In conclusion, even if compound (II) shows half protons and symmetry in crystallography, no dynamic behaviour is observed in the crystals. The reason is probably that in this case tautomerism involves the transformation of a strand of an infinite number of molecules into another strand of the same length, and this requires too much energy.

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Structure of 4-Methoxyphenyl Methyl Sulfone and a Redetermination of the Structure of Methyl Phenyl Sulfone

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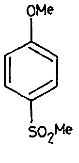
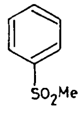
Abstract. $C_8H_{10}O_3S$, $M_r = 186.2$, monoclinic, $P2_1/c$, $a = 5.638\,(3)$, $b = 7.828\,(2)$, $c = 20.045\,(3)$ Å, $\beta = 95.05\,(2)°$, $V = 881.3$ Å^3, $Z = 4$, $D_x = 1.40$ g cm^{-3}, monochromated Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 3.2$ cm^{-1}, $F(000) = 392$, $T = 293$ K, $R = 0.041$ and $wR = 0.055$ for 1499 observed reflections with $|F^2| > 2\sigma(F^2)$. Bond lengths: S—O1 1.431 (2), S—O2 1.437 (2), S—C1 1.761 (2) and S—C7 1.755 (3) Å. $C_7H_8O_2S$, $M_r = 156.2$, monoclinic, $P2_1/c$, $a = 8.172\,(2)$, $b = 9.095\,(2)$, $c = 10.844\,(13)$ Å, $\beta = 111.66\,(5)°$, $V = 749.0$ Å^3, $Z = 4$, $D_x = 1.39$ g cm^{-3}, monochromated Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 3.5$ cm^{-1}, $F(000) = 328$, $T = 293$ K, $R = 0.045$ and $wR = 0.060$ for 1427 observed reflections with $|F^2| > 2\sigma(F^2)$. Bond lengths: S—O1 1.436 (2), S—O2 1.442 (2), S—C1 1.765 (2) and S—C7 1.751 (3) Å.

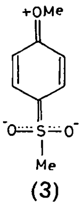
Introduction. In connection with our interest in the preparation of organic materials for non-linear optics, we prepared the chiral sulfoxide (*S*)-4-methoxyphenyl methyl sulfoxide, and obtained, in addition, a small amount of the corresponding sulfone, (1). The structure of the material was determined, and it was thought desirable to compare this with the unsubstituted analogue, methyl phenyl sulfone, (2). This structure has been determined previously (Vorontsova, 1965) but the *R* factor was 19%, so that the bond lengths which were needed for comparison were in some doubt.



(1)



(2)



(3)

Experimental. 4-Methoxyphenyl methyl sulfone, (1), was isolated as a by-product (by flash chromatography, SiO_2, cyclohexane/EtOCOMe) from an oxidation of 4-methoxyphenyl methyl sulfide to obtain the sulfoxide using cumene hydroperoxide as oxidant in the presence of tetra(isopropoxy)titanium and (−)-(*S*,*S*)-diethyl tartrate (Zhao, Samuel & Kagan, 1989). Good-quality crystals were obtained by recrystallization from warm hexane. A crystal of dimensions 0.35 × 0.20 × 0.08 mm was cut from a flat needle and used for data collection. Unit-cell parameters by least-squares fit of 25 reflections in the range $12 < 2\theta < 21°$, space group $P2_1/c$ from systematic absences of $0k0$, k odd and $h0l$, l odd, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, θ–2θ scan, $\Delta\theta = (0.8 + 0.35\tan\theta)°$, maximum scan time 1 min, 2478 measured reflections for $2 < \theta < 28°$ and h 0→7, k 0→10, l −26→26, 2281 unique reflections, $R_{\rm int} = 0.012$, 1499 observed reflections with $|F^2| > 2\sigma(F^2)$, $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/{\rm Lp}$. Two standard reflections measured every hour showed a 3.7% decrease in intensity and a correction was applied to the data; Lorentz and polarization corrections, no absorption or extinction corrections. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985), refinement by full-matrix least squares on F, non-H atoms with anisotropic thermal parameters. H atoms were located from the difference map and refined with isotropic thermal parameters. With a weighting scheme of $w = 1/\sigma^2(F)$, $\sum w(|F_o| - |F_c|)^2$ minimized, the final residuals were $R = 0.041$, $wR = 0.055$ for 1499 observed reflections, 149 variables, $S = 1.6$, $(\Delta/\sigma)_{\rm max} = 0.02$, $(\Delta\rho)_{\rm max,min} = 0.22$, -0.23 e Å^{-3} on a final difference map. Atomic parameters are given in Table 1 and selected bond distances and angles are presented in Table 2.* Fig. 1 shows the molecular structure and the numbering scheme and Fig. 2 the crystal packing.

