

Iodo-nitroarenesulfonamides: interplay of hard and soft hydrogen bonds, $I \cdots O$ interactions and aromatic $\pi \cdots \pi$ stacking interactions

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Molecules of *N*-(4'-iodophenylsulfonyl)-4-nitroaniline, 4-O₂NC₆H₄NHSO₂C₆H₄I-4' (1), are linked by three-centre $I \cdots O_2N$ interactions into chains and these chains are linked into a three-dimensional framework by C—H \cdots O hydrogen bonds. In the isomeric *N*-(4'-nitrophenylsulfonyl)-4-iodoaniline, 4-IC₆H₄NHSO₂C₆H₄NO₂-4' (2), the chains generated by the $I \cdots O_2N$ interactions are again linked into a three-dimensional framework by C—H \cdots O hydrogen bonds. Molecules of *N,N*-bis(3'-nitrophenylsulfonyl)-4-iodoaniline, 4-IC₆H₄N(SO₂C₆H₄NO₂-3')₂ (3), lie across twofold rotation axes in space group *C2/c* and they are linked into chains by paired $I \cdots O=S$ interactions: these chains are linked into sheets by a C—H \cdots O hydrogen bond, and the sheets are linked into a three-dimensional framework by aromatic $\pi \cdots \pi$ stacking interactions. In *N*-(4'-iodophenylsulfonyl)-3-nitroaniline, 3-O₂NC₆H₄NHSO₂C₆H₄I-4' (4), there are $R_2^2(8)$ rings formed by hard N—H \cdots O=S hydrogen bonds and $R_2^2(24)$ rings formed by two-centre $I \cdots \text{nitro}$ interactions, which together generate a chain of fused rings: the combination of a C—H \cdots O hydrogen bond and aromatic $\pi \cdots \pi$ stacking interactions links the chains into sheets. Molecules of *N*-(4'-iodophenylsulfonyl)-4-methyl-2-nitroaniline, 4-CH₃-2-O₂NC₆H₃NHSO₂C₆H₄I-4' (5), are linked by N—H \cdots O=S and C—H \cdots O(nitro) hydrogen bonds into a chain containing alternating $R_2^2(8)$ and $R_2^2(10)$ rings, but there are no $I \cdots O$ interactions of either type. There are two molecules in the asymmetric unit of *N*-(4'-iodophenylsulfonyl)-2-nitroaniline, 2-O₂NC₆H₄NHSO₂C₆H₄I-4' (6), and the combination of an $I \cdots O=S$ interaction and a hard N—H \cdots O(nitro) hydrogen bond links the two types of molecule to form a cyclic, centrosymmetric four-component aggregate. C—H \cdots O hydrogen bonds link these four-molecule aggregates to form a molecular ladder. Comparisons are made with structures retrieved from the Cambridge Structural Database.

1. Introduction

In diaryl sulfones the dominant mode of supramolecular aggregation is *via* the formation of soft (Braga *et al.*, 1995) C—H \cdots O=S hydrogen bonds, although where nitro groups are present their O atoms can act competitively as hydrogen-bond acceptors (Sime & Woodhouse, 1974; Glidewell *et al.*, 2001). In

aryl sulfonamides, on the other hand, the dominant mode of supramolecular aggregation involves $N-H \cdots O=S$ hydrogen bonds, generally with the formation of $C(4)$ chains or $R_2^2(8)$ rings (Vorontsova, 1966; Klug, 1968, 1970; Cotton & Stokely, 1970; Blaschette *et al.*, 1986; Brink & Mattes, 1986; Lightfoot *et al.*, 1993; Tremayne *et al.*, 1999). When I atoms and nitro groups are both present, $I \cdots O$ interactions can also play an important role in the supramolecular aggregation (Allen *et al.*, 1994; Thalladi *et al.*, 1996; Masciocchi *et al.*, 1998; Ranganathan & Pedireddi, 1998; McWilliam *et al.*, 2001).

Combining these themes, we have now investigated the supramolecular aggregation in a cognate series of substituted sulfonamides (I): *N*-(4'-iodophenylsulfonyl)-4-nitroaniline (1), *N*-(4'-nitrophenylsulfonyl)-4-iodoaniline (2), *N,N*-bis(3'-nitrophenylsulfonyl)-4-iodoaniline (3), *N*-(4'-iodophenylsulfonyl)-3-nitroaniline (4), *N*-(4'-iodophenylsulfonyl)-4-methyl-2-nitroaniline (5) and *N*-(4'-iodophenylsulfonyl)-2-nitroaniline (6). In all these compounds one aryl ring carries an I substituent and the other a nitro group, hence opening the possibility of a very wide range of different but competitive supramolecular interactions: these include hard (Braga *et al.*, 1995) hydrogen bonds of both $N-H \cdots O=S$ and $N-H \cdots O(\text{nitro})$ types; soft hydrogen bonds of $C-H \cdots O=S$ and $C-H \cdots O(\text{nitro})$ types; $I \cdots O$ interactions in which O can belong either to nitro or to sulfonyl groups; and aromatic $\pi \cdots \pi$ stacking interactions. All these interactions are observed in one or another of this series, generally in combination with others and the net out-turn is that in (1)–(3) the overall supramolecular aggregation is three-dimensional, in (4) it is two-dimensional, and in both (5) and (6) the aggregation is just one-dimensional. We also compare these structures with a number of related systems retrieved from the Cambridge Structural Database (CSD: Allen & Kennard, 1993).

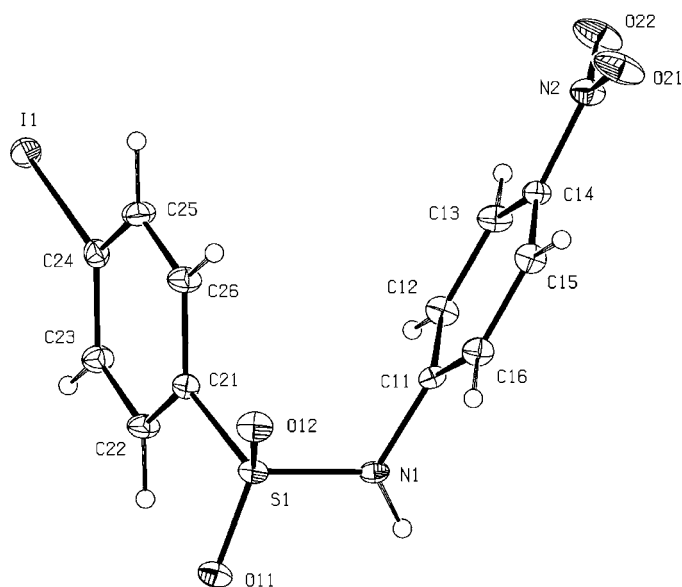
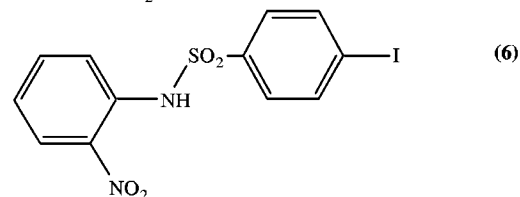
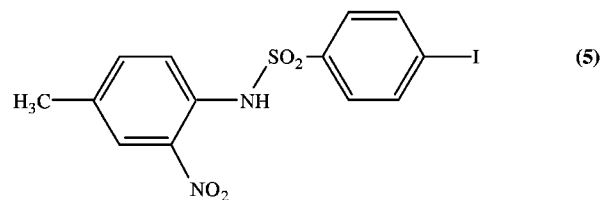
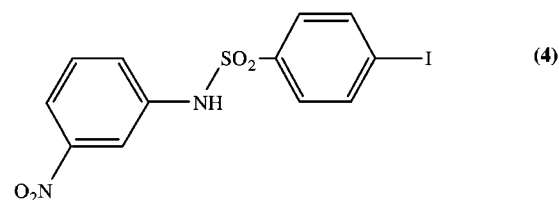
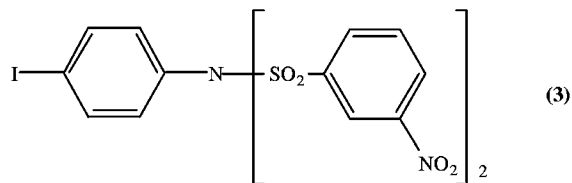
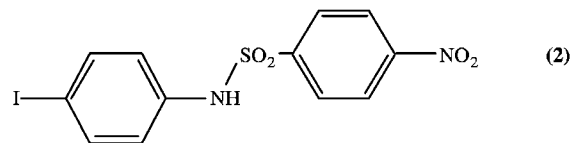
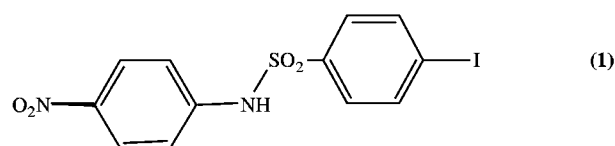


Figure 1
The molecule of (1) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.



2. Experimental

2.1. Synthesis

Compounds $RNH(SO_2R')$ and $RN(SO_2R')_2$ were prepared by the reaction of appropriate combinations of RNH_2 and $R'SO_2Cl$, in the presence of Et_3N , in either chloroform or 1,2-dichloroethane solution. Purification was by TLC and crystals suitable for single-crystal X-ray diffraction were obtained from 1,2-dichloroethane solution [for (2)] and otherwise from ethanol solutions.

2.2. Data collection, structure solution and refinement

Diffraction data for (1)–(6) were collected at 150 (2) K using a Nonius Kappa-CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Other details of cell data, data collection and refinement are

summarized in Table 1, together with details of the software employed (Ferguson, 1999; Nonius, 1997; Otwinowski & Minor, 1997; Sheldrick, 1997*a,b*; Spek, 2001).

