Molecular Structure of Trimethylene Sulfide as Studied by Gas Electron Diffraction with Joint Use of Rotational Constants

Ken-ichi KARAKIDA and Kozo KUCHITSU

Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113

(Received March 5, 1975)

The molecular structure of trimethylene sulfide (thietane) has been determined by an analysis of electron diffraction intensities combined with the rotational constants determined by microwave spectroscopy by Harris *et al.*: r_g(C–S)=1.847±0.002 Å, r_g(C–C)=1.549±0.003Å, r_g(C_α–H)=1.09±0.02 Å, r_g(C_β–H)=1.12±0.04 Å, ∠C-S-C(r_{av})=76.8±0.3°, ∠H–C_α–H(r_{av})=112±4°, ∠H–C_β–H(r_{av})=114±5° and the dihedral angle, ∠C_2SC_4–$C_2C_3C_4$(r_{av})=26±2°. The uncertainties represent estimated limits of error. The definitions of the geometrical parameters have the usual physical significance except that the normal coordinate representing the large-amplitude ring-puckering motion is extrapolated to its equilibrium position. The conventional formula used in the joint analysis has been modified to account for the large-amplitude vibration.

The ring-puckering motion of trimethylene sulfide (Fig. 1) has been studied in detail by spectroscopy[1,2] by Harris *et al.*, and the potential function is found to have a double minimum with a barrier of 274 cm^{-1} at the planar configuration. The bond distances and angles in this molecule were not determined with high accuracy, however. The present study was undertaken to determine the molecular structure by electron diffraction for a quantitative comparison with those of related molecules.

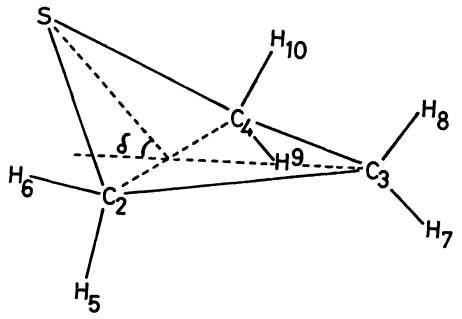

Fig. 1. Trimethylene sulfide.

The C–C, C–S and the weighted average of C–H distances were determined uniquely from electron diffraction intensities[3]. However, since the two ring diagonal distances, r(C···C) and r(C···S), are closely spaced and constitute a single peak in the radial distribution curve, it is difficult to resolve the distances with high accuracy from the electron diffraction data alone. In addition, the diffraction data has strong correlation between the hydrogen parameters in the α and β positions. Spectroscopic rotational constants A and B provide information on the r(C···C) and r(C···S) distances, respectively, and on the hydrogen parameters. Therefore, the diffraction intensities and the rotational constants have been used jointly in the present study[4]. The conventional formula used in the analysis has been modified to account for the large-amplitude ring-puckering vibration.

Experimental

The sample (bp 94 °C/752 Torr) used for the short camera length was prepared[5] in the laboratory of Professor I. Tabushi at Kyoto University. The infrared, NMR and mass spectra, and gas chromatographic analysis indicated that the sample was free from any significant impurities. The sample used for the long camera length was purchased from Tokyo Kasei Co., Ltd. (purity over 96%). Since the major impurities of the sample were solid polymers with negligible vapor pressures, it was used without further purification.

Electron diffraction photographs were taken[6] with an r^3-sector at the camera lengths of 107.73±0.02 and 243.29±0.02 mm. The electron wavelength (about 0.06 Å) was calibrated with reference to the r_a(C=O) distance of carbon dioxide (1.164$_6$ Å) measured under the same experimental conditions. The sample gas was maintained in thermal equilibrium with its liquid phase at room temperature. The pressure of the sample gas was about 30 Torr, and the exposure times were about 100 and 60 s for the short and long camera lengths, respectively. Other experimental details are described elsewhere.[6,7] The optical densities (0.17—0.62) were assumed to be proportional to electron intensities. The observed molecular intensity covering the range of s=3.5—37.7 $Å^{-1}$ was used in the analysis. The data taken with the short and long camera lengths[8] were linked at s=9.4 $Å^{-1}$. The elastic and inelastic scattering factors and the phase shifts were taken from the tables[9] prepared by

