

## Bis(3-nitrophenyl) disulfide forms no C—H...O hydrogen bonds

Debbie Cannon,<sup>a</sup> Christopher Glidewell,<sup>b\*</sup> John N. Low<sup>c†</sup> and James L. Wardell<sup>c</sup>

<sup>a</sup>Department of Electronic Engineering and Physics, University of Dundee, Nethergate, Dundee DD1 4HN, Scotland, <sup>b</sup>School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, and <sup>c</sup>Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland

Correspondence e-mail: cg@st-andrews.ac.uk

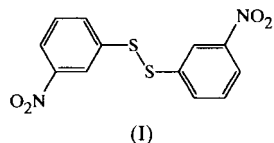
Received 4 July 2000

Accepted 19 July 2000

In the title compound, C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>, the molecules lie across twofold rotation axes in the space group *C2/c*. There are no intermolecular C—H...O hydrogen bonds, but the molecules are linked into chains along [001] by aromatic  $\pi$ ... $\pi$  stacking interactions.

### Comment

Although the structures of bis(2-nitrophenyl) disulfide and bis(4-nitrophenyl) disulfide were determined many years ago from photographic data (Ricci & Bernal, 1969, 1970), we have recently used low-temperature CCD data to redetermine these structures and to analyse the extensive intermolecular aggregation (Glidewell *et al.*, 2000; Wardell *et al.*, 2000). In the 2,2'-isomer, the molecules act as single donors of C—H...O hydrogen bonds and as single acceptors, so that chain formation results; the chains are further linked into sheets by aromatic  $\pi$ ... $\pi$  stacking interactions. Molecules of the 4,4'-isomer lie across twofold rotation axes and act as twofold donors and twofold acceptors of hydrogen bonds; the resulting sheets are linked into a three-dimensional framework by aromatic  $\pi$ ... $\pi$  stacking interactions. It is noteworthy that for both compounds, the original structure reports indicated that there were no intermolecular interactions.



As a continuation of this study, we have now determined the structure of the 3,3'-isomer, *i.e.* bis(3-nitrophenyl) disulfide, (I), whose structure turns out to contain no C—H...O hydrogen bonds, in contrast to the 2,2'- and 4,4'-isomers. The molecules in (I) lie across twofold rotation axes in space group

<sup>†</sup> Postal address: Department of Electronic Engineering & Physics, University of Dundee, Nethergate, Dundee DD1 4HN, Scotland.

*C2/c* (Fig. 1), just as in the 4,4'-isomer, but there are only two intermolecular C...O contacts of less than 3.50 Å and these are associated with H...O distances greater than 2.75 Å and C—H...O angles well below 120°. All other intermolecular C...O distances are greater than 3.50 Å with H...O distances greater than 2.85 Å.

The absence of any C—H...O hydrogen bonds in (I) is highly unusual, as such interactions are generally the dominant feature of the crystal structures of compounds containing nitroarene thiolate (O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SX) fragments (Kucsmann *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).

Despite the absence of hydrogen bonds, the molecules of (I) are nonetheless linked into chains by means of aromatic  $\pi$ ... $\pi$  stacking interactions. The aryl ring at (*x*, *y*, *z*) is part of a molecule lying across the rotation axis along (0, *y*,  $\frac{1}{2}$ ); this ring forms a  $\pi$ ... $\pi$  stacking interaction across the inversion centre at the origin with the ring at (−*x*, −*y*, −*z*), which is part of a

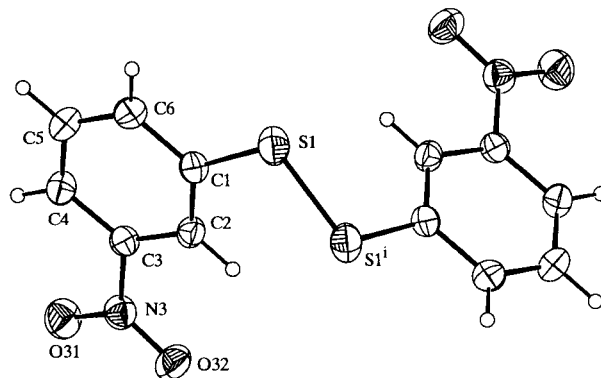


Figure 1

The molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level [symmetry code: (i)  $-x, y, \frac{1}{2} - z$ ].

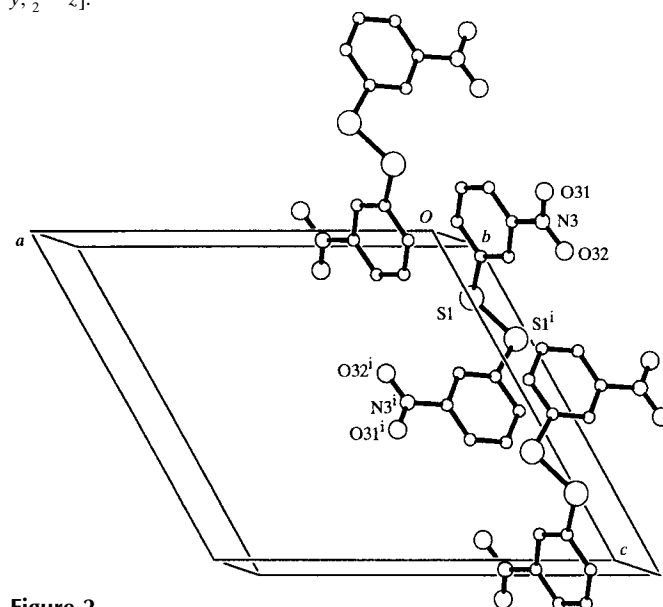


Figure 2

Part of the crystal structure of (I) showing one of the [001] chains formed by the aromatic  $\pi$ ... $\pi$  stacking interactions. H atoms have been omitted for the sake of clarity.

