

Crystal Structure of 1,2-Bis(*p*-methoxyphenylsulfonyl)ethane at 86 K

Bjørn C. Hauback, Klara M. Helgemo and Frode Mo

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

Hauback, B. C., Helgemo, K. M. and Mo, F., 1988. Crystal Structure of 1,2-Bis(*p*-methoxyphenylsulfonyl)ethane at 86 K. – Acta Chem Scand., Ser. A 42: 37–44.

1,2-Bis(*p*-methoxyphenylsulfonyl)ethane. $C_{16}H_{18}O_6S_2$, was studied by X-ray diffraction at 86 K. The space group is triclinic, $P\bar{1}$, with cell dimensions $a = 9.114(1)$, $b = 10.400(2)$, $c = 4.776(1)$ Å, $\alpha = 93.81(2)$, $\beta = 105.78(2)$, $\gamma = 109.09(2)^\circ$ and $Z = 1$. Counter data were collected to $(\sin\theta)/\lambda = 0.704$ Å⁻¹ with MoK α radiation. Refinements were made both in the conventional mode (all data), and with data from distinct shells in reciprocal space. The best model of the structure was obtained with $(\sin\theta)/\lambda \geq 0.60$ Å⁻¹, and the refined bond lengths in a fragment containing S and the phenyl ring were corrected for thermal motion. Relative to the values from the conventional refinement, the uncorrected phenyl C–C bonds are lengthened on average 0.0045 Å. The two 1,4-substituents of the ring act in concert to create a system with a significant degree of π -bond localization. Superposed on the pattern of alternating short and long bonds, there are smaller differences between pairs of bonds over the 1,4 diagonal. This bond asymmetry, presumably effected by the methoxy group in a near-coplanar orientation with the ring, provides support for previous *ab initio* calculations on anisole and anisole derivatives. Except for the shortened S–C(phenyl) bond, the structural details of the sulfone group are in very good agreement with average values for aromatic sulfones.

Dedicated to Professor Olav Foss on his 70th birthday

This work is part of a crystallographic investigation of small S-containing molecules to study details of bonding at S in the solid state and its dependence on differences in oxidation state and environment. The general formula for these molecules is $R^1-X^1(CH_2)_2X^2-R^2$, and so far various combinations: $X^1, X^2 = S, SO$ or SO_2 and $R^1, R^2 = Me, Ph$ have been analyzed.^{1–3} We present here a low-temperature X-ray study of 1,2-bis(*p*-methoxyphenylsulfonyl)ethane with $X^1, X^2 = SO_2$ and $R^1, R^2 = Ph-OCH_3$. This is the first structure in the series with a *para*-substituted phenyl ring.

Experimental

Single crystals of 1,2-bis(*p*-methoxyphenylsulfonyl)ethane, PMO, from acetone were prismatic along c , with principal faces (100), (010) and ($\bar{1}02$). The unit cell parameters were determined

by least-squares refinement from the MoK α_1 peaks of 19 reflections with 2θ in the range 55–62°. The calculations were performed twice before and once during the data collection. The variation in all parameters was within 1σ . Table 1 gives the crystal data at 86 K.

A total of 2635 reflections were measured without attenuators to the limit $(\sin\theta)/\lambda = s = 0.704$ Å⁻¹ ($-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $0 \leq l \leq 6$) with Nb-filtered MoK α radiation on a Picker FACS-I diffractometer controlled by the Vanderbilt disk-oriented program system.⁵ The crystal was cooled by a gas-flow N₂(liq.) cryostat. The scan mode was $\omega/2\theta$ at 2° min⁻¹, basic scan width $2\theta(\bar{\alpha}) - 0.90^\circ$ to $2\theta(\bar{\alpha}) + 0.90^\circ$, and backgrounds were measured for 20 s at each end of the scan. Intensities below $2\theta \sim 14^\circ$ were remeasured semi-manually with reduced low-angle scans to minimize errors caused by the NbK absorption edge. The intensity variation of three standard

Table 1. Crystal data for 1,2-bis(*p*-methoxyphenyl-sulfonyl)ethane.