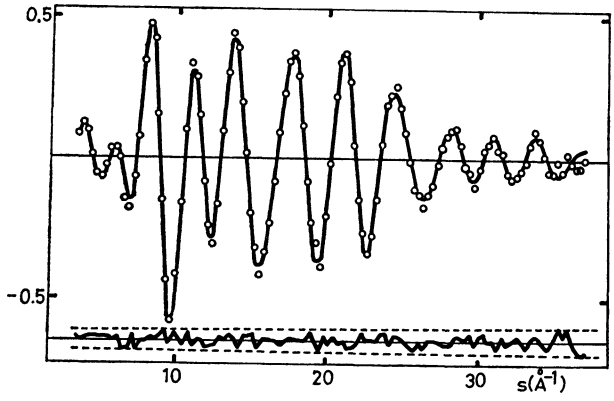

Fig. 2. Experimental and theoretical molecular intensities for trimethylene sulfide.
Typical observed $sM(s)$ values are shown in open circles, and the best-fit theoretical is shown in the solid curve. The indices of resolution are 0.84±0.03 and 0.96±0.03 for the long and short camera regions, respectively. 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.

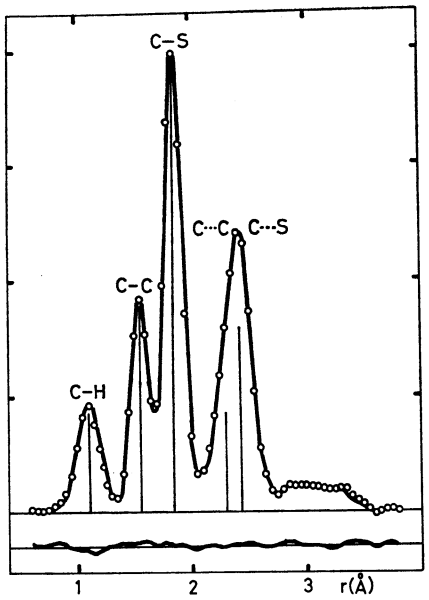

Fig. 3. Experimental (open circles) and theoretical radial distribution curves for trimethylene sulfide. The lower curve represents residuals. Vertical bars correspond to principal internuclear distances. A damping factor, $\exp(-0.0019\,s^2)$, was used.

Schäfer *et al.* The molecular intensity is illustrated in Fig. 2, and the corresponding radial distribution curve is given in Fig. 3. Most of the calculations were carried out on a HITAC 8800/8700 operating system in the Computer Center of the University of Tokyo.

Analysis

Analysis of Diffraction Intensities. The C–S, C–C and the weighted average C–H distances and their mean amplitudes were determined without assumptions or constraints.[3]

In order to get further information on the rest of the structural parameters, the following assumptions were made in the analysis:

a) The average positions of the hydrogen atoms are such that the H–C–H plane is perpendicular to the plane defined by one carbon and two adjacent ring atoms, and the angle bisectors are colinear.

b) The C_α–H and C_β–H distances are equal.

c) The H–C_α–H and H–C_β–H angles in the r_α^0 structure are equal to the corresponding angles in trimethylene oxide,[10] 110.3° and 110.7°, respectively.

Since this molecule has a large-amplitude motion, the conventional formulas based on infinitesimal vibrational amplitudes have to be modified to calculate the mean amplitudes and vibrational corrections. The zero-point average structure in the present study is defined as the r_α^0 structure[11] where the normal coordinate representing the large-amplitude ring-puckering motion (Q) takes its equilibrium value (Q_e). Mean amplitudes and vibrational corrections for bonded pairs are calculated from the conventional formulas[11] but contributions from the large-amplitude vibration are not included.

