

Interplay of hydrogen bonds, iodo···nitro interactions and aromatic π ··· π stacking interactions in iodo-nitroanilines

Simon J. Garden,^a Silvia P. Fontes,^a James L. Wardell,^b Janet M. S. Skakle,^c John N. Low^{c†} and Christopher Glidewell^{d*}

^aInstituto de Química, Departamento de Química Orgânica, Universidade Federal do Rio de Janeiro, CP 68563, 21945-970 Rio de Janeiro RJ, Brazil, ^bInstituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, CP 68563, 21945-970 Rio de Janeiro RJ, Brazil, ^cDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, UK, and ^dSchool of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, UK

† Present Address: School of Engineering, University of Dundee, Dundee DD1 4HN, UK

Correspondence e-mail: cg@st-andrews.ac.uk

Received 12 April 2002

Accepted 30 April 2002

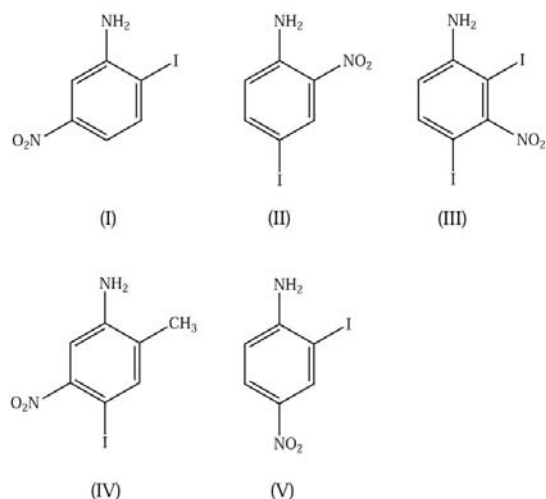
Molecules of 2-iodo-5-nitroaniline (I) are linked by N—H···O hydrogen bonds into centrosymmetric dimers and by asymmetric three-centre iodo···nitro interactions into chains, so forming chains of fused centrosymmetric rings: these chains are linked by aromatic π ··· π stacking interactions to form a three-dimensional structure. In the isomeric 4-iodo-2-nitroaniline (II), each of the two independent molecules forms hydrogen-bonded chains that are linked by two-centre iodo···nitro interactions into sheets of two types, each containing only a single type of molecule: π ··· π stacking interactions are absent. In 2,4-diiodo-3-nitroaniline (III), where the nitro group is almost orthogonal to the aryl ring, a combination of N—H···O hydrogen bonds and two distinct two-centre iodo···nitro interactions links the molecules into a three-dimensional framework that is reinforced by aromatic π ··· π stacking interactions. Bond lengths and conformations are discussed and comparisons are drawn with related compounds.

1. Introduction

In simple nitroanilines, the supramolecular structures are generally dominated by the effects of N—H···O hydrogen bonds, although the detailed supramolecular arrangement may be subtly influenced by the presence of other substituents, even those as modest as C-methyl groups (Ploug-Sørensen & Andersen, 1986; Tonogaki *et al.*, 1993; Ellena *et al.*, 1999; Cannon *et al.*, 2001; Ferguson *et al.*, 2001). Likewise, the supramolecular structures of the extended 4-nitroaniline analogues 4-H₂NC₆H₄-(C≡C)_n-C₆H₄NO₂-4' (for n = 0–3) are controlled by the N—H···O hydrogen bonds (Graham *et al.*, 1989). When nitro groups are present with I atoms in benzenoid compounds, the resulting intermolecular iodo···nitro interactions can 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; Kelly *et al.*, 2002). Finally, aromatic molecules of this type may engage in aromatic π ··· π stacking interactions.

Substituted iodo-nitroanilines thus provide very compact molecular systems within which to investigate the interplay of N—H···O (and possibly C—H···O) hydrogen bonding, iodo···nitro interactions (which may be of two-centre and/or three-centre type) and π ··· π stacking interactions. To this end, we have now investigated three carefully selected examples: 2-iodo-5-nitroaniline (I), 4-iodo-2-nitroaniline (II) and 2,4-diiodo-3-nitroaniline (III), having in (I) an isolated nitro group with no ring neighbours other than H, in (II) a similarly isolated I substituent and in (III) a nitro group sandwiched

between two I substituents. We compare the resulting patterns of supramolecular aggregation with those of the closely related compounds 4-iodo-2-methyl-5-nitroaniline (IV) (Garden, Glidewell *et al.*, 2001) and 2-iodo-4-nitroaniline (V) (McWilliam *et al.*, 2001): it may be noted here that compounds (I), (II) and (V) are isomeric.



2. Experimental

2.1. Synthesis

Compounds (I)–(III) were prepared by iodination of the appropriate nitroaniline using $K[ICl_2]$ in methanol (Larsen *et al.*, 1956; Garden, Torres *et al.*, 2001). Iodination of 2-nitroaniline gave (II), m.p. 395–396 K. Iodination of 3-nitroaniline gave a mixture of (I) and (III) (m.p. 429–431 K and 391–392 K, respectively), separated by thin-layer chromatography using chloroform and light petroleum as eluants; in addition, a third product was formed in this reaction in very low yield, but so far this has not been purified sufficiently for definitive identification. Crystals of (I)–(III) suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in ethanol.

2.2. Data collection, structure solution and refinement

Diffraction data for compounds (I)–(III) were collected at 150 (2) K, using a Bruker SMART-100 CCD for (I) and Nonius KappaCCD for (II) and (III), diffractometers 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 (Bruker, 1997; Ferguson, 1999; Nonius, 1997; Otwinowski & Minor, 1997; Sheldrick, 1997*a,b*).

