  -60.0000    1.0044  108.9588  120.0000
               1.0000  109.8852 -120.0000    1.0044  108.9588  120.0000
               1.0044  108.9588  120.0000    1.0000  109.8852 -120.0000
UPPER BOUND    1.3000    1.4000  130.0000    1.6000  130.0000  180.0000
               1.6000  140.0000 -170.0000    1.1000  130.0000  200.0000
               1.1000  130.0000  180.0000    1.1000  130.0000  140.0000
               1.1000  130.0000 -100.0000    1.1000  130.0000  180.0000
               1.1000  130.0000  140.0000    1.1000  130.0000 -100.0000
USE 2-POINT FORMULA IN INTEGRAL DERIVATIVES WITH STEP  0.00002000
STANDARD DEVIATION ON ENERGY   (KCAL)        0.000001494
STANDARD DEVIATION ON GRADIENT (KCAL/A,RD,RD)  0.0000497 0.0001079 0.0000667

CRITERION IS ENERGY (KCAL/MOLE)
```

Note 1

```
SIMULATED ANNEALING SECTION
---------------------------

* * * SYSTEM LOOKS FROZEN AT TEMPERATURE   13.1072 KCAL
NORMAL END AFTER  1006 CALLS TO CRITERION
LAST CONFORMATION GENERATED IN ANNEALING:
         HEAT OF FORMATION       =    66.516811 KCAL
CURRENT COORDINATES (ANGSTROMS, DEGREES)
   1.2188    1.3293  114.4778    1.5500  118.2967   55.8230    1.5757  116.8484
-187.2265    0.9592  111.6816  167.0184    0.9648  102.2175   94.9139    1.0814
 114.6948  102.9156    1.0716  100.9768 -126.3852    1.0321  125.0580  144.3631
   0.9304  108.9727  119.5472    0.9003  119.7909 -139.7948
ELAPSED TIME IN ANNEALING    453.77 SECONDS
TABLE OF NEARLY IDENTICAL CONFIGURATIONS AT THRESHOLD =  1.20 A
CRITERION  ,CONFIGURATIONS    (A "*" MEANS IDENTICAL)
             2 4 6 8 0 2 4 6 8 0 2 4 6 8                                        Note 2
 -4.1274   1*
  2.7782   2.*
  4.7276   3.**
  5.5361   4..**
  7.4967   5.****
 10.9376   6.*****
 12.0619   7*.....*
 12.2925   8*.*....*
 12.7461   9******..*
 15.3811  10.*.**..***
 16.5111  11..........*
 16.6978  12.*****...*.*
 17.5031  13............*
 17.5708  14.............*
 18.5427  15..............*
 19.3623  16.****..***.*...*
 23.7621  17................*
 24.0258  18..........*......*
 24.0401  19.*.***...*.*...*..*
 24.8657  20.*****..**.*...*..**
 25.2134  21**...**......*....***
 25.3259  22..****..*..*.......*.*
 26.3481  23.................*....*
 26.4419  24..........*...*.......**
 26.8325  25*.****.***.....*...*....*
 28.6571  26..............*..........*
 30.7957  27.......*.....*............*
 36.3078  28*.****..*......*...*.*..*..*
 66.5168  29.*.**..**..*......*.......***

NUMBER OF SELECTED CONFIGURATION  7                                            Note 3
CRITERIA:   -4.1274    2.7782   16.5111   17.5031   17.5708   18.5427   23.7621


QUENCHING OF REMAINING POINTS AFTER CLUSTERING ANALYSIS
-------------------------------------------------------
DONE WITHOUT PERIODIC BOUNDARIES                                               Note 4
MINIMIZE ENERGY USING BFGS ALGORITHM                                           Note 5


RESULTS OF QUENCHING No  1
..........................
         HEAT OF FORMATION       =   -46.811195 KCAL                           Note 6
CURRENT COORDINATES (ANGSTROMS, DEGREES)
   1.2471    1.3812  120.7162    1.4279  121.7107   -0.2405    1.5088  121.7646
-180.0300    0.9889  119.4871  180.6395    1.1240  110.3478  -61.0596    1.1239
 110.2519  118.9434    1.1206  109.6701 -120.5636    1.1164  110.5649  119.7728
   1.1165  110.5338  120.9236    1.1172  108.6915 -119.5522

RESULTS OF QUENCHING No  2
..........................
         HEAT OF FORMATION       =   -47.270462 KCAL                           Note 7
CURRENT COORDINATES (ANGSTROMS, DEGREES)
```

```
   1.2473    1.3814  121.2169    1.4266  123.0793   -1.8892    1.5097  121.5281
-180.3660    0.9901  119.0243  183.9219    1.1233  110.1066    6.8220    1.1237
 109.9086  120.1345    1.1242  110.4455 -120.1890    1.1165  110.3845  117.3045
   1.1163  110.6779  120.9546    1.1173  108.6833 -119.4269

RESULTS OF QUENCHING No  3
.........................
         HEAT OF FORMATION       =   -47.128784 KCAL
CURRENT COORDINATES (ANGSTROMS, DEGREES)
   1.2479    1.3825  118.8950    1.4240  123.3902 -185.3137    1.5059  121.8792
-178.8534    0.9937  117.6314  189.4792    1.1238  110.5028   48.2984    1.1222
 109.5000  119.7062    1.1253  111.3788 -120.2180    1.1166  110.8075 -126.8641
   1.1172  108.7817  120.0614    1.1171  110.0167 -120.6121

RESULTS OF QUENCHING No  4
.........................
         * * * QUENCHING INTERRUPTED: POINT PREVIOUSLY FOUND.

RESULTS OF QUENCHING No  5
.........................
         * * * QUENCHING INTERRUPTED: POINT PREVIOUSLY FOUND.

RESULTS OF QUENCHING No  6
.........................
         * * * CRITERION =   -47.128782 POINT PREVIOUSLY FOUND.
TABLE OF NEARLY IDENTICAL CONFIGURATIONS AT THRESHOLD =  1.32 A
CRITERION  ,CONFIGURATIONS    (A "*" MEANS IDENTICAL)
             2
-47.2705   1*
-47.1288   2.*
-46.8112   3*.*

NUMBER OF SELECTED CONFIGURATION  2
CRITERIA:  -47.2705  -47.1288

DETAILS ON NON EQUIVALENT STATIONARY POINTS FOUND
-------------------------------------------------

STATIONARY POINT No  1
......................
         HEAT OF FORMATION       =   -47.270462 KCAL
         RMS GRADIENT NORM       =     0.058934 KCAL/ANGSTROMS
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I   NA  NB  NC
     1     C
     2     O          1.24732 *                                   1
     3     N          1.38138 *      121.21688 *                  1   2
     4     C          1.42663 *      123.07925 *    -1.88918 *    3   1   2
     5     C          1.50971 *      121.52805 *  -180.36601 *    1   2   3
     6     H          0.99015 *      119.02432 *   183.92185 *    3   1   4
     7     H          1.12326 *      110.10656 *     6.82203 *    4   3   1
     8     H          1.12374 *      109.90861 *   120.13450 *    4   3   7
     9     H          1.12417 *      110.44552 *  -120.18905 *    4   3   7
    10     H          1.11647 *      110.38454 *   117.30453 *    5   1   2
    11     H          1.11633 *      110.67787 *   120.95459 *    5   1  10
    12     H          1.11733 *      108.68327 *  -119.42690 *    5   1  10

    ORDERED CARTESIAN (INERTIA FRAME)  AND  INTERNAL COORDS (A, DEGREES)
   NO.    X         Y         Z              BOND     ANGLE   DIHEDRAL A  B  C
 1( 2)   0.45306   1.33007  -0.00179
 2( 3)  -0.67950  -0.66170  -0.01529        2.29129                    1
 3( 4)  -1.97984  -0.07535   0.00861        1.42663    95.35           2  1
 4( 5)   1.78968  -0.67437   0.00593        2.40923    63.32   178.63  1  2  3
 5( 1)   0.48379   0.08313  -0.00142        1.24732    31.04   178.41  1  2  3
 6(12)   2.63022   0.06097  -0.02873        1.11733    82.51   177.76  4  1  2
 7( 8)  -2.59484  -0.47346  -0.84349        1.12374   109.91   126.07  3  2  1
 8( 9)  -2.50394  -0.32148   0.97219        1.12417   110.45  -114.25  3  2  1
 9(11)   1.85989  -1.34757  -0.88179        1.11633   122.28    70.03  4  1  2
10(10)   1.88004  -1.28462   0.93649        1.11647   120.15   -74.64  4  1  2
11( 7)  -1.90176   1.04118  -0.08618        1.12326   110.11     5.94  3  2  1
```

Note 8

Note 9