The mean amplitude for a nonbonded pair is calculated by[12]

$$l^2 = (\langle r_e(Q)^2\rangle_T - \langle r_e(Q)\rangle_T^2) + \langle \Delta z^2\rangle_T' \quad (1)$$

where T denotes thermal average at T kelvin and the prime outside the bracket denotes the sum of contributions from all the small-amplitude modes, and r_e is an instantaneous distance for the nonbonded pair when all the small-amplitude coordinates take their equilibrium positions. The r_g distance for a nonbonded pair is defined as

$$r_g = \langle r_e(Q)\rangle_T + \langle \Delta r\rangle_T' \quad (2)$$

which can be rewritten by use of a diatomic approximation[13,14] as

$$r_g \cong \langle r_e(Q)\rangle_T + \frac{3}{2}a_3\langle \Delta z^2\rangle_T' \quad (3)$$

The r_g distance is assumed to satisfy the equation,

$$r_g = r_a + \frac{l^2}{r_a} \quad (4)$$

where r_a is directly derived from the diffraction intensities. Since the radial distribution of the principal nonbonded pairs in trimethylene sulfide are practically Gaussian as shown in Fig. 3, Eq. (4) appears to be a sufficient approximation. The r_α distance for a nonbonded pair is defined as

$$r_\alpha = r_e(Q_e) + \langle \Delta z\rangle_T' \quad (5)$$

where Q_e is an equilibrium value of the large-amplitude coordinate. Equation (5) can be rewritten by use of a diatomic approximation as

$$r_\alpha \cong r_e(Q_e) + \frac{3}{2}a_3\langle \Delta z^2\rangle_T' - \frac{\langle \Delta x^2\rangle_T' + \langle \Delta y^2\rangle_T'}{2r_e(Q_e)} \quad (6)$$

The r_α parameters can be extrapolated to zero kelvin (r_α^0) by using a diatomic approximation for the bonded parameters and neglecting temperature dependence of the angle parameters.[11] From Eqs. (3), (4) and (6), the vibrational correction, $d=r_a-r_\alpha$, is given by

$$d = [\langle r_e(Q)\rangle_T - r_e(Q_e)] - \frac{l^2}{r_a} + \frac{\langle \Delta x^2\rangle_T' + \langle \Delta y^2\rangle_T'}{2r_e(Q_e)} \quad (7)$$

Since neither the force constants nor the vibrational frequencies for trimethylene sulfide were available except for the puckering motion, the contributions from the small-amplitude modes to the terms in Eqs. (1) and (7) were calculated from the Urey-Bradley force constants listed in Table 1 transferred from ethylmethyl sulfide,[15] diethyl sulfide[15] and thietanone-3.[16] The contributions from the large-amplitude mode were calculated from the following molecular model: The ring-puckering motion causes a change in the dihedral angle, $\delta = \angle C_2SC_4 - C_2C_3C_4$, and a deformation of $\alpha = \angle$C–S–C angle, but retains the C–S, C–C, C–H distances and H–C–H angles constant. The dependence of α on δ is assumed to satisfy the following relation derived from the microwave study:[1]

$$\rho = [r(C\cdots S) - r^0(C\cdots S)]/[r(C\cdots C) - r^0(C\cdots C)] = 0.54 \quad (8)$$

where r^0 is a nonbonded distance at the planar configuration ($\delta=0°$). The potential function for the puckering motion is taken from Ref. 1.

The mean amplitudes and vibrational corrections for bonded pairs were calculated from the force constants listed in Table 1, and their uncertainties were

Table 1. Force constants for trimethylene sulfide[a]

K(C-S)	1.75	H(C-S-C)	0.24	F(C-S-C)	0.21
K(C-C)	2.10	H(S-C-C)	0.07	F(S-C-C)	0.70
K(C-H)	4.25	H(C-C-C)	0.32	F(C-C-C)	0.21
Y(C-S)	0.02	H(C-C-H)	0.21	F(C-C-H)	0.54
Y(C-C)	0.02	H(S-C-H)	0.17	F(S-C-H)	0.39
		H(H-C-H)	0.35	F(H-C-H)	0.20

a) Estimated force constants taken from ethylmetyl sulfide,[15] diethyl sulfide[15] and thietanone-3.[16] The torsional force constants (Y) are in mdyn·Å and the others are in mdyn/Å units.