Composition	C ₁₆ H ₁₈ O ₆ S ₂	V/Å ³	405.6(1)
<i>M_r</i>	370.45	<i>T</i> /K	86(1)
Space group	<i>P</i> $\bar{1}$	$\lambda\alpha_1/\text{\AA}$	0.70930
<i>a</i> /Å	9.114(1)	$\lambda\alpha_2/\text{\AA}$	0.71359
<i>b</i> /Å	10.400(2)	<i>Z</i>	1
<i>c</i> /Å	4.776(1)	<i>D_x</i> /Mg m ⁻³	1.5166(4)
α°	93.81(2)	μ/mm^{-1}	0.343 ^a
β°	105.78(2)	Size/mm	~0.15×0.18×0.40
γ°	109.09(2)	<i>M.p.</i> /K	478–479

^aMass absorption coefficients taken from Ref. 4.

reflections monitored every 70 reflections was less than $\pm 1.5\%$. The data were scaled with a polynomial fit to the average standard curve and corrected for coincidence loss, Lorentz factor, polarization and absorption. The recovery constant was estimated as $6.0 \cdot 10^{-8}$ counts⁻¹. Absorption corrections *A** in the range 1.045–1.075 were calculated with a modified version of the program ABSOR.⁶ The intensities of ten reflections were corrected for superposition in the background or scan range of the β peak of a higher-order reflection. The maximum correction was 79%.

252 equivalent pairs, *h**h**k*0 and $\bar{h}\bar{h}k$ 0, and 22 other reflections measured twice were merged, the agreement index $D = \sum |F_1^2 - F_2^2| / \sum F_w^2 = 0.021$. F_w^2 is the weighted average of F_1^2 and F_2^2 . For an individual observation, $\sigma(F_i^2) = \sigma(I_i) (Lp)^{-1}$

(scale)*A**, and $\sigma^2(I_i) = \sigma_{i,\text{counts}}^2 + (SI_{i,\text{net}})^2$; $i = 1, 2$. *S* was taken as 0.010 to obtain a Gaussian distribution of the weighted means of the differences $\Delta_i = |F_i^2 - F_w^2|$. Of the 2361 unique reflections, 113 with $F^2 < \sigma(F^2)$ were weighted zero. Another six reflections were deleted: five at low 2 θ with the NbK edge within the range of their peak scans and one with a counting rate outside the range for coincidence loss corrections.

The position of the S atom was located from a Patterson map, while the C, N, O and H atoms were found by the difference Fourier technique. Anisotropic temperature factors were assigned to the non-H atoms and isotropic ones to H. The function $\sum w(|F_o| - k|F_c|)^2$ with $w = 1/\sigma^2(F_o)$ was minimized by the full-matrix least-squares method. Refinements with different low *s* cut-off values were carried out. Notwithstanding the limited range in *s* ($\leq 0.704 \text{\AA}^{-1}$), a refinement with the high-order data, i.e. $s > 0.60 \text{\AA}^{-1}$, was tried out in order to obtain a structure model possibly less biased by bonding effects. Table 2 summarizes three of the refinements. With all data (refinement I), the final difference electron density is within -0.33 and 0.40 e \AA^{-3} , and all extrema $> 0.26 \text{ e \AA}^{-3}$ in magnitude correspond to bonding features. The final atomic parameters are given in Table 3.⁸

Scattering factors were those of Doyle and Turner;⁷ however, for H, the values of Stewart *et al.*⁸ were used. Anomalous dispersion values for S

Table 2. Survey of refinements.

Refinement	I	II	III
$s = (\sin\theta)/\lambda$ range/Å ⁻¹	>0.0	>0.30	>0.60
Scale factor, <i>k</i>	4.970(7)	4.889(8)	4.875(59)
Number of reflections with $w \neq 0$, NO	2242	2177	839
Number of reflections with $w = 0$	113	108	53
Number of variables, NV	145	145	109 ^a
$R(F) = \sum F_o - k F_c / \sum F_o $	0.033	0.031	0.034
$R_w(F) = [\sum w(F_o - k F_c)^2 / \sum w F_o^2]^{1/2}$	0.031	0.028	0.027
GOF = $[\sum w(F_o - k F_c)^2 / (\text{NO} - \text{NV})]^{1/2}$	2.57	2.04	1.28
Max. shift/error	0.002	0.004	0.008

^aH atom parameters fixed at values from refinement II.

