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MOLECULAR STRUCTURE OF TRIMETHYLENE SULFIDE STUDIED BY GAS ELECTRON DIFFRACTION

Ken-ichi KARAKIDA, Kozo KUCHITSU, and Robert K. BOHN*
Department of Chemistry, Faculty of Science,
The University of Tokyo, Bunkyo-ku, Tokyo 113 Japan
*Department of Chemistry and Institute of Material Science,
University of Connecticut, Storrs, Connecticut 06268 U.S.A.

The skeletal structure of trimethylene sulfide (thietane) has been studied by gas electron diffraction. The bond distances (r_g) and angles (r_α) with their limits of error are: r(C-S) = 1.847 ± 0.002 Å, r(C-C) = 1.550 ± 0.003 Å, r(C-H) = 1.101 ± 0.006 Å, ∠CSC = 77.0 ± 0.5° and the effective average value of the dihedral angle, $\angle C_2SC_4$-$C_2C_3C_4$ = 26 ± 4°.

The ring-puckering motion in trimethylene sulfide $(CH_2)_3S$ has been studied by spectroscopy,1) and the potential function is found to have a double minimum with a barrier of 274 cm^{-1} at the planar configuration.2) Nevertheless, the bond distances and angles in this molecule have never been determined with high accuracy. The present letter reports on the C-S and C-C distances determined by gas electron diffraction.

The sample was prepared in the laboratory of Professor Tabushi at Kyoto University.3) Diffraction photographs were taken4) at room temperature with a vapor pressure of about 30 Torr with 40 kV electrons at a camera length of 107.73 ± 0.02 mm. The molecular intensity obtained by a standard procedure5) in the s range, 6.9–34.5 $Å^{-1}$, (Fig. 1) was analyzed by a least-squares method.6) A typical radial distribution curve is illustrated in Fig. 2.

The C-S, C-C and weighted average C-H distances and their mean amplitudes were determined without assumptions or constraints. In order to get further information on the rest of the structural parameters, the following assumptions

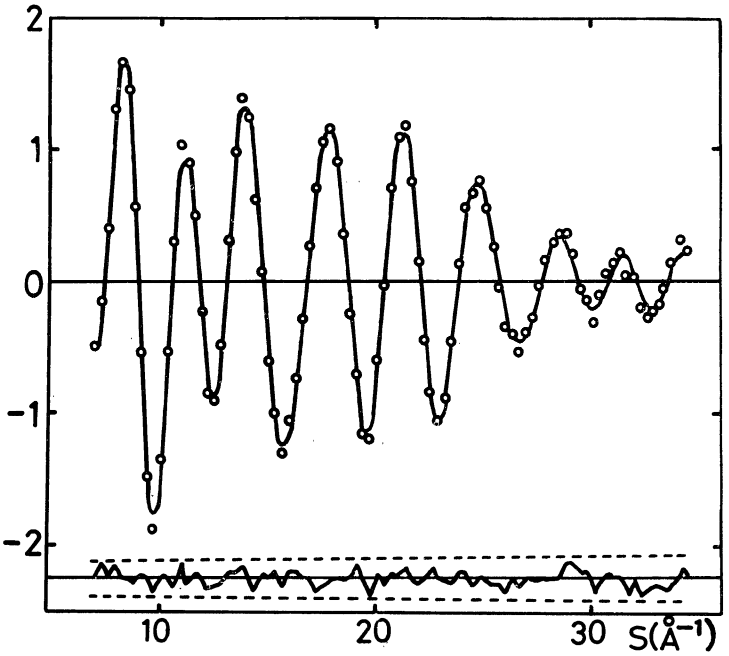


Fig. 1. Experimental and theoretical molecular intensities for trimethylene sulfide. Typical observed sM(s) values are shown in dots, and the best-fit theoretical is shown in the solid curve. The index of resolution is 1.01 ± 0.05. The lower solid and broken curves represent the residuals and the error limits in the sM(s) to a fractional error of 1 × 10^{-3} of the original photocurrent, respectively.

were made in the analysis:

1) The average positions of the hydrogen atoms are such that the plane defined by one carbon and two adjacent ring atoms is perpendicular to the H-C-H plane and the angles bisect each other.
2) All the C-H distances are equal.
3) The H-C_α-H and H-C_β-H angles in the r_α structure are equal to the corresponding angles in trimethylene oxide,[7,8] 110.3° and 110.7°, respectively.

