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Microwave Spectrum of Ethylene Episulfone

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Microwave spectra of normal, ^{13}C-, and ^{34}S-isotopic species of ethylene episulfone have been investigated. Analysis of the spectra shows that the molecule has the C_{2v} symmetry. The structural parameters obtained from the spectral data for the normal and ^{13}C-ethylene episulfone are: r(C–C)$=1.590\pm0.011$ Å, r(C–S)$=1.731\pm0.006$ Å, r(S–O)$=1.439\pm0.006$ Å, ∠CSC$=54°40'\pm15'$, and ∠OSO$=121°26'\pm30'$, on the assumption that the C–H distances and the ∠HCH and ∠H_2CC angles are the same as those of ethylene sulfide. Stark-effect measurements have yielded a value of 4.41 ± 0.05 D for the dipole moment along the a axis. The structure obtained has been compared with those of other related molecules.

Molecules containing the sulfur atom have recently acquired great importance in the field of organic chemistry because they exhibit specific behavior in their chemical reactions. One of the best ways to understand the characteristics of the sulfur-containing compounds is to consider them from the point of view of the molecular structure.

Fundamental molecules which contain sulfur atoms in various oxidation states have been studied by microwave spectroscopy. The r_s structure of dimethyl sulfide was determined by Pierce and Hayashi[1] and by Dreizler and Rudolph,[2] while that of dimethyl sulfoxide was determined by Feder *et al.*[3] As for the structure of three-membered ring compounds, Cunningham *et al.*[4] obtained the r_0 structure of ethylene episulfide, and Saito,[5] that of ethylene episulfoxide. Alkyl sulfones have not been subjected to study by microwave spectroscopy, though there have been a number of investigations by means of X-ray crystallography.[6–8] Desiderato and Sass reported an unusually long distance (1.60 Å) for the ring carbon-carbon bond and a rather short distance (1.73 Å) for the carbon-sulfur bond for *cis*-2-butene episulfone.[8] They pointed out that the anomalies could be explained by a model in which the charge and/or bonds were highly delocalized. Pochan *et al.*[9] determined the three-membered ring stucture of cyclopropanone by microwave spectroscopy; their finding was somewhat similar to that of *cis*-2-butene episulfone in the point of the long carbon-carbon bond.

We have studied the microwave spectrum of ethylene episulfone with the aim of determining its molecular structure accurately. The results obtained settle the controversy regarding the carbon-carbon bonds of episulfone compounds in a convincing way, and, when combined with earlier microwave spectroscopic studies of the simplest and fundamental sulfides and sulfoxides, they provide further insight into the properties of alkyl sulfone compounds.

Experimental

The spectra were observed with a conventional 110 kHz square- or sinusoidal wave Stark modulated spectrometer. Frequencies were reproducible to ±0.1 MHz or better. The sample of ethylene episulfone used in this study was prepared by passing the sulfur dioxide gas through an ether solution of diazomethane cooled at about −20°C according to the method of Hesse and Majmudar[10] and then stored at −10°C. Measurements were made at room temperature at a pressure of about 0.01 mmHg. The intensity of the lines decreased slowly in a few hours because of the decomposition or adsorption of the sample in the absorption cell. For the measurement of the ^{13}C-isotopic species, the sample was allowed to flow through the cell in order to maintain the signal-to-noise ratio as high as possible.

Results

A. Microwave Spectrum. The spectrum of the normal isotopic ethylene episulfone was observed

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[3] W. Feder, H. Dreizler, H. D. Rudolph and V. Typke, *ibid.*, *A*, **24**, 266 (1969).

[4] G. L. Cunningham, Jr., A. W. Boyd, R. J. Myers and W. D. Gwinn, *J. Chem. Phys.*, **19**, 676 (1951).

[5] S. Saito, This Bulletin, **42**, 663 (1969).

[6] G. A. Jeffrey, *Acta Crystallogr.*, **4**, 58 (1951).

[7] D. E. Sands, *Z. Kristallogr.*, **119**, 245 (1963).

[8] R. Desiderato and R. L. Sass, *Acta Crystallogr.*, **23**, 430 (1967).

[9] J. M. Pochan, J. E. Baldwin and W. H. Flygare, *J. Amer. Chem. Soc.*, **91**, 1896 (1969); **90**, 1072 (1968).