Table 2. Mean amplitudes and vibrational corrections (I) (Å)

	l_{obsd}[a]	l_{calcd}[b]	r_a-r_α[c]
C-S	0.055±0.005	0.054±0.003	−0.0010±0.0010
C-C	0.052±0.005	0.053±0.003	−0.0005±0.0001
C-H	0.080±0.008	0.078±0.004	0.0070±0.0007
C···S	0.051±0.008	0.057±0.006	0.0072±0.0025
C···C	0.057±0.015	0.068±0.007	0.0126±0.0045

a) Observed mean amplitudes derived from diffraction intensities. b) Mean amplitudes calculated from the force constants listed in Table 1 and the molecular model described in the text. The uncertainties were estimated from those in the force constants and the model. c) Vibrational corrections calculated from the force constants and the model described in the text. The uncertainties for the nonbonded pairs mainly originate from those in the model.

estimated to be ±10%. The mean amplitudes and vibrational corrections for nonbonded pairs consisted of the contributions from the small-amplitude and large-amplitude modes. The former contributions were calculated from the force constants and were estimated to have uncertainties of ±20%, while the latter contributions calculated classically and numerically from the model were estimated to have uncertainties of ±30%. The quoted errors for l_{calcd} and r_a-r_α in Table 2 represent these uncertainties. The asymmetry parameters[12] κ for the C–H, C–C and C–S bonds were estimated to be 1.2×10^{-5}, 2.7×10^{-6} and 2.7×10^{-6} Å^3, respectively, from the anharmonicity parameters[14] a_3 for CH, CC and CS assumed to be 1.98, 2.13 and 1.95 Å^{-1}, respectively. The κ parameters for nonbonded pairs were ignored since the observed radial distribution peaks of the nonbonded pairs were symmetric within estimated experimental error.

A least squares analysis was carried out with an empirical diagonal weight matrix.[17] The C–H, C–C and C–S distances, ∠C–S–C and dihedral angles, mean amplitudes for C–H, C–C, C–S, C···C and C···S pairs and the indices of resolution for the long and short camera regions were taken as independent variable parameters. The mean amplitudes fixed in the analysis are shown in Table 3 with vibrational corrections for the corresponding pairs. The r_α^0 parameters determined in the analysis are shown in Table 4, and the observed mean amplitudes are compared in Table 2 with the calculated values.

Systematic errors originating from slight modifications in assumptions b) and c) above had negligible effects on the structural parameters. The uncertainty in the vibrational corrections for the C···C pair caused a systematic error in the C–S–C angle, ±0.1°, and those for the other atomic pairs were unimportant compared to the random errors in the structural parameters. The uncertainty in the r_α to r_α^0 conversion was also negligible. The nonbonded mean amplitudes fixed at the calculated values (Table 3) in the analysis were estimated to have uncertainties of ±20% as mean values. Changing the value by that fraction caused a significant systematic variation only in the dihedral angle, ±2°. The fixed κ parameters caused no significant systematic errors in the distances. The error limits quoted in Table 4 include 2.5 times the

Table 3. Mean amplitudes and vibrational corrections (II)[a] (Å)

Pair	l_{calcd}	r_a-r_α	Pair	l_{calcd}	r_a-r_α
C_2-H_7	0.104	0.015	H_6-H_8	0.169	0.016
C_3-H_5	0.104	0.012	H_5-H_7	0.170	0.016
C_2-H_9	0.157	−0.003	H_6-H_7	0.150	0.019
C_2-H_{10}	0.105	0.002	H_5-H_8	0.134	0.017
S-H_5	0.110	0.006	H_5-H_9	0.289	−0.020
S-H_8	0.165	−0.003	H_5-H_{10}	0.151	0.001
S-H_7	0.103	0.004	H_6-H_{10}	0.183	−0.003

a) Mean amplitudes listed in this table were fixed in the least squares analysis. Uncertainties were estimated to be ±20%. See footnotes b) and c) of Table 2.

