Bis(4-nitrophenyl) disulfide at 150 K, a three-dimensional framework built from C—H···O hydrogen bonds and aromatic π···π stacking interactions

James L. Wardell,[a] John Nicolson Low[b]* and Christopher Glidewell[c]

[a]Department of Chemistry, University of Aberdeen, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, [b]University of Dundee, Nethergate, Dundee DD1 4HN, Scotland, and [c]School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland

Correspondence e-mail: j.n.low@dundee.ac.uk

In the title compound, $(4\text{-}O_2NC_6H_4)_2S_2$ or $C_{12}H_8N_2O_4S_2$, the molecules lie across twofold rotation axes. A single type of C—H···O hydrogen bond, with C···O = 3.394 (3) Å and C—H···O = 158°, links the molecules into continuous two-dimensional sheets built from a single type of $R_4^4(44)$ ring. These sheets are linked by aromatic π···π stacking interactions to form a continuous three-dimensional framework.

Comment

The structure of bis(4-nitrophenyl) disulfide, (I), at room temperature was reported many years ago (Ricci & Bernal, 1969). The structure was refined to $R = 0.101$ using 597 visually estimated intensities which were not corrected for either absorption or crystal decay; typical s.u.'s reported were 0.01 Å for bond lengths, 1° for bond angles and 2° for torsion angles. We have now redetermined the structure of (I) using low-temperature CCD data. Not only is the structure reported here more precisely determined but some of the intramolecular parameters show material differences from those reported earlier. More significantly, the present analysis has revealed a three-dimensional supramolecular framework built from a combination of C—H···O hydrogen bonds and aromatic π···π stacking interactions. The formation of this framework is the focus of the present report.
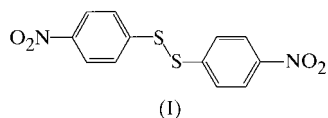
The cell dimensions and refined atomic coordinates show that the same polymorph has been used in both studies. The molecules (Fig. 1) lie across twofold rotation axes in $C2/c$, with a C—S—S—C torsion angle of 88.11 (11)° in (I) compared with a value of 90.14° reported by Ricci & Bernal (1969).
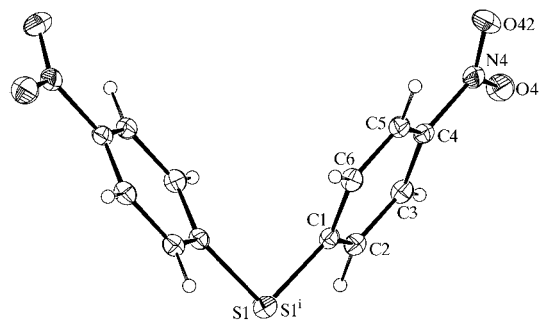
Figure 1
A molecule of (I) showing the atom-labelling scheme [symmetry code: (i) $-x, y, \frac{1}{2} - z$]. Displacement ellipsoids are drawn at the 30% probability level.
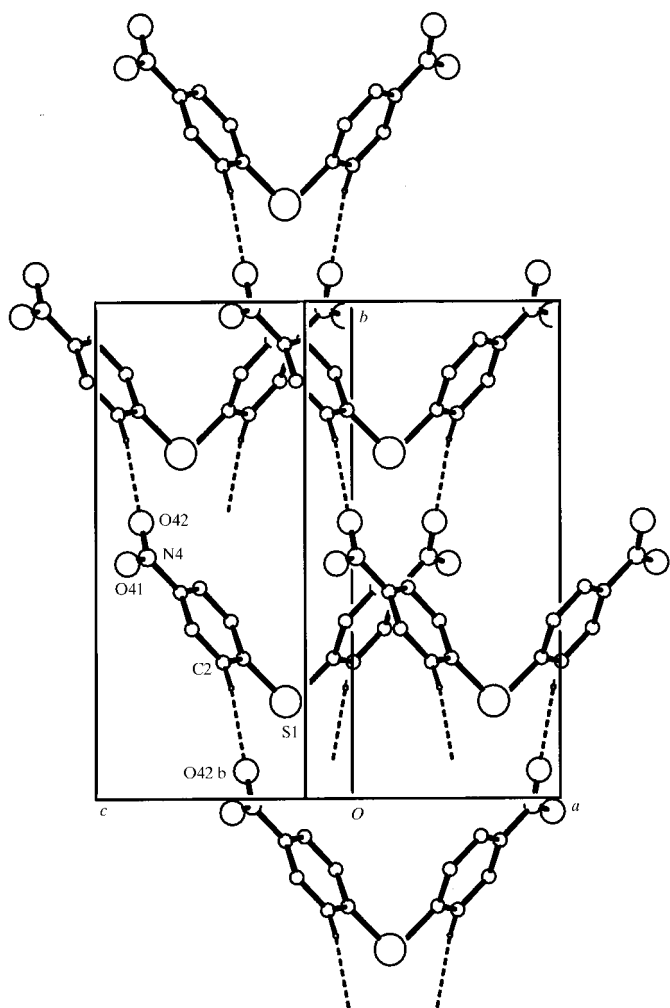
Several of the key bond distances reported here (Table 1) differ significantly from those reported earlier and this must cast some doubt on the validity of at least some of the lengthy discussion of these parameters (Ricci & Bernal, 1969).

