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Polymorphs and pseudopolymorphs of *N*,*N*′-dithiobisphthalimide

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N,*N*′-Dithiobisphthalimide, $C_{16}H_8N_2O_4S_2$ (I), forms a wide range of polymorphs and solvates (pseudopolymorphs). When (I) is crystallized from methanol it yields a solvent-free polymorph (4), in $Pna2_1$ with $Z' = 1$, in which the molecules are linked into chains by a single C—H···O hydrogen bond: crystallization from either acetonitrile or dimethylformamide produces a monoclinic polymorph (5), in $P2_1/c$ with $Z' = 2$, also solvent-free, in which the molecules are linked into molecular ladders. Nitromethane forms a monosolvate, $C_{16}H_8N_2O_4S_2{\cdot}CH_3NO_2$ (6), in $P2_1/c$ with $Z' = 1$, in which the solvent molecules are linked to the molecules of (I) not only *via* a conventional C—H···O hydrogen bond but also *via* a polarized multicentre interaction involving all three C—H bonds of the solvent molecule. Chlorobenzene forms a precise hemisolvate, $C_{16}H_8N_2O_4S_2{\cdot}0.5C_6H_5Cl$ (7), in $P\bar{1}$ with $Z' = 1$, while ethylbenzene forms an approximate hemisolvate $2C_{16}H_8N_2O_4S_2{\cdot}0.913C_6H_5C_2H_5{\cdot}0.087H_2O$ (8), in $P2_1/c$ with eight molecules of (I) per unit cell. In both solvates the molecules of (I) are linked, in (7) by $\pi\cdots\pi$ stacking interactions augmented by weak C—H···O hydrogen bonds and in (8) by stronger C—H···O hydrogen bonds: the solvent molecules lie in isolated cavities, disordered across inversion centres in (7) and fully ordered in general positions in (8). Crystallization of (I) either from tetrahydrofuran or from wet *tert*-butanol yields isomorphous solvates (9) and (10), respectively, in $C2/c$ with $Z' = 0.5$, in which molecules of (I) lie across twofold rotation axes and are linked by $\pi\cdots\pi$ stacking interactions and very weak C—H···O hydrogen bonds, forming a framework enclosing continuous channels: highly disordered solvent molecules lie within these channels. *p*-Xylene and toluene form isomorphous hemisolvates (11) and (12) with unit cells metrically very similar to those of (9) and (10), but in $P2_1/n$ with $Z' = 1$: in these two solvates the molecules of (I) are linked into a framework by very short C—H···O hydrogen bonds; the solvent molecules lie within continuous channels, but they are localized across inversion centres so that the toluene is disordered across an inversion centre.

1. Introduction

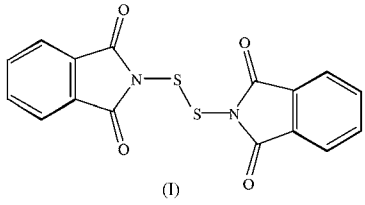
We recently reported (Skakle *et al.*, 2001) two distinct crystalline forms of *N*,*N*′-dithiobisphthalimide, $C_{16}H_8N_2O_4S_2$ (I). When crystallized from ethyl acetate, (I) gave a solvent-free polymorph (1) in which the molecules were linked into a three-dimensional framework by a combination of C—H···O hydrogen bonds and aromatic $\pi\cdots\pi$ stacking interactions. By contrast, when (I) was crystallized from dichloromethane or from ethanol, two solvated forms (2) and (3), respectively,

Table 1
Polymorphs and pseudopolymorphs of (I).

Z' values refer to molecules of (I). In (6) there is one molecule of solvent per molecule of (I) and each of (7), (8), (11) and (12) contains 0.5 molecules of solvent per molecule of (I). For solvates (9) and (10) the *SQUEEZE* option in *PLATON* (Spek, 2001) was employed.

Form	Solvent for crystallization	Space group	Z'
Solvent-free polymorphs			
(1)	$CH_3COOC_2H_5$	$P2_1/c$	2
(4)	CH_3OH	$Pna2_1$	1
(5)	CH_3CN or $HCON(CH_3)_2$	$P2_1/c$	2
Polymorphs with solvent hydrogen-bonded to (I)			
(6)	CH_3NO_2	$P2_1/c$	1
Solvent molecules are in isolated cavities			
(7)	C_6H_5Cl	$P\bar{1}$	1
(8)	$C_6H_5C_2H_5$	$P2_1/c$	2
Solvent molecules are non-localized in channels			
(2)	CH_2Cl_2	$C2/c$	0.5
(3)	C_2H_5OH	$C2/c$	0.5
(9)	C_4H_8O	$C2/c$	0.5
(10)	$(CH_3)_3COH/H_2O$	$C2/c$	0.5
Solvent molecules are localized in channels			
(11)	1,4-$(CH_3)_2C_6H_4$	$P2_1/n$	1
(12)	$C_6H_5CH_3$	$P2_1/n$	1

were obtained. In these forms, there are no hydrogen bonds but the molecules are linked by aromatic $\pi\cdots\pi$ stacking interactions into chains, between which are continuous linear channels which account for *ca* 20% of the unit-cell volume. The solvent molecules in (2) and (3) lie within the channels, but they are intractably disordered and possibly mobile as well.



(I)

Our further investigation of this intriguing system was prompted not only by the sharp difference between the solvent-free form (1) and the solvates (2) and (3), but by two recent reports on the formation of multiple polymorphs and solvates (pseudopolymorphs; Threlfall, 1995) in comparatively simple molecular systems (Kooijman *et al.*, 2000; Bingham *et al.*, 2001); in particular, the drug sulfathiazole, $H_2NC_6H_4SO_2N(C_3H_3NS)$, has been found to form more than one hundred distinct solvates (Bingham *et al.*, 2001).

Here we report a number of further polymorphs and pseudopolymorphs of (I) which, taken together with those reported earlier (Skakle *et al.*, 2001), appear to fall into several distinct groups or families (Table 1): solvent-free polymorphs, solvates where the molecules of (I) and the solvent are linked by C—H$\cdots$O hydrogen bonds; and three types of solvate where the solvent molecules are not hydrogen bonded to the framework formed by the molecules of (I): those where the solvent molecules are in isolated cavities, channel polymorphs in which localized solvent molecules in the channels are readily refinable, and channel polymorphs analogous to (2) and (3) in which the solvent molecules are disordered and/or mobile within the channels (non-localized solvent molecules).

2. Experimental

2.1. Sample preparation

A sample of *N*,*N*′-dithiobisphthalimide (I) was obtained from Aldrich: crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in the appropriate solvents. Compound (I) proved to be insufficiently soluble in cyclohexane for crystals to be obtained from this solvent. Compound (I) is also only poorly soluble in both pyridine and dimethylsulfoxide, and the only identifiable crystalline materials isolated from these solutions proved to be phthalimide and elemental sulfur, respectively, presumably resulting from hydrolysis and thermal decomposition. Attempts to grow crystals of (I) from 3-pentanone gave only powdery material.

2.2. Data collection, structure solution and refinement

Diffraction data for (4)–(12) were collected at either 120 (2) or 150 (2) K using a Nonius Kappa-CCD diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). Other details of cell data, data collection and refinement are summarized in Table 2, together with details of the software employed.

