

AN ABSTRACT OF THE THESIS OF

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Abstract approved:

Kenneth Hedberg

The method of gas-phase electron diffraction is a very useful tool for determining the geometry of a molecule in the gas-phase to a high degree of accuracy. In this thesis, the structures of tropone and tropolone, which are similar molecules that are both based on a 7-carbon ring, were investigated with the method of gas-phase electron diffraction, using molecular orbital calculations and microwave rotational constants as auxiliary data. This experiment was undertaken with two goals in mind. The first was to determine how the addition of the hydroxyl group in tropolone altered the structure of the carbon skeleton from that of tropone. The second was to reinvestigate the location of the enolic hydrogen atom in tropolone, which had been raised in a previous study.

Key Words: gas electron diffraction, tropone, tropolone

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Structural Similarities and Differences in Tropone and Tropolone:

A Gas-Phase Electron Diffraction Study

by

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I understand that my project will become part of the permanent collection of Oregon State University, University Honors College. My signature below authorizes release of my project to any reader upon request.

Eric J. Titus, Author

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Structural Similarities and Differences in Tropone and Tropolone: A Gas-Phase Electron Diffraction Study

The Gas Electron Diffraction Method

Introduction and Theory

Gas phase-electron diffraction (GED) is a method that uses the diffraction pattern produced by an electron beam as it passes through a jet of vaporized molecules to yield information about the arrangement of the atoms in the gas-phase molecules¹.

The GED apparatus at Oregon State University consists of a chamber evacuated to ca 10^{-6} Torr, in which a nozzle is used to inject vaporized sample into the chamber, where it intersects a 60 kV beam of electrons (the vapor then condenses on a liquid nitrogen cooled cold trap). The resulting electron diffraction pattern is captured on electron image film at the bottom of the chamber. The diffraction pattern consists of a series of concentric rings of decreasing intensity. Due to the rapidly decreasing intensity of these rings, a rotating sector is placed directly above the film, which is designed to allow more scattered electrons impact the film at points further from the center of the scattering. This allows for a diffraction pattern of more even intensity, and allows more of the captured diffraction pattern to be used in data analysis. The apparatus is designed to take photographs using two different nozzle-to-film distances (nominally 30cm and 75cm) to achieve a larger range of scattering.

Once the films containing the diffraction pattern have been removed from the apparatus, they are developed. Next, the blackness (optical density) of the film is read

into a computer using a modified microdensitometer, which gives about 500 data points that represent the density across the diameter of the film. Since the films containing the diffraction pattern have all been exposed for different lengths of time, the optical density measurements of each film are on an arbitrary scale. These points are then converted from their arbitrary scale to a scale of optical density using optical density standards on the microdensitometer. This gives intensity data for each film that can be compared with data from other films and be used in structure refinement. The means of obtaining information about the molecule from the intensity pattern is a least-squares matching of a theoretical intensity curve (based on the theoretical model of the molecule) to the observed intensity curve. The formula for a theoretical intensity curve is seen in Equation 1:

$$sI_m(s) = k \sum_{i \neq j} A_i(s) A_j(s) r_{ij}^{-1} \cos(\eta_i - \eta_j) \exp(-l_{ij}^2 s^2 / 2) \sin(s(r_{ij} - K_{ij} s^2)) \quad (1)$$

$$s = (4\pi/\lambda)\sin(\theta) \quad (\text{with the scattering angle} = 2\theta)$$

A_i = atomic scattering amplitude for electrons

η_i = phase shift coefficient

r_{ij} = interatomic distance

l_{ij}^2 = mean square of amplitude

K_{ij} = anharmonicity constant

The curve given by (1) represents the molecular scattering intensity as a function of s . The variable s is the variable that takes into account the scattering angle of the electrons, or the radial distance of the scattering (as captured by the electron image film) from the center of the pattern. The actual intensity striking the film during an experiment actually contains the molecular scattering, background scattering from the sample, and background scattering from the apparatus, which are all affected by the function of the rotating sector ($\alpha(s)$), and a geometric factor ($G(2\theta)$). The formula for the total observed scattering is as follows:

$$I_{film} = I_{total} \cdot \alpha(s) \cdot G(2\theta) = \left(\frac{I_m(s)}{s^4} + \frac{I_{Atomic}}{s^4} + I_{app} \right) \cdot \alpha(s) \cdot G(2\theta) \quad (2)$$

The geometric factor, $G(2\theta)$ is there to correct for the fact that not all points on the film are the same distance away from the source of the scattering, i.e. the film is a flat surface, and the intensity formula is for scattering intensity at the surface of a sphere. This correction is $\cos^3(2\theta)$. This now gives the total scattering as:

$$s^4 I_{Total} = \frac{s^4 I_{film}}{\alpha(s) \cdot \cos^3(2\theta)} = I_m(s) + I_{atomic} + s^4 I_{app} \quad (3)$$

Solving for $sI_m(s)$ gives the following

$$\left(\frac{s^4 I_{film}}{\alpha(s) \cdot \cos^3(2\theta)} - I_{atomic} - s^4 I_{app} \right) \cdot s = \left(\frac{s^4 I_{film}}{\alpha(s) \cdot \cos^3(2\theta)} - Background \right) \cdot s = s \cdot I_m(s) \quad (4)$$

To calculate the background, a least squares fit is used. This is done using an intensity curve that is generated from a theoretical model of the molecule. The following equation is then fit:

$$I_m^{\text{exp}}(s) = a \cdot I_m^{\text{theor}} + b \cdot I_{\text{atomic}} + \sum_{i=0}^n c_i x^i \quad \text{with}$$

$$b \cdot I_{\text{atomic}} + \sum_{i=0}^n c_i x^i = \text{Background} \quad (5)$$

The values for I_{atomic} are calculated as follows:

$$I_{\text{atomic}} = s^4 \cdot \sum_i F_i^2 + s^4 \cdot \sum_i I_i \quad (6)$$

F_i = Elastic scattering amplitude

I_i = Inelastic scattering intensity

The values of F_i and I_i are available from tables. The background can now be calculated and subtracted. The calculation of the background proceeds differently depending on the nominal nozzle to film distance. For pictures taken at the 75cm distance, the I_{atomic} term is used, and the fit uses a 4th degree polynomial. For pictures taken at the 30cm distance, the I_{atomic} term is not used, and an 8th degree polynomial is used.

When describing the geometry of molecules, there are several interatomic distance parameters that can be used. This has to do with the fact that the atoms in a molecule are not stationary, but that the atom is constantly vibrating and rotating in different ways.

There are three types of interatomic distance parameters that are used in GED. They are

as follows:

r_{α} : The distance between average atomic positions

r_a : The distance used in the intensity formula

r_g : The thermal average interatomic distance

For refinements, the molecule is determined in terms of r_{α} , which gives a geometrically consistent model of the molecule. This is then converted to r_a for refinements using the intensity function. The distance r_g is the average distance between two atoms at a specific temperature. The relationships between these distances are shown below in equations (7) and (8).

$$r_g = r_{\alpha} + K + \delta r \quad (7)$$

$$r_a = r_g - l^2/r_{\alpha} \quad (8)$$

The quantity K is the perpendicular amplitude correction, and it is a correction to take into account the effect of the vibration of the molecule on the interatomic distance due to vibrational modes that have a component that is perpendicular to the bond. To understand the reason that the amplitude affects bond distances, imagine the vibrations of the linear molecule CO_2 . Looking at the symmetric bending vibration of this molecule (where both oxygen atoms end up above or below the carbon atom making a V shape), it should be noted that the distance between the two oxygen atoms is actually at its longest (equal to twice the carbon-oxygen bond distance) when the vibration passes through the point where CO_2 is linear, and gets shorter as the vibration takes the molecule further from this point, which makes the actual average distance between the oxygen atoms shorter than twice the length of each carbon-oxygen bond. This is corrected for in the refinement calculations with the perpendicular amplitude correction factor. The quantity δr is the

correction due to centrifugal distortion. This corrects for the slight lengthening of bonds due to centrifugal distortion in molecules that are in an excited rotational state. The parameters K , δr and l are all calculated in the program ASYM40, which is described in the next section.

Programs Used for Data Analysis

Introduction

The procedure for data analysis of GED photographs is a multi-step process involving the use of several different programs written specifically for GED in the Fortran77 computer programming language. The main idea of this process is to take a theoretical electron diffraction curve, which is generated from parameters describing the molecule under investigation, and use a least squares regression to adjust these parameters to try to match the experimentally generated diffraction pattern, which then yields experimentally refined structural parameters for the molecule.

Data Analysis Overview

Once the optical density of the diffraction films has been read, a program named DATRED (a DATA REDuction program) is used to take the data from multiple films, make corrections to it, take experimental conditions into account, while compiling the data from multiple films into one data file. Next, the background scattering is removed with the program BACKGD. After the background subtraction, the program ASYM40 is used to calculate various parameters needed for refinement. Once this has been done, the process of refinement can start. This process involves two programs, one of which is referred to as VARLS (a VARIABLE Least Squares curve fitting program), and a program referred to as DISTAN, which is just used to define the molecule based on distance and angle parameters. The parameters that are input into DISTAN are generated from theoretical calculations carried out using the commercial program Gaussian03.

Data Reduction: DATRED

Once the films have been scanned using the microdensitometer, the sets of data representing the blackness of the films are reduced by program DATRED in several steps. The input for this program includes the nozzle-to-film distance, the temperature of the experiment, and calibration information, as well as the raw data from the microdensitometer. DATRED first converts the digitized film blackness data from an arbitrary density scale to the scale of optical density using standards from the microdensitometer. The next operation that the program performs is a centering routine. Since the densitometer scans across the entire plate (which may not be exactly centered on the densitometer), each half of the trace needs to be lined up and averaged. The program does this using a least squares fit. Now that an average curve has been produced, the program interpolates the data to give a set of intensities corresponding to s values with $\Delta s = 0.25 \text{ \AA}^{-1}$, which is calculated using the nozzle-to-plate distance and the radial distance from the center of the film. As noted in a previous section, the value $s = (4\pi/\lambda)\sin(\theta)$, where θ is half of the scattering angle, and λ is the wavelength of the electrons in the beam. The result of this is a set of intensity data that has been reduced to between 50 and 100 data points at even intervals (down from about 500).

