X-Ray Study at Room Temperature of 1,2-Bis(phenylsulfonyl)ethane

F. Mo and G. Thorkildsen*

Institutt for røntgenteknikk, Universitetet i Trondheim-NTH,
N-7034 Trondheim-NTH, Norway

Mo, F. and Thorkildsen, G., 1986. X-Ray Study at Room Temperature of 1,2-Bis(phenylsulfonyl)ethane. – Acta Chem. Scand. A 40: 481–488.

1,2-Bis(phenylsulfonyl)ethane, $Ph-SO_2(CH_2)_2SO_2-Ph$, was studied by X-ray diffraction at 293K. The space group is $P2_1/n$, $a = 8.518(2)$, $b = 10.187(2)$, $c = 9.084(2)$ Å, $\beta = 115.99(1)°$ and $Z = 2$. Two equivalent sets of counterdata were collected to a maximum $(\sin\theta)/\lambda = 0.923$ Å^{-1}. Corrections for losses due to counting coincidences, scan truncation and absorption were applied to the intensities before averaging. Least-squares refinements were carried out with various subsets of data. The aromatic $C-C$ distances expanded significantly with increasing low cut-off in $(\sin\theta)/\lambda$; the average value obtained at convergence $((\sin\theta)/\lambda > 0.65$ Å$^{-1})$, 1.3936(9) Å, lengthened to 1.401 Å when a correction for rigid-body motion was included. The $S-C$ bond lengths seemed rather insensitive to changes in $(\sin\theta)/\lambda$ cut-off. The O parameters did not reach convergence with this limited set of data. The present study confirmed previous observations that the $O-S-O$ and the average $C(central)-S-O$ bond angles in the fragment $-CH_2-SO_2-R$ are respectively 2° larger and 1–1.5° smaller when R = phenyl compared to R = methyl.

Crystallographic studies are in progress on small S-containing molecules with the general formula $R_1-X_1(CH_2)_2X_2-R_2$, where X = S, SO or SO$_2$ and R = various organic substituents (Ref. 1 and references therein). A major objective for the work is to obtain detailed descriptions of bonding at sulfur in various oxidation states and environments, and to study the influence on structural parameters caused by changes in the electronic properties of the R groups.

In this paper, we discuss an X-ray study at room temperature of 1,2-bis(phenylsulfonyl)ethane, $X_1=X_2=SO_2$, $R_1=R_2=Ph$. Preliminary results have been communicated previously.[2]

Experimental

Single crystals of 1,2-bis(phenylsulfonyl)ethane, PPDS, were obtained by slow evaporation of an acetone solution. The specimen selected for analysis had principal faces (101), (110) and (011). The unit cell parameters and crystal orientation were determined by least-squares refinement from the setting angles of 22 reflections in the 2θ-range 39–45°. The calculations were repeated 6 times during and after the intensity measurements. The maximum shift in any parameter was about 1.5σ. Table 1 gives the crystal data at 293 K.

The intensities of 4919 $+h+k\pm l$ reflections (set 1) and 4929 $-h+k\pm l$ (set 2) excluding extinctions were measured without attenuators to $(\sin\theta)/\lambda = s = 0.923$ Å^{-1} with Nb-filtered MoKα radiation on a diffractometer controlled by the Vanderbilt disk-oriented program system.[3] Reflections below 2θ ~ 12° were remeasured with reduced low-angle scans.[4] 27 reflections were deleted at this stage, 23 with counting rates $>10^5$ cps, exceeding the range for coincidence loss corrections, and two pairs of weak reflections with very large differences in intensity. The data were corrected in 3 separate blocks for long-range fluctuations by scaling with polynomials fitted to the average curve for a group of standard reflections. Corrections were made for coincidence loss[4]

---

*Present address: Rogaland Distriktshøgskole, Ulland-haug, N-4000 Stavanger, Norway.

Table 1. Crystal data, 1,2-bis(phenylsulfonyl)ethane.

Composition	$C_{14}H_{14}O_4S_2$	$T(K)$	293.0(5)
M_r	310.393	$\lambda(\text{Å})$	0.71073
Space group	$P2_1/n$	Z	2
$a(\text{Å})$	8.518(2)	$D_x(\text{Mg m}^{-3})$	1.455(1)
b	10.187(2)	$\mu(\text{mm}^{-1})$	0.368[a]
c	9.084(2)	Size (mm)	~0.81×0.75×0.38
$\beta(°)$	115.99(1)	M.p.(K)	456–457
$V(\text{Å}^3)$	708.5(3)		

[a]Mass absorption coefficients taken from International Tables for X-Ray Crystallography, Vol. IV(1974).

based on an experimental recovery constant, scan truncation errors following Denne[5] and absorption as described previously.[4] Details of the data collection and processing are given in Table 2.

