

## Conformational preferences in 2-nitrophenylthiolates: *S*-(2-nitrophenyl) 4-toluenethiosulfonate

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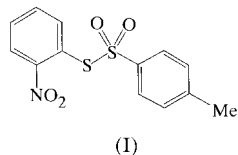
Received 18 February 2000

Accepted 2 March 2000

In the title compound,  $C_{13}H_{11}NO_4S_2$ , the nitro group is rotated by  $44.1(1)^\circ$  out of the plane of the adjacent aryl ring and the toluenethiosulfonate group is almost orthogonal to the plane of the nitrated aryl ring. There are three types of  $C-H\cdots O$  hydrogen bond in the structure [ $C\cdots O$  range  $3.324(3)$ – $3.503(3)$  Å;  $C-H\cdots O$  range  $160$ – $173^\circ$ ] and these link the molecules into a three-dimensional framework.

### Comment

In the solid state, 2-nitrophenylthiolates,  $2-O_2NC_6H_4SX$ , fall into two distinct conformational classes (Low *et al.*, 2000). In one, corresponding to the global energy minimum for the isolated molecules, the nitro group is essentially coplanar with the adjacent aryl ring and the *S*-substituent *X* also lies in this plane. In the other conformation, corresponding to a local energy minimum for the isolated molecules, the substituent *X* is twisted out of the  $C_6S$  plane and the nitro group is also twisted out of this plane; these two rotations are mutually disrotatory. In general, the planar conformation is observed where there are no intermolecular hydrogen bonds in the crystal structure (Ruostesuo *et al.*, 1989; Aupers *et al.*, 1999; Low *et al.*, 2000), while the observation of the twisted conformation is usually associated with the occurrence of



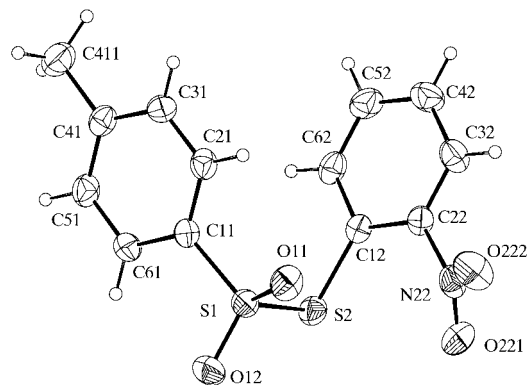
intermolecular  $C-H\cdots O$  hydrogen bonds (Aupers *et al.*, 1999; Kucsman *et al.*, 1984; Low *et al.*, 2000). We report here the structure of *S*-(2-nitrophenyl)-4-toluenethiosulfonate, (I),  $2-O_2NC_6H_4SSO_2C_6H_4CH_3-4$  (*i.e.*  $X = SO_2C_7H_7$ ), which provides a further test of the conformational generalization

outlined above. The compound adopts the twisted nitro conformation and, at the same time, an extensive series of  $C-H\cdots O$  hydrogen bonds links the molecules into a continuous three-dimensional framework.

The molecular conformation of (I) can be described by four independent torsional angles. The  $S-S-C-C$  angles are all close to  $90^\circ$  (Fig. 1 and Table 1), so that the projection of the  $S-S$  bond is approximately normal to the aryl ring. As usual, this rotation of the substituent *X* out of the plane of the nitrated aryl ring is associated with a disrotatory twist of the nitro group out of this plane, here by  $44.1(1)^\circ$ . The disposition of the two aryl rings about the central  $S-S$  bond is synclinal, with one of the sulfone O atoms (O12) antiperiplanar to the nitrophenyl group (Fig. 1, Table 1).