Background Subtraction: BACKGD

The next program that is used on the data is program BACKGD. This program fits the experimental intensity curve to a theoretical intensity curve generated from the starting model and uses this data to subtract the background scattering from the data as described earlier.

ASYM40

The next program that is run is program ASYM40², which calculates several values that are needed for refinement. This program calculates the mean amplitude of vibration (l), the perpendicular amplitude correction (K) and the correction due to centrifugal distortion (δr), which allow for the calculation of the various distance parameters. To calculate these values, ASYM40 uses Cartesian force constants and fundamental frequencies, either experimental or theoretical, as input from Gaussian03. Another function of ASYM40 is to modify rotational constants from spectroscopic experiments to allow them to be used as auxiliary data in the structure refinement. Rotational constants from spectroscopy are given for the ground rotational state, denoted as B_0 . The interatomic distances (denoted r_0) that figure in the definition of the rotational constants are not consistent with those from GED. To remedy this, both the B_0 and the r values from GED are extrapolated from the temperature of the experiment down to 0° K. After this correction, the interatomic distances that give the corrected rotational constants are equivalent to the GED corrected r_α values (denoted r_α^0).

Structure Definition and Refinement: Program VARLS0 and Subroutine DISTAN

The actual refinement of structural parameters actually uses 2 programs that are linked together: Program VARLS0 and the subroutine DISTAN. The program DISTAN is a subroutine (which is run with VARLS0) created specifically for each molecule under investigation. The purpose of this program is to take various structural parameters of a molecule like bond lengths and bond angles and construct the molecule in Cartesian coordinates from this data. The definition of the molecule in this way allows for all interatomic distances to be calculated easily by the program. The distances between atoms

calculated by DISTAN correspond to their r_{α} separations, but this program also converts them to r_g and r_a values (using the parameters calculated by ASYM40) as well.

Once the interatomic distances have been calculated for a molecule using the program DISTAN, these distances are used by VARLS0 to create a theoretical intensity curve based on these distances. The data is now ready for refinement. The refinement process, which is carried out using VARLS0, is a non-linear least squares refinement that attempts to fit the theoretical intensity curve to the experimental curves that have been collected. To fit the theoretical curve to the data, VARLS0 alters both the structural parameters used to describe the molecule in DISTAN, as well as the amplitudes of vibration (I) for each distance. The refinement is an iterative process, with each iteration controlled by the user. During a refinement, structural parameters and amplitudes are released either one-by-one, or in small groups to keep the refinement from diverging. This stepwise approach is necessary to control parameters and/or amplitudes that either diverge or converge to values that are not reasonable, as VARLS0 is only a refinement program. Once the parameters and/or amplitudes that have been released for refinement have converged, the refined curve is taken as the starting point for the next set of refinements, in which more or different parameters and amplitudes are released for refinement. This process continues until the theoretical intensity data has reached a satisfactory convergence to the experimental data as determined by the user.

Generating Radial Distribution Data: INTRD4

Another important part of the data refinement process is the radial distribution curve. A radial distribution curve (for the purpose of this experiment) is a plot of the probability density of the distance between atoms. The radial distribution curve for a

molecule is related to its electron diffraction intensity curve (shown in Equation 1) through a Fourier transform. The radial distribution curve is composed of an overlay of peaks centered at each interatomic distance, with a width determined based on the amplitude of vibration of the pair of atoms. To generate radial distribution curves from intensity data, the program INTRD4 is used. A radial distribution curve is useful in visualizing the way different distances contribute to the diffraction pattern. The program INTRD4 allows the user to generate and compare radial distribution curves from both experimental and theoretical data, giving a plot of each curve as well as a plot of the difference between the two curves. This function of the program can be useful in troubleshooting a refinement where certain parameters are not converging properly.

Another aspect of the radial distribution curve that needs to be discussed is its significance to earlier diffraction studies. Before the implementation of computerized molecular orbital calculations in determining the structure of a molecule, the radial distribution curve generated from the experimental diffraction patterns was one of the main resources in determining what the rough structure of the molecule was. If the structure of a molecule under investigation was completely unknown, the radial distribution curve was a means of determining a rough model for the molecule, which could then be refined using diffraction data.

Theoretical Calculations: Gaussian03

Before looking at experimental data, several sets of *ab initio* molecular orbital calculations are performed using the commercial quantum-mechanical program Gaussian03³. This program is used to run optimization and frequency calculations on the molecules to be studied. These calculations provide the starting model for the refinement

of the molecule being studied. The force constants and fundamental frequencies of the molecule that are calculated in this program are also used later in the refinement of data. The levels of theory/basis sets that were used in this study were HF/6-31G* and B3LYP/cc-pVTZ.

Apparatus Calibration

Because the GED pattern is dependent on the wavelength of the scattered electrons, the wavelength of the electrons coming from the electron gun needs to be precisely known. One matter that complicates this is that, due to the nature of the electrical system, the actual voltage accelerating the electrons in the gun is different than the accelerating voltage measured by the electrical system (which is what is used in data analysis). This difference will be stable over the course of several experiments, but a calibration procedure is performed after any apparatus maintenance that could affect this difference takes place. This calibration procedure is used to determine what the difference is between the electron accelerating voltage displayed by the apparatus and the actual voltage used to accelerate the electrons.

Calibration of the apparatus is accomplished by taking diffraction photographs of carbon dioxide (CO₂), which has bond lengths that are well known. The process of CO₂ calibration is identical to the process used for any other sample, with the exception that when refinement takes place, the VARLS0 program compares the experimentally determined distances for the C=O and O·O distances with standard CO₂ distances. The program accounts for the differences between the standard data and experimental data by adjusting the calculated electron wavelength, which comes out as a correction to the

electron accelerating voltage. This correction is then applied to the diffraction data from other experiments.

The Experiment

Tropone and Tropolone

In this study, the method of GED was used to examine the structure of two similar compounds, tropone and tropolone, which are each based on a 7 carbon ring. Diagrams of the two molecules are seen below in Figure 1.

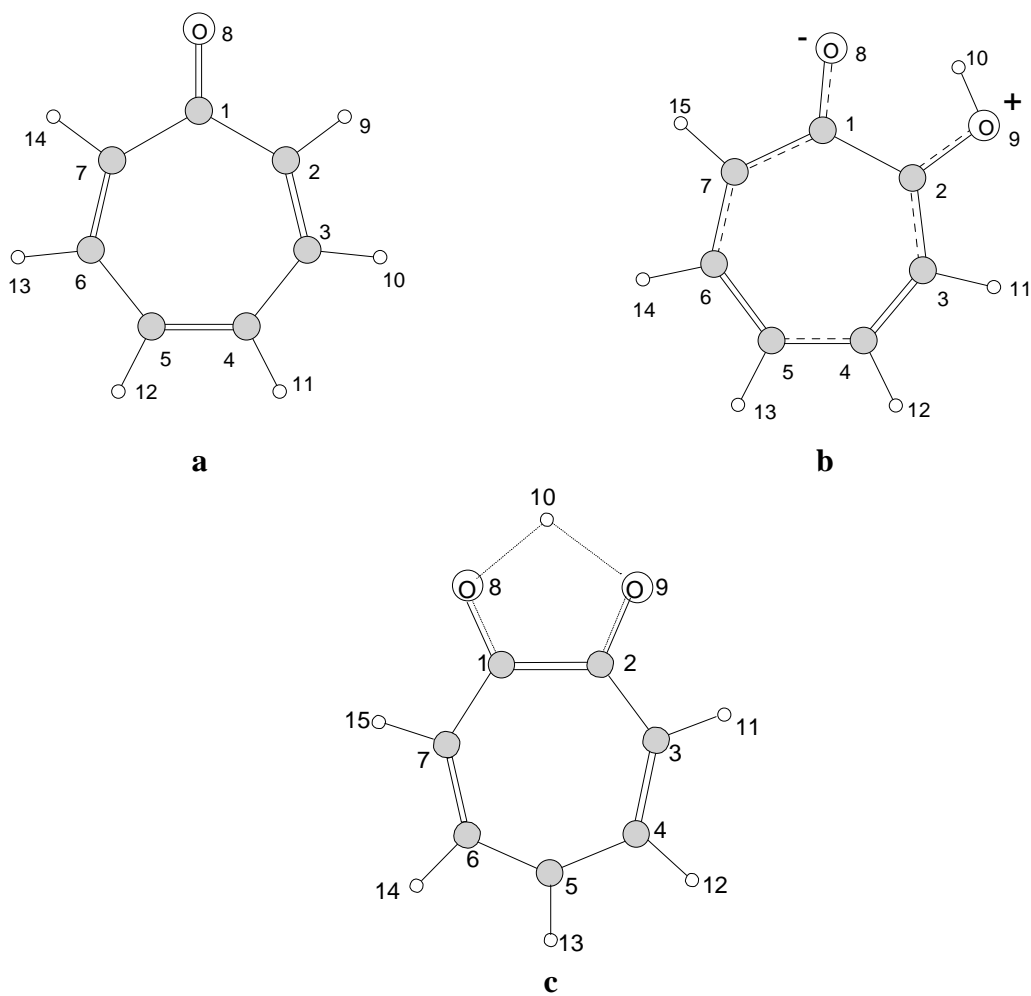


Figure 1: Models of tropone and tropolone. Tropone is labeled as **a**. Molecules **b** and **c** are both proposed structures for tropolone.

Although this report focuses on these two molecules, this study started with an examination of the structural differences between 1,3,5-cycloheptatriene (a molecule similar to tropone, but with the double bonded oxygen replaced with a hydrogen atom) and tropone. The 1,3,5-cycloheptatriene molecule is not planar (the ring is in a boat shape), while tropone is a planar molecule⁴. This change in structure suggested that the addition of the double bonded oxygen atom allows for increased conjugation of the C-C bonds around the ring. This also led to a reinvestigation of the structure of the similar molecule tropolone (also planar), which has been the subject of a GED study in the distant past⁵. The objectives of this reinvestigation of tropolone were to answer the question of where the enolic hydrogen lay in the molecule, and to examine the differences in ring structure caused by the additional hydroxyl group in tropolone. The data from the previous GED study fit well to a symmetric model of tropolone (molecule **c** in Figure 1) , placing the hydrogen atom exactly between the two oxygen atoms, and giving the molecule C_{2v} symmetry. Although the previous study achieved a good fit for the data with a symmetric model, the authors noted that the data did not rule out the possibility of an unsymmetric molecule (molecule **b** in Figure 1). For the current GED study, fits were performed for both the symmetric and unsymmetric forms of the molecule to determine which form the data matched, along with theoretical calculations for each form.