[10] G. Hesse and S. Majmudar, *Chem. Ber.*, **93**, 1129 (1960); G. Hesse, E. Reichold and S. Majmudar, *ibid.*, **90**, 2106 (1957).

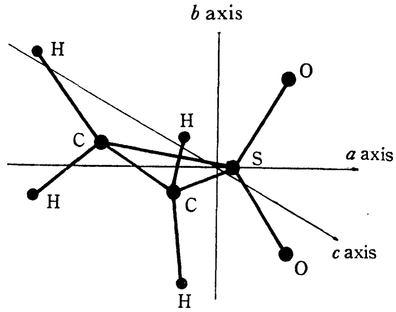

Fig. 1. Principal axes in ethylene episulfone.

by using an oscilloscope. All the *a*-type *R*-branch transitions of $J=2\leftarrow1$ and $3\leftarrow2$ were assigned by means of their well-resolved Stark patterns. Several *Q*-branch transitions were measured by means of a recorder. It was found that the intensities of the transitions depended upon the parity of the limiting prolate quantum number, K_{-1}; the ratios of the intensities of the transitions with even values of K_{-1} to those of the transitions with odd values were about ten to six. This fact suggests that the ethylene episulfone molecule has a C_2 symmetry along the *a* axis, and that there are two sets of two hydrogen atoms interchangeable by rotation about the C_2 axis.[11] Hence, it can be concluded that ethylene episulfone has the C_{2v} molecular symmetry, as shown in Fig. 1. The frequencies of the observed transitions are given in Table 1. The *R*-branch transitions of the ^{34}S-isotopic species in natural abundance were easily identified by means of their Stark effects and by their locations relative to the lines of the normal species. Since the ^{13}C-isotopic species has two equivalent carbon positions, the spectral lines will exhibit half the intensity of the lines for the ^{34}S-isotopic species. It was, however, difficult to assign the transitions of the ^{13}C-isotopic species in natural abundance, because their S/N ratios were about 20 and they were apt to be masked or disturbed by other strong lines. Since the vapor pressure of ethylene episulfone is low below 0°C, it was impossible to increase the intensity of the ground-state lines by cooling the absorption cell. Among the nine *R*-branch transitions of $J=1\leftarrow0$, $2\leftarrow1$, and $3\leftarrow2$, only five transitions were observed and assigned. The observed transitions for ^{13}C- and ^{34}S-isotopic species are listed in Table 2.

Table 1. Observed microwave transition frequencies of normal ethylene episulfone (MHz)

Transition	ν_{obsd}[a]	$\nu_{obsd}-\nu_{calcd}$
$1_{01} \leftarrow 0_{00}$	8684.43	0.00
$2_{02} \leftarrow 1_{01}$	16951.80	−0.26
$2_{12} \leftarrow 1_{11}$	16204.49	−0.24
$2_{11} \leftarrow 1_{10}$	18532.84	−0.15
$3_{03} \leftarrow 2_{02}$	24648.25	−0.19
$3_{13} \leftarrow 2_{12}$	24079.99	−0.17
$3_{12} \leftarrow 2_{11}$	27471.37	−0.46
$3_{22} \leftarrow 2_{21}$	26052.83	−0.46
$3_{21} \leftarrow 2_{20}$	27457.41	−0.73
$4_{04} \leftarrow 3_{03}$	32073.25[b]	−0.72
$4_{14} \leftarrow 3_{13}$	31793.60[b]	−0.41
$3_{22} \leftarrow 3_{03}$	11159.11[c]	0.00
$4_{13} \leftarrow 4_{14}$	10995.50[c]	0.01
$4_{23} \leftarrow 4_{04}$	13488.11[c]	−0.10
$5_{23} \leftarrow 5_{24}$	8230.87[c]	0.01

a) Accuracy, ±0.1 MHz, unless otherwise indicated. b) ±0.2 MHz. c) ±0.3 MHz.

