Molecular Structure and Conformation of Ethyl Methyl Sulfide as Studied by Gas Electron Diffraction

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The bond distances (r_g) and angles (r_a structure) in ethyl methyl sulfide have been determined by gas electron diffraction as follows: average of C(methyl)–S and C(methylene)–S=1.813±0.004 Å, C–C=1.536±0.008 Å, C–H=1.111±0.008 Å, ∠C–S–C=97.1±1.1°, ∠S–C–C=114.0±0.5°, ∠H–C–H=109.6±1.4°, where uncertainties represent estimated limits of experimental error. The two C–S lengths have been estimated independently with the aid of the rotational constants for the *trans* conformer reported by Hayashi *et al.*: C(methyl)–S=1.806±0.027 Å, C(methylene)–S=1.818±0.027 Å. The dihedral angle for the *gauche* conformer (66±9°) and the relative abundance of the *trans* and *gauche* conformers in the gas phase at 20 °C, $n_t/(n_t+n_g)=0.25\pm0.15$, have also been determined.

In the preceding paper,[1] the conformation of ethyl methyl ether was studied by gas electron diffraction, and the *trans* conformer was found to be more stable than the *gauche* conformer. The conformations of normal alkanes have also been investigated in detail by this method.[2,3] Electron diffraction is an important tool for such a conformational analysis,[4,5] since it provides, in principle, information on all interatomic distances in a molecule. However, conformations about the C–S bond in saturated compounds have never been studied by gas electron diffraction except for that in ethyl methyl disulfide.[6] Ethyl methyl sulfide is one of the simplest compounds that have internal rotation about the C–S bond. The vibrational spectra of this molecule have been observed and the conformation has been discussed.[7–11] The conformation was also investigated by a calculation based on molecular mechanics.[12] These studies have shown that there exist two conformers, the *gauche* and *trans* forms, in the gas and liquid phases. Spectroscopic experiments concluded that the two conformers had nearly the same energy in the gas phase,[8] the *gauche* conformer being 30±50 cal/mol more stable.[11]

In the present study, the frame structure and the mixing ratio of the two conformers have been derived from electron diffraction. In addition, the rotational constants of the *trans* conformer of the normal species determined by microwave spectroscopy[13] were used with our electron diffraction data to estimate the individual C–S bond lengths.

Experimental

A commercial sample (Tokyo Kasei Co., Ltd.) was purified by distillation. The purity was checked by gas chromatography, and the sample was found to be more than 99% pure.

Diffraction photographs were taken at camera lengths of 107.7 and 243.3 mm with an apparatus equipped with an r^3-sector.[14] The accelerating voltage was about 40 kV and was stabilized within 0.01% during the experiment. The sample was maintained at thermal equilibrium with its liquid phase at room temperature. The vapor pressure was about 100 Torr, and the exposure times were about 15 and 30 s for the long and short camera lengths, respectively. The scale factors of the diffraction patterns were calibrated with reference to the C=O distance (r_a) of carbon dioxide (1.1646 Å) measured under the same experimental conditions. Other experimental details are described elsewhere.[14,15]

Three photographic plates at each camera length were selected for the analysis. The optical density (0.15—0.45) was measured by a microphotometer and an integrating digital voltmeter, and it was assumed to be proportional to the molecular intensities. After correction for the imperfections of the r^3-sector shape and hand drawing of a smooth background, molecular intensities were obtained in the range s=3.7—18.8 (long) and 7.9—34.5 Å (short) at intervals of $s=\pi/10$ Å^{-1}.[16]

Since they agreed with each other in the overlapping region within their experimental errors, they were joined at s=11 Å^{-1}. The elastic and inelastic scattering factors and the phase shifts, which were required to remove the atomic and inelastic scattering, were taken from the tables prepared by Schäfer *et al.*[17] A typical molecular intensity and the corresponding

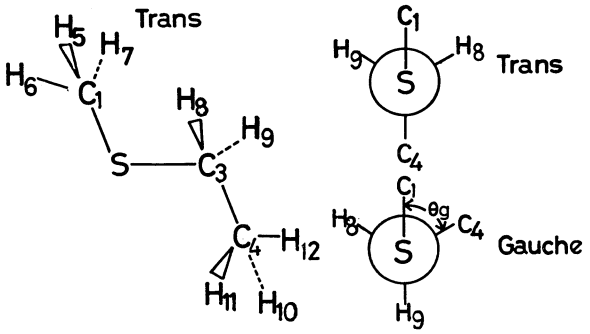

Fig. 1. Ethyl methyl sulfide. The dihedral angle for the *gauche* conformer measured from *cis* position is denoted by θ_g.