Slight modifications in assumptions 2) and 3) had negligible effects on the structural parameters derived from the analysis.

Since neither the force constants nor the vibrational frequencies for trimethylene sulfide except for the puckering motion[2] were available, the mean amplitudes were estimated as listed in Table 1 from the experimental and theoretical mean amplitudes for dimethyl sulfide,[9-11] cyclobutane,[12-14] tetrahydrothiophene,[15] silacyclobutane,[16-18] dichlorosilacyclobutane,[17,18] 7-thianorbornane,[19] and ethane-1,2-thiol,[20] with allowance for the differences in the C-S and C-C bond lengths and in the puckering potential functions. The mean amplitudes were also estimated by use of an approximate set of the Urey-Bradley force constants taken from those for thietanone-3.[21] The skeletal mean amplitudes (bonded and nonbonded C-S and C-C) and the bonded C-H amplitude were varied in the analysis. The mean amplitudes for nonbonded atom pairs involving hydrogen were fixed at the following estimates: 0.11 Å for the next to bonded C-H or S-H pairs and 0.12 Å for the pairs between C or S and the hydrogen atoms bonded to the diagonal carbon atom. These nonbonded amplitudes were estimated to have an uncertainty of 20% as mean values. Changing the values by that fraction caused a significant variation only in the dihedral angle (about 2°). This uncertainty was included in the error limits given in Table 1. In any case, the dihedral angle listed in the table represents an effective average value over the ring-puckering vibration instead of an equilibrium value, since no explicit account of the effect of this

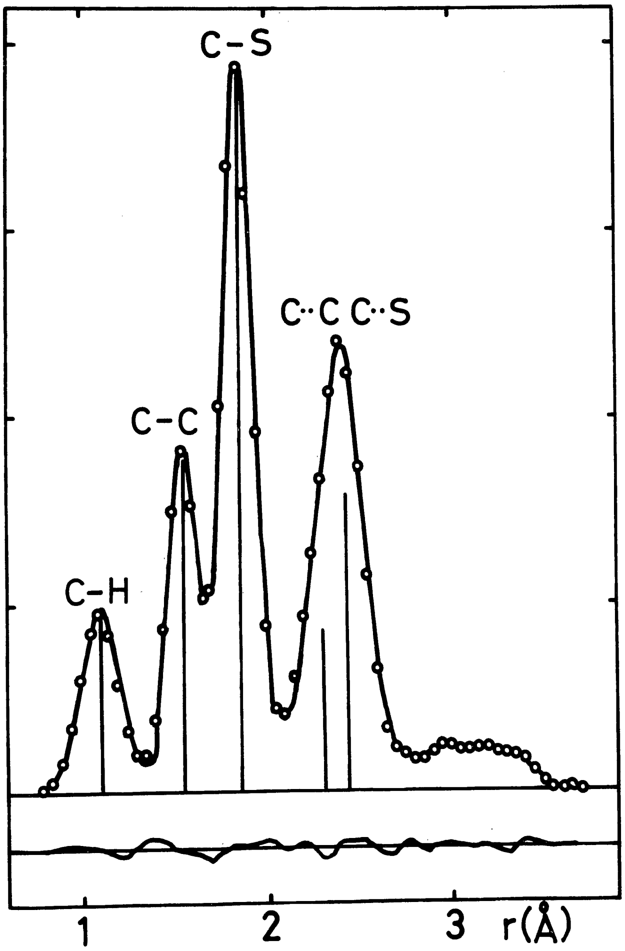


Fig. 2. Experimental (dots) and theoretical radial distribution curves for trimethylene sulfide. The lower curve represents residuals. Vertical bars correspond to principal internuclear distances. A damping factor, exp(-0.0019 s^2), was used.

