THE STRUCTURAL CHEMISTRY OF CHOLINERGIC NEURAL TRANSMISSION SYSTEMS

by

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Abstract

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The results of INDO molecular orbital calculations on the molecular geometries and electronic structures of acetylcholine, choline, muscarine, nicotine, acetyl-α-methylcholine, acetyl-β-methylcholine and acetyl-α,β-dimethylcholine[1,2,3,4] are presented. The conformations predicted to be preferred in the free space approximation are discussed in terms of intramolecular interactions, and the calculated potential energy surfaces and electronic charge distributions for each compound are considered in terms of crystallographic, spectroscopic and bio-assay data. Local minima in the potential energy surfaces can be identified with crystal geometries, the geometries implicated in muscarinic and nicotinic neural transmission systems, and the geometry favorable for hydrolysis by acetylcholinesterase. A total consideration of the above results in a biological perspective, and a critical evaluation of the current theories of cholinergic action are presented.

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A. Introduction:

A.1 Objectives. It is the aim of this study to characterize as fully as possible the structural chemistry of acetylcholine (Ach) and a series of its congeners through use of self consistent field (SCF) molecular orbital theory (MOT) at the intermediate neglect of differential overlap (INDO) level of approximation. This work involves the systematic calculation of expectation values for total energy and atomic charge densities as functions of atomic internal displacement coordinates. The potential energies calculated in the free space approximation are used to construct surfaces of conformational energy, and detailed considerations of charge density as a function of conformation are carried out in order that they might provide theoretical evidence for the nature of stabilizing intramolecular interactions. Consideration of theoretical evidence for such interactions is facilitated through the reduction of the expression for total energy into monoatomic and diatomic contributions, (energy breakup). Evaluation is made of the similarities and differences in the above results for selected cholinergic compounds, and the relationship between these results and results reported from x-ray crystallography, molecular spectroscopy and molecular pharmacology is fully developed. Current thought concerning the role of structure and conformation in cholinergic action is developed in the context of accumulated data.

A.2 Background. The transmission of information in neural systems involves the passage of impulses of electrical current throughout a network of nerve cells (neurons). When the membrane potential of a neuron is decreased below a critical level, an action potential mechanism is triggered. The action potential sweeps along the axonal fiber and invades the terminal region of the cell. For impulse propagation, the excitation must then be transferred across the synapse to the next cells in sequence, be they other neurons or operator cells such as those of smooth or striated muscle. In many nervous transmission systems, this transfer is mediated by the liberation of acetylcholine, which according to currently accepted theory[5] interacts with specific receptor sites[6]; the exact sequence of events is still an area of active research. This interaction effects a structural reorganization of the post-synaptic membrane, resulting in an increased ionic permeability. The influx, particularly of sodium ions, depresses the membrane potential below the critical level and initiates an action potential, thereby transmitting the nerve impulse. Acetylcholine is rapidly removed from the synaptic region by an enzyme-catalyzed hydrolysis, allowing the entire process to be repeated at a rate of several hundred times a second for brief periods.

The spatial conformation and electronic structural characteristics of acetylcholine in neurohumoral transmission are specifically complementary to some yet unelucidated structural entity incorporated in the post-synaptic membrane. A number of neurochemically active substances appear to function by adopting geometries and electronic charge distributions resembling those of acetylcholine, and interacting with acetylcholine receptors. Cholinergic receptors have traditionally been characterized

on the bases of the biological activities of these structural analogs of acetylcholine. Data accumulated in this regard make possible a rough differentiation of acetylcholine receptors into two types: muscarinic, where the action of acetylcholine is mimicked by muscarine and blocked by atropine, and nicotinic, where the action of acetylcholine is mimicked by nicotine and inhibited by curare and hexamethonium.[7,8] Further classification is no doubt possible since nicotinic receptors in motor endplates and ganglia are preferentially blocked by different methonium compounds,[5] and some receptors considered nicotinic are not necessarily activated by nicotine.[9] The evidence with regard to polyfunctional active sites complicates matters still further.[10] Nevertheless, the muscarinic/nicotinic terminology is in wide clinical use, and the molecular structural basis of this differentiation, and of the enzymatic hydrolysis of cholinergic substances by the cholinesterases is of considerable importance in molecular pharmacology.

An understanding of all types of cholinergic neural transmission systems, clearly, requires a detailed knowledge of the molecular electronic structural properties of acetylcholine. For future reference the molecular geometry of acetylcholine can be specified in terms of the four dihedral angles: τ(C5-C4-N-C3), τ(O1-C5-C4-N), τ(C6-O1-C5-C4) and τ(O2-C6-O1-C5), defined with respect to the numbering system given in Fig. 1. In the crystal structures of a large number of Ach analogs, the coordinates τ(C5-C4-N-C3) and τ(O2-C6-O1-C5) are observed to be antiplanar and symplanar respectively.[8] Interesting variations are found in τ(O1-C5-C4-N), which positions the ester oxygen with respect to the trimethylammonium cationic head, and in τ(C6-O1-C5-C4), which positions the acetate moiety with respect to the choline group.

The crystal structure of acetylcholine bromide has been investigated by Canepa, Pauling and Sörum[11] following up earlier work by Sörum;[12] the geometry reported is shown in Fig. 1. The C5-C4-N-C3 sequence of atoms does form an antiplanar extended chain, τ(C5-C4-N-C3) = 180°, as expected on the basis of steric factors. The acetoxy group is planar with τ(O2-C6-O1-C5) = 0°, presumably stabilized by the partial double bond character of the C6-O1 bond. Since no large variation in τ(C5-C4-N-C3) or τ(O2-C6-O1-C5) is observed over the crystal geometries of a number of Ach's structural analogs,[8] specification of the geometry of Ach in terms of τ(O1-C5-C4-N) and τ(C6-O1-C5-C4) is sufficient to characterize the three dimensional molecular structure. In the geometry reported for acetylcholine bromide, τ(O1-C5-C4-N) = 77° and τ(C6-O1-C5-C4) = 79°, henceforth denoted as {77°,79°}. The structure of acetylcholine chloride was reported by Herdklotz and Sass[13] as (Fig.2) {85°,-168°}. The nature of the forces stabilizing τ(O1-C5-C4-N) in a synclinal conformation is of considerable interest, since an antiplanar form would be favored from purely steric considerations. The possibility of intramolecular N-C-H ··· O hydrogen bonding in this structure was originally suggested by Sutor[14] based on the proximity of the trimethylammonium hydrogens and ester oxygen. A number of laboratory investigations have been directed toward gaining infrared spectroscopic evidence with regard to intramolecular hydrogen bonding.[15] No strong supportive data have been reported,but the collected results[16] are not inconsistant with such interactions. Culvenor and Ham report nuclear magnetic resonance spin coupling evidence that a synclinal conformation of τ(O1-C5-C4-N) persists in aqueous solution as well as in the crystalline solids, but specific intramolecular hydrogen bonding was unresolvable.[17] In a lively review, Donahue discounts collected evidence for intramolecular C-H···O hydrogen bonding on the grounds

that unequivocally observed C-H···O distances are not appreciably less than the expected van der Waals contact distance of 2.5-2.6Å.

Theoretical calculations of the conformational stability of acetylcholine have been reported by Liquori, Damiani and de Coen using[18] pairwise interaction potential functions and by Kier using extended[19] Hückel molecular orbital theory (EHT). Four energy minima in a four dimensional potential energy hypersurface were found in the Liquori et al. analysis; two minima involve antiplanar conformations of τ(O1-C5-C4-N) and two favor synclinal conformations around this coordinate. EHT gives a positive synclinal τ(O1-C5-C4-N) of 80°.

The angle τ(C6-O1-C5-C4) specifies the orientation of the acetoxy group with respect to the rest of the molecule. This angle establishes another geometrical parameter important for biological activity: the distance between the trimethylammonium cationic head and the electronegative carbonyl oxygen atom. Early studies of Ach and related compounds[20] established this distance as ca. 4.5Å; this played a key role in the design of a drug (pyridine-2-aldoxime methiodide, PAM) to interact with the acetylcholine receptor on acetylcholinesterase. PAM is now used clinically to treat alkyl fluorophosphate poisoning.

In crystalline acetylcholine bromide with τ(C6-O1-C5-C4) at 79°, the acetoxy group is folded around toward the cationic head. For acetylcholine in solution, infrared spectral studies of the carbonyl vibrational frequency of acetylcholine and related compounds have been reported,[15] but the structural implications are inconclusive. The nmr spectral data for acetylcholine in D_2O[16] support an antiplanar conformation, as normally expected for a primary ester. Two of the four minima on the Liquori energy surface[18] correspond to antiplanar

τ(C6-O1-C5-C4) as does the geometry reported for EHT calculations.

Most recently, the investigation of conformational aspects of acetylcholine has focused on the coordinate τ(O1-C5-C4-N). Subsequent to the Culvenor and Ham[16] study, methylene proton spin coupling analyses of nmr spectra of acetylcholine have been reported by Cushley and Mautner,[21] Casy, Hassan and Wu,[22] Inch, Chittenden and Dean,[23] and Partington, Feeney and Burgen.[24] There is unamimous agreement that τ(O1-C5-C4-N) is synclinal in aqueous solution. The detailed analysis of Partington et al. shows the system exclusively with this orientation. Casy et al.[22] report synclinal values of τ(O1-C5-C4-N) for a range of solvents, with chloroform the least polar. They concluded that the energetically preferred conformation on this coordinate was established by intramolecular interactions.

Muscarine and nicotine each have recognizable analogs of τ(O1-C5-C4-N) and τ(C6-O1-C5-C4) with asymetrically substituted atoms imparting a possible degree of stereospecificity. The active form of muscarine was determined by Waser[25] to be the C6(S),C9(R),C5(S) isomer shown in Fig. 3. The crystal geometry for this isomer as determined by Jellinek[26] corresponds to $\{74^{\circ},144^{\circ}\}$. For nicotine, the naturally occuring 2(S) isomer has been demonstrated by Barlow and Hamilton[27] to be more active than the 2(R) form, but the difference in activity depended somewhat on the preparation. The crystal structure of nicotine-1(R), 2(S)-dihydroiodide as determined by Koo and Kim,[28] and given in Fig. 4, corresponds to the $\{-60^{\circ},180^{\circ}\}$ geometry. Theoretical calculations on muscarine have been described by Liquori[29] using empirical classical energy calculations,[19] and for muscarine and nicotine by Kier and Pullman[30] using molecular quantum mechanics.

Many other cholinergic substances bear obvious structural similarities to Ach and usually have clearly defined analogs of τ(O1-C5-C4-N) and τ(C6-O1-C5-C4). Recent papers dealing with the structural basis of cholinergic action are due to Kier,[31] Pauling, Chothia and coworkers,[32,33] and Beers and Reich;[34] the area has recently been reviewed by Shefter.[35] The proposed theories differ mainly in relative emphasis on functional groups and molecular conformation. The trimethylammonium group is generally accepted as a primary effector in both muscarinic and nicotinic action. The ideas that the ester oxygen of Ach (or its equivalent in a structural analog) figures in muscarinic activity whereas the carbonyl oxygen of Ach or its equivalent is pertinent to nicotinic action are evident in early work in this area.[5,19,31] Kier studied the role of conformation by comparing the molecular structure of Ach with muscarine, muscarone and nicotine. He proposed that the geometry of Ach at nicotinic receptors differs from that at muscarinic receptors, and appears to implicate the Ach carbonyl oxygen in muscarinic activity. From Fig. 4 of Ref. 31, his muscarinic conformer appears to be {-sc,ap} with τ(O2-C6-O1-C5) = 0°; his nicotinic Ach conformer, Fig. 12 of Ref. 31, is {-sc,ap} with τ(O2-C6-O1-C5) = -90°.

Chothia and Pauling[33] correlated the crystal structure analyses of six nicotinic agonists and proposed the Ach geometry implicated in nicotinic action to be {75°,180°}. Baker, Chothia, Pauling and Petcher[32] considered ten muscarinic agonists of varying potency, and concluded that the Ach geometry complementary to muscarinic receptors was {85°,150°}. The acetate methyl group but not the carbonyl oxygen was implicated in the muscarinic pharmacophore. The resonance energy stabilizing a synplanar orientation of τ(O2-C6-O1-C5) was presented as 24 kcal/mol, which would preclude the geometry proposed by Kier for

the nicotinic pharmacophore. Earlier Chothia,[36] reasoning from the observation that the muscarinic and nicotinic Ach geometries were nearly the same, identified the side of Ach having the cationic head, acetate methyl group and ester oxygen on the periphery with muscarinic action, and the side with the cationic head and carbonyl oxygen on the periphery with nicotinic activity. The basis for these conclusions rested on the blocking actions of C4 and C5 substituents, which presumably interfere with the agonist-receptor interaction. Related studies by Chothia and Pauling[37] describe collected evidence that a $\{150^\circ, 180^\circ\}$ geometry is optimal for the hydrolysis of Ach by acetylcholinesterase,[38] consistent with the model proposed by Krupka and Laidler.[34]

Beers and Reich presented structural correlations of twelve muscarinics and eight nicotinics in support of the role of the cationic head and ester oxygen in muscarinic action, and the cationic head and carbonyl oxygen in nicotinic action. The presence of the acetate methyl group or its equivalent was not necessary for muscarinic action, but when present seemed to potentiate the effect. No role for a carbonyl oxygen in muscarinic action was indicated. The correlations were based on possible conformations deduced from molecular models, rather than from consideration of experimentally observed or calculated preferred structures.

Studies by Smissman et al.[80] on rigid ring analogs of acetylcholine and other cholinergic substances implicate an antiplanar τ(O1-C5-C4-N) in muscarinic activity.

Of all the cholinergic substances considered in the correlations described above, the compounds most closely related to Ach but with more specific activities are the α and β methyl and dimethyl Ach derivatives.

Considerable structural information is available on each compound. In addition, this set of compounds includes significant possible exceptions to each of the theories previously described. The methyl and dimethyl derivatives of Ach figure significantly in current structural theories of cholinergic action; but the actual roles of the α and β methyl groups are not clearly established. There are several mechanisms by which a change such as addition of a substituent methyl group to a neurotransmitter may influence its biological activity. The substituent may sterically prevent the compound from accessing a biologically active conformation which properly orients the functional groups, or electronically influence the position of preferred conformations. Alternatively, the substituent group may conceivably cause a charge redistribution on functional groups leading to either enhancement or decrease in biological activity. Finally, it is possible for substituent groups to have direct bonded or non-bonded interactions with biological receptors. Such interactions might be of a steric, hydrophobic or electrostatic nature, and might enhance or diminish biological activity.

The crystal structure analysis of acetyl-α(R)-methylcholine by Chothia and Pauling[39] revealed two polymorphic forms, $\{90^\circ, 170^\circ\}$ and $\{212^\circ, 176^\circ\}$. In Chothia's theory[36] the α(R) substituent blocks the methyl(muscarinic) side, leaving the nicotinic side available. Acetyl-α(R)-methylcholine is indeed a nicotinic agonist, but according to Lesser[9] so is acetyl-α(S)-methylcholine, wherein the carbonyl (nicotinic) side of Ach would be at least partially blocked. The active enantiomer of the β-methyl derivative as determined by Ellenbroek and van Rossum[40] and Beckett, Harper and Clitherow[41] is

acetyl-β(S)-methylcholine, which Chothia and Pauling[42] have found to be in the $\{85°, 203°\}$ conformation in the crystalline solid. Beckett et al.[43] observed that the β(R) derivative is not hydrolyzed by acetylcholinesterase, and inferred that a positive orientation of τ(O1-C5-C4-N) is complementary to the cholinesterase receptor; this is not inconsistant with the (+)-antiperiplanar form proposed by Pauling and Chothia. Casy, Hassan and Wu[22] presented nuclear magnetic resonance data showing that a $\{sc, ap\}$ conformation of acetyl-β-methylcholine in solution, while a lack of conformational preference was reported for τ(O1-C5-C4-N) in acetyl-α-methylcholine.

The pharmacological properties of erythro and threo dimethylacetylcholine have been studied by Smissman, Nelson, LaPidus, and Day.[44] The erythro($\pm$) derivative has 10% the muscarinic activity of Ach, and is negligibly hydrolyzed by cholinesterase, whereas the threo($\pm$) derivative shows negligible muscarinic activity and 10% the hydrolysis rate of Ach. The crystallography of erythro-α(S),β(R)- and threo-α(R),α(R)-dimethylacetylcholine was determined to be $\{284°, 155°\}$ and $\{217°, 95°\}$ respectively.[45] Shefter[35] tested the Chothia theory with these compounds and pointed out that whereas the muscarinic side would be predicted to be blocked in erythro-α(R), β(S)-dimethylacetylcholine and open in threo-α(S),β(S)-dimethylacetylcholine, the erythro isomer is observed to be a more potent muscarinic agonist. All of the methyl and dimethyl derivatives possess the functional groups necessary for dual muscarinic and nicotinic action along the lines described by Beers and Reich;[34] the observed specificity indicates that these conditions can be necessary but not sufficient for agonist action.

Conformational energy maps as functions of τ(O1-C5-C4-N) and τ(C6-O1-C5-C4) for acetyl-α-methylcholine, acetyl-β-methylcholine, and acetyl-α,β-dimethylcholine as well as for Ach itself have recently been contributed by Pullman et al.[46,47] using the PCILO-CNDO method. These studies as well as the recent theoretical calculations on Ach by Ajo et al.[48] and Froimowitz and Gans[49] using pairwise potential functions, and by Genson and Cristofferson[50] and Port and Pullman[51] using non-empirical theoretical methods will be discussed with the presentation of the INDO results.

A.3 Rationale. As described in the preceding section, the relationship for cholinergic agonists between structure, conformation and biological activity has been studied through means of x-ray crystallography, molecular spectroscopy, molecular quantum mechanics and bio-assay techniques. At the outset of the thesis research described herein, however, the stabilization of τ(O1-C5-C4-N) in cholinergic compounds was incompletely understood, and several geometries for Ach and cholinergic agonists were implicated in the crystalline solid, solution and in the theoretical free space approximation. Thus a total energy minimization of Ach as a function of conformation was in order. The aim here was to locate energy minima in the surface, to develop an understanding of the minima in terms of structural forces, and to consider the relationship between the calculated minima and molecular geometries considered in experimental studies.

Examination of Fig. 1 shows that if bond lengths and angles for heavy atoms are directly adopted from crystallographic data, and if hydrogen bond lengths and angles are assumed to be standard, conformational designation of Ach reduces to an 8 parameter problem: τ(C5-C4-N-C3), τ(O1-C5-C4-N), τ(C6-O1-C5-C4), τ(O2-C6-O1-C5) and the four dihedral angles which position the methyl hydrogens of the acetate and trimethylammonium groups. It has been noted in the preceding section that τ(C5-C4-N-C3) and τ(O2-C6-O1-C5) can be taken to be antiplanar and synplanar respectively, based upon the crystallographic results on a large number of cholinergic compounds.[8] The validity of these assumptions are readily confirmed by INDO MOT.[3] The methyl hydrogens are expected to be freely rotating in a biological solution but should be positioned at a minimum energy configuration for input

to the INDO wavefunction routine. This configuration of methyl hydrogens can be determined through study of Ach and model compounds such as tetramethylammonium (TMA) and choline.[2] Thus with six parameters fixed, a total energy minimization of Ach reduces to a consideration of τ(O1-C5-C4-N) and τ(C6-O1-C5-C4). Accordingly the INDO potential energy surface of Ach as a function of τ(O1-C5-C4-N) and τ(C6-O1-C5-C4) was generated.[1,3] Accumulated data were studied both in terms of basic stereochemical principles, and the conformations of Ach proposed to be active at cholinergic receptors. Further characterization of the nature of the intramolecular forces stabilizing a gauche conformation of the cholinergic O-C-C-N group is developed through study of the model compound choline with an energy breakup.[2]

With the molecular electronic structure of acetylcholine well characterized on a theoretical basis, the next logical step in an approach to a comprehensive theoretical treatment of cholinergic neural transmission systems involves a systematic study of the potential energy surfaces and electronic structures of nicotinic and muscarinic substances at a comparable level of approximation, and a detailed consideration of the similarities and differences between energetically preferred conformations of cholinergic substances and those found for acetylcholine. The α and β methyl derivatives of Ach are of particular interest in this regard, and thus are subjected to systematic study in terms of conformational energy and atomic charge densities.[3] The structural similarities and differences of these muscarinic and nicotinic substances should manifest themselves naturally from this approach, and the energetically preferred conformations should match with the analogous local minima on the Ach potential surface. Theories currently offered on the

structural chemistry of cholinergic action may be constructively criticized on this basis, and reorganized to a more comprehensive form.

B. Specific Aims:

The specific aims of this study are as follows:

1. The quantum theoretical calculation of Ach's τ(O1-C5-C4-N) vs. τ(C6-O1-C5-C4) potential energy surface and molecular electronic structure using approximate SCF MOT including all valence electrons.
   a. Methyl hydrogens are positioned through preliminary calculations on Ach, choline and TMA.
   b. The symplanar orientation of τ(O2-C6-O1-C5) is confirmed through calculation of a preliminary INDO potential energy surface as a function of τ(O2-C6-O1-C5) and τ(C6-O1-C5-C4), (τ(O1-C5-C4-N) is held antiplanar).

2. Consideration of the above results in terms of basic stereochemical principles, and specific evaluation of intramolecular interactions which stabilize the gauche orientation of the O-C-C-N group in the model cholinergic compound choline. The latter is accomplished through use of an energy breakup.

3. The calculation of potential energy surfaces and profiles, and atomic charge densities analogous to those generated for Ach for the compounds:
   muscarine
   nicotine
   acetyl-α-methylcholine
   acetyl-β-methylcholine
   erythro-α,β-dimethylacetylcholine
   threo-α,β-dimethylacetylcholine.

4. The computerized plotting of the potential energy surfaces for accurate presentation and location of minima, and the computerized stereographic display of energetically preferred conformations of each substance under consideration..

5. A detailed development of the relationship between the results of the quantum theoretical calculations and results reported from x-ray crystallography and molecular spectroscopy for each molecule.

6. A detailed comparison and correlation of energetically preferred conformations of the muscarinic compounds, the nicotinic compounds, and of the preferred muscarinic and nicotinic conformations with Ach conformations corresponding to minima on the Ach potential energy surface.

7. Total consideration of the above results in a biological perspective and a critical evaluation and reconsideration of current theories of the structural chemistry of cholinergic action.

C. Methods and Theory:

The calculation of a potential energy surface for a molecule involves the calculation of the total energy of the system as a function of internal atomic displacement coordinates. In quantum mechanical systems, the energy is an expectation value of of the Hamiltonian operator and molecular wavefunction, and thus a calculation of the wavefunction at a number of points in configuration space is required. For the Hamiltonian operator H and molecular wavefunction Ψ energy is given as

$$E = \int \Psi_H \Psi \, d\tau \tag{1}$$

Molecular wavefunctions computed in this research are based on spin-restricted molecular orbital theory, with the 2n-electron wave function ψ considered as a Slater determinant of the molecular orbitals ψ_i

$$\Psi = |\psi_1(1)\bar{\psi}_1(2)\psi_2(3)\bar{\psi}_2(4)\cdots\psi_n(2n-1)\bar{\psi}_n(2n)| \tag{2}$$

The molecular orbitals are individually expanded as linear combinations of atomic orbitals (LCAO) ϕ_μ centered on constituent atoms

$$\psi_i = \sum_\mu c_{\mu i}\phi_\mu \tag{3}$$

where the $c_{\mu i}$ are linear expansion coefficients. The calculation of the molecular wavefunction reduces to the determination of the coefficients by matrix Hartree-Fock self-consistent field procedures.[52] The total energy of the system at a given geometry is given by the expression

$$E = \sum\sum_{\mu\nu} P_{\mu\nu}(H_{\mu\nu} + G_{\mu\nu}) + \sum_{A<B} Z_A Z_B R_{AB}^{-1} \tag{4}$$

where the summations over greek and latin letters refer to orbitals and atoms respectively. The first term on the right hand side of equation 4 is the electronic energy of the system and involves $H_{\mu\gamma}$, the one-electron matrix elements between atomic orbitals ϕ_μ and ϕ_γ, and is representative of the kinetic and nuclear attraction operators. The $G_{\mu\gamma}$ are elements of the matrix representative of electron repulsion operators. The density matrix elements $P_{\mu\gamma}$ are defined in terms of the LCAO coefficients as

$$P_{\mu\gamma} = 2\sum_{i}^{n} c_{\mu i} c_{\gamma i} \qquad (5)$$

and specify the distribution of electronic charge in the system. The second term on the right side of equation 4 accounts for internuclear repulsions, and involves the core charges Z_A, Z_B and the internuclear separation between atoms A and B, R_{AB}.

Theoretical studies of neurotransmitter structure have used methods ranging from empirical pairwise potential functions to a variety of approaches based on molecular quantum mechanics. The quantum mechanical methods currently being used treat σ and π electrons explicitly, and fall into four basic categories: approximate independent molecular orbital theory, approximate self consistent field molecular orbital theory, approximate configurational interaction (CI) methods and ab initio SCF-MO methods.

In calculating electronic wavefunctions, one considers simultaneously the attractive between electrons and atomic nuclei of a molecule and the interelectron repulsions in the framework of molecular orbital theory. However, the size of the mathematical problem goes up as least as N^4, where N is the number of electrons.

Thus for large bio-organic molecules the calculation of precise wavefunctions is beyond the time limitations of our present generation of computers. In view of this, considerable effort has been devoted to developing molecular orbital methods capable of treating large organic and bio-organic molecules with sufficient accuracy to provide the information necessary for the treatment of scientific problems in chemistry and molecular biology.[53] The quantum mechanical methods which are currently being used are mentioned above, and these methods as well as those used in early work are discussed in the following paragraphs.

Approximate molecular orbital theories began with methods limited to pi-electrons of unsaturated molecules such as in Hückel theory,[54] which has been extensively applied to problems in biochemistry by Pullman and collaborators.[55] Methods of this type have often been criticized on the grounds of giving too many approximations to to be a basis for reliable theory, since inter-electron repulsions are neglected. A more refined approach to pi-electron theory including inter-electron repulsion in a self-consistent field manner was introduced by Pariser, Parr and Pople[56] and has been highly successful in accounting especially for the wavelengths of electron absorption bands in ultraviolet spectra. The consideration of all chemically effective electrons in a molecule in approximate molecular orbital theory was developed in the form of Extended Hückel Theory by Hoffman[57] but is subject to criticism with regard to inter-electron repulsions, just as was simple Hückel theory. EHT falls into the category of approximate independent electron molecular orbital theory and has been widely used by Hoffman[58] in innovative studies of organic reaction mechanisms. The quantitative application of this method to conformational

problems has proved less successful, with bond lengths sometimes unreliable, and bond angles and dihedral angles giving some reasonable agreement with experiment in certain systems. The well known limitations of independent electron molecular orbital theory in treating heteroatomic systems is a special disadvantage for neurotransmitter structures, as evidenced in the molecular electronic charge distributions computed using EHT.[19]

Self-consistent field molecular orbital theory has provided a framework for the development of a series of approximate methods for theoretical studies of polyatomic molecules. The principle approximations are the neglect of differential overlap in two-electron repulsion integrals, and a semi-empirical parameterization of certain one electron integrals. Valence electron SCF theories involving complete neglect of differential overlap (CNDO) and intermediate neglect of differential overlap (INDO), where differential overlap is neglected only in polycentric electron repulsion integrals were developed by Pople, Segal, Santry, Beveridge and Dobosh, and parameterized for elements of the first row of the periodic table.[59,60] Generally these methods produce good electronic charge distributions as evidenced by the agreement between theory and experiment for electric dipole moments,[53] and they are among the best approximate molecular orbital methods currently available for treating large organic and bio-organic molecules. Bond lengths and angles are reasonably well accomodated, with certain exceptions.[53] The agreement between theory and experiment to be expected for rotational barriers and dihedral angles has been well documented.[61] The methods have shown success tempered with significant inadequacies, such as failure to reproduce the planar geometry of unsaturated polyenic hydrocarbons.[62] Bond ionization

excitation energies are poorly reproduced by INDO and CNDO,[53] but a modification of INDO due to Dewar (MINDO)[63] has proved to accomodate bond energies and ionization energies.[64] Jaffe and del Bene have reworked the CNDO method for excitation energies. Extension of the methodology to second row elements and transition metals has proved to be quite complicated, although some progress has been recently achieved.[65,66]

An alternative approach to the quantum mechanical calculation of conformational energy is the PCILO method,[67] where the energy is developed using perturbative configuration interaction methods on a localized molecular orbital basis. A wide range of applications of the PCILO method to biological molecules has been reported by Pullman and coworkers,[68] using atomic integrals evaluated in the CNDO approximation. This approach has some basic theoretical and technical advantages for conformational problems, since with the purturbation expansion carried to third order some representation of electron correlation is introduced, and since there is no iterative matrix eigenvalue problem to solve, the calculations are relatively fast even for large molecules. Energy variation with respect to dihedral angles in PCILO/CNDO calculations is significantly less than that for SCF/CNDO calculations due to a natural tendency of configuration interaction to depress higher energy regions relatively more than lower energy regions, and rotational barriers may be too low. The PCILO localized orbital basis may be designed using basic chemical intuition, and as chosen appears to correct for tendencies in the approximate SCF methods to overestimate intramolecular effects such as hydrogen bonding.

Molecules the size of chemical neurotransmitters are just coming within the reach of ab initio molecular quantum mechanical calculations. The molecular fragments approach of Christofferson,[50,69] and ab initio SCF MO calculations (Port and Pullman)[51] have been applied to acetylcholine.

With modest amounts of computer time available, however, molecular orbital theory with atomic integrals evaluated at the INDO level of approximation does provide a quantum mechnanical computational vantage point tractable for extensive calculation of conformational energy maps of molecules of the size considered herein.

Using the INDO method, the total energy of the system is calculated using equation 4 with the appropriate integral approximations included. The net electrical charges Δq_A associated with each of the atoms A in the molecule is given by

$$\Delta q_A = Z_A - \sum_{\mu}^{A} P_{\mu\mu} \tag{6}$$

where the summation includes all $P_{\mu\mu}$ for orbitals centered on atom A. The electric dipole moment $\underset{\sim}{\mu}$ at the INDO level is given by the expression

$$\underset{\sim}{\mu} = \underset{\sim}{\mu}_{chg} + \underset{\sim}{\mu}_{hyb} \tag{7}$$

where

$$\underset{\sim}{\mu}_{chg} = 2.546 \sum_{A} \Delta P_{AA} \underset{\sim}{R}_A \tag{8}$$

and, e.g.

$$(\mu_{hyb})_x = -14.674 \sum_{A(\neq H)} \zeta_A^{-1} P_{2S_A 2P_{XA}} \tag{9}$$

where ζ is the orbital exponent of the orbitals centered on atom A.

In computing conformational stability, the total energy E is calculated as a function of the appropriate internal displacement coordinates, and the calculated energy E can be partitioned into monoatomic and diatomic contributions E_A and E_{AB} respectively such that[70]

$$E = \sum_A E_A + \sum_{A<B} E_{AB} \tag{10}$$

and the variation of individual terms examined separately. The expressions for E_A and E_{AB} are:

$$\begin{aligned} E_A = \sum_{\mu}^{A} P_{\mu\mu} \; [\; & 2U_{\mu\mu} + .25P_{SS}F^\circ + P_{SS}(P_{SX}+P_{SY}+P_{SZ})(F^\circ - .167G^1) \\ & + .5(P_{XX}^2+P_{YY}^2+P_{ZZ}^2)(.5F^\circ+(4/50)F^2)+2(P_{XX}P_{YY}+P_{XX}P_{ZZ}+P_{YY}P_{ZZ})(F^\circ-7F^2) \\ & + .5(P_{SX}^2+P_{SY}^2+P_{SZ}^2)(G^1-F^\circ)+(P_{XY}^2+P_{XZ}^2+P_{YZ}^2)((11/50)F^2-(1/2)F^\circ) \;] \end{aligned} \tag{11}$$

$$\begin{aligned} E_{AB} = \sum_{\mu}^{A}\sum_{\gamma}^{B} & P_{\mu\gamma}[(\beta_A^\circ+\beta_B^\circ)S_{\mu\gamma}-(1/2)P_{\mu\gamma}\gamma_{AB}] \\ & + (1/2)[P_{AA}(P_{BB}-2Z_B)+P_{BB}(P_{AA}-2Z_A)]\delta_{AB} \end{aligned} \tag{12}$$

where $U_{\mu\mu}$ is a monoatomic core integral; F^0, F^2 and G^1 are Slater-Condon notation for one-center radial atomic integrals; γ_{AB} is a two center repulsion integral; β_A° and β_B° are bonding parameters; and $S_{\mu\gamma}$ is an overlap between atomic orbitals ϕ_μ and ϕ_γ. Values for these quantities are assigned as described in Ref. 53. Elucidation of the factors responsible for the conformational stability of the gauche O-C-C-N^+ grouping is approached by examining the variation in E and individual E_A and E_{AB} for choline and norcholine as a function of τ(O1-C5-C4-N). A significant variation in an E_A term may be ascribed to charge redistribution and rehybridization effects, while a variation in E_{AB} signals a change in bonding.

The fortran routines which have the capability of performing SCF-MO calculations at the INDO level of approximation require as input total molecular charge, indication if the calculation is to be carried out in the ground state or an excited state (ground state for all calculations presented herein), and atomic number and cartesian coordinates for each atom in the molecule. Once these data are provided, the INDO wavefunction and the properties calculatable therefrom are uniquely defined, and thus are obtainable through an automatic computational procedure. This system is conveniently interfaced with the model builder system (SUBROUTINE ZMAT in Appendix C) which accepts as input intramolecular bond lengths and angles, and four atom torsions, and generates cartesian coordinates in an arbitrary frame. Thus the completion of INDO calculations reduces to a problem of geometrical input. For the calculations presented herein, great value has been placed upon the results of crystal structure determinations for input. Although this approach has possible limitations, it has the advantage

of keeping the input to the MO calculation well in contact with physical reality, and obviates the extensive preliminary setting of numerous geometrical parameters. A fortran routine XTAL was specifically developed for convenient workup of crystallographic data. A part of this program frequently employed in the work presented herein is SUBROUTINE UNZMAT which accepts cartesian coordinates (derived directly from the crystal unit cell) and generates input to model builder. A listing of XTAL is presented in Appendix A.

Intramolecular steric interactions have the capability of significantly influencing INDO calculated potential energy surfaces. Thus it is advantageous to have access to a computationally inexpensive method of evaluating intramolecular steric interactions before the relatively more expensive MO calculations are undertaken. Accordingly a routine SZMAT was developed which accepts input to model builder, and also parameters for systematic incrementing of crucial bond lengths or angles, or more frequently, four atom torsions. The routine preserves on peripheral storage devices the interatomic distance arrays of all pairs of atoms which anywhere in the conformations considered have an interatomic distance of less than 3Å. Toward completion of the routine these arrays are printed with a summary steric grid which clearly defines sterically permitted and forbidden regions in conformational space. These steric grids can have significant correlation with INDO calculated potential energy surfaces. A listing of SZMAT is provided in Appendix B.

During the course of thesis research modifications were inserted into the INDO routines which reduced the requirement for computer central memory from $57{,}000_{10}$ 60 bit words to $16{,}000_{10}$ 60 bit words, (for 35 atoms and 80 basis functions). This was

effected by use of peripheral devices for storing the core hamiltonian, and other coding changes. The smaller version does not require significantly greater amounts of computer time than the original routine, and is presented in Appendix C.

Data acquired in the course of quantum mechanical calculations as described above must be reduced to a form suitable for developing a detailed understanding of each individual system and for cross-comparison of each system with others. In this regard, extensive use is made of computer graphics for display of potential energy surfaces and conformations of molecules. Here reliance is placed on two programs: CONSURF and ORTEP.

CONSURF is a fortran program for graphic display of contour lines representative of a function of two variables. This routine is used to contour potential energy surfaces as functions of atomic internal displacement coordinates. An example of CONSURF output is presented in Fig. 8 .

ORTEP is a modification of the fortran coded Oak Ridge Thermal Ellipsoid Plot program which was developed by C.K. Johnson.[72] This routine provides for automatic drawing of molecular geometries on an incremental plotter. Input of cartesian or crystallographic coordinates of a molecular system is accepted, and output like that presented in Fig. 2 is produced. Accurate display of molecular geometry in this manner substantively aids in the elucidation of common structural features of sets of compounds.

D. Results:

As noted in sections A.3 and B, prior to the calculations of a τ(O1-C5-C4-N) vs. τ(C6-O1-C5-C4) potential energy surface for Ach or other cholinergic substances, it is valuable to know the minimum energy configurations of the trimethylammonium group's methyl hydrogens. Accordingly calculations were carried out on the model compound tetramethylammonium (TMA), which is a structural analogy of Ach's cationic head, and has 1% of Ach's nicotinic activity. A priori, it is expected that due to steric factors the minimum energy configuration is the one where all methyl hydrogens are staggered, i.e. maximally distant from one another as depicted in Fig. 5 . Prior to studying τ(H-C-N-C), a minimization of the total energy as a function of the N-C bondlengths was carried out and the result is presented in Fig. 6 , (hydrogens were held staggered). The energetically preferred N-C bondlength is calculated to be 1.44Å. Using this datum, an energy was calculated for TMA with the hydrogens eclipsed, as shown in Fig. 7 , and the result shows that the staggered form is favored over the eclipsed by ~25 kcal/mol. This steric placement of trimethylammonium methyl hydrogens is readily demonstratable in choline[2] and Ach, and is thus applied to the calculations on cholinergic substances described herein.

The potential energy surface for acetylcholine as a function of τ(O1-C5-C4-N) and τ(C6-O1-C5-C4) as calculated from INDO molecular orbital theory is presented in Fig. 8. This conformational energy map was traced from a computer generated contour surface based on 144 calculated grid points with

contour levels spaced at intervals of 0.22 kcal/mol. The minima on the surface are labelled A,B,C...G in order of increasing energy and are summarized in Table 1. Other extrema in the surface are potential energy maxima.

The absolute minimum on the surface, labeled A on Fig. 8, is located at $\{50^\circ,270^\circ\}$ and a local minimum at $\{50^\circ,50^\circ\}$, point B, is calculated to be 3.68 kcal/mol above $\{50^\circ,270^\circ\}$. The $\{50^\circ,270^\circ\}$ and $\{50^\circ,50^\circ\}$ conformers are closely related in that both positive and negative synclinal minima in the τ(C6-O1-C5-C4) would be required by symetry if τ(O1-C5-C4-N) were synplanar. With τ(O1-C5-C4-N) = 50°, a residual tendency toward the paired synclinal energy minima remains, showing up as points A and B on the surface.

The conformation associated with the calculated minimum at $\{50^\circ,50^\circ\}$ can be identified with the $\{77^\circ,79^\circ\}$ geometry observed for Ach in the bromide crystal. While this is not the absolute minimum in the surface, a comparison of molecular models of the $\{50^\circ,50^\circ\}$ and $\{50^\circ,270^\circ\}$ geometries reveals the $\{50^\circ,50^\circ\}$ would be more favorable for closest packing of molecules in the crystalline solid. This rationale is tempered, however, by the fact that the conformation of Ach in the salt of the chloride is {sc,app}.

Local minima D and H at $\{40^\circ,180^\circ\}$ and $\{180^\circ,180^\circ\}$, respectively, can be identified with conformations relevant to biological functions of Ach. The $\{40^\circ,180^\circ\}$ conformation corresponds closely to the geometry of Ach implicated in muscarinic and nicotinic aspects of cholinergic action by Chothia and Pauling.[33,36] The $\{180^\circ,180^\circ\}$ geometry corresponds to the staggered, extended conformer considered by Chothia and Pauling to be complementary

to the Ach receptor of acetylcholinesterase and the nicotinic conformer discussed by Martin-Smith, Smail, and Stenlake.[73]

The existence of a number of local minima calculated from quantum mechanical considerations as described above may be readily understood on the basis of fundamental priciples of structural chemistry and organic stereochemistry. With τ(O1-C5-C4-N) held in a positive synclinal position, the calculated minima in τ(C6-O1-C5-C4) shown in Fig. 9 correspond roughly to the minima of 60°, 180° and 300° expected in a potential energy profile for rotation of tetrahedrally hybridized atoms about an essential single bond. With τ(C6-O1-C5-C4) held in an antiplanar position, analogous considerations apply to the minima in τ(O1-C5-C4-N) shown in Fig. 10. The local minima at points E and F correspond to conformations wherein both τ(O1-C5-C4-N) and τ(C6-O1-C5-C4) fall near 60°, 180° or 300°, and thus, all the minima on the surface with the exception of point C can be accounted for on this basis. The local minimum at point C appears to arise from an interaction of methyl hydrogens of the trimethylammonium group and a methylene hydrogen of C4. This interaction stabilizes τ(O1-C5-C4-N) at 120°. No experimental data with regard to the conformations of points A, C, E or F have been reported.

For both τ(O1-C5-C4-N) and τ(C6-O1-C5-C4), the synclinal conformations are calculated to be more stable than the other accessible conformations; cf. Figs. 9 and 10. An understanding of the forces stabilizing the synclinal positions of both torsional angles can be developed in terms of intramolecular hydrogen bonding. Intramolecular hydrogen bonding is most commonly found in circumstances involving an A-H$\cdots$X structure, where A and X are both electronegative with respect

to hydrogen; the structure is stabilized by a combination of Coulomb, van der Waals, and charge-transfer forces.[74] In C-H bonds, the bond polarity is ordinarily very small, leading to little propensity for hydrogen bonding. However, for C-H bonds incorporated into a trimethylammonium cationic head, the electronegative quarternary nitrogen may effectively withdraw electrons from all the methyl C-H groups, activating the methyl hydrogens for hydrogen bonding. An accurate account of hydrogen bonding energies is somewhat beyond the capability of the level of calculations presented herein, since van der Waals forces are not accomodated in the orbital approximation and since the semiempirical nature of the INDO methodology introduces considerable uncertainty in the calculated energies and energy differences. Nevertheless, a contribution from Coulomb forces should appear, and the corresponding trends in the relative energies and calculated charge distributions should be recognizable. This is significant in that the Coulomb energy is generally held to be the dominant attractive contribution to weak hydrogen bonds.[75]

The calculated net atomic charges for Ach in the conformations $\{180^\circ,180^\circ\}$, $\{40^\circ,180^\circ\}$, $\{50^\circ,270^\circ\}$, and $\{50^\circ,50^\circ\}$ are shown in Figs. 11 -14 . The extended totally antiplanar $\{180^\circ,180^\circ\}$ conformer serves as a convenient reference for a discussion of general aspects of Ach charge distributions, since secondary intramolecular interactions are minimal in this geometry. As expected, the positive charge associated with the quarternary nitrogen in the principal valence structure is delocalized over the entire cationic head, and the nitrogen atom due to its intrinsic electronegativity is in fact the least negative of the heavy atoms in the trimethylammonium group. The

methyl carbons and hydrogens carry net positive charges of +.12 and +.03, respectively. The net atomic charges of all the atoms in the $-CH_2N(CH_3)_3$ cationic head grouping sum to +.91. The ester oxygen and carbonyl oxygen both carry net negative charges, and the high net positive charge of the carbonyl carbon is consistent with the electrophilicity attributed to this atom from infrared and reaction kinetic investigations.[76] The ester linkage is not dipositive and, to the extent these calculated net atomic charges are correct, the hydrolysis of Ach by acetylcholinesterase must be considered an exception to Pullman's dipositive bond theory of enzymatic hydrolysis.

The electronic charge distributions of Ach in other conformations corresponding to energy minima may be best understood in terms of perturbations on the distribution for the $\{180^\circ,180^\circ\}$ geometry. In the $\{40^\circ,180^\circ\}$ conformer the synclinal orientation of τ(O1-C5-C4-N) is marked by a charge-redistribution involving the ester oxygen and a methyl hydrogen H_a. The net negative charge of the ester oxygen O(1) and the positive net charge of H_a are both increased from their respective values at $\{180^\circ,180^\circ\}$. The net charges in the cationic head still sum to +.91, indicating that there is a charge polarization within the cationic head without significant charge transfer to other regions of the molecule. This polarization occurs in such a way as to increase Coulombic attraction between the ester oxygen and proximal methyl hydrogens, and correlates with a potential energy minimum. The $H_a\cdots O(1)$ distance at $\{40^\circ,180^\circ\}$ is 1.88Å, well within the van der Waals contact distance. The results are all consistent with an interpretation of the stabilization of $\{40^\circ,180^\circ\}$ in terms of intramolecular hydrogen bonding.

In the paired $\{50^\circ,50^\circ\}$ and $\{50^\circ,270^\circ\}$ forms of Ach, the

charge polarization effects characteristic of intramolecular hydrogen bonding show up for the trimethylammonium group and both the ester oxygen and the carbonyl oxygen. In $\{50^{\circ},50^{\circ}\}$, the ester oxygen interaction involves two hydrogens of the same methyl group with the critical interatomic distances O(1)...H_a and O(1)···H_c being 1.98 and 2.65Å, respcetively. A methylene hydrogen of C(5) is also proximal to O(2) and carries a correspondingly high net positive charge. In the $\{50^{\circ},270^{\circ}\}$ geometry O(1) interacts with H_a at a distance of 1.98Å and O(2) interacts with H_d at a distance of 2.1Å. The net charges of the atoms of the cationic head in $\{50^{\circ},270^{\circ}\}$ sum to +.92, indicating slight electronic charge transfer out of this region.

Thus, a characteristic feature of synclinal geometries associated with energy minima in acetylcholine's potential energy surface is charge polarization expected to be concomitant with the formation of weak intramolecular hydrogen bonds. The combination of energy stabilization, charge polarization, and intermediate distances within the van der Waals contact value indicate that the synclinal stabilization of τ(O1-C5-C4-N) and τ(C6-O1-C5-C4) in calculations at the INDO level of approximation is due to intramolecular hydrogen bonding. More detailed theoretical considerations are in order on this point and will be presented below.

Subsequent to the calculation of Ach's potential energy surface which was presented in the paragraphs immediately preceding, two other Ach conformational energy maps were generated. The first of these tests our assumption that τ(C7-C6-O1-C5) is antiplanar for all variations in τ(C6-O1-C5-C4). The INDO calculated potential energy

surface of Ach as a function of τ(C6-O1-C5-C4) and τ(C7-C6-O1-C5) with τ(O1-C5-C4-N) held antiplanar is given in Fig.15. There are three minima on the surface, all with τ(C7-C6-O1-C5) = 180°. Rotations of the latter coordinate out of the antiplanar configuration is accomplished by an increase in energy to 20 kcal/mol, consistent with the expected double bond character of the C6-O1 bond as discussed by Baker et al. This coordinate is maintained antiplanar in all subsequent calculations.

In order to obtain more detail, a second SCF-INDO conformational energy map of Ach as a function of τ(O1-C5-C4-N) and τ(C6-O1-C5-C4) with a closer grid of 20° on the full range of 360° in both variables was generated.[3] The results are relevant to succeeding discussion and are given in Fig.16. The global minimum on the surface is in the {-sc,sc} region, and local minima D and H can be identified with the bromide and chloride crystal geometries, respectively. The qualitative features are in accord with chemical intuition as described above. On a more detailed level the SCF-INDO calculations place the synclinal minima of both coordinates somewhat inside the experimentally observed values, with in some cases non-bonded atoms coming within van der Waals contact distances.[49] Using the wavefunctions generated in the latter calculation, the dipole moment of Ach was calculated to be 1.5 to 9.8 debye, depending on the conformation. An experimentally observed value for Ach in chloroform was estimated to be 2.65 debye.[77] While a number of assumptions on structure and polarizabilities are involved in reduction of the experimental data, this relatively low value suggests that the structure of Ach in chloroform may resemble the crystalline bromide

geometry rather than the crystalline chloride geometry also observed for Ach in D_2O.

Since the publication of the SCF-INDO conformational energy map for Ach, analogous calculations have been reported by Pullman, Courriere and Coubeils[30] using the PCILO-CNDO method. Studies on acetylcholine at the SCF-CNDO level have been reported by Savran and Govil.[78] The pairwise potential function method was elaborated to include a coulombic term and applied to Ach by Ajo, Bossa, Damiani, Fidenzi, Oigli, Lanzi and Lapiccinella.[48] Net atomic charges were adopted from EHT and CNDO calculations on a single conformer.[49] Froimowitz and Gans reported similar calculations based on the net atomic charges computed in the INDO approximation. The only non-empirical theoretical studies reported to date are the SCF-FSGO molecular fragment calculation by Genson and Cristofferson,[50] and the SCF-MO study by Port and Pullman.[51]

There is considerable but not total accord in the results on Ach from these diverse theoretical points of view. The SCF-CNDO should and do give results identical to those obtained at the INDO level. The corresponding PCILO-CNDO surface is somewhat flatter, with a total variation of 6 kcal/mol in sterically permitted regions, (11 kcal/mol for SCF-INDO). Pullman and Courreire have studied the sensitivity of the results to the geometrical input of the calculations and have found that calculations based on the bromide geometries give low-energy {sc,sc} minima, and calculations based on the chloride geometry give low energy {sc,ap} minima. Froimowitz and Gans have provided a detailed comparison between the pairwise potential function methods and the quantum mechanical

studies, showing similar results to those of Fig. 8. A slight tendency of the INDO method to allow non-bonded atoms to come within van der Waals radii of one another was empirically adjusted in their repulsive potentials. This problem is probably avoided in the PCILO calculations by the choice of localized molecular orbital basis functions.

The non-empirical calculation of Ach by Genson and Cristoffer-[50] son produced signigicantly different results, with a considerably wider variation in energy with respect to both coordinates, and minima synperiplanar and antiperiplanar in τ(O1-C5-C4-N). The experimentally observed synclinal value is near an energy maximum, with a variation in energy with respect to τ(O1-C5-C4-N) with τ(C6-O1-C5-C4) = 180° of 50 kcal/mol, vs. 5 kcal/mol for INDO and 3 kcal/mol for PCILO. The synclinal minimum is developed by non-covalent intramolecular bonding interactions, and this questions the ability of the molecular fragments procedure to describe this effect with functions positioned in covalent bonding regions, although evidence from calculations on other systems indicate no special problems on this point. Recent thoughts relate the problem to the limited basis set. The ab initio SCF calculation at the STO-3G level gives a synclinal minimum in τ(O1-C5-C4-N) with a barrier to the antiperiplanar form of 3 kcal/[51] mol.

Most of the theoretical and experimental studies of conformation in cholinergic substances presented above indicated a synclinal stabilization of τ(O1-C5-C4-N). In order to quantitatively determine the stabilizing force on the O-C-C-N group,

a partitioning on the model compound choline of the INDO total energy into individual monoatomic and diatomic contributions was carried out. Calculations on choline[2] are compared with those obtained for electrically neutral norcholine, where activation of hydrogens by Sutor's mechanism is precluded.[85] Fig. 17 presents the structure of choline.

The calculated total energies of choline and norcholine are displayed as a function of γ(O1-C5-C4-N) in Fig. 18. Norcholine shows synclinal and antiplanar minima in the range displayed. The pattern is characteristic of the torsional potential expected in rotation about saturated carbon atoms, with all minima falling in a range of 1 kcal/mol. Analogous minima can be identified on the choline curve, but here the synclinal minimum is preferentially stabilized to the extent of 4-5 kcal/mol. The O···H distance in the synclinal minimum of choline (40°) is 2.07Å.

The electronic charge distribution calculated for choline is given in Figs.[19,20] The antiplanar conformer serves as a convenient point of reference, since intramolecular interactions are minimal in this geometry. As expected, the positive charge associated with the quarternary nitrogen in the principal valence structure is delocalized over the entire cationic head, and the methyl carbons and hydrogens carry net positive charges of 0.12 and 0.03, respectively. The nitrogen atom, consistent with its intrinsic electronegativity is the least positive (0.0907) of the heavy atoms in the trimethylammonium group. The charge on the acyloxy oxygen is -0.279, and the net charge on the atoms $-CH_2-N(CH_3)_3$ comprising the cationic head sum to 0.901.

The principal change in charge density from the antiplanar to synclinal geometries of choline is the increased net positive

charge (0.048) found on the methyl hydrogen proximal to the oxygen, and increased net negative charge on the oxygen (-0.311). The nitrogen also has a small increase in net positive charge, from 0.091 to 0.094. The net charges of the cationic heads for the antiplanar and synclinal conformers are 0.907 and 0.906, respectively.

The calculated electronic charge distribution for norcholine is presented in Fig.21,22. In the antiplanar conformer, the dimethylammonium group is nearly electrically neutral. The nitrogen and methyl hydrogens are net negative, and the methyl carbons show net positive charges; a charge alternation effect discussed more generally by Pople and Gordon[79]. The oxygen net charge is -0.302. Going over to the synclinal conformer, there is a decrease in negative charge on the oxygen and an increase in negative charge on the nitrogen, directly opposite to the trend calculated for choline. As in choline, there is a decrease in negative charge on the methyl hydrogen proximal to the oxygen.

Before proceeding to a detailed consideration of the results of Fig.26, it is useful to consider the extent to which the minima are sensitive to the specific orientation of the trimethylammonium hydrogens assumed for calculation. To consider the orientation of the methyl groups, an energy surface for each compound was generated as a function of τ(O1-C5-C4-N) and τ(H-C1-N-C2), with the other methyl hydrogens geared for minimal steric repulsions. The results for choline and norcholine are given in Figs.23 and 24, respectively. The minima for both synclinal and antiplanar conformers occur for $\tau(H\text{-}C1\text{-}N\text{-}C2) = 60^{\circ}$ in both compounds; furthermore the synclinal and antiplanar conformers

are minimal for any slice of τ(H-C1-N-C2). The results of Fig. 18 are thus independent of methyl group orientation.

At this point a more detailed characterization of the factors contributing to the variation in energy as a function of τ(O1-C5-C4-N) is in order. For each value of τ(O1-C5-C4-N) considered, the calculated total energy was partitioned into monoatomic and diatomic contributions. The variation in many individual contributions exceeded the variation in the calculated total energy, emphasizing the extent to which the total energy is a subtle balance of widely varying terms. Each E_A and E_{AB} was individually examined as a function of τ(O1-C5-C4-N), and the significant results are collected in Figs. 25 and 26 . All relevant contributions decreasing in the synclinal region of τ(O1-C5-C4-N) are represented in these figures, as are particularly interesting contributions on the increase.

Selected monoatomic contributions to the total energy of choline are plotted together with the total energy as functions of τ(O1-C5-C4-N) in Fig. 25, and the analogous plots for selected diatomic contributions are given in Fig. 26. The calculated net stabilization of syn conformers over anti conformers is correlated with stabilizing contributions from the monoatomic oxygen term, the the monoatomic contribution of the methyl carbon proximal to the oxygen and the diatomic oxygen-hydrogen term for the methyl hydrogen proximal to the oxygen. The diatomic oxygen-nitrogen term shows only a small variation over the range of τ studied. For the stabilization of the synclinal conformer with respect to the synplanar, the stabilization contributed by the oxygen-methyl hydrogen interaction

is dominant, acting in concert with the monoatomic nitrogen term. Thus the calculated stabilization of the energetically preferred conformation with respect to τ(O1-C5-C4-N) is directly associated with the interaction between the oxygen and the cationic head, with the interaction between the oxygen and the proximal methyl hydrogen indicated as a significant factor.

An important point to consider is the comparison between the calculated results and experimental observation. Theory and experiment concur on the existance of a preferred conformation in the synclinal region of τ(O1-C5-C4-N). The calculated energy minimum falls at τ(O1-C5-C4-N) = 40°, as compared to the experimentally observed value of 84°. In view of the fact that the the energy curve is rather flat (total calculated variation of the order of 5 kcal/mol), this can be considered reasonable accord between approximate molecular orbital theory and experiment. A point of contention arises in the consideration of the nature of the O···H-C-N interaction. At $\tau = 40^{\circ}$, $R_{O\cdots H} = 2\text{Å}$, well within the sum of the van der Waals radii of hydrogen and oxygen. At $\tau = 84^{\circ}$, $R_{O\cdots H} = 2.5\text{Å}$, just beyond the sum of the van der Waals radii and just beyond the O···H distance expected for hydrogen bond formation. The O···H interaction plays a significant role in the stabilization of the INDO calculated synclinal energy minimum, but the possibility that this interaction is over-estimated by the INDO method must not be excluded. The INDO calculations indicate that a hydrogen -bonding interaction would go smoothly over to an electrostatic interaction as the O···H distance increases in choline, and thus the question here is more one of degree than of

fundamental character.

With the structural chemistry of acetylcholine and the cholinergic O-C-C-N grouping well characterized by molecular quantum mechanics at the INDO level of approximation, study at this level of approximation was addressed to the important cholinergic agonists: muscarine, nicotine, acetyl-α-methylcholine, acetyl-β-methylcholine and acetyl-α,β-dimethylcholine.[3] The result of this work is presented in the following paragraphs.

Muscarine. Muscarine has been studied from a theoretical viewpoint by a variety of methods with no substantive disagreement.[18,19,30] A conformational study of muscarine reduces to a one parameter problem, with τ(C6-O1-C5-C4) constrained to 144° by the intramolecular five membered ring. Calculations were carried out on the C6(S),C9(R), C5(S) isomer shown in Fig.3 , and for the related compounds C6(S),C9(S),C5(S) epi-muscarine, C6(R),C9(S),C5(S) allo-muscarine and C6(R),C9(R),C5(S) epiallo-muscarine. The INDO conformational energy of muscarine plotted as a function of τ(O1-C5-C4-N) is presented in Fig.[27]. The calculations show a global minimum at 60° in accord with the observed crystal geometry. A local minimum appears at 160° in τ(O1-C5-C4-N) at an energy 7 kcal/mol above the local minimum. The results for epi-muscarine, allo-muscarine, and epiallo-muscarine are essentially identical; these compounds differ from muscarine only in the absolute configuration of the methylated and hydroxylated ring carbon atoms and in their biological activities to be discussed in the next section. The calculated net atomic charges for muscarine in the $\{60^\circ, 144^\circ\}$ conformation are given in Fig. 3 . The calculated electric dipole moment is 8.05 debye.

Nicotine. The crystal geometry for nicotine dihydroiodide as determined by Koo and Kim[28] is shown in Fig. 4. Here τ(C8-C7-C2-N) is analogous to τ(O1-C5-C4-N) in Ach, and τ(C9-C8-C7-C2) holds some analogy to τ(C6-O1-C5-C4). With the latter coordinate constrained antiplanar by the pyridine ring, the crystal geometry can be represented as $\{-60^{\circ},180^{\circ}\}$. Rotation of the pyridine ring by 180° places N2 in a position analogous to the carbonyl oxygen of Ach in the $\{60^{\circ},180^{\circ}\}$ conformation. The pyrollidine ring deviates somewhat from planarity, with τ(C5-C2-N1-C3) = 17° and τ(N1-C3-C6-C5) = 14°. Simple steric considerations indicate that interactions between pyridine hydrogens and hydrogens attached to the pyrollidine ring and N-methyl group may strongly influence the conformational energy about τ(C8-C7-C2-N1).

While rapid inversion of the absolute configuration around nicotine's pyrollidine nitrogen is likely in solution, the the 1(R), 2(S) configuration of nicotine is studied here since crystal data is available for this epimer.

In the initial SCF-INDO calculations on nicotine, a conformational energy map was generated as a function of τ(C8-C7-C2-N1) and τ(H_a-C4-C2-N1), the latter coordinate specifying the orientation of the N-methyl hydrogens. Two energy minima were found, differing in energy by less than 1 kcal/mol and both corresponding to τ(H_a-C4-N1-C3) = 80°. The calculated energy vs. τ(C8-C7-C2-N1) with τ(H_a-C4-N1-C3) = 80° is shown Fig.[28]. The energy minima correspond to (C8-C7-C2-N1) = 0° and 160°, both somewhat removed from the observed value of -60°. In an attempt to understand the discrepancy between the calculated and observed values, we explored the effect of deviations in hydrogen positions on the calculated result. The coordinates specifying the

hydrogen positions were adjusted slightly in the direction expected to reduce steric effects and calculation of conformational energy vs. τ(C8-C7-C2-N1) was repeated. The resulting plot is also presented in Fig. 28. The barrier heights were reduced by 1.5to 2 kcal/mole, but the positions of the minima were essentially unchanged. Superimposed on the same plot are the interatomic distances of hydrogen atoms coming within van der Waals contact distance of one another. At τ(C8-C7-C2-N1) = 40° to 80°, the H_a-H_d distance and the H_b-H_c are very low resulting in an increased conformational energy. At τ(C8-C7-C2-N1) = 220° to 260° the H_a-H_c and H_b-H_d distances are close, also destabilizing the system. Our calculated minima correspond roughly to regions where all these interatomic distances are simultaneously maximal. Thus in spite of the lack of a calculated energy minimum in the region of the observed geometry, our results are understandable, and represent the degree of agreement to be achieved assuming the crystal geometry for non-hydrogen atoms. Conformations of nicotine with τ(C8-C7-C2-N1) from 100° to 200° and from -40° to 20° are energetically removed from the absolute minimum by less than 2.5 kcal/ mole. The calculated charge distribution for nicotine at the crystal geometry is recorded in Fig. 4, and the calculated dipole moment ranged from 7.4 to 8.9 debye.

The calculations on nicotine reported by other investigators leave the relation between calculated and observed geometries incompletely resolved. The study reported by Kier using extended Hückel theory gave good agreement with experiment but assumed a planar pyrollidine ring and computed energies on a 60° grid. INDO calculations performed on 1(R), 2(S) nicotine with the pyrollidine ring planar yield minima in τ(C8-C7-C2-N1) at -40° and 140°. However, it is difficult to justify

comparison of this result with that of the crystallographic study. Pullman et al.[30] using the PCILO method and an unspecified 1(R), 2(S) standard geometry obtained minima at τ(C8-C7-C2-N1) = -40° and 120°, in improved agreement with the crystal geometry.

Acetyl-α-methylcholine. The SCF-INDO conformational energy map of α(R)-methyl acetylcholine is presented in Fig.[29]. The conformational map for α(S)-methyl acetylcholine, the enantiomer, can be generated through the transformation $\{x,y\} \rightarrow \{x,-y\}$. The global minimum for the α(R) derivative occurs in the vicinity of $\{80°, 240°\}$. The nine other local minima are listed in Table [2]. The crystal geometry at $\{90°,170°\}$ is calculated to be 4 kcal/mole above the absolute minimum, and the $\{212°, 176°\}$ crystal result can be identified with a local minimum at $\{180°, 180°\}$. In the latter case, with τ(O1-C5-C4-N) = 180° the shape of the surface indicates considerable lability in τ(C6-O1-C5-C4) from 80° to 240°. Steric interference of the α(R) methyl group with the acetate carbonyl group precludes conformations with τ(O1-C5-C4-N) and τ(C6-O1-C5-C4) simultaneously in the range of 40° to 200°, and -40° to 60°, respectively. The calculated magnitudes of angles of the {sc,sc} minima are increased over that calculated for Ach, but comparison of Fig.[16] and Fig.[29] show that the overall effect of α-methyl substitution of the conformational energy map is relatively minor. None of the local minima on the Ach potential surface are energetically precluded for the α-methyl derivative. The α-methyl surface is slightly flatter than that of Ach, consistent with the results indicated in NMR studies.

The calculated net atomic charges for the $\{80°, 240°\}$ conformation of α(R)-methyl acetylcholine are presented in Fig. [30]. Comparison of Fig.30 with the charge distribution reported for acetylcholine in Fig. [2]

show that there is a charge redistribution induced by α-methyl substitution. There is a decrease in positive charge on N, C1 and C6, and a decrease an increase in negative charge on O1 and O2, respectively. The calculated dipole moment ranges from 0.5 to 9.1 debye.

Acetyl-β-methyl acetylcholine. The conformational energy map computed for β(S) methyl acetylcholine using the INDO method is given in Fig.31. The surface may be viewed in marked contrast to that of Ach, with 50% of the conformational space sterically excluded. The primary source of the steric effect is the interaction between the β-methyl group and the trimethylammonium methyl groups, important for all values of τ(O1-C5-C4-N) above 180°. The global minimum on the surface is located at $\{60°, 30°\}$, with a local minimum at $\{60°, 240°\}$ computed to be about 4.8 kcal/mole higher in energy. The latter local minimum may be identified with the crystal geometry at $\{85°, 203°\}$.

The calculated charge distribution for the $\{60°, 240°\}$ conformer of β(S)methyl Ach is given in Fig.32. A comparison with the calculated charge distribution for Ach show that the effect of β-methyl substitution is to decrease positive charge on N, C1 and C6, and to decrease and increase negative charge on O1 and O2, respectively. These charge redistributions are directly analogous to those which occur on α- methyl substitution. The calculated dipole ranges from 1.4 to 11.4 debye in the sterically allowed region of space.

Acetyl-α,β-dimethylcholine. The SCF-INDO conformational map calculated for threo-α(R), β(R)-dimethylacetylcholine is presented in Fig. 33. Here 87% of the surface is sterically unfavored. All conformers with τ(O1-C5-C4-N) between 40° and 200° are excluded due to interactions between β-methyl and trimethylammonium hydrogens, and

conformers with γ(C6-O1-C5-C4) between 200° and 260° have unfavorable interactions between the β-methyl group and the carbonyl oxygen. The global minimum on the surface is at {280°, 140°}, with a local minimum at about the same energy at {220°, 60°}, separated by a barrier computed to be less than 2 kcal/mole. A second local minimum is present at {280°, 300°}, separated from the first by a barrier of some 25 kcal/mole. The experimentally observed crystal geometry for the threo-α(R), β(R) derivative is {217°;95°}. .Figure 34 presents the computed net atomic charges for the {80°,220°} conformer of threo-α(S), β(S)-dimethylacetylcholine. In comparison with the calculated net atomic charge densities for acetylcholine, there is a decrease in positive charge on N, an increase on C6, and an increase in negative charge on O1. Charges on other atoms are essentially unchanged from those of acetylcholine. The calculated electric dipole moment ranges from 0.9 to 8.8 debye.

The conformational energy map for erythro-α(S),β(R)-dimethylacetylcholine is given in Fig. 35 . Steric interactions analogous to those described above exclude above 86% of the conformers on this surface In the remaining area, the global minimum is located at {280°, 120°}, with a local minimum at {240°, 80°} and {280°, 280°} at relative energies of 1.91 and 3.34 kcal/mole, respectively. The latter two minima are separated by a computed barrier of 6 kcal/mole. The crystal geometry is {280°, 160°} , a point computed to be 1.7 kcal/mole above the global minimum. The charge distribution for erythro-α(R),β(S)-dimethyl acetylcholine, as presented in Fig.36, is similar to that presented for the threo derivative except that C6 does not evidence an increase in positive charge over the analogous atom in Ach. The calculated dipole ranges from .9 to 9.0 debye.

E. Discussion:

The results of the preceding section can be used together with the biological activity data to approach a deeper understanding of the role of α-and β-methyl substituents in cholinergic action, and to gain perspective on general aspects of the structural chemistry of cholinergic transmision. Since the methyl derivatives of Ach have all of the functional groups necessary for either muscarinic or nicotinic activity, the present data may be used to examine the role of molecular conformation vis-a-vis the direct interaction of the methyl groups with the cholinergic receptor. To the extent molecular conformation is a dominant factor, compounds in this series with a particular type of activity should have the appropriate functional groups disposed in three dimensional space in a common pattern. In terms of structural parameters, this disposition is specified by sterically permitted or energetically preferred values of τ(O1-C5-C4-N) and τ(C6-O1-C5-C4), and any common pattern should be revealed by a comparison of allowed regions or energy minima in the {τ(O1-C5-C4-N), τ(C6-O1-C5-C4)} conformational maps.

The conformational data presented in the preceding section has been reduced to tabular form and collected with the biological activity data in Table 2 , Each compound considered is represented by a row of the table, containing from left to right its muscarinic activity, nicotinic activity and enzymatic hydrolysis rate; each given as percentages with respect to available data on Ach. The biological data represent results from a variety of preparations and experimental conditions, and the relative activities listed are thus of qualitative or semi-quantitative significance at best.

Further to the right of Table 2, the positions of energy minima calculated for the substance are enumerated. The columns of the table in this region are organized with respect to the calculated energy minima for Ach given in the top row; entries in the same column down the table indicate corresponding energetically preferred conformations in different substances. All preferred conformations energetically within 20kcal/mole of the global minimum of each compound are included.

