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On the Molecular Structure of Bis(trichloromethyl) Sulfone from Electron Diffraction and Vibrational Spectra of Bis(trichloromethyl) and Bis(tribromomethyl) Sulfone

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Gaseous $(CCl_3)_2SO_2$ was studied by electron diffraction at a nozzle temperature of 100 °C, while $(CBr_3)_2SO_2$ decomposed at a temperature of 140 °C.

Infrared spectra of the two sulfones as pellets, as melts and as solutes in various solvents were recorded in the region 4000–50 cm^{-1}. Raman spectra of the sulfones as polycrystalline solids, as saturated solutions in benzene and carbon tetrachloride, as a melt ($(CCl_3)_2SO_2$) and as a single crystal ($(CBr_3)_2SO_2$) were obtained. The electron diffraction analysis of $(CCl_3)_2SO_2$ yielded C_2 symmetry with the two CCl_3 groups twisted in the opposite direction from the C_{2v} position by 12° and tilted by 5° from each other. The most important geometrical data in terms of r_g and $\angle_\alpha$ parameters are: S=O 1.419(3) Å, S–C 1.894(5) Å, C–Cl 1.757(4) Å, ∠O–S–C 106.5(3)°, ∠C–S–C 109.8(4)°, ∠O–S–O 120.8(1.0)°, ∠Cl–C–Cl 110.2(1)°.

For both compounds the vibrational spectra could be interpreted either in terms of C_{2v} or C_2 symmetry. Apart from the two torsional modes expected below 50 cm^{-1}, the fundamentals for both compounds have been assigned.

The molecular structures of a relatively large series of sulfone derivatives with various ligands have recently been determined.[1,2] The observed structural variations were interpreted primarily in terms of the valence shell electron pair repulsion model.[2,3] The molecular structures and vibrational spectra of halogenated sulfones $(CX_3)_2SO_2$ seemed interesting for testing these observations on molecules with relatively bulky substituents.

EXPERIMENTAL

Commercial samples (K&K ICN Pharmaceuticals) were used in the electron diffraction, infrared and Raman experiments without further purification. Gas chromatographic analysis revealed that both compounds were more than 99 % pure.

The electron diffraction patterns of both compounds were recorded on the Balzers Eldigraph KD-G2 in Oslo. For $(CCl_3)_2SO_2$ (TCMS) the standard experimental conditions [4,5] were applied with a nozzle temperature of 100 °C. The reduced molecular intensities are shown in Fig. 1. Neither the experiment nor the structure analysis showed any indication of decomposition of the TCMS sample during the electron diffraction experiment. For $(CBr_3)_2SO_2$ (TBMS) both the standard [4,5] and the low pressure [6] techniques were used for recording the electron diffraction pattern, the latter in order to keep the experimental temperature as low as possible to prevent decomposition of the compound in the vapour phase. Nevertheless, the data analysis of the bromine compound showed a considerable degree of decomposition in the vapour. Since we were not able to overcome this difficulty, the molecular geometry of TBMS could not be determined.

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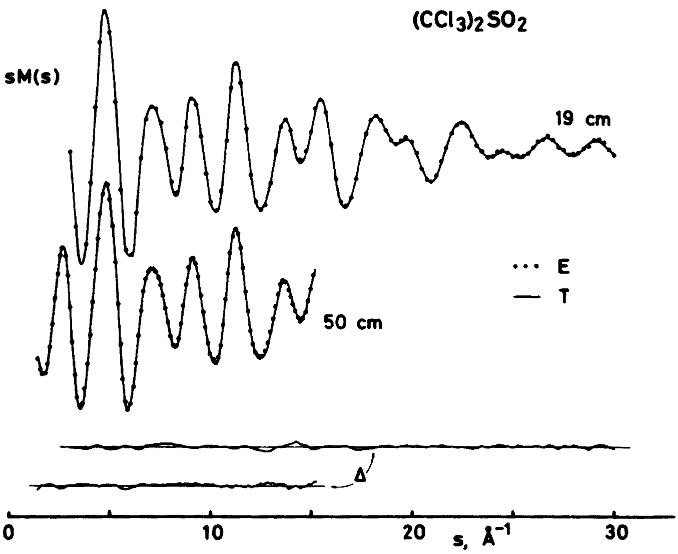

Fig. 1. Experimental (E) and theoretical (T) molecular intensities and their differences (△D) for $(CCl_3)_2SO_2$.

The infrared spectra were recorded with a Perkin-Elmer model 225 (4000–200 cm^{-1}) spectrometer and an evacuable, fast scan Fourier transform spectrometer (Bruker 114c) (600–50 cm^{-1}). Crystalline solids of TCMS and TBMS were recorded as KBr, KI and polyethylene pellets. Solutions in CCl_4, CS_2, C_6H_6 and C_6H_{12} were recorded in sealed cells with windows of KBr and polyethylene. Both compounds were recorded as melts between CsI plates, TCMS was perfectly stable as a melt. For TBMS a slight decomposition occurred at 100 °C, at 150 °C the spectrum changed considerably in 30 min.

The Raman spectra were recorded on a modified Cary 81 spectrometer, excited by an argon ion laser (CRL 52 G) using the 5145 Å line for excitation.