⁸ Lists of anisotropic displacement factors for the non-H atoms and observed and calculated structure factors have been deposited.

Table 3. Final atomic parameters. Coordinates are: $\times 10^5$ for S, C and O, and $\times 10^3$ for H. Equivalent isotropic thermal parameters for non-H atoms U_{eq} (10^4 \AA^2), are calculated from $U_{\text{eq}} = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^* a_i \cdot a_j$, where U_{ij} are defined by $T(\theta) = \exp[-2\pi^2 (U_{11}a^{*2}h^2 + \dots + 2U_{12}a^*b^*hk + \dots)]$. Isotropic thermal parameters, U (10^4 \AA^2), for H are defined by $\exp[-8\pi^2 U(\sin^2\theta/\lambda^2)]$. For non-H atoms; first row: refinement I; second row: refinement II; third row: refinement III. For H atoms: entries only for two first rows. E.s.d.'s are in parentheses.

Atom	x	y	z	U_{eq} (or U for H)
S	-11935(4)	13055(3)	13067(7)	147(1)
	-11936(3)	13060(3)	13076(6)	139(1)
	-11922(4)	13070(4)	13088(8)	136(4)
O(1)	-23683(10)	2833(9)	22844(21)	193(4)
	-23670(10)	2837(9)	22868(18)	190(4)
	-23678(15)	2844(14)	22942(28)	186(6)
O(2)	2181(10)	23149(9)	35027(20)	198(4)
	2177(10)	23149(9)	35010(18)	195(4)
	2221(16)	23201(14)	35071(28)	194(5)
O(3)	-45183(11)	40488(9)	-72238(23)	228(4)
	-45205(10)	40477(9)	-72290(20)	221(4)
	-45167(17)	40498(14)	-72287(34)	213(6)
C(1)	-4437(15)	4052(13)	-9363(28)	157(6)
	-4425(13)	4052(12)	-9417(24)	154(5)
	-4412(17)	4079(16)	-9400(29)	154(6)
C(2)	-22232(15)	21433(12)	-11223(28)	155(6)
	-22220(13)	21441(11)	-11208(24)	153(5)
	-22207(18)	21440(15)	-11174(31)	148(6)
C(3)	-13327(15)	33444(13)	-19534(30)	190(6)
	-13308(14)	33444(11)	-19542(27)	184(5)
	-13245(18)	33471(16)	-19539(35)	175(6)
C(4)	-21409(16)	39644(13)	-39887(32)	201(6)
	-21392(14)	39661(12)	-39899(27)	197(5)
	-21360(20)	39686(16)	-39935(37)	187(7)
C(5)	-38453(15)	33809(13)	-52062(29)	179(6)
	-38459(14)	33794(11)	-52082(25)	173(5)
	-38467(19)	33807(16)	-52185(34)	164(6)
C(6)	-47285(16)	21903(14)	-43462(31)	194(6)
	-47311(14)	21893(12)	-43491(27)	192(5)
	-47322(18)	21874(17)	-43505(36)	184(7)
C(7)	-39083(15)	15715(13)	-23140(30)	181(6)
	-39094(13)	15697(12)	-23128(26)	176(5)
	-39118(18)	15652(16)	-23150(35)	173(6)
C(8)	-62565(17)	34479(16)	-86576(36)	257(7)
	-62533(15)	34474(14)	-86572(32)	246(6)
	-62495(22)	34515(20)	-86480(44)	241(7)
H(11)	24(2)	107(1)	-168(3)	207(38)
	29(2)	109(2)	-165(4)	194(34)
H(12)	-136(2)	-17(1)	-253(4)	234(40)
	-143(2)	-20(2)	-261(4)	276(39)
H(3)	-12(2)	373(1)	-119(3)	137(34)
	-15(2)	373(1)	-120(3)	137(31)
H(4)	-158(2)	480(2)	-470(3)	216(38)
	-156(2)	480(2)	-471(3)	174(33)
H(6)	-587(2)	183(2)	-509(4)	234(39)
	-590(2)	181(2)	-516(4)	213(35)
H(7)	-449(2)	79(2)	-172(4)	261(41)
	-448(2)	77(2)	-168(4)	246(38)
H(81)	-651(2)	404(2)	-1010(4)	285(43)
	-646(2)	402(2)	-997(4)	317(43)
H(82)	-684(2)	341(2)	-713(4)	293(44)
	-683(2)	343(2)	-729(5)	304(41)
H(83)	-653(2)	252(2)	-975(4)	295(43)
	-653(2)	256(2)	-973(4)	235(37)