The structure contains a single type of C—H···O hydrogen bond, which is reasonably strong for its type (Table 2). This interaction, when propagated by the space-group symmetry, serves to link the molecules into deeply puckered two-dimensional sheets parallel to (001). The reference molecule (Fig. 1) lies across the twofold axis at $(0, y, \frac{1}{4})$ and the two symmetry-related halves of this molecule are thus at $(\frac{1}{2}, y, z)$ and $(-x, y, \frac{1}{2} - z)$; the midpoint of the S—S bond has $y = ca$ 0.195. Atom C2 at (x, y, z) acts as a hydrogen-bond donor to O42 at $(\frac{1}{2} + x, -\frac{1}{2} + y, z)$, a component of the molecule centred at $(\frac{1}{2}, -\frac{1}{2} + y, \frac{1}{4})$, while the symmetry-related C2 atom at $(-x, y, \frac{1}{2} - z)$ acts as donor to O42 at $(-\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, itself a component of the molecules centred at $(-\frac{1}{2}, -\frac{1}{2} + y, \frac{1}{4})$. The reference molecule also acts as an acceptor of two C—H···O hydrogen bonds from the molecules centred at $(\frac{1}{2}, \frac{1}{2} + y, \frac{1}{4})$ and $(-\frac{1}{2}, \frac{1}{2} + y, \frac{1}{4})$. Hence, each molecule is hydrogen bonded to four others, resulting in the formation of a two-dimensional sheet built from a single type of $R_4^4(44)$ ring (Fig. 2). The formation of this sheet utilizes just half of the unit-cell contents, so that two such sheets run through each cell, although adjacent sheets are not interwoven.
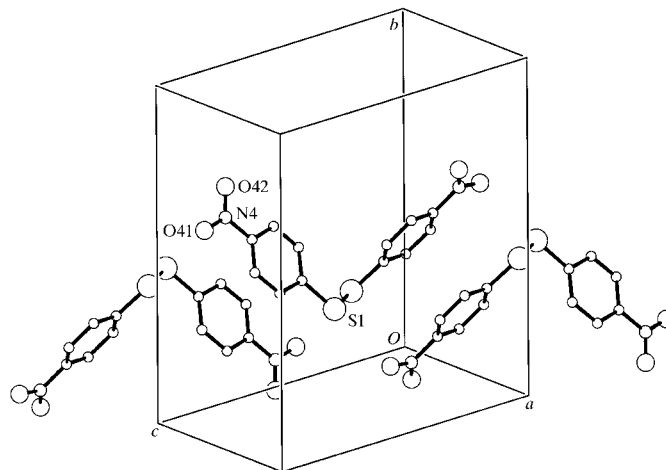
However, the (001) sheets are linked into a three-dimensional continuum by means of aromatic π···π stacking interactions across centres of inversion. The aryl ring at (x, y, z) forms a π···π interaction with that at $(-\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$ across the inversion centre at $(-\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ (Fig. 3). The perpendicular distance between the ring planes is 3.372 (3) Å and the centroid offset is 1.325 (3) Å; these dimensions are ideal for the development of stacking interactions (Hunter, 1994). Hence, the reference molecule, centred at $(0, y, \frac{1}{4})$, is linked to molecules centred at $(-\frac{1}{2}, \frac{1}{2} - y, \frac{3}{4})$ and $(\frac{1}{2}, \frac{1}{2} - y, -\frac{1}{4})$, which in turn are similarly linked to molecules centred at $(-1, y, \frac{5}{4})$ and $(1, y, -\frac{3}{4})$, respectively, so generating a chain running parallel to the $[10\bar{1}]$ direction.