Weighted averages of F^2 and $\sigma(F^2)$ were calculated for 491 reflections measured twice, and the equivalent pairs of the two sets were then weight-averaged to yield 4662 $<F_o^2>$. The agreement index $D = \Sigma|F_1^2-F_2^2|/\Sigma<F_o^2>$ is 0.0209 for all equivalent pairs with $<F_o^2>$ above threshold. The fraction of weak reflections increases markedly above $s \sim 0.70$ Å^{-1}. Table 2 shows that 48 % of the $<F_o^2>$ in the s-range 0.80–0.93 Å^{-1} are above threshold, and D for these data is 0.172. For an F_i^2, $\sigma(F_i^2) = \sigma(I_i) (\text{Lp})^{-1} (y(x) \cdot y_t)^{-1} \cdot A^*$ and $\sigma^2(I_i) = \sigma^2_{i \text{ count}} + (SI_{\text{net}})^2$; $i = 1,2$. The parameter S was adjusted to 0.016 to obtain a normal distribution of the weighted means of the differences $\Delta_i = (F_i^2 - <F_o^2>)$ in the full s range. Calculation of $\sigma(<F_o^2>)$ was by standard methods. Reflections with $<F_o^2> < p \cdot \sigma(<F_o^2>)$ were zero-weighted

(see Table 2 for values of p). Analyses and processing of the data were made with a set of local programs.

The structure was solved by Patterson and difference Fourier (ΔF) maps. The quantity $\Sigma w(|F_o|-k|F_c|)^2$ with $w = \sigma^{-2}(F_o)$ was minimized by the full-matrix least-squares method. Scattering factors for C, O and S were those of Doyle and Turner;[6] for H, the values of Stewart, Davidson and Simpson[7] were used. Scattering at S was corrected for anomalous dispersion.[8] Anisotropic temperature factors were assigned only to C, O and S.

The effects on refined atomic parameters caused by asymmetric deviations from the isolated spherical atom model were studied by refinements with data from distinct shells of reciprocal space. Such studies make use of the fact that the contribution to scattering from the outer (bonding) electrons decreases and becomes negligible with increasing magnitude of s;[9,10] therefore, refinements with data at higher angles pro-

Table 2. Data collection and processing.

$2\theta_{max}(°)$	82	Number of refl. recorded		9848
Scan mode	$\omega/2\theta$	Range of scaling function, $y(x)$		0.96–1.02
Scan speed (° min^{-1}) in 2θ	2	Range of scan truncation corr., y_t		0.98–1.00
Scan width (°)	$[2\theta(\alpha_1)-0.75, 2\theta(\alpha_2)+0.9]$	Range of absorption corr., A^*		1.13–1.26
Single backgr. counting time (s)	20	Recovery constant (counts^{-1})		$9.5 \cdot 10^{-8}$
Number of std. refl. and period	3/70	Instability factor, S		0.016

Range in $(\sin\theta)/\lambda$ (Å^{-1})	0–0.65	0.65–0.80	0.80–0.93	0–0.93
Threshold value of p in $p \cdot \sigma(<F_o^2>)$	1	2	3	–
Total number of refl.	1606	1418	1638	4662
Number of refl. with $w=0$	34	296	855	1185
Agreement index D, sets 1 and 2	0.0159	0.0640	0.1722	0.0209

duce structure models less biased by bonding effects.[11,12] Notwithstanding the limited range in s (≤ 0.923 Å^{-1}) in the present case, the results are of interest in relation both to a room temperature study of 1,2-bis(methylsulfonyl)ethane, MMDS ($s_{max} = 1.0$ Å^{-1}),[13] and to studies of related structures extended to larger reciprocal distances. Some characteristics of these refinements are given in Table 3; Table 4 shows 4 of the corresponding final sets of atomic positional and thermal parameters. H parameters were fixed at values from refinement III ($s > 0.30$ Å^{-1}) in all runs with $s > 0.60$ Å^{-1}. A list of structure factors is available from the authors.

