Molecular Structure of Divinyl Sulphone as Studied by Electron Diffraction, Vibrational Spectroscopy, and Semiempirical CNDO/2 Molecular-orbital Calculations

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An electron-diffraction structure analysis has yielded the following bond lengths (r_a) for the title compound: S=O 1.438(3), S–C 1.769(4), C=C 1.332(4), and C–H 1.118(6) Å. Of the bond angles, the following two are reliably determined: O=S=O 119.5(12) and S–C=C 121.5(3)°. CNDO/2 molecular-orbital calculations indicate the coexistence of three conformers. At least two, possibly more, conformers are present in the vapour according to the electron-diffraction data, which also indicate that the C=C bonds tend to eclipse the other bonds. Comparison of a number of bands in the i.r. and Raman spectra for different states of the compound shows the coexistence of at least two, possibly more, conformers in the liquid and in the supercooled liquid, while there is only one form in the crystalline phase. The S=O bond lengths and stretching frequencies are consistent with empirical relations found for a relatively large series of sulphones.

THE present work is an extension of our structural studies on simple sulphone molecules XSO_2Y employing electron diffraction ($X = Y = Cl$,[1] Me,[2] or NMe_2;[3] X = Me, Y = F [4] or Cl;[5] X = OMe, Y = F [6] or Cl;[7] X = Cl, Y = Ph,[8] NMe_2,[9] or CH_2=CH [10]), vibrational spectroscopy including normal co-ordinate analysis (n.c.a.) (X = Me, Y = F,[11,12] Cl,[11,12] or Br;[12] X = OMe, Y = Cl [13]), and semiempirical molecular-orbital (m.o.) calculations using the CNDO/2 approximation (X = Y = Me [14]). These studies are primarily aimed at determining and correlating geometrical, vibrational, and bonding properties of the molecular configurations around the sulphur atom. In particular, as the nature of the ligands X and Y changes, geometrical variations are observed and interpreted by electron-pair repulsions and nonbonded interactions.[15] *Ab initio* m.o. calculations have

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also been initiated.[16] Correlations between stretching vibrational frequencies, force constants, and bond lengths have been examined in detail.[17] The above investigations are well supplemented by microwave spectroscopic studies of the molecular geometry of several derivatives including: X = Y = F [18] or Me;[19,20] X = Me, Y = F [19] or Cl;[21] X = F, Y = OMe,[6] Cl,[22] or Br.[23]

It was of interest to determine the sulphur-bond configuration when X = Y = CH_2=CH, and correlate it with previous observations. In addition, divinyl sulphone is expected to possess interesting conformational properties.

CNDO/2 CALCULATIONS

This technique is known to be preferable for the conformational analysis of localized systems.[24] The preliminary results of the electron-diffraction analysis indicated C=C and S–C bond lengths in divinyl sulphone which suggested no appreciable delocalization as compared with the structures of ethylene [25] and dimethyl sulphone.[2] Pople's original (*spd*) parametrization [26] was used. All the computations were performed on an IBM 370/168 computer (C.N.R.S., Orsay, France).

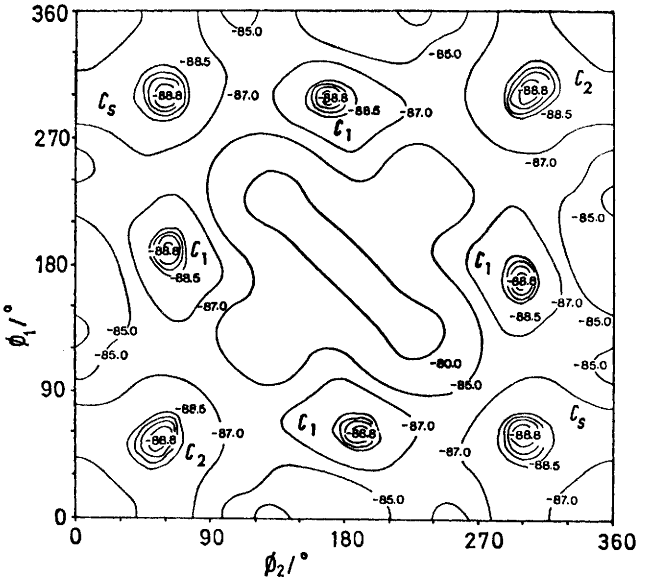

FIGURE 1 Map of total energy (*E*) against the rotational angles ϕ_1 and ϕ_2. Values of $E + 50\,300$ kcal mol^{-1} are indicated

The angles of rotation around the S–C bonds (ϕ_1 and ϕ_2) were defined in such a way that 0° corresponded to an all-*anti* C=C–S–C=C chain whose plane bisected the O=S=O angle, and $\phi_1 = \phi_2$ characterized the model with C_2 symmetry. Geometrical parameters from the early results of the electron-diffraction analysis were utilized in the calculations. These parameters were little different from those presented in Table 4. Figure 1 shows a map of isoenergy curves describing the variation of the total energy as a function of the angles of rotation (30° was used as $\Delta\phi$ step). The molecular models corresponding to the energy minima are shown in Figure 2. The total energy was rather insensitive to changes of several degrees in the bond angle C–S–C. This is noted since this parameter was not well determined by electron diffraction.

