Conformational Analysis. 11. 2-Aminoethanethiol. An Electron-Diffraction Investigation of the Molecular Structure, Conformational Composition, and Anti–Gauche Energy and Entropy Differences; Evidence for an Intramolecular SH···N Hydrogen Bond

Sarah L. Barkowski and Kenneth Hedberg*

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. *Received May 6, 1987*

Abstract: The structure and conformational composition of gaseous 2-aminoethanethiol have been investigated by electron diffraction at nozzle temperatures of 372 and 580 K. Species corresponding to heavy-atom gauche and anti arrangements were observed. The structure analysis was based on refinements of electron-diffraction data, augmented by rotational constants and dipole-moment components for two gauche-type conformers from the microwave spectroscopic literature. The results verify the conclusion of the microwave workers (Nandi, Boland, and Harmony): one of the gauche conformers (I) has an intramolecular S—H···N hydrogen bond (the H···N distance is equal to 2.39 (10) Å), but the structure of the other (II) is incompatible with such bonding. The mole fraction of the anti conformer is essentially temperature independent; the values with estimated 2σ uncertainties were found to be 0.227 (54) and 0.212 (46) at 372 and 580 K, respectively. The corresponding internal energy difference, $\Delta E° = E°_G - E°_A$, is 0.18 (42) kcal·mol^{-1} (i.e., insignificantly different from zero), and the entropy difference, $\Delta S° = S°_G - S°_A - R \ln 2$, is 1.5 (9) cal·deg^{-1}·mol^{-1}. With the assumption that the heavy-atom structures of the gauche and anti forms are the same except for the torsion angle τ(CC), the values of some of the more important parameters at 372 K with 2σ values including estimates of systematic error and correlations among observations were found to be r_g(N–H) = 1.051 (3) Å, r_g(C–H) = 1.120 (3) Å, r_g(S–H) = 1.371 (12) Å, r_g(C–N) = 1.481 (2) Å, r_g(C–C) = 1.526 (2) Å, r_g(C–S) = 1.828 (3) Å, $\angle_\alpha$CCS = 113.1 (4)°, $\angle_\alpha$CCN = 111.2 (12)°, $\angle_\alpha \mathrm{CC_SH}$ = 108.0 (15)°, $\angle_\alpha \mathrm{CC_NH}$ = 108.9 (15)°, $\tau(\mathrm{CC})_{\mathrm{I}}$ = 63.4 (24)°, $\tau(\mathrm{CN})_{\mathrm{I}}$ = −49 (18)°, $\tau(\mathrm{CS})_{\mathrm{I}}$ = −21 (28)°, $\tau(\mathrm{CC})_{\mathrm{II}}$ = 63.8 (13)°, $\tau(\mathrm{CN})_{\mathrm{II}}$ = 47 (19)°, $\tau(\mathrm{CS})_{\mathrm{II}}$ = −72 (11)°, l(N–H) = 0.053 (5) Å, l(C–H) = 0.057 (5) Å, l(S–H) = 0.060 (5) Å, l(C–N) = 0.049 (4) Å, l(C–C) = 0.057 (4) Å, l(C–S) = 0.055 (4) Å. (The zero position for torsion angles corrresponds to cis; the plus sense for torsion is counterclockwise rotation of the nearest group when viewing from S to C, or N to C, along the S–C or N–C bonds.)