RESULTS

Structural analysis. The molecular model and numbering of the atoms in TCMS are shown in Fig. 2. Since TBMS decomposed during the ED experiments, no structural results for this compound were obtained. Although in similar symmetrically substituted X_2SO_2 sulfones the molecular symmetry is usually C_{2v} (either determined or assumed) with such bulky ligands as CCl_3 and CBr_3, we did not feel justified in making such an assumption. The IR and Raman spectra of TCMS and TBMS could be reasonably well interpreted in terms of C_{2v} symmetry, but small deviations due to arrangements of the trichloromethyl groups could not be excluded.

Keeping these arguments in mind for the electron diffraction structure refinement, the rotation of the CCl_3 groups around the S–C axis as well as the tilt of the trichloromethyl groups from the same axis were taken into account. In this way the C_{2v} symmetry was decreased to either C_2, C_s or even C_1. The only assumptions regarding the molecular geometry were: (i) The OSO plane bisects the CSC plane, (ii) The local symmetry of the CCl_3 groups is C_{3v}.

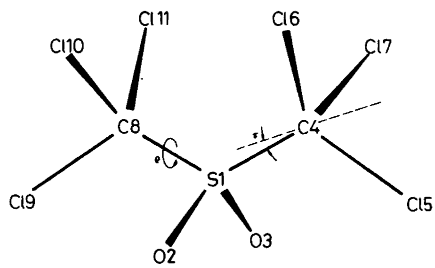

Fig. 2. C_{2v} symmetry molecular model for $(CCl_3)_2SO_2$.

The geometry of the molecule was then determined by the following eight parameters: $r(S=O)$, $r(C-Cl)$, $r(S-C)$, $\angle O-S-O$ (or $r(O\cdots O)$, see later), $\angle S-C-Cl$, $\angle O-S-C$, ρ (rotation angle of the CCl_3 groups around the S−C axis; the angle is zero in the C_{2v} position shown in Fig. 2) and τ (tilt of the CCl_3 groups; *i.e.* rotation of CCl_3 in the CSC plane around an axis through C and perpendicular to the CSC plane; the positive sign of this angle means the two CCl_3 groups move away from each other).

Our experience with the structure analysis of simple sulfones [7] showed that one of the most sensitive and not very well determined parameters is the O=S=O angle. At the first stage of the structure refinement we therefore made use of the observed invariance of the $r(O\cdots O)$ distances in the sulfone series [1,2] and kept it at 2.485 Å. In the final stage of the refinement, however, this constraint was removed. Although the O···O non-bonded distance decreased considerably (about 0.02 Å) this parameter influenced the other structural parameters only within their experimental errors.

Normal coordinate analysis was carried out based upon the experimental vibrational frequencies. Since the two lowest torsional frequencies were not observed in the spectra and the calculated vibrational amplitudes (both parallel and perpendicular) are quite sensitive to the torsional force constant, we proceeded in the following way. The value of the torsional force constant was varied in a wide range 0.005−0.030 mdyn Å rad^{-2} and the calculated parallel mean vibrational amplitudes were compared with the experimental values. The set closest to the experimental one and corresponding to τ=0.025 mdyn Å rad^{-2} was selected and its perpendicular amplitudes were used to transform the r_a to r_α parameters. The least squares refinement of the molecular structure was carried out on the r_α structure. Although the large amplitude torsional motion of the CCl_3 groups introduces some uncertainty into these correction terms, our test calculations for this molecule as well as our experience with other CCl_3 derivatives, *viz.* CCl_3SO_2Cl,[11] showed no appreciable bond angle changes in terms of r_a/r_α refinements.

The best agreement with the experimental data was achieved with a C_2 symmetry model, in which the two CCl_3 groups were rotated 12° in the opposite direction from the C_{2v} position shown in Fig. 2 and tilted away from each other about 5°.

The experimental radial distribution curve and the difference between the experimental and the theoretical curve for the final C_2 symmetry model is shown in Fig. 3. The positions of the interatomic distances with their relative weights are also indicated.

The geometrical parameters determined for TCMS together with the experimental and calculated vibrational amplitudes are collected in Table 1.

Spectral interpretations. IR spectrum of a capillary film of molten TCMS between CsI plates at

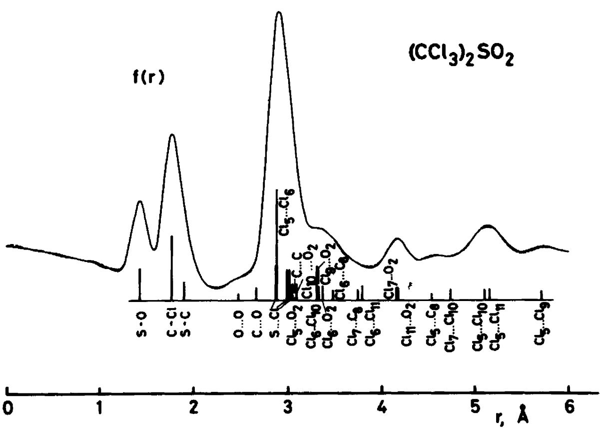

Fig. 3. Experimental (E) and theoretical (T) radial distribution curves for the final C_2 symmetry model of $(CCl_3)_2SO_2$.

