

N,N'-Dithiobisphthalimide–1,4-dioxan (1/0.6): a *C2/c* solvate with disordered solvent molecules localized in channels

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N,N'-Dithiobisphthalimide crystallizes from 1,4-dioxan solution as a solvate, $3C_{16}H_8N_2O_4S_2 \cdot 1.8C_4H_8O_2$, having space group *C2/c*. Four of the 12 $C_{16}H_8N_2O_4S_2$ molecules in the unit cell lie on twofold rotation axes, while the other eight lie in general positions. These molecules are linked by aromatic π – π -stacking interactions and by C–H...O hydrogen bonds to form a framework enclosing continuous channels running parallel to the [101] direction, which account for *ca* 20% of the unit-cell volume. The dioxan molecules lie in these channels disordered across two sets of sites, with one set across an inversion centre and the other across a twofold rotation axis.

Comment

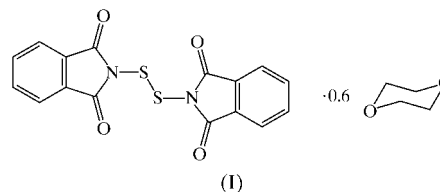
We have recently described a number of solvates (pseudo-polymorphs) of *N,N'*-dithiobisphthalimide, as well as several solvent-free polymorphs (Skakle *et al.*, 2001; Farrell *et al.*, 2002). The solvates studied to date fall into four distinct groups. The first group comprises solvates where the bisphthalimide molecules and the solvent are linked by C–H...O hydrogen bonds. In the remaining three types of solvate, the solvent molecules are not hydrogen bonded to the framework formed by the bisphthalimide. These three types are where the solvent molecules are in isolated cavities, or channel polymorphs in which localized solvent molecules in the channels are readily refinable, or channel polymorphs in which the solvent molecules are disordered and/or mobile

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within the channels (non-localized solvent molecules). Continuing this study, we report here the structure of the title dioxan solvate, (I), which is a further channel polymorph containing localized solvent molecules, but which differs from any other example so far examined.



Compound (I) crystallizes in space group *C2/c* with 12 bisphthalimide molecules per unit cell. Based upon the bisphthalimide molecules only, a *Z'* value of $\frac{3}{2}$ is obtained, which is very uncommon in this space group (Brock & Dunitz, 1994). Four of the bisphthalimide molecules, the type-1 molecules containing atom S1 (Fig. 1*a*), lie across twofold rotation axes, while the eight type-2 molecules containing atoms S11 and S21 (Fig. 1*b*) lie in general positions.

Each type of molecule forms chains in which the molecules are linked by aromatic π – π -stacking interactions. In the type-2 molecule at (x, y, z) , the C11–C16 ring forms a π – π -stacking interaction with the C21–C26 ring in the molecule at $(x, 1 - y, z - \frac{1}{2})$, in which the interplanar angle is $1.5(3)^\circ$, the interplanar spacing is 3.362(3) Å and the centroid separation is 3.657(3) Å. Similarly, the C11–C16 ring at $(x, 1 - y, z - \frac{1}{2})$ in turn forms a stacking interaction with the C21–C26 ring at $(x, y, z - 1)$, so generating a chain of type-2 molecules running parallel to the [001] direction. Four chains of this type run