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 ethylenediamine[1] show the molecule to exist mainly in the gauche heavy-atom conformation at 90 °C. Preliminary electron-diffraction results[2] from our laboratory for the same molecule at several sample temperatures confirm the earlier conclusions. In addition, the use of auxiliary data from microwave[3] and vibrational[4] spectroscopy led to identification of two gauche forms of ethylenediamine distinguished by different values of the torsion angles τ(CN) and τ(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 a similar electron-diffraction investigation of ethane-1,2-dithiol,[5] which also made use of experimental results from microwave[6] and vibrational[7] spectroscopy, showed that in the gas phase the molecules exist as a mixture of nearly equal amounts of anti (τ(SCCS) = 180°) and gauche (τ(SCCS) = 69°) conformers. The values of the C–S torsion angles of the gauche conformation were found to place one of the $\mathrm{H_S}$ 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 investigated[8] by Nandi, Boland, and Harmony (NBH). These authors were able to identify the presence of two different gauche conformers (Figure 1), but they did not identify an anti form. NBH reported values of rotational constants for parent species of the two gauche forms and for two different N-deuteriated species of each gauche form. From these six sets of rotational constants and two sets of dipole-moment components they determined values for five structural parameters for each of the gauche conformers (three torsion angles, τ(CC), τ(CS), and τ(CN); one bond distance, r(C–N); and one bond angle, $\angle$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. For 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 we undertook the investigation described herein. The spectroscopic data of NBH were expected to be very important for our analysis. We could not hope to determine the values of the C–N and C–S torsion angles using electron-diffraction intensities alone because the types of scattering terms which determine these angles, $\mathrm{S \cdots H_N}$, $\mathrm{C \cdots H_N}$, $\mathrm{N \cdots H_S}$, and $\mathrm{C \cdots H_S}$, are relatively weak. It has been our experience, however, that when rotational constants and dipole-moment components are used to complement the set of diffraction intensities, 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 at nozzle-tip temperatures of 372 and 580 K. Experiments at higher temperatures were precluded by sample decomposition, as noted by subtle

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[1] Yokozeki, A.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2926.

[2] Kazerouni, M. R.; Hedberg, L.; Hedberg, K., unpublished results.

[3] Marstokk, K. M.; Møllendal, H. *J. Mol. Struct.* **1978**, *49*, 221.

[4] Sabatini, A.; Califano, S. *Spectrochim. Acta* **1960**, *16*, 677.

[5] Barkowski, S. L.; Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1986**, *108*, 6898. The reported value of 0.41 (86) kcal·mol^{-1} for $\Delta E°$ is inconsequentially in error. The corrected value is 0.26 (86) kcal·mol^{-1}.

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[7] Hayashi, M.; Shiro, Y.; Oshima, T.; Murata, H. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1734.

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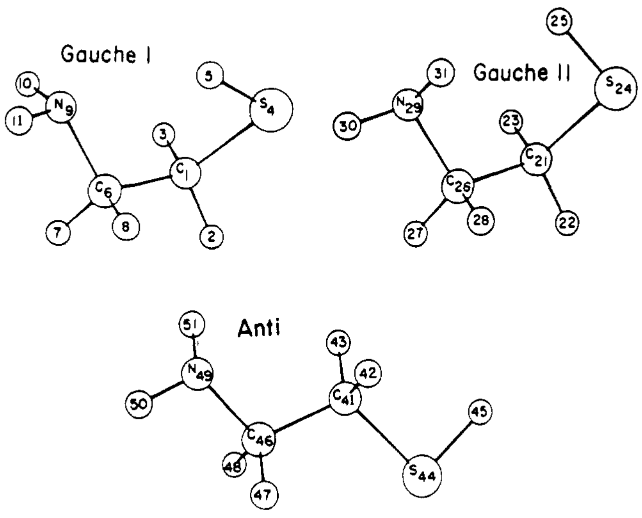

Figure 1. Atomic numbering for the conformers of 2-aminoethanethiol.