Crystallographic programs for structure solution and refinement were from the X-RAY 76 system.[14] Molecular drawings were made with ORTEP.[15]

Discussion

Refinement results. Bond lengths and angles calculated from the various coordinate sets in Table 4 are shown in Tables 5 and 6. As expected, the C—C distances in the ring expand with increasing low cut-off in s, which corresponds to a decreasing contribution of the aspherical electron density to scattering. Convergence was reached for $s_{min} \sim 0.6$–0.65 Å^{-1}. The weight-averaged phenyl C—C bond from refinement VII ($s > 0.65$ Å^{-1}), 1.3936(9) Å, is significantly longer than the value after refinement I ($s < 0.65$ Å^{-1}), 1.3825(22) Å.

In the former run, no C—C bond differs by more than $\sim 2\sigma$ from the average. The apparent shrinkage of benzene rings from refinements with low-angle data has been noted before.[16,4] The *average* shortening of the phenyl C—C bonds due to the influence of bonding electrons is about 0.010 Å in the present study. The same value was obtained in a previous room temperature analysis of a related structure.[4] Changes in the s range have only minor effects on the S—C distances which show a slight maximum for $s > 0.40$ Å^{-1}: S—C(1) 1.7882(8) and S—C(2) 1.7646(9) Å (cf. Ref. 13). The values for $s > 0.65$ Å^{-1} are nearly the same as, or smaller than, those from refinement I.

The two S—O bonds which are equal after refinement I behave slightly differently with increasing s_{min}. However, both bonds continue to expand and are 1.4473(17) and 1.4446(19) Å with $s > 0.7$ Å^{-1}. The limited range in s does not allow a satisfactory refinement of the O parameters.

All C—H bonds apparently lengthen from run I to run III. Further increase of s_{min} leads to shortening, which is most pronounced in the phenyl C—H bonds; thus, 0.906(7) after I, 0.949(11) after III and 0.768(31) Å after V. But the effect is already present with $s > 0.40$ Å^{-1} (IV): 0.903(6) Å. Hope and Ottersen obtained the shortest X—H bonds (X = C, N) with $s_{min} = 0.50$ Å^{-1} in their low temperature analyses of s-diformohydrazide[17] and carbonohydrazide.[18] In both studies, refinements with data above 0.65 Å^{-1} (C—H) and 0.75 Å^{-1} (N—H), led to improved X—H dis-

Table 3. Survey of refinements.

Ref.	s	k	NO	NZ	NV	$R(F)$	$R_w(F)$	GOF
I	<0.65	13.896(32)	1572	34	119	0.029	0.039	5.05
II	>0.00	13.777(19)	3477	1185	119	0.038	0.040	3.73
III	>0.30	13.640(21)	3332	1185	119	0.037	0.036	3.13
IV	>0.40	13.480(23)	3114	1183	119	0.037	0.032	2.56
V	>0.50	13.501(28)	2757	1176	119	0.037	0.027	1.84
VI	>0.60	13.367(48)	2227	1169	91[a]	0.044	0.030	1.61
VII	>0.65	13.017(69)	1905	1151	91[a]	0.047	0.033	1.51
VIII	>0.70	12.787(115)	1554	1087	91[a]	0.053	0.039	1.44

s = $(\sin\theta)/\lambda$ (Å^{-1})
k = scale factor
NO = number of reflections with $w \neq 0$
NZ = number of reflections with $w = 0$

NV = number of variables
$R(F)$ = $\Sigma| |F_o| - k|F_c| |/\Sigma|F_o|$
$R_w(F)$ = $[\Sigma w(|F_o| - k|F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$
GOF = $[\Sigma w(|F_o| - k|F_c|)^2/(NO - NV)]^{\frac{1}{2}}$

[a]H atom parameters fixed at values from refinement III.

