BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 92—94(1972)

The Microwave Spectrum of Dimethyl Sulfone

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(Received June 24, 1971)

The microwave spectra of normal and ^{13}C-isotopic species of dimethyl sulfone have been investigated, and the rotational constants of both species have been determined. The following r_0-structural parameters have been determined: $r(\mathrm{C{-}S})=1.777\pm0.006$ Å, $r(\mathrm{S{-}O})=1.431\pm0.004$ Å, $\angle\mathrm{CSC}=103°17'\pm10'$, and $\angle\mathrm{OSO}=121°1'\pm15'$, assuming that $r(\mathrm{C{-}H})=1.091$ Å and $\angle\mathrm{HCH}=109°34'$. The variations in the structural parameters among the related alkyl sulfides, alkyl sulfoxides, and alkyl sulfones have been discussed. The dipole moment has been determined to be $\mu=4.432\pm0.041$ D along the b axis. This value is consistent with the results of a bond-moment calculation based on the dipole moment of dimethyl sulfoxide.

Recently, ethylene episulfone, $(\mathrm{CH_2})_2\mathrm{SO_2}$[1], has been subjected to a microwave spectroscopic study; we have found an r_0 structure characterized by a long C–C bond (1.590 Å) and rather short C–S bonds (1.731 Å). These distinct features have been considered to arise from the ring strain. Dimethyl sulfone, $(\mathrm{CH_3})_2\mathrm{SO_2}$, may be a typical molecule with no ring strain, corresponding to ethylene episulfone. In fact, the structural comparison mentioned above was made with reference to the structure of dimethyl sulfone, which was determined by X-ray crystallography, not by microwave spectroscopy. Sands[2] reported that $r(\mathrm{C{-}S})=1.78$Å, a little shorter than the distance of the normal single C–S bond, $r(\mathrm{S{-}O})=1.44$ Å, $\angle\mathrm{CSC}=103°$, and $\angle\mathrm{OSO}=117.9°$, slightly smaller than the $\angle$OSO angle for the normal sulfone group. To make the situation clear, it may be desirable to compare the structure of ethylene episulfone with those of simple alkyl sulfones as accurately determined by microwave spectroscopy. Feairheller and Katon[3] observed the infrared and Raman spectra for dimethyl sulfone with detailed frequency assignments; they pointed out that this molecule is roughly an accidental spherical top. A normal-coordinate analysis of dimethyl sulfone was carried out by Carter, Freeman, and Henshall.[4] There have been a few reports on the dipole moment for this molecule as studied by the dielectric-constant method.[5–7]

In this paper we wish to report the results of the determination of the molecular structural parameters and the dipole moment for dimethyl sulfone from its microwave spectrum.

Experimental

The dimethyl sulfone sample used was obtained from the Tokyo Kasei Kogyo Co. A ^{13}C-enriched sample (6 at. % of ^{13}C) was prepared by oxidizing ^{13}C-enriched dimethyl sulfide with potassium permanganate.[8] The enriched dimethyl sulfide was formed by the reaction[9] of sodium sulfide on methyl iodide enriched to about 6 at. % of ^{13}C. The spectra were observed with a 110-kHz Stark-modulation microwave spectrometer.[10] As the vapor pressure of dimethyl sulfone was about 0.02 mmHg at about 20°C, all the measurements were carried out at room temperature. A high-precision dc-voltage power supply (Fluke, Model 415B) was used in the Stark-effect measurements.

Table 1. Rotational transitions of normal dimethyl sulfone (MHz)[a)]