Methyl phenyl sulfone, (2), was purchased from Lancaster Synthesis. Good-quality crystals were obtained by recrystallization from CH_2Cl_2/hexane. A crystal of dimensions 0.25 × 0.15 × 0.10 mm was used for data collection. Unit-cell parameters by least-squares fit of 25 reflections in the range $8 < \theta < 12°$, space group $P2_1/c$ from systematic absences of $0k0$, k odd and $h0l$, l odd, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, θ–2θ scan, $\Delta\theta = (0.8 + 0.35\tan\theta)°$, maximum scan time 1 min, 2027 measured reflections for $2 < \theta < 28°$ and h 0→10, k 0→12, l −14→14, 1915 unique reflections, $R_{\rm int} = 0.013$, 1427 observed

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3) *for* (1)

$U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{\rm eq}$
S	1348.0 (10)	4394.6 (8)	4004.4 (3)	51.3 (1)
O1	−1142 (3)	4722 (3)	4024.6 (9)	87 (1)
O2	2317 (4)	2877 (2)	4327.5 (9)	81 (1)
O3	3806 (3)	4146 (2)	1216.0 (8)	65 (1)
C1	1996 (3)	4334 (2)	3161.0 (9)	41 (1)
C2	4045 (4)	3513 (3)	2993.9 (11)	49 (1)
C3	4570 (4)	3471 (3)	2342.2 (11)	51 (1)
C4	3083 (4)	4244 (2)	1841.2 (10)	44 (1)
C5	1007 (4)	5063 (3)	2004.8 (10)	45 (1)
C6	483 (3)	5098 (3)	2667.2 (10)	46 (1)
C7	2965 (5)	6143 (3)	4353.6 (11)	64 (1)
C8	2336 (5)	4856 (4)	671.5 (12)	72 (1)

Table 2. *Intramolecular distances* (Å) *and angles* (°) *for* (1)

S—O1	1.431 (2)	S—O2	1.437 (2)
S—C1	1.761 (2)	S—C7	1.755 (3)
O3—C4	1.354 (3)	O3—C8	1.424 (3)
C1—C2	1.389 (3)	C1—C6	1.384 (3)
C2—C3	1.365 (3)	C3—C4	1.389 (3)
C4—C5	1.399 (3)	C5—C6	1.386 (3)
O1—S—O2	118.0 (1)	O1—S—C1	108.6 (1)
O1—S—C7	109.0 (1)	O2—S—C1	107.9 (1)
O2—S—C7	107.5 (1)	C1—S—C7	105.0 (1)
C4—O3—C8	119.0 (2)	S—C1—C2	119.4 (1)
S—C1—C6	120.5 (2)	C2—C1—C6	120.1 (2)
C1—C2—C3	119.8 (2)	C2—C3—C4	120.9 (2)
O3—C4—C3	115.7 (2)	O3—C4—C5	124.7 (2)
C3—C4—C5	119.6 (2)	C4—C5—C6	119.2 (2)
C1—C6—C5	120.4 (2)		

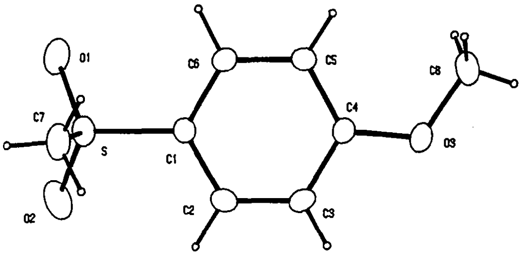


Fig. 1. Molecular structure and numbering scheme for 4-$MeOC_6H_4SO_2Me$.

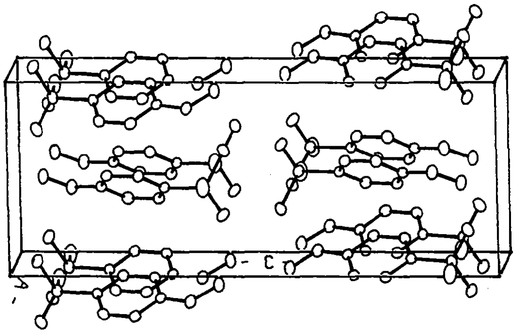


Fig. 2. Packing diagram for 4-$MeOC_6H_4SO_2Me$.