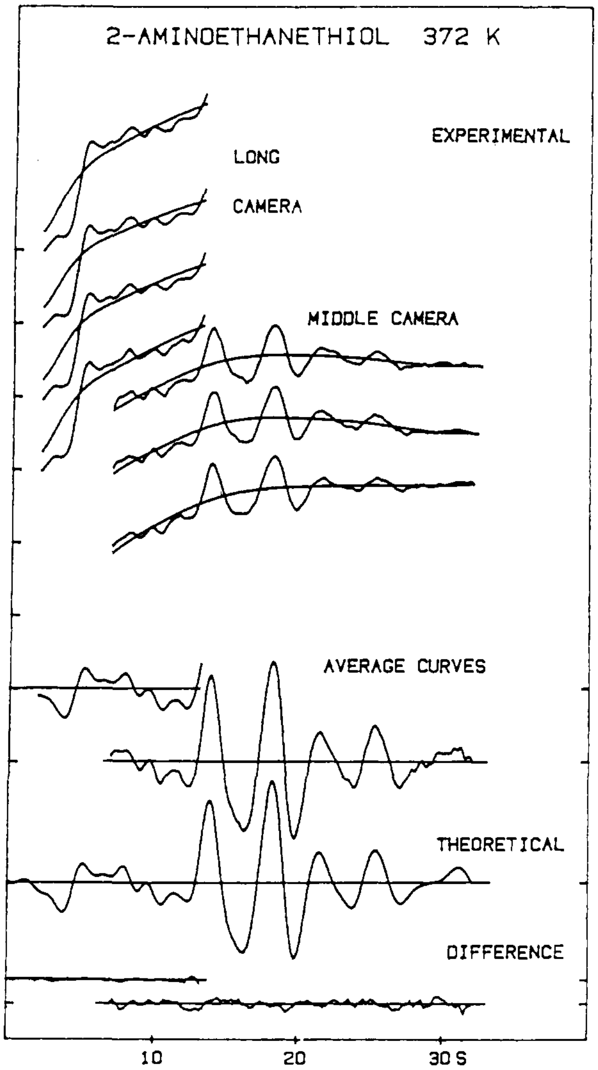

Figure 2. Intensity curves for 372 K. The s^4I_t curves from each plate are shown superimposed on the final backgrounds and are magnified 6 times relative to the backgrounds. The average curves are $s(s^4I_t - B) = sI_m$. The theoretical curve is for the final model. The difference curves are experimental minus theoretical.

changes in the mass spectrum. 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.[5] The structure analysis was based on four (three) plates from the long (intermediate) camera distances at 372 K and five (four) plates at the long (intermediate) distances at 580 K. The ranges of data were $2.00 \le s/\text{Å}^{-1} \le 13.25$ ($7.00 \le s/\text{Å}^{-1} \le 32.00$) from the long (intermediate) camera distance at 372 K and $2.00 \le s/\text{Å}^{-1} \le 13.50$ ($8.00 \le s/\text{Å}^{-1} \le 30.00$) from the long (intermediate) distance at 580 K. The data interval was $\Delta s = 0.25$ Å^{-1}. Figure 2 shows curves of the total intensities superimposed on their background 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.

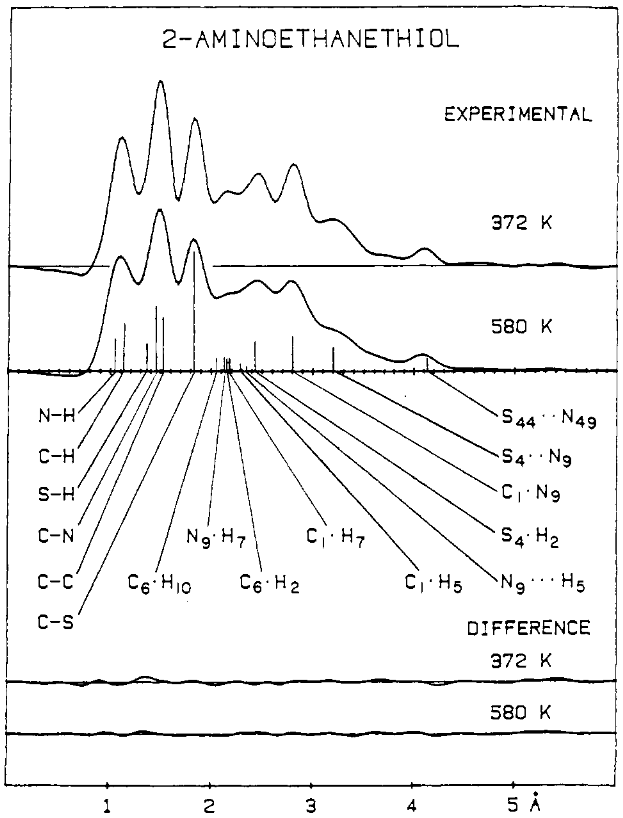

Figure 3. Radial distribution curves for 2-aminoethanethiol. The experimental curves were calculated from composites of molecular intensities from the two camera distances with $B = 0.0025$ Å^2. Distances are indicated by vertical lines of height proportional to the area of the corresponding peak component. Bars for nonbond distances through more than one angle are not shown except for $S_4 \cdot\cdot N_9$, $S_{44} \cdot\cdot N_{49}$, and the hydrogen bond distance $N_9 \cdots H_5$. The difference curves are experimental minus theoretical.