In examination of the data for compounds with signifincant muscarinic activity, it is again evident that the geometry common to muscarinic agonists is {sc,ac-ap}, consistent with ideas proposed by Pauling and co-workers. For Ach and muscarine this geometry (column 2 in the conformational energies of Table 2) corresponds to a calculated energy minimum and is thus energetically preferred. For the active β(S)-methyl derivative and the erythro-α(R), β(S)-dimethyl derivative (probably the active erythro-dimethyl enantiomer), this geometry does not correspond to local energy minima but is not sterically excluded. Beyond this, it appears that β(S)-methyl or methylenic substitution actually enhances the muscarinic activity of an agonist. Bioassay data (see Table 2) for muscarine, acetyl-β(S)-methylcholine and erythro-α(R),β(S)-dimethylacetylcholine show these compounds to have 270%, 133% and 14% of the muscarinic activity of Ach, respectively. The muscarinic activities of erythro-α(R),β(S)-dimethylacetylcholine and α(R)-methylacetylcholine are 14% and .6% relative to Ach. Examination of the conformational maps and calculated electronic charge distributions for these molecules shows no outstanding detail which could explain the enhancement of muscarinic activity for a β(S) substituent simply in terms of molecular

conformation and other molecular properties. Therefore it appears that the variation in the level of muscarinic activity in these compounds may involve a direct interaction of the methyl substituents with the muscarinic receptor.

Table [2] also lists a number of compounds which have calculated energetically preferred conformations in the vicinity of {sc,-ac} yet have low muscarinic activity. Both α(R)- and α(S)-methyl derivatives fall into this category, with α(S)-methyl substitution diminishing muscarinic activity by a factor of 10 more than α(R)-methyl substitution. Since no significant portion of the Ach conformational map is sterically precluded for the α(R)- or α(S)-methyl derivative, simple conformational effects cannot be responsible. A direct interaction of the α-methyl substituents with the receptor, contributing destructively to agonist activity, can explain the observed reduction in muscarinic potency. The loss of muscarinic activity upon α-methyl substitution is also seen in the dimethyl derivatives. Erythro- α(R), β(S)-dimethylacetylcholine has an energetically preferred conformation at {sc,-ac} and a muscarinic activity in the racemate of 14% relative to Ach, compared to 133% for β(S)-methylacetylcholine. The greater reduction in muscarinic activity for α(S)-methyl substitution as compared with α(R) substitution is evidenced again by the lack of activity in threo-α(S), β(S)-dimethylacetylcholine whereas the erythro- α(R), β(S) derivative elicits small but significant muscarinic activity.

Analogous conclusions can be drawn from a consideration of the calculated energy profiles of muscarine, given in Fig. 27, as compared with those for epi-muscarine, allo-muscarine and epiallo-muscarine. The energy profiles are similar while the observed activities

as listed in Table 2 are quite different. Neither conformational effects or a variation in electronic charge distribution can explain the variance in activity, and a direct interaction of functional groups with the receptor is indicated. The observed activities appear to implicate muscarine's hydroxyl oxygen and ring methyl group in positions analogous to the carbonyl oxygen and acetate methyl of Ach in muscarinic action.

Consideration of the data for compounds with significant nicotinic activity leads to additional information on the role of conformational effects in nicotinic action. As noted by others, nicotinic activity is clearly less stereospecific than muscarinic action, but a {sc, ac-ap} conformation has been implicated. Both α(R)- and α(S)-methyl derivatives are nearly as active at nicotinic sites as Ach. Methyl substitution at either β(R)-or β(S)- positions significantly reduces the nicotinic activity of an agonist. In consideration of the widely different effects of β(R) and β(S) substitution on conformational preferences, and that the {sc,-ac} is permitted if not preferred in the β(S) derivative, a direct interaction of methyl groups with the nicotinic receptor is indicated.

Consideration of the relative rates of cholinesterase mediated hydrolysis for the various compounds alongside the calculated results on structure and properties for methyl Ach derivatives points also towards some direct interaction of the methyl groups with the active site of the enzyme. Both α(R)- and α(S)-methylacetylcholine can achieve any point on the $\{\tau$(O1-C5-C4-N), τ(C6-O1-C5-C4)$\}$ conformational map accessible to Ach, and have no significant differences in charge distributions. Thus the observed decreased hydrolysis rate of the α(R) derivative compared to the α(S) derivative of Ach does not appear to be dependent upon conformational effects,

and may likely involve methyl groups directly. For the β-methyl derivatives, β(R) substitution reduces the hydrolysis rate to zero whereas β(S) substitution shows 54% the hydrolysis of Ach. This indicates positive synclinal and anticlinal values of γ(O1-C5-C4-N) lead to conformations complementary to the cholinesterase receptor. The calculated conformational map for β(S)-methylacetylcholine shows local minima for (+)-synclinal values of γ(O1-C5-C4-N), but none for ac to ap values. The $\{150^{\circ}, 180^{\circ}\}$ geometry implicated by Pauling et al. in enzymatic hydrolysis lies 12 kcal/mole above the global minimum.

For hydrolysis, the effects of α- and β-substitution may again be extrapolated to the α, β-dimethyl derivatives. The decreased hydrolysis rate for an α(R) derivative explains the negligible rate observed for erythro-α(R), β(S)-dimethylacetyl choline. We predict the hydrolysis rate for threo-α(S), β(S)-dimethylacetylcholine to be higher.

Overall, we can ascertain from these results that structures implicated in various aspects of cholinergic action can be identified with regions of conformational energy sterically permitted but not necessarily energetically preferred in the isolated molecule. This seems reasonable since a change in membrane permeability is probably a structural adaptation to agonist-receptor interaction, and a conformational effect on the agonist is certainly possible. Structural modifications in both enzyme and substrate are evident from spectral studies of enzymatic reactions.

In comparing theory and experiment, the structural detail presented in the results section must be considered in the perspective of a physiochemical system. At physiological and room temperatures

many conformations will be thermally populated, and in solid and solution, environmental effects are surely important. Intramolecular hydrogen bonding and the various conformations of Ach in the $\{\tau(O1\text{-}C5\text{-}C4\text{-}N),\ \tau(C6\text{-}O1\text{-}C5\text{-}C4)\}$ surface would be influenced significantly by solvent polarity. The bromide crystal geometry B and the related conformation A in Fig.16 have both the acetoxy and acyloxy oxygen atoms in the interior of a roughly spheroidal structure with C-H bonds on the exterior. In solution these geometries would likely be favored by low solvent polarity, although Ach as a cation has proved sparingly soluble in such solvents. Geometries such as D and G exposing one or both oxygens could be preferentially stabilized by highly polar, intermolecularly hydrogen bonding solvents.

The natural selection of acetylcholine as a chemical neurotransmitter has been attributed in part to its relatively non-substituted structure and subsequent conformational flexibility; being adaptable to nicotinic, muscarinic and possibly many other receptor sites. In light of the possible solvent effects on Ach's conformational flexibility, local biological environments could also serve to preferentially stabilize conformations complementary to specific receptor sites, and thus contribute to optimum biological function.

F. Summary and Conclusions:

The INDO molecular orbital calculations on acetylcholine reveal a number of energy minima with respect to the torsional angles τ(O1-C5-C4-N) and τ(C6-O1-C5-C4). Certain of the minima can be closely identified with the Ach crystal geometries, the geometries implicated in muscarinic and nicotinic aspects of cholinergic action, and the geometry considered favorable for hydrolysis by cholinesterase. The energy stabilization of synclinal values of both τ(O1-C5-C4-N) and τ(C6-O1-C5-C4) in Ach is attributed to intramolecular hydrogen bonding as evidenced by an electronic charge redistribution in a manner consistent with polarization effects expected for hydrogen bonding structures.

Thus a number of proposed structural aspects of the neurobiological action of Ach can be understood and unified on the basis of quantum mechanical calculations, considering local minima in the potential energy surface and corresponding molecular electronic properties.

The conformational energy maps and electronic charge distributions for muscarine, nicotine, the α and β methyl, and dimethyl derivatives of Ach have been considered in terms of physiochemical studies, the available bioassay data on cholinergic substances, and current theories of the structural chemistry of cholinergic transmission. Geometries observed from crystallographic and solution spectral studies for each compound may be identified with energetically preferred geometries.(local minima) on the calculated conformational energy maps. General aspects of

cholinergic activity are seen to be related to regions of conformational space sterically allowed, but are not always directly associated with energetically preferred geometries. The variance in bioassay data for active compounds cannot be explained in terms of simple conformational effects and distributions of electronic charge, and direct interactions of methyl substituents with cholinergic receptors are indicated.

Table 1

Identification on Figure 8	Relative energy, kcal/mol	Geometry		Physiochemical or biological significance
		Calcd	Exptl	
A	0.00	{50°, 270°}		See text
B	3.68	{50°, 50°}	{77°, 79°}	Observed in crystalline acetylcholine bromide
C	4.98	{120°, 300°}		See text
D	6.27	{40°, 180°}	{75°, 180°} {60°-120°, 144°-213°}	Implicated in nicotinic action Implicated in muscarinic action
E	7.72	{200°, 330°}		See text
F	7.84	{160°, 30°}		See text
G	9.98	{180°, 180°}	{180°, 150°}	Implicated in nicotinic action and hydrolysis by cholinesterase

Table 2 Summary of Biological and Conformational Data

Compound	Muscarinic Activity*	Nicotinic Activity*	Susceptibility to Hydrolysis*	Calculated Conformational Energies ** (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
acetylcholine	100.	100.	100.	{40°,60°} D,4.14	{40°,180°} H,6.42	{60°,260°} B,0.74	{160°, 40°} J,7.62	{180°,180°} K,10.20	{120°,320°} F,4.97	{200°,320°} I,7.61	{240°,60°} E,4.73	{300°,100°} A,0.0	{320°,180°} G,6.11	{320°,300°} C,3.97
acetyl-β(R)-methylcholine	3.6[a],7.7[b]	100[c,d]	78[e]	{80°,80°} C,1.87	y	{80°,240°} A,0.0	{180°,40°} F,2.28	{180°,180°} K,5.09	{120°,260°} B,2.06	{180°,260°} J,4.11	{220°,60°} E,2.68	{300°,120°} B,0.45	{300°,200°} H,3.25	{300°,320°} G,3.20
acetyl-β(S)-methylcholine	.4[a],.7[b]	100[c,d]	97[e]	{60°,40°} G,3.20	{60°,160°} H,3.25	{60°,240°} B,0.45	{180°,100°} J,4.11	{180°,180°} K,5.09	{140°,300°} E,2.68	{180°,320°} F,2.28	{240°,100°} D,2.06	{300°,120°} A,0.0	y	{280°,280°} C,1.87
acetyl-β(R)-methylcholine	.4[a],.5[b]	0[c,d]	weak[e] inhibitor	x	x	x	x	x	x	x	{240°,60°} C,5.15	{300°,120°} B,4.77	y	{300°,330°} A,0.0
acetyl-β(S)-methylcholine	99,133[a,b]	0[c,d]	54[e]	{60°,30°} A,0.0	y	{60°,240°} B,4.77	x	x	{120°,300°} C,5.15	x	x	x	x	x
erythro-acetyl-α(R),β(S) dimethylcholine	14[f]	—	0[g]	{80°,80°} C,3.34	y	{80°,240°} A,0.0	x	y	{120°,280°} B,1.91	x	x	{340°,120°} E,8.40	{340°,180°} D,6.36	x
erythro-acetyl-α(S),β(R) dimethylcholine				x	{20°,180°} D,6.36	{20°,240°} E,8.40	x	y	x	x	{240°,80°} B,1.91	{280°,120°} A,0.0	y	{280°,280°} C,3.34
threo-acetyl-α(R),β(R) dimethylcholine	.04[f]	—	9[g]	x	{0°,160°} D,8.06	x	x	y	x	x	{220°,60°} B,0.30	{280°,140°} A,0.0	y	{280°,300°} C,2.13
threo-acetyl-α(S),β(S) dimethylcholine				{80°,60°} C,2.13	y	{80°,220°} A,0.0	x	y	{140°,300°} B,0.30	x	x	x	{360°,200°} D,8.06	x
C2(S),C3(R),C5(S) muscarine	270[h]	15,25[i,j]	-	x	{60°,144°} A,0.0	x	x	{60°,144°} B,6.9	x	x	x	x	x	x
C2(S),C3(S),C5(S) epimuscarine	.3[h]	2,2.5[i,j]	-	x	{60°,144°} A,0.0	x	x	{60°,144°} B,6.9	x	x	x	x	x	x
C2(S),C3(R),C5(R) allo-muscarine	.5[h]	1.5,2.5[i,j]	-	x	{60°,144°} A,0.0	x	x	{60°,144°} B,6.9	x	x	x	x	x	x
C2(S),C3(S),C5(R) epi-allo-muscarine	.8[h]	30, 50[i,j]	-	x	{60°,144°} A,0.0	x	x	{60°,144°} B,6.9	x	x	x	x	x	x
1(R),2(S) nicotine	0[k]	100[l]	-	x	{100°,180°}	x	y	y	x	x	x	x	y	x

Key for Table 2:

a. Guinea pig ileum, Ref. 81.

b. Cat blood pressure, Ref. 81.

c. Frog rectus muscle, Ref. 44 and Ref. 82.

d. Blood pressure rise with atropine, and cat gastrocnemius stimulation, Ref. 83.

e. Hydrolysis by a standard bovine erythrocyte acetylcholinesterase homogenate, Ref. 41.

f. Guinea pig ileum, Ref. 44.

g. Hydrolysis by true acetylcholinesterase from the electric organ of the eel, Ref. 44.

h. Cat blood pressure, Ref. 25.

i. Blockage of cat superior cervical ganglion, Ref. 25.

j. Curariform action on cat gastrocnemius muscle, Ref. 25.

k. Guinea pig ileum during anoxia, Ref. 84.

l. Cat superior cervical ganglion, Ref. 7.

*Bio-assay data are given as percentages relative to Ach.

**x - sterically forbidden conformations.
y - sterically allowed conformations.

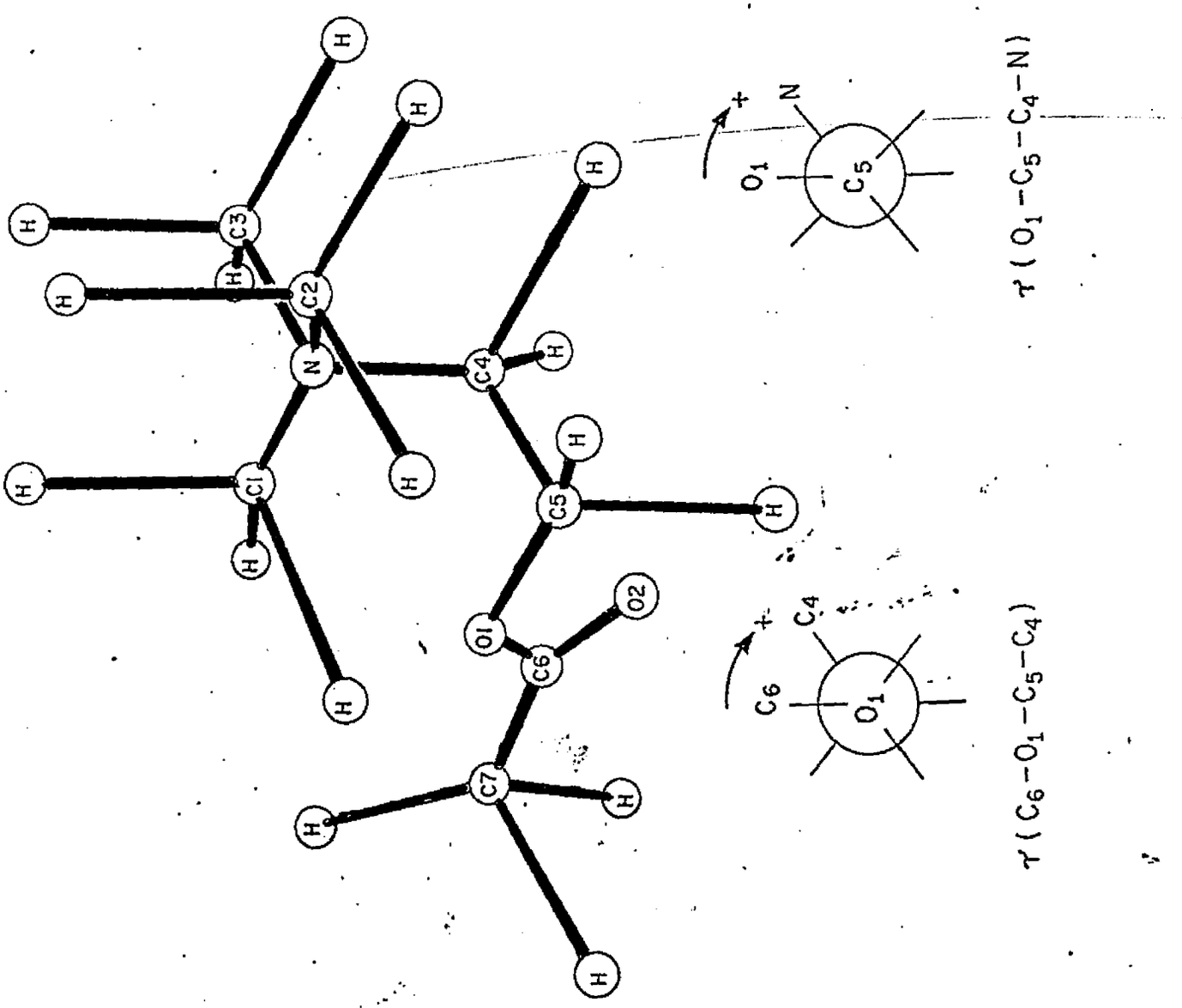
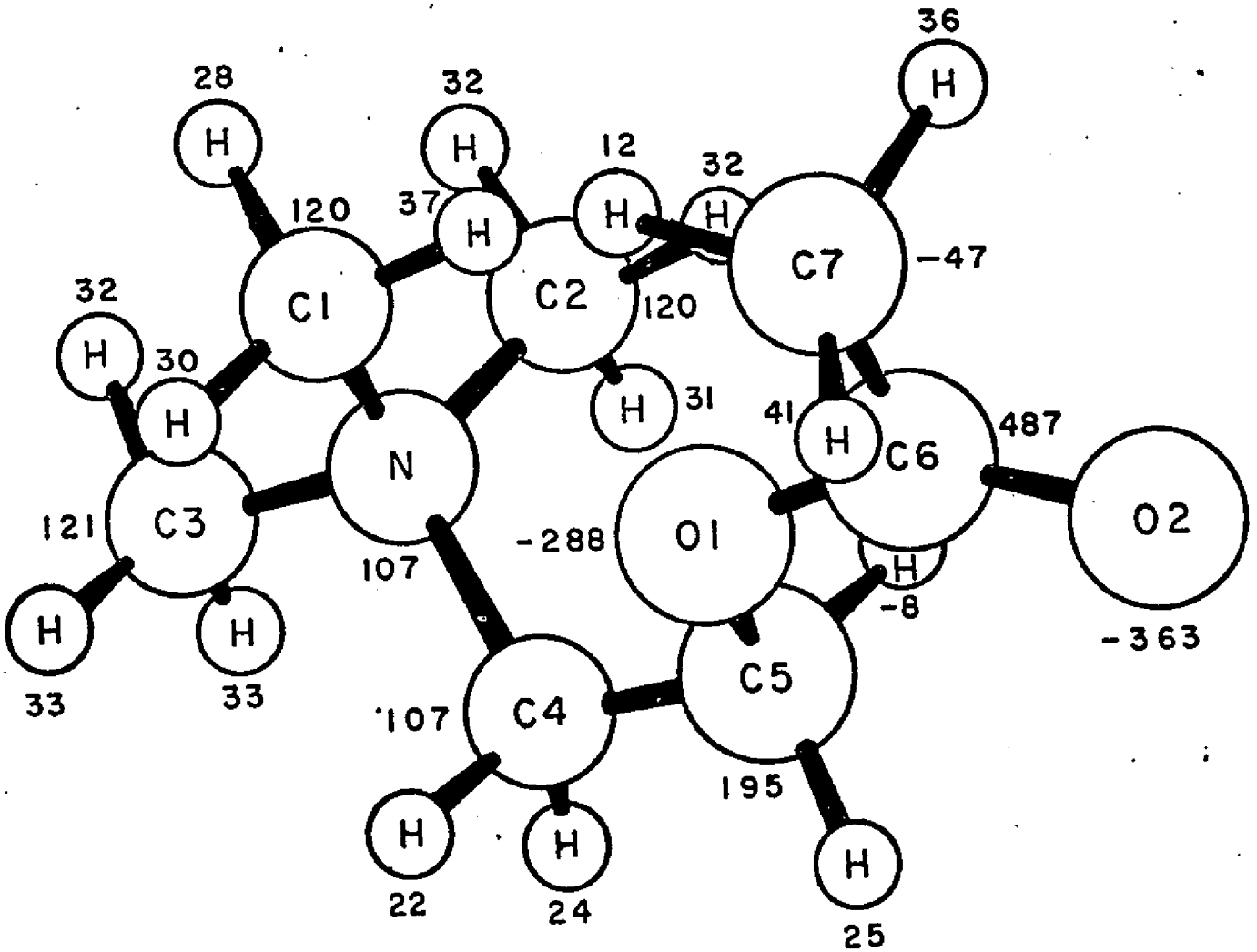


Figure 1


36
H
28
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32
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12
32
120
37
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C7
-47
C1
C2
120
32
H
30
H
31
41
H
C6
487
N
C3
121
-288
O1
O2
H
-8
107
H
H
-363
33
33
C5
107
C4
195
H
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H
22
24
25

Figure 2

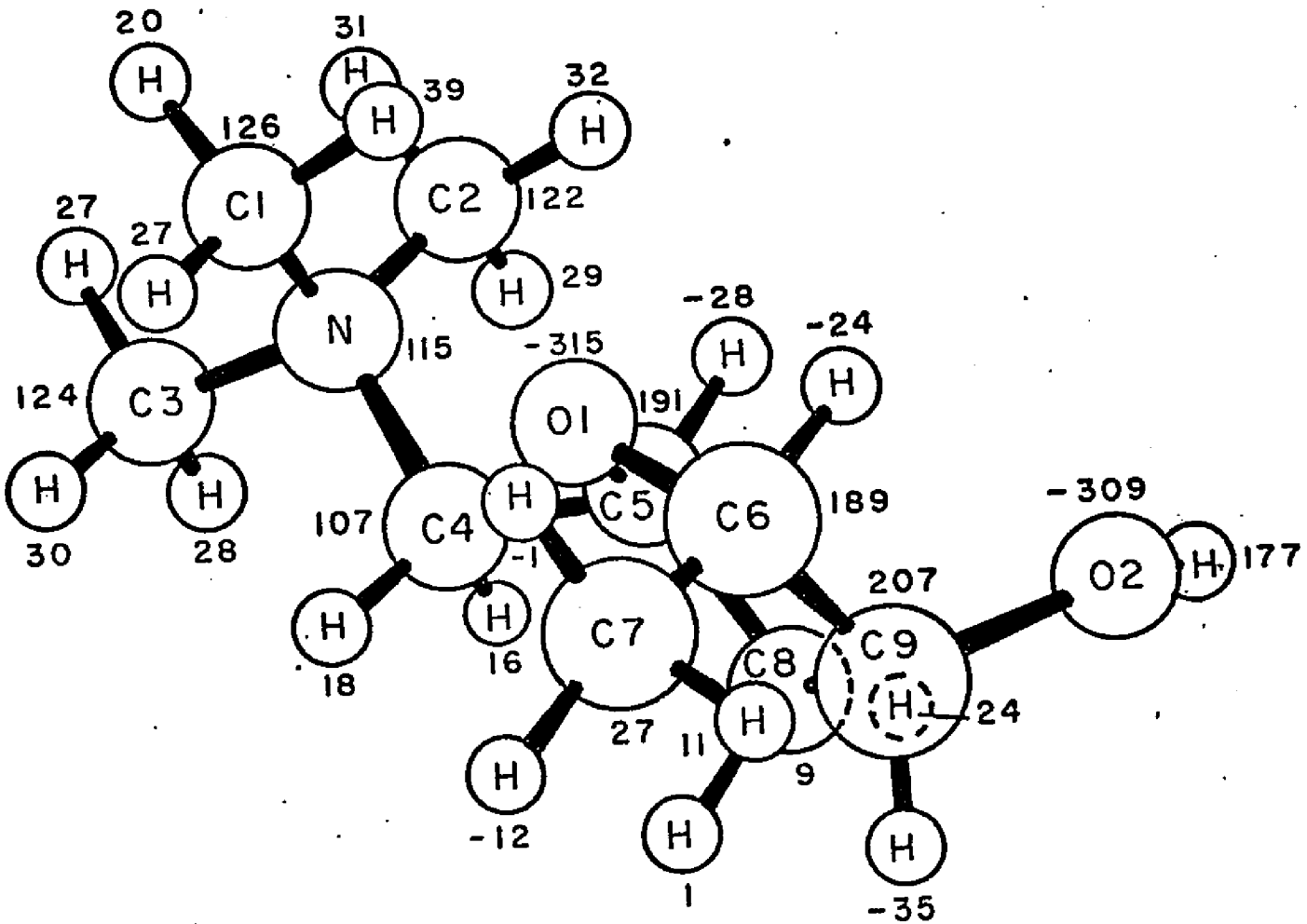

20
31
H
H
39
32
H
H
126
H
C1
C2
122
27
27
H
H
29
H
-28
-24
N
-315
H
H
115
124
C3
O1
191
H
H
H
C5
C6
189
-309
H
H
107
C4
-1
O2
H
177
H
H
207
C7
C8
C9
16
18
H
H
24
27
11
H
9
H
H
-12
1
-35

Figure 3

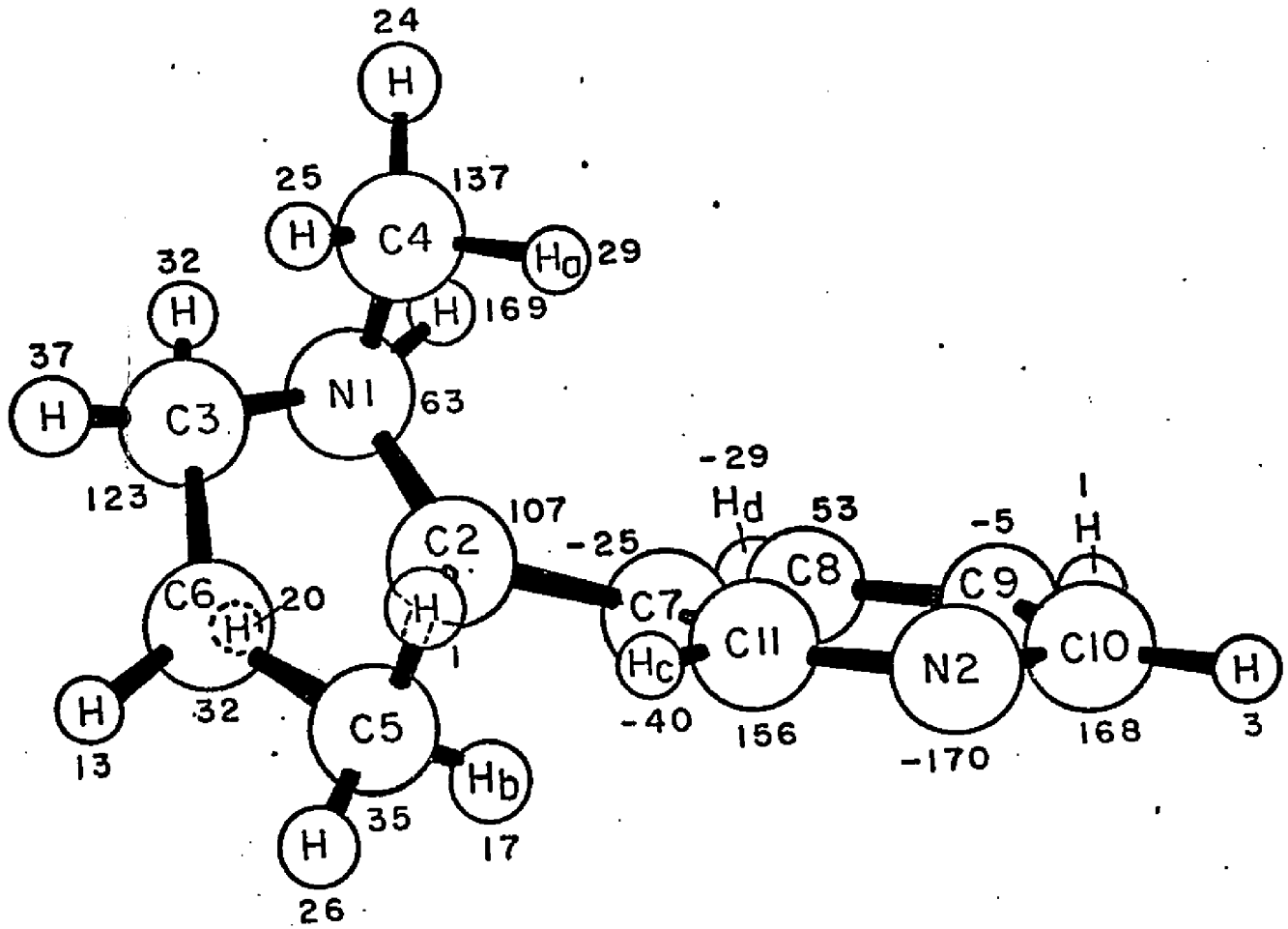

24
H
25
H
137
C4
Ha
29
H
169
32
H
37
H
C3
N1
63
123
C2
107
-25
-29
Hd
53
-5
1
H
C8
C9
C6
20
H
H
C7
C11
N2
C10
H
Hc
-40
156
-170
168
3
H
13
32
C5
Hb
35
17
H
26

Figure 4

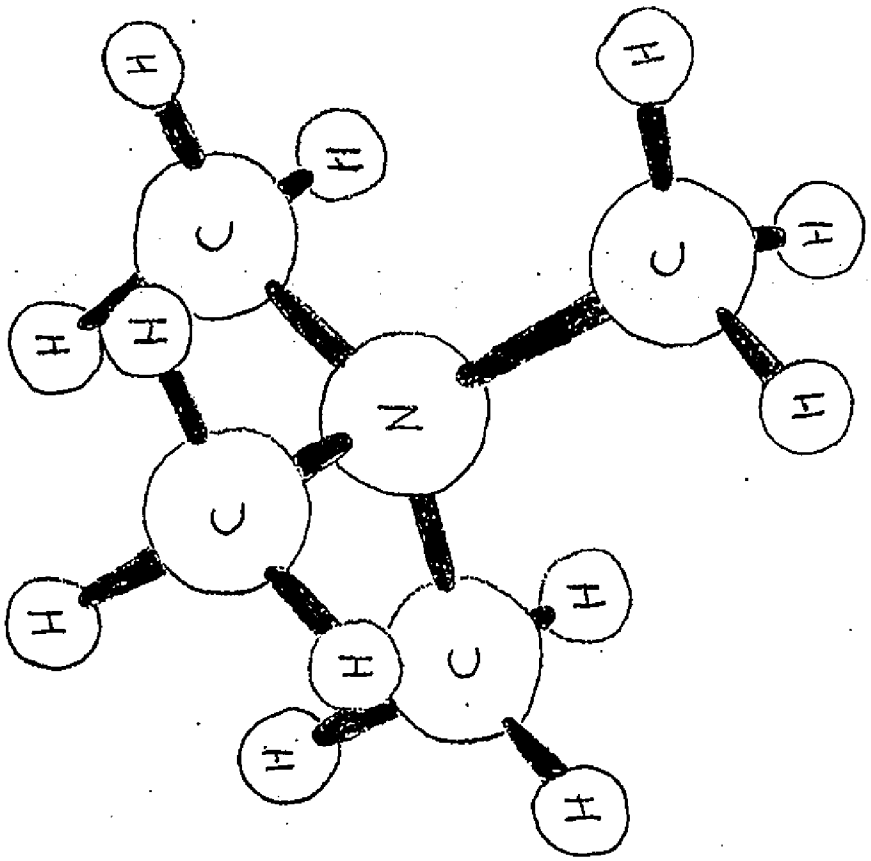


Figure 5

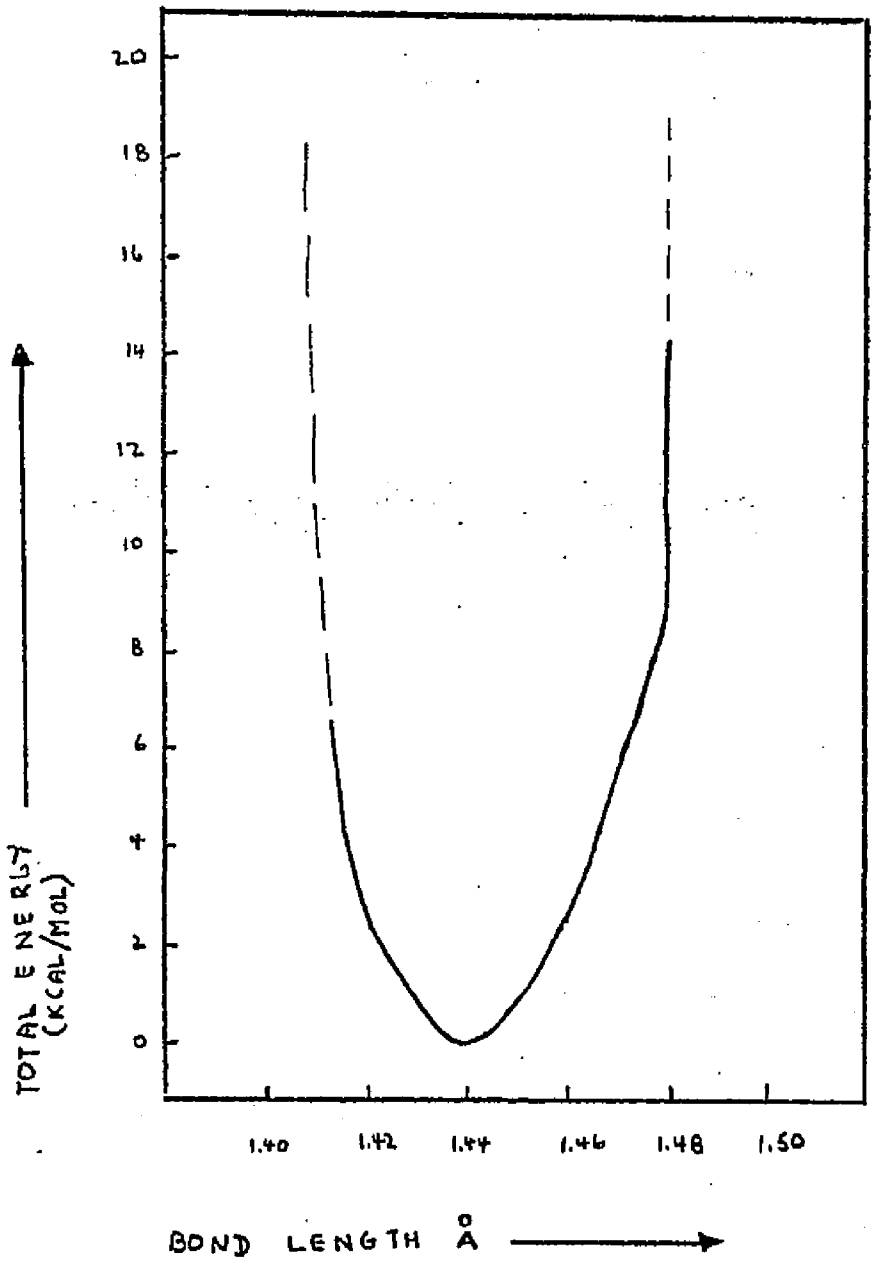

TOTAL ENERGY (KCAL/MOL)
20
18
16
14
12
10
8
6
4
2
0
1.40
1.42
1.44
1.46
1.48
1.50
BOND LENGTH Å

Figure 6

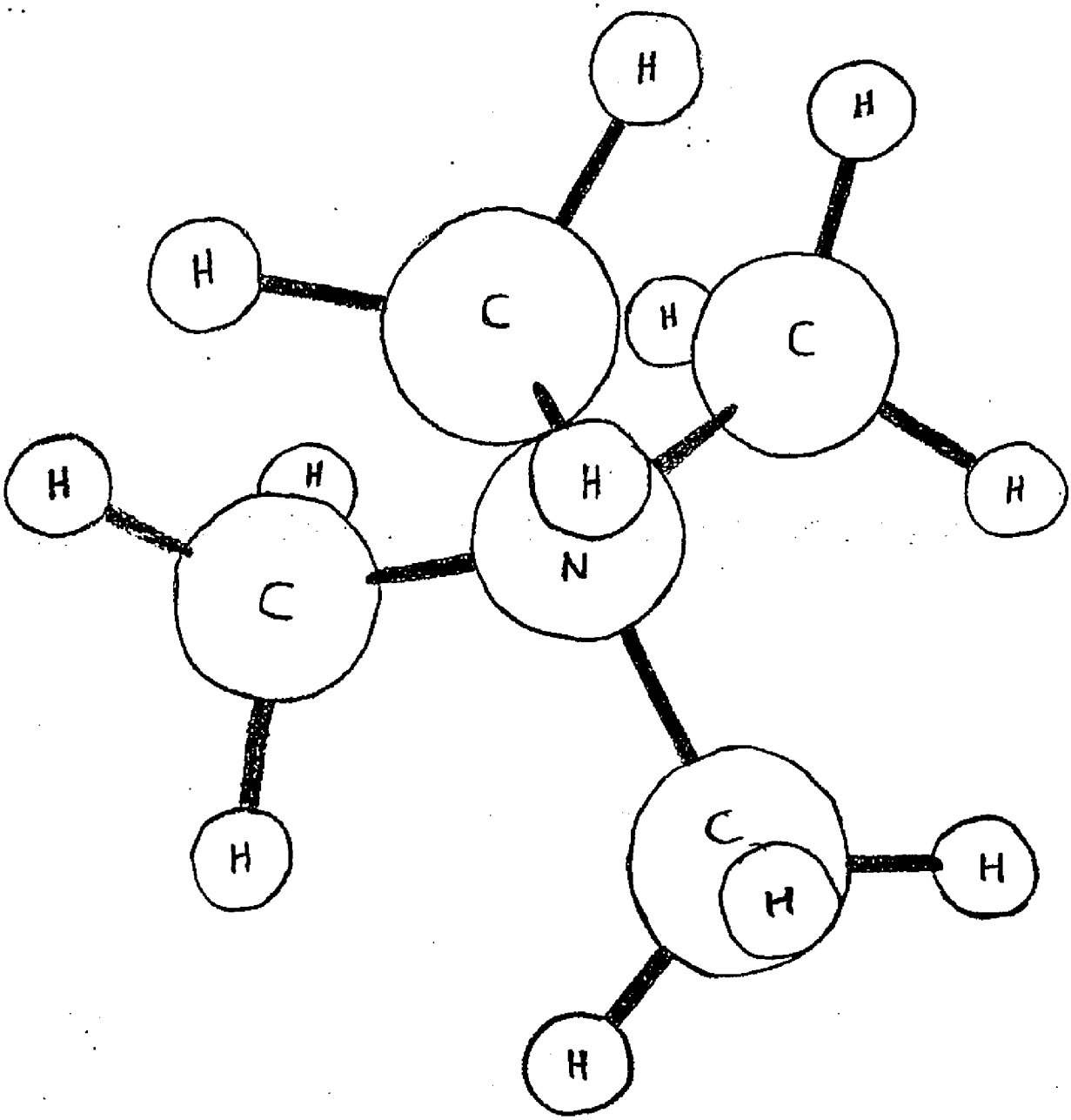


Figure 7

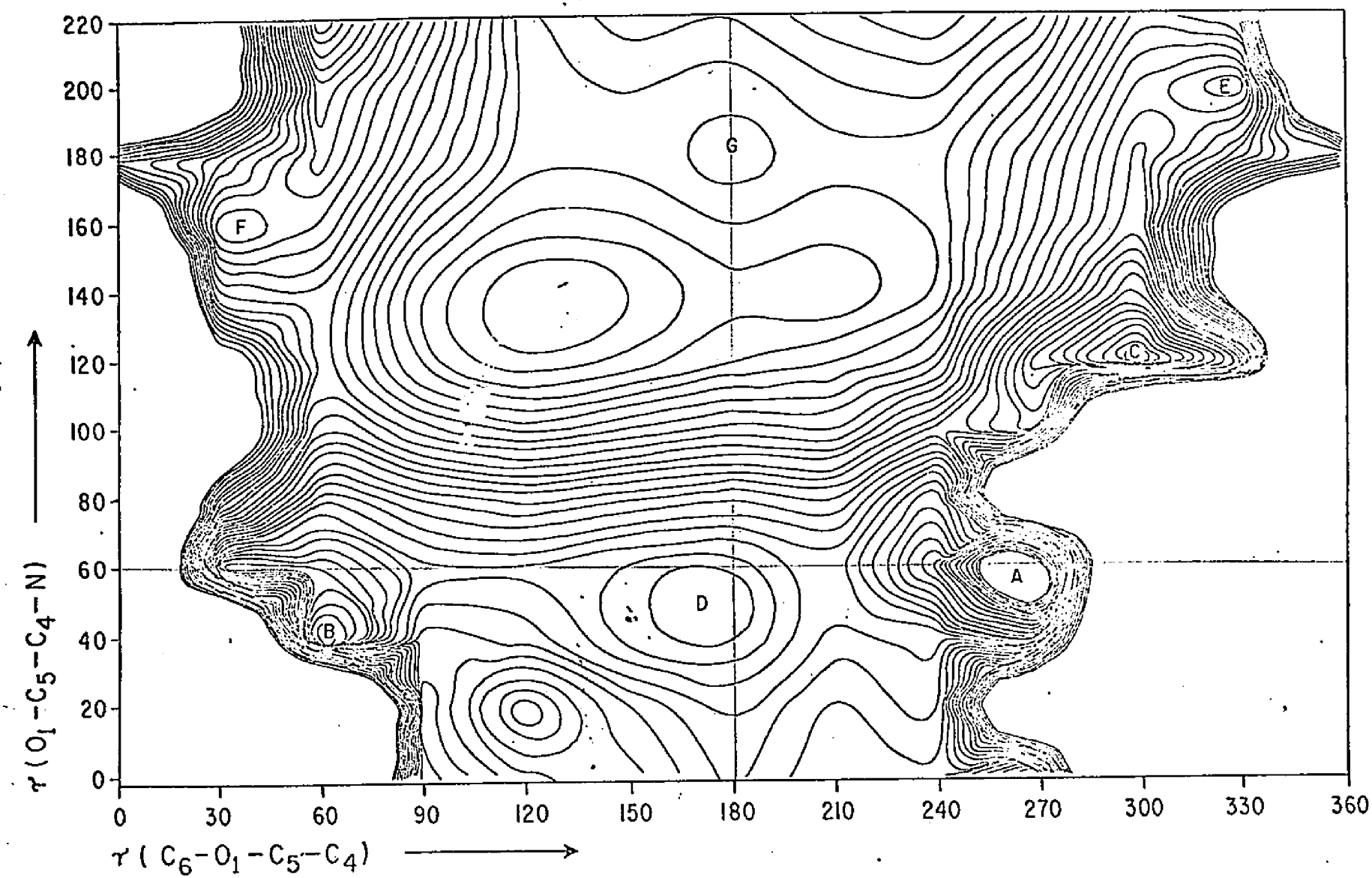

220
200
180
160
140
120
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
330
360
A
B
C
D
E
F
G
τ (O1 – C5 – C4 – N)
τ (C6 – O1 – C5 – C4)

Figure 8

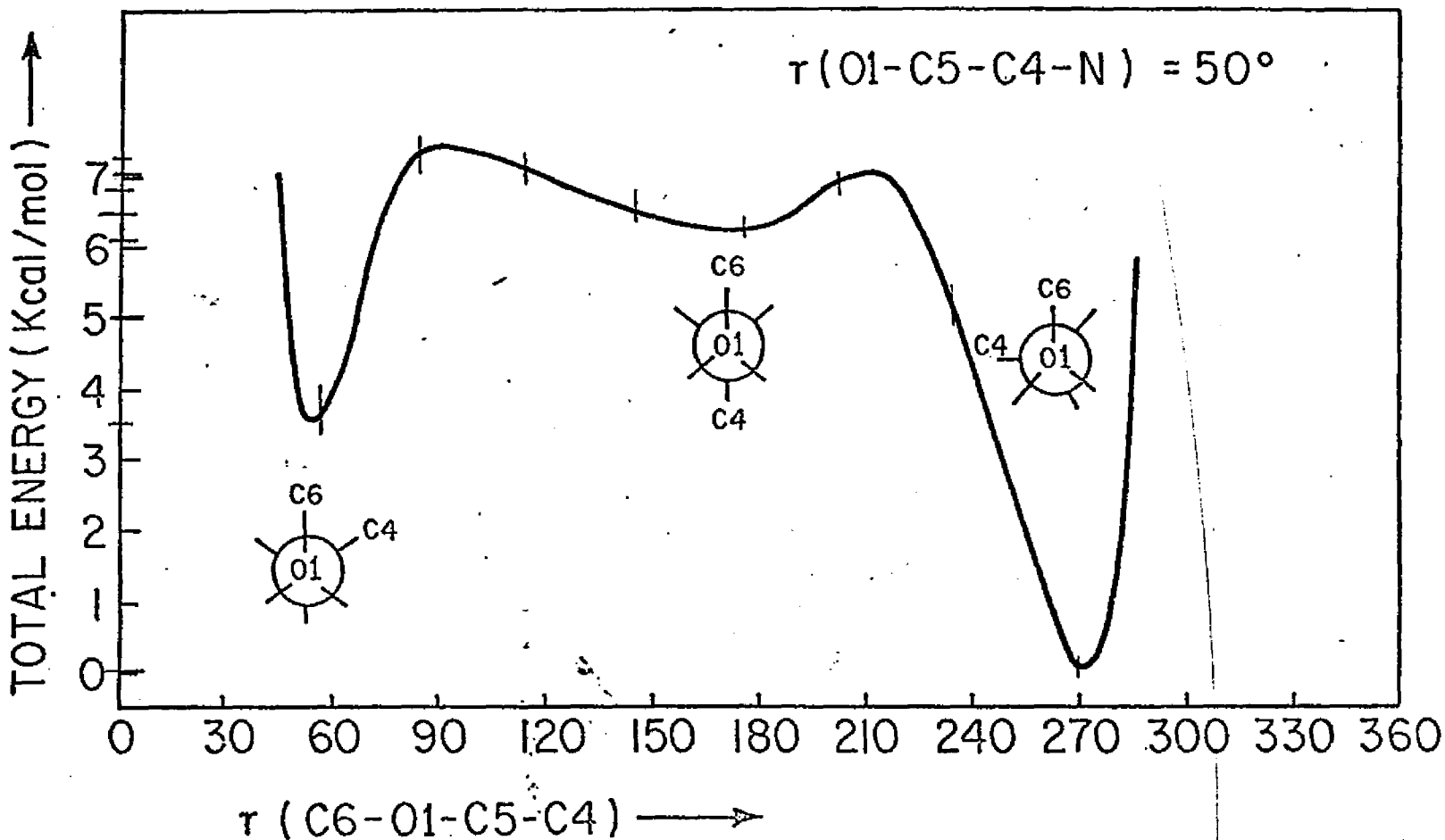

τ(O1-C5-C4-N) = 50°
TOTAL ENERGY (Kcal/mol)
0
1
2
3
4
5
6
7
0 30 60 90 120 150 180 210 240 270 300 330 360
τ (C6-O1-C5-C4)
C6
O1
C4
C6
O1
C4
C6
C4
O1

Figure 9

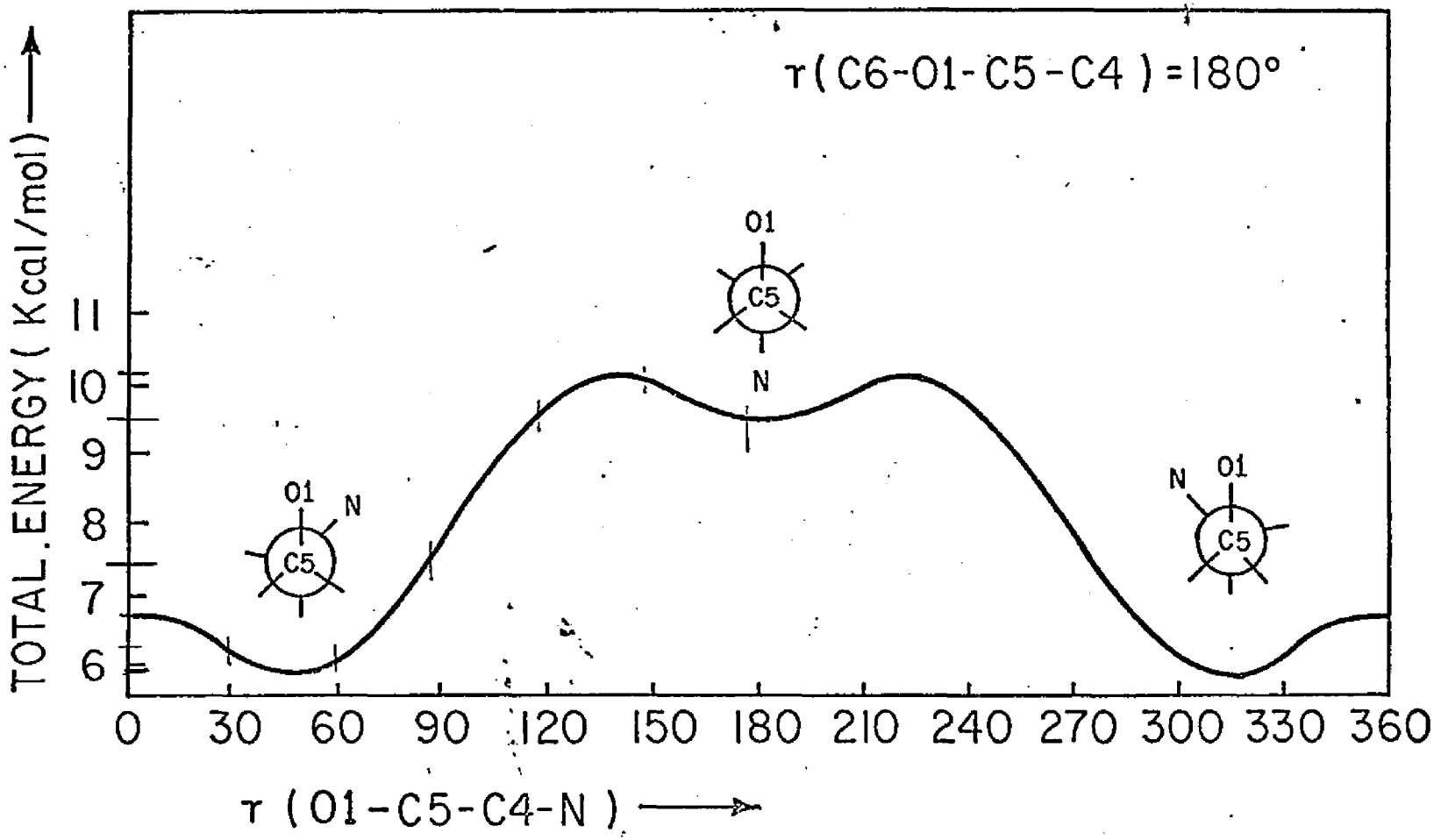
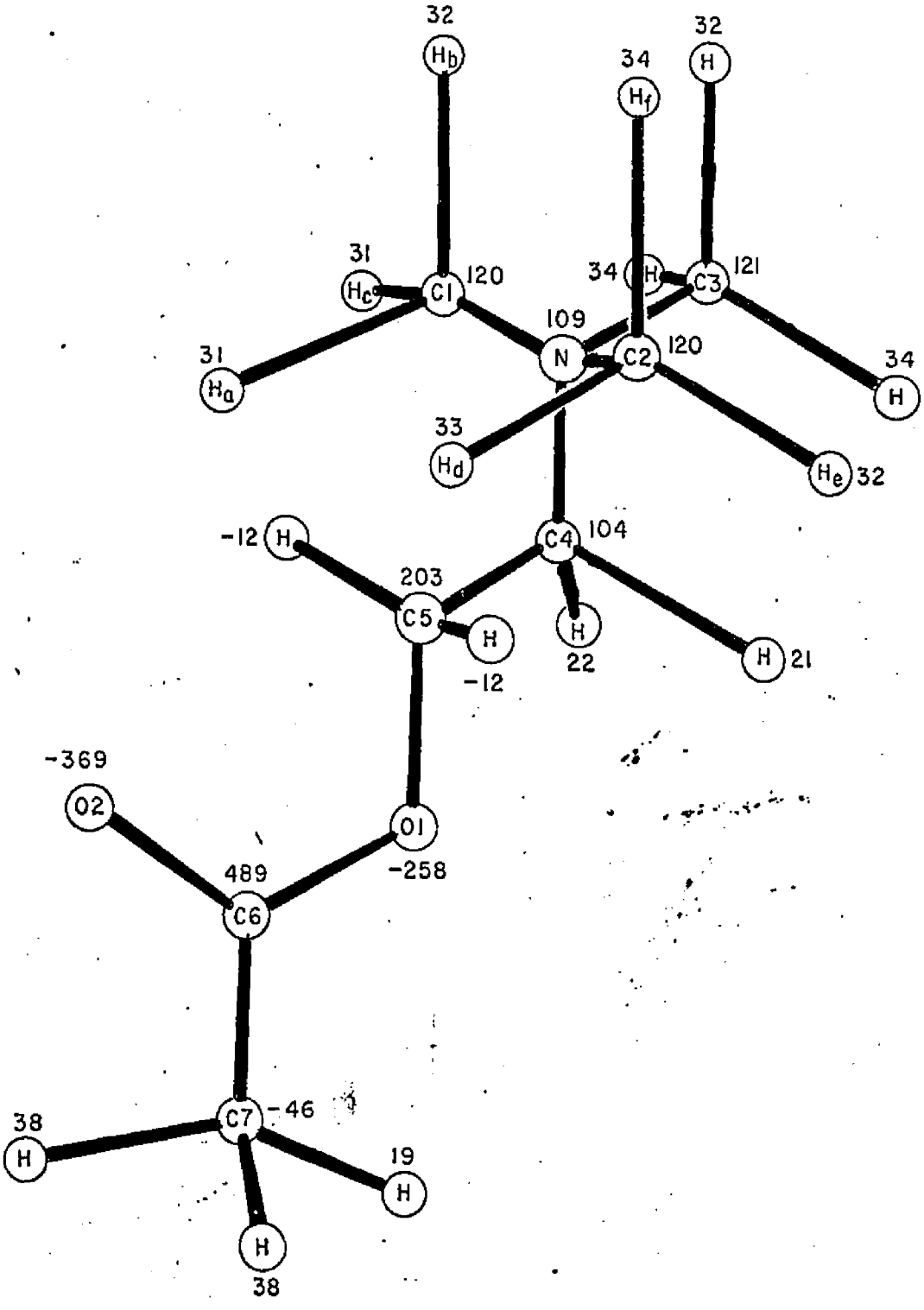

τ(C6-01-C5-C4) =180°
TOTAL. ENERGY (Kcal/mol)
11
10
9
8
7
6
0 30 60 90 120 150 180 210 240 270 300 330 360
τ (01-C5-C4-N)
01
C5
N

Figure 10


32
Hb
34
Hf
32
H
31
Hc
C1
120
34
H
C3
121
109
31
Ha
N
C2
120
34
H
33
Hd
He
32
-12
H
C4
104
203
C5
H
-12
H
22
H
21
-369
O2
O1
489
-258
C6
C7
-46
38
H
19
H
H
38

v

Figure 11

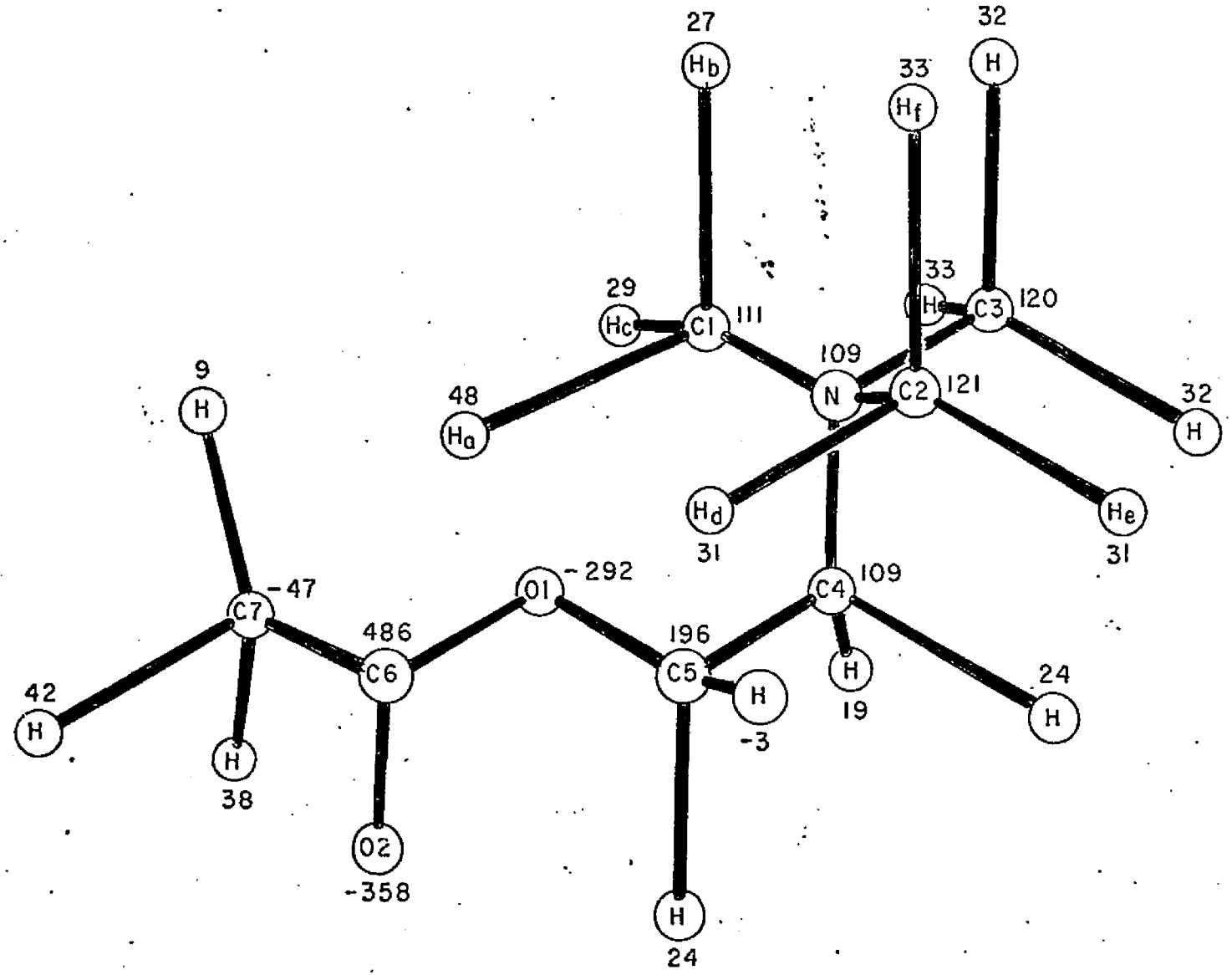

27
Hb
32
H
33
Hf
29
Hc
C1
111
33
He
C3
120
109
9
H
48
Ha
N
C2
121
32
H
Hd
31
He
31
-47
C7
-292
O1
C4
109
486
196
C6
C5
H
-3
H
19
24
H
42
H
H
38
O2
-358
H
24

Figure 12

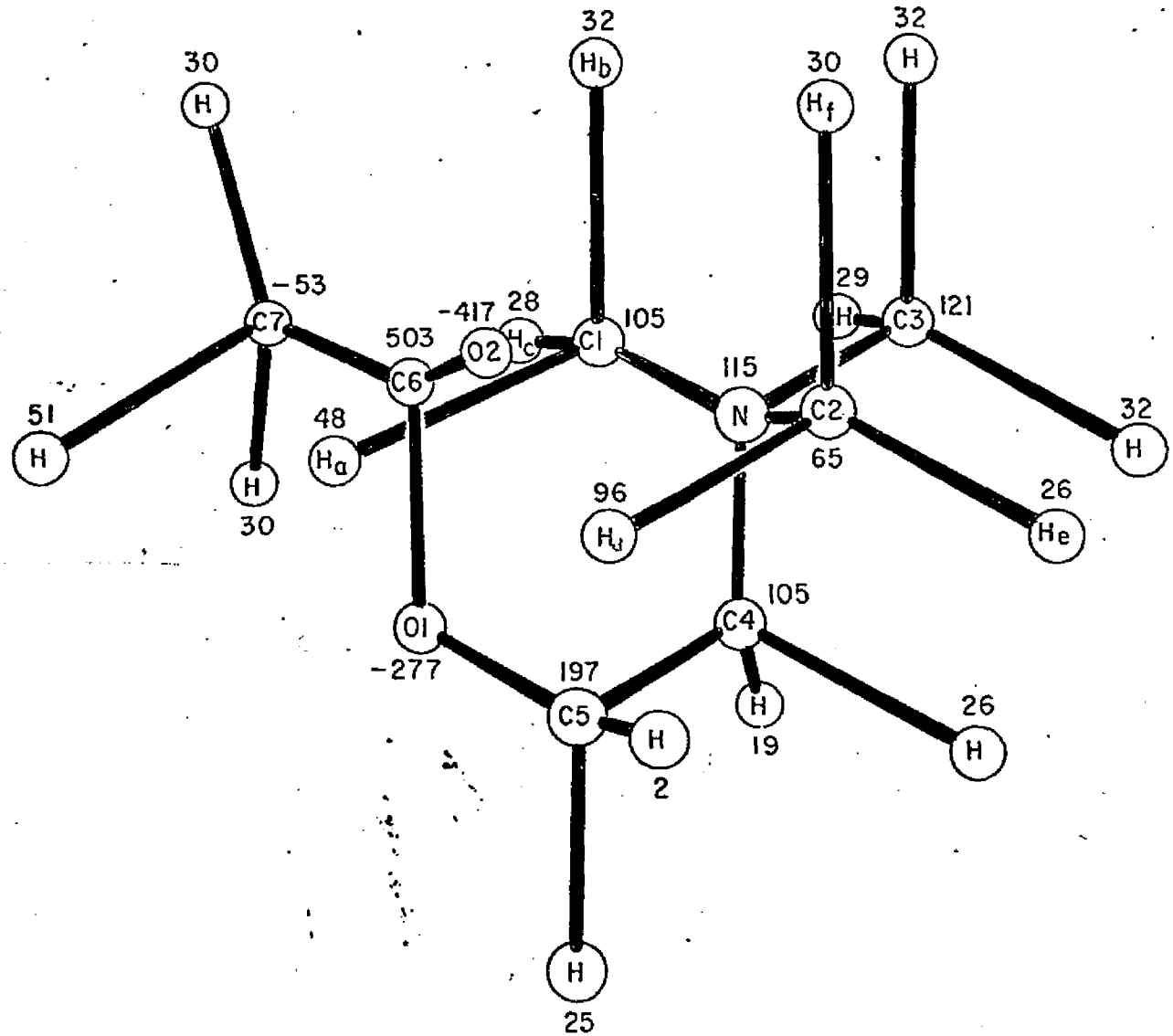

32
Hb
30
H
30
Hf
32
H
-53
C7
-417
28
O2
Hc
503
C6
C1
105
29
He
C3
121
115
N
C2
32
H
51
H
48
Ha
H
30
65
96
Hd
26
He
105
C4
O1
-277
197
C5
H
2
H
19
26
H
H
25

Figure 13

27
Hb
31
H
32
Hf
36
H
41
Hc
C1
109
111
N
C2
119
C3
121
32
H
37
Ha
26
H
31
Hd
31
He
-277
O1
-51
C7
98
C4
200
C6
489
C5
H
-6
H
44
H
21
H
48
H
28
O2
-404
H
25

Figure 14

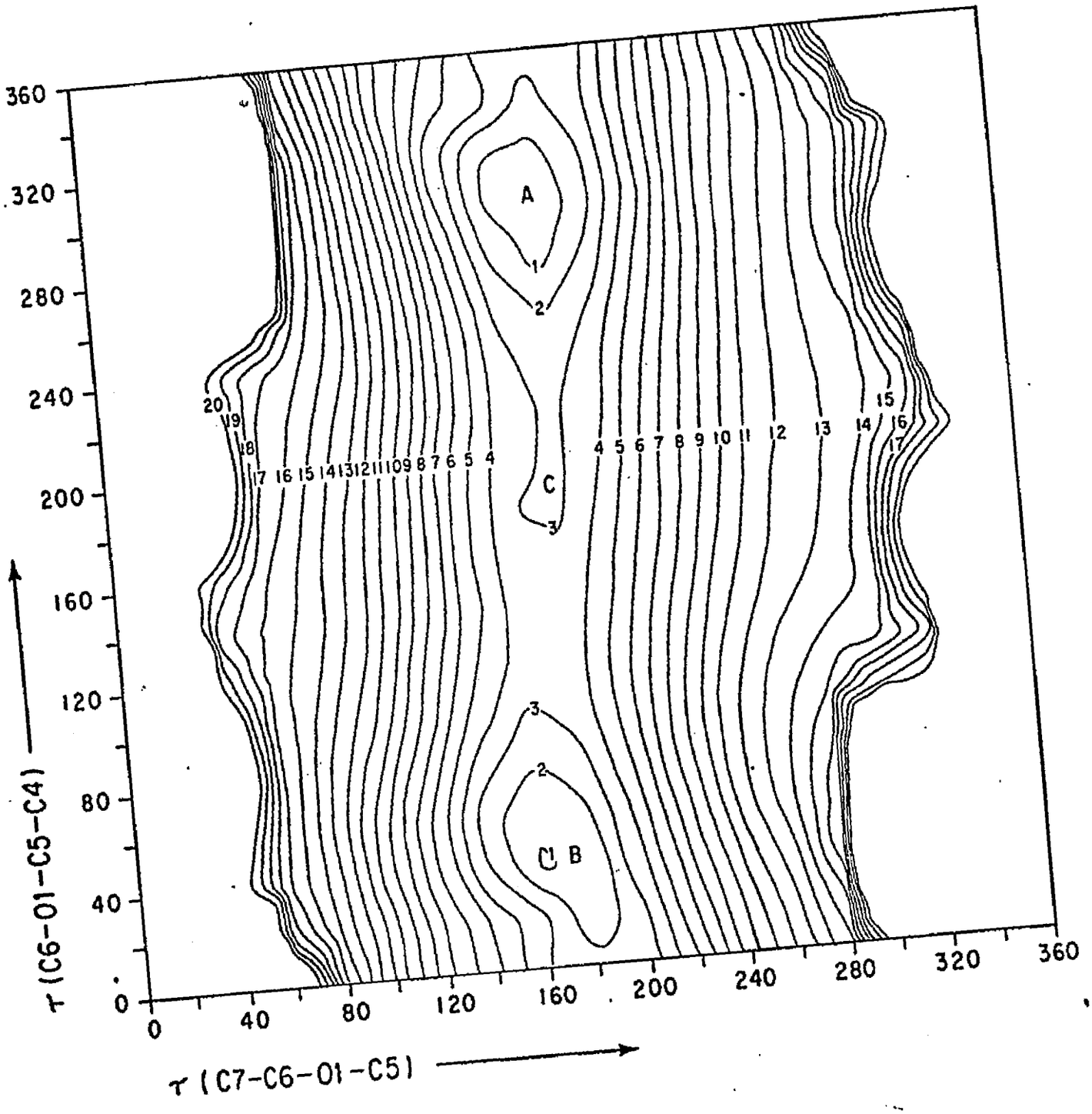

360
320
280
240
200
160
120
80
40
0
0
40
80
120
160
200
240
280
320
360
τ (C6-01-C5-C4)
τ (C7-C6-01-C5)
A
B
C
1
2
3
4 5 6 7 8 9 10 11 12 13 14 15 16 17
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4

