

# Conformational preferences and supramolecular aggregation in 2-nitrophenylthiolates: disulfides and thiosulfonates

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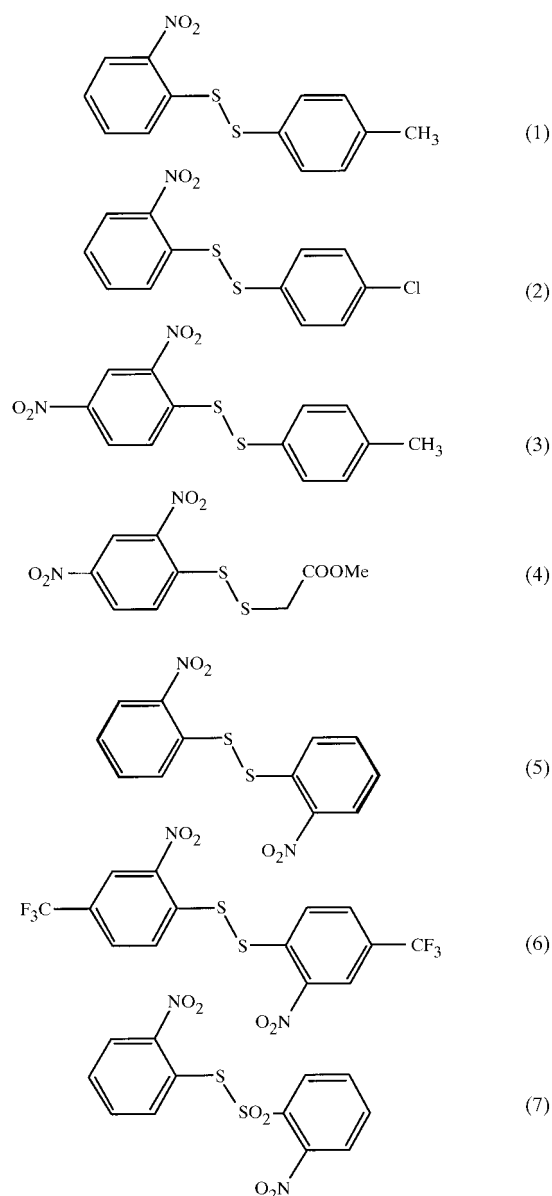
In each of the asymmetrically substituted disulfides 2-nitro-4'-methylphenyl disulfide, C<sub>13</sub>H<sub>11</sub>NO<sub>2</sub>S<sub>2</sub> (1), 2-nitro-4'-chlorodiphenyl disulfide, C<sub>12</sub>H<sub>8</sub>ClNO<sub>2</sub>S<sub>2</sub> (2), 2,4-dinitro-4'-methylphenyl disulfide, C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (3), and 2,4-dinitrophenyl-2'-methoxycarbonylmethyl disulfide, C<sub>9</sub>H<sub>8</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub> (4), and in both of the symmetrically substituted disulfides bis(2-nitrophenyl) disulfide, C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (5), and bis(2-nitro-4-trifluoromethylphenyl) disulfide, C<sub>14</sub>H<sub>6</sub>F<sub>6</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (6), the 2-nitro groups are essentially coplanar with the adjacent aryl ring and the S atom remote from the nitrated aryl ring is also essentially coplanar and *transoid* to the nitro group. In *S*-(2-nitrophenyl) 2-nitrobenzene thiosulfonate, C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub> (7), which contains three independent molecules in the asymmetric unit, all six of the independent nitro groups are twisted out of the plane of the adjacent aryl rings. The crystal structures of (1)–(3) contain isolated molecules, that of (4) contains centrosymmetric dimers held together by C–H···O hydrogen bonds, while in the structures of (5)–(7), respectively, the C–H···O hydrogen bonds generate one-, two- and three-dimensional arrays. The interplay between molecular conformation and supramolecular aggregation is discussed.

## 1. Introduction

The structures of 2-nitrophenylthiolates, O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SX, fall into two distinct conformational classes (Low, Storey *et al.*, 2000; Low, Glidewell & Wardell, 2000). In one, the nitro group is essentially planar with the adjacent aryl ring and the  $\alpha$ -atom of the group X also lies in the plane, *trans* to the nitro group; in the other, the nitro group is twisted away from the plane of the adjacent aryl ring, generally by between 30 and 50°, and at the same time the group X is also displaced from the C<sub>6</sub>S plane. Molecular modelling (Low, Storey *et al.*, 2000) has shown that the near-planar conformer represents the global energy minimum and that any rotation of the nitro group out of this plane incurs an energy cost. Experimental crystal structure determinations have shown that, for the examples reported so far, the near-planar conformer is always observed in the absence of significant intermolecular interactions such as C–H···O hydrogen bonds (Aupers *et al.*, 1999; Ruostesuo *et al.*, 1989). On the other hand, the presence of such interactions appears to be a necessary although not sufficient condition for the occurrence of the twisted conformer. Thus, the twisted conformer is observed when X = SnPh<sub>3</sub> (Aupers *et al.*, 1999), C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>-2,4 (Aupers *et al.*, 1999), C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-2 (Kuczman *et al.*, 1984) and COPh (Low, Storey *et al.*, 2000), where there are well defined C–H···O hydrogen bonds in each case, although when X = *N*-succinimido (Low, Storey *et al.*, 2000), *N*-phthalimido (Iwasaki & Masuko, 1986) or CH=CHPh (Low, Storey

*et al.*, 2000) the planar conformer is observed, despite the presence of C—H...O hydrogen bonds.

Only a single example of a 2-nitrophenyl disulfide has to date been structurally characterized. The structure of bis-(2-nitrophenyl) disulfide, (O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>S)<sub>2</sub>, was determined many years ago from photographic data and refined to *R* = 0.062 for 826 room-temperature data uncorrected for absorption, but no close intermolecular contacts were noted (Ricci & Bernal, 1970). Closely related to diaryl disulfides ArSSAr' are the thiosulfonate esters ArSSO<sub>2</sub>Ar'. The structures of several such esters have been reported (Caputo *et al.*, 1984; Ferguson *et al.*, 2000; Low *et al.*, 2000), but only one example has so far been reported in which a 2-nitro group is present (Low *et al.*, 2000). In the ester *S*-(2-nitrophenyl) 4-toluenethiosulfonate, O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, the nitro group is rotated by 44.1 (1)° out of the plane of the adjacent aryl ring, and there



are three different types of C—H...O hydrogen bond linking the molecules into a three-dimensional framework.

As part of a systematic structural study of compounds containing the 2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>—S—S— fragment we have now determined the structures of (1)–(7) from low-temperature CCD data, including a more precise re-determination for (O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>S)<sub>2</sub> (5).

## 2. Experimental

### 2.1. Synthesis

The asymmetrically substituted compounds (1)–(4), ArSSR, were prepared by the reaction of the appropriate combinations of arenesulfonyl chlorides, ArSO<sub>2</sub>Cl, and tributyltin mercaptides, Bu<sub>3</sub>SnSR (Wardell & Grant, 1969). The products were crystallized from ethanol, for (1), or methanol, for (2)–(4), and showed m.p.s of 347–348, 376–377, 376–377 and 372–373 K, respectively. The symmetrically substituted compounds (5) and (6), ArSSAr, were both obtained by reaction of the appropriate chloroarene ArCl with Na<sub>2</sub>S<sub>2</sub>: after crystallization from ethanol they showed m.p.s of 466–467 K for (5) and 433–435 K for (6). Compound (7) was isolated from the reaction of 2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl with Bu<sub>3</sub>SnSC<sub>6</sub>H<sub>4</sub>SM<sub>4</sub>-4; crystals with m.p. 380–381 K were obtained from methanol solution.

### 2.2. Data collection, structure solution and refinement

Details of cell data, data collection and refinement are summarized in Table 1 (Blessing, 1995, 1997; Ferguson, 1999; Nonius, 1997; Otwinowski & Minor, 1997; Sheldrick, 1997*a,b*; Spek, 2000).<sup>1</sup> For (1), (5) and (6), the space group *P*2<sub>1</sub>/*c* was uniquely assigned from the systematic absences; (2), (4) and (7) are triclinic and for each the space group *P*1̄ was assumed, and subsequently confirmed by the structure analysis. For (3), the systematic absences permitted the space groups *P*2<sub>1</sub> and *P*2<sub>1</sub>/*m*. The unit-cell dimensions indicated *Z* = 2, rendering *P*2<sub>1</sub>/*m* implausible, and so *P*2<sub>1</sub> was chosen, and subsequently confirmed by the successful structure analysis. Compound (7) diffracted only weakly, with only *ca* 37% of the reflections labelled observed at the 2σ level, even at 150 (2) K. The structures were all solved by direct methods using *SHELXS97* (Sheldrick, 1997*a*) and refined with all data on *F*<sup>2</sup> using *SHELXL97* (Sheldrick, 1997*b*). A weighting scheme based upon  $P = [F_o^2 + 2F_c^2]/3$  was employed in order to reduce statistical bias (Wilson, 1976). All H atoms were located from difference maps and all were included in the refinements as riding atoms. The methyl group atoms in (1), (3) and (4) were disordered and in each the H atoms were modelled using two sets of sites, offset by a 60° rotation about the exocyclic C—C bond and each with 0.50 occupancy. For the symmetrically substituted compounds (5) and (6), a search for possible additional symmetry made using the *ADDSYM* facility in *PLATON* (Spek, 2000) indicated that the space group assignment was correct: similarly for (3), no additional symmetry was found, but an attempt to determine by Flack

<sup>1</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0107). Services for accessing these data are described at the back of the journal.

refinement (Flack, 1983) the absolute configuration for the crystal selected for data collection was inconclusive: hence, the Friedel equivalent reflections were merged before the final refinements. Compound (7) has  $Z = 6$ ,  $Z' = 3$ , but again an ADDSYM search for the possible missing symmetry showed that the space group assignment was correct. However, in (7) molecules 1 and 2 (containing S1 and S3, respectively) are related by a pseudo- (non-crystallographic) twofold rotation axis parallel to [001], as are molecules 2 and 3 (containing S3 and S5, respectively), but no such relationship is obtained between molecules 1 and 3 (but see also §3.2.4). Supramolecular analyses were made, and the diagrams were prepared, with the aid of *PLATON* (Spek, 2000).