```
12( 6)  -0.61791  -1.64943   0.01615        0.99015   146.74  -175.17  2  1  3

STATIONARY POINT No  2
.....................
         HEAT OF FORMATION       =   -47.128784 KCAL
         RMS GRADIENT NORM       =     0.026377 KCAL/ANGSTROMS
   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I   NA  NB  NC
     1     C
     2     O          1.24795 *                                   1
     3     N          1.38248 *      118.89498 *                  1   2
     4     C          1.42403 *      123.39018 *  -185.31369 *    3   1   2
     5     C          1.50591 *      121.87920 *  -178.85343 *    1   2   3
     6     H          0.99365 *      117.63135 *   189.47925 *    3   1   4
     7     H          1.12376 *      110.50278 *    48.29844 *    4   3   1
     8     H          1.12217 *      109.49999 *   119.70618 *    4   3   7
     9     H          1.12528 *      111.37877 *  -120.21797 *    4   3   7
    10     H          1.11658 *      110.80751 *  -126.86414 *    5   1   2
    11     H          1.11721 *      108.78166 *   120.06144 *    5   1  10
    12     H          1.11708 *      110.01675 *  -120.61208 *    5   1  10

    ORDERED CARTESIAN (INERTIA FRAME)  AND  INTERNAL COORDS (A, DEGREES)
   NO.    X         Y         Z              BOND     ANGLE   DIHEDRAL A  B  C
 1( 2)  -1.55526  -0.77990  -0.02254
 2( 3)   0.70703  -0.66653   0.04934        2.26626                     1
 3( 4)   1.93301   0.05364  -0.02927        1.42403   152.00            2  1
 4( 5)  -0.62113   1.44195   0.00833        2.41043    64.32   -10.16  1  2  3
 5( 1)  -0.53514  -0.06149   0.00239        1.24795    32.28    -9.48  1  2  3
 6( 8)   2.78366  -0.62343   0.24865        1.12217   109.50   173.46  3  2  1
 7(11)  -1.68740   1.74183  -0.13763        1.11721    82.87   174.19  4  1  2
 8( 9)   2.11241   0.44589  -1.06860        1.12528   111.38   -66.46  3  2  1
 9(12)  -0.26182   1.84163   0.98762        1.11708   117.75   -78.06  4  1  2
10( 7)   1.92226   0.92736   0.67737        1.12376   110.50    53.76  3  2  1
11(10)  -0.00140   1.87794  -0.81179        1.11658   124.44    65.76  4  1  2
12( 6)   0.73879  -1.65832  -0.00248        0.99365    88.87  -166.83  2  1  3
ELAPSED TIME IN QUENCHING    108.58 SECONDS
CALLS TO CRITERION IN QUENCHING:  175
AM1 GNORM=0.1 PRECISE T=3500 NOINT NOXYZ ANNE LIMIT FILTER=1.2
 METHYL-N-METHYL-AMIDE
 ANNEALING, RIGID SYSTEM


    SCF FIELD WAS ACHIEVED

                              AM1    CALCULATION
                                                          VERSION 5.0

                                                     06-Mar-93

         FINAL HEAT OF FORMATION =     -47.270461 KCAL
         ELECTRONIC ENERGY       =   -3372.708738 EV
         CORE-CORE REPULSION     =    2364.400358 EV
         GRADIENT NORM           =       0.322214
         IONISATION POTENTIAL    =       9.919666 EV
         NO. OF FILLED LEVELS    =      15
         MOLECULAR WEIGHT        =      73.094
         SCF CALCULATIONS        =    1182
         COMPUTATION TIME        =     563.41 SECONDS

   ATOM    CHEMICAL   BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   SYMBOL     (ANGSTROMS)     (DEGREES)     (DEGREES)
   (I)                   NA:I          NB:NA:I      NC:NB:NA:I   NA  NB  NC
     1     C
     2     O          1.24732 *                                   1
     3     N          1.38138 *      121.21688 *                  1   2
     4     C          1.42663 *      123.07925 *    -1.88918 *    3   1   2
     5     C          1.50971 *      121.52805 *  -180.36601 *    1   2   3
     6     H          0.99015 *      119.02432 *   183.92185 *    3   1   4
     7     H          1.12326 *      110.10656 *     6.82203 *    4   3   1
     8     H          1.12374 *      109.90861 *   120.13450 *    4   3   7
```

Note 10

```
     9     H          1.12417 *      110.44552 *  -120.18905 *    4   3   7
    10     H          1.11647 *      110.38454 *   117.30453 *    5   1   2
    11     H          1.11633 *      110.67787 *   120.95459 *    5   1  10
    12     H          1.11733 *      108.68327 *  -119.42690 *    5   1  10

                 EIGENVALUES
-39.45404 -35.30080 -31.04639 -26.47663 -21.39548 -17.84156 -16.95942 -16.02728
-14.48195 -14.32135 -13.60292 -12.85761 -12.84133 -10.79838  -9.91967   1.47533
  2.22084   3.64127   3.94952   4.04499   4.19134   4.31369   4.50258   4.66526
  5.45627   6.27159   7.15117

         NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS
        ATOM NO.   TYPE          CHARGE        ATOM  ELECTRON DENSITY
          1         C           0.3002          3.6998
          2         O          -0.3705          6.3705
          3         N          -0.3917          5.3917
          4         C          -0.0753          4.0753
          5         C          -0.2429          4.2429
          6         H           0.2202          0.7798
          7         H           0.1178          0.8822
          8         H           0.0668          0.9332
          9         H           0.0629          0.9371
         10         H           0.0976          0.9024
         11         H           0.0973          0.9027
         12         H           0.1176          0.8824
DIPOLE (DEBYE)   X         Y         Z       TOTAL
POINT-CHG.    -2.782     0.353     0.025     2.805
HYBRID        -0.702     0.092     0.062     0.711
SUM           -3.484     0.444     0.087     3.512