were from Cromer and Liberman.⁹ A set of local programs was used for analyses and reduction of the data. Programs for structure solution and refinement were from X-RAY 76.¹⁰ Thermal parameters were analysed in terms of rigid-body motion using THMA11.¹¹ Molecular drawings were made with ORTEP.¹²

All calculations were performed on a SPERRY 1100 computer.

Discussion

The molecular structure. The sequence C(1')–C(1)–S–C(2) is oriented *trans*, as shown in Fig. 1. The phenyl ring is approximately planar, with largest atomic distances from the mean ring plane within ± 0.005 Å.

Bond lengths and angles from the three refinements surveyed in Table 2 are given in Table 4. In run III, the range in s is rather small, viz. $0.60 \leq s \leq 0.704$ Å⁻¹; nevertheless, the ratio of the number of observations to the number of variables is still satisfactory: NO/NV ~ 7.7 (Table 2). All C–C and C–S bond lengths converged to their final values in this refinement, and the goodness-of-fit for the structure model is significantly improved. The R -factors are comparable to those from runs I and II. Also, the bond lengths of the phenyl ring confirm that the best model for PMO is that from refinement III. Our discussion of the molecular structure will be based on this model.

Relative to the bond lengths from the refinement with all data below 0.704 Å⁻¹ (I), the phenyl C–C bonds from III are lengthened on the average 0.0045 Å. In two previous *room-temperature* studies of structures with phenyl rings we found that these bonds lengthened by about 0.010 Å in high-order refinements.^{2,3} The present results indicate the relative contribution at room temperature of the atomic thermal vibra-

tions to the apparent shrinkage of phenyl rings in conventional refinements.

The central C–C and S–C bonds are moderately influenced by the cut-off in s . The values from refinements I and III differ by no more than 1.5σ . The two S–O distances are unchanged from I to II, but expand in III. Data at much higher resolution are needed to carry out a satisfactory least-squares refinement for the O atoms.

The physical significance of the thermal parameters from refinement III was checked by a Hirshfeld rigid-bond test.¹³ The differences in the mean-square displacement amplitude for pairs of all bonded atoms in the fragment S–Ph range from $2 \cdot 10^{-4}$ to $15 \cdot 10^{-4}$ Å², the rms value being $9 \cdot 10^{-4}$ Å². According to Rosenfield, Trueblood and Dunitz,¹⁴ *all* interatomic distances within a truly rigid body should remain invariant. The distances for the phenyl ring including S are in good agreement with this extended criterion, the mean-square displacement amplitude for all possible pairs of atoms being in the range $1 - 21 \cdot 10^{-4}$ Å², with rms value $10 \cdot 10^{-4}$ Å². An analysis of this fragment in terms of the rigid-body model of Schomaker and Trueblood¹⁵ gave $[\sum_{ij}\{w_{ij}[(U_{ij})_{\text{obs}} - (U_{ij})_{\text{RB}}]\}^2/\sum w_{ij}^2]^{1/2} = 3 \cdot 10^{-4}$ Å², with $w_{ij} = 1/\sigma^2[(U_{ij})_{\text{obs}}]$, compared to $\langle \sigma^2[U_{\text{obs}}] \rangle^{1/2} = 5 \cdot 10^{-4}$ Å². Bond lengths corrected for rigid-body motion are given in Table 4 under the entry IIIRB.