Radial distribution curves were calculated by Fourier transformation of functions $I'(s) = sI_m(s)Z_SZ_CA_S^{-1}A_C^{-1}\exp(-Bs^2)$ with use of intensity data from theoretical curves in the unobserved or uncertain region $s < 2.75$ Å^{-1}. Figure 3 shows the final experimental curves 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 NH_2 and 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 and 3.2 Å correspond primarily to the S··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 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 values for rotational constants (three for the parent species of each of the two gauche forms and three for each of the two N-monodeuteriated species of each gauche form) and (2) a total of 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 $r_\alpha{}^0 = r_z$ type of distance. For the gauche conformers, conversions of the B_0's to B_z's consistent with these $r_\alpha{}^0$'s, and the $r_\alpha{}^0$'s to r_a's consistent with the electron-diffraction data, were done in a fashion similar to that described for ethane-1,2-dithiol.[5] (Although only diffraction data were available for the anti conformer of AET, our model formulation of the system, described below, required similar conversion of the 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 Å^{-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-dithiol[5] and ethylenediamine.[2] 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. On the basis of 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 analysis has become quite common, similar use of dipole-moment components is new and promises to be especially valuable in cases like AET. In our recent analysis of the ethane-1,2-dithiol system,[5] for example, 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 CH_2SH portion of the molecule and one for the CH_2NH_2 portion. The CH_2SH 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 CH_2NH_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 CH_2SH and 101° for CH_2NH_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 amimo 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 detailed description of this process will be presented in a separate article.

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 $\sum w_i B_i{}^2 : \sum w_i (s_i I_i(s))^2 : \sum w_i (\mu_i)^2 = 500000:300:1$. Each of the dipole-moment components and each of the rotational constants were given equal weights.

Table I. Results for Structural Parameters of 2-Aminoethanethiol

parameter	372 K[a]	580 K[a]	NBH[b]
⟨C–H,N–H⟩[c]	1.078 (3)	1.076 (3)	[1.063]
Δ(C–H,N–H)[c]	[0.077 (21)]	[0.077 (73)]	[0.080]
S–H	1.335 (12)	1.315 (15)	[1.349]
⟨C–C,C–N⟩[c]	1.500 (2)	1.503 (2)	1.515[d]
Δ(C–C,C–N)[c]	[0.045 (20)]	[0.045 (23)]	0.030[d]
C–S	1.824 (3)	1.822 (3)	[1.805]
∠(CCS)	113.1 (5)	112.9 (5)	[113.2]
∠(CSH)	[90.0 (27)]	[90.0 (35)]	[94.5]
∠(HCH)	[109.0 (55)]	[109.0 (103)]	[108.9],[e] [109.8][f]
⟨CC_SH,CC_NH⟩[c]	108.5 (15)	108.6 (14)	[110.45]
Δ(CC_SH,CC_NH)[c]	[–0.9 (43)]	[–0.9 (47)]	[0.5]
∠$(C–C–N)_I$	111.0 (14)	110.9 (12)	110.9 (1)
∠$(C–C–N)_{II}$	111.3 (10)	111.0 (9)	109.6 (1)
∠(C–N–H)	[108.0 (67)]	[108.0 (53)]	[110.4]
∠(H–N–H)	[109.0 (146)]	[109.0 (127)]	[109.0]
$\tau(C–C)_I$	63.4 (24)	63.8 (19)	63.8 (2_0)
$\tau(C–C)_{II}$	63.8 (13)	64.7 (12)	67.0 (2_0)
$\tau(C–S)_I$	–21 (28)	[–21 (21)]	–26.9 (3_0)
$\tau(C–S)_{II}$	–72 (11)	–71 (9)	–56.7 (3_0)
$\tau(C–N)_I$	–49 (18)	–42 (22)	–44.6 (2_0)
$\tau(C–N)_{II}$	47 (19)	48 (18)	54.7 (2_0)
X_A[g]	0.227 (54)	0.212 (50)	
R[h]	0.096	0.090	

