

AN ABSTRACT OF THE THESIS OF

Sarah Lee Barkowski for the degree of Doctor of Philosophy
in Chemistry presented on May 1, 1987.

Title: Gaseous Electron-Diffraction Investigations. Molecular
Structure, Intramolecular Hydrogen Bonding, and Anti-Gauche
Composition of Ethane-1,2-dithiol and 2-Aminoethanethiol.

Abstract approved: Redacted for Privacy
Kenneth Hedberg

The molecular structures and conformational compositions of ethane-1,2-dithiol and 2-aminoethanethiol have been determined. For ethane-1,2-dithiol, one of the H_S atoms is positioned to form a $S-H\cdots S$ hydrogen bond with the $H\cdots S$ distance equal to 2.70(8) Å. The mole fractions of the gauche form at 350 and 445 K are 0.459(86) and 0.479(100), respectively; the internal energy (entropy) difference, $\Delta E^\circ = E_G^\circ - E_A^\circ$ ($\Delta S^\circ = S_G^\circ - S_A^\circ - R \ln 2$), is 0.26(86) kcal·mol⁻¹ (-1.0(22) cal·deg⁻¹·mol⁻¹). The values of some of the parameters at 350 K with 2σ values that include estimates of systematic error and correlations among observations are C-H: $r_g = 1.118(11)$, $l = 0.086(8)$; S-H: $r_g = 1.373(15)$, $l = 0.090(8)$; C-C: $r_g = 1.537(6)$, $l = 0.054(5)$; C-S: $r_g = 1.824(2)$, $l = 0.059(3)$, all in Å; $\angle_{-\alpha} CCS = 113.1(4)$, $\angle_{-\alpha} HCH = 103.7(57)$, $\angle_{-\alpha} CCH = 111.1(13)$, $\angle_{-\alpha} SCH = 108.8(13)$, $\tau(CC) = 69.0(15)$, all in deg. The $\tau(CS)$ angles in the gauche form have values of -40(30) and -141(22)° measured in the sense of a counterclockwise rotation of

the S-H bonds with the zero position represented by the cis arrangement.

For 2-aminoethanethiol, which exists in two gauche and one anti conformation, one of the gauche forms (I) has a S-H \cdots N hydrogen bond with the H \cdots N distance equal to 2.39(10) Å, but the structure of the other gauche conformer (II) is incompatible with hydrogen bonding. The mole fractions of the anti form at 372 and 580 K were found to be 0.227(54) and 0.212(46), respectively; the internal energy (entropy) difference, $\Delta E^\circ = E^\circ_G - E^\circ_A$ ($\Delta S^\circ = S^\circ_G - S^\circ_A - R \ln 2$), is 0.18(42) kcal \cdot mol $^{-1}$ (1.5(9) cal \cdot deg $^{-1}\cdot$ mol $^{-1}$). The values of some of the more important parameters at 372 K with 2σ values including estimates of systematic error and correlations among observations are N-H: $\underline{r}_g = 1.051(3)$, $\underline{l} = 0.053(5)$; C-H: $\underline{r}_g = 1.120(3)$, $\underline{l} = 0.057(5)$; S-H: $\underline{r}_g = 1.371(12)$, $\underline{l} = 0.060(5)$; C-N: $\underline{r}_g = 1.481(2)$, $\underline{l} = 0.049(4)$; C-C: $\underline{r}_g = 1.526(2)$, $\underline{l} = 0.057(4)$; C-S: $\underline{r}_g = 1.828(3)$, $\underline{l} = 0.055(4)$; all in Å, $\underline{\angle}_{\alpha} \text{CCS} = 113.1(4)$, $\underline{\angle}_{\alpha} \text{CCN} = 111.2(12)$, $\underline{\angle}_{\alpha} \text{CC}_S\text{H} = 108.0(15)$, $\underline{\angle}_{\alpha} \text{CC}_N\text{H} = 108.9(15)$, $\tau(\text{CC})_{\text{I}} = 63.4(24)$, $\tau(\text{CN})_{\text{I}} = -49(18)$, $\tau(\text{CS})_{\text{I}} = -21(28)$, $\tau(\text{CC})_{\text{II}} = 63.8(13)$, $\tau(\text{CN})_{\text{II}} = 47(19)$, $\tau(\text{CS})_{\text{II}} = -72(11)$, all in deg. The plus sense for the torsion angles is counterclockwise rotation of the nearest group when viewing from S to C, or N to C.

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GASEOUS ELECTRON-DIFFRACTION INVESTIGATIONS.
MOLECULAR STRUCTURE, INTRAMOLECULAR HYDROGEN BONDING,
AND ANTI-GAUCHE COMPOSITION OF
ETHANE-1,2-DITHIOL AND 2-AMINOETHANETHIOL

by

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A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Doctor of Philosophy

Completed May 1, 1987

Commencement June 1987

APPROVED:

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Date thesis is presented _____ May 1, 1987

ACKNOWLEDGMENTS

I want to express my sincere gratitude to my research advisor, Professor Kenneth Hedberg, for his guidance and encouragement throughout my graduate education.

I am very grateful to Lise Hedberg for her help and advice with many calculations. Her endless patience and willingness to contribute helped make this experience an enjoyable one.

I am grateful to Dr. Richard French and M. Rahim Kazerouni for their help during these investigations.

I am grateful to Professor M. Harmony for his consultation and revised results on ethane-1,2-dithiol.

Financial support through Oregon State University Chemistry Department and grants from the National Science Foundation is gratefully acknowledged.

I want to express special appreciation to my husband, Tim, for his patience and understanding, particularly through the writing of this thesis.

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**Gaseous Electron-Diffraction Investigations.
Molecular Structure, Intramolecular Hydrogen Bonding,
and Anti-Gauche Composition of
Ethane-1,2-dithiol and 2-Aminoethanethiol**

I. INTRODUCTION

This thesis describes molecular structure investigations of ethane-1,2-dithiol and 2-aminoethanethiol by gaseous electron diffraction. These molecules are part of a class of molecules, the 1,2-disubstituted ethanes, which generally exist as mixtures of conformers. The two possible heavy-atom conformers, gauche and anti, are defined by the value for the torsion angle $\tau(\text{CC})$; values nominally equal to $\pm 60^\circ$ and $+180^\circ$ correspond to the gauche and anti forms respectively. Additional conformers may be generated by rotation about the terminal torsion angles, for example $\tau(\text{CS})$ or $\tau(\text{CN})$.

Thermodynamic information about the conformational equilibrium of a 1,2-disubstituted ethane can be revealed from an investigation of the temperature dependence of the conformational composition. Assuming a system to consist of two components in equilibrium, the anti and gauche conformers, one can determine the internal energy- and entropy differences, $\Delta E^\circ = E_G^\circ - E_A^\circ$ and $\Delta S^\circ = S_G^\circ - S_A^\circ - R \ln 2$, where

the statistical weight of the gauche form has been removed from S_G° , from the formula

$$R\ln(\chi_G/\chi_A) = -\Delta E^\circ(1/T) + \Delta S^\circ + R\ln 2$$

in which χ_G and χ_A represent the gauche- and anti mole fraction. The energy difference reveals information about the relative importance of the factors which stabilize each form. The gauche form may be stabilized by intramolecular hydrogen bonding of the type $X-H\cdots Y$ where X and Y are substituents and/or the "gauche effect"¹ while the anti form is mainly stabilized by steric repulsion. In addition, a rough estimate of the relative strength of the hydrogen bonds formed in two different 1,2-disubstituted ethane molecules may be had from comparison of the ΔE° values if the effect of steric hindrance and the gauche effect may be assumed to be approximately equal.

Table I.1 summarizes in a systematic fashion the results of numerous gaseous molecular structure investigations (microwave and/or electron-diffraction) of 1,2-disubstituted ethane molecules involving the groups or atoms $-NH_2$, $-OH$, $-SH$, $-F$, and/or $-Cl$. The corresponding references for these molecules are cited in the table. The trends can be summarized as follows. All molecules containing two first row atoms exist predominantly (83 to 95%) in the gauche form at room temperature. Intramolecular hydrogen bonds have been found in all of these molecules, except of course 1,2-difluoroethane, for which the stabilizing factor is presumed to be the gauche effect. Two different gauche forms, distinguishable by their terminal torsion angles $\tau(CN)$,

Table I.1. Summary of Electron-Diffraction and Microwave Results Including Conformational Composition and Hydrogen Bonding for Various 1,2-Disubstituted Ethane Molecules^a

	2 Group V	1 Group V + 1 Group VI	1 Group V + 1 Group VII or 2 Group VI	1 Group VI + 1 Group VII	2 Group VII
	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	$\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$	$\text{OHCH}_2\text{CH}_2\text{OH}$	$\text{OHCH}_2\text{CH}_2\text{F}$	$\text{FCH}_2\text{CH}_2\text{F}$
Two	ED:83%G at 373 K	ED:93%G at 357 K	ED:95%G at 376 K	ED:90%G at 429 K	ED:95%G at 295 K
First	N-H...N	O-H...N	O-H...O	O-H...F	ref 9
Row	ref 2	ref 4	ref 2	ref 8	
Atoms	MW:N-H...N ref 3	MW:O-H...N ref 5	MW:O-H...O ref 6 $\text{NH}_2\text{CH}_2\text{CH}_2\text{F}$ ED:88%G at 355 K N-H...F ref 4 MW:N-H...F ref 7		
		$\text{NH}_2\text{CH}_2\text{CH}_2\text{SH}$	$\text{OHCH}_2\text{CH}_2\text{SH}$	$\text{OHCH}_2\text{CH}_2\text{Cl}$	$\text{FCH}_2\text{CH}_2\text{Cl}$
One First		ED:77%G at 372 K	MW:O-H...S ref 12	ED:90%G at 310 K ref 13	
Row and		S-H...N ref 10		MW:O-H...Cl ref 14	
One Second		MW:S-H...N ref 11	$\text{NH}_2\text{CH}_2\text{CH}_2\text{Cl}$	$\text{SHCH}_2\text{CH}_2\text{F}$	
Row Atom					
			$\text{SHCH}_2\text{CH}_2\text{SH}$	$\text{SHCH}_2\text{CH}_2\text{Cl}$	$\text{ClCH}_2\text{CH}_2\text{Cl}$
Two			ED:38%G at 343 K ref 15	MW:incomplete assignment ref 11	ED:21%G at 313 K ref 18
Second					
Row			ED:46%G at 350 K see text ref 16		
Atoms			MW:see text ref 17		

^a For clarity of presentation only the composition of the heavy atom conformers is given.

have been found for ethylenediamine and 2-fluoroethylamine. For both of these molecules both of the gauche forms exhibit an intramolecular hydrogen bond. Of the six molecules containing one first row and one second row atom only three have been investigated. The results are similar to those for the molecules containing two first row atoms in that the predominant species is the gauche form and intramolecular hydrogen bonds have been identified. For 2-aminoethanethiol, which is one subject of this thesis, the results of a microwave-spectroscopy study indicate the presence of two gauche forms, distinguishable primarily by their terminal torsion angles $\tau(\text{CN})$ and $\tau(\text{CS})$, only one of which is compatible with an intramolecular hydrogen bond.

For the three molecules containing two second row atoms a decrease in the percentage existing in the gauche form is observed, in agreement with prediction based on atomic size and steric repulsion. The trend of 95 to 21% gauche when going from 1,2-difluoro- to 1,2-dichloroethane indicates an increased effect of steric hindrance and a decreased gauche effect as predicted by the periodic trends in atomic size and/or electronegativity. Since the assignment of spectral lines for 2-chloroethanethiol is incomplete and no electron-diffraction experiment has been done for this species, no valid statement can be made concerning a possible $\text{S-H}\cdots\text{Cl}$ hydrogen bond. However the microwave spectrum does indicate that both anti and gauche forms are present and, based on line intensities, that the anti form is predominant. For ethane-1,2-dithiol, another subject of this thesis, both electron-diffraction and microwave experiments had been done prior to the conclusion of this investigation. The electron-diffraction

study, which was done prior to the microwave study, indicated the anti form to be the predominant species. Without the availability of spectroscopic data no statement could be made about a possible S-H...S hydrogen bond. The microwave results, which were published during the course of this investigation, were interpreted to give a gauche form incompatible with hydrogen bonding. However the microwave data were later reanalyzed to give, in agreement with our results, a gauche form which is compatible with hydrogen bond formation.

This thesis is comprised of two main sections, each of which is a manuscript of a structure investigation except for minor editorial changes (none in content). The ethane-1,2-dithiol manuscript has been published in the Journal of American Chemical Society and the 2-aminoethanethiol manuscript will soon be submitted to the same journal. A general discussion of the theory and experimental procedures of electron diffraction and a list of pertinent references is given in Appendix A. It is included only to provide information to the reader not familiar with electron diffraction. Appendix B contains a discussion of why and how dipole-moment components are used in an electron-diffraction analysis. The details of this discussion are not likely to be found in the current literature.

Each section and appendix has a separate list of references in addition to there being a complete bibliography (Section IV). The supplementary material mentioned in each manuscript is available in the laboratory archives or from the appropriate journal.

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II. CONFORMATIONAL ANALYSIS. ETHANE-1,2-DITHIOL.
AN ELECTRON-DIFFRACTION INVESTIGATION OF THE MOLECULAR
STRUCTURE, CONFORMATIONAL COMPOSITION, AND ANTI-GAUCHE ENERGY
AND ENTROPY DIFFERENCES. EVIDENCE FOR AN
INTRAMOLECULAR S-H...S HYDROGEN BOND

Introduction

The molecules of 1,2-disubstituted ethanes exist as mixtures of anti and gauche conformers as a result of rotation about the C-C bond. Which of these forms is the more stable for a given substance depends on the relative importance of steric repulsion on the one hand, and internal hydrogen bonding and/or the "gauche effect"¹ on the other. Substances that afford the possibility of hydrogen-bond formation, such as ethylenediamine^{2,3}, ethylene glycol⁴, 2-fluoroethanol⁵, 2-aminoethanol⁶, 2-mercaptoethanol⁷, and 2-chloroethanol⁸ are found to be 80-99% gauche in the gas at room temperature. In 1,2-difluoroethane where hydrogen-bond formation is not possible, but where the gauche effect is presumed to be important, the molecules are found to be about 95% gauche.⁹ In the absence of either a strong gauche effect or hydrogen bonding, such as in 1,2-dichloroethane, the anti form predominates (60-90%).