Figs. 1–7 show the molecular units in compounds (1)–(7), and Figs. 8–17 show aspects of the crystal structures. Tables 2–4 contain selected geometrical parameters and Table 5 gives details of the hydrogen bonding.

### 3. Results and discussion

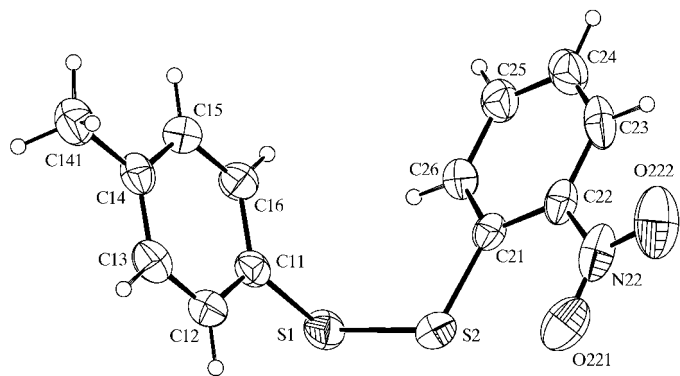
#### 3.1. Molecular structures

**3.1.1. Molecular conformations.** In crystals of (1)–(7), the molecules all lie in general positions and hence have no symmetry imposed upon them. All adopt conformations of  $C_1$  symmetry, and hence in the solid state the individual mole-

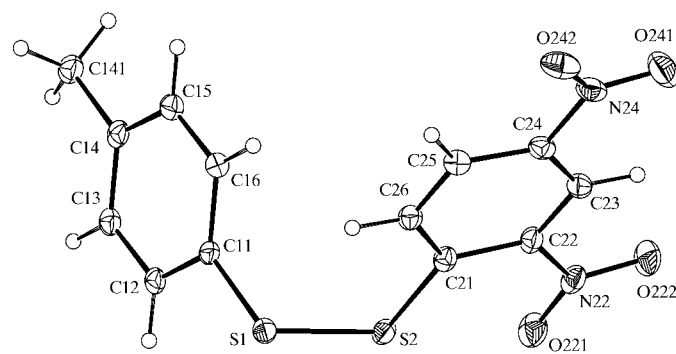
cules are all chiral: since, however, (1), (2) and (4)–(7) all crystallize in centrosymmetric space groups, in these compounds equal numbers of each enantiomer are present in the solid state.

In the asymmetrically substituted disulfides (1)–(4) (Table 2) and in the symmetrically substituted disulfides (5) and (6) (Table 3), the C–S–S–C torsional angles are all within  $10^\circ$  of  $\pm 90^\circ$ . The value of this torsional angle is dominated by the  $3p$  lone pairs on the two S atoms, which seek to become orthogonal in order to minimize their mutual overlap and repulsion integrals. The conformation about the central S–S bond in each of the independent molecules of the thiosulfonate (7) (Table 4) has one of the S–O bonds antiperiplanar to the remote aryl ring Cn1–Cn6 ( $n = 2, 4$  or  $6$ ). This conformation is that usually observed in S-aryl arenethiosulfonates ArSSO<sub>2</sub>Ar' (Caputo *et al.*, 1984; Ferguson *et al.*, 2000; Low, Glidewell & Wardell, 2000) in preference to the alternative conformation having the two aryl groups antiperiplanar, rather than synclinal.

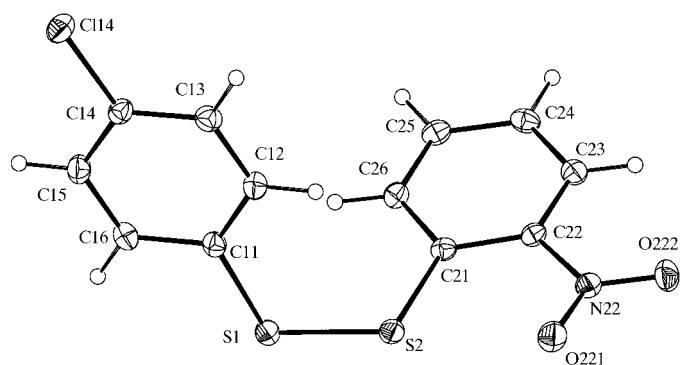
In each of (1)–(6), the 2-nitro groups are only slightly rotated out of the plane of the adjacent aryl ring and accordingly the S1–S2–C21–C22 torsional angles are all close to  $180^\circ$ . According to SCF calculations of molecular energies, described earlier (Low, Storey *et al.*, 2000), at the global energy minimum for 2-nitrophenylthiolates, O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SX, the substituent X and the nitro group are both



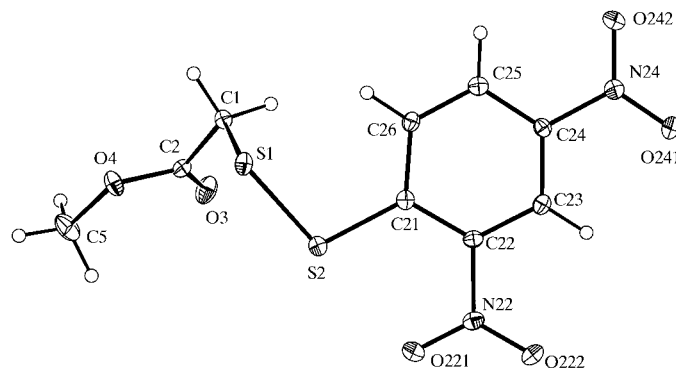
**Figure 1**  
The asymmetric unit of (1), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.



**Figure 3**  
The asymmetric unit of (3), showing the atom-labelling scheme. Atoms are depicted as in Fig. 1.



**Figure 2**  
The asymmetric unit of (2), showing the atom-labelling scheme. Atoms are depicted as in Fig. 1.



**Figure 4**  
The asymmetric unit of (4), showing the atom-labelling scheme. Atoms are depicted as in Fig. 1.

**Table 1**  
Experimental details.

	(1)	(2)	(3)	(4)	(5)
<b>Crystal data</b>					
Chemical formula	C <sub>13</sub> H <sub>11</sub> NO <sub>2</sub> S <sub>2</sub>	C <sub>12</sub> H <sub>8</sub> ClNO <sub>2</sub> S <sub>2</sub>	C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub>	C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>
Chemical formula weight	277.35	297.76	322.35	304.3	308.32
Cell setting	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	6.6384 (2)	7.0434 (5)	10.1301 (2)	8.1655 (3)	7.1028 (11)
<i>b</i> (Å)	24.4389 (7)	7.8315 (5)	6.3474 (1)	8.2415 (3)	22.925 (4)
<i>c</i> (Å)	7.9478 (3)	11.3709 (8)	11.1133 (2)	9.3887 (4)	7.7769 (14)
$\alpha$ (°)	90	82.576 (4)	90	72.1417 (15)	90
$\beta$ (°)	93.6346 (10)	80.690 (3)	106.644 (8)	83.3965 (14)	95.536 (12)
$\gamma$ (°)	90	83.189 (3)	90	80.332 (3)	90
<i>V</i> (Å <sup>3</sup> )	1286.82 (7)	610.71 (7)	684.64 (2)	591.48 (4)	1260.4 (4)
<i>Z</i>	4	2	2	2	4
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.432	1.619	1.564	1.709	1.625
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	2935	2960	1695	2629	1862
$\theta$ range (°)	1.66–27.38	2.94–30.19	2.10–27.50	2.92–29.31	3.01–28.47
$\mu$ (mm <sup>-1</sup> )	0.406	0.645	0.406	0.476	0.437
Temperature (K)	150 (2)	150 (2)	150 (2)	150 (2)	150 (2)
Crystal form	Block	Plate	Needle	Needle	Needle
Crystal size (mm)	0.25 × 0.20 × 0.10	0.20 × 0.15 × 0.02	0.55 × 0.10 × 0.08	0.35 × 0.05 × 0.03	0.40 × 0.07 × 0.07
Crystal colour	Yellow	Yellow	Yellow	Yellow	Yellow
<b>Data collection</b>					
Diffractometer	KappaCCD	KappaCCD	KappaCCD	KappaCCD	KappaCCD
Data collection method	$\varphi$ and $\omega$ scans with $\kappa$ offsets	$\varphi$ and $\omega$ scans with $\kappa$ offsets	$\varphi$ and $\omega$ scans with $\kappa$ offsets	$\varphi$ and $\omega$ scans with $\kappa$ offsets	$\varphi$ and $\omega$ scans with $\kappa$ offsets
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
<i>T</i> <sub>min</sub>	0.9054	0.8818	0.8077	0.8512	0.8447
<i>T</i> <sub>max</sub>	0.9606	0.9872	0.9702	0.9882	0.9701
No. of measured reflections	13 605	6846	7452	6105	3982
No. of independent reflections	2935	2960	1695	2629	1862
No. of observed reflections	1639	2327	1615	1969	1135
Criterion for observed reflections	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )
<i>R</i> <sub>int</sub>	0.072	0.036	0.072	0.050	0.059
$\theta$ <sub>max</sub> (°)	27.38	28.50	27.50	27.50	25.00
Range of <i>h, k, l</i>	–8 → <i>h</i> → 8 –31 → <i>k</i> → 31 –10 → <i>l</i> → 10	–9 → <i>h</i> → 9 –10 → <i>k</i> → 10 –13 → <i>l</i> → 15	–13 → <i>h</i> → 13 –7 → <i>k</i> → 8 –12 → <i>l</i> → 14	–10 → <i>h</i> → 10 –9 → <i>k</i> → 10 –11 → <i>l</i> → 11	–8 → <i>h</i> → 7 –27 → <i>k</i> → 28 –7 → <i>l</i> → 10
<b>Refinement</b>					
Refinement on	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	0.0459	0.0440	0.0392	0.0435	0.0557
<i>wR</i> ( <i>F</i> <sup>2</sup> )	0.1465	0.1159	0.1069	0.1105	0.1352
<i>S</i>	1.028	1.049	1.044	1.044	1.027
No. of reflections used in refinement	2935	2960	1695	2629	1862
No. of parameters used	164	163	191	173	181
H-atom treatment	H atoms constrained	H atoms constrained	H atoms constrained	H atoms constrained	H atoms constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0738P)^2]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0742P)^2 + 0.0709P]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2]$ , where $P = (F_o^2 + 2F_c^2)/3$
( $\Delta/\sigma$ ) <sub>max</sub>	0.001	0.001	0.000	0.008	0.000
$\Delta\rho$ <sub>max</sub> (e Å <sup>-3</sup> )	0.226	0.398	0.395	0.356	0.326
$\Delta\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	–0.247	–0.419	–0.514	–0.376	–0.286
Extinction method	None	None	None	None	None

