The Molecular Structure of Dimethyl Sulfide*

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The gas-phase molecular structure of dimethyl sulfide, $(CH_3)_2S$, has been investigated by means of electron diffraction. By a joint analysis of the diffraction results and the spectroscopic moments of inertia by Pierce and Hayashi, the structure parameters, the distances in r_g and the angles in φ_{av}, were determined (with parenthesized limits of error) to be as follows: S–C=1.807(2) Å, C–H=1.116(3) Å, ∠CSC=99.05(4)°, and ∠HCH=109.3(5)°. A tilt of 2.35° and the local C_{3v} symmetry of the methyl groups were assumed. The isotope effects of deuterium substitution were examined, and the DCD angle was found to be larger than HCH in the zero-point average structure.

The present authors have, for some time, been investigating the structures of molecules which contain one or two methyl groups. The combined use of diffraction and spectroscopic data has been successful in obtaining more accurate values of the structure parameters. By this technique, the uncertainties of the hydrogen parameters were especially reduced to ±0.003—6 Å for C–H distances and ±0.5—1.0° for the HCH angles.[1] Furthermore, it was possible in some favourable cases to obtain information on the isotope effects in structure parameters for the deuterium substitution.[2] In the present study, the structure of dimethyl sulfide was determined by applying the technique of the joint analysis.

The microwave spectra of this molecule were extensively studied by Pierce and Hayashi.[3] They measured and analyzed the spectra of several isotopic species as well as the parent species. The spectrum of the parent species was measured also by Rudolph, Dreizler, and Maier.[4] As for the diffraction study, there were the visual works by Brockway and Jenkins[5] and by Schomaker,[6] but no high-precision data have been available.[7] Therefore, the electron-diffraction data were newly obtained in the present study by the sector-microphotometer method. The moments of inertia reported by Pierce and Hayashi were used in the joint analysis.

Experimental

A sample of grade G. R. purchased from Nakarai Chemicals, Ltd., was used without further purification. The diffraction experiments were made by means of the Hokkaido University apparatus[8] at room temperature, using an r^3-sector and two nozzle-to-plate distances, 244.3 and 109.3 mm. The other experimental conditions are as follows: accelerating voltage, 42 kV; beam current, 0.1 μA; exposure times, 100—180 s; and sample pressure, 60—70 Torr (1 Torr=133.322 Pa). The scale factor for $L\lambda$ was calibrated using the diffraction patterns of CS_2 taken in the same sequence of exposures. Data obtained from three selected plates for the long and short camera distances covered the approximate s ranges of 3—17, and 7—40 Å^{-1} respectively.[9]

The theoretical molecular intensities from the best-fit model and the differences (experimental minus theoretical) are shown in Fig. 1.[10] The vertical scale of the difference is four times as large as that of the molecular intensity. The

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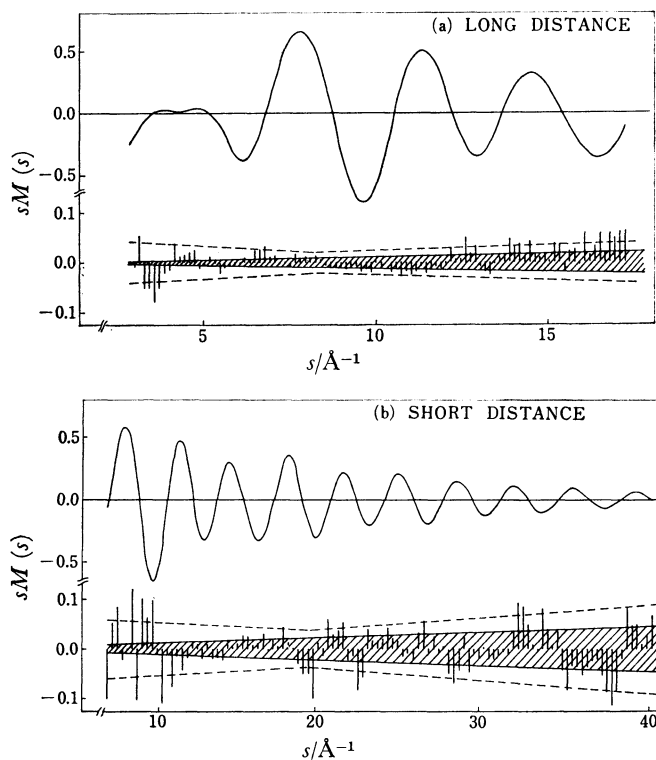* 1 Å=100 pm is used throughout this paper.