Figure 15

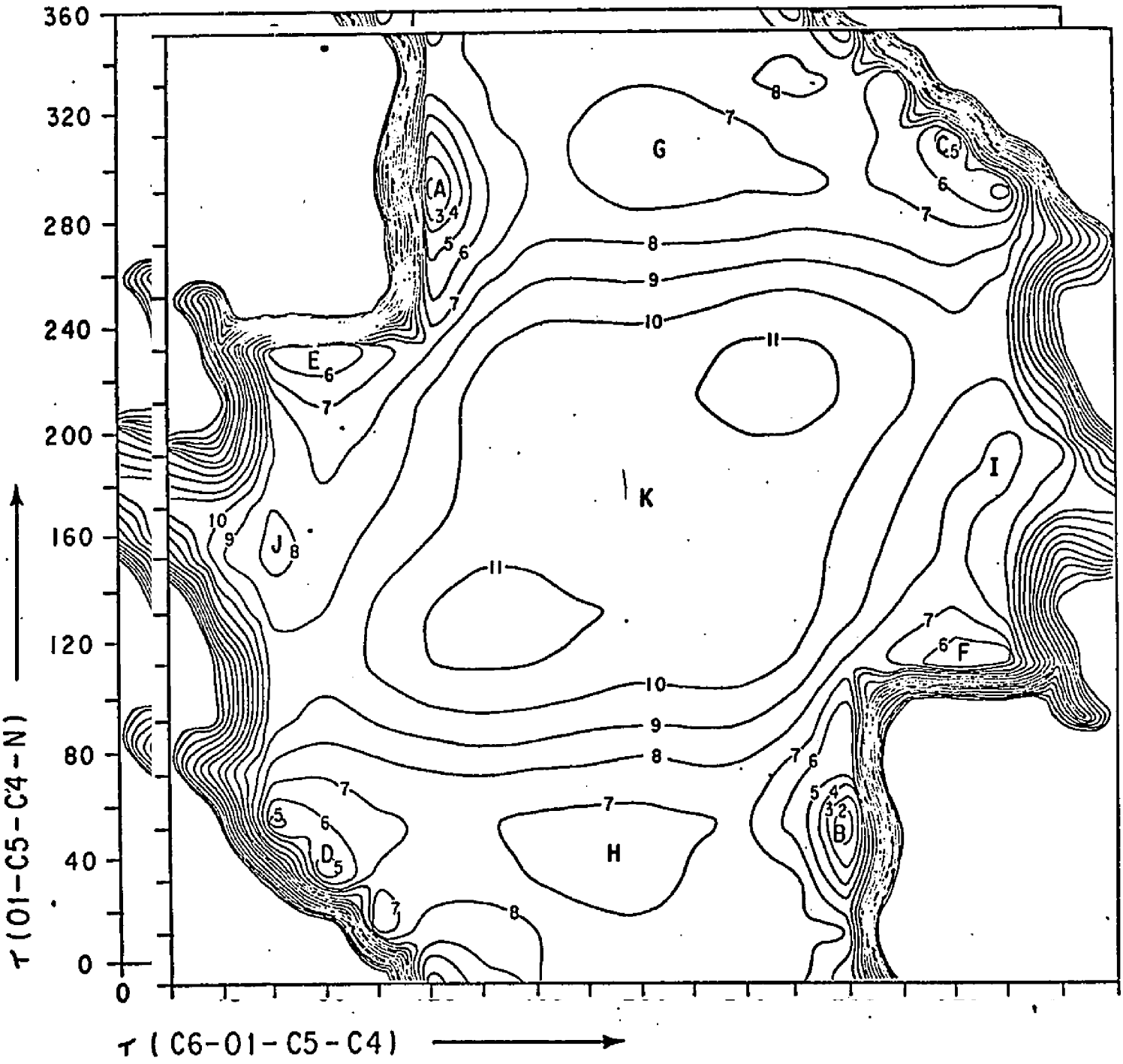

360
320
280
240
200
160
120
80
40
0
0
τ(O1-C5-C4-N)
τ(C6-O1-C5-C4)
A
B
C5
D5
E6
F
G
H
I
J8
K
3
4
5
6
7
8
9
10
11

Figure 16

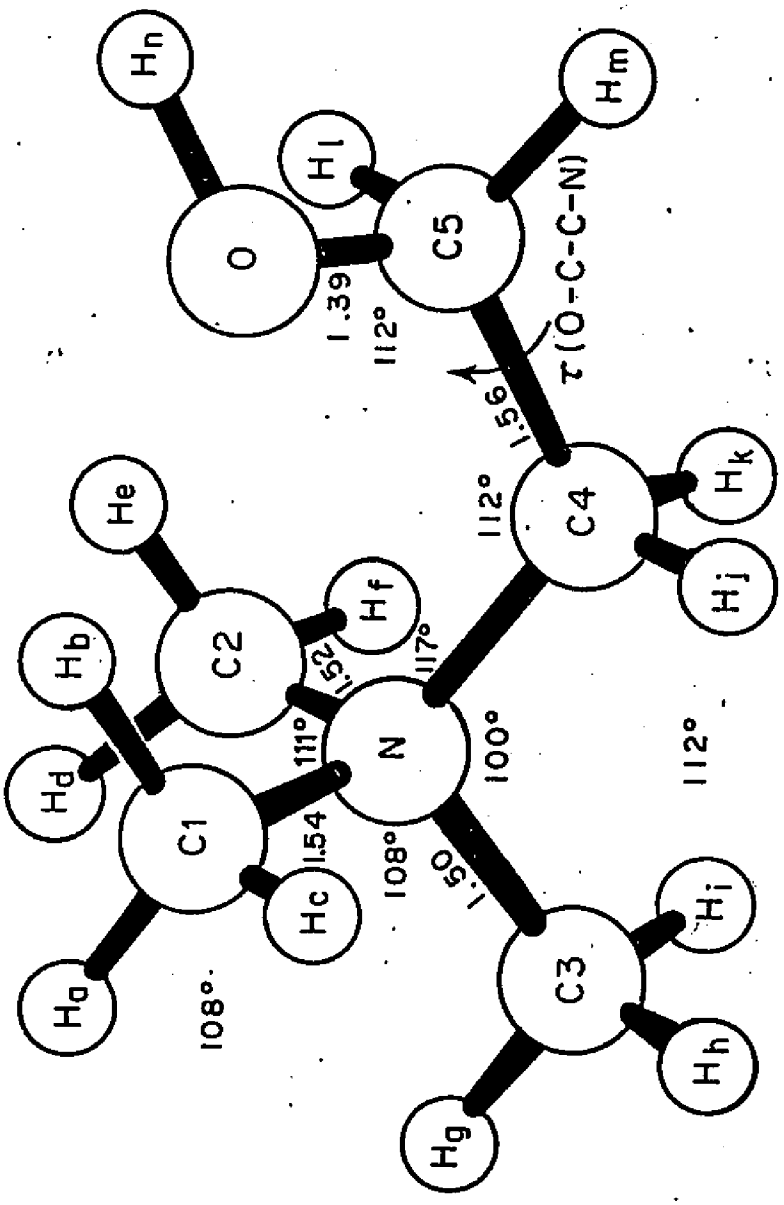

Hn
Hl
Hm
O
C5
1.39
112°
τ(O-C-C-N)
1.59
112°
C4
Hk
Hj
He
Hf
Hb
C2
1.52
117°
111°
N
100°
112°
Hd
C1
1.54
108°
1.50
Hc
Ha
108°
C3
Hi
Hg
Hh

Figure 17

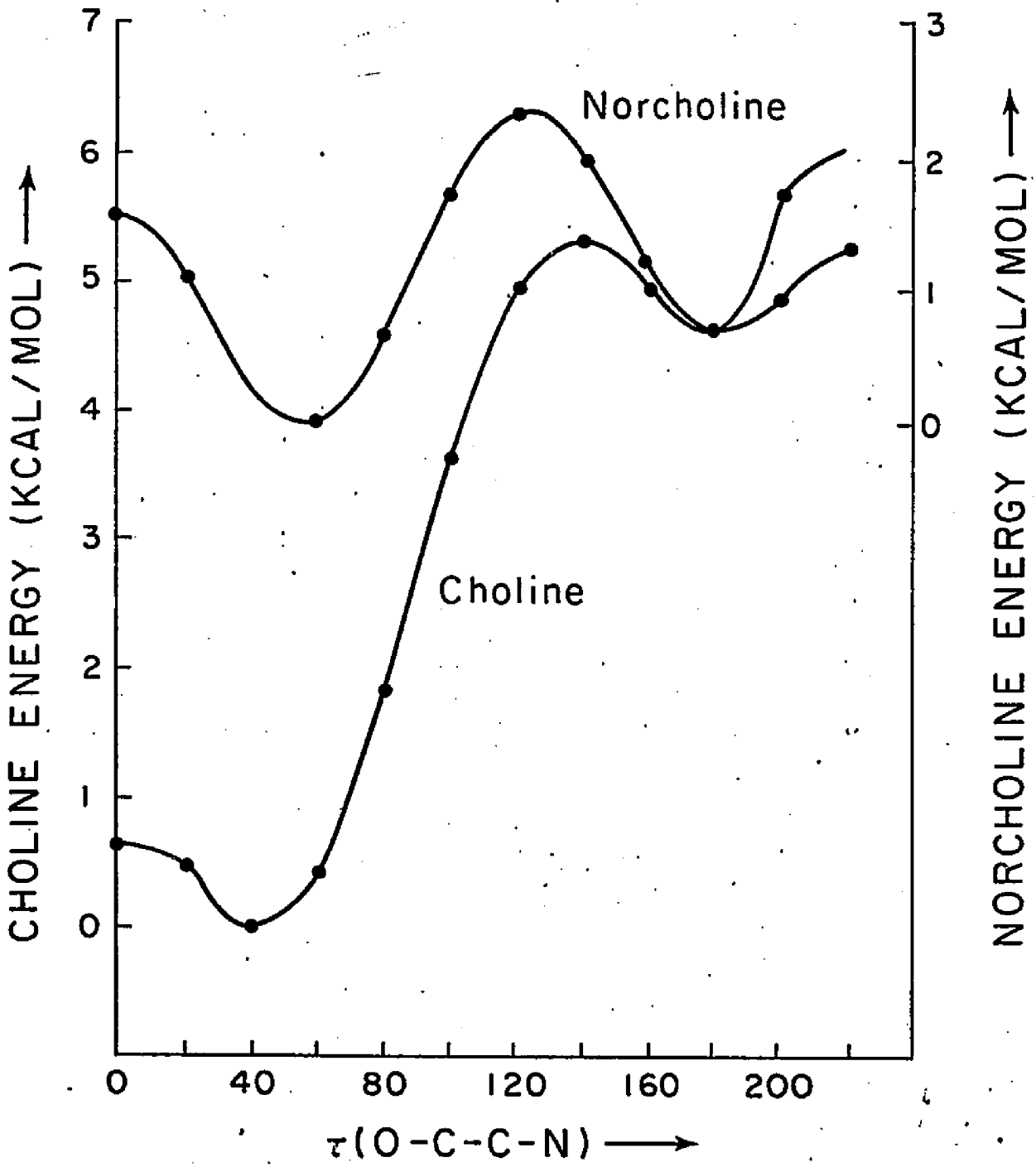

Norcholine
Choline
CHOLINE ENERGY (KCAL/MOL)
NORCHOLINE ENERGY (KCAL/MOL)
τ(O-C-C-N)
0
40
80
120
160
200
7
6
5
4
3
2
1
0
3
2
1
0

Figure 18

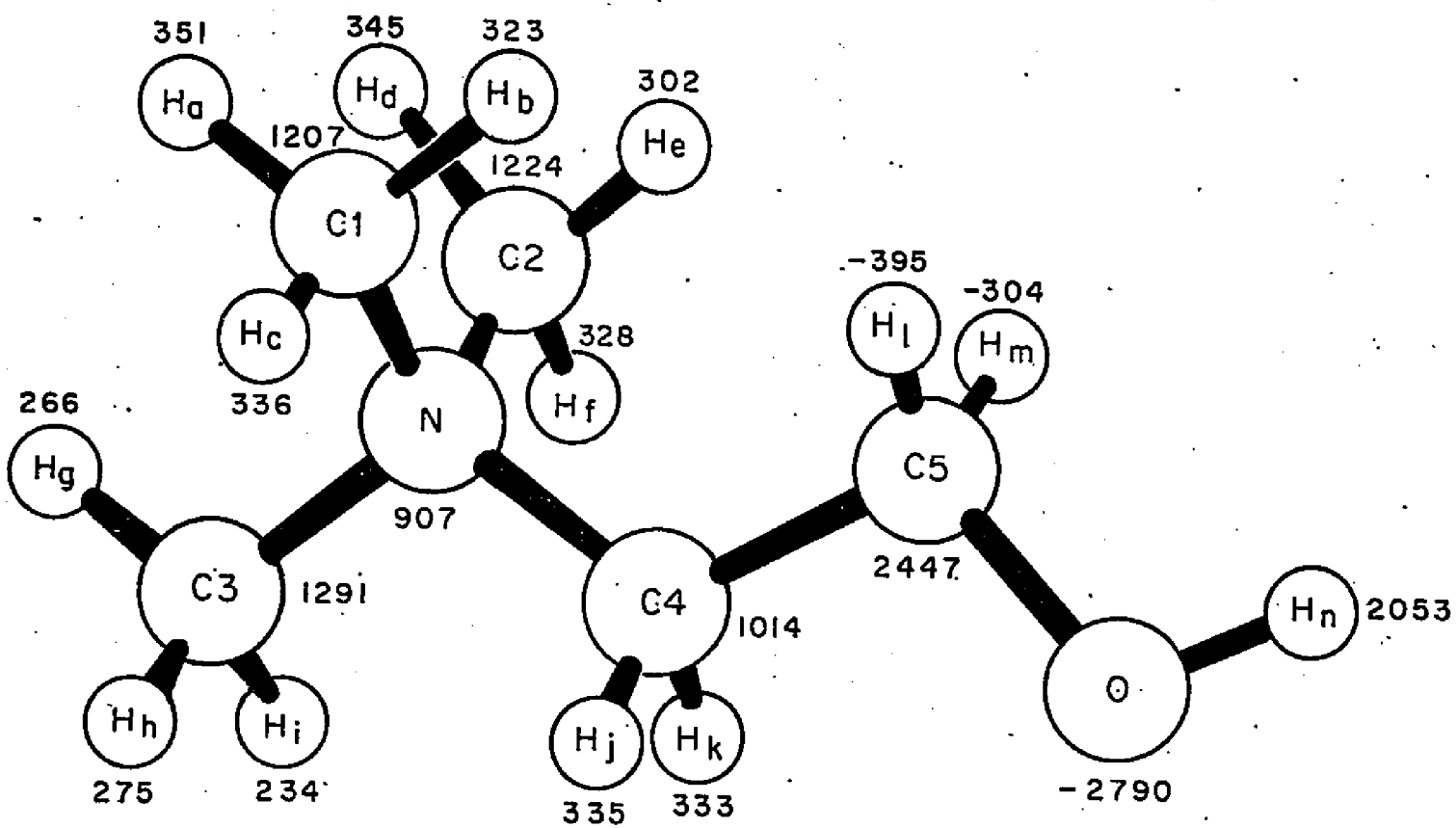

351
345
323
Ha
Hd
Hb
302
He
1207
1224
C1
C2
-395
-304
Hl
Hm
328
Hc
Hf
336
N
266
Hg
C5
907
C3
1291
C4
1014
2447
Hn
2053
Hh
Hi
Hj
Hk
O
275
234
335
333
-2790

Figure 19

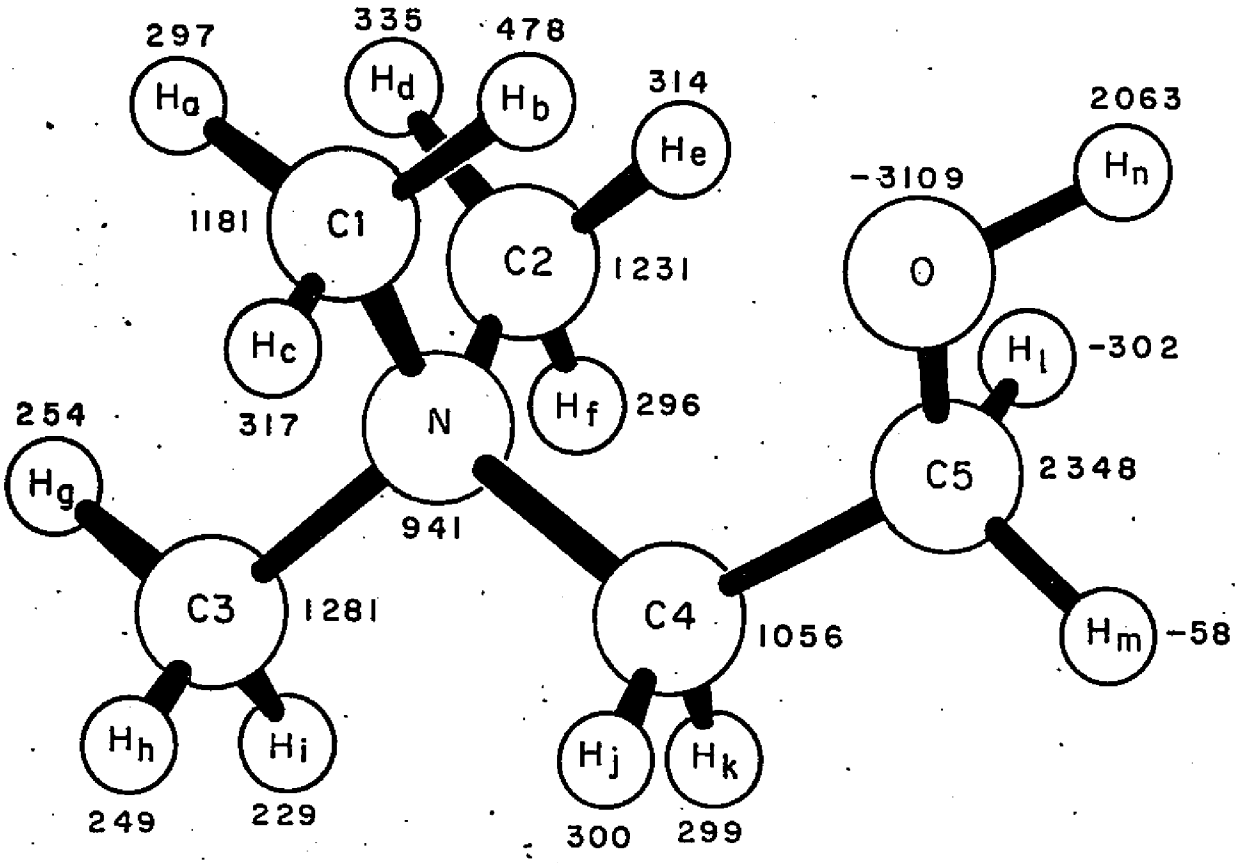

297
335
478
314
2063
Ha
Hd
Hb
He
Hn
-3109
1181
C1
C2
1231
O
Hc
Hl
-302
317
N
Hf
296
254
2348
Hg
C5
941
C3
1281
C4
1056
Hm
-58
Hh
Hi
Hj
Hk
249
229
300
299

Figure 20

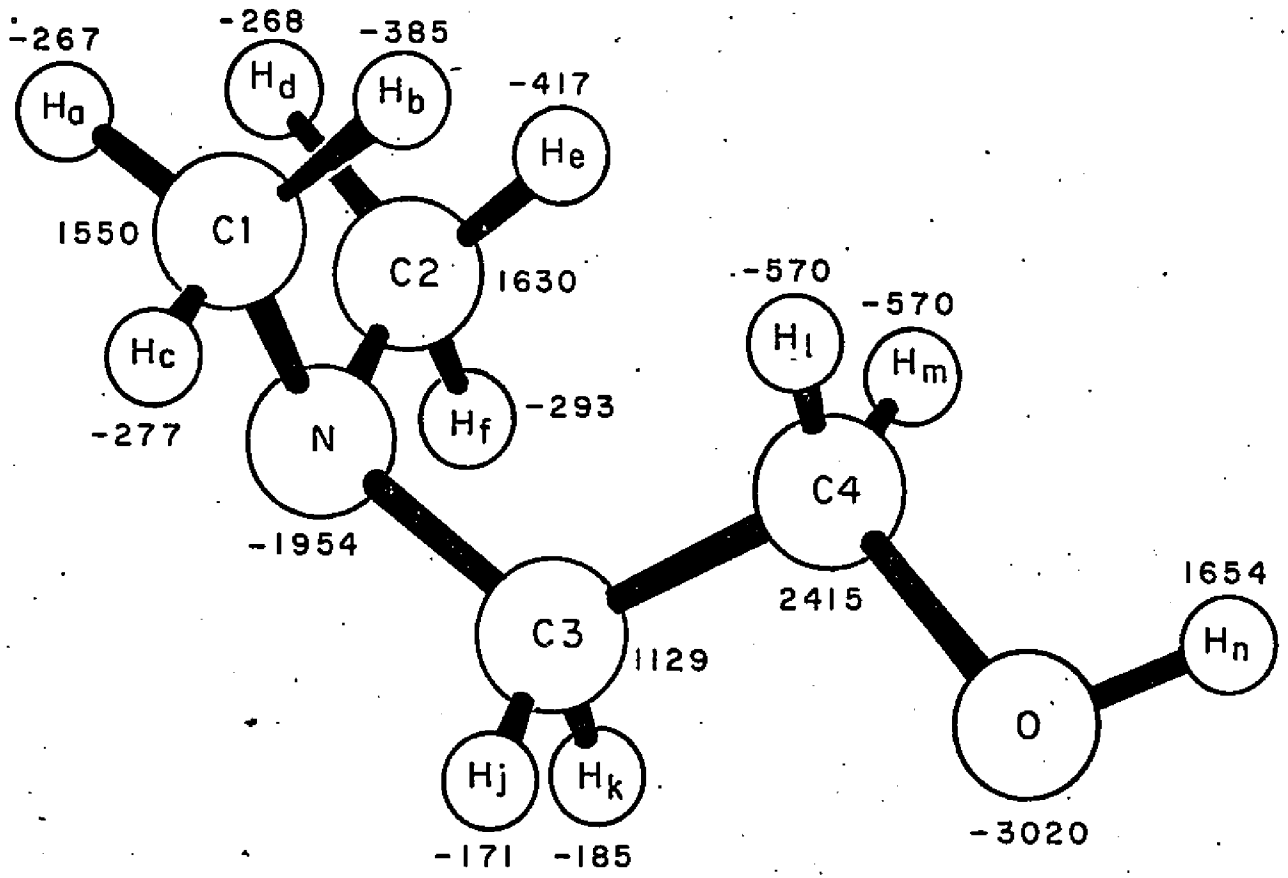

-267
Ha
-268
Hd
-385
Hb
-417
He
1550
C1
C2
1630
-570
Hl
-570
Hm
Hc
-277
N
Hf
-293
-1954
C4
2415
1654
Hn
C3
1129
O
Hj
Hk
-171
-185
-3020

Figure 21

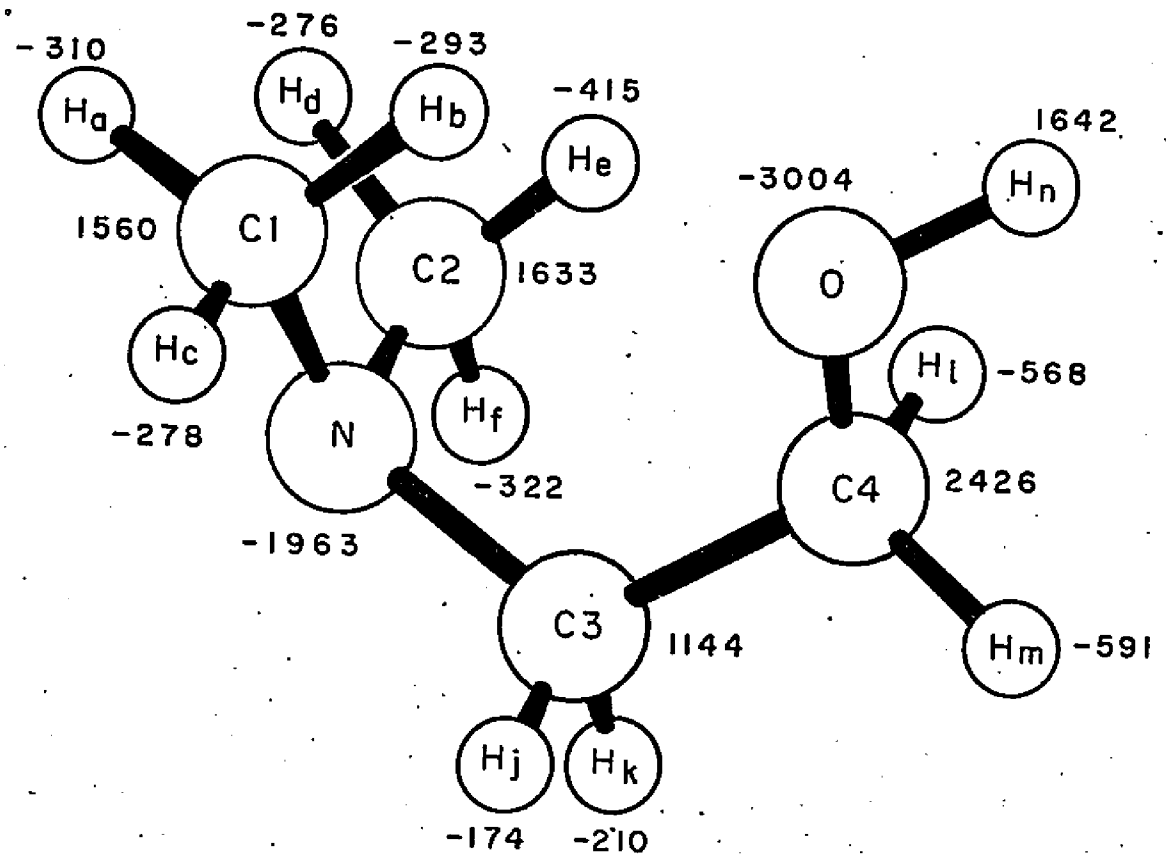

-310
-276
-293
-415
1642
Ha
Hd
Hb
He
Hn
-3004
1560
C1
C2
1633
O
Hc
Hl
-568
-278
N
Hf
-322
C4
2426
-1963
C3
1144
Hm
-591
Hj
Hk
-174
-210

Figure 22

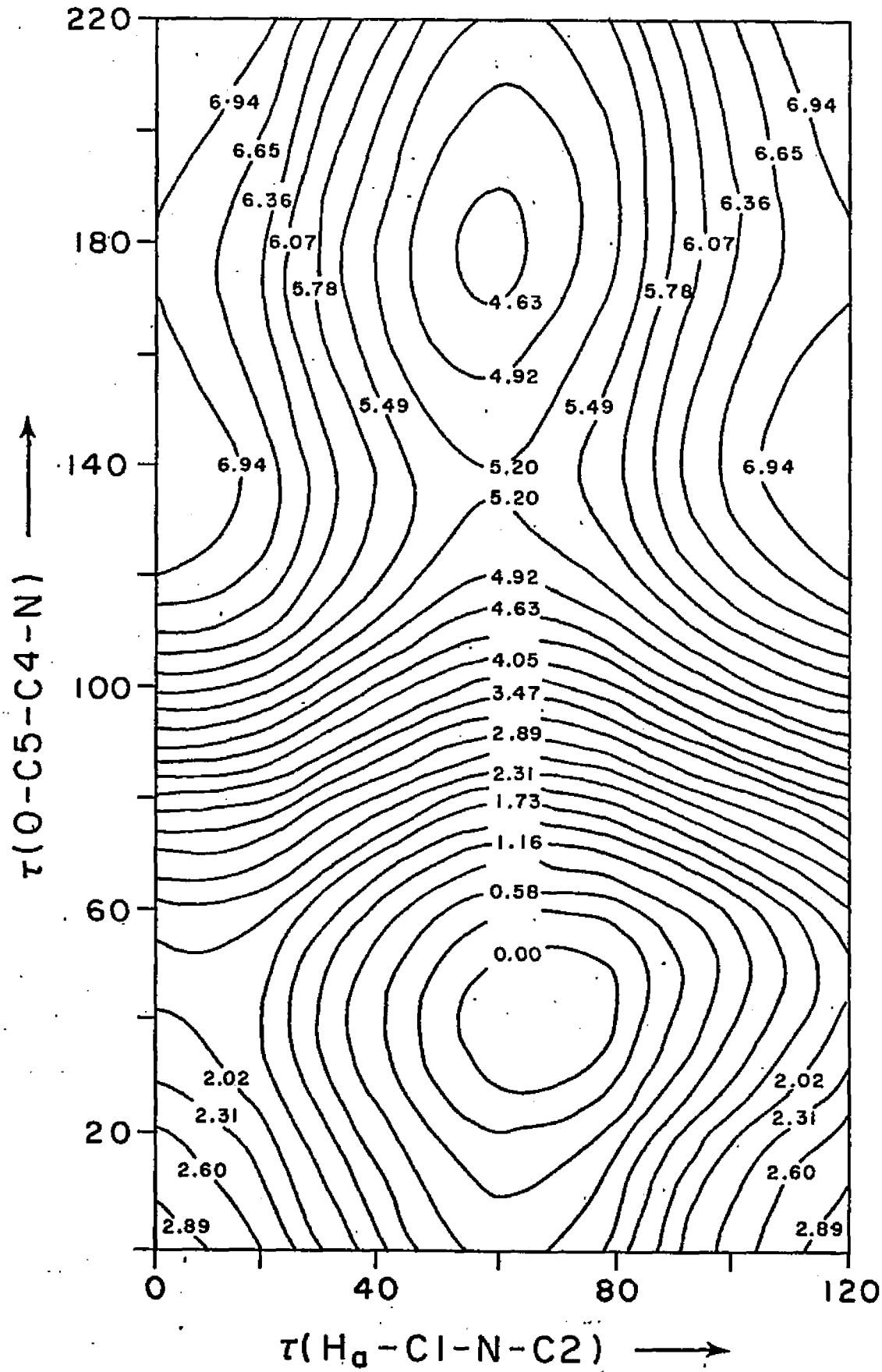

220
180
140
100
60
20
0
40
80
120
τ(O-C5-C4-N)
τ(Hα-C1-N-C2)
6.94
6.65
6.36
6.07
5.78
5.49
5.20
4.92
4.63
4.05
3.47
2.89
2.31
1.73
1.16
0.58
0.00
2.02
2.31
2.60
2.89

Figure 23

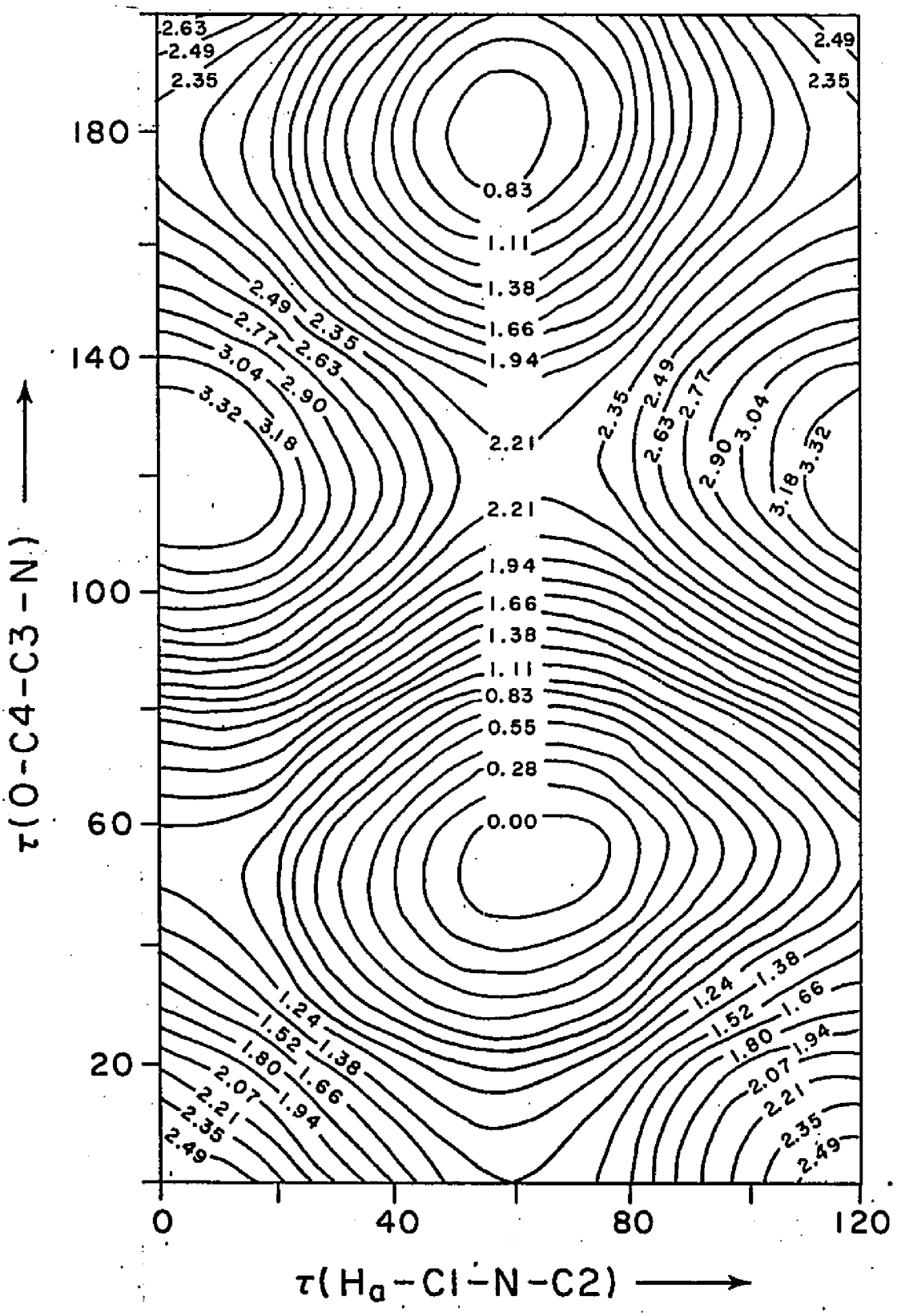

τ(O-C4-C3-N)
τ(Hα-C1-N-C2)
180
140
100
60
20
0
40
80
120
0.83
1.11
1.38
1.66
1.94
2.21
2.49
2.35
2.63
2.77
3.04
2.90
3.32
3.18
0.55
0.28
0.00
1.24
1.52
1.80
2.07

Figure 24

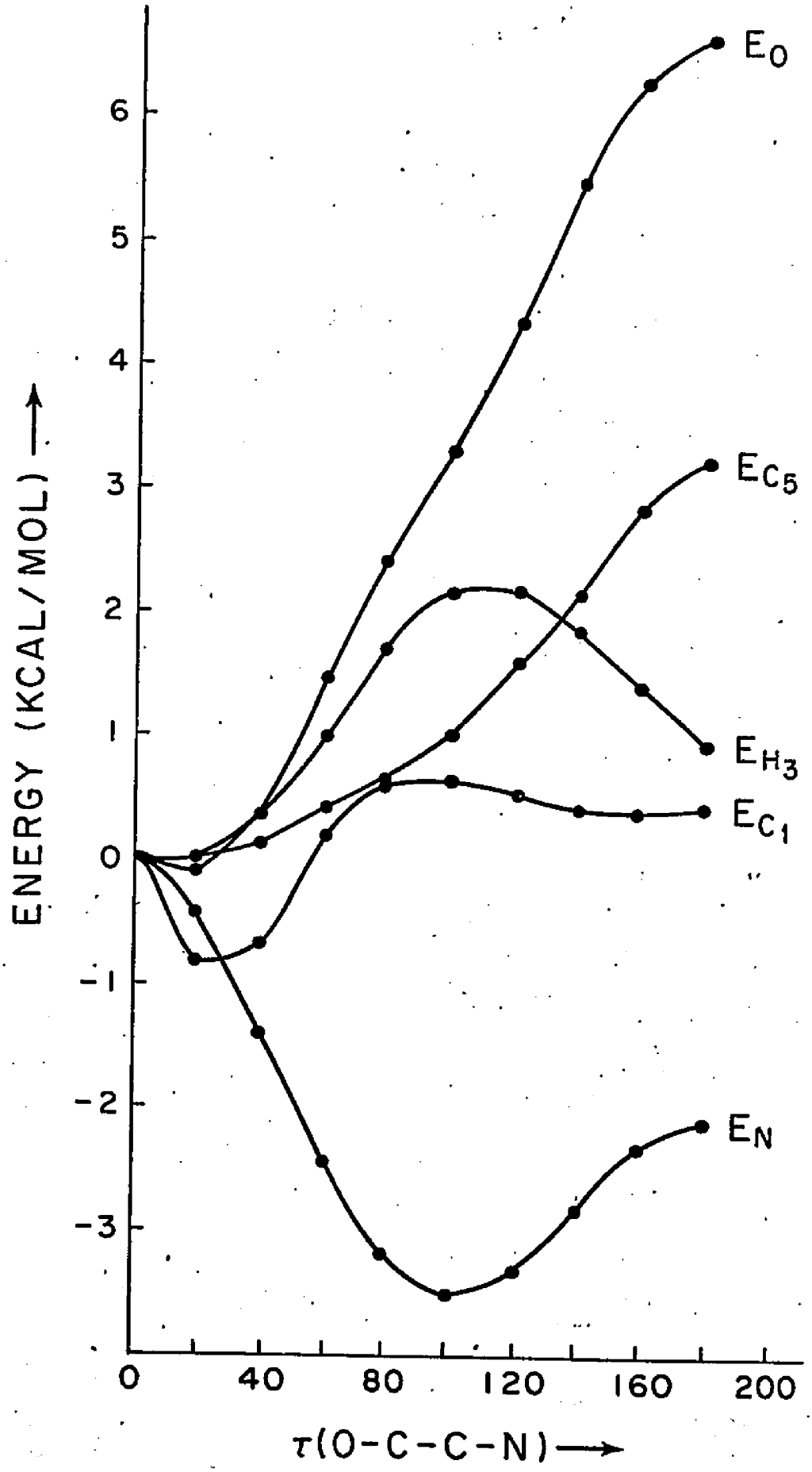

ENERGY (KCAL/MOL) ⟶
6
5
4
3
2
1
0
-1
-2
-3
0
40
80
120
160
200
τ(O-C-C-N) ⟶
E0
EC5
EH3
EC1
EN

Figure 25

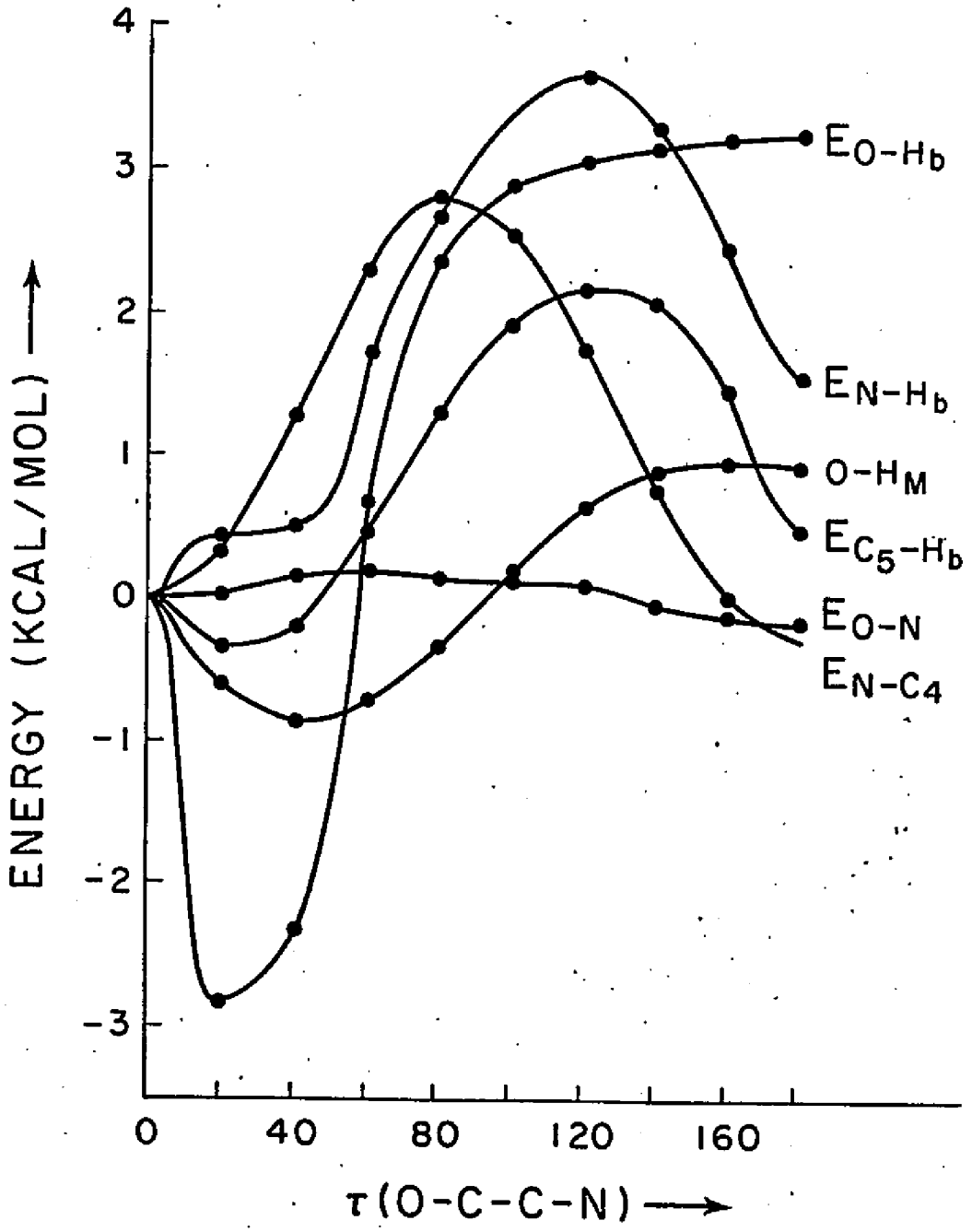

4
3
2
1
0
-1
-2
-3
ENERGY (KCAL/MOL) ⟶
0
40
80
120
160
τ(O-C-C-N) ⟶
E_{O-H_b}
E_{N-H_b}
$O-H_M$
$E_{C_5-H_b}$
E_{O-N}
E_{N-C_4}

Figure 26

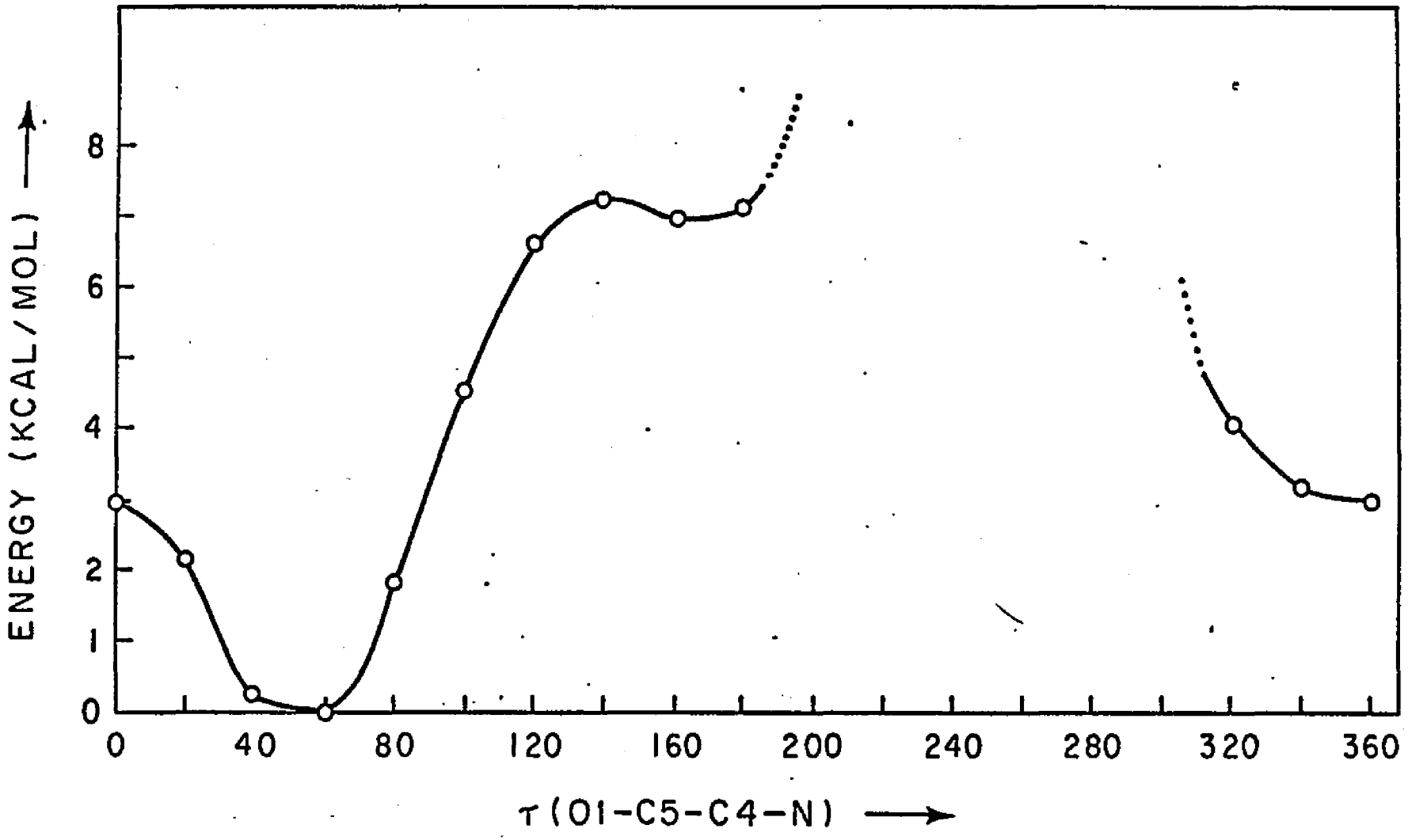

ENERGY (KCAL/MOL)
0
1
2
4
6
8
0
40
80
120
160
200
240
280
320
360
τ(O1-C5-C4-N)

Figure 27

Figure 28

ENERGY (KCAL/MOL)
0
2
4
6
8
10
τ(C8-C7-C2-N)
0
40
80
120
160
200
240
280
320
360
INTERATOMIC DISTANCE (Å)
1
2
3
4
5

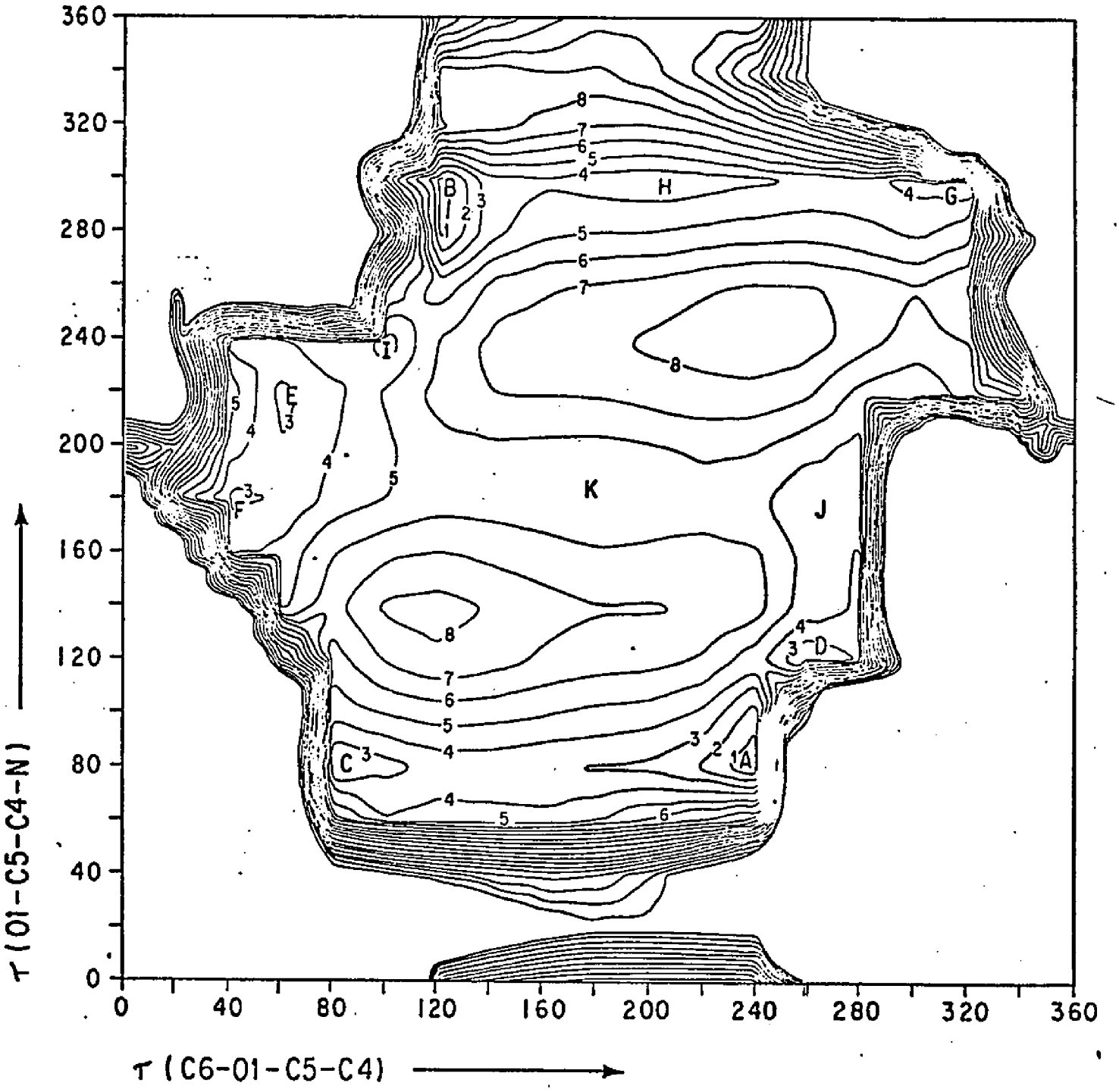

360
320
280
240
200
160
120
80
40
0
0
40
80
120
160
200
240
280
320
360
τ(01-C5-C4-N)
τ(C6-01-C5-C4)
A
B
C
D
E
F
G
H
I
J
K

Figure 29

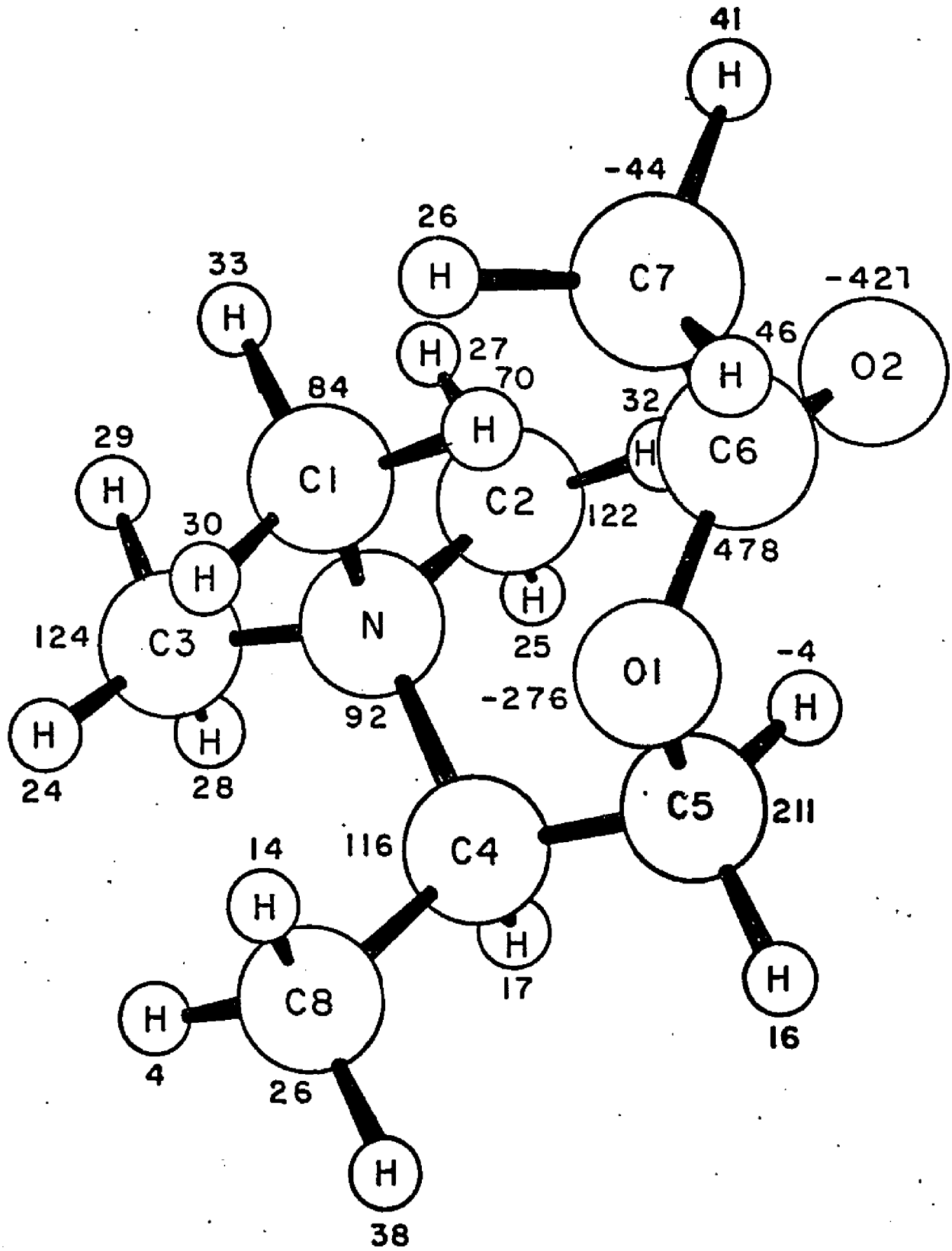

41
H
-44
26
H
C7
-421
33
H
H
27
70
46
O2
84
H
32
H
C6
29
H
C1
H
C2
122
30
478
H
H
N
124
C3
25
O1
-4
H
-276
H
H
92
24
28
C5
211
116
C4
14
H
H
17
H
C8
H
4
26
16
H
38

Figure 30

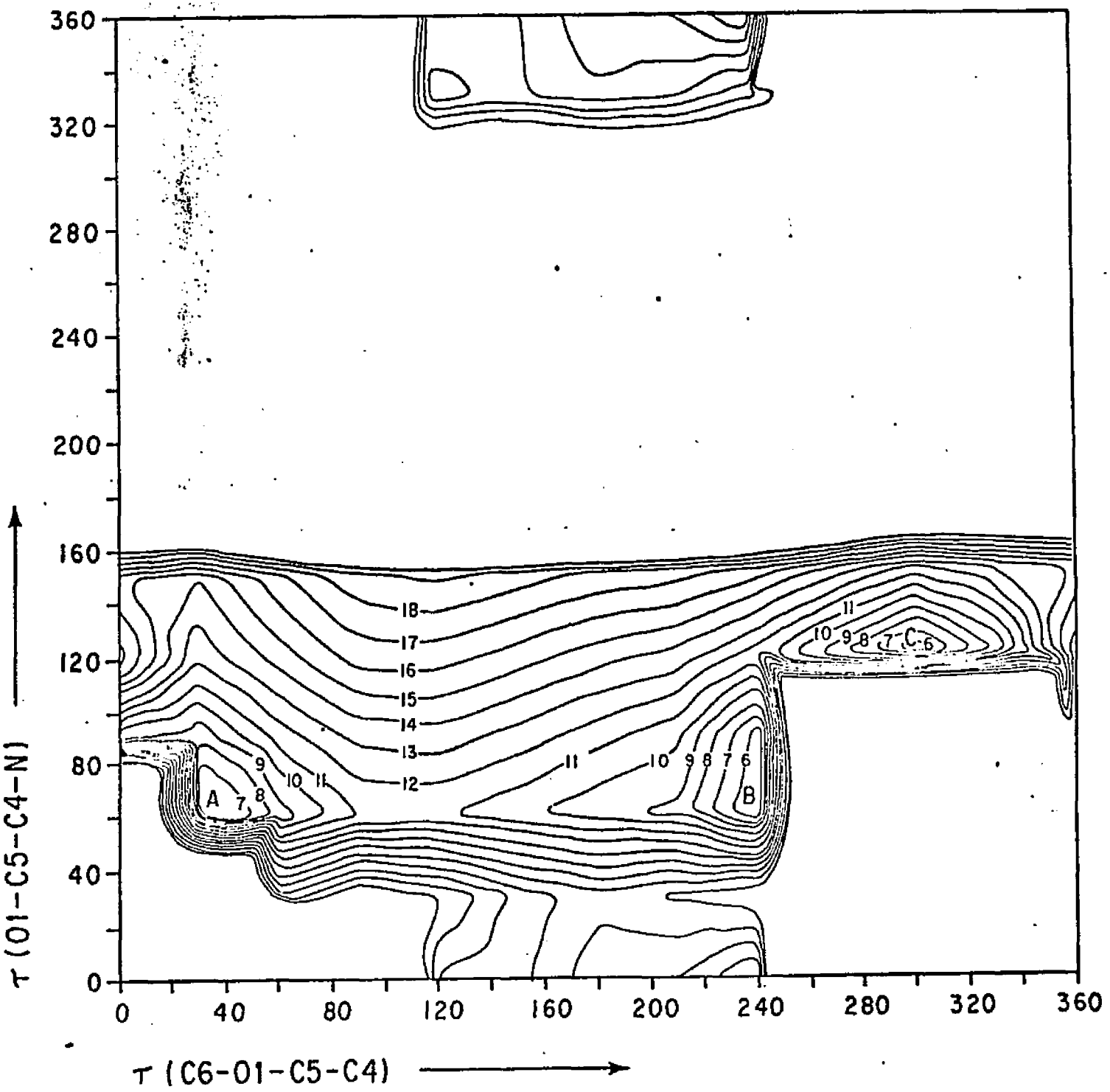

360
320
280
240
200
160
120
80
40
0
0
40
80
120
160
200
240
280
320
360
τ (O1-C5-C4-N)
τ (C6-O1-C5-C4)
18
17
16
15
14
13
12
11
10
9
8
7
6
A
B
C

Figure 31

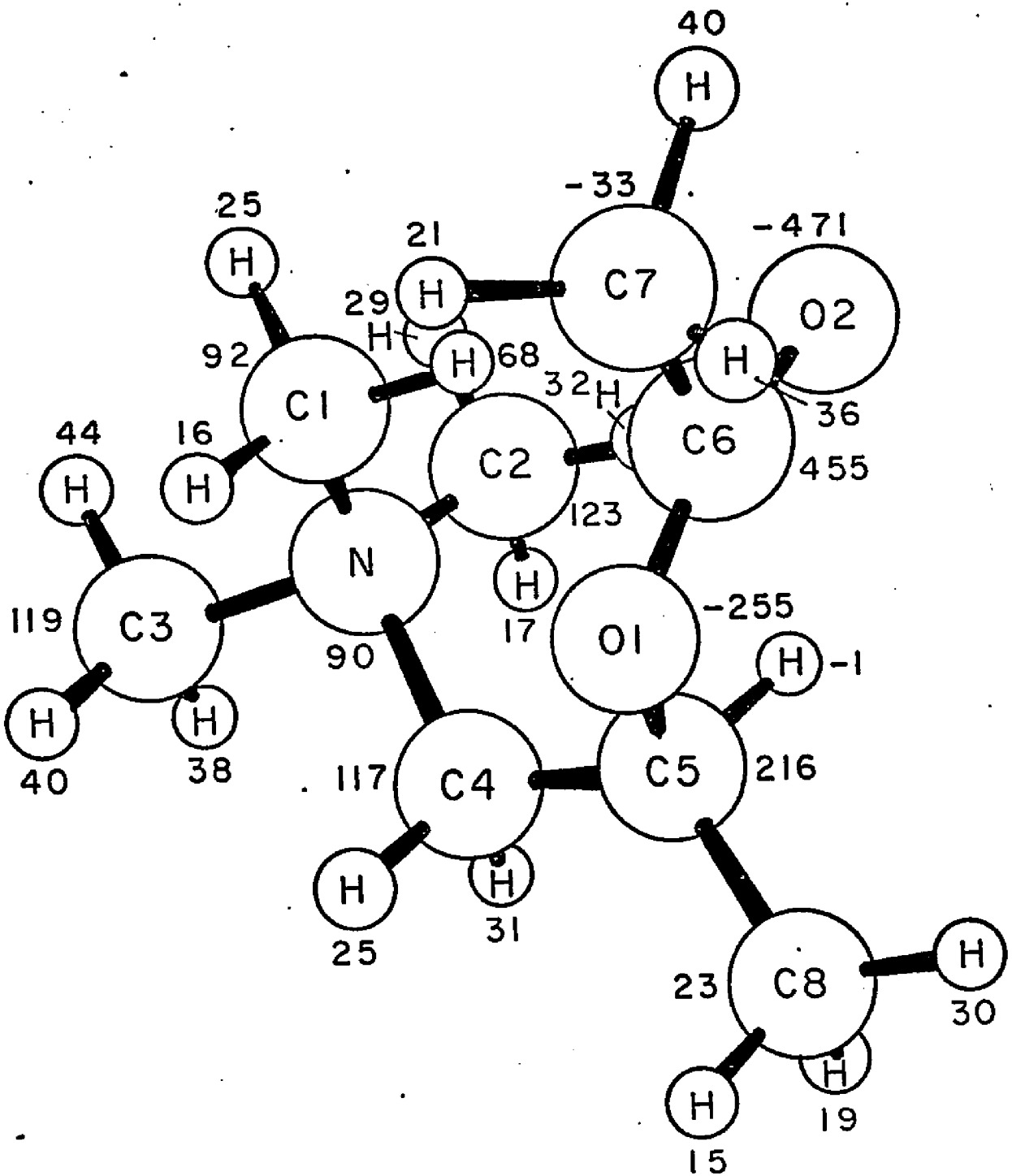

40
H
-33
25
H
21
H
C7
-471
O2
29
H
H
68
92
C1
32
H
H
36
C6
44
16
C2
455
H
H
123
N
H
17
119
C3
O1
-255
90
H
-1
H
H
40
38
117
C4
C5
216
H
H
31
25
23
C8
H
30
H
H
19
15

Figure 32

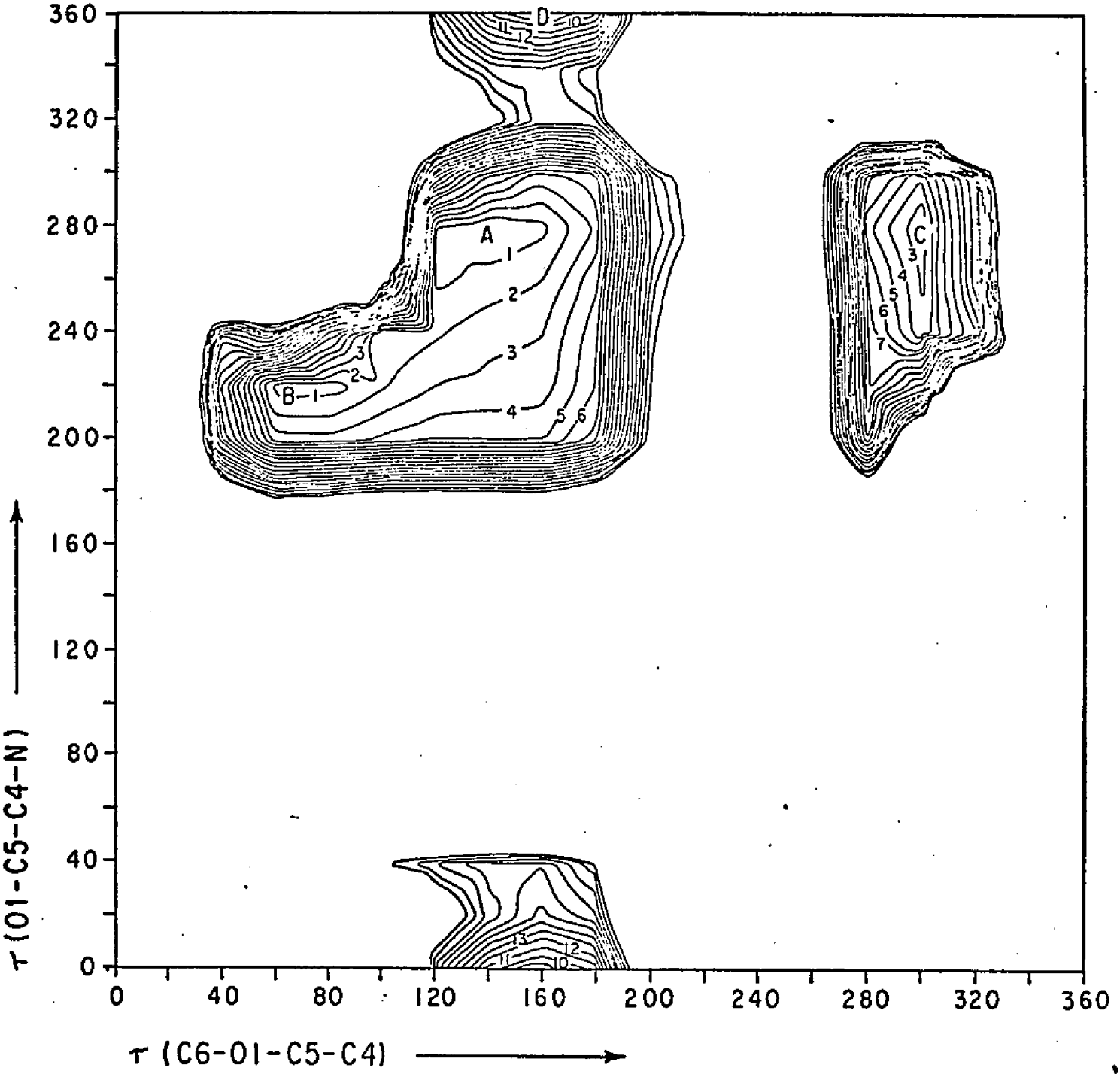

360
320
280
240
200
160
120
80
40
0
0
40
80
120
160
200
240
280
320
360
τ (O1-C5-C4-N)
τ (C6-O1-C5-C4)
A
B-1
C
D
1
2
3
4
5
6
7
10
11
12
13

Figure 33

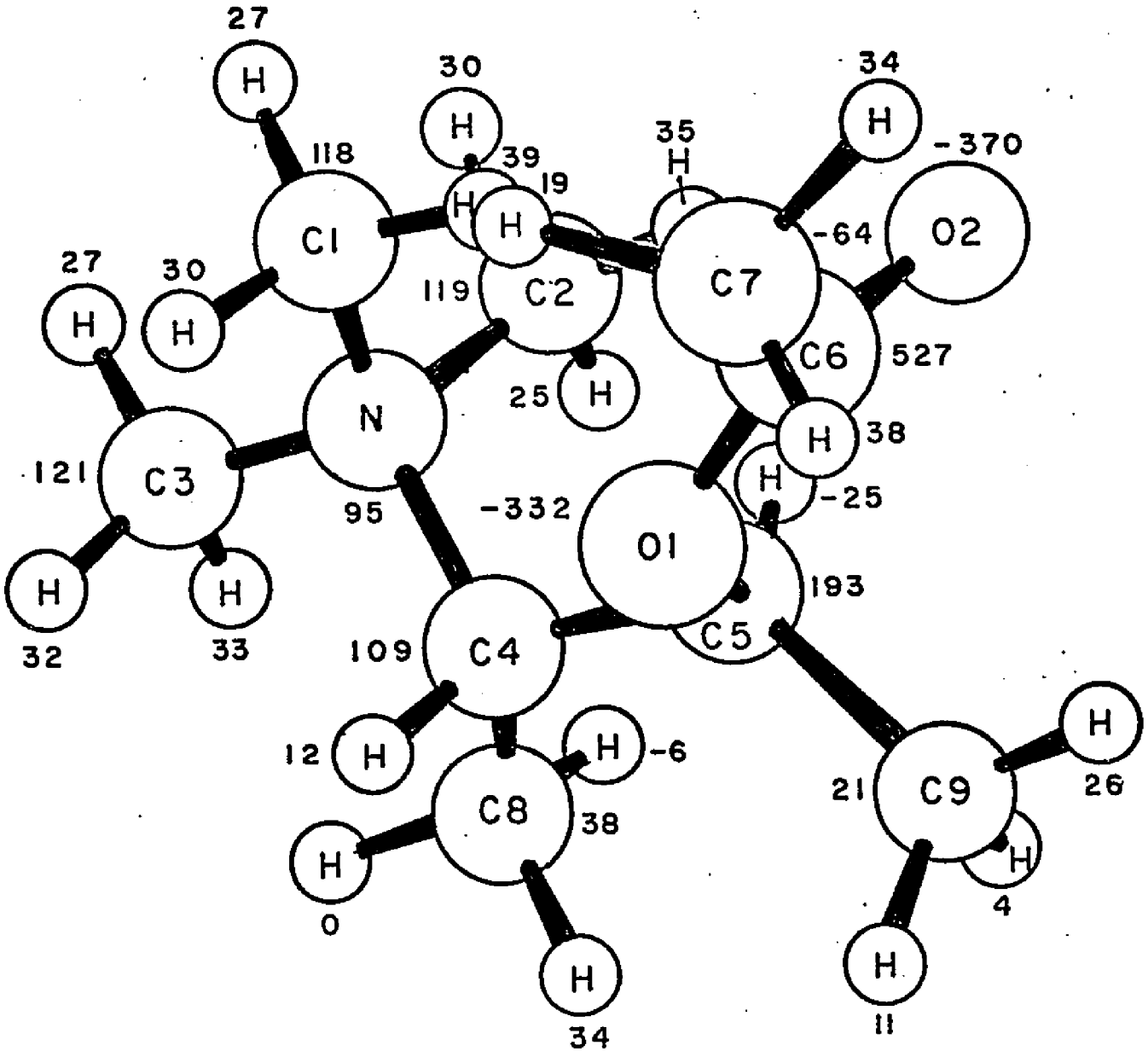

27
H
118
C1
30
H
39
H
19
H
35
H
34
H
-370
O2
-64
C7
27
H
30
H
119
C2
C6
527
25
H
N
H
38
121
C3
H
-25
95
-332
O1
193
H
H
C5
32
33
109
C4
12
H
H
-6
C8
38
21
C9
H
26
H
H
4
0
H
H
34
11