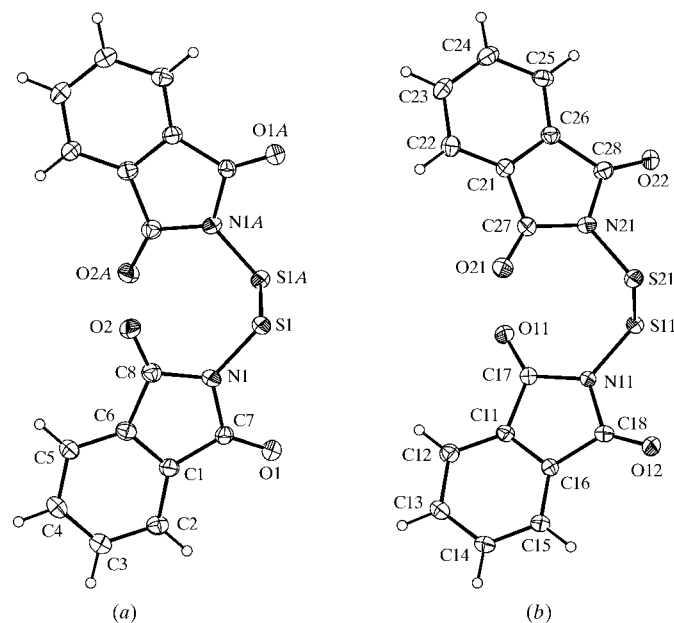


Figure 1

The two independent molecules of *N,N'*-dithiobisphthalimide in (I), showing the atom-labelling scheme; (a) a molecule of type 1, where the atoms with the suffix *A* are at the symmetry position $(-x, y, \frac{1}{2} - z)$, and (b) a molecule of type 2. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

through each unit cell. The reference chain lies in the domain $0.06 < x < 0.27$, $0.28 < y < 0.72$, and the other three lie in the domains $0.23 < x < 0.44$, $0.78 < y < 1.22$, $0.56 < x < 0.77$, $0.78 < y < 1.22$, and $0.73 < x < 0.94$, $0.28 < y < 0.72$. There are thus two pairs of adjacent chains running through each unit cell (Fig. 2).

In the type-1 molecule which lies across the twofold rotation axis along $(0, y, \frac{1}{4})$, the two aryl rings are at (x, y, z) and $(-x, y, \frac{1}{2} - z)$. The ring at (x, y, z) forms a π - π -stacking interaction with that at $(-x, -y, -z)$, part of the type-1 molecule lying across the rotation axis along $(0, -y, -\frac{1}{4})$; the interplanar spacing is 3.347 (4) Å and the centroid separation is 3.754 (4) Å. Similarly, the ring at $(-x, y, \frac{1}{2} - z)$, also part of the molecule across $(0, y, \frac{1}{4})$, forms a stacking interaction with the ring at $(x, -y, \frac{1}{2} + z)$, which is part of the molecule across the twofold axis along $(0, -y, \frac{3}{4})$. In this manner, a second [001] chain is generated, and there are two chains of this type running through each unit cell, related by the C -centring operation and lying in the domains $-0.10 < x < 0.10$, $-0.20 < y < 0.20$, and $0.40 < x < 0.60$, $0.30 < y < 0.70$ (Fig. 3). The type-1 chains thus fit neatly in the gaps between the pairs of type-2 chains, giving a sequence of types along [100] of the form ...122122122..., and these stacked chains are linked along the [010] direction by weak C—H...O hydrogen bonds (Table 2).

The C—H...O hydrogen bond involving atoms of a type-2 molecule as both donor and acceptor (Table 2, Fig. 1) simply reinforces the π - π -stacked type-2 chain along [001] by

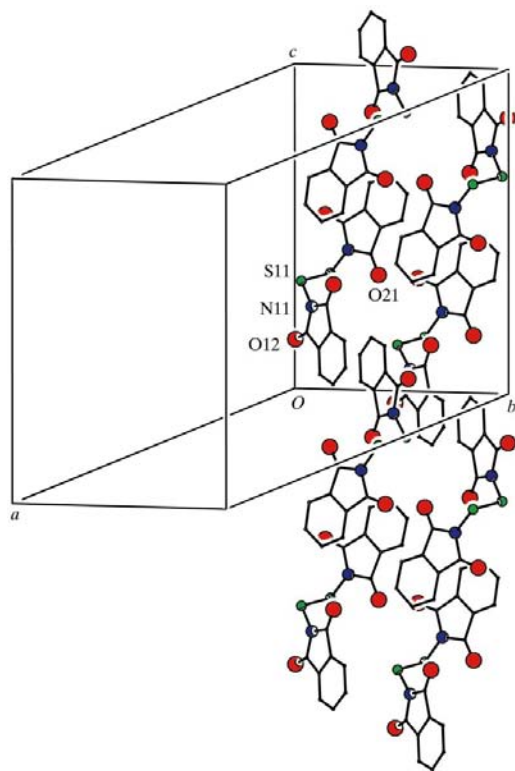


Figure 2

Part of the crystal structure of (I), showing the two π - π -stacked chains of type-2 molecules in the domain $0 < x < \frac{1}{2}$. For the sake of clarity, H atoms have been omitted.