         ATOMIC ORBITAL ELECTRON POPULATIONS
  1.22279   0.88645   0.84224   0.74836   1.91674   1.09968   1.87911   1.47494
  1.45975   1.09563   1.06084   1.77547   1.22341   1.01518   0.83832   0.99840
  1.23018   1.01720   0.96554   1.02997   0.77979   0.88222   0.93315   0.93714
  0.90243   0.90270   0.88237
FULL COMPUTATION TIME :   563.440 SECONDS
```

Note 1: These are the upper and lower boundaries along with the initial values for each coordinate.

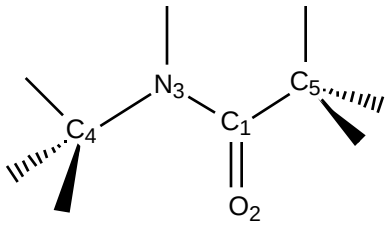
Note 2: This table lists which configurations it has identified as identical and eliminated.

Note 3: This line lists the energies of the selected configurations as this is an ANNE search rather than a MANN search, in which case the gradient norms would have been printed.

Note 4: This notation reminds the user that constraints imposed by use of the LIMIT keyword in the annealing section have been removed for quenching.

Note 5: Again, this is an energy minimization and the default BFGS/DFP algorithm is used.

Note 6: The first minima located is the trans-saddle point, corresponding to an eclipsed C_4-H / N_3-H bond arrangement via rotation of the methyl group attached to N_3 (see below). In an ideal situation, this point should not have been located, as it is NOT an energetic minima. This is a failing of the BFGS/DFP algorithm that can cause problems for the unwary. See Section 5.15 for a more complete description.



Note 7: This is the trans-minimum geometry.

Note 8: This in the cis-minimum geometry.

Note 9: At this stage in the calculation, the trans-saddle point is discarded due to its geometric similarity to the trans-minima. It is possible to retain all three of the points by lowering the filtering factor, specifying FILTER=1.0 on the keyword line.

Note 10: A full set of results is reported for the trans-minima, the most stable configuration according to the energy criteria.

CHAPTER 10: AMSOL MODELS

(This Chapter of the manual was adapted from AMSOL–version 4.1, manual by C. J. Cramer, G. D. Hawkins, G. C. Lynch, D. G. Truhlar, and D. A. Liotard.)

10.1 Introduction

The AMSOL models, also often referred to as the SMx models, installed in AMPAC calculate the free energies of solvation of molecules and ions in aqueous solution. They are based on NDDO semiempirical molecular orbital theory in which terms representing the solvent are included in and directly perturb the solute Hamiltonian. The current version of AMPAC includes all solvation models included in AMSOL—version 4.1. In particular, it includes the SM1, SM1a, SM2, and SM2.1 solvation models based on using the AM1 semiempirical model for the solute electronic Hamiltonian and the SM3 solvation model based on using the PM3 semiempirical model for the solute electronic Hamiltonian. The free energy of solvation is based on two terms:

1. A generalized Born contribution that accounts for electric polarization of the continuum-dielectric solvent, i.e., for the electronic, atomic, and orientational polarization of the solvent molecules and for the resulting feedback of this effect on the solute charge distribution.

2. An accessible-surface-area term that accounts for the free energy of cavity formation, dispersion interactions, and hydrophobic and hydrophilic effects such as solvent structure alterations. The surface tension term, being semiempirical, adjusts for errors in AM1 or PM3 as well.

As mentioned above, five general parameterizations are available for the solvation terms: AM1-SM1 and AM1-SM1a (originally released in the Version 1 of AMSOL), AM1-SM2 and PM3-SM3 (originally released in the Version 3.0 of AMSOL), and AM1-SM2.1 (released in the present AMSOL-version 4.1). In every case, the nomenclature indicates the underlying gas-phase Hamiltonian which is employed followed by the designation of the Solvation Model. The parameters for all of the models have been determined semiempirically, and the original model and method for determination of the parameters are described for SM1 and SM1a in the literature.[19] The AM1-SM1 model is the original general parameter set which can be used for ionic or neutral systems containing H, C, N, O, F, S, Cl, Br, and I atoms.[20] The AM1-SM1a model is a more specialized parameter set which is applicable to neutral molecules that are composed of the same atoms as in the SM1 model but that do not have hypervalent centers, three-center bonds, or unusual hybridization at N or O. The SM2 model[21] was introduced in 1992, and is an improved solvation model for the atoms in the SM1 model plus P. AM1-SM1

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19 Cramer, C. J.; Truhlar, D. G. J. Am. Chem. Soc. 1991 , 113, 8305, 9901.

20 Use of atoms other than these with the keyword SM1, SM2, SM2.1, or SM3 is allowed, but no accessible-surface-area dependent correction will be applied, i.e., the surface tension factor is 0.00.

21 Cramer, C. J.; Truhlar, D. G. Science 1992 , 256, 213.

parameters for P were also introduced at that time. SM3[22] is similar to SM2 but is based on the PM3 Hamiltonian rather than AM1. SM2.1[23] is similar to SM2, but is based on a more accurate and stable radial quadrature scheme in the dielectric screening algorithm. A full comparison of the first four methods together with a detailed description of both the models is available in the literature.[24] The computational methodologies employed in AMSOL-version 4.1 and the current AMPAC implementation of AMSOL are described in the paper above where SM2.1 was introduced.

AMSOL modifies AMPAC so that, in addition to Heats of Formation (ΔH_f), the free energies of solvation can also be computed. Modifications to the AMPAC program are transparent unless one of the four keywords which indicate application of a specific solvation model is included. The keywords are "SM1", "SM1A", "SM2", "SM2.1", and "SM3" (both upper and lower case letters are allowed). Use of any one of these keywords requires specification of the gas-phase Hamiltonian, either AM1 (for SM1, SM1a, SM2 and SM2.1) or PM3 (for SM3). (Note that while it is possible to successfully use other combinations, e.g., PM3-SM2, the results are of dubious value since the SMx parameters should be used with the Hamiltonian for which they were optimized.)

If an AMSOL solvation model is specified, one of the three keywords, "NOPOL", "DERINU", or "1SCF" must also be included or the program will halt execution after reading the data file. (See below for a discussion of NOPOL and Chapter 3 for definition of DERINU and 1SCF.) The keyword "DERINU" is used for geometry optimizations with any solvent model activated at all stages of the calculation. (DERINU is required for this task because the default procedure in AMPAC calculates each gradient as the sum of all of the contributions from all possible pairwise combinations of atoms (the matrix operations are considerably simplified by restricting them to two-atom combinations). However, when an AMSOL model is used, the individual gradients CANNOT be calculated in this manner, and instead, energy calculations must be performed for the entire molecule with each movement of an atom. DERINU accomplishes this.) Any of the supplied methods for optimization may be used provided the gradients themselves are calculated by the DERINU option. The keyword "1SCF" performs a single SCF calculation at the input geometry optimizing the electronic distribution to reflect aqueous solvation.

Three other keywords, "TEXPN=x.xx", "TONE=x.xx" and "EXTM" are available for use with the SM2.1 model, providing additional flexibility in the step sizes for the radial quadrature of the dielectric screening algorithm. The most computationally expensive step in the SMx algorithms is the calculation of the electrostatic free energy of a sphere (representing an atom in a molecule), of radius ρ_k, centered at the origin, embedded in an infinite continuum dielectric medium of relative permittivity ε but shielded from this medium by a set of (N–1) nearby "coulomb spheres" (representing the other atoms), centered at points x_k' and having radii ρ_k' and relative permittivities of 1 (where N is the number of atoms in the solute). Some of the nearby spheres may partially overlap the

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22 Cramer, C. J.; Truhlar, D. G. J. Comput. Chem. 1992 , 13, 1089.

23 Liotard, D. A.; Hawkins, G. D.; Lynch, G. C.; Cramer, C. J.; Truhlar, D. G. in press .

24 Cramer, C. J.; Truhlar, D. G. J. CAMD 1992 , 6, 629.

sphere at the origin or one another. The critical step in this calculation is the evaluation of the radial quadrature

$$\frac{1}{\alpha_k} = \int_{\rho_k}^{\infty} \frac{dr}{r^2} \frac{A\left(r_1\{\mathbf{x}_{k'},\rho_{k'}\}\right)}{4\pi r^2} \qquad (51)$$

where $A\left(r\{\mathbf{x}_{k'},\rho_{k'}\}\right)$ *is the exposed area of a sphere at the origin of radius r in the presence of the (N–1) other spheres characterized by the (2N–2) parameters in the set* $\{\mathbf{x}_{k'},\rho_{k'}\}$. *(The exposed area is the area* <u>*not contained*</u> *in any other sphere.) The computational expense is due to the repetitive evaluation of exposed surface areas at the quadrature nodes of the radial integration.*

The quadrature is carried out numerically using a sequence of increasing step sizes $T_1, T_2, \ldots, T_M$ *corresponding to the distances between a sequence of M concentric shells. The step size* T_i *for step i of the radial quadrature is calculated from an initial step size* T_1 *and a step size expansion factor TEXPN as follows:*

$$T_{i+1} = TEXPN \times T_i\ , \qquad i = 1, 2, \ldots.$$