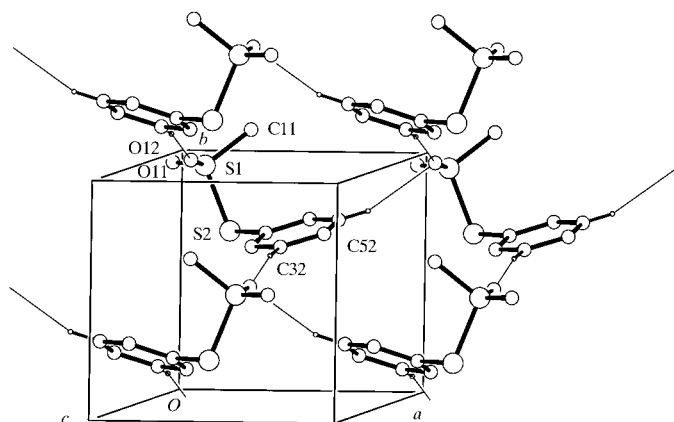
The  $C-C$  distances and the  $C-C-C$  angles on the nitrated aryl ring, and the exocyclic  $C-N$  bond distance are similar to those observed in the related carbothiolate ester  $2-O_2NC_6H_4SCOPh$  (Low *et al.*, 2000). Neither ester exhibits the very pronounced fixation, of quinoid type, observed for the nitrated ring in the styryl derivative,  $2-O_2NC_6H_4SCH=CHPh$  (Low *et al.*, 2000), where the  $C-C$  bond lengths in this ring range from  $1.310(4)$  to  $1.374(5)$  Å and where the corresponding intra-ring  $C-C-C$  angles range from  $111.6(3)$  to  $125.3(3)^\circ$ ; the reasons underlying this bond fixation remain unclear. The bond lengths are all typical of their types (Allen *et al.*, 1987). The  $O-S-O$  and  $O-N-O$  angles are both much larger than the ideal tetrahedral or trigonal values, respectively, doubtless as a consequence of the substantial negative charge on the paired O atoms in each unit.

The molecules in (I) are linked into a continuous three-dimensional framework by means of  $C-H\cdots O$  hydrogen bonds. Each molecule acts as a threefold donor and as a threefold acceptor, but the O atoms of the nitro group are not involved. Sulfone atom O11 acts as a double acceptor, and O12 as a single acceptor of hydrogen bonds. The overall hydrogen-bonding scheme is most easily described in terms of the individual one-dimensional motifs, which combine to form the framework. Atom C52 in the nitrated aryl ring at  $(x, y, z)$  acts as donor to O11 at  $(1+x, y, z)$ , so generating by translation a  $C(7)$  chain running parallel to the  $[100]$  direction.



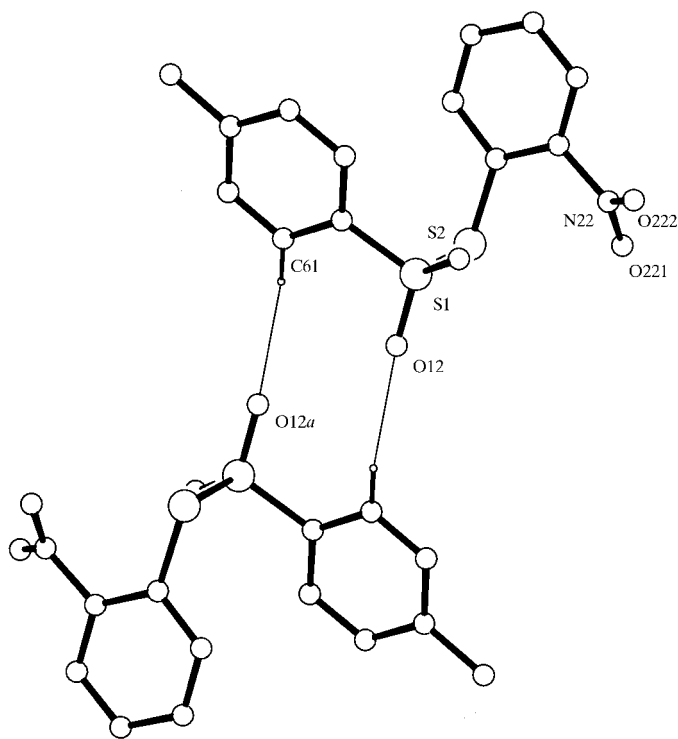
**Figure 1**

A view of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 2**  
Part of the crystal structure of (I) showing one of the (001) sheets built from  $R_4^3(20)$  rings. For clarity, all atoms of the nitrated ring except C11 and all H atoms except H32 and H52 have been omitted.