Compound (1) is monoclinic and the space group $P2_1/n$ was uniquely assigned from the systematic absences: (4)–(6) are all triclinic and in each case the space group $P\bar{1}$ was assumed and confirmed by structure analysis. For (2) and (3) the unit-cell volumes and the systematic absences permitted Cc (with $Z' = 1$) and $C2/c$ (with $Z' = 0.5$) as possible space groups: Cc was chosen for (2) and $C2/c$ was chosen for (3), and for each the choice was confirmed by the subsequent analysis. For (2) the

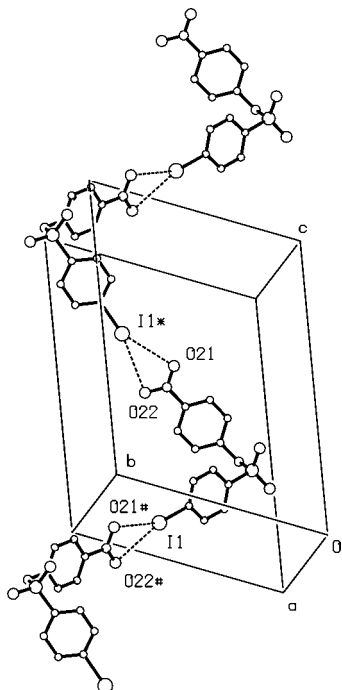


Figure 2
Part of the crystal structure of (1) showing the formation of a $[10\bar{1}]$ chain by $I \cdots O_2N$ interactions. For the sake of clarity H atoms are omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(-\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$ and $(\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z)$, respectively.

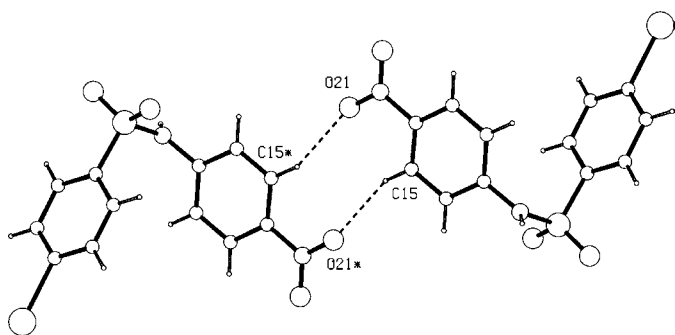


Figure 3
Part of the crystal structure of (1) showing the $R_2^2(10)$ ring motif which links the $[10\bar{1}]$ chains into a (101) sheet. For the sake of clarity the unit-cell box is omitted. The atoms marked with an asterisk (*) are at the symmetry position $(-x, 1 - y, 1 - z)$.

absolute structure was determined by refinement of the Flack parameter (Flack, 1983; Flack & Bernardinelli, 2000), giving a value of 0.00 (2). 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). All H atoms were located from difference maps and included in the refinements as riding atoms with N–H 0.88, C–H 0.95 Å.

The diagrams were prepared with the aid of *PLATON* (Spek, 2001). Details of $I \cdots O$ interactions are given in Table 2, hydrogen-bond dimensions in Table 3 and other selected dimensions in Table 4.¹ Figs. 1–17 show the molecular components, with the atom-labelling schemes, and aspects of the supramolecular structures. Table 5 gives details of $I \cdots O$ interactions in cognate structures retrieved from the CSD, illustrated in Figs. 18–23.

3. Results and discussion

3.1. Supramolecular aggregation is one-dimensional

3.1.1. *N*-(4'-Iodophenylsulfonyl)-4-nitroaniline (1). The supramolecular aggregation in (1) (Fig. 1) is dominated by a slightly asymmetric, three-centre $I \cdots O_2N$ interaction which leads to chain formation. Atom I1 in the molecule at (x, y, z) is linked to both nitro O atoms in the molecule at $(\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z)$ (Table 2), while I1 at $(\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z)$ is similarly linked to the nitro O atoms of the molecule at $(1 + x, y, -1 + z)$, thus producing a chain running parallel to the $[10\bar{1}]$ direction and generated by the n glide plane at $y = 0.75$ (Fig. 2). Two such chains run through each unit cell and they are linked by a single C–H \cdots O hydrogen bond to form sheets; these sheets are, in turn, linked by two weaker C–H \cdots O hydrogen bonds.

Atom C15 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the nitro O21 atom in the molecule at $(-x, 1 - y, 1 - z)$, thus producing a centrosymmetric $R_2^2(10)$ motif linking antiparallel $[10\bar{1}]$ chains across the inversion centre at $(0, \frac{1}{2}, \frac{1}{2})$ (Fig. 3). The molecules at $(1 + x, y, -1 + z)$ and $(1 - x, 1 - y, -z)$ are similarly linked across the inversion centre at $(1, \frac{1}{2}, -\frac{1}{2})$ and hence a molecular ladder is generated (Fig. 3). Within this ladder, the molecules at (x, y, z) and $(1 - x, 1 - y, -z)$ form $I \cdots O_2N$ links to the molecules at $(\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z)$ and $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, respectively, and these latter two molecules are themselves linked, by C–H \cdots O hydrogen bonds having C22 as the donor, to those at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$ and $(\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z)$, respectively, in neighbouring ladders along the $[010]$ direction. In this manner, the action of the 2_1 screw axes links all the $[10\bar{1}]$ ladders into a (101) sheet.

The (101) sheets are linked by two C–H \cdots O hydrogen bonds (Table 3): C22 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the nitro O22 atom in the molecule at $(\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ in the adjacent (101) sheet, while C22 at $(\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ in turn acts as a donor to O22 at $(x,$

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0127). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	(1)	(2)	(3)
Crystal data			
Chemical formula	C ₁₂ H ₉ IN ₂ O ₄ S	C ₁₂ H ₉ IN ₂ O ₄ S	C ₁₈ H ₁₂ IN ₃ O ₈ S ₂
Chemical formula weight	404.17	404.17	589.33
Cell setting, space group	Monoclinic, <i>P</i> ₂ <i>1</i> / <i>n</i>	Monoclinic, <i>C</i> <i>c</i>	Monoclinic, <i>C</i> ₂ / <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.0825 (1), 13.0448 (3), 20.5648 (6)	5.0246 (1), 13.0735 (4), 20.8840 (6)	18.1057 (4), 11.3671 (3), 11.1174 (3)
β (°)	92.7786 (9)	96.8350 (13)	113.2717 (16)
<i>V</i> (Å ³)	1361.85 (6)	1362.10 (6)	2101.91 (9)
<i>Z</i>	4	4	4
<i>D</i> _x (Mg m ⁻³)	1.971	1.971	1.862
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
No. of reflections for cell parameters	3088	2659	2378
θ range (°)	3.12–27.48	1.96–28.31	3.26–27.48
μ (mm ⁻¹)	2.519	2.518	1.775
Temperature (K)	150 (2)	150 (2)	150 (2)
Crystal form, colour	Plate, colourless	Block, colourless	Plate, colourless
Crystal size (mm)	0.30 × 0.18 × 0.08	0.30 × 0.20 × 0.10	0.10 × 0.09 × 0.07
Data collection			
Diffractometer	KappaCCD	KappaCCD	KappaCCD
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
Absorption correction	Multi-scan	Multi-scan	Multi-scan
<i>T</i> _{min}	0.5187	0.5188	0.8425
<i>T</i> _{max}	0.8239	0.7868	0.8858
No. of measured, independent and observed parameters	12 123, 3088, 2691	7110, 2659, 2610	6830, 2378, 2154
Criterion for observed reflections	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)
<i>R</i> _{int}	0.0657	0.0613	0.0366
θ _{max} (°)	27.48	28.31	27.48
Range of <i>h</i> , <i>k</i> , <i>l</i>	−6 → <i>h</i> → 6 −16 → <i>k</i> → 16 −26 → <i>l</i> → 26	−6 → <i>h</i> → 5 −16 → <i>k</i> → 16 −27 → <i>l</i> → 26	−23 → <i>h</i> → 23 −13 → <i>k</i> → 14 −14 → <i>l</i> → 14
Refinement			
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.0367, 0.096, 1.037	0.0279, 0.0836, 1.118	0.026, 0.0653, 1.054
No. of reflections and parameters used in refinement	3088, 181	2659, 182	2378, 147
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.6779P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 0.5195P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0238P)^2 + 2.5253P]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.000	0.000	0.000
$\Delta\rho$ _{max} , $\Delta\rho$ _{min} (e Å ⁻³)	0.963, −1.329	0.725, −0.993	0.441, −0.604
Extinction method	None	<i>SHELXL</i>	None
Extinction coefficient	–	0.0083 (6)	–
	(4)	(5)	(6)
Crystal data			
Chemical formula	C ₁₂ H ₉ IN ₂ O ₄ S	C ₁₃ H ₁₁ IN ₂ O ₄ S	C ₁₂ H ₉ IN ₂ O ₄ S
Chemical formula weight	404.17	418.2	404.17
Cell setting, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.6482 (2), 8.4274 (3), 10.8790 (3)	5.4333 (2), 10.9336 (5), 12.5713 (7)	8.1228 (2), 13.0723 (2), 14.4738 (3)
α , β , γ (°)	88.8029 (12), 75.8302 (12), 83.5777 (11)	95.5668 (18), 93.0809 (17), 101.4226 (17)	113.4712 (11), 100.7181 (9), 97.3706 (10)
<i>V</i> (Å ³)	675.58 (4)	726.52 (6)	1349.76 (5)
<i>Z</i>	2	2	4
<i>D</i> _x (Mg m ⁻³)	1.987	1.912	1.989
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
No. of reflections for cell parameters	3037	3174	5161
θ range (°)	2.96–27.49	1.63–27.44	3.14–26.01
μ (mm ⁻¹)	2.538	2.364	2.541
Temperature (K)	150 (2)	150 (2)	150 (2)
Crystal form, colour	Plate, colourless	Plate, colourless	Plate, colourless
Crystal size (mm)	0.20 × 0.20 × 0.10	0.15 × 0.10 × 0.04	0.20 × 0.15 × 0.10
Data collection			
Diffractometer	KappaCCD	KappaCCD	KappaCCD
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

Table 1 (continued)