In the SM1, SM1a, SM2, and SM3 models, these step sizes are used without further change in a quadrature method[25] *called the force rectangle rule. In the SM2.1 model, the quadrature is carried out by a higher-order method called the force trapezoid rule. In the force rectangle algorithm, the concentric shells expanded about each atom in the numerical integration sequence do not necessarily end at the precise point where the rest of the molecule is engulfed by the shell. Rather, the progression continues a partial step past that point. In the force trapezoid quadrature scheme the value of* T_1 *is adjusted downwards by the minimum change required to constrain one of the steps to end at the minimal radial distance that totally engulfs the coulomb spheres of all the other atoms. This downwards adjustment means that the value actually used for* T_1 *is typically a few percent less than the default or input value.*

The values finally adopted for T_1 *were 0.1 Å for SM1 and SM1a and 0.02 Å for SM2 and SM3, and TEXPN was fixed at 1.5 in all four methods that use the force rectangle rule. These choices lead to small,but significant systematic errors in the integrals, and these were explicitly absorbed in the parameterization. These values should not be changed by the user because the systematic errors in the quadrature must be consistent with the parameterization of these methods. In the SM2.1 method, the parameters were obtained using the more efficient force trapezoid rule with default values of* T_1 *and TEXPN such that the integrals were well converged. As a consequence, the user has the freedom to perform less well converged calculations by increasing* T_1 *and/or TEXPN from their default values, which are 0.15 Å and 1.2 respectively. The user may also require that the quadrature for each atom be carried out with a fixed number M of shells. These options are controlled by the TONE, TEXPN, and EXTM keywords explained below.*

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[25] *Still, W. C.; Tempczak, A.; Hawley, R.C.; and Hendrickson, T. J. Am. Chem. Soc. 1990 , 112, 6127.*

In addition to the reporting of energies, use of a solvation model keyword automatically requires that the accessible-surface-area terms are output in kcal/mol, by individual atom as well as summed over the atoms. The effective Born radii and effective interatomic distances are printed out in block matrix form. The atomic Born energies are printed out in block matrix form and summed over individual atoms as well as atomic number. Note that these energies will be significantly more negative than the actual electronic contribution to the free energy of solvation since there is an energy loss associated with the gas-phase portion of the SCF calculation due to electronic reorganization. One additional item worthy of note is that the ionization potential and the HOMO energy are no longer adequately predicted by Koopman's theorem. Hence, AMSOL reports the HOMO energy labeled as such.

Note that AMSOL model RESTARTs are not supported in AMPAC. Be sure to specify enough time using the T= keyword to complete the calculation.

10.2 AMSOL Dedicated Keywords

EXTM

This keyword (EXTernal M values) allows manual specification of the M values (see previous section) for the individual atoms in the AMSOL force trapezoid radial quadrature. By default, the values of M are consequences of the default values of TONE and TEXPN plus the requirement that sphere M engulf the whole molecule. The EXTM option allows the user to fix M to other values. If EXTM is specified, the value of TONE is not used, and the sequence of step sizes is a consequence of TEXPN and M. This keyword <u>should be used only in conjunction with the SM2.1 keyword</u>, not with the other solvation models. The default (no EXTM keyword) causes the program to use the standard prescription for M values. If EXTM is specified, the program will look for M values following Z-matrix data on any non-dummy atom line in the data file. When EXTM is specified, the TEXPN keyword is allowed, but TONE is not. (If EXTM is not specified in the keyword line, then TEXPN or TONE or both are allowed.)

The Z-matrix must be fully padded out with zeros (even for the first two atoms) in order to use the EXTM option. Note that if the SPARKLE option is used (where the charges are input after the Z-matrix in the data file) with the EXTM option, the M values should be placed before the SPARKLE charges on the Z matrix rows.

The primary reason why one might wish to use the EXTM option is to force the calculated results to be independent of the initial guess and to be continuous functions of geometry. The default values of M may change (typically by ± 1) as functions of the initial guess, and although the resulting differences in the calculated geometries, energies, and other properties should be small and within the limits of precision of other parts of the calculation, the discontinuous nature of the change could be undesirable in certain applications, e.g., when following a reaction path. As a guide to users who wish to fix M, when the SM2.1 option is used the values of M are printed on the output. Thus a recommended course of action would be to run SM2.1 without the EXTM keyword. If problems are encountered with M varying from run to run, then the EXTM option should be invoked with M values one or two units larger than the ones that were obtained without the EXTM option; as long as M is increased and not decreased from those

default values, the accuracy should be adequate and reliable. Abbreviation: None

NOPOL

The keyword "NOPOL" indicates that the program is to proceed with a normal gas-phase calculation Upon completion, the output free energy of solvation is that which would be obtained using the gas-phase geometry and wavefunction. In particular, the solvation free energy depends on the atomic charges and bond orders calculated from the solute wavefunction. Often considerably smaller polarization free energies are obtained with the geometry and wavefunction "frozen" this way than when they are re-optimized in the presence of solvent. Abbreviation: None

TEXPN=x.xx

The TEXPN keyword sets the expansion factor used for concentric shells expanded about each atom in the radial quadrature of the AMSOL dielectric screening algorithm. As an example, the use of the keyword TEXPN=1.5 will yield a sequence of quadrature shells where each shell has a radius 50% larger than its immediate precursor. It is important to note that SMx runs with x = 1, 1a, 2, and 3) must use the default value for TEXPN, since the parameters for these solvation models make up for systematic errors in the force rectangle quadratures obtained with these values. However TEXPN > 1.2 may be used with SM2.1 as a way to decrease computer time in calculations where high precision is unnecessary (e.g., exploratory investigations). The TEXPN keyword can be used in conjunction with the TONE or EXTM keywords if desired. Abbreviation: None

TONE=x.xx

The TONE keyword sets the thickness T_1 of the first shell in the radial quadrature of the AMSOL dielectric screening algorithm, as explained above. It is important to note that all SMx runs with x = 1, 1a, 2, or 3 must use the default value for TONE, since the parameters for the solvation models have been developed using this default value, and they are only consistent with runs in which the same systematic differences from converged quadratures occur.. The TONE keyword can be used in conjunction with the TEXPN keyword if desired. Abbreviation: None

TRUES, HGAS=n.nn

The keyword TRUES requires AMPAC to calculate the true solvation free energy when one of the AMSOL models is applied. This true solvation energy is the heat of formation plus solvation free energy for the optimized geometry in solution minus the final heat of formation for the optimized gas-phase geometry. When the keyword TRUES is specified, The keyword HGAS=n.nn must be used to supply the heat of formation for the optimized gas-phase geometry in kcal/mol. Abbreviation: None

10.3 Notes and Background

The determination of the effective Born radii is the slowest step in the calculation. This calculation, as well as the calculation of the CDS term, involves computing the exposed surface area of a sphere in a set of spheres.

This version of AMPAC includes the improved exposed surface area algorithm of AMSOL–version 4.1 mentioned above, in which exposed surface areas are calculated analytically (this the ASA keyword in AMSOL). It also includes a more efficient radial integration scheme for the dielectric screening computation as explained above.

The keyword PRECISE affects only the SCF calculation (two-point central differences are the default for geometry optimization) if a solvation model is specified. In general when using the AMSOL models, the default SCF termination criteria of 0.00001 in AMPAC is too loose and the output results are questionable. The recommended course of action is to use the keyword phrase SCFCRT=0.000001; this makes the tolerance ten times as stringent and usually produces accurately converged heats of formation and energies. Using PRECISE or still tighter tolerances occasionally causes the SCF calculation to converge very slowly due to the numerical discontinuities in the generalized Born terms.

The changes implemented in the atomic data in AMSOL have been removed in AMPAC. These involved replacement of the weighted average natural abundance atomic masses with the exact masses of the most abundant isotopes. Users should be aware of this and expect very slight differences from AMSOL-version 4.1 results. Users may use the exact masses used in AMSOL by defining the isotopic values described in Section 2.3 of this manual.

CHAPTER 11: EIGENVECTOR FOLLOWING

(Note: This Chapter of the manual was adapted from the EF Manual by Frank Jensen.)

The eigenvector following (EF) geometry optimization algorithm, contributed by Frank Jensen, has been added to AMPAC. The current version of the EF optimization routine is a combination of the original EF algorithm of Simons et al.[26] as implemented by Baker[27] along with the QA algorithm of Culot et al.[28] Additional features have also been added to improved stability.

11.1 Introduction

