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N,N′-Dithiobisphthalimide–nitrobenzene (2/1): a *Pn* solvate with localized solvent molecules ordered head-to-tail in channels

Katharine F. Bowes,[a] George Ferguson,[a]† Christopher Glidewell,[a]* John N. Low[b]‡ and Antonio Quesada[c]§

[a]School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [c]Department of Electronic Engineering and Physics, University of Dundee, Dundee DD1 4HN, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

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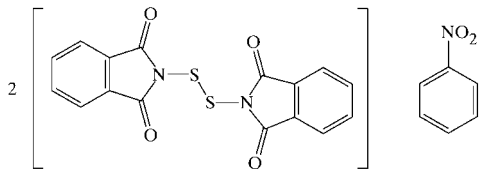
N,N′-Dithiobisphthalimide crystallizes from nitrobenzene solution as a solvate, $2C_{16}H_8N_2O_4S_2\cdot C_6H_5NO_2$, having space group *Pn*. The bisphthalimide molecules are linked by C—H···O hydrogen bonds and by aromatic π–π-stacking interactions, forming a framework enclosing continuous channels running along the [100] direction and accounting for *ca* 20% of the unit-cell volume. The nitrobenzene molecules lie in these channels, ordered in a head-to-tail fashion and linked to the bisphthalimide framework by C—H···O and C—H···π(arene) hydrogen bonds.

Comment

We have recently described a number of solvates of *N,N′*-dithiobisphthalimide, as well as some solvent-free polymorphs (Skakle *et al.*, 2001; Bowes *et al.*, 2002; Farrell *et al.*, 2002). In some of the solvates the bisphthalimide molecules and the solvent are linked by C—H···O hydrogen bonds, while in other solvates the bisphthalimide molecules form structures containing either isolated cavities or continuous channels in which the solvent molecules reside without being hydrogen bonded to the bisphthalimide frameworks. Thus, for example, nitromethane forms a monosolvate, $C_{16}H_8N_2O_4S_2\cdot CH_3NO_2$, in which the solvent molecules are linked to the bisphthalimide molecules not only *via* a conventional C—H···O hydrogen bond but also *via* a polarized multi-centre interaction involving all three C—H bonds of the solvent molecule (Farrell *et al.*, 2002). On the other hand, in the chlorobenzene solvate, $2C_{16}H_8N_2O_4S_2\cdot C_6H_5Cl$, the solvent molecules lie in isolated cavities, while in the toluene solvate, $2C_{16}H_8N_2O_4S_2\cdot C_7H_8$, the solvent molecules lie within continuous channels (Farrell *et al.*, 2002).



(I)

Seeking to combine the specific hydrogen-bonding capacity manifest in nitromethane with the steric requirements of aromatic solvent molecules, such as chlorobenzene and toluene, we have now prepared and structurally characterized the nitrobenzene solvate $2C_{16}H_8N_2O_4S_2\cdot C_6H_5NO_2$, (I), which turns out to exhibit a channel structure containing fully ordered and bound solvent molecules.

Compound (I) (Fig. 1) crystallizes in space group *Pn* with four molecules of the bisphthalimide per unit cell, and these molecules, whose internal dimensions do not differ significantly from those observed in other polymorphs and solvates (Skakle *et al.*, 2001; Bowes *et al.*, 2002; Farrell *et al.*, 2002), are linked by a combination of C—H···O hydrogen bonds (Table 1) and aromatic π–π-stacking interactions. The substructure formed by the bisphthalimide molecules alone is effectively centrosymmetric (100% fit to $P2_1/n$), but the presence of the nitrobenzene component precludes the higher symmetry. Each type of bisphthalimide molecule (type 1 contains S1 and S2, and type 2 contains S3 and S4) forms chains by means of C—H···O hydrogen bonds reinforced by

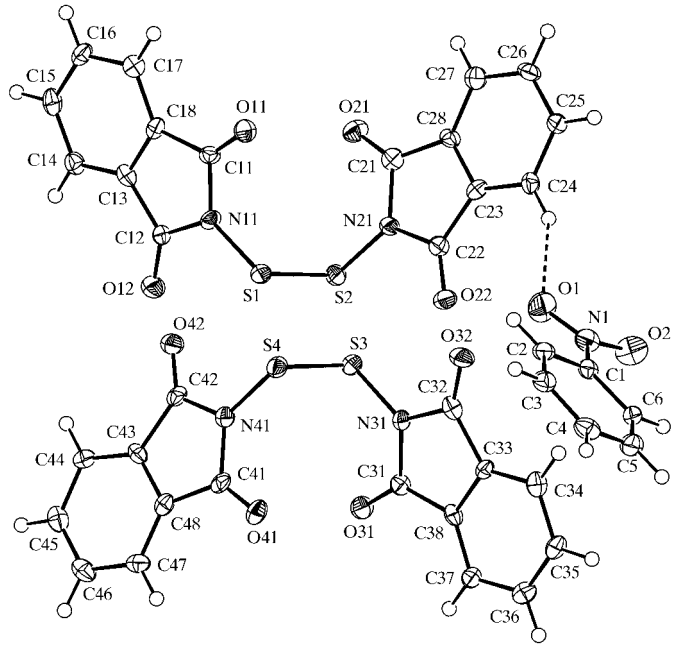


Figure 1
The independent molecular components in (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