	(4)	(5)	(6)
Absorption correction	Multi-scan	Multi-scan	Multi-scan
T_{\min}	0.6307	0.7181	0.6304
T_{\max}	0.7854	0.9114	0.7852
No. of measured, independent and observed parameters	10 353, 3037, 2687	9313, 3174, 2802	13 324, 5161, 4442
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0695	0.0548	0.0920
θ_{max} (°)	27.49	27.44	26.01
Range of h, k, l	$-9 \rightarrow h \rightarrow 9$ $-10 \rightarrow k \rightarrow 10$ $-13 \rightarrow l \rightarrow 14$	$-7 \rightarrow h \rightarrow 7$ $-13 \rightarrow k \rightarrow 13$ $-16 \rightarrow l \rightarrow 16$	$-10 \rightarrow h \rightarrow 9$ $-16 \rightarrow k \rightarrow 16$ $-17 \rightarrow l \rightarrow 17$
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.0329, 0.0796, 1.041	0.032, 0.0818, 1.078	0.0434, 0.1195, 1.001
No. of reflections and parameters used in refinement	3037, 181	3174, 191	5161, 361
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 0.8392P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	0.001	0.001	0.001
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.777, -1.053	0.712, -1.022	1.099, -2.486
Extinction method	None	None	None

$-1 + y, z$) in the original sheet. Similarly, C13 at (x, y, z) acts as a donor to sulfonamide O11 at $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, while C13 at $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$ acts as a donor to O11 at $(x, 1 + y, z)$. These two antiparallel chains thus combine to produce a $C(7)C(11)[R_2^2(10)]$ chain of rings generated by the 2_1 screw axis along $(\frac{3}{4}, y, \frac{1}{4})$ (Fig. 4), and propagation of this motif serves to link all of the (101) sheets into a continuous framework.

It is noteworthy that in two of the C—H...O hydrogen bonds, the acceptors are the two O atoms of the nitro group,

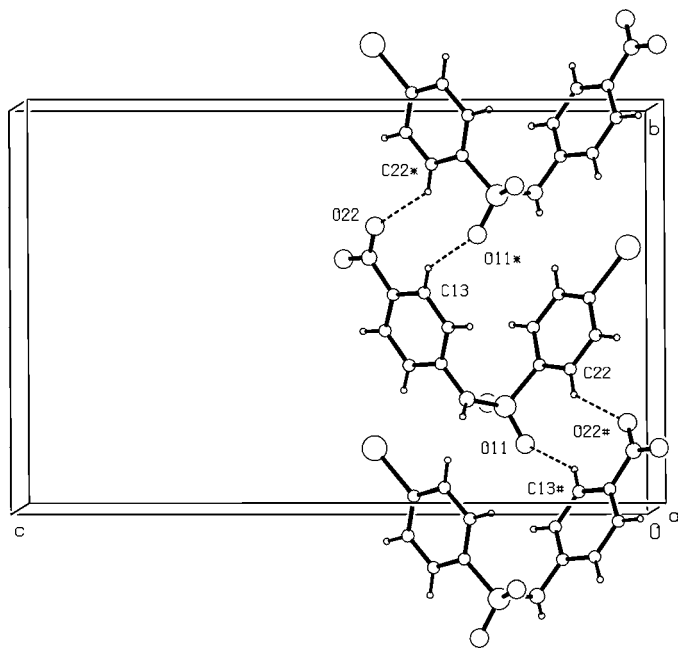


Figure 4
Part of the crystal structure of (1) showing the formation of the $C(7)C(11)[R_2^2(10)]$ chain of rings parallel to $[010]$. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$ and $(\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, respectively.

which thus participate in both the hydrogen bonding and the I...O interactions. By contrast, the O atoms of the sulfonamide unit participate only in the C—H...O hydrogen bonding but not in the I...O interactions; nor does the N—H participate in the hydrogen bonding so that hard (Braga *et al.*, 1995) hydrogen bonds are absent. There are no aromatic $\pi \cdots \pi$ stacking interactions in (1).

3.1.2. N-(4'-Nitrophenylsulfonyl)-4-iodoaniline (2). The molecular constitution of (2) (Fig. 5) is similar to that of (1), differing only in the notional exchange of the iodo and nitro substituents between the two aryl rings. Although the space groups of the two compounds are different [$P2_1/n$ for (1) and Cc for (2)], the unit-cell dimensions are rather similar (Table 1). While the I...O interactions are similar in (2) to those in

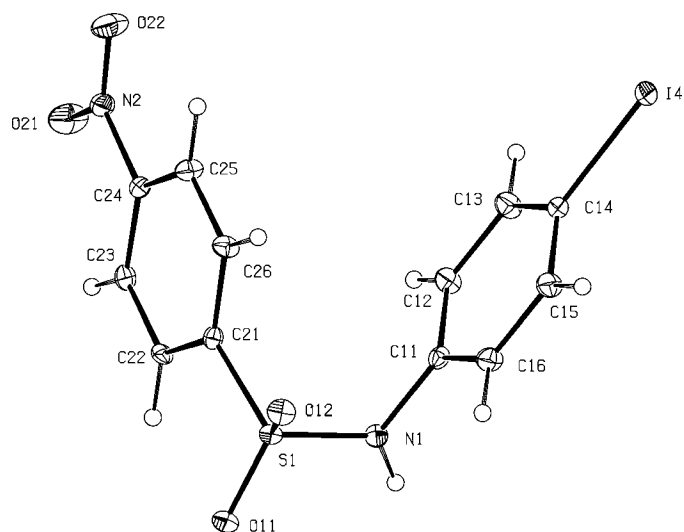


Figure 5
The molecule of (2) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 2
 Geometric parameters for I···O interactions (Å, °).

C—I···O—X	C—I	I···O	O—X	C—I···O	I···O—X
(1)					
C24—I1···O21 ⁱ —N2 ⁱ	2.100 (3)	3.320 (3)	1.223 (4)	156.23 (10)	103.84 (19)
C24—I1···O22 ⁱ —N2 ⁱ	2.100 (3)	3.459 (3)	1.226 (4)	166.62 (9)	96.8 (2)
(2)					
C14—I4···O21 ⁱⁱ —N2 ⁱⁱ	2.115 (4)	3.380 (4)	1.248 (6)	162.36 (14)	104.0 (3)
C14—I4···O22 ⁱⁱ —N2 ⁱⁱ	2.115 (4)	3.551 (4)	1.229 (6)	159.14 (15)	95.1 (3)
(3)					
C1—I1···O2 ⁱⁱⁱ —S1 ⁱⁱⁱ	2.098 (2)	3.2787 (14)	1.4273 (14)	155.03 (3)	146.45 (8)
(4)					
C24—I1···O21 ^{iv} —N2 ^{iv}	2.097 (3)	3.125 (2)	1.232 (4)	172.07 (9)	116.27 (18)
(5)					
No I···O interactions†					
(6)					
C44—I2···O11 ^v —S1 ^v	2.096 (4)	3.188 (3)	1.433 (3)	171.19 (13)	124.87 (17)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (iii) $x, 1 + y, z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $2 - x, -y, -z$. † C—I 2.102 (3); N—O 1.222 (4) and 1.234 (4) Å.

Table 3
 Hydrogen-bond parameters (Å, °).

D—H···A	H···A	D···A	D—H···A
(1)			
C13—H13···O11 ⁱ	2.53	3.330 (4)	143
C15—H15···O21 ⁱⁱ	2.40	3.280 (4)	153
C22—H22···O22 ⁱⁱⁱ	2.41	3.149 (4)	134
(2)			
C15—H15···O21 ^{iv}	2.49	3.416 (6)	164
C25—H25···O11 ^v	2.44	3.167 (6)	133
(3)			
C12—H12···O12 ⁱⁱ	2.55	3.500 (2)	177
(4)			
N1—H1···O11 ^{vi}	2.01	2.894 (3)	179
C22—H22···O22 ^{vii}	2.47	3.187 (4)	132
(5)			
N1—H1···O22	1.94	2.615 (3)	132
N1—H1···O12 ^{viii}	2.52	3.144 (3)	128
C13—H13···O21 ^{ix}	2.44	3.342 (4)	158
(6)			
N1—H1···O21	1.99	2.659 (5)	131
N3—H3···O21	2.27	3.049 (5)	147
C35—H35···O41 ^x	2.43	3.308 (7)	153
C43—H43···O32 ^{xi}	2.38	3.320 (5)	172

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

(1) leading to chain formation, the linking of these chains into a three-dimensional framework is markedly different.

In (2) the asymmetric I···O₂N interaction (Table 2) links I4 in the molecule at (x, y, z) to the two nitro O atoms at $(\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, thus producing a chain parallel to $[10\bar{1}]$, as in (1), but generated in this case by the *n* glide plane at $y = 0.25$.

Two of these chains pass through each unit cell and they are linked by two C—H···O hydrogen bonds. In the soft hydrogen bond with the larger C—H···O angle (Table 3), C15 in the iodinated ring at (x, y, z) acts as a donor to nitro O21 at $(1 + x, -y, -\frac{1}{2} + z)$, thus producing a *C*(12) chain running parallel to the $[20\bar{1}]$ direction and generated by the *c* glide plane at $y = 0$ (Fig. 6). The combination of these $[20\bar{1}]$ chains with the I···O₂N $[10\bar{1}]$ chains generates a (010) sheet.

The second C—H···O hydrogen bond links these sheets: atom C25 in the nitrated aryl ring at (x, y, z) acts as a hydrogen-bond donor to sulfonamide O11 at $(\frac{1}{2} + x, \frac{1}{2} + y, z)$, thus generating by translation a *C*(6) chain parallel to $[110]$ (Fig. 7). It is noteworthy that both nitro and sulfonamide O atoms participate in the C—H···O hydrogen bonding in (2).