[a] Distances ($r_\alpha{}^0$) in angstroms, angles ($\angle_\alpha$) in degrees. Values in brackets were assumed. Values in parentheses attached to values in brackets are σ_{LS} (see text for explanation); other values in parentheses are $2\sigma_{tot}$ which include estimates of systematic error and correlations among observations. [b] Calculated from ref 8. Values in parentheses "should encompass errors in the assumed parameters". [c] See text for definitions. [d] Reported as C–C = [1.530] Å, $C–N_I$ = 1.489 (15) Å, and $C–N_{II}$ = 1.511 (15) Å. [e] Thiol end. [f] Amino end. [g] Mole fraction of anti conformation. [h] $R = [\sum w_i \Delta_i{}^2 / \sum w_i (s_i I_i(\text{obsd}))^2]^{1/2}$ where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

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 all 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. (NBH report[8] 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 distances 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 $\langle r(\text{CH,NH})\rangle = [2r(\text{C–H}) + r(\text{N–H})]/3$, $\Delta r(\text{CH,NH}) = r(\text{C–H}) - r(\text{N–H})$, r(C–S), $\langle r(\text{CC,CN})\rangle = [r(\text{C–C}) + r(\text{C–N})]/2$, $\Delta r(\text{CC,CN}) = r(\text{C–C}) - r(\text{C–N})$, and r(S–H); and the angles ∠CCS, ∠CSH, ∠HCH, $\langle CC_SH, CC_NH\rangle = [\angle CC_SH + \angle CC_NH]/2$, $\Delta[CC_SH, CC_NH] = \angle CC_SH - \angle CC_NH$, ∠CCN, ∠CNH, and ∠HNH. The unique set of parameters was chosen to be the six torsion angles $\tau(CC)_I$, $\tau(CC)_{II}$, $\tau(CS)_I$, $\tau(CS)_{II}$, $\tau(CN)_I$, and $\tau(CN)_{II}$. The zero value for these angles corresponds to eclipsed C–N and C–S bonds for τ(CC), eclipsed S–H and C–C bonds for τ(CS), and an eclipsing of the nitrogen lone pair and the C–C bond for τ(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

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(10) Kojima, T. *J. Phys. Soc. Jpn.* **1960**, *15*, 1284.
(11) Takagi, K.; Kojima, T. *J. Phys. Soc. Jpn.* **1971**, *30*, 1145.

Table II. Distances ($r_\alpha{}^0$, r_g, and r_a) and Amplitudes (l) in 2-Aminoethanethiol[a,b]