Table 1. Structural parameters of $(CCl_3)_2SO_2$.

Parameters	$r_a, \angle_\alpha$ Å, degree	l(ED) Å	l(calc) Å	K(calc) Å
Independent				
S=O	1.418(3)	0.038(2)	0.036	0.0085
C−Cl	1.756(4)	0.046(2)	0.055	0.0154
S−C	1.892(5)	0.059(6)	0.056	0.0049
O···O	2.464(15)	0.099(16) [c]	0.060	0.0124
O−S−C	106.5(3)			
S−C−Cl [a]	108.8(1)			
ρ [b]	12.4(4)			
τ [b]	4.9(3)			
Dependent				
O···C	2.665(8)	0.122 [c]	0.084	0.0081
S···Cl_5	2.873(10)	0.091(2) [d]	0.094	0.0121
Cl_5···Cl_6	2.878(6)	0.074 [d]	0.077	0.0224
S···Cl_7	2.989(6)	0.080 [e]	0.078	0.0119
S···Cl_6	3.022(7)	0.077(3) [e]	0.076	0.0115
Cl_5···O_2	3.052(13)	0.168 [e]	0.163	0.0145
C···C	3.091(9)	0.099 [l]	0.099	0.0028
Cl_{10}···O_2	3.092(13)	0.152 [e]	0.151	0.0146
Cl_6···Cl_{10}	3.309(14)	0.271 [f]	0.285	0.0204
Cl_9···O_2	3.326(12)	0.143 [f]	0.157	0.0130
Cl_6···O_2	3.371(12)	0.137(6) [f]	0.151	0.0125
Cl_6···C_8	3.482(11)	0.163 [f]	0.177	0.0092
Cl_7···C_8	3.746(11)	0.151(16) [g]	0.178	0.0072
Cl_6···Cl_{11}	3.799(20)	0.295 [g]	0.318	0.0082
Cl_7···O_2	4.160(9)	0.090(5) [h]	0.081	0.0106
Cl_{11}···O_2	4.168(9)	0.094 [h]	0.084	0.0103
Cl_5···C_8	4.539(12)	0.113(13) [i]	0.106	0.0037
Cl_7···Cl_{10}	4.740(18)	0.269 [i]	0.258	0.0033
Cl_5···Cl_{10}	5.112(12)	0.173(6) [j]	0.197	0.0053
Cl_5···Cl_{11}	5.156(12)	0.141 [j]	0.165	0.0040
Cl_5···Cl_9	5.726(19)	0.129(14) [k]	0.148	0.0045
O−S−O	120.8(10)			
C−S−C	109.8(3)			
Cl−C−Cl	110.2(1)			

[a] Mean value, refers to the untilted position of the CCl_3 groups. [b] For definition, see the text. [c–k] Mean amplitudes refined in groups. [l] Fixed at the calculated value.

60 °C is shown in Fig. 4, while a far IR spectrum of a saturated solution in cyclohexane is presented in Fig. 5. A Raman spectrum of TCMS melted in an evacuated tube is shown in Fig. 6.

For TBMS IR spectra of KBr and polyethylene pellets are shown in Figs. 7 and 8, respectively. A far IR spectrum of TBMS in benzene solution is given in Fig. 9, whereas a Raman spectrum of a single crystal is presented in Fig. 10. The wave numbers of the observed IR and Raman bands of TCMS and TBMS are listed in Tables 2 and 3, respectively.

As discussed above, the present compounds can have C_{2v}. C_2, C_s or C_1 symmetry. In principle it should be possible to determine the molecular symmetry from the vibrational spectra. However, no vapour spectra could be recorded due to the very low volatilities. Moreover, there was a

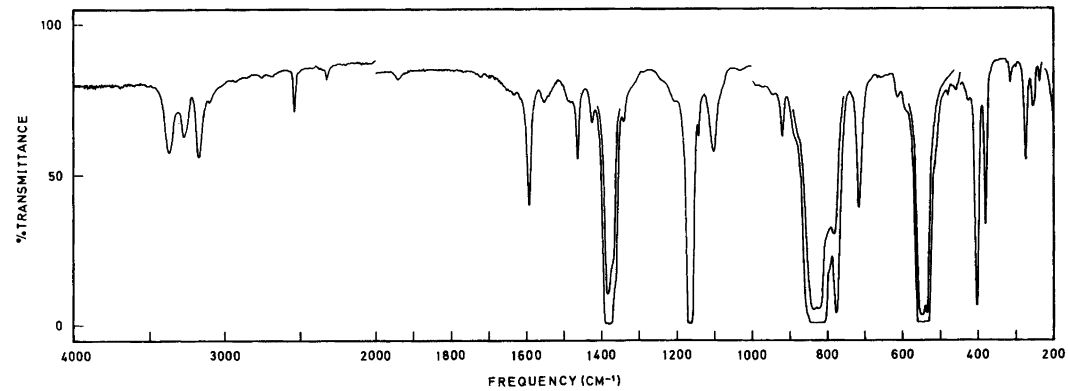

Fig. 4. Infrared spectrum of $(CCl_3)_2SO_2$ as a capillary melt at *ca.* 70 °C between CsI plates.

considerable overlap of bands particularly in the low frequency region, making the spectral data incomplete. For both compounds the IR and Raman data could be interpreted in terms of C_{2v} symmetry (9 a_1, 5 a_2, 7 b_1 and 6 b_2) as previously done for dimethylsulfone [8] and diphenylsulfone.[9] The a_2 modes should in this case be depolarized in Raman and inactive in IR, and very few such cases were observed in the spectra. Preliminary force constant calculations revealed that practically all the a_2 modes overlapped other modes. Both for TCMS and TBMS the spectra were easily interpreted in terms of C_{2v} symmetry and the number of polarized Raman bands agreed quite well with the 9 a_1 modes expected.