3.1.3. *N,N*-Bis(3'-nitrophenylsulfonyl)-4-iodoaniline (3). In (3) (Fig. 8) the molecules lie on twofold rotation axes in space group *C2/c* and they are linked into chains by means of symmetrically paired I···O interactions involving sulfonamide

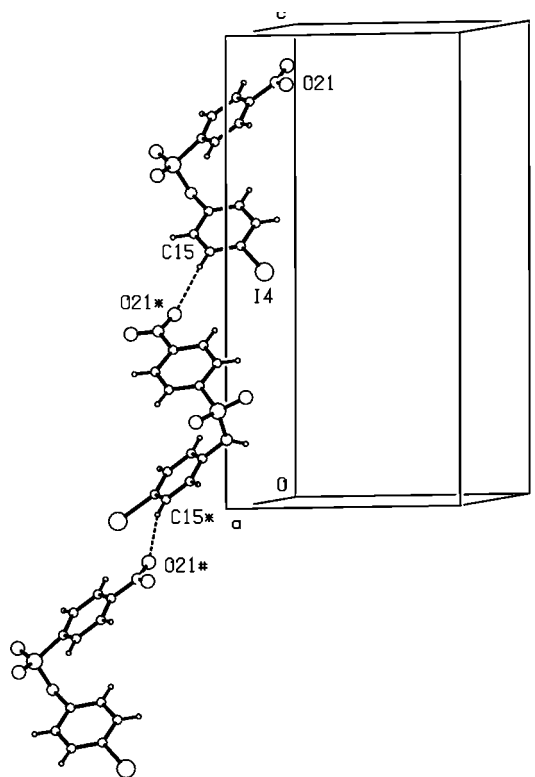


Figure 6
 Part of the crystal structure of (2) showing the formation of a *C*(12) chain parallel to $[20\bar{1}]$. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1 + x, -y, -\frac{1}{2} + z)$ and $(2 + x, y, 1 + z)$, respectively.

O, rather than nitro O atoms. These chains are linked into sheets by a single C—H···O hydrogen bond, which again involves sulfonamide O: thus, the nitro O atoms in (3) play no part whatsoever in the supramolecular aggregation.

The I1 atom in the reference molecule at (x, y, z) lies on the twofold rotation axis along $(0, y, \frac{3}{4})$. This atom forms short I···O contacts with the two sulfonamide O11 atoms in the molecule at $(x, 1 + y, z)$, thus generating a six-membered ring,

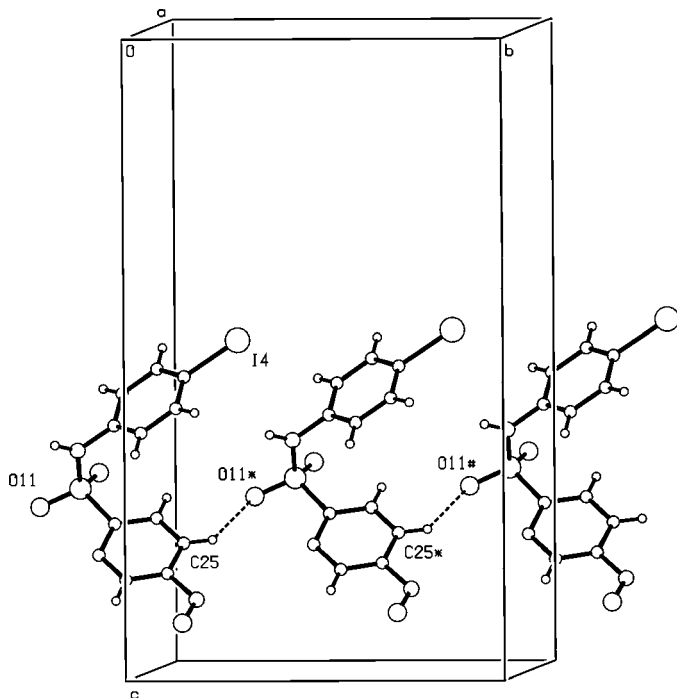


Figure 7
Part of the crystal structure of (2) showing the formation of a $C(6)$ chain parallel to $[110]$. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(\frac{1}{2} + x, \frac{1}{2} + y, z)$ and $(1 + x, 1 + y, z)$, respectively.

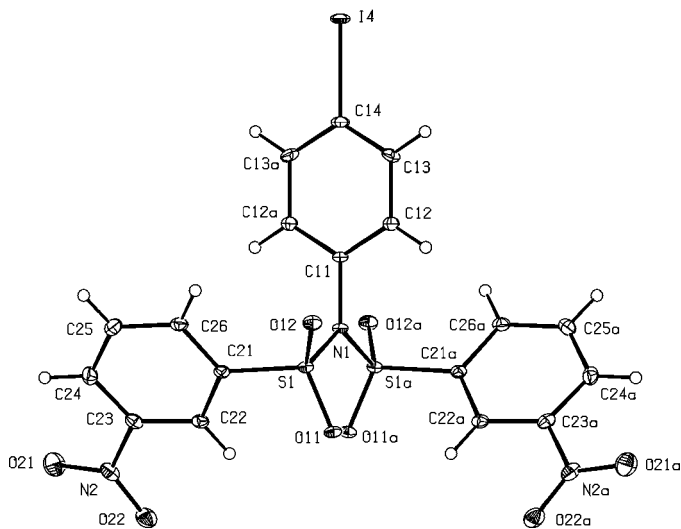


Figure 8
The molecule of (3) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atoms marked 'a' are at the symmetry position $(-x, y, \frac{3}{2} - z)$.

having the skew-boat conformation with a sum of bond angles of *ca* 683°. These interactions produce a strictly linear chain along the $[010]$ direction (Fig. 9). There are four such chains passing through each unit cell, along each of the twofold axes, and they are linked into two sheets by means of a single C—H···O hydrogen bond.

Atom C12 in the iodinated ring of the reference molecule at (x, y, z) lies in the $[010]$ chain along $(0, y, \frac{3}{4})$ and it acts as a hydrogen-bond donor to sulfonamide O12 at $(-x, 1 - y, 1 - z)$, which itself lies in the antiparallel chain along $(0, y, \frac{1}{4})$: C12 at $(-x, 1 - y, 1 - z)$ in turn acts as a donor to O12 at (x, y, z) , thus producing an $R_2^2(12)$ ring. The symmetry-related C12 in the $(0, y, \frac{1}{4})$ chain is at $(x, 1 - y, -\frac{1}{2} + z)$ and this atom acts as a hydrogen-bond donor to O12 at $(-x, y, \frac{1}{2} - z)$, part of the $[010]$ chain along $(0, y, -\frac{1}{4})$. Propagation of this hydrogen bond thus generates a molecular ladder (Fig. 10), running parallel to $[001]$, in which the uprights are formed by $C_2^2(10)$ chains and the rungs by the central C—N bonds. The combination of the $[010]$ and $[001]$ motifs generates a (100) sheet containing three types of ring.

Adjacent sheets are weakly linked by aromatic $\pi \cdots \pi$ stacking interactions. The nitrated ring at (x, y, z) forms a stacking interaction with the corresponding ring at $(\frac{1}{2} - x, -\frac{3}{2} - y, 2 - z)$: the interplanar spacing between these strictly parallel rings is 3.845 (2) Å and the centroid offset is

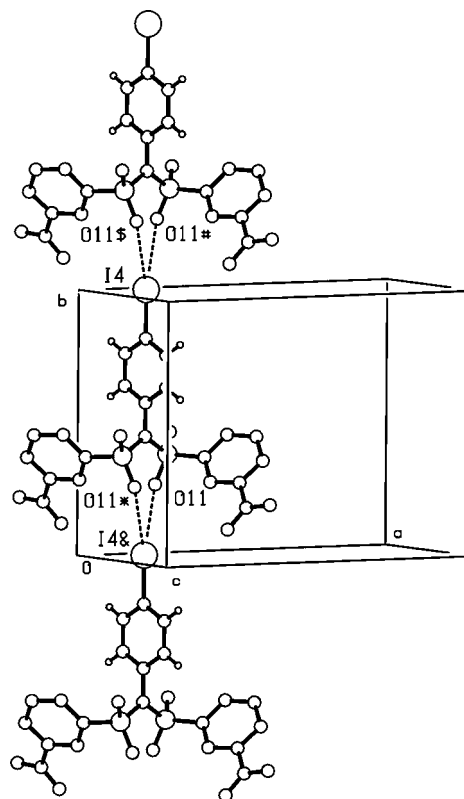


Figure 9
Part of the crystal structure of (3) showing the formation of a chain of rings parallel to $[010]$. The atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(-x, y, \frac{3}{2} - z)$, $(x, 1 + y, z)$ and $(-x, 1 + y, \frac{3}{2} - z)$, respectively.

1.744 (2) Å. The ring at (x, y, z) lies in the $[010]$ chain along $(0, y, \frac{3}{4})$ and is part of the (100) sheet at $x = 0$, while the ring at $(\frac{1}{2} - x, -\frac{3}{2} - y, 2 - z)$ lies in the $[010]$ chain along $(\frac{1}{2}, y, 1.25)$, which is part of the (100) sheet at $x = 0.5$. Propagation of this interaction by the twofold rotation axis links each (100) sheet to its two immediate neighbours, leading to supramolecular aggregation which, overall, is three-dimensional.

3.1.4. General comparison of three-dimensional structures. We draw attention briefly here to the differences between the supramolecular aggregation modes of the foregoing three structures. In both (1) and (2), the $I \cdots O$ interactions involve the nitro group only, while the two $C-H \cdots O$ hydrogen bonds both have nitro O acceptors in (1), but one nitro and one

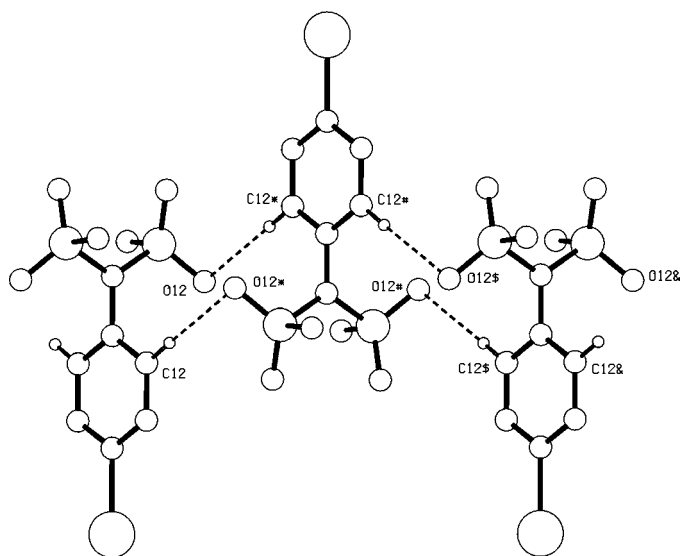


Figure 10
Part of the crystal structure of (3) showing the formation of a molecular ladder along $[001]$. For the sake of clarity the unit-cell box is omitted. The atoms marked with an asterisk (*), hash (#), dollar sign (\$) or ampersand (&) are at the symmetry positions $(-x, 1 - y, 1 - z)$, $(x, 1 - y, -\frac{1}{2} + z)$, $(-x, y, \frac{1}{2} - z)$ and $(x, y, -1 + z)$, respectively.

