organic compounds

S-(4-Nitrophenyl) 4-nitrobenzene-thiosulfonate

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The title compound, $C_{12}H_8N_2O_6S_2$, (I), is a positional isomer of S-(2-nitrophenyl) 2-nitrobenzenethiosulfonate [Glidewell, Low & Wardell (2000). *Acta Cryst.* B**56**, 893–905], (II). The most obvious difference between the two isomers is the rotation of the nitro groups with respect to the planes of the adjacent aryl rings. In (I), the nitro groups are only slightly rotated out of the plane of the adjacent aryl ring [2.4 (6) and 6.7 (7)°], while in (II) the nitro groups are rotated by between 37 and 52°, in every case associated with S—S—C—C torsion angles close to 90°. Other important differences between the isomers are the C—S—S(O₂)—C torsion angle [78.39 (2)° for (I) and 69.8 (3)° for (II) (mean)] and the dihedral angles between the aromatic rings [12.3 (3)° for (I) and 28.6 (3)° for (II) (mean)]. There are two types of C—H···O hydrogen bond in the structure [C···O = 3.262 (7) Å and C—H···O = 144°; C···O = 3.447 (7) Å and C—H···O = 166°] and these link the molecules into a two-dimensional framework. The hydrogen-bond-acceptor properties differ between the two isomers.

Comment

This paper forms part of our continuing study of the synthesis and structural characterization of divalent sulfur compounds (Brito *et al.*, 2008, and references therein). The title compound, (I), was isolated during attempts to synthesize sulfenamides by a condensation reaction between 4-nitrobenzenesulfenyl chloride, (III), and secondary amines. Compound (III) was purchased from Aldrich (purity 95%, CAS No. 937–32-6). Impurities were not identified in the technical information accompanying the compound, but we believe that (I) was probably an impurity in the commercial sample of (III). To our knowledge, compound (I) is not commercially available. We report here the structure of (I), 4-O₂NC₆H₄SSO₂C₆H₄O₂N-4.

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. Compound (I) is a positional isomer of S-(2-nitrophenyl) 2-nitrobenzenethiosulfonate, (II), which crystallizes with $Z = 3$ and S—S bond distances in the range 2.070 (2)–2.076 (2) Å (Glidewell *et al.*, 2000). The two isomers exhibit important differences with respect to bonding geometries and conformation. The S—S bond distance in (I) is somewhat longer than that in (II). The S—S distances vary upon oxidation of the S-atom centers in the order S—S < SO₂—S (Aucott *et al.*, 2005). A survey of C—S—S—C fragments (Allen *et al.*, 1987) found that S—S bond distances are bimodally distributed: for torsion angles in the ranges 75–105 and 0–20°, the mean S—S bond distances are 2.031 (15) and 2.07 (2) Å, respectively.
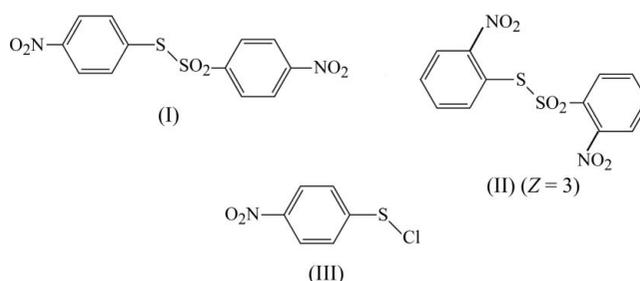
The nitro groups are rotated by 6.7 (7) and 2.4 (6)° in (I), while in (II) the nitro groups are rotated by between 37 and 52°, in every case associated with S—S—C—C torsion angles close to 90°, and at the same time the SO₂C₆H₄O₂N group is also displaced from the C₆S plane. In general, this conformation is observed where there are intermolecular C—H···O hydrogen bonds in the crystal structure, although this is not a sufficient condition for the occurrence of the twisted conformer (Aupers *et al.*, 1999; Kucsman *et al.*, 1984; Low, Storey *et al.*, 2000). Other important differences between the isomers are the C—S—S(O₂)—C torsion angle [78.39 (2)° for (I) and 69.8 (3)° for (II) (mean)] and the torsion angles between the aromatic rings [12.3 (3)° for (I) and 28.6 (3)° for (II) (mean)].