atom pair	372 K					580 K				
	$r_\alpha{}^0$	r_g	r_a	l		$r_\alpha{}^0$	r_g	r_a	l	
For All Conformers										
N–H	1.027	1.051	1.048 (3)	0.053	(5)	1.025	1.049	1.041 (4)	0.089	(6)
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	(4)	1.481	1.485	1.482 (3)	0.072	(5)
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)	
$C_6{\cdot}H_{10}$	2.043	2.056	2.052 (3)	0.097	(10)	2.045	2.058	2.053 (4)	0.103	(9)
$N_9{\cdot}H_7$	2.118	2.128	2.123 (24)	0.101		2.119	2.129	2.123 (24)	0.109	
$C_6{\cdot}H_2$	2.139	2.149	2.143 (21)	0.109		2.142	2.152	2.145 (18)	0.119	
$C_1{\cdot}H_7$	2.151	2.161	2.156 (19)	0.107		2.154	2.164	2.158 (18)	0.116	
$C_1{\cdot}H_5$	2.261	2.280	2.274 (8)	0.119		2.247	2.267	2.259 (11)	0.121	
$S_4{\cdot}H_2$	2.424	2.432	2.428 (20)	0.105		2.421	2.429	2.424 (17)	0.115	
$C_1{\cdot}N_9$	2.475	2.479	2.477 (20)	0.073	(6)	2.477	2.481	2.476 (17)	0.108	(8)
$S_4{\cdot}C_6$	2.798	2.801	2.799 (8)	0.081		2.794	2.799	2.794 (9)	0.121	
For Gauche I Conformer										
$N_9{\cdot\cdot}H_2$	3.410	3.416	3.413 (25)	0.110		3.411	3.418	3.414 (22)	0.117	
$N_9{\cdot\cdot}H_3$	2.682	2.689	2.677 (55)	0.179		2.681	2.688	2.673 (46)	0.205	
$S_4{\cdot\cdot}H_7$	3.762	3.769	3.765 (12)	0.112		3.756	3.764	3.760 (11)	0.123	
$S_4{\cdot\cdot}H_8$	2.960	2.967	2.956 (31)	0.183		2.951	2.960	2.944 (26)	0.212	
$C_1{\cdot\cdot}H_{10}$	2.759	2.770	2.761 (134)	0.158		2.816	2.829	2.818 (172)	0.178	
$C_1{\cdot\cdot}H_{11}$	3.345	3.354	3.351 (34)	0.106		3.334	3.344	3.340 (55)	0.113	
$C_6{\cdot\cdot}H_5$	2.472	2.490	2.472 (130)	0.206		2.465	2.485	2.461 (11)	0.241	
$S_4{\cdot\cdot}N_9$	3.211	3.217	3.208 (6)	0.173 (17)[c]		3.212	3.221	3.206 (6)	0.221 (20)[b]	
For Gauche II Conformer										
$S_4{\cdot\cdot\cdot}H_{10}$	3.709	3.720	3.702 (232)	0.260		3.791	3.805	3.779 (262)	0.313	
$S_4{\cdot\cdot\cdot}H_{11}$	4.049	4.059	4.052 (147)	0.173		3.988	4.001	3.990 (202)	0.206	
$N_9{\cdot\cdot\cdot}H_5$	2.368	2.392	2.367 (102)	0.248		2.379	2.407	2.370 (15)	0.296	
$N_{29}{\cdot\cdot}H_{22}$	3.411	3.418	3.414 (21)	0.110		3.413	3.420	3.416 (18)	0.118	
$N_{29}{\cdot\cdot}H_{23}$	2.683	2.690	2.678 (38)	0.179		2.676	2.684	2.668 (33)	0.206	
$S_{24}{\cdot\cdot}H_{27}$	3.760	3.767	3.763 (13)	0.112		3.757	3.765	3.761 (10)	0.123	
$S_{24}{\cdot\cdot}H_{28}$	2.954	2.961	2.950 (23)	0.183		2.944	2.952	2.937 (19)	0.212	
$C_{21}{\cdot\cdot}H_{30}$	3.345	3.355	3.351 (33)	0.110		3.348	3.358	3.354 (31)	0.119	
$C_{21}{\cdot\cdot}H_{31}$	2.779	2.789	2.780 (154)	0.156		2.774	2.785	2.774 (149)	0.177	
$C_{26}{\cdot\cdot}H_{25}$	2.904	2.920	2.901 (114)	0.233		2.886	2.904	2.877 (97)	0.277	
$S_{24}{\cdot\cdot}N_{29}$	3.221	3.227	3.218 (13)	0.173 (17)[c]		3.223	3.232	3.216 (13)	0.225 (20)[b]	
$S_{24}{\cdot\cdot\cdot}H_{30}$	4.190	4.201	4.194 (66)	0.164		4.187	4.200	4.191 (66)	0.196	
$S_{24}{\cdot\cdot\cdot}H_{31}$	2.892	2.905	2.883 (194)	0.248		2.886	2.903	2.872 (183)	0.297	
$N_{29}{\cdot\cdot\cdot}H_{25}$	2.691	2.712	2.680 (157)	0.294		2.678	2.703	2.656 (133)	0.356	
For Anti Conformer										
$N_{49}{\cdot\cdot}H_{42}$	2.693	2.702	2.692 (40)	0.161		2.695	2.705	2.692 (35)	0.183	
$S_{44}{\cdot\cdot}H_{47}$	2.978	2.985	2.975 (30)	0.170		2.975	2.983	2.971 (24)	0.195	
$C_{41}{\cdot\cdot}H_{50}$	2.670	2.680	2.673 (7)	0.135		2.670	2.680	2.671 (8)	0.152	
$C_{41}{\cdot\cdot}H_{51}$	3.353	3.363	3.357 (7)	0.135		3.353	3.363	3.357 (8)	0.152	
$C_{46}{\cdot\cdot}H_{45}$	3.654	3.666	3.662 (11)	0.124		3.638	3.651	3.646 (15)	0.134	
$S_{44}{\cdot\cdot}N_{49}$	4.126	4.128	4.127 (7)	0.081		4.124	4.128	4.125 (8)	0.096	
$S_{44}{\cdot\cdot}H_{50}$	4.373	4.379	4.375 (7)	0.142		4.370	4.377	4.371 (8)	0.162	
$S_{44}{\cdot\cdot\cdot}H_{51}$	4.839	4.846	4.841 (8)	0.142		4.837	4.844	4.839 (8)	0.162	
$N_{49}{\cdot\cdot\cdot}H_{45}$	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] Average calculated values for those amplitudes (l/Å) that were refined were, at 372 K (580 K), as follows. N–H, 0.075 (0.075); C–N, 0.075 (0.087); C–S, 0.052 (0.058); $C_6{\cdot}H_{10}$, 0.104 (0.107); $C_1{\cdot\cdot}N_9$, 0.154 (0.189); $S_{24}{\cdot\cdot}N_{29}$, 0.154 (0.196); differences within refined groups are the calculated ones. [c] The $S_4{\cdot\cdot}N_9$ amplitudes for the gauche I and II conformers were tied during the refinement.