Transition	ν_{obs}[b)]	$\nu_{obs}-\nu_{calc}$[d)]
$2_{02}\leftarrow1_{11}$	16576.64	−0.07
$2_{12}\leftarrow1_{01}$	17169.78	0.25
$2_{21}\leftarrow1_{10}$	18091.48	−0.11
$2_{20}\leftarrow1_{11}$	18235.73	0.11
$3_{03}\leftarrow2_{12}$	25071.70[c)]	−0.15
$3_{13}\leftarrow2_{02}$	25475.84	0.14
$3_{22}\leftarrow2_{11}$	26445.73[c)]	−0.11
$3_{21}\leftarrow2_{12}$	26922.32[c)]	0.09
$3_{31}\leftarrow2_{20}$	27415.78	−0.20
$3_{30}\leftarrow2_{21}$	27445.40	0.11
$4_{13}\leftarrow3_{22}$	33194.18	−0.54
$4_{04}\leftarrow3_{13}$	33529.75	−0.30
$4_{14}\leftarrow3_{03}$	33765.00	0.05
$4_{23}\leftarrow3_{12}$	34738.66	−0.28
$4_{22}\leftarrow3_{13}$	35772.55	−0.19
$4_{32}\leftarrow3_{21}$	35835.07	−0.17
$4_{31}\leftarrow3_{22}$	35981.21	0.08
$4_{41}\leftarrow3_{30}$	36705.33	−0.03
$4_{40}\leftarrow3_{31}$	36709.35	−0.02
$5_{14}\leftarrow4_{23}$	41832.38	−1.09
$5_{05}\leftarrow4_{14}$	41946.27	−0.39
$5_{15}\leftarrow4_{04}$	42065.75	−0.43
$5_{24}\leftarrow4_{13}$	42980.98	−0.26
$5_{33}\leftarrow4_{22}$	44179.05	−0.35
$5_{32}\leftarrow4_{23}$	44598.87	−0.23
$5_{42}\leftarrow4_{31}$	45171.33	−0.23
$5_{41}\leftarrow4_{32}$	45199.40	−0.27

a) First ten transitions were used in least squares fit.

b) Accuracy better than ±0.1 MHz, unless otherwise indicated.

c) ±0.2 MHz.

d) Calculated frequencies were obtained using rotational constants in Table 3.

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Microwave Spectrum

Most of the measurements were made using a recorder, because the spectral lines were all weak. The assignment of the spectral lines for the normal species was performed by observing the Stark effect on each transition. The frequencies of the observed transitions are listed in Table 1. The rotational constants for the normal species were determined by a least-squares fitting of the lowest ten transitions. The centrifugal distortion effect was discarded in the analysis, because only low-J transitions were observed. Although the ^{13}C-enriched sample was used, it was difficult to assign the spectral lines of the ^{13}C species. This is because the expected frequency regions for low-J transitions of the ^{13}C species were densely covered with other strong lines. Observation had to be made very carefully of the Stark effect for each candidate line and of its relative intensity in the natural sample and in the ^{13}C-enriched sample. A simple relation between the moments of inertia, $\Delta I = I_c - (I_a + I_b)$, was also helpful for the assignment, because it remains essentially unchanged for the isotopic substitution of the atoms in the CSC plane. Ten observed transitions of the ^{13}C species are listed in Table 2. Most of them were used to calculate the rotational constants. The observed rotational constants and moments of inertia are given in Table 3. The three rotational constants thus obtained differ from one another only by a few hundred megahertz, so the dimethyl sulfone molecule is a nearly accidental spherical-top, as has been pointed out by Feairheller and Katon.[3] Table 3 also shows that the ΔI's for the normal species and the ^{13}C species agree very well. This indicates that the effect of zero-point vibrations can be disregarded.

Table 2. Observed rotational transitions of ^{13}C-enriched dimethyl sulfone (MHz)

Transition	ν_{obs} [a]	$\nu_{obs} - \nu_{calc}$ [c]
$2_{12} \leftarrow 1_{01}$	16846.45	−0.30
$3_{03} \leftarrow 2_{12}$	24504.85	−0.21
$3_{13} \leftarrow 2_{02}$	24950.96	−0.13
$3_{22} \leftarrow 2_{11}$	26058.90	0.10
$4_{13} \leftarrow 3_{22}$	32427.73 [b]	−0.86
$4_{14} \leftarrow 3_{03}$	33036.88	−0.19
$4_{23} \leftarrow 3_{12}$	34147.74	0.53
$4_{22} \leftarrow 3_{13}$	35376.13	0.03
$4_{32} \leftarrow 3_{21}$	35401.52 [b]	0.02
$4_{41} \leftarrow 3_{30}$	36394.31	−0.19

a) Accuracy better than ±0.2 MHz.
b) Not included in least squares fit.
c) Calculated frequencies were obtained using rotational constants in Table 3.