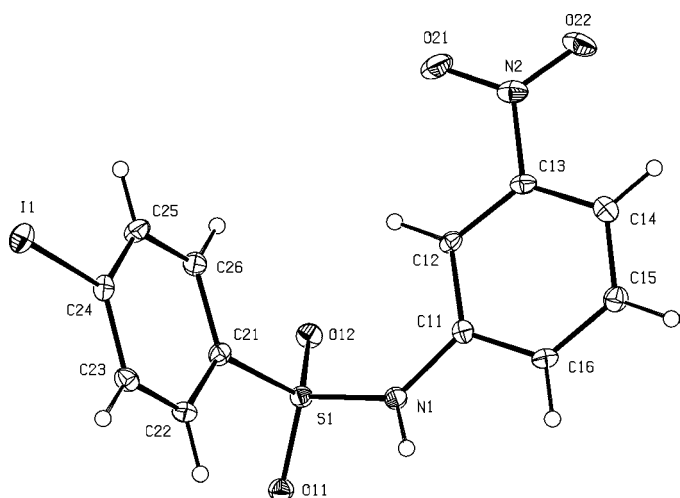


Figure 11
The molecule of (4) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

sulfonamide O in (2). In (3), by contrast, both the $I \cdots O$ interaction and the $C-H \cdots O$ hydrogen bond involve only the sulfonamide O, and there are, in addition, aromatic $\pi \cdots \pi$ stacking interactions which are absent from the structures of both (1) and (2).

3.2. Supramolecular aggregation is two-dimensional

3.2.1. *N*-(4'-Iodophenylsulfonyl)-3-nitroaniline (4). Compound (4) (Fig. 11) shows a number of significant differences from (1) in terms of its mode of supramolecular aggregation. First, the $I \cdots$ nitro interaction involves only one O per nitro group; second, both the $N-H$ and the SO_2 units are involved in hydrogen bonding; third, there are aromatic $\pi \cdots \pi$ stacking interactions present. The combination of $I \cdots$ nitro interactions and $N-H \cdots O=S$ hydrogen bonds leads to chain formation, and the chains are linked into sheets by a combination of soft (Braga *et al.*, 1995) hydrogen bonds and $\pi \cdots \pi$ stacking interactions.

The $I \cdots$ nitro interaction generates a cyclic centrosymmetric motif, with I1 in the molecule at (x, y, z) forming a very short (Table 2) interaction with nitro O21 at $(1 - x, 1 - y, 1 - z)$ (Fig. 12). Adapting the graph-set notation commonly used for hydrogen-bond motifs (Bernstein *et al.*, 1995; Grell *et al.*, 1999; Motherwell *et al.*, 1999) to more general non-covalent interactions (Starbuck *et al.*, 1999), the resulting ring can be described as being of $R_2^2(24)$ type. At the same time, sulfon-

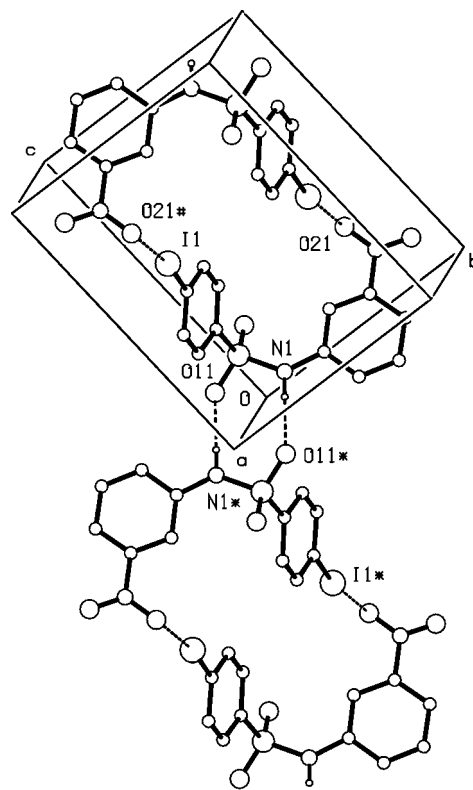


Figure 12
Part of the crystal structure of (4) showing the formation of a $[011]$ chain of fused $R_2^2(8)$ and $R_2^2(24)$ rings. For the sake of clarity H atoms bonded to C are omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1 - x, -y, -z)$ and $(1 - x, 1 - y, 1 - z)$, respectively.

amido N1 at (x, y, z) acts as a hydrogen-bond donor to sulfonamide O11 at $(1 - x, -y, -z)$, forming a second ring, of $R_2^2(8)$ type (Fig. 12). The hydrogen-bonding behaviour of (4) [in contrast to that of (1)] is far more typical of that observed in sulfonamides in general (Lightfoot *et al.*, 1993; Tremayne *et al.*, 1999). The combination of the two types of ring generates a chain of fused rings running parallel to the [011] direction, in which the hydrogen-bonded $R_2^2(8)$ rings are centred at $(\frac{1}{2}, n, n)$ ($n = \text{zero or integer}$) and the $I \cdots \text{nitro } R_2^2(24)$ rings are centred at $(\frac{1}{2}, n + \frac{1}{2}, n + \frac{1}{2})$ ($n = \text{zero or integer}$; Fig. 12).

The nitrated aryl ring C11–C16 in the molecule at (x, y, z) forms an aromatic $\pi \cdots \pi$ stacking interaction with the symmetry-related C11–C16 ring at $(-x, 1 - y, 1 - z)$ in the adjacent [011] chain. These two rings are strictly parallel, with an interplanar spacing of 3.404 (2) Å; the centroid separation is 3.758 (2) Å and the centroid offset is 1.592 (2) Å. Propagation of this interaction links the [011] chains into a (111) sheet and the $\pi \cdots \pi$ interactions are reinforced by the soft hydrogen bonds: C22 in the molecule at (x, y, z) acts as a hydrogen-bond donor to nitro O22 in the molecule at $(1 + x,$

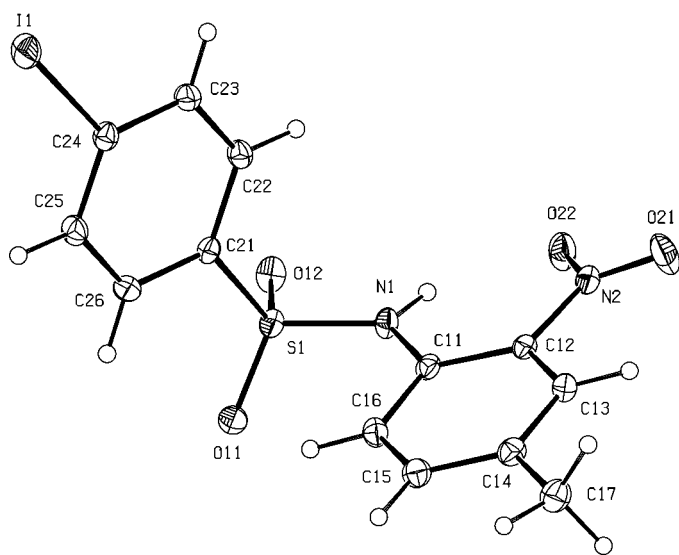


Figure 13
The molecule of (5) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

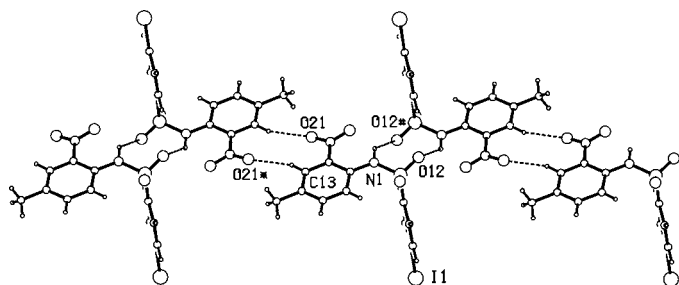


Figure 14
Part of the crystal structure of (5) showing the formation of a chain of rings parallel to [210]. For the sake of clarity the unit-cell box is omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(2 - x, 1 - y, -z)$ and $(-x, -y, -z)$, respectively.

$-1 + y, z)$, which lies in an adjacent [011] chain. This same molecule at $(1 + x, -1 + y, z)$ is involved in a $\pi \cdots \pi$ interaction with the molecule at $(1 - x, -y, -z)$, which itself is linked by the hard hydrogen bonds to the molecule at (x, y, z) .