formation of a $C(7)$ motif. The combination of the other two hydrogen bonds links the chains of different types. In the type-1 molecule across the twofold rotation axis $(0, y, \frac{1}{4})$, the two symmetry-related C4 atoms are at (x, y, z) and $(-x, y, \frac{1}{2} - z)$. These act as hydrogen-bond donors to atoms O22 in the type-2 molecules at $(x, -y, z - \frac{1}{2})$ and $(-x, -y, 1 - z)$, respectively, while atoms C22 in these two molecules act as donors to atoms O1 at $(x, y - 1, z)$ and $(-x, y - 1, \frac{1}{2} - z)$, which both lie in the same type-1 molecule (Fig. 4). In this way, a molecular ladder is generated, with a pair of $C_2^2(14)$ chains related by the twofold axis acting as the uprights, and with the central N—S—S—N fragments of the type-1 molecules acting as the rungs, which enclose $R_4^4(36)$ rings. There are four of these ladders running through each unit cell, and they link the π - π -stacked [001] chains into a (100) sheet.

The overall framework generated by the bisphthalimide molecules occupies only 80% of the unit-cell volume [*i.e.* 20% solvent-accessible volume, as estimated using *PLATON* (Spek, 2002)], which is typical of the channel polymorphs described earlier (Skakle *et al.*, 2001; Farrell *et al.*, 2002), and, in fact, the remaining volume takes the form of continuous channels, two per unit cell, which run parallel to the [101] direction (Fig. 5). It is within these channels that the dioxan molecules lie, each disordered over two partially occupied sets of sites at different special positions. The dioxan molecules containing atoms O41 and O51 are disordered across the centre of inversion at $(\frac{1}{4}, \frac{3}{4}, \frac{1}{2})$, with occupancies of 0.509 (10) and 0.429 (10), respectively (Fig. 6a), while that containing atoms

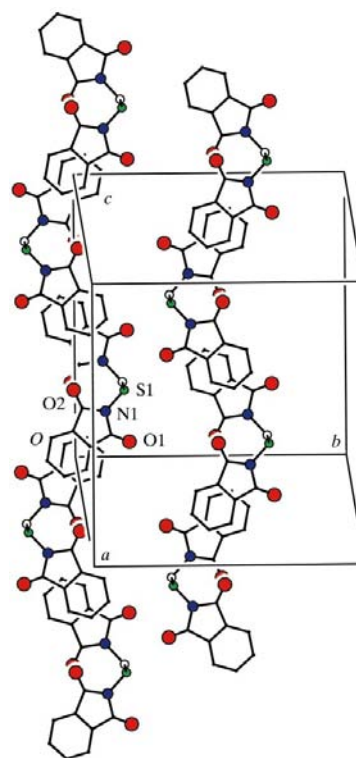


Figure 3

Part of the crystal structure of (I), showing π - π -stacked chains of type-1 molecules in the domains $-0.10 < x < 0.10$ and $0.40 < x < 0.60$. For the sake of clarity, H atoms have been omitted.

O31 and O34 is disordered across the twofold rotation axis along $(0, y, \frac{1}{4})$, centred approximately at $(0, \frac{3}{4}, \frac{1}{4})$, with occupancy 0.431 (7) (Fig. 6*b*). These partially occupied dioxan sites, taken together, correspond to 7.2 molecules of dioxan per unit cell. With the 12 molecules of dithiobisphthalimide in the unit cell, this gives the composition for (I) as $C_{16}H_8N_2O_4S_2 \cdot 0.6C_4H_8O_2$.

It is interesting to note the structural contrast between the dioxan solvate, (I), and the tetrahydrofuran (THF) solvate (Farrell *et al.*, 2002). Despite the rather close similarity between the solvent molecules, the THF solvate has $Z' = \frac{1}{2}$ in $C2/c$ (based upon the bisphthalimide molecules) and the solvent molecules are intractably disordered within continuous channels along [001].