The molecule ethane-1,2-dithiol (hereafter EDT) diagrammed in

Figure II.1 also poses the possibility of intramolecular hydrogen-bond formation. Although a bond of the type $S-H\cdots S$ in the gauche conformer would surely be weak because of the unfavorable electronegativity of the sulfur atom, bonds -- or at least arrangements -- of the type $S-H\cdots N$ and $O-H\cdots S$ apparently exist (in 2-aminoethanethiol¹⁰ and 2-mercaptoethanol⁷) and show that sulfur may act either as donor or acceptor of hydrogen. The structure and composition of EDT at about 70 °C has previously been investigated¹¹ by electron diffraction, from which it was concluded that the anti form was the more stable by about 0.8 kcal/mol. The vibrational spectrum of EDT has also been studied¹² and led to a similar conclusion about the relative stability of the conformers. The results are consistent with that for 1,2-dichloroethane (which is isoelectronic with EDT) and suggest that internal hydrogen bonding, if it exists at all in EDT, is too weak to stabilize the gauche form.

Although the overall picture of the structure and composition of EDT seemed quite clear from the electron diffraction and spectroscopic studies, there remained some interesting questions. One of these was the internal energy and entropy differences of the conformers. (Because the original diffraction work was done at only one temperature the energy difference cited is ΔG° .) Accordingly, we decided to reinvestigate the EDT system by electron diffraction with elucidation of ΔE° and ΔS° for the conformers our main object. The other question concerned the location of the H_S hydrogen atoms in the gauche conformer. From the structural point of view, the question of whether or not intramolecular hydrogen bonding occurs in EDT depends upon a

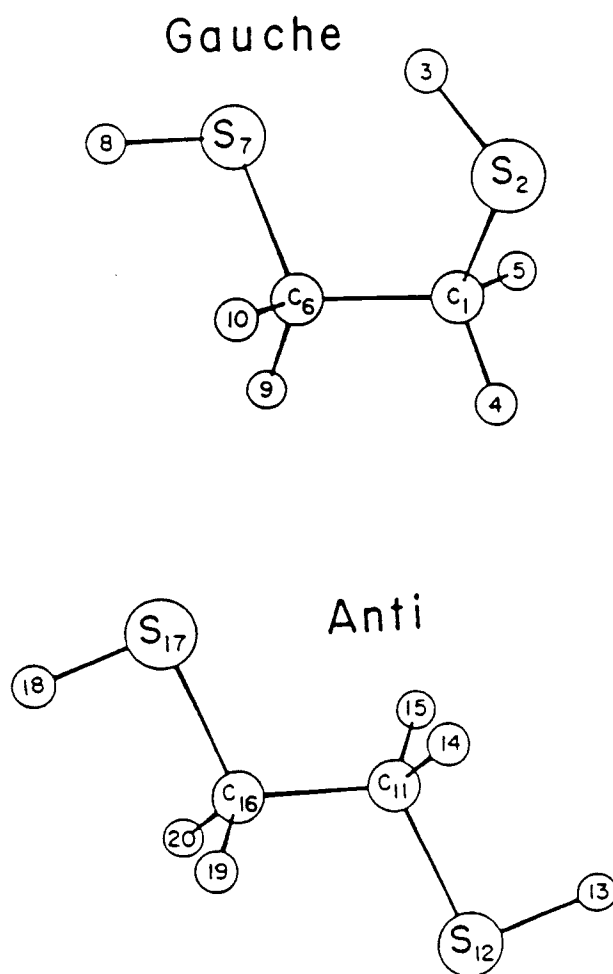


Figure II.1. Atomic numbering for the conformers of ethane-1,2-dithiol.

determination of the positions of the H_S atoms in the molecular frame of reference. It was clear that the diffraction data alone would not settle this question because the scattering terms which determine these positions, $S \cdots H_S$ and $C \cdots S_H$, are relatively weak. As it turned out, measurements of rotational constants and dipole-moment components from microwave spectroscopy^{13a} became available for the gauche conformer during the course of our work. These data, when combined with our diffraction data, have permitted us to determine the likely positions of the H_S atoms in the gauche conformer. One of these positions corresponds to the hydrogen-bond arrangement $S \cdots H-S$. An account of our work follows.

Experimental Section

The sample of EDT (>96%) was obtained from the Aldrich Chemical Co. and was distilled under reduced pressure (35 torr) through a 30 cm column packed with glass helices. A middle fraction was collected (b.p. 61.5 °C) for the diffraction experiments. The boiling temperature was essentially unchanged throughout the distillation.

Diffraction photographs were made in the Oregon State apparatus with an r^3 sector at nozzle-tip temperatures of 350 and 445 K. (Sample decomposition above about 500 K noted by changes in the mass spectrum ruled out a desirable third experiment at a higher temperature.) The 8 x 10 in Kodak projector slide plates (medium contrast) were developed for 10 min in D-19 developer diluted 1:1. Other experimental conditions were as follows: nominal nozzle-to-plate

distances, 70 and 30 cm (long and intermediate cameras); beam currents, 0.42 - 0.48 A; exposure times, 45-185 s; ambient apparatus pressures during exposures, $3.0 - 5.9 \times 10^{-6}$ torr; electron wavelengths, 0.05487 - 0.05494 Å (calibrated from CO₂ with $r_a(C=0) = 1.1646$ Å and $r_a(O=O) = 3.3244$ Å); ranges of data, $2.00 \leq s \leq 13.00$ Å⁻¹ (long, 350 and 445 K), $6.00 \leq s \leq 33.00$ Å⁻¹ (intermediate, 350 K) and $6.00 \leq s \leq 32.00$ Å⁻¹ (intermediate, 445 K); data interval 0.25 s .

Analysis of the structure was based on five plates from the long and three plates from the intermediate camera distance at 350 K, and three plates from each camera distance at 445 K. Procedures for obtaining the total intensities ($s^4 I_t(s)$) and molecular intensities ($s I_m(s)$) have been described.^{14,15} Figure II.2 shows curves of the total scattered intensities, averaged intensities, and the final background for the experiment at 350 K. The corresponding curves for 445 K as well as all of the intensity and background data are available as supplementary material.

Radial distribution curves were calculated in the usual way by Fourier transformation of functions $I'(s) = s I_m(s) Z_S Z_C A_S^{-1} A_C^{-1} \exp(-Bs^2/2)$ with the artificial damping factor, B, equal to 0.0025 Å². Figure II.3 shows the final experimental curves. Data in the unobserved or uncertain region $s < 3.75$ Å⁻¹ were taken from theoretical curves. Electron scattering amplitudes and phases for these calculations and later refinements were obtained from tables.¹⁶

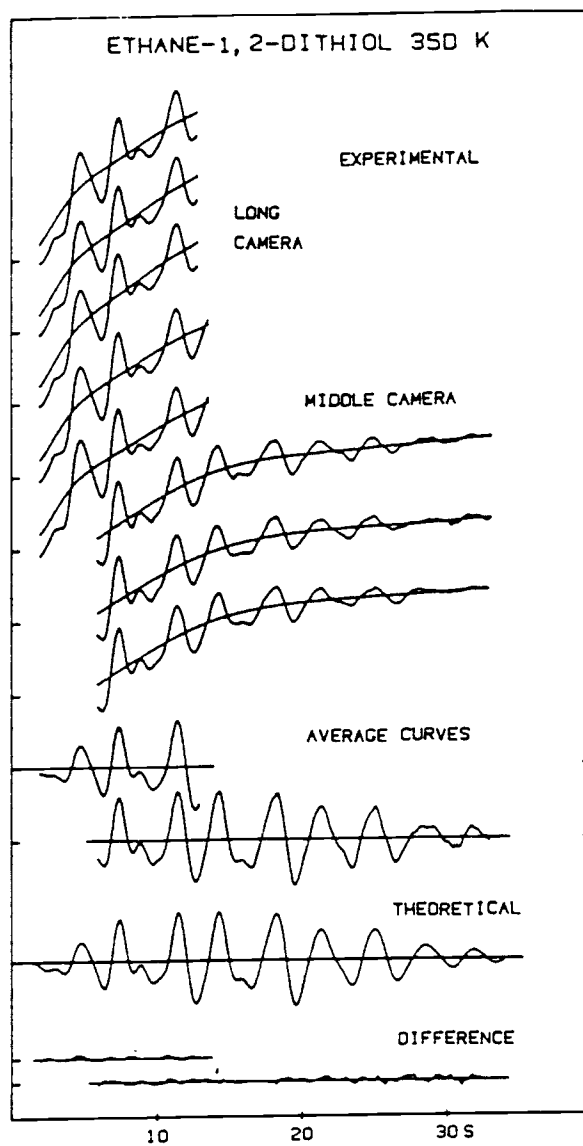


Figure II.2. Intensity curves for 350 K. The $\underline{s}^4 \underline{I}_t$ curves from each plate are shown superimposed on the backgrounds and are magnified 7 times relative to the backgrounds. The average curves are $\underline{s}(\underline{s}^4 \underline{I}_t - B) = \underline{sI}_m$. The theoretical curve is for the final model. The difference curves are experimental minus theoretical.

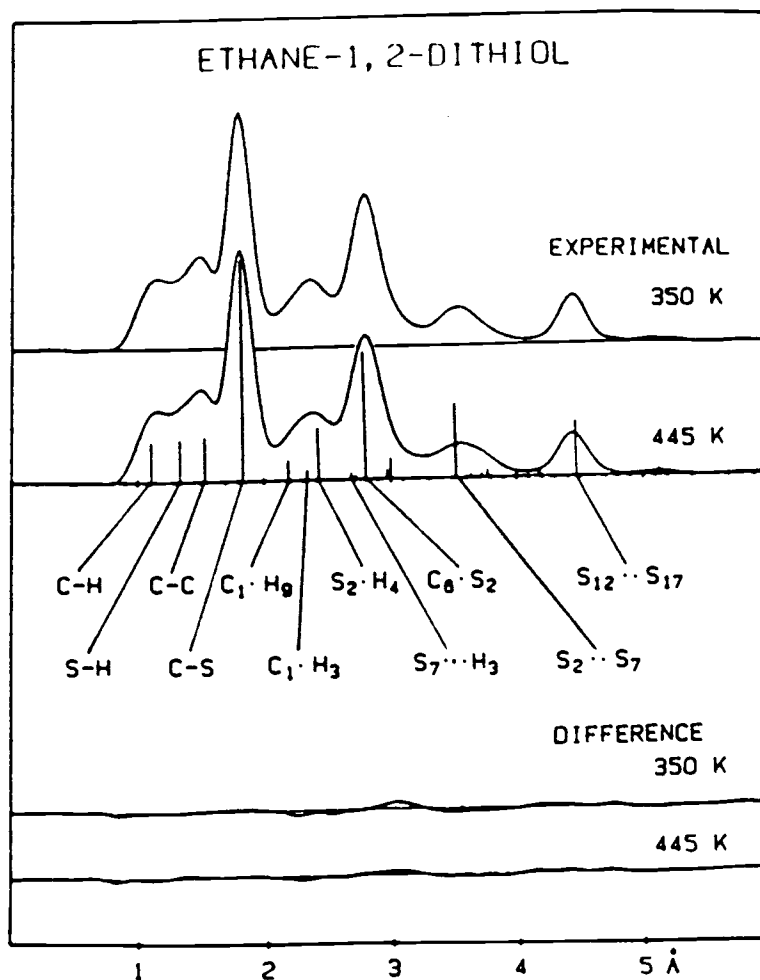


Figure II.3. Radial distribution curves for ethane-1,2-dithiol. The experimental curves were calculated from composites of molecular intensities from the two camera distances. Distances are indicated by vertical lines of height proportional to the area of the corresponding peak component. Bars for nonbond distances through more than one angle involving hydrogen are unlabeled except the hydrogen bond distance, $S_7 \cdots H_3$. The difference curves are experimental minus theoretical.

Structure Analysis

The experimental radial distribution curves gave clear evidence of the presence of substantial amounts of both anti and gauche heavy atom conformations; the peaks at approximately 3.5 Å and 4.4 Å are built up primarily from the S··S distances of the gauche and anti conformers, respectively. In most of our work involving conformational analysis of this type it has been found satisfactory to assume that the structures of the conformers differ only in their torsion angles, and that assumption was adopted for EDT. The common set of parameters was chosen to be the bond distances $\underline{r}(\text{C-H})$, $\underline{r}(\text{S-H})$, $\underline{r}(\text{C-C})$, and $\underline{r}(\text{C-S})$; and the angles $\underline{\angle}\text{CCS}$, $\underline{\angle}\text{CSH}$, $\underline{\angle}\langle\text{CCH},\text{SCH}\rangle = (\underline{\angle}\text{CCH} + \underline{\angle}\text{SCH})/2$, and $\Delta(\text{CCH},\text{SCH}) = \underline{\angle}\text{CCH} - \underline{\angle}\text{SCH}$. Specification of the gauche form of the molecule required three more parameters, taken to be the torsion angles $\tau(\text{SCCS})$, $\tau(\text{CCSH}_3)_G$, and $\tau(\text{CCSH}_8)_G$. The composition of the system was represented by the mole fraction of the anti form χ_A , which was assumed to have equilibrium C_{2h} symmetry with the S-H groups anti to the C-C bond. Because displacements of the coordinate $\tau(\text{SCCS})$ in the anti form (τ_A) were expected to decrease significantly the average values of the torsion-sensitive distances, we followed previous practice¹⁷ and introduced the parameter σ_A , the root-mean-square-amplitude of this torsion. Each distance sensitive to τ_A was divided into nine components with values of τ_A equal to 0, $\pm 0.5\sigma_A$, $\pm 1.0\sigma_A$, $\pm 1.5\sigma_A$, and $\pm 2.0\sigma_A$, and weighting each according to $P(\tau_A) = Q^{-1} \exp[-\tau_A^2 / (2\sigma_A)^2]$. With exclusion of the unimportant H.H terms, our model of the system thus had 35 different distances each with its

associated "frame" amplitude of vibration. In accordance with usual practice, the individual amplitudes known or found to be nonrefinable because of their weak contribution to the scattering were either held at values calculated from the force fields described below or collected into refinable groups in which the amplitude differences of the group members were set at the calculated values.