Table 3. Rotational constants (MHz) and moments of inertia (amuÅ^2)[a] for dimethyl sulfone

	Normal species	^{13}C-species
A	4638.15 ± 0.02	4606.03 ± 0.05
B	4295.44 ± 0.02	4219.71 ± 0.05
C	4177.13 ± 0.02	4080.24 ± 0.05
I_a	108.961 ± 0.0006	109.721 ± 0.0015
I_b	117.654 ± 0.0006	119.766 ± 0.0015
I_c	120.987 ± 0.0006	123.859 ± 0.0015
ΔI	−105.628	−105.627

a) Conversion factor = 5.05376×10^5 amuÅ^2 MHz for amu based on the ^{12}C scale.
b) $\Delta I = I_c - (I_a + I_b)$.

Dipole Moment

The second-order Stark effect was measured for six transitions, as is shown in Table 4. The electrode spacing was calibrated using the $J = 1 \leftarrow 0$ transition of OCS.[11] From the Stark coefficients, the dipole moment along the b axis was determined to be 4.432 ± 0.041 D, where the error quoted was 2.5 times the standard deviation. This value is in agreement with the values (μ=4.25—4.26 D) obtained by the dielectric-constant measurements.[5-7]

Table 4. Stark coefficients and dipole moments of dimethyl sulfone

Transition		$\Delta\nu / E^2_{obs}$ [a]	μ_{obs}(D)
$2_{20} - 1_{11}$	$M=1$	2.536×10^{-4}	4.484
$3_{03} - 2_{12}$	$M=1$	-0.6268×10^{-4}	4.411
$3_{30} - 2_{21}$	$M=1$	-0.6665×10^{-4}	4.439
$3_{30} - 2_{21}$	$M=2$	-2.483×10^{-4}	4.455
$3_{31} - 2_{20}$	$M=1$	-1.571×10^{-4}	4.436
$3_{31} - 2_{20}$	$M=2$	-6.083×10^{-4}	4.367
$\mu = \mu_b = 4.432 \pm 0.041$D [b]			

a) Values in MHz (V/cm)$^{-2}$.
b) Error is 2.5 times the standard deviation.

Structure

Dimethyl sulfone has six independent structural parameters. Among them, it is hard to determine the two parameters related to methyl groups without information on the deuterated species. As has been discussed in the cases of ethylene episulfoxide[10] and ethylene episulfone[1], it may be reasonable to assume that the structure of the methyl groups for dimethyl sulfone is the same as that of dimethyl sulfide[12]: r(C–H) = 1.091 Å and ∠HCH = 109°34′. The remaining four structural parameters, the C–S and S–O bond distances and the ∠CSC and ∠OSO bond angles, were determined by fitting to the three moments of inertia for the normal species and I_a for the ^{13}C species; this choice of moments of inertia was found to be the most suitable for determining the four structural parameters. The results are

Table 5. r_0 structure of dimethyl sulfone

r(C–S)	1.777 ± 0.006Å
r(S–O)	1.431 ± 0.004Å
∠CSC	103°17′ ± 10′
∠OSO	121°1′ ± 15′
Assumed parameters [a]	
r(C–H)	1.091Å
∠HCH	109°34′

a) Ref. 12.

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TABLE 6. OBSERVED AND CALCULATED MOMENTS OF INERTIA (amuÅ^2)

	Observed	$I_{obs}-I_{calc}$[a]
Normal species		
I_a	108.961	0.000
I_b	117.654	0.000
I_c	120.987	0.000
^{13}C species		
I_a	109.721	0.000
I_b	119.766	−0.001
I_c	123.859	0.001

a) Based on the structure given in Table 5.

given in Table 5. The uncertainties estimated are due to the experimental uncertainties of the rotational constants and the assumption regarding the methyl groups. The moments of inertia for dimethyl sulfone are calculated using the structure thus obtained; they are compared with the observed values in Table 6. The agreement between them is good.

Discussion

As the comparison in Table 7 shows, the structure of dimethyl sulfone obtained by Sands[2] is in good agreement with our results except for the value of the ∠OSO angle. The ∠OSO angle of 121°1′ which was obtained by this work seems quite reasonable for the ∠OSO angle of alkyl sulfone compounds.

