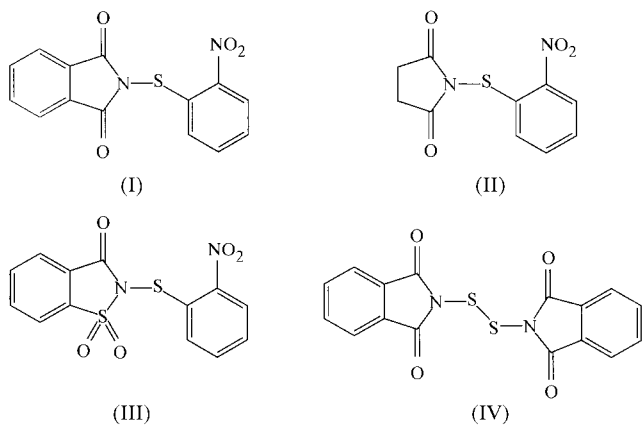


Solvated and solvent-free forms of  
*N,N'*-dithiodipthalimideJanet M. S. Skakle,<sup>a</sup> James L. Wardell,<sup>a</sup> John N. Low<sup>a</sup> and  
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*N,N'*-Dithiodipthalimide, C<sub>16</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>, crystallizes from ethyl acetate with two independent molecules in the asymmetric unit, in which the N—S—S—N torsion angles are −83.59 (19) and 92.9 (2)°. The molecules are linked by C—H···O hydrogen bonds and aromatic  $\pi$ – $\pi$ -stacking interactions into a three-dimensional framework. When crystallized from either dichloromethane or ethanol, solvates are formed in which the molecules of the title compound lie across twofold rotation axes in space group *C2/c*, with N—S—S—N torsion angles of 93.54 (7) and 96.14 (11)°. There are no hydrogen bonds in these solvates, but the molecules are linked by aromatic  $\pi$ – $\pi$ -stacking interactions into chains, between which there are continuous channels. Disordered solvent molecules occupy these channels, which account for *ca* 20% of the unit-cell volume.

## Comment

In each of *N*-(2-nitrophenylthio)phthalimide, (I) (Iwasaki & Masuko, 1986), *N*-(2-nitrophenylthio)succinimide, (II) (Low *et al.*, 2000), and *N*-(2-nitrophenylthio)saccharin, (III) (Glidewell *et al.*, 2000a), the molecular conformations are dominated

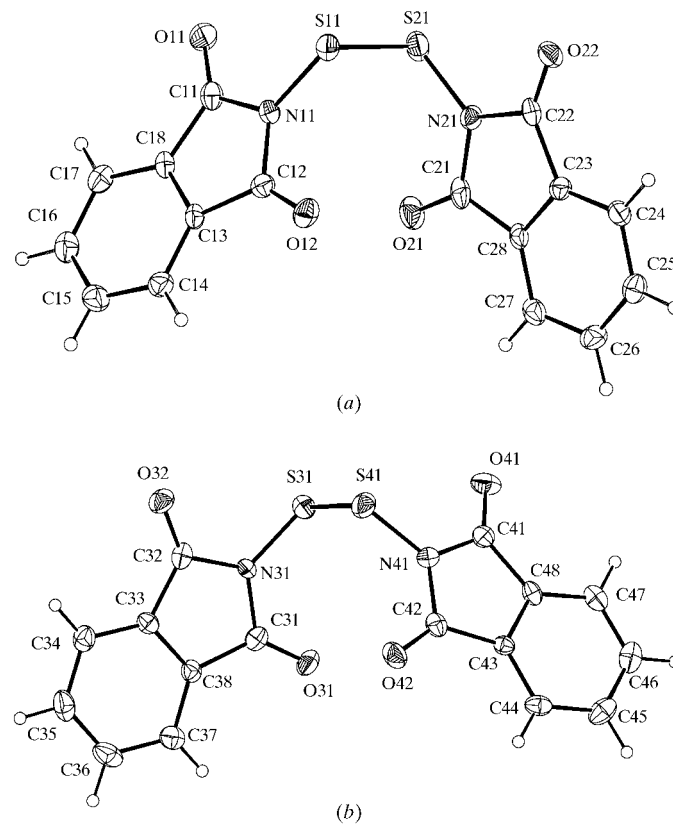


by the near orthogonality of the lone pairs at N and S. Similarly, in diaryl disulfides, *RSSR'*, the molecular conformations