Experimental Procedure

Samples of tropone and tropolone for this experiment were obtained from Aldrich Chemical Co. (97% pure and 98% pure, respectively) and were used without further purification. Scattering photographs of each molecule were taken at both middle camera (MC) and long camera (LC) distances, which have nominal distances of 30 cm and 75

cm. Samples were introduced into the chamber by placing a small amount of sample in a glass sample bulb equipped with a Teflon valve. Proper vapor pressures of the samples were obtained by heating the sample bulb in an oil bath, and condensation in the bulb was reduced by heating the upper portion of the sample bulb with heating tape. The nozzle was heated to prevent condensation of sample in the nozzle. Experimental conditions are as follows: sample temperature, 95-103° C; nozzle temperature, 113-122° C; electron beam current, 0.50-0.62 μ A; nominal electron accelerating voltage, 60 kV; apparatus pressure during experiment, 2-4 x 10⁻⁶ Torr; exposure times, 45-90s (LC distance) and 120-255s (MC distance); film used, Kodak 8x10 in electron image film; developer, Kodak D19 diluted 1:1. For tropone, 1 film was used from the LC exposures, and 2 films were used from the MC exposures. For tropolone, 3 films from the LC exposures were used, and 4 films from the MC exposures were used. The density of each film was read 3 times using the microdensitometer and then the average of the three scans was used for analysis.

Theoretical Calculations

Quantum mechanical calculations for tropone and each of the two models of tropolone were carried out using Gaussian03W at the HF/6-31G* and B3LYP/cc-pVTZ levels of theory/basis sets. The planarity of both tropone and tropolone was assumed in both the theoretical and experimental calculations. The theoretical results from Gaussian predict that tropolone assumes the form with C_s symmetry; the B3LYP/cc-pVTZ calculations predict that the C_s form of tropolone is lower in energy by 5.315 kcal·mol⁻¹. The B3LYP/cc-pVTZ optimized geometries were used as the starting models for refinement of the experimental data.

Harmonic frequency calculations were also carried out for tropone and both models of tropolone at the levels of theory and basis sets mentioned above. Using the Cartesian force fields and vibrational frequencies obtained from the B3LYP/cc-pVTZ calculation for tropone and tropolone, normal-coordinate calculations were done using the program ASYM40 to calculate the constants needed for the interconversion of distances as noted in the section on ASYM40 earlier in this report. These frequency calculations also predicted that the C_{2v} conformation of tropolone exists as a transition state, so the results of the calculations on this form were not used in program ASYM40.

Structural Models

Tropone

Assuming that tropone is a planar molecule with C_{2v} symmetry, the entire structure can be defined using 11 parameters. These were the bond lengths $r(C1-C2)$, $r(C2=C3)$, $r(C4=C5)$, $r(C1=O8)$, the ring angles $\Delta(C2-C1-C7)$ and $\Delta(C1-C2-C3)$, and the cross-ring distance as defined by the distance between C1 and the center of the C4=C5 bond. The hydrogen atoms were defined using the average carbon-hydrogen bond length $\langle r(C-H) \rangle$, and the angles $\Delta(C3-C4-H9)$, $\Delta(C2-C3-H11)$, and $\Delta(C5-C4-H13)$. In this model, there are 38 different distances, given that all C-H bonded distances were assumed to be equal, and that all H-H distances in the molecule were ignored. The vibrational amplitudes for the distances were formed into 15 groups for refinement. Amplitudes that are grouped are refined together while preserving amplitude differences predicted by theory. Groupings can be seen in Appendix A.

Tropolone

To describe the geometry of the C_s conformation of tropolone (the conformation predicted by the results of the theoretical calculations), 23 parameters were used. Due to the number of parameters used in refinement, many distances and angles were input as averages and differences. The benefit of this is that although the same precision is obtained for each individual parameter, the value calculated for the average is more precise. In this model of tropolone, there were 86 distances, which excludes H··H distances. The 86 corresponding amplitudes of vibration were then formed into 16 groups for refinement. These can be seen in Appendix B. A model of tropolone with C_{2v} symmetry was also constructed from the results of the theoretical calculations.

Refinement Results

Tropone

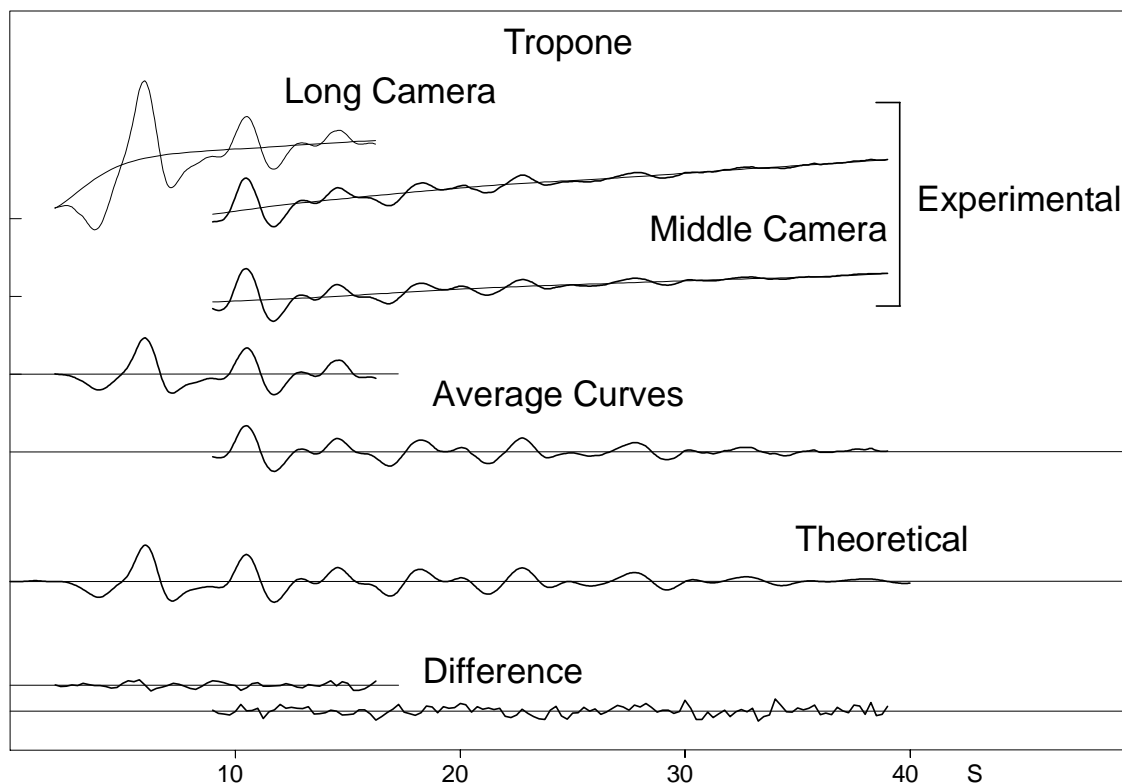
Structure refinement was carried out using the method described in the background section of this report by simultaneously fitting the three experimental curves collected to the theoretical curve generated using results from the theoretical calculations. Rotational constants from a previous microwave spectroscopy experiment were also used as auxiliary data in the refinement.⁶ As can be seen in the table of distances included in Appendix A, several of the non-bonded O··H amplitudes could not be refined, or have a large uncertainty associated with them due to the low weight of the scattering. The experimentally refined parameters for tropone are listed in Table 1, along with their initial values (predicted by theory). Figure 2 below shows the experimental intensity curve data collected from the tropone diffraction films, along with the intensity curve generated from

the refined model of the molecule. Figure 3 shows the radial distribution curve of the interatomic distances in the molecule, along with peak assignments.

Table 1: Refinement Parameters for Tropone^a

Parameter	Experiment (r_e, Δ_e)	Theory (r_e, Δ_e) ^b
$\langle r(\text{C-H}) \rangle$	1.067(7)	1.084
$r(\text{C=O})$	1.200(3)	1.229
$r(\text{C1-C2})$	1.460(14)	1.468
$r(\text{C2=C3})$	1.343(13)	1.354
$r(\text{C4=C5})$	1.384(34)	1.357
$\Delta(\text{C2-C1-C7})$	120.7(18)	121.7
$\Delta(\text{C1-C2-C3})$	133.0(28)	131.0
Cross-ring distance ^c	3.147(9)	3.165
$\Delta(\text{C3-C2-H9})$	113.2(37)	117.5
$\Delta(\text{C2-C3-H10})$	109.3(56)	115.5
$\Delta(\text{C5-C4-H11})$	117.0(94)	116.7

^aAll distances (r) are given in Angstroms (\AA), with all angles (Δ) in degrees. ^bValues calculated at the B3LYP/cc-pVTZ level of theory/basis set. ^cCross-ring distance is the distance between C1 and the C4=C5 bond.