Table 4. Final atomic parameters. Coordinates are: $\times 10^5$ for S, C and O, and $\times 10^3$ for H. Thermal parameters, U_{ij} ($\mathring{A}^2 \times 10^4$) for C, O and S, and $U(\mathring{A}^2 \times 10^4)$ for H are defined by: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \cdots + 2U_{12}a^*b^*hk + \cdots)]$ and $\exp[-8\pi^2 U(\sin^2\theta/\lambda^2)]$, respectively. For non-H atoms: first row: refinement I (0–0.65 $\mathring{A}^{-1}$); second row: refinement III ($s > 0.30$ $\mathring{A}^{-1}$]; third row: refinement V ($s > 0.50$ $\mathring{A}^{-1}$); fourth row: refinement VII ($s > 0.65$ $\mathring{A}^{-1}$). For H atoms: entries only for three first rows, see text. E.s.d.'s are in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	16487(4)	10454(3)	22589(4)	367(2)	386(2)	362(2)	−31(1)	188(1)	−40(1)
	16485(2)	10457(2)	22587(2)	357(1)	374(1)	351(1)	−29(1)	183(1)	−39(1)
	16484(2)	10454(2)	22592(2)	354(1)	370(1)	347(1)	−28(1)	180(1)	−38(1)
	16487(3)	10459(3)	22600(3)	345(1)	360(1)	339(1)	−25(1)	175(1)	−35(1)
O(1)	22166(14)	5339(11)	38860(11)	613(6)	665(7)	356(5)	−104(5)	236(5)	−22(4)
	22169(10)	5338(8)	38888(8)	602(4)	660(4)	344(3)	−104(3)	232(3)	−21(3)
	22184(11)	5338(9)	38945(7)	592(3)	661(4)	337(2)	−99(3)	227(2)	−20(2)
	22213(20)	5273(17)	38975(12)	578(6)	647(6)	319(3)	−95(5)	215(3)	−12(3)
O(2)	6176(14)	22226(10)	18140(15)	492(6)	452(5)	745(7)	77(4)	348(5)	−45(5)
	6183(9)	22226(7)	18161(10)	488(3)	448(3)	741(5)	73(3)	349(3)	−45(3)
	6143(10)	22282(7)	18108(12)	490(3)	435(3)	739(4)	75(2)	351(3)	−45(3)
	6124(18)	22284(13)	18058(23)	480(5)	424(4)	707(7)	69(3)	340(5)	−44(4)
C(1)	4055(17)	−2225(13)	8859(15)	374(6)	386(7)	367(7)	−59(5)	148(5)	16(5)
	4044(11)	−2233(8)	8852(9)	367(3)	383(4)	349(3)	−66(3)	137(3)	18(3)
	4043(9)	−2247(7)	8871(7)	372(2)	375(3)	337(2)	−68(2)	129(2)	23(2)
	4034(13)	−2220(11)	8876(13)	361(3)	372(4)	331(3)	−67(3)	126(2)	24(2)
C(2)	34733(15)	12743(11)	18511(14)	310(6)	344(6)	327(6)	−33(4)	129(5)	−48(4)
	34718(9)	12745(7)	18494(9)	304(3)	337(3)	323(3)	−26(2)	126(2)	−38(2)
	34704(7)	12734(6)	18504(7)	299(2)	327(2)	325(2)	−19(2)	128(2)	−22(2)
	34678(11)	12729(8)	18514(10)	294(3)	314(3)	318(3)	−19(2)	127(2)	−22(2)
C(3)	34771(19)	23142(14)	8738(18)	419(7)	434(7)	466(7)	16(6)	208(6)	61(6)
	34711(12)	23161(9)	8715(11)	420(4)	421(4)	465(4)	7(3)	219(3)	64(3)
	34641(11)	23225(8)	8661(10)	419(3)	418(3)	476(3)	12(3)	230(3)	83(2)
	34634(17)	23236(13)	8657(16)	417(4)	408(4)	472(5)	8(3)	235(4)	83(4)
C(4)	49287(21)	25096(17)	5868(21)	544(9)	624(10)	573(9)	−98(7)	316(7)	66(7)
	49285(14)	25148(12)	5839(14)	530(5)	621(6)	573(5)	−96(4)	320(4)	60(4)
	49272(14)	25227(13)	5824(14)	521(4)	628(5)	590(4)	−78(4)	333(4)	76(4)
	49246(25)	25265(22)	5825(25)	503(6)	621(8)	594(7)	−75(6)	332(5)	76(6)
C(5)	63347(20)	16759(20)	12686(21)	398(8)	830(12)	593(9)	−112(8)	278(7)	−105(8)
	63398(13)	16750(13)	12703(14)	394(4)	816(7)	590(5)	−97(5)	274(4)	−96(5)
	63486(12)	16769(15)	12665(14)	387(3)	814(7)	593(4)	−75(4)	273(3)	−67(4)
	63466(20)	16836(28)	12615(27)	379(4)	807(12)	594(7)	−66(6)	269(5)	−58(7)
C(6)	63097(20)	6360(19)	22240(21)	347(7)	698(10)	587(9)	82(7)	148(7)	−44(8)
	63171(13)	6359(13)	22279(14)	340(4)	700(6)	589(5)	75(4)	160(4)	−42(5)
	63257(11)	6287(13)	22364(14)	329(3)	706(5)	593(4)	79(3)	174(3)	−19(4)
	63268(17)	6277(25)	22383(25)	322(4)	705(9)	590(7)	74(4)	179(4)	−12(6)
C(7)	48811(18)	4219(14)	25399(17)	387(7)	434(7)	437(7)	34(6)	128(6)	20(6)
	48770(11)	4177(9)	25404(11)	370(4)	427(4)	436(4)	42(3)	126(3)	18(3)
	48791(9)	4159(8)	25438(10)	353(3)	431(3)	446(3)	49(2)	130(2)	27(2)
	48789(15)	4157(13)	25450(16)	337(3)	421(4)	446(4)	50(3)	125(7)	30(3)