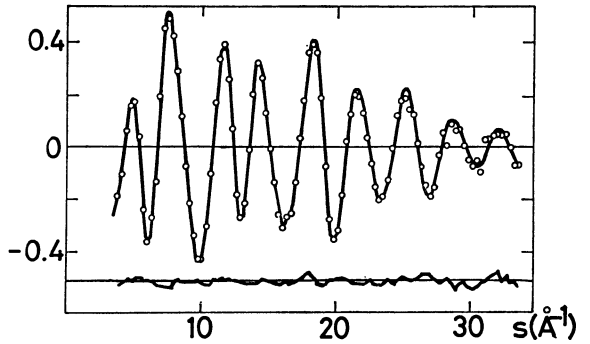

Fig. 2. Molecular intensities for ethyl methyl sulfide. Observed values are shown as open circles, and the solid curve represents the best-fit theoretical intensity. The lower solid curve represents the residuals.

radial distribution curve are illustrated in Figs. 2 and 3, respectively. Most of the calculations were carried out on a HITAC 8800/8700 in the Computer Center of the University of Tokyo.

Results and Discussion

Analysis of the Diffraction Data. The radial distribution curve has the following features: All the distances are contained in the 1.0—2.0 Å region. The peak at 1.1 Å is due to the C–H distance, and the C–C distance makes a small peak at 1.5 Å. The prominent peak contains the two C–S distances. The peaks at 2.4 and 2.9 Å are due to the nonbonded distances independent of the torsion about the C(methylene)–S axis. The shoulder at 3.2 Å and the small peak at 4.2 Å are due to the torsion-dependent C(methyl)···C(methyl) distances; the former shoulder and the latter peak come from the *gauche* and the *trans* conformers, respectively. Thus, their relative populations in the gas phase are determined from the contour of these peaks, *i.e.*, from the contributions of the C(methyl)···C(methyl) distances. On the basis of this analysis, it was concluded that two principal conformers existed in the gas phase at room temperature. By comparing the observed radial distribution curve with the curves calculated from various mixing ratios, the *gauche* conformer was inferred to be dominant. This is consistent with the conclusion derived from spectroscopy. The mean amplitudes for the C(methyl)···C(methyl) nonbonded pairs are so large that the intensity contributions from these pairs fade out in larger scattering angles. Therefore, the ratio of the two conformers is determined by the molecular intensities in the range of $s<5$ Å^{-1}. On the other hand, the r_α structure of the skeleton is determined by a least-squares analysis of molecular intensities in the larger s range ($s>5$ Å^{-1}), since in this range correlation between the parameters for the frame structure and the mixing ratio is not significant.

In this least-squares analysis the following approximations were made in order to decrease the number of the structural parameters:

1) Each of the methyl groups has C_{3v} symmetry and has no tilt.

2) For the methylene group, the bisectors of the H–C–H angle and the S–C–C angle are colinear.

3) All the C–H bond lengths are equal.

4) The difference in the two C–S bond distances is 0 ± 0.01 Å, on the basis of the structural data for dimethyl sulfide,[18] 1,2-ethanedithiol.[19] (The need for this assumption was removed in a later stage).

5) The geometrical parameters of the two conformers are equal except for the dihedral angles about the C(methylene)–S bond. (This assumption was examined in a later stage).

6) The *trans* conformer has C_s symmetry.