are dominated by the near orthogonality of the lone pairs on the two adjacent S atoms (Glidewell *et al.*, 2000b). Developing these earlier studies, and combining the themes of lone-pair orthogonality in >N—S— and —S—S— pairs, we have now investigated the structure of *N,N'*-dithiodipthalimide, (IV), where the central N—S—S—N fragment comprises four contiguous atoms bearing lone pairs with those on adjacent atoms expected to be pairwise orthogonal. Compound (IV) has been obtained both in an unsolvated form and as two different solvates, to which the term 'pseudo-polymorph' (Kooijman *et al.*, 2000) can be applied; in these solvated forms, there are channels containing disordered solvent molecules.

The title compound, (IV), crystallizes from ethyl acetate to yield a solvent-free polymorph (1), which is monoclinic, with *Z'* = 2 in *P2<sub>1</sub>/c*. The dimensions of the two independent molecules (Fig. 1) are very similar (Table 1), and the molecular conformations are determined by the N—S—S—N and C—N—S—S torsion angles, which are all close to 90° (Table 1), indicating that the N and S lone pairs are approximately orthogonal. The five-membered rings are planar, with internal bond angles which are all considerably less than the ideal value of 120° for each of the planar three-connected atoms within this ring. All other bond distances and angles are typical of their types.

The molecules in polymorph (1) are linked into a continuous three-dimensional framework by a combination of C—



**Figure 1**  
The two independent molecules in form (1) of (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

H $\cdots$ O hydrogen bonds and aromatic  $\pi$ - $\pi$ -stacking interactions. Molecule *A*, containing S11 and S21 (Fig. 1), is a triple acceptor of C—H $\cdots$ O hydrogen bonds, while molecule *B*, containing S31 and S41, is a triple donor (Table 1); these hydrogen-bonding characteristics and the molecular conformations (Fig. 1) together preclude the possibility of any higher symmetry.

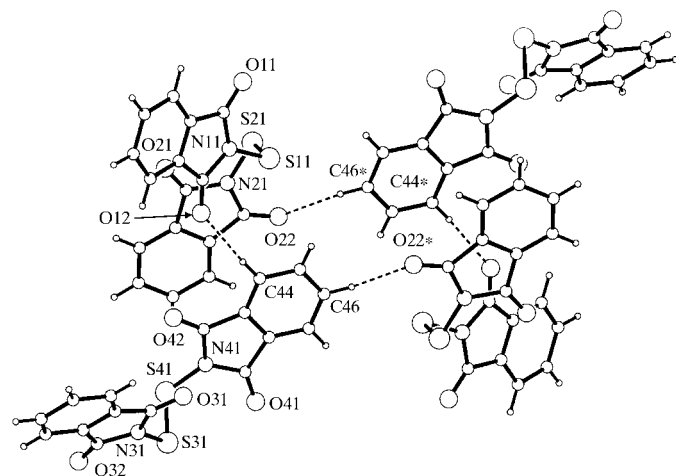
Utilizing the substructure approach (Gregson *et al.*, 2000), the three-dimensional framework structure can readily be analysed in terms of a cyclic centrosymmetric tetramer containing two molecules of each type, and thence in terms of the connections between these tetramers. Within the selected asymmetric unit (Fig. 1), atom C44 in molecule *B* acts as hydrogen-bond donor to O12 in molecule *A* (Table 2); at the same time, C46 in molecule *B* at  $(x, y, z)$  acts as donor to O22 in molecule *A* at  $(-x, -y, 1 - z)$ , while C46 at  $(-x, -y, 1 - z)$  acts as donor to O22 at  $(x, y, z)$ . These two hydrogen bonds thus generate a tetramer, characterized by an  $R_4^4(26)$  motif centred at  $(0, 0, \frac{1}{2})$  (Fig. 2); the second such tetramer in the unit cell is centred at  $(0, \frac{1}{2}, 0)$ .