Table 2. Observed microwave transition frequencies of ^{34}S- and ^{13}C-isotopic species (MHz)

Transition	ν_{obsd}[a]	$\nu_{obsd}-\nu_{calcd}$
^{34}S-Species		
$2_{02} \leftarrow 1_{01}$	16937.96	0.00
$2_{11} \leftarrow 1_{10}$	18513.55	0.00
$3_{03} \leftarrow 2_{02}$	24629.87[b]	−0.61
$3_{13} \leftarrow 2_{12}$	24059.79	−0.52
$3_{21} \leftarrow 2_{20}$	27426.90	0.00
^{13}C-Species		
$2_{12} \leftarrow 1_{11}$	15957.48	0.00
$2_{11} \leftarrow 1_{10}$	18161.58	0.00
$3_{12} \leftarrow 2_{11}$	26955.56	0.54
$3_{22} \leftarrow 2_{21}$	25589.54	0.23
$3_{21} \leftarrow 2_{20}$	26862.16	0.00
$4_{14} \leftarrow 3_{13}$	31356.00[b]	−1.59

a) Accuracy, ±0.1 MHz, unless otherwise indicated. b) ±0.2 MHz.

B. Rotational Constants. The rotational constants of the normal species were determined in the rigid-rotor approximation by using the frequency of the $1_{01}\leftarrow0_{00}$ transition and the values of $(A\text{-}C)/2$ and κ obtained from $(A\text{-}C)/2$ *versus* κ plots of the *Q*-branch transitions. The results thus obtained are shown in Table 3. The rotational constants for the ^{13}C- and ^{34}S-isotopic species were calculated from three low-*J* transitions; they are also listed in Table 3. Large errors associated with the *A* rotational constants for the ^{13}C- and ^{34}S-isotopic species arose from the lack of observed

Table 3. Rotational constants (MHz) and moments of inertia (amu·Å^2)[a] for ethylene episulfone

	Normal species	^{34}S-Species	^{13}C-Species
A	6676.58±0.2	6673.87±2.0	6623.35±2.0
B	4924.28±0.1	4918.66±0.1	4815.91±0.1
C	3760.15±0.1	3757.57±0.1	3713.86±0.1
I_a	75.717	75.748	76.326
I_b	102.661	102.778	104.971
I_c	134.444	134.537	136.120

a) Conversion factor is 5.05531 × 10^5 MHz·amu·Å^2.

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[11] C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York (1955), p. 104.

Q-branch lines. Using the rotational constants shown in Table 3, the transition frequencies were calculated; the differences between the calculated and the observed frequencies are given in Tables 1 and 2. The discrepancies seem to be primarily due to the neglect of the centrifugal distortion effects.

C. Dipole Moment. The Stark-effect coefficients were measured for the $M=0$, $1_{01}\leftarrow 0_{00}$ transition and for the $M=0$ and 1 components of the $2_{02}\leftarrow 1_{01}$ transition. The effective electrode spacing was determined from the measurements of the Stark effect of the $1\leftarrow 0$ transition of OCS, using its dipole moment of 0.71521 D obtained by Muenter.[12] The observed values of the Stark coefficients are shown in Table 4. The dipole moment was determined to be 4.41±0.05 D along the a axis.

TABLE 4. STARK COEFFICIENTS[a] AND DIPOLE MOMENTS OF ETHYLENE EPISULFONE

Transition		$\Delta\nu/E^2_{obsd}$	Dipole moment
$1_{01}\leftarrow 0_{00}$	$M=0$	2.980×10^{-4}	4.380D
$2_{02}\leftarrow 1_{01}$	$M=0$	-0.884×10^{-4}	4.417D
	$M=1$	0.671×10^{-4}	4.425D
$\mu=\mu_a=4.41\pm 0.05\,\mathrm{D}$			

a) Values in $\mathrm{MHz}\cdot(\mathrm{V/cm})^{-2}$.