With these assumptions, the molecular structure is described by six parameters: the C–C bond length, the average of the C–S bond lengths, the C–H bond length, the S–C–C angle, the C–S–C angle, the weighted average of the H–C–H angles, and the dihedral angle about the C(methylene)–S bond for the *gauche* conformer. The corresponding dihedral angle for the *trans* conformer was fixed to 180° according to assumption 6).

Table 1. Mean amplitudes (l_{ij}) and shrinkage corrections (r_a-r_α) for *trans* and *gauche* ethyl methyl sulfide[a] (in 10^{-4} Å)

trans	l_{ij}	r_a-r_α		l_{ij}	r_a-r_α
C_1–H_5	786	78	S···H_8	1104	2
C_1–H_6	786	66	S···C_4	727	−10
C_3–H_8	786	87	C_1···C_3	890	−16
C_4–H_{10}	786	76	C_1···H_8	2099	−68
C_4–H_{11}	786	63	S···H_{11}	1706	114
C_3–C_4	525	10	S···H_{10}	1011	−67
C_1–S	522	8	C_3···H_5	1099	−149
C_3–S	535	−4	C_1···C_4	855	−244
C_3···H_{10}	1067	24	C_4···H_6	2018	251
C_3···H_{11}	1066	18	C_1···H_{11}	1790	−339
C_4···H_8	1070	19	C_1···H_{10}	1326	−249
S···H_5	1073	19	C_4···H_5	1145	−341
S···H_6	1071	13	C_3···H_6	2049	−53
gauche	l_{ij}	r_a-r_α		l_{ij}	r_a-r_α
C_1–H_5	786	69	C_1–H_7	786	62
C_1–H_6	786	65	C_3–H_8	786	97
C_3–H_9	786	96	C_1···H_{11}	2476	443
C_4–H_{10}	786	113	C_4···H_7	2792	405
C_4–H_{11}	786	89	C_4···S	728	−16
C_4–H_{12}	786	106	C_1···C_3	892	−22
C_3–C_4	526	6	C_3···H_6	2045	26
C_1–S	522	−5	C_3···H_7	1957	38
C_3–S	535	4	C_1···H_8	2086	41
C_3···H_{10}	1067	53	S···H_{11}	1706	4
C_3···H_{11}	1066	9	S···H_{12}	1936	−19
C_3···H_{12}	1066	36	C_1···C_4	1956	25
C_4···H_8	1070	22	C_4···H_6	3448	−58
C_4···H_9	1070	26	C_1···H_{12}	3608	−136
S···H_5	1073	0	S···H_{10}	1011	−72
S···H_6	1071	−2	C_3···H_5	1101	−164
S···H_7	1071	−6	C_1···H_9	1773	8
S···H_8	1104	19	C_4···H_5	1944	−120

a) Calculated at 20 °C. See Fig. 1 for the numbering of the atoms. Nonlinear shrinkages due to the C (methylene) –S torsion and the methyl torsions are included. (See text.) The values for H···H pairs are not listed.

The asymmetry parameter κ[20] for the C–H bond was estimated to be 1.3×10^{-5} Å^3 from the anharmonicity parameter a_3 for the C–H bond, which was assumed to be 1.98 Å^{-1}.[21] The asymmetry parameters for other atom pairs were ignored, since they did not contribute to molecular intensities significantly. The mean amplitudes and the shrinkage corrections (r_a-r_α)[22,23] for all the atom pairs were calculated on the basis of the modified Urey-Bradley force field,[9] as listed in Table 1. The frequencies of the skeletal and methyl torsions may be so low that a large-amplitude treatment is necessary. Since the frequencies and the potential functions for the skeletal torsions were not known, the contributions from these vibrational modes were estimated by Karle's method.[24-26] The three-fold potential barrier for the C(methylene)–S torsion was estimated to be about 500 cm^{-1} from those of methanethiol[27] and ethanethiol[28] assuming additivity of the contributions from substituted atoms or atom groups to the potential barrier.[29] The mean amplitudes estimated from the barrier height

turned out to be smaller than those estimated by the usual approximation of infinitesimal displacements. Karle's correction had the largest effect on the mean amplitude of the C(methyl)···C(methyl) nonbonded pair for the *gauche* conformer. The only significant effect of this torsion on the $r_a - r_\alpha$ is that for the C(methyl)···C(methyl) nonbonded atom pair, 0.0094 Å. The effect of the methyl torsions was estimated from the threefold potential barrier of about 700 cm^{-1} for the C(methyl)–S group and about 1400 cm^{-1} for the C(methyl)–C group, which were assumed from those of related molecules.[28,30] The uncertainties in the mean amplitudes and the shrinkage corrections were assumed to be 100% for the contributions from the C(methylene)–S and methyl torsions and 10% for those from the other modes.

