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A second monoclinic polymorph of *S*-(4-tolyl) 4-toluenethiosulfonate at 150 and 293 K

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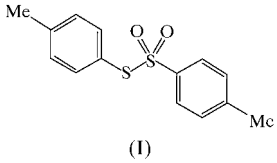
The title compound, $C_{14}H_{14}O_2S_2$, contains discrete molecules and is a polymorph of a structure reported previously by Caputo, Palumbo, Nardelli & Pelizzi [*Gazz. Chim. Ital.* (1984), **114**, 421–430]. The present structure contains no intermolecular C—H···O hydrogen bonds, whereas in the previous polymorph, the molecules are linked into continuous chains by such interactions.

Comment

The structure of *S*-(4-tolyl) 4-toluenethiosulfonate, (I), 4-CH_3-$C_6H_4SO_2SC_6H_4CH_3$-4, was reported several years ago (Caputo *et al.*, 1984). The compound crystallized in space group $P2_1/n$ with $Z = 4$, and we refer to this as polymorph *A*. This sample was synthesized in acetone solution and, in the absence of any further information in the original report (Caputo *et al.*, 1984), it may reasonably be assumed that polymorph *A* was obtained by crystallization from acetone.



(I)

We have now observed a second monoclinic polymorph of (I), denoted polymorph *B*, by crystallization from ethanol. Although both polymorphs crystallize in space group No. 14 with $Z = 4$, they have slightly different unit-cell volumes at 293 K and their unit-cell dimensions are entirely different. In particular, the ratio V/b at 293 (2) K is 115.8 (1) Å^2 for polymorph *A* and 203.1 (1) Å^2 for polymorph *B*. Polymorph *B* is unchanged upon lowering the temperature from 293 (2) K to 150 (2) K: apart from a 3.0% change in the unit-cell volume, the structures of polymorph *B* at these two temperatures are essentially identical. Hence, only the more precise results from the low-temperature determination are discussed here.

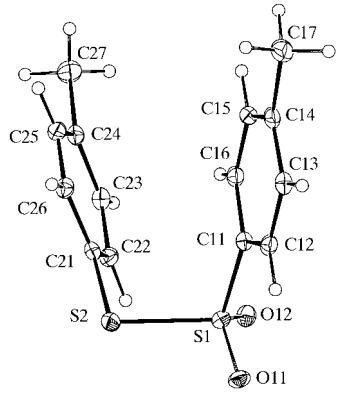


Figure 1
The molecular conformation of (I) in polymorph *B*, showing the atom-labelling scheme used in this work. Displacement ellipsoids are drawn at the 30% probability level and only the major conformation is shown for the methyl groups; the minor-occupancy O atoms have been omitted.

The molecular structures of (I) found in the two polymorphs are very similar, although not identical. While the overall conformations are broadly similar, with an anti-periplanar arrangement of an aryl ring and a sulfone O atom about the $S^{II}—S^{VI}$ bond (Figs. 1 and 2, Table 1), the key torsional angles exhibit detailed but significant differences from one polymorph to the other (Table 1). Most of the bond lengths and angles are typical of their types (Allen *et al.*, 1987), but noteworthy are the very large $O—S^{VI}—O$ angles and the correspondingly small $C—S^{VI}—S^{II}$ angle.

Apart from the sulfone O atoms, the rest of the heavy-atom skeleton has a conformation close to C_2 rotational symmetry. This is possibly connected with the observation in the present polymorph *B* of minor orientational disorder. At 150 (2) K, 6.25% of the molecules adopt an orientation in which the S^{VI} and S^{II} sites are interchanged, so that the O atoms occupy two pairs of sites, with site-occupation factors of 0.938 and 0.062, respectively. In the determination at 293 (2) K, the site-occupation factors were 0.96 and 0.04, so that 4% of the molecules adopt the alternative orientation; however, since for practical reasons different crystals had been used for the two data collections, the difference between these two measures of disorder is not significant. No such disorder was reported for polymorph *A*, or for the related esters $PhSO_2SPh$ and 4-Cl-$C_6H_4SO_2SC_6H_4Cl$-4 (Caputo *et al.*, 1984).