Experimental data applicable to the EDT structural problem were the scattered intensities from electron diffraction (which derive from the mixture of conformers), and the rotational constants and dipole-moment components measured for the gauche conformer by microwave spectroscopy. It is now common practice in electron-diffraction work to refine molecular structures with inclusion of, say, a set of three rotational constants as observables together with the diffraction data; because of their precision, the former serve as important constraints and lead to more reliable results than can be obtained by diffraction alone. Dipole-moment components do not appear to have been used in a similar way, most likely because the connection between structural parameters and charge distributions is uncertain at best. Nevertheless, since these components are very sensitive functions of some structural parameters, such as the orientations of the S-H groups in EDT that tests showed could not be unequivocally defined even by combinations of rotational constants and diffraction data, we decided to include them in our analysis.

Use of dipole-moment components required the development of a suitable method for calculation of their structure dependence. We began by adopting the approach of Nandi, et al.,¹⁰ who considered the

dipole vector in EDT to be the resultant of two $-\text{CH}_2\text{SH}$ group moments.^{13a} The group moment was assigned the magnitude found for CH_3SH ,¹⁸ and a direction defined by the angle made with the C-S bond. At first this angle was given the value found for CH_3SH (153°), but toward the end of the work it was found that better overall agreement was given by a slightly different value, 156° . The group moment was resolved into two "bond" components, one colinear with the C-S bond comprising a $\text{H}_3\text{C-S}$ fragment and the other colinear with the S-H bond; their directions were taken such as to have the sulfur atom negative with respect both to hydrogen and the methylene group. These components were used throughout the structure analysis. During each cycle of refinement cartesian coordinates for the atoms of the gauche molecule were calculated in the principal axis system. These coordinates led to the orientation of the "bond" components of the dipole moment and in turn to the axial components. A more detailed description of this process is included in Appendix B.

Least-squares refinements of the structure were made by simultaneously fitting the rotational constants and dipole-moment components for the gauche conformer and the diffraction intensity data. Because the effect of vibrational averaging is manifested in different ways in these different types of observables, it was convenient to define the model in terms of the distance type \underline{r}_α^0 . Conversions of the B_0 's to B_z 's and the \underline{r}_α^0 's to \underline{r}_a 's appearing in the scattering equations were then necessary. Although diffraction data only were available for the anti form of the molecule, the formulation of our model of the EDT system required similar conversion

of the r 's for it. The procedures used to estimate the corrections were very similar to those previously described.¹⁹ The corrections for the distances sensitive to τ_A were calculated with elimination of the torsional mode. Values for the Morse anharmonicity parameter a_3 required for the distance corrections were 1.981, 2.131, 1.84, and 1.943 \AA^{-1} for C-H, C-C, S-H, and C-S, respectively.²⁰ The quadratic force fields used in these conversions consisted of combinations of bond stretching-, angle bending-, and torsional constants taken from molecules similar to EDT and adjusted to fit the 24 fundamental wavenumbers observed¹² for each of the conformers to an accuracy of at least 99 per cent. In the case of the anti form the internal coordinate combinations were symmetrized to C_{2h} ; for the gauche form of no symmetry the same combinations were used. These force fields have no special spectroscopic significance, but were satisfactory for use in estimation of the distance and rotational constant corrections, which are generally insensitive to minor changes in it. The symmetry coordinates, force fields, observed and calculated wavenumbers, and potential energy distributions are available as supplementary material.

The least-squares refinements were carried out under a variety of conditions with regard to the weights of the various observables and the parameters which were refined. The general idea was to allow the diffraction data to dominate the refinement of the heavy atom framework while the microwave observables were allowed to dominate the refinement of the C-S torsion angles. For the final refinement the weights were assigned to the observables such that the sum of the weighted squares

of the rotational constants was about 1000 times the sum of the weighted squares of the diffraction intensities which in turn was about 200 times the sum of the weighted squares of the dipole-moment components. The relative weight of the dipole-moment components was 2:1:1 for μ_a , μ_b , and μ_c respectively; μ_a was found to be considerably more sensitive to the C-S torsions and was thus given twice the weight of the other two dipole-moment components. The three rotational constants were given equal weights.

It was found during the structure analysis that the parameters $\angle\text{CSH}$ and $\Delta(\angle\text{CCH}, \angle\text{SCH})$ could not be reliably refined. The CSH angle was varied from 90° to 97° in 1° increments and then fixed at 94° , the value which gave the best fit. The parameter $\Delta(\angle\text{CCH}, \angle\text{SCH})$ was similarly varied and then fixed at 2.3° .

The final results obtained for the structure of EDT at each of the two temperatures are given in Tables II.1 and II.2. Table II.3 shows the correlation matrix corresponding to the lower temperature results; that for the higher temperature is very similar.

Discussion

As is seen in the data of Table II.1, our analysis of the EDT structure (at 350 K) has given values for the bond distances and bond angles, including the torsion angle $\tau(\text{SCCS})$, in excellent agreement with the earlier work of Schultz and Hargittai¹¹ (hereafter SH). We differ slightly with SH in our estimate of the mole fraction of the anti form present in the sample, but the difference is more apparent

Table II.1. Results for Structural Parameters of Ethane-1,2-dithiol^a

parameter	350 K	445 K	^b Harmony	Schultz and Hargittai ^c
C-H $\left\{ \begin{array}{l} r_a \\ r_\alpha^0 \end{array} \right.$	1.112(11) 1.103(11)	1.113(8) 1.104(8)	1.103	1.12 ₀ (2 ₆)
S-H $\left\{ \begin{array}{l} r_a \\ r_\alpha^0 \end{array} \right.$	1.367(15) 1.338(15)	1.367(12) 1.337(12)	1.339	1.40 ₀ (5 ₆)
C-C $\left\{ \begin{array}{l} r_a \\ r_\alpha^0 \end{array} \right.$	1.535(6) 1.534(6)	1.542(5) 1.539(5)	1.534	1.53 ₀ (5 ₆)
C-S $\left\{ \begin{array}{l} r_a \\ r_\alpha^0 \end{array} \right.$	1.822(2) 1.820(2)	1.823(2) 1.821(2)	1.817	1.819(12)
$\angle(\text{C-C-S})$	113.1(4)	112.7(4)	113.6	112.0(26)
$\angle(\text{H-C-H})$	103.7(57)	103.9(55)	103.5	[109.8]
$\langle \angle\text{CCH}, \angle\text{SCH} \rangle^{\text{d}}$	109.9(13)	110.0(13)	--	--
$\Delta(\angle\text{CCH}, \angle\text{SCH})^{\text{d}}$	[2.3]	[2.3]	--	--
$\angle(\text{C-C-H})$	111.1(13)	111.1(13)	111.2	110.4 ^e
$\angle(\text{S-C-H})$	108.8(13)	108.8(13)	108.4	107.0(6.2)
$\angle(\text{C-S-H})$	[94.0]	[94.0]	94.0	90.5(90)
$\tau(\text{S-C-C-S})_{\text{G}}$	69.0(15)	69.1(14)	66.9	73.7(100)
$\tau(\text{C-C-S-H}_3)_{\text{G}}$	-40(30)	-41(29)	-25.5	[180.0]
$\tau(\text{C-C-S-H}_8)_{\text{G}}$	-141(22)	-152(17)	-144.3	[180.0]
$\angle\sigma_{\text{A}}^{\text{f}}$	14.9(52)	16.5(55)	--	--
X_{A}^{g}	0.541(86)	0.521(100)	--	0.62 ₀ (8 ₄)
\underline{R}^{h}	0.079	0.074	--	--

Continued.

^aDistances in angstroms, angles (\angle_{α}) in degrees. Values in parentheses are 2σ and include estimates of systematic error and correlations among observations. Values in brackets were assumed.

^bThe values in this column satisfy the B_z and μ_g values of Table II.4 essentially exactly. The values (with no uncertainties given or implied) suggest that the structural variations needed to fit the microwave data alone are relatively small. See ref 13b. ^cRef 11.

^dSee text for definitions. ^eCalculated using the reported values for $\angle(\text{SCH})$, $\angle(\text{CCH})$, and $\angle(\text{CCS})$. ^fRoot mean square torsional

amplitude for the anti form. ^gMole fraction of anti conformation.

$$h_R = \left[\frac{\sum w_i \Delta_i^2}{\sum w_i (s_i I_i(\text{obsd}))^2} \right]^{1/2} \text{ where } \Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd}).$$

Table II.2. Distances (r_{α}^0 , r_g , and r_a) and Amplitudes (l)^a

atom pair	350 K				445 K			
	r_{α}^0	r_g	r_a	l	r_{α}^0	r_g	r_a	l
C-H	1.103	1.118	1.112(11)	0.086	1.104	1.119	1.113(8)	0.078
S-H	1.338	1.373	1.367(15)	0.090	1.337	1.372	1.367(12)	0.082
C-C	1.534	1.537	1.535(6)	0.054(5)	1.539	1.543	1.542(5)	0.053(5)
C-S	1.820	1.824	1.822(2)	0.059(3)	1.821	1.825	1.823(2)	0.062(3)
C ₁ -H ₃	2.333	2.353	2.345(10)	0.134	2.333	2.353	2.345(8)	0.137
C ₁ -H ₉	2.187	2.196	2.188(14)	0.134	2.194	2.202	2.193(15)	0.138
S ₂ -H ₄	2.413	2.420	2.412(16)	0.136	2.415	2.422	2.414(16)	0.141
C ₁ -S ₇	2.802	2.805	2.802(5)	0.081(5)	2.802	2.805	2.802(5)	0.092(5)
Gauche Form								
S ₂ ···S ₇	3.515	3.522	3.517(16)	0.139(19)	3.507	3.517	3.508(13)	0.177(25)
C ₁ ···H ₈	3.610	3.624	3.617(126)	0.160	3.663	3.677	3.669(77)	0.170
C ₆ ···H ₃	2.686	2.704	2.685(238)	0.223	2.689	2.707	2.685(232)	0.242
S ₂ ···H ₈	4.091	4.104	4.081(325)	0.310	4.229	4.244	4.215(232)	0.349
S ₇ ···H ₃	2.675	2.701	2.669(81)	0.294	2.667	2.695	2.655(87)	0.325
S ₂ ···H ₉	3.772	3.778	3.775(10)	0.111	3.774	3.780	3.777(10)	0.116
S ₂ ···H ₁₀	2.967	2.973	2.962(47)	0.176	2.964	2.971	2.959(47)	0.189
Anti Form								
S ₁₂ ···S ₁₇	4.469	4.471	4.469(7)	0.089(12)	4.468	4.470	4.468(7)	0.102(15)
C ₁₁ ···H ₁₈	3.723	3.735	3.730(14)	0.128	3.725	3.737	3.732(12)	0.133
S ₁₂ ···H ₁₈	5.131	5.140	5.135(11)	0.154	5.131	5.140	5.135(10)	0.163
S ₁₂ ···H ₁₉	2.999	3.004	2.997(8)	0.148	2.999	3.005	2.997(7)	0.156

^a Values in angstroms. Parenthesized quantities are 2σ , those in curly brackets were refined as a group, those without attached uncertainties were calculated from the force field and were not refined.

Table II.3 Correlation Matrix (x100) for Parameters of Ethane-1,2-dithiol at 350 K

	^a σ_{LS} x100	\underline{r}_1	\underline{r}_2	\underline{r}_3	\underline{r}_4	\angle_5	$\langle \rangle_6$	τ_7	τ_8	τ_9	σ_{10}	\underline{l}_{11}	\underline{l}_{12}	\underline{l}_{13}	\underline{l}_{14}	\underline{l}_{15}	\underline{l}_{16}	\underline{l}_{17}	χ_{18}	
1	$\underline{r}(\text{C-H})$	0.39	100	55	27	-6	-15	-53	5	-2	-1	-5	11	-7	<1	9	8	2	1	-3
2	$\underline{r}(\text{S-H})$	0.54		100	46	-7	-27	-43	6	-2	-6	-5	19	8	15	15	11	4	4	-4
3	$\underline{r}(\text{C-C})$	0.19			100	-1	-67	-24	18	-3	-13	-13	25	2	4	15	14	6	5	-4
4	$\underline{r}(\text{C-S})$	0.05				100	-26	-11	11	-1	-5	7	-2	-4	-11	1	-21	-2	2	-1
5	$\angle(\text{C-C-S})$	13.					100	8	-53	30	12	45	-19	<1	-1	-13	26	-15	-1	2
6	$\langle \angle \text{CCH}, \angle \text{SCH} \rangle^b$	46.						100	-26	41	-43	-13	-4	1	-2	-23	<1	3	-5	-1
7	$\tau(\text{SCCS})_G$	52.							100	-18	72	-23	2	-1	<1	8	-27	12	-2	10
8	$\tau(\text{CCSH})_3G$	1100.								100	11	18	1	<1	-1	-16	26	-1	-3	5
9	$\tau(\text{CCSH})_8G$	770.									100	14	-8	<1	<1	5	-5	1	-2	14
10	\angle_A^c	180.										100	-8	-1	-3	4	11	-22	-13	13
11	$\underline{l}(\text{C-S})$	0.07											100	10	8	39	-4	11	15	-7
12	$\underline{l}(\text{C-H})$	0.27												100	34	10	3	3	2	<1
13	$\underline{l}(\text{C-C})$	0.16													100	12	4	3	2	-1
14	$\underline{l}(\text{C}_1 \cdot \text{S}_7)$	0.12														100	-10	2	14	-8
15	$\underline{l}(\text{C}_1 \cdot \text{H}_9)$	0.75															100	<1	-4	6
16	$\underline{l}(\text{S}_{12} \cdot \text{S}_{17})$	0.40																100	-38	67
17	$\underline{l}(\text{S}_2 \cdot \text{S}_7)$	0.66																	100	-63
18	χ_A^d	3.1																		100

^a Standard deviations from least-squares. Distances (\underline{r}) and amplitudes (\underline{l}) in angstroms; angles in degrees. ^b See text for definition. ^c Root mean square torsional amplitude. ^d Mole fraction of anti form.

than real since SH did not attempt a realistic assessment of the uncertainty attached to their measurement of this parameter. Our results go beyond those of SH, however, in providing estimates of the energy- and entropy differences of the conformers (described below) and in providing values for $\tau(\text{CCSH}_3)$ and $\tau(\text{CCSH}_g)$ in the gauche form of the molecule; we find $\tau(\text{CCSH}_3)$ to be such as to place the hydrogen atom between the sulfur atoms and thus to imply hydrogen-bond formation, whereas SH assumed the S-H bonds to be anti to the C-C bond. We note that the rms amplitudes of vibration reported by SH agree very well with ours except for that associated with the S··S distance in the anti form of the molecule. Because we introduced the rms amplitude of SCCS torsion as a parameter, our S··S amplitude does not reflect torsional motion. Our "frame" value is thus about 0.03 Å smaller than the S··S amplitude found by SH with their assumption of a torsionally rigid trans orientation of the anti conformer.