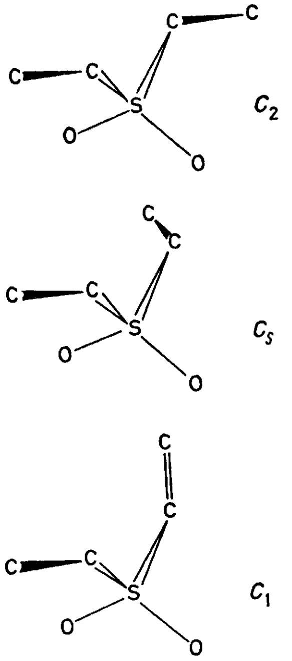

FIGURE 2 Some of the possible forms of divinyl sulphone which are characterized by the following angles of rotation:

	$\phi_1/°$	$\phi_2/°$
C_2	60	60
C_s	60	300
C_1	60	180

VIBRATIONAL ANALYSIS

The Raman spectrum of liquid divinyl sulphone has been recorded by Aleksanyan *et al.*[27] without assignment of the vibrational frequencies. Feairheller and Katon [28] compared the vibrational frequencies of the SO_2 group in divinyl sulphone to those in related compounds. No complete i.r. data have been published. We recorded the i.r. and Raman spectra and carried out a tentative assignment of the vibrational frequencies by comparing them with the spectra of

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TABLE 1

Vibrational spectrum (cm^{-1}) of divinyl sulphone

Infrared					Raman			
crystal *ca.* 120 K	supercooled liquid	liquid	solution in CCl_4	gas	crystal *ca.* 120 K	supercooled liquid	liquid	Assignment
3 210w		3 208w					3 214w,p	$2\nu_4$
3 116w 3 108w 3 098m 3 095m	3 112m 3 097w	3 102m	3 098m	3 100w	3 104m	3 113w 3 100vw	3107m,dp	ν_1, ν_{24}
3 071m 3 058vs 3 046m	3 062w 3 052vs	3 061 (sh) 3 055s	3 062 (sh) 3 052m		3 059m	3 063w 3 054m	3 060m,dp	ν_2, ν_{25}
3 033w	3 028w	3 020m	3 016m	3 028w	3 022m	3 031s	3 026vs,p	ν_3, ν_{26}
2 974m 2 967m	2 976w	2 967w	2 960w		2 972w	2 978vw	2 972w,p	$\nu_4 + \nu_5$
2 924 (sh)								
2 915w								
2 847w 2 838vw	2 840— 2 850vw	2 845w	2 845w					
2 645vw,br	2 640vw	2 630vw						
2 619vw	2 612vw							
2 606vw								
2 598vw								
2 426w	2 430vw	2 430vw	2 450w					
2 390vw								
2 259w			2 260vw,br					
2 252w	2 253vw	2 250vw,br	2 230vw,br					
2 027vw								
2 021vw								
1 995vw								
1 964w								
1 958w	1 959w							
1 948vw								
1 943vw		1 945w,br		1 942w				
1 933w			1 931w					
1 918w								
1 742w	1 743w	1 730w	1 735w	1 768w				
1 695w	1 698vw	1 680w	1 685w					
1 618vs	1 618m	1 604m	1 605w	1 610w	1 608vs	1 613vs	1 609vs,p	ν_4, ν_{27}
1 580w						1 588vw	1 586w,dp	ν_{27}?
1 401 (sh)								
1 395vs	1 392vs	1 381s	1 373s	1 389m	1 395s	1 398m	1 388s, 0.5	ν_5, ν_{28}
					1 391s			
						1 377m	1 372w (sh), dp	ν_5, ν_{28} (II)
1 309vs	1 309vs	1 310vs	1 320vs	1 352s	1 316m	1 316m	1 317w,dp	ν_{18}
1 298 (sh)								
1 286w								
1 259 (sh)	1 264m	1 254m	1 250m	1 260w	1 266m	1 265m	1 259m, 0.5	ν_6, ν_{29}
1 245vs	1 252m	1 242m	1 240m	1 230w	1 253vw	1 250m		ν_6, ν_{29} (II)
1 186w								
1 169vw								
1 146m (sh)						1 145vw	1 136w	
1 136vs	1 138vs	1 124vs	1 130vs	1 150vs	1 125vs	1 122vs	1 127vs,p	ν_7
1 125(sh)								
1 114(sh)								
1 078w								
1 042vw								
1 024m	1 025m	1 017w (sh)	1 020 (sh)	1 025m	1 016s	1 027m	1 019m,dp	ν_{13}, ν_{19}
						1 012m		
1 008vs	1 004vs	1 007w (sh)	999w (sh)	1 004vs	993w	997w	1 007m,dp	ν_8, ν_{30}
999 (sh)								
987s	989vs	984s		989vs				ν_{20}
975 (sh)	979 (sh)			979 (sh)				
967s	969s	964 (sh)	964s	969s	962w	972w	962w,dp	ν_4
		942m			955w			
804s								
		778 (sh)		792vs				
783vs	794vs	772s		771s			782vw,dp	ν_{31}
774 (sh)								
722vs	721vs	710s		715m	724vs	728vs	713vs,p	ν_9
		685vw	680w (sh)				691w, (p)	ν_{15}, ν_{21} (II)
	666w	654w	638w		654w	670w	659w,dp	ν_{21}
643 (sh)								
638m	637m	632w	618w		637m	647m	636m, (p)	ν_{15}
604m	608s	599s	580m		608m	605w	601w,dp	ν_{22}
597m (sh)								
	561 (sh)							