Table 1
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_6H_5IN_2O_2$	$C_6H_5IN_2O_2$	$C_6H_4I_2N_2O_2$
Chemical formula weight	264.02	264.02	389.91
Cell setting, space group	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.4236 (15), 7.4979 (18), 8.293 (2)	26.5541 (9), 7.0445 (2), 16.4416 (5)	7.6069 (3), 12.5917 (4), 10.2546 (3)
α , β , γ (°)	71.422 (4), 85.285 (4), 86.125 (4)	90, 101.1548 (16), 90	90, 106.6693 (16), 90
<i>V</i> (Å ³)	376.98 (16)	3017.47 (16)	940.95 (6)
<i>Z</i>	2	16	4
<i>D_x</i> (Mg m ⁻³)	2.326	2.325	2.752
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	1674	3426	2144
θ range (°)	2.60–28.44	3.0–27.48	3.23–27.46
μ (mm ⁻¹)	4.195	4.192	6.647
Temperature (K)	120 (2)	120 (2)	120 (2)
Crystal form, colour	Plate, orange	Plate, orange	Plate, colourless
Crystal size (mm)	0.24 × 0.12 × 0.04	0.25 × 0.20 × 0.05	0.28 × 0.24 × 0.08
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_{min}</i>	0.434	0.380	0.180
<i>T_{max}</i>	0.850	0.811	0.618
No. of measured, independent and observed reflections	2274, 1674, 1620	10470, 3426, 2696	8456, 2144, 1950
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
<i>R_{int}</i>	0.0248	0.0556	0.1038
θ_{max} (°)	28.44	27.48	27.46
Range of <i>h</i> , <i>k</i> , <i>l</i>	–8 → <i>h</i> → 7 –10 → <i>k</i> → 9 –10 → <i>l</i> → 10	–34 → <i>h</i> → 33 –8 → <i>k</i> → 9 –21 → <i>l</i> → 21	–9 → <i>h</i> → 8 –14 → <i>k</i> → 16 –13 → <i>l</i> → 13
Refinement			
Refinement on $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	<i>F</i> ² 0.0375, 0.1022, 1.069	<i>F</i> ² 0.0322, 0.0815, 1.046	<i>F</i> ² 0.0445, 0.1215, 1.131
No. of reflections and parameters used in refinement	1674, 100	3426, 193	2144, 110
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0823P)^2] + 0.6322P$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2] + 3.2146P$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2] + 3.8878P$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001	0.001	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	1.291, –1.864	1.222, –1.551	2.356, –2.261
Extinction method	None	None	SHELXL
Extinction coefficient	0	0	0.0044 (5)

Computer programs used: SMART (Bruker, 1997), SHELXTL (Bruker, 1997), SHELXS97 (Sheldrick, 1997*b*), SHELXL97 (Sheldrick, 1997*a*), PRPKAPPA (Ferguson, 1999), KappaCCD server software (Nonius, 1997), DENZO-SMN (Otwinowski & Minor, 1997).

Compound (I) is triclinic: space group $P\bar{1}$ was selected and confirmed by the analysis. For compound (II), the systematic

Table 2
Selected geometric parameters.

	Intramolecular distances (Å)				
	Compound (I)		Compound (II)		Compound (III)
	<i>n</i> = nil	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = nil	
<i>Cn1</i> — <i>Cn2</i>	1.406 (6)	1.421 (5)	1.404 (4)	1.404 (10)	
<i>Cn2</i> — <i>Cn3</i>	1.392 (6)	1.399 (5)	1.409 (5)	1.394 (8)	
<i>Cn3</i> — <i>Cn4</i>	1.387 (7)	1.370 (5)	1.357 (5)	1.380 (8)	
<i>Cn4</i> — <i>Cn5</i>	1.389 (6)	1.398 (5)	1.397 (5)	1.398 (9)	
<i>Cn5</i> — <i>Cn6</i>	1.372 (6)	1.366 (5)	1.366 (5)	1.370 (9)	
<i>Cn6</i> — <i>Cn1</i>	1.415 (6)	1.405 (5)	1.417 (6)	1.409 (9)	
<i>Cn2</i> — <i>In2</i>	2.099 (4)	—	—	2.099 (6)	
<i>Cn4</i> — <i>In4</i>	—	2.095 (4)	2.099 (4)	2.089 (6)	
<i>Cn1</i> — <i>Nn1</i>	1.361 (6)	1.343 (5)	1.344 (5)	1.380 (8)	
<i>Cnm</i> — <i>Nnm</i> †	1.469 (6)	1.433 (5)	1.426 (5)	1.484 (8)	

Bond angles (°)

Compound (I)			
N1—C1—C2	122.8 (4)	N5—C5—C4	118.7 (4)
N1—C1—C6	120.4 (4)	N5—C5—C6	117.3 (4)
C2—C1—C6	116.7 (4)	C4—C5—C6	124.0 (4)
I2—C2—C1	119.0 (3)	C1—C2—C3	121.9 (4)
I2—C2—C3	119.1 (3)		
Compound (II)			
N11—C11—C12	124.2 (4)	N21—C21—C22	124.9 (4)
N11—C11—C16	120.0 (4)	N21—C21—C26	119.3 (4)
C12—C11—C16	115.8 (3)	C22—C21—C26	115.8 (3)
N12—C12—C11	121.6 (3)	N22—C22—C21	121.5 (3)
N12—C12—C13	116.8 (3)	N22—C22—C23	116.6 (3)
C11—C12—C13	121.6 (3)	C21—C22—C23	121.9 (3)
I14—C14—C13	119.4 (3)	C23—C24—C25	119.0 (3)
I14—C14—C15	121.0 (3)	I24—C24—C23	120.3 (3)
C13—C14—C15	119.6 (3)	I24—C24—C25	120.7 (3)
Compound (III)			
N1—C1—C2	123.4 (6)	I2—C2—C1	119.1 (4)
N1—C1—C6	119.8 (6)	I2—C2—C3	121.4 (5)
C2—C1—C6	116.7 (6)	C1—C2—C3	119.5 (6)
N3—C3—C2	118.0 (5)	I—C4—C3	123.4 (5)
N3—C3—C4	119.0 (5)	I4—C4—C5	118.9 (4)
C2—C3—C4	122.9 (6)	C3—C4—C5	117.7 (5)