The tetramers are linked into chains by means of aromatic  $\pi$ - $\pi$ -stacking interactions. Ring C43–C48 in molecule *B* at  $(x, y, z)$  forms a stacking interaction with ring C23–C28 in molecule *A* at  $(1 + x, y, z)$ ; the angle between the ring planes is  $0.3(2)^\circ$  and the minimum perpendicular distance between the planes is  $3.375(3) \text{ \AA}$ , with a centroid offset of *ca*  $1.62 \text{ \AA}$  (Fig. 3). The symmetry-related ring C43–C48 within the tetramer centred at  $(0, 0, \frac{1}{2})$  is at  $(-x, -y, 1 - z)$  and this forms a stacking interaction with ring C23–C28 at  $(-1 - x, -y, 1 - z)$ ; hence, these stacking interactions link the tetramers into a continuous chain running parallel to  $[100]$  and lying along the line  $(x, 0, \frac{1}{2})$ .

Finally, the  $[100]$  chains are all weakly linked together by a third C—H $\cdots$ O hydrogen bond: C36 in molecule *B* at  $(x, y, z)$  acts as hydrogen-bond donor to O21 in molecule *A* at  $(1 + x, \frac{1}{2} - y, \frac{1}{2} + z)$ . The molecules at  $(1 + x, \frac{1}{2} - y, \frac{1}{2} + z)$  form part of the tetramer centred at  $(1, \frac{1}{2}, 1)$ , whose other components are at

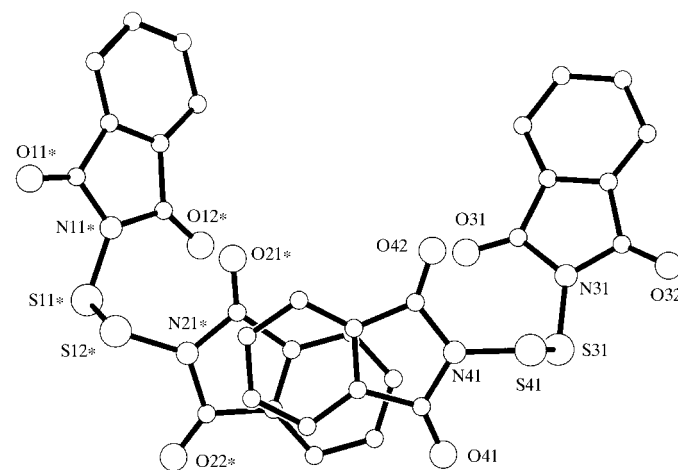
$(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$ , and this tetramer is a component of the  $[100]$  chain along  $(x, \frac{1}{2}, 1)$ . Atom C36 at  $(1 + x, \frac{1}{2} - y, \frac{1}{2} + z)$  acts as donor to O21 at  $(2 + x, y, 1 + z)$ , a component of the chain along  $(x, 0, \frac{1}{2})$ , while C36 at  $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$  is donor to O21 at  $(-x, 1 - y, 1 - z)$ , a component of the chain along  $(x, 1, \frac{1}{2})$ . Propagation of this hydrogen bond by the space group serves to link all of the  $[100]$  chains. Thus, for example, the chain along  $(x, \frac{1}{2}, 1)$  is thereby linked to the four chains along  $(x, 0, \frac{1}{2})$ ,  $(x, 0, \frac{3}{2})$ ,  $(x, 1, \frac{1}{2})$  and  $(x, 1, \frac{3}{2})$ . The linking of the  $[100]$  chains in this manner is at the cost of a rather short non-bonded O41 $\cdots$ O41<sup>iii</sup> contact of  $2.835(7) \text{ \AA}$  [symmetry code: (iii)  $-x, -y, 2 - z$ ]. It must be emphasized that although the C36—H36 $\cdots$ O21<sup>ii</sup> hydrogen bond [symmetry code: (ii)  $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$ ] is probably fairly weak, as judged by the C—H $\cdots$ O angle, in all of the C—H $\cdots$ O hydrogen bonds observed here, the unnormalized H $\cdots$ O distances are below  $2.40 \text{ \AA}$  and the C $\cdots$ O distances are below  $3.40 \text{ \AA}$ , well within the currently accepted limits for such interactions (Desiraju, 1991).