Of special interest in the present work are the possible structural changes induced by a methoxy substituent in the *para* position of the phenyl ring. Investigations of the angular distortions in multi-substituted benzene rings have indicated that the substituent effects to a good approximation can be considered independent and additive.^{16,17} After refinement III the deviations from 120° in the PMO ring are: $\Delta\alpha = 0.9$, $\Delta\beta = -0.3$, $\Delta\gamma = -0.3$, and $\Delta\delta = 0.4^\circ$ (see 1). The differences are in reasonably good agreement with

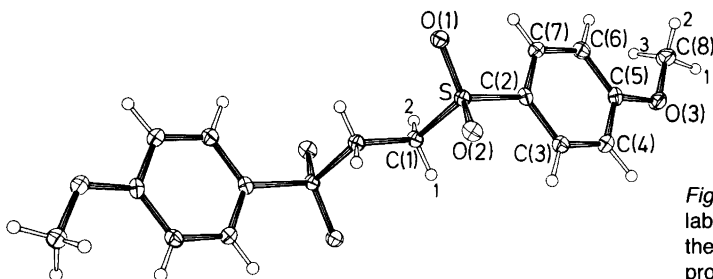


Fig. 1. Molecular conformation and labelling of atoms. Thermal ellipsoids of the non-H atoms correspond to 50% probability.

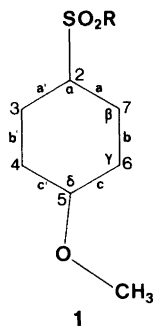
Table 4. Bond lengths (Å) and angles (°) with e.s.d.'s. For explanation of Roman numerals, see Table 2.

	I	II	III	III ^a
Bond				
S–O(1)	1.4449(10)	1.4447(9)	1.4476(14)	
S–O(2)	1.4468(8)	1.4459(8)	1.4499(11)	
S–C(1)	1.7817(16)	1.7850(14)	1.7837(19)	
S–C(2)	1.7500(14)	1.7494(13)	1.7480(17)	1.749
C(1)–C(1')	1.5222(21)	1.5233(18)	1.5256(24)	
C(2)–C(3)	1.3981(18)	1.3981(16)	1.4027(22)	1.405
C(3)–C(4)	1.3811(21)	1.3826(18)	1.3849(25)	1.385
C(4)–C(5)	1.4016(18)	1.4035(16)	1.4070(21)	1.409
C(5)–C(6)	1.3947(19)	1.3948(17)	1.3993(23)	1.402
C(6)–C(7)	1.3849(21)	1.3873(18)	1.3884(25)	1.389
C(7)–C(2)	1.3850(17)	1.3869(15)	1.3902(20)	1.393
C(5)–O(3)	1.3540(18)	1.3558(16)	1.3515(24)	
O(3)–C(8)	1.4403(16)	1.4357(14)	1.4351(22)	
Angle				
O(1)–S–O(2)	118.74(6)	118.74(5)	118.69(8)	
O(1)–S–C(1)	107.46(6)	107.48(6)	107.61(8)	
O(1)–S–C(2)	108.73(6)	108.81(5)	108.78(8)	
O(2)–S–C(1)	106.87(6)	106.84(6)	106.87(8)	
O(2)–S–C(2)	109.85(6)	109.83(5)	109.77(8)	
C(1)–S–C(2)	104.19(7)	104.14(6)	104.12(8)	
S–C(1)–C(1')	109.05(10)	108.78(8)	108.83(10)	
S–C(2)–C(3)	119.73(9)	119.74(8)	119.64(11)	
S–C(2)–C(7)	119.56(10)	119.45(9)	119.40(12)	
C(2)–C(3)–C(4)	119.67(11)	119.69(10)	119.55(13)	
C(3)–C(4)–C(5)	119.67(12)	119.54(11)	119.66(15)	
C(4)–C(5)–C(6)	120.39(13)	120.56(11)	120.40(16)	
C(5)–C(6)–C(7)	119.58(12)	119.50(10)	119.69(14)	
C(6)–C(7)–C(2)	120.05(12)	119.98(11)	119.82(14)	
C(7)–C(2)–C(3)	120.63(13)	120.73(11)	120.88(15)	
O(3)–C(5)–C(4)	115.15(12)	115.09(10)	115.04(14)	
O(3)–C(5)–C(6)	124.45(11)	124.35(10)	124.57(14)	
C(5)–O(3)–C(8)	117.29(11)	117.27(10)	117.12(15)	