Polymorph (4) is orthorhombic and the systematic absences permitted $Pna2_1$ and *Pnam* as possible space groups: the unit-cell volume indicated Z = 4 and accordingly $Pna2_1$ was selected and subsequently confirmed by the analysis. For polymorphs (5), (6) and (8) the space group $P2_1/c$ was uniquely assigned from the systematic absences; likewise the space group $P2_1/n$ was uniquely assigned for (11) and (12); polymorph (7) is triclinic and space group $P\bar{1}$ was chosen, and confirmed by the analysis; for (9) and (10) the systematic absences permitted *Cc* and *C*2/*c* as possible space groups and in both cases *C*2/*c* was chosen and confirmed by the analysis.

The structures were solved by direct methods and refined with all data on F^2. A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976). Two complete data sets were collected for polymorph (5), as crystallized from acetonitrile and *N*,*N*-dimethylformamide, respectively. The data set from the acetonitrile sample was somewhat larger: 6776 unique data of which 5280 were labelled 'observed', as opposed to 5999 unique, of which 4769 were labelled 'observed', and it gave lower R values, R = 0.041 and wR = 0.120, as opposed to R = 0.059 and wR = 0.141. Accordingly, all results reported here for form (5) are based on the first of these data sets. For (4), despite the presence of S, the refined value, −0.26 (11), of the Flack parameter (Flack, 1983) was inconclusive (Flack & Bernardinelli, 2000) and the absolute structure could not be

Table 2
Experimental details.

	(4)	(5)	(6)	(7)	(8)
Crystal data					
Chemical formula	$C_{16}H_8N_2O_4S_2$	$C_{16}H_8N_2O_4S_2$	$C_{16}H_8N_2O_4S_2\cdot CH_3NO_2$	$C_{16}H_8N_2O_4S_2\cdot 0.5C_6H_5Cl$	$C_{19.652}H_{12.652}N_2O_{4.043}S_2$
Chemical formula weight	356.36	356.36	417.41	412.64	405.63
Cell setting, space group	Orthorhombic, $Pna2_1$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/c$
a, b, c (Å)	7.1298 (2), 30.7247 (13), 6.8691 (2)	13.5052 (2), 7.8740 (1), 29.2050 (5)	22.5545 (9), 4.8545 (2), 16.7095 (14)	7.6257 (10), 10.3369 (2), 11.6392 (2)	13.7600 (4), 16.4924 (4), 16.0450 (5)
α, β, γ (°)	90, 90, 90	90, 98.9640 (5), 90	90, 102.4670 (17), 90	81.5440 (8), 77.8600 (8), 78.8480 (13)	90, 92.951 (1), 90
V (Å^3)	1504.75 (9)	3067.73 (8)	1786.40 (18)	874.59 (12)	3636.35 (18)
Z	4	8	4	2	8
D_x (Mg m^{-3})	1.573	1.543	1.552	1.567	1.482
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	2913	6776	3397	3946	8251
θ range (°)	2.93–27.46	2.95–27.45	3.31–27.45	3.01–27.50	2.96–27.48
μ (mm^{-1})	0.378	0.371	0.340	0.411	0.323
Temperature (K)	120 (2)	120 (2)	120 (2)	120 (2)	120 (2)
Crystal form, colour	Needle, colourless	Plate, colourless	Lath, colourless	Block, colourless	Block, colourless
Crystal size (mm)	0.35 × 0.08 × 0.07	0.20 × 0.07 × 0.02	0.40 × 0.16 × 0.10	0.34 × 0.30 × 0.28	0.16 × 0.14 × 0.08
Data collection					
Diffractometer	Kappa–CCD	Kappa–CCD	Kappa–CCD	Kappa–CCD	Kappa–CCD
Data collection method	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{min}	0.8791	0.9295	0.8759	0.8729	0.9501
T_{max}	0.9740	0.9926	0.9668	0.8936	0.9746
No. of measured, independent and observed parameters	6890, 2913, 2154	26 075, 6776, 5280	8059, 3397, 2883	8059, 3946, 3616	32 961, 8251, 5880
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0543	0.0882	0.0325	0.0325	0.0601
θ_{max} (°)	27.46	27.45	26.05	27.50	27.48
Range of h, k, l	$-5 \rightarrow h \rightarrow 9$ $-39 \rightarrow k \rightarrow 39$ $-7 \rightarrow l \rightarrow 6$	$-17 \rightarrow h \rightarrow 17$ $-10 \rightarrow k \rightarrow 10$ $-37 \rightarrow l \rightarrow 37$	$-28 \rightarrow h \rightarrow 27$ $-6 \rightarrow k \rightarrow 5$ $-21 \rightarrow l \rightarrow 20$	$-9 \rightarrow h \rightarrow 9$ $-13 \rightarrow k \rightarrow 13$ $-15 \rightarrow l \rightarrow 15$	$-17 \rightarrow h \rightarrow 16$ $-21 \rightarrow k \rightarrow 21$ $-20 \rightarrow l \rightarrow 20$
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0446, 0.0998, 1.058	0.0411, 0.1202, 1.042	0.0367, 0.0926, 1.06	0.0381, 0.1084, 1.127	0.0464, 0.1291, 1.035
No. of reflections and parameters used in refinement	2913, 217	6776, 433	3397, 254	3946, 253	8251, 510
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0238P)^2 + 0.4375P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0713P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 1.0483P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0560P)^2 + 0.3058P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0693P)^2 + 0.8270P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.000	0.002	0.000	0.000	0.001
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.244, −0.313	0.608, −0.6	0.25, −0.377	0.392, −0.523	0.47, −0.506
Extinction method	None	None	None	None	None

	(9)	(10)	(11)	(12)
Crystal data				
Chemical formula	$C_{16}H_8N_2O_4S_2$	$C_{16}H_8N_2O_4S_2$	$C_{16}H_8N_2O_4S_2\cdot 0.5C_8H_{10}$	$C_{16}H_8N_2O_4S_2\cdot 0.5C_7H_8$
Chemical formula weight	356.36	356.36	409.44	402.45
Cell setting, space group	Monoclinic, $C2/c$	Monoclinic, $C2/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a, b, c (Å)	14.4180 (6), 16.0502 (7), 7.6616 (3)	14.3752 (5), 15.9349 (10), 7.631 (10)	14.2629 (5), 16.1851 (4), 7.7835 (2)	14.3126 (4), 16.1270 (4), 7.6990 (2)
β (°)	93.369 (2)	93.845 (2)	94.3917 (9)	94.3216 (13)

Table 2 (continued)