TABLE 1 (*Continued*)

Infrared					Raman			
crystal, *ca.* 120 K	supercooled liquid	liquid	solution in CCl_4	gas	crystal, *ca.* 120 K	supercooled liquid	liquid	Assignment
557m	557m	560w	540w			555vw		ν_{10}
	511m							(II)
	499m							(II)
492s	487s	478m	470m		486m	491m	484w,dp	ν_{32}
	454m	445vw	428vw		450w	456m	449m, 0.3	ν_{11}
402 (sh)								
	403s				402s	410w	410w,dp	ν_{16}
399m					389vs	395s	384s, 0.6	ν_{12}
						358w	354w,dp	ν_{12} (II)
					281vs	290m		
						273m	267s,br	ν_{11}, ν_{33} (II)
					249vs	261m		ν_{33}
						238w	235—240 (sh)	?
					182w	175w		
					165w			ν_{17}, ν_{23}
					147vs	135vs		
					122w	122s		Lattice vibrations ?
						95w		
						80w		

s = Strong, m = medium, w = weak, sh = shoulder, br = broad, p = polarized, dp = depolarized. Polarization ratios are indicated and (II) marks the assignment to a second isomer.

similar compounds, such as divinyl sulphide,[29] divinyl sulphoxide,[30] penta-1,4-diene,[31] divinyl ether,[32] methyl vinyl sulphone,[28] and vinylsilanes,[33] by analysing the spectra in various states, by measuring the Raman polarization data, and carrying out a n.c.a. based on the general valence force field.

The sample of divinyl sulphone (from FERAK, Berlin-West) was used after rectification at 79 °C (4 Torr),* *n* (293 K, 589.3 nm) = 1.4743. The i.r. spectra of the liquid film between KBr windows, of the gaseous sample (10-cm path length, KBr windows, atmospheric pressure), and of the solution in CCl_4 (161 μm path length; in the 2 800—3 400 cm^{-1} region, 1 048 μm path length) were recorded on a Perkin-Elmer model 621 spectrophotometer, and the Raman spectra of the liquid sample on a GDM 1000 grating double monochromator (VEB Carl Zeiss Jena) equipped with an ILA 120 argon laser. For the solid sample, the i.r. spectra were recorded on a UR 10 spectrophotometer and the Raman spectra on a Coderg PHO spectrophotometer equipped with a Spectra Physics model 125 helium–neon laser. The frequencies, intensities, and tentative assignments of the observed bands are listed in Table 1.

The 33 fundamentals corresponding to the conformations considered may be divided into the following irreducible representations: for C_{2v} (*anti-anti*), (*syn-syn*), $12A_1 + 5A_2 + 6B_1 + 10B_2$; for C_2, $17\,A + 16\,B$; for C_s (*e.g.* ϕ_1 60 and ϕ_2 300°), $18\,A' + 15\,A''$; for C_s (*syn-anti*), $22\,A' + 11\,A''$; for C_1, 33 A. The A_1, A', and A vibrations give rise to polarized Raman bands. The C_{2v} *syn-syn* conformation and one of the C_s forms (*syn-anti*) may be excluded for steric reasons.

The Raman spectrum of the *anti-anti* form should exhibit 21 depolarized or nearly depolarized lines, while five vibrations should be i.r. inactive. The Raman spectrum of the second C_s form (ϕ_1 60 and ϕ_2 300°) should exhibit polarized $\nu_{sym}(SO_2)$ and $\rho(SO_2)$ lines. The most probable conformation should be the C_2 ($\phi_1 = \phi_2$) form with 17 polarized and 16 depolarized lines in the Raman spectrum. The C_1 form cannot be completely excluded, although in the spectrum there are many polarized lines. Table 2 shows the distribution of the fundamentals among the various species of symmetry.