3.3. Supramolecular structures are one-dimensional

3.3.1. *N*-(4'-Iodophenylsulfonyl)-4-methyl-2-nitroaniline (5). Compound (5) (Fig. 13) differs from both (1) and (4) in that there are no $I \cdots O$ interactions present, but there is an intramolecular $N-H \cdots O$ hydrogen bond, generating the $S(6)$ motif (Dhaneshwar *et al.*, 1978; Cannon *et al.*, 2001) typical of 2-nitroanilines. The supramolecular aggregation is determined by a combination of hard and soft hydrogen bonds having sulfonamide and nitro O, respectively, as the acceptors. Sulfonamide N1 in the molecule at (x, y, z) acts as a hydrogen-bond donor to sulfonamide O12 in the molecule at $(-x, -y, -z)$, thus generating a cyclic centrosymmetric $R_2^2(8)$ motif

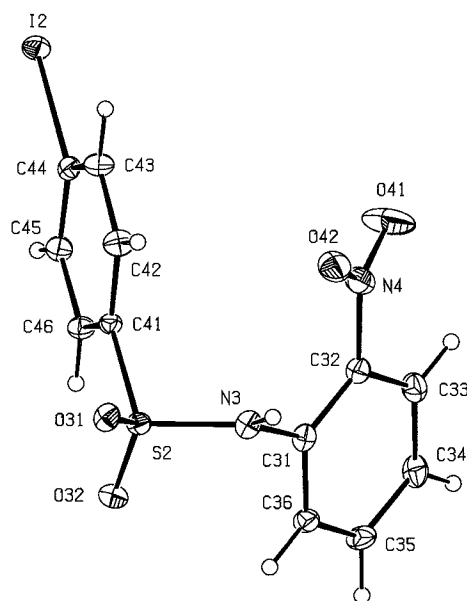
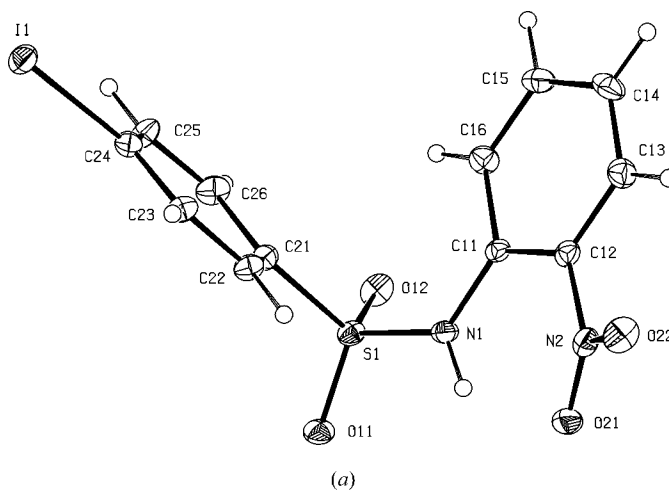


Figure 15
The two independent molecules of (6) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 4
Selected torsional angles ($^{\circ}$).

	(1)	(2)	(3)	(4)	(5)	(6)
N1—S1—C21—C22	88.0 (2)	91.2 (4)	86.9 (2)	-78.8 (2)	54.7 (3)	-44.9 (4)
O11—S1—C21—C22	-25.6 (3)	-22.5 (4)	-33.6 (2)	32.3 (3)	172.5 (2)	66.3 (4)
O12—S1—C21—C22	-157.9 (2)	-155.6 (4)	-166.7 (2)	164.1 (2)	-57.3 (3)	-161.9 (3)
O21—N2—C14—C13	175.9 (3)	-7.0 (6) [†]	11.5 (3) [‡]	8.7 (4) [§]	-9.2 (4) [¶]	-154.8 (4) ^{¶¶}
O22—N2—C14—C13	-4.6 (5)	175.2 (4) ^{††}	-169.0 (2) ^{‡‡}	-170.0 (3) ^{§§}	170.3 (3) ^{¶¶}	23.8 (6) ^{¶¶}

[†] O21—N2—C24—C23. [‡] O21—N2—C23—C24. [§] O21—N2—C13—C12. [¶] O21—N2—C12—C13. ^{††} O22—N2—C24—C23. ^{‡‡} O22—N2—C23—C24. ^{§§} O22—N2—C13—C12. ^{¶¶} O22—N2—C12—C13.

(Fig. 14), and atom C13 in the molecule at (x, y, z) acts as a hydrogen-bond donor to nitro O21 in the molecule at $(2 - x, 1 - y, -z)$, thus generating a cyclic centrosymmetric $R_2^2(10)$ motif (Fig. 14). Propagation of these two centrosymmetric motifs generates a $C_2^2(13)[R_2^2(8)][R_2^2(10)]$ chain of rings (Fig. 14) running parallel to the $[210]$ direction, in which the rings involving sulfonamide O are centred at $(2n, n, 0)$ ($n = \text{zero or integer}$) and those involving nitro O are centred at $[(2n + 1), (2n + 1)/2, 0]$ ($n = \text{zero or integer}$). There are no interactions between adjacent chains, other than van der Waals contacts, so that the supramolecular aggregation is strictly one-dimensional.

3.3.2. *N*-(4'-Iodophenylsulfonyl)-2-nitroaniline (6). The molecular constitution of (6) differs from that of (5) only in the absence of the 4-methyl group: although both compounds crystallize in space group $P1$, (5) and (6) have $Z' = 1$ and $Z' = 2$, respectively. In (6) only one of the two independent mole-

cules forms an intramolecular N—H \cdots O hydrogen bond, while the two independent molecules are linked within the asymmetric unit by such a bond (Fig. 15). In addition to this hard intermolecular hydrogen bond, (6) also differs from (5) in exhibiting I \cdots O interactions; it differs from (1), (4) and (5) in that the I \cdots O interactions involve sulfonamide O rather than nitro O. The hard hydrogen bond and I \cdots O interactions link molecules of types 1 and 2 (containing atoms S1 and S2, respectively) into large rings: there are also two soft C—H \cdots O hydrogen bonds, one each with nitro O and sulfonamide O as acceptors, and these generate a molecular ladder containing only molecules of type 2.

Atom I2 in the asymmetric unit at (x, y, z) forms a short I \cdots O interaction with sulfonamide O11 at $(2 - x, -y, -z)$, thus generating a cyclic four-component aggregate (Fig. 16), centred at $(1, 0, 0)$. Thus, the hard hydrogen bond and the I \cdots O interaction combine to generate a finite, zero-dimen-

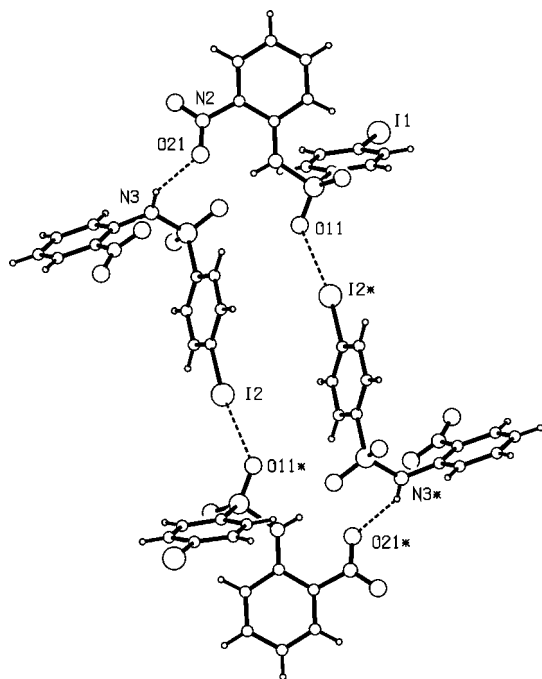


Figure 16
Part of the crystal structure of (6) showing a cyclic, centrosymmetric aggregate formed from type 2 molecules only. For the sake of clarity the unit-cell box is omitted. The atoms marked with an asterisk (*) are at the symmetry position $(2 - x, -y, -z)$.

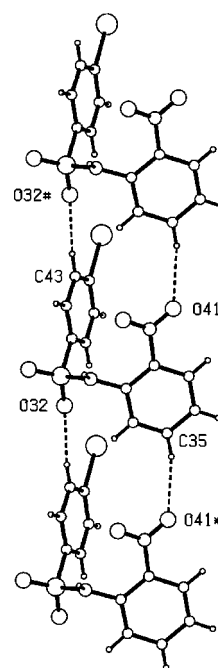


Figure 17
Part of the crystal structure of (6) showing the formation of a molecular ladder. For the sake of clarity the unit-cell box is omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(-1 + x, y, z)$ and $(1 + x, y, z)$, respectively.

Table 5
Geometric parameters for I...O interactions in compounds retrieved from the CSD (Å, °).

C—I...O—X	C—I	I...O	O—X	C—I...O	I...O—X
ITNOBE01 (7)					
C1—I1...O3 ⁱ —N2 ⁱ	2.082 (6)	3.267 (7)	1.205 (7)	161.1 (2)	99.7 (4)
C1—I1...O3 ⁱⁱ —N2 ⁱⁱ	2.082 (6)	3.267 (7)	1.205 (7)	161.1 (2)	99.7 (4)
DIMYUT10 (8)					
C1—I1...O1 ⁱⁱⁱ —N1 ⁱⁱⁱ	2.043 (8)	3.448 (7)	1.206 (10)	146.9 (2)	89.0 (4)
C1—I1...O2 ⁱⁱⁱ —N1 ⁱⁱⁱ	2.043 (8)	3.042 (8)	1.206 (10)	168.9 (2)	110.0 (6)
DIMYED10 (9)					
C1—I1...O1 ^{iv} —N1 ^{iv}	2.061	3.075	1.21 (4)	173.9	117.5
CUGDEN (10)					
C1—I1...O7 ^v —N4 ^v	2.083 (4)	3.194 (5)	1.212 (6)	123.33 (14)	139.4 (3)
KOVGEH (11)					
C1—I1...O3 ^{vi} —N2 ^{vi}	2.069 (7)	3.032 (6)	1.228 (9)	179.0 (2)	116.0 (5)
C1—I2...O2 ^{vii} —N1 ^{vii}	2.086 (8)	3.101 (6)	1.232 (9)	172.7 (2)	111.3 (4)
C3—I3...O7 ^{viii} —N4 ^{viii}	2.066 (9)	3.196 (8)	1.227 (10)	168.6 (3)	105.3 (5)
C3—I3...O8 ^{viii} —N4 ^{viii}	2.066 (9)	3.482 (8)	1.196 (10)	151.8 (2)	91.6 (5)
C3—I4...O4 ^{ix} —N2 ^{ix}	2.082 (9)	3.258 (8)	1.195 (10)	164.7 (2)	152.5 (5)
ZEMKUX (12)					
C2—I1...O1 ^x —N1 ^x	2.093 (7)	3.551 (8)	1.227 (10)	146.8 (2)	87.9 (5)
C2—I1...O2 ^x —N1 ^x	2.093 (7)	3.054 (8)	1.238 (10)	176.1 (2)	112.9 (5)
C1—I2...O2 ^{xi} —N1 ^{xi}	2.085 (7)	3.400 (7)	1.238 (10)	141.9 (2)	166.4 (5)
KORXEU (13)					
C2—I1...O2 ^{xii} —S4 ^{xii}	2.083 (6)	2.922 (6)	1.498 (4)	174.4 (2)	123.4 (3)
C7—I2...O1 ^{xiii} —S2 ^{xiii}	2.087 (6)	3.408 (7)	1.486 (5)	148.3 (2)	92.4 (2)
KORXUK (14)					
C2—I1...O1 ^{xiv} —S2 ^{xiv}	2.089 (16)	2.992 (14)	1.506 (14)	177.6 (5)	108.5 (7)