	(9)	(10)	(11)	(12)
V (Å^3)	1769.92 (13)	1744 (2)	1791.52 (9)	1772.03 (8)
Z	4	4	4	4
D_x (Mg m^{-3})	1.337	1.357	1.518	1.508
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	1993	1974	4089	3467
θ range (°)	3.20–27.48	3.21–27.49	2.89–29.78	2.92–28.04
μ (mm^{-1})	0.321	0.326	0.329	0.331
Temperature (K)	120 (2)	120 (2)	120 (2)	120 (2)
Crystal form, colour	Block, colourless	Block, colourless	Block, colourless	Block, colourless
Crystal size (mm)	0.10 × 0.10 × 0.08	0.15 × 0.10 × 0.08	0.25 × 0.15 × 0.10	0.25 × 0.10 × 0.10
Data collection				
Diffractometer	Kappa–CCD	Kappa–CCD	Kappa–CCD	Kappa–CCD
Data collection method	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{min}	0.9686	0.9527	0.9224	0.9219
T_{max}	0.9747	0.9744	0.9679	0.9677
No. of measured, independent and observed parameters	5857, 1993, 1633	5498, 1974, 1437	14 107, 4089, 3275	9295, 3467, 2827
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0595	0.0733	0.0724	0.0541
θ_{max} (°)	27.48	27.49	27.45	26.05
Range of h, k, l	$-18 \rightarrow h \rightarrow 18$ $-19 \rightarrow k \rightarrow 20$ $-8 \rightarrow l \rightarrow 9$	$-17 \rightarrow h \rightarrow 18$ $-20 \rightarrow k \rightarrow 20$ $-9 \rightarrow l \rightarrow 9$	$-14 \rightarrow h \rightarrow 18$ $-20 \rightarrow k \rightarrow 20$ $-10 \rightarrow l \rightarrow 10$	$-17 \rightarrow h \rightarrow 17$ $-19 \rightarrow k \rightarrow 19$ $-9 \rightarrow l \rightarrow 9$
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.1268, 1.063	0.054, 0.1538, 1.032	0.039, 0.1172, 1.089	0.0393, 0.1073, 1.034
No. of reflections and parameters used in refinement	1993, 109	1974, 109	4089, 255	3467, 254
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0708P)^2 + 0.7470P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0908P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2 + 0.0637P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 0.3414P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.000	0.000	0.001	0.013
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.45, −0.562	0.411, −0.656	0.369, −0.439	0.329, −0.413
Extinction method	None	None	*SHELXL*	None
Extinction coefficient	–	–	0.016 (2)	–

PRPKAPPA (Ferguson, 1999), *Kappa-CCD server software* (Nonius, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS*97 (Sheldrick, 1997*a*), *SHELXL*97 (Sheldrick, 1997), *PLATON* (Spek, 2001).

established. For (8) the occupancy of the solvent sites by ethylbenzene was only partial and the remaining sites were occupied by water molecules: in both (9) and (10) the solvent molecules in the channels were intractably disordered and the *SQUEEZE* option in *PLATON* (Spek, 2001) was employed.

All H atoms in (I) and in localized organic components were located from difference maps, and included in the refinements as riding atoms with C—H 0.95 (aromatic) or 0.98 Å (methyl). The diagrams were prepared with the aid of *PLATON*. Details of the hydrogen-bond dimensions are given in Table 3.[1]

[1] Supplementary data for this paper, including diagrams of the molecule of (I) in polymorphs (7)–(12) showing the atom-labelling schemes and anisotropic displacement parameters, are available from the IUCr electronic archives (Reference: NA0132). Services for accessing these data are described at the back of the journal.

3. Results and discussion

3.1. Solvent-free polymorphs

Polymorph (1) of (I) crystallizes from a solution in ethyl acetate with $Z' = 2$ in space group $P2_1/c$ (Skakle *et al.*, 2001). In this solvent-free polymorph, the molecules are linked by C—H···O hydrogen bonds into centrosymmetric aggregates containing four molecules, two of each type, and these four-molecule aggregates are further linked by aromatic $\pi\cdots\pi$ stacking interactions and by weak C—H···O hydrogen bonds to form a continuous three-dimensional framework.

When (I) is crystallized from methanol, a second solvent-free polymorph (4) (Fig. 1) is obtained having $Z' = 1$ in space group $Pna2_1$, in which the molecules are linked into simple spiral chains by a single C—H···O hydrogen bond (Table 3). Aromatic C16 at (x, y, z) acts as a hydrogen-bond donor to O21 at $(-x, -y, \frac{1}{2}+z)$, while C16 at $(-x, -y, \frac{1}{2}+z)$ in turn

Table 3
Hydrogen bonds and short intermolecular contacts (Å, °).

	D—H···A	H···A	D···A	D—H···A	Motif direction
(4)					
C16—H16···O21^{i}	2.51	3.343 (6)	147	$C(11)$	[001]
(5)					
C14—H14···O21^{ii}	2.53	3.358 (2)	146	$R_2^2(20)$	–
C16—H16···O32	2.37	3.245 (2)	153	D	–
C34—H34···O31^{iii}	2.45	3.198 (3)	136	$C(6)$	[010]
C45—H45···O41^{iv}	2.53	3.175 (3)	126	$C(7)$	[010]
(6)					
C17—H17···O32	2.41	3.352 (3)	172	D	–
C24—H24···O22^{ii}	2.46	3.334 (3)	153	$R_2^2(10)$	–
C31—H31C···O11	2.51	3.463 (3)	165	D	–
C31—H31A···O21^{iii}	2.84	2.914 (3)	85	$C_2^2(14)$	[010]
C31—H31B···O21^{iii}	2.72	2.914 (3)	91	$C_2^2(14)$	[010]
C31—H31C···O21^{iii}	2.70	2.914(3)	93	$C22_2^2(14)$	[010]
(7)					
C15—H15···O22^{iv}	2.54	3.299 (2)	137	$C(11)$	[010]
C24—H24···O12^{v}	2.55	3.384 (2)	147	$R_2^2(20)$	–
C26—H26···O11^{vi}	2.51	3.445 (2)	170	$C(11)$	[001]
(8)					
C35—H35···O31^{vii}	2.45	3.230 (3)	140	$C(7)$	[001]
C44—H44···O41^{viii}	2.48	3.258 (2)	139	$C(6)$	[001]
C46—H46···O22	2.44	3.249 (2)	143	D	–
(9)					
C5—H5···O1^{ix}	2.55	3.344 (3)	142	$C(7)$	[101]
(10)					
C5—H5···O1^{ix}	2.55	3.353 (5)	142	$C(7)$	[101]
(11)					
C15—H15···O11^{x}	2.09	3.023 (2)	168	$C(7)$	[101]
C26—H26···O22^{xi}	2.39	3.209 (2)	144	$C(7)$	[010]
(12)					
C15—H15···O11^{x}	2.11	3.029 (2)	163	$C(7)$	[101]
C26—H26···O22^{xi}	2.38	3.179 (2)	142	$C(7)$	[010]

Symmetry codes: (i) $-x, -y, \frac{1}{2}+z$; (ii) $-x, 2-y, -z$; (iii) $x, 1+y, z$; (iv) $x, -1+y, z$; (v) $1-x, 2-y, -z$; (vi) $x, y, -1+z$; (vii) $x, \frac{3}{2}-y, -\frac{1}{2}+z$; (viii) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (ix) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (x) $-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z$; (xi) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$.

acts as a donor to O21 at $(x, y, 1+z)$. Hence, a $C(11)$ chain is produced running parallel to [001] and generated by the 2_1 screw axis along (0, 0, z) (Fig. 2): a second such chain is generated by the 2_1 axis along ($\frac{1}{2}$, $\frac{1}{2}$, z), but there are neither hydrogen bonds nor aromatic $\pi\cdots\pi$ stacking interactions between neighbouring chains.