The quantities $\Delta E^\circ = E_G^\circ - E_A^\circ$ and $\Delta S^\circ = S_G^\circ - S_A^\circ - R \ln 2$ may be determined from the usual formula $R \ln(N_G/N_A) - R \ln 2 = -\Delta E^\circ/T + \Delta S^\circ$, where the statistical weight of the gauche form has been removed from S_G° . The results are $\Delta E^\circ = 0.26(86) \text{ kcal mol}^{-1}$ and $\Delta S^\circ = -1.0(2.2) \text{ cal mol}^{-1} \text{ K}^{-1}$. The value $0.63 \text{ kcal mol}^{-1}$ was obtained by Hayashi, et al.¹² from measurements of the vibrational spectrum, and SH's value for the Gibbs free energy difference was $0.8 \text{ kcal mol}^{-1}$. We regard the agreement as good.

Our location of the H_S atoms was made possible by recent measurements of the rotational constants and dipole-moment components of EDT by Nandi, et al.^{13a} These authors concluded that the H_S

atoms were positioned in a manner incompatible with hydrogen-bond formation, but Professor Harmony has recently reinterpreted^{13b} their data and finds that the location of these atoms is entirely consistent with our determination. Table II.1 includes a set of parameters supplied by him which satisfies the microwave data (B_z 's and μ_g) essentially exactly. The fits provided by our structure, and incidentally SH's structure, to the rotational constants and dipole-moment components are given in Table II.4. The apparently poor fit provided by SH's structure is due almost entirely to their assumption of C_2 symmetry for the gauche form of the molecule with the S-H bonds anti to the C-C.

The most interesting feature of our model of EDT is the position of one of the H_S atoms (H_3) between the two S atoms. The distance of H_3 from the acceptor atom S_7 is about 2.70 Å -- about 0.4 Å less than the sum of the van der Waals radii.²¹ Also, the orientation of the S_7 -H bond is such that an electron pair on S points toward H_3 . These data suggest the existence of intramolecular hydrogen bonding in EDT. It is clear, however, that the hydrogen bond must be very weak.

A crude estimate of its energy may be had from a comparison for the isoelectronic molecule 1,2-dichlorethane²² with the value $\Delta E^\circ \approx 0$ we find for the conformers of EDT. With the assumption that repulsive forces tending to stabilize the anti conformers in the two molecules are about the same, the energy of the hydrogen bond in EDT is predicted to be about a kilocalorie per mole.

To the extent that torsion around the C-C bond is a good representation of one of the normal coordinates, the value of the

Table II.4. Observed and Calculated Values for Rotational Constants and Dipole-Moment Components^a

	Observed		Calculated ^b	
	B_0^c	B_z^d	This Work 350 K	Schultz and Hargittai ^e
A	9292.451	9289.79	9289.61	9906.24
B	2239.194	2236.23	2233.91	2128.79
C	1935.557	1934.56	1935.85	1890.74
μ_a	0.774		0.65	0.0
μ_b	1.749		1.65	2.43
μ_c	0.683		0.66	0.0

^aRotational constants are in MHz, dipole moments are in debye.

^b $B_z = 505379/I_z$. ^cRef 13a. ^dCorrections calculated from the force field. ^eCalculated from results in ref 11.

parameter σ_A allows a crude estimate of the wavenumber for the torsional mode.¹⁷ The result calculated from the formula $\omega = (2\pi c)^{-1}(k/\mu)^{1/2}$ is 87(24) cm^{-1} , where the figure in parentheses is an estimated 2σ uncertainty. The observed¹² wavenumber is 115 cm^{-1} . The value of k was estimated to be 0.071(35) aJ/rad^2 from the formula $k = V^*/2 = RT/\sigma_A^2$; here σ_A is a weighted average from our experiments at the two temperatures.

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III. CONFORMATIONAL ANALYSIS. 2-AMINOETHANETHIOL.
AN ELECTRON-DIFFRACTION INVESTIGATION OF THE MOLECULAR
STRUCTURE, CONFORMATIONAL COMPOSITION, AND ANTI-GAUCHE ENERGY
AND ENTROPY DIFFERENCES; EVIDENCE FOR AN
INTRAMOLECULAR S-H...N HYDROGEN BOND

Introduction

The molecular structures and conformational compositions of ethylenediamine and ethane-1,2-dithiol have been the subject of numerous investigations. The results of an electron-diffraction investigation of ethylenediamine¹ show that at 90°C the molecule exists predominantly in the gauche heavy-atom conformation. Preliminary electron-diffraction results² from our laboratory for the same molecule at several sample temperatures confirm the earlier conclusions. In addition, the use of auxiliary data from microwave³ and vibrational⁴ spectroscopy led to identification of two gauche forms that are distinguished by different values of the torsion angles $\tau(\text{CN})$ and $\tau(\text{CC})$. The gauche forms are presumably stabilized relative to the anti form in part by the formation of an intramolecular N-H...N hydrogen bond. Our recent results from the electron-diffraction investigation⁵ of ethane-1,2-dithiol described in section II of this thesis, which also made use of experimental results from microwave⁶ and vibrational⁷ spectroscopy, showed that in the gas phase the

molecules exist as an almost equal mixture of anti ($\tau(\text{SCCS}) = 180^\circ$) and gauche ($\tau(\text{SCCS}) = 69^\circ$) conformers. The values of the C-S torsion angles of the gauche conformation are found to place one of the H_S atoms in a position compatible with an intramolecular S-H...S hydrogen bond.

The microwave spectrum of the molecule 2-aminoethanethiol, a "hybrid" of ethylenediamine and ethane-1,2-dithiol, has been investigated⁸ by Nandi, Boland, and Harmony (NBH). These authors found the compound to exist as a mixture of two gauche conformers (Figure III.1); they were not able to observe any of the anti form. NBH reported values of rotational constants for parent species of the two gauche forms, and for two different N-deuterated species of each gauche form. From these six sets of rotational constants and two sets of dipole-moment components they determined values of five structural parameters for each of the gauche conformers (three torsion angles $\tau(\text{CC})$, $\tau(\text{CS})$, and $\tau(\text{CN})$, one bond distance $r(\text{C-N})$, and one bond angle $\angle\text{CCN}$) based on assumed values for the remaining structural parameters. One of the gauche conformers was found to be compatible with an intramolecular hydrogen bond of the type S-H...N.

We have under way a continuing series of electron-diffraction studies of compounds exhibiting rotational isomerism. In the cases of the 1,2-disubstituted ethanes, the objective has been, in part, to determine the conformational composition as a function of sample temperature, and from the results to estimate the energy- and entropy differences of the rotamers. The molecule 2-aminoethanethiol (hereafter AET) is an important member of this series and accordingly

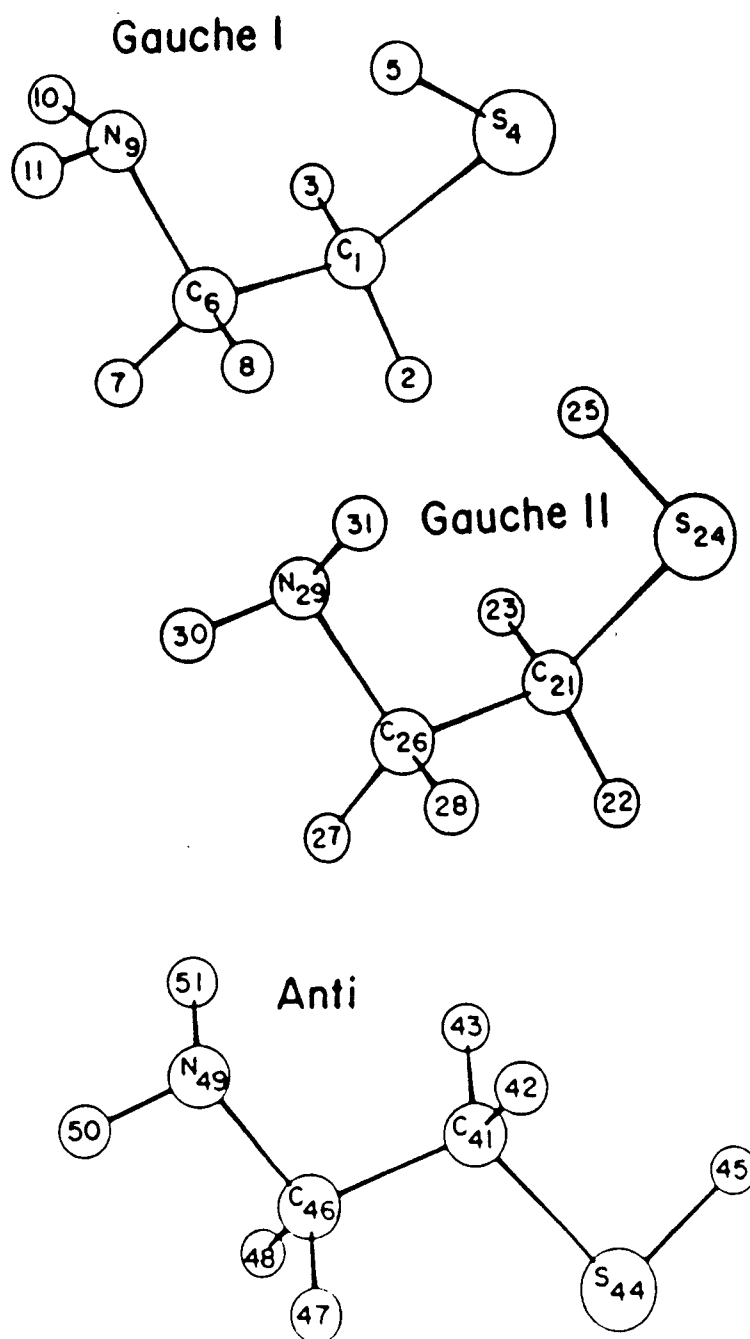


Figure III.1. Atomic numbering for the conformers of 2-aminoethanethiol.

we undertook the investigation described herein. NBH's spectroscopic data were expected to be very important for our analysis. We could not hope to independently determine the values of the C-N and C-S torsion angles using electron-diffraction intensities alone because the scattering terms which determine these angles, $S \cdots H_N$, $C \cdots H_N$, $N \cdots H_S$, and $C \cdots H_S$, are relatively weak. We have found from past experiences, however, that when rotational constants and dipole-moment components are used to complement the set of electron-diffraction intensities, the parameters such as the torsion angles mentioned can be determined with reasonable precision.

Experimental Section

The sample of AET, (Fluka Chemical Co., >98%) was sublimed under reduced pressure onto a cold finger and then transferred from the cold finger to the electron-diffraction sample tube under an atmosphere of dry nitrogen.

Diffraction photographs were made in the Oregon State apparatus with an r^3 sector at nozzle-tip temperatures of 372 and 580 K. Sample decomposition above about 650 K noted by subtle changes in the mass spectrum precluded a desirable third experiment at a higher temperature. The experimental conditions, the wavelength calibration, and the data reduction- and calculational procedures were very similar to those used for the ethane-1,2-dithiol work. Analysis of the structure was based on data from four long camera and three intermediate camera plates at 372 K and five long camera and four

intermediate camera plates at 580 K. The ranges of data were at 372 K: $2.00 \leq \underline{s}/\text{\AA}^{-1} \leq 13.25$ (long) and $7.00 \leq \underline{s}/\text{\AA}^{-1} \leq 32.00$ (intermediate) and at 580 K: $2.00 \leq \underline{s}/\text{\AA}^{-1} \leq 13.50$ (long) and $8.00 \leq \underline{s}/\text{\AA}^{-1} \leq 30.00$ (intermediate). The data interval was $\Delta \underline{s} = 0.25 \text{\AA}^{-1}$. Figure III.2 shows curves of the total intensities superimposed on their backgrounds and the averaged intensities for the experiment at 372 K. The corresponding curves for 580 K as well as all of the intensity and background data are available as supplementary material.

Radial distribution curves were calculated by Fourier transformation of functions $\underline{I}'(\underline{s}) = \underline{s} \underline{I}_m(\underline{s}) Z_S Z_C A_S^{-1} A_C^{-1} \exp(-B \underline{s}^2/2)$ with use of intensity data from theoretical curves in the unobserved or uncertain region $\underline{s} < 2.75 \text{\AA}^{-1}$. Figure III.3 shows the final experimental and difference curves.

Structure Analysis

It was known from NBH's microwave study of AET that there exist two forms of the molecule with a gauche heavy-atom conformation that differ mainly in the orientations of the $-\text{NH}_2$ and $-\text{SH}$ groups. NBH did not identify a form with an anti heavy-atom arrangement, but the radial distribution curve calculated from our electron-diffraction data reveals immediately that this form as well as the gauche is present: the peaks at approximately 4.1\AA and 3.2\AA correspond primarily to the $\text{S} \cdots \text{N}$ distances of the anti and gauche conformers, respectively.