TABLE 2

Distribution of the fundamentals among the various symmetry species

C_{2v}	A_1	A_2	B_1	B_2
C_2	A	A	B	B
C_s [a]	A'	A''	A'	A''
C_s' [b]	A'	A''	A''	A'
C_1	A	A	A	A

ν_1 $\nu_{asym}(CH_2)$	ν_{13} $\tau(CH_2)$	ν_{18} $\nu_{asym}(SO_2)$	ν_{24} $\nu_{asym}(CH_2)$
ν_2 $\nu(CH)$	ν_{14} $\omega(CH_2)$	ν_{19} $\tau(CH_2)$	ν_{25} $\nu(CH)$
ν_3 $\nu_{sym}(CH_2)$	ν_{15} $\delta(CH)$ [c]	ν_{20} $\omega(CH_2)$	ν_{26} $\nu_{sym}(CH_2)$
ν_4 $\nu(CC)$	ν_{16} $\tau(SO_2)$	ν_{21} $\delta(CH)$ [c]	ν_{27} $\nu(CC)$
ν_5 $\delta(CH_2)$	ν_{17} τ(vinyl) $\downarrow\uparrow$	ν_{22} $\rho(SO_2)$	ν_{28} $\delta(CH_2)$
ν_6 $\delta(CH)$ [d]		ν_{23} τ(vinyl) $\downarrow\downarrow$	ν_{29} $\delta(CH)$ [d]
ν_7 $\nu_{sym}(SO_2)$			ν_{30} $\delta(CH_2)$
ν_8 $\rho(CH_2)$			ν_{31} $\nu_{asym}(CS)$
ν_9 $\nu_{sym}(CS)$			ν_{32} $\omega(SO_2)$
ν_{10} $\delta(SO_2)$			ν_{33} $\delta(CCS)$
ν_{11} $\delta(CCS)$			
ν_{12} $\delta(CSC)$			

[a] $\phi_1 = 60$, $\phi_2 = 300°$. [b] *syn-anti* conformation. [c] Out of plane. [d] In plane.

In the vibrational spectra of monovinyl compounds three bands in the C–H stretching region are expected. The spectra of divinyl sulphone show four bands in this region, the highest two being split in the crystal spectra. In accordance with previously published data,[31–34] the Raman lines at 3 107, 3 060, and 3 026 cm^{-1} corresponding to the i.r. bands at 3 102, 3 055, and 3 020 cm^{-1} are assigned to $\nu_{asym}(CH_2)$, $\nu(CH)$, and $\nu_{sym}(CH_2)$, respectively. As a consequence of the relatively large mass of the SO_2 group, a mass coupling of the two vinyl groups seems to be almost

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* Throughout this paper: 1 Torr = (101 325/760) Pa; 1 cal = 4.184 J; 1 dyn = 10^{-5} N.

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excluded; therefore we have assigned the lowest frequency in the CH-stretching region (i.r. 2 967w cm^{-1}, Raman 2 972w,p cm^{-1}) to the combination $\nu_4 + \nu_5$. The assumption of a small mass coupling is supported by the coincidence of some other vinyl-group vibrations such as ν(C=C), τ(CH$_2$), ρ(CH$_2$), and δ(CH) (out of plane); the latter two are also split in the Raman spectra of the crystalline compound. Normal co-ordinate analyses have been carried out [33,34] using deuteriated compounds in order to confirm that τ(CH$_2$) has the highest frequency of the three non-planar deformation vibrations. Therefore the weak i.r. band at 1 017 cm^{-1} has been assigned to this vibration, corresponding to a nearly depolarized Raman line at 1 019 cm^{-1}. Overtones of ω(CH$_2$) may be observed in comparable spectra (here a broad band at 1 930 cm^{-1}); and we assign the absorption at 970 cm^{-1} to ω(CH$_2$).

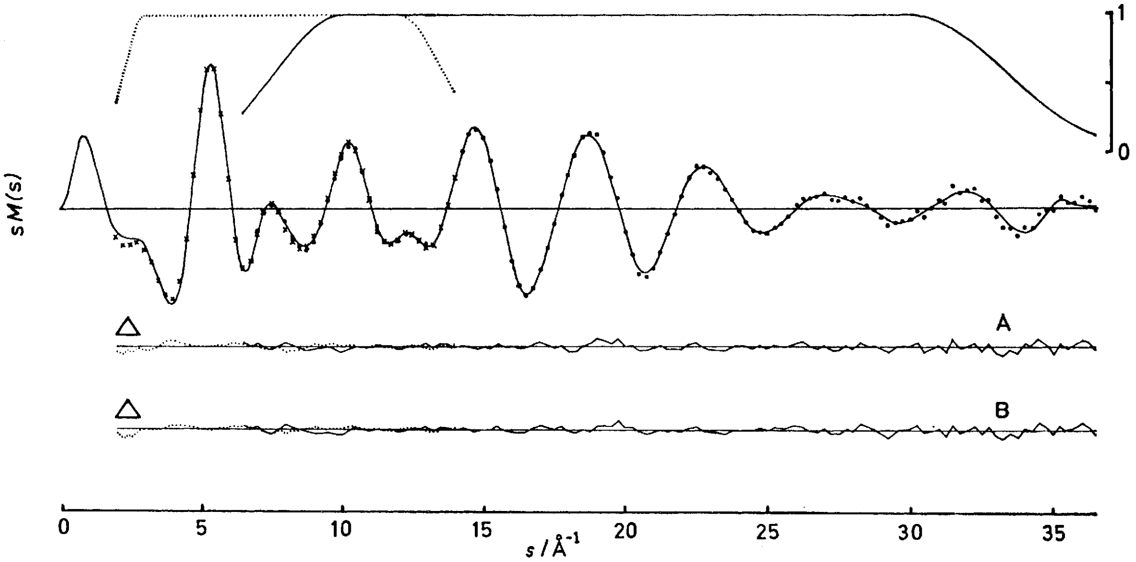

FIGURE 3 Experimental (× and ● for 50- and 19-cm camera ranges) and theoretical (——, corresponding to column A of Table 4) molecular intensities $sM(s)$, difference curves (△) for A and B, and weights $W(s)$ used in the least-squares refinements