Table 1 (continued)

	(1)	(2)	(3)	(4)	(5)
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for X-ray Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for X-ray Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for X-ray Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for X-ray Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs					
Data collection	KappaCCD server software (Nonius, 1997)	KappaCCD server software (Nonius, 1997)	KappaCCD server software (Nonius, 1997)	KappaCCD server software (Nonius, 1997)	KappaCCD server software (Nonius, 1997)
Cell refinement	<i>DENZO</i> (Otwinowski & Minor, 1997)	<i>DENZO</i> (Otwinowski & Minor, 1997)	<i>DENZO</i> (Otwinowski & Minor, 1997)	<i>DENZO</i> (Otwinowski & Minor, 1997)	<i>DENZO</i> (Otwinowski & Minor, 1997)
Data reduction	<i>DENZO</i> (Otwinowski & Minor, 1997)	<i>DENZO</i> (Otwinowski & Minor, 1997)	<i>DENZO</i> (Otwinowski & Minor, 1997)	<i>DENZO</i> (Otwinowski & Minor, 1997)	<i>DENZO</i> (Otwinowski & Minor, 1997)
Structure solution	<i>SHELXS97</i> (Sheldrick, 1997a)	<i>SHELXS97</i> (Sheldrick, 1997a)	<i>SHELXS97</i> (Sheldrick, 1997a)	<i>SHELXS97</i> (Sheldrick, 1997a)	<i>SHELXS97</i> (Sheldrick, 1997a)
Structure refinement	<i>SHELXL97</i> (Sheldrick, 1997b)	<i>SHELXL97</i> (Sheldrick, 1997b)	<i>SHELXL97</i> (Sheldrick, 1997b)	<i>SHELXL97</i> (Sheldrick, 1997b)	<i>SHELXL97</i> (Sheldrick, 1997b)
Preparation of material for publication	<i>SHELXL97</i> and <i>WordPerfect</i> macro PRPKAPPA (Ferguson, 1999)	<i>SHELXL97</i> and <i>WordPerfect</i> macro PRPKAPPA (Ferguson, 1999)	<i>SHELXL97</i> and <i>WordPerfect</i> macro PRPKAPPA (Ferguson, 1999)	<i>SHELXL97</i> and <i>WordPerfect</i> macro PRPKAPPA (Ferguson, 1999)	<i>SHELXL97</i> and <i>WordPerfect</i> macro PRPKAPPA (Ferguson, 1999)
		(6)		(7)	
Crystal data					
Chemical formula		C <sub>14</sub> H <sub>5</sub> F <sub>6</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>		C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub>	
Chemical formula weight		444.33		340.32	
Cell setting		Monoclinic		Triclinic	
Space group		<i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>		<i>P</i> $\bar{1}$	
<i>a</i> (Å)		14.1617 (5)		8.8211 (18)	
<i>b</i> (Å)		5.3367 (2)		11.042 (2)	
<i>c</i> (Å)		22.6233 (10)		21.258 (4)	
$\alpha$ (°)		90		101.06 (3)	
$\beta$ (°)		91.7376 (13)		91.97 (3)	
$\gamma$ (°)		90		91.07 (3)	
<i>V</i> (Å <sup>3</sup> )		1709.01 (12)		2030.3 (7)	
<i>Z</i>		4		6	
<i>D</i> <sub>x</sub> (Mg m <sup>-3</sup> )		1.727		1.670	
Radiation type		Mo <i>K</i> $\alpha$		Mo <i>K</i> $\alpha$	
Wavelength (Å)		0.71073		0.71073	
No. of reflections for cell parameters		3812		8996	
$\theta$ range (°)		2.33–27.45		2.93–29.68	
$\mu$ (mm <sup>-1</sup> )		0.400		0.426	
Temperature (K)		150 (2)		150 (2)	
Crystal form		Needle		Plate	
Crystal size (mm)		0.35 × 0.10 × 0.05		0.05 × 0.05 × 0.01	
Crystal colour		Yellow		Yellow	
Data collection					
Diffractometer		KappaCCD		KappaCCD	
Data collection method		$\varphi$ and $\omega$ scans with $\kappa$ offsets		$\varphi$ and $\omega$ scans with $\kappa$ offsets	
Absorption correction		Multi-scan		Multi-scan	
<i>T</i> <sub>min</sub>		0.8728		0.9790	
<i>T</i> <sub>max</sub>		0.9803		0.9958	
No. of measured reflections		14 106		19 285	
No. of independent reflections		3812		8996	
No. of observed reflections		1646		3364	
Criterion for observed reflections		<i>I</i> > 2 $\sigma$ ( <i>I</i> )		<i>I</i> > 2 $\sigma$ ( <i>I</i> )	
<i>R</i> <sub>int</sub>		0.081		0.075	
$\theta$ <sub>max</sub> (°)		27.45		27.50	
Range of <i>h</i> , <i>k</i> , <i>l</i>		–18 → <i>h</i> → 18 –6 → <i>k</i> → 6 –28 → <i>l</i> → 29		–11 → <i>h</i> → 10 –11 → <i>k</i> → 14 –29 → <i>l</i> → 27	
Refinement					
Refinement on		<i>F</i> <sup>2</sup>		<i>F</i> <sup>2</sup>	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]		0.0534		0.0788	

Table 1 (continued)

	(6)	(7)
$wR(F^2)$	0.1492	0.1892
$S$	0.941	0.917
No. of reflections used in refinement	3812	8996
No. of parameters used	253	595
H-atom treatment	H atoms constrained	H atoms constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2]$ , where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.000	0.001
$\Delta\rho_{\max}$ ( $e \text{ \AA}^{-3}$ )	0.373	0.733
$\Delta\rho_{\min}$ ( $e \text{ \AA}^{-3}$ )	-0.247	-0.429
Extinction method	None	None
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs		
Data collection	KappaCCD server software (Nonius, 1997)	KappaCCD server software (Nonius, 1997)
Cell refinement	DENZO (Otwinowski & Minor, 1997)	DENZO (Otwinowski & Minor, 1997)
Data reduction	DENZO (Otwinowski & Minor, 1997)	DENZO (Otwinowski & Minor, 1997)
Structure solution	SHELXS97 (Sheldrick, 1997a)	SHELXS97 (Sheldrick, 1997a)
Structure refinement	SHELXL97 (Sheldrick, 1997b)	SHELXL97 (Sheldrick, 1997b)
Preparation of material for publication	SHELXL97 and WordPerfect macro PRPKAPPA (Ferguson, 1999)	SHELXL97 and WordPerfect macro PRPKAPPA (Ferguson, 1999)

essentially coplanar with the aryl ring with *X* *transoid* to the NO<sub>2</sub> group. The symmetrically substituted compounds (5) and (6), having a 2-nitro group in each ring, thus adopt conformations in which both S—S—C—C fragments are nearly planar. By contrast, in (1)–(4) the S2—S1—C11—C12 [in (1)–(3)] or S2—S1—C1—C2 [in (4)] torsional angles vary between 4.7 (2)° in (2) and 99.6 (2)° in (3), although the rings C11—C16 differ in (2) and (3) only in the nature of the 4-substituent, chloro *versus* methyl. All of the six independent 2-nitro groups in (7) are rotated out of the plane of the adjacent aryl ring by between 37 and 52°, in every case associated with S—S—C—C torsional angles close to 90° (Table 4). It is interesting to note (§3.2) that in (7) there is a much more extensive network of C—H···O hydrogen bonds than in any of (1)–(6). A similar S—S—C—C torsional angle, close to 90°, is also observed in 2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, associated with a nitro-group twist angle of 44.1 (1)°.