Atom C32 at  $(x, y, z)$ , in the same aryl ring, acts as a donor to O11 at  $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ , so generating a second  $C(7)$  motif in the form of a spiral chain around the  $2_1$  screw axis along  $(\frac{1}{4}, y, \frac{1}{4})$ . The combination of these two orthogonal chains produces a sheet parallel to (100) and built from a single type  $R_4^3(20)$  ring (Fig. 2). Two such sheets pass through each unit cell, one in the domain  $0 < z < \frac{1}{2}$  and the other in the domain  $\frac{1}{2} < z < 1$ . Thus, the adjacent sheets are not interwoven; they are, however, linked by further C—H...O hydrogen bonds, so



**Figure 3**  
Part of the crystal structure of (I) showing one of the  $R_2^2(10)$  rings which link the (001) sheets built from  $R_4^3(20)$  rings. For clarity, all H atoms except H61 have been omitted.

forming a three-dimensional continuum. Atom C61 at  $(x, y, z)$  acts as a donor to sulfone O12 at  $(-x, 2 - y, -z)$ , so forming an  $R_2^2(10)$  motif centred at  $(0, 1, 0)$  (Fig. 3); by means of such paired hydrogen bonds, each sheet is linked to the two neighbouring sheets.

Examination of the structure with *PLATON* (Spek, 1999) showed that there were no solvent-accessible voids in the crystal lattice.

## Experimental

Compound (I) was obtained from the reaction of 2-nitrobenzenesulphenyl chloride with  $\text{Ph}_3\text{GeOS(O)C}_6\text{H}_4\text{Me-4}$  in  $\text{CCl}_4$  (Taylor & Wardell, 1976). Crystals were obtained from a solution in EtOH (m.p. 367–369 K).

### Crystal data

$\text{C}_{13}\text{H}_{11}\text{NO}_4\text{S}_2$   
 $M_r = 309.35$   
 Monoclinic,  $P2_1/n$   
 $a = 7.2971$  (4) Å  
 $b = 7.0999$  (4) Å  
 $c = 27.0085$  (15) Å  
 $\beta = 95.620$  (10)°  
 $V = 1392.55$  (13) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.476$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 2444 reflections  
 $\theta = 1.51$ – $25.00$ °  
 $\mu = 0.394$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Block, colourless  
 $0.38 \times 0.20 \times 0.18$  mm

### Data collection

Bruker SMART area-detector diffractometer  
 Peak integration from area-detector frames (*SAINIT*; Bruker, 1999)  
 Absorption correction: multi-scan (*SADABS*; Bruker, 1999)  
 $T_{\min} = 0.865$ ,  $T_{\max} = 0.933$   
 8612 measured reflections

2444 independent reflections  
 1907 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.026$   
 $\theta_{\max} = 25$ °  
 $h = -8 \rightarrow 8$   
 $k = -8 \rightarrow 8$   
 $l = -26 \rightarrow 32$   
 Intensity decay: negligible

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.083$   
 $S = 1.002$   
 2444 reflections  
 182 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0486P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 0.18$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.21$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

S1—O11	1.4275 (15)	S2—C12	1.7683 (19)
S1—O12	1.4320 (14)	C22—N22	1.474 (2)
S1—C11	1.7575 (19)	N22—O221	1.219 (2)
S1—S2	2.0910 (8)	N22—O222	1.223 (2)
O11—S1—O12	120.41 (10)	C11—S1—S2	105.09 (6)
O11—S1—C11	108.85 (9)	C12—S2—S1	99.24 (6)
O12—S1—C11	110.56 (9)	O221—N22—O222	124.84 (19)
O11—S1—S2	107.96 (7)	O221—N22—C22	118.70 (18)
O12—S1—S2	102.75 (8)	O222—N22—C22	116.5 (2)
S2—S1—C11—C21	-90.42 (15)	C12—C22—N22—O221	44.2 (3)
S2—S1—C11—C61	83.62 (16)	C32—C22—N22—O221	-135.9 (2)
S1—S2—C12—C62	-89.91 (15)	C12—C22—N22—O222	-136.6 (2)
S1—S2—C12—C22	88.75 (15)	C32—C22—N22—O222	43.3 (2)

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C32—H32...O11 <sup>i</sup>	0.93	2.40	3.324 (3)	173
C52—H52...O11 <sup>ii</sup>	0.93	2.54	3.435 (3)	160
C61—H61...O12 <sup>iii</sup>	0.93	2.58	3.503 (3)	171

Symmetry codes: (i)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (ii)  $1 + x, y, z$ ; (iii)  $-x, 2 - y, -z$ .

H atoms were treated as riding, with C—H = 0.93–0.96 Å. The methyl group was modelled by six H-atom sites of occupancy 0.5.

Data collection: *SAINT* (Bruker, 1999); cell refinement: *SMART* (Bruker, 1999); data reduction: *SMART*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected by members of staff in the Chemistry Department of the University of Aberdeen. The authors thank the staff for all their help and advice.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1372). Services for accessing these data are described at the back of the journal.

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