The molecules in (I) are linked into a continuous two-dimensional framework by means of C—H···O hydrogen bonds. The C—H···O(S) hydrogen bonds connect the mol-
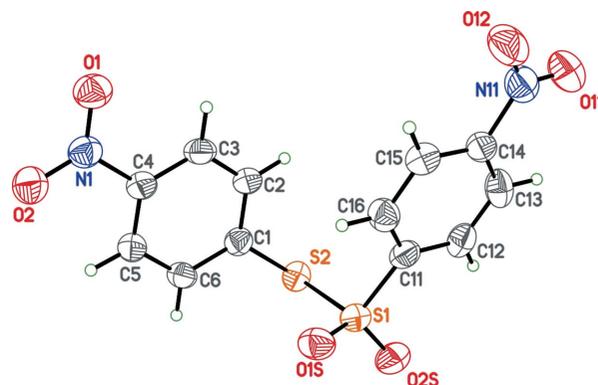

Figure 1
A displacement ellipsoid plot (50% probability level) of (I), showing the atom-numbering scheme.

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ecules to form chains running along the diagonal between the *a* and *b* axes. Pairs of these chains, which are perpendicular to each other, are further connected by C—H···O(N) hydrogen bonds (Table 2 and Fig. 2).

The aromatic C—H bonds between the nitro and sulfone groups (C13—H13 and C15—H15) are expected to be the most acidic bonds in the molecule and thus to show the highest propensity for C—H···O hydrogen-bond formation. Each molecule in (I) acts as a twofold donor at (x, y, z) and as a twofold acceptor; sulfone atom O1S acts as a single acceptor and nitro group atom O11 as an acceptor of hydrogen bonds at $(-x + 2, y - \frac{1}{2}, -z + \frac{1}{2})$ and $(x - 1, y + 1, z)$, respectively, while in (II) both of the sulfone O atoms acts as hydrogen-bond acceptors. The nitro group O atoms of the *S*-(4-nitrophenyl) fragment are not involved. The hydrogen-bond acceptor properties differ between the isomers.

The molecular conformation of (I) can be described by four independent torsion angles. The S—S—C—C angles are all close to 90° (Fig. 1 and Table 1), so that the projection of the S—S bond is approximately normal to both aryl rings. The conformation about the central S—S bond in (I) has one of the S—O bonds antiperiplanar to the remote C1–C6 aryl ring. This same conformation is observed in (II) and is that usually observed in *S*-aryl arenethiosulfonates, ArSSO$_2$Ar′ (Caputo *et al.*, 1984; Ferguson *et al.*, 2000; Low, Glidewell & Wardell, 2000), in preference to the alternative conformation having the two aryl groups antiperiplanar rather than synclinal. The S—SO$_2$ distance is somewhat larger than that in (II) [2.095 (2) Å for (I) and 2.073 (2) Å (mean) for (II)] and is characteristic in esters of this type.

A search of the Cambridge Structural Database (CSD; Version 5.31; Allen 2002) for phenylthiolate fragments C$_6$H$_{5-y}$S*X* (*X* = SO$_2$C$_6$H$_{5-y}$; *y* = 0, 1) yielded seven structures: benzenethiosulfonic acid phenyl ester (CSD refcode BILCII10; Caputo *et al.*, 1984), *S*-(*p*-tolyl) *p*-toluenethiosulfonate (refcode BILCOO01; Ferguson *et al.*, 2000), *p*-tolylthiosulfonic acid *p*-tolyl ester (refcode BILCOO10; Caputo *et al.*, 1984), di(*p*-bromophenyl) thiosulfonate (refcode BPTSLF; Noordik & Vos, 1967), *S*-(2-nitrophenyl) 2-nitro-benzenethiosulfonate (refcode FUQMIN; Glidewell *et al.*, 2000), *S*-(2-nitrophenyl) *p*-toluenethiosulfonate (refcode LIYQOZ; Low, Glidewell &Wardell, 2000) and bis[2-(*N,N*-dipropylcarbamoyl)phenyl] thiosulfinate (refcode NAJBIJ; Kim *et al.*, 1996), with an average S—SO$_2$ distance of 2.087 (4) Å (restraints used in the search: only three-dimensional coordinates available; no private communication; only one sulfone group and no cyclic disulfide). The O—S—O angle is much larger than the ideal tetrahedral values, doubtless as a consequence of both the substantial negative charge on the geminal O atoms (Table 1), which is observed also in (II) as well as in the seven compounds found in the search of the CSD described above, and the π-bonding/double S=O bonds.