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

sional aggregate. The soft hydrogen bonds, by contrast, generate a molecular ladder: atom C35 in the nitrated aryl ring of the type 2 molecule at (x, y, z) acts as a hydrogen-bond donor to nitro O41 in the type 2 molecule at $(-1 + x, y, z)$, while C43 in the iodinated ring of the type 2 molecule at (x, y, z) acts as a hydrogen-bond donor to sulfonamide O32 in the type 2 molecule at $(1 + x, y, z)$. These two hydrogen bonds thus individually generate $C(7)$ and $C(6)$ chains, respectively, both running parallel to the $[100]$ direction, and together they generate a molecular ladder in which the $C(7)$ and $C(6)$ chains act as the uprights and the $\text{SO}_2\text{-NH-Ar}$ units act as the rungs. Between the rungs there are $R_2^2(17)$ rings (Fig. 17).

Two of these molecular ladders, related to one another by the centres of inversion and thus mutually antiparallel, run through each unit cell: the ladders are pairwise linked by means of the four component aggregates (Fig. 16), where the two type 2 molecules lie in antiparallel ladders. There are no further interactions between the paired ladders, so that as in (5), the supramolecular aggregation in (6) is strictly one-dimensional.

3.4. Molecular conformations and dimensions

The intramolecular dimensions show no unusual features. Two aspects of the molecular conformations, however, are

worthy of brief comment. In all compounds studied here the orientation of the sulfonamide group relative to the S-aryl ring is such that one of the O atoms is close to the plane of this ring; hence the N-aryl ring is markedly displaced from this plane with C—C—S—N torsional angles having magnitudes in the range $44.9(4)\text{--}91.2(4)^\circ$ (Table 4). The nitro groups are all to some extent twisted out of the plane of the adjacent aryl ring and, in general, the magnitude of this twist increases from 4-nitro, *via* 3-nitro, to the 2-nitro groups.

3.5. Related compounds

The I...nitro interaction as an important determinant of supramolecular organization has been described for a number of simple examples, including 4-iodonitrobenzene [Cambridge Structural Database (CSD) code (Allen & Kennard, 1993) ZUNYIK; Thalladi *et al.*, 1996], 4-iodo-4'-nitrobiphenyl (CSD code RAYCID01; Masciocchi *et al.*, 1998), 1,4-diiodobenzene-1,4-dini-

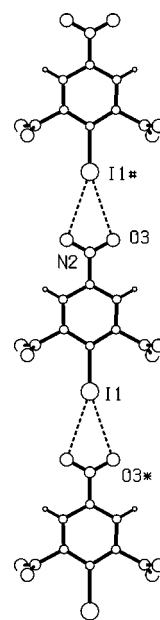
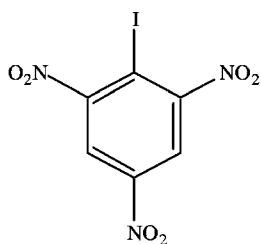


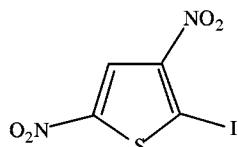
Figure 18

Part of the crystal structure of ITNOBE01 (Weiss *et al.*, 1999) showing the formation of a linear $[110]$ chain by means of a symmetric three-centre I...O₂N interaction. For the sake of clarity the unit-cell box is omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(-1 + x, -1 + y, z)$ and $(1 + x, 1 + y, z)$, respectively.

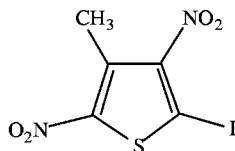
trobenzene (1/1) (CSD code YESZEB; Allen *et al.*, 1994), 1,4-dinitrobenzene–4-iodocinnamic acid (1/2) (CSD code ZONYOQ; Thalladi *et al.*, 1996) and 1,4-diiodobenzene–3,5-dinitrobenzoic acid (1/2) (CSD code PUQQIB; Ranganathan & Pedireddi, 1998). All of these systems are based on aromatic components and most have equal numbers of I atoms and nitro groups present. In view of the very wide range of behaviour described earlier (§§3.1–3.4) for (1)–(6), it is of interest to consider other examples retrieved from the CSD, including examples having a mismatch between the numbers of I and nitro groups present and those based on non-benzeneoid skeletons (II). We also comment on two further examples exhibiting $I \cdots O=S$ interactions. It is noteworthy that for the examples retrieved from the CSD, the original reports do not, in general, make any comment whatsoever on the supramolecular aggregation.



(7)



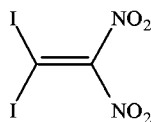
(8)



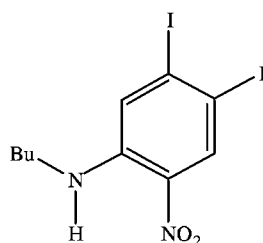
(9)

 $IC_8(NO_2)_7$

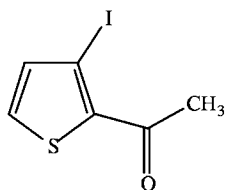
(10)



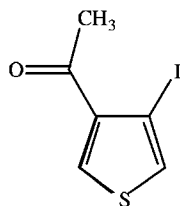
(11)



(12)



(13)



(14)

In 2,4,6-trinitroiodobenzene [(7); picryl iodide; CSD code ITNOBE01; Weiss *et al.*, 1999], the molecules lie across twofold rotation axes in space group $P4_32_12_1$ (No. 96) and they are linked into strictly linear chains by symmetrical, planar three-centre $I \cdots O_2N$ interactions (Fig. 18). However, there are neither $C-H \cdots O$ hydrogen bonds nor aromatic $\pi \cdots \pi$ stacking interactions present in ITNOBE01. In the two thiophene derivatives (8) (CSD code DIMYUT10; Consiglio *et al.*, 1997) and (9) (CSD code DIMYED10; Consiglio *et al.*, 1997), the molecular constitutions are different only by the presence, in (9), of a methyl group at a site remote from I: both crystallize in space group $P2_12_12_1$, but the nature of the intermolecular $I \cdots$ nitro interaction is different in the two compounds, although in both it is only the nitro group adjacent to I which participates. In (8) there is an asymmetric, three-centre $I \cdots O_2N$ interaction leading to the formation of spiral chains parallel to [001] (Fig. 19); by contrast, in (9) only one O of the 3-nitro substituent participates and in this case the spiral chain runs parallel to [100] (Fig. 20). In neither (8) nor (9) are there any $C-H \cdots O$ hydrogen bonds or any aromatic $\pi \cdots \pi$ stacking interactions.

For the rather unusual iodoheptanitrocubane [(10); CSD code CUGDEN; Zhang *et al.*, 2000], the supramolecular analysis is complicated by disorder: the molecules lie across twofold rotation axes in space group $C2/c$, so that I and one nitro group have 0.5 occupancy. Nonetheless, there is a short $I \cdots O$ interaction which leads to chain formation by translation.

Turning to an acyclic example containing equal numbers of I and nitro groups, 1,1-diiodo-2,2-dinitroethene [(11); CSD code KOVGEH; Baum *et al.*, 1992] crystallizes with $Z' = 2$ in space group $P\bar{1}$ and the behaviour of the two independent molecules is entirely different. While both nitro groups in the type 1 molecule (containing I1 and I2) are involved in $I \cdots$ nitro interactions, only one of the nitro groups in the type 2 molecule (containing I3 and I4) participates. In molecules of type 1, I1 and I2 both form a single short $I \cdots O$ contact with another type 1 molecule, leading to the formation of a (001) sheet in the form of a (4,4) net built from $R_4^4(18)$ rings (Fig. 21). In the type 2 molecules, on the other hand, I3 forms a three-centre $I \cdots O_2N$ interaction with a single nitro group in another type 2 molecule, leading to simple chain formation along the [010] direction (Fig. 22). In space group $P\bar{1}$ there are two (001) sheets of type 1 molecules passing through each unit cell, related to one another by the centres of inversion; similarly there are two [010] chains of type 2 molecules per cell. The final type of $I \cdots O$ interaction, involving I4, links the sheets of type 1 molecules to the chains of type 2 molecules.