molecule lying across the rotation axis along  $(0, y, -\frac{1}{4})$ . The separation of the ring planes is 3.587 (3) Å and the centroid offset is 1.429 (3) Å. The symmetry-related ring in the reference molecule lying across the axis along  $(0, y, \frac{1}{4})$  is at  $(-x, y, \frac{1}{2} - z)$  and this in turn forms a stacking interaction across the inversion centre at  $(0, 0, \frac{1}{2})$  with the ring at  $(x, -y, \frac{1}{2} + z)$ ; this ring is itself part of a molecule lying across the twofold axis along  $(0, y, \frac{3}{4})$ . Propagation of this  $\pi \cdots \pi$  stacking interaction by the inversion centres at  $(0, 0, n/2)$  ( $n = \text{zero or integer}$ ) and the twofold rotation axes along  $(0, y, \frac{1}{4} + n/2)$  ( $n = \text{zero or integer}$ ) produces a chain parallel to the [001] direction (Fig. 2). A second such chain related to the first by the action of the *C*-centring operation is generated by the glide plane at  $y = 0.5$ , and these two chains accommodate all the unit-cell contents and thus are sufficient to define the entire crystal structure.

Molecules of the 2,2'-, 3,3'- and 4,4'-isomers of dinitrophenyl disulfide are thus hydrogen bonded to two, zero and four other molecules, respectively, and are linked *via*  $\pi \cdots \pi$  stacking interactions to one, two and two other molecules, respectively. Very modest changes to the molecular constitutions lead to significant changes in the supramolecular aggregation.

The bond lengths and angles which show significant differences between the three isomers are listed in Table 1. Particularly noteworthy are the C—C—C and S—C—C angles at the *ipso* position, the C—S—S—C torsion angles and the torsion angles defining the twist of the nitro groups with respect to the plane of the adjacent aryl ring.

## Experimental

A sample of compound (I) was obtained from Aldrich. Crystals suitable for single-crystal X-ray diffraction were grown from a solution in ethanol.

### Crystal data

$C_{12}H_8N_2O_4S_2$	$D_x = 1.560 \text{ Mg m}^{-3}$
$M_r = 308.32$	Mo $K\alpha$ radiation
Monoclinic, <i>C2/c</i>	Cell parameters from 2212 reflections
$a = 13.6731 (9) \text{ \AA}$	$\theta = 2.86\text{--}24.92^\circ$
$b = 8.9078 (6) \text{ \AA}$	$\mu = 0.419 \text{ mm}^{-1}$
$c = 12.4539 (8) \text{ \AA}$	$T = 306 (2) \text{ K}$
$\beta = 120.070 (1)^\circ$	Block, yellow
$V = 1312.70 (15) \text{ \AA}^3$	$0.47 \times 0.26 \times 0.16 \text{ mm}$
$Z = 4$	

### Data collection

Bruker 1000 CCD diffractometer	983 reflections with $I > 2\sigma(I)$
$\varphi$ - $\omega$ scans	$R_{\text{int}} = 0.018$
Absorption correction: multi-scan (SADABS; Bruker, 1997)	$\theta_{\text{max}} = 25^\circ$
$T_{\text{min}} = 0.831, T_{\text{max}} = 0.940$	$h = -10 \rightarrow 16$
4030 measured reflections	$k = -10 \rightarrow 9$
1156 independent reflections	$l = -14 \rightarrow 14$
	Intensity decay: negligible

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 0.2399P]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.089$	$(\Delta/\sigma)_{\text{max}} = 0.005$
$S = 1.047$	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
1156 reflections	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
91 parameters	
H-atom parameters constrained	

**Table 1**

Comparison of geometric parameters (Å, °) for (I) and its 2,2'- and 4,4'-isomers.

	2,2'-Isomer	(I)	4,4'-Isomer
S—S	2.057 (2)	2.0260 (10)	2.099 (8)
S—C—C	122.5 (3)	114.77 (14)	115.31 (16)
	121.5 (3)	125.03 (13)	124.33 (16)
	121.2 (4)		
	121.6 (4)		
C—C(S)—C	116.2 (4)	120.18 (16)	120.3 (2)
	117.2 (4)		
C—C(NO <sub>2</sub> )—C	122.7 (4)	123.13 (16)	122.2 (2)
	121.6 (4)		
C—S—S—C	−84.4 (3)	97.63 (9)	88.11 (11)
C—C—N—O	−7.6 (7)	4.7 (2)	−7.2 (3)
	−16.7 (5)		

Compound (I) crystallized in the monoclinic system; space group *C2/c* was assigned from the systematic absences and confirmed by the analysis. The H atoms were treated as riding with C—H = 0.93 Å. Examination of the structure with PLATON (Spek, 2000) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2000); software used to prepare material for publication: SHELXL97 and WordPerfect macro PRPKAPPA (Ferguson, 1999).

X-ray data were collected at the University of Aberdeen using a Bruker SMART 1000 diffractometer. The authors thank Dr W. Harrison for his assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1410). Services for accessing these data are described at the back of the journal.

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