Crystallization from either acetonitrile or dimethylformamide yields a third solvent-free monoclinic polymorph (5) also having $Z' = 2$ in $P2_1/c$ analogous to form (1), but with cell dimensions very different from those of form (1). The conformations of both molecules in (5) (Fig. 3) are similar to those observed for forms (I)–(III), with N—S—S—N and C—N—S—S torsional angles all close to 90°, but the form of the supramolecular aggregation in (5) is entirely different from that observed in (1) and (4). Molecules of type 2 in (5), containing S31 and S41 (Fig. 3), form a molecular ladder, from which the type 1 molecules containing S11 and S21 are pendent. Atom C34 in the type 2 molecule at (x, y, z) acts as a hydrogen-bond donor to O31 in the type 2 molecule at $(x, 1+y, z)$, while C45 at (x, y, z) acts as a hydrogen-bond donor to O41 at $(x, -1+y, z)$. In this way, antiparallel $C(6)$ and $C(7)$ chains are generated by translation along the [010] direction. These chains represent the two uprights of a molecular ladder in which the central C31—N—S—S—N—C41 fragments represent the rungs: there are $R_2^2(21)$rings (Fig. 4) between the rungs of the ladder and a molecule of type 1 is linked to each atom of type O32 (Table 3). There are four such ladders running through each unit cell, along the approximate lines (0.18, y, 0.23), (0.18, y, 0.73), (0.82, y, 0.27) and (0.82, y, 0.77), and these ladders are linked in pairs by a further C—H···O hydrogen bond. Atom C14 in the type 1 molecule at (x, y, z), part of the ladder running along (0.18, y, 0.23), acts as a hydrogen-bond donor to O21 in the type 1 molecule at

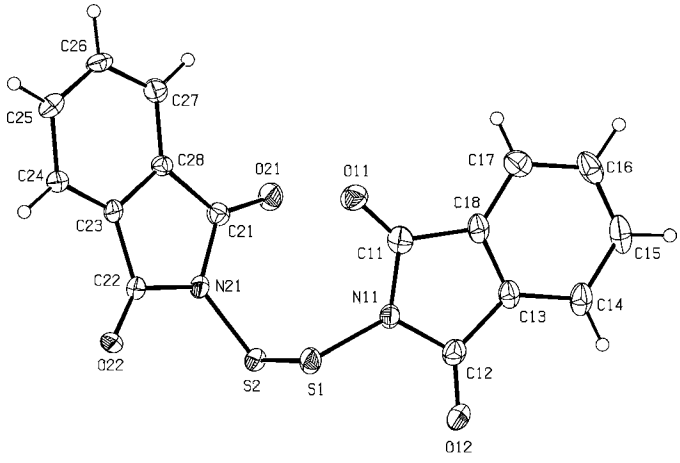


Figure 1
The molecule of (I) in (4), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

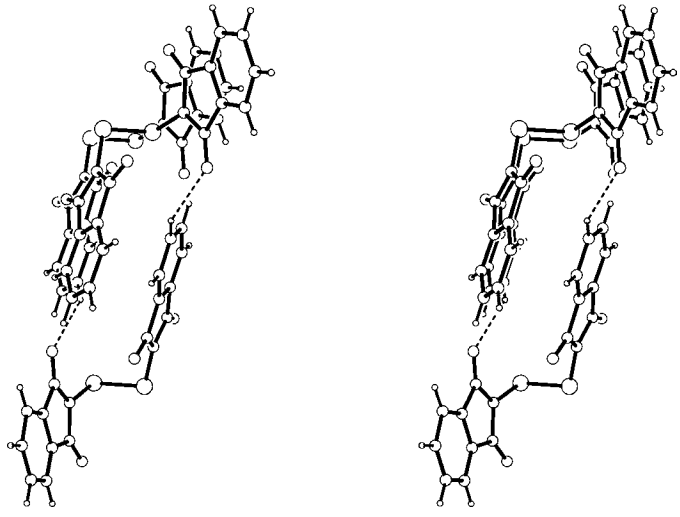


Figure 2
Stereoview of part of the crystal structure of (4) showing the formation of a $C(11)$ chain along [001]. For the sake of clarity the unit-cell box is omitted.

$(-x, 2-y, -z)$, part of the ladder along $(-0.18, y, -0.23)$. The centrosymmetric $R_2^2(20)$ motif thus formed (Fig. 5) serves to link the two ladders, but there are no further interactions between the ladders. In particular, there are no aromatic $\pi\cdots\pi$ stacking interactions as observed in form (1). The overall supramolecular structure can itself be regarded as another molecular ladder, with the type 2 molecules providing the uprights and the dimers of type 1 molecules forming the rungs.

3.2. A solvate with solvent molecules hydrogen-bonded to (I)

When crystallized from nitromethane, (I) forms a monosolvate $C_{16}H_8N_2O_4S_2\cdot CH_3NO_2$ (6). Both molecular components lie in general positions in space group $P2_1/c$ and the solvent molecule acts as both a donor and an acceptor of C—H$\cdots$O hydrogen bonds. Within the asymmetric unit (Fig. 6) aromatic C17 in (I) acts as a hydrogen-bond donor to nitromethane O32 and nitromethane C31 acts as a donor, *via* H31*C*, to O11, so completing an $R_2^2(9)$ ring. These two-component units are linked into centrosymmetric four-component aggregates by a third C—H$\cdots$O hydrogen bond: C24 in the molecule of (I) at (x, y, z) acts as a hydrogen-bond donor to O22 in the molecule of (I) at $(-x, 2-y, -z)$, thus generating an $R_2^2(10)$ ring centred at (0, 1, 0) (Fig. 7).

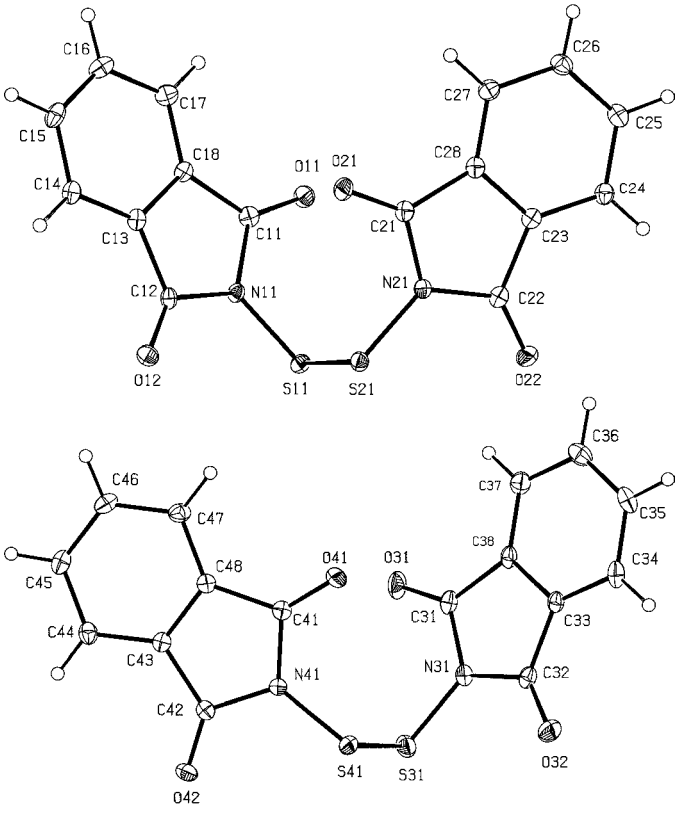


Figure 3
The two independent molecules of (I) in (5), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

These four-component aggregates are linked into chains running parallel to the [010] direction by an uncommon type of multicentre interaction. The amidic O21 at (x, y, z) forms rather short contacts with the three nitromethane H atoms at $(x, -1+y, z)$ and a very short contact with the corresponding methyl C31 (Table 2, Fig. 8). All three C—H$\cdots$O angles are close to 90° and so these interactions cannot be regarded as conventional soft hydrogen bonds. However, the presence of the nitro group generates significant partial positive charges on the H atoms of the nitromethane molecule, while the amidic O atoms carry significant partial negative charges; this combination of polarized molecular components leads to a favourable electrostatic interaction between the methyl group of the solvent nitromethane and a carbonyl group of (I).