**3.1.2. Molecular dimensions.** The C—N bond distances vary between 1.448 (5) Å in (5) and 1.486 (8) Å in (7): these values are typical of C(aryl)—NO<sub>2</sub> distances, where the mean value is 1.468 Å (Allen *et al.*, 1987), with upper and lower

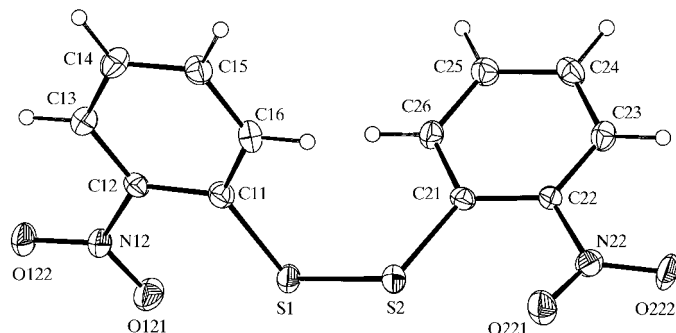


Figure 5 The asymmetric unit of (5), showing the atom-labelling scheme. Atoms are depicted as in Fig. 1.

quartile values of 1.476 and 1.460 Å, respectively. Similarly, the C—C distances within the aryl rings are reasonably uniform. None of (1)–(7) exhibits the quinonoid-type bond fixation observed in 2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SCH=CHPh, where the C—N distance is only 1.383 (4) Å, well below the typical range for such bonds, and the C—C distances in the nitrated ring vary between 1.310 (4) and 1.374 (5) Å. The C(aryl)—S distances show no significant variation between the differently substituted aryl groups, nor between those involving two- or four-coordinate S, as in (7). The S—SO<sub>2</sub> distances in (7) are somewhat larger than the simple S—S distances in (1)–(6), as typically observed in esters of this type. Other bond lengths are typical of their types (Allen *et al.*, 1987).

Within the nitrated aryl rings, the C—C—C angles show significant deviations from 120° in all compounds, but in all cases these are in reasonable accord with the values predicted by the use of additive substituent constants (Domenicano & Murray-Rust, 1979). The O—N—O and O—S—O angles are

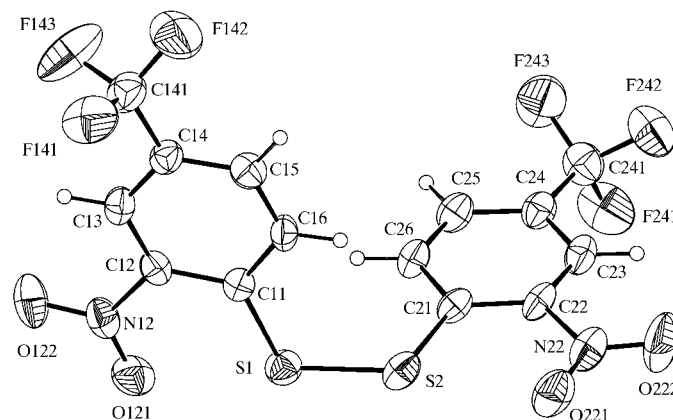
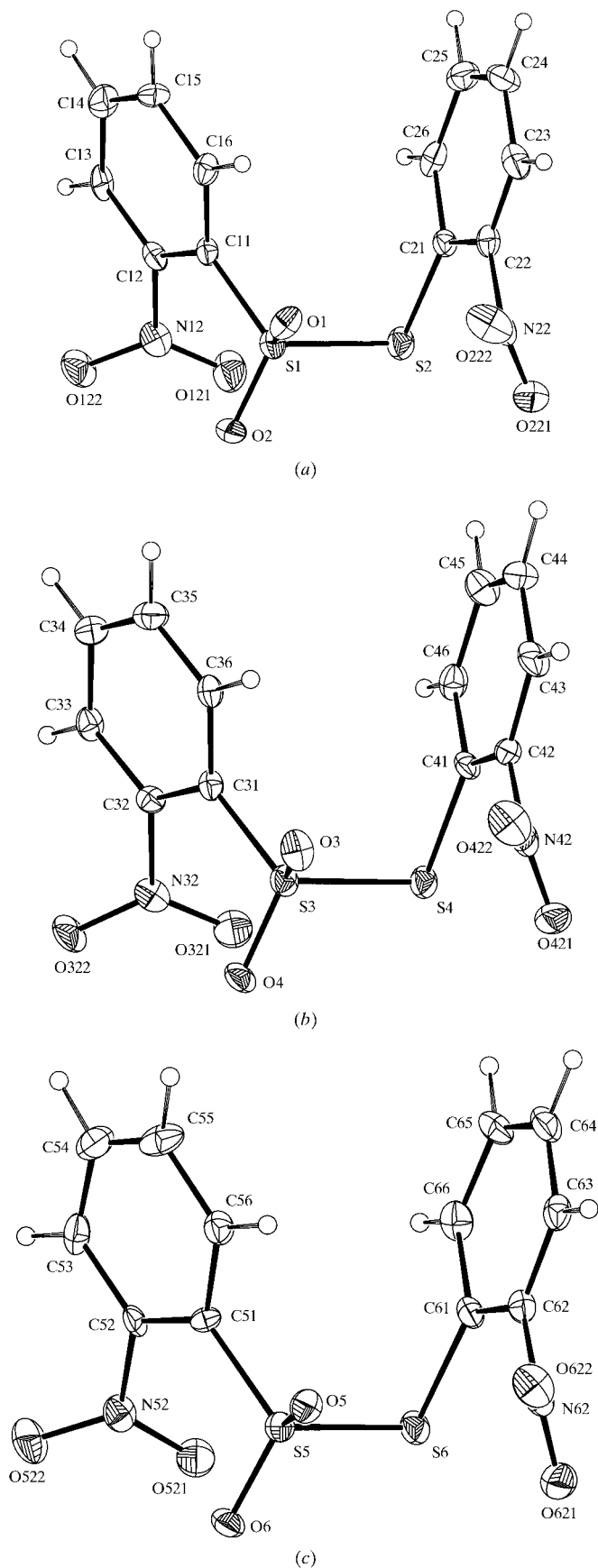


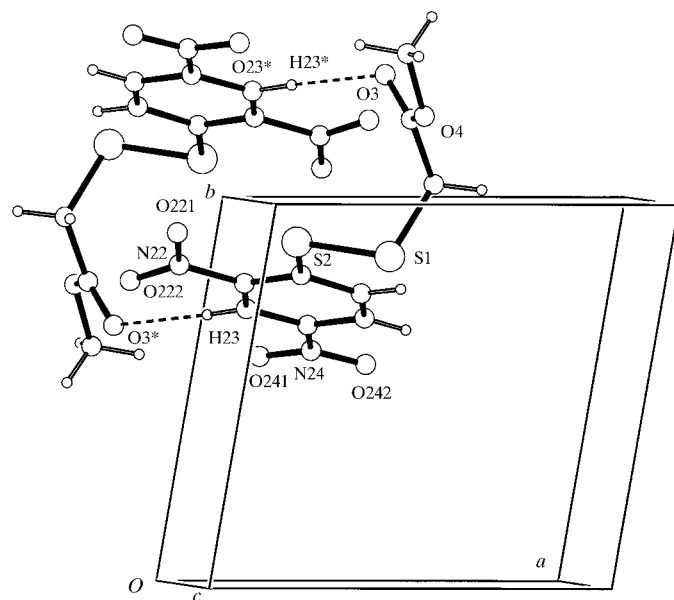
Figure 6 The asymmetric unit of (6), showing the atom-labelling scheme. Atoms are depicted as in Fig. 1.



**Figure 7**  
The three individual molecules in the asymmetric unit of (7), showing the atom-labelling scheme. Atoms are depicted as in Fig. 1.

**Table 2**  
Selected geometric parameters (Å, °) for (1)–(4).

	(1)	(2)	(3)	(4)
S1–S2	2.054 (1)	2.040 (1)	2.059 (1)	2.046 (1)
S1–C11	1.776 (3)	1.784 (2)	1.784 (3)	–
S2–C21	1.781 (2)	1.789 (2)	1.774 (3)	1.777 (2)
C22–N22	1.453 (4)	1.460 (2)	1.461 (4)	1.467 (3)
N22–O221	1.224 (4)	1.230 (2)	1.217 (4)	1.229 (3)
N22–O222	1.222 (4)	1.223 (2)	1.238 (3)	1.222 (2)
C24–N24	–	–	1.464 (4)	1.468 (3)
N24–O241	–	–	1.233 (4)	1.224 (3)
N24–O242	–	–	1.220 (4)	1.228 (2)
S1–C1	–	–	–	1.819 (2)
C14–C14	–	1.743 (2)	–	–
C11–S1–S2	102.07 (8)	105.25 (7)	102.51 (9)	–
C1–S1–S2	–	–	–	102.72 (8)
C21–S2–S1	105.22 (8)	103.78 (7)	104.7 (1)	104.16 (7)
O221–N22–O222	123.1 (3)	123.3 (2)	123.5 (3)	123.7 (2)
O221–N22–C22	117.7 (3)	117.4 (2)	118.4 (3)	117.2 (2)
O222–N22–C22	119.1 (3)	119.2 (2)	118.1 (3)	119.2 (2)
O241–N24–O242	–	–	123.9 (3)	124.0 (2)
O241–N24–C24	–	–	117.7 (3)	118.2 (2)
O242–N24–C24	–	–	118.3 (3)	117.7 (2)
C12–C11–C16	118.5 (2)	120.0 (2)	119.7 (3)	–
C22–C21–C26	116.0 (2)	116.0 (2)	116.0 (3)	115.6 (2)
C21–C22–C23	122.5 (3)	122.7 (2)	122.5 (3)	123.6 (2)
C11–S1–S2–C21	85.4 (2)	–81.50 (9)	94.6 (2)	–
S1–S2–C21–C22	–169.8 (2)	–172.0 (2)	–178.5 (2)	171.1 (2)
S2–S1–C11–C12	83.8 (2)	4.7 (2)	99.4 (2)	–
C21–C22–N22–O221	–3.6 (4)	–4.5 (3)	–1.7 (4)	11.0 (3)
C23–C24–N24–O241	–	–	7.5 (4)	0.4 (3)
C1–S1–S2–C21	–	–	–	84.0 (2)
S2–S1–C1–C2	–	–	–	67.0 (2)
S1–C1–C2–O3	–	–	–	–115.4 (2)
S1–C1–C2–O4	–	–	–	66.0 (2)



**Figure 8**  
Part of the crystal structure of (4) showing the formation of a centrosymmetric  $R_2^2(18)$  motif. H atoms not involved in the hydrogen-bonding motif shown are omitted for the sake of clarity. Atoms marked with a star (\*) are at the symmetry position  $(-x, 2 - y, 1 - z)$ .