have the extended conformation with staggered N–H and C–H bonds, as shown in Figure 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 reported 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 the 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 nondeuteriated 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 nondeuteriated 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 deuteriated forms. (The very small isotopic effects such as $r_\alpha{}^0$(N–D) − $r_\alpha{}^0$(N–H) were ignored.) The purpose of these

Table III. Correlation Matrix (×100) for 2-Aminoethanethiol at 372 K[a]

		σ_{LS}[b] × 100	$\langle\ \rangle_1$ 0.064	r_2 0.083	$\langle\ \rangle_3$ 0.098	r_4 0.43	$\angle 5$ 15	$\langle\ \rangle_6$ 51	$\angle_7$ 80	τ_8 84	τ_9 990	τ_{10} 630	χ_{11} 1.9
1	⟨C–C,C–N⟩[c]	0.064	100	37	17	15	−22	−13	−50	50	−42	3	1
2	r(C–S)	0.083	36	100	13	6	−51	30	−17	27	−25	−11	3
3	⟨C–H,N–H⟩[c]	0.098	17	12	100	37	<1	−19	−28	29	−28	−4	<1
4	r(S–H)	0.42	15	5	36	100	−4	−8	−19	21	−20	−2	7
5	∠(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	∠(CCN)	34	−49	−14	−29	−19	8	70	100	−93	62	−69	−9
8	τ(C–C)	47	55	38	33	25	−34	−35	−77	100	−68	76	4
9	τ(C–S)	370	40	28	32	25	−29	−4	−2	−15	100	−43	−4
10	τ(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

[a] The right-hand side of the diagonal represents conformer I; the left-hand side represents conformer II. Distances (r) and amplitudes (l) in angstroms; angles in degrees. [b] Standard deviations from least squares. [c] See text for definitions. [d] Mole fraction of anti form.