Our analysis of the AET system was intended to yield not only the heavy-atom structures of the conformers at the two temperatures of our

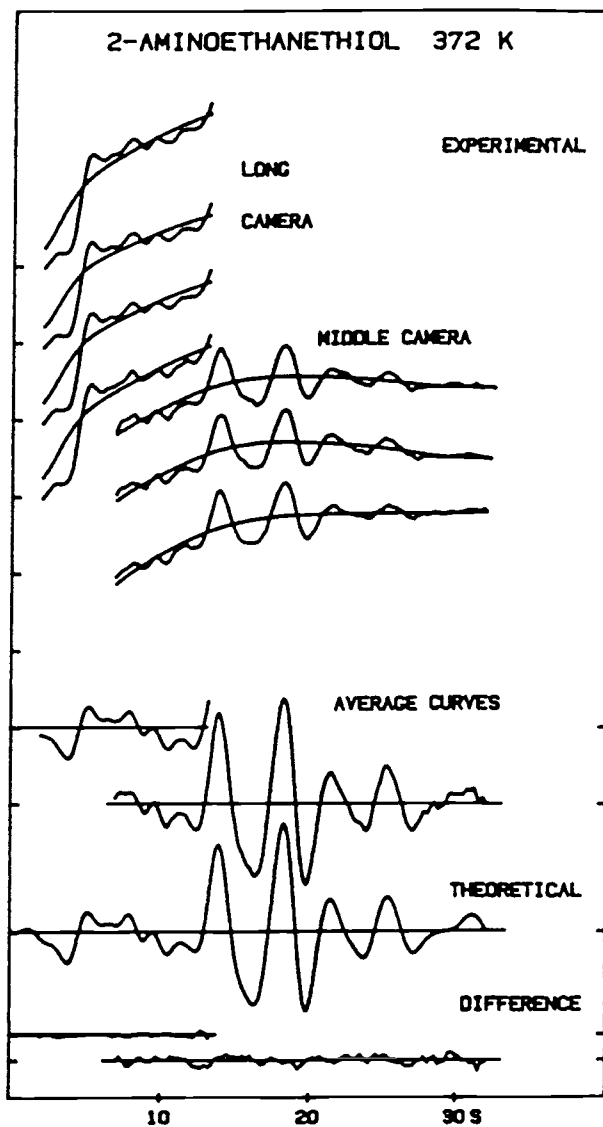


Figure III.2. Intensity curves for 372 K. The $\underline{s}^4 \underline{I}_t$ curves from each plate are shown superimposed on the final backgrounds and are magnified 6 times relative to the backgrounds. The average curves are $\underline{s}(\underline{s}^4 \underline{I}_t - B) = \underline{sI}_m$. The theoretical curve is for the final model. The difference curves are experimental minus theoretical.

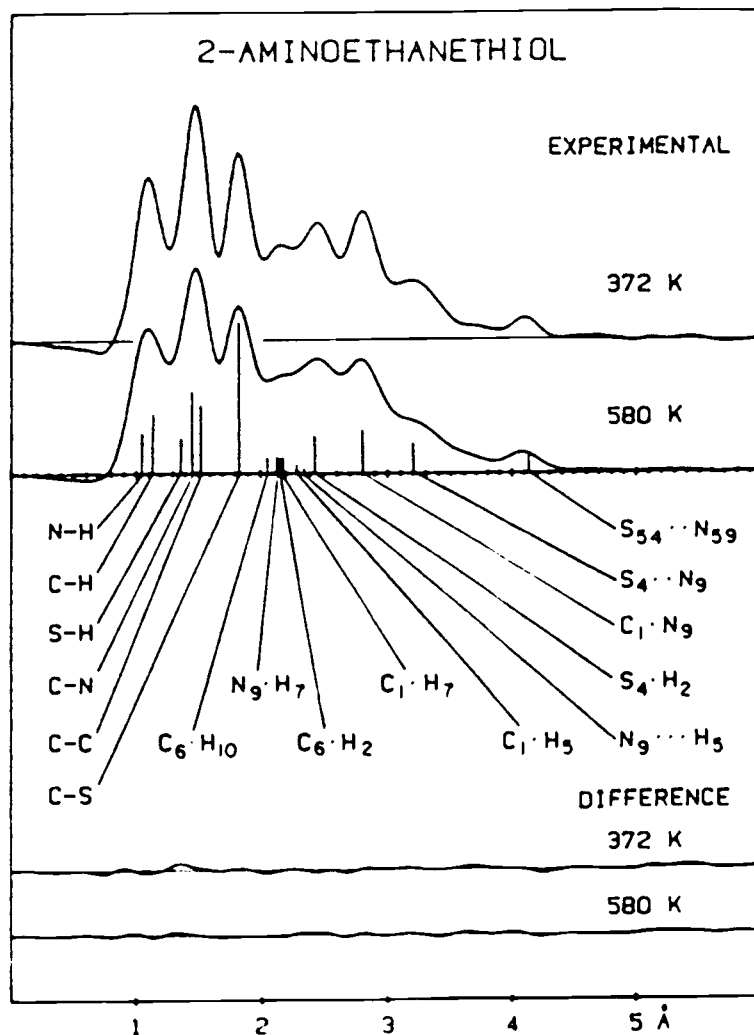


Figure III.3. Radial distribution curves for 2-aminoethanethiol. The experimental curves were calculated from composites of molecular intensities from the two camera distances with $B = 0.0025 \text{ \AA}^2$. Distances are indicated by vertical lines of height proportional to the area of the corresponding peak component. Bars for nonbond distances through more than one angle are not shown except the gauche I distances $S_4 \cdot \cdot \cdot N_9$ and $N_9 \cdot \cdot \cdot H_5$ - the hydrogen bond distance. The difference curves are experimental minus theoretical.

experiments, but also details of the structures and orientations of the -NH_2 and -SH groups. In addition to our electron-diffraction data, the data available for this task were those from NBH's work: 1) a total of 18 rotational constant values (three for the parent species of each of the two gauche forms and three of each of the two corresponding N-monodeuterated species of each of the two gauche forms) and 2) a total of the six dipole-moment components (three for the parent species of each gauche form). The integration of NBH's data, which apply to individual conformers, with the diffraction intensities that derive from a mixture of conformers, is a complicated task in itself. It was made more so by the limitations of our least squares program for structure refinement that allows the inclusion of only one set of three rotational constants and one set of dipole-moment components as auxiliary data. The iterative procedure adopted to solve this problem is described later.

Vibrational Corrections. Models of the AET system were defined in terms of the $\underline{r}_\alpha^0 = \underline{r}_z$ type of distance. For the gauche conformers, conversions of the B_0 's to B_z 's consistent with these \underline{r}_α^0 's, and the r_α^0 's to \underline{r}_a 's consistent with the electron-diffraction data, were done in a fashion similar to that described for ethane-1,2-dithiol. (Although only diffraction data were available for the anti conformer, our model formulation of the AET system, described below, required similar conversion of the \underline{r} 's for it.) Values for the Morse anharmonicity parameter a_3 needed for the distance corrections were 1.84, 1.889, 1.945, 1.981, 2.131, and 2.268 \AA^{-1} for S-H, N-H, C-S, C-H, C-C, and C-N respectively;⁹ anharmonicities of nonbonds were

ignored. The quadratic force field used to calculate the conversion terms consisted of combinations of bond stretching-, angle bending-, and torsional constants taken from ethane-1,2-dithiol⁵ and ethylenediamine². There are apparently no experimental fundamental wavenumbers for AET which would allow adjustment of the force field; the alternative was to "average" the force fields from the two molecules mentioned. Based on past experience, the resulting force field for AET was expected to be satisfactory for use in estimation of the distance- and rotational constant corrections, which are generally insensitive to small changes in force constants. The symmetry coordinates and force field are available as supplementary material.

Dipole-Moment Components. Although use of rotational constant values as auxiliary data in electron-diffraction structure analyses has become quite common, similar use of dipole-moment components is new and promises to be especially valuable in cases like AET. For example, in the analysis of the ethane-1,2-dithiol system, described previously, the dipole-moment components were found to be very sensitive functions of the orientations of the S-H groups. Without these components the S-H orientations could not be unequivocally defined even with the constraints imposed by values of the rotational constants.

The method for calculation of the dipole-moment components was similar to that used for ethane-1,2-dithiol. The molecular dipole vector in AET was considered to be the resultant of that from two group moments, one for the $-\text{CH}_2\text{SH}$ portion of the molecule and one for the $-\text{CH}_2\text{NH}_2$. The $-\text{CH}_2\text{SH}$ group moment was assigned the magnitude found for CH_3SH ¹⁰ and a direction defined by the angle made with

the C-S bond. Similarly, the $-\text{CH}_2\text{NH}_2$ group moment was assigned to have the magnitude found for CH_3NH_2 ¹¹ and a direction defined by the angle made with the C-N bond. Each of these angles was initially given the value found in the parent compounds, (153° for $-\text{CH}_2\text{SH}$ and 101° for $-\text{CH}_2\text{NH}_2$). In the course of the analysis values of these angles differing as much as 20° from those in the parent compounds were tested, and toward the end of the work it was found that the values 158° and 98° , for the thiol and amino groups respectively, gave a bit better overall agreement. Each of the group moments was resolved into "bond" components, the orientations of which were determined during each refinement iteration from the cartesian coordinates for the atoms in the principal axis system. A more detailed description of this process is included in Appendix B.

Weighting of Data. Because both the numerical values and the associated uncertainties of the different kinds of observables differ greatly, the weighting had to be chosen carefully. In the final stages of the work the ratios of the weighted sums of squares of rotational constants, diffraction intensities, and dipole-moment components were $(\sum w_i B_i^2 : \sum w_i (s_i I_i(\underline{s}))^2 : \sum w_i (\mu_i)^2) = 500,000 : 300 : 1$. Each of the dipole-moment components and each of the rotational constants were given equal weights.

Modeling the System. Systems containing a mixture of rotational conformers are conveniently described by a "common" set of structural parameters -- those assumed to be the same for all conformers -- and a "unique" set which defines structural variations among the conformers. With rare exception it has been found satisfactory for each of the

cases studied in this laboratory to assume that the skeletal parameters of the rotamers are the same except for the torsion angles. We investigated the validity of this assumption for the (heavy-atom) gauche and anti conformers of AET by doing test refinements in which small differences between the average gauche and anti C-N bond lengths, and the corresponding C-C-N bond angles, were allowed. The results showed that the two values for each parameter lay within one standard deviation of the overall averages. (We note that NBH report⁸ somewhat different C-N bond distances (1.489(15) Å and 1.511(15) Å) and slightly different C-C-N bond angles (110.9(1)° and 109.6(1)°) for the two gauche forms I and II. A part of these differences may derive from their assumptions about the values of parameters they did not measure.) Accordingly, it seemed appropriate to adopt the assumption that the C-N distance and C-C-N angle did not differ significantly from conformer to conformer, and they were included in the set of parameters common to all forms.

The common set of parameters was chosen to be the distances $\langle \underline{r}(\text{CH}, \text{NH}) \rangle = [2\underline{r}(\text{C-H}) + \underline{r}(\text{N-H})]/3$, $\Delta \underline{r}(\text{CH}, \text{NH}) = \underline{r}(\text{C-H}) - \underline{r}(\text{N-H})$, $\underline{r}(\text{C-S})$, $\langle \underline{r}(\text{CC}, \text{CN}) \rangle = [\underline{r}(\text{C-C}) + \underline{r}(\text{C-N})]/2$, $\Delta \underline{r}(\text{CC}, \text{CN}) = \underline{r}(\text{C-C}) - \underline{r}(\text{C-N})$, and $\underline{r}(\text{S-H})$; and the angles $\angle \text{CCS}$, $\angle \text{CSH}$, $\angle \text{HCH}$, $\langle \angle \text{CC}_\text{S}\text{H}, \text{CC}_\text{N}\text{H} \rangle = [\angle \text{CC}_\text{S}\text{H} + \angle \text{CC}_\text{N}\text{H}]/2$, $\Delta[\angle \text{CC}_\text{S}\text{H}, \text{CC}_\text{N}\text{H}] = \angle \text{CC}_\text{S}\text{H} - \angle \text{CC}_\text{N}\text{H}$, $\angle \text{CCN}$, $\angle \text{CNH}$, and $\angle \text{HNH}$. The unique set of parameters was chosen to be the six torsion angles $\tau(\text{CC})_\text{I}$, $\tau(\text{CC})_\text{II}$, $\tau(\text{CS})_\text{I}$, $\tau(\text{CS})_\text{II}$, $\tau(\text{CN})_\text{I}$, and $\tau(\text{CN})_\text{II}$. The zero value for these angles corresponds to eclipsed C-N and C-S bonds for $\tau(\text{CC})$, eclipsed S-H and C-C bonds for $\tau(\text{CS})$, and an eclipsing of the nitrogen lone pair and the C-C bond for $\tau(\text{CN})$; the positive sense

for torsion is counterclockwise rotation of the nearest group when viewed from S to C or N to C. The conformational composition of the system was represented by the mole fraction of the anti form χ_A , which was assumed to have the extended conformation with staggered N-H bonds, as shown in Figure III.1. The relative amount of the gauche forms I and II could not be determined since the electron-diffraction intensities are almost completely insensitive to the structural differences of these conformers; these conformers were assumed to be present in the ratio obtained by NBH, i.e., 39% I and 61% II. The value of $1 - \chi_A$ is thus the sum of the mole fractions of the two gauche conformers. Excluding unimportant H·H terms, our model of the system had 43 different distances each with an associated amplitude of vibration. Of these many vibrational amplitude parameters, a few were chosen to be independent, some were fixed at values calculated from the force fields described below, and others were collected into refinable groups wherein amplitude differences of group members were fixed at the values taken from the calculations.

Refinement Procedure. It has been mentioned above that an iterative procedure for refinement of the structure and composition of the AET system was necessary in order to make use of NBH's spectroscopic data. The procedure was as follows. First, the dipole-moment components and the rotational constants for the nondeuterated gauche I species were used together with the electron-diffraction intensities to refine the structures of the gauche I and anti conformers. The effect of the gauche II conformer on the diffraction intensities was taken into account by including it in an

amount equal to 61% of the total gauche composition (the amount suggested by NBH's work), but of its parameters, only those belonging to the common set experienced refinement. Next, the dipole-moment components and rotational constants of the gauche I form were replaced by those for the nondeuterated gauche II and a similar refinement of the structures of the gauche II and anti conformers was carried out. This procedure was repeated twice, each time with use of sets of rotational constants for the deuterated forms. The purpose of these six refinements was to determine average values for the torsion angles $\tau(\text{CS})$ and $\tau(\text{CN})$ in each of the two gauche forms that would provide the best simultaneous fit to the three sets of rotational constants and to the dipole-moment components. Two final refinements, one for each gauche conformer, with $\tau(\text{CS})$ and $\tau(\text{CN})$ held at their average values, were carried out with use of values for rotational constants for the nondeuterated species and dipole-moment components as auxiliary data.