tances. In the present case, refinement of H parameters with $s_{min} > 0.60$ $\mathring{A}^{-1}$ was not successful, as some of the coordinates became unstable. We ascribe this mainly to the facts that the data in this s range are comprised of a large fraction of weak reflections, (see Table 2), and the contribution to scattering from H is relatively small in PPDS, which contains two S atoms.

We have checked the physical validity of the thermal parameters from refinement VII by a

Table 4. (cont.)

Atom	x	y	z	U	Atom	x	y	z	U
H(11)	−49(2)	−42(1)	124(2)	493(40)	H(5)	727(3)	188(2)	110(2)	721(55)
	−50(2)	−46(1)	124(2)	562(32)		736(3)	192(2)	114(2)	820(46)
	−45(4)	−40(3)	127(3)	577(46)		725(15)	186(10)	156(12)	1115(176)
H(12)	115(2)	−94(1)	108(2)	521(45)	H(6)	728(3)	11(2)	271(2)	725(55)
	112(2)	−98(1)	106(2)	508(31)		736(3)	11(2)	281(2)	729(41)
	116(5)	−96(3)	106(4)	667(57)		707(9)	24(5)	260(7)	840(91)
H(3)	257(2)	284(2)	42(2)	612(49)	H(7)	486(2)	−28(2)	316(2)	522(43)
	246(2)	288(2)	37(2)	638(36)		484(2)	−27(1)	320(2)	474(28)
	275(5)	284(4)	62(4)	681(60)		481(4)	−22(3)	308(3)	597(48)
H(4)	491(2)	319(2)	−8(3)	710(53)					
	490(2)	318(2)	−11(2)	660(36)					
	509(7)	301(6)	21(7)	831(91)					

Hirshfeld rigid-bond test.[19] The calculated differences between the vibration amplitudes along the bonds range from 0.0001 to 0.0013 Å for the bonded non-H atoms. The rms difference is 0.0007 Å². This is a satisfactory result.

The molecular structure. Fig. 1 shows the molecular conformation of PPDS. The bond sequence C−C−S−C(Ph) has a *gauche* orientation, found also in the MMDS structure. Excluding the C−H bond lengths, we believe that the parameters obtained with $s > 0.65$ Å^{-1} are the best description of the structure, uncorrected for thermal effects. As already mentioned, the S−O distances are probably less reliable. The thermal motion of the phenyl ring including S can be fitted to a rigid-body (RB) model. An analysis according to Schomaker and Trueblood[20] gave the averages $< |(U_{ij})_{exp} - (U_{ij})_{RB}| > = 0.0006$ Å² as compared to $< \sigma(U_{ij})_{exp} > = 0.0004$ Å². The parent corrections of bond lengths are given in Table 5 under the entry VII RB. The average ring C−C distance after correction is 1.401 Å (range 1.397−

Table 5. Bond lengths (Å) with standard deviations. For explanation of Roman numerals, see Tables 2 and 3.