Figure 34

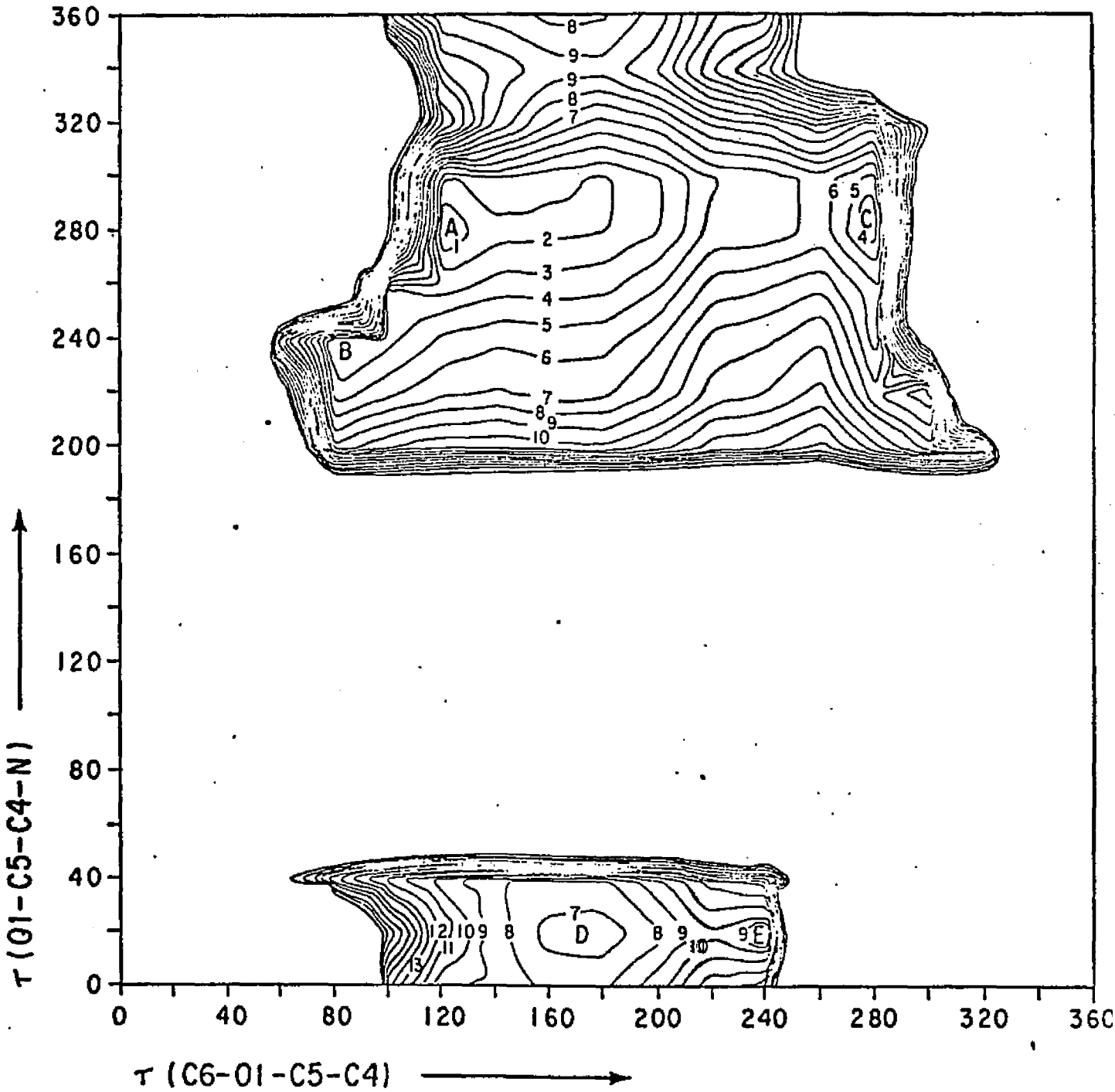

360
320
280
240
200
160
120
80
40
0
τ(01-C5-C4-N)
0
40
80
120
160
200
240
280
320
360
τ (C6-01-C5-C4)
A
B
C
D
E

Figure 35

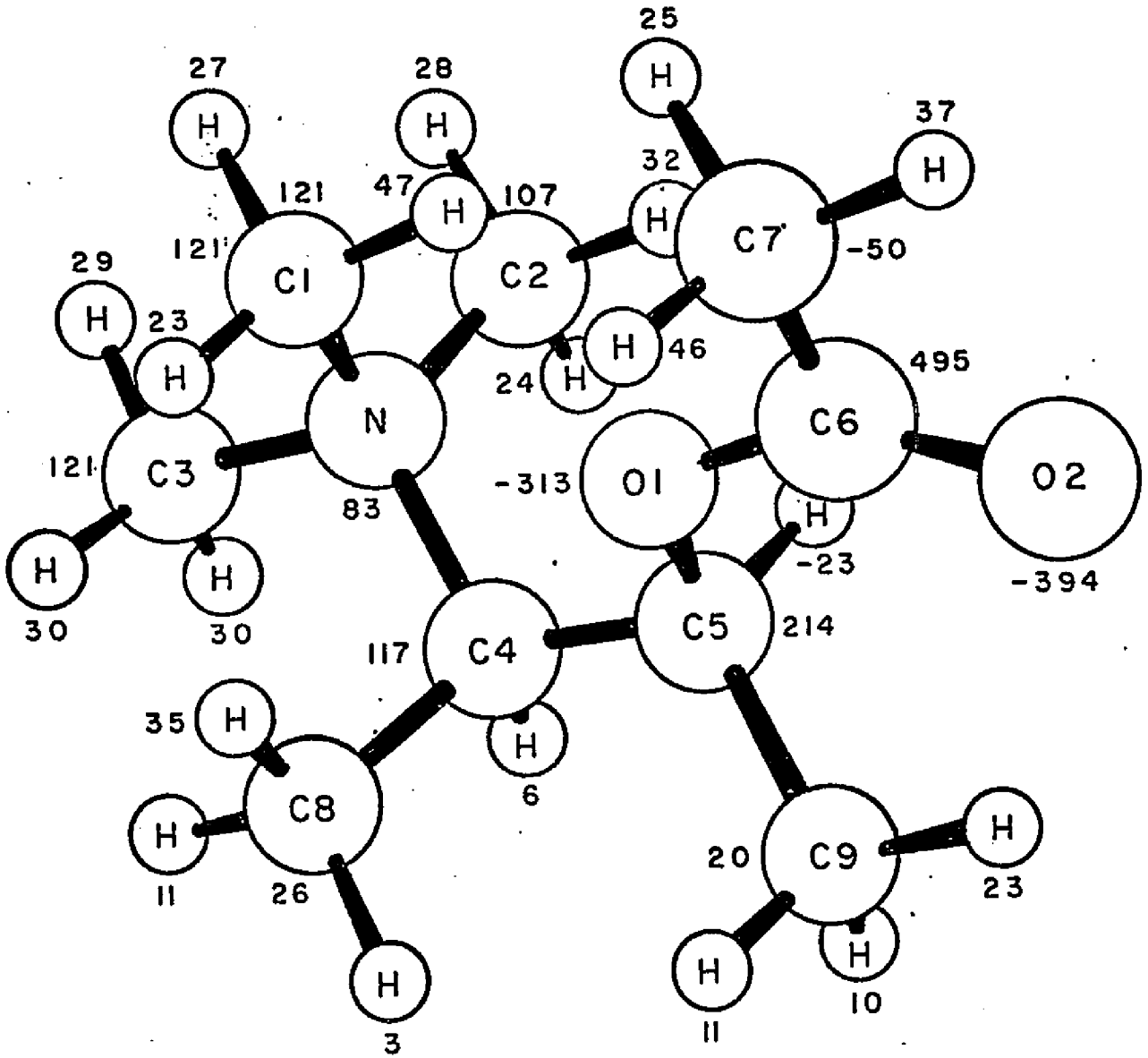

25
H
27
H
28
H
37
H
32
H
47
H
107
H
121
121
C1
C2
C7
-50
29
H
23
H
H
46
24
H
495
N
C6
121
C3
-313
O1
O2
83
H
-23
-394
H
30
H
30
117
C4
C5
214
35
H
H
6
C8
H
20
C9
H
23
11
26
H
H
H
10
3
11

Figure 36

Appendix A:

XTAL accepts the coordinates of an orthorhombic crystal unit cell, and the dimensions of the unit cell. From this data it generates the cartesian coordinates of the system, and an interatomic distance array. The cartesian coordinates are transformed into the model builder frame where the first atom is at the origin of a right handed coordinate system, the second atom lies on the Z axis, and the thirdatom lies in the X-Z plane. XTAL then calls SUBROUTINE UNZMAT which generates all bond angles and four atom torsions, and writes input to M. Gordon's model builder routine ZMAT. The generated input to ZMAT is tested by SUBROUTINE ZTEST which calls SUBROUTINE ZMAT. The latter routine generates an interatomic distance array from the UNZMAT generated input to ZMAT, and compares this new interatomic distance array to the one calculated from the input crystal data. The input format for the dimensions of the unit cell and unit cell coordinates is (3F20.10).

```
=RJR,LIST=ALL
=100,NEW1=100
      PROGRAM XTAL(INPUT,OUTPUT,PUNCH)                                  0
C     REVISED ZMAT GENERATING VERSION                                   0
      DIMENSION                                 YC(60,3)                0
C      TEST INSERTION                                                   0
      COMMON/ARAN/ZS(3,3)                                               0
      DIMENSION CT(3,3),TZ(3,3)                                         0
      DIMENSION CY(3,3)                                                 0
      INTEGER AN                                                        0
      COMMON/ATOM/AN                                                    0
      COMMON/BONDS/ANCIM(40,40),NCIM                                    0
      DIMENSION AN(40)                                                  0
      COMMON/TRANZ/ AFILL(3,3)                                          0
      DIMENSION INTER(60)                                               0
      COMMON/IIII/LTEST                                                 0
      COMMON/JJJJ/BONDBL                                                0
      COMMON/INFO/QRS                                                   0
      DIMENSION QRS(60,3)                                               0
      DIMENSION          RR(60,3),HHHH(60),QQQQ(60),SSSS(60)            0
      DIMENSION ZZ(3,3),Z(60,3),AR12(60),AR23(60),AR31(60)              0
      DIMENSION C(60,3),R(60,60),FF(3,3),            F(3,3)             0
      DIMENSION T(3,3)    ,CCC(3,60),EE(3,60)                           0
      DIMENSION Y(60,60),TRANS(3,3)                                     0
      DIMENSION E(60,3),TRANT(3,3)                                      0
      DIMENSION BC(3,3)                                                 0
      DIMENSION DC(1,3)                                                 0
      DIMENSION IDENT(20)                                               0
  199 CONTINUE                                                          0
C         INPUT                                                         0
      READ 999, (IDENT(I),I=1,20)                                       0
      PUNCH 999,(IDENT(I),I=1,20)                                       0
      READ 8888, LFIN,LPUN,NCIM                                         0
 8888 FORMAT(3I4)                                                       0
      IF(LFIN .EQ. 1) GO TO  765                                        0
  999 FORMAT (20A4)                                                     0
      PRINT 998, (IDENT(I),I=1,20)                                      0
  998 FORMAT(1H1,////,20A4,///)                                         0
      READ 4538, APH, BET, GAM,ACCC,ADDD                                0
 4538 FORMAT (3F20.10,2F10.5)                                           0
      PRINT 342, APH, BET, GAM                                          0
  342 FORMAT (///,1X,6HAPH = ,F10.5,3X,6HBET = ,F10.5,3X,6HGAM = ,F10.5,0
     *///)                                                              0
      READ 1, AA,BB,CC                                                  0
    1 FORMAT (3F20.10)                                                  0
      PRINT 2, AA,BB,CC                                                 0
    2 FORMAT (1H ,///,3X,23HDIMENSIONS OF UNIT CELL,5X,2HA=,2X,F10.5,5X,0
     *2HB=,2X,F10.5,5X,2HC=,2X,F10.5)                                   0
      READ 3,NN,LIN,BONDBL                                              0
    3 FORMAT (2I4,F10.5)                                                0
      IF(BONDBL .EQ. 0) BONDBL = 1.65                                   0
    4 FORMAT (//,3X,17HNUMBER OF ATOMS =,I4)                            0
```

```
      PRINT 4, NN
      IF(LIN .NE. 0) GO TO 556
      DO 5 I =1,NN
    5 READ 6,((C(I,J),J=1,3),AN(I),INTER(I))
    6 FORMAT (3F20.10,I5,A4)
      GO TO 557
  556 CONTINUE
      DO 558 I=1,NN
  558 READ 559, (AN(I),(C(I,J),J=1,3),INTER(I))
  559 FORMAT (I4,3(3X,F12.7),A4)
  557 CONTINUE
      IF(NCIM .NE. 1)  GO TO 1733
      DO 1734  IR = 1,NN
      READ 1735,  (NNCIM(IR,JR),JR=1,NN)
 1734 CONTINUE
 1735 FORMAT (80I1)
 1733 CONTINUE
      DO 4239 I=1,NN
      IF(AN(I) .EQ.0) AN(I) = 6
 4239 CONTINUE
C*************************************************************************
C*****GENERATE CARTESIAN COORDINATES
      PRINT 7
    7 FORMAT (///,3X,21HUNIT CELL COORDINATES,///)
      CALL COUT(C,NN)
      DO 10 I =1,NN
      C(I,1) = AA*C(I,1)
      C(I,2) = BB*C(I,2)
      C(I,3) = CC*C(I,3)
   10 CONTINUE
      PRINT 4513
 4513 FORMAT(//,1X,57HCARTESIAN COORDINATES WITHOUT ORTHOGONALIZATION PRO
     *OCEDURE,//)
      CALL COUT(C,NN)
       CALL DIST(C,NN,R)
      CALL OUT(R,NN)
C     CALL REF(C,NN)
C     PRINT 457
  457 FORMAT (//,1X,70HCARTESIAN COORDINATES WITHOUT ORTHOGONALIZATION RO
     *EFERRED TO THE ORIGIN,//)
C       CALL COUT(C,NN)
C      CALL DIST(C,NN,R)
C     CALL OUT(R,NN)
      DO 7174  IN = 1,3
       DO 7174  JN = 1,3
       CY(IN,JN) = C(IN,JN)
 7174 CONTINUE
       CALL CLINT (CY,CT,TZ)
      CALL MULT(C,TZ,C,NN)
C     PRINT 898
  898 FORMAT (//,1X,40HCARTESIAN COORDINATES SUBJECTED TO CLINT,//)
C          CALL COUT(E,NN)
```

```
C       CALL DIST(E,NN,R)                                               C
C      CALL OUT(R,NN)                                                   C
       CALL REF(C,NN)                                                   C
       PRINT 8743                                                       C
 8743 FORMAT(//,1X,95HCARTESIAN COORDINATES SUBJECTED TO CLINT AND REFERO
     *RED TO THE ORIGIN (WITHOUT ORTHOGONALIZATION),//)                  C
            CALL COUT(C,NN)                                             C
       CALL DIST(C,NN,R)                                                C
      CALL OUT(R,NN)                                                    C
C      PRINT 88                                                         C
C      CALL COUT(C,NN)                                                  C
       IF((APH .EQ. 90.0) .AND. (BET .EQ. 90.0) .AND. (GAM . EQ. 90.0)) GO
     *GO TO 498                                                         C
       DO 9134 IZ=1,3                                                   C
        DO 9134  JZ = 1,3                                               C
        AFILL(IZ,JZ) = 0.                                               C
 9134 CONTINUE                                                          C
C       PRINT 1213                                                      C
 1213 FORMAT(//,1X,26HNON-ORTHOGONAL COORDINATES,//)                    C
C      CALL COUT(C,NN)                                                  C
C      CALL DIST(C,NN,R)                                                C
C      CALL OUT(R,NN)                                                   C
       CALL CFIX(C,APH,BET,GAM,NN)                                      C
       CALL MULT(C,AFILL,E,NN)                                          C
       PRINT 327                                                        C
  327 FORMAT  (//,1X,31HCFIX ORTHOGONALIZED COORDINATES,//)             C
       CALL COUT(E,NN)                                                  C
       CALL DIST(E,NN,R)                                                C
       CALL OUT(R,NN)                                                   C
       CALL DFIX(C,APH,BET,GAM,NN)                                      C
       CALL MULT(C,ZS,C,NN)                                             C
       PRINT 2861                                                       C
 2861 FORMAT (//,1X,31HDFIX ORTHOGONALIZED COORDINATES,//)              C
       CALL COUT(C,NN)                                                  C
       CALL DIST(C,NN,R)                                                C
       CALL OUT(R,NN)                                                   C
  498 CONTINUE                                                          C
       IF((APH .EQ. 90.) .AND. (BET .EQ. 90.) .AND. (GAM .EQ. 90.)) PRINTO
     *1015                                                              C
 1015 FORMAT (//,1X,24HTHE SYSTEM IS ORTHOGONAL,//)                     C
       DO 8712 I = 1,NN                                                 C
       DO 8712 J = 1,3                                                  C
 8712 YC(I,J) = C(I,J) + 1. 0                                           C
       CALL UNZMAT(YC,R,NN,AN,INTER)                                    C
       CALL COUT(C,NN)                                                  C
C*******************************************************************C
C*****CREATE ZMAT CONVENTION COORDINATES FOR FIRST THREE ATOMS        C
       COA = ((R(1,3)**2) + (R(1,2)**2) -(R(2,3)**2))/                  C
     *(2*(R(1,3))*(R(1,2)) )                                            C
       ALPH =  ACOS(COA)                                                C
       SIA =  SIN(ALPH)                                                 C
       COAA =  COS(ALPH)                                                C
```

```
      PRINT 135, ALPH,SIA,COA,COAA                                      C
  135 FORMAT (//,3X,4F10.5)                                             C
C     CONVERSION TO DEGREES                                             C
      BLPH = ALPH * (180./3.141592654)                                  C
      PRINT 136, BLPH                                                   C
  136 FORMAT (//,3X,16HALPH IN DEGREES=,F10.5,//)                       C
      DO 501 I = 1,3                                                    C
  501 F(1,I) = 0.0                                                      C
      DO 500 J = 1,2                                                    C
  500 F(2,J) = 0.0                                                      C
      F(2,3) = R(1,2)                                                   C
      F(3,1) = R(1,3)* SIN(ALPH)                                        C
      F(3,2) = 0.0                                                      C
      F(3,3) = R(1,3)* COS(ALPH)                                        C
      DO 502 I = 1,3                                                    C
      DO 502 J = 1,3                                                    C
  502 FF(J,I) = F(I,J) + 1.                                             C
C*******************************************************************C
      DO 85 I = 1,3                                                     C
      DO 85 J = 1,3                                                     C
      TRANS(I,J) = 0.0                                                  C
   85 T(I,J) = 0.0                                                      C
      DO 81 I = 1,3                                                     C
      DO 81 J = 1,3                                                     C
   81 BC(J,I) = C(I,J) + 1.                                             C
      CALL RRED(C,NN,TRANS)                                             C
      DO 2221 I = 1,3                                                   C
      DO 2221 J = 1,3                                                   C
 2221 TRANT(I,J) = TRANS(I,J)                                           C
C     CALL TMAT(TRANT,FF,T)                                             C
      CALL TMAT(BC,FF,T)                                                CC
C*****GENERATE ZMAT CONVENTION COORDINATES                              C
C*******************************************************************CC
      CALL MULT(C,T,E,NN)                                               CC
      CALL REF(E,NN)                                                    CC
C*******************************************************************CC
      PRINT 187                                                         CC
  187 FORMAT (//,3X,40HCARTESIAN COORDINATES IN ZMAT CONVENTION,//)     CC
      CALL COUT(E,NN)                                                   CC
      CALL DIST(E,NN,R)                                                 CC
      PRINT 888                                                         CC
      CALL OUT(R,NN)                                                    CC
  888 FORMAT (///,3X,21HINTERATOMIC DISTANCES,///)                      CC
      IF(LPUN .NE. 1) GO TO 199                                         CC
      DO 1111 I =1,NN                                                   CC
 1111 PUNCH 6, (E(I,J),J=1,3)                                           CC
      GO TO 199                                                         CC
  765 CONTINUE                                                          CC
      END                                                               CC
      SUBROUTINE DFIX(C,APH,BET,GAM,NN)                                 CC
      COMMON/ARAN/ A(3,3)                                               CC
      COMMON/ARRAYS/AB(3,3),VT(3,3),X(3,3)                              CC
```

```
      COMMON/1/GAMMA(3),BETA(3),BETASQ(3),  D(3),W(3),XYZ(60)
      DIMENSION C(6C,3)
      PT=3.141592654/180.
      SINA=SIN(APH*PT)
      COSA=COS(APH*PT)
      SINB=SIN(BET*PT)
      COSB=COS(BET*PT)
      SING=SIN(GAM*PT)
      COSG=COS(GAM*PT)
      DO 37 I=1,3
      DO 37 J=1,3
      AB(I,J)=0.0
   37 CONTINUE
      AB(1,1)=1.0
      AB(2,1)=COSG
      AB(3,1)=COSB
      AB(2,2)=1.0
      AB(3,2)=COSA
      AB(3,3)=1.0
      CALL EIGN(3,0.000001)
      DO 38 J=1,3
      DO 38 I=1,3
   38 VT(I,J)=VT(I,J)/SQRT(D(J))
      DO 39 I=1,3
      DO 39 J=1,3
   39 A(I,J)=VT(J,I)
      RETURN
      END
      SUBROUTINE EIGN(NN,RHO)
C     RHO= UPPER LIMIT FOR OFF-DIAGONAL ELEMENT
C     NN= SIZE OF MATRIX
C     A = F MATRIX (ONLY LOWER TRIANGLE IS USED + THIS IS DESTROYED)
C     EIG = RETURNED EIGENVALUES IN ALGEBRAIC ASCENDING ORDER
C     VEC = RETURNED EIGENVECTORS IN COLUMNS
C     IND = ERROR RETURN INDICATOR
C     0 FOR NORMAL RETURN
C     1 SUM OF EIGENVALUES NOT RQUAL TO TRACE
C     2 SUM OF EIGENVALUES SQUARED NOT EQUAL TO NORM
C     3 BOTH OF THESE ERRORS
      COMMON/ARRAYS/A(3,3),VEC(3,3),X(3,3)
      COMMON/1/GAMMA(3),BETA(3),BETASQ(3),EIG(3),W(3),XYZ(60)
C     THE FOLLOWING DIMENSIONED VARIABLES ARE EQUIVALENCED
      DIMENSION P(80),Q(80)
      EQUIVALENCE (P(1),BETA(1)),(Q(1),BETA(1))
      DIMENSION IPOSV(80),IVPOS(80),ICRD(80)
      EQUIVALENCE (IPOSV(1),GAMMA(1)),(IVPOS(1),BETA(1)),
     1(ICRD(1),BETASQ(1))
      ABSF(X) = ABS(X)
      SQRTF(X) = SQRT(X)
      RHOSQ=RHO*RHO
      N=NN
C     RESET ERROR RETURN INDICATOR
```

```
      IND=0
      IF (N .EQ. 0) 640,10
   10 N1=N-1
      N2=N-2
C     COMPUTE THE TRACE AND EUCLIDIAN NORM OF THE INPUT MATRIX
C     LATER CHECK AGAINST SUM AND SUM OF SQUARES OF EIGENVALUES
      ENORM=0.
      TRACE=0.
      DO 30 J=1,N
      DO 20 I=J,N
   20 ENORM=ENORM+A(I,J)**2
      TRACE=TRACE+A(J,J)
   30 ENORM=ENORM-.5*A(J,J)**2
      ENORM=ENORM+ENORM
      GAMMA(1)=A(1,1)
      IF(N2) 200,190,40
   40 DO 180 NR=1,N2
      B=A(NR+1,NR)
      S=0.
      DO 50 I=NR,N2
   50 S=S+A(I+2,NR)**2
C     PREPARE FOR POSSIBLE BYPASS OF TRANSFORMATION
      A(NR+1,NR)=0.
      IF (S) 170,170,60
   60 S=S+B*B
      SGN=+1.
      IF (B) 70,80,80
   70 SGN=-1.
   80 SQRTS=SQRTF(S)
      D=SGN/(SQRTS+SQRTS)
      TEMP=SQRTF(.5+B*D)
      W(NR)=TEMP
      A(NR+1,NR)=TEMP
      D=D/TEMP
      B=-SGN*SQRTS
C     D IS FACTOR OF PROPORTIONALITY. NOW COMPUTE AND SAVE W VECTOR.
C     EXTRA SINGLY SUBSCRIPTED W VECTOR USED FOR SPEED.
      DO 90 I=NR,N2
      TEMP=D*A(I+2,NR)
      W(I+1)=TEMP
   90 A(I+2,NR)=TEMP
C     PREMULTIPLY VECTOR W BY MATRIX A TO OBTAIN P VECTOR.
C     SIMULTANEOUSLY ACCUMULATE DOT PRODUCT WP,(THE SCALAR K)
      WTAW=0.
      DO 140 I=NR,N1
      SUM=0.
      DO 100 J=NR,I
  100 SUM=SUM+A(I+1,J+1)*W(J)
      I1=I+1
      IF(N1-I1) 130,110,110
  110 DO 120 J=I1,N1
  120 SUM=SUM+A(J+1,I+1)*W(J)
```

```
  130 P(I)=SUM                                                          C
  140 WTAW=WTAW+SUM*W(I)                                                C
C     P VECTOR AND SCALAR K  NOW STORED. NEXT COMPUTE Q VECTOR          C
      DO 150 I=NR,N1                                                    C
  150 Q(I)=P(I)-WTAW*W(I)                                               C
C     NOW FORM PAP MATRIX. REQUIRED PART                                C
      DO 160 J=NR,N1                                                    C
      QJ=Q(J)                                                           C
      WJ=W(J)                                                           C
      DO 160 I=J,N1                                                     C
  160 A(I+1,J+1)=A(I+1,J+1)-2.*(W(I)*QJ+WJ*Q(I))                        C
  170 BETA(NR)=B                                                        C
      BETASQ(NR)=B*B                                                    C
  180 GAMMA(NR+1)=A(NR+1,NR+1)                                          C
  190 B=A(N,N-1)                                                        C
      BETA(N-1)=B                                                       C
      BETASQ(N-1)=B*B                                                   C
      GAMMA(N)=A(N,N)                                                   C
  200 BETASQ(N)=0.                                                      C
C     ADJOIN AN IDENTIFY MATRIX TO BE POSTMULTIPLIED BY ROTATIONS.      C
      DO 220 I=1,N                                                      C
      DO 210 J=1,N                                                      C
  210 VEC(I,J)=0.                                                       C
  220 VEC(I,I)=1.                                                       C
      M=N                                                               C
      SUM=0.                                                            C
      NPAS=1                                                            C
      GO TO 350                                                         C
  230 SUM=SUM+SHIFT                                                     C
      COSA=1.                                                           C
      G=GAMMA(1)-SHIFT                                                  C
      PP=G                                                              C
      PPBS=PP*PP+BETASQ(1)                                              C
      PPBR=SQRTF(PPBS)                                                  C
      DO 320 J=1,M                                                      C
      COSAP=COSA                                                        C
      IF(PPBS .NE. 0.) 250,240                                          C
  240 SINA=0.                                                           C
      SINA2=0.                                                          C
      COSA=1.                                                           C
      GO TO 290                                                         C
  250 SINA=BETA(J)/PPBR                                                 C
      SINA2=BETASQ(J)/PPBS                                              C
      COSA=PP/PPBR                                                      C
C     POSTMULTIPLY IDENTITY BY P-TRANSPOSE MATRIX                       C
      NT=J+NPAS                                                         C
      IF(NT .GE. N) 260,270                                             C
  260 NT=N                                                              C
  270 DO 280 I=1,NT                                                     C
      TEMP=COSA*VEC(I,J)+SINA*VEC(I,J+1)                                C
      VEC(I,J+1)=-SINA*VEC(I,J)+COSA*VEC(I,J+1)                         C
  280 VEC(I,J)=TEMP                                                     C
```

```
  290 DIA=GAMMA(J+1)-SHIFT
      U=SINA2*(G+DIA)
      GAMMA(J)=G+U
      G=DIA-U
      PP=DIA*COSA-SINA*COSAP*BETA(J)
      IF(J .NE. M) 310,300
  300 BETA(J)=SINA*PP
      BETASQ(J)=SINA2*PP*PP
      GO TO 330
  310 PPBS=PP*PP+BETASQ(J+1)
      PPBR=SQRTF(PPBS)
      BETA(J)=SINA*PPBR
  320 BETASQ(J)=SINA2*PPBS
  330 GAMMA(M+1)=G
C     TEST FOR CONVERGENCE OF LAST DIAGONAL ELEMENT
      NPAS=NPAS+1
      IF(BETASQ(M) .GT. RHOSQ) 370,340
  340 EIG(M+1)=GAMMA(M+1)+SUM
  350 BETA(M)=0.
      BETASQ(M)=0.
      M=M-1
      IF(M .EQ. 0) 400,360
  360 IF(BETASQ(M) .LE. RHOSQ) 340,370
C     TAKE ROOT OF CORNER 2 BY 2 NEAREST TO LOWER DIAGONAL IN VALUE
C     AS ESTIMATE OF EIGENVALUE TO USE FOR SHIFT
  370 A2=GAMMA(M+1)
      R2=.5*A2
      R1=.5*GAMMA(M)
      R12=R1+R2
      DIF=R1-R2
      TEMP=SQRTF(DIF*DIF+BETASQ(M))
      R1=R12+TEMP
      R2=R12-TEMP
      DIF=ABSF(A2-R1)-ABSF(A2-R2)
      IF(DIF .LT. 0.) 390,380
  380 SHIFT=R2
      GO TO 230
  390 SHIFT=R1
      GO TO 230
  400 EIG(1)=GAMMA(1)+SUM
C     INITIALIZE AUXILIARY TABLES REQUIRED FOR REARRANGING THE VECTORS
      DO 410 J=1,N
      IPOSV(J)=J
      IVPOS(J)=J
  410 IORD(J)=J
C     USE A TRANSPOSITION SORT TO ORDER THE EIGENVALUES
      M=N
      GO TO 450
  420 DO 440 J=1,M
      IF (EIG(J) .GE. EIG(J+1)) 440,430
  430 TEMP=EIG(J)
      EIG(J)=EIG(J+1)
```

```
      EIG(J+1)=TEMP
      ITEMP=IORD(J)
      IORD(J)=IORD(J+1)
      IORD(J+1)=ITEMP
  440 CONTINUE
  450 M=M-1
      IF(M .NE. 0) 420,460
  460 IF(N1 .EQ. 0) 510,470
  470 DO 500 L=1,N1
      NV=IORD(L)
      NP=IPOSV(NV)
      IF(NP .EQ. L) 500,480
  480 LV=IVPOS(L)
      IVPOS(NP)=LV
      IPOSV(LV)=NP
      DO 490 I=1,N
      TEMP=VEC(I,L)
      VEC(I,L)=VEC(I,NP)
  490 VEC(I,NP)=TEMP
  500 CONTINUE
  510 ESUM=0.
      ESSQ=0.
C     BACK TRANSFORM THE VECTORS OF THE TRIPLE DIAGONAL MATRIX
      DO 570 NRR=1,N
      K=N1
  520 K=K-1
      IF(K .LE. 0) 560,530
  530 SUM=0.
      DO 540 I=K,N1
  540 SUM=SUM+VEC(I+1,NRR)*A(I+1,K)
      SUM=SUM+SUM
      DO 550 I=K,N1
  550 VEC(I+1,NRR)=VEC(I+1,NRR)-SUM*A(I+1,K)
      GO TO 520
  560 ESUM=ESUM+EIG(NRR)
  570 ESSQ=ESSQ+EIG(NRR )**2
      TEMP=ABSF(128.*TRACE)
      IF((ABSF(TRACE-ESUM)+TEMP)-TEMP.NE.0.) 580,590
  580 IND=IND+1
  590 TEMP=256.*FNORM
      IF((ABSF(FNORM-ESSQ)+TEMP)-TEMP.NE.0.)  600,610
  600 IND=IND+2
  610 CONTINUE
C     REVERSE ORDER OF EIGENVALUES AND EIGENVECTORS
      NHALF=N/2
      DO 620 I=1,NHALF
      TEMP=EIG(I)
      EIG(I)=EIG(N+1-I)
  620 EIG(N+1-I)=TEMP
      DO 630 I=1,N
      DO 630 J=1,NHALF
      TEMP=VEC(I,J)
```

```
      VEC(I,J)=VEC(I,N+1-J)
  630 VEC(I,N+1-J)=TEMP
  640 RETURN
      END
      SUBROUTINE CLINT (C,CC,T)
      DIMENSION C(3,3),CC(3,3),T(3,3),Z(3),ZUNI(3),A(3),Y(3),YUNI(3),
     *AX(3),BY(3),CZ(3)
      DIMENSION XUNI(3)
C     THIS ROUTINE ACCEPTS A (3,3) COORDINATE SYSTEM, AND GENERATES A (3
C     TRANSFORMATION MATRIX WHICH IS USED TO TRANSFORM A (NN,3) COORDINA
C     SYSTEM INTO  THE ZMAT CONVENTION)  HERE BL(1,2) LIES IN THE Z AXIS
C     AND THE FIRST THREE ATOMS LIE IN THE X-Z PLANE (Y=0).
      Z(1) = C(2,1) - C(1,1)
      Z(2) = C(2,2) - C(1,2)
      Z(3) = C(2,3) - C(1,3)
      ZMAG =  SQRT (Z(1)**2 + Z(2)**2 + Z(3)**2)
      ZUNI(1) = Z(1)/ZMAG
      ZUNI(2) = Z(2)/ZMAG
      ZUNI(3) = Z(3)/ZMAG
      A(1) = C(3,1) - C(1,1)
      A(2) = C(3,2) - C(1,2)
      A(3) = C(3,3) - C(1,3)
      CALL   VECPRD(Y,Z,A)
      YMAG = SQRT(Y(1)**2  + Y(2)**2 + Y(3)**2)
      YUNI(1) = Y(1)/YMAG
      YUNI(2) = Y(2)/YMAG
      YUNI(3) = Y(3)/YMAG
      CALL VECPRD (XUNI,YUNI,ZUNI)
      DO 993 II=1,3
      AX(II) = 0.
      BY(II) = 0.
      CZ(II) = 0.
  993 CONTINUE
      AX(1) = 1.
      BY(2) = 1.
      CZ(3) = 1.
      T(1,1) = DOTPRD (XUNI,AX)
       T(1,2) = DOTPRD (XUNI,BY)
      T(1,3) = DOTPRD(XUNI,CZ)
      T(2,1) = DOTPRD(YUNI,AX)
      T(2,2) = DOTPRD (YUNI,BY)
       T(2,3) =  DOTPRD (YUNI,CZ)
       T(3,1) =  DOTPRD (ZUNI,AX)
       T(3,2) = DOTPRD (ZUNI,BY)
        T(3,3) =  DOTPRD (ZUNI,CZ)
      PRINT 10
      DO 5 I=1,3
      PRINT 6,  (T(I,J),J=1,3)
 5    CONTINUE
 6    FORMAT (1X,F10.5,2X,F10.5,2X,F10.5)
 10   FORMAT (//,2X, 21HTRANSFORMATION MATRIX,//)
       RETURN
```

```
            END
      FUNCTION DOTPRD (X,Y)
      DIMENSION X(3),  Y(3)
       C=0.
       DO 1 I=1,3
       C=C + X(I)*Y(I)
    1  CONTINUE
       DOTPRD = C
       RETURN
            END
       SUBROUTINE  MULT(C,T,E,NN)
C      THIS ROUTINE USES A (3,3) TRANSFORMATION MATRIX TO TRANSFORM A
C      (3,NN) ARRAY  (THE TRANSPOSE OF THE(NN,3) )    TO A RESULTANT
C      (3,NN) ARRAY, AND THEN TRANSPOSES THE (3,NN) BACK TO A (NN,3).
       DIMENSION C(60,3),T(3,3),E(60,3),CC(3,60),EE(3,60)
       DIMENSION CCC(3,3)
       DO 1 I=1,NN
         DO 1J=1,3
      CC(J,I) = C(I,J)
    1  CONTINUE
         DO 83 I=1,3
       DO 83 J=1,NN
       EE(I,J) = 0.
       DO 83 K = 1,3
   83  EE(I,J) = EE(I,J) + T(I,K)*CC(K,J)
       DO 3 I=1,NN
       DO 3 J=1,3
      E(I,J) = EE(J,I)
    3  CONTINUE
      RETURN
      END
      SUBROUTINE COUT(C,NN)
C     THIS ROUTINE PRINTS A (NN,3) ARRAY
      DIMENSION C(60,3)
      COMMON/ATOM/AN(40)
      DIMENSION EL(9)
      INTEGER AN
      DATA ((EL(I),I=1,9)=4H   H,4H  HE,4H  LI,4H  BE,4H   B,4H   C,
     *4H   N,4H   O,4H   F)
      PRINT 1
    1 FORMAT(21X,1HX,10X,1HY,10X,1HZ,///)
      DO 8 I =1,NN
      IND1 = AN(I)
    8 PRINT 9, I,EL(IND1),  (C(I,J), J=1,3)
    9 FORMAT (3X,I4,3X,A4,3X,3F10.5)
      RETURN
      END
      SUBROUTINE OUT(R,NN)
C     THIS ROUTINE PRINTS AN (NN,NN) ARRAY.
      DIMENSION R(60,60)
      KITE = 0
   20 KITE = KITE + 1
```

```
      KITE = KITE + 12
      KITE = AMINO(KITE,NN)
      PRINT 19,(I,I=LOW,KITE)
   19 FORMAT (//,6X,12(I9,1X),///)
      DO 32 I =1,NN
   32 PRINT 18,I,(R(I,J),J=LOW,KITE)
   18 FORMAT (2X,I4,3X,12F10.4)
      IF(NN-KITE) 40,40,20
   40 RETURN
      END
      SUBROUTINE TMAT(A,B,T)
C     TO SOLVE MATRIX EQ B = T*A FOR T GIVEN A AND B
      DIMENSION A(3,3),B(3,3),C(3,3),D(3,3),T(3,3),E(3,3)
      DIMENSION AL(2),BL(2),CL(2),DL(2),EL(2),FL(2)
      DATA ((AL(I),I=1,2)=4HMATR,4HIX A)
      DATA ((BL(I),I=1,2)=4HMATR,4HIX B)
      DATA ((CL(I),I=1,2)=4HINVE,4HRSE )
      DATA ((DL(I),I=1,2)=4HCK I,4HNVER)
      DATA ((EL(I),I=1,2)=4HTRAN,4HS MT)
      DATA ((FL(I),I=1,2)=4HCK T,4HRANS)
C     ************************************
C     INPUT SECTION
  999 CONTINUE
      CALL MOUTPT(A,3,3,3,3,AL)
      CALL MOUTPT(B,3,3,3,3,BL)
C     ************************************
C     SOLUTION FOR T IS T = B*A-INVERSE
C     FORM INVERSE OF A
C     CALCULATE MATRIX OF COFACTORS OF A IN D
      D(1,1) = A(2,2)*A(3,3)-A(2,3)*A(3,2)
      D(1,2) = -(A(2,1)*A(3,3)-A(2,3)*A(3,1))
      D(1,3) = A(2,1)*A(3,2)-A(2,2)*A(3,1)
      D(2,1) = -(A(1,2)*A(3,3)-A(1,3)*A(3,2))
      D(2,2) = A(1,1)*A(3,3)-A(1,3)*A(3,1)
      D(2,3) = -(A(1,1)*A(3,2)-A(1,2)*A(3,1))
      D(3,1) = A(1,2)*A(2,3)-A(1,3)*A(2,2)
      D(3,2) = -(A(1,1)*A(2,3)-A(1,3)*A(2,1))
      D(3,3) = A(1,1)*A(2,2)-A(1,2)*A(2,1)
C     ************************************
C     CALCULATE DETERMINANT OF A AND OUTPUT
      DET = A(1,1)*D(1,1)+A(1,2)*D(1,2)+A(1,3)*D(1,3)
      IF( ABS(DET).LT.1.0E-5) GO TO 5
      GO TO 6
    5 PRINT 1002, DET
 1002 FORMAT(//,24H MATRIX SINGULAR, DET = ,D15.5,//)
      STOP
    6 CONTINUE
      PRINT 1000, DET
 1000 FORMAT(//,7H DET = ,D15.5,//)
C     ************************************
C     FORM ELEMENTS OF INVERSE
      DO 1 I=1,3
```

```
      DO 1 J=1,3                                                        C
    1 C(I,J) = D(J,I)/DET                                               C
      CALL MOUTPT(C,3,3,3,3,CL)                                         C
C     ***********************************                               C
C     CHECK INVERSE                                                     C
      DO 2 I=1,3                                                        C
      DO 2 J=1,3                                                        C
      D(I,J) = 0.                                                       C
      DO 2 K=1,3                                                        C
    2 D(I,J) = D(I,J)+A(I,K)*C(K,J)                                     C
      CALL MOUTPT(D,3,3,3,3,DL)                                         C
C     ***********************************                               C
C     FORM TRANSFORMATION MATRIX                                        C
      DO 3 I=1,3                                                        C
      DO 3 J=1,3                                                        C
      T(I,J) = C                                                        C
      DO 3 K=1,3                                                        C
    3 T(I,J) = T(I,J)+B(I,K)*C(K,J)                                     C
      CALL MOUTPT(T,3,3,3,3,EL)                                         C
C     ***********************************                               C
C      CHECK TRANSFORMATION MATRIX                                      C
      DO 4 I=1,3                                                        C
      DO 4 J = 1,3                                                      C
      F(I,J) = 0                                                        C
      DO 4 K=1,3                                                        C
    4 E(I,J) = F(I,J)+T(I,K)*A(K,J)                                     C
      CALL MOUTPT(E,3,3,3,3,FL)                                         C
 1111 CONTINUE                                                          C
      RETURN                                                            C
      END                                                               C
      SUBROUTINE MOUTPT(A,M,N,MDIM,NDIM,NAME)                           C
C     OUTPUT OF M X N MATRIX DIMENSIONED TO MDIM X NDIM                 C
      DIMENSION NAME(2)                                                 C
      DIMENSION A(MDIM,NDIM)                                            C
      REAL NAME                                                         C
      PRINT 1000,NAME                                                   C
 1000 FORMAT (/,3X,2A4,//)                                              C
      KITE = 0                                                          C
   20 LOW = KITE+1                                                      C
      KITE = KITE+14                                                    C
      KITE = MINO(KITE,N)                                               C
      PRINT 19,(I,I=LOW,KITE)                                           C
   19 FORMAT( //     ,4X,14(6X,I2),/)                                 C
      DO 32 I=1,M                                                       C
   32 PRINT 18,I,(A(I,J),J=LOW,KITE)                                    C
   18 FORMAT(I4,2X,14F10.4)                                             C
      IF(N-KITE) 40,40,20                                               C
   40 RETURN                                                            C
      END                                                               C
      SUBROUTINE UNZMAT(C,R,NN,AN,INTER)                                C
C     THIS ROUTINE ACCEPTS A COORDINATE SYSTEM, AND AN INTERATOMIC      C
C     DISTANCE MATRIX, AND GENERATES BOND ANGLES AND DIHEDRAL ANGLES.   C
```

```
C       IT THEN GENERATES AND TESTS INPUT TO ZMAT.                      C
        COMMON/IIII/LTEST                                               C
        COMMON/BONDS/NNCIM(40,40), NCIM                                 C
        COMMON/JIM/IJIM                                                 C
        COMMON/INFO/QRS                                                 C
        COMMON/JJJJ/BONDBL                                              C
        INTEGER AN                                                      C
        DIMENSION EL(9)                                                 C
        DIMENSION R(60,60),RR(40,40)                                    C
        DIMENSION LUU(40)                                               C
        DIMENSION QRS(60,3)                                             C
        DATA((EL(I),I=1,9)=4H   H,4H  HE,4H  LI,4H  BE,4H   B,4H   C,   C
       *4H   N,4H   O,4H   F)                                           C
        INTEGER Z                                                       C
        DIMENSION T(40,40,40)                                           C
        DIMENSION INTER(60)                                             C
        DIMENSION AN(40),Z(60,4),BL(40),ALPHA(40),BETA(40)              C
        DIMENSION C(60,3),RA(60,60),                                    C
       *                    A(3,3)                                      C
        DATA(HOUS=4HHOUS)                                               C
        LTEST=0                                                         C
        DO 8180 I=1,NN                                                  C
        DO 8180 J=1,NN                                                  C
        DO 8180 K=1,NN                                                  C
        RR(I,J) = 0.                                                    C
        T(I,J,K) = 0.                                                   C
        Z(I,4) = 0                                                      C
        Z(I,3) = 0                                                      C
        Z(I,2) = 0                                                      C
        Z(I,1) = 0                                                      C
        ALPHA(I) = 0.                                                   C
        BETA(I) = 0.                                                    C
        BL(I) = 0.                                                      C
 8180 CONTINUE                                                          C
C       CALCULATE BOND ANGLES                                           C
        DO 7777 JJ = 1,NN                                               C
        DO 7777 KK = 1,NN                                               C
        DO 7777 LL = 1,NN                                               C
        IF(JJ .EQ.LL) GO TO 7777                                        C
        IF(JJ .EQ. KK) GO TO 7777                                       C
        IF(LL .EQ. KK) GO TO 7777                                       C
        IF(JJ .LT. LL) GO TO 7777                                       C
        IF(JJ .LT. KK)  GO TO 7777                                      C
        IF((NCIM.EQ.1).AND.(NNCIM(JJ,KK).EQ.1).AND.(NNCIM(KK,LL).EQ.1))GO C
       *TO 1001                                                         C
        IF((R(JJ,KK) .LT. BONDBL) .AND. (R(KK,LL) .LT. BONDBL)) GO TO   C
       *1001                                                            C
        GO TO 7777                                                      C
 1001 CONTINUE                                                          C
        CT = C.0                                                        C
        DO 1130 I = 1,3                                                 C
 1130 CT = CT-(C(LL,I) - C(KK,I)) * (C(KK,I) - C(JJ,I))                 C
```

```
      CT = CT/(R(JJ,KK)*R(KK,LL))
      XXXX = (1.0 - CT*CT)
      IF(XXXX .LT. 0.0) GO TO 1200
       GO TO 1201
 1200 PRINT 1202
 1202 FORMAT (/,3X,11HXXXX IS NEG./)
 1201 CONTINUE
      ST =  SQRT ( ABS(1.0  - CT*CT)            )
      T(JJ,KK,LL) =(180./3.141592654)       *ATAN2(ST,CT)
      PRINT 8, JJ,KK,LL,T(JJ,KK,LL),R(JJ,KK),R(KK,LL)
    8 FORMAT (/3X,6HANGLE(,I2,1H,,I2,1H,,I2,2H)=,F10.5,20X,2F10.5)
 7777 CONTINUE
C*****CALCULATE DIHYDRAL ANGLES
      DO 1949 JJ= 1,NN
      DO 1949 KK= 1,NN
      DO 1949 LL = 1,NN
      IF(  T(JJ,KK,LL)  .EQ. 0) GO TO 1949
      DO 1948 MM= 1,NN
      IF(JJ.LT.MM) GO TO 1948
      IF((JJ.EQ.LL).OR.(JJ.EQ.KK).OR.(LL.EQ.KK).OR.(LL.EQ.MM))GO TO
     *1948
      IF((MM.EQ.KK) .OR. (MM.EQ.JJ)) GO TO 1948
      IF((NCIM.EQ.1).AND.(NNCIM(LL,MM).EQ.1)) GO TO 13
      IF(R(LL,MM) .LT. BONDBL) GO TO 13
      GO TO 14
   13 CONTINUE
C     AT THIS POINT JJ,KK,LL,MM ARE SEQUENTIALLY BONDED ATOMS. WHERE JJ
C     IS GREATER THAN MM
      CC=0.0
      DO 1240 I = 1,3
 1240 CC = CC+(C(KK,I)-C(JJ,I))*(C(LL,I)-C(KK,I))
      CC = CC/(R(JJ,KK)*R(KK,LL))
      DO 1230 I = 1,3
 1230 A(1,I)=(C(LL,I)-C(KK,I))/R(KK,LL)
      DO 1250 I = 1,3
      YYYY = (1.0 - CC*CC)
      IF (YYYY .LT. 0.0) GO TO 1205
       GO TO 1206
 1205 PRINT 1202
 1206 CONTINUE
 1250 A(2,I)=(-(C(KK,I)-C(JJ,I))/R(JJ,KK)+CC*(C(LL,I)-C(KK,I))/R(KK,LL))
     */ SQRT( ABS(1.0 -CC*CC)         )
      A(3,1)=A(1,2)*A(2,3)-A(1,3)*A(2,2)
      A(3,2)=A(2,1)*A(1,3)-A(1,1)*A(2,3)
      A(3,3)=A(1,1)*A(2,2)-A(2,1)*A(1,2)
      ZO=0.0
      YO=0.0
      DO 1260 I=1,3
      ZO=ZO+A(3,I)*(C(MM,I)-C(KK,I))
 1260 YO=YO+A(2,I)*(C(MM,I)-C(KK,I))
      CT = YO
      ST = ZO
```

```
      TAU=( 180./3.141592654)          * ATAN2(ST,CT)
      IF(JJ .EQ. 4) BETA4 = TAU
      IF(MM .EQ. 5)  PRINT 2712
 2712 FORMAT(1X,6HMM = 5)
        PRINT 9, JJ,KK,LL,MM,TAU,R(JJ,KK),R(KK,LL),R(LL,MM)
    9 FORMAT (/10X,4HTAU(,I2,1H,,I2,1H,,I2,1H,,I2,2H)=,F10.5,20X,3F10.5
     *)
C     GENERATE ZMAT
      IF(Z(JJ,1).NE. 0) GO TO 1949
      Z(JJ,1) = KK
      BL(JJ) = R(JJ,KK)
      Z(JJ,2) = LL
      ALPHA(JJ) = T(JJ,KK,LL)
      IF(INTER(JJ) .EQ.  HOUS)  GO TO 6238
      AAAA=0.
      DO 6139 LO=1,NN
      IF((LO.EQ.KK) .OR.(LO.EQ.JJ)) GO TO 6139
      IF(LO .EQ. LL) GO TO 6139
      IF(T(JJ,KK,LO) .NE.0.) GO TO 6138
      GO TO 6139
 6138 Z(JJ,3) = LO
      BETA(JJ) = T(JJ,KK,LO)
      Z(JJ,4) = 1
      AAAA =1.
 6139 CONTINUE
      IF(AAAA.EQ.0.)  GO TO 6238
      GO TO 1949
 6238 BETA(JJ) = TAU
      Z(JJ,3) = MM
      Z(JJ,4) = 0
   14 CONTINUE
 1948 CONTINUE
 1949 CONTINUE
C     ZMAT FOR ATOM 2
      BL(2) = R(1,2)
      Z(2,1) = 1
C     ZMAT FOR ATOM 3
      IF(Z(3,1) .NE. 0) GO TO 7612
      DO 1297 I=1,2
      IF((NCIM.EQ.1).AND.(NNCIM(3,I).EQ.1)) Z(3,1) = I
      IF(R(3,I) .LT. BONDBL) Z(3,1) = I
 1297 CONTINUE
      KA =Z(3,1)
      BL(3) = R(3,KA)
      DO 1296 I=1,2
      KA =Z(3,1)
      IF(T(3,KA     ,1)  .NE. 0) Z(3,2) = I
 1296 CONTINUE
      KA =Z(3,1)
      KB = Z(3,2)
       ALPHA(3) = T(3,KA,KB)
 7612 CONTINUE
```

```
C       ZMAT FOR ATOM 4
        IF(Z(4,1) .NE. 0) GO TO 7613
        DO 1295 I=1,3
        IF((NCIM.EQ.1).AND.(NNCIM(4,I).EQ.1))  Z(4,1) = I
        IF(R(4,I) .LT. BONDBL) Z(4,1) = I
 1295 CONTINUE
        KC = Z(4,1)
        BL(4) = R(4,KC)
        NMN = 0
        IK=0
 1909 CONTINUE
        DO 1294 I=1,3
        KC = Z(4,1)
        IF((NMN.EQ.0).AND.(T(4,KC     ,I).NE.0))GO TO 1336
        IF((NMN.EQ.1).AND.(T(4,KC     ,I).NE.0))GO TO 1337
        GO TO 1294
 1336 IJ=I
        NMN = NMN+1
        GO TO 1909
 1337 IK = I
 1294 CONTINUE
C       IF(IK .EQ. 0.)  ATOM 4 FORMS ONLY ONE BOND ANGLE AND THEREFORE MUS
C       BE DESIGNATED BY A DIHEDRAL
        IF(IK .EQ. 0) GO TO 1207
        GO TO 1208
 1207 Z(4,2) = IJ
        KC = Z(4,1)
        KD = Z(4,2)
        ALPHA(4) = T(4,KC,KD)
        Z(4,3) = (6- (KC+KD))
        KE = Z(4,3)
        Z(4,4) = 0
        BETA(4) =  BETA4
        GO TO 7613
 1208 Z(4,2) = IK
        Z(4,3) = IJ
        Z(4,4) = 1
        KC = Z(4,1)
        KD = Z(4,2)
        ALPHA(4) = T(4,KC,KD)
        KE = Z(4,3)
         BETA(4) = T(4,KC,KE)
 7613 CONTINUE
C       CHECK TO SEE IF ATOM 5 IS DESIGNATED PROPERLY.  IF IT IS POSSIBLE
C       TO DESIGNATE 5 BY A DIHYDRAL, THE ZMAT FOR ATOM 5 IS WRITTEN
C       PROPERLY.  IF NOT, NO ZMAT IS WRITTEN FOR 5.  UNZMAT MUST WRITE
C       IT NOW.
        IF(Z(5,1) .NE. 0) GO TO 9190
        DO 9180 I=1,NN
        IF((NCIM.EQ.1).AND.(NNCIM(5,I).EQ.1))  GO TO 9181
        IF(R(5,I) .LT. BONDBL)  GO TO 9181
        GO TO 9180
```

```
 9181 Z(5,1) = I
      BL(5) = R(5,I)
      GO TO 9185
 9180 CONTINUE
 9185 CONTINUE
      LORS = 0
      DO 9182 I=1,NN
      JJ=Z(5,1)
      IF((T(5,JJ,I) .NE. 0) .AND. (LORS .EQ.0)) GO TO 9183
      IF((T(5,JJ,I) .NE. 0) .AND. (LORS .NE.0)) GO TO 9184
      GO TO 9182
 9183 KK=I
      LORS = LORS + 1
      GO TO 9186
 9184 LL=I
      GO TO 9187
 9186 CONTINUE
 9182 CONTINUE
 9187 CONTINUE
      ALPHA(5) = T(5,JJ,LL)
      Z(5,2) = LL
      BETA(5) = T(5,JJ,KK)
      Z(5,3) = KK
      Z(5,4) = 1
 9190 CONTINUE
C     THIS CODE TESTS IF AN ATOM IS DESIGNATED BY A DIHYDRAL, AND
C     DETERMINES IF DESIGNATION BY MORE THAN ONE DIHYDRAL IS POSSIBLE.
C     IF THE LATTER CASE IS TRUE, AND THE POSSIBLE DIHYDRALS IN QUESTION
C     ARE TAU(J,K,L,M), THE DIHYDRAL WITH THE LARGER VALUE OF K
C     IS EMPLOYED.  THIS FREQUENTLY IS OF VALUE IN GEARING RINGS.
      DO 8322 J=5,NN
      IF(Z(J,4) .NE. 0) GO TO 7015
      LWIN = 0
      DO 7010 K=1,NN
      DO 7016 L=1,NN
      IF(T(J,K,L) .EQ. 0) GO TO 7016
      DO 7018 M=1,NN
      IF(J .LT. M) GO TO 7018
      IF((J.LT.K).OR.(J.LT.L)) GO TO   7018
      IF((J .EQ. L) .OR. (J.EQ.K) .OR. (L.EQ.K).OR.(L.EQ.M)) GO TO 7018
      IF((M.EQ.K).OR.(M.EQ.J)) GO TO 7018
      IF((NCIM.EQ.1).AND.(NNCIM(L,M).NE.1))       GO TO 7018
      IF((R(L,M) .GT. BONDBL)) GO TO 7018
      IF(LWIN .GT. 0) GO TO 7012
      GO TO 7099
 7012 PRINT 7013, J
 7013 FORMAT (///,3X,4HATOM,3X,I4,3X,51HCAN BE DESIGNATED BY MORE THAN
     *ONE DIHYDRAL ANGLE.)
      CALL TAUFIX(BL,ALPHA,BETA,J,K,L,M,T,R,Z,C)
 7099 CONTINUE
      LWIN = LWIN +1
 7018 CONTINUE
```

```
 7016 CONTINUE
 7010 CONTINUE
 7015 CONTINUE
 8322 CONTINUE
C      WRITE OUT COMPLETED ZMAT
       PRINT 1997
 1997 FORMAT(////)
C      PRINT 1998
 1998 FORMAT (1X,8HZ MATRIX,//,42H NO AN   (1)    BL    (2)     ALPHA    (3)
     *     ,10HBETA    (4))
       DO 900 J = 1,NN
       IND1 = AN(J)
C      PRINT 1999,(J,AN(J),Z(J,1),BL(J),Z(J,2),ALPHA(J),Z(J,3),BETA(J),
C     *Z(J,4))
  900 CONTINUE
 1999 FORMAT (2I3,I4,F7.4,2(I4,F11.6),I4)
       DATA(HOUS=4HHOUS)
       DO 7196 IME = 4,NN
 1325  FORMAT (1X,2HHI)
       IF((Z(IME,4) .EQ. 0) .OR. (Z(IME,4) .EQ. 2))  GO TO 7196
       CALL Z4FIX(C,Z,IME)
 7196 CONTINUE
       CALL ZTEST (R,RR,AN,Z,BL,ALPHA,BETA,NN)
       IF(LTEST .EQ. 1) GO TO 1984
       NMNJ = 1
       DO 1979 I=1,NN
       IF(Z(I,4) .NE. 0)  GO TO 1978
       GO TO 1979
 1978 LUU(NMNJ) = I
       NMNJ = NMNJ+1
 1979 CONTINUE
       NMNJ =NMNJ-1
       DO 4224 J=1,NMNJ
       I=LUU(J)
 4224 Z(I,4) = 1
       CALL       ZTEST(R,RR,AN,Z,BL,ALPHA,BETA,NN)
       IF(LTEST .EQ.1) GO TO 1984
       IAOK = 0
       LOST = NMNJ + 1
       DO 7007 JKK=1,LOST
       LJKK = JKK-1
       IF(IAOK .EQ. 0) GO TO 7008
       LKK = LUU (LJKK)
       Z(LKK,4) = Z(LKK,4)*(-1)
 7008 CONTINUE
       DO 7000 I=1,NMNJ
       DO 7001 J=1,NMNJ
       IF(J.EQ.1) GO TO 7002
       KM1=K
       Z(KM1,4) =Z(KM1,4)*(-1)
 7002 K=LUU(J)
       Z(K,4) = Z(K,4)*(-1)
```

```
      CALL        ZTEST(R,RR,AN,Z,BL,ALPHA,BETA,NN)
      IF(LTEST .EQ.1) GO TO 1984
      DO 7004 IK=1,NMNJ
      II=LUU(IK)
      Z(II,4) = Z(II,4)*(-1)
 7004 CONTINUE
      CALL ZTEST(R,RR,AN,Z,BL,ALPHA,BETA,NN)
      IF(LTEST .EQ.1) GO TO 1984
      DO 7005 IL=1,NMNJ
      II=LUU(IL)
      Z(II,4) = Z(II,4)*(-1)
 7005 CONTINUE
 7001 CONTINUE
      K=LUU(I)
 7000 Z(K,4) = Z(K,4)*(-1)
      IF(IACK .EQ. 0) GO TO 7009
      Z(LKK,4) = Z(LKK,4)*(-1)
 7009 CONTINUE
      IACK = IACK + 1
 7007 CONTINUE
      RETURN
      SUBROUTINE Z4FIX (C,Z,IME)
C     THIS ROUTINE THANKS TO CLINT COOK PROPERLY SETS Z(I,4) IN THE
C     ZMAT WHICH IS GENERATED BY UNZMAT, IFTHE ATOM I IS
C     SPECIFIED BY TWO BOND ANGLES.
      INTEGER Z
      DIMENSION C(60,3),              Z(60,4), Q1(3),Q2(3),Q3(3),MY(4),
     *QC(3),QD(3),QE(3),QL1(3),QL2(3),QL3(3),DIM1(3),DIM2(3)
      MY(1)=Z(IME,2)
      MY(2)=Z(IME,1)
      MY(3)=Z(IME,3)
      MY(4)=IME
 1202 FORMAT (2HBO)
      DO 14 I=1,3
      IF(I.EQ.1) GO TO 5
      GO TO 6
    5 CONTINUE
      MOS=MY(2)
      MOR=MY(1)
    6 CONTINUE
      IF(I.EQ.2) GO TO 7
      GO TO 8
    7 CONTINUE
      MOS=MY(3)
      MOR=MY(2)
    8 CONTINUE
      IF(I.EQ.3) GO TO 9
      GO TO 10
    9 CONTINUE
      MOS=MY(4)
      MOR=MY(2)
   10 CONTINUE
```

```
      DO 11 J=1,3
      QC(J)=C(MQS,J)-C(MQR,J)
   11 CONTINUE
      IF(I.EQ.1) CALL UNIVEC(QL1,QC)
      IF(I.EQ.2) CALL UNIVEC(QL2,QC)
      IF(I.EQ.3) CALL UNIVEC(QL3,QC)
   14 CONTINUE
      CALL VECPRD(DIM1,QL1,QL2)
      CALL SCLPRD(DIM2,DIM1,QL3)
      ALPA=C.0
      DO 25 K=1,3
      ALPA=DIM2(K)+ALPA
   25 CONTINUE
      IF(ALPA.GT.0.0) GO TO 100
      GO TO 101
  100 CONTINUE
      Z(IME,4) = 1
      GO TO 103
  101 CONTINUE
      Z(IME,4) =-1
  103 CONTINUE
      RETURN
      END
      SUBROUTINE SCLPRD(VP,X,Y)
C*****VP IS THE VECTOR PRODUCT OF X DOT Y.
      DIMENSION VP(3),X(3),Y(3)
      DO 1 I=1,3
      VP(I) = X(I) * Y(I)
 1    CONTINUE
      RETURN
      END
      SUBROUTINE REF(E,NN)
      DIMENSION E(60,3), A(1,3), R(60,60)
   99 FORMAT (//,1X, 40HCARTESIAN COORDINATES SUBJECTED TO CLINT,//)
      DO 1 I=1,3
      A(1,I) = E(1,I)
    1 CONTINUE
      DO 2 I=1,NN
      DO 2 J=1,3
      E(I,J) = E(I,J) - A(1,J)
    2 CONTINUE
  100 FORMAT (//,1X, 66HCATESIAN COORDINATES SUBJECTED TO CLINT AND REFE
     *RRED TO THE ORIGIN.//)
      RETURN
      END
      SUBRCUTINE CFIX(C,APH,BET,GAM,NN)
      COMMON/TRANZ/ A(3,3)
      DIMENSION C(60,3)
      AAPH = APH * 3.141592654/180.
      ABET = BET * 3.141592654/180.
      AGAM = GAM * 3.141592654/180.
      ACON = 90. * 3.141592654/180.
```

```
      SINA = SIN(AAPH - ACON)
      COSA = COS(AAPH - ACON)
      SINB = SIN(ABET - ACON)
      COSB = COS(ABET - ACON)
      SING = SIN (AGAM - ACON)
      COSG = COS(AGAM - ACON)
      IF((APH .EQ. 90.) .AND. (GAM .EQ. 90.))  GO TO 55
      GO TO 66
   55 CONTINUE
      PRINT 98
   98 FORMAT (//,1X,24HTHE SYSTEM IS MONOCLINIC,//)
      GO TO 56
   66 CONTINUE
      IF(( APH .EQ. 90.) .AND. (BET .EQ. 90.) .AND. (GAM .EQ. 120.))  G
     *TO 61
      GO TO 62
   61 CONTINUE
      PRINT 99
   99 FORMAT (//,1X,23HTHE SYSTEM IS HEXAGONAL,//)
      GO TO 67
   62 CONTINUE
      IF((APH .NE. BET) .AND. (BET .NE. GAM) .AND. (GAM.NE. APH)) GO TO
     *81
      GO TO 82
   81 CONTINUE
      PRINT 100
  100 FORMAT (//,2X,23HTHE SYSTEM IS TRICLINIC,//)
      GO TO 83
   82 CONTINUE
      IF((APH .EQ. BET) .AND. (APH .EQ. GAM))  GO TO 91
      GO TO 92
   91 CONTINUE
      IF((APH .LT. 120.))  GO TO 93
      GO TO 94
   93 CONTINUE
      PRINT 101
  101 FORMAT (//,2X,22HTHE SYSTEM IS TRIGONAL,//)
      GO TO 95
   94 CONTINUE
   92 CONTINUE
      PRINT 102
  102 FORMAT (//,1X,77HTHE SYSTEM IS NOT ORTHORHOMBIC, MONOCLINIC, HEXAG
     *ONAL, TRICLINIC OR TRIGONAL.,//)
      GO TO 70
   56 CONTINUE
      D = COSB
      A(1,1) = COSB/D
      A(1,2) = 0.
      A(1,3) = 0.
      A(2,1) = 0.
      A(2,2) = 1.
      A(2,3) = 0.
```

```
      A(3,1) = SINB/D
      A(3,2) = C.
      A(3,3) = 1.0/D
      GO TO 70
   67 CONTINUE
      D = COSG
      A(1,1) = COSG/D
      A(1,2) = 0.
      A(1,3) = 0.
      A(2,1) = SING/D
      A(2,2) = 1.0/D
      A(2,3) = 0.
      A(3,1) = 0.
      A(3,2) = 0.
      A(3,3) = 1.
      GO TO 70
   83 CONTINUE
      GO TO 70
   95 CONTINUE
      GO TO 70
   70 CONTINUE
      RETURN
      END
      SUBROUTINE DIST(C,NN,R)
C     THIS ROUTINE ACCEPTS A SET OF CARTESIAN COORDINATES AND GENERATES
C     THE INTERATOMIC DISTANCE MATRIX
      DIMENSION C(60,3), R(60,60)
      DO 1 I=1,NN
      DO 1 J=1,NN
      R(I,J) = SQRT((C(I,1)-C(J,1))**2 + (C(I,2)-C(J,2))**2        +
     *(C(I,3)- C(J,3))**2)
    1 CONTINUE
      RETURN
      END
      SUBROUTINE RREO(AMAT,IROWS,TRANS)
       DIMENSION TRANS(3,3),AMAT(60,3)
      DIMENSION COPY(60,3)
      DO 1 I=1,IROWS
      DO 1 J=1,3
    1 COPY(I,J)=AMAT(I,J)
      L=0
      DO 30 I=1,3
      IF (COPY(I,I)) 8,4,8
    4 L=L+1
      IF (I+L-IROWS) 5,5,30
    5 IF (COPY(I+L,I)) 6,4,6
    6 CONTINUE
      DO 7II=1,3
      M=I
      HOLD=COPY(II,M)
      COPY(II,M)=COPY(II+L,M)
    7 COPY(II+L,M) = HOLD
```

```
      L = 0
    8 CONTINUE
      DO 3 J=1,3
    3 COPY(I,J)=COPY(I,J)/COPY(I,I)
      DO 9 K=1,IROWS
      IF (K+I-IROWS) 10,10,30
   10 CONTINUE
      DO 9 J=I,3
    9 COPY(I+K,J)=COPY(I+K,J) - COPY(I+K,I)*COPY(I,J)
   30 CONTINUE
      DO 40 I=1,IROWS
   40 PRINT 50,(COPY(I,J),J=1,3)
   50 FORMAT(3F20.10)
      DO 60 I=1,3
      DO 60 J=1,3
   60 TRANS(I,J)=COPY(I,J)
      RETURN
      END
      SUBROUTINE ZTEST(R,RR,AN,Z,BL,ALPHA,BETA,NN)
C     THIS ROUTINE ACCEPTS AS INPUT THE ZMAT GENERATED BY UNZMAT, AND
C     USES SUBROUTINE ZMAT TO GENERATE THE INTERATOMIC DISTANCE MATRIX.
C     ZTEST THEN COMPARES THIS INTERATOMIC DISTANCE MATRIX TO THAT
C     GENERATED FROM THE CARTESIAN COORDINATES ACCEPTED AS INPUT TO XTAL
C     IF THE ZMAT WORKS, ZTEST SAYS SO, AND ALSO SETS LTEST = 1 SO THAT
C     UPON RETURN TO UNZMAT THE MACHINE EXITS TO XTAL.
      INTEGER Z
      COMMON/IIII/LTEST
      COMMON/JIM/IJIM
      COMMON/INFO/ORS
      DIMENSION ORS(60,3)
      DIMENSION RRRR(40,40)
      DIMENSION R(60,60),RR(40,40),AN(40),Z(60,4),BL(40),ALPHA(40),
     *BETA(40)
      IJIM = 0
      CALL ZMAT(AN,Z,BL,ALPHA,BETA,NN,RR)
      DO 2212 I=1,NN
      DO 2212 J=1,NN
 2212 RRRR(I,J) = R(I,J) - RR(I,J)
      DO 2213 I=1,NN
      DO 2213 J=1,NN
      IF(ABS(RRRR(I,J)) .GT. .0001) GO TO 2214
      GO TO 2213
 2214 GO TO 9999
 2213 CONTINUE
      IJIM = IJIM + 1
      CALL ZMAT(AN,Z,BL,ALPHA,BETA,NN,RR)
      PRINT 99
   99 FORMAT (///,3X,20HTHE ABOVE ZMAT WORKS,///)
      LTEST = 1
      DO 6969 I=1,NN
      PUNCH 1003, AN(I),Z(I,1),BL(I),Z(I,2),ALPHA(I),Z(I,3),BETA(I),
     *Z(I,4)
```

```
 1003 FORMAT (I3,I4,F7.4,I4,F11.6,I4,F11.6,I4)
 6969 CONTINUE
 9999 RETURN
      END
      SUBROUTINE ZMAT(AN,Z,BL,ALPHA,BETA,NN,R)
C     *(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT,PUNCH)
C     THIS PROGRAM ACCEPTS A DEFINITION OF A MOLECULE IN TERMS OF
C     ATOMIC NUMBERS, BOND LENGTHS, BOND ANGLES AND DIHEDRAL ANGLES
C     AND CALCULATES THE CARTESIAN COORDINATES IN ANGSTROMS
C     ADAPTED FROM MARK GORDONS MBLD SYSTEM BY D L BEVERIDGE
C     CODED IN CDC SCOPE 3.1 LEVEL FORTRAN FOR THE CIMS CDC 6600
      DIMENSION Z(60,4),BL(40),ALPHA(40),BETA(40)
      DIMENSION V1(3),V2(3),V3(3),VJ(3),VP(3),L1(3),L2(3),L3(3),L4(3),
     * A(80),B(80),D(80)
      TYPE REAL L1,L2,L3,L4
      COMMON/JIM/IJIM
      DIMENSIONC(60,3)
      DIMENSION BTB(60),ALB(60),BLB(60)
      DIMENSION AN(40)
      COMMON/INFO/C
      TYPE INTEGER AN,CHARGE,Z,PUNCH
      DIMENSION R(40,40)
      COMMON/IDENT/IDENT(10)
      COMMON/ELORB/EL(104),ORB(4,7)
      TYPE INTEGER ORB
      DATA((EL(I),I=1,36 )=4H   H,4H  HE,4H  LI,4H  BE,4H   B,4H   C,
     14H   N,4H   O,4H   F,4H  NE,4H  NA,4H  MG,4H  AL,4H  SI,4H   P,
     24H   S,4H  CL,4H  AR,4H   K,4H  CA,4H  SC,4H  TI,4H   V,4H  CR,
     34H  MN,4H  FE,4H  CO,4H  NI,4H  CU,4H  ZN,4H  GA,4H  GE,4H  AS,
     44H  SE,4H  BR,4H  KR)
      DATA((EL(I),I=37,71)=4H  RB,4H  SR,4H   Y,4H  ZR,4H  NB,4H  MO,
     14H  TC,4H  RV,4H  RH,4H  PD,4H  AG,4H  CD,4H  IN,4H  SN,4H  SB,
     24H  TE,4H   I,4H  XE,4H  CS,4H  BA,4H  LA,4H  CE,4H  PR,4H  ND,
     34H  PM,4H  SM,4H  EU,4H  GD,4H  TB,4H  DY,4H  HO,4H  ER,4H  TM,
     44H  YB,4H  LU)
      DATA((EL(I),I=72,102)=4H  HF,4H  TA,4H   W,4H  RE,4H  OS,4H  IR,
     14H  PT,4H  AU,4H  HG,4H  TL,4H  PB,4H  BI,4H  PO,4H  AT,4H  RN,
     24H  FR,4H  RA,4H  AC,4H  TH,4H  PA,4H   U,4H  NP,4H  PU,4H  AM,
     34H  CM,4H  BK,4H  CF,4H  ES,4H  FM,4H  MD,4H  NO)
      SINF(X)=SIN(X)
      COSF(X)=COS(X)
      ABSF(X)=ABS(X)
      SIGNF(X,Y)=SIGN(X,Y)
      SQRTF(X) = SQRT(X)
      ATANF(X)=ATAN(X)
C     ************************************
C     INPUT AND OUTPUT OF INPUT
      PUNCH = 8HPUNCH
      M=NN
      NATOMS=NN
  999 CONTINUE
C     READ 1000,(IDENT(I),I=1,10)
```

```
C       IF(EOF,5) 1,2
C     1 STOP
      2 CONTINUE
C       PRINT 998
   998 FORMAT(1H1)
C       PRINT 2006
  2006 FORMAT(/,14H INPUT DATA..../)
C       PRINT 1000,(IDENT(I),I=1,10)
  1000 FORMAT(10A8)
C       IF(IDENT(10).EQ.PUNCH)3,4
C     3 PRINT 2008
  2008 FORMAT(/,16H PUNCH OPTION ON,/)
C       PUNCH 1000,(IDENT(I),I=1,10)
      4 CONTINUE
C       READ 1001, NATOMS,CHARGE,MULTIP
  1001 FORMAT(3I2)
C       PRINT1002, NATOMS,CHARGE,MULTIP
  1002 FORMAT(//,10H NATOMS = ,I4,2X,10H CHARGE = ,I4,2X,10H MULTIP =  ,I4
     .  *,I4,//)
C       IF(IDENT(10).EQ.5HPUNCH) 5,6
C     5 PUNCH 8,NATOMS,CHARGE,MULTIP
      8 FORMAT(3I4)
      6 CONTINUE
C       PRINT 1004
  1004 FORMAT(//,9H Z MATRIX,//)
C       **********************************
C       CALCULATION OF COORDINATES
        DO 6969 I=1,M
C       READ  1003,   AN(I),Z(I,1),BL(I),Z(I,2),ALPHA(I),Z(I,3),BETA(I),
C      1Z(I,4)
  1003 FORMAT(I3,I4,F7.4,I4,F11.6,I4,F11.6,I4,F10.5)
C6969 PRINT 1003,   AN(I),Z(I,1),BL(I),Z(I,2),ALPHA(I),Z(I,3),BETA(I),
C      1Z(I,4)
  6969 CONTINUE
        DO 232 I=1,M
        BTB(I) = BETA(I)
        ALB(I) = ALPHA(I)
        BLB(I) = BL(I)
   232 CONTINUE
        DO 502 J=1,M
   502 ALPHA(J) = ALPHA(J)*3.141592654/180.
        DO 503 J=1,M
   503 BETA(J) = BETA(J)*3.141592654/180.
        DO 504 J= 1,3
   504 C(1,J)=0.0
        C(2,1)=0.0
        C(2,2)=0.0
        C(2,3)=BL(2)
        C(3,1)=BL(3)*SINF(ALPHA(3))
        C(3,2)=0.0
C       **********************************
C       THE FOLLOWING IS AN ADDITION TO COORD FINDEP PROGRAM TO BE USED
```

```
C       IF THE MOLECULE UNDER CONSIDERATION HAS ONLY ONE HEAVY ATOM OR FOR
C       A MOLECULE SUCH AS NEOPENTANE IN WHICH THE CENTRAL ATOM HAS NO
C       HYDROGENS BONDED TO IT
        IF(Z(3,1).EQ.1) 505,506
  505 C(3,3) = BL(3)*COSF(ALPHA(3))
        GO TO 507
  506 C(3,3) = C(2,3)-BL(3)*COSF(ALPHA(3))
  507 I=3
        IF(ABSF(C(3,1)).LT..00001) 550,510
  550 DO 509 I = 4,1000
        IF(I.LE.M.AND.ABSF(C(I-1,1)).LT..00001) 508,510
  508 C(I,1) = BL(I)*SINF(ALPHA(I))
        C(I,2) = 0.0
        ITEMP = Z(I,1)
        JTEMP = Z(I,2)
       0C(I,3) = C(ITEMP,3)-BL(I)*COSF(ALPHA(I))*SIGNF(1.,C(ITEMP,3)-C(JTE
       1MP,3))
  509 CONTINUE
  510 CONTINUE
        IF(I.EQ.3) 511,512
  511 K=4
        GO TO 513
  512 K=I
  513 CONTINUE
        IF(K.GT.M) 601,600
  600 CONTINUE
        DO 533 J = K,M
        IF(Z(J,4).EQ.0) 514,517
C       **********************************
C       THIS PART IS USED IF THE ATOM IS BEING DEFINED BY A DIHEDRAL ANGLE
  514 CALL RELVEC(V1,Z(J,2),Z(J,3))
        CALL UNIVEC(L1,V1)
C       V1 IS A VECTOR FROM ATOM Z(J,3) TO ATOM Z(J,2)
C       L1 IS A UNIT VECTOR OF V1.  BL(Z(J,2)) I2 BONDLENGTH OF ATOM Z(J,2
        CALL RELVEC(V2,Z(J,1),Z(J,2))
        CALL UNIVEC(L2,V2)
C       V2 IS THE VE3TOR FROM ATOM Z(J,2) TO AT04 Z(J,1)
C       L2 IS THE UNIT VECTOR OF V2.   BL(Z(J,1)@ IS BONDLENGTH  DEFINING
C       ATOM Z(J,1)
        CALL VECPRD(VP,L1,L2)
        DO 515 I = 1,3
  515 L3(I) = VP(1)/SQRTF(1.-(L1(1)*L2(1)+L1(2)*L2(2)+L1(3)*L2(3))**2)
C       L3 IS THE UNIT VECTOR OF VP.ALPHA(Z(J,1))IS THE ANGLE DEFINING
C       ATOM Z(J,1)
        CALL VECPRD(L4,L3,L2)
C       L4,L3,L2 ARE A NEW SET OF MUTUALLY ORTHOGONAL AXES. WE WILL NOW
C       OBTAIN COORD OF ATOM J IN TERMS OF THESE AXES RELATIVE TO ATOM Z(J
        DO 516 I=1,3
      0VJ(I) = BL(J)*(-L2(I)*COSF(ALPHA(J))+L4(I)*SINF(ALPHA(J))*COSF(BET
       1A(J))+L3(I)*SINF(ALPHA(J))*SINF(BETA(J)))
C       VJ IS THE VECTOR FROM ATOM Z(J,1) TO ATOM J
        ITEMP = Z(J,1)
```

```
      C(J,I) = VJ(I) + C(ITEMP,I)
  516 CONTINUE
      GO TO 533
  517 IF(Z(J,4).EQ.1.OR.Z(J,4).EQ.-1) 549,528
C     ********************************
C     THIS PART IS USED IF ATOM IS DEFINED BY TWO BONDANGLES
  549 CALL RELVEC(V1,Z(J,1),Z(J,3))
      CALL UNIVEC(L1,V1)
      CALL RELVEC(V2,Z(J,2),Z(J,1))
      CALL UNIVEC(L2,V2)
      ZETA = -(L1(1)*L2(1)+L1(2)*L2(2)+L1(3)*L2(3))
      A(J) = (-COSF(BETA(J))+ZETA*COSF(ALPHA(J)))/(1.-ZETA**2)
      B(J) = (COSF(ALPHA(J))-ZETA*COSF(BETA(J)))/(1.-ZETA**2)
      PI = 3.141592654
      IF(ZETA.LT.0) 518,519
  518 TEMP = PI
      GO TO 520
  519 TEMP = 0.0
  520 CONTINUE
      IF(ZETA.EQ.0) 521,522
  521 GAMMA = PI/2.
      GO TO 523
  522 GAMMA = ATANF(SQRTF(1.-ZETA**2)/ZETA) +TEMP
  523 CONTINUE
      IF (ABSF(GAMMA+ALPHA(J)+BETA(J)-2.*PI).LT..0000C0C1) 524,525
  524 D(J) = 0.0
      GO TO 526
  5250D(J) = Z(J,4)*(SQRTF(1.+A(J)*COSF(BETA(J))-B(J)*COSF(ALPHA(J))))/S
     1QRTF(1.-ZETA**2)
  526 CONTINUE
      CALL VECPRD(V3,L1,L2)
      DO 527 I = 1,3
      L3(I) = A(J)*L1(I)+B(J)*L2(I)+D(J)*V3(I)
      VJ(I) = BL(J)*L3(I)
      ITEMP = Z(J,1)
      C(J,I) = VJ(I)+C(ITEMP,I)
  527 CONTINUE
      GO TO 533
C     ************************************
C     THIS PART IS USED IF ATOM IS DEFINED BY ONE BONDANGLE AND BY THE
C     ANGLE WHICH BOND Z(J,1)-J MAKES WITH THE PLANE OF Z(J,1),Z(J,2)
C     AND Z(J,3)
  528 CALL RELVEC(V1,Z(J,1),Z(J,3))
      CALL UNIVEC(L1,V1)
      CALL RELVEC(V2,Z(J,2),Z(J,1))
      CALL UNIVEC(L2,V2)
      ZETA = -(L1(1)*L2(1)+L1(2)*L2(2)+L1(3)*L2(3))
      CALL VECPRD(V3,L1,L2)
C     BETA(J) HERE REFERS TO 90-ANGLE WHICH BOND Z(J,1)-J MAKES WITH THE
C     AFOREMENTIONED PLANE
      A(J) = COSF(BETA(J))/(1.-ZETA**2)
      IF(Z(J,4).EQ.2) 530,529
```

```
  529 B(J)= -SQRTF((1.-COSF(ALPHA(J))**2-A(J)*COSF(BETA(J)))/(1.-ZETA**2
     1))
      GO TO 531
  530 B(J)=SQRTF((1.-COSF(ALPHA(J))**2-A(J)*COSF(BETA(J)))/(1.-ZETA**2))
  531 CONTINUE
      D(J) = B(J)*ZETA+COSF(ALPHA(J))
      DO 532 I=1,3
      L3(I) = B(J)*L1(I)+D(J)*L2(I)+A(J)*V3(I)
      VJ(I) = BL(J)*L3(I)
      ITEMP = Z(J,I)
      C(J,I) = VJ(I) + C(ITEMP,I)
  532 CONTINUE
  533 CONTINUE
  601 CONTINUE
C     **********************************
C     OUTPUT SECTION
C     PRINT 2007
      IF(IJIM .EQ. 0) GO TO 11
      PRINT 1998
 1998 FORMAT (1X,8HZ MATRIX,//,42H NO AN   (1)    BL    (2)     ALPHA    (3)
     *    ,20HBETA    (4)      EL    ,8X,1HX,11X,1HY,12X,1HZ)
 2007 FORMAT(//,15H OUTPUT DATA....,/)
C1998 FORMAT (//,20X,11HCOORDINATES,//4X,10HNO OF ATOM,3X,6HSYMBOL,10X,
C    11HX,10X,1HY,10X,1HZ,/)
      DO 900 J=1,M
      IND1=AN(J)
  900 PRINT 1999,J,AN(J),Z(J,1),BLB(J),Z(J,2),ALB(J),Z(J,3),BTB(J),
     *Z(J,4),EL(IND1),(C(J,I),I=1,3)
 1999 FORMAT (2I3,I4,F7.4,2(I4,F11.6),I4,6X,A4,4X,3F12.8)
C 900 PRINT 1999    ,J,EL(IND1),(    C(J,I),I=1,3)
C1999 FORMAT(8X,I2,5X,A4,4X,3F12.8)
C     IF(IDENT(10).EQ.PUNCH) 7,11
C    7 PUNCH 9,(AN(I),(C(I,J),J=1,3),I=1,NATOMS)
     9 FORMAT(I4,3(3X,F12.7))
    11 CONTINUE
       DO 10I=1,NATOMS
       DO 10J=1,NATOMS
    10 R(I,J) = SQRT((C(I,1)-C(J,1))**2+(C(I,2)- C(J,2))**2+(C(I,3)-C(J,
     *))**2)
C     CALL MOUTP (R,NATOMS,NATOMS,40,40,10H DISTANCES)
      DO 1502 J=1,M
      ALPHA(J) = ALPHA(J) * 180./3.141592654
      BETA(J) = BETA(J) * 180./3.141592654
 1502 CONTINUE
      RETURN
      END
      SUBROUTINE RELVEC(R,J,K)
      COMMON/INFO/C
      DIMENSIONC(60,3)
          DIMENSION R(3)
          TYPE REAL C,R
          TYPE INTEGER J,K,I
```

```
          DO 1 I=1,3
    1           R(I)=C(J,1)-C(K,I)
C         R IS THE RELATIVE VECTOR FROM ATOM K TO ATOM J
      RETURN
      END
      SUBROUTINE UNIVEC(L,R)
          DIMENSION L(3),R(3)
      SQRTF(X)=SQRT(X)
          TYPE REAL L,R
          TYPE INTEGER I
          DO 2 I=1,3
    2           L(I)=R(I)/SQRTF(R(1)**2 + R(2)**2 + R(3)**2)
C     L IS THE UNITVECTOR OF R
      RETURN
      END
      SUBROUTINE VECPRD(VP,X,Y)
          DIMENSION VP(3),X(3),Y(3)
          TYPE REAL VP,X,Y
          VP(1)=X(2)*Y(3)-X(3)*Y(2)
          VP(2)=X(3)*Y(1)-X(1)*Y(3)
          VP(3)=X(1)*Y(2)-X(2)*Y(1)
C     VP IS THE VECTOR PRODUCT OF X CROSSED Y
      RETURN
      END
      SUBROUTINE MOUTP (A,M,N,MDIM,NDIM,NAME)
C     OUTPUT OF M X N MATRIX DIMENSIONED TO MDIM X NDIM
      DIMENSION A(MDIM,NDIM)
      XMINOF(I,J)=MINO(I,J)
      PRINT 1000,NAME
 1000 FORMAT(//,A10)
      KITE = 0
   20 LOW = KITE+1
      KITE = KITE+14
      KITE = XMINOF(KITE,N)
      PRINT 19,(I,I=LOW,KITE)
   19 FORMAT( //     ,4X,14(6X,I2),/)
      DO 32 I=1,M
   32 PRINT 18,I,(A(I,J),J=LOW,KITE)
   18 FORMAT(I4,2X,14F8.4)
      IF(N-KITE) 40,40,20
   40 RETURN
      END
           SUBROUTINE TAUFIX(BL,ALPHA,BETA,JJ,KK,LL,MM,T,R,Z,C)
C     THIS ROUTINE CALCULTAES  TAU(J,K,L,M) AND IS USED BY UNZMAT TO
C     GEAR RINGS.
      INTEGER Z
      DIMENSION A(3,3)
      DIMENSION C(60,3)
      DIMENSION BL(40),ALPHA(40),BETA(40),T(40,40,40),R(60,60)
      DIMENSION Z(60,4)
C     AT THIS POINT JJ,KK,LL,MM ARE SEQUENTIALLY BONDED ATOMS WHERE JJ
C     IS GREATER THAN MM
```

```
      CC=0.0
      DO 1240 I = 1,3
 1240 CC = CC+(C(KK,I)-C(JJ,I))*(C(LL,I)-C(KK,I))
      CC = CC/(R(JJ,KK)*R(KK,LL))
      DO 1230 I = 1,3
 1230 A(1,I)=(C(LL,I)-C(KK,I))/R(KK,LL)
      DO 1250 I = 1,3
      YYYY = (1.0 - CC*CC)
      IF (YYYY .LT. 0.0) GO TO 1205
       GO TO 1206
 1205 PRINT 1202
 1202 FORMAT(///,36HSORT HAS NEGATIVE ARGUMENT IN TAUFIX,///)
 1206 CONTINUE
 1250 A(2,I)=(-(C(KK,I)-C(JJ,I))/R(JJ,KK)+CC*(C(LL,I)-C(KK,I))/R(KK,LL))
     */ SQRT( ABS(1.0 -CC*CC)        )
      A(3,1)=A(1,2)*A(2,3)-A(1,3)*A(2,2)
      A(3,2)=A(2,1)*A(1,3)-A(1,1)*A(2,3)
      A(3,3)=A(1,1)*A(2,2)-A(2,1)*A(1,2)
      ZO=0.0
      YO=0.0
      DO 1260 I=1,3
      ZO=ZO+A(3,I)*(C(MM,I)-C(KK,I))
 1260 YO=YO+A(2,I)*(C(MM,I)-C(KK,I))
      CT = YO
      ST = ZO
      TAU=( 180./3.141592654)          * ATAN2(ST,CT)
      Z(JJ,1) = KK
      BL(JJ) = R(JJ,KK)
      Z(JJ,2) = LL
      ALPHA(JJ) = T(JJ,KK,LL)
      Z(JJ,3) = MM
      BETA(JJ) = TAU
      RETURN
      END
) NOT FOUND IN NM DIRECTORY.  STOWED WITH TTR.
E WAS 00010000
```