Structure Results. The final results for the structure of AET are given in Tables III.1 and III.2. The correlation matrices corresponding to the lower temperature results are found in Table III.3; those for the higher temperature results are similar. The contents of Tables III.1 and III.2 require comment. As outlined above, each step of the iterative procedure made use of only one set of spectroscopic data -- that corresponding to either gauche I or gauche II, parent or monodeuterated. Although each model system consisted of gauche I, gauche II, and anti forms in their indicated proportions, only the parameters peculiar to one of the gauche forms, plus the parameters common to all forms, were refined during each

Table III.1. Results for Structural Parameters of 2-Aminoethanethiol

parameter	372 K ^a	580 K ^a	NBH ^b
$\langle\text{C-H,N-H}\rangle^{\text{c}}$	1.078(3)	1.076(3)	[1.063]
$\Delta(\text{C-H,N-H})^{\text{c}}$	[0.077(21)]	[0.077(73)]	[0.080]
S-H	1.335(12)	1.315(15)	[1.349]
$\langle\text{C-C,C-N}\rangle^{\text{c}}$	1.500(2)	1.503(2)	1.515 ^d
$\Delta(\text{C-C,C-N})^{\text{c}}$	[0.045(20)]	[0.045(23)]	0.030 ^d
C-S	1.824(3)	1.822(3)	[1.805]
$\angle(\text{CCS})$	113.1(5)	112.9(5)	[113.2]
$\angle(\text{CSH})$	[90.0(27)]	[90.0(35)]	[94.5]
$\angle(\text{HCH})$	[109.0(55)]	[109.0(103)]	[108.9] ^e , [109.8] ^f
$\langle\text{CC}_{\text{S}}\text{H,CC}_{\text{N}}\text{H}\rangle^{\text{c}}$	108.5(15)	108.6(14)	[110.45]
$\Delta(\text{CC}_{\text{S}}\text{H,CC}_{\text{N}}\text{H})^{\text{c}}$	[-0.9(43)]	[-0.9(47)]	[0.5]
$\angle(\text{C-C-N})_{\text{I}}$	111.0(14)	110.9(12)	110.9(1)
$\angle(\text{C-C-N})_{\text{II}}$	111.3(10)	111.0(9)	109.6(1)
$\angle(\text{C-N-H})$	[108.0(67)]	[108.0(53)]	[110.4]
$\angle(\text{H-N-H})$	[109.0(146)]	[109.0(127)]	[109.0]
$\tau(\text{C-C})_{\text{I}}$	63.4(24)	63.8(19)	63.8(2 ₀)
$\tau(\text{C-C})_{\text{II}}$	63.8(13)	64.7(12)	67.0(2 ₀)
$\tau(\text{C-S})_{\text{I}}$	-21(28)	[-21(21)]	-26.9(3 ₀)
$\tau(\text{C-S})_{\text{II}}$	-72(11)	-71(9)	-56.7(3 ₀)
$\tau(\text{C-N})_{\text{I}}$	-49(18)	-42(22)	-44.6(2 ₀)
$\tau(\text{C-N})_{\text{II}}$	47(19)	48(18)	54.7(2 ₀)
$\chi_{\text{A}}^{\text{g}}$	0.227(54)	0.212(50)	--
$\underline{\text{R}}^{\text{h}}$	0.096	0.090	--

Table III.1. Continued.

^aDistances (r_{α}^0) in angstroms, angles (\angle_{α}) in degrees. Values in brackets were assumed. Values in parentheses attached to values in brackets are $1\sigma_{LS}$ (see text for explanation); other values in parentheses are $2\sigma_{tot}$ which include estimates of systematic error and correlations among observations. ^bCalculated from ref 8. Values in parentheses "should encompass errors in the assumed parameters". ^cSee text for definitions. ^dReported as C-C = [1.530], C-N_I = 1.489(15), and C-N_{II} = 1.511(15)Å. ^eThiol end. ^fAmino end. ^gMole fraction of anti conformation. $h_R = \left(\frac{\sum w_i \Delta_i^2}{\sum w_i (s_{i-i}(obsd))^2} \right)^{1/2}$ where $\Delta_i = s_{i-i}(obsd) - s_{i-i}(calcd)$.

Table III.2. Distances (\underline{r}_α^0 , \underline{r}_g , and \underline{r}_a) and Amplitudes (\underline{l}) in 2-Aminoethanethiol^a

atom pair	372 K				580 K			
	\underline{r}_α^0	\underline{r}_g	\underline{r}_a	\underline{l}	\underline{r}_α^0	\underline{r}_g	\underline{r}_a	\underline{l}
N-H	1.027	1.051	1.048(3)	0.053	1.025	1.049	1.041(4)	0.089
C-H	1.104	1.120	1.117(3)	0.057	1.102	1.118	1.110(4)	0.093
S-H	1.335	1.371	1.368(12)	0.060	1.315	1.350	1.343(16)	0.096
C-N	1.478	1.481	1.480(3)	0.049	1.481	1.485	1.482(3)	0.072
C-C	1.523	1.526	1.524(2)	0.057	1.526	1.531	1.527(3)	0.082
C-S	1.824	1.828	1.826(3)	0.055(4)	1.822	1.828	1.825(3)	0.076(4)
C ₆ · H ₁₀	2.043	2.056	2.052(3)	0.097	2.045	2.058	2.053(4)	0.103
N ₉ · H ₇	2.118	2.128	2.123(24)	0.101	2.119	2.129	2.123(24)	0.109
C ₆ · H ₂	2.139	2.149	2.143(21)	0.109	2.142	2.152	2.145(18)	0.119
C ₁ · H ₇	2.151	2.161	2.156(19)	0.107	2.154	2.164	2.158(18)	0.116
C ₁ · H ₅	2.261	2.280	2.274(8)	0.119	2.247	2.267	2.259(11)	0.131
S ₄ · H ₂	2.424	2.432	2.428(20)	0.105	2.421	2.429	2.424(17)	0.115
C ₁ · N ₉	2.475	2.479	2.477(20)	0.073	2.477	2.481	2.476(17)	0.108
S ₄ · C ₆	2.798	2.801	2.799(8)	0.081	2.794	2.799	2.794(9)	0.121
CONFORMER I								
N ₉ · · H ₂	3.410	3.416	3.413(25)	0.110	3.411	3.418	3.414(22)	0.117

Table III.2. Continued.

N ₉ ···H ₃	2.682	2.689	2.677(55)	0.179	2.681	2.688	2.673(46)	0.205
S ₄ ···H ₇	3.762	3.769	3.765(12)	0.112	3.756	3.764	3.760(11)	0.123
S ₄ ···H ₈	2.960	2.967	2.956(31)	0.183	2.951	2.960	2.944(26)	0.212
C ₁ ···H ₁₀	2.759	2.770	2.761(134)	0.158	2.816	2.829	2.818(172)	0.178
C ₁ ···H ₁₁	3.345	3.354	3.351(34)	0.106	3.334	3.344	3.340(55)	0.113
C ₆ ···H ₅	2.472	2.490	2.472(130)	0.206	2.465	2.485	2.461(11)	0.241
S ₄ ···N ₉	3.211	3.217	3.208(6)	0.173(17) ^b	3.212	3.221	3.206(6)	0.221(20) ^b
S ₄ ···H ₁₀	3.709	3.720	3.702(232)	0.260	3.791	3.805	3.779(262)	0.313
S ₄ ···H ₁₁	4.049	4.059	4.052(147)	0.173	3.988	4.001	3.990(202)	0.206
N ₉ ···H ₅	2.368	2.392	2.367(102)	0.248	2.379	2.407	2.370(15)	0.296
CONFORMER II								
N ₂₉ ···H ₂₂	3.411	3.418	3.414(21)	0.110	3.413	3.420	3.416(18)	0.118
N ₂₉ ···H ₂₃	2.683	2.690	2.678(38)	0.179	2.676	2.684	2.668(33)	0.206
S ₂₄ ···H ₂₇	3.760	3.767	3.763(13)	0.112	3.757	3.765	3.761(10)	0.123
S ₂₄ ···H ₂₈	2.954	2.961	2.950(23)	0.183	2.944	2.952	2.937(19)	0.212
C ₂₁ ···H ₃₀	3.345	3.355	3.351(33)	0.110	3.348	3.358	3.354(31)	0.119
C ₂₁ ···H ₃₁	2.779	2.789	2.780(154)	0.156	2.774	2.785	2.774(149)	0.177
C ₂₆ ···H ₂₅	2.904	2.920	2.901(114)	0.233	2.886	2.904	2.877(97)	0.277

Table III.2. Continued.

S ₂₄ ···N ₂₉	3.221	3.227	3.218(13)	0.173(17) ^b	3.223	3.232	3.216(13)	0.225(20) ^b
S ₂₄ ···H ₃₀	4.190	4.201	4.194(66)	0.164	4.187	4.200	4.191(66)	0.196
S ₂₄ ···H ₃₁	2.892	2.905	2.883(194)	0.248	2.886	2.903	2.872(183)	0.297
N ₂₉ ···H ₂₅	2.691	2.712	2.680(157)	0.294	2.678	2.703	2.656(133)	0.356
ANTI								
N ₄₉ ···H ₄₂	2.693	2.702	2.692(40)	0.161	2.695	2.705	2.692(35)	0.183
S ₄₄ ···H ₄₇	2.978	2.985	2.975(30)	0.170	2.975	2.983	2.971(24)	0.195
C ₄₁ ···H ₅₀	2.670	2.680	2.673(7)	0.135	2.670	2.680	2.671(8)	0.152
C ₄₁ ···H ₅₁	3.353	3.363	3.357(7)	0.135	3.353	3.363	3.357(8)	0.152
C ₄₆ ···H ₄₅	3.654	3.666	3.662(11)	0.124	3.638	3.651	3.646(15)	0.134
S ₄₄ ···N ₄₉	4.126	4.128	4.127(7)	0.081	4.124	4.128	4.125(8)	0.096
S ₄₄ ···H ₅₀	4.373	4.379	4.375(7)	0.142	4.370	4.377	4.371(8)	0.162
S ₄₄ ···H ₅₁	4.839	4.845	4.841(8)	0.142	4.837	4.844	4.839(8)	0.162
N ₄₉ ···H ₄₅	4.734	4.744	4.740(12)	0.144	4.723	4.733	4.728(14)	0.160

^a Values in angstroms. Parenthesized quantities are 2σ , those in curly brackets were refined as a group, those without attached uncertainties were calculated from the force field and were not refined. ^b The S₄···N₉ amplitudes for the gauche I and II conformers were tied during the refinement.

Table III.3. Correlation Matrix (x100) for Parameters of 2-Aminoethanethiol at 372 K^a

		$\langle \rangle_1$	\underline{r}_2	$\langle \rangle_3$	\underline{r}_4	\underline{l}_5	$\langle \rangle_6$	\underline{l}_7	τ_8	τ_9	τ_{10}	χ_{11}	
	σ_{LS}^b x100	0.064	0.083	0.098	0.43	15.	51.	50.	84.	990.	630.	1.9	
1	$\langle C-C, C-N \rangle^c$	0.064	100	37	17	15	-22	-13	-50	50	-42	3	1
2	$\underline{r}(C-S)$	0.083	36	100	13	6	-51	30	-17	27	-25	-11	3
3	$\langle C-H, N-H \rangle^c$	0.098	17	12	100	37	<1	-19	-28	29	-28	-4	<1
4	$\underline{r}(S-H)$	0.42	15	5	36	100	-4	-8	-19	21	-20	-2	7
5	$\underline{l}(CCS)$	17.	-25	-43	-6	-7	100	-53	-3	-30	19	-11	11
6	$\langle CC_{S,N}^H \rangle^c$	51.	-15	30	-21	-10	-32	100	68	-51	29	-46	-6
7	$\underline{l}(CCN)$	34.	-49	-14	-29	-19	8	70	100	-93	62	-69	-9
8	$\tau(C-C)$	47.	55	38	33	25	-34	-35	-77	100	-68	76	4
9	$\tau(C-S)$	370.	40	28	32	25	-29	-4	-2	-15	100	-43	-4
10	$\tau(C-N)$	670.	-18	<1	-15	-10	54	34	42	-7	-50	100	5
11	χ_A^d	1.9	2	7	1	8	4	<1	-4	<1	4	-2	100

^aThe right hand side of the diagonal represents conformer I; the left hand side represents conformer II. Distances (\underline{r}) and amplitudes (\underline{l}) in angstroms; angles in degrees. ^bStandard deviations from least-squares. ^cSee text for definitions. ^dMole fraction of anti form.

step. It is pleasing that after several such steps the parameter values obtained from these refinements differed very little: the ranges of each defined by the associated uncertainties always overlapped well. The tabulated values are averages from the two final refinements based on the parent species of gauche I and gauche II. The uncertainties are essentially those from the two final refinements, but they have been expanded slightly in some cases to encompass the ranges from both. It should be noted that these ranges do not reflect the effect of uncertainties in the assumptions -- the bracketed quantities in Table III.1. However, rough guesses of the effect of error in these assumptions may be had from the values of σ_{LS} attached to their values in Table III.1. It is estimated that an error of this magnitude in one of the assumptions would project into the measured parameter values as a change of less than half the magnitude of their listed uncertainties.

Discussion

Electron-Diffraction and Microwave Structures. Table III.1 offers a comparison of our results of the investigation of AET with those NBH obtained from microwave spectroscopy. Ours, of course, reflect a combination of the diffraction- and spectroscopic data and are correspondingly more extensive. NBH's limited but precise data required them to make a number of structural assumptions in order to obtain values for the more interesting parameters. That they have done so judiciously is seen in the generally good agreement between theirs

and our results, and between the calculated locations of the H_N atoms (Table III.4) that depend on the orientation of the molecule in the principal axis system. A few sizable differences are found in the parameter values of the gauche II conformer. It is likely that these arise from some of NBH's structural assumptions that deviate appreciably, but not unreasonably, from our measured values. In any case, none of the structural differences have any bearing on NBH's principal conclusions about the structures of the gauche forms, with which we are in complete accord.

Table III.5 shows the observed and calculated values for the rotational constants and dipole-moment components of the electron-diffraction and microwave structures. The fit provided by the latter is of course excellent. We regard the fit of our structure to the B_2 's to be very good: the maximum error of less than 0.1% is smaller than the correction term used to convert the B_0 's to B_2 's. The fit of our structure to the dipole-moment components is excellent in view of uncertainties in the calculated values that are expected to be about 0.1 - 0.2 D. Table III.6 shows the observed and calculated values of the N-deuterated rotational constants for the two structures. Here the corrections to the B_0 's calculated from the force field are an average of those for the $-NH_2$ and $-ND_2$ species. Again, the fit of the microwave structure is excellent. For the electron-diffraction structure, the largest error in the fit of the calculated B_2 's to the observed is about 0.3%.