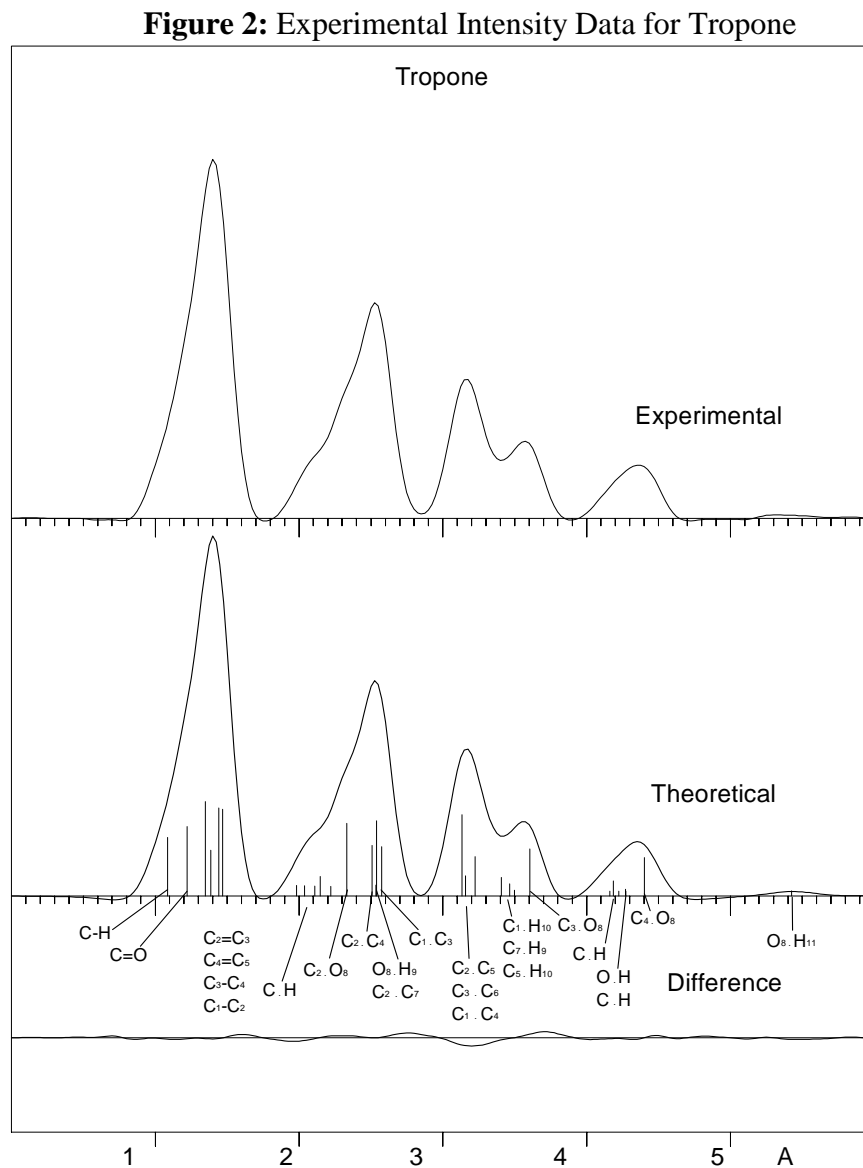


Figure 3: Radial Distribution Curve for Tropone

Tropolone

Structural refinement was carried out by simultaneously fitting the seven experimental curves collected to the theoretical curve generated from the theoretical calculation (of tropolone with C_s symmetry). Rotational constants from a previous microwave spectroscopy experiment were also used as auxiliary data in the refinement.⁷

During the refinement, several of the parameters were unable to be refined due to low scattering weight and were left at theoretical values throughout the refinement. These parameters were all of the C-C bonded distance differences, all of the $\Delta(\text{C-C-C})$ and $\Delta(\text{C-C-O})$ ring-angle differences, and the hydrogen defining angles $\Delta(\text{C-C-H})$ and $\Delta(\text{C-O-H})$. Upon refinement, each of these parameters either did not converge or had a large error associated with them. To test the assumption that alteration of the C-C bonded distance differences would not have a significant impact on the refinement of the overall structure, these values were each modified by a few hundredths of an angstrom and following each modification, the structure was refined again. This test showed that the impact of modifying these differences was small enough to justify fixing them at their theoretical values. The intensity curves from the tropolone films can be seen below in Figure 4, with the radial distribution curves for the final model given in Figure 5. Table 2, shown below, lists the refined values for all parameters used to define the molecule, as well as their initial (predicted by theory) values. A full list of refined interatomic distances is can be seen in Appendix B.

After a set of refinements fitting the theoretical intensity curve generated from the C_s symmetry of tropolone, another set of refinements were carried out which attempted to fit the theoretical curve generated using the C_{2v} model of tropolone to the same experimental curves. After completing this set of refinements, the goodness of fit parameter of this set of refinements was compared with that of the refinements on the C_s model, and showed that the experimental data gave a much better fit to the C_s model of tropolone (as predicted by the theoretical calculations).

Table 2: Refinement Parameters for Tropolone^a

Parameter	Experiment (r_e, Δ_e) ^b	Theory (r_e, Δ_e) ^c
$\langle r(\text{C-H}) \rangle$	1.086(6)	1.0833
$\langle r(\text{C2-O9}), r(\text{C1=O8}) \rangle$	1.280(6)	1.28695
$r(\text{C2-O9}) - r(\text{C1=O8})$	0.091(12)	0.0849
$\langle r(\text{C1-C2}), r(\text{C1-C7}) \rangle$	1.465(8)	1.45741
$r(\text{C1-C2}) - r(\text{C1-C7})$	0.05 ^d	0.05
$\langle r(\text{C2=C3}), r(\text{C6=C7}) \rangle$	1.391(13)	1.36985
$r(\text{C2=C3}) - r(\text{C6=C7})$	0.00322 ^d	0.00322
$\langle r(\text{C3-C4}), r(\text{C5-C6}) \rangle$	1.380(16)	1.4082
$r(\text{C3-C4}) - r(\text{C5-C6})$	-0.00405 ^d	0.00405
$\langle \Delta(\text{C2-C1-O8}), \Delta(\text{C7-C1-O8}) \rangle$	117.0(6)	118.388
$\Delta(\text{C2-C1-O8}) - \Delta(\text{C7-C1-O8})$	-7.3519 ^d	-7.3519
$\langle \Delta(\text{C1-C2-C3}), \Delta(\text{C1-C7-C6}) \rangle$	126.9(10)	130.1828
$\Delta(\text{C1-C2-C3}) - \Delta(\text{C1-C7-C6})$	-0.4062 ^d	0.4062
$\langle \Delta(\text{C2-C3-C4}), \Delta(\text{C5-C6-C7}) \rangle$	132.7(13)	129.7063
$\Delta(\text{C2-C3-C4}) - \Delta(\text{C5-C6-C7})$	-1.3862 ^d	1.3862
$r(\text{O9-H10})$	0.985(41)	0.9909
$\Delta(\text{C1-C2-O9})$	113.7(15)	111.122
$\Delta(\text{C4-C3-H11})$	116.538 ^d	116.538
$\Delta(\text{C5-C4-H12})$	115.94 ^d	115.94
$\Delta(\text{C6-C5-H13})$	115.876 ^d	115.876
$\Delta(\text{C7-C6-H14})$	114.855 ^d	114.855
$\Delta(\text{C1-C7-H15})$	112.297 ^d	112.297
$\Delta(\text{C2-O9-H10})$	102.9341 ^d	102.934

^aAll distances (r) are given in Angstroms (\AA), with all angles (Δ) in degrees.

^bExperimental values taken from refinements on model b. ^cValues calculated at the B3LYP/cc-pVTZ level of theory/basis set. ^dNot refined and held at theoretical values due to low scattering weight associated with the parameter.

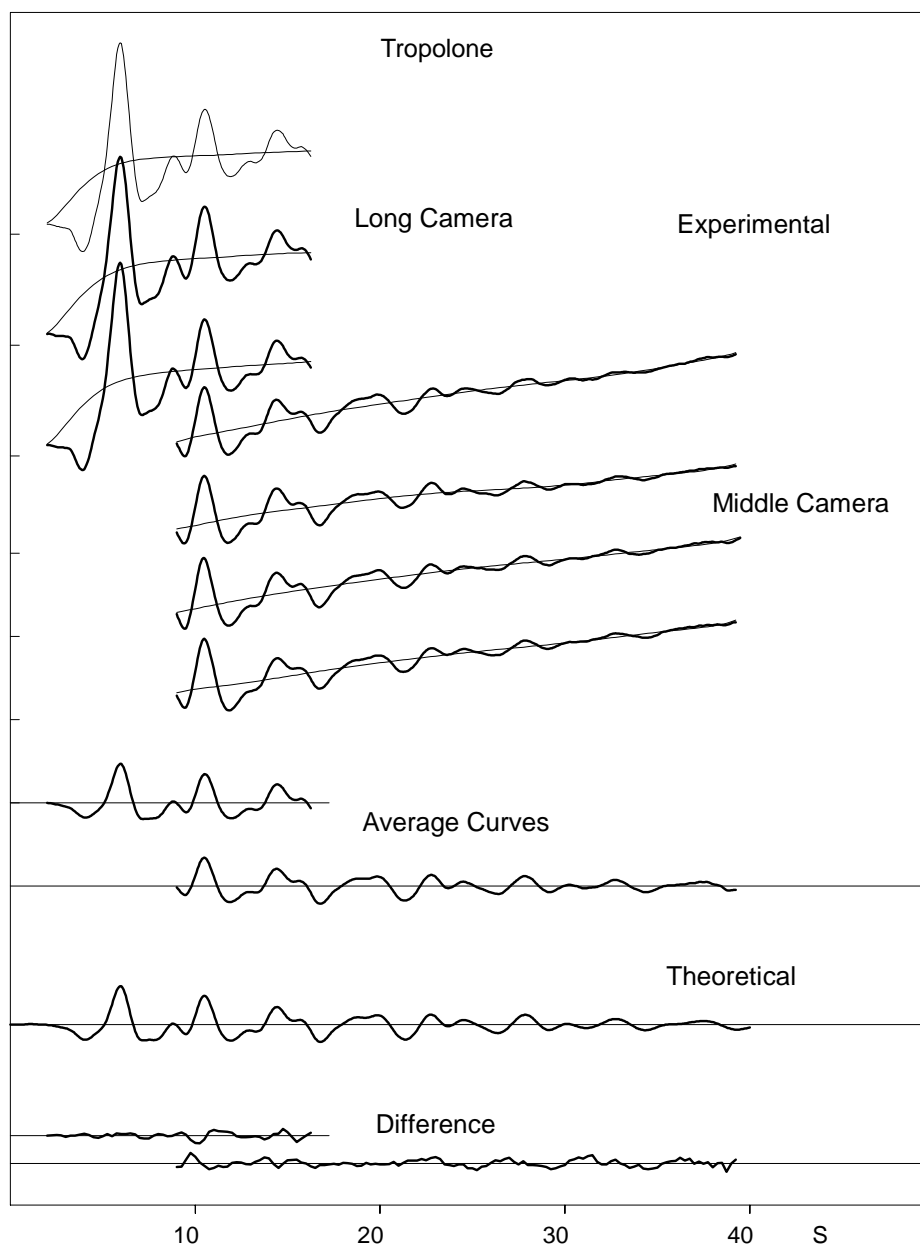


Figure 4: Experimental Intensity Data for Tropolone

Discussion

Table 3, given below, contains the final refined parameters (as r_α and Δ_α) for both tropone and tropolone.