Since the results obtained from electron diffraction favoured C_2 symmetry for TCMS (see above), we have interpreted the spectra of both compounds in terms of this symmetry. The vibrational fundamentals should divide themselves between 14 *a* and 13 *b*, the former should be polarized, the latter depolarized in Raman. The assigned fundamentals for TCMS and TBMS are listed in Table 4, together with the calculated frequencies.

As is apparent from Table 4, the majority of

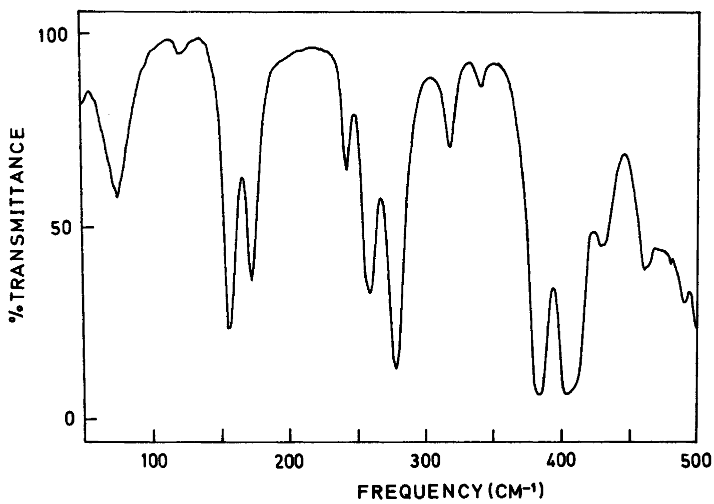

Fig. 5. Infrared spectrum of $(CCl_3)_2SO_2$ as a saturated solution in C_6H_{12}, 1 mm polyethylene cell, 6 μm beamsplitter.

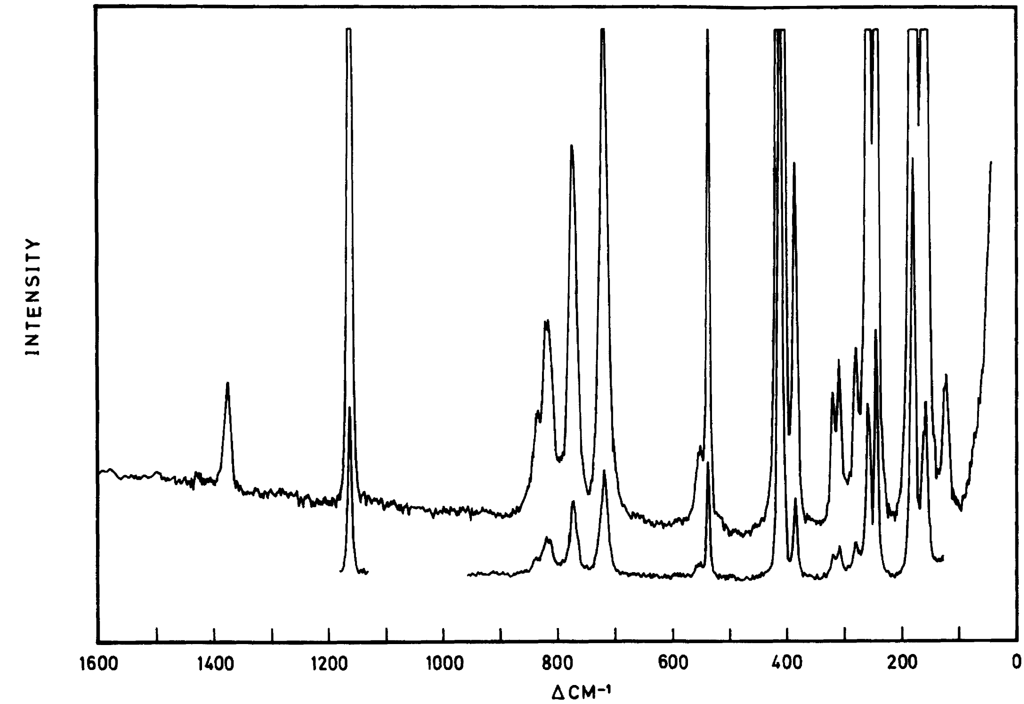

Fig. 6. Raman spectrum of $(CCl_3)_2SO_2$ as a melt at *ca.* 70 °C.

the *a*-fundamentals of TCMS and TBMS were experimentally observed as polarized in Raman. Since the polarization ratios of *a*-fundamentals can lie close to 3/4, the apparent depolarized bands assigned as ν_7 and ν_8 of TCMS and as ν_4 of TBMS represent no serious objection to the interpretations. On the other hand, no polarized Raman bands were assigned as *b*-fundamentals except those overlapping *a*-fundamentals.