Bonds and angles involving H

Type	Number	I		II		σ_{av}
		Range	Mean	Range	Mean	
C–H(ali)	5	0.93–1.01	0.97	0.91–1.01	0.96	0.02
C–H(aro)	4	0.92–0.99	0.96	0.94–1.00	0.97	0.02
X–C–H; X=S,O,C	7	106–113	109	104–113	109	1
C–C–H(phenyl)	8	117–124	120	118–123	120	1
H–C–H	4	108–113	110	108–112	111	1

^aBonds lengths corrected for rigid-body motion using the program THMA11.



those calculated from tabulated values¹⁷ for the OMe and SO₂Me groups: $\Delta\alpha = 0.5$, $\Delta\beta = -0.2$, $\Delta\gamma = -0.4$ and $\Delta\delta = 0.8^\circ$.

The methoxy group atoms O(3) and C(8) lie nearly in the ring plane; the distances from this plane are -0.032 and -0.114 Å, respectively. The methyl group forms a short contact with the *ortho* H atom [$\text{H}(82)\cdots\text{H}(6) = 2.22$, $\text{H}(83)\cdots\text{H}(6) = 2.34$ Å*], inducing a pronounced in-plane bending of the C(5)–O(3) bond [$\text{O}(3)\text{--C}(5)\text{--C}(4) = 115.0(1)$ and $\text{O}(3)\text{--C}(5)\text{--C}(6) = 124.6(1)^\circ$]. The C–O–CH₃ angle is $117.1(2)^\circ$. These angle values are characteristic for near-planar methoxy-substituted benzenes.^{18,19} The two O atoms in the SO₂ group are 0.200 [O(1)] and 0.688 Å [O(2)] above the ring plane. This is not close enough to cause a similar bending of the S–C(2) bond [$\text{S--C}(2)\text{--C}(3) = 119.6(1)$ and $\text{S--C}(2)\text{--C}(7) = 119.4(1)^\circ$].

Pairs of bonds over the C(2)–C(5) diagonal in the benzene ring show small, but systematic differences. Using the values corrected for rigid-body motion these are $a' - a = 0.012$, $b' - b = -0.004$ and $c' - c = 0.007$ Å (see 1), i.e. the discrepancies, Δl , are in the range 1 to 4 $\sigma(\Delta l)$. A similar trend was not found in the high-angle refinements for the *mono*-substituted 1,2-bis(phenylsulfonyl)ethane studied at 85K.²⁰ Insofar as the differences are real, it is reasonable to ascribe them largely to the OCH₃-group. Di Rienzo *et al.*²¹ compared the results of room-temperature studies of some fifteen *para*-substituted anisoles. Their observations of asymmetry in the bonds (but not in the angles) are in qualitative agreement with ours. Theoretical calcula-

* All contacts with H have been calculated with C(aromatic)–H and C(aliphatic)–H distances normalized to 1.09 and 1.10 Å, respectively.

tions at the STO–3G level of accuracy have been performed by Korschin on anisole,²² *p*-dimethoxybenzene²³ and *p*-methoxyphenol.²⁴ All calculations confirm the geometry: $a' > a$, $b' < b$, $c' > c$; in *p*-dimethoxybenzene the effect is enhanced due to the presence of two OCH₃ groups. The feature $a' > a$ and $b' < b$ is consistent with a larger contribution from the resonance form (I) than from (II).^{18,21} This is also in accordance with calculated π charges on C(4) and C(6) in anisole, viz. -0.056 and -0.070 , respectively.²⁵