The spectra also indicate the possible existence of a second isomer. We observed an apparently depolarized shoulder (1 372 cm^{-1}) to low frequency of the intense line at 1 388 cm^{-1} in the Raman spectrum of the liquid, two clearly split lines of comparable intensity in the spectrum of the supercooled liquid at 1 398 and 1 377 cm^{-1}, but only two small resolved lines at 1 395 and 1 391 cm^{-1} in the spectrum of the crystal. In the i.r. spectrum of liquid divinyl sulphone two hardly resolved bands appear at 1 254 and 1 242 cm^{-1} (ν_6 and ν_{29}), the latter being of increased intensity in CCl$_4$ solution. The same effect may be observed in the spectrum of the crystal. Furthermore, the Raman lines at 691, 456, 358, 273, and 238 cm^{-1} are absent from the spectra of the crystal, as are the i.r. bands observable in the spectra of the liquid and the supercooled liquid at 685, 665, 561, 511, 499, and 454 cm^{-1}. This may be an indication of the existence of other conformers.

For C_2 symmetry, six polarized and five depolarized or nearly depolarized Raman lines are predicted below 700 cm^{-1}. The spectrum of the liquid shows four polarized lines at 691, 636, 449, and 384 cm^{-1}, four depolarized or nearly depolarized lines at 659, 484, 410, and 354 cm^{-1}, and a complex band below 300 cm^{-1}, the depolarization ratio of which could not be determined.

The assignment of the four deformation vibrations of the sulphonyl group is difficult, since there are no regularities in their order for various sulphonyl compounds. We have used the Raman polarization data and the results of the calculation of the potential-energy distribution as criteria for the assignment in this region. In Table 1 the vibration with the highest potential energy is also given at a stronger coupling. The strong overlapping of the bands below 300 cm^{-1} and the uncertain determination of the depolarization ratio do not allow a reliable assignment in this region.

The deformation-vibration region between 700 and 200 cm^{-1} is the most sensitive part of the spectrum for the distinction of several conformers. There are 11 lines in this region of the Raman spectrum, and three bands and shoulders at 561, 511, and 495 cm^{-1} in the i.r. spectrum of the liquid. Bands lower than 200 cm^{-1} arise after cooling or crystallization. Since only 11 fundamentals are expected in this region for one conformer, we conclude that at least two conformers are present in the liquid state. Moreover, since the Raman line at 691 cm^{-1} as well as the i.r. band at 685 cm^{-1} vanish on cooling the liquid, it seems that a third conformer is possible. The most important evidence for the existence of two or more conformers is that a few bands present in the spectra of the liquid or the supercooled liquid (the Raman lines at 691, 456, 358, 273, and 238 cm^{-1} and the i.r. bands and shoulders at 685, 665, 561, 511, 499, and 454 cm^{-1}) are absent from the spectra of the crystal.

A n.c.a. has been carried out using the *GF* matrix method,[35] and for the solution of the inverse eigenvalue problem the Becher–Mattes stepwise-coupling method [36] was employed. The divinyl sulphone molecule was assumed to have C_{2v} (*anti-anti*) symmetry, in order to reduce the degree of the secular equation. The bond lengths and angles are given in the electron-diffraction section. The C–S–C bond angle was taken as 104.6°. The calculated

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bond force constants are compared with corresponding values for divinyl sulphide,[29] dimethyl sulphide,[37] dimethyl sulphone,[37] and ethylene [38] in Table 3.

TABLE 3

Force constants (mdyn Å^{-1})

Force constant	$S(CH_2=CH)_2$ [a]	$(CH_2=CH)_2SO_2$ [b]	SMe_2 [c]	Me_2SO_2 [c]	Ethylene [d]
f_{CH}	5.33	5.45			
f_{CH_2}	5.45	5.47			
f_{CH_3}			4.85	4.98	
f_{CC}	8.37	8.61			9.21
f_{CS}	3.22	3.89	3.19	3.25	
f_{SO}		8.89		9.61	
$f_{SO/SO}$		−0.5		−0.6	

[a] Ref. 29. [b] Present work. [c] Ref. 37. [d] Ref. 38.

The frequencies for the three isomers of symmetry C_2, C_s, and C_1 were calculated using the force field obtained by means of the above symmetry. The differences between equivalent frequencies of the different isomers are too small to support a reliable assignment.