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* Lists of structure factors, anisotropic temperature factors, H-atom parameters, complete bond distances and angles, least-squares planes, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54791 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0512]

reflections with $|F^2| > 2\sigma(F^2)$, $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/\mathrm{Lp}$. Two standard reflections measured every hour showed a 14.7% decrease in intensity and a correction was applied to the data: Lorentz and polarization corrections, no absorption or extinction corrections. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985), refinement by full-matrix least squares on *F*, non-H atoms with anisotropic thermal parameters. H atoms were located from the difference map and refined with isotropic thermal parameters. With a weighting scheme of $w = 1/\sigma^2(F)$, $\sum w(|F_o| - |F_c|)^2$ minimized, the final residuals were $R = 0.045$, $wR = 0.060$ for 1427 observed reflections, 123 variables, $S = 1.9$, $(\Delta/\sigma)_{\max} = 0.03$, $(\Delta\rho)_{\max,\min} = 0.31$, -0.58 e Å^{-3} on a final difference map. Atomic parameters are given in Table 3 and selected bond distances and angles are presented in Table 4. Fig. 3 shows the molecular structure and the numbering scheme and Fig. 4 the crystal packing.

Programs from the Enraf–Nonius *SDP-Plus* package (Frenz, 1984) were run on a MicroVAX II computer. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Drawings by *PLUTO* (Motherwell, 1976).

Discussion. The structure of methyl phenyl sulfone, (2), is essentially the same as that previously determined (Vorontsova, 1965) but the bond lengths and angles now seem to be within the more normal ranges for this type of compound. The structures of 1,2-bis(phenylsulfonyl)ethane (Mo & Thorkildsen, 1986) and 1,2-bis(4-methoxyphenylsulfonyl)ethane (Hauback, Helgemo & Mo, 1988) have been determined previously and compared using high-quality data. For $PhSO_2CH_2CH_2SO_2Ph$ the data with high-angle cutoff (which most closely compares with ours) gave a value of 1.764 (1) Å for the length of the bond from S to the aryl C atom, and 1.437 (1) and 1.436 Å for the S—O bond lengths. By contrast, the values for the methoxy-substituted compound were C_{Ar}—S = 1.750 (1), S—O = 1.445 (1), 1.447 (1) Å. Thus the S—C_{Ar} bond in the substituted compound is distinctly shorter than in most related structures, while the unsubstituted bis(sulfone) gave an essentially normal value. Also the S—O bond distances are longer for the methoxylated compound than for the unsubstituted analogue. The authors concluded that the difference between the two bond lengths reflected a contribution from a dipolar resonance form such as (3). The comparison in our examples is less convincing. The S—C_{Ar} bond lengths for the methoxyphenyl methyl sulfone and the unsubstituted analogue are respectively 1.761 (2) and 1.765 (2) Å. While the difference is in the expected direction, it is not large enough to establish a real contribution from a dipolar form. This

Table 3. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3) *for* (2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
S	3677.2 (6)	1393.7 (5)	1671.5 (5)	41 (0)
O1	3100 (2)	148 (2)	804 (2)	65 (1)
O2	4538 (2)	1111 (2)	3073 (3)	59 (1)
C1	1849 (2)	2542 (2)	1448 (2)	38 (1)
C2	274 (3)	2304 (2)	392 (2)	47 (1)
C3	− 1150 (3)	3184 (3)	261 (2)	58 (1)
C4	− 1014 (3)	4282 (3)	1160 (2)	63 (1)
C5	567 (3)	4520 (3)	2216 (2)	60 (1)
C6	2005 (3)	3653 (2)	2367 (2)	49 (1)
C7	5104 (3)	2435 (3)	1148 (2)	56 (1)

Table 4. *Intramolecular distances* (Å) *and angles* (°) *for* (2)

S—O1	1.436 (2)	S—O2	1.442 (2)
S—C1	1.765 (2)	S—C7	1.751 (3)
C1—C2	1.388 (2)	C1—C6	1.392 (3)
C2—C3	1.377 (3)	C3—C4	1.371 (4)
C4—C5	1.391 (3)	C5—C6	1.374 (3)
O1—S—O2	117.6 (1)	O1—S—C1	108.66 (9)
O1—S—C7	108.1 (1)	O2—S—C1	108.0 (1)
O2—S—C7	108.3 (1)	C1—S—C7	105.5 (1)
S—C1—C2	120.1 (2)	S—C1—C6	118.8 (1)
C2—C1—C6	121.1 (2)	C1—C2—C3	119.0 (2)
C2—C3—C4	120.5 (2)	C3—C4—C5	120.4 (2)
C4—C5—C6	120.2 (2)	C1—C6—C5	118.9 (2)

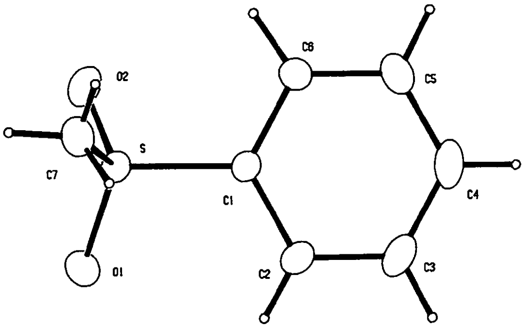

Fig. 3. Molecular structure and numbering scheme for $PhSO_2Me$.