Table 4. Average structures of trimethylene sulfide[a]

	r_α^0 [b]	r_{av}[c]	r_g[d]
C-S	1.846±0.002	1.846±0.002	1.847±0.002
C-C	1.547±0.003	1.548±0.003	1.549±0.003
C-H_{av}[e]	1.085±0.006	1.086±0.006	1.100±0.006
C_α-H	—	1.08 ±0.02	1.09 ±0.02
C_β-H	—	1.11 ±0.04	1.12 ±0.04
∠C-S-C	77.0±0.5	76.8±0.3	—
δ[f]	26 ±4	26 ±2	—
∠H-C-H_{av}[e]	—	112 ±2	—
∠H-C_α-H	(110.3)[g]	112 ±4	—
∠H-C_β-H	(110.7)[g]	114 ±5	—
C···S	2.421±0.010	2.421±0.003	2.430±0.003
C···C	2.286±0.015	2.294±0.006	2.309±0.006
∠C-C-S	90.6±0.5	90.6±0.3	—
∠C-C-C	95.3±0.8	95.6±0.4	—

a) Distances in Å units, angles in degrees. b) Derived from diffraction intensities. Uncertainties are estimated limits of error. c) Derived from a joint analysis of diffraction intensities and rotational constants. Uncertainties are estimated limits of error. See text for the definition. The final structural parameters for the angles. d) Derived from the r_{av} structure. The final structural parameters for internuclear distances. e) Weighted average value. f) Dihedral angle, ∠C_2SC_4-$C_2C_3C_4$. g) Assumed value.

standard deviations plus the systematic errors estimated above.

In the next step the rotational constants determined[1] in the microwave study were combined[4] with the diffraction intensities in order to obtain more accurate angle parameters and hydrogen parameters for the α and β positions.

Joint Analysis of Diffraction Intensities and Rotational Constants. The rotational constants A, B and C for the ground and excited states (up to $v=4$) have been determined by microwave spectroscopy[1] by Harris *et al.* They expressed the rotational constants as a power series in the coordinate of the large-amplitude mode,

$$A = 10013.44 + 17.52Q^2 - 0.088Q^4 \quad (9a)$$

$$B = 6670.78 + 5.01Q^2 - 0.76Q^4 \quad (9b)$$

$$C = 4335.74 + 19.15Q^2 - 0.087Q^4 \quad (9c)$$

This procedure is based on the fact that the vibration-rotation interactions in this molecule are given simply by the quantum mechanical averaging of the rotational constant over the puckering motion, and Coriolis interactions are relatively unimportant.[1,2] The potential function for the vibration has been determined[1] by numerically fitting the experimentally determined rotational constants to the power series without assumptions on the details of the vibrational motion,

$$V(Q) = 7.0207Q^4 - 87.7581Q^2 \text{ cm}^{-1} \quad (10)$$

which has a minimum at $Q=Q_e=2.500$ (amu)$^{1/2}$ Å. Substitution of Q by Q_e in Eq. (9) leads to the rotational constants for the ground vibrational state (A'_0, B'_0 and C'_0) where the normal coordinate representing the large-amplitude motion takes its equilibrium value. A similar treatment has been applied to the rotational constants of trimethylene oxide by Chan *et al.*[10] in order to obtain a set of structural parameters corresponding to the equilibrium or nonvibrating values for the large-amplitude mode. The rotational constants A'_0, B'_0 and C'_0 were conventionally transformed into the average rotational constants[18] A_z, B_z and C_z by subtracting the vibration-rotation interactions for all the small-amplitude modes.