ELECTRON DIFFRACTION

The source of the sample was the same as in the vibrational spectroscopic analysis. The electron-diffraction patterns were obtained with the Budapest EG-100A apparatus.[39,40] The temperature of the so-called membrane-nozzle system was *ca.* 100—108 °C during the exposures. Other experimental conditions and the procedure for data reduction were essentially the same as in some of the other studies mentioned above.[2,5,6] The ranges of intensity data used were $2.0 \leqslant s \leqslant 14.0$ Å^{-1} (Δs 0.125 Å^{-1}) and $6.5 \leqslant s \leqslant 36.5$ Å^{-1} (Δs 0.25 Å^{-1}) for the 50- and 19-cm camera ranges, respectively. The total experimental intensity values have been deposited as Supplementary Publication No. SUP 22250 (3 pp.).* The molecular intensities are shown in Figure 3. The experimental radial distribution (Figure 4) provided some valuable direct information on the S–C bond and evidence for two coexisting conformers since the slight maxima at *r ca.* 4.55 and 4.85 Å can be interpreted only as contributions from the rotation-dependent $C_\beta \cdots C_\beta$ distances.

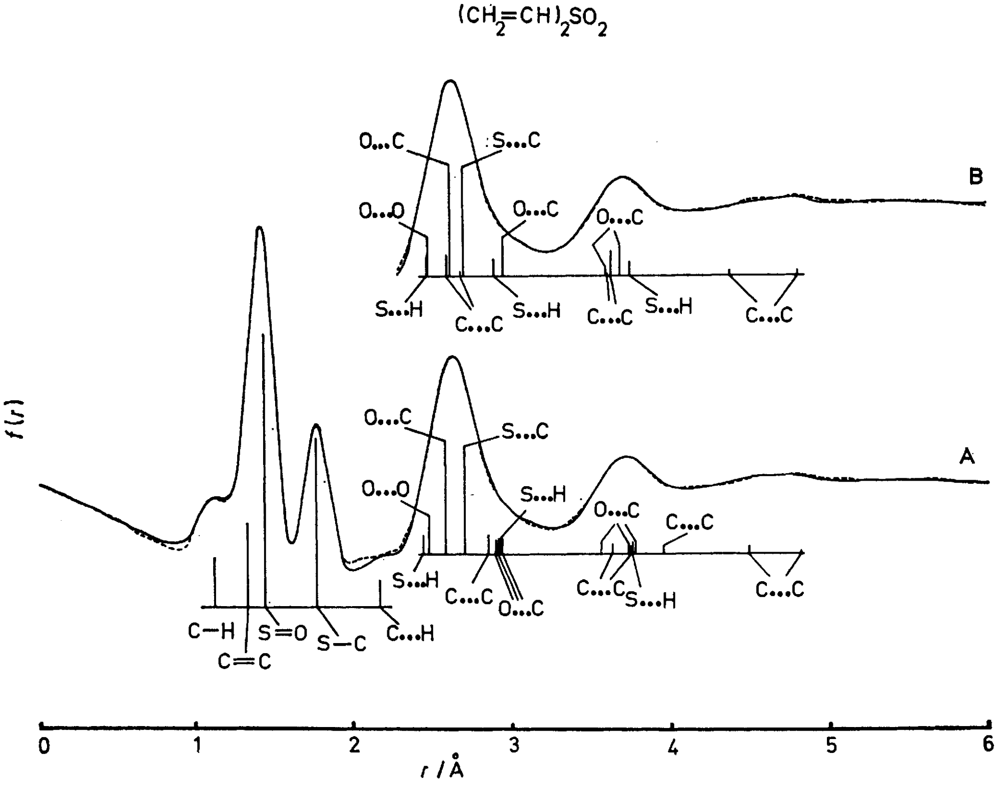

FIGURE 4 Experimental (— — —) and theoretical (——) radial distributions $f(r)$ corresponding to columns B and A of Table 4. Vertical bars represent contributions from some of the interatomic distances

The molecular models considered in the structure refinement were characterized by the independent geometrical parameters listed in Table 4. Thus mean values of the length and vibrational amplitude (l) were determined for the C–H bonds. The bonds around the sulphur atom retained C_{2v} symmetry. The geometrical parameters were assumed to be the same in the different conformers except for the angles of rotation. Since some rotation-independent non-bonded distances, *e.g.* $r(O \cdots O)$ or $r(O \cdots C)$, have been observed to be nearly constant (2.485 and 2.61 Å, respectively) in a relatively large series of simple sulphone

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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molecules, it was convenient to use them as independent geometrical parameters. The experimental radial distribution and structural data on analogous systems provided data for the trial structures. The least-squares method based on the molecular intensities[41] was used for the structure refinement. For the expression of the form in which the molecular intensities were used see ref. 5. The coherent and incoherent scattering factors were taken from refs. 42 and 43, respectively.