Experimental

Crystal data

C$_{12}$H$_8$N$_2$O$_6$S$_2$	$V = 1340.0$ (2) Å^3
$M_r = 340.32$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 5.2585$ (7) Å	$\mu = 0.43$ mm^{-1}
$b = 6.0483$ (5) Å	$T = 173$ K
$c = 42.133$ (4) Å	$0.32 \times 0.12 \times 0.12$ mm

Data collection

Stoe IPDS II two-circle diffractometer	5902 measured reflections
Absorption correction: multi-scan (*MULABS*; Spek, 2009; Blessing, 1995)	2453 independent reflections
	1791 reflections with $I > 2\sigma(I)$
$T_{min} = 0.875$, $T_{max} = 0.950$	$R_{int} = 0.096$

Table 1
Selected geometric parameters (Å, °).

|			
S1—O1S	1.431 (5)	N1—O1	1.216 (6)
S1—O2S	1.440 (4)	N1—O2	1.230 (6)
S1—C11	1.767 (6)	C14—N11	1.466 (8)
S1—S2	2.095 (2)	N11—O11	1.228 (7)
S2—C1	1.801 (5)	N11—O12	1.217 (7)
C4—N1	1.478 (7)		
O1S—S1—O2S	121.0 (3)	O1—N1—O2	123.4 (5)
O1S—S1—C11	107.5 (3)	O1—N1—C4	118.5 (5)
O2S—S1—C11	109.4 (2)	O2—N1—C4	118.0 (5)
O1S—S1—S2	107.92 (17)	O12—N11—O11	123.1 (6)
O2S—S1—S2	103.46 (19)	O12—N11—C14	118.5 (5)
C11—S1—S2	106.77 (19)	O11—N11—C14	118.4 (6)
C1—S2—S1	99.05 (18)		
S1—S2—C1—C2	86.1 (5)	S2—S1—C11—C12	−90.6 (4)
S1—S2—C1—C6	−96.1 (4)	S2—S1—C11—C16	86.8 (4)
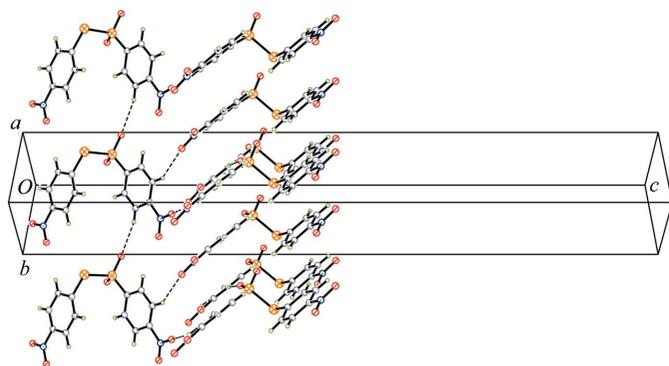
Figure 2
The C—H···O(S) hydrogen bonds connect the molecules to form chains running along the [1$\bar{1}$0] diagonal between the *a* and *b* axes. Pairs of these chains, which are perpendicular to each other, are further connected by C—H···O(N) hydrogen bonds.

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Table 2
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C13—H13$\cdots$O11^i	0.95	2.45	3.262 (7)	144
C15—H15$\cdots$O2S^{ii}	0.95	2.52	3.447 (7)	166

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$	$\Delta\rho_{max} = 0.67$ e Å^{-3}
$wR(F^2) = 0.157$	$\Delta\rho_{min} = -0.37$ e Å^{-3}
$S = 0.97$	Absolute structure: Flack (1983),
2453 reflections	948 Friedel pairs
199 parameters	Flack parameter: 0.06 (18)
H-atom parameters constrained	

All H atoms could be located by difference Fourier synthesis but were ultimately placed in calculated positions and treated as riding, with C—H distances of 0.95 Å and fixed individual displacement parameters $[U_{iso}(H) = 1.2U_{eq}(C)]$. The absolute structure was determined on the basis of 950 measured Bijvoet pairs (coverage 99%). Since the molecule is achiral, the directions of the polar axes had been determined. Two reflections were not included in the data set as they were either partially obscured by the beam stop or were eliminated during data reduction.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL-Plus* (Release 4.1; Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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