Table 3: Comparison of Refined Parameters from Tropone and Tropolone (r_α and Δ_α

Values)^a

Tropone			Tropolone		
Parameter	Experimental	Theoretical ^b	Parameter	Experimental ^c	Theoretical ^b
C2=C3	1.343(13)	1.3542	C2 ≡ C3	1.392(13)	1.3715
C4=C5	1.384(34)	1.3569	C4 ≡ C5	1.408(29)	1.3714
C6=C7	1.343(13)	1.3542	C6 ≡ C7	1.389(13)	1.3682
C1-C2	1.460(14)	1.4676	C1-C2	1.490(8)	1.4824
C1-C7	1.460(14)	1.4676	C1 ≡ C7	1.440(8)	1.4324
C3-C4	1.427(13)	1.4292	C3=C4	1.378(16)	1.4062
C5-C6	1.427(13)	1.4292	C5=C6	1.382(16)	1.4102
C1-O8	1.200(3)	1.2291	C1 ≡ O8	1.234(5)	1.2445
C2-O9			C2 ≡ O9	1.325(11)	1.3294
$\Delta(7-1-2)$	120.7(18)	121.736	$\Delta(7-1-2)$	125.9(12)	123.224
$\Delta(1-2-3)$	133.0(28)	130.956	$\Delta(1-2-3)$	126.7(10)	129.980
$\Delta(2-3-4)$	128.2(19)	130.123	$\Delta(2-3-4)$	132.0(13)	129.013
$\Delta(3-4-5)$	128.5(5)	128.054	$\Delta(3-4-5)$	128.4(8)	129.465
$\Delta(4-5-6)$	128.5(5)	128.054	$\Delta(4-5-6)$	126.5(8)	127.532
$\Delta(6-7-1)$	133.0(28)	130.956	$\Delta(6-7-1)$	127.1(10)	130.386

^aExperimental distances and angles are given as r_α (Å) and Δ_α (degrees), with theoretical distances and angles given as r_e (Å) and Δ_e , (degrees). ^bValues calculated at the B3LYP/cc-pVTZ level of theory/basis set. ^cExperimental values taken from refinements on model b.

From information presented in Table 3, it is possible to make inferences into the differences in the bonding nature of these 7- member conjugated rings. For both of these molecules, the conjugation of the C-C bonds and the C-O bonds in the ring play an important role in their structures. When comparing the bonds around the carbon ring of these two molecules, it is important to note how the bond orders around the ring have changed. In tropone, the ring has alternating bond lengths around the ring, with the C2-

C3, C4-C5, and C6-C7 bonds all significantly shorter than the other C-C bonds in the ring, which is reflected by their representation as double bonds. In tropolone, the data based on model **b** suggests that these bonds are longer, while the other bonds in the ring (represented as single bonds in tropone) are shorter in tropolone, with the exception of the C1-C2 bond; the lengthening of this bond is due to its conjugation between the two C-O bonds. The differences in bonding between these molecules are enough to make the C3-C4 and the C5-C6 bonds the shortest C-C bonds in tropolone. Form **b** of tropolone reflects this, and based on this model, it appears that the addition of the hydroxyl group to the ring injected additional electrons and allowed for this increased conjugation around the ring.

The other objective of this experiment was to reexamine the structure of tropolone to determine the location of the hydrogen atom of the hydroxyl group; although this position can not be measured directly because of the low scattering power of the hydrogen atom, it may be inferred from the structure of the ring. The question that had been raised in the previous study of tropolone was whether the molecule had C_s symmetry (model **b**) or C_{2v} symmetry (model **c**). As stated previously, the authors found that the data obtained in their experiment fit well to a symmetric model of tropolone, but did not rule out the unsymmetric form. After attempting to fit the experimental data to each model of tropolone, it was determined that a better fit to the experimental data was obtained with the C_s form. This determination was possible because the level of precision of the results from electron diffraction experiments has increased dramatically over the almost 60 years that have elapsed since the original study. These advances have allowed

for enough precision in the data obtained in this experiment to be able to determine which structure better fit the experimental data.

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APPENDICES

Appendix A. Experimental and Theoretical Distances in Tropone

Distance	Experiment				Theory	
	r_{α}^a	r_g	r_a	ℓ^b	r_e	ℓ
C-H	1.067(7)	1.093	1.086	0.089(8)	1.084	0.076
C1=O8	1.200(3)	1.222	1.220	0.045(4)	1.229	0.039
C2=C3	1.343(13)	1.351	1.349	0.052(8)	1.354	0.043
C4=C5	1.384(34)	1.388	1.386	0.052(8)	1.357	0.043
C3-C4	1.427(13)	1.444	1.442	0.057(6)	1.429	0.047
C1-C2	1.460(14)	1.471	1.469	0.059(6)	1.468	0.049
C1·H9	2.127(69)	2.157	2.154	0.081(40)	2.121	0.102
C3·H9	2.019(44)	2.042	2.039	0.076(40)	2.089	0.097
C2·H10	1.972(64)	1.985	1.982	0.076(40)	2.067	0.097
C4·H10	2.194(71)	2.223	2.220	0.078(40)	2.120	0.099
C3·H11	2.108(112)	2.144	2.141	0.077(40)	2.131	0.099
C5·H11	2.096(89)	2.112	2.110	0.075(40)	2.083	0.097
C2·O8	2.304(5)	2.334	2.333	0.058(4)	2.329	0.057
O8·H9	2.484(88)	2.542	2.535	0.133 ^c	2.465	0.133
C3·C5	2.532(36)	2.542	2.540	0.066(5)	2.505	0.057
C2·C4	2.492(20)	2.510	2.509	0.066(5)	2.524	0.057
C1·C3	2.572(7)	2.575	2.573	0.068(5)	2.568	0.059
C2·C7	2.538(47)	2.541	2.539	0.072(5)	2.564	0.062
C3·C6	3.159(39)	3.160	3.159	0.078(7)	3.119	0.071
C2·C6	3.134(16)	3.137	3.134	0.080(7)	3.135	0.073
C2·C5	3.118(15)	3.132	3.130	0.077(7)	3.139	0.071
C1·C4	3.222(10)	3.226	3.225	0.076(7)	3.237	0.069
C3·O8	3.595(6)	3.607	3.606	0.066(6)	3.622	0.060
C4·O8	4.402(10)	4.404	4.402	0.090(14)	4.447	0.069
C7·H9	3.454(73)	3.464	3.461	0.091(16)	3.471	0.100
C4·H9	3.380(35)	3.412	3.410	0.088(16)	3.453	0.097
C1·H10	3.399(54)	3.409	3.407	0.090(16)	3.479	0.099
C5·H10	3.482(67)	3.500	3.498	0.088(16)	3.404	0.097
C2·H11	3.377(76)	3.409	3.407	0.088(16)	3.421	0.097
C6·H11	3.446(64)	3.469	3.467	0.088(16)	3.436	0.096
C1·H11	4.264(34)	4.277	4.273	0.125(41)	4.295	0.099
C2·H13	4.159(29)	4.164	4.160	0.127(41)	4.204	0.102
C2·H12	4.168(36)	4.193	4.189	0.125(41)	4.205	0.100
C3·H14	4.184(25)	4.194	4.191	0.127(41)	4.194	0.102
C3·H13	4.222(46)	4.228	4.224	0.126(41)	4.180	0.100
C4·H14	4.160(18)	4.185	4.181	0.125(41)	4.205	0.100
O8·H10	4.257(74)	4.276	4.270	0.158(236)	4.388	0.109
O8·H11	5.427(44)	5.432	5.428	0.146(137)	5.488	0.100

^aAll values in Å. ^bSquare brackets indicate vibrational amplitude refinement groups. ^cNot refined and held at theoretical value due to low scattering weight of the distance.

Appendix B. Experimental and Theoretical Distances in Tropolone

Distance	Experiment				Theory	
	r_{α}^a	r_g	r_a	ℓ^b	r_e	ℓ
C-H	1.086(7)	1.105	1.102	0.063(1)	1.0072	0.074
O9-H10	0.985(41)	1.007	1.002	0.074 ^c	1.0970	0.076
C1=O8	1.234(5)	1.242	1.241	0.039(9)	1.2508	0.040
C2-O9	1.325(11)	1.332	1.331	0.043(9)	1.3349	0.045
C2=C3	1.392(13)	1.398	1.396	0.051(5)	1.3756	0.044
C4=C5	1.408(29)	1.414	1.412	0.051(5)	1.3761	0.044
C6=C7	1.389(13)	1.395	1.393	0.051(5)	1.3729	0.044
C1-C2	1.490(8)	1.494	1.492	0.058(5)	1.4846	0.051
C1-C7	1.440(8)	1.447	1.445	0.055(5)	1.4380	0.048
C3-C4	1.378(16)	1.384	1.382	0.053(5)	1.4111	0.046
C5-C6	1.382(16)	1.389	1.387	0.054(5)	1.4164	0.047
O8-H10	1.846(49)	1.863	1.849	0.163 ^c	1.7914	0.163
C1·C3	2.576(10)	2.579	2.578	0.059(6)	2.5880	0.062
C1·C6	2.533(10)	2.538	2.536	0.056(6)	2.5458	0.058
C2·C4	2.531(14)	2.535	2.534	0.054(6)	2.5104	0.057
C2·C7	2.61(18)	2.613	2.612	0.061(6)	2.5658	0.063
C3·C5	2.508(18)	2.514	2.513	0.055(6)	2.5163	0.058
C4·C6	2.491(18)	2.497	2.496	0.055(6)	2.5003	0.058
C5·C7	2.545(14)	2.552	2.550	0.055(6)	2.5278	0.058
C1·O9	2.359(17)	2.365	2.364	0.06(7)	2.3259	0.060
C2·O8	2.281(12)	2.288	2.287	0.057(7)	2.3059	0.056
C3·O9	2.35(14)	2.358	2.356	0.059(7)	2.3325	0.058
C7·O8	2.327(12)	2.338	2.336	0.058(7)	2.3533	0.057
O8·O9	2.513(25)	2.524	2.517	0.138 ^c	2.4926	0.086
C1·H15	2.107(8)	2.126	2.122	0.095(11)	2.1121	0.101
C2·H10	1.82(31)	1.835	1.830	0.089(11)	1.8371	0.095
C2·H11	2.055(21)	2.070	2.066	0.093(11)	2.0798	0.099
C3·H12	2.091(13)	2.107	2.103	0.093(11)	2.1137	0.099
C4·H11	2.101(16)	2.116	2.112	0.093(11)	2.1338	0.099
C4·H13	2.141(31)	2.156	2.152	0.092(11)	2.1045	0.097
C5·H12	2.122(26)	2.137	2.133	0.092(11)	2.0973	0.098
C5·H14	2.05(28)	2.068	2.064	0.093(11)	2.1209	0.099
C6·H13	2.098(16)	2.115	2.111	0.093(11)	2.1332	0.099
C6·H15	2.156(18)	2.171	2.167	0.092(11)	2.1095	0.098
C7·H14	2.092(12)	2.107	2.103	0.092(11)	2.0819	0.098
C1·C4	3.209(17)	3.211	3.209	0.082(8)	3.2098	0.073
C1·C5	3.21(16)	3.213	3.211	0.081(8)	3.2116	0.072
C2·C5	3.185(10)	3.188	3.186	0.08(8)	3.1428	0.070
C2·C6	3.154(15)	3.156	3.154	0.083(8)	3.1379	0.073
C3·C6	3.086(30)	3.089	3.087	0.083(8)	3.1264	0.074