Torsional angles (°)

Compound (I)		Compound (II)	
C4—C5—N5—O51	−176.1 (5)	C11—C12—N12—O11	170.8 (4)
C4—C5—N5—O52	3.2 (7)	C11—C12—N12—O12	−9.3 (6)
		C21—C22—N22—O21	−178.0 (4)
		C21—C22—N22—O22	2.2 (6)
Compound (III)			
C2—C3—N3—O131	−100.3 (6)		
C2—C3—N3—O132	80.4 (7)		

† For N of nitro group, in compound (I), *m* = 5; in (II), *m* = 2; in (III), *m* = 3.

absences permitted *C2/c* and *Cc* as possible space groups: *C2/c* was selected and confirmed by the analysis. For compound (III), the space group *P2₁/c* was uniquely assigned from the systematic absences. The structures were solved by direct methods and refined with all data on *F*². A weighting scheme based on $P = [F_o^2 + F_c^2]/3$ 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 Å and C—H = 0.95 Å.

Supramolecular analyses were made with the aid of *PLATON* (Spek, 2002). Details of molecular dimensions,

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

<i>D</i> —H··· <i>A</i>	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>	Motif	Direction
Compound (I)					
N1—H1B···O51 ⁱ	2.51	3.311 (6)	152	<i>R</i> ₂ ² (14)	—
Compound (II)					
N11—H11A···O11 ⁱⁱ	2.24	3.005 (5)	146	C(6)	[010]
N11—H11B···O12	2.01	2.642 (4)	128	S(6)	—
N21—H21A···O21 ⁱⁱⁱ	2.19	2.979 (5)	149	C(6)	[010]
N21—H21B···O22	2.00	2.626 (4)	127	S(6)	—
C15—H15···O12 ⁱⁱⁱ	2.63	3.524 (4)	157	C(7)	[001]
C25—H25···O22 ^{iv}	2.55	3.495 (4)	172	C(7)	[001]
Compound (III)					
N1—H1B···O132 ^v	2.46	3.128 (8)	133	C(7)	[201]

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

Table 4
Geometric parameters for I···O interactions (Å, °).

	C—I···O— <i>X</i>	I···O	C—I···O	I···O— <i>X</i>
Compound (I)				
C2—I2···O51 ⁱ —N5 ⁱ		3.521 (4)	154.0 (2)	93.2 (3)
C2—I2···O52 ⁱ —N5 ⁱ		3.239 (4)	167.6 (2)	107.2 (3)
Compound (II)				
C14—I14···O11 ⁱⁱ —N12 ⁱⁱ		3.177 (3)	167.6 (2)	122.7 (2)
C24—I24···O21 ⁱⁱⁱ —N22 ⁱⁱⁱ		3.161 (3)	166.9 (2)	119.9 (2)
Compound (III)				
C2—I2···O132 ^{iv} —N3 ^{iv}		3.165 (5)	176.4 (2)	115.0 (4)
C4—I4···O132 ^v —N3 ^v		3.382 (5)	155.2 (2)	116.9 (4)
In (I)				
O51 ⁱ ···I2···O52 ⁱ		36.92 (9)		
In (III)				
I2 ^{vi} ···O132···I4 ^v		91.3 (2)		

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

hydrogen-bonding geometry and I···O interactions are given in Tables 2, 3 and 4, respectively. The diagrams were prepared with the aid of *PLATON* (Spek, 2002). Figs. 1, 2 and 3 show the molecules (I)–(III) with the atom-labelling schemes, and Figs. 4–10 show aspects of the supramolecular structures.

Lists of atomic coordinates, anisotropic displacement parameters, geometric parameters and structure factors have been deposited with the IUCr.¹

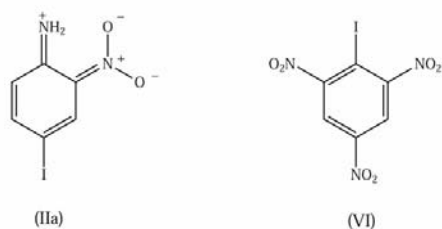
3. Results and discussion

3.1. Molecular dimensions and conformations

In compound (I) (Fig. 1), where the amino and nitro groups are *meta* to one another, the C1—N1 and C5—N5 distances (Table 2) are, within experimental uncertainty, identical to the mean values (1.355 Å and 1.468 Å, respectively) for C(ar)—NH₂ and C(ar)—NO₂ distances (Allen *et al.*, 1987): at the same time, there is no evidence for any significant bond

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0135). Services for accessing these data are described at the back of the journal.

fixation in the aryl ring, so the ring-delocalized form (I) is an adequate representation of the molecular-electronic structure. By contrast, the $Cn1-Nn1$ and $Cn2-Nn2$ distances ($n = 1$ or 2 for the two independent molecules) in (II) (Fig. 2), where the amino and nitro groups are mutually *ortho*, are both short for their types, while amongst the ring C—C bonds $Cn3-Cn4$ and $Cn5-Cn6$ are systematically much shorter than the remainder, pointing to the importance of the charge-separated quinonoid form (IIa) as a significant contributor.