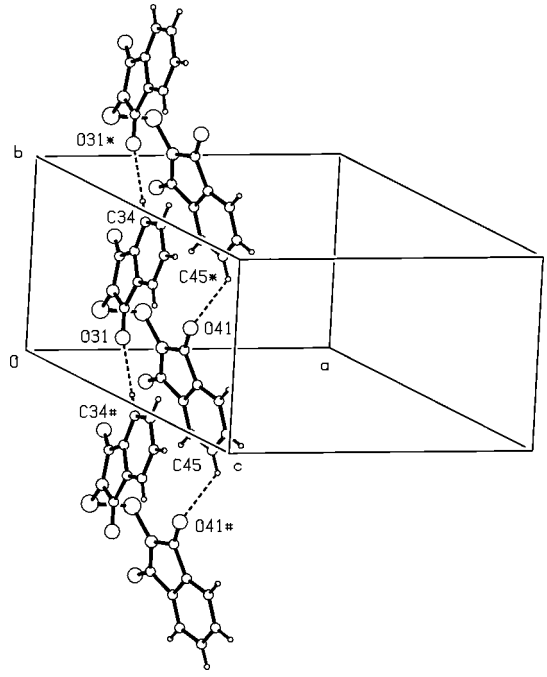


Figure 4
Part of the crystal structure of (5) showing the formation of a molecular ladder along [010]. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x, 1+y, z)$ and $(x, -1+y, z)$, respectively.

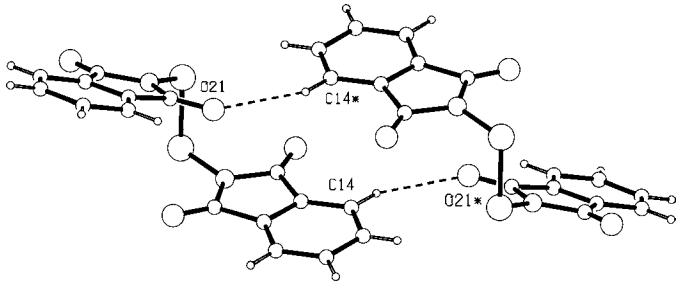
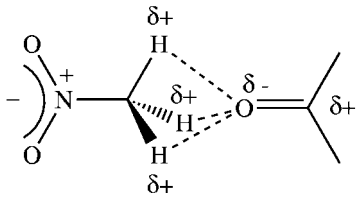


Figure 5
Part of the crystal structure of (5) showing the formation of a centrosymmetric $R_2^2(20)$ ring motif linking pairs of molecular ladders. The atoms marked with an asterisk (*) are at the symmetry position $(-x, 2-y, -z)$.



Although this geometry represents an uncommon type of intermolecular interaction, an analogous multicentre C—H···O system has recently been observed in the salt $[HN(CH_2CH_2)_3NH]^{2+}\cdot[(C_4H_5O_6)^-]_2$ formed between 1,4-diazabicyclo[2.2.2]octane and racemic tartaric acid, where a single O in a tartrate anion forms close contacts with all four H atoms in one of the $-CH_2-CH_2-$ bridges of the cation with H···O distances in the range 2.42–2.55 Å and C—H···O angles in the range 78–100° (Farrell *et al.*, 2002).

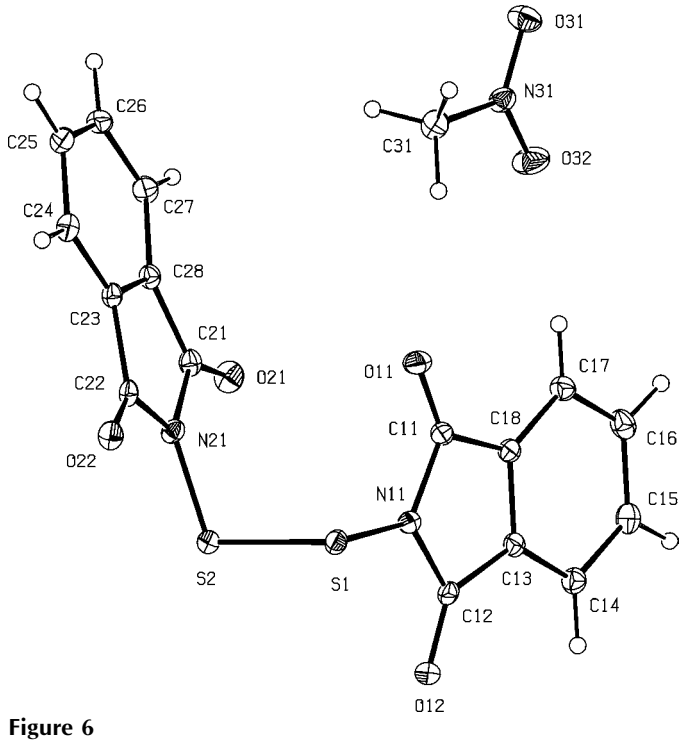


Figure 6
The molecular components in (6), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

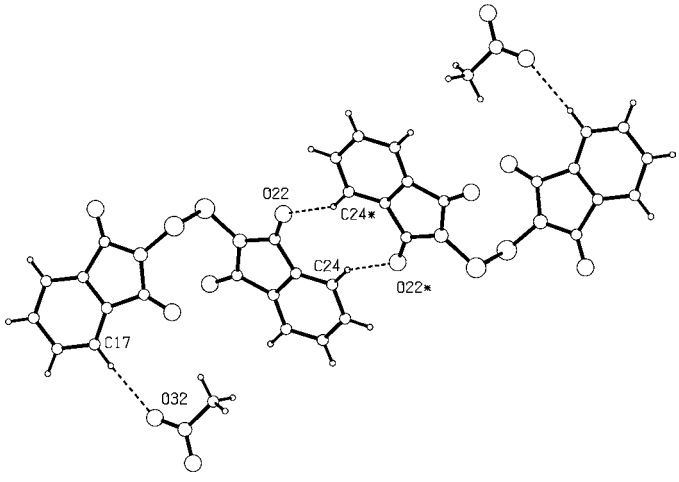


Figure 7
Part of the crystal structure of (6) showing the formation of a centrosymmetric four-molecule aggregate. The atoms marked with an asterisk (*) are at the symmetry position $(-x, 2-y, -z)$.

3.3. Solvates with solvent molecules in isolated cavities

3.3.1. Chlorobenzene hemisolvate in space group $P\bar{1}$. The hemisolvate formed by chlorobenzene, $(C_{16}H_8N_2O_4S_2)_2\cdot C_6H_5Cl$ (7), crystallizes in space group $P\bar{1}$. In this solvate the molecules of (I) occupy general positions and they are again linked by a combination of aromatic $\pi\cdots\pi$ stacking interactions and weak C—H···O hydrogen bonds; both ring systems of (I) form $\pi\cdots\pi$ stacking interactions with adjacent molecules. The ring system containing atoms C1*n* in the molecule at (x, y, z) form a $\pi\cdots\pi$ stacking interaction across the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with the symmetry-related ring containing C1*n* in the molecule at $(1-x, 1-y, 1-z)$: the interplanar spacing is 3.563 (2) Å. Similarly, the ring system at (x, y, z) containing atoms C2*n* forms a $\pi\cdots\pi$ stacking interaction across the inversion centre at (0, 1, 0) with the symmetry-related ring containing C2*n*, at $(-x, 2-y, -z)$; here, the interplanar spacing is 3.527 (2) Å. Propagation of these two $\pi\cdots\pi$ stacking interactions generates a chain along the $[1\bar{1}1]$ direction (Fig. 9) and adjacent chains are linked by the soft hydrogen bonds.

