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2-Nitrophenyl 4-nitrophenyl disulfide

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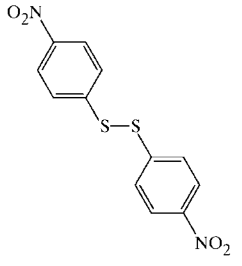
The structure of the title compound, $C_{12}H_8N_2O_4S_2$, contains no direction-specific intermolecular interactions, *i.e.* no C—H$\cdots$O hydrogen bonds, no aromatic π–π-stacking interactions and no C—H$\cdots\pi$(arene) interactions. This behaviour is compared with the three known symmetrical isomers of bis(nitrophenyl) disulfide, having the nitro groups on the two 2-, 3- or 4-positions, all of which exhibit direction-specific supramolecular aggregation.

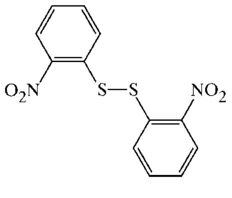
Comment

In bis(4-nitrophenyl) disulfide, $(4\text{-}O_2NC_6H_4)_2S_2$, (I), where the molecules lie across twofold rotation axes in space group $C2/c$, a single C—H$\cdots$O hydrogen bond suffices to link the molecules into sheets, which are then linked by aromatic π–π-stacking interactions to give a three-dimensional framework structure (Wardell *et al.*, 2000). In the isomeric bis(2-nitrophenyl) disulfide, (II), the molecules are linked into chains by a single C—H$\cdots$O hydrogen bond, and the chains are further linked into sheets by means of aromatic π–π-stacking interactions (Glidewell *et al.*, 2000). The structure of bis(3-nitrophenyl) disulfide, (III), on the other hand, contains no C—H$\cdots$O hydrogen bonds, but the molecules are nonetheless linked into chains by aromatic π–π-stacking interactions (Cannon *et al.*, 2000).

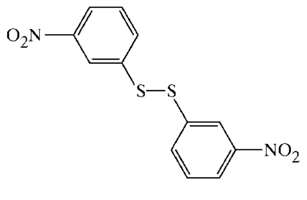
Intrigued by the different supramolecular structures adopted by the isomers (I)–(III), we have now investigated the 'intermediate' isomer 2-nitrophenyl 4-nitrophenyl disulfide, (IV). The intramolecular dimensions and overall molecular conformation of (IV) are comparable with those in (I)–(III), with both nitro groups in (IV) nearly coplanar with the adjacent aryl rings (Fig. 1). Also noteworthy are the C—C—C, C—C—S and C—C—N angles at the *ipso* positions (Table 1), where the C—C—C angles, in particular, are consistent with the electron-donating and electron-withdrawing properties of thiolate and nitro substituents, respectively (Domenicano & Murray-Rust, 1979). We also note that the S2—S1—C11—C12 torsion angle is close to 180°, consistent (Low *et al.*, 2000) with the near coplanarity of the 2-nitro group and the C11–C16 ring.



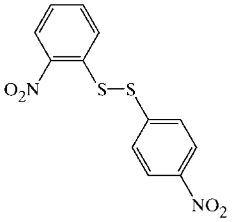
(I)



(II)



(III)



(IV)

However, the striking feature of the structure of (IV) is the complete absence of C—H$\cdots$O hydrogen bonds and of both aromatic π–π-stacking interactions and C—H$\cdots\pi$(arene) interactions, so that there are no direction-specific intermolecular interactions. By not forming C—H$\cdots$O hydrogen bonds, (IV) resembles (III), rather than (I) and (II). The supramolecular structures of (I)–(IV), as defined by the direction-specific intermolecular interactions, are thus three-, two-, one- and zero-dimensional, respectively, with very modest changes in molecular constitution leading to significant changes in the supramolecular aggregation.