Fig. 1. Theoretical $sM(s)$ from the best-fit model and the differences (experimental minus theoretical) for the long (a) and short (b) camera distances. The vertical scale of the difference is four times as large as that of the $sM(s)$. See text.

narrower shaded boundaries in the difference correspond to ±2 in the last digit of the digital voltmeter used in photometry, that is the, limit of the detectable changes in the intensity. The outer boundaries, drawn in broken lines, indicate the normally expected range of the random scattering of differences. Some points are outside this boundary for accidental reasons. A least-squares refinement with zero-weights for these points showed that the effects of these extraordinary data on the final parameter-values were negligibly small.

Analysis of the Diffraction Data

The skeletal parameters, S–C, S⋯H, and C⋯C distances, were determined by the least-squares method.[9] The C–H and H⋯H r_a distances of the methyl group were fixed at 1.107, and 1.783 Å respectively. The local C_{3v} symmetry of the methyl

group was assumed. The other non-bonded distances were fixed at the values calculated from the reported r_s-structure.[3] The rms amplitudes of vibration were fixed at the values calculated by Gebhardt and Cyvin.[11] The Hartree-Fock elastic scattering factors were generated by a computer program for the partial-waves method.[12] The inelastic scattering factors were taken from the literature.[13] The results of the least-squares procedure are summarized in Table 1.

TABLE 1. RESULTS OF THE LEAST-SQUARES ANALYSIS OF THE DIFFRACTION DATA FOR DIMETHYL SULFIDE
(in Å units)[a]

	S–C	S···H	C···C
Long camera distance			
r_a	1.8056	2.4098	2.7616
σ_1[b]	8	37	91
σ_2	3	37	64
ε[c]	31	101	243
Short camera distance			
r_a	1.8055	2.3943	2.7567
σ_1	10	91	201
σ_2	3	22	60
ε	33	239	524
Weighted averages			
r_a	1.805_6[d]	2.408_1	2.76_1
ε	2_2	9_3	2_2

a) Index of resolution; 0.82—0.94. b) For the definitions of σ_1 and σ_2, see Ref. 14. c) The limit of error, ε, was estimated from $2.6\sigma_1$ and the systematic error of the scale factor, 0.13% for the long, and 0.11% for the short, camera distance. d) r_g(S–C); 1.806_9 Å.

The r_a values from the data of the long and short camera distances are in good agreement with each other for all three distances. The weighted averages of them give the most probable values of the bond distances as obtained by the diffraction method. For the S–C distance, the long- and short-distance data make nearly equal contributions, while for the S···H and C···C distances, the weights of the long-distance data are much larger than those of the short-distance data.

It is noted that the S–C distance might be affected by the assumed value of the intra-methyl H···H distance, because they are very close to each other. Thus, in the final refinement the value of the H···H was changed to 1.804 Å, a value which was given from the results of the joint analysis, and the least-squares procedure was carried out again. The values of the parameters shifted within only 10% of the standard deviations.

Joint Analysis of the Diffraction Results and the Spectroscopic Moments of Inertia

More detailed structure information was obtained by a joint analysis of the diffraction data and the spectroscopic data on the moments of inertia. Since the data from both methods were combined on the r_z-basis (the zero-point average structure),[15] the vibrational effects of the moments of inertia or the vibrational

TABLE 2. MOMENTS OF INERTIA OF DIMETHYL SULFIDE
(in amu Å² units)[a]

	$I^{(0)}$	ΔI	$I^{(z)}$
$(CH_3)_2S$			
a	28.376	0.143(0.143)	28.519
b	66.314	0.209(0.210)	66.522
c	88.387	0.101(0.101)	88.488
γ[b]	(3.262)	0.015(−0.004)	3.277
$(CD_3)SCH_3$			
a	32.646	0.151	32.797
b	76.619	0.227	76.846
c	99.731	0.112	99.843

a) $I^{(0)}$: observed effective values for the ground vibrational state, taken from Ref. 3. The numerical values are, however, slightly different from Ref. 3 because of the use of the conversion factor of 505376 Mc amu Å² in this work. ΔI; calculated vibrational corrections. The values in parentheses were obtained by an approximate method. See text. $I^{(z)}$: moments of inertia for the zero-point average structure. b) γ indicates the torsional coordinate of the methyl tops.

corrections were calculated by using the force field reported by Gebhardt and Cyvin.[11] The barrier to the internal rotation of the methyl top of this molecule is reported to be about 2.1 kcal/mol.[3] The method of calculating the vibrational corrections for molecules with large-amplitude internal motion was applied.[16,17] The moments of inertia and the vibrational corrections are shown in Table 2.