Table 1. Molecular Structure and Mean Amplitudes for Trimethylene Sulfide[a)]

	Distances and Angles	ℓ(obsd)[b)]	ℓ(estd)[b)]
C – S	1.847(2)	0.056(5)	0.058(3)
C – C	1.550(3)	0.054(5)	0.055(3)
C – H	1.101(6)	0.083(8)	0.079(2)
S --C_3	2.421(10)	0.055(15)	0.065(6)
C_2--C_4	2.300(15)	0.058(20)	0.066(7)
∠CSC	77.0(5)	——	——
δ[c)]	26(4)	——	——

a) Bond distances (r_g) are in Å units. Angles in degrees are calculated on the basis of r_α structure. The numbers in parentheses represent estimated limits of error attached to the last significant figures.

b) Observed and estimated mean amplitudes.

c) Dihedral angle, $\angle C_2SC_3$-$C_2C_4C_3$.

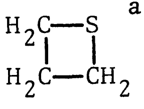
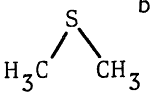
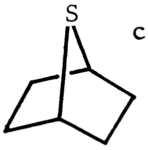
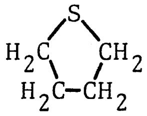
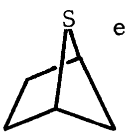
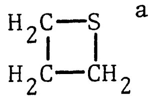
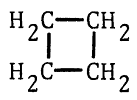
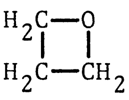
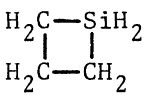
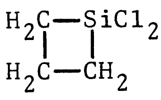
Table 2. Observed and Calculated Rotational Constants for Trimethylene Sulfide (in MHz)

	MW[a)]		ED[b)]
A_0	10110.15	A_α	10040(100)
B_0	6673.90	B_α	6663(80)
C_0	4441.04	C_α	4431(35)

a) Rotational constants for the ground vibrational state determined by microwave spectroscopy.[2)]

b) Effective average rotational constants calculated from the r_α structure determined in the present study with no vibrational correction.

Table 3. Comparison of Structures

	 a)	 b)	 c)	 d)	 e)
r(C-S)	1.847(2)r_g	1.805(3)r_g	1.837(6)r_g	1.839(2)r_a	1.866(4)r_g
∠CSC	77.0(5)r_α	99.0(3)r_{av}	80.1(8)r_α	93.4(5)r_a	69.7(5)r_α
	 a)	 f)	 g)	 h)	 i)
r(C-C)	1.550(3)r_g	1.548(3)r_a	1.549(3)	1.58_5(1)r_a	1.59(2)r_a

a) Trimethylene sulfide, determined by the present study.

b) Dimethyl sulfide. Ref. 11. c) 7-thiabicyclo[2.2.1]heptane. Ref. 19.

d) Tetrahydrothiophene. Ref. 15. e) 5-thiabicyclo[2.1.1]hexane. Ref. 19.

f) Cyclobutane. Ref. 12. g) Trimethylene oxide. Refs. 7 and 8.

h) 1-silacyclobutane. Ref. 17. i) 1,1-dichloro-1-silacyclobutane. Ref. 17.

large-amplitude motion[22)] has yet been taken. Harris et al. determined the dihedral angle of the potential minimum to be about 30°.[2)]

The effective average rotational constants calculated from the r_α structure determined in the present study with no vibrational correction are listed in Table 2 with the rotational constants for the ground vibrational state determined by microwave spectroscopy.[2)]

The skeletal structure of trimethylene sulfide is compared in Table 3 with those of analogous molecules studied by either electron diffraction or spectroscopy. Sulfur-carbon bond lengths in 4-membered rings are clearly longer than in other environments, a trend also observed among carbon-carbon bond lengths.

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