The leading dimensions (Table 1) of the two independent bisphthalimide molecules in (I) do not differ significantly, and they are typical of those observed in other polymorphs and

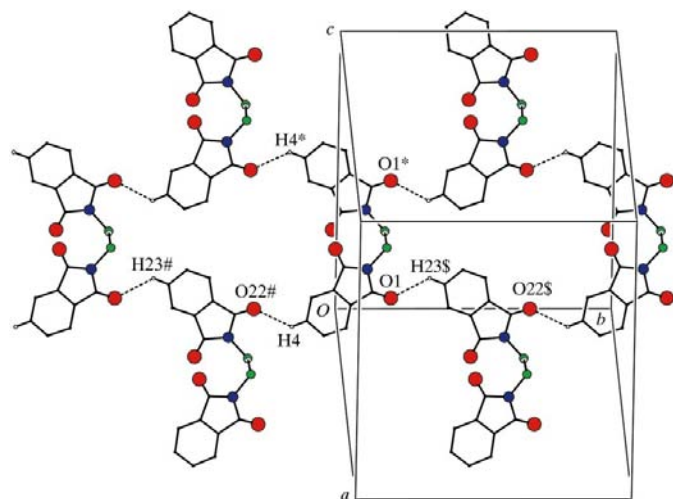


Figure 4
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded molecular ladder parallel to [010] linking the π - π -stacked chains. Atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(-x, y, \frac{1}{2} - z)$, $(x, -y, z - \frac{1}{2})$ and $(x, 1 - y, z - \frac{1}{2})$, respectively.

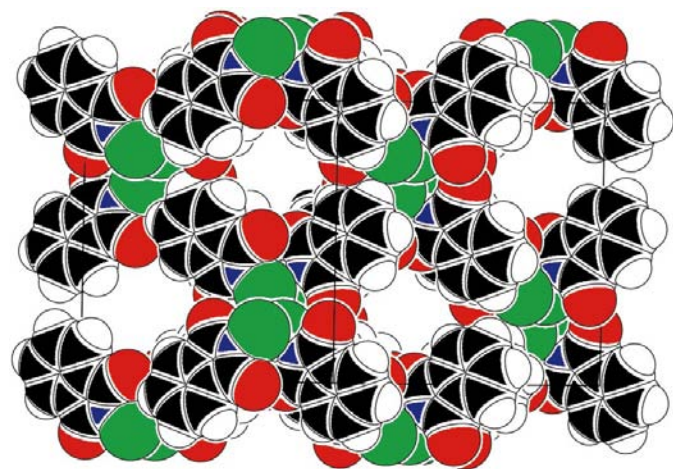


Figure 5
A space-filling representation of the molecules of N,N' -dithiobisphthalimide in (I), showing the continuous channels running parallel to [101].

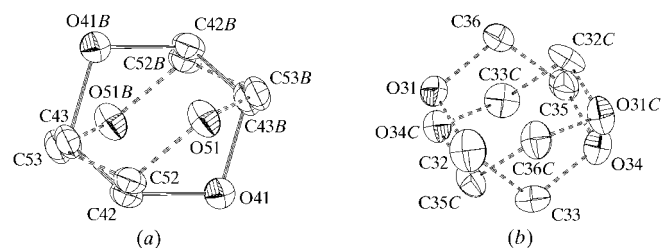


Figure 6
The disordered dioxan molecules in (I), (a) at the inversion centre $(\frac{1}{4}, \frac{3}{4}, \frac{1}{2})$, where atoms with suffix B are at the symmetry position $(\frac{1}{2} - x, \frac{3}{2} - y, 1 - z)$, and (b) across the twofold rotation axis $(0, y, \frac{1}{4})$, where atoms with suffix C are at the symmetry position $(-x, y, \frac{1}{2} - z)$. For the sake of clarity, H atoms have been omitted.

solvates of N,N' -dithiobisphthalimide. We note in particular the planarity at N and the torsion angles within the N—S—S—N fragments, which indicate that the formally non-bonding lone pairs at adjacent N and S atoms are essentially orthogonal.