For the vibrational correction in the case of a large-amplitude torsional motion, it is necessary to calculate the n_{is} matrix as well as the l_{is} matrix.[16] The n_{is} is the derivative of the l_{is} viewed on the top-fixed axis with respect to the torsional coordinate. The requirement of calculating the n_{is} matrix makes the whole procedure tedious and complicated. If the n_{is} matrix can be neglected, though, the l_{is} matrix may easily be obtained by ordinary normal-cordinate calculations. The vibrational corrections for the parent species calculated by neglecting the n_{is} matrix were found to be good approximations for ΔI except for ΔI_γ, as is shown in the parentheses in Table 2. A similar comparison was made for propane and 2-fluoropropane. The maximum deviation of the approximate value was found to be 0.006 amu Å². The vibrational corrections for the CD_3SCH_3 species in Table 2 were calculated by this approximated method.

The r_g(C–S) distance by diffraction, 1.806_9 Å, was converted into r_α^0 ($\approx r_z$), $1.804_8 \pm 0.002$ Å, by the use of anharmonic stretching, 0.0003 Å, the correction for the perpendicular motion, 0.0009 Å, and centrifugal stretching, 0.0009 Å. All these corrections were calculated by the use of the force field by Gebhardt and Cyvin.[11]

As was the case in our previous papers,[1,2] the structure of the molecule including the isotope effects for the deuterium substitution was determined by using the $I^{(z)}$ values of $(CH_3)_2S$ and CD_3SCH_3 species and r_α^0(S–C) from diffraction. The value of r_α^0 (S–C) and its limit of error determine the allowable region of the S–C distance. For each S–C value within this region, three

structure parameters, C–H $\angle$HCH, and $\angle$CSC, were determined from the three moments of inertia of the parent species, by assuming a local C_{3v} symmetry of the methyl top and a tilt of 2.35°.[18] The equilibrium conformation of the methyl group was determined by the microwave study[3] to be such that one of the C–H bonds lies on the CSC plane in the position trans to the S–C bond.

By using the structure parameters of the parent species, the deuterium-isotope effects were determined from the $I^{(z)}$ values of the d_3-species. The isotope effects in C–D, $\angle$DCD, and $\angle$CSC were also taken into consideration. Among them the isotope effect in C–D was estimated by assuming a Morse-type potential and using a diatomic approximation.[19] The values of $\angle$DCD and $\angle$CSC were adjusted to give a good fit for the three $I^{(z)}$ values of the d_3-species. It was found that there was no satisfactory solution for them in the r(S–C)$<$1.803 Å region, just outside the region allowed by the diffraction results. The moments of inertia of the ^{13}C and ^{34}S species were found to be consistent with the parameters of the parent species, in and around the region of the S–C distance examined by the present
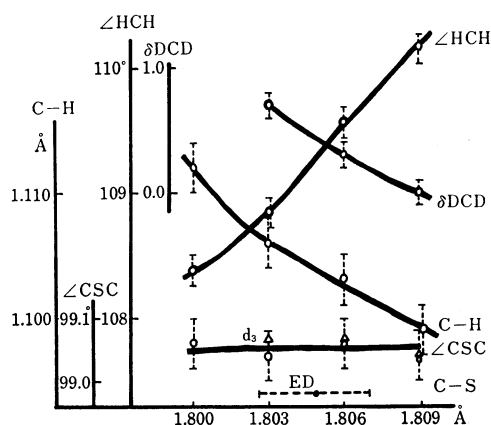

Fig. 2. Variations of structure parameters determined by moments of inertia along the change of the S–C distance. Vertical broken lines show the uncertainties due to ± 0.01 amu Å^2 of I$^{(z)}$. $\triangle$ show the CSC angle of d_3-species. The range of S–C allowed by the diffraction result is indicated as ED. No solution was found for $\angle$DCDh and $\angle$CSC (d_3) in the region of S–C$<$1.803.

TABLE 3. ZERO-POINT AVERAGE STRUCTURE OF DIMETHYL SULFIDE[a]

	r_{av}, ϕ_{av}	ε_1	ε_2	ε_3	ε_4	ε_0
S–C	1.805	0.002	—	—	—	0.002
C–H	1.104	0.002	0.002	—	—	0.003
$\angle$CSC	99.05	0.01	0.04	—	—	0.04
$\angle$HCH	109.30	0.48	0.12	—	0.03	0.50
δ(CSC)[b]	0.01	0.02	0.03	0.01	—	0.04
δ(DCD)[b]	0.40	0.20	0.10	0.08	—	0.25

r_g; S–C 1.807, C–H 1.116

a) The distances are in Å, and the angles, in degree units. ε_1 through ε_4 are uncertainties from various origins, and ε_0 is the estimate of the total uncertainty. See text. b) δ(CSC)$=\angle$CSC(in d_3)$-\angle$CSC(h_6); δ(DCD)$=\angle$DCD$-\angle$HCH.

analysis. The variations of the parameters with the change in the S–C distance are shown in Fig. 2.

