(ii) H_2O_2 and strong reductants such as sulfide[5] and thiosulfate[20] ions in neutral solution without and with catalyst, respectively; and (iii) H_2O_2 and the weak reductant SCN^- with Cu(II) ion present in strong alkaline environment. Although the mechanism of the oscillatory behavior is now understood only for the Bray reaction, it seems safe to state that the chemical background of the periodicity and multistability is rather different in each case.

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Registry No. H_2O_2, 7722-84-1; SCN^-, 302-04-5; Cu, 7440-50-8; NH_4^+, 7664-41-7.

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Conformational Analysis. 10. Ethane-1,2-dithiol. Electron-Diffraction Investigation of the Molecular Structure, Conformational Composition, and Anti–Gauche Energy and Entropy Differences. Evidence for an Intramolecular SH···S Hydrogen Bond

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Abstract: The structure and conformational composition of gaseous ethane-1,2-dithiol have been investigated at nozzle temperatures of 350 and 445 K. The analysis was based on refinements of electron-diffraction data augmented by rotational constants and, in a newly developed method, dipole-moment components from the literature. The most important discovery is that one of the H_S atoms is positioned so as to form a S–H···S hydrogen bond in the gauche form of the molecule with the H···S distance equal to 2.70 (8) Å, about 0.4 Å less than the sum of the van der Waals radii. The mole fractions of the gauche conformer at 350 and 445 K are 0.459 (86) and 0.479 (100), respectively, from which the internal energies of the gauche and anti forms are calculated not to be significantly different ($\Delta E° = E_G° - E_A° = 0.41$ (86) kcal mol^{-1}) and the entropy difference $\Delta S° = S_G° - S_A° - R \ln 2$ to be −1.0 (22) cal deg^{-1} mol^{-1}. Assuming that the conformers differ only in their C–C and C–S torsion angles, the values of some of the more important parameters at 350 K with 2σ values that include estimates of systematic error and correlations among observations are r_g(C–H) = 1.118 (11) Å, r_g(S–H) = 1.373 (15) Å, r_g(C–C) = 1.537 (6) Å, r_g(C–S) = 1.824 (2) 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)°, τ(SCCS) = 69.0 (15)°, l(C–H) = 0.086 (8) Å, l(S–H) = 0.090 (8) Å, l(C–C) = 0.054 (5) Å, l(C–S) = 0.059 (3) Å, σ_A(root mean square amplitude of C–C_A torsion) = 14.9 (52)°. The torsion angles CCSH in the gauche form have values equal to −40 (30)° and −141 (22)° measured in the sense of a counterclockwise rotation of the S–H bonds relative to an eclipsed arrangement of these bonds with τ(SCCS) equal to 0.0°. The frequency of the torsional vibration in the anti form of the molecule is calculated from σ_A to be 87 (24) cm^{-1} in good agreement with the experimental value 115 cm^{-1}.

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 glycol,[4] 2-fluoroethanol,[5] 2-aminoethanol,[6] 2-mercaptoethanol,[7] and 2-chloroethanol,[8] 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 1 also poses the possibility of intramolecular hydrogen-bond formation. Although a bond of the type S–H···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···N and O–H···S apparently exist (in 2-aminoethanethiol[10] and 2-mercapoethanol[7]) and show that sulfur may act either as a donor or an acceptor of hydrogen. The structure and composition of EDT at about 70 °C have previously been investigated[11] by electron diffraction, from which it was concluded that the anti form was the more stable by about 0.8

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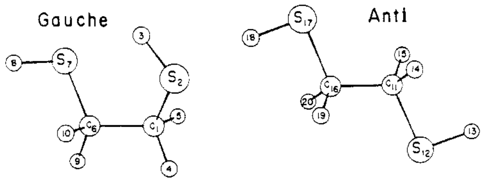

Figure 1. Atomic numbering for the conformers of ethane-1,2-dithiol.

kcal/mol. The vibrational spectrum of EDT has also been studied[12] and has 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 $\Delta G°$). Accordingly, we decided to reinvestigate the EDT system by electron diffraction, with elucidation of $\Delta E°$ and $\Delta S°$ for the conformers to be 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 determination of the *positions* of the H_S atom 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 (bp 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 × 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, $3.0\text{–}5.9 \times 10^{-6}$ torr; electron wavelengths, 0.05487–0.05494 Å (calibrated from CO_2 with $r_a(C{=}O) = 1.1646$ Å and $r_a(O \cdot O) = 3.3244$ Å); ranges of data, $2.00\ Å^{-1} \leq s \leq 13.00\ Å^{-1}$ (long, 350 and 445 K), $6.00\ Å^{-1} \leq s \leq 33.00\ Å^{-1}$ (intermediate, 350 K) and $6.00\ Å^{-1} \leq s \leq 32.00\ Å^{-1}$ (intermediate, 445 K); data interval, $0.25\ Å^{-1}$.