C3·C7	3.167(15)	3.170	3.167	0.085(8)	3.1527	0.076
C4·C7	3.175(10)	3.180	3.178	0.082(8)	3.1359	0.073
C3·O8	3.600(11)	3.604	3.604	0.056(13)	3.6190	0.061
C4·O9	3.682(14)	3.687	3.686	0.060(13)	3.6782	0.064
C6·O8	3.628(10)	3.634	3.633	0.057(13)	3.6487	0.062
C7·O9	3.726(15)	3.730	3.729	0.062(13)	3.6746	0.066
C1·H10	2.182(30)	2.194	2.188	0.119(18)	2.1300	0.137
C1·H11	3.471(17)	3.479	3.477	0.084(18)	3.4967	0.101
C1·H14	3.453(9)	3.465	3.463	0.081(18)	3.4550	0.099
C2·H12	3.432(12)	3.444	3.442	0.08(18)	3.4154	0.097
C2·H15	3.511(15)	3.521	3.519	0.084(18)	3.4823	0.101
C3·H10	3.115(35)	3.126	3.125	0.074(18)	3.1061	0.091
C3·H13	3.440(20)	3.453	3.451	0.08(18)	3.4428	0.097
C4·H14	3.385(28)	3.399	3.397	0.08(18)	3.4134	0.097
C5·H11	3.436(22)	3.447	3.445	0.08(18)	3.4349	0.098
C5·H15	3.482(19)	3.496	3.494	0.08(18)	3.4569	0.098
C6·H12	3.417(19)	3.431	3.429	0.08(18)	3.4303	0.097
C7·H13	3.442(13)	3.455	3.454	0.08(18)	3.4373	0.097
O8·H15	2.483(15)	2.506	2.498	0.133 ^c	2.5199	0.133
O9·H11	2.449(35)	2.465	2.457	0.134 ^c	2.4766	0.134
C4·O8	4.407(16)	4.408	4.407	0.083(8)	4.4192	0.071
C5·O8	4.433(15)	4.436	4.434	0.083(8)	4.4460	0.072
C5·O9	4.493(11)	4.496	4.494	0.084(8)	4.4574	0.073
C6·O9	4.451(17)	4.452	4.451	0.086(8)	4.4320	0.075
C1·H12	4.273(16)	4.280	4.276	0.13(31)	4.2744	0.102
C1·H13	4.269(13)	4.277	4.273	0.129(31)	4.2744	0.101
C2·H13	4.254(12)	4.263	4.259	0.128(31)	4.2110	0.100
C2·H14	4.227(18)	4.234	4.230	0.13(31)	4.2085	0.102
C3·H14	4.143(36)	4.153	4.149	0.13(31)	4.1925	0.102
C3·H15	4.228(16)	4.235	4.231	0.132(31)	4.2177	0.104
C4·H10	4.347(32)	4.354	4.351	0.131(31)	4.3376	0.103
C4·H15	4.248(11)	4.259	4.255	0.129(31)	4.2060	0.101
C6·H11	4.157(32)	4.164	4.160	0.13(31)	4.1946	0.102
C7·H10	3.622(26)	3.630	3.621	0.172(32)	3.5611	0.144
C7·H11	4.228(21)	4.235	4.231	0.132(31)	4.2189	0.104
C7·H12	4.242(10)	4.252	4.248	0.129(31)	4.2051	0.101
O8·H11	4.330(18)	4.338	4.334	0.139(31)	4.3644	0.110
O8·H14	4.418(10)	4.430	4.426	0.137(31)	4.4201	0.109
O9·H12	4.426(16)	4.438	4.433	0.139(31)	4.4284	0.111
O9·H15	4.461(14)	4.468	4.464	0.141(31)	4.4206	0.113
C5·H10	4.930(25)	4.935	4.930	0.152(32)	4.8880	0.124
C6·H10	4.609(24)	4.614	4.608	0.166(32)	4.5737	0.137
O8·H12	5.451(16)	5.455	5.452	0.13(31)	5.4613	0.101
O8·H13	5.480(13)	5.485	5.482	0.13(31)	5.4952	0.101
O9·H13	5.548(15)	5.555	5.552	0.131(31)	5.5108	0.102

O9·H14	5.509(18)	5.514	5.511	0.132(31)	5.4814	0.104
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^aAll values in Å. ^bSquare brackets indicate vibrational amplitude refinement groups. ^cNot refined and held at theoretical values due to low scattering weight associated with the distance

Appendix C. DISTAN Subroutine for Tropone

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SUBROUTINE DISTAN(RA,IBJ,L1,L2)
C  SUBROUTINE FOR TROPONE
C  Written in Fortran77 by Eric Titus

COMMON/ATOMS/ISYM(80),AMASS(80),XYZPA(80,3),NATOMS,NISOT,NSKIP
CHARACTER*2 ISYM
REAL*8 AMASS,XYZPA

COMMON/CONST/DCHECK,DEG,RAD,DELR,DELA,CHECK,DISFAC,AMPFAC,
$          SNORM2,DISLIM,ANGLIM,AMPLIM,ALFLIM,
$          DAMFAC,RCONV,FCONV,ITER
REAL*8 DCHECK,DEG,RAD

COMMON/MODEL/DIST(400),IDG(300),OCCUR(300),ALPHA(300),R(400),
$          AMP(300),CAP(300),IDM(300,2),IDGN(300),PNAME(30),
$          II(300),JJ(300),CORR(300),RF(300),RG(300),JAMP(30),
$          NDIS,NAMP,NALPHA,NCAP,NSCAL,NDEPAR,NEGALPH,NC
CHARACTER*4 IDG
CHARACTER*8 PNAME,DIST
C  DIST must be CHAR*8 to accomodate labels for NDEPAR

COMMON/PARAM/VAR(30),IDV(30),VNAME(30), PRED(30),IDPR(30),
$          PRUNC(30),PRWGT(30),NTVAR,NIVAR,IPRED
CHARACTER*8 VNAME

COMMON/SCRATCH/TITLE(10),TITLEX(10),X(80),Y(80),Z(80),DIFA(300),
$          TI(3,3),V(3,3),DIFG(300),DUMSCR(744)
CHARACTER*8 TITLE,TITLEX
REAL*8 X,Y,Z,TI,V

DIMENSION RA(L1)
REAL*8 E1(3)

C*****List of Parameters*****

C  VAR(1)= AVE H DIST
C  VAR(2)= C=O DIST
C  VAR(3)= 1-2 DIST
C  VAR(4)= 2-4 DIST
C  VAR(5)= 6-7 DIST
C  VAR(6)= 2-1-3 ANG
C  VAR(7)= 1-2-4 ANG
C  VAR(8)= 1 TO 6-7 BOND
C  VAR(9)= 4-2-9 ANG
C  VAR(10)= 2-4-11 ANG
C  VAR(11)= 7-6-13 ANG
C
C  1-7 ARE CARBONS, 8 IS OXYGEN, AND 9-14 ARE HYDROGENS

DATA II/ 2,1,2,6,4,1,1,4, 2, 6, 4, 7,2,8,4,2,1,2,4,2,2,1,4,6,3,6,
$          1, 7, 2, 5, 1, 2, 2, 4, 4, 6, 8, 8,262*0/

```

```
DATA JJ/ 9,8,4,7,6,2,9,9,11,11,13,13,8,9,7,6,4,3,5,5,7,6,8,8,9,9,
$      11,11,13,13,13,12,14,10,12,10,11,13,262*0/
```

```
DATA ISYM/ 7*2HC , 2HO , 6*2HH , 66*2H /
DATA AMASS/ 7*12., 16.994915, 6*1.007825, 66*0. /
```

C Statement function:

$$\text{ARG}(I,J,K) = (\text{RF}(I)**2 + \text{RF}(J)**2 - \text{RF}(K)**2)/(2.0*\text{RF}(I)*\text{RF}(J))$$

C*****Set all Coordinates to (0,0,0)

```
NC = 14
NATOMS=14
DO 14 I=1,NC
  X(I)=0.
  Y(I)=0.
  Z(I)=0.
14 CONTINUE
IDVAR=L2
```

C*****Convert parameters to variables

```
ANG124= VAR(7) *RAD
ANG213= VAR(6) *RAD
ANG429= VAR(9) *RAD
ANG2411= VAR(10) *RAD
ANG7613= VAR(11) *RAD
```

```
R18 = VAR(2)
R12 = VAR(3)
R24 = VAR(4)
R67 = VAR(5)
CROSSRING = VAR(8)
```

```
RH = VAR(1)
```

C *****CALCULATION OF C1,C2,C4,C6 INTO VERTICAL POSITION*****

```
X(1)=0
Y(1)=0
```

```
ANG= ANG213 / 2
X(2)= SIN(ANG)*R12
Y(2)= -COS(ANG)*R12
```

```
PHI= 180*RAD - (ANG213)/2
ANG= ANG124-PHI
```

```
X(4)= SIN(ANG)*R24 +X(2)
Y(4)= -COS(ANG)*R24 +Y(2)
```

```
X(6)= R67 * 0.5
Y(6)= -CROSSRING
```

```

C   ****MIRRORS CARBONS 2,4,6 ONTO C3,C5,C7****
      DO 27 J=3,7,2
          Y(J)=Y(J-1)
          X(J)=X(J-1)*(-1)
      27 CONTINUE