Atoms C15 and C26 in the molecule at (x, y, z) act as hydrogen-bond donors to O22 at $(x, -1+y, z)$ and to O11 at $(x, y, -1+z)$, respectively, so linking adjacent chains in the [010] and [001] directions. Similarly, C24 at (x, y, z) acts as a hydrogen-bond donor to O12 at $(1-x, 2-y, -z)$ again linking adjacent chains in the [010] direction. The combination

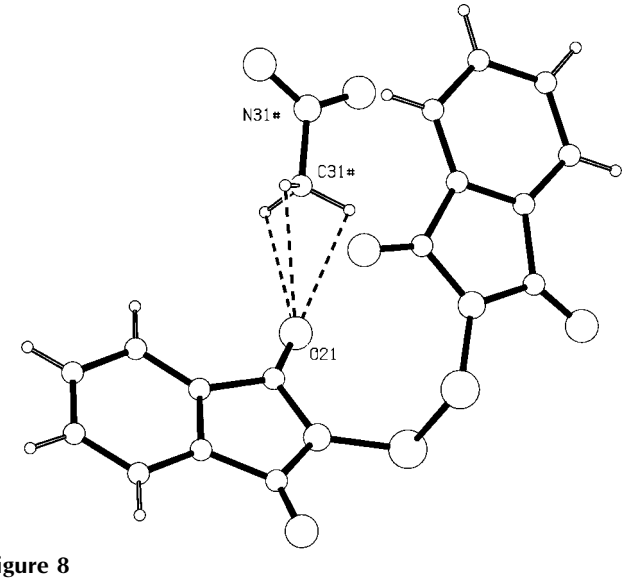


Figure 8
Part of the crystal structure of (6) showing the very short contacts between O21 and three C—H bonds in a nitromethane molecule with the C—H···O contacts shown as dotted lines; the atoms marked with a hash (#) are at the symmetry position $(x, -1+y, z)$.

of the two independent $\pi\cdots\pi$ stacking interactions and the three independent C—H$\cdots$O hydrogen bonds links all the molecules of (I) in (7) into a continuous three-dimensional framework. However, the molecules of (I) occupy only *ca* 82.8% of the total volume of the unit cell of (7), leaving substantial voids around the centres of inversion (0, 0.5, 0) and so on. The solvent chlorobenzene molecules are located at the centres on inversion within these voids, disordered over two sets of sites such that the Cl site has 0.5 occupancy; however, there are no C—H$\cdots$O hydrogen bonds involving the solvent molecules.

3.3.2. Ethylbenzene hemisolvate in space group $P2_1/c$. Crystallization of (I) from ethylbenzene yields an approximate hemisolvate, also containing some adventitious water molecules $(C_{16}H_8N_2O_4S_2)_2\cdot0.913C_6H_5C_2H_5\cdot0.087H_2O$ (8) in space group $P2_1/c$, in which all of the independent molecular components, two molecules of (I), the partial molecule of ethylbenzene and the trace of water, all lie in general positions. The unit-cell dimensions do not in any way resemble those found for the chlorobenzene solvate (§3.3.1; Table 2).

The type 2 molecules of (I) in this solvate (those containing S3 and S4) are linked into molecular ladders by a combination of C—H$\cdots$O hydrogen bonds and aromatic $\pi\cdots\pi$ stacking interactions. Atoms C35 and C44 in different aryls rings of the type 2 molecule at (x, y, z) act as hydrogen-bond donors, respectively, to O31 and O41 in the type 2 molecules at $(x, \frac{3}{2}-y, -\frac{1}{2}+z)$ and $(x, \frac{3}{2}-y, \frac{1}{2}+z)$, thus producing a molecular ladder running parallel to the [001] direction and generated by the *c*-glide plane at $y = 0.75$ (Fig. 10). The uprights consist of antiparallel $C(6)$ and $C(7)$ chains, each generated by one hydrogen bond, while the molecular cores act as the rungs of the ladder. Between the rungs there are $R_2^2(21)$ rings. At the same time, there are $\pi\cdots\pi$ stacking interactions between adjacent type 2 molecules within the ladder, which serve to reinforce the effect of the hydrogen bonds: the interplanar spacings are *ca* 3.33 Å with an aryl-centroid offset of *ca* 1.25 Å. The type 1 molecules are pendent from this ladder: within the asymmetric unit, C46 in the type 2 molecule acts as a hydrogen-bond donor to O22 in the type 1 molecule.

Two molecular ladders pass through each unit cell, in the domains $0.03 < x < 0.52$ and $0.48 < x < 0.97$, respectively, but there are no significant directed interactions between the adjacent ladders. The ladders together account for only 78.9% of the unit-cell volume and the remaining space is occupied by fully ordered ethylbenzene molecules in general positions. There are no hydrogen bonds or $\pi\cdots\pi$ stacking interactions between the molecules of (I) and those of ethylbenzene, nor are there any solvent-accessible connections between adjacent solvent cavities.

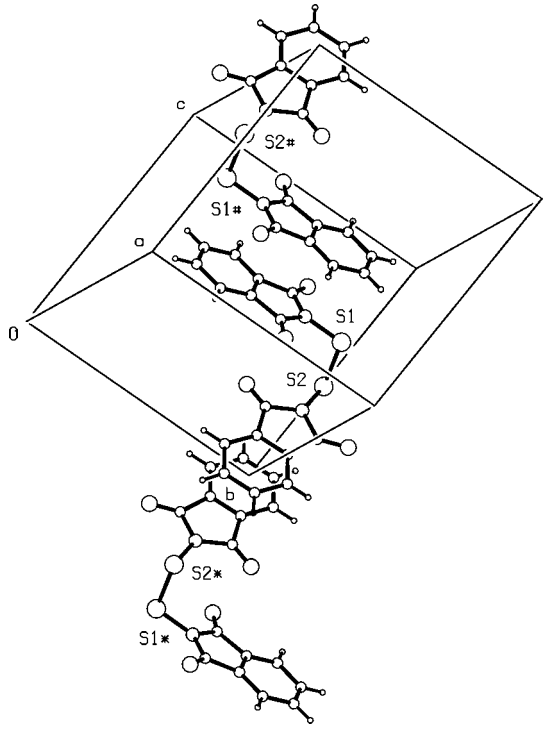


Figure 9
Part of the crystal structure of (7) showing the formation, by means of aromatic $\pi\cdots\pi$ stacking interactions, of a chain of molecules of (I) along the $[1\bar{1}1]$ direction. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(-x, 2-y, -z)$ and $(1-x, 1-y, 1-z)$, respectively.