None of these intermolecular interactions was discussed in the original report on the structure of (I) (Ricci & Bernal, 1969). Indeed, the authors specifically remarked that apart from S···O contacts close to, but greater than, the sum of the

organic compounds

van der Waals radii, 'no other features of the packing appear to merit special comment'. It is therefore of interest to compare the intermolecular interactions in (I) with those in the crystal structures of related compounds retrieved from the Cambridge Structural Database (CSD; Allen & Kennard, 1993). Neither the isomeric $(2\text{-}O_2NC_6H_4)_2S_2$ (CSD refcode ODNPDS10; Ricci & Bernal, 1970) nor its bis-chlorinated analogue $(5\text{-}Cl\text{-}2\text{-}O_2NC_6H_3)_2S_2$ (ZEXNEV; Garcia *et al.*, 1995) exhibit any C—H···O hydrogen bonding. Similarly, in $(4\text{-}O_2N\text{-}C_6H_4CH_2O)_2S_2$ (RIJDAP; Borghi *et al.*, 1997), a chain-extended analogue of (I) containing the unusual –O—S—S—O– fragment, there are again no short ($D\cdots A < 3.4$ Å) C—H···O contacts having C—H···O angles above 130°. The behaviour of $(2\text{-}O_2NC_6H_4)_2S_2$ may, in turn, be contrasted with that of the monosulfide $(2\text{-}O_2NC_6H_4)_2S$ (DEKDIG; Kucsman *et al.*, 1984), where the molecules are linked by two types of C—H···O hydrogen bond into two-dimensional sheets (Low *et al.*, 2000). The factors leading to the presence or absence of C—H···O hydrogen bonding in systems of this type will plainly repay further study.

Figure 3
Part of the crystal structure of (I), showing one of the $\pi\cdots\pi$ stacked chains running parallel to [$10\bar{1}$].

Figure 2
Part of the crystal structure of (I), showing the formation of one of the (001) sheets built from $R_4^4(44)$ rings.

Experimental

A sample of (I) was prepared by oxidative coupling of $4\text{-}O_2NC_6H_4SH$ and was crystallized from ethanol.

Crystal data

$C_{12}H_8N_2O_4S_2$	$D_x = 1.609$ Mg m^{-3}
$M_r = 308.34$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 1411
$a = 7.1167$ (7) Å	reflections
$b = 14.1692$ (15) Å	$\theta = 3.21–27.49°$
$c = 12.6473$ (14) Å	$\mu = 0.433$ mm^{-1}
$\beta = 93.753$ (4)°	$T = 150$ (2) K
$V = 1272.6$ (2) Å^3	Plate, yellow
$Z = 4$	$0.10 \times 0.05 \times 0.05$ mm

Data collection

KappaCCD diffractometer	1062 reflections with $I > 2\sigma(I)$
φ and ω scans with κ offsets	$R_{int} = 0.061$
Absorption correction: multi-scan	$\theta_{max} = 27.49°$
(*SORTAV*; Blessing, 1995, 1997)	$h = -9 \rightarrow 8$
$T_{min} = 0.958$, $T_{max} = 0.979$	$k = -18 \rightarrow 18$
4579 measured reflections	$l = -15 \rightarrow 16$
1411 independent reflections	Intensity decay: negligible

Table 1
Selected geometric parameters (Å, °).

S1—S1^i	2.0299 (8)	N4—O41	1.227 (3)
S1—C1	1.779 (2)	N4—O42	1.226 (3)
C4—N4	1.465 (3)		
C1—S1—S1^i	105.80 (7)	O41—N4—C4	118.2 (2)
O41—N4—O42	123.4 (2)	O42—N4—C4	118.4 (2)
C1^i—S1^i—S1—C1	88.11 (11)	C3—C4—N4—O41	−7.2 (3)
S1^i—S1—C1—C6	−22.0 (2)	C3—C4—N4—O42	172.3 (2)
S1^i—S1—C1—C2	160.6 (15)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 0.5922P]$
$wR(F^2) = 0.107$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.082$	$(\Delta/\sigma)_{max} = 0.001$
1411 reflections	$\Delta\rho_{max} = 0.39$ e Å^{-3}
91 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}
H-atom parameters constrained	

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C2-H2\cdots O42^i$	0.95	2.49	3.394 (3)	158

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

Compound (I) crystallized in the monoclinic system and space group $C2/c$ was assumed from the systematic absences. H atoms were treated as riding with a C—H distance of 0.95 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

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