The uncertainties in A_z, B_z and C_z were estimated from the following sources: a) Uncertainties in the corrections for the large-amplitude mode were estimated from the deviations[1] of the observed rotational constants from the values calculated by use of Eq. (9) to be ±1, ±3 and ±1 MHz for A_z, B_z and C_z, respectively. b) Uncertainties in the corrections for all the small-amplitude modes were estimated to be $\pm10\%$ of the corrections, or ±4, ±2 and ±0.5 MHz for A_z, B_z and C_z, respectively. The A_z, B_z and C_z are compared in Table 5 with the rotational constants A^0_α, B^0_α and C^0_α calculated from the r^0_α parameters determined in the foregoing electron diffraction analy-

TABLE 5. ROTATIONAL CONSTANTS FOR TRIMETHYLENE SULFIDE[a] (MHz)

	B[b]	B_z[c]	B^0_α[d]	B_{av}[e]
A	10110.15	10096 (4)	10079 (50)	10096 (4)
B	6673.90	6660 (4)	6667 (30)	6660 (4)
C	4441.04	4450 (1)	4437 (30)	4450 (1)

a) Uncertainties attached to the last significant digits are given in parentheses. b) Effective rotational constants for the ground vibrational state determined by microwave spectroscopy. Ref. 1. c) Zero-point average rotational constants calculated from the effective rotational constants for the ground and excited vibrational states by subtracting the vibration-rotation interactions for the large-amplitude mode and the small-amplitude modes. d) Rotational constants calculated from r^0_α parameters listed in Table 4 determined in the analysis of diffraction intensities. Uncertainties are propagated from those in the r^0_α parameters. e) Best-fit rotational constants corresponding to the r_{av} structure listed in Table 4, derived from a combined analysis of electron diffraction and microwave data. Uncertainties represent 2.5 times the estimated standard deviations.

TABLE 6. ERROR MATRIX FOR TRIMETHYLENE SULFIDE[a]

	k_1	k_2	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	l_1	l_2	l_3	l_4
k_1	218													
k_2	55	181												
x_1	15	−7	6											
x_2	−27	15	−4	11										
x_3	27	−58	−6	−9	55									
x_4	63	74	−5	−12	−68	111								
x_5	17	−21	−3	10	16	17	21							
x_6	−86	14	−4	−10	−36	−69	−46	124						
x_7	73	−92	13	27	78	−62	65	−142	215					
x_8	125	135	15	9	−87	155	28	−149	−36	314				
l_1	12	39	−2	4	−12	15	−4	4	−19	27	10			
l_2	13	38	−2	3	−12	15	−5	5	−21	28	8	14		
l_3	27	44	0	7	−18	29	15	−26	39	−7	9	9	31	
l_4	25	50	−4	7	−24	36	17	−7	40	−60	11	10	39	62

a) k_1, k_2=indices of resolution for the long and short camera regions, respectively, $x_1=r$(C-S), $x_2=r$(C-C), $x_3=r(C_\alpha\text{-H})$, $x_4=r(C_\beta\text{-H})$, $x_5=\angle$C-S-C, $x_6=\delta$, $x_7=\angle H\text{-}C_\alpha\text{-H}$, $x_8=\angle H\text{-}C_\beta\text{-H}$, $l_1=l$(C-S), $l_2=l$(C-C), $l_3=l$(C···S) and $l_4=l$(C···C). Units ($\times10^{-4}$) for the distances and mean amplitudes are Å, those for the angles are rad, and those for the indices are dimensionless.

sis. The diffraction and spectroscopic constants agree within the experimental error of the former.

The rotational constants A_z, B_z and C_z were combined with the diffraction intensities into a joint least squares analysis, where the assumptions b) and c) made in the analysis of diffraction intensities were excluded. The mean amplitudes for C_α–H and C_β–H pairs were fixed at the calculated values. The relative weight for the rotational constants were adjusted empirically so that 2.5 times the standard errors in the rotational constants were nearly equal to their uncertainties. The weights used in the analysis were 1.5×10^6, 1.5×10^6 and 2×10^7 for A_z, B_z and C_z, respectively, where a unit weight was assigned to the molecular intensities from $s=6.3$ to 26.7 Å^{-1} taken at $\pi/10$ intervals. A typical error matrix is shown in Table 6.