Appendix B:

SZMAT accepts as input a description of a geometrical system of atoms in terms of bond lengths and angles, and four atom torsions, (model builder input to ZMAT of M. Gordon). It also accepts parameters for the systematic incrementing of up to two bond lengths, bond angles or four atom torsions. Having read the above input, SZMAT calculates an interatomic distance array for each of the configurations designated by the input. If any interatomic distance in any of the configurations goes below the arbitrarily set value of 3.0Å, the atoms which did this are recorded in an array, KNOWL. Having the knowledge of which interatomic distances are sterically significant, SZMAT recalculates these distances and stores them on a peripheral disk. After all the distances are written on the disk, they are systematically examined to determine if they change as a function of conformation. If they do not, they cannot account for changes in conformational energy, and SZMAT makes note of this in an array LCIM. SZMAT then generates a summary steric grid (which for all interatomic distances which change as a function of conformation), writes for a conformation the following words based on the lowest interatomic distance:

BAD	under .7 Å
FAIL	between .7 Å and 1.5 Å
CLOS	between 1.5 Å and 2.0 Å

The symbol .... is printed if all changing interatomic distances are above 2.0 Å. The appearance of the steric grid is constructed for ease in visual scanning, and this relatively fast geometrical procedure can yield interesting information regarding steric intramolecular interactions.

```
./ JOB.LIST=ALL
./ NEW1=100
      BLOCK DATA
        IMPLICIT REAL*8(A-H,O-Z)
      COMMON/LIT/IBLANK,ITMAT,IBL,IALPHA,IBETA,ICLEAR,III,II2
C      TEST INSERTION
C     COMMON/ARRAYS/ABC(19200)
C     COMMON/TAPE/RWTAPE,TPOSTN,ADDRSS(40)
C     COMMON/AUXINT/A(17),B(17)
C     COMMON/PERTBL/EL(18)
C     DIMENSION EL(18)
C     COMMON/ORB/ORB(9)
C     COMMON/1/XYZ(2000)
C     COMMON/INFO1/CZ(35),U(80),ULIM(35),LLIM(35),NELECS,OCCA,OCCB
C     COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF
C     COMMON/ENGY/IC,BQE(3),RQE(3)
C     COMMON/SIMRUN/ID,I1,I2,II,III,BL(80),ANG1(80),ANG2(80),IE,DELTA,IS
C    A,ISS,PMIN
C      DATA EL(1),EL(2),EL(3),EL(4),EL(5),EL(6),EL(7),EL(8),EL(9) /'H',
C    *'HE','LI','BE','B','C','N','O','F'/
C     COMMON/NTMAT/LTMAT,NVAR,LID
C          INTEGER  OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF
C          INTEGER OFF
C          INTEGER ORB,EL,AN,CHARGE
C     COMMON/ZETA/EMU(18)
C     COMMON/GUESS/IGES,IGUESS
C     DIMENSION EGRID(1600)
C    14H DYZ,4HDX-Y,4H DXY)
C     DATA(INDO=4HINDO)
C     DATA(OPEN=6HOPEN  )
C     DATA(CLOSED=6HCLOSED)
C     DATA IZMAT/'ZMAT'/
C     DATA (IZMAT = 4HZMAT)
C     DATA(OFF = 3HOFF)
C     DATA(IGUESS = 5HGUESS)
C     DATA(IOUT = 4H OUT)
      COMMON/IPR/IOUT,LOUTT
      DATA IOUT/' OUT'/
      DATA III/'I1'/
      DATA II2/'I2'/
      DATA IALPHA/'ALPH'/
      DATA IBETA/'BETA'/
      DATA IBLANK/'    '/
      DATA ICLEAR/'    '/
      DATA IBL/'BL  '/
      DATA ITMAT/'TMAT'/
C     DATA(IBETA=5HBETA )
C     DATA(IBLANK=8H        )
C     DATA(ICLEAR=5H     )
C     DATA(IBL=5HBL   )
C     DATA(III=2HI1)
C     DATA ((LCAL(I),I=1,6)=4H    ,4H    ,4H    ,4H    ,4H    ,4H    )
```

```
C      DATA(II2=2HI2)
C      DATA (IALPHA=5HALPHA)
C      DATA(ITMAT=4HTMAT)
       END
       IMPLICIT REAL*8(A-H,O-Z)
C      PROGRAM SZMAT
C     *(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT,PUNCH,TAPE10,TAPE11)
       INTEGER*2 LCIM,KNOW1,KNOW2
       DIMENSION LCAL(6)
       COMMON/LIT/IBLANK,ITMAT,IBL,IALPHA,IBETA,ICLEAR,III,II2
       COMMON/IPR/IOUT,LOUTT
       COMMON/LAB/I1STOR,I2STOR,TOP
       COMMON/STR/JS1,JSS1,JS2,JSS2
       COMMON/KNOW/KNOW1(600),KNOW2(600)
       COMMON/CIM/JKJL,JKJLMN,LCIM
       COMMON/COUNT/NOOO
C      INPUT IS READ IN THE FOLLOWING ORDER
C      (1) OPTION CARD WITH THE FOLLOWING INFORMATION
C        (A) OPTION (WAVEFUNCTION OPTION) IN COLUMNS 1 - 4.  THE KEY
C            WORDS ARE          INDO                    CNDO
C        (B) OPNCLO (OPEN OR CLOSED SHELL) IN COLUMNS 5 - 10.  THE KEY
C            WORDS ARE          OPEN                  CLOSED
C        (C) INPUT (TO READ IN THE MOLECULE IN TERMS OF BONDLENGTHS, BON
C            ANGLES, AND DIHEDRAL ANGLES, IN COLUMNS 11 - 14. THE KEY
C            WORD IS            ZMAT
C        (D) IONOFF (TO SUPPRESS MOST PRINTED OUTPUT) IN COLUMNS 15 - 17.
C            ANGLE(S), OR DIHEDRAL ANGLE(S) SPECIFIED IN LVAR1,IS1, AND
C            ISS1 IS (OR ARE) TO BE VARIED BY THE AMOUNT DELTA1. I1 IS
C            SPECIFIED IN I3 FORMAT IN COLUMNS 27 - 29.
C        (H) LVAR1 (WHICH SPECIFIES WHAT IS TO BE VARIED) IN COLUMNS
C            30 - 34.  THE KEY WORDS ARE
C                               ALPHA                BETA                BL
C        (I - J) IS1 AND ISS1 (THE SUBSCRIPT OF LVAR1) IN COLUMNS
C            35 - 38 AND 39 - 42 RESPECTIVELY (EACH) IN I4 FORMAT.  EACH
C            MAY BE ANY POSITIVE INTEGER FROM 1 TO THE NUMBER OF ATOMS IN
C            THE MOLECULE.  IF ONLY ONE IS BEING VARIED, LEAVE ISS1 BLANK
C        (K) DELTA1 (THE AMOUNT BY WHICH LVAR1(IS1) AND/OR LVAR1(ISS1) IS
C            OR ARE BEING VARIED) IN COLUMNS 43 - 53 (IN F11.6 FORMAT)
C        (L - P) G - K ARE REPEATED TO PERMIT A SECOND VARIABLE, LVAR2,
C            SUBSCRIPTED BY IS2 AND ISS2 TO BE VARIED BY DELTA2 SO THAT
C            A GRID SEARCH CAN BE CONDUCTED I2 TIMES.
C            I2 (IN I3 FORMAT) IS IN COLUMNS 54 - 56.
C            LVAR2 IS IN COLUMNS 57 - 61.
C            IS2 AND ISS2 ARE IN COLUMNS 62 - 65 AND 66 - 69
C          OF THE RUN.
C      (2) AN IDENTIFICATION CARD WHICH IS PRINTED AT THE BEGINNING
C            DELTA2 IS IN COLUMNS 70 - 80 (IN F11.6 FORMAT).
C            RESPECTIVELY (EACH IN I4 FORMAT).
C      (3) NATOMS, CHARGE, MULTIPLICITY        FORMAT (3I2)
C      (4) ATOMIC NUMBER, X COORDINATE, Y COORDINATE, Z COORDINATE ON
C          ONE CARD.  FORMAT (I4,3(3X,F12.7))
C          DECIMAL POINTS IN COLUMNS 12, 27, AND 42
```

```
      DATA IBCD/'IBCD'/
      DATA IOK/'....'/
      DATA IFAIL/'FAIL'/
      DATA IBAD/' BAD'/
       DATA ICLOS/'CLOS'/
        INTEGER AN, CHARGE
      DIMENSION JGRD(36,36)
      DIMENSION C(60,3),AN(60)
      DIMENSION LCIM(60,60)
      COMMON/INFO/C       ,NATOMS,CHARGE,MULTIP,AN     ,          N
      DIMENSION EEEEE(18,18), DOST(1000)
      DIMENSION TOP(36), SIDE(36)
      DIMENSION BOE(3), ROE(3),                    BL(60),ANG1(60),ANG2(60)
      COMMON/NTMAT/LTMAT,NVAR,LID
C     COMMON/LIT/IBLANK,ITMAT,IBL,IALPHA,IBETA,ICLEAR,II1,II2
      COMMON/SIMRUN/BL,ANG1,ANG2,ID,I1,I2,II,III,IE,DELTA,IS
     A,ISS,KMIN
      COMMON/ENGY/   BOE,ROE       ,IC
      SQRTF(X) = DSQRT(X)
  996 CONTINUE
      NOOO=0
      KKK = 0
      DO 9031 I = 1,60
      DO 9031 J = 1,60
 9031 LCIM(I,J)= 0
      JKJLMN = 0
      JKJL = 1
      DO 4404 I=1,600
      KNOW1(I) = 0
      KNOW2(I) = 0
 4404 CONTINUE
      PRINT 9123
 9123 FORMAT (1H1)
      NSCR = 10
      NDISK = 11
C     DEFINE FILE 11(10,2400,U,IDUMP),10(1,400,U,JDUMP)
      REWIND NDISK
       REWIND NSCR
      IC=0
      JD = 1
      JDD = 2
      READ 4444, LFIN
 4444 FORMAT (I4)
      IF(LFIN .EQ. 1)  GO TO 998
      READ 40,                                        II,LVAR1,IS1,ISS1,
     XDELTA1,I2,LVAR2,IS2,ISS2,DELTA2
      I1STOR = I1
      I2STOR = I2
C     IF(EOF(5)) 998,997
  997 CONTINUE
      JS1 = IS1
      JSS1 = ISS1
```

```
      JS2 = IS2
      JSS2 = ISS2
      I1 = I1STOR
      I2 = I2STOR
      LID = III
      ID=1
      JD=I1
      NVAR=LVAR1
      IS=IS1
      ISS=ISS1
      DELTA=DELTA1
      IF(IABS(I1).EQ.0) GO TO 999
  992 CONTINUE
      DO 990 JD=1,I1
      LID = III
      ID=JD
      GO TO 999
  991 CONTINUE
      DO 993 JDD=2,I2
       LID = II2
      ID=JDD
  999 CONTINUE
      IC=IC + 1
      IF=IC
      IF (IC.LT.3) GO TO  3470
 3471 CONTINUE
C     IF (LTMAT.NE.ITMAT) GO TO3476
C3477 CALL TMAT
 3476 IC=1
 3470 CONTINUE
      IF(JKJLMN .NE.2) GO TO 51
      IF((LOUTT .NE. IOUT) .AND. (IE .EQ. 1)) GO TO 8015
      IF(LOUTT .NE. IOUT)  GO TO 51
 8015 CONTINUE
      IF(NQQQ.NE.0) GO TO 51
      PRINT 41,                                          I1,LVAR1,IS1,ISS1,
     ZDELTA1,I2,LVAR2,IS2,ISS2,DELTA2,ID,DELTA
C     CALL TIM
C     IF (INPUT.NE.IZMAT) GO TO 52
   51 CALL ZMAT
      GO TO 53
   52 CONTINUE
C     READ 20,(AN(I),I=1,10)
C     PRINT 30,(AN(I),I=1,10)
C     READ 50,NATOMS,CHARGE,MULTIP,IUNITS
C  50 FORMAT(4I4)
C     PRINT 60,NATOMS,CHARGE,MULTIP,IUNITS
C  60 FORMAT(/5X,I4,18H ATOMS   CHARGE  =,I4,18H   MULTIPLICITY  =,I4,12
C    1H   IUNITS = ,I4,/)
C     DO 10 I = 1,NATOMS
C     READ 70,AN(I), C(I,1),C(I,2),C(I,3)
C     PRINT 70,AN(I), C(I,1),C(I,2),C(I,3)
```

```
C       CONVERSION OF COORDINATES FROM ANGSTROMS TO ATOMIC UNITS
C       IF(IUNITS.EQ.1) GO TO 10
C   11  CONTINUE
C       DO 9 J=1,3
C     9 C(I,J) = C(I,J)/.529167
C    10 CONTINUE
    53  CONTINUE
C       IF (OPTION.NE.INDO) GO TO 6
      1 DO 5 I=1,NATOMS
        IF (AN(I).LE.9) GO TO 4
      2 PRINT 3
      3 FORMAT(47H THIS PROGRAM DOES NOT DO INDO CALCULATIONS FOR,
       1 51H MOLECULES CONTAINING ELEMENTS HIGHER THAN FLUORINE)
        STOP
      4 CONTINUE
      5 CONTINUE
      6 CONTINUE
        IF(JKJLMN .NE. 2)  GO TO 96
        KGRD = IBCD
        DO 99 I=2,NATOMS
        IM1 = I-1
        DO 99 J=1,IM1
        IF(LCIM(I,J) .NE. 0) GO TO 99
        R=SQRTF((C(I,1)-C(J,1))**2+(C(I,2)-C(J,2))**2+(C(I,3)-C(J,3))**2)
       1 *0.529167
        IF(KGRD.EQ.IFAIL) GO TO 7173
        IF(R .LE. 1.5) KGRD = IBAD
        IF((R.GT.1.5).AND.(R.LT.2.).AND.(KGRD.NE.IBAD)) KGRD = ICLOS
 7173   CONTINUE
        IF(JKJLMN .NE. 2) GO TO 9009
        IF((LOUTT .NE. IOUT) .AND. (IE .EQ. 1)) GO TO 2093
        IF(LOUTT .NE. IOUT)    GO TO 9009
 2093   CONTINUE
        IF((R .LE. 1.5 ) .AND. (R .GT. .7)) PRINT 7093, I,J,R
 9009   CONTINUE
 7093   FORMAT ( 45H STERIC INTERACTION IS LIKELY SINCE          .  3H R(,
       *I4,I4,4H) = ,F10.5)
        IF(R .GE. .7)  GO TO 4445
          KGPD = IFAIL
        IF(JKJLMN .NE.2) GO TO 99
        IF((LOUTT .NE. IOUT) .AND. (IE .EQ. 1)) GO TO 1387
        IF(LOUTT .NE. IOUT)  GO TO 99
 1387   CONTINUE
        IF(NOOO .NE. 0) GO TO 99
   98   PRINT 97,I,J,R
   97   FORMAT(   45H MO CALCULATION OF THIS CONFORMATION BYPASSED,3H R(,
       *I4 ,I4,4H) = ,F10.5)
C       GO TO 96
 4445   CONTINUE
   99   CONTINUE
        IF(KGRD .EQ. IBCD)  GO TO 1920
        GO TO 1921
```

```
 1920 KGRD = IOK
 1921 CONTINUE
      WRITE (NSCR) KGRD
C     CALL OVERLAY(6LCNINDO,1,0)
C     CALL OVERLAY(6LCNINDO,2,0)
C     KKK = KKK + 1
C     FGRID(KKK) = BOE(1)
C     CALL TIM
   96 CONTINUE
 7679 FORMAT (3X,3HI2=,I4,3X,4HLID=,A4,3H11=,I4 )
      IF ((I2.GT.0).AND.(LID.EQ.III)) GO TO 994
 5432 FORMAT (3X,1HW)
      GO TO 993
  994 CONTINUE
 5433 FORMAT (3X,1HX)
      NVAR=LVAR2
      IS=IS2
      ISS=ISS2
      DELTA=DELTA2
      GO TO 991
  993 CONTINUE
       LID = III
      NVAR=LVAR1
      IS=IS1
      ISS=ISS1
      DELTA=DELTA1
      ID=JD
  990 CONTINUE
C     IF ((IC.EQ.3).AND.(LTMAT.EQ.ITMAT)) 3570,3571
C3570 CALL TMAT
 3571 CONTINUE
      IF(JKJLMN .NE. 2)  GO TO 49
      IF(I1 .EQ. 0) GO TO 915
      GO TO 916
  915 I1 = 1
  916  CONTINUE
      IF(I2 .EQ. 0) GO TO 917
      GO TO 918
  917 I2 = 1
  918 CONTINUE
      DO 394 I = 1,I2
  394 TOP(I) = (I-1)*DELTA2
      DO 395 I = 1,I1
  395  SIDE(I) = (I-1)*DELTA1
      REWIND NSCR
      DO 331 = 1,I1
        DO 33J=1,I2
   33 READ(NSCR) JGRD(I,J)
      IF(JKJLMN .NE. 2) GO TO 49
      PRINT 74
   74 FORMAT (//,2X,38HGRID OF STERICALLY EXCLUDED CONFORMERS,//)
      PRINT 974
```

```
  974 FORMAT (1X,5HKEY= ,3X,22HFAIL - R LESS THAN 0.7,/,9X,43HBAD  - R L
     *ESS THAN 1.5 AND GREATER THAN 0.7,/,9X,43HCLOS - R LESS THAN 2.0 A
     *ND GREATER THAN 1.5,//)
      KITE = 0
   22 LOW = KITE + 1
      KITE = KITE + 14
      KITE = AMINO(KITE,I2)
      PRINT 19, (TOP(I),I=LOW,KITE)
      PRINT 9124
 9124 FORMAT(//)
   19 FORMAT (//,5X,14(2X,F6.2),/)
      DO 32 I = 1,I1
   32 PRINT 18,  SIDE(I),(JGRD(I,J),J=LOW,KITE)
   18 FORMAT (1X,F6.2,14(2X,A4,2X))
      IF(I2-KITE) 49,49,22
   49 CONTINUE
      IF(JKJLMN .NE. 1) GO TO 1281
C     PRINT 9225, JKJL
 9225 FORMAT(I10)
      CALL KFIX
      KOW = I1*I2
      DO 4231  MHO = 1,JKJL
      JHO = 1
      KHO = 1
      REWIND NDISK
      DO 4228 KEEP = 1,KOW
      DO 3225 IHO = 1,JKJL
      READ (NDISK) DOST(IHO)
 3225 CONTINUE
      EEEEE(JHO,KHO) = DOST(MHO)
      IF(KHO .EQ. I2)  GO TO 3227
      GO TO 3228
 3227 CONTINUE
      JHO = JHO + 1
      KHO = 1
      GO TO 4227
 3228 CONTINUE
      KHO = KHO + 1
 4227 CONTINUE
 4228 CONTINUE
      CALL MOUTPT(EEEEE,I1,I2,18,18,LCAL)
      CALL ROUT(EEEEE,MHO)
 4231 CONTINUE
 1281 CONTINUE
      JKJLMN = JKJLMN + 1
      IF((JKJLMN .EQ. 1) .OR. (JKJLMN .EQ. 2)) GO TO 9293
      GO TO 996
 9293 CONTINUE
      NQQQ=0
      IC=0
      JD=1
      JDD = 2
```

```
      GO TO 997
  998 CONTINUE
C     PUNCH 888, (EGRID(I),I=1,KKK)
  888 FORMAT (8F10.5)
      PRINT 80
   20 FORMAT(10A8)
   30 FORMAT( //,10A8)
   40 FORMAT (2(I3,A4,1X,2I4,F11.6))
   41 FORMAT (/////                                    ///,6H I1 = ,I4,9H LV
     CAR1 = ,A5,6H IS1 =,1X,I4,5X,8H ISS1 = ,I4,5X,10H DELTA1 = ,F11.6,/
     D/,6H I2 = ,I4,9H LVAR2 = ,A5,7H IS2 = ,I4,5X,8H ISS2 = ,I4,5X,10H
     EDELTA2 = ,F11.6,///,14H CURRENT ID = ,I4,10X,17H CURRENT DELTA = ,
     FF12.6)
   70 FORMAT(I4,3(3X,F12.7))
   80 FORMAT(16H END OF THIS RUN)
 4443 CONTINUE
      END
      SUBROUTINE ZMAT
      IMPLICIT REAL*8(A-H,O-Z)
      INTEGER*2 LCIM,KNOW1,KNOW2
C     THIS PROGRAM ACCEPTS A DEFINITION OF A MOLECULE IN TERMS OF
C     ATOMIC NUMBERS, BOND LENGTHS, BOND ANGLES AND DIHEDRAL ANGLES
C     AND CALCULATES THE CARTESIAN COORDINATES IN ANGSTROMS
C     ADAPTED FROM MARK GORDONS MBLD SYSTEM BY D L BEVERIDGE
C     CODED IN CDC SCOPE 3.1 LEVEL FORTRAN FOR THE CIMS CDC 6600
      DIMENSION Z(60,4),ALPHA(60),BETA(60)
      COMMON/TAU/ALPHA,BETA
      DATA JCIM/'JCIM'/
      DIMENSION V1(3),V2(3),V3(3),VJ(3),VP(3),L1(3),L2(3),L3(3),L4(3),
     * A(60),B(60),D(60)
      DIMENSION BOE(3), ROE(3),AN(60),C(60,3),BL(60),ANG1(60),ANG2(60)
      COMMON/COUNT/NOOO
      COMMON/INFO/C,M      ,CHARGE,MULTIP,AN,  N
      COMMON/IPR/IOUT,LOUTT
      COMMON/CIM/JKJL,JKJLMN,LCIM
      DIMENSION LCIM(60,60)
      COMMON/STR/JS1,JSS1,JS2,JSS2
      COMMON/KNOW/KNOW1(600),KNOW2(600)
           INTEGER AN,CHARGE,Z,PUNCH
      EQUIVALENCE(M,NATOMS)
       REAL*8 L1,L2,L3,L4
      DIMENSION BLB(60),ALB(60),BTB(60)
      DIMENSION R(60,60)
      DIMENSION IDENT(20)
      DIMENSION EL(17), ORB(4,7)
           INTEGER ORB
      COMMON/ENGY/   BOE,ROE       ,IC
      COMMON/SIMRUN/BL,ANG1,ANG2,ID,I1,I2,II,III,IF,DELTA,IS
     A,ISS,RMIN
      COMMON/LIT/IBLANK,ITMAT,IBL,IALPHA,IBETA,ICLEAR,II1,II2
      COMMON/NTMAT/LTMAT,NVAR,LID
           INTEGER FL
```

```
      INTEGER  OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF
      INTEGER OFF
C     COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF
C     DATA (OFF = 3HOFF)
      DIMENSION NAL(6)
      DATA NAL(1),NAL(2),NAL(3),NAL(4),NAL(5),NAL(6)/'INTE','RATO',
     *'MIC ','DIST','ANCE','S   '/
      DATA EL(1),EL(2),EL(3),EL(4),EL(5),EL(6),EL(7),EL(8),EL(9) /'H',
     *'HE','LI','BE','B','C','N','O','F'/
C     DATA((NAL(I),I=1,6)=4HINTE,4HRATO,4HMIC ,4HDIST,4HANCE,4HS    )
C     DATA ((EL(I),I=1,9)=4H   H,4H  HE,4H  LI,4H  BE,4H   B,4H   C,
C    *4H   N,4H   O,4H   F)
C     **********************************
C     FORTRAN II TO IV CONVERSION
      ABSF(X) =DABS(X)
      ATANF(X) =DATAN(X)
      COSF(X) = DCOS(X)
      SINF(X) =DSIN(X)
      SIGNF(X,Y) =DSIGN(X,Y)
      SQRTF(X) =DSQRT(X)
C     INPUT AND OUTPUT OF INPUT
C     PUNCH = 8HPUNCH
      NBFN = 0
      IF (IE.EQ.1) GO TO 999
      GO TO 2919
  999 CONTINUE
      IF(JKJLMN .NE. 0)  GO TO 2
      READ 1000,(IDENT(I),I=1,20)
      GO TO 1324
C     IF(EOF(5)) 999,2
    2 CONTINUE
      DO 1325 IKL=1,NATOMS
      ALPHA(IKL) = ALPHA(IKL)*180./3.141592654
      BETA(IKL) = BETA(IKL)*180./3.141592654
 1325 CONTINUE
 1324 CONTINUE
 2919 CONTINUE
      IF(NOOO .NE. 0)  GO TO 4
      IF((JKJLMN .EQ. 0) .AND. (IE .EQ. 1)) GO TO 7091
      IF(JKJLMN .NE. 2) GO TO 4
      IF((LOUTT . NE. IOUT) .AND. (IE .EQ. 1)) GO TO 7091
      IF(LOUTT .NE. IOUT)  GO TO 4
 7091 CONTINUE
      PRINT 1111, (IDENT(I),I=1,20)
 1000 FORMAT(20A4)
 1111 FORMAT (//,20A4)
C     IF(IDENT(10).EQ.PUNCH)3,4
C   3 PRINT 2008
 2008 FORMAT(/,16H PUNCH OPTION ON,/)
C     PUNCH 1000,(IDENT(I),I=1,10)
    4 CONTINUE
      IF (IE.EQ.1)  GO TO 101
```

```
      GO TO 102
  101 CONTINUE
      IF(JKJLMN .NE. 0)  GO TO 102
      READ 1001, NATOMS,CHARGE,MULTIP
 1001 FORMAT(3I2)
  102 CONTINUE
      IF(JKJLMN .NE. 2)  GO TO 6
      IF((LOUTT .NE. IOUT) .AND. (IE .EQ. 1)) GO TO 6091
      IF(LOUTT .NE. IOUT)  GO TO 6
 6091 CONTINUE
      IF(NOOO .NE. 0) GO TO 6
      PRINT1002, NATOMS,CHARGE,MULTIP
 1002 FORMAT(//,10H NATOMS = ,I4,2X,10H CHARGE = ,I4,2X,10H MULTIP = ,I4
     *,I4,//)
C     IF(IDENT(10).EQ.5HPUNCH) 5,6
C    5 PUNCH 8,NATOMS,CHARGE,MULTIP
    8 FORMAT(3I4)
    6 CONTINUE
      IF((JKJLMN .EQ. 0) .AND. (IE .EQ. 1)) READ 4919, LDENT   ,LOUTT
 4919 FORMAT (2A4)
C     **********************************
C     CALCULATION OF COORDINATES
      IF (IE.GT.1) GO TO 104
  103 CONTINUE
      DO 6969 I=1,M
      IF(JKJLMN .NE. 0) GO TO 1193
      READ 1003,AN(I),Z(I,1),BL(I),Z(I,2),ALPHA(I),Z(I,3),BETA(I),Z(I,
     *4),(LCIM(I,IRO),IRO=1,10)
 1193 CONTINUE
 1003 FORMAT (I3,I4,F7.4,I4,F11.6,I4,F11.6,I4,1X,10I3)
C     ANG1 AND ANG2 STORE THE ANGLES ALPHA AND BETA IN DEGREE FORM
C     ANG1 AND ANG2 STORE THE ANGLES ALPHA AND BETA IN DEGREE FORM
      ANG1(I)=ALPHA(I)
      ANG2(I)=BETA(I)
      IF(AN(I) .LE. 10) GO TO 361
      NBFN = NBFN + 9
      GO TO 371
  361 IF(AN(I) .LT. 3) GO TO 362
      NBFN = NBFN + 4
      GO TO 371
  362 NBFN = NBFN + 1
  371 CONTINUE
 6969 CONTINUE
      IF((JKJLMN .EQ. 0) .AND. (IE .EQ. 1) .AND. (LDENT .EQ. JCIM))
     * GO TO 4920
      GO TO 4921
 4920 DO 4148 IT = 1,NATOMS
 4148 READ 4149, (LCIM(IT,JT),JT=1,NATOMS)
 4149 FORMAT (80I1)
 4921 CONTINUE
      IF(IE .EQ. 1) GO TO 388
      GO TO 389
```

```
  388 CONTINUE
      IF(JKJLMN .NE. 0) GO TO 399
      AALPHA = ALPHA(JS1)
      ABETA = BETA(JS1)
      ABL = BL(JS1)
      BALPHA = ALPHA(JS2)
      BBETA = BETA(JS2)
      BBL = BL(JS2)
      GO TO 389
  399 CONTINUE
      ALPHA(JS1) = AALPHA
      BETA(JS1) = ABETA
      BL(JS1) = ABL
      ALPHA(JS2) = BALPHA
      BETA(JS2) = BBETA
      BL(JS2) = BBL
      ANG2(JS1) =  BETA(JS1)
      ANG2(JS2) =  BETA(JS2)
      ANG1(JS1) = ALPHA(JS1)
      ANG1(JS2) = ALPHA(JS2)
  389 CONTINUE
      IF(JKJLMN .NE. 2)  GO TO 104
      IF((LOUTT .NE. IOUT) .AND. (IE .EQ. 1)) GO TO 5091
      IF(LOUTT .NE. IOUT)  GO TO 6
 5091 CONTINUE
      PRINT 374, NBFN,NATOMS
  374 FORMAT (/,3X,I4, 29H BASIS FUNCTIONS REQUIRED FOR,I3,6H ATOMS,/)
  104 CONTINUE
      DO 232 I = 1,M
      BTB(I) = BETA(I)
      ALB(I) = ALPHA(I)
      BLB(I) = BL(I)
  232 CONTINUE
      IF ((NVAR.EQ.ICLEAR).OR.(ID.EQ.1)) GO TO 7000
 7001 CONTINUE
      IF (NVAR.EQ.IBL) GO TO 7002
      GO TO 7003
 7002 BL(IS)=BL(IS) + DELTA
      IF (ISS.EQ.0) GO TO 7000
      BL(ISS)=BL(ISS) + DELTA
      GO TO 7000
 7003 CONTINUE
      IF (NVAR.EQ.IALPHA) GO TO 7004
      GO TO 7005
 7004 ANG1(IS)=ANG1(IS) + DELTA
      IF (ISS.EQ.0) GO TO 7000
      ANG1(ISS)=ANG1(ISS) + DELTA
      GO TO 7000
 7005 CONTINUE
      IF (NVAR.EQ.IBETA) GO TO 7006
      GO TO 7007
 7006 ANG2(IS)=ANG2(IS) + DELTA
```

```
      IF (ISS.EQ.0) GO TO 7000                                          C
      ANG2(ISS)=ANG2(ISS) + DELTA                                       C
      GO TO 7000                                                        C
 7007 CONTINUE                                                          C
      PRINT 7008                                                        C
 7008 FORMAT (/////, 55H ERROR ON FIRST CARD IN COLUMNS 30 - 34 OR 57 - C
     C61,///,37H PROGRAM TERMINATED DUE TO THIS ERROR,///,60H CHECK PERM
     DISSIBLE STATEMENTS FOR THESE COLUMNS AND RESUBMIT,///)            C
      GO TO 1984                                                        C
 7000 CONTINUE                                                          C
      IF (IE.EQ.1) GO TO 106                                            C
  105 CONTINUE                                                          C
      DO 109 I = 1,M                                                    C
      ALB(I) = ANG1(I)                                                  C
      BTB(I) = ANG2(I)                                                  C
      BLB(I) = BL(I)                                                    C
      ALPHA (I) = ANG1(I)                                               C
      BETA(I) = ANG2(I)                                                 C
  109 CONTINUE                                                          C
  106 CONTINUE                                                          C
      IF ((NVAR.NE.ICLEAR).AND.(ID.EQ.I2).AND.(LID.EQ.II2)) GO TO 7201  C
      GO TO 7200                                                        C
 7201 DID=I2 - 1                                                        C
      IF (NVAR.EQ.IBL) GO TO 7202                                       C
      GO TO 7203                                                        C
 7202 BL(IS)=BL(IS) - (DID * DELTA)                                     C
      IF (ISS.EQ.0) GO TO 7200                                          C
      BL(ISS)=BL(ISS) - (DID * DELTA)                                   C
      GO TO 7200                                                        C
 7203 CONTINUE                                                          C
      IF (NVAR.EQ.IALPHA) GO TO 7204                                    C
      GO TO 7205                                                        C
 7204 ANG1(IS)=ANG1(IS) - (DID * DELTA)                                 C
      IF (ISS.EQ.0) GO TO 7200                                          C
      ANG1(ISS)=ANG1(ISS) - (DID * DELTA)                               C
      GO TO 7200                                                        C
 7205 ANG2(IS)=ANG2(IS) - (DID * DELTA)                                 C
      IF (ISS.EQ.0) GO TO 7200                                          C
      ANG2(ISS)=ANG2(ISS) - (DID * DELTA)                               C
 7200 CONTINUE                                                          C
      IF((LTMAT.EQ.ITMAT).AND.(NVAR.NE.ICLEAR).AND.(IC.EQ.2)) GO TO 7401C
      GO TO 7400                                                        C
 7401 CONTINUE                                                          C
      IF (NVAR.EQ.IBL) GO TO 7402                                       C
      GO TO 7403                                                        C
 7402 RQE(2)=BL(IS)                                                     C
      GO TO 7406                                                        C
 7403 CONTINUE                                                          C
      IF (NVAR.EQ.IALPHA) GO TO 7404                                    C
      GO TO 7405                                                        C
 7404 RQE(2)=ANG1(IS)                                                   C
      GO TO 7406                                                        C
```

```
 7405 ROE(2)=ANG2(IS)
 7406 ROE(1)= ROE(2) - DELTA
      ROE(3)= ROE(2) + DELTA
 7400 CONTINUE
      DO 502 J=1,M
  502 ALPHA(J) = ALPHA(J)*3.141592654/180.
      DO 503 J=1,M
  503 BETA(J) = BETA(J)*3.141592654/180.
      DO 504 J= 1,3
  504 C(1,J)=0.0
      IF(M .EQ. 1) GO TO 601
      C(2,1)=0.0
      C(2,2)=0.0
      C(2,3)=BL(2)
      IF(M .EQ. 2) GO TO 601
      C(3,1)=BL(3)*SINF(ALPHA(3))
      C(3,2)=0.0
C     **********************************
C     THE FOLLOWING IS AN ADDITION TO COORD FINDER PROGRAM TO BE USED
C     IF THE MOLECULE UNDER CONSIDERATION HAS ONLY ONE HEAVY ATOM OR FOR
C     A MOLECULE SUCH AS NEOPENTANE IN WHICH THE CENTRAL ATOM HAS NO
C     HYDROGENS BONDED TO IT
      IF(Z(3,1).EQ.1) GO TO 505
      GO TO 506
  505 C(3,3) = BL(3)*COSF(ALPHA(3))
      GO TO 507
  506 C(3,3) = C(2,3)-BL(3)*COSF(ALPHA(3))
  507 I=3
      IF(ABSF(C(3,1)).LT..00001) GO TO 550
      GO TO 510
  550 DO 509 I = 4,1000
      IF(I.LE.M.AND.ABSF(C(I-1,1)).LT..00001) GO TO 508
      GO TO 510
  508 C(I,1) = BL(I)*SINF(ALPHA(I))
      C(I,2) = 0.0
      ITEMP = Z(I,1)
      JTEMP = Z(I,2)
     0C(I,3) = C(ITEMP,3)-BL(I)*COSF(ALPHA(I))*SIGNF(1.,C(ITEMP,3)-C(JTE
     1MP,3))
  509 CONTINUE
  510 CONTINUE
      IF(I.EQ.3) GO TO 511
      GO TO 512
  511 K=4
      GO TO 513
  512 K=I
  513 CONTINUE
      IF(K.GT.M) GO TO 601
  600 CONTINUE
      DO 533 J = K,M
      IF(Z(J,4).EQ.0) GO TO 514
      GO TO 517
```

```
C      ************************************
C      THIS PART IS USED IF THE ATOM IS BEING DEFINED BY A DIHEDRAL ANGLE
  514 CALL RELVEC(V1,Z(J,2),Z(J,3))
      CALL UNIVEC(L1,V1)
C      V1 IS A VECTOR FROM ATOM Z(J,3) TO ATOM Z(J,2)
C      L1 IS A UNIT VECTOR OF V1.  BL(Z(J,2)) IS BONDLENGTH OF ATOM Z(J,2
      CALL RELVEC(V2,Z(J,1),Z(J,2))
      CALL UNIVEC(L2,V2)
C      V2 IS THE VECTOR FROM ATOM Z(J,2) TO ATOM Z(J,1)
C      L2 IS THE UNIT VECTOR OF V2.   BL(Z(J,1)) IS BONDLENGTH  DEFINING
C      ATOM Z(J,1)
      CALL VECPRD(VP,L1,L2)
      XXX = 0.0
      XXX =                (1.-(L1(1)*L2(1)+L1(2)*L2(2)+L1(3)*L2(3))**2)
      IF(XXX .LT. 0.0) GO TO 1888
      GO TO 1889
 1888 PRINT 1913, XXX
 1913 FORMAT (3X,32HARGUMENT OF DSQRT IS LESS THAN 0.6H XXX =,F40.20)
 1889 CONTINUE
      DO 515 I = 1,3
  515 L3(I) = VP(I)/SQRTF(DABS(1.-(L1(1)*L2(1)+L1(2)*L2(2)+L1(3)*L2(3))
     ***2))
 1985 FORMAT(3X,1HA)
C      L3 IS THE UNIT VECTOR OF VP.ALPHA(Z(J,1))IS THE ANGLE DEFINING
C      ATOM Z(J,1)
      CALL VECPRD(L4,L3,L2)
C      L4,L3,L2 ARE A NEW SET OF MUTUALLY ORTHOGONAL AXES. WE WILL NOW
C      OBTAIN COORD OF ATOM J IN TERMS OF THESE AXES RELATIVE TO ATOM Z(J
      DO 516 I=1,3
     OVJ(I) = BL(J)*(-L2(I)*COSF(ALPHA(J))+L4(I)*SINF(ALPHA(J))*COSF(BET
     1A(J))+L3(I)*SINF(ALPHA(J))*SINF(BETA(J)))
C      VJ IS THE VECTOR FROM ATOM Z(J,1) TO ATOM J
      ITEMP = Z(J,1)
      C(J,I) = VJ(I) + C(ITEMP,I)
  516 CONTINUE
      GO TO 533
  517 IF(Z(J,4).EQ.1.OR.Z(J,4).EQ.-1) GO TO 549
      GO TO 528
C      ************************************
C      THIS PART IS USED IF ATOM IS DEFINED BY TWO BONDANGLES
  549 CALL RELVEC(V1,Z(J,1),Z(J,3))
      CALL UNIVEC(L1,V1)
      CALL RELVEC(V2,Z(J,2),Z(J,1))
      CALL UNIVEC(L2,V2)
      ZETA = -(L1(1)*L2(1)+L1(2)*L2(2)+L1(3)*L2(3))
      A(J) = (-COSF(BETA(J))+ZETA*COSF(ALPHA(J)))/(1.-ZETA**2)
      B(J) = (COSF(ALPHA(J))-ZETA*COSF(BETA(J)))/(1.-ZETA**2)
      PI = 3.141592654
      IF(ZETA.LT.0) GO TO 518
      GO TO 519
  518 TEMP = PI
      GO TO 520
```

```
  519 TEMP = 0.0
  520 CONTINUE
      IF(ZETA.EQ.0) GO TO 521
      GO TO 522
  521 GAMMA = PI/2.
      GO TO 523
  522 GAMMA = ATANF(SQRTF(1.-ZETA**2)/ZETA) +TEMP
 1986 FORMAT (3X,1HB)
  523 CONTINUE
      IF (ABSF(GAMMA+ALPHA(J)+BETA(J)-2.*PI).LT..CCCCCCC1) GO TO 524
      GO TO 525
  524 D(J) = 0.0
      GO TO 526
  525 CONTINUE
      VXY = (1.-ZETA**2)
      IF(ABSF(SQRTF(ABSF(VXY))) .GT. .0001)   GO TO 1209
      PRINT 1210,VXY,J
 1210 FORMAT (///,3X,4HVXY=,3X,F10.5,4HJ = ,I4,///)
 1209 CONTINUE
      XYZ = (1.+A(J)*COSF(BETA(J))-B(J)*COSF(ALPHA(J)))
      IF(XYZ .GE.0.) GO TO 1204
      PRINT 1206
 1206 FORMAT (///,3X,4HBUGS,///)
 1204 CONTINUE
      IF(VXY .GE.0.) GO TO 1207
      PRINT 1208
 1208 FORMAT(///,3X,5HBUGS2,///)
 1207 CONTINUE
      D(J)=Z(J,4)*(SQRTF(    ABSF(1.+A(J)*COSF(BETA(J))-B(J)*COSF(ALPHA(
     *J))))    )/SQRTF(ABSF(1.-ZETA**2))
 1987 FORMAT (3X,1HC)
  526 CONTINUE
      CALL VECPRD(V3,L1,L2)
      DO 527 I = 1,3
      L3(I) = A(J)*L1(I)+B(J)*L2(I)+D(J)*V3(I)
      VJ(I) = BL(J)*L3(I)
      ITEMP = Z(J,1)
      C(J,I) = VJ(I)+C(ITEMP,I)
  527 CONTINUE
      GO TO 533
C     ************************************
C     THIS PART IS USED IF ATOM IS DEFINED BY ONE BONDANGLE AND BY THE
C     ANGLE WHICH BOND Z(J,1)-J MAKES WITH THE PLANE OF Z(J,1),Z(J,2)
C     AND Z(J,3)
  528 CALL RELVEC(V1,Z(J,1),Z(J,3))
      CALL UNIVEC(L1,V1)
      CALL RELVEC(V2,Z(J,2),Z(J,1))
      CALL UNIVEC(L2,V2)
      ZETA = -(L1(1)*L2(1)+L1(2)*L2(2)+L1(3)*L2(3))
      CALL VECPRD(V3,L1,L2)
C     BETA(J) HERE REFERS TO 90-ANGLE WHICH BOND Z(J,1)-J MAKES WITH THE
C     AFOREMENTIONED PLANE
```

```
      A(J) = COSF(BETA(J))/(1.-ZETA**2)                                 C
      IF(Z(J,4).EQ.2) GO TO 530                                         C
  529 B(J)= -SQRTF((1.-COSF(ALPHA(J))**2-A(J)*COSF(BETA(J)))/(1.-ZETA**2C
     1))                                                                C
 1988 FORMAT (3X,1HD)                                                   C
      GO TO 531                                                         C
  530 B(J)=SQRTF((1.-COSF(ALPHA(J))**2-A(J)*COSF(BETA(J)))/(1.-ZETA**2))C
 1989 FORMAT (3X,1HE)                                                   C
  531 CONTINUE                                                          C
      D(J) = B(J)*ZETA+COSF(ALPHA(J))                                   C
      DO 532 I=1,3                                                      C
      L3(I) = B(J)*L1(I)+D(J)*L2(I)+A(J)*V3(I)                          C
      VJ(I) = BL(J)*L3(I)                                               C
      ITEMP = Z(J,1)                                                    C
      C(J,I) = VJ(I) + C(ITEMP,I)                                       C
  532 CONTINUE                                                          C
  533 CONTINUE                                                          C
  601 CONTINUE                                                          C
C     ***********************************                             C
C     OUTPUT SECTION                                                    C
      IF(JKJLMN .NE. 2) GO TO 1994                                      C
      IF((LOUTT .NE. IOUT) .AND. (IE .EQ. 1))  GO TO 4093               C
      IF(LOUTT .NE. IOUT)  GO TO 1994                                   C
 4093 CONTINUE                                                          C
      IF(NOOO .NE. 0) GO TO 1994                                        C
      PRINT 1998                                                        C
 1998 FORMAT (1X,8HZ MATRIX,//,42H NO AN  (1)   BL    (2)    ALPHA   (3) C
     *    ,20HBETA   (4)     EL    ,8X,1HX,11X,1HY,12X,1HZ)             C
      DO 900 J = 1,M                                                    C
      IND1 = AN(J)                                                      C
  900 PRINT 1999,J,AN(J),Z(J,1),BLB(J),Z(J,2),ALB(J),Z(J,3),BTB(J),     C
     *Z(J,4),EL(IND1),(C(J,I),I=1,3)                                    C
 1999 FORMAT (2I3,I4,F7.4,2(I4,F11.6),I4,6X,A4,4X,3F12.8)               C
C     IF(IDENT(10).EQ.PUNCH) 7,11                                       C
C    7 PUNCH 9,(AN(I),(C(I,J),J=1,3),I=1,NATOMS)                        C
     9 FORMAT(I4,3(3X,F12.7))                                           C
    11 CONTINUE                                                         C
 1994 CONTINUE                                                          C
      DO 10I=1,NATOMS                                                   C
      DO 10J=1,NATOMS                                                   C
   10 R(I,J)=SQRTF((C(I,1)-C(J,1))**2+(C(I,2)- C(J,2))**2+(C(I,3)-C(J,3 C
     *))**2)                                                            C
      IF((JKJLMN .EQ.0) .AND. (IE . EQ. 1)) PRINT 8081                  C
 8081 FORMAT (///,3X,68H STERICALLY AND/OR ELECTRONICALLY SIGNIFICANT INC
     *TERATOMIC DISTANCES.,//,3X,5HORDER,6X,1HI,8X,1HJ,6X,6HR(I,J),6X,  C
     * 31H CONFORMATION FIRST ENCOUNTERED,//)                           C
      IF(JKJLMN .EQ. 0)  CALL RSEARC (R)                                C
      IF((JKJLMN .EQ. 1) .AND. (IE .EQ. 1)) GO TO 8188                  C
      GO TO 8199                                                        C
 8188 CONTINUE                                                          C
      IF((JKJLMN .EQ. 1) .AND. (IE .EQ. 1))   JKJL = JKJL - 1           C
      DO 8210 IX = 1,JKJL                                               C
```

```
C       PRINT 8211,KNOW1(IX),KNOW2(IX)
 8210 CONTINUE
 8211 FORMAT(2I8)
 8199 CONTINUE
      IF(JKJLMN .EQ. 1)  CALL DOUT(R)
 2222 FORMAT(3X,2HNN)
   13 CONTINUE
      IF(JKJLMN .NE. 2) GO TO 1995
      IF((LOUTT .NE. IOUT) .AND. (IE . EQ. 1))  GO TO 3093
      IF(LOUTT .NE. IOUT)  GO TO 1995
 3093 CONTINUE
      IF(NQQQ . NE. 0) GO TO 1995
      CALL MOUTPT(R,NATOMS,NATOMS,60,60,NAL)
 1995 CONTINUE
   12 CONTINUE
C       CONVERT COORDINATES TO ATOMIC UNITS
      DO 90 I=1,NATOMS
      DO 90 J=1,3
   90 C(I,J) = C(I,J)/0.529167
 1984 CONTINUE
      RETURN
      END
      SUBROUTINE RELVEC(R,J,K)
      IMPLICIT REAL*8(A-H,O-Z)
      INTEGER CHARGE, AN
      COMMON/INFO/C(60,3),M      ,CHARGE,MULTIP,AN(60),N
          DIMENSION R(3)
               INTEGER J,K,I
          DO 1 I=1,3
     1         R(I)=C(J,I)-C(K,I)
C         R IS THE RELATIVE VECTOR FROM ATOM K TO ATOM J
      RETURN
      END
      SUBROUTINE UNIVEC(L,R)
      IMPLICIT REAL*8(A-H,O-Z)
          DIMENSION L(3),R(3)
      REAL*8 L
      SQRTF(X) = DSQRT(X)
               INTEGER I
          DO 2 I=1,3
     2         L(I)=R(I)/SQRTF(R(1)**2 + R(2)**2 + R(3)**2)
C       L IS THE UNITVECTOR OF R
      RETURN
      END
      SUBROUTINE VECPRD(VP,X,Y)
      IMPLICIT REAL*8(A-H,O-Z)
          DIMENSION VP(3),X(3),Y(3)
          VP(1)=X(2)*Y(3)-X(3)*Y(2)
          VP(2)=X(3)*Y(1)-X(1)*Y(3)
          VP(3)=X(1)*Y(2)-X(2)*Y(1)
C       VP IS THE VECTOR PRODUCT OF X CROSSED Y
      RETURN
```

```
      END
      SUBROUTINE MOUTPT(A,M,N,MDIM,NDIM,NAL)
      IMPLICIT REAL*8(A-H,O-Z)
C     OUTPUT OF M X N MATRIX DIMENSIONED TO MDIM X NDIM
      DIMENSION NAL(6)
      DIMENSION A(MDIM,NDIM)
      PRINT 1000,NAL
 1000 FORMAT (//,2X, 6A4)
      KITE = 0
   20 LOW = KITE+1
      KITE = KITE+14
      KITE = AMINO(KITE,N)
      PRINT 19,(I,I=LOW,KITE)
   19 FORMAT( //     ,4X,14(6X,I2),/)
      DO 32 I=1,M
   32 PRINT 18,I,(A(I,J),J=LOW,KITE)
   18 FORMAT(I4,2X,14F8.4)
      IF(N-KITE) 40,40,20
   40 RETURN
      END
      SUBROUTINE RSEARC (R)
      IMPLICIT REAL*8(A-H,O-Z)
      INTEGER*2 LCIM,KNOW1,KNOW2
      DIMENSION R(60,60)
      COMMON/TAU/ALPHA(60),BETA(60)
      COMMON/KNOW/KNOW1(600),KNOW2(600)
      COMMON/STR/JS1,JSS1,JS2,JSS2
      COMMON/CIM/JKJL,JKJLMN,LCIM
      COMMON/INFO/C(60,3),NATOMS,CHARGE,MULTIP,AN(60),N
      INTEGER AN, CHARGE
      DIMENSION LCIM(60,60)
      DO 9 I=1,NATOMS
      ALPHA(I) = ALPHA(I)*180./3.141592654
      BETA(I) = BETA(I)*180./3.141592654
    9 CONTINUE
      DO 1 I=2,NATOMS
      IM1=I-1
      DO 1 J=1,IM1
      IF(LCIM(I,J) .NE. 0) GO TO 1
      IF(R(I,J) .LT. 3.00)   GO TO 2
      GO TO 3
    2 CONTINUE
      DO 5 II=1,JKJL
      IF((I .EQ. KNOW1(II)) .AND. (J .EQ. KNOW2(II))) GO TO 1
      IF((J .EQ. KNOW1(II)) .AND. (I .EQ. KNOW2(II))) GO TO 1
    5 CONTINUE
      PRINT 7, JKJL,I,J,R(I,J),BETA(JS1),BETA(JS2)
    7 FORMAT (3I8,3(3X,F10.5))
      KNOW1(JKJL) = I
      KNOW2(JKJL) = J
      JKJL = JKJL + 1
    3  CONTINUE
```

```
    1 CONTINUE
      DO 10 I=1,NATOMS
      ALPHA(I) = ALPHA(I)*3.141592654/180.
      BETA(I) = BETA(I)*3.141592654/180.
 10   CONTINUE
      RETURN
      END
      SUBROUTINE OUT(AGR )
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION AGR(18,18)
      COMMON/LAB/LROW,LCOL,A
      DIMENSION A(36)
      KITE = 0
   20 LOW = KITE + 1
      KITE = KITE + 12
      KITE = AMINO(KITE,LCOL)
      PRINT 19, (A(I),I=LOW,KITE)
   19 FORMAT (//,6X,12F10.1,///)
      PRINT 212
  212 FORMAT (//)
      DO 32 I =1,LROW
   32 PRINT 18,A(I),(AGR (I,J),J=LOW,KITE)
   18 FORMAT(2X,F5.1,2X,12F10.4)
      IF(LCOL-KITE) 40,40,20
   40 RETURN
      END
      SUBROUTINE DOUT(R)
      IMPLICIT REAL*8(A-H,O-Z)
      INTEGER*2 LCIM,KNOW1,KNOW2
      COMMON/TAU/ALPHA(60),BETA(60)
      COMMON/STR/JS1,JSS1,JS2,JSS2
      COMMON/CIM/JKJL,JKJLMN,LCIM
      COMMON/INFO/C(60,3),NATOMS,CHARGE,MULTIP,AN(60),N
      DIMENSION LCIM(60,60)
      INTEGER CHARGE,AN
      COMMON/KNOW/KNOW1(600),KNOW2(600)
      DIMENSION R(60,60)
      DO 20 I=1,NATOMS
      ALPHA(I) = ALPHA(I) * 180./3.141592654
      BETA(I) = BETA(I)*180./3.141592654
   20 CONTINUE
      NDISK = 11
      DO 1 I=1,NATOMS
      IM1=I-1
      DO 1 J=1,IM1
      DO 1 K=1,JKJL
      LL = KNOW1(K)
      MM = KNOW2(K)
C     IF((I .EQ. LL) .AND. (J .EQ. MM)) WRITE(NDISK) R(I,J)
C     IF((I .EQ. MM) .AND. (J .EQ. LL)) WRITE(NDISK) R(I,J)
      IF((I .EQ. LL) .AND. (J .EQ. MM)) GO TO 5
      GO TO 6
```

```
    5  CONTINUE
       WRITE(NDISK) R(I,J)
       PRINT 8,R(I,J),I,J,BETA(JS1),BETA(JS2)
    8  FORMAT (3X,11HLL MM NDISK,3X,F10.5,2I3,2F10.5)
    6  CONTINUE
       IF((I .EQ. MM) .AND. (J .EQ.LL)) GO TO 9
       GO TO 10
    9  CONTINUE
       WRITE(NDISK) R(I,J)
       PRINT11,R(I,J),I,J,BETA(JS1),BETA(JS2)
   11  FORMAT (3X,11HMM LL NDISK,3X, F10.5,2I3,2F10.5)
   10  CONTINUE
    1  CONTINUE
       DO 30 I=1,NATOMS
       ALPHA(I) = ALPHA(I)*3.141592654/180.
       BETA(I) = BETA(I)*3.141592654/180.
   30  CONTINUE
       RETURN
       END
       SUBROUTINE KFIX
       IMPLICIT REAL*8(A-H,O-Z)
        INTEGER*2 LCIM,KNOW1,KNOW2
       ABSF(X) = DABS(X)
       COMMON/KNOW/KNOW1(600),KNOW2(600)
       COMMON/CIM/JKJL,JKJLMN,LCIM
       DIMENSION LCIM(60,60)
       KKLL = JKJL - 1
 2394  CONTINUE
       MOOSE = 0
       DO 2333 IH = 1,KKLL
       IF(KNOW1(IH) .EQ. KNOW1(IH+1)) GO TO 2395
       GO TO 2396
 2395  CONTINUE
       IF(KNOW2(IH) .GT. KNOW2(IH+1)) GO TO 2397
       GO TO 2398
 2397  CONTINUE
       MOOSE = MOOSE + 1
       IHOLD2 = KNOW2(IH)
       JHOLD2 = KNOW2(IH+1)
       KNOW2(IH) = JHOLD2
       KNOW2(IH+1) = IHOLD2
 2398  CONTINUE
 2396  CONTINUE
       IF(KNOW1(IH) .GT. KNOW1(IH+1))  GO TO 2387
       GO TO 2398
 2387  CONTINUE
       MOOSE = MOOSE + 1
       IHOLD1 = KNOW1(IH)
       JHOLD1 = KNOW1(IH+1)
       IHOLD2 = KNOW2(IH)
       JHOLD2 = KNOW2(IH+1)
       KNOW1(IH) = JHOLD1
```

```
      KNOW2(IH) = JHOLD2                                                C
      KNOW1(IH+1) = IHOLD1                                              C
      KNOW2(IH+1) = IHOLD2                                              C
 3398 CONTINUE                                                          C
 2333 CONTINUE                                                          C
      IF(MOOSE .NE. 0)  GO TO 2394                                      C
       RETURN                                                           C
      END                                                               C
      SUBROUTINE ROUT (EEEEE,MHO)                                       C
      IMPLICIT REAL*8(A-H,O-Z)                                          C
       INTEGER*2 LCIM,KNOW1,KNOW2                                       C
      DIMENSION EEEEE(18,18)                                            C
      COMMON/KNOW/KNOW1(600),KNOW2(600)                                 C
      COMMON/CIM/JKJL,JKJLMN,LCIM                                       C
      COMMON/LAB/I1,I2,A                                                C
      DIMENSION A(36)                                                   C
      ABSF(X) = DABS(X)                                                 C
      DIMENSION LCIM(60,60)                                             C
      DO 1178 IQ = 1,I1                                                 C
      DO 1178 JQ = 1,I2                                                 C
      DO 1178 IR = 1,I1                                                 C
      DO 1178 JR = 1,I2                                                 C
      IF(ABSF   (EEEEE(IQ,JQ) - EEEEE(IR,JR)) .GT. .00001)  GO TO 1179  C
 1178 CONTINUE                                                          C
      EDD = EEEEE(1,1)                                                  C
      PRINT 1174, KNOW1(MHO), KNOW2(MHO)     ,EDD                       C
 1174 FORMAT (3X,2HR(,I3,3H , ,I3,5H ) = ,F10.5,3X,48H,  AND IS CONSTANTC
     * FOR THE ROTATIONS CONSIDERED.)                                   C
      IHEL =  KNOW1(MHO          )                                      C
      IHEV = KNOW2(MHO)                                                 C
      LCIM(IHEV,IHEL) = 1                                               C
      LCIM(IHEL,IHEV) = 1                                               C
      GO TO 1864                                                        C
 1179 CONTINUE                                                          C
      PRINT 1171,KNOW1(MHO), KNOW2(MHO)                                 C
 1171 FORMAT (///,11H GRID OF R(,I3,3H , ,I3, 3H ) ,31H AS A FUNCTION OFC
     * CONFORMATION.,///)                                               C
      CALL OUT(EEEEE)                                                   C
 1864 CONTINUE                                                          C
      RETURN                                                            C
      END                                                               C
NOT FOUND IN NM DIRECTORY.  STOWED WITH TTR.
WAS-00000000
```