The mean amplitudes of the C–C, the average of the C–S amplitudes and the weighted average of the C–H amplitudes were varied as parameters in the subsequent analysis. Other mean amplitudes were fixed to the values listed in Table 1. A conventional diagonal weight matrix was used in the analysis.[31] In this stage, the structural parameters obtained were the weighted *trans* and *gauche* parameters. The r_α structure and the r_g distances derived from the r_α structure are listed in Table 2. The error limits listed in this table were estimated from random and systematic errors including those originating from the approximations mentioned above.[32,33]

Table 2. Structure and mean amplitudes for ethyl methyl sulfide derived from electron diffraction data (in Å and degrees)

	r_α	r_g	ε[a]
$(C-S)_{av}$	1.811	1.813	0.004
$C_{methyl}-S$[b]	1.804	1.806	0.027
$C_{methylene}-S$[b]	1.816	1.818	0.027
C–C	1.534	1.536	0.008
C–H	1.096	1.111	0.008
∠C–S–C	97.1		1.1
∠S–C–C	114.0		0.5
∠H–C–H	109.6		1.4
θ_g[c]	66		9
$n_t/(n_t+n_g)$[d]	0.25		0.10
l(C–H)	0.079		0.005
l(C–C)	0.058		0.007
$l(C-S)_{av}$	0.054		0.004

a) Estimated limits of error. b) These distances were determined separately by a joint analysis. The rest of the parameters obtained by the joint analysis were essentially equal to those given in this Table. c) The dihedral angle for the *gauche* conformer measured from the *cis* position. d) Relative abundance of the *trans* conformer at room temperature estimated by the method of background function. See text.

Analysis of Diffraction Data with Supplementary Use of the Rotational Constants. The observed diffraction intensity carries information on the structures of the two conformers. On the other hand, the rotational constants are known only for the less abundant *trans* conformer, but the structure of this conformer has not been determined from the rotational constants. In order to take these rotational constants into the analysis as additional experimental information, the difference in the geometrical parameters for the *trans* and the *gauche* conformers had to be assumed. In the analysis of normal alkanes,[34] the C–C–C angle in the *gauche* conformer was estimated to be $0.1 \pm 1°$ larger than the corresponding angle in the *trans* conformation on account of the *gauche* C–C interaction, while their C–C bond lengths were assumed to be equal. Since existing spectroscopic data[11] and calculations based on molecular mechanics[12] suggest little enthalpy difference between the two conformers, it seems unlikely that intramolecular strain in the *gauche* conformer causes its skeletal structure to differ greatly from that of the *trans* conformer. Therefore, the possible differences in the skeletal C–C–S and C–S–C angles in the *gauche* and *trans* conformers were assumed to be 0—2°. It was also assumed that all the bond lengths were equal in the two conformers. Since the rotational constants for the *trans* conformer have different dependence on the two C–S bond lengths, it was possible to treat these distances as independent parameters in the joint analysis.

Table 3. Observed and calculated rotational constants for *trans* ethyl methyl sulfide[a] (in cm^{-1})

	B_0[b]	B_z[c]	B_α^0[d]	B_{av}[e]
A	0.5342879	0.537(5)	0.526(15)	0.533(5)
B	0.106293	0.1063(2)	0.1056(20)	0.1058(8)
C	0.0933749	0.0934(1)	0.0923(12)	0.0930(5)

a) Uncertainties attached to the last significant digits are given in parentheses. b) Observed rotational constants for the ground vibrational state. Uncertainties are not listed in the original reference. Ref. 13. c) Zero-point average rotational constants calculated from A_0, B_0, and C_0 with corrections for vibrational effects. d) Rotational constants calculated from r_α parameters given in Table 2 determined in the analysis of electron diffraction intensities. Uncertainties are estimated from those in the r_α parameters. e) Best-fit rotational constants corresponding to the r_α sturcture, listed in Table 2, derived from the combined analysis of diffraction and microwave data. Uncertainties represent 2.5 times the estimated standard deviations.