Effect of Other Conformers of AET. As far as conformation is concerned, the electron-diffraction data from the AET system provide

Table III.4. Atomic Coordinates in Principal Axis System for H_N Atoms

	This Work ^a				NBH ^b				
	372 K		580 K		Substitution		Calculated		
					Coordinates ^c		Coordinates ^d		
	I	II	I	II	I	II	I	II	
	x	-1.12(8)	0.12(20)	-1.08(12)	0.13(20)	-1.074(13)	0.151(90)	-1.093	0.182
H10(30)	y	-0.59(8)	-0.85(10)	-0.55(8)	-0.86(10)	-0.625(20)	-0.905(14)	-0.604	-0.916
	z	2.09(22)	2.74(7)	2.19(26)	2.74(7)	2.131(7)	2.693(5)	2.143	2.706
	x	0.42(13)	0.23(18)	0.47(12)	0.21(18)	0.455(81)	0.204(40)	0.437	0.041
H11(31)	y	-1.06(12)	-1.50(2)	-1.11(15)	-1.50(2)	-1.110(31)	-1.508(4)	-1.107	-1.497
	z	2.53(16)	1.20(14)	2.46(21)	1.20(14)	2.467(16)	1.159(6)	2.481	1.173
H·H dist		1.672(5)	1.672(5)	1.667(6)	1.671(5)	1.639(77)	1.649(10)	1.646	1.645

^aUncertainties for coordinates are $2\sigma_{LS}$. For the H·H distance they are $2\sigma_{tot}$ which include estimates of systematic error and correlation among observations. ^bRef 8. Signs have been changed to agree with our convention. ^cUncertainties are based on 3σ uncertainties in rotational constants and vibration-rotation uncertainty of 0.0015/g, g = a,b,c. ^dCorresponds to parameter values of Table I.1.

Table III.5. Observed and Calculated Values of Rotational Constants and Dipole-Moment Components of 2-Aminoethanethiol^a

	Observed		Calculated ^b	
	B_0^c	B_z^d	This Work (372 K) ^e	NBH ^f
CONFORMER I				
A	12040.1(113)	12044.7	12043.8	12042.4
B	3352.24(3)	3348.2	3346.2	3351.86
C	2881.99(3)	2880.3	2880.7	2881.14
μ_a	2.68(1)		2.64	2.66
μ_b	0.88(2)		0.89	0.89
μ_c	0.37(5)		0.37	0.39
CONFORMER II				
A	11929.9(102)	11934.8	11933.8	11927.0
B	3395.01(3)	3390.9	3389.9	3394.66
C	2877.82(3)	2876.3	2874.2	2877.39
μ_a	1.51(11)		1.58	1.49
μ_b	0.0(2)		0.03	0.15
μ_c	0.62(15)		0.50	0.63

^aRotational constants are in MHz, dipole moments are in debye.

^b $B_z = 505379/I_z$. ^cRef 8. Values in parentheses are 3σ .

^dCorrections $B_0 - B_z$ calculated from the force field. ^eA, B, C values should be compared to those for the B_z 's. ^fCalculated from results in ref 8. A, B, C values should be compared to those for the B_0 's.

Table III.6. Observed and Calculated Values of Rotational Constants of N-Deuterated Forms of 2-Aminoethanethiol^a

		Observed		Calculated ^b	
		B_0^c	B_z^d	This Work (372 K) ^e	NBH ^f
CONFORMER I					
-NH ₁₀ D ₁₁	A	11663.54(2000)	11668.1	11705.5	11672.2
	B	3217.56(16)	3213.8	3206.1	3216.0
	C	2766.97(16)	2765.4	2762.7	2765.2
-ND ₁₀ H ₁₁	A	11629.60(621)	11634.2	11629.2	11629.2
	B	3231.03(3)	3227.3	3227.3	3228.7
	C	2802.81(2)	2801.3	2805.3	2801.4
CONFORMER II					
-NH ₁₀ D ₁₁	A	11323.00(300)	11328.3	11339.1	11339.0
	B	3363.37(5)	3359.5	3358.6	3363.0
	C	2820.08(3)	2818.6	2819.4	2819.7
-ND ₁₀ H ₁₁	A	11713.25(1020)	11718.5	11731.2	11703.3
	B	3236.74(6)	3232.9	3229.9	3234.7
	C	2752.12(6)	2750.7	2748.6	2750.4

^aValues are in MHz. ^b $B_z = 505379/I_z$. ^cRef 8. Values in parentheses are 3σ . ^dCorrections $B_0 - B_z$ calculated from the force field are an average of those for -NH₂ and -ND₂. ^eValues should be compared to those for B_z 's. ^fCalculated from results in ref 8. Values should be compared to those for B_0 's.

information principally about the heavy-atom gauche-anti composition, but they reveal little or nothing about the identities and relative amounts of conformers that are distinguished mainly by different C-S and C-N torsion angles. NBH's spectroscopic data on the other hand, hold no information about the gauche-anti heavy-atom composition (nor in fact about the presence of any anti conformers), but permitted those authors to identify two conformers with similar gauche heavy-atom arrangements and different C-S and C-N torsion angles. Our models of the AET system have included only three of the several possible conformers, of which NBH's pair have been taken as representative of all possible gauche forms. Because the diffraction data are insensitive to the C-S and C-N torsion angles, our results for the gauche-anti composition are independent of the presence of species with still other combinations of these angles.

Internal Hydrogen Bonding. Among the more interesting of our structural results for AET is the firm establishment of the orientations of the peripheral groups in gauche conformers I and II. As NBH also concluded, the former has an S-H...N arrangement consistent with formation of an N...H_S hydrogen bond. (The N...H_S distance is about 2.39 Å and is shorter than the sum of the van der Waals radii by about 0.3 Å.) A clue to the strength of such a hydrogen bond is to be found in the energy difference between the gauche and anti forms of the molecule. A crude estimate of the internal energy (and entropy) differences of these classes of conformers may be obtained from the usual formula $R \ln(N_G/N_A) - R \ln 2 = -\Delta E^\circ/T + \Delta S^\circ$, where $\Delta E^\circ = E_G^\circ - E_A^\circ$ and the statistical weight of the heavy-atom gauche forms has been

removed according to $\Delta \underline{S}^\circ = \underline{S}_G - \underline{S}_A - R \ln 2$. The results are $\Delta \underline{E}^\circ = 0.18(42) \text{ kcal} \cdot \text{mol}^{-1}$ and $\Delta \underline{S}^\circ = 1.5(9) \text{ cal} \cdot \text{deg}^{-1} \cdot \text{mol}^{-1}$. The former is nearly identical with the value found in ethane-1,2-dithiol (EDT, $\underline{E}_G^\circ - \underline{E}_A^\circ = 0.26(86) \text{ kcal} \cdot \text{mol}^{-1}$), a molecule that judged from the position of one of the hydrogen atoms, appears to form an intramolecular S-H \cdots S hydrogen bond. After taking account of steric repulsion, expected to be greater for the gauche forms, we estimated the energy of the hydrogen bond in EDT to be about a kilocalorie per mole. Assumption of steric repulsions of similar magnitude in AET suggests a similar value for the energy of its internal hydrogen bond.

In the gauche I form of AET the H_S atom points toward the unshared electron pair on the N atom. In the gauche II form the NH₂ and SH group rotations are such as to place one of the H_N atoms and the H_S atom approximately at the van der Waals distance; this form is clearly incompatible with hydrogen-bond formation. It is interesting that NBH find gauche II to be more stable than gauche I by 0.274(90) kcal·mol⁻¹. They explain their result in terms of the torsion angles $\tau(\text{CN})$ and $\tau(\text{CS})$. In their structures the values of these angles for the gauche II conformer lie closer to the torsional energy minima than do those for gauche I (Table III.1). Our torsion-angle values are consistent with this interpretation, but the uncertainties associated with the measurements themselves suggest coincidence rather than proof.

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V. APPENDICES

Appendix A: Theoretical and Experimental Overview
of Molecular Structure Determination
by Gaseous Electron Diffraction

Appendix A contains a brief description of an electron-diffraction experiment and the interpretation of the intensity data to yield structural information. This appendix is intended to provide the reader not familiar with electron diffraction the information necessary to understand the body of this thesis. Readers interested in a more thorough treatise of the technique are referred to the literature cited herein.

A schematic of the OSU electron-diffraction apparatus is shown in Figure V.1. A 45 kV electron beam is focused down through an evacuated chamber (10^{-6} torr) and is scattered by a molecular beam entering the chamber through a nozzle. The scattered electrons within a certain range of the scattering angle 2θ are allowed to strike an 8 x 10 inch photographic plate which is mounted perpendicular to and centered around the undiffracted electron beam. The pattern produced generally consists of a set of concentric rings of varying intensity. The rate of flow of the gaseous sample, as judged by the chamber pressure, can be regulated by a valve on the sample holder and/or by controlling the sample temperature. After passing through the nozzle the sample is condensed onto a liquid nitrogen cooled trap to prevent the chamber pressure from building up.

Mounted a few millimeters above the photographic plate is a rotating sector which reduces the fraction of the scattered beam that

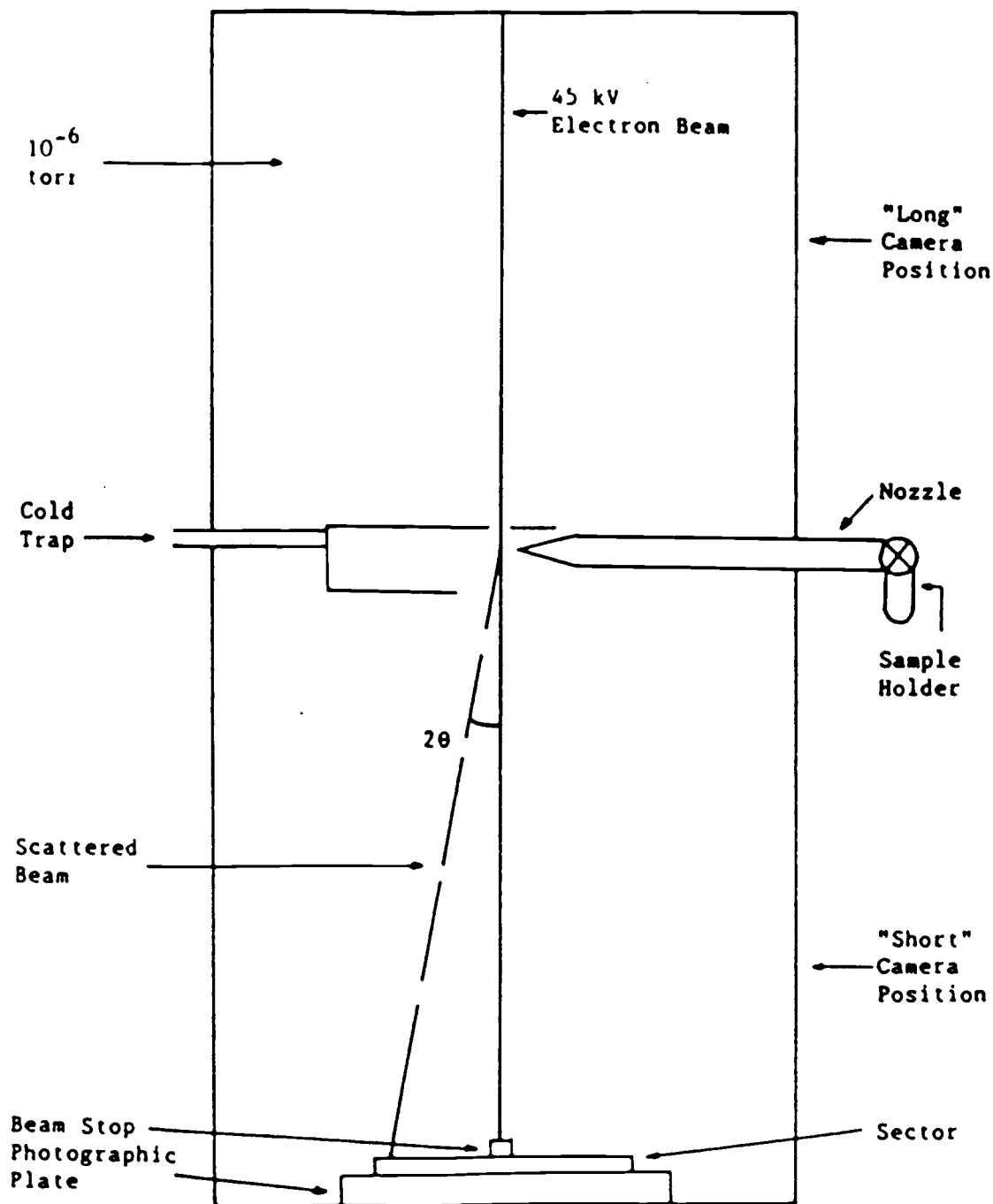


Figure V.1. Schematic of electron-diffraction apparatus.

is allowed to strike the plate at low scattering angles relative to that at high scattering angles. The scattered intensity drops off very rapidly with increasing scattering angle; without the sector most of the scattering would exceed the latitude of the photographic emulsion. In order to maximize the 2θ range over which data are recorded, experiments may be done at different nozzle positions. In the "long" camera position the distance from the scattering center to the photographic plate, termed the "height", is nominally 75 cm and the 2θ range is 1.0 to 6.5°. In the "middle" ("short") camera position, height = 30 cm (12 cm), the 2θ range is 3.0 to 16.6 (11.0 to 30.4°). For a more thorough description of the OSU apparatus, see for example the thesis by Danielson¹ and for experimental techniques of gas-phase electron-diffraction in general, see the book by Davis².

After the photographic plates are developed they are scanned on a microdensitometer to obtain the "raw data" curves which are digital readings proportional to optical density as a function of distance across the plate. These raw data curves are read into a data reduction program³ which (1) converts the measurements to optical density using the numbers obtained by the scan of a standard step tablet, (2) determines the center of the curves by matching derivative forms of the two halves using least squares, (3) calculates an \underline{s} value ($\underline{s} = 4\pi/\lambda \sin 2\theta$, λ = wavelength of the electron beam) for each datum from the height and the radial distance from the center of the plate, (4) interpolates the data at 0.25 \underline{s} values, (5) removes the effect of the sector, (6) applies a geometric correction resulting from nonsphericity of the plate, and (7) averages the two halves of the scan and multiplies the

result by \underline{s}^4 .