† Permanent address: Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.
‡ Postal address: Department of Electronic Engineering & Physics, University of Dundee, Dundee DD1 4HN, Scotland.
§ Permanent address: Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain.

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aromatic π–π-stacking interactions, but only one type of chain needs to be described, because of the pseudosymmetry.

Atom C15 in the type 1 molecule at (x, y, z) acts as hydrogen-bond donor to O11 in the type 1 molecule at ($-\frac{1}{2}+x$, $1-y$, $\frac{1}{2}+z$), and propagation of this hydrogen bond produces a $C(7)$ chain running parallel to the [10$\bar{1}$] direction, and generated by the n-glide plane at $y=\frac{1}{2}$ (Fig. 2). At the same time, the C13–C18 aryl ring at (x, y, z) forms a π–π-stacking interaction with the C23–C28 ring at ($-\frac{1}{2}$ x, $1-y$, $\frac{1}{2}+z$), so reinforcing the action of the C—H···O hydrogen bond (Fig. 2); the interplanar angle is only 0.6 (2)°, with a centroid separation of 3.598 (2) Å and an interplanar spacing of 3.361 (2) Å, giving a centroid offset of 1.284 (2) Å. The antiparallel [10$\bar{1}$] chains formed individually by the two types of bisphthalimide molecule are linked by further C—H···O hydrogen bonds involving both types. Atom C26 in the type 1 molecule at (x, y, z) acts as hydrogen-bond donor to O42 in the type 2 molecule at ($\frac{1}{2}+x$, $1-y$, $-\frac{1}{2}+z$), while C46 at ($\frac{1}{2}+x$, $1-y$, $-\frac{1}{2}+z$) acts as donor to O22 at (x, $1+y$, z), so forming a $C_2^2(14)$ chain running parallel to [010] (Fig. 3).

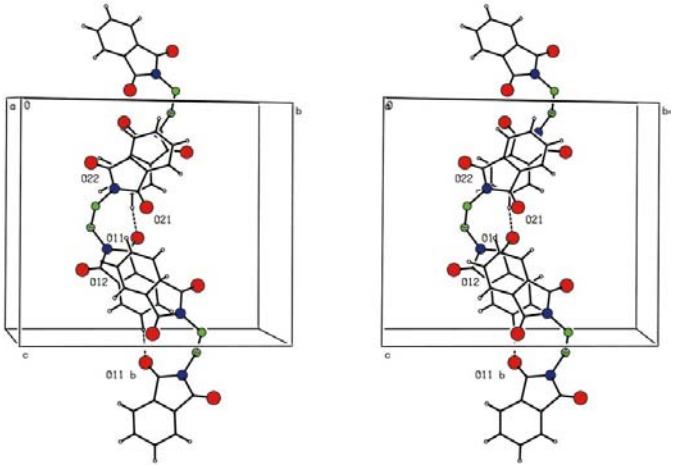

Figure 2
Stereoview of part of the crystal structure of (I), showing the formation of a [10$\bar{1}$] chain of type 1 molecules built from C—H···O hydrogen bonds and aromatic π–π-stacking interactions.