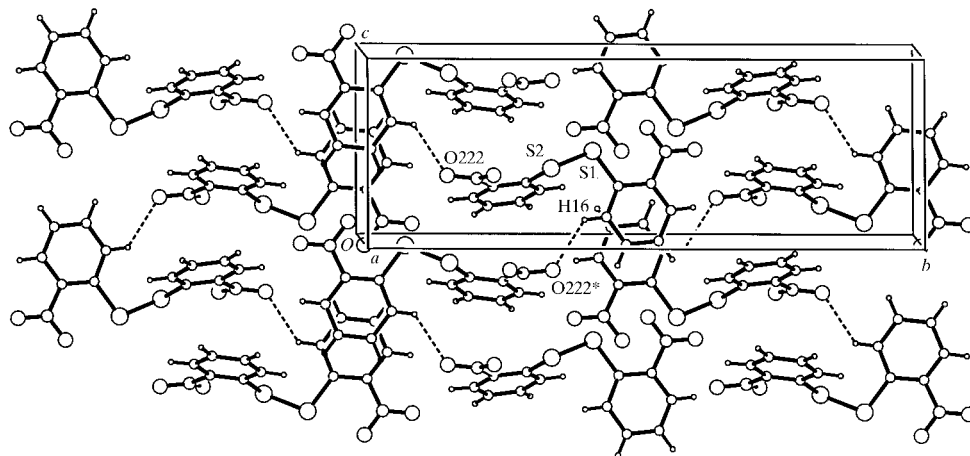
**Table 3**  
Selected geometric parameters (Å, °) for (5) and (6).

	(5)	(6)
S1—S2	2.057 (2)	2.048 (2)
S1—C11	1.784 (4)	1.777 (3)
S2—C21	1.795 (5)	1.787 (3)
C12—N12	1.460 (5)	1.455 (4)
N12—O121	1.236 (4)	1.225 (4)
N12—O122	1.217 (4)	1.217 (4)
C22—N22	1.448 (5)	1.467 (5)
N22—O221	1.232 (5)	1.217 (4)
N22—O222	1.228 (4)	1.211 (4)
C11—S1—S2	105.1 (2)	104.7 (2)
C21—S2—S1	104.4 (2)	104.5 (2)
O121—N12—O122	122.6 (4)	123.2 (3)
O121—N12—C12	117.6 (4)	118.1 (3)
O122—N12—C12	119.7 (3)	118.7 (4)
O221—N22—O222	122.4 (4)	123.8 (4)
O221—N22—C22	117.9 (4)	117.5 (4)
O222—N22—C22	119.6 (4)	118.7 (4)
C12—C11—C16	116.2 (4)	116.2 (3)
C11—C12—C13	122.7 (4)	122.7 (3)
C22—C21—C26	117.2 (4)	116.6 (3)
C21—C22—C23	121.6 (4)	122.5 (3)
C11—S1—S2—C21	−84.4 (3)	−89.9 (2)
S1—S2—C21—C22	−159.6 (3)	−170.2 (2)
S2—S1—C11—C12	−167.5 (4)	−173.6 (2)
C11—C12—N12—O121	−7.6 (7)	1.1 (5)
C21—C22—N22—O221	−16.7 (5)	0.3 (5)

all greater than the ideal trigonal or tetrahedral values, respectively: this can be traced to the substantial negative charges on the paired O atoms in these units.

It is notable that in (7) the S—S—C angles at the four-coordinate sulfur atoms, *Sm* ( $m = 1, 3, 5$ ), are all close to 107° (Table 4) and are thus similar to the S—S—C angles in the disulfides (1)–(6) (Tables 2 and 3). On the other hand, the S—S—C angles at the two-coordinate sulfur atoms in (7), *Sn* ( $n = 2, 4, 6$ ) are all significantly smaller, close to 97°.

**3.1.3. Molecular dimensions in (5).** The structure of (5) has been reported earlier (Ricci & Bernal, 1970): it was refined



**Figure 9**  
Part of the crystal structure of (5) showing C(9) chains running parallel to [001] and linked by  $\pi \cdots \pi$  stacking interactions. Atoms are depicted as in Fig. 8. The atom marked with a star (\*) is at the symmetry position ( $x, \frac{1}{2} - y, -\frac{1}{2} + z$ ).

**Table 4**  
Selected geometric parameters (Å, °) for (7).

	Molecule (1) ( $m, n = 1, 2$ )	Molecule (2) ( $m, n = 3, 4$ )	Molecule (3) ( $m, n = 5, 6$ )
<i>Sm</i> — <i>Sn</i>	2.073 (2)	2.070 (2)	2.076 (2)
<i>Sm</i> — <i>Om</i>	1.430 (4)	1.428 (4)	1.427 (4)
<i>Sm</i> — <i>On</i>	1.433 (4)	1.440 (4)	1.437 (4)
<i>Sm</i> — <i>Cm1</i>	1.764 (6)	1.773 (6)	1.771 (6)
<i>Sn</i> — <i>Cn1</i>	1.768 (6)	1.782 (6)	1.781 (6)
<i>Cm2</i> — <i>Nm2</i>	1.477 (7)	1.471 (7)	1.464 (7)
<i>Nm2</i> — <i>Om21</i>	1.214 (6)	1.219 (6)	1.223 (6)
<i>Nm2</i> — <i>Om22</i>	1.242 (7)	1.237 (6)	1.233 (7)
<i>Cn2</i> — <i>Nn2</i>	1.486 (8)	1.483 (7)	1.466 (8)
<i>Nn2</i> — <i>On21</i>	1.219 (6)	1.226 (6)	1.226 (6)
<i>Nn2</i> — <i>On22</i>	1.226 (6)	1.237 (6)	1.221 (6)
<i>Om</i> — <i>Sm</i> — <i>On</i>	119.3 (3)	119.1 (3)	118.7 (3)
<i>Sn</i> — <i>Sm</i> — <i>Cm1</i>	107.4 (2)	107.6 (2)	106.2 (2)
<i>Sm</i> — <i>Sn</i> — <i>Cn1</i>	97.6 (2)	97.3 (2)	97.4 (2)
<i>Om21</i> — <i>Nm2</i> — <i>Om22</i>	125.9 (6)	125.5 (6)	123.7 (5)
<i>Om21</i> — <i>Nm2</i> — <i>Cm2</i>	118.4 (6)	118.2 (5)	119.1 (6)
<i>Om22</i> — <i>Nm2</i> — <i>Cm2</i>	115.7 (5)	116.2 (5)	117.2 (5)
<i>On21</i> — <i>Nn2</i> — <i>On22</i>	125.4 (6)	124.7 (6)	124.0 (5)
<i>On21</i> — <i>Nn2</i> — <i>Cn2</i>	118.9 (5)	118.8 (5)	118.1 (5)
<i>On22</i> — <i>Nn2</i> — <i>Cn2</i>	115.6 (5)	116.4 (5)	117.8 (5)
<i>Cm2</i> — <i>Cm1</i> — <i>Cm6</i>	117.5 (6)	118.3 (6)	118.3 (5)
<i>Cm1</i> — <i>Cm2</i> — <i>Cm3</i>	121.6 (6)	120.9 (6)	120.9 (6)
<i>Cn2</i> — <i>Cn1</i> — <i>Cn6</i>	116.3 (6)	118.2 (6)	118.2 (6)
<i>Cn1</i> — <i>Cn2</i> — <i>Cn3</i>	122.3 (6)	122.1 (6)	121.4 (6)
<i>Cm1</i> — <i>Sm</i> — <i>Sn</i> — <i>Cn1</i>	71.3 (3)	69.7 (3)	68.4 (3)
<i>Om</i> — <i>Sm</i> — <i>Sn</i> — <i>Cn1</i>	−42.5 (3)	−44.5 (3)	−45.9 (3)
<i>On</i> — <i>Sm</i> — <i>Sn</i> — <i>Cn1</i>	−171.3 (3)	−173.4 (3)	−174.3 (3)
<i>Sm</i> — <i>Sn</i> — <i>Cn1</i> — <i>Cn2</i>	84.3 (5)	80.5 (5)	79.2 (5)
<i>Sn</i> — <i>Sm</i> — <i>Cm1</i> — <i>Cm2</i>	85.2 (5)	88.1 (5)	87.8 (5)
<i>Cm1</i> — <i>Cm2</i> — <i>Nm2</i> — <i>Om21</i>	−50.5 (8)	−52.3 (7)	−49.8 (8)
<i>Cn1</i> — <i>Cn2</i> — <i>Nn2</i> — <i>On21</i>	43.4 (8)	37.3 (8)	37.9 (8)

from room-temperature photographic data, uncorrected for absorption, to  $R = 0.062$ . The structure reported here from absorption-corrected CCD data at 150 K shows that no change of phase has occurred and that the structure is essentially the same at the two temperatures. The s.u.s on the bond distances and angles reported here are typically less than half those reported earlier. However, subject to this, corresponding pairs of derived geometric parameters for the two determinations are all within  $3\sigma$ , with the sole exception of the S—S distance found here as 2.057 (2) Å and reported earlier as 2.045 (3) Å.