3.4. Channel polymorphs with non-localized solvent molecules

Crystallization of (I) from either tetrahydrofuran (THF) or wet 2-methyl-2-propanol (Me_3COH) yields solvates (9) and (10), which are isomorphous with the solvates (2) and (3) previously reported (Skakle *et al.*, 2001). Thus, the molecules of (I) in polymorphs (9) and (10) lie across twofold axes in space group $C2/c$; they are linked into chains along $[10\bar{1}]$ by $\pi\cdots\pi$ stacking interactions, as in (2) and (3), together with weak C—H$\cdots$O hydrogen bonds. These hydrogen bonds have

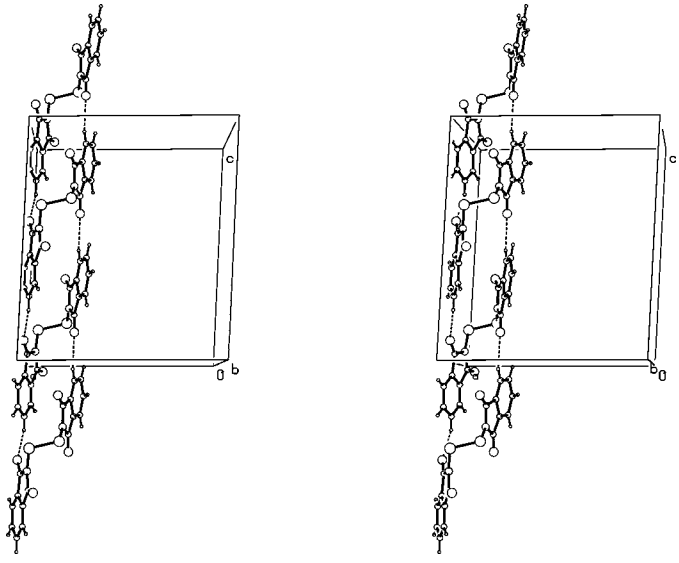


Figure 10
Stereoview of part of the crystal structure of (8) showing the formation of a molecular ladder parallel to [001].

H···O distances of 2.55 Å in both (9) and (10); the corresponding contacts in (2) and (3) have H···O distances of 2.61 and 2.65 Å, respectively, and on this basis were not regarded as structurally significant. The important feature in both (9) and (10) is the formation of channels along [001], whose volumes represent 20.0 and 19.7%, respectively, of the unit-cell volume. There are solvent molecules within these channels which are intractably disordered and possibly mobile, as suggested in the case of polymorphs (2) and (3) (Skakle *et al.*, 2001). In (10) there is a continuous ribbon of electron density along the channel, consistent with the presence of mobile water molecules, rather than of Me_3COH molecules, whose presence is, in any case, unlikely for geometric reasons.

3.5. Channel polymorphs with localized solvent molecules

When (I) is crystallized from either *p*-xylene or toluene, two further solvates are obtained, $(C_{16}H_8N_2O_4S_2)_2\cdot C_8H_{10}$ (11) and $(C_{16}H_8N_2O_4S_2)_2\cdot C_7H_8$ (12), respectively, which are isomorphous and which contain 0.5 molecules of solvent per molecule of (I). In these two polymorphs the molecules are packed so as to form continuous channels, analogous to those in forms (2), (3), (9) and (10). However, forms (11) and (12) crystallize in space group $P2_1/n$, a subgroup of the space group $C2/c$ found for (2), (3), (9) and (10), with cell dimensions very similar to those in the $C2/c$ forms. Moreover, while in (2), (3), (9) and (10) the solvent molecules are intractably disordered, the solvent molecules in (11) and (12) are localized in the channels across centres of inversion and are readily refined; the toluene molecules in (12) are disordered over two sets of sites having equal occupancy.

Space group $P2_1/n$ differs from $C2/c$ in that it lacks the twofold rotation axes: in forms (2), (3), (9) and (10), the molecules lie across these twofold axes, whereas in (11) and (12) they lie in general positions. The molecules in (11) and (12) are linked by very short C—H···O hydrogen bonds, whose effect is reinforced by aromatic $\pi\cdots\pi$ stacking interactions. Atom C15 at (x, y, z) acts as a hydrogen-bond donor to O11 at $(-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z)$, while C15 at $(-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z)$ in turn acts as a donor to O11 at $(-1+x, y, -1+z)$, thus producing a $C(7)$ chain running parallel to the [101] direction (Fig. 11). In addition, the aryl ring C13–C18 in the molecule at (x, y, z) forms a $\pi\cdots\pi$ stacking interaction with the aryl ring C23–C28 in the molecule at $(-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z)$: these two rings are parallel within 1°; the interplanar spacing is 3.552 (2) Å in (11) [3.549 (2) Å in (12)] and the centroid offset is 1.310 (2) Å in (11) [1.320 (2) Å in (12)]. This interaction reinforces the chain running parallel to [101] (Fig. 11). The [101] chain formed by the combined effect of the C—H···O hydrogen bonds and the $\pi\cdots\pi$ stacking interactions is generated by the glide plane at $y = 0.75$; there is a second parallel chain generated by the glide plane at $y = 0.25$ and these two chains are linked by a second

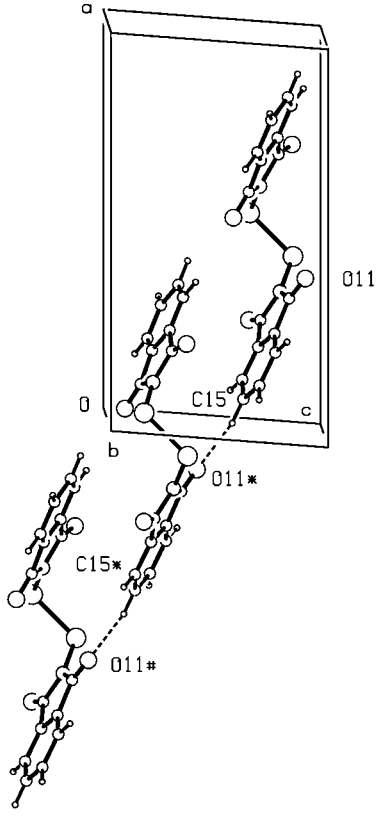


Figure 11
Part of the crystal structure of (11) showing the formation of a $C(7)$ chain along [101]. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z)$ and $(-1+x, y, -1+z)$, respectively.

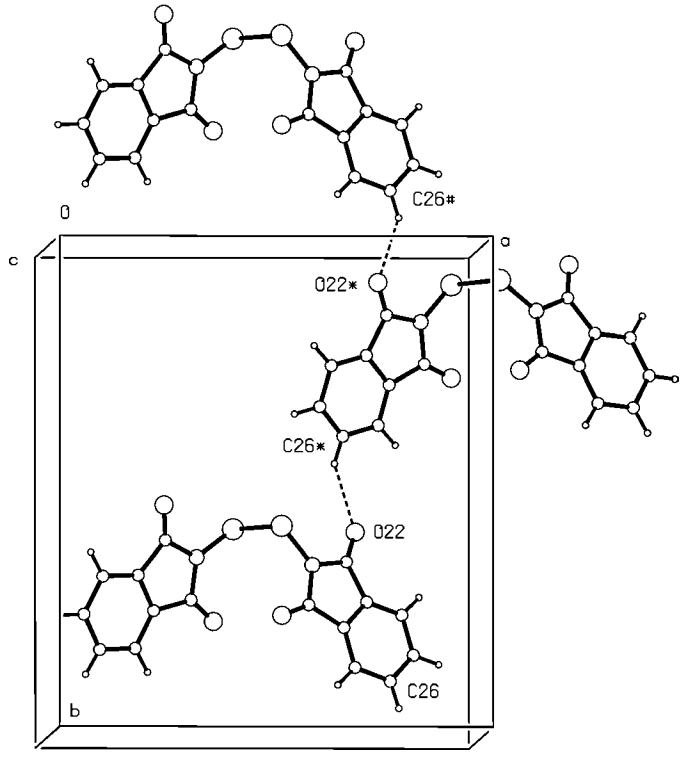


Figure 12
Part of the crystal structure of (11) showing the formation of a $C(6)$ chain along [010]. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z)$ and $(x, 1+y, z)$, respectively.