An unusual example of a compound containing more I than nitro groups is provided by 1,2-diiodo-4-nitro-5-(butylamino)benzene [(12); CSD code ZEMKUX; Senskey *et al.*, 1995]. In this compound, which crystallizes in space group $P\bar{1}$ with $Z' = 1$, one of the I atoms in the molecule at (x, y, z) , that *para* to the nitro group, forms an asymmetric three-centre $I \cdots O_2N$ interaction with the nitro group at $(1+x, -1+y, z)$, thus generating by translation a chain parallel to the [110] direction (Fig. 23); the other I in the molecule at (x, y, z) forms a simple

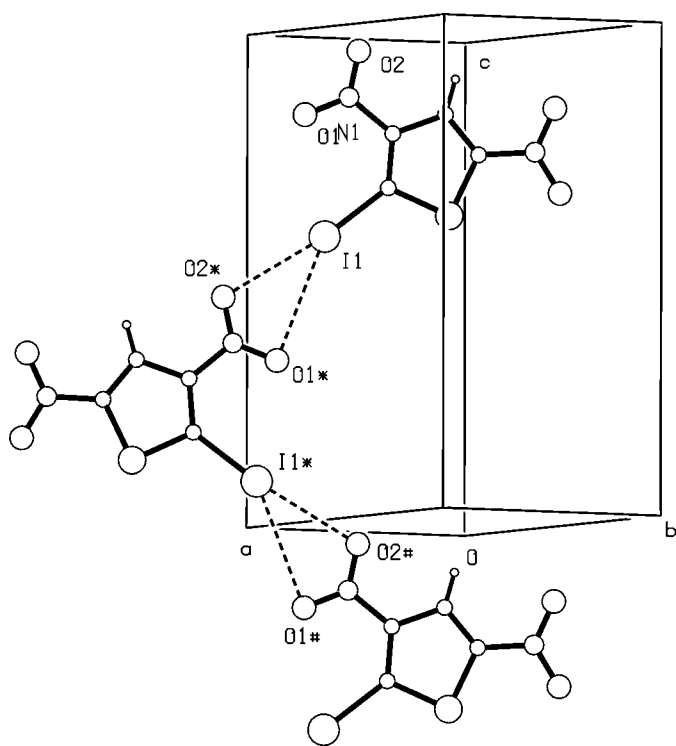


Figure 19
Part of the crystal structure of DIMYUT10 (Consiglio *et al.*, 1997) showing the formation of a spiral [001] chain by means of an asymmetric three-centre I...O₂N interaction. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z)$ and $(x, y, -1 + z)$, respectively.

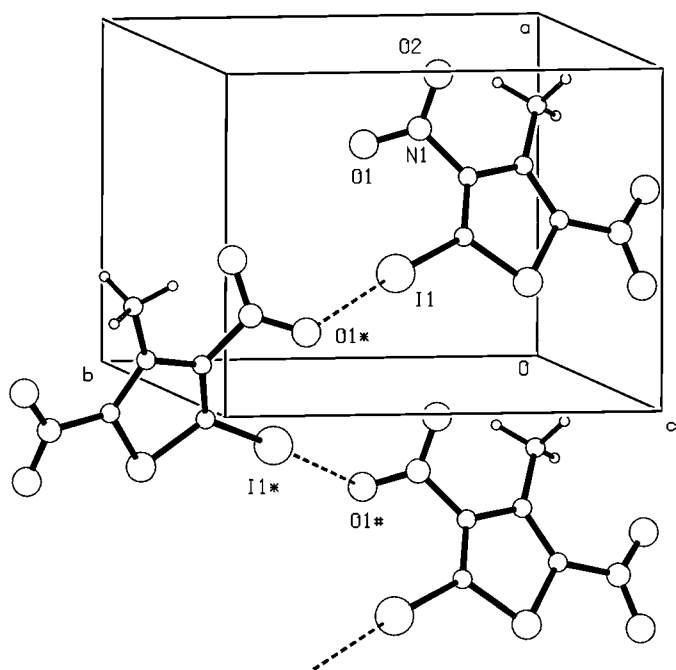


Figure 20
Part of the crystal structure of DIMYED10 (Consiglio *et al.*, 1997) showing the formation of a spiral [100] chain by means of a two-centre I...O₂N interaction. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(-\frac{1}{2} + x, \frac{3}{2} - y, 2 - z)$ and $(-1 + x, y, z)$, respectively.

I...O interaction with the molecule at $(-x, 2 - y, -z)$, and propagation of these interactions leads to the formation of a chain of fused centrosymmetric rings, with $R_2^2(10)$ and $R_2^2(12)$ rings alternating. The butyl groups lie on the exterior of this chain, effectively preventing any further interactions between the chains either of I...O type or of C-H...O type.

Examples where the supramolecular aggregation is controlled by I...O=S interactions are uncommon, but two examples based on substituted thiophenes have been reported. Compound (13) (CSD code KORXEU; Folli *et al.*, 1991) has $Z' = 2$ and there are two distinct chain motifs, each involving just one of the two I; in each type of chain the molecules are linked by a combination of I...O=S interactions and C-H...O=S hydrogen bonds, and the combination of the two chain motifs, along [102] and [010], respectively, generates a $(10\bar{2})$ sheet. The isomeric compound (14) (CSD code KORXUK; Folli *et al.*, 1991) crystallizes with $Z' = 1$ and there are both I...O=S interactions and C-H...O=S hydrogen bonds which again link the molecules into (100) sheets.

3.6. I...nitro and I...O=S geometries

For the compounds studied in this work which exhibit I...nitro interactions, (1), (2) and (4), the C-I...O angles are all above 150° with I...O-N angles around 110° (Table 2); this generalization also holds for those examples retrieved from the CSD (Table 5), with the exception of CUGDEN and

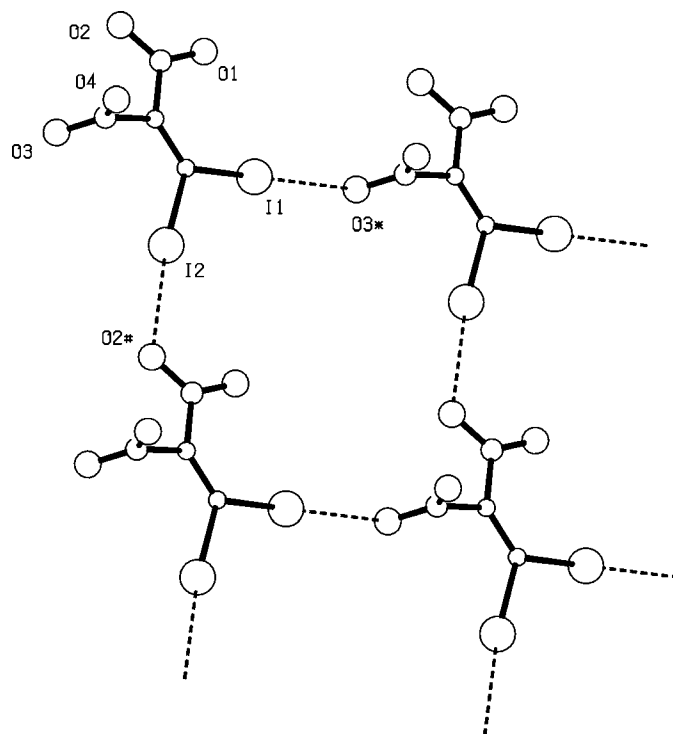


Figure 21
Part of the crystal structure of KOVGEH (Baum *et al.*, 1992) showing the formation of a (001) sheet built from type 1 molecules only. For the sake of clarity the unit-cell box is omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1 + x, y, z)$ and $(x, -1 + y, z)$, respectively.

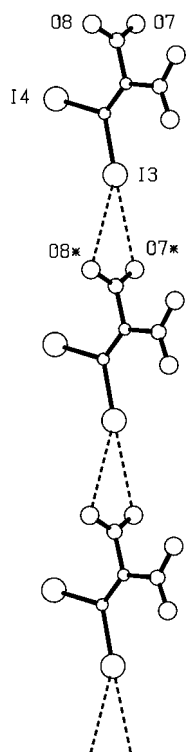


Figure 22
Part of the crystal structure of KOVGEH (Baum *et al.*, 1992) showing the formation of a [010] chain built from type 2 molecules only. For the sake of clarity the unit-cell box is omitted. The atoms marked with an asterisk (*) are at the symmetry position $(x, 1 + y, z)$.

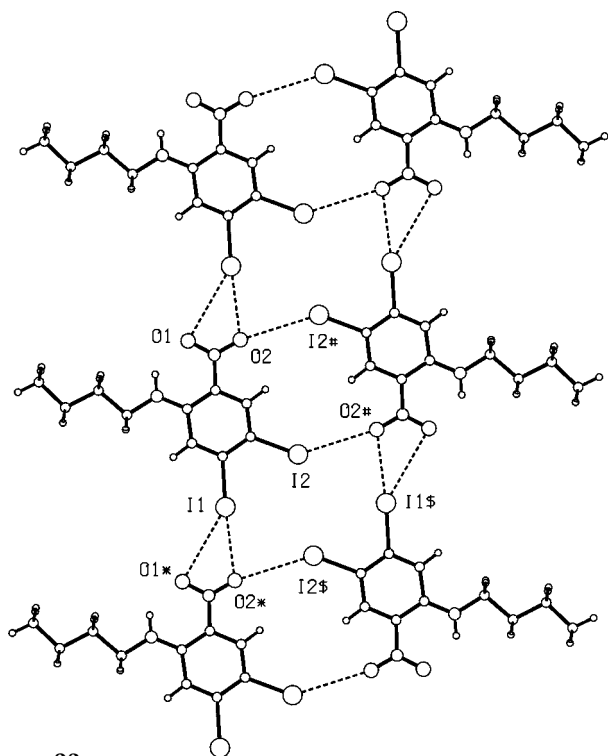


Figure 23
Part of the crystal structure of ZEMKUX (Senskey *et al.*, 1995) showing the formation of a $[1\bar{1}0]$ chain of fused $R_2^2(10)$ and $R_2^2(12)$ rings. For the sake of clarity the unit-cell box is omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(1 + x, -1 + y, z)$, $(-x, 2 - y, -z)$ and $(1 - x, 1 - y, -z)$, respectively.

one of the interactions in ZEMKUX. In general, also, the $I \cdots O$ distances tend to be somewhat shorter in two-centre systems than in three-centre systems. The short $I \cdots O= S$ interactions exhibit similar angular properties, except for the longer of the two interactions in KORXEU: we draw attention to the very short $I \cdots O$ contacts in the sulfoxide derivatives KORXEU and KORXUK.

4. Conclusions

Within the series of substituted arenesulfonamides studied here, (1)–(6), all the types of distinct intermolecular interactions possible for these molecular units are observed, although not all possible combinations in interactions. The variety of observed combinations, even within this short series, means that the aggregation pattern of one compound cannot be predicted from knowledge of the patterns in the remainder. Contrasts of this kind provide continuing challenges to attempts at the prediction from first principles of the crystal structures of comparatively simple molecular compounds (Lommerse *et al.*, 2000).

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