TABLE 4

Results of electron-diffraction refinements[a]

	Set A: $C_2 + C_1$ r_a	Set A: $C_2 + C_1$ l	Set B: $C_2 + C_s + C_1$ r_a	Set B: $C_2 + C_s + C_1$ l
(*a*) Independent distances[b]				
S=O	1.438 4(4)	0.036[c]	1.438 3(4)	0.036[c]
S–C	1.769 1(9)	0.054(1)	1.767 5(9)	0.053(1)
C=C	1.332(2)	0.040[c]	1.332(2)	0.040[c]
C–H	1.118(3)	0.065(3)	1.121(3)	0.065(3)
O · · · O	2.485[c]	0.069[c]	2.485[c]	0.069[c]
O · · · C	2.591(1)	0.064(2)[d]	2.631(2)	0.102(2)[j]
S · · · C	2.714(2)	0.059[d]	2.710(4)	0.097[j]
C · · · H	2.167(6)	0.100[c]	2.151(7)	0.100[c]
(*b*) Dependent angles[b]				
O=S=O	119.49(4)		119.50(3)	
O=S–C	107.30(4)		109.89(6)	
C–S–C	107.7(2)		95.0(3)	
S–C=C	121.5(1)		121.2(2)	
C=C–H	124.2(4)		122.3(4)	
(*c*) Dependent distances[b]				
C · · · C	2.856(4)	0.058[c]	2.606(6)	0.058[c]
S · · · H	2.451(6)	0.097[c]	2.478(5)	0.097[c]
S · · · H	3.773(2)	0.096[c]	3.763(2)	0.096[c]
S · · · H	2.942(7)	0.141[c]	2.904(6)	0.141[c]
(*d*) Conformer C_2				
α	0.31(8)[e]		0.40[c]	
ϕ_1	76(3)[f]		60[c]	
ϕ_2	76[f]		60[c]	
O · · · C	2.913(4)	0.185(13)[g]	2.960(4)	0.182(17)[k]
O · · · C	3.737(9)	0.097(12)[h]	3.696(2)	0.146(5)[l]
C · · · C	3.75(2)	0.117[h]	3.638(6)	0.146[l]
C · · · C	4.83(3)	0.070[c]	4.818(5)	0.046(25)
(*e*) Conformer C_s				
α	0		0.40[c]	
ϕ_1			300[c]	
ϕ_2			60[c]	
O · · · C			3.696(2)	0.146[l]
O · · · C			2.960(4)	0.182[k]
C · · · C			3.638(6)	0.146[l]
C · · · C			4.395(6)	0.130[l]
(*f*) Conformer C_1				
α	0.69[e]		0.20[c]	
ϕ_1	272(3)		60[c]	
ϕ_2	48(3)		180[c]	
O · · · C	3.784(7)	0.097[h]	2.960(4)	0.182[k]
O · · · C	2.946(8)	0.185[g]	3.696(2)	0.146[l]
O · · · C	3.57(1)	0.065(14)[i]	3.610(2)	0.146[l]
O · · · C	2.925(5)	0.185[g]	3.610(2)	0.146[l]
C · · · C	3.64(2)	0.075[i]	3.638(6)	0.146[l]
C · · · C	3.96(1)	0.37(2)	2.686(8)	0.182[k]
C · · · C	4.50(3)	0.150[c]	3.615(9)	0.186[l]
k_{19}	2.82(3)		2.82(3)	
k_{50}	2.80(2)		2.81(2)	
R	0.065		0.065	

[a] r_a and l in Å, angles in °. Values in parentheses are standard deviations from the least-squares refinement and refer to the last digit. α is the mol fraction of the conformer, k_{50} and k_{19} are the scale factors for the two camera ranges, and $R = \{\Sigma[M^E(s) - M^T(s)]^2W(s)/\Sigma[M^E(s)]^2W(s)\}^{\frac{1}{2}}$ where superscripts E and T indicate experimental and theoretical molecular intensities. [b] Common for the two (A) or three (B) conformers. [c] Fixed parameter. [d–l] Groups of parameters.

Mixtures of models having C_s and C_2 symmetry were chosen to reproduce the features assigned to the $C_\beta \cdots C_\beta$ distances in the experimental radial distribution. These features were subsequently found to correspond to two of the forms suggested by the CNDO/2 calculations. The third, less symmetric (C_1), conformer was added only after the semiempirical calculations. This somewhat improved the agreement between calculated and experimental data. Refinement of the relative abundances of the conformers was possible only when certain geometrical and vibrational parameters were frozen. In such cases, however, the results consistently indicated the two symmetric forms to be prevailing.