C—H···O hydrogen bond. Atom C26 at (x, y, z) is part of the chain lying in the domain $0.56 < y < 0.94$ and it acts as a hydrogen-bond donor to O22 at $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$, which lies in the domain $1.06 < y < 1.44$. Propagation of this second hydrogen bond produces a $C(7)$ chain running parallel to the [010] direction (Fig. 12) which links the [101] chains into a $(10\bar{1})$ sheet.

As in the $C2/c$ polymorphs, the molecules of (I) in (11) and (12) do not occupy the entire unit-cell volume: in (11) the framework formed by (I) occupies only 79.2% of the cell volume, in (12) 79.8%. The residual space forms continuous channels parallel to [001] (Fig. 13) and the solvent molecules are localized across centres of inversion within these channels. In polymorph (11) the *p*-xylene lies across the centre of inversion at $(1, \frac{1}{2}, \frac{1}{2})$, while in polymorph (12) the toluene is disordered across this inversion centre such that the methyl groups have 0.5 occupancy. There are no short contact distances between the solvent molecules and the framework formed by (I); in particular, the shortest C—H···O contact of this kind has an H···O distance of 2.63 Å associated with a C—H···O angle of 100°.

Thus, the $P2_1/n$ polymorphs (11) and (12) differ from the $C2/c$ forms (2), (3), (9) and (10) in the following ways: the molecules in the $P2_1/n$ form lie in general positions and are linked by very strong C—H···O hydrogen bonds, as well as by the $\pi\cdots\pi$ stacking interaction, whereas in the $C2/c$ polymorphs, where the molecules lie across twofold axes, the C—H···O hydrogen bonds are either very weak or absent; secondly, the chains in the $P2_1/n$ polymorphs lie along the [101] direction, while in the $C2/c$ forms they are parallel to the $[10\bar{1}]$ direction; finally, in the $P2_1/n$ forms the solvent molecules are localized within the channels, whereas in the $C2/c$ polymorphs the individual solvent molecules cannot be resolved.

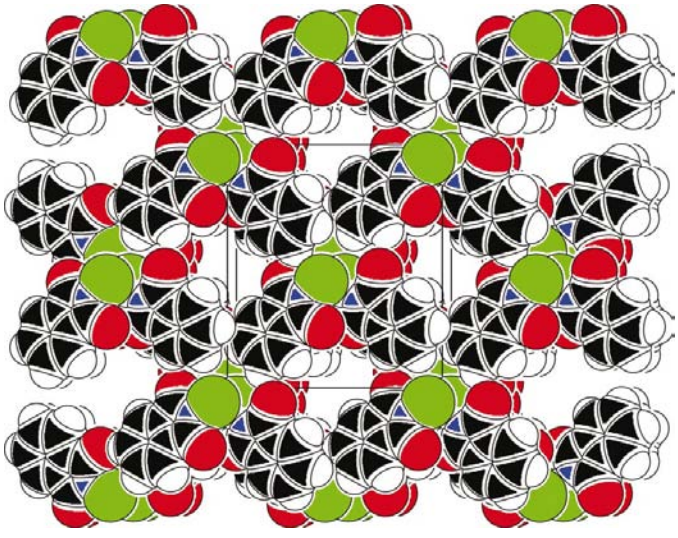


Figure 13
Space-filling representation of the molecules of (I) in (11) showing the continuous channels along [001].

3.6. Molecular dimensions and conformations

The intramolecular dimensions of the molecules of (I) in the various polymorphs and pseudopolymorphs show no unusual features: all forms adopt conformations similar to those previously observed (Skakle *et al.*, 2001), with essentially orthogonal lone pairs at the adjacent N and S atoms.

4. Conclusions

The crystallization of *N*,*N*′-dithiobisphthalimide (I) from common organic solvents has yielded a rich variety of polymorphs and solvates (pseudopolymorphs): including those reported in our earlier structural investigation of this compound (Skakle *et al.*, 2001), we have now found around a dozen different forms. The occurrence in particular of three quite different solvent-free polymorphs, forms (1), (4) and (5) (Table 1) provides, as indeed do all occurrences of polymorphism, a rigorous test for methods aimed at the *ab initio* prediction of the crystal structures of simple molecular compounds (Lommerse *et al.*, 2000). In a similar way, the rather different solvates formed with chlorobenzene form (7), toluene form (12) and ethylbenzene form (8) indicate that even solvent molecules with nearly identical sizes and shapes generate significantly different solvates.

In a recent study, based on the Cambridge Structural Database (CSD; Allen & Kennard, 1993), Nangia & Desiraju (1999) have 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: of these 13, we have in this study excluded the use of benzene, chloroform and carbon tetrachloride on safety grounds and we have excluded acetic acid on the grounds of its solvolytic reactivity towards (I), but all of the remaining nine solvents have been investigated here.

It is interesting to note that the highest ranked solvent (Nangia & Desiraju, 1999) is dimethylformamide, which yielded here the solvent-free polymorph (4): similarly, acetonitrile and methanol, which appear high in the frequency list, both form solvent-free polymorphs, (4) and (5), respectively. On the other hand, the single solvent observed here to exhibit specific multi-point interactions with (I), nitromethane in (6), does not appear in the top 20 solvents in the CSD-based list. Of solvents lower down the list, both ethyl acetate and ethanol formed part of our earlier study (Skakle *et al.*, 2001): both have been found (Nangia & Desiraju, 1999) to form specific and characteristic hydrogen-bonding interactions with host molecules. However, with (I) ethyl acetate gives the solvent-free polymorph (I), while in the ethanol solvate (3), the solvent molecules are intractably disordered, and possibly mobile, within the framework channels: whether the ethanol is mobile or static, there is no evidence of specific hydrogen-bonding interactions between ethanol and (I). All in all, therefore, the

solvation characteristics of (I) seem to be rather atypical of the solvates in the CSD as a whole.

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References

Allen, F. H. & Kennard O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Bingham, A. L., Hughes, D. S., Hursthouse, M. B., Lancaster, R. W., Taverner, S. & Threlfall, T. L. (2001). *Chem. Commun.* pp. 603–604.
Farrell, D. M. M., Ferguson, G., Lough, A. J. & Glidewell, C. (2002). *Acta Cryst.* B**58**, 272–288.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Flack, H. D. & Bernardinelli, G. (2000). *J. Appl. Cryst.* **33**, 1143–1148.
Kooijman, H., van Bommel, K. J. C., Verboom, W., Reinhoudt, D. N., Kroon, J. & Spek, A. L. (2000). *Acta Cryst.* C**56**, 749–757.
Lommerse, J. P. M., Motherwell, W. D. S., Ammon, H. L., Dunitz, J. D., Gavezzotti, A., Hofmann, D. W. M., Leusen, F. J. J., Mooij, W. T. M., Price, S. L., Schweizer, B., Schmidt, M. U., van Eijck, B. P., Verwer, P. & Williams, D. E. (2000). *Acta Cryst.* B**56**, 697–714.
Nangia, A. & Desiraju, G. R. (1999). *Chem. Commun.* pp. 605–606.
Nonius (1997). *Kappa-CCD Server Software.* Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sheldrick, G. M. (1997*a*). *SHELXL*97. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXS*97. University of Göttingen, Germany.
Skakle, J. M. S., Wardell, J. L., Low, J. N. & Glidewell, C. (2001). *Acta Cryst.* C**57**, 742–746.
Spek, A. L. (2001). *PLATON*. University of Utrecht, The Netherlands.
Threlfall, T. L. (1995). *Analyst*, **120**, 2435–2460.
Wilson, A. J. C. (1976). *Acta Cryst.* A**32**, 994–996.