Table IV. Atomic Coordinates in the Principal Axis System for H_N Atoms

		this work[a]				NBH[b]			
		372K		580 K		substitution coordinates[c]		calculated coordinates[d]	
		I	II	I	II	I	II	I	II
H10(30)	x	−1.12 (8)	0.12 (20)	−1.08 (12)	0.13 (20)	−1.074 (13)	0.151 (90)	−1.093	0.182
	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
H11(31)	x	0.42 (13)	0.23 (18)	0.47 (12)	0.21 (18)	0.455 (81)	0.204 (40)	0.437	0.041
	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

[a] Uncertainties 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. [b] Reference 8. Signs have been changed to agree with our convention. [c] Uncertainties are based on 3σ uncertainties in rotational constants and vibration–rotation uncertainty of 0.0015/g, g = a,b,c. [d] Corresponds to parameter values of Table I.

Table V. 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

[a] Rotational constants are in MHz, dipole moments are in debye. [b] $B_z = 505379/I_z$. [c] Reference 8. Values in parentheses are 3σ. [d] Corrections $B_0 - B_z$ calculated from the force field. [e] A, B, C values should be compared to those for the B_z's. [f] Calculated from results in reference 8. A, B, C values should be compared to those for the B_0's.

six refinements was to determine average values for the torsion angles τ(CS) and τ(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 τ(CS) and τ(CN) held at their average values, were carried out with use of values for rotational constants for the nondeuteriated species and dipole-moment components as auxiliary data.

Structure Results. The final results for the structure of AET are given in Tables I and II. The correlation matrices corresponding to the lower temperature results are found in Table III; those for the higher temperature results are similar. The contents of Tables I and II 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 monodeuteriated. 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 step. It is pleasing that after several such steps the parameter values obtained from these refinements differed very little: the ranges of each parameter 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 I. 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 I. 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 I 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 their and our results, and between the calculated locations of the H_N atoms (Table IV) 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,

Table VI. Observed and Calculated Values of Rotational Constants of N-Deuteriated 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			
$-NH_{30}D_{31}$	*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
$-ND_3H_{31}$	*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

[a] Values are in MHz. [b] $B_z = 505379/I_z$. [c] Reference 8. Values in parentheses are 3σ. [d] Corrections $B_0 - B_z$ calculated from the force field are an average of those for NH_2 and ND_2. [e] Values should be compared to those for B_z's. [f] Calculated from results in ref 8. Values should be compared to those for B_0's.

with which we are in complete accord.

Table V 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_z'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_z'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 VI shows the observed and calculated values of the N-deuteriated 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_z's to the observed is about 0.3%.

Effect of Other Conformers of AET. It is possible that conformers distinguished by C–S and C–N torsion angles different from those taken into account in our analysis are also present in gaseous AET. However, their presence would have no effect on our principal conclusions. As far as conformation is concerned, the electron-diffraction data from the AET system provide information about the heavy-atom gauche–anti composition, but are rather insensitive to the 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. In our models of the AET system, NBH's pair are thus satisfactorily representative of all possible gauche forms.

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 $N\cdots H_S$ hydrogen bond. (The $N\cdots H_S$ 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 $R \ln (N_G/N_A) - R \ln 2 = -\Delta E°/T + \Delta S°$, where $\Delta E° = E_G° - E_A°$ and the statistical weight of the heavy-atom gauche forms has been removed according to $\Delta S° = S_G - S_A - R \ln 2$. The results are $\Delta E° = 0.18\ (42)$ kcal·mol^{-1} and $\Delta S° = 1.5\ (9)$ cal·deg^{-1}·mol^{-1}. The former is nearly identical with the value found for ethane-1,2-dithiol (EDT, $E_G° - E_A° = 0.26\ (86)$ kcal·mol^{-1}), a molecule that, judged from the position of one of the hydrogen atoms, appears to form an intramolecular S—H···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 NH_2 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 τ(CN) and τ(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 I). 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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Supplementary Material Available: Tables of total intensities, final backgrounds, and average molecular intensities for both temperatures; table of symmetry coordinates; table of force constants; and a figure of total intensities with backgrounds for 580 K (27 pages). Ordering information is given on any current masthead page.