	I	III	V	VII	VII RB[a]
S−O(1)	1.4365(11)	1.4390(8)	1.4429(8)	1.4470(13)	
S−O(2)	1.4359(11)	1.4353(8)	1.4419(8)	1.4427(14)	
S−C(1)	1.7854(13)	1.7867(8)	1.7869(7)	1.7857(10)	
S−C(2)	1.7640(16)	1.7637(10)	1.7623(8)	1.7597(12)	1.7649
C(1)−C(1′)	1.5162(18)	1.5156(11)	1.5195(9)	1.5185(15)	
C(2)−C(3)	1.3831(20)	1.3837(13)	1.3919(11)	1.3944(17)	1.4028
C(3)−C(4)	1.3852(28)	1.3909(18)	1.3938(17)	1.3924(30)	1.3965
C(4)−C(5)	1.3745(23)	1.3817(16)	1.3911(16)	1.3893(29)	1.3970
C(5)−C(6)	1.3755(28)	1.3756(19)	1.3900(20)	1.3993(37)	1.4069
C(6)−C(7)	1.3846(27)	1.3928(17)	1.3946(16)	1.3951(25)	1.3993
C(7)−C(2)	1.3878(18)	1.3893(11)	1.3919(9)	1.3931(14)	1.4016
C(1)−H[b]	0.932(17)−0.968(21)	0.948(15)−0.985(19)	0.947(38)−0.959(37)		
C(1)−H[c]	0.946(18)	0.962(18)	0.953(6)		
C(Ph)−H[b]	0.883(18)−0.919(20)	0.918(18)−0.976(17)	0.654(68)−0.828(34)		
C(Ph)−H[c]	0.906(7)	0.949(11)	0.768(31)		

[a] Bonds corrected for rigid-body motion according to formalism by Schomaker and Trueblood[20]; [b] Range; [c] Mean value with weighted sample error.

1.407 Å). This compares well with the vibration-corrected values from neutron diffraction studies of benzene, 1.398 Å,[21] and a benzene derivative, 1.397 Å.[22]

There are significant distortions of the regular D_{6h} symmetry of the benzene ring caused by the RSO_2 substituent.[23] Deviations from 120° in the endocyclic angles are: $\Delta\alpha = +2.0$; $\overline{\Delta\beta} = -1.4$, $\overline{\Delta\gamma} = +0.2$; and $\Delta\delta = +0.4°$, where $\alpha = ipso$, $\beta = ortho$, $\gamma = meta$ and $\delta = para$ relative to the substituent. The e.s.d. in these angles are in the range 0.1–0.2°. The deviations are in good agreement with those of the related 1-(methylsulfonyl)-2-(phenylsulfonyl)ethane, $MPSO_2$,[4] and, in general, also with the values given by Domenicano and Murray-Rust[24] for a $MeSO_2$ substituent.

In the study of $MPSO_2$, it was observed that the O–S–O and C(central)–S–O angles in the phenyl end were, respectively, 2° larger and 1.5° smaller than in the methyl end of the molecule.[4] Simple models for bonding, including the VSEPR model,[25] however, predict both angles near phenyl to be larger. The X-ray analyses of PPDS and MMDS[13] confirm our previous observations: the average O–S–O and C(central)–S–O angles for the three structures are 119.0[0.25]* and 107.1[1.9]°, respectively, when $R = Ph$ in the fragment $-CH_2-SO_2-R$, and 117.0[0.05] and 108.2[1.8]°, respectively, when $R = Me$. These results may be summarized in the following signed differences $\delta(O-S-O) = +2.0$ and $\delta(C_c^\dagger-S-O) = -1.1°$.

Electron diffraction studies of gaseous $PhSO_2Cl$ and $MeSO_2Cl$[26] show the same trend in O–S–O and Cl–S–O angles, namely $\delta(O-S-O) = +1.7$ and $\delta(Cl-S-O) = -1.6°$. The magnitudes of the O–S–O angles are larger, however: 122.5(36) and 120.8(8)°, respectively. In a recent electron diffraction study of MMDS,[27] this angle was determined at 119.0°. In general, it appears to be $\geq120°$ in gaseous sulfones. Even taking into account that the error in this parameter is rather large in some of the published gas phase studies,[26] the O–S–O angle seems to be distinctly different in crystalline and free sulfones, being more contracted in the crystalline state.

_____

* Values in square brackets denote range of observations.

† $C_c = $ C(central).

Table 6. Valency angles (°) with standard deviations. For explanation of Roman numerals, see Tables 2 and 3.