D. Molecular Structure. As has been described above, the microwave data are strongly indicative of the C_{2v} symmetry for ethylene episulfone; hence, the structural calculations have been carried out on this basis. Since no studies have been made of the deuterated species of ethylene episulfone, scarcely no structural information about the methylene groups was obtained from the moments of inertia for the normal, ^{13}C-, and ^{34}S-isotopic species. We assume that the structural parameters related to the methylene groups are the same as those of ethylene sulfide, that is, $r(\mathrm{C{-}H})=1.078$Å, $\angle\mathrm{HCH}=116°0'$, and $\angle\mathrm{H_2CC}=151°43'$,[4] as were assumed for ethylene episulfoxide.[5] Moreover, the moments of inertia for the ^{34}S-isotopic species cannot be used to obtain the molecular structure, for the sulfur atom is located only 0.24 Å from the center of gravity. Four structural parameters between heavy atoms, the S–O and C–S distances and the ∠OSO and ∠CSC angles, were calculated from the moments of inertia for the normal and ^{13}C-isotopic species. First, we used all the moments of inertia simultaneously, but this led to an unreasonable structure, because the I_a and I_c of the normal species and the corresponding moments of inertia for the ^{13}C-species had an almost parallel dependence on the structural parameters to be determined. Therefore, the structure of ethylene episulfone was determined from three moments of inertia for the normal species and the I_b of the ^{13}C-species. The results are given in Table 5. The errors quoted were estimated from the uncertainties of the rotational constants.

Discussion

Two distinct features of the structure of ethylene episulfone are the long C–C bond and the rather short C–S bond. Though the C–C and C–S bond distances obtained above deviate from the corresponding normal single-bond distances by amounts considerably larger than the estimated errors, it is valuable to consider the accuracies of the structure determined in this study. Besides the errors associated with the uncertainties of the rotational constants, there are uncertainties which originate in the assumption made with regard to the methylene groups. It might be expected that the C–H bond distances of ethylene episulfone are different from those of episulfides and episulfoxides, for α hydrogen atoms are highly activated by the introduction of a sulfone group.[13] To estimate the uncertainties due to the unestablished C–H bond distances, a trial calculation was done on an assumption that the C–H distances are longer by 0.01 Å than the value cited in Table 5. The calculated results show that the changes of the distances are −0.002 Å for the C–C bond and +0.001 Å for the C–S bonds; both values are within the estimated uncertainties listed in Table 5. Thus, an unusually long C–C bond and short C–S bonds have been established for ethylene episulfone in spite of the tentatively-assumed C–H distances.

TABLE 5. r_0 STRUCTURE OF ETHYLENE EPISULFONE

r(S–O)	1.439±0.006 Å
r(C–S)	1.731±0.006 Å
r(C–C)[a]	1.590±0.011 Å
∠OSO	121°26′±30′
∠CSC	54°40′±15′
Assumed parameters	
r(C–H)	1.078 Å
∠CHC	116° 0′
∠$\mathrm{H_2CC}$	151°43′

a) C–C distance is not independent of the other parameters listed above.

In order to make the remarkable properties of ethylene episulfone clear, it would be helpful to compare the C–C and C–S bond distances and the ∠CSC and ∠OSO bond angles of related compounds. Table 6 indicates that the three-membered-ring structure of ethylene episulfone is very similar to that of *cis*-2-butene episulfone, although the structure of the former was determined by gas-phase microwave spectroscopy, and that of the

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[12] J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).

[13] S. Oae, "Chemistry of Organic Sulfur Compounds," Vol. II, Kagakudojin, Kyoto (1969), p. 315.

TABLE 6. C–S, C–C AND S–O BOND DISTANCES (Å), AND ∠CSC AND ∠OSO ANGLES IN VARIOUS COMPOUNDS

Molecule		r(C–S)	r(C–C)	r(S–O)	∠CSC	∠OSO
$(CH_2)_2SO_2$a)	r_0	1.731	1.590	1.439	54°40′	121°26′
$(CH_2)_2SO$b)	r_0	1.822	1.504	1.483	48°46′	—
$(CH_2)_2S$c)	r_0	1.819	1.492	—	48°25′	—
$(CH_3)_2SO_2$d)	Xn)	1.78	—	1.44	103°	117.9°
$(CH_3)_2SO$e)	r_s	1.799	—	1.485	96°34′	—
$(CH_3)_2S$f)	r_s	1.802	—	—	98°52′	—
$(CH_3CH)_2SO_2$g)	Xn)	1.73o)	1.60p)	1.42_5r)	55.4°	120.4°
Thiopheneh)	r_s	1.71_4	—	—	92°10′	—
CSi)	r_e	1.5349	—	—	—	—
$(CH_2)_2CO$j)	r_s	—	1.575q)	—	—	—
$(CH_2)_2NH$k)	r_0	1.480	—	—	—	—
$(CH_2)_2PH$l)	r_s	—	1.502	—	—	—
$(CH_2)_2O$c)	r_0	—	1.472	—	—	—
SO_2m)	r_e	—	—	1.4307_6	—	119°19.8′