Compound (III) (Fig. 3) is similar to (I) in having the amino and nitro substituents in *meta* positions, but differs from (I) in that there is an I substituent interposed between the amino and nitro groups. There is again no bond fixation within the ring, as judged by the C—C distances, but both of the C—N distances are rather long and indeed both are just above the upper quartile values for their types, 1.372 Å and 1.476 Å, respectively (Allen *et al.*, 1987). Closely associated with these long C—N bonds is the overall conformation of (III), which differs markedly from those observed in (I) and (II). It has been clearly demonstrated (Domenicano *et al.*, 1990) that while the coplanar conformation of a nitro group bonded to a benzenoid ring represents an energy minimum, the barrier to rotation about a C(ar)—NO₂ bond is rather small (probably no more than 15 kJ mol⁻¹). A contributory factor to the stabilization of the planar conformation may be the attractive interaction between the negatively polarized O atoms of the nitro group and the positively polarized H atoms *ortho* to the nitro group. Thus, in both (I) and (II) the twist of the nitro groups away from the ring plane is very modest (Table 2),

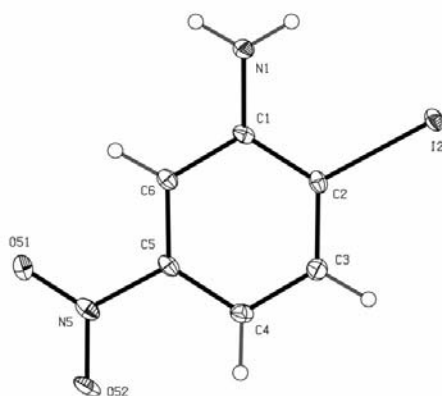


Figure 1
A molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

whereas in (III), where the nitro group lies between two I substituents, the nitro group is almost perpendicular to the

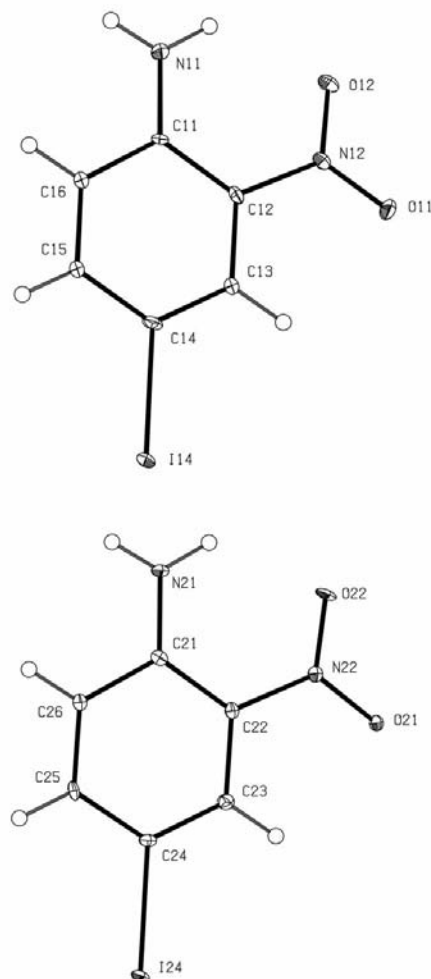


Figure 2
The two independent molecules of (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

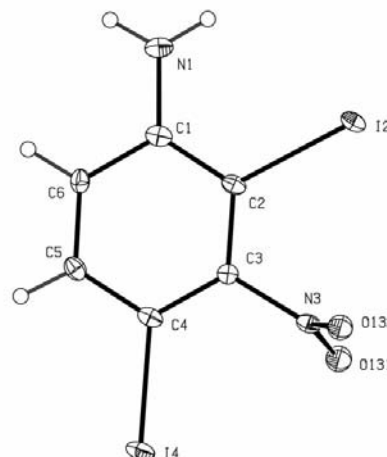


Figure 3
A molecule of (III) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

ring plane. We have noted previously (Garden, Glidewell *et al.*, 2001) that intramolecular interactions between mutually *ortho* I and nitro substituents on aryl rings appear to be repulsive, although intermolecular I...nitro interactions are generally attractive. The twist of the nitro group in (III), as well as those in (IV) and 2,4,6-trinitroiodobenzene (VI) [Cambridge Structural Database (CSD; Allen & Kennard, 1993) refcode ITNOBE01 (Weiss *et al.*, 1999)], indicates repulsion between *ortho* I and nitro. It is interesting to note that in ITNOBE01 the C–N distances for the 2-nitro and 4-nitro groups (the molecules lie on twofold rotation axes in space group $P4_32_12$) are 1.476 (9) Å and 1.451 (8) Å associated with nitro-group twist angles of 75.2 (9)° and 7.8 (8)°, respectively.

Further evidence of repulsive interactions between adjacent substituents can be gleaned from the bond angles at the *ipso* C atoms, although here it is necessary also to take into consideration the well established effects of substituent electro-negativity on the internal C–C–C angle at the *ipso* C atoms (Domenicano & Murray-Rust, 1979). From the values in Table 2 and those in other iodo-nitroanilines and related compounds (Weiss *et al.*, 1999; Garden, Glidewell *et al.*, 2001; McWilliam *et al.*, 2001), the following general comments can be made:

(i) The internal C–C–C angle *ipso* to an amino group is always small, regardless of other substituents, consistent with the electron-donor characteristics of this substituent.

(ii) The internal C–C–C angle *ipso* to a nitro group is large, consistent with the electron-withdrawing behaviour of this substituent, provided only that there are no *ortho* substituents.

(iii) The internal C–C–C angle *ipso* to I is close to 120°; mutually *ortho* amino and nitro groups are repulsive, as indicated here by the angles $Nn1-Cn1-Cn2$ and $Nn2-Cn2-Cn3$ in compound (II).

(iv) Mutually *ortho* I and nitro substituents are repulsive, as indicated here by the $I4-C4-C3$ angle in (III) and by the nitro conformation.

While no indications can be drawn from the present data concerning mutually *ortho* I and amino substituents, it is unfortunate that there appear to be no structures in the CSD for simple iodoanilines having no further substituents.

3.2. Supramolecular dimensions

3.2.1. Hydrogen bonds. It is noteworthy that in compound (II), where the charge-separated form (IIa) is significant, the intermolecular N–H...O hydrogen bonds are characterized by shorter H...O and N...O distances (Table 3) than those in compounds (I) and (III), where the development of comparable charge-separated forms is not possible. This is consistent with and supportive of the general concept of resonance-enhanced hydrogen bonding (Gilli *et al.*, 1994). Likewise, it is only in compound (II) that there is a C–H...O hydrogen bond, albeit a comparatively weak example as judged by the H...O and C...O distances.