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 ($s^4I_t(s)$) and molecular intensities ($sI_m(s)$) have been described.[14,15] Figure 2 shows curves of the total scattered intensities, averaged intensities, and the final backgrounds 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.

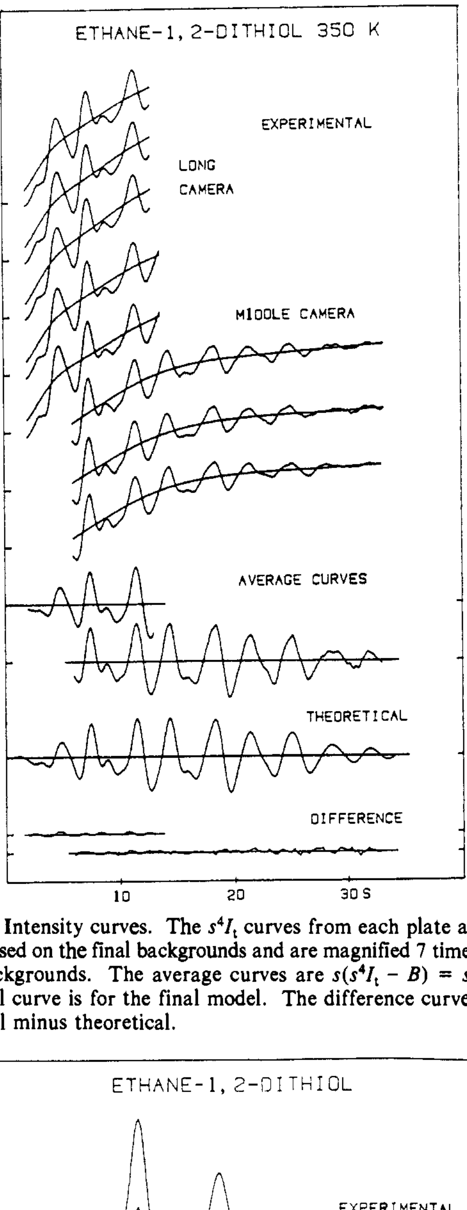

Figure 2. Intensity curves. The s^4I_t curves from each plate are shown superimposed on the final backgrounds and are magnified 7 times relative to the backgrounds. The average curves are $s(s^4I_t - B) = sI_m$. The theoretical curve is for the final model. The difference curves are experimental minus theoretical.

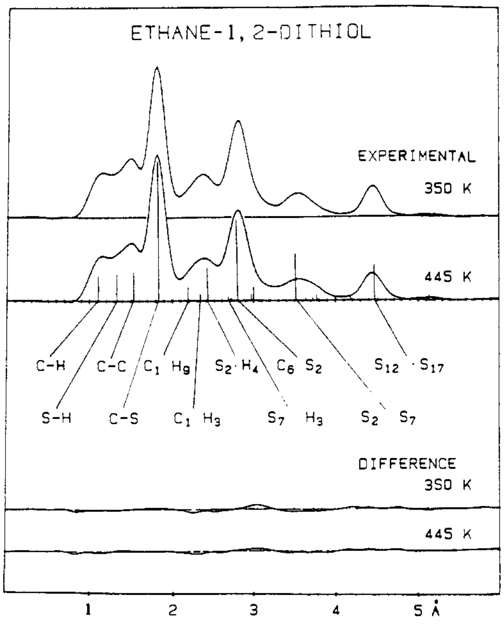

Figure 3. Radial distribution curves. The experimental curves were calculated from composites of molecular intensities from the two camera distances. Distances are indicated by vertical lines of height proportional to the area of the corresponding peak component. Bars for nonbond distances through more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