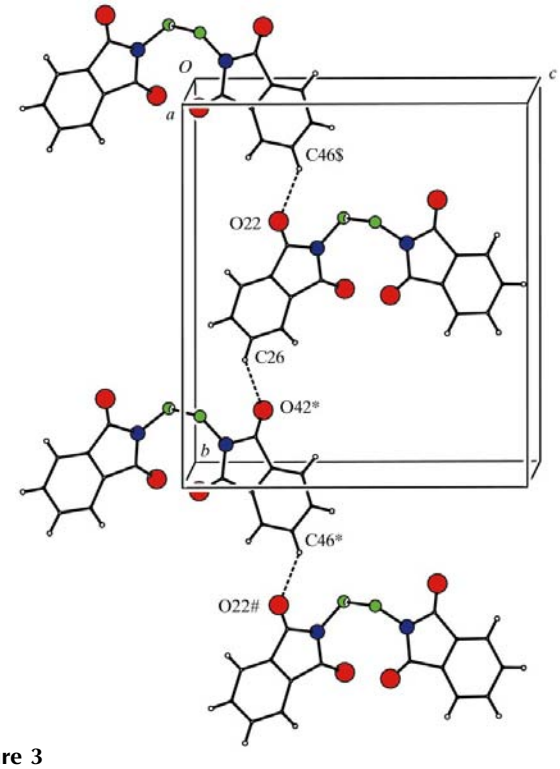

Figure 3
Part of the crystal structure of (I), showing the formation of a $C_2^2(14)$ chain along [010]. Atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions ($\frac{1}{2}+x$, $1-y$, $-\frac{1}{2}+z$), (x, $1+y$, z) and ($\frac{1}{2}+x$, $-1-y$, $-\frac{1}{2}+z$), respectively.

The bisphthalimide molecules occupy only *ca* 80% of the unit-cell volume [*i.e.* 20% solvent-accessible volume as estimated using *PLATON* (Spek, 2002)]; the remaining volume takes the form of continuous channels running along [100] (Fig. 4). There are two such channels passing through each unit cell, along the lines (x, $\frac{1}{4}$, 0) and (x, $\frac{3}{4}$, $\frac{1}{2}$), and having a mean diameter of *ca* 5.4 Å, and it is in these channels that the nitrobenzene molecules lie, arranged in an ordered head-to-tail fashion.

The ordering of the nitrobenzene molecules contrasts with the disorder of the chlorobenzene and toluene molecules across centres of inversion in their respective solvates. The ordering in (I) is due to specific multi-point recognition between the bisphthalimide framework and the nitrobenzene solvate molecules, involving both C—H···O and C—H···π(arene) hydrogen bonds (Table 1). The nitrobenzene molecule at (x, y, z) accepts, *via* O1, a rather weak hydrogen bond from C24 in the type 1 molecule at (x, y, z), while nitrobenzene C6 acts as donor to O42 in the type 2 molecule at

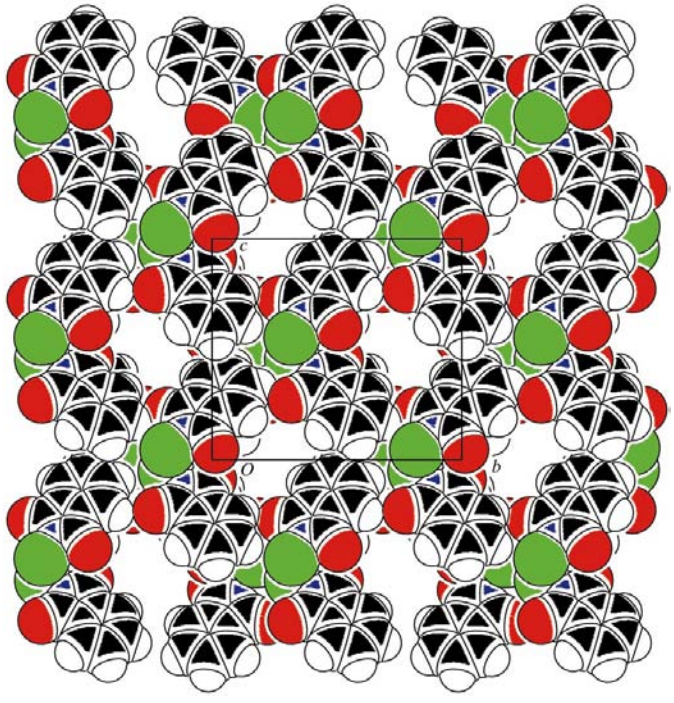

Figure 4
Space-filling representation of the bisphthalimide framework, showing the continuous channels along [100].

$(1 + x, y, -1 + z)$. In addition to these two C—H···O hydrogen bonds, there are two C—H···π(arene) hydrogen bonds, in which the C1–C6 nitrobenzene ring at (x, y, z), centroid $Cg1$, accepts C—H···π hydrogen bonds from C14 at $(1 + x, y, -1 + z)$ and from C34 at $(1 + x, y, z)$, with one such hydrogen bond on each face of the ring (Fig. 5).

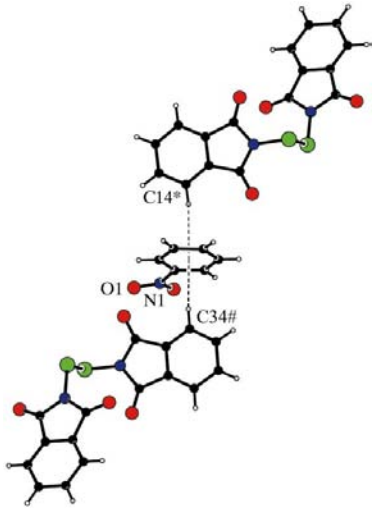

Figure 5
Part of the crystal structure of (I), showing the linking of the nitrobenzene to the bisphthalimide framework by C—H···π(arene) hydrogen bonds. For the sake of clarity, the unit-cell box has been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1 + x, y, -1 + z)$ and $(1 + x, y, z)$ respectively.