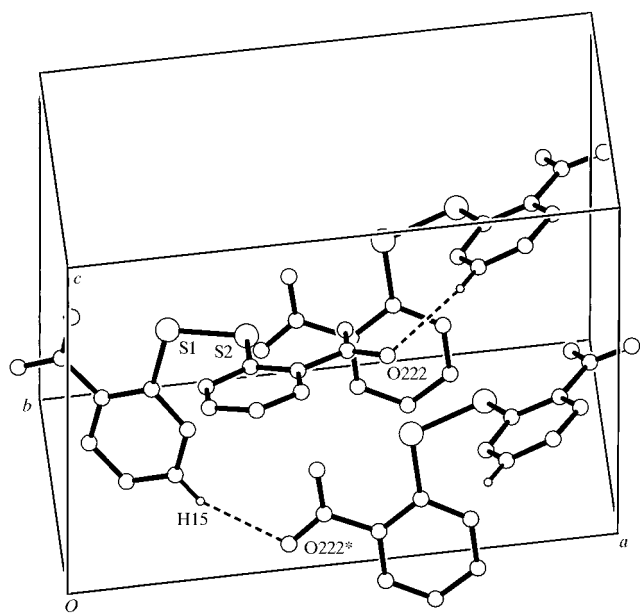
### 3.2. Supramolecular structures

It has recently been noted that the criteria for acceptance of non-covalent contacts involving hydrogen as genuine hydrogen bonds seem to be undergoing continual relaxation (Cotton *et al.*, 1997). It therefore seems desirable to specify the acceptance criteria adopted here for the hydrogen bonds listed in

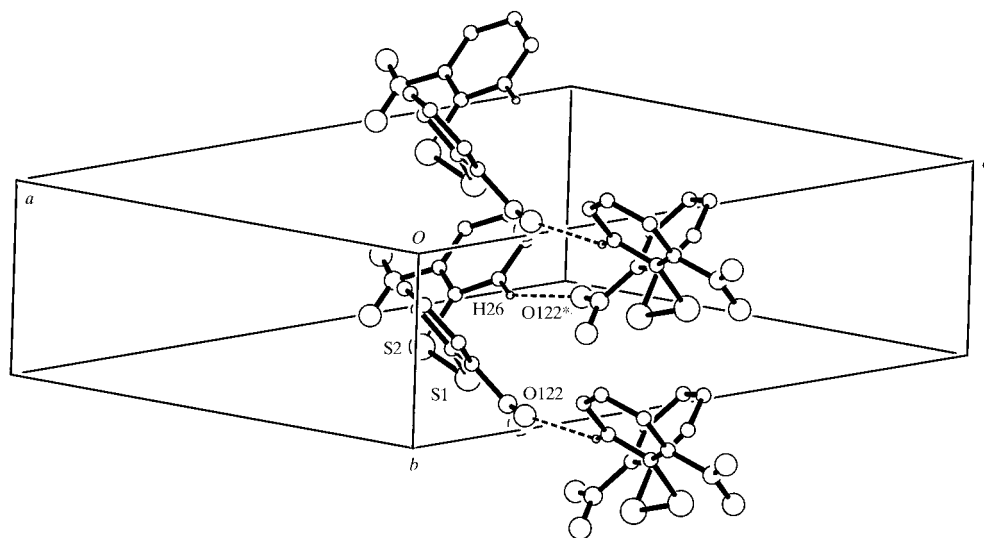


Table 5. The C—H···O hydrogen bonds in Table 5 all involve aromatic C—H bonds and all have C···O distances below 3.50 Å and C—H···O angles not less than 130°: these values are within the ranges now accepted for such bonds (Desiraju, 1991, 1996; Braga *et al.*, 1995).

In (1)–(3) there are neither C—H···O hydrogen bonds nor aromatic  $\pi\cdots\pi$  stacking interactions so that the structures consist of isolated molecules. By contrast in (4)–(7), the C—H···O hydrogen bonds generate supramolecular structures of dimensionality zero, one, two and three, respectively. Thus, in (4) the molecules are linked by C—H···O hydrogen bonds



**Figure 10**  
Part of the crystal structure of (6) showing a  $C(10)$  spiral running parallel to  $[010]$ . H atoms not involved in the hydrogen-bonding motif shown, and the  $\text{CF}_3$  groups, are omitted for the sake of clarity. The atom marked with a star (\*) is at the symmetry position  $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ .



**Figure 11**  
Part of the crystal structure of (6) showing a  $C(9)$  spiral running parallel to  $[010]$ . Atoms are depicted as in Fig. 10. The atom marked with a star (\*) is at the symmetry position  $(-x, -\frac{1}{2} + y, \frac{1}{2} - z)$ .

**Table 5**  
Hydrogen bond dimensions (Å, °) for (4)–(7).

<i>D</i>	H	<i>A</i>	<i>D</i> ··· <i>A</i>	H··· <i>A</i>	<i>D</i> —H··· <i>A</i>
Compound (4)					
C23	H23	O3 <sup>i</sup>	3.299 (3)	2.35	176
Compound (5)					
C16	H16	O222 <sup>ii</sup>	3.197 (5)	2.49	131
Compound (6)					
C15	H15	O222 <sup>iii</sup>	3.421 (5)	2.57	152
C26	H26	O122 <sup>iv</sup>	3.239 (5)	2.46	141
Compound (7)					
C14	H14	O4	3.209 (8)	2.37	147
C34	H34	O6	3.183 (9)	2.41	139
C35	H35	O621 <sup>v</sup>	3.298 (9)	2.56	134
C44	H44	O6 <sup>v</sup>	3.502 (8)	2.56	172
C54	H54	O1 <sup>vi</sup>	3.459 (8)	2.55	161
C64	H64	O2 <sup>vii</sup>	3.403 (8)	2.49	161
C13	H13	O3 <sup>viii</sup>	3.214 (7)	2.52	130
C46	H46	O222 <sup>ix</sup>	3.466 (8)	2.53	168
C56	H56	O622 <sup>x</sup>	3.320 (8)	2.53	141
C63	H63	O5 <sup>x</sup>	3.277 (7)	2.57	131

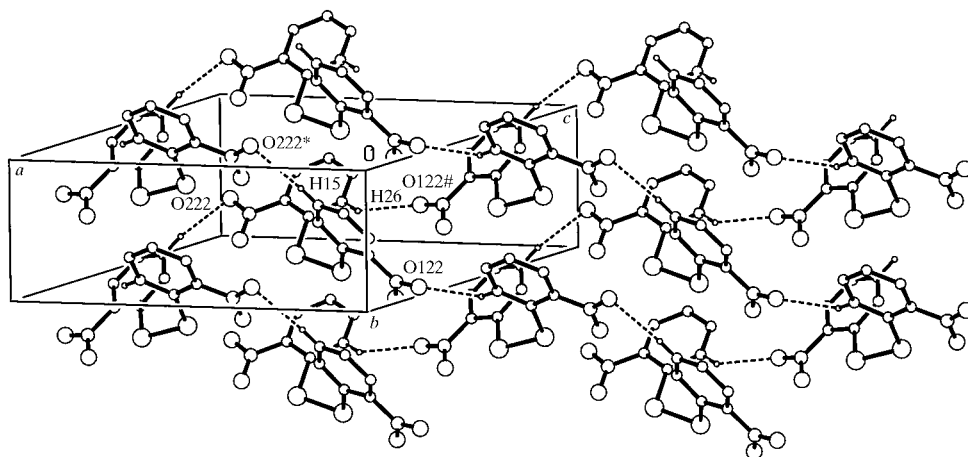
Symmetry codes: (i)  $-x, 2 - y, 1 - z$ ; (ii)  $x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (iii)  $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (iv)  $-x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (v)  $x, -1 + y, z$ ; (vi)  $x, y, 1 + z$ ; (vii)  $x, 1 + y, 1 + z$ ; (viii)  $1 - x, -y, 1 - z$ ; (ix)  $2 - x,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

into finite, *i.e.* zero-dimensional, dimers, while in (5) they are linked into chains. In (6) and (7) the C—H···O hydrogen bonds link the molecules into sheets and into a continuous three-dimensional framework, respectively. The chains in (5) are further linked by aromatic  $\pi\cdots\pi$  stacking interactions.

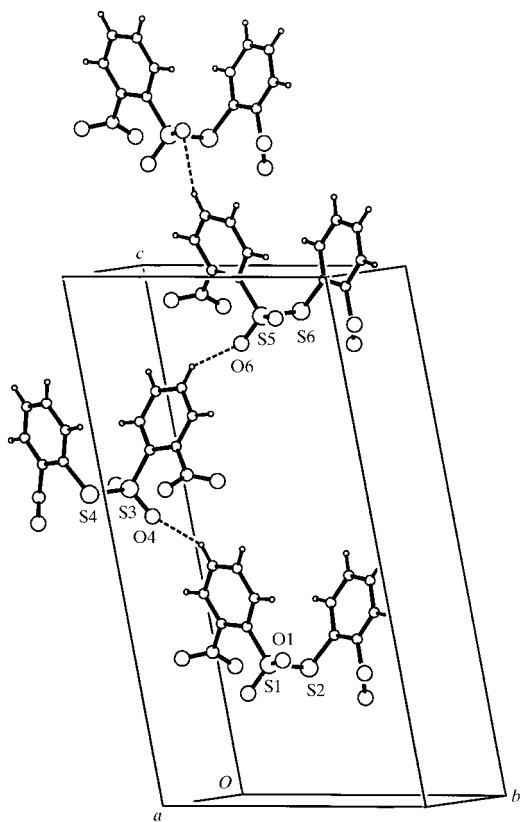
**3.2.1. Zero-dimensional hydrogen bonding.** In (4) the aromatic C—H bond between the two nitro groups (C23—H23; Fig. 4) is expected to be the most acidic bond in the molecule, and thus to show the highest propensity for C—H···O hydrogen-bond formation. Accordingly, C23 at  $(x, y, z)$  acts as a donor to carbonyl O3 at  $(-x, 2 - y, 1 - z)$ , so forming a centrosymmetric  $R_2^2(18)$  motif, centred at  $(0, 1, \frac{1}{2})$  (Fig. 8).