Perhaps the most prominent feature of the benzene ring in PMO is the significant relative contraction of the bonds C(3)–C(4) and C(6)–C(7), average ~ 0.015 Å. The exocyclic S–C(2) bond length, $1.749(2)$ Å, is distinctly shorter than the mean S–C(aromatic) distance, $1.765(3)$ Å, in some well refined sulfone structures.¹ At the opposite end of the ring, the C(5)–O(3) bond length, $1.352(2)$ Å,[†] is comparable to that of the corresponding bond in several *p*-alkoxybenzoic acids,¹⁸ but falls below the typical range, i.e. $1.367\text{--}1.377$ Å, for methoxybenzenes where the benzene ring is part of a larger ring system.¹⁹ Crystal structure data for anisole itself, which would have been valuable for this comparison, apparently do not exist. All these structural details are in consonance, indicating a substantial

[†] A thermal correction to this bond length is very small, of the order of 0.001 Å.

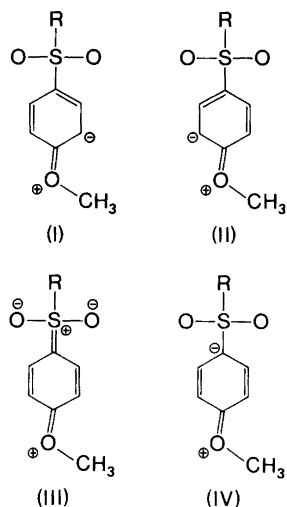
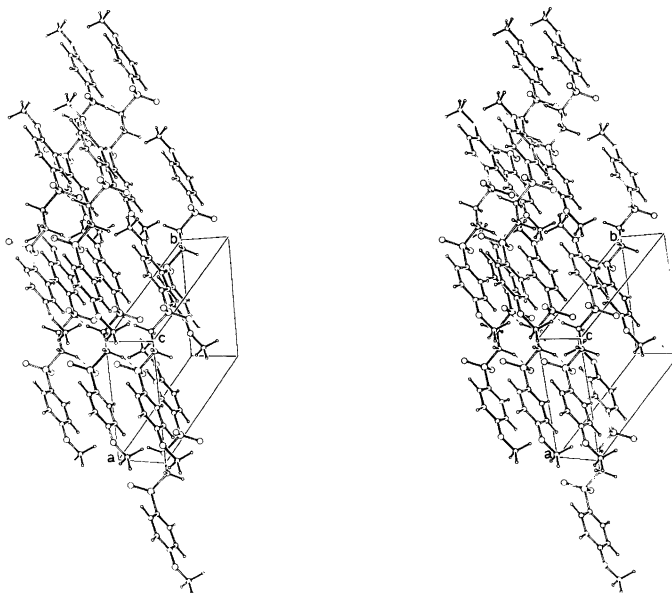


Fig. 2. Stereo drawing of the molecular packing. The two shortest O...H distances, 2.40 and 2.44 Å, are shown as broken lines.



degree of conjugation due to the two 1,4-substituents acting concertedly through their opposite π -electronic properties. The resulting ring geometry with partially localized double bonds can be described as being the result of contributions from resonance structures like (III) and (IV).

The sulfone S–C(1) bond length is very close to the mean value for non-terminal S–C(aliphatic) bonds, viz. 1.781(2) Å.¹ The angles O(1)–S–O(2) = 118.7(1), O(1)–S–C(1) = 107.6(1) and O(2)–S–C(1) = 106.9(1)° are in good agreement with average values for an SO₂ group bonded to a phenyl ring.² The angle C(1)–S–C(2) is slightly smaller than the mean value (105.2°) for the structures PPDS² and MPDSO₂.³ Atom O(1) makes a short intramolecular contact with H(7) of 2.50 Å.