The EF geometry optimization algorithm is based on a second order Taylor expansion of the energy about the current point. At this point the energy, the gradient, and an estimate of the Hessian matrix are explicitly available. A distinction must be made between searches for minima (entered using the master keyword "EF") and transition states (entered using the master keyword "TS") since for a minimum on the PES, the correct Hessian has only positive eigenvalues by definition and for a TS the correct Hessian has exactly one negative eigenvalue, and the corresponding eigenvector should be in the direction of the reaction coordinate. There are three fundamental steps in determining the next geometry based on this information, and each is described below.

> *Stage 1: Locate the best step within or on the hypersphere using the current trust radius.*

The actual geometry step is determined using a shift factor which ensures that the steplength is within or on the hypersphere. If the Hessian has the correct structure at this point, a pure Newton-Raphson step is attempted. (This corresponds to setting the shift factor to zero.) If this step is found to be longer than the trust radius, a P-RFO step is projected and if this is also too long, then the best step on the hypersphere is determined by the QA formula. This three step procedure is the default and is implemented automatically. Note that certain EF keywords can alter the default procedure (see NONR and RSCAL below).

> *Stage 2: Determine if this step should be retained based on various criteria.*

Using the geometry increment determined from Stage 1, the new energy and gradient are evaluated. Two sets of criteria are used depending on whether the search is for a minimum or a transition state:

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26 J. Simons, A. Banerjee, N. Adams, R. Shepard, Journal of Physical Chemistry 89, 52 (1985).

27 J. Baker, Journal of Computational Chemistry 7, 385 (1986).

28 P. Culot, G. Dive, V. H. Nguyen, J. M. Ghuysen, Theoretica Chimica Acta 82, 189 (1992).

Minimum: *The new energy should be lower than the previous step. If this is not the case, the step is rejected and the trust radius is halved for the new step.*

TS: *In this case, two criteria are used in determining whether the step is appropriate. The first is the ratio between the actual and predicted energy change which should ideally be 1.00. If it deviates substantially from this value, the second order Taylor expansion about the present point is no longer valid. Limits on how far from 1.00 the ratio can deviate before the step is rejected are governed by the keywords RMIN and RMAX (see below). If the ratio is outside the defined limits, the step is rejected, the trust radius halved, and a new step predicted. The second criteria for TS searches is that the eigenvector along which the energy is being maximized should not change substantially between iterations. The minimum overlap of the TS eigenvector with that of the previous iteration should be larger than a set value (see OMIN below), otherwise the step is rejected. Large values for RMIN and RMAX as well as setting OMIN to zero effectively inhibits step rejection.*

Stage 3 : Update the trust radius.

As before, Stage 3 is dependent on whether the EF search is for a minimum or for a transition state.

Minimum: *The trust radius is increased by a factor of* $\sqrt{2}$ *if the ratio between actual and predicted energy change is above 0.5. If the ratio is within ±0.1 of 1.0, it is multiplied by 2.*

TS: *During a TS search, more restrictive criteria are used. If the ratio is within ±0.1 of 1.0, the trust radius is multiplied by 2. If the ratio is between 0.75 and 0.9, or 1.1 and 1.33, the radius is increased by a factor* $\sqrt{2}$ *. If the ratio is less than 0.1 or larger than 3, the trust radius is halved.*

In either case above, the updating of the trust radius can be inhibited by specifying the keyword NOUPD (see below). Other trust radius parameters can be adjusted via special keywords (see DMAX, DDMAX, and DDMIN below).

Note that in all cases, as the optimization approaches the stationary point the energy changes become very small, and the actual/predicted ratio may vary wildly. For this reason, step rejection based on this ratio is only performed if both the actual and the predicted energy changes are larger than 0.02. Similarly the trust radius is only updated if both changes are larger than this value, or if the gradient norm is larger than 5. The gradient norm condition is imposed to avoid stalling the optimization when it is distant from the stationary point. Below these limits, a fixed trust radius of 0.10 is used for each step.

11.2 EF Strategies

1. An examination of the Hessian matrix may be obtained by specifying CYCLES=0. This will cause the routine to process the HESS option, diagonalize the Hessian, and automatically set PRNT=3 (unless PRNT is given explicitly). This procedure is useful for selecting the MODE to follow in TS searches. After inspection of the output, the calculation can be restarted by specifying RESTART (to pickup the Hessian from the jobname.RES file) or HESS=2. The appropriate value for MODE can now be specified with confidence.

2. Repeated use of HESS=2, varying the value of MODE, is useful for following several different TS modes from the same initial geometry. (Note that the jobname.RES and jobname.DEN files must be copied over the name of the jobname.DAT file to be properly read.)

3. If very highly converged geometries and wavefunctions are required, AMPAC options combined with EF options can be used to obtain them. The default value for GNORM is usually sufficient to ensure that the energy is optimized to within 0.01 kcal/mol without PRECISE, and 0.0001 kcal/mol when PRECISE is active. In general, it will be quite difficult to converge structures to a gnorm of less than 0.01. SCFCRT should be tightened and HESS=3 used instead.

4. The RMIN, RMAX, and OMIN features (see below) have been introduced in the current version of EF to improve the stability of TS optimizations. Setting RMIN and RMAX close to 1.00 will give a very stable, albeit very slow, optimization. Wide limits on RMIN and RMAX may in certain cases give a faster convergence, but there is always the risk that very poor steps are accepted, causing the optimization to diverge to unprofitable regions of the potential surface. The default values of 0.00 and 4.00 rarely reject steps which would lead to faster convergence, but may occasionally accept poor steps. If a TS search is not converging properly, the first solution is to lower the limits to RMIN=0.50 and RMIN=2.00. Tighter limits such as these will usually slow the optimization substantially, but may be necessary in some cases.

5. The EF algorithm has the capability of following Hessian eigenvectors other than the one with the lowest eigenvalue toward a TS. Such higher mode following procedures are always much more difficult to converge than descent along the lowest eigenvector. Ideally, as the optimization progresses, the mode being followed by EF should become the lowest eigenvector. Care must be taken during the optimization, however, that the nature of the mode does not suddenly change, leading to optimization of a different TS than the one desired. OMIN is designed to ensure that the nature of the TS mode changes gradually by requiring some level of overlap between TS modes. While this concept at first appears quite promising, it is not without problems when the Hessian is updated. As the updated Hessian in each step is only approximately correct (not completely re-computed), there is a upper limit on a practical value for TS mode overlap. Tests have shown that 0.9 is a rough practical limit to the value of OMIN. However, a combination of RECALC=1 and OMIN=0.9 allows EF to locate very difficult transition state structures.

6. Following modes other than those with the lowest eigenvalue toward a TS indicates that the starting geometry is not "close" to the desired TS. It may possess multiple negative eigenvalues and be at a complex point on the potential

surface. There are cases where it is very difficult to locate a starting geometry which has a Hessian with a well-defined eigenvector, and mode following may be of some use.

7. Using the RECALC=1 option will force computation of a full Hessian matrix at each step in the calculation. (Using the HESS=5 keyword will use the rapid LTRD algorithm for this purpose.) This is very costly in terms of time and computational effort but can be useful in locating difficult points on the PES.

11.3 Dedicated EF Keywords

Below is a complete list of keywords associated with the various EF optimizers:

DDMAX=n.n

The maximum size of the trust radius used in the three-step geometry projection algorithm above is specified by this keyword. (Default=0.5 for EF, 0.3 for TS) Abbreviation: None

DDMIN=n.n

The maximum size of the trust radius used in the three-step geometry projection algorithm above is specified by this keyword. If the trust radius drops below the default value of 0.001, the optimization is terminated with a warning message. Abbreviation: None

DMAX=n.n

The initial trust radius used in the three step geometry optimization procedure above may be directly specified using this keyword. (Default=0.20) Abbreviation: None

HESS=n

This keyword indicates to the EF algorithm where to obtain its original Hessian matrix based on the value of n. Abbreviation: None

- n=0 : use a diagonal matrix (default for EF)
- n=1 : calculate by numerical differentiation (default for TS)
- n=2 : read just the Hessian matrix from a previous EF restart file, jobname.RES
- n=3 : calculate by double numerical differentiation
- n=4 : restart EF using jobname.RES
- n=5 : compute a full Hessian using LTRD in either Cartesian or internal coordinates

IUPD=n

This keyword directs updating of the Hessian matrix during the course of optimization based on the particular value of n. Abbreviation: None

n=0 : no update
n=1 : Powell update (default for TS)
n=2 : BFGS update (default for EF)

MODE=n