There are no aromatic  $\pi\cdots\pi$  stacking interactions, so the supramolecular aggregation in this structure is limited to the formation of these dimeric units. Entirely analogous  $R_2^2(18)$  dimers formed by paired C—H···O hydrogen bonds have been observed in the structure of 4-ferrocenylcarbonyl-4'-chlorocarbonylbiphenyl (Ahmed *et al.*, 1999).

**3.2.2. One-dimensional hydrogen bonding.** The crystal structure of (5) exhibits a combination of C—H···O hydrogen bonds and aromatic  $\pi\cdots\pi$  stacking interactions. The hydrogen bonds link the molecules into zigzag chains: C16 at  $(x, y, z)$  acts as a donor to O222


**Figure 12**

Part of the crystal structure of (6) showing an (001) sheet built from  $R_4^4(38)$  rings. Atoms are depicted as in Fig. 10. The atoms marked with a star (\*) or a hash (#) are at the symmetry positions  $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$  and  $(-x, -\frac{1}{2} + y, \frac{1}{2} - z)$ , respectively.


**Figure 13**

Part of the crystal structure of (7) showing a  $C_3^3(21)$  chain parallel to [001] built from molecules of types 1, 2 and 3. Atoms are depicted as in Fig. 8.

at  $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ , while C16 at  $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$  in turn acts as a donor to O222 at  $(x, y, -1 + z)$ . In this way, a  $C(9)$  chain running parallel to [001] is generated by the action of the glide plane at  $y = 0.25$  (Fig. 9). A similar, but antiparallel, chain is generated by the glide plane at  $y = 0.75$ , and neighbouring pairs of chains are linked by means of aromatic  $\pi \cdots \pi$  stacking interactions into a sheet. The rings containing C11–C16 in the

molecules at  $(x, y, z)$  and  $(-x, 1 - y, -z)$  are parallel, with an interplane spacing of 3.62 Å and a centroid offset of 1.34 Å, so forming a  $\pi \cdots \pi$  stacking contact across the inversion centre at  $(0, \frac{1}{2}, 0)$ . Propagation of this interaction serves to generate multiple links between pairs of adjacent chains. Each molecule in (5) is thus linked to three others, two *via* the hydrogen bonds and one *via* the  $\pi \cdots \pi$  stacking.

In the earlier account of this structure, no significant intermolecular interactions were reported. Indeed the packing diagram given by Ricci & Bernal (1970), viewed down the [001]

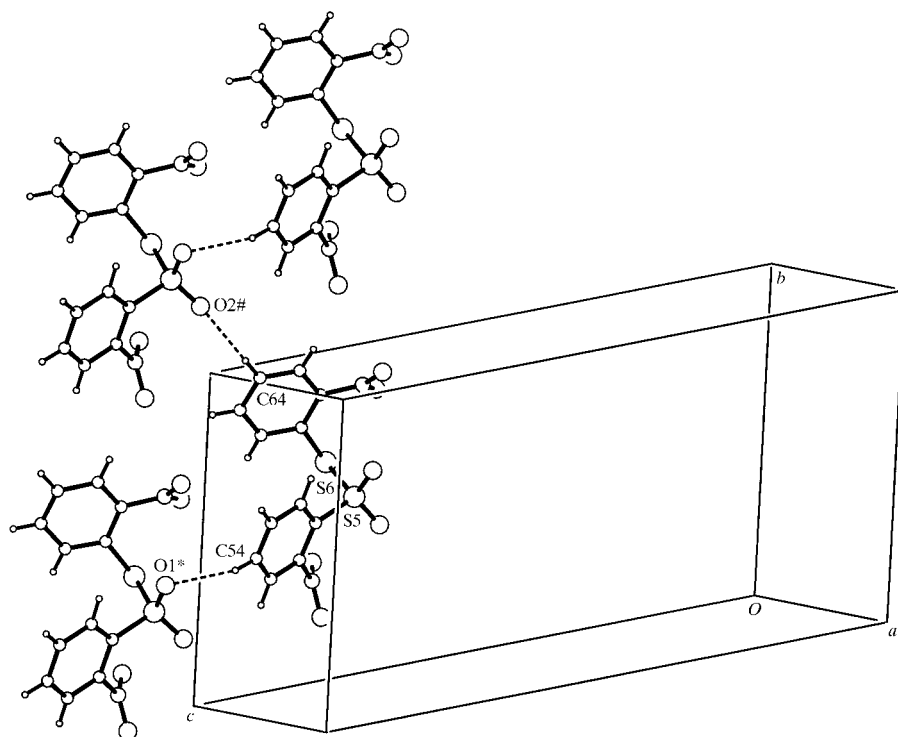
direction, necessarily obscures the effect of the C–H $\cdots$ O hydrogen bonds.

**3.2.3. Two-dimensional hydrogen bonding.** There are two different types of C–H $\cdots$ O hydrogen bond in the structure of the symmetrically substituted compound (6): these involve aromatic C–H bonds at different sites in the two rings, and give rise to different hydrogen-bonding motifs so precluding any possibility that the molecules of (6) could exhibit internal symmetry. The two types of hydrogen bond generate spiral motifs around different  $2_1$  screw axes and together they generate a two-dimensional sheet.

Atom C15 in the molecule at  $(x, y, z)$  (Fig. 6) acts as a hydrogen-bond donor to O222 at  $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ : propagation of this interaction generates a  $C(10)$  spiral chain, running parallel to [010] and lying around the  $2_1$  axis along  $(\frac{1}{2}, y, \frac{1}{4})$  (Fig. 10). At the same time, C26 in the other aryl ring of the molecule at  $(x, y, z)$  (Fig. 6) acts as a donor to O122 at  $(-x, -\frac{1}{2} + y, \frac{1}{2} - z)$ : this generates a second spiral motif running parallel to [010], this time a  $C(9)$  chain lying around the  $2_1$  axis along  $(0, y, \frac{1}{4})$  (Fig. 11).

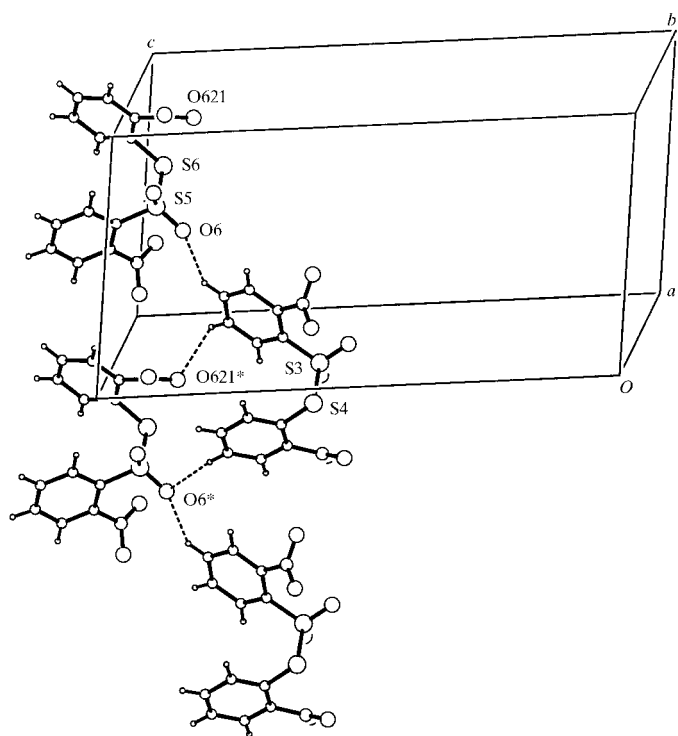
The combination of these two spiral motifs leads to the production of a continuous sheet parallel to (001) built from a single type of  $R_4^4(38)$  ring (Fig. 12). The formation of one such sheet utilizes only half of the contents of the unit cell, lying in the domain  $0 < z < \frac{1}{2}$ . There is a second sheet running through each unit cell, related to the first by the action of the centres of inversion and lying in the domain  $\frac{1}{2} < z < 1.0$ . Adjacent parallel sheets are thus not interwoven.

**3.2.4. Three-dimensional hydrogen bonding.** The three independent molecules in compound (7) (Fig. 7) all show different behaviour as donors and acceptors of hydrogen bonds (Table 5). In all three molecules, both of the sulfone O atoms act as hydrogen-bond acceptors, but O6 in molecule 3 is the only double acceptor. Of the 12 independent O atoms in the nitro groups, only O222 in molecule 1 and O621 and O622, both in molecule 3 act as hydrogen-bond acceptors. Thus, the hydrogen-bond acceptor properties alone serve to discrimi-



**Figure 14**

Part of the crystal structure of (7), showing a  $C_2^2(15)$  chain parallel to  $[010]$  built from molecules of types 1 and 3 only. Atoms are depicted as in Fig. 8. The atoms marked with a star (\*) or a hash (#) are at the symmetry positions  $(x, y, 1 + z)$  and  $(x, 1 + y, 1 + z)$ , respectively.



**Figure 15**

Part of the crystal structure of (7) showing a  $C_2^1(13)$  chain embodying  $R_2^2(18)$  rings parallel to  $[010]$  and built from molecules of types 2 and 3 only. Atoms are depicted as in Fig. 8. Atoms marked with a star (\*) are at the symmetry position  $(x, -1 + y, z)$ .

nate between the three independent molecules, hence confirming the correctness of  $Z' = 3$ . In terms of hydrogen-bond donor properties, molecule 1 is a double donor, while molecules 2 and 3 are both quadruple donors, but these two molecules utilize a different selection of C—H bonds in hydrogen-bond formation. The donor properties thus also discriminate between the three molecules in the asymmetric unit.