The structure parameters obtained by the analysis are summarized in Table 3. Uncertainties from various origins were estimated and are also listed in the table. They are: ε_1, from the half-width of the variation of the parameter values in the allowed region; ε_2, from the uncertainties of $I^{(z)}$, assumed to be ± 0.01 amu Å^2; ε_3, from the uncertainty of the estimated isotope effect in C–D ± 0.0015 Å, and ε_4, from the uncertainty in the tilt, $\pm 0.37°$.[20] The total estimates of the uncertainty are shown as ε_0, obtained by means of the square-root of the sum of the squares of ε_1 through ε_4.

Discussion

The bond-angles in the zero-point average structure shown in Table 3 are close to the values of the r_s-structure reported by Pierce and Hayashi, while the r_z distances are longer than r_s.[21] The final structure in Table 3 leads to the r_a values of 2.418, 2.748, and 1.804 Å for S$\cdots$H, C$\cdots$C, and H$\cdots$H respectively, neglecting the anharmonicity in bond-angles. The S$\cdots$H and C$\cdots$C distances are judged to be consistent with the diffraction results in Table 1. The HCH angle, 109.3(5)°, of this molecule is in the range, 107.9—110.8°, of the HCH angles of acetyl halides,[1] acetone,[2] acetaldehyde,[16] propane,[22] and 2-chloropropane,[23] which were determined by the technique of joint analysis. The C–H distance, 1.116 Å, in r_g is, however, longer than the C–H distances of these molecules, 1.101—1.109 Å. This may be an effect of the neighbouring hetero-atom sulfur, used in place of carbon, on the structure of the methyl group.

A positive isotope effect in the DCD angle (the effect giving a $\angle$DCD larger than $\angle$HCH) is similar to that found in acetone and several other molecules. As was discussed in a previous paper on acetone,[2] it may be attributed to the repulsive interaction between the two methyl tops. It is interesting to note that the nearest H$\cdots$H distance between the two tops is 2.82 Å in acetone and 2.76 Å in dimethyl sulfide. The skeletal bond-distances are very different in the two molecules, but the smaller CSC angle of dimethyl sulfide compensates for the longer S–C distance, and the H$\cdots$H distance becomes almost the same. Therefore, the effect of the H$\cdots$H interaction, if any, may be expected to exist to a similar extent.

In the case of acetone, the isotope effect in the CCC angle was found to be 17'(2); that is, the angle for the d_6-species is less than that for the h_6-species. For dimethyl sulfide, however, the isotope effect in the CSC angle of the d_3-species is essentially zero. According to the idea that the isotope effect in the CSC angle is due to the anharmonicity of the symmetric rocking mode of the two methyl groups,[2] the effect in the d_3-species may be roughly estimated to be about one third of what would be observed for the d_6-species. The present result for the d_3-species does not necessarily exclude the possibility of the existence of the isotope effect in the d_6-species of an amount similar to that of acetone. Unfortunately, the spectroscopic data of the d_6-species

are not available.

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17) Equation 33 of Ref. 16 contains an error. It should read

$$I_{\alpha\gamma} = \Sigma_i m_i\{\lambda_\alpha \boldsymbol{\sigma}_i{}^2 - (\boldsymbol{\sigma}_i)_\alpha(\lambda \cdot \boldsymbol{\sigma}_i)\}$$
$$+ \Sigma_t(l_{ts} \times n_{ts})_\alpha Q_s{}^2 - (\lambda \times L_{R's})_\alpha Q_s.$$

The same applies to Eq. 8 of Ref. 2.
18) The tilt angle is determined from $\angle$CSC and the angle between the two top-axes, 2θ. The value of 2θ was determined to be 103.77 ° by the analysis of the torsional splittings.[3] In the present analysis, the variation in the $\angle$CSC within the allowed region was so small that the tilt was fixed at 2.35°.
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20) One and a half of the reported uncertainty in 2θ in Ref. 3, namely, three times as much as that of the tilt. Note that the uncertainty in $\angle$CSC is much smaller.
21) r_s-structure: S–C 1.802(2) Å, C–H 1.091(5) Å, $\angle$CSC 98.9(2)°, and $\angle$HCH 109.6(3)°. Ref. 3.
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