Possibly the most striking difference between the crystal structures of the two polymorphs is the absence of any C—H···O hydrogen bonding in polymorph *B*. Since sulfone O atoms are usually particularly effective acceptors, and aromatic C—H are particularly effective donors in such systems (Ferguson *et al.*, 1999), the absence of such interactions in polymorph *B* is unexpected. There are, indeed, some non-bonded contacts in polymorph *B* with $C_{aryl}\cdots O$ distances less than 3.5 Å, but all are associated with C—H···O angles

less (sometimes very much less) than 120°; hence none of these contacts can be regarded either as C—H···O hydrogen bonds or as being structurally significant. By contrast, there are two distinct types of C—H···O hydrogen bond in polymorph *A* (Caputo *et al.*, 1984), with $C_{aryl}\cdots O$ distances of 3.485 (7) and 3.460 (7) Å associated with C—H···O angles of 140 and 150°, respectively, and these interactions serve to link the molecules into continuous spiral chains. Similarly, in $PhSO_2SPh$ (Caputo *et al.*, 1984) there are two types of intermolecular C—H···O hydrogen bond, with C···O distances of 3.318 (8) and 3.265 (8) Å associated with C—H···O angles of 126 and 135°, respectively, which link the molecules into chains.

It is of interest to compare the intermolecular interactions in (I) with those in the series of related compounds 4-$(CH_3C_6H_4SO_2)_2S_x$ (x = 0–3). While there are no atom coordinates available in the Cambridge Structural Database (Allen & Kennard, 1993) for the bis-sulfone corresponding to (I), (4-$CH_3C_6H_4SO_2)_2$ (x = 0; ZZZEQK; Dawson *et al.*, 1948), the centrosymmetric molecules in the close analogue $(PhSO_2)_2$ (DPDSON; Kiers & Vos, 1972) act as fourfold donors and fourfold acceptors in C—H···O hydrogen bonds, with C···O distances of 3.361 (3) and 3.462 (3) Å, and C—H···O angles of 136 and 151°, respectively. All four O atoms in the molecule act as hydrogen-bond acceptors and the molecules are thus linked into continuous two-dimensional sheets. Despite the well developed hydrogen bonding in $(PhSO_2)_2$, this aspect of the structure was not discussed by Kiers & Vos (1972), possibly because at the time of their report, the reality of C—H···O hydrogen bonds appeared to have been definitively demolished (Donohue, 1968). While there are no intermolecular C—H···O hydrogen bonds for x = 1 (ZZZMPW01; Foss *et al.*, 1985), for both x = 2 (ZZZGNK10; Foss *et al.*, 1985) and x = 3 (ZZZVGG01; Foss *et al.*, 1985) the molecules are linked into chains by C—H···O hydrogen bonds, with $C_{aryl}\cdots O$ distances of 3.376 (3) (ZZZGNK10) and 3.347 (5) Å (ZZZVGG01) associated with C—H···O angles of 135 and 136°, respectively. Hence, the absence of C—H···O hydrogen bonds in polymorph *B* of (I) is unusual and unexpected. It is interesting to note that, at 293 (2) K, the hydrogen-bonded polymorph *A* of compound (I) has a molecular volume (*V*/*Z*) *ca* 4% greater than that of polymorph *B*, which exhibits no hydrogen bonding.

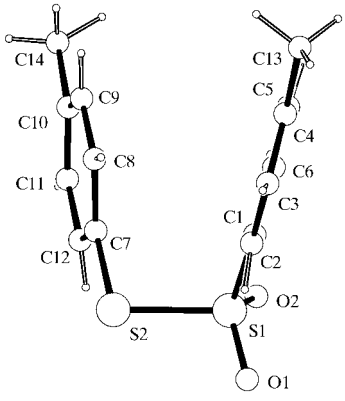


Figure 2
The molecular conformation of (I) in polymorph *A* (Caputo *et al.*, 1984), using their atom-labelling scheme. The atoms are all drawn as spheres of arbitrary radii.

Experimental

Compound (I) was obtained from the reaction between 4-tolylsulfinyl chloride and triphenylstannyllithium in dry tetrahydrofuran. After hydrolysis, (I) was isolated by thin-layer chromatography on silica gel with benzene as the solvent. Crystals suitable for single-crystal X-ray diffraction were grown from a solution in ethanol (m.p. 356–357 K) [literature m.p.: 346–348 K (solvent unspecified; Caputo *et al.*, 1984) and 349–351 K (H_2O/ethanol, 1:3 *v*/*v*; Klivenyi *et al.*, 1955)].