Some of the fundamentals are good group frequencies like ν_1, ν_5 and ν_{15} connected with O=S=O, symmetric stretch, bend and asymmetric stretch, respectively. Various correlations between the wave numbers of these modes and

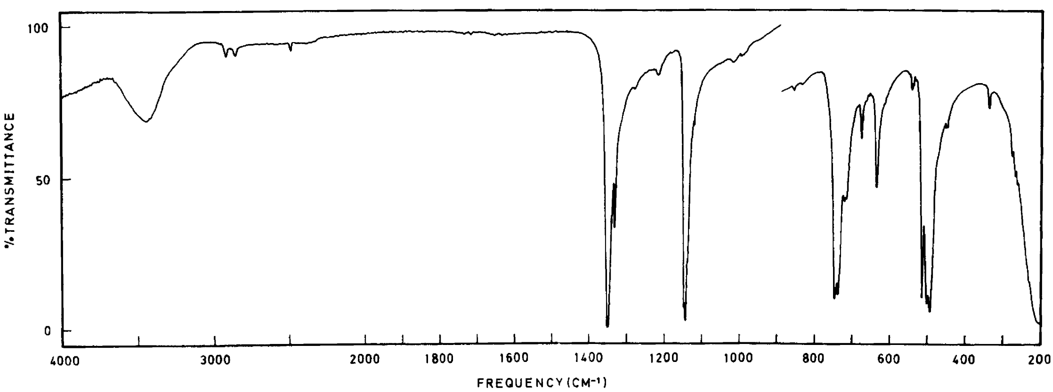

Fig. 7. Infrared spectrum of $(CBr_3)_2SO_2$ in a KBr pellet.

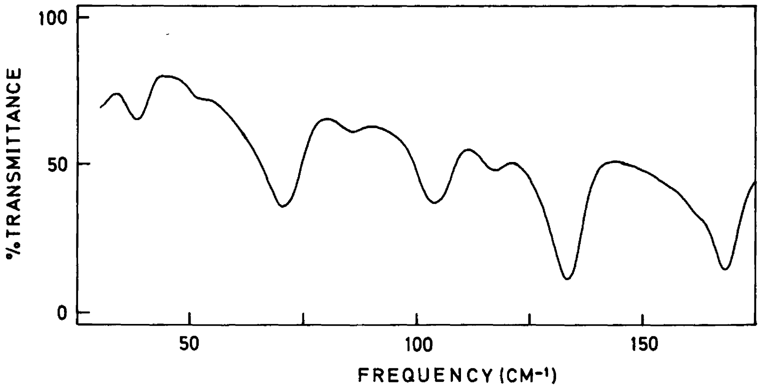

Fig. 8. Infrared spectrum of $(CBr_3)_2SO_2$, 50 mg in a polyethylene pellet, 12 μm beamsplitter.

the O=S=O bond angle and bond distance have been proposed.[1,2] The six C-halogen stretching modes for thhese compounds are spread over a large frequency region and are mixed with C−S stretch. The various CX_3 bending modes give rise to a number of distinct IR and Raman bands below *ca.* 380 cm^{-1} for TCMS and 240 cm^{-1} for TBMS. Although the positions of the torsional frequencies ν_{14} and ν_{27} are very uncertain, they are probably situated below 35 cm^{-1} for both compounds. With local C_{3v} symmetry they are probably quite weak both in IR and in Raman, and it is not surprising that they remain unobserved.

As is apparent from Table 4, the agreement between the observed and calculated fundamentals was quite satisfactory. The result of the force constant calculations was a great help

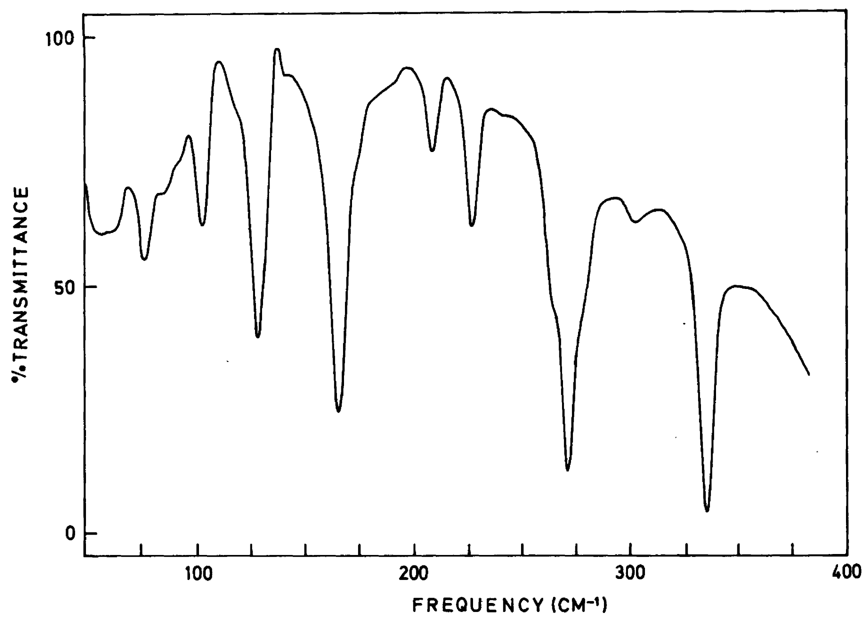

Fig. 9. Infrared spectrum of $(CBr_3)_2SO_2$ as a saturated solution in C_6H_6, 1 mm polyethylene cell, 3 μm beamsplitter.