TABLE 7. C–S AND S–O BOND DISTANCES (Å) AND ∠CSC AND ∠OSO ANGLES IN VARIOUS COMPOUNDS

Molecule		r(C–S)	r(S–O)	∠CSC	∠OSO
$(CH_3)_2SO_2$[a]	r_0	1.777	1.431	103°17′	121°1′
$(CH_3)_2SO_2$[b]	X	1.78	1.44	103°	117.9°
$(CH_3)_2S$[c]	r_s	1.802	—	98°52′	—
$(CH_2)_2S$[d]	r_0	1.819	—	48°25′	—
$(CH_3)_2SO$[e]	r_s	1.799	1.485	96°34′	—
$(CH_2)_2SO$[f]	r_0	1.822	1.483	48°46′	—
$(CH_2)_2SO_2$[g]	r_0	1.731	1.439	54°40′	121°26′
$(CH_3CH_2)_2SO_2$[h]	X	1.73[j]	1.42_5[k]	55°24′	120°24′
SO_2[i]	r_e	—	1.4307_6	—	119°19.8′

a) This work. b) Ref. 2. c) Ref. 12. d) Ref. 14.
e) Ref. 13. f) Ref. 10. g) Ref. 1.
h) R. Desiderato and R. L. Sass, *Acta Crystallogr.*, **23**, 430 (1967).
i) S. Saito, *J. Mol. Spectrosc.*, **30**, 1 (1969).
j) The mean value of 1.72 Å and 1.74 Å.
k) The mean value of 1.41 Å and 1.44 Å.

For the purpose of comparison, the four main structural parameters of several related compounds are also listed in Table 7. The C–S bond of dimethyl sulfone is shorter than those of dimethyl sulfide[12] and dimethyl sulfoxide.[13] On the other hand, the C–S bond of ethylene episulfone[1] is distinctly shorter than that of dimethyl sulfone, but, contrary to the case of ethylene episulfone, the C–S bonds of other ring compounds, ethylene episulfide[14] and ethylene episulfoxide,[10] are slightly longer than those of the corresponding compounds, dimethyl sulfide and dimethyl sulfoxide respectively. The former fact means that the sulfone group has a strong electron withdrawing force, resulting in the decrease of the C–S bond distances. The latter fact suggests that the ring strain has some effect on the structures of ring compounds. The behavior of the ring strain can be understood by comparing the ∠CSC bond angles listed in Table 7. The ∠CSC angle of dimethyl sulfone is appreciably wider than those of dimethyl sulfide and dimethyl sulfoxide, so the corresponding ring compound, ethylene episulfone, suffers from severe ring strain. The unusually short C–S bonds of ethylene episulfone may be formed by the combined effects of the weakened long C–C bond and the migration of electrons from the C–C bond to the C–S bonds caused by the strong electron-withdrawing force of the sulfone group. The variation in the ∠CSC bond angle among alkyl sulfides, alkyl sulfoxides, and alkyl sulfones can be explained by the degree of the *s*-character of the C–S bond, which itself depends on the oxidation state of the sulfur atom. However, another point remains to be discussed why the C–S bond distances of ethylene episulfide and ethylene episulfoxide increase slightly, contrary to the case of ethylene episulfone. It is difficult to say why this is so, but it may be said that both the ring strain and the electron-withdrawing force around the sulfur atom in ethylene episulfide and ethylene episulfoxide are so weak that the ring-structures depend on a balance between the two forces. It must be noted that the S–O bond distance and the ∠OSO bond angle of the sulfone group are nearly constant, regardless of the structure of the alkyl group.

Finally, it is interesting to divide the dipole moment of dimethyl sulfone into the C–S and S–O bond moments. When the C–S and S–O bond moments are assumed to be 1.47 D and 2.70 D respectively, values which are derived from the moment of dimethyl sulfoxide,[13] the dipole moment of dimethyl sulfone can be estimated to be 4.47 D. This agrees with the observed value, 4.432 D, given in Table 4. In the same way, the dipole moment of ethylene episulfone can be calculated to be 4.36 D by using the C–S and S–O bond moments of ethylene episulfoxide.[10] The observed value for ethylene episulfone is 4.41 D.[1]

The authors would like to thank Professor Yonezo Morino for his helpful discussions.

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