By contrast, the title compound crystallizes from both dichloromethane and ethanol as a solvate, in space group  $C2/c$ , where the molecules lie across twofold rotation axes (Fig. 4). The solvated crystals obtained from dichloromethane, form



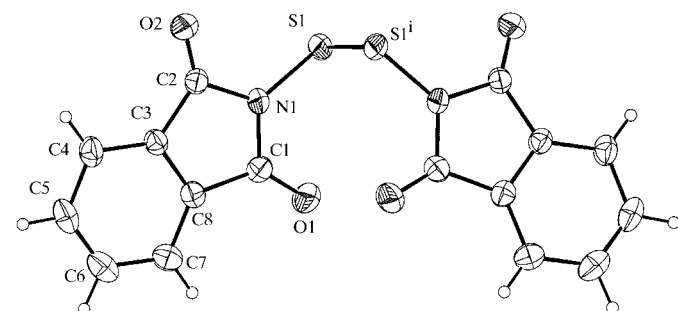
**Figure 2**

Part of the crystal structure of form (1) of (IV), showing the formation of a centrosymmetric hydrogen-bonded tetramer. Atoms marked with an asterisk (\*) are at the symmetry position  $(-x, -y, 1 - z)$ .



**Figure 3**

Part of the crystal structure of form (1) of (IV), showing the  $\pi$ - $\pi$ -stacking interaction. For the sake of clarity, H atoms have been omitted. Atoms marked with an asterisk (\*) are at the symmetry position  $(1 + x, y, z)$ .

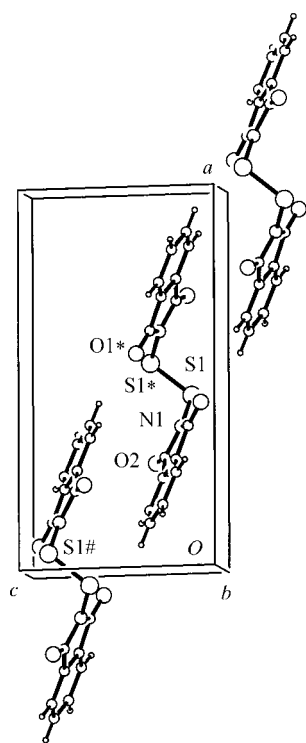


**Figure 4**

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

(2), provided a much better data set at ambient temperature than those obtained from ethanol, form (3), even at 150 (2) K. It is clear, however, from the unit-cell dimensions and the refined atom coordinates that these forms have the same structure, and therefore only that of form (2) will be discussed in detail (geometry given in Table 3). Nonetheless, it may be noted that the unit-cell volume of form (2) at 295 (2) K is slightly less than that of form (3) at 150 (2) K. The molecular dimensions and molecular conformation are essentially the same as found in form (1); the important differences occur in the supramolecular structure.

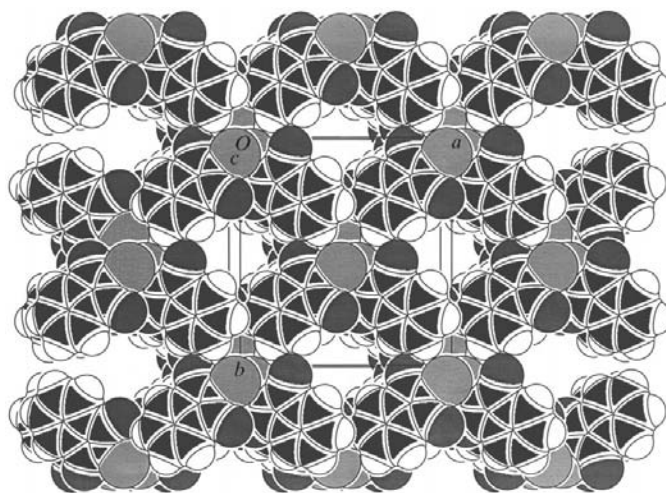
There are no C—H···O hydrogen bonds between the molecules of (IV) in forms (2) and (3), despite the presence of four carbonyl groups per molecule. The molecules are, however, weakly linked by means of aromatic  $\pi$ – $\pi$ -stacking interactions. The aromatic ring at  $(x, y, z)$  is a component of the molecule lying across the twofold rotation axis along  $(\frac{1}{2}, y, \frac{1}{4})$ ; this ring forms a  $\pi$ – $\pi$ -stacking interaction, across the inversion centre at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ , with the aromatic ring at  $(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$ , which is a component of the molecule lying across the rotation axis along  $(0, y, \frac{3}{4})$ . The interplanar spacing is 3.409 (2) Å and the centroid offset is 1.476 (2) Å, and propagation of this interaction by the space group generates a chain of  $\pi$ – $\pi$ -stacked molecules running parallel to the  $[\bar{1}01]$  direction (Fig. 5). This chain is generated by the glide plane at  $y = \frac{1}{4}$  and it lies in the domain  $0.07 < y < 0.43$ ; a second, similar chain lying in the domain  $0.57 < y < 0.93$  is generated by the glide plane at  $y = \frac{3}{4}$ .