The rotational constants for the ground vibrational states, A_0, B_0, and C_0, were converted to the zero-point average rotational constants, A_z, B_z, and C_z, by the harmonic corrections[35] listed in Table 3. The uncertainties in these corrections were assumed to be 100% for the contributions from the C–S and methyl torsions and 10% for those from all the other small amplitude modes. The uncertainties in the average rotational constants originate mainly from these corrections. The r_α structure determined by electron diffraction was extrapolated to zero kelvin by estimating the difference $r_\alpha - r_\alpha^0$.[23] In order to check the consistency of the diffraction data and the rotational constants, the rotational constants, A_α^0, B_α^0, and C_α^0 for the *trans* conformer were calculated from the r_α^0 structure and compared with A_z, B_z, and C_z. The agreement was

Table 4. Error matrix[a] and correlation matrix[b] for ethyl methyl sulfide[c]

	k_1	k_2	x_1	x_2	x_3	x_4	x_5	x_6	x_7	l_1	l_2	l_3
	102	358	31	6	16	76	36	100	567	19	24	14
k_1	100	52	−23	−16	32	−57	48	46	19	57	10	58
k_2		100	83	−58	61	−65	−34	58	18	82	78	96
x_1			100	−51	54	−52	−69	56	24	62	66	77
x_2				100	−41	33	−27	−45	−19	−47	−42	−55
x_3					100	−37	−25	53	−6	46	46	60
x_4						100	−48	−76	−42	−55	−47	−64
x_5							100	15	−29	−19	−34	−27
x_6								100	43	50	43	56
x_7									100	12	16	16
l_1										100	61	80
l_2											100	71
l_3												100

a) Error matrix. Units ($\times 10^{-4}$) for the distances and mean amplitudes are Å, those for the angles are rad, and those for the indices are dimensionless. b) Correlation matrix ($\times 10^{-2}$). c) k_1,k_2=indices of resolution for the long and short distance data, respectively, $x_1=r$(C–C), $x_2=r$(C–S)$_{av}$, $x_3=r$(C–H)$_{av}$, $x_4=\angle$C–S–C, $x_5=\angle$S–C–C, $x_6=\angle$H–C–H, x_7=dihedral angle for the *gauche* conformer, $l_1=l$(C–H), $l_2=l$(C–S), and $l_3=l$(C–C).

within the experimental uncertainties of A_α^0, B_α^0, and C_α^0, as shown in Table 3. Hence, these constants were used with the diffraction intensities as subsidiary observables. The weights for the rotational constants used in this analysis were estimated by the procedure mentioned in Ref. 1; they are 1×10^3, 1×10^4, and 1×10^4 for A_z, B_z, and C_z, respectively, where a unit weight was assigned to the molecular intensities from $s=10.5$ to 25.1 Å^{-1} taken at $s=\pi/10$ Å^{-1} intervals. A typical error matrix is shown in Table 4. The r_{av} structure[23] agreed with the r_α^0 structure, and the mean amplitudes also converged to essentially the same values as those obtained in the analysis of the electron diffraction data alone. The assumption 4) made in the analysis of the diffraction intensities was now removed, and the two C–S bond distances were varied independently. The two C–S bond lengths estimated separately in the present analysis are listed in Table 2. Their limits of uncertainty include the systematic uncertainties caused by the various assumptions described above, the main origin of the uncertainties being the assumed differences in the skeletal C–C–S and C–S–C angles in the *gauche* and *trans* conformers. The average of the C–S distances is equal to that obtained from electron diffraction.