The selection of which eigenvector to follow towards the transition state in a TS optimization at Stage 2 above is given by MODE=n, where n is the number of the Hessian eigenvector to follow. The default value of n is 1, but if the TS mode changes to some higher mode during the optimization this can present a problem. To turn off mode following, and thus always follow the mode with the lowest eigenvalue, set MODE=0. Abbreviation: None

NONR

The Newton-Raphson phase of the three step procedure outlined above for projecting the next geometry is skipped in favor of the P-RFO method. Abbreviation: None

NOUPD

This keyword suppresses updating of the trust radius at Stage 3 above. Abbreviation: None

OMIN=n.n

This value is the minimum overlap between the old vector along which energy is maximized and the projected vector along which energy is maximized for a TS search in Stage 2 above. If a step is rejected on this basis, one (or possibly more) lines with the same CYCLE number appear in the output file. The default OMIN value is 0.8, which allows fairly large changes to occur, and should be suitable for most simple systems. Abbreviation: None

PRNT=n

Defines print level for the EF routine according to the value of n.. Specific items output at various levels are listed below. Abbreviation: None

n=0 : a one line summary for each step (default)
n=1 : details regarding step construction, trust radius, TS mode
n=2 : geometries and gradients
n=3 : Hessian eigenvalues and eigenvectors
n=4 : Hessian matrices
n=5 : debug print (beware, huge output)

RECALC=n

Requires that an exact Hessian be computed every n steps. The default value for n is set very high (99999), resulting in essentially no recalculation but only approximate updates based on the three step procedure above. While specifying RECALC to a lower value will certainly make the optimization more stable, but vastly slower as diagonalization of the Hessian matrix is a very slow step computationally. Abbreviation: None

RSCAL=n.n

Rather than defaulting to the QA search of the hypersphere for projecting the next geometry in the three step protocol described above, the user may choose to scale the P-RFO step down to the trust radius by a multiplicative constant. This can be accomplished by specifying RSCAL. Abbreviation: None

RMIN=n.n

This is the minimum ratio of actual to predicted energy change for accepting geometry steps at Stage 2 above (default=0.00). Abbreviation: None

RMAX=n.n

This is the maximum ratio of actual to predicted energy change for accepting geometry steps at Stage 2 above (default=4.00) Abbreviation: None

The following standard AMPAC keywords are also active in the EF routine, with similar functions to those they serve in the main program:

CYCLES=n
RESTART
GNORM=n.n

CHAPTER 12: ERROR MESSAGES PRODUCED BY AMPAC

AMPAC produces several hundred messages, all of which are intended to be self-explanatory. However, when an error occurs it is often useful to have more information than is given in the message text itself. The following alphabetical list gives more complete definitions of the messages printed.

ATOM NUMBER nn IS ILLDEFINED

The rules for definition of atom connectivity are:

1. *Atom 2 must be connected to atom 1 (default - no override)*

2. *Atom 3 must be connected to atom 1 or 2, and make an angle with 2 or 1.*

3. *All other atoms must be defined in terms of already-defined atoms: these atoms must all be different. Thus atom 9 might be connected to atom 5, make an angle with atom 6, and have a dihedral with atom 7. If the dihedral was with atom 5, then the geometry definition would be faulty.*

If any of these rules are broken, a fatal error message is printed and the calculation stopped.

ATOMIC NUMBER nn IS NOT AVAILABLE...

An element has been requested for which parameters are not available. This check is not exhaustive, in that even if the elements are acceptable there are some combinations of elements within MINDO3 that are not allowed. This is a fatal error message.

ATOMIC NUMBER OF nn ?

An atom has been specified with a negative or zero atomic number. This is normally caused by forgetting to specify an atomic number or symbol. This is a fatal error message.

ATOMS nn AND nn ARE SEPARATED BY nn.nnnn ANGSTROMS

Two genuine atoms (not dummies) are separated by a very small distance. This can occur when a complicated geometry is being optimized, in which case the user may wish to continue. This can be done by using the key-word GEO-OK. More often, however, this message indicates a mistake, and the calculation is stopped by default.

ATTEMPT TO GO DOWNHILL IS UNSUCCESSFUL...

A quite rare message, produced by the NLLSQ gradient norm minimization protocol. NLLSQ attempts to minimize the gradient norm by searching the gradient space for a minimum. Apparently a minimum has been found, but not recognized as such. The program has searched in all (3N-6) directions, and found no way down, but the criteria for a minimum have not been satisfied. A different gradient minimization technique is recommended.

C.I. NOT ALLOWED WITH UHF

There is no UHF configuration interaction calculation in AMPAC. Either remove the key-word that implies CI or the word UHF.

CALCULATION ABANDONED AT THIS POINT

This error may occur during a geometry optimization or gradient minimization and usually indicates that a dihedral angle is about to become undefined. This happens when the three atoms used to define a fourth's dihedral approach a straight line. The ways to circumvent this error are to redefine the connectivity of the molecule, use Cartesian coordinates, or use one or more dummy atoms. Note that if the three atoms are in an exactly straight line, this message will not be triggered.

CARTESIAN COORDINATES READ IN, AND CALCULATION...

If Cartesian coordinates are read in, but the calculation is to be carried out using internal coordinates, then either all possible geometric variables must be optimized, or none can be optimized. If only some are marked for optimization then ambiguity exists. For example, if the "X" coordinate of atom 6 is marked for optimization, but the "Y" is not, then when the conversion to internal coordinates takes place, the first coordinate becomes a bond-length, and the second an angle. These bear no relationship to the "X" or "Y" coordinates. This is a fatal error.

ERROR DURING READ AT ATOM NUMBER...

Something is wrong with the geometry data. In order to help find the error, the geometry already read in is printed. The error lies either on the last line of the geometry printed, or on the next (unprinted) line. This is a fatal error.

ERROR - TO MANY POINTS GENERATED IN SURFACE
REDUCE NSURF, SCALE, DEN, OR SCINCR

This is an error from the ESP charge routine and should not generally appear. It indicates that the maximum number of probe points has been exceeded in the ESP fit of the molecule's surface. See Section 7.5 for an explanation of how this figure is computed. You should only see this error if you have altered the keywords noted in the error message.

FAILED IN SEARCH, SEARCH CONTINUING

This is not a fatal error. The McIver-Komornicki (SIGMA) gradient minimization method involves use of a line-search to find the lowest gradient. This message is merely advice. However, if SIGMA minimization runs for an excessive period of time, consider another method such as POWELL or NLLSQ.

*<<<<----**** FAILED TO ACHIEVE SCF. ****---->>>>*

The SCF calculation (definition of the wavefunction) failed to converge. There are a number of possible reasons why this might occur, but they are usually related in one way or another to charge (electron) oscillations. In a system where a biradical can form, such as ethane decomposing into two CH_3 units or a hydrogen shift, the normal RHF procedure can fail to achieve self-consistence. If the system has significant biradicaloid character, BIRADICAL or UHF/TRIPLET will often prove successful in circumventing the error condition.

This problem can be demonstrated with H-Cl by steadily increasing the interatomic distance. At bonding distance the covalent bond will be strong, and a self-consistent field is readily obtained. As the bond is stretched, it becomes increasingly ionic. Electrons are polarized toward the chlorine and the hydrogen becomes electropositive. As the energy increases electrons are attracted by the positive charge on the hydrogen. At some point, an electron will suddenly "jump" from the chlorine to the hydrogen causing a re-organization of the density matrix. There is a good chance the electron will oscillate between the hydrogen and the chlorine, and SCF will not be achieved This can be prevented by using BIRADICAL, and in this instance exactly one electron will end up on hydrogen. A similar result can be obtained by specifying TRIPLET in a UHF calculation.

If this message does appear, suspect first that the input calculation requested might be faulty. If after examination the input appears correct, add SHIFT= or invoke PULAY. If this is not successful, then consider slackening SCFCRT. This will allow heats of formation to be calculated with reasonable precision, but the gradients are likely to be imprecise.

GEOMETRY TOO UNSTABLE FOR EXTRAPOLATION...

In a reaction coordinate calculation the initial geometry for a point is calculated by quadratic extrapolation using the previous three points.

If a quadratic fit is likely to lead to an inferior geometry, then the geometry of the last point calculated will be used. The total effect is to slow down the calculation, but no user action is recommended.

ILLEGAL ATOMIC NUMBER

An element has been specified by an atomic number which is not in the range 1 to 106. Check the data. The first item on one of the geometry specification lines is likely faulty.

IMPOSSIBLE NUMBER OF OPEN SHELL ELECTRONS

The keyword OPEN(n1,n2) has been used, but for an even-electron system n1 was specified as odd or for an odd-electron system n1 was specified as even. Either way, there is a conflict which the user must resolve.

IMPOSSIBLE OPTION REQUESTED

A general catch-all. This message will be printed if two incompatible options are used, such as both MINDO3 and AM1 being specified. The user must check the key-words and manually resolve the conflict.