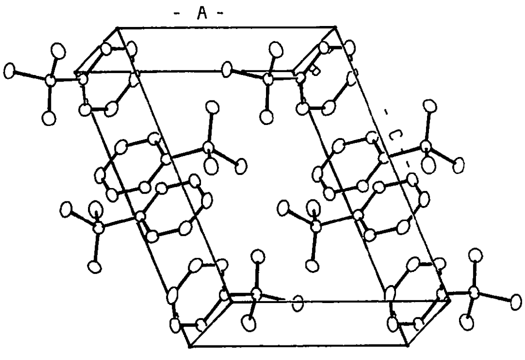

Fig. 4. Packing diagram for $PhSO_2Me$.

negative conclusion is reinforced by noting that the differences in the S—O bond lengths are *not* in the expected direction, suggesting that crystal packing forces may play a dominant role. The corresponding C—S bond length in 3-MeO-4-$MeSO_2C_6H_3$-$CONHCH_2CH_2NEt_2$ is 1.760 (3) Å (Houttemane, Boivin, Nowogrocki, Thomas, Bonte & Debaert, 1983) and in 2,4-$(MeO)_2C_6H_3SO_2CH(SO_2Me)_2$ it is 1.730 (4) Å (Grossert, Hoyle, Cameron, Roe & Vincent, 1987).

It is of some interest to compare the packing diagrams for the two sulfones (Figs. 2 and 4). In the methoxy-substituted compounds the molecules are 'paired' with clear π–π interactions between the aromatic rings. Longer range interactions are also of the 'head-to-head' and 'tail-to-tail' variety. The structure of methyl phenyl sulfone is in sharp contrast, with no obvious π–π interactions and antiparallel chains of molecules in a 'head-to-tail' arrangement. There is no obvious explanation for this difference. Further studies of this type of compound are underway.

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Structures Cristallines de Deux Dérivés de l'Oxaphénalène: les 2-Benzoyl- et 2-(4-Methoxybenzoyl)-6-méthoxynaphto[1,8-*bc*]pyranes

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(*Reçu le* 18 *avril* 1991, *accepté le* 30 *septembre* 1991)

Abstract. 6-Methoxynaphtho[1,8-*bc*]pyran-2-yl phenyl ketone, (I), $C_{20}H_{14}O_3$, monoclinic, $M_r = 302.3$, $P2_1/n$, $a = 10.522$ (9), $b = 12.63$ (2), $c = 11.644$ (6) Å, $\beta = 103.40$ (3)°, $V = 1505$ Å^3, $Z = 4$, $D_x = 1.334$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, graphite monochromator, $\mu = 0.733$ mm^{-1}, $F(000) = 632$, $T = 298$ K, $R = 0.042$ for the 2058 observed reflections. 6-Methoxynaphtho[1,8-*bc*]pyran-2-yl 4-methoxyphenyl ketone, (II), $C_{21}H_{16}O_4$, monoclinic, $M_r = 332.4$, $P2_1/n$, $a = 14.310$ (2), $b = 16.260$ (1), $c = 7.62$ (1) Å, $\beta = 115.20$ (1)°, $V = 1604$ Å^3, $Z = 4$, $D_x = 1.376$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, graphite monochromator, $\mu = 0.74$ mm^{-1}, $F(000) = 696$, $T = 298$ K, $R = 0.044$ for the 2540 observed reflections. The oxaphenalene nuclei of compounds (I) and (II) are quasiplanar and the double bond between C(2) and C(3) shows a greater ethylenic character than that observed in the naphthofuran series, in good agreement with ^{1}H and ^{13}C NMR data.

Introduction. Parmi les substances les plus génotoxiques actuellement connues figurent certains dérivés des arénofuranes et particulièrement des 2-nitronaphto[2,1-*b*]furanes (Royer & Buisson, 1986; Ajana, Bideau, Cotrait, Buisson, Demerseman, Einhorn & Royer, 1988).

Plus récemment, il a été montré que des 2-nitrooxaphénalènes, méthoxylés ou non, possèdent

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