The r_{av} structure listed in Table 4 agrees with the r_α^0 structure derived from the electron diffraction data alone except that the angle parameters are appreciably more accurate. The final r_g structure derived from the r_{av} structure is shown in Table 4. The structural parameters of this molecule determined earlier by the visual method of gas electron diffraction[19–21] are in good agreement with the present results to within their uncertainties: r(C–S)$=1.85_1\pm$ 0.02 Å, r(C–C)$=1.54_9\pm0.03$ Å, ∠C–S–C$=78\pm1°$ and ∠C–C–C$=97\pm5°$.

The dihedral angle determined in the present study is nearly equal to that estimated by Harris *et al.*,[1,2] 28°. The skeletal structure of trimethylene sulfide was compared[3] with those of analogous molecules. Sulfur-carbon bond lengths in 4-membered rings are clearly longer than in other environments, a trend also observed among carbon-carbon bond lengths.[22]

The authors are indebted to Professor Iwao Tabushi, Dr. Yoshinao Tamaru and Mrs. Kazumi Mizuno for preparation of the sample and to Professor Robert K. Bohn for helpful comments.

References

1) D. O. Harris, H. W. Harrington, A. C. Luntz, and W. D. Gwinn, *J. Chem. Phys.*, **44**, 3467 (1966); see also L. H. Scharpen, *ibid.*, **48**, 3552 (1968). The authors wish to thank Professr Harris for his comments on the microwave analysis of his group.

2) W. D. Gwinn and A. Luntz, *Trans. Amer. Cryst. Assoc.*, **2**, 90 (1966).

3) K. Karakida, K. Kuchitsu, and R. K. Bohn, *Chem. Lett.*, **1974**, 159.

4) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1967).

5) G. M. Bennett and A. L. Hock, *J. Chem. Soc.*, **1927**, 2496.

6) Y. Murata, K. Kuchitsu, and M. Kimura, *Jap. J. Appl. Phys.*, **9**, 591 (1970).

7) M. Tanimoto, K. Kuchitsu, and Y. Morino, This Bulletin, **43**, 2766 (1970).

8) Numerical experimental data of the leveled total intensity have been deposited with the Chemical Society of Japan (Document No. 7512).

9) L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, **55**, 3055 (1971).

10) S. I. Chan, J. Zinn, and W. D. Gwinn, *ibid.*, **34**, 1319 (1961). The structure for trimethylene oxide was deduced in this literature from the rotational constants extrapolated to a hypothetical planar state.

11) K. Kuchitsu and S. J. Cyvin, "Molecular Structures and Vibrations," ed. by S. J. Cyvin, Elsevier, Amsterdam (1972), Chapter 12.

12) K. Kuchitsu, This Bulletin, **40**, 498 (1967).

13) L. S. Bartell, *J. Chem. Phys.*, **23**, 1219 (1955).

14) K. Kuchitsu and Y. Morino, This Bulletin, **38**, 805 (1965).

15) M. Ohsaku, Y. Shiro, and H. Murata, *ibid.*, **46**, 1399 (1973).

16) C. S. Blackwell, Thesis, Massachusetts Institute of Technology (1971).

17) Y. Morino, K. Kuchitsu, and Y. Murata, *Acta Crystallogr.*, **18**, 549 (1965).

18) M. Toyama, T. Oka, and Y. Morino, *J. Mol. Spectrosc.*, **13**, 193 (1964).

19) E. Goldish, Thesis, California Institute of Technology (1956).

20) E. Goldish, *J. Chem. Educ.*, **36**, 408 (1959).

21) Y. Etienne, R. Soulas, and H. Lumbroso, "Heterocyclic Compounds with Three- and Four-Membered Rings," Part II, A. Weissberger, Ed., Interscience, Chapter 5 (1964).

22) K. Kuchitsu, "Gas Electron Diffraction, HTP International Review of Science, A Biennial Series, Physical Chemistry," Vol. 2, ed. by G. Allen, Medical and Technical Publishers, Oxford (1972), Chap. 6.