**Figure 5**  
Part of the crystal structure of form (2) of (IV) showing one of the  $[\bar{1}01]$  chains of  $\pi$ – $\pi$ -stacked molecules. For the sake of clarity, H atoms have been omitted. Atoms marked with an asterisk (\*) or hash (#) are at the symmetry positions  $(1 - x, y, \frac{1}{2} - z)$  and  $(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$ , respectively.

The molecules in these chains occupy only some 79.5% of the total volume of the unit cell in form (2) [and 79.4% of the slightly larger unit cell in form (3)]; the remaining space comprises two continuous channels per unit cell, running parallel to the  $[001]$  direction (Fig. 6). The average cross-sectional area of each channel is *ca* 23.6 Å<sup>2</sup> in form (2) and 24.3 Å<sup>2</sup> in form (3), corresponding to an average diameter of *ca* 5.5 Å in both forms. In these solvated forms, the dichloromethane molecules in form (2) and ethanol molecules in form (3) occupy the channels between the *N,N'*-dithiodipthalimide molecules within which they are intractably disordered and, indeed, possibly mobile.

The *SQUEEZE* option in *PLATON* (Spek, 2001) indicated that in form (2), the electron density within the channels summed to 116 electrons per unit cell; this is most simply interpreted as 2.76 molecules of CH<sub>2</sub>Cl<sub>2</sub> per unit cell. Similarly, in form (3), with 113 electrons per unit cell in the channels, this is most simply interpreted as 4.35 molecules of ethanol per unit cell. Alternative assignments, such as four molecules of ethanol and 0.9 molecules of water per cell are also possible. However, a definitive distinction between these (and other, similar) formulations is not possible from analytical and spectroscopic evidence only. The crucial point, however, regardless of the precise assignment, is the very low density of the solvent molecules within the channels, which increases the likelihood of their being continuously mobile. The occurrence of the channel-forms (2) and (3) at both 295 (2) and 150 (2) K indicates that the choice of polymorph, solvated *versus* unsolvated, is determined largely by the crystallization solvent, rather than by temperature. The absence of any C—H···O hydrogen bonding between the molecules in forms (2) and (3) is most readily rationalized in terms of the  $\pi$ – $\pi$ -stacking and the presence of the solvent molecules. Atom O1 is adjacent to a channel and may be utilized in C—H···O hydrogen-bond formation by dichloromethane and in O—H···O hydrogen-bond formation by the ethanol molecules, while the geometry of the  $\pi$ – $\pi$ -stacking



**Figure 6**  
Space-filling representation of form (3) of (IV) showing the continuous channels between the molecules.

interactions effectively precludes formation of C—H...O hydrogen bonds to either acceptor.

The striking difference found here between the solvent-free form (1) and the open-channel solvates (2) and (3) is sufficient to provide a serious challenge for the attempted prediction from first principles of the crystal structures of comparatively simple molecular compounds (Lommerse *et al.*, 2000).

## Experimental

A sample of compound (IV) was obtained from Aldrich. Crystals of forms (1), (2) and (3) suitable for single-crystal X-ray diffraction were obtained by slow evaporation of solutions in ethyl acetate, dichloromethane and ethanol, respectively.

### Form (1) of compound (IV)

#### Crystal data

C<sub>16</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>  
*M<sub>r</sub>* = 356.38  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 7.6037 (3) Å  
*b* = 33.9046 (14) Å  
*c* = 11.9404 (6) Å  
 $\beta$  = 93.058 (2)°  
*V* = 3073.9 (2) Å<sup>3</sup>  
*Z* = 8

#### Data collection

KappaCCD diffractometer  
 $\varphi$  scans, and  $\omega$  scans with  $\kappa$  offsets  
 Absorption correction: multi-scan  
 (SORTAV; Blessing, 1995, 1997)  
*T*<sub>min</sub> = 0.947, *T*<sub>max</sub> = 0.971  
 17 261 measured reflections  
 6603 independent reflections

#### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.061  
*wR* (*F*<sup>2</sup>) = 0.115  
*S* = 0.86  
 6603 reflections  
 433 parameters

*D<sub>x</sub>* = 1.540 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 6603 reflections  
 $\theta$  = 2.9–27.4°  
 $\mu$  = 0.37 mm<sup>-1</sup>  
*T* = 150 (2) K  
 Needle, colourless  
 0.15 × 0.09 × 0.08 mm

2314 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.176  
 $\theta$ <sub>max</sub> = 27.4°  
*h* = -9 → 9  
*k* = -41 → 43  
*l* = -15 → 15

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0005P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 ( $\Delta/\sigma$ )<sub>max</sub> = 0.001  
 $\Delta\rho$ <sub>max</sub> = 0.37 e Å<sup>-3</sup>  
 $\Delta\rho$ <sub>min</sub> = -0.48 e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °) for form (1) of compound (IV).

S11—S21	2.0164 (17)	S31—S41	2.0190 (19)
S11—N11	1.685 (3)	S31—N31	1.679 (3)
N11—C11	1.410 (5)	N31—C32	1.415 (5)
N11—C12	1.430 (5)	N31—C31	1.424 (5)
S21—N21	1.683 (3)	S41—N41	1.683 (3)
N21—C21	1.424 (5)	N41—C41	1.414 (5)
N21—C22	1.427 (5)	N41—C42	1.421 (5)
N11—S11—S21	106.08 (14)	N31—S31—S41	105.31 (15)
C11—N11—C12	111.6 (4)	C32—N31—C31	111.7 (4)
C11—N11—S11	124.6 (3)	C32—N31—S31	123.4 (3)
C12—N11—S11	122.5 (3)	C31—N31—S31	124.9 (3)
N21—S21—S11	104.95 (14)	N41—S41—S31	104.77 (14)
C21—N21—C22	110.8 (4)	C41—N41—C42	111.4 (4)
C21—N21—S21	123.0 (3)	C41—N41—S41	122.9 (3)
C22—N21—S21	126.2 (3)	C42—N41—S41	125.6 (3)
N11—S11—S21—N21	-83.59 (19)	N31—S31—S41—N41	92.9 (2)
S21—S11—N11—C11	-93.8 (4)	S41—S31—N31—C31	-85.0 (4)
S11—S21—N21—C21	83.7 (4)	S31—S41—N41—C41	80.3 (4)

**Table 2**

Hydrogen-bonding geometry (Å, °) for form (1) of compound (IV).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C44—H44...O12	0.95	2.38	3.325 (5)	171
C46—H46...O22 <sup>i</sup>	0.95	2.35	3.204 (6)	150
C36—H36...O21 <sup>ii</sup>	0.95	2.39	3.112 (6)	132

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

### Form (2) of compound (IV)

#### Crystal data

C<sub>16</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>  
*M<sub>r</sub>* = 356.38  
 Monoclinic, *C*2/*c*  
*a* = 14.3782 (13) Å  
*b* = 16.0723 (14) Å  
*c* = 7.7910 (7) Å  
 $\beta$  = 93.256 (2)°  
*V* = 1797.5 (3) Å<sup>3</sup>  
*Z* = 4

#### Data collection

Bruker SMART 1000 CCD diffractometer  
 $\varphi$ - $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 1997)  
*T*<sub>min</sub> = 0.911, *T*<sub>max</sub> = 0.988  
 6105 measured reflections

#### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.043  
*wR* (*F*<sup>2</sup>) = 0.079  
*S* = 1.01  
 2648 reflections  
 109 parameters

*D<sub>x</sub>* = 1.317 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 2648 reflections  
 $\theta$  = 1.9–30.2°  
 $\mu$  = 0.32 mm<sup>-1</sup>  
*T* = 295 (2) K  
 Plate, colourless  
 0.30 × 0.10 × 0.04 mm

2648 independent reflections  
 1286 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.030  
 $\theta$ <sub>max</sub> = 30.2°  
*h* = -19 → 19  
*k* = -22 → 11  
*l* = -10 → 11

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0225P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 ( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho$ <sub>max</sub> = 0.19 e Å<sup>-3</sup>  
 $\Delta\rho$ <sub>min</sub> = -0.23 e Å<sup>-3</sup>

**Table 3**

Selected geometric parameters (Å, °) for form (2) of compound (IV).