Radial distribution curves were calculated in the usual way by Fourier transformation of functions $I'(s) = sI_m(s)Z_SZ_CA_S^{-}A_C^{-1}\exp(-Bs^2/2)$ with

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the artificial damping factor B equal to 0.0025 Å^2. Figure 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]

Table I. Results for Structural Parameters of Ethane-1,2-dithiol[a]

parameter	temp, K 350	temp, K 445	Harmony[b]	Schultz–Hargittai[c]
C–H				
r_a	1.112 (11)	1.113 (8)		1.12$_0$ (2$_6$)
$r_\alpha{}^0$	1.103 (11)	1.104 (8)	1.103	
S–H				
r_a	1.367 (15)	1.367 (12)		1.40$_0$ (5$_6$)
$r_\alpha{}^0$	1.338 (15)	1.337 (12)	1.339	
C–C				
r_a	1.535 (6)	1.542 (5)		1.53$_0$ (5$_6$)
$r_\alpha{}^0$	1.534 (6)	1.539 (5)	1.534	
C–S				
r_a	1.822 (2)	1.823 (2)		1.819 (12)
$r_\alpha{}^0$	1.820 (2)	1.821 (2)	1.817	
∠(C–C–S)	113.1 (4)	112.7 (4)	113.6	112.0 (26)
∠(H–C–H)	103.7 (57)	103.9 (55)	103.5	[109.8]
⟨∠CCH,∠SCH⟩[d]	109.9 (13)	110.0 (13)		
Δ(∠CCH,∠SCH)[d]	[2.3]	[2.3]		
∠(C–C–H)	111.1 (13)	111.1 (13)	111.2	110.4[e]
∠(S–C–H)	108.8 (13)	108.8 (13)	108.4	107.0 (62)
∠(C–S–H)	[94.0]	[94.0]	94.0	90.5 (90)
τ(S–C–C–S)$_G$	69.0 (15)	69.1 (14)	66.9	73.7 (100)
τ(C–C–S–H$_3$)$_G$	−40 (30)	−41 (29)	−25.5	[180.0]
τ(C–C–S–H$_8$)$_G$	−141 (22)	−152 (17)	−144.3	[180.0]
∠σ_A[f]	14.9 (52)	16.5 (55)		
X_A[g]	0.541 (86)	0.521 (100)		0.62$_0$ (8$_4$)
R[h]	0.079	0.074		

[a] Distances in angstroms, angles ($\angle_\alpha$) in degrees. Values in parentheses are 2σ and include estimates of systematic error and correlations among observations. Values in brackets were assumed. [b] The values in this column satisfy the B_z and μ_g values of Table IV 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. [c] Reference 11. [d] See text for definitions. [e] Calculated by using the reported values for ∠(SCH), ∠(CCH), and ∠(CCS). [f] Root-mean-square torsional amplitude for the anti form. [g] Mole fraction of anti conformation. [h] $R = [\sum w_i\Delta_i^2/\sum w_i(s_iI_i(\text{obsd}))^2]^{1/2}$ where $\Delta_i = s_iI_i(\text{obsd}) - s_iI_i(\text{calcd})$.

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 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 this assumption was adopted for EDT. The common set of parameters was chosen to be the bond distances r(C–H), r(S–H), r(C–C), and r(C–S); and the angles ∠CCS, ∠CSH, ⟨∠CCH,∠SCH⟩ = (∠CCH + ∠SCH)/2, and Δ(∠CCH,∠SCH) = ∠CCH − ∠SCH. Specification of the gauche form of the molecule required three more parameters, taken to be the torsion angles τ(SCCS), τ(CCSH$_3$)$_G$, and τ(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 τ(SCCS) in the anti form (τ_A) were expected to decrease significantly the average values of the torsion-sensitive distances, we followed previous practice[17] 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 corresponding to values of τ_A equal to 0, $\pm 0.5\sigma_A$, $\pm 1.0_A$, $\pm 1.5\sigma_A$, and $\pm 2.0\sigma_A$. Each component was weighted 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 CH$_2$SH group moments.[13a] The group moment was assigned the magnitude found for CH$_3$SH[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$_3$SH (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 H$_3$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. We intend to describe the process in greater detail in another article.