3.2.2. Iodo...nitro interactions. The iodo...nitro interactions in compounds (I)–(III) display a wide variety of structural types, with an asymmetric three-centre interaction in (I) where the longer component is perhaps at the margin of significance, two similar two-centre interactions in (II), one for each independent molecule, and an unusual type of three-centre interaction in (III) involving two different I atoms linked to the same O atom, which is the same O that acts as the acceptor in the N–H...O hydrogen bond in (III). The I...O distances in two-centre I...nitro interactions are, in general, shorter than those in three-centre systems of I...(O)₂ type, as deduced not only from a study of iodo-nitro-arenesulfonamides (Kelly *et al.*, 2002) but also from an analysis of iodo...nitro interactions in compounds retrieved from the CSD (Allen & Kennard, 1993). The I...O distances in compounds (I) and (II) (Table 4) certainly conform to this pattern, while the two distances in the (I)₂...O system of compound (III) differ significantly from one another.

3.3. Supramolecular structures

The supramolecular structures of compounds (I)–(III) are characterized by a combination of N–H...O hydrogen bonds, two-centre and three-centre iodo...nitro interactions and aromatic π ... π stacking interactions (Tables 3 and 4); however, structurally significant C–H...O hydrogen bonds are generally absent. To codify the hydrogen-bonding motifs we employ the now-familiar graph-set notation (Etter, 1990; Bernstein *et al.*, 1995; Motherwell *et al.*, 1999), and for the iodo...nitro interactions we employ the recently described (Starbuck *et al.*, 1999) extension of this notation to encompass secondary bonding, wherein we regard the negatively polarized O atoms of the nitro group as ‘donors’ and the positively polarized I atoms as ‘acceptors’.

3.3.1. Compound (I). The supramolecular structure of compound (I) (Fig. 1) is characterized by hard hydrogen bonds of the N–H...O type, asymmetric three-centre I...NO₂ interactions and weak aromatic π ... π stacking interactions. The absence of intermolecular C–H...O hydrogen bonds may be ascribed firstly to the adequacy of the hard-hydrogen-bond donors, since there are equal numbers of N–H bonds and of nitro O acceptors, and secondly to the involvement of both O atoms in the iodo...nitro interaction. The hydrogen bonds and the iodo...nitro interactions together produce a chain of fused rings, while adjacent chains are linked by the π ... π stacking interactions.

Atom I2 in the molecule at (x, y, z) is linked to both O51 and O52 in the molecule at (1 + x, y, –1 + z), so generating by translation a chain parallel to [101], and pairs of these chains are linked by a single N–H...O hydrogen bond. Atom N1 at (x, y, z) acts as hydrogen-bond donor, *via* H1B, to O51 at (–x, 1 – y, 1 – z). Propagation of the hydrogen bond in combination with the I...nitro interactions generates a chain of fused centrosymmetric rings (Fig. 4) in which hydrogen-bonded R₂²(14) rings are centred at (n, 0.5, 0.5 – n) (n = zero or integer) and twelve-membered rings built from a combi-

nation of hydrogen bonds and $I \cdots O$ interactions are centred at $(0.5 - n, 0.5, n)$ ($n = \text{zero or integer}$).

The aryl ring of the molecule at (x, y, z) participates in aromatic $\pi \cdots \pi$ stacking interactions with the strictly parallel rings in molecules both at $(1 - x, 1 - y, 1 - z)$ and at $(1 - x, -y, 1 - z)$ (Fig. 5); the corresponding interplanar spacings are 3.410 (3) Å and 3.567 (3) Å, respectively, associated with ring-centroid offsets of 1.413 (3) Å and 1.430 (3) Å. In this way, the molecule at $(-x, 1 - y, 1 - z)$, which forms part of the reference $[10\bar{1}]$ chain, is linked to that at $(-1 + x, y, z)$, so generating a chain parallel to $[100]$, and to that at $(-1 + x, 1 + y, z)$, so producing a chain parallel to $[1\bar{1}0]$. The combination of chain motifs along $[100]$ and $[1\bar{1}0]$ and propagation of these two interactions by translation and inversion serves to link all of the $[10\bar{1}]$ chains into a single three-dimensional continuum.

3.3.2. Compound (II). Compound (II) crystallizes with $Z' = 2$ in space group $C2/c$. Each of the two molecular types (Fig. 2; the type 1 molecule contains I14 and the type 2