Appendix C:

The following routine is a modification of the INDO routine of Pople, Beveridge and Dobosh which allows for a significant reduction in required computer central memory. Central to this modification is the EIGN subroutine of P. Dobosh which diagonalizes an array and outputs the resulting array within the same area of computer memory. Other changes in the routine were in SUBROUTINES INTGRL, HUCKCL, SCFCL and CPRINT. The central change in the SCFCL circuitry was the storage of the core hamiltonian on peripheral disk, and the reading of this disk file upon the entry to SCFCL. Thus one area of central memory at different times stores the overlap intgral matrix (INTGRL), core hamiltonian (HUCKCL), Fock matrix (SCFCL) and density matrix (SCFCL). These changes were designed by Professor Beveridge, and coded by R.J.R.

```
=RJR.LIST=ALL
=JOB,MSG=1,CC
      IMPLICIT REAL*8(A-H,O-Z)                                          CC
C     TO CHANGE THE SIZE OF THE ROUTINE AS A FUNCTION OF IAT AND IBF    CC
C     CHANGE ALL DIMENSION STATEMENTS IN THE MAIN PROGRAM, AND ALSO     CC
C      TEST INSERTION                                                   CC
C      TEST INSERTION                                                   CC
C     IN EIGN AND EIGOUT                                                CC
C     ALSO RESET THE VALUES FOR IAT AND IBF IN THE MAIN PROGRAM.        CC
       DIMENSION PDIAG( 90),Q( 90),CZ(50),U( 90),ULIM(50),LLIM(50),     CC
     *XXX( 90),ASDA( 90, 90),GAMMA(50,50),Z(50,4),BL(50),ALPHA(50),     CC
     *BETA(50),NUM( 90),C(50,3),AN(50)                                  CC
       INTEGER*4 U,ULIM                                                 CC
       INTEGER*4 CZ                                                     CC
      COMMON/ENGY/BOF(3),BOE(3),FTOT,VOL,DP,IC                          CC
       COMMON/INFO/N,NATOMS,CHARGE,MULTIP                               CC
      COMMON/SIMRUN/DELTA,RMIN,ID,I1,I2,II,III,IE,IS,ISS                CC
      INTEGER*4 Z                                                       CC
      COMMON/JRCOV/IRCOV,IJC,IDISK,IRCCC,JDISK                          CC
C     IRCOV=TEST FOR CONVERGENCE                                        CC
C     IJC=PLACE IN GRID                                                 CC
C     IDISK=SEQUENTIAL DISK ASSIGNMENT                                  CC
C     IRCCC = TEST FOR INITIALLY CONVERGED CALCULATION                  CC
      COMMON/NTMAT/LTMAT,NVAR,LID                                       CC
       INTEGER OFF                                                      CC
      COMMON/PERTBL/FL( 9)                                              CC
      COMMON/ORB/ORB(9)                                                 CC
      COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF   CC
      COMMON/LIT/IBLANK,ITMAT,IBL,IALPHA,IBETA,ICLEAR,III,II2           CC
           INTEGER  OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF   CC
           INTEGER ORB,FL,AN,CHARGE                                     CC
       DIMENSION EGRD(18,18),VGRD(18,18),DGRD(18,18)                    CC
       COMMON/GRID/LROW,LCOL                                            CC
      DATA IZMAT/'ZMAT'/                                                CC
       DATA IBLK/'    '/                                                CC
       DATA OFF/'OFF'/                                                  CC
C     INPUT IS READ IN THE FOLLOWING ORDER                              CC
C     (1) OPTION CARD WITH THE FOLLOWING INFORMATION                    CC
C       (A) OPTION (WAVEFUNCTION OPTION) IN COLUMNS 1 - 4.  THE KEY     CC
C           WORDS ARE          INDO                 CNDO              CC
C       (B) OPNCLO (OPEN OR CLOSED SHELL) IN COLUMNS 5 - 10.  THE KEY   CC
C           WORDS ARE          OPEN                 CLOSED            CC
C           WORDS ARE          OPEN                 CLSD              CC
C       (C) INPUT (TO READ IN THE MOLECULE IN TERMS OF BONDLENGTHS, BONDCC
C           ANGLES, AND DIHEDRAL ANGLES. IN COLUMNS 11 - 14. THE KEY     CC
C           WORD IS            ZMAT                                      CC
C       (D) IONOFF (TO SUPPRESS MOST PRINTED OUTPUT) IN COLUMNS 15 - 17.CC
C           THE KEY WORD IS                 OFF                          CC
C       (E) IGES IN COLUMNS 18 - 22.  THE KEY WORD IS       GUESS        CC
C       (F) LTMAT (TO SET THE ENERGIES OF THREE CONSECUTIVE OUTPUT SETS CC
C           TO  A PARABOLA IN ORDER TO FIND THE MINIMUM ENERGY           CC
C           CONFIGURATION) IN COLUMNS 23 - 26.  THE KEY WORD IS          CC
```

```
C
C
C
C
C
C                                TMAT                                   OC
C        (G) I1 (THE NUMBER OF TIMES THAT THE BONDLENGTH(S), BOND       OC
C            ANGLE(S), OR DIHEDRAL ANGLE(S) SPECIFIED IN LVAR1,IS1, AND OC
C            ISS1 IS (OR ARE) TO BE VARIED BY THE AMOUNT DELTA1. I1 IS  OC
C            SPECIFIED IN I3 FORMAT IN COLUMNS 27 - 29.                 OC
C        (H) LVAR1 (WHICH SPECIFIES WHAT IS TO BE VARIED) IN COLUMNS    OC
C            30 - 34.  THE KEY WORDS ARE                                OC
C                              ALPHA              BETA              BL    OC
C        (I - J) IS1 AND ISS1 (THE SUBSCRIPT OF LVAR1) IN COLUMNS       OC
C            35 - 38 AND 39 - 42 RESPECTIVELY (EACH) IN I4 FORMAT.  EACH OC
C            MAY BE ANY POSITIVE INTEGER FROM 1 TO THE NUMBER OF ATOMS INOC
C            THE MOLECULE.  IF ONLY ONE IS BEING VARIED, LEAVE ISS1 BLANKOC
 3128 CONTINUE                                                          OC
C        (K) DELTA1 (THE AMOUNT BY WHICH LVAR1(IS1) AND/OR LVAR1(USS1) ISOC
C            OR ARE BEING VARIED) IN COLUMNS 43 - 53 (IN F11.6 FORMAT)  OC
C            SUBSCRIPTED BY IS2 AND ISS2 TO BE VARIED BY DELTA2 SO THAT OC
C        (L - P) G - K ARE REPEATED TO PERMIT A SECOND VARIABLE, LVAR2, OC
C            A GRID SEARCH CAN BE CONDUCTED I2 TIMES.                   OC
C            I2 (IN I3 FORMAT) IS IN COLUMNS 54 - 56.                   OC
C            LVAR2 IS IN COLUMNS 57 - 61.                               OC
C            IS2 AND ISS2 ARE IN COLUMNS 62 - 65 AND 66 - 69            OC
C            RESPECTIVELY (EACH IN I4 FORMAT).                          OC
C            DELTA2 IS IN COLUMNS 70 - 80 (IN F11.6 FORMAT).            OC
C      (2) AN IDENTIFICATION CARD WHICH IS PRINTED AT THE BEGINNING     OC
C          OF THE RUN.                                                  OC
C      (3) NATOMS, CHARGE, MULTIPLICITY      FORMAT (3I2)               OC
C      (4) ATOMIC NUMBER, X COORDINATE, Y COORDINATE, Z COORDINATE ON   OC
C          ONE CARD.  FORMAT (I4,3(3X,F12.7))                           OC
C          DECIMAL POINTS IN COLUMNS 12, 27, AND 42                     OC
  996 CONTINUE                                                          OC
      IAT=50                                                            OC
      IBF=90                                                            OC
      IJC = 0                                                           OC
       K1 = 1                                                           OC
        K2 = 1                                                          OC
       JDISK = 10                                                       OC
       IDISK = 11                                                       OC
      IRCCC=0                                                           OC
      IC=0                                                              OC
      JD=1                                                              OC
      JDD=2                                                             OC
      READ 40,  OPTION,OPNCLO,INPUT,IONOFF,IGES,LTMAT,I1,LVAR1,IS1,ISS1,OC
     XDELTA1,I2,LVAR2,IS2,ISS2,DELTA2                                   OC
      IF(OPTION.EQ.IBLK) GO TO 998                                      OC
  997 CONTINUE                                                          OC
      LID = II1                                                         OC
      ID=1                                                              OC
      JD=I1                                                             OC
      NVAR=LVAR1                                                        OC
      IS=IS1                                                            OC
      ISS=ISS1                                                          OC
      DELTA=DELTA1                                                      OC
```

```
C
C
C
      IF(IABS(I1) .EQ. 0) GO TO 999                                     00
  992 CONTINUE                                                          00
C LOOP OVER VARIABLE ZMAT ELEMENTS                                      00
      DO 990 JD=1,I1                                                    00
      LID = III                                                         00
      ID=JD                                                             00
      GO TO 999                                                         00
  991 CONTINUE                                                          00
      DO 993 JDD=2,I2                                                   00
      LID = II2                                                         00
      ID=JDD                                                            00
  999 CONTINUE                                                          00
      IC=IC + 1                                                         00
      IF=IC                                                             00
      IF (IC .GT. 3) GO TO 3471                                         00
      GO TO 3470                                                        00
 3471 CONTINUE                                                          00
      IF (LTMAT .EQ. ITMAT) GO TO 3477                                  00
      GO TO 3476                                                        00
 3477 CONTINUE                                                          00
      CALL TMAT                                                         00
 3476 IC=1                                                              00
 3470 CONTINUE                                                          00
      PRINT 41, OPTION,OPNCLO,INPUT,IONOFF,IGES,LTMAT,I1,LVAR1,IS1,ISS1,00
     *DELTA1,I2,LVAR2,IS2,ISS2,DELTA2                                   00
      CALL TIM                                                          00
      IF (INPUT .EQ. IZMAT) GO TO 51                                    00
      GO TO 52                                                          00
   51 CONTINUE                                                          00
      CALL ZMAT(ALPHA,BETA,C,BL,ALPHA,BETA,GAMMA,AN,IAT,IBF,Z)          00
      CALL MINERT(C,AN,IBF,IAT)                                         00
      DO 90 I=1,NATOMS                                                  00
      DO 90 J=1,3                                                       00
   90 C(I,J)=C(I,J)/0.529167D0                                          00
 6178 FORMAT(2I10)                                                      00
      IJC = IJC + 1                                                     00
      GO TO 53                                                          00
   52 CONTINUE                                                          00
      READ 20,(AN(I),I=1,10)                                            00
      PRINT 30,(AN(I),I=1,10)                                           00
      READ 50,NATOMS,CHARGE,MULTIP,IUNITS                               00
   50 FORMAT(4I4)                                                       00
      PRINT 60,NATOMS,CHARGE,MULTIP,IUNITS                              00
   60 FORMAT(/5X,I4,18H ATOMS   CHARGE  =,I4,18H   MULTIPLICITY  =,I4,12C0
     1H   IUNITS = ,I4,/)                                               00
      DO 10 I = 1,NATOMS                                                00
      READ 70,AN(I), C(I,1),C(I,2),C(I,3)                               00
      PRINT 70,AN(I), C(I,1),C(I,2),C(I,3)                              00
C     CONVERSION OF COORDINATES FROM ANGSTROMS TO ATOMIC UNITS           00
      IF(IUNITS .EQ. 1)GO TO 10                                         00
      GO TO 11                                                          00
   11 CONTINUE                                                          00
```

```
C
C
      DO 9 J=1,3                                                        OC
    9 C(I,J)=C(I,J)/0.529167D0                                          OC
   10 CONTINUE                                                          OC
   53 CONTINUE                                                          OC
      IF(OPTION .EQ. INDO) GO TO 1                                      OC
       GO TO 6                                                          OC
    1 DO 5 I=1,NATOMS                                                   OC
      IF(AN(I).GT.9) GO TO 2                                            OC
      GO TO 4                                                           OC
    2 PRINT 3                                                           OC
    3 FORMAT(47H THIS PROGRAM DOES NOT DO INDO CALCULATIONS FOR,        OC
     1 51H MOLECULES CONTAINING ELEMENTS HIGHER THAN FLUORINE)          OC
      STOP                                                              OC
    4 CONTINUE                                                          OC
    5 CONTINUE                                                          OC
    6 CONTINUE                                                          OC
C     DEFAULT IF ANY ATOMS ARE TOO CLOSE TOGETHER                       OC
      KKK = KKK+1                                                       OC
      DO 99 I=2,NATOMS                                                  OC
      IM1 = I-1                                                         OC
      DO 99 J=1,IM1                                                     OC
C     CHECK FOR BONDED ATOMS                                            OC
C     ELSE CHECK FOR CLOSEST APPROACH                                   OC
      R=DSQRT((C(I,1)-C(J,1))**2+(C(I,2)-C(J,2))**2+(C(I,3)-C(J,3))**2) OC
     1*0.529167D0                                                       OC
      IF(R.GE.0.5)GO TO 99                                              OC
C     SET DEFAULT VALUES                                                OC
      ETOT=999.99D0                                                     OC
      VOL=0.0D0                                                         OC
      DP=99.99D0                                                        OC
   98 PRINT 97,I,J,R                                                    OC
   97 FORMAT(//,45H MO CALCULATION OF THIS CONFORMATION BYPASSED,3H R(,  OC
     *I4,1H,,I4,4H) = ,F10.5,//)                                        OC
      GO TO 96                                                          OC
   99 CONTINUE                                                          OC
        CALL INTGRL(ASDA,C,GAMMA,CZ,U,ULIM,LLIM,AN,IBF,IAT)             OC
      CALL HUCKCL(PDIAG,Q,GAMMA,GAMMA,ASDA,C,AN,IAT,IBF,CZ,U,ULIM,LLIM,XOO
     *XX,NUM)                                                           OO
       CALL SCFCL(GAMMA,GAMMA,ASDA,C,AN,IAT,IBF,PDIAG,Q,CZ,U,ULIM,LLIM,XOO
     *XX,NUM)                                                           OO
         CALL CPRINT(GAMMA,ASDA,C,AN,IBF,IAT,XXX,CZ,U,ULIM,LLIM,PDIAG,OOO
     *,NUM)                                                             OO
   96 CONTINUE                                                          OO
        IF(I1.EQ.0.AND.I2.EQ.0)  GO TO 1750                             OO
C     TUCK AWAY CURRENT VALUES OF RESULTS                               OO
       EGRD(K1,K2) = ETOT                                               OO
        VGRD(K1,K2) = VOL                                               OO
       DGRD(K1,K2) = DP                                                 OO
        IF(K2 .LT. I2)  GO TO 1748                                      OO
       GO TO 1749                                                       OO
 1748 CONTINUE                                                          OO
       K2 = K2 + 1                                                      OO
```

```
C
C
C
      GO TO 1750                                                        00
 1749 CONTINUE                                                          00
      K2 = 1                                                            00
      K1 = K1 + 1                                                       00
 1750 CONTINUE                                                          00
      CALL TIM                                                          00
      IF ((I2.GT.0).AND.(LID.EQ.II1)) GO TO 994                         00
      GO TO 993                                                         00
  994 CONTINUE                                                          00
      NVAR=LVAR2                                                        00
      IS=IS2                                                            00
      ISS=ISS2                                                          00
      DELTA=DELTA2                                                      00
      GO TO 991                                                         00
  993 CONTINUE                                                          00
      LID = II1                                                         00
      NVAR=LVAR1                                                        00
      IS=IS1                                                            00
      ISS=ISS1                                                          00
      DELTA=DELTA1                                                      00
      ID=JD                                                             00
  990 CONTINUE                                                          00
C     END OF LOOP OVER VARIABLE ZMAT ELEMENTS                           00
      IF(I1.EQ.0.AND.I2.EQ.0) GO TO 996                                 00
C     FILL GRDVERT ARRAYS                                               00
      KKK=0                                                             00
      LROW = I1                                                         00
      LCOL = I2                                                         00
      DELT = DELTA1                                                     00
      CALL GRDVER (EGRD,VGRD,DGRD,DELT)                                 00
      GO TO 9999                                                        00
 3569 CONTINUE                                                          00
      IF ((IC.EQ.3).AND.(LTMAT.EQ.ITMAT)) GO TO 3570                    00
       GO TO 3571                                                       00
 3570 CONTINUE                                                          00
      CALL TMAT                                                         00
 3571 CONTINUE                                                          00
 9999 CONTINUE                                                          00
      GO TO 996                                                         00
  998 CONTINUE                                                          00
      PRINT 80                                                          00
   20 FORMAT(10A8)                                                      00
   30 FORMAT( //,10A8)                                                  00
   40 FORMAT (A4,A6,A4,A3,A5,A4,2(I3,A5,2I4,F11.6))                     00
   41 FORMAT(/,1X,A4,3X,A6,3X,A4,3X,A3,3X,A5,3X,A4,//,6H I1 = ,I4, 9H LVOC
     CAR1 = ,A5,6H IS1 =,1X,I4,5X,8H ISS1 = ,I4,5X,10H DELTA1 = ,F11.6,/OC
     D/,6H I2 = ,I4,9H LVAR2 = ,A5,7H IS2 = ,I4,5X,8H ISS2 = ,I4,5X,10H OC
     *DELTA2 = ,F11.6)                                                  00
   70 FORMAT(I4,3(3X,F12.7))                                            00
   80 FORMAT(16H END OF THIS RUN)                                       00
      END                                                               00
       BLOCK DATA                                                       00
```

```
C
C
C
C
      COMMON/PERTBL/EL(9)                                                   CC
       COMMON/ORB/ORB(9)                                                    CC
      COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF       CC
      COMMON/LIT/IBLANK,ITMAT,IBL,IALPHA,IBETA,ICLEAR,III,II2               CC
           INTEGER  OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF       CC
           INTEGER ORB,EL,AN,CHARGE                                         CC
      DATA EL(1),EL(2),EL(3),EL(4),EL(5),EL(6),EL(7),EL(8),EL(9) /'H',      CC
     *'HE','LI','BE','B','C','N','O','F'/                                   CC
      DATA ORB(1),ORB(2),ORB(3),ORB(4),ORB(5),ORB(6),ORB(7),ORB(8),         CC
     *ORB(9) /'  S',' PX',' PY',' PZ',' DZ2',' DXZ',' DYZ','DX-Y',          CC
     *' DXY'/                                                               CC
      DATA CNDO/'CNDO'/                                                     CC
      DATA INDO/'INDO'/                                                     CC
      DATA OPEN/'OPEN'/                                                     CC
      DATA CLOSED/'CLSD'/                                                   CC
      DATA III/'I1'/                                                        CC
      DATA II2/'I2'/                                                        CC
      DATA ITMAT/'TMAT'/                                                    CC
      DATA IBLANK/'    '/                                                   CC
      DATA ICLEAR/'    '/                                                   CC
      DATA IBL/'BL  '/                                                      CC
      DATA IALPHA/'ALPH'/                                                   CC
      DATA IBETA/'BETA'/                                                    CC
      END                                                                   CC
      SUBROUTINE MOUTPT(A,M,N,MDIM,NDIM,NAL)                                CC
C     OUTPUT OF M X N MATRIX DIMENSIONED TO MDIM X NDIM                     CC
      IMPLICIT REAL*8(A-H,O-Z)                                              CC
      DIMENSION NAL(6)                                                      CC
      DIMENSION A(MDIM,NDIM)                                                CC
      PRINT 1000,NAL                                                        CC
 1000 FORMAT (//,2X, 6A4)                                                   CC
      KITE = 0                                                              CC
   20 LOW = KITE+1                                                          CC
      KITE = KITE+14                                                        CC
      KITE = AMIN0(KITE,N)                                                  CC
      PRINT 19,(I,I=LOW,KITE)                                               CC
   19 FORMAT( //    ,4X,14(6X,I2),/)                                       CC
      DO 32 I=1,M                                                           CC
   32 PRINT 18,I,(A(I,J),J=LOW,KITE)                                        CC
   18 FORMAT(I4,2X,14F8.4)                                                  CC
      IF(N-KITE) 40,40,20                                                   CC
   40 RETURN                                                                CC
      END                                                                   CC
      SUBROUTINE TMAT                                                       CC
      IMPLICIT REAL*8(A-H,O-Z)                                              CC
C     TO SOLVE MATRIX EQ B = T*A FOR T GIVEN A AND B                        CC
      COMMON/ENGY/B(3),R(3),ETOT,VOL,DP,IC                                  CC
      COMMON/SIMRUN/DELTA,RMIN,ID,I1,I2,II,III,IE,IS,ISS                    CC
      COMMON/LIT/IBLANK,ITMAT,IBL,IALPHA,IBETA,ICLEAR,III,II2               CC
      COMMON/NTMAT/LTMAT,NVAR,LID                                           CC
      DIMENSION A(3,3),C(3,3),D(3,3),T(3)                                   CC
C     ***************************************************************** CC
```

```
C
C
C
C
C
C
C     INPUT SECTION                                                     00
      DO 9 J=1,3                                                        00
      A(1,J)=1.0D0                                                      00
      A(2,J)=R(J)                                                       00
    9 A(3,J)=R(J)*R(J)                                                  00
      CALL MOUTPT(A,3,3,3,3,9H MATRIX A)                                00
      CALL MOUTPT(B,1,3,1,3,9H MATRIX B)                                00
C     ******************************************************************0
C     SOLUTION FOR T IS T = B*A-INVERSE                                 00
C     FORM INVERSE OF A                                                 00
C     CALCULATE MATRIX OF COFACTORS OF A IN D                           00
      D(1,1)=A(2,2)*A(3,3)-A(2,3)*A(3,2)                                00
      D(1,2)=-(A(2,1)*A(3,3)-A(2,3)*A(3,1))                             00
      D(1,3)=A(2,1)*A(3,2)-A(2,2)*A(3,1)                                00
      D(2,1)=-(A(1,2)*A(3,3)-A(1,3)*A(3,2))                             C
      D(2,2)=A(1,1)*A(3,3)-A(1,3)*A(3,1)                                0
      D(2,3)=-(A(1,1)*A(3,2)-A(1,2)*A(3,1))                             0
      D(3,1)=A(1,2)*A(2,3)-A(1,3)*A(2,2)                                0
      D(3,2)=-(A(1,1)*A(2,3)-A(1,3)*A(2,1))                             C
      D(3,3)=A(1,1)*A(2,2)-A(1,2)*A(2,1)                                0
C     ******************************************************************C
C     CALCULATE DETERMINANT OF A AND OUTPUT                             C
      DET=A(1,1)*D(1,1)+A(1,2)*D(1,2)+A(1,3)*D(1,3)                     0
      IF (DABS(DET).LT.1.0D-18) GO TO 5                                 C
      GO TO 6                                                           C
    5 PRINT 1002, DET                                                   0
 1002 FORMAT(//,24H MATRIX SINGULAR, DET = ,E15.5,//)                   C
      STOP                                                              0
    6 CONTINUE                                                          0
      PRINT 1000, DET                                                   0
 1000 FORMAT(//,7H DET = ,E15.5,//)                                     C
C     ******************************************************************0
C     FORM ELEMENTS OF INVERSE                                          C
      DO 1 I=1,3                                                        0
      DO 1 J=1,3                                                        0
    1 C(I,J)=D(J,I)/DET                                                 C
      CALL MOUTPT(C,3,3,3,3,8H INVERSE)                                 C
C     ******************************************************************C
C     CHECK INVERSE                                                     0
      DO 2 I=1,3                                                        C
      DO 2 J=1,3                                                        C
      D(I,J)=0.0D0                                                      C
      DO 2 K=1,3                                                        C
    2 D(I,J)=D(I,J)+A(I,K)*C(K,J)                                       C
      CALL MOUTPT(D,3,3,3,3,7H CK INV)                                  C
C     ******************************************************************C
C     FORM TRANSFORMATION MATRIX                                        C
      DO 3 J=1,3                                                        C
      T(J)=0.0D0                                                        C
      DO 3 K=1,3                                                        C
    3 T(J)=T(J)+B(K)*C(K,J)                                             C
      CALL MOUTPT(T,1,3,1,3,10H TRANS MAT)                              C
```

```
C
C
C
C
C
      RMIN=-T(2)/(2.0D0*T(3))                                          000
      PRINT 750, RMIN                                                  000
  750 FORMAT (//,8H RMIN = ,F20.16)                                    000
      RETURN                                                           000
      END                                                              000
      SUBROUTINE TIM                                                   000
      IMPLICIT REAL*8(A-H,O-Z)                                         000
C      CALL S19V1(TIME)                                                000
C       PRINT 1111, TIME                                               000
C1111 FORMAT(1X,A8)                                                    000
      RETURN                                                           000
      END                                                              000
       SUBROUTINE DMAT(PDIAG,XXX,B,C,N,OCCA,IBF,AN,IAT,CZ,U,ULIM,LLIM,NU000
     *M)                                                               000
       IMPLICIT REAL*8(A-H,O-Z)                                        000
        DIMENSION CZ(IAT),U(IBF),ULIM(IAT),LLIM(IAT)                   000
       DIMENSION NUM(IBF)                                              000
       INTEGER*4 CZ                                                    000
      INTEGER *4 U,ULIM                                                000
            DIMENSION C(IAT,3), AN(IAT)                                000
      DIMENSION XXX(IBF)                                               000
      DIMENSION PDIAG(IBF)                                             000
C     THIS ROUTINE ACCEPTS THE COEFFICIENTS OR EIGENVECTORS IN B       000
C     AND GENERATES THE DENSITY MATRIX ALSO IN B                       000
      INTEGER OCCA                                                     000
      DIMENSION B(IBF,IBF)                                             000
      COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF  000
      INTEGER OPTION,OPNCLO,HUCKEL,CNDO,CLOSED,OPEN                    000
       INTEGER OFF                                                     000
       DATA OFF/'OFF'/                                                 000
       IF(IONOFF .EQ. OFF)  GO TO 2222                                 000
       PRINT 1111                                                      000
 1111 FORMAT(13H COEFFICIENTS)                                         000
            CALL SCFOUT(C,AN,B,CZ,U,ULIM,LLIM,NUM,0,1,IBF,IAT)         000
 2222 CONTINUE                                                         000
       DO 140 I=1,N                                                    000
       DO 120 J=1,N                                                    000
       XXX(J) = 0.D0                                                   000
      DO 110 K=1,OCCA                                                  000
  110 XXX(J) = XXX(J) + 2.D0*B(I,K)*B(J,K)                             000
  120 CONTINUE                                                         000
        DO 130 J=1,N                                                   000
  130 B(I,J) = XXX(J)                                                  000
  140 CONTINUE                                                         000
      DO 150 I=1,N                                                     000
       DO 150 J=1,N                                                    000
      PDIAG(I) = B(I,I)                                                000
  150 B(J,I) = B(I,J)                                                  000
C     WRITE THE DIAGONAL OF THE NEWLY GENERATED DENSITY MATRIX ON DISK 000
C     KDISK = 11                                                       000
C     IKDISK=12                                                        000
C      REWIND IKDISK                                                   000
```

```
C
C
C
C
C      REWIND KDISK                                                    000
C      DO 2222 IY=1,N                                                  000
C      DO 2222 JY=1,N                                                  000
C      IF(IY .NE. JY)  GO TO 2222                                      000
C      WRITE (KDISK) B(IY,JY)                                          000
C      WRITE (IKDISK) B(IY,JY)                                         000
C2222 CONTINUE                                                         000
       IF(IONOFF .EQ. OFF)  GO TO 4444                                 000
       PRINT 3333                                                      000
 3333 FORMAT (15H DENSITY MATRIX)                                      000
            CALL SCFOUT(C,AN,B,CZ,U,ULIM,LLIM,NUM,0,1,IBF,IAT)         000
 4444 CONTINUE                                                         000
       RETURN                                                          000
            END                                                        000
      SUBROUTINE EIGN(NN,RHO,IBF,A)                                    000
      IMPLICIT REAL*8(A-H,O-Z)                                         000
C      ONE MATRIX VERSION                                              000
C      RHO= UPPER LIMIT FOR OFF-DIAGONAL ELEMENT                       000
C      NN= SIZE OF MATRIX                                              000
C      A = F MATRIX (ONLY LOWER TRIANGLE IS USED + THIS IS DESTROYED)  000
C      EIG = RETURNED EIGENVALUES IN ALGEBRAIC ASCENDING ORDER         000
C      VEC = RETURNED EIGENVECTORS IN COLUMNS                          000
      DIMENSION A(IBF,IBF)                                             000
      DIMENSION W( 90),GAMMA( 90),BETA( 90),BETASQ( 90),IPOSV( 90),IVPOS000
     *( 90),IORD( 90)                                                  000
      COMMON/BYE/EIG( 90)                                              000
C      THE FOLLOWING DIMENSIONED VARIABLES ARE EQUIVALENCED            000
C      DIMENSION VEC(IBF,IBF)                                          000
C      EQUIVALENCE (A(1),VEC(1))                                       000
C      EQUIVALENCE (VEC,A)                                             000
      DIMENSION P(50),Q(50)                                            000
      EQUIVALENCE (P(1),BETA(1)),(Q(1),BETA(1))                        000
      EQUIVALENCE (IPOSV(1),GAMMA(1)),(IVPOS(1),BETA(1)),              000
     1(IORD(1),BETASQ(1))                                              000
      ABSF(X) =DABS(X)                                                 000
      SQRTF(X) =DSQRT(X)                                               000
C      PRINT 1917                                                      000
 1917 FORMAT( 8H IN EIGN)                                              000
      RHOSQ=RHO*RHO                                                    000
      N=NN                                                             000
      IF(N .EQ. 0) GO TO 560                                           000
    1 N1=N-1                                                           000
      N2=N-2                                                           000
      GAMMA(1)=A(1,1)                                                  000
      IF(N2) 280,270,120                                               000
  120 DO 260 NR=1,N2                                                   000
      B=A(NR+1,NR)                                                     000
      S=0.D0                                                           000
      DO 130 I=NR,N2                                                   000
  130 S=S+A(I+2,NR)**2                                                 000
C      PREPARE FOR POSSIBLE BYPASS OF TRANSFORMATION                   000
      A(NR+1,NR)=0.D0                                                  000
```

```
C
C
C
      IF (S) 250,250,140                                                00
  140 S=S+B*B                                                           00
      SGN=+1.D0                                                         00
      IF (B) 150,160,160                                                00
  150 SGN=-1.D0                                                         00
  160 SQRTS=SQRTF(S)                                                    00
      TSQR = SQRTS +SQRTS                                               00
C     PRINT 1111,TSQR                                                   00
 1111 FORMAT (F80.60)                                                   00
      D=SGN/(SQRTS+SQRTS)                                               00
      TEMP=SQRTF(.500+B*D)                                              00
      W(NR)=TEMP                                                        00
      A(NR+1,NR)=TEMP                                                   00
C     PRINT 1111,TEMP                                                   00
      D=D/TEMP                                                          00
      B=-SGN*SQRTS                                                      00
C     D IS FACTOR OF PROPORTIONALITY. NOW COMPUTE AND SAVE W VECTOR.    00
C     EXTRA SINGLY SUBSCRIPTED W VECTOR USED FOR SPEED.                 00
      DO 170 I=NR,N2                                                    00
      TEMP=D*A(I+2,NR)                                                  00
      W(I+1)=TEMP                                                       00
  170 A(I+2,NR)=TEMP                                                    00
C     PREMULTIPLY VECTOR w BY MATRIX A TO OBTAIN P VECTOR.              00
C     SIMULTANEOUSLY ACCUMULATE DOT PRODUCT WP.(THE SCALAR K)           00
      WTAW=0.D0                                                         00
      DO 220 I=NR,N1                                                    00
      SUM=0.D0                                                          00
      DO 180 J=NR,I                                                     00
  180 SUM=SUM+A(I+1,J+1)*W(J)                                           00
      I1=I+1                                                            00
      IF(N1-I1) 210,190,190                                             00
  190 DO 200 J=I1,N1                                                    00
  200 SUM=SUM+A(J+1,I+1)*W(J)                                           00
  210 P(I)=SUM                                                          00
  220 WTAW=WTAW+SUM*W(I)                                                00
C     P VECTOR AND SCALAR K  NOW STORED. NEXT COMPUTE Q VECTOR          00
      DO 230 I=NR,N1                                                    00
  230 Q(I)=P(I)-WTAW*W(I)                                               00
C     NOW FORM PAP MATRIX. REQUIRED PART                                00
      DO 240 J=NR,N1                                                    00
      QJ=Q(J)                                                           00
      WJ=W(J)                                                           00
      DO 240 I=J,N1                                                     00
  240 A(I+1,J+1)=A(I+1,J+1)-2.D0*(W(I)*QJ+WJ*Q(I))                      00
  250 BETA(NR)=B                                                        00
      BETASQ(NR)=B*B                                                    00
  260 GAMMA(NR+1)=A(NR+1,NR+1)                                          00
  270 B=A(N,N-1)                                                        00
      BETA(N-1)=B                                                       00
      BETASQ(N-1)=B*B                                                   00
      GAMMA(N)=A(N,N)                                                   00
  280 BETASQ(N)=0.D0                                                    00
```

```
C
C
C
C
C
C
      DO 800 I=1,N                                                      00
      DO 810 J=I,N                                                      00
  810 A(I,J)=0.D0                                                       00
  800 A(I,I)=1.D0                                                       00
C      FORM PRODUCT P1*P2*...*PN-2                                      00
      K=N                                                               00
  540 KP=K                                                              00
      K=K-1                                                             00
      KM=K-1                                                            00
      DO 550 J=KP,N                                                     00
      DO 580 I=K,N                                                      00
      SUM=0.D0                                                          00
      DO 600 L=K,N                                                      00
  600 SUM=SUM+A(L,KM)*A(L,J)                                            00
      SUM=SUM+SUM                                                       00
  580 W(I)=A(I,J)-SUM*A(I,KM)                                           00
      DO 620 I=K,N                                                      00
  620 A(I,J)=W(I)                                                       00
  550 CONTINUE                                                          00
      DO 640 I=KP,N                                                     00
  640 A(I,K)=-2.D0*A(I,KM)*A(K,KM)                                      00
      A(K,K)=1.D0-2.D0*A(K,KM)*A(K,KM)                                  00
      IF(K .GE. 3)  GO TO 540                                           00
  660 CONTINUE                                                          00
      DO 900 I=2,N                                                      00
  900 A(I,1)=0.D0                                                       00
      M=N                                                               00
      SUM=0.D0                                                          00
      GO TO 400                                                         00
  310 SUM=SUM+SHIFT                                                     00
      COSA=1.D0                                                         00
      G=GAMMA(1)-SHIFT                                                  00
      PP=G                                                              00
      PPBS=PP*PP+BETASQ(1)                                              00
      PPBR=SQRTF(PPBS)                                                  00
      DO 370 J=1,M                                                      00
      COSAP=COSA                                                        00
      IF(PPBS .NE. 0.D0) GO TO 320                                      00
  311 SINA=0.D0                                                         00
      SINA2=0.D0                                                        00
      COSA=1.D0                                                         00
      GO TO 350                                                         00
  320 SINA=BETA(J)/PPBR                                                 00
C      PRINT 1111, PPBR                                                 00
C      PRINT 1111, PPBS                                                 00
      SINA2=BETASQ(J)/PPBS                                              00
      COSA=PP/PPBR                                                      00
C     POSTMULTIPLY P1*...*PN-2 BY ROTATION MATRIX   (P-TRANSPOSE)       00
  330 DO 340 I=1,N                                                      00
C     TEMP=COSA*VEC(I,J)+SINA*VEC(I,J+1)                                00
      TEMP=COSA*  A(I,J)+SINA*  A(I,J+1)                                00
C     VEC(I,J+1)=-SINA*VEC(I,J)+COSA*VEC(I,J+1)                         00
```

```
C
C
C
C
        A(I,J+1)=-SINA*  A(I,J)+COSA*  A(I,J+1)                          00
C 340 VEC(I,J)=TEMP                                                      00
  340   A(I,J)=TEMP                                                      00
  350 DIA=GAMMA(J+1)-SHIFT                                               00
      U=SINA2*(G+DIA)                                                    00
      GAMMA(J)=G+U                                                       00
      G=DIA-U                                                            00
      PP=DIA*COSA-SINA*COSAP*BETA(J)                                     00
      IF(J .NE. M) GO TO 360                                             00
  351 BETA(J)=SINA*PP                                                    00
      BETASQ(J)=SINA2*PP*PP                                              00
      GO TO 380                                                          00
  360 PPBS=PP*PP+BETASQ(J+1)                                             00
      PPBR=SQRTF(PPBS)                                                   00
      BETA(J)=SINA*PPBR                                                  00
  370 BETASQ(J)=SINA2*PPBS                                               00
  380 GAMMA(M+1)=G                                                       00
C     TEST FOR CONVERGENCE OF LAST DIAGONAL ELEMENT                      00
      IF(BETASQ(M) .GT. RHOSQ) GO TO 410                                 00
  390 EIG(M+1)=GAMMA(M+1)+SUM                                            00
  400 BETA(M)=0.D0                                                       00
      BETASQ(M)=0.D0                                                     00
      M=M-1                                                              00
      IF(M .EQ. 0) GO TO 430                                             00
  401 IF(BETASQ(M) .LE. RHOSQ) GO TO 390                                 00
C     TAKE ROOT OF CORNER 2 BY 2 NEAREST TO LOWER DIAGONAL IN VALUE      00
C     AS ESTIMATE OF EIGENVALUE TO USE FOR SHIFT                         00
  410 A2=GAMMA(M+1)                                                      00
      R2=.5D0*A2                                                         00
      R1=.5D0*GAMMA(M)                                                   00
      R12=R1+R2                                                          00
      DIF=R1-R2                                                          00
      TEMP=SQRTF(DIF*DIF+BETASQ(M))                                      00
      R1=R12+TEMP                                                        00
      R2=R12-TEMP                                                        00
      DIF=ABSF(A2-R1)-ABSF(A2-R2)                                        00
      IF(DIF .LT. 0.D0) GO TO 420                                        00
  411 SHIFT=R2                                                           00
      GO TO 310                                                          00
  420 SHIFT=R1                                                           00
      GO TO 310                                                          00
  430 EIG(1)=GAMMA(1)+SUM                                                00
C     INITIALIZE AUXILIARY TABLES REQUIRED FOR REARRANGING THE VECTORS   00
      DO 440 J=1,N                                                       00
      IPOSV(J)=J                                                         00
      IVPOS(J)=J                                                         00
  440  IORD(J)=J                                                         00
C     USE A TRANSPOSITION SORT TO ORDER THE EIGENVALUES                  00
      M=N                                                                00
      GO TO 470                                                          00
  450 DO 460 J=1,M                                                       00
      IF (EIG(J) .LE. EIG(J+1)) GO TO 460                                00
```

```
      C
      C
      C
  451 TEMP=EIG(J)                                                       000
      EIG(J)=EIG(J+1)                                                   000
      EIG(J+1)=TEMP                                                     000
      ITEMP=IORD(J)                                                     000
      IORD(J)=IORD(J+1)                                                 000
      IORD(J+1)=ITEMP                                                   000
  460 CONTINUE                                                          000
  470 M=M-1                                                             000
      IF(M .NE. 0) GO TO 450                                            000
  471 IF(N1 .EQ. 0) GO TO 500                                           000
  472 DO 490 L=1,N1                                                     000
      NV=IORD(L)                                                        000
      NP=IPOSV(NV)                                                      000
      IF(NP .EQ. L) GO TO 490                                           000
  473 LV=IVPOS(L)                                                       000
      IVPOS(NP)=LV                                                      000
      IPOSV(LV)=NP                                                      000
      DO 480 I=1,N                                                      000
C     TEMP=VEC(I,L)                                                     000
      TEMP=  A(I,L)                                                     000
C     VEC(I,L)=VEC(I,NP)                                                000
        A(I,L)=  A(I,NP)                                                000
C 480  VEC(I,NP)=TEMP                                                   000
  480   A(I,NP)=TEMP                                                    000
  490 CONTINUE                                                          000
  500 CONTINUE                                                          000
  560 CONTINUE                                                          000
C      PRINT 1919                                                       000
 1919 FORMAT(13H LEAVING EIGN)                                          00
      RETURN                                                            00
      END                                                               00
      SUBROUTINE EIGOUT(M,K)                                            00
      IMPLICIT REAL*8(A-H,O-Z)                                          00
C     THIS ROUTINE IS CALLED IN SCFOUT TO PRINT THE EIGENVALUES M TO K  00
      COMMON/BYE/EPSILN( 90)                                            00
      PRINT 10,(EPSILN(I),I=M,K)                                        00
   10 FORMAT(//,15H EIGENVALUES---,10F9.4,//)                           00
      RETURN                                                            00
      END                                                               00
      SUBROUTINE SCFOUT(C,AN,A,CZ,U,ULIM,LLIM,NUM,OP,MOP,IBF,IAT)       00
      IMPLICIT REAL*8(A-H,O-Z)                                          00
C     THIS ROUTINE PRINTS THE ARRAY IN COMMON/ARRAYS/ WHICH IS DESIGNATE00
C     MOP. IF OP = 1 THE EIGENVALUES CONTAINED IN COMMON/1/ ARE ALSO    00
C     PRINTED. IF OP= 0 THE EIGENVALUES ARE NOT PRINTED                 00
      DIMENSION C(IAT,3), AN(IAT)                                       00
      DIMENSION A(IBF,IBF)                                              00
      COMMON/INFO/N,NATOMS,CHARGE,MULTIP                                00
      INTEGER*4 CHARGE,OCCA,OCCB,UL,ANI                                 00
      COMMON/ORB/ORB(9)                                                 00
      COMMON/INFO1/NELECS,OCCA,OCCB                                     00
      DIMENSION CZ(IAT),U(IBF),ULIM(IAT),LLIM(IAT)                      00
      COMMON/PERTBL/EL(9)                                               00
```

```
      DIMENSION NUM(IBF)                                                00
      INTEGER*4 OP,AN,ANII,CZ,U,ORB,ULIM,EL                             00
      DO 10 I = 1,N                                                     00
   10 NUM(I) = I                                                        00
      DO 120 M=1,N,11                                                   00
      K=M+10                                                            00
      IF(K.GT.N) GO TO 20                                               00
      GO TO 30                                                          00
   20 K=N                                                               00
   30 CONTINUE                                                          00
      PRINT 100                                                         00
      IF(OP.EQ.1) GO TO 40                                              00
      GO TO 50                                                          00
   40 CONTINUE                                                          00
   50 CONTINUE                                                          00
      PRINT 60,(NUM(I),I=M,K)                                           00
   60 FORMAT(13X,11I9)                                                  00
      DO 110 I=1,N                                                      00
      II=U(I)                                                           00
      ANII=AN(II)                                                       00
      L=I-LLIM(II)+1                                                    00
   70 PRINT 80,I,II,EL(ANII),ORB(L),(A(I,J),J=M,K)                      00
   80 FORMAT(1X,I2,I3,A4,1X,A4,11F9.4)                                  00
      IF(I.EQ.ULIM(II)) GO TO 90                                        00
      GO TO 110                                                         00
   90 PRINT 100                                                         00
  100 FORMAT(1X)                                                        00
  110 CONTINUE                                                          00
  120 CONTINUE                                                          00
      PRINT 100                                                         00
      PRINT 100                                                         00
      RETURN                                                            00
      END                                                               00
      SUBROUTINE ZMAT(ALPHA,BETA,C,BL,ANG1,ANG2,R,AN,IAT,IBF,Z)         00
      IMPLICIT REAL*8(A-H,O-Z)                                          00
       REAL*8 L1,L2,L3,L4                                               00
      DIMENSION ALPHA(IAT),BETA(IAT),Z(IAT,4),C(IAT,3),AN(IAT),BL(IAT), 00
     *ANG1(IAT),ANG2(IAT)                                               00
       COMMON/INFO/N,NATOMS,CHARGE,MULTIP                               00
C     THIS PROGRAM ACCEPTS A DEFINITION OF A MOLECULE IN TERMS OF       00
C     ATOMIC NUMBERS, BOND LENGTHS, BOND ANGLES AND DIHEDRAL ANGLES     00
C     AND CALCULATES THE CARTESIAN COORDINATES IN ANGSTROMS             00
C     ADAPTED FROM MARK GORDONS MBLD SYSTEM BY D L BEVERIDGE            00
C     CODED IN CDC SCOPE 3.1 LEVEL FORTRAN FOR THE CIMS CDC 6600        00
      DIMENSION V1(3),V2(3),V3(3),VJ(3),VP(3),L1(3),L2(3),L3(3),L4(3)   00
      COMMON/JDENT/IDENT                                                00
           INTEGER AN,CHARGE,Z,PUNCH                                    00
      DIMENSION R(IAT,IAT)                                              00
      DIMENSION IDENT(20)                                               00
       DIMENSION EL(9)                                                  00
      COMMON/ENGY/BOE(3),ROE(3),ETOT,VOL,DP,IC                          00
      COMMON/SIMRUN/DELTA,RMIN,ID,I1,I2,II,III,IE,IS,ISS                00
```

```
      COMMON/OPTION/OPTION,OPNCLO,HUCKCL,CNDO,INDO,CLOSED,OPEN,IONOFF  000
          INTEGER  OPTION,OPNCLO,HUCKCL,CNDO,INDO,CLOSED,OPEN,IONOFF   000
      COMMON/LIT/IBLANK,ITMAT,IBL,IALPHA,IBETA,ICLEAR,II1,II2          000
      COMMON/NTMAT/LTMAT,NVAR,LID                                      000
          INTEGER EL                                                   000
          INTEGER OFF                                                  000
      DIMENSION NAL(6)                                                 000
      DATA NAL(1),NAL(2),NAL(3),NAL(4),NAL(5),NAL(6)/'INTE','RATO',    000
     *'MIC ','DIST','ANCE','S   '/                                     000
       DATA OFF/'OFF'/                                                 000
      DATA EL(1),EL(2),EL(3),EL(4),EL(5),EL(6),EL(7),EL(8),EL(9) /'H',  000
     *'HE','LI','BE','B','C','N','O','F'/                             000
C     ************************************                             000
C     FORTRAN II TO IV CONVERSION                                      000
      ABSF(X) =DABS(X)                                                 000
      ATANF(X) =DATAN(X)                                               000
      COSF(X) = DCOS(X)                                                000
      SINF(X) =DSIN(X)                                                 000
      SIGNF(X,Y) =DSIGN(X,Y)                                           000
      SQRTF(X) =DSQRT(X)                                               000
C     INPUT AND OUTPUT OF INPUT                                        000
      NBEN = 0                                                         000
      IF (IE.EQ.1) GO TO 999                                           000
      GO TO 2                                                          000
  999 CONTINUE                                                         000
      READ 1000,(IDENT(I),I=1,20)                                      000
    2 CONTINUE                                                         000
      PRINT 1111, (IDENT(I),I=1,20)                                    000
 1000 FORMAT(20A4)                                                     000
 1111 FORMAT (//,20A4)                                                 000
 2008 FORMAT(/,16H PUNCH OPTION ON,/)                                  000
    4 CONTINUE                                                         000
      IF (IE.EQ.1)  GO TO 101                                          000
      M = NATOMS                                                       000
      GO TO 102                                                        000
  101 CONTINUE                                                         000
      READ 1001, NATOMS,CHARGE,MULTIP                                  000
      M = NATOMS                                                       000
 1001 FORMAT(3I2)                                                      000
  102 CONTINUE                                                         000
      PRINT1002, NATOMS,CHARGE,MULTIP                                  000
 1002 FORMAT(//,10H NATOMS = ,I4,2X,10H CHARGE = ,I4,2X,10H MULTIP = ,I400
     *,I4,//)                                                          00
    8 FORMAT(3I4)                                                      00
    6 CONTINUE                                                         00
C     ************************************                             00
C     CALCULATION OF COORDINATES                                       00
      IF (IE.GT.1) GO TO 104                                           00
  103 CONTINUE                                                         00
      DO 6969 I=1,M                                                    00
      READ 1003,  AN(I),Z(I,1),BL(I),Z(I,2),ALPHA(I),Z(I,3),BETA(I),Z(I,00
     B4)                                                               00
```

```
 1003 FORMAT (I3,I4,F7.4,I4,F11.6,I4,F11.6,I4)                          00
C     ANG1 AND ANG2 STORE THE ANGLES ALPHA AND BETA IN DEGREE FORM      00
      ANG1(I)=ALPHA(I)                                                  00
      ANG2(I)=BETA(I)                                                   00
      IF(AN(I) .LE. 10) GO TO 361                                       00
      NBFN = NBFN + 9                                                   00
      GO TO 371                                                         00
  361 IF(AN(I) .LT. 3) GO TO 362                                        00
      NBFN = NBFN + 4                                                   00
      GO TO 371                                                         00
  362 NBFN = NBFN + 1                                                   00
  371 CONTINUE                                                          00
 6969 CONTINUE                                                          00
      PRINT 374, NBFN,NATOMS                                            00
  374 FORMAT (/,3X,I4, 29H BASIS FUNCTIONS REQUIRED FOR,I3,6H ATOMS,/)  00
  104 CONTINUE                                                          00
C     DO 1124 I=1,NATOMS                                                00
C      PRINT 1125,AN(I),Z(I,1),BL(I),Z(I,2),ALPHA(I),Z(I,3),BETA(I),    00
C    *Z(I,4)                                                            00
C1124 CONTINUE                                                          00
C1125 FORMAT(I3,I4,F7.4,I4,F11.6,I4,F11.6,I4)                           00
      IF ((NVAR.EQ.ICLEAR).OR.(ID.EQ.1)) GO TO 7000                     00
 7001 CONTINUE                                                          00
      IF (NVAR.EQ.IBL) GO TO 7002                                       00
      GO TO 7003                                                        00
 7002 BL(IS)=BL(IS) + DELTA                                             00
      IF (ISS.EQ.0) GO TO 7000                                          00
      BL(ISS)=BL(ISS) + DELTA                                           00
      GO TO 7000                                                        00
 7003 CONTINUE                                                          00
      IF (NVAR.EQ.IALPHA) GO TO 7004                                    00
      GO TO 7005                                                        00
 7004 ANG1(IS)=ANG1(IS) + DELTA                                         00
      IF (ISS.EQ.0) GO TO 7000                                          00
      ANG1(ISS)=ANG1(ISS) + DELTA                                       00
      GO TO 7000                                                        00
 7005 CONTINUE                                                          00
      IF (NVAR.EQ.IBETA) GO TO 7006                                     00
      GO TO 7007                                                        00
 7006 ANG2(IS)=ANG2(IS) + DELTA                                         00
      IF (ISS.EQ.0) GO TO 7000                                          00
      ANG2(ISS)=ANG2(ISS) + DELTA                                       00
      GO TO 7000                                                        00
 7007 CONTINUE                                                          00
      PRINT 7008                                                        00
 7008 FORMAT (/////, 55H ERROR ON FIRST CARD IN COLUMNS 30 - 34 OR 57 - 00
     C61,///,37H PROGRAM TERMINATED DUE TO THIS ERROR,///,60H CHECK PERM00
     DISSIBLE STATEMENTS FOR THESE COLUMNS AND RESUBMIT,///)            00
      GO TO 1984                                                        00
 7000 CONTINUE                                                          00
C     DO 1127 I=1,NATOMS                                                00
C      PRINT 1125,AN(I),Z(I,1),BL(I),Z(I,2),ALPHA(I),Z(I,3),BETA(I),    00
```

```
C     *Z(I,4)                                                          00C
C1127 CONTINUE                                                         00C
C       CONVERT TO RADIANS                                             00C
      DO 502 J=1,M                                                     00C
  502 ALPHA(J)=ALPHA(J)*3.141592654D0/180.0D0                          00C
      DO 503 J=1,M                                                     00C
  503 BETA(J)=BETA(J)*3.141592654D0/180.0D0                            00C
      DO 504 J= 1,3                                                    00C
  504 C(1,J)=0.0D0                                                     00C
      IF(M .EQ. 1) GO TO 601                                           00C
      C(2,1)=0.0D0                                                     00C
      C(2,3)=BL(2)                                                     00C
      C(2,2)=0.0D0                                                     00C
      IF(M .EQ. 2) GO TO 601                                           00C
      C(3,1)=BL(3)*SINF(ALPHA(3))                                      00C
      C(3,2)=0.0D0                                                     00C
C     ***********************************                              00C
C     IF THE MOLECULE UNDER CONSIDERATION HAS ONLY ONE HEAVY ATOM OR FOR00C
C     THE FOLLOWING IS AN ADDITION TO COORD FINDER PROGRAM TO BE USED  00C
C     A MOLECULE SUCH AS NEOPENTANE IN WHICH THE CENTRAL ATOM HAS NO   00C
C     HYDROGENS BONDED TO IT                                           00C
      IF(Z(3,1).EQ.1) GO TO 505                                        00C
      GO TO 506                                                        00C
  505 C(3,3) = BL(3)*COSF(ALPHA(3))                                    00C
      GO TO 507                                                        00C
  506 C(3,3) = C(2,3)-BL(3)*COSF(ALPHA(3))                             00C
  507 I=3                                                              00C
      IF(ABSF(C(3,1)).LT.0.00001D0) GO TO 550                          00C
      GO TO 510                                                        00C
  550 DO 509 I = 4,1000                                                00C
      IF(I.LE.M.AND.ABSF(C(I-1,1)).LT.0.00001D0) GO TO 508             00C
      GO TO 510                                                        00C
  508 C(I,1) = BL(I)*SINF(ALPHA(I))                                    00C
      C(I,2)=0.0D0                                                     00C
      ITEMP = Z(I,1)                                                   00C
      JTEMP = Z(I,2)                                                   00C
      C(I,3)=C(ITEMP,3)-BL(I)*COSF(ALPHA(I))*SIGNF(1.0D0,C(ITEMP,3)-   00C
     1C(JTEMP,3))                                                      00C
  509 CONTINUE                                                         00C
  510 CONTINUE                                                         00C
      IF(I.EQ.3) GO TO 511                                             00C
      GO TO 512                                                        00C
  511 K=4                                                              00C
      GO TO 513                                                        00C
  512 K=I                                                              00C
  513 CONTINUE                                                         00C
      IF(K.GT.M) GO TO 601                                             00C
  600 CONTINUE                                                         00C
      DO 533 J = K,M                                                   00C
      IF(Z(J,4).EQ.0) GO TO 514                                        00C
      GO TO 517                                                        00C
C     ***********************************                              00C
```

```
C
C
C
C     THIS PART IS USED IF THE ATOM IS BEING DEFINED BY A DIHEDRAL ANGLE
  514 CONTINUE
      CALL RELVEC(V1,Z(J,2),Z(J,3),IAT,IBF,C)
      CALL UNIVEC(L1,V1)
C     V1 IS A VECTOR FROM ATOM Z(J,3) TO ATOM Z(J,2)
C     L1 IS A UNIT VECTOR OF V1.  BL(Z(J,2)) IS BONDLENGTH OF ATOM Z(J,2
      CALL RELVEC(V2,Z(J,1),Z(J,2),IAT,IBF,C)
      CALL UNIVEC(L2,V2)
C     V2 IS THE VECTOR FROM ATOM Z(J,2) TO ATOM Z(J,1)
C     L2 IS THE UNIT VECTOR OF V2.   BL(Z(J,1)) IS BONDLENGTH  DEFINING
C     ATOM Z(J,1)
      CALL VECPRD(VP,L1,L2)
      XXX=0.0D0
      XXX=(1.0D0-(L1(1)*L2(1)+L1(2)*L2(2)+L1(3)*L2(3))**2)
      IF(XXX.LT.0.0D0) GO TO 1888
      GO TO 1889
 1888 PRINT 1913, XXX
 1913 FORMAT (3X,32HARGUMENT OF DSQRT IS LESS THAN 0,6H XXX =,F40.20)
 1889 CONTINUE
      DO 515 I = 1,3
  515 L3(I)=VP(I)/SQRTF(DABS(1.0D0-(L1(1)*L2(1)+L1(2)*L2(2)+
     1L1(3)*L2(3))**2))
 1985 FORMAT(3X,1HA)
C     L3 IS THE UNIT VECTOR OF VP.ALPHA(Z(J,1))IS THE ANGLE DEFINING
C     ATOM Z(J,1)
      CALL VECPRD(L4,L3,L2)
C     L4,L3,L2 ARE A NEW SET OF MUTUALLY ORTHOGONAL AXES. WE WILL NOW
C     OBTAIN COORD OF ATOM J IN TERMS OF THESE AXES RELATIVE TO ATOM Z(J
      DO 516 I=1,3
     0VJ(I) = BL(J)*(-L2(I)*COSF(ALPHA(J))+L4(I)*SINF(ALPHA(J))*COSF(BET
     1A(J))+L3(I)*SINF(ALPHA(J))*SINF(BETA(J)))
C     VJ IS THE VECTOR FROM ATOM Z(J,1) TO ATOM J
      ITEMP = Z(J,1)
      C(J,I) = VJ(I) + C(ITEMP,I)
  516 CONTINUE
      GO TO 533
  517 IF(Z(J,4).EQ.1.OR.Z(J,4).EQ.-1) GO TO 549
      GO TO 528
C     **********************************
C     THIS PART IS USED IF ATOM IS DEFINED BY TWO BONDANGLES
  549 CONTINUE
      CALL RELVEC(V1,Z(J,1),Z(J,3),IAT,IBF,C)
      CALL UNIVEC(L1,V1)
      CALL RELVEC(V2,Z(J,2),Z(J,1),IAT,IBF,C)
      CALL UNIVEC(L2,V2)
      ZETA = -(L1(1)*L2(1)+L1(2)*L2(2)+L1(3)*L2(3))
      A=(-COSF(BETA(J))+ZETA*COSF(ALPHA(J)))/(1.0D0-ZETA**2)
      B=(COSF(ALPHA(J))-ZETA*COSF(BETA(J)))/(1.0D0-ZETA**2)
      PI=3.14159265D0
      IF(ZETA.LT.0.0D0) GO TO 518
      GO TO 519
  518 TEMP = PI
```

```
C
C
C
C
C
C
      GO TO 520                                                         000
  519 TEMP=0.0D0                                                        000
  520 CONTINUE                                                          000
      IF(ZETA.EQ.0.0D0) GO TO 521                                       000
      GO TO 522                                                         000
  521 GAMMA=PI/2.0D0                                                    000
      GO TO 523                                                         000
  522 GAMMA=ATANF(SQRTF(1.0D0-ZETA**2)/ZETA)+TEMP                       000
 1986 FORMAT (3X,1HB)                                                   000
  523 CONTINUE                                                          000
      IF(ABSF(GAMMA+ALPHA(J)+BETA(J)-2.0D0*PI).LT.0.00000001D0)         000
     1GO TO 524                                                         000
      GO TO 525                                                         000
  524 D = 0.D0                                                          000
      GO TO 526                                                         000
  525 D=Z(J,4)*(SQRTF(1.0D0+A*COSF(BETA(J))-B*COSF(ALPHA(J))))          000
     1/SQRTF(1.0D0-ZETA**2)                                             000
 1987 FORMAT (3X,1HC)                                                   000
  526 CONTINUE                                                          000
      CALL VECPRD(V3,L1,L2)                                             000
      DO 527 I = 1,3                                                    000
      L3(I) = A*L1(I)+B*L2(I)+D*V3(I)                                   000
      VJ(I) = BL(J)*L3(I)                                               000
      ITEMP = Z(J,1)                                                    000
      C(J,I) = VJ(I)+C(ITEMP,I)                                         000
  527 CONTINUE                                                          000
      GO TO 533                                                         000
C     ************************************                            000
C     THIS PART IS USED IF ATOM IS DEFINED BY ONE BONDANGLE AND BY THE  000
C     ANGLE WHICH BOND Z(J,1)-J MAKES WITH THE PLANE OF Z(J,1),Z(J,2)   000
C     AND Z(J,3)                                                        000
  528 CONTINUE                                                          000
      CALL RELVEC(V1,Z(J,1),Z(J,3),IAT,IBF,C)                           000
      CALL UNIVEC(L1,V1)                                                000
      CALL RELVEC(V2,Z(J,2),Z(J,1),IAT,IBF,C)                           000
      CALL UNIVEC(L2,V2)                                                000
      ZETA = -(L1(1)*L2(1)+L1(2)*L2(2)+L1(3)*L2(3))                     000
      CALL VECPRD(V3,L1,L2)                                             000
C     BETA(J) HERE REFERS TO 90-ANGLE WHICH BOND Z(J,1)-J MAKES WITH THE000
C     AFOREMENTIONED PLANE                                              000
      A=COSF(BETA(J))/(1.0D0-ZETA**2)                                   000
      IF(Z(J,4).EQ.2) GO TO 530                                         000
  529 B=-SQRTF((1.0D0-COSF(ALPHA(J))**2-A*COSF(BETA(J)))/               000
     1(1.0D0-ZETA**2))                                                  000
 1988 FORMAT (3X,1HD)                                                   000
      GO TO 531                                                         000
  530 B=SQRTF((1.0D0-COSF(ALPHA(J))**2-A*COSF(BETA(J)))/                000
     1(1.0D0-ZETA**2))                                                  000
 1989 FORMAT (3X,1HE)                                                   000
  531 CONTINUE                                                          000
      D = B*ZETA+COSF(ALPHA(J))                                         000
      DO 532 I=1,3                                                      000
```

```
C
C
C
C
C
C
      L3(I) = B*L1(I)+D*L2(I)+A*V3(I)                                   000
      VJ(I) = BL(J)*L3(I)                                               000
      ITEMP = Z(J,1)                                                    000
      C(J,I) = VJ(I) + C(ITEMP,I)                                       000
  532 CONTINUE                                                          000
  533 CONTINUE                                                          000
  601 CONTINUE                                                          000
C     ************************************                            000
C      CONVERT ALPHA AND BETA BACK TO DEGREES                           000
       DO 9173 LL1=1,NATOMS                                             000
       ALPHA(LL1) = ALPHA(LL1)* 180.D0/3.14159265D0                     000
       BETA(LL1) =  BETA(LL1)* 180.D0/3.14159265D0                      000
 9173 CONTINUE                                                          000
C     OUTPUT SECTION                                                    001
      PRINT 1998                                                        001
 1998 FORMAT (1X,8HZ MATRIX,//,42H NO AN  (1)   BL   (2)    ALPHA   (3) 001
     *   ,20HBETA   (4)    EL   ,8X,1HX,11X,1HY,12X,1HZ)                001
      DO 900 J = 1,M                                                    001
      IND1 = AN(J)                                                      001
  900 PRINT 1999,J,AN(J),Z(J,1),BL(J),Z(J,2),ALPHA(J),Z(J,3),BETA(J),   001
     *Z(J,4),EL(IND1),(C(J,I),I=1,3)                                    001
 1999 FORMAT (2I3,I4,F7.4,2(I4,F11.6),I4,6X,A4,4X,3F12.8)               001
    9 FORMAT(I4,3(3X,F12.7))                                            001
   11 CONTINUE                                                          001
       IF(IONOFF .EQ. OFF)  GO TO 3137                                  001
      DO 10I=1,NATOMS                                                   001
      DO 10J=1,NATOMS                                                   001
   10 R(I,J)=SQRTF((C(I,1)-C(J,1))**2+(C(I,2)- C(J,2))**2+(C(I,3)-C(J,3 001
     *))**2)                                                            001
 3137 CONTINUE                                                          001
 2222 FORMAT(3X,2HNN)                                                   001
   13 CONTINUE                                                          001
      IF(IONOFF.NE.OFF)CALL MOUTP1(R,NATOMS,NATOMS,IAT,IAT,NAL)         001
   12 CONTINUE                                                          001
 1984 CONTINUE                                                          001
      IF ((NVAR.NE.ICLEAR).AND.(ID.EQ.I2).AND.(LID.EQ.II2)) GO TO 7201  001
      GO TO 7200                                                        001
 7201 DID=I2 - 1                                                        001
      IF (NVAR.EQ.IBL) GO TO 7202                                       001
      GO TO 7203                                                        001
 7202 BL(IS)=BL(IS) - (DID * DELTA)                                     001
      IF (ISS.EQ.0) GO TO 7200                                          001
      BL(ISS)=BL(ISS) - (DID * DELTA)                                   001
      GO TO 7200                                                        001
 7203 CONTINUE                                                          001
      IF (NVAR.EQ.IALPHA) GO TO 7204                                    001
      GO TO 7205                                                        001
 7204 ANG1(IS)=ANG1(IS) - (DID * DELTA)                                 001
      IF (ISS.EQ.0) GO TO 7200                                          001
      ANG1(ISS)=ANG1(ISS) - (DID * DELTA)                               001
      GO TO 7200                                                        001
 7205 ANG2(IS)=ANG2(IS) - (DID * DELTA)                                 001
```

```
      IF (ISS.EQ.0) GO TO 7200                                          001
      ANG2(ISS)=ANG2(ISS) - (DID * DELTA)                               001
 7200 CONTINUE                                                          001
      IF((LTMAT.EQ.ITMAT).AND.(NVAR.NE.ICLEAR).AND.(IC.EQ.2)) GO TO 7401001
      GO TO 7400                                                        001
 7401 CONTINUE                                                          001