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 $r_\alpha{}^0$. Conversions of the B_0's to B_z's and the $r_\alpha{}^0$'s to 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 Å^{-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 observed[12] for each of the conformers to an accuracy of at least 99%.

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Table II. Distances (r_α^0, r_g, and r_a) and Amplitudes (l) in Ethane-1,2-dithiol[a]

	350 K				445 K			
atom pair	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 } (8)	1.104	1.119	1.113 (8)	0.078 } (6)
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)
$C_1 \cdot H_3$	2.333	2.353	2.345 (10)	0.134	2.333	2.353	2.345 (8)	0.137
$C_1 \cdot H_9$	2.187	2.196	2.188 (14)	0.134 } (22)	2.194	2.202	2.193 (15)	0.138 } (21)
$S_2 \cdot H_4$	2.413	2.420	2.412 (16)	0.136 }	2.415	2.422	2.414 (16)	0.141 }
$C_1 \cdot S_7$	2.802	2.805	2.802 (5)	0.081 (5)	2.802	2.805	2.802 (5)	0.092 (5)
				Gauche Form				
$S_2 \cdot\cdot S_7$	3.515	3.522	3.517 (16)	0.139 (19)	3.507	3.517	3.508 (13)	0.177 (25)
$C_1 \cdot\cdot H_8$	3.610	3.624	3.617 (126)	0.160	3.663	3.677	3.669 (77)	0.170
$C_6 \cdot\cdot H_3$	2.686	2.704	2.685 (238)	0.223	2.689	2.707	2.685 (232)	0.242
$S_2 \cdots H_8$	4.091	4.104	4.081 (325)	0.310	4.229	4.244	4.215 (232)	0.349
$S_7 \cdots H_3$	2.675	2.701	2.669 (81)	0.294	2.667	2.695	2.655 (87)	0.325
$S_2 \cdot\cdot H_9$	3.772	3.778	3.775 (10)	0.111	3.774	3.780	3.777 (10)	0.116
$S_2 \cdot\cdot H_{10}$	2.967	2.973	2.962 (47)	0.176	2.964	2.971	2.959 (47)	0.189
				Anti Form				
$S_{12} \cdot\cdot S_{17}$	4.469	4.471	4.469 (7)	0.089 (12)	4.468	4.470	4.468 (7)	0.102 (15)
$C_{11} \cdot\cdot H_{18}$	3.723	3.735	3.730 (14)	0.128	3.725	3.737	3.732 (12)	0.133
$S_{12} \cdot\cdot H_{18}$	5.131	5.140	5.135 (11)	0.154	5.131	5.140	5.135 (10)	0.163
$S_{12} \cdot\cdot H_{19}$	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 III. Correlation Matrix for Parameters of Ethane-1,2-dithiol at 350 K (X100)

		$100\sigma_{LS}$[a]	r_1	r_2	r_3	r_4	$\angle_5$	$\langle\,\rangle_6$	τ_7	τ_8	τ_9	σ_{10}	l_{11}	l_{12}	l_{13}	l_{14}	l_{15}	l_{16}	l_{17}	χ_{18}
1	r(C–H)	0.39	100	55	27	−6	−15	−53	5	−2	−1	−5	11	−7	<1	9	8	2	1	−3
2	r(S–H)	0.54		100	46	−7	−27	−43	6	−2	−6	−5	19	8	15	15	11	4	4	−4
3	r(C–C)	0.19			100	−1	−67	−24	18	−3	−13	−13	25	2	4	15	14	6	5	−4
4	r(C–S)	0.05				100	−26	−11	11	−1	−5	7	−2	−4	−11	1	−21	−2	2	−1
5	$\angle$(C–C–S)	13					100	8	−53	30	12	45	−19	<1	−1	−13	26	−15	−1	2
6	$\langle\angle$CCH,$\angle$SCH$\rangle$[b]	46						100	−26	41	−43	−13	−4	1	−2	−23	<1	3	−5	−1
7	$\tau(SCCS)_G$	52							100	−18	72	−23	2	−1	<1	8	−27	12	−2	10
8	$\tau(CCSH_3)_G$	1100								100	11	18	1	<1	−1	−16	26	−1	−3	5
9	$\tau(CCSH_8)_G$	770									100	14	−8	<1	<1	5	−5	1	−2	14
10	$\angle\sigma_A$[c]	180										100	−8	−1	−3	4	11	−22	−13	13
11	l(C–S)	0.07											100	10	8	39	−4	11	15	−7
12	l(C–H)	0.27												100	34	10	3	3	2	<1
13	l(C–C)	0.16													100	12	4	3	2	−1
14	$l(C_1 \cdot S_7)$	0.12														100	−10	2	14	−8
15	$l(C_1 \cdot H_9)$	0.75															100	<1	−4	6
16	$l(S_{12} \cdot\cdot S_{17})$	0.40																100	−38	67
17	$l(S_2 \cdot\cdot S_7)$	0.66																	100	−63
18	χ_A[d]	3.1																		100