a) This work. b) Ref. 5. c) Ref. 4. d) Ref. 7. e) Ref. 3. f) Ref. 1. g) Ref. 8. h) Ref. 14. i) R. C. Mockler and G. R. Bird, *Phys. Rev.*, **98**, 1837 (1955). j) Ref. 9. k) Ref. 15. l) Ref. 16. m) Ref. 17. n) X-Ray crystallography. o) The mean value of 1.72Å and 1.74Å. p) Ring carbon-carbon bond. q) The C–C bond perpendicular to the CO bond. r) The mean value of 1.41Å and 1.44Å.

latter, by X-ray crystallography.8) The C–S bond distances of dimethyl sulfide1) and dimethyl sulfoxide3) are nearly equal, and those of ethylene episulfide4) and ethylene sulfoxide5) are also almost identical. The C–S distance is 0.02 Å longer for alkyl episulfone than for dialkyl sulfone. This difference may be attributable to the ring strain. In accord with the fact that the C–S distance of dimethyl sulfone is shorter than those of dimethyl sulfide and dimethyl sulfoxide, the C–S distance of ethylene episulfone is also shorter than those of ethylene episulfide and ethylene episulfoxide. The decrease is, however, remarkable for the latter; it amounts to 0.09 Å, and, in fact, the C–S distance is almost equal to that of thiophene.14) Thus, it can be concluded that the C–S bond of ethylene episulfone has a considerable double-bond character.

Contrary to the well-known fact that the C–C bonds of usual three-membered-ring compounds, such as ethylene oxide,4) ethylene episulfide,4) ethylene episulfoxide,5) ethylenimine,15) and phosphirane,16) are shorter than the normal C–C single bond, the C–C bond of ethylene episulfone is longer than the normal C–C single bond by the unusually long distance of 0.05 Å. The C–C distance obtained by the present study seems to be the longest among those of the three-membered-ring molecules studied so far by microwave spectroscopy or by other spectroscopic methods. According to the recent study of cyclopropanone by Pochan *et al.*, the length of the C–C bond perpendicular to the CO bond is unusually long (1.575 Å), while that of the C–C bond adjacent to the CO bond is considerably short (1.475 Å).9) They stated that the 1.575 Å C–C bond was the longest, but in actuality the C–C bond in ethylene episulfone is longer by 0.015 Å.

It is most likely that the unusually long C–C bond distance is strongly correlated with the short C–S bond distance; for instance, the migration of electrons from the C–C bond to the C–S bonds would bring about the increase in the double-bond nature of the latter and the loosening of the former bond. At any rate, the above findings will be interesting in connection with the molecular orbital calculations and will be important and suggestive for the consideration of the reaction mechanisms involving these molecules. Furthermore, the similarity between the structures of ethylene episulfone and cyclopropanone gives interesting support to the similarities between the chemistry of carbonyl and sulfone compounds.

The structures of the SO_2 group of ethylene episulfone, dimethyl sulfone, and *cis*-2-butene episulfone are approximately the same as that of sulfur dioxide.17) It must be added that the observed value of the dipole moment of ethylene episulfone is close to the sum of the bond moment of the C–S bond for ethylene sulfide4) and that of the S–O bond for ethylene episulfoxide.5)

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14) B. Bak, D. Christensen, L. Hansen-Nygaard and J. Rastrup-Andersen, *J. Mol. Spectrosc.*, **7**, 58 (1961).

15) T. E. Turner, V. C. Fiora and W. M. Kendrick, *J. Chem. Phys.*, **23**, 1966 (1955).

16) M. T. Bowers, R. A. Beaudet, H. Goldwhite and R. Tang, *J. Amer. Chem. Soc.*, **91**, 17 (1969).

17) S. Saito, *J. Mol. Spectrosc.*, **30**, 1 (1969); Y. Morino, Y. Kikuchi, S. Saito and E. Hirota, *ibid.*, **13**, 95 (1964).