S1—S1 <sup>i</sup>	2.0281 (10)	N1—C1	1.416 (2)
S1—N1	1.6819 (13)	N1—C2	1.433 (2)
N1—S1—S1 <sup>i</sup>	105.41 (5)	C1—N1—S1	125.02 (11)
C1—N1—C2	111.70 (13)	C2—N1—S1	123.27 (12)
N1—S1—S1 <sup>i</sup> —N1 <sup>i</sup>	93.54 (7)	C2—N1—S1—S1 <sup>i</sup>	90.17 (12)
C1—N1—S1—S1 <sup>i</sup>	-90.03 (13)		

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

### Form (3) of compound (IV)

#### Crystal data

C<sub>16</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>  
*M<sub>r</sub>* = 356.38  
 Monoclinic, *C*2/*c*  
*a* = 14.8129 (11) Å  
*b* = 15.9280 (13) Å  
*c* = 7.6616 (6) Å  
 $\beta$  = 91.671 (2)°  
*V* = 1806.9 (2) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.310 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 3256 reflections  
 $\theta$  = 1.9–32.5°  
 $\mu$  = 0.32 mm<sup>-1</sup>  
*T* = 150 (2) K  
 Block, colourless  
 0.30 × 0.20 × 0.20 mm

## Data collection

Bruker SMART 1000 CCD diffractometer	3256 independent reflections
$\varphi$ - $\omega$ scans	1486 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1997)	$R_{\text{int}} = 0.062$
$T_{\text{min}} = 0.912$ , $T_{\text{max}} = 0.940$	$\theta_{\text{max}} = 32.5^\circ$
9221 measured reflections	$h = -20 \rightarrow 22$
	$k = -24 \rightarrow 23$
	$l = -11 \rightarrow 8$

## Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.062$	$w = 1/[\sigma^2(F_o^2) + (0.0935P)^2]$
$wR(F^2) = 0.184$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.92$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3256 reflections	$\Delta\rho_{\text{max}} = 0.50 \text{ e } \text{\AA}^{-3}$
109 parameters	$\Delta\rho_{\text{min}} = -0.41 \text{ e } \text{\AA}^{-3}$

The solvent-free form (1) of compound (IV) is monoclinic and the space group  $P2_1/c$  was uniquely assigned from the systematic absences. For the solvated forms (2) and (3), the systematic absences permitted  $Cc$  and  $C2/c$  as possible space groups;  $C2/c$  was chosen and confirmed by the successful structure solution and refinement. The crystals of all three forms diffracted rather poorly. For form (1), two complete data sets were collected at 150 (2) K, using two different crystals; for both, only some 35% of the reflections were labelled 'observed', and both data sets gave rather high  $R_{\text{int}}$  values. The data set employed here is marginally the better of the two. The crystal quality for form (1) is uniformly indifferent, but no solvent system has yet been found which provides better quality crystals of the solvent-free polymorph. Similarly for the solvated forms (2) and (3), the diffraction was rather poor, with *ca* 49% of the reflections labelled 'observed' for the dichloromethane solvate at 295 (2) K and *ca* 46% labelled 'observed' for the ethanol solvate at 150 (2) K. It was apparent from an early stage that (2) and (3) were both solvated, but the disorder of the solvent molecules proved to be intractable in each case. With the solvent omitted, *PLATON* (Spek, 2001) indicated void space of  $368.2 \text{ \AA}^3$  per unit cell in (2) and  $372.3 \text{ \AA}^3$  per unit cell in (3); consequently, the *SQUEEZE* option in *PLATON* was employed, which indicated that these voids accommodated electron density summing to 116 and 113 electrons per unit cell in (2) and (3), respectively. Final refinements were made using the solvent-free reflection data. All H atoms were located from difference maps and were treated as riding atoms with C–H distances in the range 0.93–0.95 Å.

For form (1), data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data

reduction: *DENZO*. For forms (2) and (3), data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*. For all forms, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997) and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, using a Nonius KappaCCD diffractometer, and data for forms (2) and (3) were collected at the University of Aberdeen using a Bruker SMART 1000 CCD diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1049). Services for accessing these data are described at the back of the journal.

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