Table 2. Infrared and Raman spectral data [a] for bis(trichloromethyl) sulfone (TCMS).

IR				Raman		Interpretation
Melt	Solution		Solid Pellet	Melt	Solution CCl_4	
	CCl_4 [b]	C_6H_6				
1464 m [c]	1470 m					
				1445 vw P?	1445 vw	
1426 w						
1382 vs,bd	1392 vs		1384 s	1384 w D	1389 w D	ν_{15} *b*
1366 m,sh	1373 m		1366 w,sh			
1340 vw			1341 vw,bd?			
1167 s	1168 s		1268 s	1168 s P	1169 s P	ν_1 *a*
1161 m,sh	1165 m		1266 w,sh			
1143 vw			1133 vw			
1104 vw	1108 vw,bd		1105 vw,bd			
947 vw	944 vw					
921 w	921 w		922 vw			
886 w	888 w					
858 s,sh	858 s,sh		860 vw,sh		859 vw ?	
836 vs,bd	837 vs		836 s	836 w D	838 w D	ν_2 *a*, ν_{16} *b*
820 vs,bd	822 vs		821 ms,sh	821 w P	822 w P	ν_3 *a*
794 w					795 w,sh P?	ν_{17} *b*
778 s			777 mw	774 m D	778 m D	ν_{18} *b*
				755 vw D?	755 vw,sh	
717 m	719 m		718 mw	723 s,bd P	723 m,bd P?	ν_4 *a*
614 vw	615 vw					
592 vw	592 vw					
561 s,sh						
549 vs	554 vs		554 vs	555 w D	555 w D	ν_{19} *b*
	544 vw					
536 vs	536 s		538 vs	542 s P	540 m P	ν_5 *a*
512 w,sh	512 w,sh			517 vw P	520 vw P?	
481 vw						
458 vw	457 vw	459 m?				
					438 vw P?	
429 vw	418 w	426 m	428 vw	418 vs P	417 vs P	ν_6 *a*
406 s	404 s	410 s	406 s			ν_{20} *b*
383 s	384 s	386 vs	385 s	387 m D	387 m D	ν_{21} *b*
318 w		317 w	318 w	320 m D?		ν_7 *a*
302 vw?				308 m D?		ν_8 *a*
277 m	278 m	277 m	276 m	280 m D?	281 w D?	ν_{22} *b*
258 w	258 w	256 m	258 w	259 vs D	258 vs D	ν_9 *a*, ν_{23} *b*
253 vw,sh						ν_{24} *b*
241 vw	237 vw	241 w	243 w	245 vs P	245 vs P	ν_{10} *a*
	227 vw			225 vw?		
	172 m	173 m	172 m	180 vs P	180 vs P	ν_{11} *a*, ν_{25} *b*
	154 m	155 m	155 m	162 s D	158 s D	ν_{26} *b*
		120 w	118 w	122 m P	122 m P	ν_{12} *a*
		82 vw				
		73 w	74 m			ν_{13} *a*
			50 vw?			

[a] Data listed in the region 1500–40 cm^{-1}. [b] C_6H_{12} solution employed in the region 500–40 cm^{-1}. [c] Abbreviations used: s, strong; m, medium; w, weak; v, very; bd, broad; sh, shoulder; P, polarized; D, depolarized.

Table 3. Infrared and Raman spectral data [a] for bis(tribromomethyl) sulfone (TBMS).