C   COORDINATES FOR HYDROGENS

C*****H9*****

      CALL UVEC(2,4,E1)
      X(9)= E1(1)
      Y(9) = E1(2)
      Z(9) = E1(3)

      COSINE=(COS(ANG429))
      SINE=(SIN(ANG429))
      CALL ROTAT(X(9),Y(9), COSINE, SINE)
      X(9) = X(9)*RH + X(2)
      Y(9) = Y(9)*RH + Y(2)

C*****H11*****

      CALL UVEC(4,2,E1)
      X(11) = E1(1)
      Y(11) = E1(2)
      Z(11) = E1(3)

      COSINE=(COS(-ANG2411))
      SINE=(SIN(-ANG2411))
      CALL ROTAT(X(11),Y(11), COSINE, SINE)
      X(11) = X(11)*RH + X(4)
      Y(11) = Y(11)*RH + Y(4)

C*****H13*****

      CALL UVEC(6,7,E1)
      X(13) = E1(1)
      Y(13) = E1(2)
      Z(13) = E1(3)

      COSINE=(COS(ANG7613))
      SINE=(SIN(ANG7613))
      CALL ROTAT(X(13),Y(13), COSINE, SINE)
      X(13) = X(13)*RH + X(6)
      Y(13) = Y(13)*RH + Y(6)

C   Mirrors hydrogens 9, 11, and 13 to create hydrogens 10, 12, and 14

      DO 30 L=10,14,2
          X(L)= (-1)*X(L-1)
          Y(L)= Y(L-1)
      30 CONTINUE

C   Coordinates for oxygen

```

```

Y(8)= R18
X(8)= 0.0
Z(8)= 0.0

```

```

C   CALCULATION OF DISTANCES

```

```

NDIS = 38
DO 34 K=1,NDIS
I=II(K)
J=JJ(K)

```

```

RF(K)=SQRT((X(I)-X(J))**2 + (Y(I)-Y(J))**2 + (Z(I)-Z(J))**2)
RG(K) = RF(K) + CORR(K)
RA(K) = RG(K) - AMP(K)**2/RF(K)

```

```

34 CONTINUE

```

```

IF(IBJ.EQ.1)RETURN

```

```

C

```

```

C   DEPENDENT PARAMETERS

```

```

NDEPAR = 11
IND = NDIS

```

```

C-1

```

```

IND = IND + 1
DIST(IND) = "3-1-2"
COSANG = ARG(6,6,18)
RA(IND) = ACOS(COSANG)*DEG

```

```

C-2

```

```

IND = IND + 1
DIST(IND) = "1-2-4"
COSANG = ARG(6,3,17)
RA(IND) = ACOS(COSANG)*DEG

```

```

C-3

```

```

IND = IND + 1
DIST(IND) = "2-4-6"
COSANG = ARG(3,5,16)
RA(IND) = ACOS(COSANG)*DEG

```

```

C-4

```

```

IND = IND + 1
DIST(IND) = "4-6-7"
COSANG = ARG(5,4,15)
RA(IND) = ACOS(COSANG)*DEG

```

```

C-5

```

```

IND = IND + 1
DIST(IND) = "2-1-8"
COSANG = ARG(6,2,13)
RA(IND) = ACOS(COSANG)*DEG

```

```

C-6

```

```

IND = IND + 1
DIST(IND) = "1-2-9"
COSANG = ARG(6,1,7)
RA(IND) = ACOS(COSANG)*DEG

```

```

C-7

```

```

IND = IND + 1
DIST(IND) = "4-2-9"
COSANG = ARG(3,1,8)

```



```

C-8  RA(IND) = ACOS(COSANG)*DEG
      IND = IND + 1
      DIST(IND) = "2-4-11"
      COSANG = ARG(3,1,9)
      RA(IND) = ACOS(COSANG)*DEG
C-9  IND = IND + 1
      DIST(IND) = "6-4-11"
      COSANG = ARG(5,1,10)
      RA(IND) = ACOS(COSANG)*DEG
C-10 IND = IND + 1
      DIST(IND) = "4-6-13"
      COSANG = ARG(5,1,11)
      RA(IND) = ACOS(COSANG)*DEG
C-11 IND = IND + 1
      DIST(IND) = "7-6-13"
      COSANG = ARG(4,1,12)
      RA(IND) = ACOS(COSANG)*DEG

      RETURN
      END

```

```

C-----+-----+-----+-----+-----+-----+-----+-----+
C                                                                 ROTAT
C  Subroutine ROTAT courtesy of Lise Hedberg
C
C  SUBROUTINE ROTAT(X, Y, COSANG, SINANG)
C  REAL*8 X,Y,XX,YY
C  XX = X
C  YY = Y
C  X = XX*COSANG - YY*SINANG
C  Y = XX*SINANG + YY*COSANG
C  RETURN
C  END

```

```

C
C-----+-----+-----+-----+-----+-----+-----+-----+
C                                                                 RLGT
C  Subroutine RLGT courtesy of Lise Hedberg
C
C  FUNCTION RLGT(I1,I2)
C  DISTANCE FROM I1 TO I2
C
C  COMMON/SCRATCH/TITLE(10),TITLEX(10),XYZ(80,3),DIFA(300),
C  $              TI(3,3),V(3,3),DIFG(300),DUMSCR(744)
C  CHARACTER*8 TITLE,TITLEX
C  REAL*8 XYZ,TI,V
C  REAL*8 SUM
C
C  SUM = 0.0D0
C  DO 10 J = 1,3
10  SUM = SUM + (XYZ(I2,J) - XYZ(I1,J))**2
      RLGT = DSQRT(SUM)

```

```
      RETURN
      END
C
C-----+-----+-----+-----+-----+-----+-----+
C
C      Subroutine UVEC courtesy of Lise Hedberg
C
C      SUBROUTINE UVEC(I1,I2,UV)
C      UNIT VECTOR FROM I1 TO I2
C
C      COMMON/SCRATCH/TITLE(10),TITLEX(10),XYZ(80,3), DIFA(300),
$          TI(3,3),V(3,3),DIFG(300),DUMSCR(744)
C      CHARACTER*8 TITLE,TITLEX
C      REAL*8 XYZ,TI,V
C      REAL*8 UV(3)
C
C      RIJ = RLGT(I1,I2)
C
C      DO 10 J = 1 , 3
10     UV(J) = (XYZ(I2,J) - XYZ(I1,J))/RIJ
C
C      RETURN
      END
```

Appendix D. DISTAN Subroutine for Tropolone

```

SUBROUTINE DISTAN(RA,IBJ,L1,L2)
C   SUBROUTINE FOR TROPOLONE
C   Written in Fortran77 by Eric Titus

COMMON/ATOMS/ISYM(500),AMASS(500),XYZPA(500,3),NATOMS,NISOT,NSKIP
CHARACTER*2 ISYM
REAL*8 AMASS,XYZPA

COMMON/CONST/DCHECK,DEG,RAD,DELRL,DELA,CHECK,DISFAC,AMPFAC,
$           SNORM2,DISLIM,ANGLIM,AMPLIM,ALFLIM,
$           DAMFAC,RCONV,FCONV,ITER
REAL*8 DCHECK,DEG,RAD

COMMON/COORD/X(500),Y(500),Z(500),NC
REAL*8 X,Y,Z

COMMON/MODEL/DIST(1100),IDG(1000),OCCUR(1000),ALPHA(1000),R(1100),
$           AMP(1000),CAP(1000),IDM(1000,2),IDGN(1000),PNAME(1000),
$           II(1000),JJ(1000),CORR(1000),RF(1000),RG(1000),
$           JAMP(1000),NDIS,NAMP,NALPHA,NCAP,NSCAL,NDEPAR,NEGALPH
CHARACTER*4 IDG
CHARACTER*8 PNAME,DIST
C   DIST must be CHAR*8 to accomodate labels for NDEPAR

COMMON/PARAM/VAR(100),IDV(100),VNAME(100), PRED(100),IDPR(100),
$           PRUNC(100),PRWGT(100),NTVAR,NIVAR,IPRED
CHARACTER*8 VNAME

COMMON/WORK1/TITLE(10),TITLEX(10),TI(3,3),V(3,3),
$           DIFA(300),DIFG(300)
CHARACTER*8 TITLE,TITLEX
REAL*8 TI,V

DIMENSION RA(L1)
REAL*8 E1(3)

C   List of Parameters

C   VAR(1)= AVE C-H DIST
C   VAR(2)= CO AVE
C   VAR(3)= CO DELTA
C   VAR(4)= 1-2,1-7 AVE
C   VAR(5)= 1-2,1-7 DELTA
C   VAR(6)= 2-3,6-7 AVE
C   VAR(7)= 2-3,6-7 DELTA
C   VAR(8)= 3-4,5-6 AVE
C   VAR(9)= 3-4,5-6 DELTA
C   VAR(10)= 2-1-8,7-1-8 AVE
C   VAR(11)= 2-1-8,7-1-8 DELTA
C   VAR(12)= 1-2-3,1-7-6 AVE
C   VAR(13)= 1-2-3,1-7-6 DELTA
C   VAR(14)= 2-3-4,5-6-7 AVE

```

```

C   VAR(15)= 2-3-4,5-6-7 DELTA
C   VAR(16)= 0-H DISTANCE
C   VAR(17)= ANG 1-2-9
C   VAR(18)= ANG 4-3-11
C   VAR(19)= ANG 5-4-12
C   VAR(20)= ANG 6-5-13
C   VAR(21)= ANG 7-6-14
C   VAR(22)= ANG 1-7-15
C   VAR(23)= ANG 2-9-10
C
C   1-7 ARE CARBONS, 8-9 ARE OXYGEN, AND 10-15 ARE HYDROGENS

DATA II/ 9, 3,1,2,2,4,6,1,1,3,5,8,1,1,2,2,3,4,5,1,2,3,7,8, 1, 2,
& 2, 3, 4, 4, 5, 5, 6, 6, 7,1,1,2,2,3,3,4,3,4,6,7, 1, 1, 1, 2, 2,
& 3, 3, 4, 5, 5, 6, 7, 8, 9,4,5,5,6, 1, 1, 2, 2, 3, 3, 4, 4, 6, 7,
& 7, 7, 8, 8, 9, 9, 5, 6, 8, 8, 9, 9, 914*0/