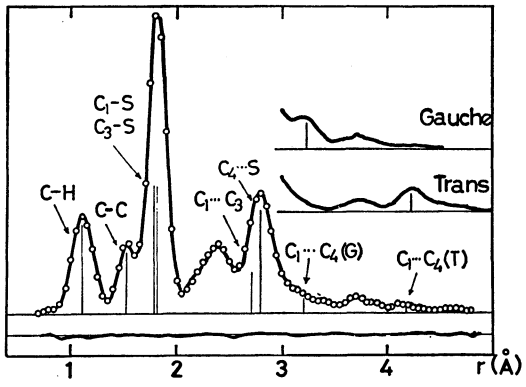

Fig. 3. Experimental and theoretical radial distribution curves. Damping factor, exp(−0.0016 s^2), was used. The residuals are shown below in the same scale.

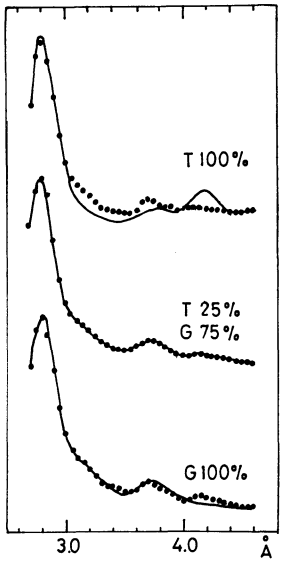

Fig. 4. Experimental and theoretical radial distribution curves illustrating the dependence on internal rotation.

Rotational Isomerism. The experimental radial distribution curve is compared in Fig. 4 with the theoretical radial distribution curves based on several different compositions of the *gauche* and *trans* conformers. The peaks from 3 to 4 Å^{-1} in the experimental curve show that in the gas phase at room temperature** the *gauche* form occupies more than 60% of the total population.

The essential experimental information about the conformation is contained in the molecular intensities from $s=2.2$ to 5.0 Å. The molecular intensity in this range is slightly influenced by the electron distributions forming chemical bonds. However, this effect[36] is less

** As discussed in Ref. 1, the above estimate of the sample temperature is based on the assumption that the thermal equilibrium at the temperature of the nozzle (room temperature) was retained in the gas jet when the electron beam was diffracted by the gas molecules.

than the error limits estimated below. The molecular intensities in this range measured at intervals of $s=\pi/10$ Å^{-1} were analyzed by the method of background function.[37,38] This method makes use of a background function $I_b(s)$ derived from the experimental total intensities $I_t(s)$ and the molecular intensities $sM(s)$ calculated from a structural model. If the structural model is correct, the I_b function should be free from fluctuations with a period similar to that of the molecular term. In other words, whether or not the I_b function oscillates with an amplitude exceeding a certain noise level is a sensitive criterion for selecting an acceptable conformation model. The I_b functions based on several different assumptions of the mixing ratio are shown in Fig. 5. Theoretical molecular intensities based on the

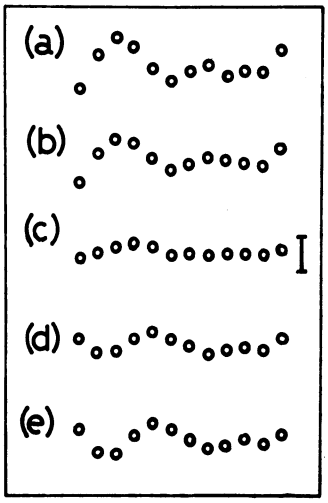

Fig. 5. Background functions I_b for different compositions of the *gauche* and *trans* isomers. (a) 60%, 40%, (b) 70%, 30%, (c) 75%, 25%, (d) 80%, 20%, and (e) 90%, 10%. The vertical bar represents 0.8% of I_b. See text.

geometrical parameters determined in the preceding section were used for the calculation of I_b. Models of A, B, C, D, and E correspond to the *trans* fractions of 40, 30, 25, 20, and 10%, respectively. A nearly flat I_b function is obtained for Model C. On the other hand, systematic fluctuations with a period of 1.6 Å^{-1} corresponding to the C_1–C_3 distance in the *trans* conformer appear in A, B, D, and E. They demonstrate that these models contain unacceptable assumptions regarding the *trans* fraction.