The output intensity curves from the data reduction program, commonly called the "reduced" curves, are in the form

$$\underline{s}^4 \underline{I}_t = \underline{I}_m(\underline{s}) + \underline{I}_{at} + \underline{s}^4 \underline{I}_{app}$$

where \underline{I}_m , \underline{I}_{at} , and \underline{I}_{app} are the intensities due to molecular-, atomic-, and extraneous scattering respectively and \underline{I}_t is the total intensity. The next step is to read the reduced curves into a background subtraction program⁴ which, as the program name implies, subtracts the background, $B = \underline{I}_{at} + \underline{s}^4 \underline{I}_{app}$, leaving only that part of the $\underline{s}^4 \underline{I}_t$ curve which contains the molecular structure information. The procedure used to determine the background involves a least-squares fitting of the curve

$$F(\underline{s}) = a \underline{I}_m^{thi} + b \underline{I}_{at} + \sum_i c_i \underline{s}^i$$

to the $\underline{s}^4 \underline{I}_t$ curve. In the expression for $F(\underline{s})$, \underline{I}_m^{thi} is the molecular scattering intensity calculated from a theoretical model of the structure, the atomic scattering intensity is calculated from tables⁵, and the polynomial is used to represent the extraneous scattering intensity. The parameters a , b , and the c_i 's are varied in the fitting procedure. The degree of the polynomial is chosen based on previous experience. Finally, the background is subtracted from the $\underline{s}^4 \underline{I}_t$ curve and the result is multiplied by \underline{s} .

The output intensity curves from the background subtraction program, called the experimental $\underline{s} \underline{I}_m(\underline{s})$ curves, are then read into the variable least-squares program^{6,7} which fits the experimental

curve to a theoretical curve having the form

$$\underline{sI}_m(\underline{s}) = k \sum_{i>j} n_{ij} \underline{r}_{ij}^{-1} A_i(\underline{s}) A_j(\underline{s}) \cos(\eta_i - \eta_j) \times \\ \exp(-\underline{l}_{ij}^2 \underline{s}^2 / 2) \sin(\underline{r}_{ij} \underline{s} - \kappa_{ij} \underline{s}^2)$$

in which n_{ij} is the multiplicity of the distance type from atom i to j , \underline{r}_{ij} is the interatomic distance, $A_i/s^2 = F_i$ is the absolute value of the complex electron scattering amplitude, η_i is the phase shift coefficient, \underline{l}_{ij}^2 is the mean-square amplitude of vibration, κ_{ij} is the anharmonicity coefficient (generally negligible), and k is a scaling constant. The $\underline{sI}_m(\underline{s})$ curve is a superposition of weighted, damped sine waves. The weighting factor is $n_{ij} A_i A_j / \underline{r}_{ij}$, the damping factor is the exponential containing the mean-square amplitude of vibration (the larger \underline{l}_{ij} the more heavily damped the sine wave), and the period of each sine wave is determined by the interatomic distance. During the fitting of the experimental and theoretical $\underline{sI}_m(\underline{s})$ curves the parameters being refined are generally the bond distances, bond angles, mean-square amplitudes of vibration, and, where applicable, torsion angles and conformational composition. The refinement program drives the quantity $\sum \underline{w}_i (\underline{s}_i \underline{I}_i(\text{obsd}) - \underline{s}_i \underline{I}_i(\text{calcd}))^2$ to a minimum by making small adjustments in the refined parameters.

A useful tool for the analysis of electron-diffraction data is the Fourier transform. It is difficult, if not impossible, to look at a $\underline{sI}_m(\underline{s})$ curve and resolve the sine waves associated with each interatomic distance. However, a radial distribution curve, which may be generated by the Fourier transformation of an altered form of a $\underline{sI}_m(\underline{s})$ curve, consists of a set of Gaussians corresponding to the set

of distances associated with the molecule and each Gaussian is centered at an interatomic distance. The area under each Gaussian is proportional to $n_{ij} Z_i Z_j / r_{ij}$ and the width at half height is related to the root-mean-square amplitude of vibration by the equation

$$w_{1/2} = 2(\ln 2)^{1/2} (4B + 2\langle l_{ij}^2 \rangle)^{1/2}$$

in which B is a damping factor introduced to eliminate series termination errors. Depending on the molecule under investigation and the temperature of the experiment, these Gaussians may be more or less resolved. Thus, the radial distribution curve is very useful in the evaluation of theoretical models calculated from the least-squares refinement program.

One weakness of electron diffraction lies in its inability to accurately determine distances involving hydrogen through two or more bond angles. It is because of this weakness that one cannot determine, from electron diffraction alone, whether or not molecules such as ethane-1,2-dithiol and 2-aminoethanethiol possess intramolecular hydrogen bonding. For ethane-1,2-dithiol the question of the presence or absence of intramolecular hydrogen bonding requires accurate determination of the distances $C \cdots H_S$ and $S \cdots H_S$, among other distances. However, these distances, through two and three bond angles respectively, are not accurately determined by electron diffraction. Fortunately, rotational constants are generally very sensitive to the positions of the terminal hydrogen atoms since these atoms tend to lie at relatively long distances from the principal axes. Thus rotational

constants were included in the structure determinations discussed in this thesis. What follows is a discussion of the incorporation of rotational constants in an electron diffraction investigation. Excellent accounts^{8,9} of this subject are available in the literature.

The interatomic distances associated with microwave spectroscopy are fundamentally different from those measured by electron diffraction because each are derived from techniques in which the averaging of the effects of molecular vibrations is done differently. For electron diffraction the distance in the interference function, $\sin(\underline{r}_{\underline{a}}s)$, is the $\underline{r}_{\underline{a}}$ interatomic distance which is related to the thermal average value of interatomic distance, $\underline{r}_{\underline{g}}$ by

$$\underline{r}_{\underline{a}} = \underline{r}_{\underline{g}} - \frac{1}{2} \frac{1}{\underline{r}_{\underline{e}}}$$

in which $\underline{r}_{\underline{e}}$ is the distance between equilibrium positions of atomic nuclei. The distance associated with microwave spectroscopy is the $\underline{r}_{\underline{0}}$ distance which reproduces the ground state rotational constants. Conversion of the electron diffraction $\underline{r}_{\underline{a}}$'s to $\underline{r}_{\underline{\alpha}}^0$'s and the microwave spectroscopy B_0 's to B_z 's allows one to directly use rotational constants in the least-squares refinement. The distances $\underline{r}_{\underline{\alpha}}^0$ and $\underline{r}_{\underline{z}}$, which reproduces B_z , represent the same physical quantity; they are simply derived from different sources.

The relationship between $\underline{r}_{\underline{a}}$ and $\underline{r}_{\underline{\alpha}}^T$, the distance between average positions of atoms at a particular temperature T, is given by

$$\underline{r}_{\underline{\alpha}} = \underline{r}_{\underline{a}} + \frac{1}{2} \frac{1}{\underline{r}_{\underline{e}}} - K - \delta \underline{r}$$

in which $\delta \underline{r}$ is the correction due to centrifugal distortion and K , the perpendicular amplitude correction, is given by

$$K = (\langle \Delta x^2 \rangle^T + \langle \Delta y^2 \rangle^T) / 2 \underline{r}_e$$

in which Δx^T and Δy^T are displacements perpendicular to the internuclear axis at a given temperature T . The values for K and $\delta \underline{r}$ for each distance in a molecule are calculated by a program written by Lise Hedberg, ASYM20, discussed later in this appendix; the value for \underline{r}_e is usually approximated by that for \underline{r}_g . The \underline{r}_α values may now be extrapolated from temperature T to zero degrees Kelvin to give the \underline{r}_α^0 values by the equation

$$\underline{r}_\alpha^0 = \underline{r}_\alpha^T + (K^T - K^0) - 3/2 a_3 [(\underline{1}^T)^2 - (\underline{1}^0)^2]$$

in which a_3 is analogous to the Morse anharmonicity parameter a for a diatomic molecule and superscripts denote temperature. For nonbond distances it is usual practice to ignore the term involving a_3 , while for bond distances a_3 is obtained from the Morse parameter for diatomics. Again, the rms amplitudes of vibration and perpendicular amplitude corrections at zero degrees Kelvin and temperature T are calculated from ASYM20.

Conversion of the B_0 rotational constants to the B_z 's follows the equation

$$B_z = B_0 + \frac{3N-6}{2} \sum_{\underline{i}=1} \underline{d}_i \underline{\alpha}_i (h)$$

in which $d_{\underline{i}}$ is the degeneracy of the i th normal mode and $\alpha_{\underline{i}}(h)$ is a set of harmonic corrections again generated from ASYM20. The calculated B_z rotational constants can now be used directly in the least-squares refinement of the $r_{\underline{\alpha}}^0$ parameter set.

The rms amplitudes of vibration, perpendicular amplitude corrections, centrifugal distortion corrections, and harmonic corrections to the rotational constants for a molecule can all be calculated at a given temperature using the program ASYM20. The program parallels the normal coordinate analysis discussed by Califano¹⁰.

Use of the ASYM20 program generally proceeds through three phases. In the first phase a diagonal matrix of internal force constants is converted using a U matrix, which describes a set of $3N - 6$ symmetrized coordinates in terms of a set of internal coordinates, to an approximate F matrix consisting of symmetrized force constants. The initial set of internal force constants is obtained from known constants of similar molecules. The second phase involves calculating the vibrational frequencies from the elements of the $G \cdot F$ matrix. The G matrix is calculated from the known masses and structure of the molecule. These vibrational frequencies are then compared to observed frequencies. The F matrix is adjusted until a satisfactory fit of the observed and calculated frequencies is obtained. In the case of 2-aminoethanethiol, for which there are no observed frequencies, the F matrix was obtained from a composite of those for ethane-1,2-dithiol and ethylenediammine. The last phase involves calculating the desired corrections and amplitudes at the desired temperatures from the final F matrix.

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Appendix B: Use of Dipole-Moment Components in an
Electron-Diffraction Analysis

Until about three years ago, dipole-moment components have not been included as additional sets of independent observables in electron-diffraction analyses. However, during the analyses of ethane-1,2-dithiol (EDT) and 2-aminoethanethiol (AET) it was found that the terminal torsion angles could not be reliably refined using electron-diffraction intensities and rotational constants alone. (In order to determine the positions of the H_S and H_N atoms in the molecular frame of reference, and thus investigate the question of a possible intramolecular hydrogen bond, these torsion angles must be determined.) The electron-diffraction intensity pattern is nearly completely insensitive to these torsion angles, since they are determined from scattering terms which contribute only very weakly to the molecular intensity. Although the rotational constants are sensitive to the terminal torsion angles, a reliable refinement of these angles cannot be done because of the high correlation among variables.¹ The availability of rotational constants for the N-deuterated species of AET², -NHD and -NDH, for both gauche I and II permit the calculation of substitution coordinates for the H_N atoms in the principal axis system. However spectral assignments for the S-deuterated species of AET and EDT² have not been obtained.³ Thus the question of intramolecular hydrogen bonding cannot be resolved at all for EDT, and at best only partially resolved for AET with use of only electron-diffraction intensities and rotational constants.

An additional set of structural dependent observables available for EDT and AET are the dipole-moment components calculated with use of second-order Stark theory.⁴ In order to use this independent set of observables in the least-squares refinement of structures one must be able to determine for each trial structure a set of "calculated" values which may be compared to the "observed" values. The question becomes: how does one calculate a set of dipole-moment components, μ_a , μ_b , and μ_c , along the principal axes from a set of structural variables? As a first approximation the components can be calculated from these structural variables and a set of bond moments, which are vector quantities acting in the direction of each bond. The components of each bond moment along each axis are calculated from the geometry of the molecule, and then summed. The resultant sums, μ_a , μ_b , and μ_c , would vary as one varied the structure. Thus, one could make small changes in the structural variables, recalculate the dipole moments, and compare the results with the observed dipole moments. The problem with this method is that the magnitudes of the bond moments are not precisely known. Smyth⁵ reports the C-H bond moment, for example, to be 0.4 D but includes a discussion which covers values ranging from 0.2 to 0.6 D, with some uncertainty as to the direction. In order to circumvent the use of imprecise bond moments, group moments may be used to represent the contributions to the molecular dipole moment from different groups within the molecule. This general idea in which one considers the molecular dipole moment to be the vector sum of two or more group moments, which was first proposed by J. J. Thomson⁶, was used by M. D. Harmony in his microwave analyses of AET² and EDT³.

In the application of this concept to the least-squares analysis of EDT, for example, the molecular dipole vector was considered to be the resultant from two $-\text{CH}_2\text{SH}$ groups. The experimentally determined molecular dipole vector for CH_3SH ⁷ was used to define the magnitude and orientation of these groups in the EDT molecule. (The contributions from the "extra" C-H bonds in CH_3SH , not present in EDT, will cancel each other as the two groups are joined; the C-C bond is assumed to have zero dipole moment.) The group moments were then used, and the EDT structural parameters, to calculate a set of "bond" components along each of the C-S and S-H bonds of EDT. (The sum contribution from the C-H bonds is colinear with the C-S bond and thus is included in the C-S "bond" component. The direction of these components were, from positive to negative, C to S and H to S.) The atomic coordinates in the molecular frame of reference were converted to those in the principal axis system and these "bond" components were resolved to give μ_a , μ_b , and μ_c . The orientation of the $-\text{CH}_2\text{SH}$ group moments in the EDT molecule was allowed to vary from the orientation of the molecular dipole vector in methylthiol by as much as 20° , however the magnitude was assumed to be the same.

With this method of analysis contained in the least-squares program, one can include a set of dipole-moment components as an additional constraint on the refinement of a structure. The value of $\sum_{abc} \{\mu(\text{obsd}) - \mu(\text{calcd})\}^2$ is minimized, in addition to values for similar expressions for the electron-diffraction intensities and rotational constants, to an extent determined by the selected weighting scheme.

References

- (1) For a given heavy-atom structure which gives a satisfactory fit to the electron-diffraction data, the terminal torsion angles could be refined using the rotational constants to give a structure which would simultaneously fit the two sets of observables. However if the values of the torsion angles were then changed by 2 or $3\sigma_{LS}$ and then held constant, the structure refinement could be repeated, and the fit to the rotational constants could be restored by making only subtle changes in the heavy-atom structure; i.e., without disrupting the electron-diffraction fit.
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