INTERNAL COORDINATES READ IN, AND SYMMETRY...

If internal coordinates are read in, but the calculation is to be carried out using Cartesian coordinates, then any symmetry relationships between the internal coordinates will not be reflected in the Cartesian coordinates. For example, if the bond-lengths of atoms 5 and 6 are equal, it does not follow that these atoms have equal values for their "X" coordinates. This is a fatal error.

THE LINE MINIMIZATION FAILED TWICE IN A ROW

This is usually found in more exotic calculations. For some reason, the heat of formation at the start of a line minimization within FLEPO was lower than any point on the line minimization, a situation that cannot occur naturally. If the gradient norm is low, ignore this message. If it is significant, a new connectivity pattern is suggested. The required accuracy may also be increased by specifying PRECISE or SCFCRT=n.n.

***** MAX. NUMBER OF ATOMS ALLOWED...*

***** MAX. NUMBER OF ORBITALS...*

***** MAX. NUMBER OF TWO ELECTRON INTEGRALS...*

Any of these messages indicate that the system being attempted exceeds the maximum size for which this version of AMPAC was prepared. Contact Semichem if you need a larger version of the program. The default number of atoms is 50 heavy (non-hydrogen) and 50 hydrogens.

*** RMS GRADIENT IS TOO LARGE TO ALLOW...*

In AMPAC 5.0, the translational and rotational "vibrations" are computed analytically and the force constant matrix is projected from the subspace of the genuine vibrations. This corrects the harmonic force field by removing the residual first order components present because the system is not exactly a stationary point. The geometry must be very near a stationary point so that third and higher order components do not corrupt the quadratic force field. Before a FORCE calculation can be performed the gradient norm must very low. If the

gradient norm is too large, the calculation will be halted. This condition may be overridden by use of the keyword LET. See Section 5.4 for a discussion of stationary points and the implications of incompletely optimized geometries.

SINCE COS HAS JUST BEEN RESET...

A non-fatal error message. After two attempts to lower the heat of formation have failed, the DFP optimization is terminated. If the gradients are acceptable, no further action is necessary; otherwise examine the geometry to see if a different numbering system will eliminate the large gradient component(s).

A rarer cause of this message is when the geometry supplied is already almost fully optimized, and it becomes optimized within the first cycle.

SYSTEM DOES NOT APPEAR TO BE OPTIMIZABLE

This is a gradient minimization message. These routines will only work if the nearest minimum to the supplied geometry in gradient-norm space is a transition state or a ground state. Gradient norm space can be visualized as the space of the scalar of the derivative of the energy space with respect to geometry. To a first approximation, there are twice as many minima in gradient norm space as there are in energy space. It is unlikely that there exists any simple way to refine a geometry that results in this message.

TEMPERATURE RANGE STARTS TOO LOW...

The thermodynamics calculation assumes that the statistical summations can be replaced by integrals. This assumption is only valid above 100K, so the lower temperature bound is set to 100, and the calculation continued.

THERE HAVE BEEN 3 ATTEMPTS...

The energy minimization routine has made three attempts to lower the heat of formation and the gradient, but while the heat of formation has reached a fairly constant value, the gradient norm is still large. This is a non-fatal error, and almost certainly the results will be useful. Use GNORM= or PRECISE to increase the convergence criteria.

THERE IS A RISK OF INFINITE LOOPING...

SCFCRT has been reset by the user, and the new value is so small that the SCF test may never be satisfied.

THREE ATOMS BEING USED TO DEFINE...

If the internal coordinates of an atom depend on the dihedral angle it makes with three other atoms, and those three atoms fall in an almost straight line, then a small change in the Cartesian coordinates of one of those three atoms can cause a

large change in its position. This is a potential source of trouble, and the data should be rearranged to make the geometric specification of the atom in question less ambiguous.

This message can appear at any time, particularly in reaction path and CHAIN calculations.

An exception to this rule is the case where three atoms fall exactly on a straight line. For example, if in propyne, the hydrogens are defined in terms of the three carbon atoms, then no error will be flagged. In such a system the three atoms in the straight line must not have the angle between them optimized, as the finite step in the derivative calculation would displace one atom off the straight line and the error-trap would take effect.

- - - - - - - TIME UP - - - - - - -

The time defined on the keyword line (3,600 seconds, if no time is specified) will be exceeded if another cycle is performed. A controlled termination of the run should follow this message. See the keyword RESTART.

TRIPLET SPECIFIED WITH ODD NUMBER OF ELECTRONS

If TRIPLET has been specified the number of electrons must be even. Check the charge on the system, the empirical formula, and whether TRIPLET was intended.

"""""""""""""""UNABLE TO ACHIEVE SELF-CONSISTENCY

See the error-message:

<<<<----**** FAILED TO ACHIEVE SCF. ****---->>>>

UNDEFINED SYMMETRY FUNCTION USED

Symmetry operations are restricted to those defined, i.e. in the range 1-21 (18 excluded). Any other symmetry operations will result in this fatal message.

UNRECOGNISED ELEMENT NAME

In the geometric specification a chemical symbol which does not correspond to any known element has been used. The error lies in the first datum on a line of geometric data.

WARNING: INTERNAL COORDINATES...

Triatomics are, by default, defined in terms of internal coordinates. This warning is only a reminder. For tetra-atomics and higher, the presence or absence of a connectivity table distinguishes internal and Cartesian coordinates, but for diatomics and triatomics there is an ambiguity. If the data are expressed in Cartesian coordinates, override the default by adding the keyword XYZ.

***** WARNING **** RMS GRADIENT IS VERY LARGE...*

The low-lying vibrations are very sensitive to third and higher order contamination of the genuine harmonic force field. The criterion for THERMO is much more stringent than that for a vibrational frequency calculation in FORCE. In contrast to the zero point energy (ZPE), it is the lowest few genuine vibrations (those most susceptible to error) that contribute the most to the internal vibrational energy, entropy, etc.

CHAPTER 13: BIBLIOGRAPHY

Note: Direct references to the contributed methods in AMPAC (AMSOL, EF, ESP, etc.) are contained in the specific manual chapters describing their function and use.

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CHAPTER 14: TESTING AND VALIDATION

AMPAC comes with an extensive set of test files along with the results of these calculations completed on Semichem's computers for your version of the program. If there is ever a doubt as to the validity of a calculation using AMPAC an example of the type needed may be run for comparison. Also, these files serve as a more extensive set of examples and templates of the various options available in AMPAC's computational module. The files are located in the "testsuite" subdirectory of the main AMPAC directory. There are three subdirectories under this one, "datfiles", "outfiles", and "arcfiles". Following are the keyword and comment lines from each file in the testsuite for easy reference and location.

TEST01.DAT:
```
AM1 PRECISE GRAD GEO-OK LICENSE
Distorted Benzene for geom. opt. tests
BFGS LICENSE
```

TEST02.DAT:
```
AM1 PRECISE GRAD DFP GEO-OK
Distorted Benzene for geom. opt. tests
DFP
```

TEST03.DAT:
```
AM1 PRECISE GRAD POWELL
s-cis-1,3-butadiene
POWELL
```

TEST04.DAT:
```
AM1 PRECISE GRAD LTRD
s-cis-1,3-butadiene
LTRD
```

TEST05.DAT:
```
AM1 PRECISE GRAD GEO-OK
Distorted Benzene for geom. opt. tests
XYZ READ, BFGS OPTIMIZATION
```

TEST06.DAT:
```
AM1 PRECISE GRAD XYZ GEO-OK
Distorted Benzene for geom. opt. tests
BFGS/XYZ
```

TEST07.DAT:
```
MNDOC PRECISE GRAD GEO-OK
Distorted Benzene for geom. opt. tests
BFGS/MNDOC
```

TEST08.DAT:
```
AM1 PRECISE POWELL T=3595 GRAD BONDS
Conrotary cyclization TS
POWELL on TS
```

TEST09.DAT:
```
MINDO3 PREC GRAD
Ethane rotational barrier
MINDO3, reaction coordinate
```

TEST10.DAT:
```
AM1 PRECISE LTRD T=3595 GRAD BONDS
Conrotary cyclization TS
LTRD on TS
```

TEST11.DAT:
```
AM1 PRECISE NLLSQ T=3595 GRAD BONDS
Conrotary cyclization TS
NLLSQ on TS
```

TEST12.DAT:
```
AM1 PRECISE SIGMA T=3595 GRAD BONDS
Conrotary cyclization TS
SIGMA on TS
```

TEST13.DAT:
```
AM1 GNORM=10.00 GRAD GEO-OK
Distorted Benzene for geom. opt. tests
BFGS, GNORM
```

TEST14.DAT:
```
AM1 PREC FORCE T=3595 GRAD LET THERMO(298,298,0) TRANS=1 +
ROT=2
Conrotary cyclization TS
FORCE on TS, POOR STRUCTURE, two keyword lines
```

TEST15.DAT:
```
AM1 PRECISE FORCE print=4 +
T=3595 GRAD +
THERMO TRANS=1 ROT=2
Conrotary cyclization TS
FORCE on TS, preoptimized structure, three input lines
```

TEST16.DAT:
```
MNDO PREC GRAD BIRADICAL
Twist ethylene
MNDO BIRADICAL
```

TEST17.DAT:
```
MNDO PREC GRAD UHF TRIPLET
Twist ethylene
MNDO UHF TRIPLET
```

TEST18.DAT:
```
MNDO PREC GRAD UHF TRIPLET SPIN
Twist ethylene
MNDO UHF TRIPLET, SPIN
```

TEST19.DAT:
```
AM1 PRECISE GRAD ESR UHF
METHYL RADICAL
AM1 ESR
```

TEST20.DAT:
```
AM1 CHAIN CYCLES=1000 T=20000 PREC GRAD
ETHANE ROTATIONAL BARRIER
AM1 CHAIN
```

TEST21.DAT:
```
AM1 PRECISE GRAD ENPART DENSITY LOCALIZE VECTORS
Benzene
AM1 DENSITY ENPART LOCALIZE VECTORS
```

TEST22.DAT:
```
AM1 NOXY NOINT GNORM=0.1 T=50000 ANNE +
FILTER=1.  PEN2 LIMIT NCHECK=10
CYCLOHEXANE
```