Compound (I) at 150 K

Crystal data

$C_{14}H_{14}O_2S_2$
M_r = 278.37
Monoclinic, $P2_1/c$
a = 13.1835 (11) Å
b = 6.5050 (4) Å
c = 15.2171 (9) Å
β = 92.217 (4)°
V = 1304.02 (16) Å^3
Z = 4
D_x = 1.418 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2266 reflections
θ = 1.54–25.01°
μ = 0.399 mm^{-1}
T = 150 (2) K
Lath, colourless
0.30 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
T_{min} = 0.890, T_{max} = 0.943
7404 measured reflections
2266 independent reflections
1849 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 25.03°
$h = -15 \rightarrow 15$
$k = -7 \rightarrow 7$
$l = -17 \rightarrow 18$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.118
S = 1.088
2266 reflections
173 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0560P)^2 + 0.9064P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I) at 150 K.

S1—O11	1.4464 (17)	S2—O21	1.428 (3)
S1—O12	1.4226 (18)	S2—O22	1.429 (3)
S1—C11	1.763 (2)	S2—C21	1.774 (2)
S1—S2	2.1011 (9)		
O11—S1—O12	119.70 (11)	O11—S1—S2	102.92 (8)
C11—S1—O11	109.23 (11)	O12—S1—S2	109.72 (8)
C11—S1—O12	108.63 (11)	C11—S1—S2	105.71 (8)
S1—S2—C21	100.25 (8)		
S1—S2—C21—C22	68.56 (19)	O11—S1—S2—C21	−176.52 (11)
S1—S2—C21—C26	−108.05 (18)	O12—S1—S2—C21	−48.04 (11)
S2—S1—C11—C12	104.09 (18)	C11—S1—S2—C21	68.92 (12)
S2—S1—C11—C16	−73.5 (2)		

Compound (I) at 293 K

Crystal data

$C_{14}H_{14}O_2S_2$
M_r = 278.37
Monoclinic, $P2_1/c$
a = 13.3579 (7) Å
b = 6.6176 (4) Å
c = 15.2123 (11) Å
β = 92.1322 (19)°
V = 1343.79 (14) Å^3
Z = 4
D_x = 1.376 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2633 reflections
θ = 1.53–26.06°
μ = 0.387 mm^{-1}
T = 293 (2) K
Plate, colourless
0.10 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
T_{min} = 0.962, T_{max} = 0.981
9656 measured reflections
2633 independent reflections
1451 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
θ_{max} = 26.06°
$h = -15 \rightarrow 15$
$k = -7 \rightarrow 8$
$l = -16 \rightarrow 18$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.148
S = 0.976
2633 reflections
173 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0752P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

All H-atom contributions were visible in difference maps and these atoms were treated as riding, with C—H = 0.95–0.98 Å in (I) at 150 K and C—H = 0.93–0.96 Å in (I) at 293 K. It was clear from the difference maps computed to determine the methyl-H contributions (at C17 and C27) that in both cases these H atoms were disordered unequally over two sites. This was then allowed for by appropriate *SHELXL*97 (Sheldrick, 1997) *HFIX*/*AFIX* commands. Difference maps computed at the closing stages of refinement showed very clearly only two peaks of height 0.5 e Å^{-3}, adjacent to S2, consistent with these being contributions from another minor orientation in which the two O atoms were bonded to S2 and not S1. In the final refinement cycles, the occupancies of O11/O12 (bonded to S1) and O21/O22 (bonded to S2) were fixed at 0.938 and 0.062, respectively, in (I) at 150 K, and 0.96 and 0.04, respectively, in (I) at 293 K (effectively making O21 and O22 contribute 0.5 e Å^{-3}), and the S2—O21, S2—O22 geometry was restrained by suitable *SHELXL*97 *DFIX* commands to be comparable with that at S1. The occupancies for the O atoms were determined from peak heights in difference maps and were not refined.

At both temperatures, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service at the University of Southampton. The authors thank the staff for all their help and advice.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1374). Services for accessing these data are described at the back of the journal.

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