IR		Raman			Interpretation
Solution CS_2 [b]	Solid Pellet	Solution CS_2	Solution C_6H_6	Solid	
1374 vs [c]	1353 vs	1374 m D	1376 m D	1351 m	ν_{15} *b*
	1344 vw?				
1358 m	1336 m				
	1151 s				
1156 vs	1146 vs	1155 s P	1156 s P	1150 s	ν_1 *a*
1149 m,sh	1141 m				
1132 vw	1123 vw		1124 vw?		
	1015 vw				
	857 vw				
784 w					
762 w					
	748 vs				
736 vs		736 m P	737 m P	742 m	ν_2 *a*, ν_{16} *b*
	739 vs				
	723 m			725 w	
720 m		718 m,bd D	718 m D		ν_3 *a*, ν_{17} *b*
	717 m			716 m	
675 w	678 w	675 m D?	678 m D?	678 m	ν_4 *a*
653 vw				656 vw	
637 m	638 m		638 w D?	642 w	ν_{18} *b*
548 vw	546 vw				
536 w	524 vw		534 vw?		
515 s	517 vs	516 w	517 w P?	518 m	ν_5 *a*
502 vs	503 vs	503 w D?	505 w D	505 vw	ν_{19} *b*
493 s	494 vs			493 w	
452 vw	453 vw				
		395 w,bd?			
334 w	340 w	333 w D	334 w D	342 m	ν_{20} *b*
277 vw,sh	281 w				ν_6 *a*
270 m	272 w	275 s P	277 s P	283 s	ν_7 *a*
262 w,sh	266 w	263 vs P	263 vs P	266 vs	ν_8 *a*, ν_{21} *b*
226 w	227 w	226 vs P	227 s P	229 s	ν_9 *a*
207 w	211 w	208 w D?	208 w D	213 w	ν_{22} *b*
				175 m,sh	ν_{23} *b*
165 m	168 m	163 s D	164 s D	165 s	ν_{10} *a*, ν_{24} *b*
	160 vw,sh?				
140 vw?	144 vw				
126 m	132 m	132 vw	132 vw?	133 vw	ν_{11} *a*
	116 vw	113 w P	113 w P	104 s	ν_{12} *a*
101 vw	103 w	100 vw,sh	100 vw D	119 m	ν_{25} *b*
81 vw	85 vw				ν_{26} *b*
61 vw,bd	69 m			67 w	ν_{13} *a*
	51 vw				
	37 w				

[a] Data listed in the region 1500–40 cm^{-1}. [b] C_6H_6 solution employed in the region 500–40 cm^{-1}. [c] Abbreviations: see footnote to Table 2.

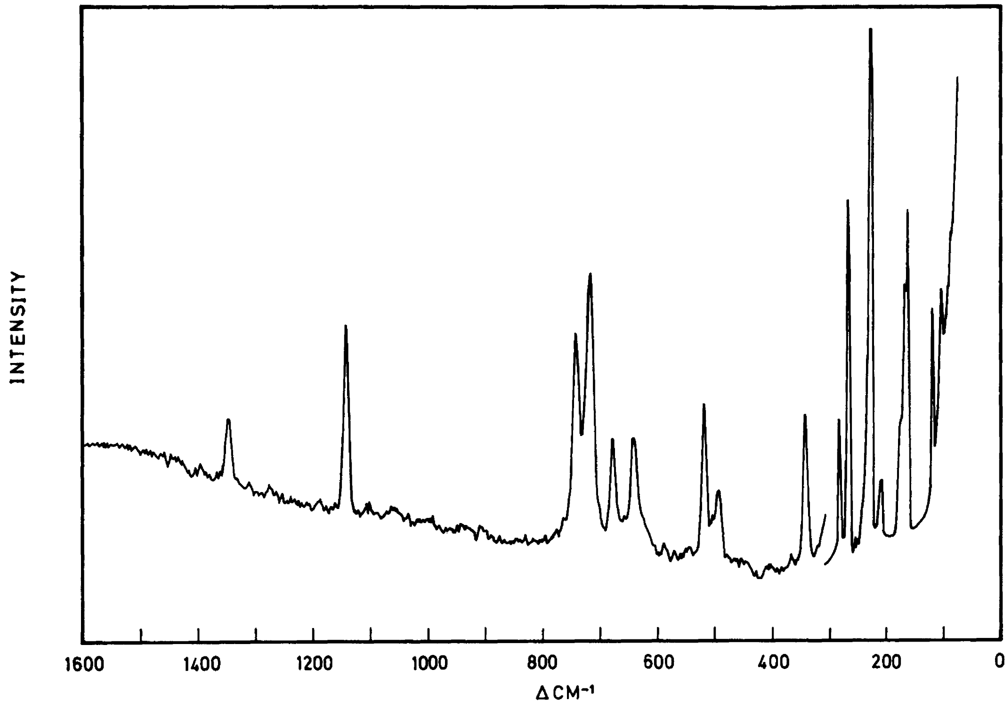

Fig. 10. Raman spectra of a single crystal of $(CBr_3)_2SO_2$.

Table 4. Observed and calculated fundamental vibrations of $(CCl_3)_2SO_2$ (TCMS) and $(CBr_3)_2SO_2$ (TBMS).

	TCMS			TBMS		
	Obs.	Calc.	Approx.description	Obs.	Calc.	Approx.description
[a]						
ν_1	1167	1158	SO_2 stretch	1156	1158	SO_2 stretch
ν_2	836 [a]	807	CCl_3 stretch	736 [a]	742	CBr_3 stretch
ν_3	820	803	CCl_3 stretch	720 [a]	729	CBr_3 stretch
ν_4	719	734	CS stretch	675	698	CS stretch
ν_5	536	554	OSO bend	515	537	OSO stretch
ν_6	418	419	CCl_3 stretch	277	296	CBr_3 stretch
ν_7	318	329		275	267	SO_2 twist
ν_8	308	326		263 [a]	235	
ν_9	258 [a]	250	SO_2 twist	226	178	
ν_{10}	245	242	CCl_3 def	165 [a]	170	CBr_3 def
ν_{11}	172 [a]	174		132	105	
ν_{12}	122	169		113	102	
ν_{13}	74	69	CSC bend	61	45	CSC bend
ν_{14}		39 [b]	torsion	–	–	torsion