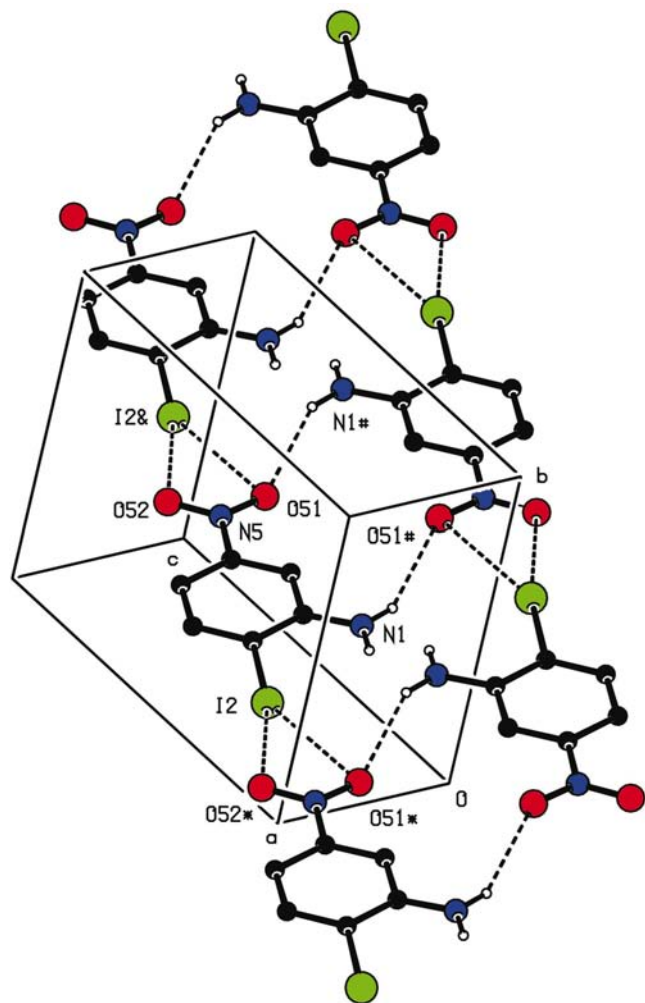


Figure 4
Part of the crystal structure of (I) showing formation of a chain of fused rings along $[10\bar{1}]$. For the sake of clarity, H atoms bonded to C are omitted. Atoms marked with (*), (#) or (&) are at the symmetry positions $(1 + x, y, -1 + z)$, $(-x, 1 - y, 1 - z)$ and $(-1 + x, y, 1 + z)$, respectively.

molecule contains I24) forms an independent two-dimensional substructure built from a combination of $N-H \cdots O$ hydrogen bonds and two-centre $I \cdots O$ interactions, but there are no direction-specific interactions between molecules of different types. Each type of molecule forms an intramolecular $N-H \cdots O$ hydrogen bond, producing an $S(6)$ motif, and the sheets formed by the two types of molecule are broadly similar, so we discuss in detail only that formed by the type 1 molecule.

Atom N11 in the type 1 molecule at (x, y, z) acts as hydrogen-bond donor *via* H11A to nitro O11 in the type 1 molecule at $(x, 1 + y, z)$, so generating by translation a $C(6)$ chain running parallel to the $[010]$ direction. Eight chains of type 1 molecules run through each unit cell, with two in each of the domains $0.17 < x < 0.20$, $0.30 < x < 0.33$, $0.67 < x < 0.70$ and $0.80 < x < 0.83$, and the chains within each domain of x are linked into sheets by means of two-centre iodo \cdots nitro interactions. Atom I14 in the type 1 molecule at (x, y, z) forms a short $I \cdots O$ contact with nitro O11 at $(x, -1 - y, \frac{1}{2} + z)$, while I14 at $(x, -1 - y, \frac{1}{2} + z)$ in turn forms a similar contact with O11 at $(x, y, 1 + z)$, so producing a chain running parallel to $[001]$ and generated by the c -glide plane at $y = -\frac{1}{2}$. The combination of the $[010]$ and $[001]$ chains generates a (100) sheet built from 20-membered rings (Fig. 6): if the notations for hydrogen bonds and for $I \cdots O$ interactions are combined, these rings are of $R_4^4(20)$ type. The molecules of type 2 form a very similar type of sheet (Fig. 7), and for each type of sheet there is also a single weak and possibly adventitious $C-H \cdots O$ hydrogen bond within the sheet (Table 3). The sheets formed by the type 2 molecules lie in the domains $0.05 < x < 0.07$, $0.43 < x < 0.45$, $0.55 < x < 0.57$ and

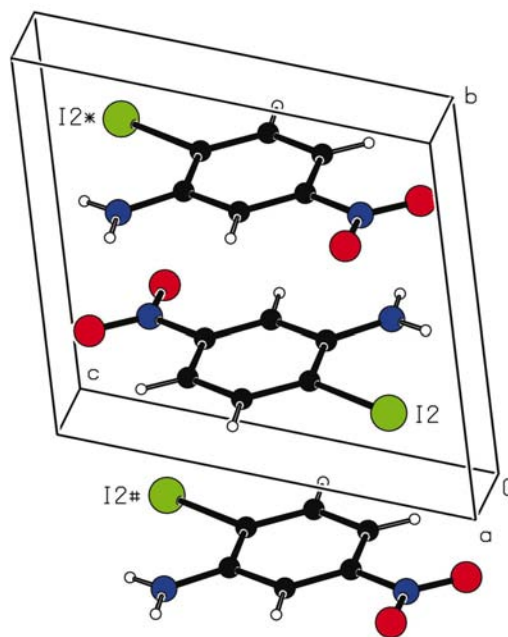
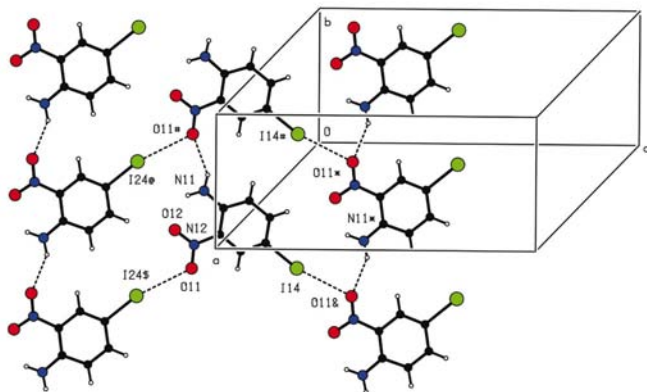
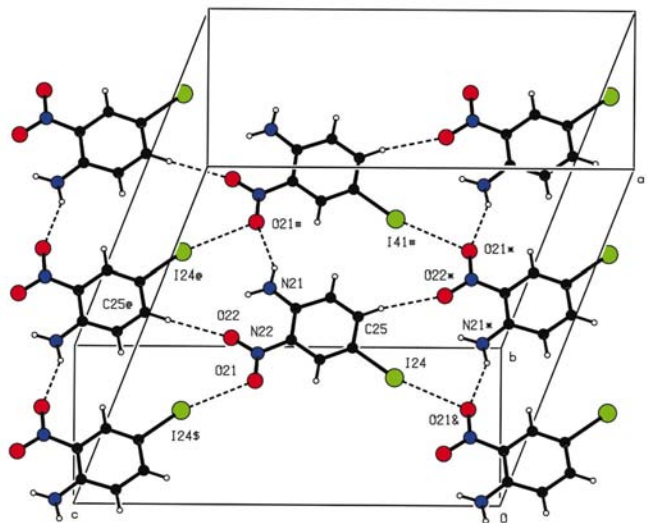