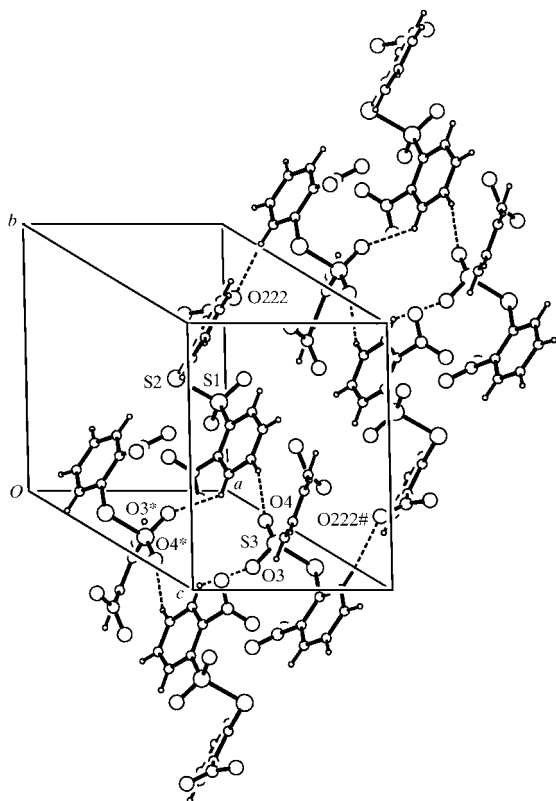
Of the ten significant hydrogen bonds in the structure of (7) (Table 5) two, C14—H14...O4 and C34—H34...O6, are within the asymmetric unit. Four others generate chain motifs by translation along the  $[010]$  and  $[001]$  directions and, together, these one-dimensional motifs generate sheets. The final four hydrogen-bond types all generate distinct centrosymmetric ring motifs, whose effect is to link the neighbouring sheets, so generating a continuous three-dimensional framework.

The chain running parallel to the  $[001]$  direction includes all three independent molecules and in each of the

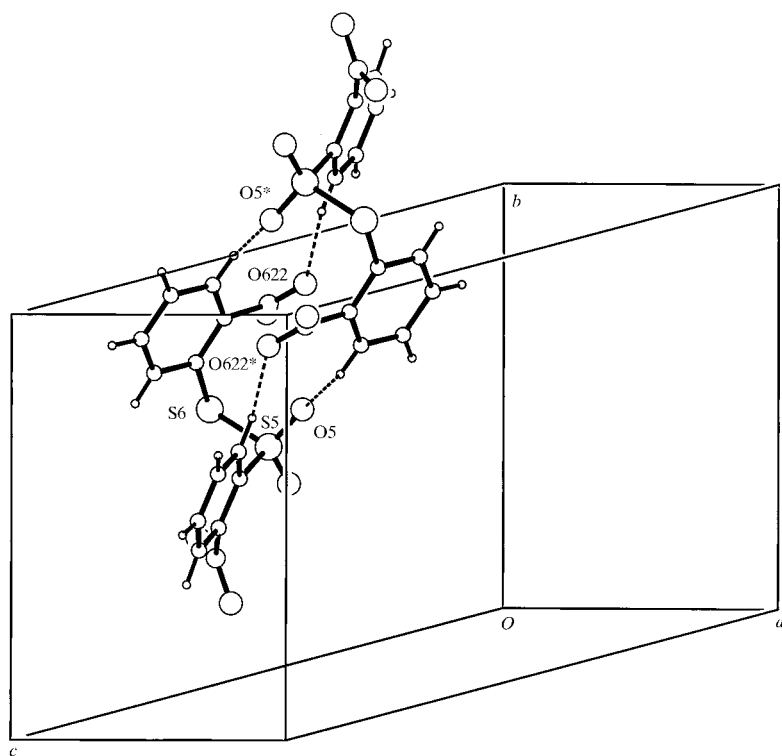
hydrogen bonds the C—H bond *para* to the  $SO_2$  unit acts as a donor to a sulfone O in the neighbouring molecule. Thus, C14 and C34 act as donors to O4 and O6, respectively, within the asymmetric unit, while C54 at  $(x, y, z)$  acts as a donor to O1 at  $(x, y, 1 + z)$ , thus forming by translation a  $C_3^3(21)$  chain (Fig. 13).

There are two distinct chain motifs running parallel to  $[010]$ . The simpler of the two involves only molecules 1 and 3: atoms C54 and C64 in molecule 3 at  $(x, y, z)$  act as hydrogen-bond donors to O1 at  $(x, y, 1 + z)$  and O2 at  $(x, 1 + y, 1 + z)$ , respectively. This pair of hydrogen bonds thus generates, again by translation, a  $C_2^2(15)$  chain (Fig. 14). The other  $[010]$  motif is a chain of rings (Bernstein *et al.*, 1995), which utilizes only molecules 2 and 3. Atoms C34 and C35 in molecule 2 at  $(x, y, z)$  and  $(x - 1 + y, z)$ , respectively, so producing a  $C_2^1(13)$  chain (Fig. 15). At the same time, C35 at  $(x, y, z)$  acts as a donor to nitro O621 at  $(x, -1 + y, z)$  producing a  $C_2^2(11)$  chain (Fig. 15), and the two parallel chains enclose  $R_2^2(18)$  rings (Fig. 15). Overall this  $[010]$  motif has graph-set descriptor  $C_2^1(13)C_2^2(11)[R_2^2(18)]$  (Bernstein *et al.*, 1995).

The combination of the various  $[010]$  and  $[001]$  chains (Figs. 13–15), all generated by translation, serves to produce a continuous two-dimensional sheet parallel to  $(100)$ . There are two of these sheets passing through each unit cell: they are related by the centres of inversion and one, containing the reference molecules at  $(x, y, z)$ , lies in the domain  $0.5 < x < 1.0$ , while the other lies in the domain  $0 < x < 0.5$ . As with the



**Figure 16**  
Part of the crystal structure of (7), showing the  $R_4^4(14)$  and  $R_4^4(34)$  rings which link adjacent (100) sheets. Atoms are depicted as in Fig. 8. The atoms marked with a star (\*) or a hash (#) are at the symmetry positions  $(1-x, -y, 1-z)$  and  $(2-x, 1-y, 1-z)$ , respectively.



**Figure 17**  
Part of the crystal structure of (7), showing concentric  $R_2^2(14)$  and  $R_2^2(34)$  rings which link adjacent (100) sheets. Atoms are depicted as in Fig. 8. The atoms marked with a star (\*) are at the symmetry position  $(2-x, 2-y, 2-z)$ .

sheets formed in the structure of (6), those in (7) are not interwoven: they are, however, extensively linked to form a continuous framework, by no fewer than four further types of C—H...O hydrogen bond involving all three independent molecules as both donors and acceptors.

Paired C—H...O hydrogen bonds involving molecules of types 1 and 2 link each sheet to its two neighbours. Atom C13 at  $(x, y, z)$  acts as a donor to sulfone O3 at  $(1-x, -y, 1-z)$ , thus generating an  $R_4^4(14)$  ring centred at  $(\frac{1}{2}, 0, \frac{1}{2})$ ; atom C46 at  $(x, y, z)$  acts as a donor to nitro O222 at  $(2-x, 1-y, 1-z)$ , thus generating an  $R_4^4(34)$  ring centred at  $(1.5, \frac{1}{2}, \frac{1}{2})$ . Propagation of these two motifs links the adjacent (100) sheets by means of a chain of fused rings running in the [110] direction (Fig. 16). Finally, C56 and C63, both at  $(x, y, z)$ , act as donors, respectively, to O622 and to O5 both at  $(2-x, 2-y, 2-z)$ , thus producing concentric  $R_2^2(18)$  and  $R_2^2(14)$  rings, centred at  $(1, 1, 1)$  and linking an adjacent pair of sheets (Fig. 17).

**3.2.5. General comments on the hydrogen bonding.** It remains difficult to predict the outcome of hydrogen bonding in this series of compounds. For example, while C—H...O hydrogen bonding in the 2,2'-dinitro compound (5) leads to the formation of chains, in the isomeric 4,4'-dinitro compound the hydrogen bonds lead to the formation of sheets (Wardell *et al.*, 2000). Similarly, (5) and (6) differ only in the presence in (6) of the trifluoromethyl groups, which play no direct role in the supramolecular aggregation: nonetheless, in (6) the hydrogen-bonded structure is two-dimensional, whereas in (5) it is only one-dimensional. However, in both of the thio-sulfonates (7) and 2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, there are three-dimensional arrays of hydrogen bonds, even though the latter ester contains only one nitro group per molecule, as opposed to two per molecule in (7). In both esters the dominant hydrogen-bond acceptors are the sulfone O atoms: indeed in 2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> the nitro group does not participate in the hydrogen-bonding scheme.

#### 4. Concluding comments

The conformational results reported here for compounds (1)–(7) and for related compounds discussed earlier are all consistent with the hypothesis that, in the absence of any specific intermolecular interactions such as hydrogen bonds, the conformation observed in the solid state will always correspond to the global energy minimum, as calculated for isolated molecules, while the presence of such interactions is a necessary but not sufficient condition for the observation of local-minimum conformers. In all these compounds, there is close but subtle interplay between the intramolecular conformation and the supramolecular aggregation.

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ampton, using an Enraf–Nonius Kappa-CCD diffractometer. The authors thank the staff for all their help and advice. The authors also thank an anonymous referee for drawing attention to pseudo-symmetric relationships in (7).

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