      IF (NVAR.EQ.IBL) GO TO 7402                                       001
      GO TO 7403                                                        001
 7402 RQE(2)=BL(IS)                                                     001
      GO TO 7406                                                        001
 7403 CONTINUE                                                          001
      IF (NVAR.EQ.IALPHA) GO TO 7404                                    001
      GO TO 7405                                                        001
 7404 RQE(2)=ANG1(IS)                                                   001
      GO TO 7406                                                        001
 7405 RQE(2)=ANG2(IS)                                                   001
 7406 RQE(1)=RQE(2)-DELTA                                               001
      RQE(3)=RQE(2)+DELTA                                               001
 7400 CONTINUE                                                          001
      RETURN                                                            001
      END                                                               001
       SUBROUTINE RELVEC(R,J,K,IAT,IBF,C)                               001
      IMPLICIT REAL*8(A-H,O-Z)                                          001
      DIMENSION C(IAT,3)                                                001
          DIMENSION R(3)                                                001
      DOUBLE PRECISION C,R                                              001
                INTEGER J,K,I                                           001
          DO 1 I=1,3                                                    001
    1           R(I)=C(J,I)-C(K,I)                                      001
C         R IS THE RELATIVE VECTOR FROM ATOM K TO ATOM J                001
      RETURN                                                            001
      END                                                               001
      SUBROUTINE UNIVEC(L,R)                                            001
      IMPLICIT REAL*8(A-H,O-Z)                                          001
          DIMENSION L(3),R(3)                                           001
      DOUBLE PRECISION L,R,X                                            001
                INTEGER I                                               001
      SQRTF(X) =DSQRT(X)                                                001
          DO 2 I=1,3                                                    001
    2           L(I)=R(I)/SQRTF(R(1)**2 + R(2)**2 + R(3)**2)            001
C     L IS THE UNITVECTOR OF R                                          001
      RETURN                                                            001
      END                                                               001
      SUBROUTINE VECPRD(VP,X,Y)                                         001
      IMPLICIT REAL*8(A-H,O-Z)                                          001
          DIMENSION VP(3),X(3),Y(3)                                     001
      DOUBLE PRECISION VP,X,Y                                           001
          VP(1)=X(2)*Y(3)-X(3)*Y(2)                                     001
          VP(2)=X(3)*Y(1)-X(1)*Y(3)                                     001
          VP(3)=X(1)*Y(2)-X(2)*Y(1)                                     001
C     VP IS THE VECTOR PRODUCT OF X CROSSED Y                           001
      RETURN                                                            001
```

```
      END                                                               001
      SUBROUTINE MINERT(C,AN,IBF,IAT)                                   001
      IMPLICIT REAL*8 (A-H,O-Z)                                         001
      DIMENSION C(IAT,3),AN(IAT)                                        001
       COMMON/INFO/NNN,NATOMS,CHARGE,MULTIP                             001
       COMMON/OPTION/OPTION,OPNCLO,HUCKCL,CNDO,INDO,CLOSED,OPEN,IONOFF  001
       INTEGER OPTION,OPNCLO,HUCKCL,CNDO,INDO,CLOSED,OPEN,IONOFF        001
       INTEGER OFF                                                      001
       DATA OFF/'OFF'/                                                  001
C     THIS PROGRAM ACCEPTS ATOMIC NUMBERS AND CARTESIAN COORDINATES OF  001
C     ALL ATOMS IN A MOLECULE AND AND CALCULATES THE MOMENT OF INERTIA  001
C     TENSOR ABOUT THE CENTER OF MASS, THE PRINCIPAL MOMENTS OF INERTIA,001
C     AND THE PRINCIPAL AXES DIRECTION COSINES AND EULER ANGLES         001
C     CODED IN SCOPE 3.1 FORTRAN BY DAVID L. BEVERIDGE                  001
      COMMON/PERTBL/EL(9)                                               001
      COMMON/ORB/ORB(9)                                                 001
      INTEGER EL,ORB                                                    001
           INTEGER CHARGE,AN                                            001
      DIMENSION AW(  9),RMASS(3),R(3),A(3,3),B(3,3),E(3,3)              001
      DATA AW/1.00797D0,4.0026D0,6.939D0,9.0122D0,10.811D0,12.01115D0,  001
     1 14.0067D0,15.9994D0,18.9984D0/                                   001
C     ************************************                              001
C     INPUT AND OUTPUT OF INPUT                                         001
  888 CONTINUE                                                          001
 9898 FORMAT(10H IN MINERT)                                             001
C     ************************************                              001
C     CALCULATION OF COORDINATES OF CENTER OF MASS IN MOLECULAR FRAME    001
       IF(IONOFF .NE. OFF)   PRINT9898                                  001
      FNUMX=0.0D0                                                       001
      FNUMY=0.0D0                                                       001
      FNUMZ=0.0D0                                                       001
      DEN=0.0D0                                                         001
      DO 2 I=1,NATOMS                                                   001
      IAN = AN(I)                                                       001
      DEN = DEN+AW(IAN)                                                 001
      FNUMX = FNUMX+AW(IAN)*C(I,1)                                      001
      FNUMY = FNUMY+AW(IAN)*C(I,2)                                      001
      FNUMZ = FNUMZ+AW(IAN)*C(I,3)                                      001
    2 CONTINUE                                                          001
      RMASS(1) = FNUMX/DEN                                              001
      RMASS(2) = FNUMY/DEN                                              001
      RMASS(3) = FNUMZ/DEN                                              001
C     TRANSLATE ORIGIN OF CENTER OF MASS TO MOLECULAR FRAME             001
      DO 3 I=1,NATOMS                                                   001
      DO 3 K=1,3                                                        001
    3 C(I,K) = C(I,K)-RMASS(K)                                          001
C     CHECKING CENTER OF MASS CALCULATION                               001
      DO 9 I=1,3                                                        001
      R(I)=0.0D0                                                        001
      DO 9 K=1,NATOMS                                                   001
      IAN = AN(K)                                                       001
    9 R(I) = R(I)+AW(IAN)*C(K,I)                                        001
```

```
C      ************************************                              00
C      CALCULATION OF ELEMENTS OF MOMENT OF INERTIA TENSOR               00
       DO 10 I=1,3                                                       00
       DO 10 J=1,3                                                       00
       A(I,J)=0.0D0                                                      00
       DO 10 K=1,NATOMS                                                  00
       IAN = AN(K)                                                       00
       IF(I.EQ.J) GO TO 11                                               00
       GO TO 12                                                          00
C      ROUTE FOR DIAGONAL ELEMENTS                                       00
   11  RKSQ = C(K,1)**2+C(K,2)**2+C(K,3)**2                              00
       A(I,J)=A(I,J)+AW(IAN)*(RKSQ-C(K,I)*C(K,J))*1.67D0                 00
       GO TO 10                                                          00
C      ROUTE FOR OFF DIAGONAL ELEMENTS                                   00
   12  A(I,J)=A(I,J)-AW(IAN)*C(K,I)*C(K,J)*1.67D0                        00
   10  CONTINUE                                                          00
C      ************************************                              00
C      DIAGONALIZATION OF MOMENT OF INERTIA TENSOR AND OUTPUT            00
       CALL TPAT(A,B,E)                                                  00
C      ORIENT COORDINATE SYSTEM ALONG PRINCIPAL AXES                     00
       DO 20 K=1,NATOMS                                                  00
       DO 21 I=1,3                                                       00
       A(I,I)=0.000                                                      00
       DO 21 J=1,3                                                       00
   21  A(I,I) = A(I,I)+B(J,I)*C(K,J)                                     00
       DO 20 J=1,3                                                       00
   20  C(K,J) = A(J,J)                                                   00
         IF(IONOFF .NE. OFF) PRINT 720                                   00
  720  FORMAT(15H LEAVING MINERT)                                        00
       RETURN                                                            00
       END                                                               00
       SUBROUTINE TPAT(A,S,ANGLE)                                        00
       IMPLICIT REAL*8(A-H,O-Z)                                          00
C      PRINCIPLE AXIS TRANSFORMATION                                     00
       DIMENSION A(3,3),S(3,3),ANGLE(3,3)                                00
            INTEGER N,I,J,P,Q,IND,LL,UL,K,NSMALL                         00
       REAL*8 RHO,THR,MU,OMEGA,SINT,COST,INT1,V1,V2,V3,A,S,SMALL         00
       SQRTF(X) =DSQRT(X)                                                00
       ABSF(X) =DABS(X)                                                  00
       ATANF(X) =DATAN(X)                                                00
       SIGNF(X,Y)=DSIGN(X,Y)                                             00
       FLOATF(I)=DFLOAT(I)                                               00
       RHO = 1.0D-6                                                      00
       N = 3                                                             00
       DO 30 I=1,N                                                       00
       DO 20 J=1,N                                                       00
   20  S(I,J)=0.0D0                                                      00
   30  S(I,I)=1.0D0                                                      00
       INT1=0.0D0                                                        00
       DO 40 I=2,N                                                       00
       UL = I-1                                                          00
       DO 40 J=1,UL                                                      00
```

```
      INT1=INT1+2.0D0*A(I,J)**2                                          001
   40 CONTINUE                                                           001
      THR = SQRTF(INT1)                                                  001
      IND = 0                                                            001
   50 THR = THR/FLOATF(N)                                                001
      IF (THR.LT.RHO) GO TO 60                                           001
      GO TO 70                                                           001
   60 THR = RHO                                                          001
   70 CONTINUE                                                           001
      DO 200 P=2,N                                                       001
      UL = P-1                                                           001
      DO 200 Q=1,UL                                                      001
      IF (ABSF(A(P,Q)).GE.THR) GO TO 80                                  001
      GO TO200                                                           001
   80 IND = 1                                                            001
      V1 = A(Q,Q)                                                        001
      V2 = A(P,Q)                                                        001
      V3 = A(P,P)                                                        001
      MU=0.5D0*(V1-V3)                                                   001
      IF(ABSF(MU).LT.0.00000100) GO TO 90                                001
      GO TO 100                                                          001
   90 OMEGA=-1.0D0                                                       001
      GO TO 110                                                          001
  100 OMEGA=-SIGNF(1.0D0,MU)*V2/SQRTF(V2**2+MU**2)                       001
  110 CONTINUE                                                           001
  120 SINT=OMEGA/SQRTF(2.0D0*(1.0D0+SQRTF(1.0D0-OMEGA**2)))              001
  130 COST=SQRTF(1.0D0-SINT**2)                                          001
      DO 190 I=1,N                                                       001
      IF (I.GE.P) GO TO 140                                              001
      GO TO 150                                                          001
  140 INT1 = A(I,Q)*COST - A(I,P)*SINT                                   001
      A(I,P) = A(I,Q)*SINT + A(I,P)*COST                                 001
      A(I,Q) = INT1                                                      001
      GO TO 180                                                          001
  150 IF (I.LT.P.AND.I.LT.Q) GO TO 160                                   001
      GO TO 170                                                          001
  160 INT1   = A(Q,I)*COST - A(P,I)*SINT                                 001
      A(P,I) = A(Q,I)*SINT + A(P,I)*COST                                 001
      A(Q,I) = INT1                                                      001
      GO TO 180                                                          001
  170 INT1   = A(I,Q)*COST - A(P,I)*SINT                                 001
      A(P,I) = A(I,Q)*SINT + A(P,I)*COST                                 001
      A(I,Q) = INT1                                                      001
  180 CONTINUE                                                           001
      INT1   = S(I,Q)*COST - S(I,P)*SINT                                 001
      S(I,P) = S(I,Q)*SINT + S(I,P)*COST                                 001
      S(I,Q) = INT1                                                      001
  190 CONTINUE                                                           001
      A(Q,Q) = V1*COST**2 + V3*SINT**2                                   001
     1-2.0D0*V2*SINT*COST                                                001
      A(P,P) = V1*SINT**2 + V3*COST**2                                   001
     1+2.0D0*V2*SINT*COST                                                001
```

```
      A(P,0) = (V1 - V3)*SINT*COST                                      00
     1         + V2*(COST**2 - SINT**2)                                 00
  200 CONTINUE                                                          00
      IF (IND.EQ.1) GO TO 210                                           00
      GO TO 220                                                         00
  210 IND = 0                                                           00
      GO TO 70                                                          00
  220 IF (THR.GT.RHO) GO TO 230                                         00
      GO TO 240                                                         00
  230 GO TO 50                                                          00
  240 CONTINUE                                                          00
      DO 280 I=1,3                                                      00
      DO 280 J=1,3                                                      00
C     IF ANGLE IS WITHIN +/- 1 MINUTE OF 90 DEGREES CALL IT 90          00
      IF(ABSF(S(I,J)).LT.0.00029D0) GO TO 250                           00
      GO TO 260                                                         00
  250 ANGLE(I,J)=90.0D0                                                 00
      GO TO 280                                                         00
  260 ANGLE(I,J)=ATANF(SQRTF(1.0D0-S(I,J)**2)/S(I,J))*57.2957800        00
      IF(ANGLE(I,J).LT.0.0D0) GO TO 270                                 00
      GO TO 280                                                         00
  270 ANGLE(I,J)=180.0D0+ANGLE(I,J)                                     00
  280 CONTINUE                                                          00
      RETURN                                                            00
      END                                                               00
      SUBROUTINE INTGRL(S,C,GAMMA,CZ,U,ULIM,LLIM,AN,IBF,IAT)            00
      IMPLICIT REAL*8(A-H,O-Z)                                          00
C     ATOMIC INTEGRALS FOR CNDO CALCULATIONS                            00
      DIMENSION CZ(IAT),U(IBF),ULIM(IAT),LLIM(IAT)                      00
      DIMENSION GAMMA(IAT,IAT)                                          00
      DIMENSION C(IAT,3),AN(IAT)                                        00
      INTEGER*4 AN,ULIM,ULK,ULL,CZ,U,CHARGE,ANL,ANK                     00
      DIMENSION         NC(18),LC(9),MC(9),E(3)                         00
      DIMENSION MU(18)                                                  00
      REAL*8 MU,NUM,K1,K2                                               00
      DIMENSION S(IBF,IBF)                                              00
      COMMON/INFO/N,NATOMS,CHARGE,MULTIP                                00
      COMMON/INFO1/NELECS,OCCA,OCCB                                     00
      INTEGER*4 OCCA,OCCB                                               00
      DIMENSION T(9,9),PAIRS(9,9),TEMP(9,9),C1(3),C2(3)                 00
      COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF   00
      INTEGER*4 OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF       00
      INTEGER*4 OFF                                                     00
      DATA OFF/'OFF'/                                                   00
      FLOATF(I)=DFLOAT(I)                                               00
      SQRTF(X)=DSQRT(X)                                                 00
      XMAXOF(I,J)=MAX0(I,J)                                             00
C     DETERMINATION OF SIZE OF AO BASIS IN AND CORE CHARGE CZ           00
 1239 FORMAT (10H IN INTGRL)                                            00
      IF(IONOFF .NE. OFF) PRINT 1239                                    00
C     PRINT 1114, IBF,NATOMS,N,CHARGE,MULTIP,NELECS,OCCA,OCCB           00
 1114 FORMAT(8I10)                                                      00
```

```
 1117 FORMAT(5H PASS)                                                   OC
C1238 PRINT 1239                                                        CO
      N=0                                                               OC
      DO 60 I=1,NATOMS                                                  OC
      LLIM(I) = N+1                                                     OC
      K=1                                                               OC
      IF(AN(I).GT.10) GO TO 10                                          OC
      GO TO 20                                                          OC
   10 N=N+9                                                             OC
      CZ(I)=AN(I)-10                                                    OC
      GO TO 50                                                          CO
   20 IF(AN(I).LT.3) GO TO 40                                           CC
   30 N=N+4                                                             OC
      CZ(I) = AN(I)-2                                                   OC
      GO TO 50                                                          OC
   40 N=N+1                                                             OC
      CZ(I)= AN(I)                                                      OC
   50 CONTINUE                                                          CO
      ULIM(I) = N                                                       CO
   60 CONTINUE                                                          OC
C     * FILL U ARRAY---U(J) IDENTIFIES THE ATOM TO WHICH ORBITAL J IS   OC
C       ATTACHED E.G. ORBITAL 32 ATTACHED TO  ATOM 7, ETC.              CO
      DO 70 K=1,NATOMS                                                  CC
      LLK = LLIM(K)                                                     OC
      ULK = ULIM(K)                                                     CC
      LIM = ULK+1-LLK                                                   OC
      DO 70 I=1,LIM                                                     OC
      J = LLK+I-1                                                       OC
   70 U(J) = K                                                          OC
C       ASSIGNMENT OF ORBITAL EXPONENTS TO ATOMS BY SLATERS RULES       OC
      MU(1)=1.200                                                       OC
      MU(2)=1.700                                                       OC
      NC(1)=1                                                           OC
      NC(2)=1                                                           OC
      DO 80 I=3,10                                                      OC
      NC(I)=2                                                           OC
   80 MU(I)=.32500*DFLOAT(I-1)                                          CO
      DO 90 I=11,18                                                     OC
      NC(I)=3                                                           OC
   90 MU(I)=(.650D0*DFLOAT(I)-4.950D0)/3.D0                             OC
C       ASSIGNMENT OF ANGULAR MOMENTUM QUANTUM NOS. TO ATOMIC ORBITALS  OC
      LC(1)=0                                                           OC
      LC(2)=1                                                           OC
      LC(3)=1                                                           OC
      LC(4)=1                                                           CC
      LC(5)=2                                                           OC
      LC(6)=2                                                           OC
      LC(7)=2                                                           OC
      LC(8)=2                                                           CO
      LC(9)=2                                                           OC
      MC(1)=0                                                           CO
      MC(2)=1                                                           OC
```

```
      MC(3)=-1                                                          CC
      MC(4)=0                                                           CC
      MC(5)=0                                                           CC
      MC(6)=1                                                           CC
      MC(7)=-1                                                          CC
      MC(8)=2                                                           CC
      MC(9)=-2                                                          CC
C     STEP THRU PAIRS OF ATOMS                                          CC
      DO 320 K=1,NATOMS                                                 CC
      DO 320 L=K,NATOMS                                                 CC
      DO 100 I=1,3                                                      CC
      C1(I) = C(K,I)                                                    CC
  100 C2(I) = C(L,I)                                                    CC
C     CALCULATE UNIT VECTOR ALONG INTERATOM AXIS,E                      CC
        CALL RLVEC(R,E,C1,C2)                                           CC
      LLK = LLIM(K)                                                     CC
      LLL = LLIM(L)                                                     CC
      ULK = ULIM(K)                                                     CC
      ULL = ULIM(L)                                                     CC
      NORBK=ULK-LLK+1                                                   CC
      NORBL=ULL-LLL+1                                                   CC
      ANK=AN(K)                                                         CC
      ANL=AN(L)                                                         CC
C     LOOP THRU PAIRS OF BASIS FUNCTIONS, ONE ON EACH ATOM              CC
      DO 200 I=1,NORBK                                                  CC
      DO 200 J=1,NORBL                                                  CC
      IF(K.EQ.L) GO TO 160                                              CC
  110 IF(MC(I).NE.MC(J)) GO TO 150                                      CC
  120 IF(MC(I).LT.0) GO TO 140                                          CC
  130 CONTINUE                                                          CC
      PAIRS(I,J)=SQRTF((MU(ANK)*R)**(2*NC(ANK)+1)*(MU(ANL)*R)**(2*NC(ANLCC
     1)+1)/(FACT(2*NC(ANK))*FACT(2*NC(ANL))))*(-1.D0)**(LC(J)+MC(J))    CC
     2*SS(NC(ANK),LC(I),MC(I),NC(ANL),LC(J),MU(ANK)*R,MU(ANL)*R)         CC
      GO TO 190                                                         CC
  140 PAIRS(I,J)=PAIRS(I-1,J-1)                                         CC
      GO TO 190                                                         CC
  150 PAIRS(I,J)=0.0D0                                                  CC
      GO TO 190                                                         CC
  160 IF(I.EQ.J) GO TO 170                                              CC
      GO TO 180                                                         CC
  170 PAIRS(I,J)=1.000                                                  CC
      GO TO 190                                                         C
  180 PAIRS(I,J)=0.000                                                  C
  190 CONTINUE                                                          C
  200 CONTINUE                                                          C
      LCULK=LC(NORBK)                                                   C
      LCULL=LC(NORBL)                                                   C
      MAXL = XMAXOF(LCULK,LCULL)                                        C
      IF(R.GT.0.00000100) GO TO 220                                     C
  210 GO TO 250                                                         C
C     ROTATE INTEGRALS FROM DIATOMIC BASIS TO MOLECULAR BASIS           C
  220 CALL HARMTR(T,MAXL,E)                                             C
```

```
C
C
C
      DO 230 I=1,NORBK                                                  C
      DO 230 J=1,NORBL                                                  C
      TEMP(I,J) = 0.DO                                                  C
      DO 230 KK=1,NORBL                                                 CC
      TEMP(I,J) = TEMP(I,J)+T(J,KK)*PAIRS(I,KK)                         CC
  230 CONTINUE                                                          CC
      DO 240 I=1,NORBK                                                  CC
      DO 240 J=1,NORBL                                                  CC
      PAIRS(I,J) = 0.DO                                                 CC
      DO 240 KK=1,NORBK                                                 CC
      PAIRS(I,J) = PAIRS(I,J)+T(I,KK)*TEMP(KK,J)                        CC
  240 CONTINUE                                                          CC
C     FILL S MATRIX                                                     CC
  250 CONTINUE                                                          CC
      DO 260 I=1,NORBK                                                  C
      DO 260 J=1,NORBL                                                  .C
  260 S(LLK+I-1,LLL+J-1) = PAIRS(I,J)                                   CC
C     COMPUTATION OF 1-CENTER COULOMB INTEGRALS OVER SLATER S FUNCTIONS CC
      N1=NC(ANK)                                                        CC
      N2=NC(ANL)                                                        CC
      K1=MU(ANK)                                                        CC
      K2=MU(ANL)                                                        CC
      IF(K.NE.L) GO TO 290                                              CC
  270 TERM1 = FACT(2*N1-1)/((2.0DO*K2)**(2*N1))                         CC
      TERM2 = 0.DO                                                      CC
      LIM = 2*N1                                                        CC
      DO 280 J=1,LIM                                                    CC
      NUM =DFLOAT(J)*(2.DO*K1)**(2*N1-J)*FACT(4*N1-J-1)                 CC
      DEN = FACT(2*N1-J)*2.DO*DFLOAT(N1)*(2.DO*(K1+K2))**(4*N1-J)       CC
      TERM2 = TERM2 + NUM/DEN                                           CC
  280 CONTINUE                                                          CC
      GO TO 310                                                         CC
C     COMPUTATION OF 2-CENTER COULOMB INTEGRALS OVER SLATER S FUNCTIONS CC
  290 TERM1=(R/2.DO)**(2*N2)*SS(0.0,0.2*N2-1,0.0.DO,2.DO*K2*R)          CC
      TERM2 = 0.DO                                                      CC
      LIM = 2*N1                                                        CC
      DO 300 J=1,LIM                                                    CC
  300 TERM2 = TERM2+(DFLOAT(J)*(2.DO*K1)**(2*N1-J)*(R/2.DO)**(2*        CC
     1N1-J+2*N2))/(FACT(2*N1-J)*2.DO*DFLOAT(N1))*SS(2*N1-J,0,0,2*N2-1,000
     2,2.DO*K1*R,2.DO*K2*R)                                             CC
  310 GAMMA(K,L) = ((2.DO*K2)**(2*N2+1)/FACT(2*N2))*(TERM1-TERM2)       CC
  320 CONTINUE                                                          CC
C     SYMMETRIZATION OF OVERLAP AND COULOMB INTEGRAL MATRICES           CC
      DO 330 I=1,N                                                      CC
      DO 330 J=I,N                                                      CC
  330 S(J,I) = S(I,J)                                                   CC
      DO 340 I=1,NATOMS                                                 CC
      DO 340 J=1,NATOMS                                                 CC
  340 GAMMA(J,I) = GAMMA(I,J)                                           CC
      IF(IONOFF.EQ.OFF) GO TO 12                                        CC
   13 CONTINUE                                                          CC
      PRINT 350                                                         CC
```

```
  350 FORMAT(24H OVERLAP INTEGRAL MATRIX)                                00
      CALL MATOUT(GAMMA,N,1,IBF,S,IAT)                                   00
      PRINT 370                                                          00
  370 FORMAT(24H COULOMB INTEGRAL MATRIX)                                00
      CALL MATOUT(GAMMA,NATOMS,2,IBF,S,IAT)                              00
   12 CONTINUE                                                           00
      RETURN                                                             00
      END                                                                00
      SUBROUTINE HARMTR(T,MAXL,E)                                        00
      IMPLICIT REAL*8(A-H,O-Z)                                           00
      DIMENSION T(9,9),E(3)                                              00
      COST = E(3)                                                        00
  301 FORMAT (10H IN HARMTR)                                             00
      IF((1.0D0-COST**2).GT.0.00C0C0C0C01D0) GO TO 20                    00
   10 SINT = 0.D0                                                        00
      GO TO 30                                                           00
   20 SINT=DSQRT(1.D0-COST**2)                                           00
   30 CONTINUE                                                           00
      IF(SINT.GT.0.C0C001D0)  GO TO 50                                   00
   40 COSP = 1.D0                                                        00
      SINP = 0.D0                                                        00
      GO TO 70                                                           00
   50 COSP = E(1)/SINT                                                   00
   60 SINP = E(2)/SINT                                                   00
   70 CONTINUE                                                           00
      DO 80 I=1,9                                                        00
      DO 80 J=1,9                                                        00
   80 T(I,J) = 0.D0                                                      00
      T(1,1) =1.D0                                                       00
      IF (MAXL.GT.1) GO TO 100                                           00
   90 IF (MAXL.GT.0) GO TO 110                                           00
      GO TO 120                                                          00
  100 COS2T = COST**2-SINT**2                                            00
      SIN2T = 2.D0*SINT*COST                                             00
      COS2P = COSP**2-SINP**2                                            00
      SIN2P = 2.D0*SINP*COSP                                             00
C     TRANSFORMATION MATRIX ELEMENTS FOR D FUNCTIONS                     00
      SQRT3=DSQRT(3.D0)                                                  00
      T(5,5) = (3.D0*COST**2-1.D0)/2.D0                                  00
      T(5,6) = -SQRT3   *SIN2T/2.D0                                      00
      T(5,8) = SQRT3    *SINT**2/2.D0                                    00
      T(6,5) = SQRT3    *SIN2T*COSP/2.D0                                 00
      T(6,6) = COS2T*COSP                                                00
      T(6,7) = -COST*SINP                                                00
      T(6,8) =-T(6,5)/SQRT3                                              00
      T(6,9) = SINT*SINP                                                 00
      T(7,5) = SQRT3    *SIN2T*SINP/2.D0                                 00
      T(7,6) = COS2T*SINP                                                00
      T(7,7) = COST*COSP                                                 00
      T(7,8) = -T(7,5)/SQRT3                                             00
      T(7,9) = -SINT*COSP                                                00
      T(8,5) = SQRT3    *SINT**2*COS2P/2.D0                              00
```

```
C
C
C
      T(8,6) = SIN2T*COS2P/2.DO                                         00
      T(8,7) = -SINT*SIN2P                                              00
       T(8,8) = (1.DO+COST**2)*COS2P/2.DO                               00
      T(8,9) = -COST*SIN2P                                              00
      T(9,5) = SQRT3   *SINT**2*SIN2P/2.DO                              00
      T(9,6) = SIN2T*SIN2P/2.DO                                         00
      T(9,7) = SINT*COS2P                                               00
      T(9,8) = (1.DO+COST**2)*SIN2P/2.DO                                00
      T(9,9) = COST*COS2P                                               00
  110 CONTINUE                                                          00
C     TRANSFORMATION MATRIX ELEMENTS FOR P FUNCTIONS                    00
      T(2,2) = COST*COSP                                                00
      T(2,3) = -SINP                                                    00
      T(2,4) = SINT*COSP                                                00
      T(3,2) = COST*SINP                                                00
      T(3,3) = COSP                                                     00
      T(3,4) = SINT*SINP                                                00
      T(4,2) = -SINT                                                    00
      T(4,4) = COST                                                     00
  120 CONTINUE                                                          00
      RETURN                                                            00
      END                                                               00
      FUNCTION SS(NN1,LL1,MM,NN2,LL2,ALPHA,BETA)                        00
      IMPLICIT REAL*8(A-H,O-Z)                                          00
C     PROCEDURE FOR CALCULATING REDUCED OVERLAP INTEGRALS               00
      DIMENSION A(17), B(17)                                            00
      INTEGER*4 ULIM                                                    00
      SQRTF(X)=DSQRT(X)                                                 00
      XABSF(I) = IABS(I)                                                00
      XMODF(I,J) = MOD(I,J)                                             00
C 100 PRINT 99                                                          00
   99 FORMAT ( 6H IN SS)                                                00
      N1=NN1                                                            00
      L1=LL1                                                            00
      M=MM                                                              00
      N2=NN2                                                            00
      L2=LL2                                                            00
      PT=(ALPHA-BETA)/2.000                                             00
      P=(ALPHA+BETA)/2.000                                              00
      X=0.DO                                                            00
      M=XABSF(M)                                                        00
C     REVERSE QUANTUM NUMBERS IF NECESSARY                              00
      IF((L2.LT.L1).OR.((L2.EQ.L1).AND.(N2.LT.N1))) GO TO 20            00
   10 GO TO 30                                                          00
   20 K = N1                                                            00
      N1= N2                                                            00
      N2= K                                                             00
      K= L1                                                             00
      L1= L2                                                            00
      L2= K                                                             00
      PT=-PT                                                            00
   30 CONTINUE
```

```
      K = XMODF((N1+N2-L1-L2),2)                                        CC
C     FIND A AND B INTEGRALS                                            CC
      CALL AINTGS(P,N1+N2,A,B)                                          CC
      CALL BINTGS(PT,N1+N2,A,B)                                         CC
      IF((L1.GT.0).OR.(L2.GT.0)) GO TO 60                               CC
C     BEGIN SECTION USED FOR OVERLAP INTEGRALS INVOLVING S FUNCTIONS    CC
C     FIND Z TABLE NUMBER L                                             CC
   40 L = (90-17*N1+N1**2-2*N2)/2                                       CC
      ULIM = N1+N2                                                      CC
      LLIM = 0                                                          CC
      DO 50 I=LLIM,ULIM                                                 CC
      NNI1=N1+N2-I+1                                                    CC
   50 X=X+ZII(I+1,L)*A(I+1)*B(NNI1)/2.D0                                CC
      SS=X                                                              CC
      GO TO 80                                                          CC
C     BEGIN SECTION USED FOR OVERLAPS INVOLVING NON-S FUNCTIONS         CC
C     FIND Y TABLE NUMBER L                                             CC
   60 L=(5-M)*(24-10*M+M**2)*(83-30*M+3*M**2)/120+                      CC
     1  (30-9*L1+L1**2-2*N1)*(28-9*L1+L1**2-2*N1)/8+                    CC
     2  (30-9*L2+L2**2-2*N2)/2                                          CC
      LLIM = 0                                                          CC
      DO 70 I=LLIM,8                                                    CC
      ULIM = 4-MOD(K+I,2)                                               CC
      DO 70 J=LLIM,ULIM                                                 CC
      ITEMP = 2*J+MOD(K+I,2)+1                                          CC
   70 X = X + YII(I+1,J+1,L)*A(I+1)*B(ITEMP)                            CC
      SS=X*(FAC1(M+1)/8.D0)**2*DSQRT(DFLOAT(2*L1+1)*FAC1(L1-M)*         CC
     * DFLOAT(2*L2+1)*FAC1(L2-M)/(4.D0*FAC1(L1+M)*FAC1(L2+M)))          CC
   80 CONTINUE                                                          CC
      RETURN                                                            CC
      END                                                               CC
      FUNCTION ZII(JHI,KHI)                                             CC
      IMPLICIT REAL*8(A-H,O-Z)                                          CC
      DIMENSION ZZ(87), JZZ(87)                                         CC
      DATA JZZ(1)/341/                                                  CC
      DATA JZZ(2)/343/                                                  CC
      DATA JZZ(3)/345/                                                  CC
      DATA JZZ(4)/347/                                                  CC
      DATA JZZ(5)/664/                                                  CC
      DATA JZZ(6)/665/                                                  CC
      DATA JZZ(7)/666/                                                  CC
      DATA JZZ(8)/667/                                                  CC
      DATA JZZ(9)/668/                                                  CC
      DATA JZZ(10)/669/                                                 CC
      DATA JZZ(11)/154/                                                 CC
      DATA JZZ(12)/156/                                                 CC
      DATA JZZ(13)/158/                                                 CC
      DATA JZZ(14)/160/                                                 CC
      DATA JZZ(15)/162/                                                 CC
      DATA JZZ(16)/164/                                                 CC
      DATA JZZ(17)/222/                                                 CC
      DATA JZZ(18)/223/                                                 CC
```

```
C
C
C
      DATA JZZ(19)/224/                                                 00
      DATA JZZ(20)/225/                                                 00
      DATA JZZ(21)/226/                                                 00
      DATA JZZ(22)/227/                                                 00
      DATA JZZ(23)/228/                                                 00
      DATA JZZ(24)/229/                                                 00
      DATA JZZ(25)/230/                                                 00
      DATA JZZ(26)/231/                                                 00
      DATA JZZ(27)/307/                                                 00
      DATA JZZ(28)/308/                                                 00
      DATA JZZ(29)/309/                                                 00
      DATA JZZ(30)/310/                                                 00
      DATA JZZ(31)/312/                                                 00
      DATA JZZ(32)/313/                                                 00
      DATA JZZ(33)/314/                                                 00
      DATA JZZ(34)/315/                                                 00
      DATA JZZ(35)/409/                                                 00
      DATA JZZ(36)/410/                                                 00
      DATA JZZ(37)/411/                                                 00
      DATA JZZ(38)/412/                                                 00
      DATA JZZ(39)/413/                                                 00
      DATA JZZ(40)/414/                                                 00
      DATA JZZ(41)/415/                                                 00
      DATA JZZ(42)/416/                                                 00
      DATA JZZ(43)/528/                                                 00
      DATA JZZ(44)/529/                                                 00
      DATA JZZ(45)/530/                                                 00
      DATA JZZ(46)/532/                                                 00
      DATA JZZ(47)/533/                                                 00
      DATA JZZ(48)/534/                                                 00
      DATA JZZ(49)/562/                                                 00
      DATA JZZ(50)/563/                                                 00
      DATA JZZ(51)/565/                                                 00
      DATA JZZ(52)/566/                                                 00
      DATA JZZ(53)/732/                                                 00
      DATA JZZ(54)/733/                                                 00
      DATA JZZ(55)/545/                                                 00
      DATA JZZ(56)/546/                                                 00
      DATA JZZ(57)/547/                                                 00
      DATA JZZ(58)/548/                                                 00
      DATA JZZ(59)/549/                                                 00
      DATA JZZ(60)/550/                                                 00
      DATA JZZ(61)/579/                                                 00
      DATA JZZ(62)/580/                                                 00
      DATA JZZ(63)/581/                                                 00
      DATA JZZ(64)/582/                                                 00
      DATA JZZ(65)/596/                                                 00
      DATA JZZ(66)/598/                                                 00
      DATA JZZ(67)/443/                                                 00
      DATA JZZ(68)/444/                                                 00
      DATA JZZ(69)/445/                                                 00
      DATA JZZ(70)/446/                                                 00
```

```
C
C
C
C
C
C
      DATA JZZ(71)/447/                                                 00
      DATA JZZ(72)/448/                                                 00
      DATA JZZ(73)/698/                                                 00
      DATA JZZ(74)/699/                                                 00
      DATA JZZ(75)/700/                                                 00
      DATA JZZ(76)/701/                                                 00
      DATA JZZ(77)/324/                                                 00
      DATA JZZ(78)/325/                                                 00
      DATA JZZ(79)/326/                                                 00
      DATA JZZ(80)/327/                                                 00
      DATA JZZ(81)/328/                                                 00
      DATA JZZ(82)/329/                                                 00
      DATA JZZ(83)/330/                                                 00
      DATA JZZ(84)/331/                                                 00
      DATA JZZ(85)/460/                                                 00
      DATA JZZ(86)/462/                                                 00
      DATA JZZ(87)/464/                                                 00
      DATA ZZ(1)/-1.D0/                                                 00
      DATA ZZ(2)/3.D0/                                                  00
      DATA ZZ(3)/-3.D0/                                                 00
      DATA ZZ(4)/1.D0/                                                  00
      DATA ZZ(5)/-1.D0/                                                 00
      DATA ZZ(6)/5.D0/                                                  00
      DATA ZZ(7)/-10.D0/                                                00
      DATA ZZ(8)/10.D0/                                                 00
      DATA ZZ(9)/-5.D0/                                                 00
      DATA ZZ(10)/1.D0/                                                 00
      DATA ZZ(11)/-1.D0/                                                00
      DATA ZZ(12)/5.D0/                                                 00
      DATA ZZ(13)/-10.D0/                                               00
      DATA ZZ(14)/10.D0/                                                00
      DATA ZZ(15)/-5.D0/                                                00
      DATA ZZ(16)/1.D0/                                                 00
      DATA ZZ(17)/-1.D0/                                                00
      DATA ZZ(18)/1.D0/                                                 00
      DATA ZZ(19)/4.D0/                                                 00
      DATA ZZ(20)/-4.D0/                                                00
      DATA ZZ(21)/-6.D0/                                                00
      DATA ZZ(22)/6.D0/                                                 00
      DATA ZZ(23)/4.D0/                                                 00
      DATA ZZ(24)/-4.D0/                                                00
      DATA ZZ(25)/-1.D0/                                                00
      DATA ZZ(26)/1.D0/                                                 00
      DATA ZZ(27)/-1.D0/                                                00
      DATA ZZ(28)/2.D0/                                                 00
      DATA ZZ(29)/2.D0/                                                 00
      DATA ZZ(30)/-6.D0/                                                00
      DATA ZZ(31)/6.D0/                                                 00
      DATA ZZ(32)/-2.D0/                                                00
      DATA ZZ(33)/-2.D0/                                                00
      DATA ZZ(34)/1.D0/                                                 00
      DATA ZZ(35)/-1.D0/                                                00
```

```
C
C
C
C
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C
      DATA ZZ(36)/3.D0/                                                 00
      DATA ZZ(37)/-1.D0/                                                00
      DATA ZZ(38)/-5.D0/                                                00
      DATA ZZ(39)/5.D0/                                                 00
      DATA ZZ(40)/1.D0/                                                 00
      DATA ZZ(41)/-3.D0/                                                00
      DATA ZZ(42)/1.D0/                                                 00
      DATA ZZ(43)/-1.D0/                                                00
      DATA ZZ(44)/4.D0/                                                 00
      DATA ZZ(45)/-5.D0/                                                00
      DATA ZZ(46)/5.D0/                                                 00
      DATA ZZ(47)/-4.D0/                                                00
      DATA ZZ(48)/1.D0/                                                 00
      DATA ZZ(49)/-1.D0/                                                00
      DATA ZZ(50)/2.D0/                                                 00
      DATA ZZ(51)/-2.D0/                                                00
      DATA ZZ(52)/1.D0/                                                 00
      DATA ZZ(53)/-1.D0/                                                00
      DATA ZZ(54)/1.D0/                                                 00
      DATA ZZ(55)/1.D0/                                                 00
      DATA ZZ(56)/-3.D0/                                                00
      DATA ZZ(57)/2.D0/                                                 00
      DATA ZZ(58)/2.D0/                                                 00
      DATA ZZ(59)/-3.D0/                                                00
      DATA ZZ(60)/1.D0/                                                 00
      DATA ZZ(61)/1.D0/                                                 00
      DATA ZZ(62)/-1.D0/                                                00
      DATA ZZ(63)/-1.D0/                                                00
      DATA ZZ(64)/1.D0/                                                 00
      DATA ZZ(65)/-1.D0/                                                00
      DATA ZZ(66)/1.D0/                                                 00
      DATA ZZ(67)/-1.D0/                                                00
      DATA ZZ(68)/1.D0/                                                 00
      DATA ZZ(69)/2.D0/                                                 00
      DATA ZZ(70)/-2.D0/                                                00
      DATA ZZ(71)/-1.D0/                                                00
      DATA ZZ(72)/1.D0/                                                 00
      DATA ZZ(73)/-1.D0/                                                00
      DATA ZZ(74)/3.D0/                                                 00
      DATA ZZ(75)/-3.D0/                                                00
      DATA ZZ(76)/1.D0/                                                 00
      DATA ZZ(77)/1.D0/                                                 00
      DATA ZZ(78)/-1.D0/                                                00
      DATA ZZ(79)/-3.D0/                                                00
      DATA ZZ(80)/3.D0/                                                 00
      DATA ZZ(81)/3.D0/                                                 00
      DATA ZZ(82)/-3.D0/                                                00
      DATA ZZ(83)/-1.D0/                                                00
      DATA ZZ(84)/1.D0/                                                 00
      DATA ZZ(85)/1.D0/                                                 00
      DATA ZZ(86)/-2.D0/                                                00
      DATA ZZ(87)/1.D0/                                                 00
```

```
      IQ = JHI + ((KHI-1)*17)                                          001
      IF((IQ .LT. 154) .OR. (IQ .GT. 733)) GO TO 71                    001
      DO 97 I=1,87                                                     001
      IF(IQ .EQ. JZZ(I)) GO TO 91                                      001
      GO TO 97                                                         001
   91 CONTINUE                                                         001
      ZII=ZZ(I)                                                        001
      GO TO 90                                                         001
   97 CONTINUE                                                         001
   71 CONTINUE                                                         001
      ZII = 0.D0                                                       001
   90 CONTINUE                                                         001
      RETURN                                                           001
      END                                                              001
      FUNCTION YII(JHI,KHI,LHI)                                        001
      IMPLICIT REAL*8(A-H,O-Z)                                         001
      DIMENSION  YY(224), JYY(224)                                     001
      DATA YY(1)/64.D0/                                                001
      DATA YY(2)/64.D0/                                                001
      DATA YY(3)/-64.D0/                                               001
      DATA YY(4)/-128.D0/                                              001
      DATA YY(5)/-64.D0/                                               001
      DATA YY(6)/-128.D0/                                              001
      DATA YY(7)/128.D0/                                               001
      DATA YY(8)/64.D0/                                                001
      DATA YY(9)/128.D0/                                               001
      DATA YY(10)/64.D0/                                               001
      DATA YY(11)/-64.D0/                                              001
      DATA YY(12)/-64.D0/                                              001
      DATA YY(13)/-96.D0/                                              001
      DATA YY(14)/32.D0/                                               001
      DATA YY(15)/-192.D0/                                             001
      DATA YY(16)/192.D0/                                              001
      DATA YY(17)/288.D0/                                              001
      DATA YY(18)/-96.D0/                                              001
      DATA YY(19)/192.D0/                                              001
      DATA YY(20)/-192.D0/                                             001
      DATA YY(21)/96.D0/                                               001
      DATA YY(22)/-288.D0/                                             001
      DATA YY(23)/-192.D0/                                             001
      DATA YY(24)/192.D0/                                              001
      DATA YY(25)/-32.D0/                                              001
      DATA YY(26)/96.D0/                                               001
      DATA YY(27)/-16.D0/                                              001
      DATA YY(28)/16.D0/                                               001
      DATA YY(29)/32.D0/                                               001
      DATA YY(30)/-16.D0/                                              001
      DATA YY(31)/-16.D0/                                              001
      DATA YY(32)/-16.D0/                                              001
      DATA YY(33)/-16.D0/                                              001
      DATA YY(34)/32.D0/                                               001
      DATA YY(35)/16.D0/                                               001
```

```
      DATA YY(36)/-16.D0/                                              00
      DATA YY(37)/48.D0/                                               00
      DATA YY(38)/-48.D0/                                              00
      DATA YY(39)/48.D0/                                               00
      DATA YY(40)/-96.D0/                                              00
      DATA YY(41)/48.D0/                                               00
      DATA YY(42)/-48.D0/                                              00
      DATA YY(43)/-48.D0/                                              00
      DATA YY(44)/96.D0/                                               00
      DATA YY(45)/-48.D0/                                              00
      DATA YY(46)/48.D0/                                               00
      DATA YY(47)/48.D0/                                               00
      DATA YY(48)/-48.D0/                                              00
      DATA YY(49)/96.D0/                                               00
      DATA YY(50)/-48.D0/                                              00
      DATA YY(51)/-48.D0/                                              00
      DATA YY(52)/48.D0/                                               00
      DATA YY(53)/-96.D0/                                              00
      DATA YY(54)/48.D0/                                               00
      DATA YY(55)/-48.D0/                                              00
      DATA YY(56)/48.D0/                                               00
      DATA YY(57)/64.D0/                                               00
      DATA YY(58)/-128.D0/                                             00
      DATA YY(59)/-64.D0/                                              00
      DATA YY(60)/64.D0/                                               00
      DATA YY(61)/128.D0/                                              00
      DATA YY(62)/-64.D0/                                              00
      DATA YY(63)/-96.D0/                                              00
      DATA YY(64)/32.D0/                                               00
      DATA YY(65)/-96.D0/                                              00
      DATA YY(66)/64.D0/                                               00
      DATA YY(67)/32.D0/                                               00
      DATA YY(68)/96.D0/                                               00
      DATA YY(69)/32.D0/                                               00
      DATA YY(70)/64.D0/                                               00
      DATA YY(71)/96.D0/                                               00
      DATA YY(72)/-32.D0/                                              00
      DATA YY(73)/32.D0/                                               00
      DATA YY(74)/-96.D0/                                              00
      DATA YY(75)/-64.D0/                                              00
      DATA YY(76)/-32.D0/                                              00
      DATA YY(77)/-96.D0/                                              00
      DATA YY(78)/-32.D0/                                              00
      DATA YY(79)/-64.D0/                                              00
      DATA YY(80)/96.D0/                                               00
      DATA YY(81)/-32.D0/                                              00
      DATA YY(82)/96.D0/                                               00
      DATA YY(83)/-144.D0/                                             00
      DATA YY(84)/96.D0/                                               00
      DATA YY(85)/-16.D0/                                              00
      DATA YY(86)/144.D0/                                              00
      DATA YY(87)/-48.D0/                                              00
```

```
C
C
C
C
      DATA YY(88)/96.D0/                                                CO
      DATA YY(89)/-96.D0/                                               00
      DATA YY(90)/48.D0/                                                00
      DATA YY(91)/-144.D0/                                              CO
      DATA YY(92)/16.D0/                                                00
      DATA YY(93)/-96.D0/                                               00
      DATA YY(94)/144.D0/                                               0C
      DATA YY(95)/144.D0/                                               00
      DATA YY(96)/-144.D0/                                              00
      DATA YY(97)/-144.D0/                                              00
      DATA YY(98)/144.D0/                                               CC
      DATA YY(99)/144.D0/                                               0C
      DATA YY(100)/-144.D0/                                             CO
      DATA YY(101)/-144.D0/                                             CO
      DATA YY(102)/144.D0/                                              0C
      DATA YY(103)/-16.D0/                                              00
      DATA YY(104)/32.D0/                                               CO
      DATA YY(105)/-16.D0/                                              00
      DATA YY(106)/16.D0/                                               00
      DATA YY(107)/-48.D0/                                              00
      DATA YY(108)/32.D0/                                               00
      DATA YY(109)/-32.D0/                                              00
      DATA YY(110)/48.D0/                                               00
      DATA YY(111)/-16.D0/                                              00
      DATA YY(112)/16.D0/                                               00
      DATA YY(113)/-32.D0/                                              00
      DATA YY(114)/16.D0/                                               00
      DATA YY(115)/64.D0/                                               00
      DATA YY(116)/-64.D0/                                              00
      DATA YY(117)/-64.D0/                                              00
      DATA YY(118)/-64.D0/                                              00
      DATA YY(119)/64.D0/                                               00
      DATA YY(120)/64.D0/                                               00
      DATA YY(121)/64.D0/                                               00
      DATA YY(122)/-64.D0/                                              00
      DATA YY(123)/-96.D0/                                              00
      DATA YY(124)/32.D0/                                               00
      DATA YY(125)/128.D0/                                              00
      DATA YY(126)/96.D0/                                               00
       DATA YY(127)/-96.D0/                                             00
      DATA YY(128)/-128.D0/                                             00
      DATA YY(129)/-32.D0/                                              00
      DATA YY(130)/96.D0/                                               CO
      DATA YY(131)/-64.D0/                                              CO
      DATA YY(132)/-128.D0/                                             00
      DATA YY(133)/64.D0/                                               00
      DATA YY(134)/128.D0/                                              00
      DATA YY(135)/128.D0/                                              00
      DATA YY(136)/64.D0/                                               CO
      DATA YY(137)/-128.D0/                                             00
      DATA YY(138)/-64.D0/                                              00
      DATA YY(139)/-16.D0/                                              CC
```

```
      DATA YY(140)/16.D0/                                              00
      DATA YY(141)/16.D0/                                              00
      DATA YY(142)/-16.D0/                                             00
      DATA YY(143)/16.D0/                                              00
      DATA YY(144)/-16.D0/                                             00
      DATA YY(145)/-16.D0/                                             00
      DATA YY(146)/16.D0/                                              00
      DATA YY(147)/-16.D0/                                             00
      DATA YY(148)/16.D0/                                              00
      DATA YY(149)/16.D0/                                              00
      DATA YY(150)/-16.D0/                                             00
      DATA YY(151)/64.D0/                                              00
      DATA YY(152)/-64.D0/                                             00
      DATA YY(153)/-128.D0/                                            00
      DATA YY(154)/128.D0/                                             00
      DATA YY(155)/64.D0/                                              00
      DATA YY(156)/-64.D0/                                             00
      DATA YY(157)/64.D0/                                              00
      DATA YY(158)/-64.D0/                                             00
      DATA YY(159)/-64.D0/                                             00
      DATA YY(160)/-64.D0/                                             00
      DATA YY(161)/64.D0/                                              00
      DATA YY(162)/64.D0/                                              00
      DATA YY(163)/64.D0/                                              00
      DATA YY(164)/-64.D0/                                             00
      DATA YY(165)/-96.D0/                                             00
      DATA YY(166)/32.D0/                                              00
      DATA YY(167)/-96.D0/                                             00
      DATA YY(168)/160.D0/                                             00
      DATA YY(169)/96.D0/                                              00
      DATA YY(170)/128.D0/                                             00
      DATA YY(171)/-96.D0/                                             00
      DATA YY(172)/96.D0/                                              00
      DATA YY(173)/-128.D0/                                            00
      DATA YY(174)/-96.D0/                                             00
      DATA YY(175)/-160.D0/                                            00
      DATA YY(176)/96.D0/                                              00
      DATA YY(177)/-32.D0/                                             00
      DATA YY(178)/96.D0/                                              00
      DATA YY(179)/-96.D0/                                             00
      DATA YY(180)/32.D0/                                              00
      DATA YY(181)/32.D0/                                              00
      DATA YY(182)/32.D0/                                              00
      DATA YY(183)/96.D0/                                              00
      DATA YY(184)/32.D0/                                              00
      DATA YY(185)/-32.D0/                                             00
      DATA YY(186)/-96.D0/                                             00
      DATA YY(187)/-32.D0/                                             00
      DATA YY(188)/-32.D0/                                             00
      DATA YY(189)/-32.D0/                                             00
      DATA YY(190)/96.D0/                                              00
      DATA YY(191)/48.D0/                                              00
```

```
C
C
C
      DATA YY(192)/-48.D0/                                              00
      DATA YY(193)/-48.D0/                                              00
      DATA YY(194)/48.D0/                                               00
      DATA YY(195)/-48.D0/                                              00
      DATA YY(196)/48.D0/                                               00
      DATA YY(197)/48.D0/                                               00
      DATA YY(198)/-48.D0/                                              00
      DATA YY(199)/48.D0/                                               00
      DATA YY(200)/-48.D0/                                              00
      DATA YY(201)/-48.D0/                                              00
      DATA YY(202)/48.D0/                                               00
      DATA YY(203)/-64.D0/                                              00
      DATA YY(204)/64.D0/                                               00
      DATA YY(205)/64.D0/                                               00
      DATA YY(206)/-64.D0/                                              00
      DATA YY(207)/-64.D0/                                              00
      DATA YY(208)/-64.D0/                                              00
      DATA YY(209)/64.D0/                                               00
      DATA YY(210)/64.D0/                                               00
      DATA YY(211)/64.D0/                                               00
      DATA YY(212)/64.D0/                                               00
      DATA YY(213)/-64.D0/                                              00
      DATA YY(214)/-64.D0/                                              00
      DATA YY(215)/16.D0/                                               00
      DATA YY(216)/-16.D0/                                              00
      DATA YY(217)/-16.D0/                                              00
      DATA YY(218)/16.D0/                                               00
      DATA YY(219)/16.D0/                                               00
      DATA YY(220)/-16.D0/                                              00
      DATA YY(221)/-64.D0/                                              00
      DATA YY(222)/64.D0/                                               00
      DATA YY(223)/64.D0/                                               00
      DATA YY(224)/-64.D0/                                              00
      DATA JYY(1)/7039/                                                 00
      DATA JYY(2)/7040/                                                 00
      DATA JYY(3)/7049/                                                 00
      DATA JYY(4)/7032/                                                 00
      DATA JYY(5)/7041/                                                 00
      DATA JYY(6)/7033/                                                 00
      DATA JYY(7)/7042/                                                 00
      DATA JYY(8)/7025/                                                 00
      DATA JYY(9)/7034/                                                 00
      DATA JYY(10)/7026/                                                00
      DATA JYY(11)/7035/                                                00
      DATA JYY(12)/7027/                                                00
      DATA JYY(13)/6904/                                                00
      DATA JYY(14)/6913/                                                00
      DATA JYY(15)/6896/                                                00
      DATA JYY(16)/6905/                                                00
      DATA JYY(17)/6906/                                                00
      DATA JYY(18)/6915/                                                00
      DATA JYY(19)/6889/                                                00
```

```
C
C
C
      DATA JYY(20)/6907/                                                00
      DATA JYY(21)/6890/                                                00
      DATA JYY(22)/6899/                                                00
      DATA JYY(23)/6891/                                                00
      DATA JYY(24)/6900/                                                00
      DATA JYY(25)/6892/                                                00
      DATA JYY(26)/6901/                                                00
      DATA JYY(27)/2854/                                                00
      DATA JYY(28)/2663/                                                00
      DATA JYY(29)/2847/                                                00
      DATA JYY(30)/2856/                                                00
      DATA JYY(31)/2865/                                                00
      DATA JYY(32)/2840/                                                00
      DATA JYY(33)/2849/                                                00
      DATA JYY(34)/2858/                                                00
      DATA JYY(35)/2842/                                                00
      DATA JYY(36)/2851/                                                00
      DATA JYY(37)/2710/                                                00
      DATA JYY(38)/2719/                                                00
      DATA JYY(39)/2711/                                                00
      DATA JYY(40)/2720/                                                00
      DATA JYY(41)/2729/                                                00
      DATA JYY(42)/2703/                                                00
      DATA JYY(43)/2712/                                                00
      DATA JYY(44)/2721/                                                00
      DATA JYY(45)/2704/                                                00
      DATA JYY(46)/2713/                                                00
      DATA JYY(47)/2722/                                                00
      DATA JYY(48)/2731/                                                00
      DATA JYY(49)/2705/                                                00
      DATA JYY(50)/2714/                                                00
      DATA JYY(51)/2723/                                                00
      DATA JYY(52)/2706/                                                00
      DATA JYY(53)/2715/                                                00
      DATA JYY(54)/2724/                                                00
      DATA JYY(55)/2707/                                                00
      DATA JYY(56)/2716/                                                00
      DATA JYY(57)/5329/                                                00
      DATA JYY(58)/5322/                                                00
      DATA JYY(59)/5340/                                                00
      DATA JYY(60)/5315/                                                00
      DATA JYY(61)/5333/                                                00
      DATA JYY(62)/5326/                                                00
      DATA JYY(63)/5185/                                                00
      DATA JYY(64)/5194/                                                00
      DATA JYY(65)/5186/                                                00
      DATA JYY(66)/5195/                                                00
      DATA JYY(67)/5204/                                                00
      DATA JYY(68)/5178/                                                00
      DATA JYY(69)/5187/                                                00
      DATA JYY(70)/5196/                                                00
      DATA JYY(71)/5179/                                                00
```