b

ν_{15}	1382	1357	SO_2 stretch	1374	1356	SO_2 stretch
ν_{16}	836 [a]	785	CCl_3 stretch	736 [a]	759	CS stretch
ν_{17}	794	785	CCl_3 stretch	720 [a]	708	CBr_3 stretch
ν_{18}	778	757	CS stretch	637	693	CBr_3 stretch
ν_{19}	554	578	SO_2 wag	502	524	SO_2 wag
ν_{20}	404	407	CCl_3 stretch	334	297	SO_2 rock
ν_{21}	384	357	SO_2 rock	263 [a]	274	CBr stretch
ν_{22}	278	283		207	198	
ν_{23}	258 [a]	241		175	179	
ν_{24}	253	239	CCl_3 def	165 [a]	162	CBr_3 def
ν_{25}	172 [a]	171		101	113	
ν_{26}	154	146		81	103	
ν_{27}		54 [b]	torsion	–	–	torsion

[a] Used twice. [b] Estimated from the electron diffraction data (see text).

for the assignments.

The force field was evaluated from the spectroscopic data on dimethyl sulfone,[8] 1,1,1-trichloroethane [15] and 1,1,1-tribromoethane.[16] Since the CS distance in TCMS is lengthened by the halogen substitution, the force constant, K_{cs}, was estimated 10 % lower for TCMS than for dimethyl sulfone. The force field is listed in Table 5.

DISCUSSION

A relatively large body of experimental data has been accumulated on the geometries of sulfone derivatives.[1,2] The most noteworthy feature of the TCMS structure is the longest S–C bond in this series and the rather large C–S–C bond angle. The lengthening of the S–C bond from 1.76 to 1.86 Å in the CH_3SO_2Cl/CF_3SO_2Cl pair as well as in the CH_3SO_2Cl/CCl_3SO_2Cl pair has already been noted.[10,11] Substitution of one of the methyl groups of dimethyl sulfone, S–C 1.771(4) Å [12] by a chlorine barely influences the length of the remaining S–C bond in CH_3SO_2Cl, S–C 1.763(5) Å.[7] The S–C bond length of CCl_3SO_2Cl has been determined, unfortunately, with relatively large uncertainty. The origin of the CH_3SO_2Cl/CF_3SO_2Cl change has been examined in detail.[2] Semiempirical molecular orbital calculations in the CNDO/2 approximation [13] have agreed with the observed changes in bond length. They were attributed primarily to the difference between the electron withdrawing ability of the CF_3 group and the electron donating ability of the CH_3 group. The somewhat smaller C–S–Cl bond angle (98.7±0.4°) of CF_3SO_2Cl as compared with the analogous bond angle of CH_3SO_2Cl (101.0±1.4°) is consistent with what could be expected from the elec-

Table 5. Suggested valence force constants for $(CCl_3)_2SO_2$ (TCMS) and $(CBr_3)_2SO_2$ (TBMS).

Constant	Value [a] TCMS	TBMS
K_{CS}	3.00	3.00
K_{SO}	9.54	9.54
K_{CX} [b]	3.35	2.83
H_{CSC}	0.83	0.83
H_{OSO}	1.39	1.39
H_{CSO}	1.10	1.10
H_{SCX}	1.12	1.13
H_{XCX}	1.21	1.25
$F_{CX/CX}$	0.35	0.30
$F_{CS/CX}$	0.32	0.29
$F_{CS/CSO}$	0.19	0.19
$F_{CS/SCX}$	0.51	0.51
$F_{CX/SCX}$, $F_{CX/XCX}$	0.64	0.56
$F_{CSO/CSO'}$	0.21	0.21
$F_{CSO/C'SO}$	–0.19	–0.19
$F_{SCX/SCX}$, $F_{SCX/XCX}$	0.10	0.16
$F_{XCX/XCX}$		
$\tau_{torsion}$	0.025 [c]	

[a] Stretch and stretch–stretch force constants in mdyn $Å^{-1}$; bending and torsional force constants in mdyn Å rad^{-2} and stretch–bend force constants in mdyn · rad^{-1}. [b] X=Cl,Br. [c] Estimated from electron diffraction data (see text).

tronegativity rule of the VSEPR model. This trend is also consistent with the supposedly greater double bond character of the S–C bond *versus* that in CF_3SO_2Cl. If the C–S–C angles of $(CH_3)_2SO_2$ and TCMS are compared, similar reasoning would suggest a smaller angle in TCMS which is clearly not the case. The only explanation may be found in the strong steric effects caused by the large space requirements of the two trichloromethyl groups in TCMS. The Cl_6---Cl_{10} non-bonded distance is 3.309(14) Å, considerably smaller than the sum of the van der Waals radii (3.60 Å). A more typical C–S–C angle would correspond to yet a smaller Cl---Cl non-bonded distance (*e.g.* 100° to 2.96 Å). The C–S–C bond angle in this molecule is, in fact, so large that the relationship $<XSY \ll X(Y)SO \ll OSO$ generally observed for XSO_2Y sulfones is not valid here. A similarly large XSX bond angle was observed for only one molecule, *viz.* N–S–N 110.5±0.4° in $(CH_3)_2NSO_2N(CH_3)_2$,[14] also with unusually large ligands on the SO_2 group.

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