In a recent study based on the Cambridge Structural Database (CSD; Allen & Kennard, 1993), Nangia & Desiraju (1999) analysed both the relative frequency of occurrence of the common organic solvents in solvated organic crystals and the specific supramolecular synthons linking the solvent molecules to the host molecules. When normalized for the frequency of usage in crystal growth, 13 solvents were found to have a significantly higher than average tendency to be included in solvates. It is interesting to note that of the *N,N′*-bisphthalimide solvates so far analysed, the two solvents found to exhibit specific multi-point interactions (nitromethane and nitrobenzene) do not appear in the top 20 solvents in the normalized CSD-based list; indeed neither solvent is mentioned in Nangia & Desiraju's (1999) analysis.

Experimental

A sample of *N,N′*-dithiobisphthalimide was purchased from Aldrich. Crystals of (I) suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of a solution in nitrobenzene.

Crystal data

$2C_{16}H_8N_2O_4S_2{\cdot}C_6H_5NO_2$
$M_r = 835.88$
Monoclinic, *Pn*
$a = 7.7070$ (2) Å
$b = 16.1001$ (3) Å
$c = 14.3067$ (4) Å
$\beta = 95.077$ (1)°
$V = 1768.26$ (8) Å^3
$Z = 2$
$D_x = 1.570$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7660 reflections
$\theta = 2.9$–27.5°
$\mu = 0.34$ mm^{-1}
$T = 120$ (2) K
Block, colourless
0.22 × 0.10 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.927$, $T_{max} = 0.972$
19 021 measured reflections
7660 independent reflections
5681 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 10$
$k = -20 \rightarrow 20$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.096$
$S = 0.97$
7660 reflections
516 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0057 (7)
Absolute structure: Flack (1983); 3603 Friedel pairs
Flack parameter = 0.32 (9)

Table 1
Hydrogen-bonding geometry (Å, °).

*Cg*1 is the centroid of the C1–C6 nitrobenzene ring.

D—H···A	D—H	H···A	D···A	D—H···A
C15—H15···O11^{i}	0.95	2.34	3.267 (5)	166
C26—H26···O42^{ii}	0.95	2.39	3.196 (6)	142
C35—H35···O31^{iii}	0.95	2.41	3.311 (5)	159
C46—H46···O22^{iv}	0.95	2.35	3.136 (6)	139
C6—H6···O42^{v}	0.95	2.51	3.245 (4)	134
C24—H24···O1	0.95	2.51	3.372 (5)	151
C14—H14···$Cg1^{vi}$	0.95	2.69	3.633 (5)	172
C34—H34···$Cg1^{vii}$	0.95	2.58	3.510 (5)	166

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

Compound (I) is monoclinic and the systematic absences permitted *Pn* and *P*2/*n* as possible space groups; *Pn* was selected and confirmed by the analysis. H atoms were treated as riding, with a C—H distance of 0.95 Å. The value of the Flack (1983) parameter [0.32 (9)] indicated racemic twinning and this was handled *via* the *TWIN* and *BASF* instructions in *SHELXL*97 (Sheldrick, 1997). Although *PLATON* (Spek, 2002) reports a 94% fit to $P2_1/n$ (and indeed a 100% fit when the nitrobenzene component is omitted), careful inspection of the reflection file indicated several strong ($0k0$) reflections with k odd, which preclude the presence of a 2_1 screw axis. In addition to the structure for (I) discussed above, we had earlier located another solution, which refined to $R = 0.046$ and $wR2 = 0.109$, and gave effectively the same supramolecular structure as that described above, but approximately related to it by the transformation $(x, y, 1 - z)$. Our attention was drawn to the unsatisfactory nature of this initial solution by the *PLATON* (Spek, 2002) checking routines, which flagged, in particular, the consistently low average C—C distance (*ca* 1.34 Å) in the phthalimide arene rings and the very large range (*ca* 0.16 Å) of the nitrobenzene C—C bond lengths; a detailed examination of the bond distances and angles then led to the decisive rejection of this solution. The lessons to be drawn from this are that, despite a satisfactory R value and a satisfactory supramolecular arrangement, the warnings of the data-validation process must be heeded and investigated, and that all of the derived geometric parameters must be scrutinized critically.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinemen and data reduction: *DENZO–SMN* (Otwinowski & Minor, 1997); structure solution: *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997) and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1574). Services for accessing these data are described at the back of the journal.

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