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

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 being 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 $\angle$CSH and $\Delta(\angle$CCH,$\angle$SCH) could not be reliably refined. The CSH angle was varied from 90° to 97° in 1-deg increments and then fixed at 94°, the value which gave the best fit. The parameter $\Delta(\angle$CCH,$\angle$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 Table I and II. Table III shows the correlation matrix corresponding to the lower temperature results; that for the higher temperature is similar.

Discussion

As is seen in the data of Table I, our analysis of the EDT structure (at 350 K) has given values for the bond distances and bond angles, including the torsion angle τ(SCCS), in excellent agreement with the earlier work of Schultz and Hargittai.[11] We differ slightly with Schultz–Hargittai in our estimate of the mole fraction of the anti form present in the sample, but the difference is more apparent than real since Schultz–Hargittai did not attempt a realistic assessment of the uncertainty attached to their measurement of this parameter. Our results go beyond those of Schultz–Hargittai, however, in providing estimates of the energy

Table IV. Observed and Calculated Values for Rotational Constants and Dipole-Moment Components[a]

	obsd		calcd[b]	
	B_0[c]	B_z[d]	this work at 350 K	Schultz–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

[a] Rotational constants are in megahertz; dipole moments are in debye. [b] $B_z = 505379/I_z$. [c] Reference 13a. [d] $B_0 - B_z$ differences calculated from the force field. [e] Calculated from results in ref 11.

and entropy differences of the conformers (described below) and in providing values for $\tau(\mathrm{CCSH_3})$ and $\tau(\mathrm{CCSH_8})$ in the gauche form of the molecule; we find $\tau(\mathrm{CCSH_3})$ to be such as to place the hydrogen atom between the sulfur atoms and thus to imply hydrogen-bond formation, whereas Schultz–Hargittai assumed the S–H bonds to be anti to the C–C bond. We note that the rms amplitudes of vibration reported by Schultz–Hargittai 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 Schultz–Hargittai with their assumption of a torsionally rigid trans orientation of the anti conformer.

The quantities $\Delta E° = E_G° - E_A°$ and $\Delta S° = S_G° - S_A° - R \ln 2$ may be determined from the usual formula $R \ln (N_G/N_A) - R \ln 2 = -\Delta E°/T + \Delta S°$, where the statistical weight of the gauche form has been removed from $S_G°$. The results are $\Delta E° = 0.41$ (86) kcal mol^{-1} and $\Delta S° = -1.0$ (2.2) cal mol K^{-1}. The value 0.63 kcal mol^{-1} for the energy difference was obtained by Hayashi et al.[12] from measurements of the vibrational spectrum, and Schultz–Hargittai's value for the Gibbs free energy difference was 0.8 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 Prof. Harmony has recently reinterpreted[13b] their data and finds that the location of these atoms is entirely consistent with our determination. Table I 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 Schultz–Hargittai's structure, to the rotational constants and dipole-moment components are given in Table IV. The apparently poor fit provided by Schultz–Hargittai'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 bonds.

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 of the value $\Delta E° = -1.05$ (10) kcal mol^{-1} for the isoelectronic molecule 1,2-dichloroethane[22] with the value $\Delta E° \simeq 0$ that 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 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 is parentheses is an estimated 2σ uncertainty. The observed[12] 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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Registry No. $HS(CH_2)_2SH$, 540-63-6.

Supplementary Material Available: Tables of total intensities, final backgrounds, and average molecular intensities for both temperatures, symmetry coordinates, force constants, observed and calculated wavenumbers, and potential energy distributions and figure of total intensities with backgrounds for 445 K (26 pages). Ordering information is given on any current masthead page.

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