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C
C
C
      DATA JYY(72)/5138/                                                00
      DATA JYY(73)/5197/                                                00
      DATA JYY(74)/5206/                                                00
      DATA JYY(75)/5180/                                                00
      DATA JYY(76)/5189/                                                00
      DATA JYY(77)/5198/                                                00
      DATA JYY(78)/5181/                                                00
      DATA JYY(79)/5190/                                                00
      DATA JYY(80)/5199/                                                00
      DATA JYY(81)/5182/                                                00
      DATA JYY(82)/5191/                                                00
      DATA JYY(83)/4375/                                                00
      DATA JYY(84)/4384/                                                00
      DATA JYY(85)/4393/                                                00
      DATA JYY(86)/4368/                                                00
      DATA JYY(87)/4386/                                                00
      DATA JYY(88)/4395/                                                00
      DATA JYY(89)/4370/                                                00
      DATA JYY(90)/4379/                                                00
      DATA JYY(91)/4397/                                                00
      DATA JYY(92)/4372/                                                00
      DATA JYY(93)/4381/                                                00
      DATA JYY(94)/4390/                                                00
      DATA JYY(95)/1900/                                                00
      DATA JYY(96)/1909/                                                00
      DATA JYY(97)/1893/                                                00
      DATA JYY(98)/1920/                                                00
      DATA JYY(99)/1895/                                                00
      DATA JYY(100)/1922/                                               00
      DATA JYY(101)/1906/                                               00
      DATA JYY(102)/1915/                                               00
      DATA JYY(103)/955/                                                00
      DATA JYY(104)/964/                                                00
      DATA JYY(105)/973/                                                00
      DATA JYY(106)/948/                                                00
      DATA JYY(107)/966/                                                00
      DATA JYY(108)/975/                                                00
      DATA JYY(109)/950/                                                00
      DATA JYY(110)/959/                                                00
      DATA JYY(111)/977/                                                00
      DATA JYY(112)/952/                                                00
      DATA JYY(113)/961/                                                00
      DATA JYY(114)/970/                                                00
      DATA JYY(115)/8155/                                               00
      DATA JYY(116)/8156/                                               00
      DATA JYY(117)/8165/                                               00
      DATA JYY(118)/8148/                                               00
      DATA JYY(119)/8157/                                               00
      DATA JYY(120)/8149/                                               00
      DATA JYY(121)/8158/                                               00
      DATA JYY(122)/8150/                                               00
      DATA JYY(123)/8020/                                               00
```

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      DATA JYY(124)/8029/                                              00
      DATA JYY(125)/8021/                                              00
      DATA JYY(126)/8013/                                              00
      DATA JYY(127)/8031/                                              00
      DATA JYY(128)/8014/                                              00
      DATA JYY(129)/8015/                                              00
      DATA JYY(130)/8024/                                              00
      DATA JYY(131)/7084/                                              00
      DATA JYY(132)/7076/                                              00
      DATA JYY(133)/7085/                                              00
      DATA JYY(134)/7086/                                              00
      DATA JYY(135)/7069/                                              00
      DATA JYY(136)/7070/                                              00
      DATA JYY(137)/7079/                                              00
      DATA JYY(138)/7071/                                              00
      DATA JYY(139)/3205/                                              00
      DATA JYY(140)/3214/                                              00
      DATA JYY(141)/3206/                                              00
      DATA JYY(142)/3215/                                              00
      DATA JYY(143)/3198/                                              00
      DATA JYY(144)/3216/                                              00
      DATA JYY(145)/3199/                                              00
      DATA JYY(146)/3217/                                              00
      DATA JYY(147)/3200/                                              00
      DATA JYY(148)/3209/                                              00
      DATA JYY(149)/3201/                                              00
      DATA JYY(150)/3210/                                              00
      DATA JYY(151)/7579/                                              00
      DATA JYY(152)/7580/                                              00
      DATA JYY(153)/7572/                                              00
      DATA JYY(154)/7573/                                              00
      DATA JYY(155)/7565/                                              00
      DATA JYY(156)/7566/                                              00
      DATA JYY(157)/5680/                                              00
      DATA JYY(158)/5681/                                              00
      DATA JYY(159)/5673/                                              00
      DATA JYY(160)/5691/                                              00
      DATA JYY(161)/5674/                                              00
      DATA JYY(162)/5692/                                              00
      DATA JYY(163)/5684/                                              00
      DATA JYY(164)/5685/                                              00
      DATA JYY(165)/7435/                                              00
      DATA JYY(166)/7444/                                              00
      DATA JYY(167)/7436/                                              00
      DATA JYY(168)/7445/                                              00
      DATA JYY(169)/7428/                                              00
      DATA JYY(170)/7437/                                              00
      DATA JYY(171)/7446/                                              00
      DATA JYY(172)/7429/                                              00
      DATA JYY(173)/7438/                                              00
      DATA JYY(174)/7447/                                              00
      DATA JYY(175)/7430/                                              00
```

```
      DATA JYY(176)/7439/                                                   00
      DATA JYY(177)/7431/                                                   00
      DATA JYY(178)/7440/                                                   00
      DATA JYY(179)/5545/                                                   00
      DATA JYY(180)/5554/                                                   00
      DATA JYY(181)/5546/                                                   00
      DATA JYY(182)/5555/                                                   00
      DATA JYY(183)/5538/                                                   00
      DATA JYY(184)/5556/                                                   00
      DATA JYY(185)/5539/                                                   00
      DATA JYY(186)/5557/                                                   00
      DATA JYY(187)/5540/                                                   00
      DATA JYY(188)/5549/                                                   00
      DATA JYY(189)/5541/                                                   00
      DATA JYY(190)/5550/                                                   00
      DATA JYY(191)/3070/                                                   00
      DATA JYY(192)/3079/                                                   00
      DATA JYY(193)/3071/                                                   00
      DATA JYY(194)/3080/                                                   00
      DATA JYY(195)/3063/                                                   00
      DATA JYY(196)/3081/                                                   00
      DATA JYY(197)/3064/                                                   00
      DATA JYY(198)/3082/                                                   00
      DATA JYY(199)/3065/                                                   00
      DATA JYY(200)/3074/                                                   00
      DATA JYY(201)/3066/                                                   00
      DATA JYY(202)/3075/                                                   00
      DATA JYY(203)/8200/                                                   00
      DATA JYY(204)/8201/                                                   00
      DATA JYY(205)/8193/                                                   00
      DATA JYY(206)/8194/                                                   00
      DATA JYY(207)/7615/                                                   00
      DATA JYY(208)/7616/                                                   00
      DATA JYY(209)/7625/                                                   00
      DATA JYY(210)/7608/                                                   00
      DATA JYY(211)/7617/                                                   00
      DATA JYY(212)/7609/                                                   00
      DATA JYY(213)/7618/                                                   00
      DATA JYY(214)/7610/                                                   00
      DATA JYY(215)/3250/                                                   00
      DATA JYY(216)/3259/                                                   00
      DATA JYY(217)/3243/                                                   00
      DATA JYY(218)/3261/                                                   00
      DATA JYY(219)/3245/                                                   00
      DATA JYY(220)/3254/                                                   00
      DATA JYY(221)/5725/                                                   00
      DATA JYY(222)/5718/                                                   00
      DATA JYY(223)/5736/                                                   00
      DATA JYY(224)/5729/                                                   00
      IQ = ((LHI-1)*45) + (9*(KHI-1)) + JHI                                 00
      IF((IQ .LT. 948) .OR. (IQ .GT. 8201))  GO TO 61                       00
      DO 87 I=1,224                                                         00
```

```
C
C
C
      IF(IO .EQ. JYY(I)) GO TO 81                                       00
      GO TO 87                                                          00
   81 CONTINUE                                                          00
      YII = YY(I)                                                       00
      GOTO  90                                                          00
   87 CONTINUE                                                          00
   61 CONTINUE                                                          00
      YII = 0.DO                                                        00
   90 CONTINUE                                                          00
       RETURN                                                           00
       END                                                              00
      FUNCTION FACT(N)                                                  00
      IMPLICIT REAL*8(A-H,O-Z)                                          00
      INTEGER*4 N,I,PRODT                                               00
      FLOATF(I)=DFLOAT(I)                                               00
C 100 PRINT 99                                                          00
   99 FORMAT ( 8H IN FACT)                                              00
      PRODT = 1                                                         00
      IF(N.EQ.0) GO TO 10                                               00
      GO TO 20                                                          00
   10 GO TO 40                                                          00
   20 DO 30 I=1,N                                                       00
   30 PRODT = PRODT*I                                                   00
   40 FACT=FLOATF(PRODT)                                                00
      RETURN                                                            00
      END                                                               00
      SUBROUTINE BINTGS(X,K,A,B)                                        00
      IMPLICIT REAL*8(A-H,O-Z)                                          00
C     FILLS ARRAY OF B-INTEGRALS. NOTE THAT B(I) IS B(I-1) IN THE       00
C     USUAL NOTATION                                                    00
C     FOR X.GT.3                        EXPONENTIAL FORMULA IS USED     00
C     FOR 2.LT.X.LE.3 AND K.LE.10       EXPONENTIAL FORMULA IS USED     00
C     FOR 2.LT.X.LE.3 AND K.GT.10       15 TERM SERIES IS USED          00
C     FOR 1.LT.X .E.2 AND K.LE.7        EXPONENTIAL FORMULA IS USED     00
C     FOR 1.LT.X.LE.2 AND K.GT.7        12 TERM SERIES IS USED          00
C     FOR .5.LT.X.LE.1 AND K.LE.5       EXPONENTIAL FORMULA IS USED     00
C     FOR .5.LT.X.LE.1 AND K.GT.5        7 TERM SERIES IS USED          00
C     FOR X.LE..5                        6 TERM SERIES IS USED          00
C     ******* ***************************************************************00
      DIMENSION A(17), B(17)                                            00
      ABSF(X)=DABS(X)                                                   00
      EXPF(X)=DEXP(X)                                                   00
C1234 PRINT 99                                                          00
   99 FORMAT (10H IN BINTGS)                                            00
      IO=0                                                              00
      ABSX=ABSF(X)                                                      00
      IF(ABSX.GT.3.0DO) GO TO 120                                       00
   10 IF(ABSX.GT.2.0DO) GO TO 20                                        00
      GO TO 40                                                          00
   20 IF(K.LE.10) GO TO 120                                             00
   30 LAST=15                                                           00
      GO TO 140                                                         00
```

```
      40 IF(ABSX.GT.1.0D0) GO TO 50                                          00
         GO TO 70                                                            00
      50 IF(K.LE.7) GO TO 120                                                00
      60 LAST=12                                                             00
         GO TO 140                                                           00
      70 IF(ABSX.GT.0.5D0) GO TO 80                                          00
         GO TO 100                                                           00
      80 IF(K.LE.5) GO TO 120                                                00
      90 LAST=7                                                              00
         GO TO 140                                                           00
     100 IF(ABSX .GT. 0.000001D0)  GO TO 110                                 00
         GO TO 170                                                           00
     110 LAST=6                                                              00
         GO TO 140                                                           00
     120 EXPX=EXPF(X)                                                        00
         EXPMX=1.D0/EXPX                                                     00
         B(1)=(EXPX-EXPMX)/X                                                 00
         DO 130 I=1,K                                                        00
     130 B(I+1)=(DFLOAT(I)*B(I)+(-1.0D0)**I*EXPX-EXPMX)/X                    00
         GO TO 190                                                           00
     140 DO 160 I=IO,K                                                       00
         Y=0.CD0                                                             00
         DO 150 M=IO,LAST                                                    00
     150 Y=Y+(-X)**M*(1.0D0-(-1.CD0)**(M+I+1))/(FACT(M)*DFLOAT(M+I+1))       00
     160 B(I+1)=Y                                                            00
         GO TO 190                                                           00
     170 DO 180 I=IO,K                                                       00
         FNUM=1.0D0-(-1.0D0)**(I+1)                                          00
         FDEN=DFLOAT(I)+1.0D0                                                00
C        FDEN = FLOAT(I)+1.                                                  00
         B(I+1) = FNUM/FDEN                                                  00
     180 CONTINUE                                                            00
     190 RETURN                                                              00
          END                                                                00
         SUBROUTINE AINTGS(X,K,A,B)                                          00
         IMPLICIT REAL*8(A-H,O-Z)                                            00
         DIMENSION A(17), B(17)                                              00
         EXPF(X)=DEXP(X)                                                     00
C    100 PRINT 99                                                            00
      99 FORMAT (10H IN AINTGS)                                              00
         A(1) = EXPF(-X)/X                                                   00
         DO 10  I=1,K                                                        00
      10 A(I+1) =(A(I)*I + EXPF(-X))/X                                       00
         RETURN                                                              00
         END                                                                 00
          SUBROUTINE MATOUT(GAMMA,N,MATOP,IBF,A,IAT)                         00
         IMPLICIT REAL*8(A-H,O-Z)                                            00
         DIMENSION A(IBF,IBF)                                                00
          DIMENSION GAMMA(IAT,IAT)                                           00
           DIMENSION NUM(50)                                                 00
         DO 10 I=1,N                                                         00
      10 NUM(I)=I                                                            00
```

```
C
C
C
      DO 80 M=1,N,11                                                    00
      K=M+10                                                            00
      IF(K.GT.N) GO TO 20                                               00
      GO TO 30                                                          00
   20 K=N                                                               00
   30 CONTINUE                                                          00
      PRINT 40,(NUM(J),J=M,K)                                           00
   40 FORMAT(//,7X,11(4X,I2,3X),//)                                     00
      DO 60 I=1,N                                                       00
      IF(MATOP .EQ. 1)  PRINT 50,I,(A(I,J),J=M,K)                       00
      IF(MATOP .EQ. 2)  PRINT 50, I, (GAMMA(I,J),J=M,K)                 00
   50 FORMAT(1X,I2,4X,11F9.4)                                           00
   60 CONTINUE                                                          00
      PRINT 70                                                          00
   70 FORMAT(//)                                                        00
   80 CONTINUE                                                          00
      RETURN                                                            00
      END                                                               00
      SUBROUTINE RLVEC(R,E,C1,C2)                                       00
      IMPLICIT REAL*8(A-H,O-Z)                                          00
      DIMENSION C1(3), C2(3)                                            00
      DIMENSION E(3)                                                    00
      SQRTF(X)=DSQRT(X)                                                 00
C 100 PRINT 99                                                          00
   99 FORMAT ( 9H IN RLVEC)                                             00
      X = 0.D0                                                          00
      DO 10 I=1,3                                                       00
      E(I) = C2(I)-C1(I)                                                00
      X = X+E(I)**2                                                     00
   10 CONTINUE                                                          00
      R = SQRTF(X)                                                      00
      DO 40 I=1,3                                                       00
      IF(R.GT.0.000001D0) GO TO 30                                      00
   20 GO TO 40                                                          00
   30 F(I) =E(I)/R                                                      00
   40 CONTINUE                                                          00
C     PRINT 98                                                          00
   98 FORMAT(14H LEAVING RLVEC)                                         00
      RETURN                                                            00
      END                                                               00
      SUBROUTINE HUCKCL(PDIAG,Q,G,GAMMA,A,C,AN,IAT,IBF,CZ,U,ULIM,LLIM,XX00
     *XX,NUM)                                                           00
      IMPLICIT REAL*8(A-H,O-Z)                                          00
      DIMENSION NUM(IBF)                                                00
      DIMENSION G(IAT,IAT),GAMMA(IAT,IAT)                               00
      DIMENSION PDIAG(IBF), Q(IBF)                                      00
      DIMENSION XXX(IBF)                                                00
C     EXTENDED HUCKEL THEORY FOR CLOSED SHELLS                          00
C     OVERLAPS ARE IN MATRIX A, COULOMB INTEGRALS (GAMMA) ARE IN MATRIX 00
      DIMENSION BETAC(18)                                               00
      DIMENSION C(IAT,3), AN(IAT)                                       00
      DIMENSIONA(IBF,IBF)                                               00
```

```
      COMMON/INFO/U,NATOMS,CHARGE,MULTIP                                CO
       DIMENSION CZ(IAT),U(IBF),ULIM(IAT),LLIM(IAT)                     CO
       COMMON/INFO1/NELECS,OCCA,OCCB                                    CO
      COMMON/JRCOV/IRCOV,IJC,IDISK,IRCCC,JDISK                          CO
       COMMON/HELLO/ENERGY                                              CO
      COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF   CO
      INTEGER*4 OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF       CO
      INTEGER*4 OFF                                                     CO
        DIMENSION ENEG(18,3)                                            CO
      INTEGER*4 CHARGE,OCCA,OCCB,UL,AN,CZ,U,ULIM,ANI                    CO
      DIMENSION G1(18),F2(18)                                           CO
      DATA OFF/'OFF'/                                                   CO
      FLOATF(I)=DFLOAT(I)                                               CO
      ABSF(X)=DABS(X)                                                   CO
      G1(3)=.092012      DO                                             CO
      G1(4)=.1407        DO                                             CO
      G1(5)=.199265      DO                                             CO
      G1(6)=.267708      DO                                             CO
      G1(7)=.346029      DO                                             CO
      G1(8)=.43423       DO                                             CO
      G1(9)=.532305      DO                                             CO
      F2(3)=.049865      DO                                             CO
 1716 FORMAT(10H IN HUCKCL)                                             CO
      F2(4)=.089125      DO                                             CO
      F2(5)=.13041       DO                                             CO
      F2(6)=.17372       DO                                             CO
      F2(7)=.219055      DO                                             CO
      F2(8)=.266415      DO                                             CO
      F2(9)=.31580       DO                                             CO
      ENEG(1,1)=7.1761   DO                                             CO
      ENEG(3,1)=3.1055   DO                                             CO
      ENEG(3,2)=1.258    DO                                             CO
      ENEG(4,1)=5.94557  DO                                             CO
      ENEG(4,2)=2.563    DO                                             CO
      ENEG(5,1)=9.59407  DO                                             CO
      ENEG(5,2)=4.001    DO                                             CO
      ENEG(6,1)=14.051   DO                                             CO
      ENEG(6,2)=5.572    DO                                             CO
      ENEG(7,1)=19.31637DO                                              CO
      ENEG(7,2)=7.275    DO                                             CO
      ENEG(8,1)=25.39017DO                                              CO
      ENEG(8,2)=9.111    DO                                             CO
      ENEG(9,1)=32.2724  DO                                             CO
      ENEG(9,2)=11.08    DO                                             CO
      ENEG(11,1)=2.804   DO                                             CO
      ENEG(11,2)=1.302   DO                                             CO
      ENEG(11,3)=0.150   DO                                             CO
      ENEG(12,1)=5.1254  DO                                             CO
      ENEG(12,2)=2.0516  DO                                             CO
      ENEG(12,3)=0.16195DO                                              CO
      ENEG(13,1)=7.7706  DO                                             CO
      ENEG(13,2)=2.9951  DO                                             CO
```

```
C
C
C
      ENEG(13,3)=0.22425D0                                                  00
      ENEG(14,1)=10.C327D0                                                  00
      ENEG(14,2)=4.1325 D0                                                  00
      ENEG(14,3)=0.337  D0                                                  00
      ENEG(15,1)=14.0327D0                                                  00
      ENEG(15,2)=5.4638 D0                                                  00
      ENEG(15,3)=0.500  D0                                                  00
      ENEG(16,1)=17.6496D0                                                  00
      ENEG(16,2)=6.989  D0                                                  00
      ENEG(16,3)=0.71325D0                                                  00
      ENEG(17,1)=21.5906D0                                                  00
      ENEG(17,2)=8.7081 D0                                                  00
      ENEG(17,3)=0.97695D0                                                  00
      BETA0(1)= -9.     D0                                                  00
      BETA0(3)= -9.     D0                                                  00
      BETA0(4)= -13.    D0                                                  00
      BETA0(5)= -17.    D0                                                  00
      BETA0(6)= -21.    D0                                                  00
      BETA0(7)= -25.    D0                                                  00
      BETA0(8)= -31.    D0                                                  00
      BETA0(9)= -39.    D0                                                  00
      BETA0(11)=-7.7203 D0                                                  00
      BETA0(12)=-9.4471 D0                                                  00
      BETA0(13)=-11.3011D0                                                  00
      BETA0(14)=-13.065 D0                                                  00
      BETA0(15)=-15.070 D0                                                  00
      BETA0(16)=-18.150 D0                                                  00
      BETA0(17)=-22.330 D0                                                  00
C     FIND NELECS AND FILL H CORE(DIAGONAL) WITH (I+A)/2                    00
      NELECS=0                                                              00
      DO 60 I=1,NATOMS                                                      00
      NELECS=NELECS+CZ(I)                                                   00
      LL =LLIM(I)                                                           00
      UL =ULIM(I)                                                           00
      ANI=AN(I)                                                             00
      L=0                                                                   00
      DO 50 J=LL,UL                                                         00
      L=L+1                                                                 00
      IF(L.EQ.1) GO TO 10                                                   00
      GO TO 20                                                              00
   10 A(J,J)  =-ENEG(ANI,1)/27.21D0                                         00
      GO TO 50                                                              00
   20 IF(L.LT.5) GO TO 40                                                   00
   30 A(J,J)=-ENEG(ANI,3)/27.21D0                                           00
      GO TO 50                                                              00
   40 A(J,J)=-ENEG(ANI,2)/27.21D0                                           00
   50 CONTINUE                                                              00
   60 CONTINUE                                                              00
      NELECS=NELECS-CHARGE                                                  00
      OCCA=NELECS/2                                                         00
C     FORM HUCKEL HAMILTONIAN IN A (OFF DIAGONAL TWO CENTER TERMS)          00
      DO 90 I=2,N                                                           00
```

```
      K=U(I)                                                            CC
      L=AN(K)                                                           CC
      UL=I-1                                                            CC
      DO 90 J=1,UL                                                      CC
      KK=U(J)                                                           CC
      LL=AN(KK)                                                         CC
      IF((L.GT.9).OR.(LL.GT.9)) GO TO 70                                CC
      GO TO 80                                                          CC
   70 A(I,J)=0.75D0*A(I,J)*(BETA0(L)+BETA0(LL))/54.42D0                 CC
      A(J,I)=A(I,J)                                                     CC
      GO TO 90                                                          CC
   80 A(I,J)=A(I,J)*(BETA0(L)+BETA0(LL))/54.42D0                        CC
      A(J,I)=A(I,J)                                                     CC
   90 CONTINUE                                                          CC
      DO 100 I=1,N                                                      CC
  100 Q(I)=A(I,I)                                                       CC
      DO 9998 IQ=1,N                                                    CC
      DO 9998 JQ=1,N                                                    CC
       A(IQ,JQ) = A(JQ,IQ)                                              CC
 9998 CONTINUE                                                          CC
C     WRITE LOWER TRIANGLE OF  CORE HAMILTONIAN ON DISK FILE 10         CC
C     WITH THE DIAGONAL ELEMENTS                                        CC
      REWIND JDISK                                                      CC
      WRITE (JDISK) ((A(IERT,KERT),KERT=1,IERT),IERT=1,N)               CC
 3334 FORMAT(1X,F10.5)                                                  CC
      IF((IJC .EQ. 1) .OR. (IRCCC.EQ. 0) )GO TO 98                      CC
      REWIND IDISK                                                      CC
      READ(IDISK)  ((A(IJQ,JJQ),IJQ=1,N),JJQ=1,N)                       CC
      PRINT 8013                                                        CC
      GO TO 96                                                          CC
   98 CONTINUE                                                          CC
 8013 FORMAT(33H READING DENSITY MATRIX FROM DISK)                      CC
      CALL EIGN(N,0,C00001D0,IBF,A)                                     CC
C     EIGENVECTORS (IN B) ARE CONVERTED INTO DENSITY MATRIX (IN B)      CC
      CALL DMAT(PDIAG,XXX,A,C,N,OCCA,IBF,AN,IAT,CZ,U,ULIM,LLIM,NUM)     CC
C     ADD V(AB) TO HCORE--CNDO                                          CC
   96 CONTINUE                                                          CC
      DO  170  I=1,N                                                    CC
      J=U(I)                                                            CC
      Q(I)=Q(I)  +0.5D0*G(J,J)                                          CC
      DO 160 K=1,NATOMS                                                 CC
  160 Q(I)=Q(I)-DFLOAT(CZ(K))*G(J,K)                                    CC
  170 CONTINUE                                                          CC
C     EXIT SEGMENT IF ONLY CNDO APPROXIMATIONS ARE DESIRED              CC
      IF(OPTION.EQ.INDO) GO TO 180                                      CC
      GO TO 290                                                         CC
C     INDO MODIFICATION (CORRECTION TO U(I,I) )                         CC
  180 DO 280 I=1,NATOMS                                                 CC
      K=AN(I)                                                           CC
      J=LLIM(I)                                                         CC
      IF((K.GT.1).AND.(K.LT.10)) GO TO 190                              CC
      GO TO 280                                                         CC
```

```
  190 IF(K.GT.3) GO TO 200                                                  00
      GO TO 210                                                             00
  200 Q(J)=Q(J)   +(DFLOAT(CZ(I))-1.5D0)*G1(K)/6.D0                         00
  210 IF(K.EQ.3) GO TO 220                                                  00
      GO TO 230                                                             00
  220 TEMP=G1(K)/12.D0                                                      00
      GO TO 260                                                             00
  230 IF(K.EQ.4) GO TO 240                                                  00
      GO TO 250                                                             00
  240 TEMP=G1(K)/4.D0                                                       00
      GO TO 260                                                             00
  250 TEMP=G1(K)/3.D0+(DFLOAT(CZ(I))-2.5D0)*2.D0*F2(K)/25.D0                00
  260 CONTINUE                                                              00
      DO 270 L=1,3                                                          00
  270 Q(J+L)=Q(J+L)+TEMP                                                    00
  280 CONTINUE                                                              00
  290 CONTINUE                                                              00
      DO 310 I=1,N                                                          00
      DO 300 J=I,N                                                          00
  300 A(J,I)=A(I,J)                                                         00
  310 CONTINUE                                                              00
      RETURN                                                                00
      END                                                                   00
        SUBROUTINE SCFCL(G,GAMMA,A,C,AN,IAT,IBF,PDIAG,Q,CZ,U,ULIM,LLIM,XXX  00
     *XX,NUM)                                                               00
      IMPLICIT REAL*8(A-H,O-Z)                                              00
       DIMENSION XXX(IBF)                                                   00
      DIMENSION NUM(IBF)                                                    00
      DIMENSION PDIAG(IBF),Q(IBF)                                           00
       DIMENSION C(IAT,3), AN(IAT)                                          00
C     CNDO/INDO CLOSED SHELL SCF SEGMENT                                    00
C     GAMMA MATRIX CONTAINED IN G, CORE HAMILTONIAN CONTAINED IN Q AND      00
C     UPPER TRIANGLE OF A, AND INITIAL DENSITY MATRIX CONTAINED IN B        00
C     OPTIONS   CNDO OR INDO                                                00
       COMMON/HELLO/ENERGY                                                  00
       DIMENSION G(IAT,IAT), GAMMA(IAT,IAT)                                 00
      DIMENSION A(IBF,IBF)                                                  00
       COMMON/INFO/N,NATOMS,CHARGE,MULTIP                                   00
       COMMON/INFO1/NELECS,OCCA,OCCB                                        00
       DIMENSION CZ(IAT),U(IBF),ULIM(IBF),LLIM(IBF)                         00
      COMMON/JRCOV/IRCOV,IJC,IDISK,IRCCC,JDISK                              00
      COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF       00
      INTEGER*4 OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF           00
      INTEGER*4 CHARGE,OCCA,OCCB,UL,ULIM,U,AN,CZ,Z                          00
      DIMENSION G1(18),F2(18)                                               00
      INTEGER*4 OFF                                                         00
      DATA OFF/'OFF'/                                                       00
      ABSF(X)=DABS(X)                                                       00
      IRCOV = 0                                                             00
      G1(3)=.092012D0                                                       00
      G1(4)=.1407  D0                                                       00
      G1(5)=.199265D0                                                       00
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      G1(6)=.26770800                                                   002
 9898 FORMAT( 9H IN SCFCL)                                              002
      G1(7)=.346029DC                                                   002
      G1(8)=.43423 DO                                                   002
      G1(9)=.532305DC                                                   002
      F2(3)=.049865DC                                                   002
      F2(4)=.08912500                                                   002
      F2(5)=.13041 DO                                                   002
      F2(6)=.17372 DO                                                   002
      F2(7)=.21905500                                                   002
      F2(8)=.26641500                                                   002
      F2(9)=.31580 DO                                                   002
      OLDENG=C.0D0                                                      002
      Z = C                                                             002
      IT = 40                                                           002
   10 CONTINUE                                                          002
      IF(IONOFF .NE. OFF)  CALL TIM                                     002
C     READ CORE HAMILTONIAN WITH DIAGONAL INTO THE LOWER TRIANGLE       002
C     OF MATRIX A                                                       002
      REWIND JDISK                                                      002
     *READ  (JDISK) ((A(IERT,KERT),KERT=1,IERT),IERT=1,N)               002
 4341 FORMAT(1X,F10.5)                                                  002
      CALL ECALC(1,ENERGY,N,IBF,A,PDIAG,Q)                              002
      IF(IONOFF .EQ. OFF)  GO TO 3791                                   002
      PRINT 3792                                                        002
 3792 FORMAT ( 84H LOWER TRIANGLE HAS CORE HAMILTONIAN, UPPER TRIANGLE A002
     *ND DIAGONAL HAS DENSITY MATRIX)                                   002
           CALL SCFOU1(C,AN,A,CZ,U,ULIM,LLIM,NUM,0,1,IBF,IAT)           002
      PRINT 3793                                                        002
 3793 FORMAT(42H DIAGONAL ELEMENTS OF THE CORE HAMILTONIAN)             002
      DO 3974 IANB=1,N                                                  002
 3974 PRINT 3975, IANB,Q(IANB)                                          002
 3975 FORMAT(1X,2HQ(,I5,2H)=,3X,F10.5)                                  002
 3791 CONTINUE                                                          002
      Z = Z+1                                                           002
      DO 40 I=1,N                                                       002
      II=U(I)                                                           002
C     A(I,I) = A(I,I) - B(I,I)*G(II,II)*0.5                             002
C     READ (KDISK)  BII                                                 002
C     A(I,I) = Q(I) - BII*G(II,II)*0.5                                  002
C      A(I,I) = Q(I) -B(I,I)*G(II,II)*0.5                               002
      A(I,I) = Q(I) -PDIAG(I)*G(II,II)*0.5D0                            002
      DO 30 K=1,N                                                       002
      JJ=U(K)                                                           002
C  30 A(I,I) = A(I,I) + B(K,K)*G(II,JJ)                                 002
C     READ  (IKDISK) BII                                                002
C  30 A(I,I) = Q(I) - BII*G(II,JJ)                                      002
C  30 A(I,I) = Q(I)+B(K,K)*G(II,JJ)                                     002
   30 A(I,I) = A(I,I) + PDIAG(K)*G(II,JJ)                               002
      LL=I+1                                                            002
      IF(LL .GT. N)  GO TO 40                                           002
   31 CONTINUE                                                          002
```

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C
C
C
      DO 41 J=LL,N                                                      00
      JJ=U(J)                                                           00
C     A(J,I)=A(J,I)-B(J,I)*G(II,JJ)*0.5                                 00
      A(J,I) = A(J,I) - A(I,J)*G(II,JJ)*0.5D0                           00
   41 CONTINUE                                                          00
   40 CONTINUE                                                          00
C     INDO MODIFICATION                                                 00
      IF (OPTION.EQ.INDO) GO TO 50                                      00
      GO TO 90                                                          00
   50 DO 80 II=1,NATOMS                                                 00
      K=AN(II)                                                          00
      I=LLIM(II)                                                        00
      IF (K.EQ.1) GO TO 80                                              00
      GO TO 60                                                          00
   60 PAA=PDIAG(I)+PDIAG(I+1)+PDIAG(I+2)+PDIAG(I+3)                     00
      A(I,I) = A(I,I)-(PAA-PDIAG(I))*G1(K)/6.D0                         00
      DO 70 J=1,3                                                       00
      A(I+J,I+J)=A(I+J,I+J)-PDIAG(I)*G1(K)/6.D0-(PAA-PDIAG(I))*7.D0*F2(K00
     *)/50.D0 + PDIAG(I+J)*11.D0*F2(K)/50.D0                            00
      A(I+J,I)=A(I+J,I)+A(I,I+J)*G1(K)/2.D0                             00
      JJ=J-1                                                            00
      IF(JJ.EQ.0) GO TO 70                                              00
      GO TO 71                                                          00
   71 CONTINUE                                                          00
      DO 72 L=1,JJ                                                      00
      A(I+J,I+L) = A(I+J,I+L)+A(I+L,I+J)*11.D0*F2(K)/50.D0              00
   72 CONTINUE                                                          00
   70 CONTINUE                                                          CO
   80 CONTINUE                                                          00
   90 CONTINUE                                                          00
      CALL ECALC(2,ENERGY,N,IBF,A,PDIAG,0)                              00
      IF(IONOFF .NE. OFF) PRINT 9999, ENERGY                            00
 9999 FORMAT(1X,F20.10)                                                 00
      IF(IONOFF .EQ. OFF)  GO TO 9123                                   00
      PRINT 2137                                                        00
 2137 FORMAT(79H LOWER TRIANGLE AND DIAGONAL HAS FOCK MATRIX, UPPER TRIA00
     *NGLE HAS DENSITY MATRIX)                                          00
  200 FORMAT(27H HARTREE-FOCK ENERGY MATRIX)                            00
          CALL SCFOU1(C,AN,A,CZ,U,ULIM,LLIM,NUM,0,1,IBF,IAT)            00
 9123 CONTINUE                                                          00
      CALL EIGN1(N,.000001D0,IBF,A)                                     00
      EDIFF = ENERGY-OLDENG                                             00
      IF(EDIFF.LT.0.0D0) GO TO 401                                      00
  400 PRINT 402,Z                                                       00
  402 FORMAT(/,30H ENERGY DIVERGING AT ITERATION, I4,/)                 00
      ENERGY = 999.9900                                                 00
      GO TO 405                                                         00
  401 CONTINUE                                                          00
      IF (ABSF(ENERGY-OLDENG).LT..000001D0) GO TO 120                   00
      GO TO 150                                                         00
  120 CONTINUE                                                          00
      PRINT 1115, Z                                                     00
```

```
C
C
C
 1115 FORMAT(1X,I5,11H ITERATIONS)                                      00
      Z=100                                                             00
      IRCCC = 1                                                         00
      IRCOV = 1                                                         00
  130 PRINT 140                                                         00
  140 FORMAT(/,17H ENERGY SATISFIED)                                    00
      GO TO 170                                                         00
  150 CONTINUE                                                          00
  160 OLDENG=ENERGY                                                     00
  170 CONTINUE                                                          00
      IF (Z.GT.IT)GO TO 220                                             00
      GO TO 240                                                         00
  220 CONTINUE                                                          00
      IF(IONOFF.EQ.OFF) GO TO 14                                        00
   15 CONTINUE                                                          00
      PRINT 230                                                         00
  230 FORMAT(28HEIGENVALUES AND EIGENVECTORS)                           00
            CALL SCFOU1(C,AN,A,CZ,U,ULIM,LLIM,NUM,1,1,IBF,IAT)          00
  240 CONTINUE                                                          00
   14 CONTINUE                                                          00
C     EIGENVECTORS (IN B) ARE CONVERTED INTO DENSITY MATRIX (IN B)      CO
      CALL DMA1(PDIAG,XXX,A,C,N,OCCA,IBF,AN,IAT,CZ,U,ULIM,LLIM,NUM)     00
      IF (Z.GT.IT) GO TO 300                                            CO
      GO TO 10                                                          00
  300 CONTINUE                                                          CO
      IF(IRCOV.NE.1)  GO TO 9133                                        00
      REWIND IDISK                                                      CO
      WRITE(IDISK)  ((A(IJQ,JJQ),IJQ=1,N),JJQ=1,N)                      00
      PRINT 8012                                                        CC
 9133 CONTINUE                                                          CC
 8012 FORMAT (31H WRITING DENSITY MATRIX ON DISK)                       CC
  405 CONTINUE                                                          CO
      RETURN                                                            00
      END                                                               00
      SUBROUTINE ECALC(JOINT,ESUM,N,IBF,A,PDIAG,Q)                      CC
      IMPLICIT REAL*8(A-H,O-Z)                                          00
      DIMENSION PDIAG(IBF), Q(IBF)                                      00
      DIMENSION A(IBF,IBF)                                              00
      IF(JOINT .EQ. 1) ESUM=0.D0                                        00
      DO 3130 IBC=1,N                                                   00
      DO 3130 JBC=1,N                                                   00
      IF(JBC .LE. IBC) GO TO 3130                                       00
      ESUM =      (A(IBC,JBC)*A(JBC,IBC)) + ESUM                        00
 3130 CONTINUE                                                          00
      IF(JOINT .EQ. 2)  GO TO 3333                                      00
      DO 3131 IBC=1,N                                                   00
      ESUM = ESUM + ((PDIAG(IBC)*Q(IBC))/2.D0)                          00
 3131 CONTINUE                                                          00
      GO TO 4444                                                        00
 3333 CONTINUE                                                          00
      DO 1234 III=1,N                                                   00
        ESUM = ESUM +((PDIAG(III)*A(III,III))/2.D0)                     00
```

```
 1234 CONTINUE
 4444 CONTINUE
      RETURN
      END
      SUBROUTINE CPRINT(G,B,C,AN,IBF,IAT,XXX,CZ,U,ULIM,LLIM,PDIAG,Q,NUM
     *)
      IMPLICIT REAL*8(A-H,O-Z)
       DIMENSION G(IAT,IAT)
      DIMENSION XXX(IBF)
      DIMENSION NUM(IBF)
       DIMENSION C(IAT,3), AN(IAT)
C     CNDO-INDO SCF CLOSED SHELL- PRINTOUT SEGMENT
       COMMON/HFLLO/ENERGY
      DIMENSION PDIAG(IBF), Q(IBF)
       DIMENSION B(IBF,IBF)
       COMMON/INFO/N,NATOMS,CHARGE,MULTIP
       COMMON/INFO1/NELECS,OCCA,OCCB
        DIMENSION CZ(IAT),U(IBF),ULIM(IAT),LLIM(IAT)
      COMMON/PERTBL/EL(9)
      COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF
       COMMON/ENGY/BOE(3),ROE(3),ETOT,MOLVOL,DP,IC
      INTEGER*4 OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF
      INTEGER*4 CHARGE,AN,U,ULIM,EL,OCCA,OCCB,UL,CZ,ANI
      DIMENSION DPM(3),DM(3),DMSP(3),DMPD(3)
      DIMENSION ATENG(18)
      DIMENSION RCH(3),DMP(3)
      REAL*8 MAXX,MINX,MAXY,MINY,MAXZ,MINZ,MOLVOL
      INTEGER*4 OFF
      DATA OFF/'OFF'/
      FLOATF(I)=DFLOAT(I)
      SQRTF(X)=DSQRT(X)
C      PRINT 9898
 9898 FORMAT(10H IN CPRINT)
      IF(ENERGY.NE.999.99D0) GO TO 400
C     SET DEFAULT VALUES
      ETOT=999.99D0
      MOLVOL=999.99D0
      DP=999.99D0
      GO TO 401
  400 CONTINUE
      IF(OPTION.EQ.INDO) GO TO 10
      GO TO 20
   10 CONTINUE
      ATENG(1)=-0.6387302462  D0
      ATENG(4)=0.0D0
      ATENG(3)=0.0D0
      ATENG(5)=0.0D0
      ATENG(6)=-5.9349548261  D0
      ATENG(7)=-10.6731741251 D0
      ATENG(8)=-17.2920850650 D0
      ATENG(9)=-26.2574377875 D0
      GO TO 30
```

```
C
C
C
   20 CONTINUE                                                          CC
      ATENG(1)=-0.6387302462  DO                                        CC
      ATENG(3)=0.0D0                                                    CC
      ATENG(4)=0.0D0                                                    CC
      ATENG(5)=0.0D0                                                    CC
      ATENG(6)=-6.1649935261  DO                                        CC
      ATENG(7)=-11.0768746252 DO                                        CC
      ATENG(8)=-18.0819658651 DO                                        CC
      ATENG(9)=-27.5491302860 DO                                        CC
      ATENG(11)=-.1977009568  DO                                        CC
      ATENG(12)=-.8671913833  DO                                        CC
      ATENG(13)=-2.0364557744 DO                                        CC
      ATENG(14)=-3.8979034686 DO                                        CC
      ATENG(15)=-6.7966009163 DO                                        CC
      ATENG(16)=-10.765817434100                                        CC
      ATENG(17)=-16.046701794000                                        CC
   30 CONTINUE                                                          CC
      K=NATOMS-1                                                        CC
   13 CONTINUE                                                          CC
      IF(IONOFF.EQ.OFF) GO TO 12                                        CC
      PRINT 40                                                          CC
   40 FORMAT(15H DENSITY MATRIX/)                                       CC
      IF(IONOFF.NE.OFF)CALL SCFOU2(C,AN,B,CZ,U,ULIM,LLIM,NUM,0.1,IBF,IATCC
     *)                                                                 CC
   12 CONTINUE                                                          CC
      DO 50 I=1,K                                                       CC
      L=I+1                                                             CC
      DO 50 J=L,NATOMS                                                  CC
      RAD=SQRTF((C(I,1)-C(J,1))**2+(C(I,2)-C(J,2))**2                   CC
     1          +(C(I,3)-C(J,3))**2)                                    CC
   50 ENERGY=ENERGY+(FLOATF(CZ(I))*FLOATF(CZ(J)))/RAD                   CC
      BWE(IC)=ENERGY                                                    CC
      PRINT 60,ENERGY                                                   CC
   60 FORMAT(//16H TOTAL ENERGY = F16.10)                               CC
      ETOT = ENERGY                                                     CC
      IF(IONOFF.EQ.OFF) GO TO 81                                        CC
      DO 70 I=1,NATOMS                                                  CC
      IAN = AN(I)                                                       CC
   70 ENERGY = ENERGY-ATENG(IAN)                                        CC
      PRINT 80,ENERGY                                                   CC
   80 FORMAT(//16HBINDING ENERGY= ,F16.10,5H A.U.)                      CC
   81 CONTINUE                                                          CC
      PRINT 82                                                          CC
   82 FORMAT(/,17H CHARGE DENSITIES,/)                                  CC
      DO 110 I=1,NATOMS                                                 CC
      FCHG=0.0D0                                                        CC
      TCHG=0.0D0                                                        CC
      LL=LLIM(I)                                                        CC
      UL=ULIM(I)                                                        CC
      DO 90 J=LL,UL                                                     CC
      FCHG = 0.D0                                                       CC
   90 TCHG = TCHG+B(J,J)                                                CC
```

```
      ANI=AN(I)                                                         CC
      DCHG=DFLOAT(CZ(I))-TCHG                                           CC
      PRINT 100,I,EL(ANI),TCHG,DCHG,FCHG                                CC
  100 FORMAT(I3,A4,8X,3F7.4)                                            CC
      XXX(I)=TCHG                                                       CC
  110 CONTINUE                                                          CC
C     CALCULATE MOLECULAR VOLUME                                        CC
      MINX = C(1,1)                                                     CC
      MAXX = C(1,1)                                                     CC
      MINY = C(1,2)                                                     CC
      MAXY = C(1,2)                                                     CC
      MINZ = C(1,3)                                                     CC
      MAXZ = C(1,3)                                                     CC
      DO 310 IA=2,NATOMS                                                CC
      MINX=DMIN1(C(IA,1),MINX)                                          CC
      MAXX=DMAX1(C(IA,1),MAXX)                                          CC
      MINY=DMIN1(C(IA,2),MINY)                                          CC
      MAXY=DMAX1(C(IA,2),MAXY)                                          CC
      MINZ=DMIN1(C(IA,3),MINZ)                                          CC
      MAXZ=DMAX1(C(IA,3),MAXZ)                                          CC
  310 CONTINUE                                                          CC
      MOLVOL=(MAXX-MINX+1.0D0)*(MAXY-MINY+1.0D0)*(MAXZ-MINZ+1.0D0)*0.529CC
     1168D0                                                             CC
      PRINT 311,MOLVOL                                                  CC
  311 FORMAT(/,20H MOLECULAR VOLUME = ,F10.5,5H A**3,/)                 CC
C     COMPUTE VECTOR COMPONENTS OF CENTER OF POSITIVE CHARGE            CC
      DO 300 I=1,3                                                      CC
      FNUM=0.0D0                                                        CC
      FDEN=0.0D0                                                        CC
      DO 301 IA=1,NATOMS                                                CC
      FNUM = FNUM+FLOATF(CZ(IA))*C(IA,I)                                CC
      FDEN = FDEN+FLOATF(CZ(IA))                                        CC
  301 CONTINUE                                                          CC
      RCH(I) = FNUM/FDEN                                                CC
C     REFER CARTESIAN COORDINATES TO CENTER OF POSITIVE CHARGE          CC
      DO 300 IA=1,NATOMS                                                CC
  300 C(IA,I) = C(IA,I)-RCH(I)                                          CC
      DO 120 I=1,3                                                      CC
      DM(I)=0.0D0                                                       CC
      DMSP(I)=0.0D0                                                     CC
  120 DMPD(I)=0.0D0                                                     CC
      DO 200 J=1,NATOMS                                                 CC
      IF(AN(J).LT.3) GO TO 180                                          CC
  130 IF(AN(J).LT.11) GO TO 140                                         CC
      GO TO 160                                                         CC
  140 INDEX=LIM(J)                                                      CC
      DO 150 K=1,3                                                      CC
  150 DMSP(K)=DMSP(K)-B(INDEX,INDEX+K)*7.33697D0/                       CC
     1 (.325D0*DFLOAT(AN(J)-1))                                         CC
      GO TO 180                                                         CC
  160 SLTR1=(.65D0*DFLOAT(AN(J))-4.95D0)/3.D0                           CC
      FACTOR=2.5416D0*7.D0/(DSQRT(5.D0)*SLTR1)                          CC
```

```
C
C
C
      INDEX=LLIM(J)                                                     CC
      DO 170 K=1,3                                                      CC
  170 DMSP(K)=DMSP(K)-B(INDEX,INDEX+K)*10.27175D0/SLTR1                 CC
      DMPD(1)=DMPD(1)-FACTOR*(B(INDEX+2,INDEX+8)+B(INDEX+3,INDEX+5)     CC
     1  +B(INDEX+1,INDEX+7)-1.D0/DSQRT(3.D0)*B(INDEX+1,INDEX+4))        CC
      DMPD(2)=DMPD(2)-FACTOR*(B(INDEX+1,INDEX+8)+B(INDEX+3,INDEX+6)     CC
     1  +B(INDEX+2,INDEX+7)-1.D0/DSQRT(3.D0)*B(INDEX+2,INDEX+4))        CC
      DMPD(3)=DMPD(3)-FACTOR*(B(INDEX+1,INDEX+5)+B(INDEX+2,INDEX+6)     CC
     1  +2.D0/DSQRT(3.D0)*B(INDEX+3,INDEX+4))                           CC
  180 DO 190 I=1,3                                                      CC
  190 DM(I)=DM(I)+(DFLOAT(CZ(J))-XXX(J))*C(J,I)*2.5416D0                CC
  200 CONTINUE                                                          CC
      DO 210 I=1,3                                                      CC
  210 DPM(I)=DM(I)+DMSP(I)+DMPD(I)                                      CC
      IF(IONOFF.EQ.OFF) GO TO 83                                        CC
      PRINT 220                                                         CC
  220 FORMAT(//16H *DIPOLE MOMENTS./)                                   CC
      PRINT 230                                                         CC
  230 FORMAT(5X,11H COMPONENTS,3X,2H X,8X,2H Y,8X,2H Z)                 CC
      PRINT 240,DM(1),DM(2),DM(3)                                       CC
  240 FORMAT(5X,10H DENSITIES,3(1X,F9.5))                               CC
      PRINT 250,DMSP(1),DMSP(2),DMSP(3)                                 CC
  250 FORMAT(5X,4H S.P,6X,3(1X,F9.5))                                   CC
      PRINT 260,DMPD(1),DMPD(2),DMPD(3)                                 CC
  260 FORMAT(5X,4H P.D,6X,3(1X,F9.5))                                   CC
      PRINT 270,DPM(1),DPM(2),DPM(3)                                    CC
  270 FORMAT(5X,6H TOTAL,4X,3(1X,F9.5),/)                               CC
   83 CONTINUE                                                          CC
      DP=SQRTF(DPM(1)**2+DPM(2)**2+DPM(3)**2)                           CC
      PRINT 280,DP                                                      CC
  280 FORMAT(15H DIPOLE MOMENT=,F9.5,7H DEBYES.//)                      CC
  401 CONTINUE                                                          CC
      RETURN                                                            CC
      END                                                               CC
      SUBROUTINE GRDVER (AGRD,VGRD,DIP,DELT)                            CC
      IMPLICIT REAL*8(A-H,O-Z)                                          CC
      DIMENSION AGRD(18,18),VGRD(18,18),DIP(18,18)                      CC
       COMMON/GRID/LROW,LCOL                                            CC
       DIMENSION A(18)                                                  CC
      MM = MAXO(LROW,LCOL)                                              CC
      DO 6 I =1,MM                                                      CC
    6 A(I) = (I-1)*(DELT)                                               CC
      PUNCH 43                                                          CC
      PRINT 43                                                          CC
   43 FORMAT ( /,3X,20HAGRD IN ATOMIC UNITS,/ )                         CC
       CALL OUT(AGRD,A)                                                 CC
      BMIN=9999.0D0                                                     CC
      DO 5555 I = 1,LROW                                                CC
      DO 5555 J = 1,LCOL                                                CC
      BMIN =  DMIN1 (BMIN,AGRD(I,J))                                    CC
 5555 CONTINUE                                                          CC
      BMAX=-1000.0D0                                                    CC
```

```
C
C
C
      DO 7777 I =1,LROW
      DO 7777 J = 1,LCOL
      IF(AGRD(I,J).EQ.0.0D0) GO TO 7676
      BMAX = DMAX1 (BMAX,AGRD(I,J))
 7676 CONTINUE
 7777 CONTINUE
      BMAX=BMAX+1.0D0
      DO 8787 I = 1,LROW
      DO 8787 J = 1,LCOL
      IF(AGRD(I,J).NE.0.0D0) GO TO 8787
      AGRD(I,J) = BMAX
 8787 CONTINUE
      DO 7 I =1,LROW
      DO 7 J =1,LCOL
    7 AGRD(I,J)=((AGRD(I,J))-(BMIN))*(628.55D0)
      DO 8765 I = 1,LROW
      DO 8765 J = 1,LCOL
      IF(AGRD(I,J).GT.9999.0D0) GO TO 8766
      GO TO 8767
 8766 AGRD(I,J)=9999.000
 8767 CONTINUE
 8765 CONTINUE
      PRINT 41
      PUNCH 41
   41 FORMAT(/,3X,17HEGRID IN KCAL/MOL,/)
       CALL OUT(AGRD,A)
      PRINT 2130
      PUNCH 2130
 2130 FORMAT(/,21H MOLVOL GRID IN CM**3,/)
        CALL OUT(VGRD,A)
      PRINT 2131
      PUNCH 2131
 2131 FORMAT(/,27H DIPOLE GRID IN DEBYE UNITS,/)
       CALL OUT(DIP,A)
      RETURN
      END
        SUBROUTINE OUT(AGR,A)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION AGR(18,18)
       COMMON/GRID/LROW,LCOL
        DIMENSION A(18)
      KITE = 0
   20 LOW = KITE + 1
      KITE = KITE + 12
      KITE = AMINO(KITE,LCOL)
      PRINT 19, (A(I),I=LOW,KITE)
   19 FORMAT ( /,6X,11F10.1,/)
      DO 32 I =1,LROW
   32 PRINT 18,A(I),(AGR (I,J),J=LOW,KITE)
   18 FORMAT(2X,F5.1,2X,12F10.4)
      IF(LCOL-KITE) 40,40,20
   40 CONTINUE
```

```
C
C
C
      IF((LCOL .EQ. 12) .OR. (LCOL .EQ. 18)) GO TO 1988                 00
      GO TO 1989                                                        00
 1988 CONTINUE                                                          00
       DO 1900 I=1,LROW                                                 00
 1900 PUNCH 5, (AGR(I,J),J=1,LCOL),AGR(I,1)                             00
      PUNCH 5, (AGR(1,J),J=1,LCOL),AGR(1,1)                             00
    5 FORMAT(8F10.5)                                                    00
      GO TO 77                                                          00
 1989 CONTINUE                                                          00
      DO 1901I=1,LROW                                                   00
 1901 PUNCH 5, (AGR(I,J),J=1,LCOL)                                      00
   77 CONTINUE                                                          00
      RETURN                                                            00
      END                                                               00
       SUBROUTINE DMA1(PDIAG,XXX,B,C,N,OCCA,IBF,AN,IAT,CZ,U,ULIM,LLIM,NUO0
     *M)                                                                00
       IMPLICIT REAL*8(A-H,O-Z)                                         00
        DIMENSION CZ(IAT),U(IBF),ULIM(IAT),LLIM(IAT)                    00
       DIMENSION NUM(IBF)                                               00
       INTEGER*4 CZ                                                     00
      INTEGER *4 U,ULIM                                                 00
            DIMENSION C(IAT,3), AN(IAT)                                 00
      DIMENSION XXX(IBF)                                                00
      DIMENSION PDIAG(IBF)                                              00
C     THIS ROUTINE ACCEPTS THE COEFFICIENTS OR EIGENVECTORS IN B         00
C     AND GENERATES THE DENSITY MATRIX ALSO IN B                        00
      INTEGER OCCA                                                      00
      DIMENSION B(IBF,IBF)                                              00
      COMMON/OPTION/OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN,IONOFF   00
      INTEGER OPTION,OPNCLO,HUCKEL,CNDO,CLOSED,OPEN                     00
       INTEGER OFF                                                      00
       DATA OFF/'OFF'/                                                  00
       IF(IONOFF .EQ. OFF)  GO TO 2222                                  00
       PRINT 1111                                                       00
 1111 FORMAT(13H COEFFICIENTS)                                          00
            CALL SCFOU1(C,AN,B,CZ,U,ULIM,LLIM,NUM,0,1,IBF,IAT)          00
 2222 CONTINUE                                                          00
       DO 140 I=1,N                                                     00
       DO 120 J=1,N                                                     00
       XXX(J) = 0.D0                                                    00
      DO 110 K=1,OCCA                                                   00
  110 XXX(J) = XXX(J) + 2.D0*B(I,K)*B(J,K)                              00
  120 CONTINUE                                                          00
        DO 130 J=1,N                                                    00
  130 B(I,J) = XXX(J)                                                   00
  140 CONTINUE                                                          00
      DO 150 I=1,N                                                      00
       DO 150 J=1,N                                                     00
      PDIAG(I) = B(I,I)                                                 00
  150 B(J,I) = B(I,J)                                                   00
C     WRITE THE DIAGONAL OF THE NEWLY GENERATED DENSITY MATRIX ON DISK  00
C     KDISK = 11                                                        00
```

```
C
C
C
C     IKDISK=12                                                          C
C      REWIND IKDISK                                                     C
C     REWIND KDISK                                                       C
C     DO 2222 IY=1,N                                                     C
C     DO 2222 JY=1,N                                                     C
C     IF(IY .NE. JY)  GO TO 2222                                         C
C     WRITE (KDISK) B(IY,JY)                                             C
C     WRITE (IKDISK) B(IY,JY)                                            C
C2222 CONTINUE                                                           C
      IF(IONOFF .EQ. OFF)  GO TO 4444                                    C
      PRINT 3333                                                         C
 3333 FORMAT (15H DENSITY MATRIX)                                        C
           CALL SCFOUT(C,AN,B,CZ,U,ULIM,LLIM,NUM,0,1,IBF,IAT)            C
 4444 CONTINUE                                                           C
      RETURN                                                             C
           END                                                           C
      SUBROUTINE MOUTP1(A,M,N,MDIM,NDIM,NAL)                             C
C     OUTPUT OF M X N MATRIX DIMENSIONED TO MDIM X NDIM                  C
      IMPLICIT REAL*8(A-H,O-Z)                                           C
      DIMENSION NAL(6)                                                   C
      DIMENSION A(MDIM,NDIM)                                             C
      PRINT 1000,NAL                                                     C
 1000 FORMAT (//,2X, 6A4)                                                C
      KITE = 0                                                           C
   20 LOW = KITE+1                                                       C
      KITE = KITE+14                                                     C
      KITE = AMINO(KITE,N)                                               C
      PRINT 19,(I,I=LOW,KITE)                                            C
   19 FORMAT( //     ,4X,14(6X,I2),/)                                  C
      DO 32 I=1,M                                                        C
   32 PRINT 18,I,(A(I,J),J=LOW,KITE)                                     C
   18 FORMAT(I4,2X,14F8.4)                                               C
      IF(N-KITE) 40,40,20                                                C
   40 RETURN                                                             C
      END                                                                C
      SUBROUTINE SCFOUT(C,AN,A,CZ,U,ULIM,LLIM,NUM,OP,MOP,IBF,IAT)        C
      IMPLICIT REAL*8(A-H,O-Z)                                           C
C     THIS ROUTINE PRINTS THE ARRAY IN COMMON/ARRAYS/ WHICH IS DESIGNATEC
C     MOP. IF OP = 1 THE EIGENVALUES CONTAINED IN COMMON/1/ ARE ALSO     C
C     PRINTED. IF OP= 0 THE EIGENVALUES ARE NOT PRINTED                  C
      DIMENSION C(IAT,3), AN(IAT)                                        C
      DIMENSION A(IBF,IBF)                                               C
      COMMON/INFO/N,NATOMS,CHARGE,MULTIP                                 C
      INTEGER*4 CHARGE,OCCA,OCCB,UL,ANI                                  C
      COMMON/ORB/ORB(9)                                                  C
      COMMON/INFO1/NELECS,OCCA,OCCB                                      C
      DIMENSION CZ(IAT),U(IBF),ULIM(IAT),LLIM(IAT)                       C
      COMMON/PERTBL/EL(9)                                                C
      DIMENSION NUM(IBF)                                                 C
      INTEGER*4 OP,AN,ANII,CZ,U,ORB,ULIM,EL                              C
      DO 10 I = 1,N                                                      C
   10 NUM(I) = I                                                         C
```

```
      DO 120 M=1,N,11                                                   00
      K=M+10                                                            00
      IF(K.GT.N) GO TO 20                                               00
      GO TO 30                                                          00
   20 K=N                                                               00
   30 CONTINUE                                                          00
      PRINT 100                                                         00
      IF(OP.EQ.1) GO TO 40                                              00
      GO TO 50                                                          00
   40 CALL EIGOUT(M,K)                                                  00
   50 CONTINUE                                                          00
      PRINT 60,(NUM(I),I=M,K)                                           00
   60 FORMAT(13X,11I9)                                                  00
      DO 110 I=1,N                                                      00
      II=U(I)                                                           00
      ANII=AN(II)                                                       00
      L=I-LLIM(II)+1                                                    00
   70 PRINT 80,I,II,EL(ANII),ORB(L),(A(I,J),J=M,K)                      00
   80 FORMAT(1X,I2,I3,A4,1X,A4,11F9.4)                                  00
      IF(I.EQ.ULIM(II)) GO TO 90                                        00
      GO TO 110                                                         00
   90 PRINT 100                                                         00
  100 FORMAT(1X)                                                        00
  110 CONTINUE                                                          00
  120 CONTINUE                                                          00
      PRINT 100                                                         00
      PRINT 100                                                         00
      RETURN                                                            00
      END                                                               00
       SUBROUTINE SCFOU2(C,AN,A,CZ,U,ULIM,LLIM,NUM,OP,MOP,IBF,IAT)      00
      IMPLICIT REAL*8(A-H,O-Z)                                          00
C     THIS ROUTINE PRINTS THE ARRAY IN COMMON/ARRAYS/ WHICH IS DESIGNATE00
C     MOP. IF OP = 1 THE EIGENVALUES CONTAINED IN COMMON/1/ ARE ALSO    00
C     PRINTED. IF OP= C THE EIGENVALUES ARE NOT PRINTED                 00
       DIMENSION C(IAT,3), AN(IAT)                                      00
      DIMENSION A(IBF,IBF)                                              00
       COMMON/INFO/N,NATOMS,CHARGE,MULTIP                               00
      INTEGER*4 CHARGE,OCCA,OCCB,UL,ANI                                 00
      COMMON/ORB/ORB(9)                                                 00
       COMMON/INFO1/NELECS,OCCA,OCCB                                    00
        DIMENSION CZ(IAT),U(IBF),ULIM(IAT),LLIM(IAT)                    00
      COMMON/PERTBL/EL(9)                                               00
      DIMENSION NUM(IBF)                                                00
      INTEGER*4 OP,AN,ANII,CZ,U,ORB,ULIM,EL                             00
      DO 10 I = 1,N                                                     00
   10 NUM(I) = I                                                        00
      DO 120 M=1,N,11                                                   00
      K=M+10                                                            00
      IF(K.GT.N) GO TO 20                                               00
      GO TO 30                                                          00
   20 K=N                                                               00
   30 CONTINUE                                                          00
```

```
      PRINT 100                                                         C
      IF(OP.EQ.1) GO TO 40                                              C
      GO TO 50                                                          C
   40 CONTINUE                                                          C
   50 CONTINUE                                                          C
      PRINT 60,(NUM(I),I=M,K)                                           C
   60 FORMAT(13X,1119)                                                  C
      DO 110 I=1,N                                                      C
      II=U(I)                                                           C
      ANII=AN(II)                                                       C
      L=I-LLIM(II)+1                                                    C
   70 PRINT 80,I,II,EL(ANII),ORB(L),(A(I,J),J=M,K)                      C
   80 FORMAT(1X,I2,I3,A4,1X,A4,11F9.4)                                  C
      IF(I.EQ.ULIM(II)) GO TO 90                                        C
      GO TO 110                                                         C
   90 PRINT 100                                                         C
  100 FORMAT(1X)                                                        C
  110 CONTINUE                                                          C
  120 CONTINUE                                                          C
      PRINT 100                                                         C
      PRINT 100                                                         C
      RETURN                                                            C
      END                                                               C
      SUBROUTINE EIGN1(NN,RHO,IBF,A)                                    C
      IMPLICIT REAL*8(A-H,O-Z)                                          C
C      ONE MATRIX VERSION                                               C
C     RHO= UPPER LIMIT FOR OFF-DIAGONAL ELEMENT                         C
C     NN= SIZE OF MATRIX                                                C
C     A = F MATRIX (ONLY LOWER TRIANGLE IS USED + THIS IS DESTROYED)    C
C     EIG = RETURNED EIGENVALUES IN ALGEBRAIC ASCENDING ORDER           C
C     VEC = RETURNED EIGENVECTORS IN COLUMNS                            C
      DIMENSION A(IBF,IBF)                                              C
      DIMENSION W( 90),GAMMA( 90),BETA( 90),BETASQ( 90),IPOSV( 90),IVPOSC
     *( 90),IORD( 90)                                                   C
      COMMON/BYE/FIG( 90)                                               C
C     THE FOLLOWING DIMENSIONED VARIABLES ARE EQUIVALENCED              C
C     DIMENSION VEC(IBF,IBF)                                            C
C     EQUIVALENCE (A(1),VEC(1))                                         C
C      EQUIVALENCE (VEC,A)                                              C
      DIMENSION P(50),Q(50)                                             C
      EQUIVALENCE (P(1),BETA(1)),(Q(1),BETA(1))                         C
      EQUIVALENCE (IPOSV(1),GAMMA(1)),(IVPOS(1),BETA(1)),               C
     1(IORD(1),BETASQ(1))                                               C
      ABSF(X) =DABS(X)                                                  C
      SQRTF(X) =DSQRT(X)                                                C
C      PRINT 1917                                                       C
 1917 FORMAT( 8H IN EIGN)                                               C
      RHOSQ=RHO*RHO                                                     C
      N=NN                                                              C
      IF(N .EQ. 0) GO TO 560                                            C
    1 N1=N-1                                                            C
      N2=N-2                                                            C
```

```
C
C
C
      GAMMA(1)=A(1,1)                                                   00
      IF(N2) 280,270,120                                                00
  120 DO 260 NR=1,N2                                                    00
      B=A(NR+1,NR)                                                      00
      S=0.DO                                                            00
      DO 130 I=NR,N2                                                    00
  130 S=S+A(I+2,NR)**2                                                  00
C     PREPARE FOR POSSIBLE BYPASS OF TRANSFORMATION                     00
      A(NR+1,NR)=0.DO                                                   00
      IF (S) 250,250,140                                                00
  140 S=S+B*B                                                           00
      SGN=+1.DO                                                         00
      IF (B) 150,160,160                                                00
  150 SGN=-1.DO                                                         00
  160 SQRTS=SQRTF(S)                                                    00
      TSQR = SQRTS +SQRTS                                               00
C     PRINT 1111,TSQR                                                   00
 1111 FORMAT (F80.60)                                                   00
      D=SGN/(SQRTS+SQRTS)                                               00
      TEMP=SQRTF(.5DC+B*D)                                              00
      W(NR)=TEMP                                                        00
      A(NR+1,NR)=TEMP                                                   00
C     PRINT 1111,TEMP                                                   00
      D=D/TEMP                                                          00
      B=-SGN*SQRTS                                                      00
C     D IS FACTOR OF PROPORTIONALITY. NOW COMPUTE AND SAVE W VECTOR.    00
C     EXTRA SINGLY SUBSCRIPTED W VECTOR USED FOR SPEED.                 00
      DO 170 I=NR,N2                                                    00
      TEMP=D*A(I+2,NR)                                                  00
      W(I+1)=TEMP                                                       00
  170 A(I+2,NR)=TEMP                                                    00
C     PREMULTIPLY VECTOR W BY MATRIX A TO OBTAIN P VECTOR.              00
C     SIMULTANEOUSLY ACCUMULATE DOT PRODUCT WP,(THE SCALAR K)           00
      WTAW=0.DO                                                         00
      DO 220 I=NR,N1                                                    00
      SUM=0.DO                                                          00
      DO 180 J=NR,I                                                     00
  180 SUM=SUM+A(I+1,J+1)*W(J)                                           00
      I1=I+1                                                            00
      IF(N1-I1) 210,190,190                                             00
  190 DO 200 J=I1,N1                                                    00
  200 SUM=SUM+A(J+1,I+1)*W(J)                                           00
  210 P(I)=SUM                                                          00
  220 WTAW=WTAW+SUM*W(I)                                                00
C     P VECTOR AND SCALAR K  NOW STORED. NEXT COMPUTE Q VECTOR          00
      DO 230 I=NR,N1                                                    00
  230 Q(I)=P(I)-WTAW*W(I)                                               00
C     NOW FORM PAP MATRIX. REQUIRED PART                                00
      DO 240 J=NR,N1                                                    00
      QJ=Q(J)                                                           00
      WJ=W(J)                                                           00
      DO 240 I=J,N1                                                     00
```

```
  240 A(I+1,J+1)=A(I+1,J+1)-2.D0*(W(I)*QJ+WJ*Q(I))                    00
  250 BETA(NR)=B                                                      00
      BETASQ(NR)=B*B                                                  00
  260 GAMMA(NR+1)=A(NR+1,NR+1)                                        00
  270 B=A(N,N-1)                                                      00
      BETA(N-1)=B                                                     00
      BETASQ(N-1)=B*B                                                 00
      GAMMA(N)=A(N,N)                                                 00
  280 BETASQ(N)=0.D0                                                  00
      DO 800 I=1,N                                                    00
      DO 810 J=I,N                                                    00
  810 A(I,J)=0.D0                                                     00
  800 A(I,I)=1.D0                                                     00
C      FORM PRODUCT P1*P2*...*PN-2                                    00
      K=N                                                             00
  540 KP=K                                                            00
      K=K-1                                                           00
      KM=K-1                                                          00
      DO 550 J=KP,N                                                   00
      DO 580 I=K,N                                                    00
      SUM=0.D0                                                        00
      DO 600 L=K,N                                                    00
  600 SUM=SUM+A(L,KM)*A(L,J)                                          00
      SUM=SUM+SUM                                                     00
  580 W(I)=A(I,J)-SUM*A(I,KM)                                         00
      DO 620 I=K,N                                                    00
  620 A(I,J)=W(I)                                                     00
  550 CONTINUE                                                        00
      DO 640 I=KP,N                                                   00
  640 A(I,K)=-2.D0*A(I,KM)*A(K,KM)                                    00
      A(K,K)=1.D0-2.D0*A(K,KM)*A(K,KM)                                00
      IF(K .GE. 3)  GO TO 540                                         00
  660 CONTINUE                                                        00
      DO 900 I=2,N                                                    00
  900 A(I,1)=0.D0                                                     00
      M=N                                                             00
      SUM=0.D0                                                        00
      GO TO 400                                                       00
  310 SUM=SUM+SHIFT                                                   00
      COSA=1.D0                                                       00
      G=GAMMA(1)-SHIFT                                                00
      PP=G                                                            00
      PPBS=PP*PP+BETASQ(1)                                            00
      PPBR=SQRTF(PPBS)                                                00
      DO 370 J=1,M                                                    00
      COSAP=COSA                                                      00
      IF(PPBS .NE. 0.D0) GO TO 320                                    00
  311 SINA=0.D0                                                       00
      SINA2=0.D0                                                      00
      COSA=1.D0                                                       00
      GO TO 350                                                       00
  320 SINA=BETA(J)/PPBR                                               00
```

```
C       PRINT 1111, PPBR                                                00
C       PRINT 1111, PPBS                                                00
        SINA2=BETASQ(J)/PPBS                                            00
        COSA=PP/PPBR                                                    00
C       POSTMULTIPLY P1*...*PN-2 BY ROTATION MATRIX   (P-TRANSPOSE)     00
  330   DO 340 I=1,N                                                    00
C       TEMP=COSA*VEC(I,J)+SINA*VEC(I,J+1)                              00
        TEMP=COSA*  A(I,J)+SINA*  A(I,J+1)                              00
C       VEC(I,J+1)=-SINA*VEC(I,J)+COSA*VEC(I,J+1)                       00
          A(I,J+1)=-SINA*  A(I,J)+COSA*  A(I,J+1)                       00
C 340 VEC(I,J)=TEMP                                                     00
  340     A(I,J)=TEMP                                                   00
  350   DIA=GAMMA(J+1)-SHIFT                                            00
        U=SINA2*(G+DIA)                                                 00
        GAMMA(J)=G+U                                                    00
        G=DIA-U                                                         00
        PP=DIA*COSA-SINA*COSAP*BETA(J)                                  00
        IF(J .NE. M) GO TO 360                                          00
  351   BETA(J)=SINA*PP                                                 00
        BETASQ(J)=SINA2*PP*PP                                           00
        GO TO 380                                                       00
  360   PPBS=PP*PP+BETASQ(J+1)                                          00
        PPBR=SQRTF(PPBS)                                                00
        BETA(J)=SINA*PPBR                                               00
  370   BETASQ(J)=SINA2*PPBS                                            00
  380   GAMMA(M+1)=G                                                    00
C       TEST FOR CONVERGENCE OF LAST DIAGONAL ELEMENT                   00
        IF(BETASQ(M) .GT. RHOSQ) GO TO 410                              00
  390   EIG(M+1)=GAMMA(M+1)+SUM                                         00
  400   BETA(M)=0.D0                                                    00
        BETASQ(M)=0.D0                                                  00
        M=M-1                                                           00
        IF(M .EQ. 0) GO TO 430                                          00
  401   IF(BETASQ(M) .LE. RHOSQ) GO TO 390                              00
C       TAKE ROOT OF CORNER 2 BY 2 NEAREST TO LOWER DIAGONAL IN VALUE   00
C       AS ESTIMATE OF EIGENVALUE TO USE FOR SHIFT                      00
  410   A2=GAMMA(M+1)                                                   00
        R2=.5D0*A2                                                      00
        R1=.5D0*GAMMA(M)                                                00
        R12=R1+R2                                                       00
        DIF=R1-R2                                                       00
        TEMP=SQRTF(DIF*DIF+BETASQ(M))                                   00
        R1=R12+TEMP                                                     00
        R2=R12-TEMP                                                     00
        DIF=ABSF(A2-R1)-ABSF(A2-R2)                                     00
        IF(DIF .LT. 0.D0) GO TO 420                                     00
  411   SHIFT=R2                                                        00
        GO TO 310                                                       00
  420   SHIFT=R1                                                        00
        GO TO 310                                                       00
  430   EIG(1)=GAMMA(1)+SUM                                             00
C       INITIALIZE AUXILIARY TABLES REQUIRED FOR REARRANGING THE VECTORS 00
```

```
C
C
C
      DO 440 J=1,N                                                      00
      IPOSV(J)=J                                                        00
      IVPOS(J)=J                                                        00
  440  IORD(J)=J                                                        00
C     USE A TRANSPOSITION SORT TO ORDER THE EIGENVALUES                 00
      M=N                                                               00
      GO TO 470                                                         00
  450 DO 460 J=1,M                                                      00
      IF (EIG(J) .LE. EIG(J+1)) GO TO 460                               00
  451 TEMP=EIG(J)                                                       00
      EIG(J)=EIG(J+1)                                                   00
      EIG(J+1)=TEMP                                                     00
      ITEMP=IORD(J)                                                     00
      IORD(J)=IORD(J+1)                                                 00
      IORD(J+1)=ITEMP                                                   00
  460 CONTINUE                                                          00
  470 M=M-1                                                             00
      IF(M .NE. 0) GO TO 450                                            00
  471 IF(N1 .EQ. 0) GO TO 500                                           00
  472 DO 490 L=1,N1                                                     00
      NV=IORD(L)                                                        00
      NP=IPOSV(NV)                                                      00
      IF(NP .EQ. L) GO TO 490                                           00
  473 LV=IVPOS(L)                                                       00
      IVPOS(NP)=LV                                                      00
      IPOSV(LV)=NP                                                      00
      DO 480 I=1,N                                                      00
C     TEMP=VEC(I,L)                                                     00
      TEMP=  A(I,L)                                                     00
C     VEC(I,L)=VEC(I,NP)                                                00
        A(I,L)=  A(I,NP)                                                00
C 480  VEC(I,NP)=TEMP                                                   00
  480    A(I,NP)=TEMP                                                   00
  490 CONTINUE                                                          00
  500 CONTINUE                                                          00
  560 CONTINUE                                                          00
C      PRINT 1919                                                       00
 1919 FORMAT(13H LEAVING EIGN)                                          00
       RETURN                                                           00
      END                                                               00
      FUNCTION FAC1(N)                                                  00
      IMPLICIT REAL*8(A-H,O-Z)                                          00
      INTEGER*4 N,I,PRODT                                               00
      FLOATF(I)=DFLOAT(I)                                               00
      PRODT = 1                                                         00
      IF(N.EQ.0) GO TO 10                                               00
      GO TO 20                                                          00
   10 GO TO 40                                                          00
   20 DO 30 I=1,N                                                       00
   30 PRODT = PRODT*I                                                   00
   40 FAC1=FLOATF(PRODT)                                                00
      RETURN                                                            00
```

END 003
NOT FOUND IN NM DIRECTORY. STOWED WITH TTR.
WAS 00000000

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