The limit of uncertainty of this background-function method depends on two sources: uncertainties in the model used for calculating the molecular terms, and random and systematic errors in the experimental intensities. In order to check the former uncertainties, background functions were calculated with various sets of the geometrical parameters. The effect of the latter was estimated by checking the reproducibility of the intensities obtained from the three different photographic plates and by examining various sources of systematic error. As a consequence, the limit of uncertainty in the background function is estimated to be $\pm$0.8%. This leads to the uncertainties of 15% in the estimates of the *gauche* and the *trans* fractions in the gas phase at room temperature, 75 and 25%, respectively.

Comparison of Structures. The skeletal structure of ethyl methyl sulfide is compared with those of related molecules in Table 5. The average of the two C–S bond lengths is nearly equal to those in dimethyl disulfide[6] and ethyl methyl disulfide.[6] There has been little information about the difference of the C(methyl)–S and C(methylene)–S distances. The present analysis suggests that the C(methylene)–S distance is slightly larger than the C(methyl)–S distance, which is nearly equal to those of dimethyl sulfide[18] and methyl vinyl sulfide.[39] This trend is similar to that observed in the C(methyl)–O and C(methylene)–O bond distances in ethyl methyl ether.[1] The C–C bond length is equal to those in normal alkanes[40,41] within the limits of error. This bond length is not affected by the adjacent sulfur atom, whereas the C–C bond in ethyl methyl ether[1] is shortened by the adjacent oxygen atom. The C–S–C angle is nearly equal to that in dimethyl sulfide and 6° smaller than that in methyl vinyl sulfide.

The population of the *gauche* conformer of ethyl methyl sulfide, 75$\pm$15% in the gas phase at room temperature, implies that the *gauche* conformer is slightly more stable than the *trans* conformer by ΔG of 0.18$\pm$0.35 kcal/mol. This conclusion is compatible with that obtained from recent Raman spectroscopy. The energy difference between the conformers may be contrasted with those for butane[2] and ethyl methyl ether,[1] where the *trans* conformer is more stable than the *gauche* conformer by 0.50$\pm$0.22 and 1.23$\pm$0.26 kcal/mol, respectively. The stability of the *gauche* conformer for ethyl methyl sulfide is the largest among these molecules.

Table 5. Comparison of the structures of related molecules[a]

	C–S	C–C	C–S–C	$n_t/(n_t+n_g)$[l]	ΔG[m]
CH_3–S–CH_2–CH_3[b]	1.813(4)[j]	1.536(8)	98.0(7)	25(15)	−0.18(35)
CH_3–S–CH_3[c]	1.807(2)	—	99.05(4)	—	—
CH_3–S–S–CH_3[d]	1.816(3)	—	—	—	—
CH_3–S–S–CH_2–CH_3[e]	1.817(4)[j]	1.540(7)	—	—	—
CH_3–S–CH=CH_2[f]	1.808(3)[k]	1.532(3)	104.6(8)	—	—
CH_3–CH_2–CH_3[g]	—	1.532(3)	—	—	—
CH_3–O–CH_2–CH_3[h]	—	1.520(4)	—	80(8)	1.23(27)
CH_3–CH_2–CH_2–CH_3[i]	—	1.531(2)	—	54(9)	0.50(22)

a) Distances (Å) in r_g and angles (deg) in r_{av} (r_a for f)). b) Present study. c) Ref. 18. d) Ref. 6. e) Ref. 6. f) Ref. 39. g) Ref. 40. h) Ref. 1. i) Ref. 2. j) Average of C_{methyl}–S and $C_{methylene}$–S distances. k) C_{methyl}–S distance. l) % *trans* form. m) Free energy difference (kcal/mol): $\Delta G=G_{gauche}-G_{trans}$.

The H···H nonbonded distances among the two methyl groups in these molecules make a reverse order; those in ethyl methyl ether are the smallest, and those in ethyl methyl sulfide are the largest. Steric effect of the rotors seems to play a dominant role in determining the relative stability of the conformers.

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