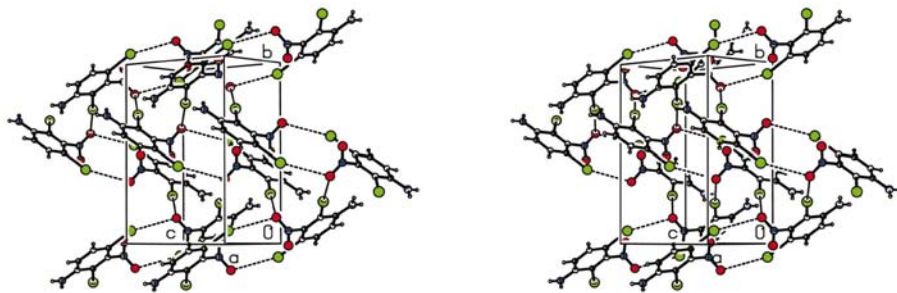
Figure 5
Part of the crystal structure of (I) showing the $\pi \cdots \pi$ stacking interactions. The atoms marked with (*) or (#) are at the symmetry positions $(1 - x, 1 - y, 1 - z)$ and $(1 - x, -y, 1 - z)$, respectively.


Figure 6

Part of the crystal structure of (II) showing the formation of a (100) sheet built from type 1 molecules only. For the sake of clarity, H atoms bonded to C are omitted. Atoms marked with (*), (#), (\$), (&) or (@) are at the symmetry positions $(x, -y, \frac{1}{2} + z)$, $(x, 1 + y, z)$, $(x, -1 - y, -\frac{1}{2} + z)$, $(x, -1 - y, \frac{1}{2} + z)$ and $(x, -y, -\frac{1}{2} + z)$, respectively.


Figure 7

Part of the crystal structure of (II) showing the formation of a (100) sheet built from type 2 molecules only. For the sake of clarity, H atoms bonded to C are omitted. Atoms marked with (*), (#), (\$), (&) or (@) are at the symmetry positions $(x, -y, -\frac{1}{2} + z)$, $(x, 1 + y, z)$, $(x, -1 - y, \frac{1}{2} + z)$, $(x, -1 - y, -\frac{1}{2} + z)$ and $(x, -y, \frac{1}{2} + z)$, respectively.


Figure 8

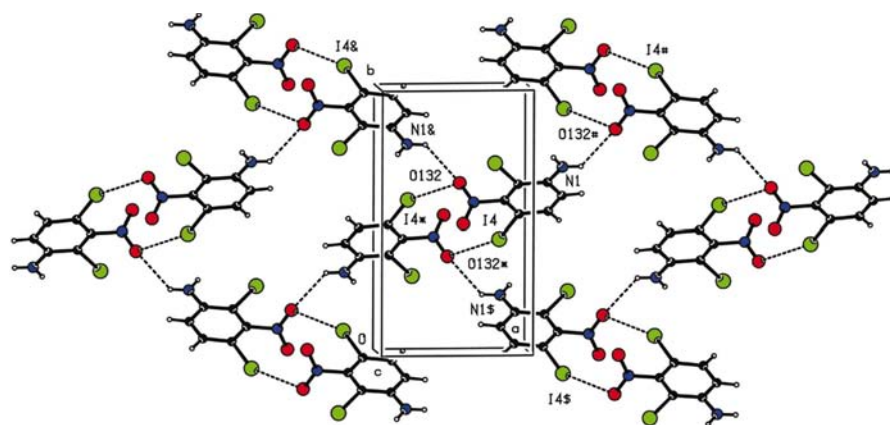
Stereoview of part of the crystal structure of (III) showing formation of a (100) sheet of $R_2^2(10)$ and $R_4^2(22)$ rings built from $I \cdots O$ interactions only.

$0.93 < x < 0.95$. Hence, the sheets of type 1 and type 2 molecules are stacked in pairs parallel to (100) thus, $\dots 11221122 \dots$, with adjacent sheets of a given type related within a pair by centres of inversion.

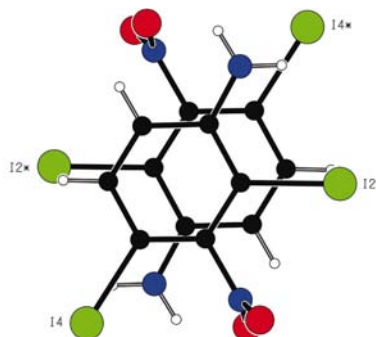
3.3.3. Compound (III). In compound (III) (Fig. 3), one of the nitro O atoms, O132, not only acts as acceptor in an intermolecular $N-H \cdots O$ hydrogen bond, but also participates in two intermolecular iodo \cdots nitro interactions involving I atoms from two different molecules. By contrast, O131 plays no role whatsoever in the intermolecular aggregation. Also unexpected is the non-participation of amino H1A in the intermolecular hydrogen bonding (Table 3). These three intermolecular interactions, one hydrogen bond and two distinct two-centre $I \cdots O$ interactions, together generate a three-dimensional framework structure, which is readily analyzed using the substructure approach (Gregson *et al.*, 2000).