Another approach to improving the agreement was to remove the constraints on the rotation angles which had been applied to preserve symmetry. Unfortunately, some of the geometrical parameters were sensitive to changes in the conformational properties of the models used in the refinements. Further uncertainty was caused by the lack of knowledge concerning the mean amplitudes of vibration. Two sets of structural parameters were selected to characterize the results obtained in various refinement schemes (Table 4). In set A only C_2 and C_1 conformers were present, but form C_1 as obtained in the refinement could be considered as a distorted C_s. Set A was also characterized by l values for non-bonded distances around the sulphur atom which were very similar to those calculated for analogous molecules (*e.g.* ethenesulphonyl chloride[10]). The other set (B) was obtained for a model containing three forms (C_2, C_s, and C_1) and was characterized by somewhat larger than expected l values for the non-bonded distances around the sulphur atom. The most important difference between sets A and B occurred in the C–S–C bond angles (107.7 and 95.0°, respectively). It is not possible to choose between these two parameter sets on the basis of statistical criteria. Set A may be preferred on the basis of somewhat more realistic l values and stereochemical considerations, *viz.* that 95° seems to be too small for divinyl sulphone when compared with analogous molecules.

Table 4 contains the standard deviations from the least-squares refinements. Our estimates for the total errors include the standard deviations from the least-squares refinements multiplied by $3^{\frac{1}{2}}$ for data correlation, and 0.2% experimental scale error for the distances, and the variations in the parameters occurring when the assumed values of $r(O \cdots O)$ were changed to cover the interval 2.470—2.500 Å. Thus we have r_a(S=O) 1.438 ± 0.003, r_a(S–C) 1.769 ± 0.004, r_a(C=C) 1.332 ± 0.004, and r_a(C–H) 1.118 ± 0.006 Å, O=S=O 119.5 ± 1.2 and S–C=C 121.5 ± 0.3°.

DISCUSSION

The bond lengths of divinyl sulphone are well determined and show no unusual features. The S=O bond is relatively long compared with other sulphones and is well correlated with the relatively small stretching frequencies. Recently, the revised empirical relations (1) and (2) were established[17] between geometrical and vibrational parameters of the SO_2 groups. The values 1.440 ± 0.004

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and 1.445 ± 0.005 Å can be estimated for r_g(S=O) from (1) and (2), respectively. The S–C bond length (1.769 ±

$$\log \nu_{asym}(S{=}O) = -4.30 \log r_g(S{=}O) + 3.801 \quad (1)$$

$$\log \nu_{sym}(S{=}O) = -3.51 \log r_g(S{=}O) + 3.612 \quad (2)$$

0.004 Å) differs very slightly from those in many other sulphones, *e.g.* Me_2SO_2 (1.771 ± 0.004) or $MeSO_2Cl$ (1.763 ± 0.005 Å). However, it is considerably shorter in ethenesulphonyl chloride (1.744 ± 0.005 Å).[10] This, together with the observed (with a large uncertainty) lengthening of the C=C bond in CH_2=$CHSO_2Cl$ may indicate greater delocalization. The C=C bond in divinyl sulphone is essentially the same as in ethylene.[25]

The value given for the bond angle O=S=O is based on the r(S=O) bond length determined from the relation angle O=S=O = 2 arcsin[(2.485/2)/r(S=O)] since the O · · · O distance is nearly constant [2,15] at *ca.* 2.485 Å in a relatively large series of sulphones, as determined mainly from microwave spectra. Another estimate can be made according to the empirical relation [17] log (angle O=S=O) = −1.929 log r(S=O) + 2.38 based mainly on electron-diffraction data, yielding 118.9 ± 0.6°. Thus the O=S=O angle of divinyl sulphone is felt to be well established. On the other hand, it was not possible to determine unambiguously the C–S–C bond angle. Neither of the values of 108 and 95° can be rejected with confidence. The former is one of the largest X–S–Y angles observed in XSO_2Y sulphones. An even larger N–S–N angle was determined in $SO_2(NMe_2)_2$ (112.6 ± 0.4° in the gas phase [3] and 110.5 ± 0.4° in the crystal phase [44]). According to the valence-shell electron-pair repulsion (VSEPR) model [45] the relative magnitude of the bond angles around the sulphur atom in sulphones is expected to be X–S–Y < X–S=O(Y–S=O) < O=S=O. This is indeed the case for all the sulphones studied so far in the vapour phase, except for $SO_2(NMe_2)_2$, and possibly divinyl sulphone, although even a C–S–C angle of 107.7° compared with 107.3° for O=S–C cannot be considered to be in serious disagreement with the VSEPR model. The value of 95° for C–S–C would fit perfectly the above relation between the bond angles. However, it would be the smallest X–S–Y bond angle among the XSO_2Y sulphones and would thus contradict other postulates (*e.g.* concerning the effects of ligand electronegativities) of the VSEPR model. The bond angle S–C=C is well determined, and is the same as that in CH_2=$CHSO_2Cl$ (121.3 ± 1.7°).[10]

The conformational properties of divinyl sulphone are not well determined. At least two forms are present in the vapour but there may be three or more. Perhaps it is reasonable to state that there is a tendency for the C=C double bond to approach a position in which it nearly eclipses another bond. A similar tendency was observed in CH_2=$CHSO_2Cl$.[10] From the vibrational analysis of divinyl sulphone it may be concluded that at least two conformers coexist in the liquid and supercooled state, while only one persists after crystallization. Conclusions on the symmetry of the several conformers cannot be drawn.

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