	I	III	V	VII
O(1)–S–O(2)	118.76(8)	118.67(5)	118.75(6)	119.16(11)
O(1)–S–C(1)	106.60(7)	106.59(5)	106.60(4)	106.45(8)
O(1)–S–C(2)	109.49(6)	109.54(4)	109.54(4)	109.48(8)
O(2)–S–C(1)	107.77(6)	107.82(4)	107.81(4)	107.60(7)
O(2)–S–C(2)	108.48(7)	108.50(5)	108.41(5)	108.35(8)
C(1)–S–C(2)	104.86(7)	104.83(4)	104.85(4)	104.85(6)
S–C(1)–C(1')	112.34(9)	112.24(6)	112.11(5)	112.33(8)
S–C(2)–C(3)	119.09(10)	118.94(6)	118.73(5)	118.78(8)
S–C(2)–C(7)	119.30(11)	119.06(7)	119.08(6)	119.16(9)
C(2)–C(3)–C(4)	118.96(13)	118.87(9)	118.63(8)	118.78(13)
C(3)–C(4)–C(5)	119.99(17)	119.79(12)	120.03(12)	120.15(20)
C(4)–C(5)–C(6)	120.59(18)	120.75(12)	120.52(12)	120.42(20)
C(5)–C(6)–C(7)	120.67(15)	120.62(10)	120.36(10)	120.20(16)
C(6)–C(7)–C(2)	118.18(15)	117.97(9)	118.29(9)	118.41(14)
C(7)–C(2)–C(3)	121.61(15)	121.99(9)	122.17(8)	122.05(12)
S–C(1)–H^a	103.3(9)–106.9(9)	105.0(8)–109.1(7)	101.4(1.6)–107.5(1.8)	
C–C(1)–H^a	110.9(8)–113.1(1.2)	111.4(7)–112.6(9)	111.9(2.2)–112.4(1.4)	
H–C(1)–H	109.8(1.6)	106.0(1.3)	111(3)	
C–C(Ph)–H^a	116.6(1.2)–122.7(1.2)	116.0(1.1)–122.9(1.1)	106(8)–129(6)	

^{a}Range.

Fig. 1. Molecular
conformation and
labelling of atoms.
Thermal ellipsoids of the
non-H atoms correspond
to a 50 % probability.
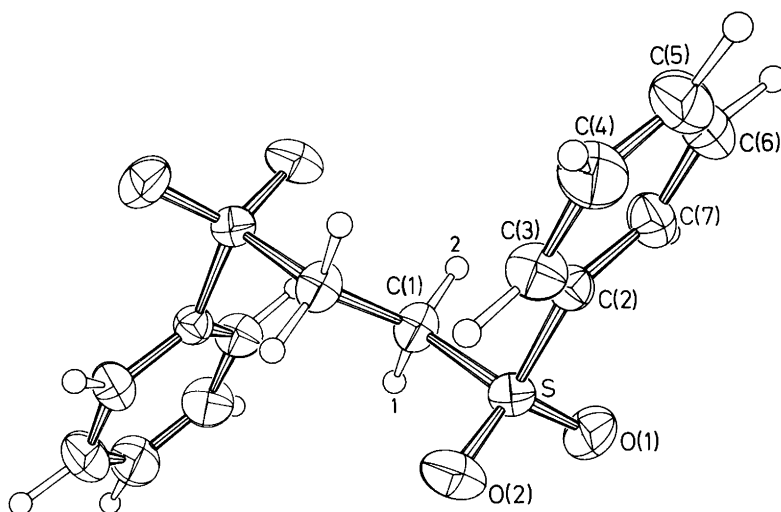
The electron diffraction studies involved several RSO_2Cl compounds with R ligands covering a wide range in electronegativity. The changes in the $Cl-S-O$ angles with ligand electronegativity were only in approximate agreement with the predictions of the VSEPR model, and it was noted by Hargittai[26] that the largest deviation from the expected result occurred for R = Me. He also pointed out the significance of non-bonded interactions for the final geometry near S. In the crystal structures of MMDS, MPSO₂ and PPDS, the observed δ values cannot be ascribed to short non-bonded interactions. The shortest intramolecular distances are found in MPSO₂ and PPDS, both structures having a nearly *syn*-planar atomic sequence O−S−C(*ipso*)−C(*ortho*)−H(*ortho*). The O···H(*ortho*) dis-

tances, 2.52 and 2.51 Å,[§] respectively, correspond to normal van der Waals contacts. Other structure parameters of the central part of PPDS have been discussed elsewhere.[1]

The crystal structure. The phenyl rings are rather loosely packed in double layers along *a* (Fig. 2), no distance between aromatic C atoms being shorter than 3.80 Å. Each asymmetric unit is involved in three C···O contacts in the normal van der Waals range: 3.236(2)–3.359(2) Å. Two contacts are formed by O(2), 2.45 Å,[§] with H atoms in adjacent molecules. These contacts are drawn as dotted lines in Fig. 2.