DATA JJ/ 10,11,8,9,3,5,7,2,7,4,6,10,3,6,4,7,5,6,7,9,8,9,8,9,15,10,
&11,12,11,13,12,14,13,15,14,4,5,5,6,6,7,7,8,9,8,9,10,11,14,12,15,
&10,13,14,11,15,12,13,15,11,8,8,9,9,12,13,13,14,14,15,10,15,11,10,
&11,12,11,14,12,15,10,10,12,13,13,14, 914*0/

DATA ISYM/ 7*2HC , 2*2HO , 6*2HH , 485*2H /
DATA AMASS/ 7*12., 2*15.994915, 6*1.007825, 485*0. /

C   Statement function:
ARG(I,J,K) = (RF(I)**2 + RF(J)**2 - RF(K)**2)/(2.0*RF(I)*RF(J))

C   Set all atoms to coordinates (0,0,0)

NATOMS= 15
NC = 15
DO 14 I=1,NC
  X(I)=0.
  Y(I)=0.
  Z(I)=0.
14 CONTINUE
IDVAR=L2

C*****DISTANCES-Conversion from Parameters to Variables
R29 = (2*VAR(2)+VAR(3))/2
R18 = R29-VAR(3)

R12= (2*VAR(4)+VAR(5))/2
R17= R12-VAR(5)
R23= (2*VAR(6)+VAR(7))/2
R67= R23-VAR(7)
R34= (2*VAR(8)+VAR(9))/2
R56= R34-VAR(9)

R910= VAR(16)
RH= VAR(1)

C*****ANGLES-Conversion from Parameters to Variables
ANG218=(2*VAR(10)+VAR(11))/2

```

ANG718=ANG218-VAR(11)
 ANG218=ANG218*RAD
 ANG718=ANG718*RAD

ANG123=(2*VAR(12)+VAR(13))/2
 ANG176=ANG123-VAR(13)
 ANG123=ANG123*RAD
 ANG176=ANG176*RAD

ANG234=(2*VAR(14)+VAR(15))/2
 ANG567=ANG234-VAR(15)
 ANG234=ANG234*RAD
 ANG567=ANG567*RAD

ANG129=VAR(17)*RAD
 ANG2910=VAR(23)*RAD

C COORDINATES FOR CARBONS 1-4

X(1)= 0
 Y(1)= 0

ANGLE= ANG218-90*RAD

X(2)= COS(ANGLE)*R12
 Y(2)= -SIN(ANGLE)*R12

ALPH=ATAN(ABS(Y(2)/X(2)))
 ANGLE=ANG123-ALPH-90*RAD

X(3)= SIN(ANGLE)*R23 + X(2)
 Y(3)= -COS(ANGLE)*R23 + Y(2)

ALPH=90*RAD-ANGLE
 ANGLE=ANG234-ALPH

X(4)= -COS(ANGLE)*R34 + X(3)
 Y(4)= -SIN(ANGLE)*R34 + Y(3)

C COORDINATES FOR CARBONS 5-7

ANGLE= ANG718-90*RAD

X(7)= -COS(ANGLE)*R17
 Y(7)= -SIN(ANGLE)*R17

ALPH=ATAN(ABS(Y(7)/X(7)))
 ANGLE=ANG176-ALPH-90*RAD

X(6)= -SIN(ANGLE)*R67 + X(7)
 Y(6)= -COS(ANGLE)*R67 + Y(7)

ALPH=90*RAD-ANGLE
 ANGLE=ANG567-ALPH

X(5)= COS(ANGLE)*R56 + X(6)
 Y(5)= -SIN(ANGLE)*R56 + Y(6)

```

C    CALCULATION OF OXYGEN O8

X(8) = 0
Y(8) = R18
Z(8) = 0

C    Calculation of Hydrogens 11-14
DO 188 L=0,3
CALL UVEC(L+3,L+4,E1)
X(L+11) = E1(1)
Y(L+11) = E1(2)
Z(L+11) = E1(3)

COSINE=COS(VAR(L+18)*RAD)
SINE=SIN(VAR(L+18)*RAD)
CALL ROTAT(X(L+11),Y(L+11), COSINE, SINE)
X(L+11) = X(L+11)*RH + X(3+L)
Y(L+11) = Y(L+11)*RH + Y(3+L)
188 CONTINUE

C    Calculation of Hydrogen 15
CALL UVEC(7,1,E1)
X(15) = E1(1)
Y(15) = E1(2)
Z(15) = E1(3)

COSINE=COS(VAR(22)*RAD)
SINE=SIN(VAR(22)*RAD)
CALL ROTAT(X(15),Y(15), COSINE, SINE)
X(15) = X(15)*RH + X(7)
Y(15) = Y(15)*RH + Y(7)

C    CALCULATION OF OXYGEN O9
CALL UVEC(2,1,E1)
X(9)=E1(1)
Y(9) = E1(2)
Z(9) = E1(3)
FACTOR = R29

COSINE=(COS(-ANG129))
SINE=(SIN(-ANG129))
CALL ROTAT(X(9),Y(9), COSINE, SINE)

X(9) = X(9)*FACTOR + X(2)
Y(9) = Y(9)*FACTOR + Y(2)
Z(9) = Z(9)*FACTOR + Z(2)

C    CALCULATION OF HYDROGEN H10
ARGUMENT=(Y(9)-Y(2))/(X(9)-X(2))
ARGUMENT=ATAN(ARGUMENT)
ARGUMENT=ANG2910-ARGUMENT

X(10)=-COS(ARGUMENT)* R910+X(9)
Y(10)= SIN(ARGUMENT)*R910 + Y(9)
C*****

```

C CALCULATION OF DISTANCES

```

NDIS = 86
DO 34 K=1,NDIS
  I=II(K)
  J=JJ(K)
  RF(K)=SQRT((X(I)-X(J))**2 + (Y(I)-Y(J))**2 + (Z(I)-Z(J))**2)
  RG(K) = RF(K) + CORR(K)
  RA(K) = RG(K) - AMP(K)**2/RF(K)

```

34 CONTINUE

```

  IF(IBJ.EQ.1) RETURN

```

C

C DEPENDENT PARAMETERS

```

NDEPAR = 7

```

```

IND = NDIS

```

C-1

```

  IND = IND + 1
  DIST(IND) = "7-1-2"
  COSANG = ARG(9,8,16)
  RA(IND) = ACOS(COSANG)*DEG

```

C-2

```

  IND = IND + 1
  DIST(IND) = "1-2-3"
  COSANG = ARG(8,5,13)
  RA(IND) = ACOS(COSANG)*DEG

```

C-3

```

  IND = IND + 1
  DIST(IND) = "2-3-4"
  COSANG = ARG(5,10,15)
  RA(IND) = ACOS(COSANG)*DEG

```

C-4

```

  IND = IND + 1
  DIST(IND) = "3-4-5"
  COSANG = ARG(10,6,17)
  RA(IND) = ACOS(COSANG)*DEG

```

C-5

```

  IND = IND + 1
  DIST(IND) = "4-5-6"
  COSANG = ARG(6,11,18)
  RA(IND) = ACOS(COSANG)*DEG

```

C-6

```

  IND = IND + 1
  DIST(IND) = "5-6-7"
  COSANG = ARG(11,7,19)
  RA(IND) = ACOS(COSANG)*DEG

```

C-7

```

  IND = IND + 1
  DIST(IND) = "6-7-1"
  COSANG = ARG(7,9,14)
  RA(IND) = ACOS(COSANG)*DEG

```

```

  RETURN

```

END

```
C-----+-----+-----+-----+-----+-----+-----+
C                                                                 ROTAT
```

C Subroutine ROTAT courtesy of Lise Hedberg

C

SUBROUTINE ROTAT(X, Y, COSANG, SINANG)

REAL*8 X,Y,XX,YY

XX = X

YY = Y

X = XX*COSANG - YY*SINANG

Y = XX*SINANG + YY*COSANG

RETURN

END

C

```
C-----+-----+-----+-----+-----+-----+-----+
C                                                                 RLGT
```

C Subroutine RLGT courtesy of Lise Hedberg

C

FUNCTION RLGT(I1,I2)

DISTANCE FROM I1 TO I2

C

***** old

C

COMMON/SCRATCH/TITLE(10),TITLX(10),XYZ(80,3),DIFA(300),

C

\$ TI(3,3),V(3,3),DIFG(300),DUMSCR(744)

C

CHARACTER*8 TITLE,TITLX

C

REAL*8 XYZ, TI, V

C

***** new

C

COMMON/WORK1/TITLE(10),TITLX(10),TI(3,3),V(3,3),

C

\$ DIFA(300),DIFG(300)

C

CHARACTER*8 TITLE,TITLX

C

REAL*8 TI, V

C

COMMON/COORD/XYZ(500,3),NC

C

REAL*8 XYZ

C

C

REAL*8 SUM

C

SUM = 0.0D0

DO 10 J = 1,3

10

SUM = SUM + (XYZ(I2,J) - XYZ(I1,J))**2

RLGT = DSQRT(SUM)

RETURN

END

C

```
C-----+-----+-----+-----+-----+-----+-----+
C                                                                 UVEC
```

C Subroutine UVEC courtesy of Lise Hedberg

C

SUBROUTINE UVEC(I1,I2,UV)

C

UNIT VECTOR FROM I1 TO I2

C

C***** OLD

C

COMMON/SCRATCH/TITLE(10),TITLX(10),XYZ(80,3), DIFA(300),

C

\$ TI(3,3),V(3,3),DIFG(300),DUMSCR(744)


```
C      CHARACTER*8 TITLE,TITLEX
C      REAL*8 XYZ, TI,V

C      *****          new
COMMON/WORK1/TITLE(10),TITLEX(10),TI(3,3),V(3,3),
$      DIFA(300),DIFG(300)
CHARACTER*8 TITLE,TITLEX
REAL*8 TI,V

COMMON/COORD/XYZ(500,3),NC
REAL*8 XYZ
C      *****

REAL*8 UV(3)
C
RIJ = RLGT(I1,I2)

DO 10 J = 1 , 3
10  UV(J) = (XYZ(I2,J) - XYZ(I1,J))/RIJ

RETURN
END
C
```