The bisphthalimide molecules in (I) conform closely to the rare space group $P2/m$ in a much smaller unit cell, derived from the observed cell by the transformation $(\frac{1}{3}, 0, \frac{1}{3}; 0, 1, 0; -\frac{1}{3}, 0, \frac{1}{6})$ and having $Z = 2$, *i.e.* $Z' = \frac{1}{2}$, which would require all of the bisphthalimide molecules to lie on twofold rotation axes, rather than just one third of them. However, the dioxan molecules do not conform to this pseudosymmetry, so that the correct space group is indeed $C2/c$.

Experimental

A sample of N,N' -dithiobisphthalimide was purchased from Aldrich. Crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow evaporation from a solution in 1,4-dioxan.

Crystal data

$3C_{16}H_8N_2O_4S_2 \cdot 1.8C_4H_8O_2$
 $M_r = 1227.68$
 Monoclinic, $C2/c$
 $a = 20.7900$ (11) Å
 $b = 16.0520$ (10) Å
 $c = 16.7780$ (9) Å
 $\beta = 105.604$ (4)°
 $V = 5392.8$ (5) Å³
 $Z = 4$

$D_x = 1.512$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 6116 reflections
 $\theta = 3.6$ – 27.6 °
 $\mu = 0.33$ mm⁻¹
 $T = 150$ (2) K
 Needle, colourless
 $0.34 \times 0.12 \times 0.10$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)
 $T_{\min} = 0.884$, $T_{\max} = 0.964$
 20 736 measured reflections

6116 independent reflections
 3050 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.127$
 $\theta_{\text{max}} = 27.6$ °
 $h = -26 \rightarrow 26$
 $k = -20 \rightarrow 20$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.072$
 $wR(F^2) = 0.183$
 $S = 1.02$
 6116 reflections
 425 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0197P)^2 + 21.0287P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.42$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.00080 (19)

Table 1

Selected geometric parameters (Å, °).

S1–N1	1.683 (4)	S1–S1 ⁱ	2.034 (3)
S11–N11	1.685 (3)	S11–S21	2.033 (2)
S21–N21	1.681 (4)		
S1–N1–C7	124.1 (3)	S11–N11–C17	124.5 (3)
S1–N1–C8	124.5 (3)	S11–N11–C18	123.1 (3)
C7–N1–C8	111.4 (3)	C17–N11–C18	112.3 (3)
N1–S1–S1 ⁱ	105.80 (16)	S21–N21–C27	125.4 (3)
N11–S11–S21	105.41 (16)	S21–N21–C28	122.7 (3)
S11–S21–N21	105.58 (17)	C27–N21–C28	111.9 (3)
S1 ⁱ –S1–N1–C7	92.2 (4)	N1 ⁱ –S1 ⁱ –S1–N1	91.52 (18)
S11–S21–N21–C27	93.1 (4)	N11–S11–S21–N21	–95.17 (19)
S21–S11–N11–C17	89.1 (4)		

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C14–H14 ⁱ ···O11 ⁱ	0.95	2.45	3.306 (6)	151
C4–H4 ⁱⁱ ···O22 ⁱⁱ	0.95	2.53	3.268 (6)	134
C23–H23 ⁱⁱⁱ ···O1 ⁱⁱⁱ	0.95	2.55	3.257 (6)	131

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

Compound (I) crystallized in the monoclinic system, and space group $C2/c$ or Cc was indicated by the systematic absences; $C2/c$ was assumed and confirmed by the analysis. H atoms were treated as riding, with $C-H = 0.95$ and 0.99 Å. One dithiobisphthalimide molecule lies about a twofold axis and another is in a general position. There are two partially occupied sites with disordered dioxan molecules. One site, with molecule O31–C36, is disordered [occupancy 0.431 (7)] about a twofold axis, and the other, with molecules

O41–C42 [occupancy 0.509 (10)] and O51–C52 [occupancy 0.429 (10)], is disordered about an inversion centre. This leads to the asymmetric unit having the formulation 3(dithiobisphthalimide)–1.8(dioxan).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC, Canada.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1551). Services for accessing these data are described at the back of the journal.

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