The absence of any C—H$\cdots$O hydrogen bonds in (III) and (IV) is highly unusual, as such interactions are generally the dominant feature of the crystal structures of compounds containing nitroarenethiolate, $O_2NC_6H_4SX$, fragments (Kucsman *et al.*, 1984; Aupers *et al.*, 1999; Low *et al.*, 2000; Glidewell *et al.*, 2000), as well as those of simple nitrobenzenes (Boonstra, 1963; Trotter & Williston, 1966; Choi & Abel, 1972; Herbstein & Kapon, 1990; Boese *et al.*, 1992; Sekine *et al.*, 1994).

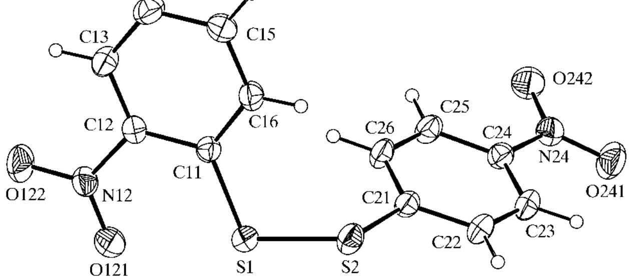


Figure 1
A view of the molecule of (IV) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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Much effort continues to be expended in attempts to compute, using a variety of *ab initio*, semi-empirical and heuristic methods, the structures of simple molecular compounds (Lommerse *et al.*, 2000; Motherwell, 2001). However, the unexpected differences between the crystal structures of members of simple series of isomeric compounds, such as compounds (I)–(IV), and other series where hard (Braga *et al.*, 1995) hydrogen bonds are absent, as reported elsewhere (Farrell *et al.*, 2002; Glidewell *et al.*, 2002), together with the entire phenomenon of polymorphism, in particular the rather frequent observation of concomitant polymorphism (Bernstein *et al.*, 1999), raise at least the suspicion that, for systems characterized by weak and/or long-range intermolecular forces, the crystal structures may, in general, be intrinsically non-computable.

Experimental

A sample of the title compound was obtained by reaction of equimolar quantities of 2-nitrobenzenesulfenyl chloride and (4-nitrobenzenethiolato)triphenylstannane in chloroform solution. Crystals of (IV) suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in ethanol [m.p. 429–431 K; literature m.p. 429 K (Lukashevich & Sergeeva, 1949)].

Crystal data

$C_{12}H_8N_2O_4S_2$
$M_r = 308.34$
Monoclinic, $P2_1/c$
$a = 11.4923$ (6) Å
$b = 7.9061$ (4) Å
$c = 14.3117$ (7) Å
$\beta = 94.3350$ (10)°
$V = 1296.63$ (11) Å^3
$Z = 4$
$D_x = 1.579$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4661 reflections
$\theta = 2.9$–32.5°
$\mu = 0.43$ mm^{-1}
$T = 298$ (2) K
Block, colourless
0.33 × 0.20 × 0.12 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.873$, $T_{\max} = 0.951$
13 378 measured reflections
4661 independent reflections
2924 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 32.5°$
$h = -17 \rightarrow 15$
$k = -11 \rightarrow 11$
$l = -21 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.105$
$S = 0.93$
4661 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.056P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1
Selected bond and torsion angles (°).

C12—C11—C16	116.33 (12)	C22—C21—S2	116.93 (10)
C12—C11—S1	121.77 (10)	C26—C21—S2	123.12 (11)
C16—C11—S1	121.88 (10)	C23—C24—C25	122.02 (13)
C11—C12—C13	122.12 (12)	C23—C24—N24	118.99 (13)
C11—C12—N12	120.57 (12)	C25—C24—N24	118.99 (12)
C22—C21—C26	119.95 (13)		
S1—S2—C21—C22	−150.29 (11)	C11—C12—N12—O121	−0.4 (2)
S2—S1—C11—C12	−175.34 (10)	C23—C24—N24—O241	6.6 (2)
C11—S1—S2—C21	−90.27 (7)		

Compound (IV) crystallized in the monoclinic system; space group $P2_1/c$ was uniquely assigned from the systematic absences. H atoms were treated as riding atoms, with C—H distances of 0.93 Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1120). Services for accessing these data are described at the back of the journal.

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