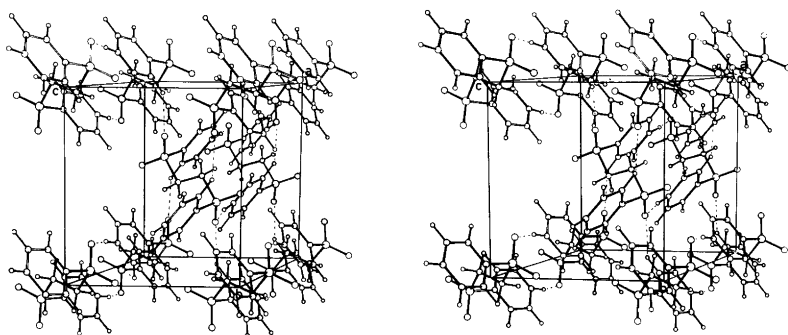[§] Calculated with C−H lengths normalized to 1.09 Å.

Fig. 2. Stereodrawing of the molecular packing. Two intermolecular O···H distances, 2.45 Å, are shown as dashed lines.

References

1. Mo, F., Hauback, B. C. and Winther, S. *Acta Crystallogr. B40* (1984) 288.
2. Mo, F., Berg, Ø., Thorkildsen, G. and Gaasdal, A. *Fifth Eur. Crystallogr. Meeting,* Copenhagen (ECM-5) 1979, Abstr. p. 352, and extended abstract.
3. Lenhert, P. G. *J. Appl. Crystallogr. 8* (1975) 568.
4. Mo, F. and Gaasdal, A. *Acta Crystallogr. B36* (1980) 2349.
5. Denne, W. A. *Acta Crystallogr. A33* (1977) 438.
6. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A24* (1968) 390.
7. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys. 42* (1965) 3175.
8. Cromer, D. T. and Liberman, D. *J. Chem. Phys. 53* (1970) 1891.
9. Stewart, R. F. *J. Chem. Phys. 48* (1968) 4882.
10. Groenewegen, P. P. M., Zeevalkink, J. and Feil, D. *Acta Crystallogr. A27* (1971) 487.
11. Ruysink, A. F. J. and Vos, A. *Acta Crystallogr. A30* (1974) 503.
12. Wang, Y., Blessing, R. H., Ross, F. K. and Coppens, P. *Acta Crystallogr. B32* (1976) 572.
13. Mo, F. and Berg, Ø. *Acta Chem. Scand. A36* (1982) 657.
14. Stewart, J. M., Ed., *The X-RAY SYSTEM,* Version of 1976, Technical Report TR-446, Computer Science Center, University of Maryland, College Park, MD 1976.
15. Johnson, C. K. *ORTEP II,* Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN 1976.
16. O'Connell, A. M., Rae, A. I. M. and Maslen, E. N. *Acta Crystallogr. 21* (1966) 208.
17. Hope, H. and Ottersen, T. *Acta Crystallogr. B34* (1978) 3623.
18. Ottersen, T. and Hope, H. *Acta Crystallogr. B35* (1979) 373.
19. Hirshfeld, F. L. *Acta Crystallogr. A32* (1976) 239.
20. Schomaker, V. and Trueblood, K. N. *Acta Crystallogr. B24* (1968) 63.
21. Bacon, G. E., Curry, N. A. and Wilson, S. A. *Proc. R. Soc. London A279* (1964) 98.
22. Bacon, G. E., Walker, C. R. and Speakman, J. C. *J. Chem. Soc. Perkin Trans. 2* (1977) 979.
23. (a) Domenicano, A., Vaciago, A. and Coulson, C. A. *Acta Crystallogr. B31* (1975) 221; (b) *Ibid.* 1630.
24. Domenicano, A. and Murray-Rust, P. *Tetrahedron Lett. 24* (1979) 2283.
25. Gillespie, R. J. In: *Molecular Geometry,* Van Nostrand-Reinhold, New York 1972.
26. Hargittai, I. In: *Lecture Notes in Chemistry: Sulphone Molecular Structures,* Springer, Berlin 1978.
27. Brunvoll, J. and Hargittai, I. *Acta Chem. Scand. A39* (1985) 667.