The crystal structure. The molecular packing is shown in Fig. 2. The O atoms interact with several aliphatic and aromatic C atoms. The three shortest O...C distances range from 3.202(2) to 3.449(3) Å for aliphatic C, and from 3.189(3) to 3.444(2) Å for aromatic C atoms. The two shortest O...H distances, O(3)...H(81) ($-1-x, 1-y, -2-z$) = 2.40 and O(1)...H(12) ($x, y, 1+z$) = 2.44 Å, are shown in Fig. 2 as broken lines. The closest van der Waals contacts involving ring

atoms are C(3)...C(3) ($-x, 1-y, -z$) = 3.521(2) and C(7)...C(7) ($-1-x, -y, -1-z$) = 3.607(2) Å.

Acknowledgements. We thank Prof. J. Dunitz and Dr. W. B. Schweizer, ETH, Zürich, for making the program version THMA11 available to us, and Prof. J. M. Bakke of this University for valuable discussions. Support for this work from Norges Almenvitenskapelige Forskningsråd (NAVF) through Grant 14.22.52.005 is gratefully acknowledged.

References

1. Mo, F., Hauback, B. C. and Winther, S. *Acta Crystallogr., Sect. B* 40 (1984) 288.
2. Mo, F. and Thorkildsen, G. *Acta Chem. Scand., Ser. A* 40 (1986) 481.
3. Mo, F. and Gaasdal, A. *Acta Crystallogr., Sect. B* 36 (1980) 2349.
4. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV.
5. Lenhart, P. G. *J. Appl. Crystallogr.* 8 (1975) 568.
6. Templeton, L. K. and Templeton, D. H. *Am. Crystallogr. Assoc. Program Abstr. Ser. 2* 1 (1973) 143.
7. Doyle, P. A. and Turner, P. S. *Acta Crystallogr., Sect. A* 24 (1968) 390.
8. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.

9. Cromer, D. T. and Liberman, D. J. *Chem. Phys.* 53 (1970) 1891.
10. 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.
11. Schomaker, V. and Trueblood, K. N. *Acta Crystallogr., Sect. A* 40 (1984) C339.
12. Johnson, C. K. *ORTEP II*: Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN 1976.
13. Hirshfeld, F. L. *Acta Crystallogr., Sect. A* 32 (1976) 239.
14. Rosenfield, R. E., Trueblood, K. N. and Dunitz, J. D. *Acta Crystallogr., Sect. A* 34 (1978) 828.
15. Schomaker, V. and Trueblood, K. N. *Acta Crystallogr., Sect. B* 24 (1968) 63.
16. Norrestam, R. and Schepper, L. *Acta Chem. Scand., Ser. A* 32 (1978) 889.
17. Domenicano, A. and Murray-Rust, P. *Tetrahedron Lett.* 24 (1979) 2283.
18. Colapietro, M. and Domenicano, A. *Acta Crystallogr., Sect. B* 34 (1978) 3277.
19. (a) van der Helm, D., Wu, K. K., Ansell, L. L., Ruehle, P. H. and Eisenbraun, E. J. *Acta Crystallogr., Sect. B* 33 (1977) 2041; (b) Rohrer, D. C. and Duax, W. L. *Acta Crystallogr., Sect. B* 34 (1978) 3475; (c) Duax, W. L., Rohrer, D. C., Blessing, R. H. and Strong, P. D. *Acta Crystallogr., Sect. B* 35 (1979) 2656; (d) White, P. S. and Neil Swindells, D. C. *Acta Crystallogr., Sect. B* 36 (1980) 491.
20. Thorkildsen, G. *Thesis*, Inst for røntgenteknikk, UNIT-NTH, Trondheim, Norway 1983.
21. Di Rienzo, F., Domenicano, A., Portalone, G. and Vaciago, A. *Abstr. 2nd Yugosl.-Ital. Crystallogr. Conf.*, Dubrovnik, Yugoslavia (1976) p. A102.
22. Korschin, H. *J. Mol. Struct. (Theochem.)* 105 (1983) 213.
23. Korschin, H. *J. Mol. Struct. (Theochem.)* 110 (1984) 311.
24. Korschin, H. *J. Mol. Struct. (Theochem.)* 110 (1984) 303.
25. Anderson, G. M., III, Kollman, P. A., Domelsmith, L. N. and Houk, K. N. *J. Am. Chem. Soc.* 101 (1979) 2344.

Received May 29, 1987.