```
            ANNEALING TEST, FLOPPY SYSTEM

TEST23.DAT: AM1 PRECISE GRAD EXCITED
            Benzene
            AM1 EXCITED

TEST24.DAT: AM1 PRECISE GRAD MECI C.I.=4 DERINU
            Benzene
            AM1 CI BY NUMERICAL DERIVATIVES

TEST25.DAT: AM1 PRECISE GRAD MECI C.I.=4
            Benzene
            AM1 CI BY ANALYTICAL DERIVATIVES

TEST26.DAT: AM1 PREC GRAD BONDS CHARGE=1
            METHANE CATION
            AM1 CHARGE

TEST27.DAT: AM1 PREC GRAD T=20000 STEP1=0.05 STEP2=0.05
            1,5-HEXADIENE INVERSION
            GRID

TEST28.DAT: AM1 PRECISE T=3595 GRAD T.V. IRC THERMO(298,298)
            Conrotary cyclization TS
            IRC

TEST29.DAT: SAM1 PRECISE GRAD GEO-OK
            Distorted Benzene for geom. opt. tests
            SAM1 BFGS

TEST30.DAT: SAM1 PRECISE GRAD MECI C.I.=4
            Benzene
            SAM1 CI

TEST31.DAT: AM1 PRECISE GRAD ISOTOPE FORCE LET
            s-cis-1,3-butadiene
            ISOTOPE FORCE

TEST32.DAT: AM1 BONDS PRECISE T=3000 DENMAT
            TRIQUINACENE
            DENMAT DUMP

TEST33.DAT: AM1 BONDS PRECISE T=3000 OLDMAT
            TRIQUINACENE
            OLDMAT PICKUP

TEST34.DAT: AM1 PRECISE GRAD DENOUT
            s-cis-1,3-butadiene
            AM1 DENOUT

TEST35.DAT: AM1 PRECISE GRAD OLDENS
            s-cis-1,3-butadiene
            AM1 OLDEN RESTART
```

TEST36.DAT: AM1 BONDS PRECISE T=300
TRIQUINACENE
restart, first run

TEST37.DAT: AM1 BONDS PRECISE T=300 RESTART
TRIQUINACENE
restart, SECOND run

TEST38.DAT: AM1 PRECISE PATH T=3595 GRAD T.V. WEIGHT
Conrotary cyclization TS
PATH

TEST39.DAT: AM1 PREC PULAY SHIFT=1000
Ethyl radical, proton exchange TS
AM1 PULAY SHIFT

TEST40.DAT: AM1 PREC CHARGE=2 SYMMETRY GRAD
WATER WITH TWO PARTIAL CHARGED SPARKLES
SPARKLES

TEST41.DAT: AM1 PRECISE GRAD GRAPH 1SCF
s-cis-1,3-butadiene
GRAPH 1SCF

TEST42.DAT: AM1 PREC GRAD BONDS ENPART
B2
AM1 WITH BORON, ENPART

TEST43.DAT: SAM1 PREC BONDS GRAD
CH3F
SAM1 HALOGENS(F)

TEST44.DAT: SAM1 PREC BONDS GRAD
CH3Cl
SAM1 HALOGENS(Cl)

TEST45.DAT: AM1 GNORM=0.1 PRECISE T=3500 NOINT NOXYZ ANNE +
LIMIT FILTER=1.0
METHYL-N-METHYL-AMIDE
ANNEALING, RIGID SYSTEM

TEST47.DAT: AM1 PREC POLAR
H2O
POLAR/SPARKLES

TEST48.DAT: AM1 PREC GRAD BONDS T=3600 CHARGE=2
WATER WITH A ++ SPARKLE
SPARKLES

TEST49.DAT: PM3 PRECISE GRAD GEO-OK
Distorted Benzene for geom. opt. tests
PM3 BFGS

TEST50.DAT: PM3 GRAD PREC T=3550

```
            GeBr2
            PM3 New Parameters
```

TEST51.DAT:
```
            AM1 PREC GRAD BONDS MULLIK NBO
            METHYLAMINE
            NBO MULLIK
```

TEST52.DAT:
```
            XYZ 1SCF ESP MNDO MMOK PRECISE CONNOLLY POTWRT
            Alanine
            ESP options
```

TEST53.DAT:
```
            MNDO GEO-OK PREC ESP SYMAVG
            methanol
            ESP
```

TEST54.DAT:
```
            MNDO 1SCF PRECISE ESP POTWRT SYMAVG
            Benzene
            ESP options
```

TEST55.DAT:
```
            SAM1 GNORM=1.00 PRECISE SYMMETRY
            h2odi (-5.0 H2O-DIMER, exp: H=-3.59(373K))
            dimer, SAM1
```

TEST56.DAT:
```
            AM1 SM2 DERINU PREC SYMMETRY TRUES HGAS=-7.283460 T=21000 +
            DEBUG ITER FLEPO PRINT=2
            ammonia
            AMSOL options
```

TEST57.DAT:
```
            DERINU SM3 CHARGE=-1 PM3 SYMMETRY PRECISE T=20000
            Acetate anion (Cs symmetry)
            AMSOL options
```

TEST58.DAT:
```
            AM1 TS PREC
            ETHANE ROTATIONAL BARRIER
            EF/TS
```

TEST59.DAT:
```
            AM1 SM2.1 DERINU PREC SYMMETRY TRUES HGAS=-7.283460 T=21000 +
            DEBUG ITER FLEPO PRINT=2
            Ammonia
            AMSOL options
```

TEST60.DAT:
```
            AM1 PRECISE TS MODE=5 RECALC=1
            MeNC to MeCN TS, following mode #5
            EF/TS options
```

TEST61.DAT:
```
            AM1 PREC KPOLAR
            H2O
            KPOLAR
```

GLOSSARY

AM1	-	*Austin Model 1*
HOMO	-	*Highest Occupied Molecular Orbital*
LUMO	-	*Lowest Unoccupied Molecular Orbital*
MERP, MEP	-	*Minimum Energy Reaction Pathway*
MINDO3	-	*Modified Intermediate Neglect of Differential Overlap, V. 3*
MO	-	*Molecular Orbital*
MM	-	*Molecular Mechanics*
NBO	-	*Natural Bond Orbital Population Analysis*
NDDO	-	*Neglect of Diatomic Differential Overlap*
PES	-	*Potential Energy Surface.*
PM3	-	*Parameterization Model 3*
SAM1	-	*Semi-ab initio Method Version 1*
SMx	-	*Solvation Model x*
TERI	-	*Two Electron Repulsion Integral*
TS	-	*Transition State*

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