Atom I4 in the molecule at (x, y, z) forms an $I \cdots O$ interaction with O132 at $(1 - x, 1 - y, 1 - z)$, so generating a centrosymmetric $R_2^2(10)$ dimeric unit centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and it is convenient to treat this zero-dimensional substructural 'dimer' as the core building unit of the structure. The second $I \cdots O$ interactions, which involves I2 rather than I4, generates a two-dimensional substructure. The atoms I2 in the reference dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ are at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, and these two atoms are involved in short $I \cdots O$ interactions with the O132 atoms at $(x, \frac{3}{2} - y, \frac{1}{2} + z)$ and $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, respectively, which themselves lie in the dimeric units centred at $(\frac{1}{2}, 1, 1)$ and $(\frac{1}{2}, 0, 0)$, respectively. The two O132 atoms in the dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, are in turn involved in $I \cdots O$ interactions with atoms I2 at $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$ and $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$, respectively, and these I atoms are components of the dimers centred at $(\frac{1}{2}, 1, 0)$ and $(\frac{1}{2}, 0, 1)$. Thus, each $R_2^2(10)$ dimeric unit is linked *via* the various $I2 \cdots O132$ interactions to four other dimers, and propagation of these interactions generates a continuous sheet parallel to (100) (Fig. 8) in which the $R_2^2(10)$ rings alternate in checkerboard fashion with $R_4^2(22)$ rings, where the four negatively charged nitro O atoms are regarded as the donors and the six positively charged I as the acceptors.

A second sheet results from the action of the hydrogen bonds: each dimer unit accepts two $N-H \cdots O$ hydrogen bonds and contains the donors in two other such bonds. The amino N-atoms at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ both lie in the dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and they act as hydrogen-bond donors, *via* H1B, to atoms O132 at $(1 + x, \frac{3}{2} - y, \frac{1}{2} + z)$ and $(-x, -\frac{1}{2} + y, \frac{1}{2} - z)$, respectively, which are components of the dimeric units centred at $(\frac{3}{2}, 1, 1)$ and $(-\frac{1}{2}, 0, 0)$, respectively. Similarly, the atoms O132 at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ accept hydrogen bonds from amino N atoms at $(-1 + x, \frac{3}{2} - y, -\frac{1}{2} + z)$ and $(2 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$, which lie in the dimers centred at $(-\frac{1}{2}, 1, 0)$ and


Figure 9

Part of the crystal structure of (III) showing the formation of a $(10\bar{2})$ sheet of $R_2^2(10)$ and $R_6^0(30)$ rings. The atoms marked with (*), (#), (\$) or (&) are at the symmetry positions $(1-x, 1-y, 1-z)$, $(1+x, \frac{3}{2}-y, \frac{1}{2}+z)$, $(2-x, -\frac{1}{2}+y, \frac{3}{2}-z)$ and $(-1+x, \frac{3}{2}-y, -\frac{1}{2}+z)$, respectively.


Figure 10

Part of the crystal structure of (III), showing the $\pi \cdots \pi$ stacking interaction. The atoms marked with (*) are at the symmetry position $(2-x, 1-y, 2-z)$.

$(\frac{3}{2}, 0, 1)$, respectively. Propagation of the hydrogen bond in combination with the $I \cdots O$ interaction that generates the dimer produces a sheet parallel to $(10\bar{2})$ (Fig. 9), in which the $R_2^2(10)$ rings alternate in checkerboard fashion with centrosymmetric $R_6^0(30)$ rings incorporating hydrogen bonds and $I \cdots O$ interactions. It may also be noted that the $N-H \cdots O$ hydrogen bond alone produces a one-dimensional substructure in the form of a $C(7)$ chain running parallel to the $[201]$ direction, generated by the glide plane at $y = 0.75$. If in both the (100) sheet and the $(10\bar{2})$ sheet the $R_2^2(10)$ dimers are regarded as the nodes of the resulting nets, then these nets are both of (4,4) type (Batten & Robson, 1998). The combination of the (100) and $(10\bar{2})$ sheets is sufficient to generate a continuous three-dimensional framework.

This framework is further reinforced by aromatic $\pi \cdots \pi$ stacking interactions between molecules at (x, y, z) and $(2-x, 1-y, 2-z)$, where the interplanar spacing and the centroid separation are 3.503 (3) Å and 3.636 (3) Å, respectively, corresponding to a centroid offset of only 0.902 (3) Å (Fig. 10): the mutual disposition of the stacked rings neatly accommodates the nearly orthogonal nitro groups.

3.3.4. General comments on the supramolecular structures. It is useful to summarize here the essential features of

the supramolecular structures of compounds (I)–(III), in order to compare these with the two related compounds (IV) and (V).

The hydrogen bond in (I) generates a finite (zero-dimensional) dimer, while the $iodo \cdots nitro$ interaction generates single chains: the combined effect of these two interactions is the formation of a strictly one-dimensional substructure (Fig. 4), while the $\pi \cdots \pi$ stacking interaction links the one-dimensional fragments into a three-dimensional whole. In (II) and in both polymorphs of (V), a compound which is isomeric with both (I) and (II), the $N-H \cdots O$ hydrogen bonds and the $iodo \cdots nitro$ interactions individually form chains,

and in combination they form sheets, but in each of these three structures the effects of the $\pi \cdots \pi$ stacking interactions are different. In the orthorhombic modification of (V), the stacking interactions link the sheets into a single three-dimensional framework; in the triclinic polymorph of (V), the sheets are pairwise linked by the stacking interactions forming bi-layers; in (II), there are no $\pi \cdots \pi$ stacking interactions and the structure is based on isolated sheets. One of the $iodo \cdots nitro$ interactions in (III) generates a finite dimer, and these units are linked into sheets of different type and direction by the second $iodo \cdots nitro$ interaction and by the hydrogen bond, so that a three-dimensional structure results from these interactions alone. This is simply reinforced by the $\pi \cdots \pi$ stacking interactions.

4. Concluding comments

The structures discussed here show that even in simple isomeric series, such as compounds (I), (II) and (V), the patterns of supramolecular aggregation and even the nature of the interactions involved may differ substantially. In effect, the aggregation pattern for any one compound is not readily predicted from knowledge of the patterns in the others, even those of its isomers. Contrasts of this kind provide continuing challenges to attempts to predict from first principles the crystal structures of comparatively simple molecular compounds (Lommerse *et al.*, 2000).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, UK. The authors thank the staff of the service for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants that have provided computing facilities for this work. SJG, SPF and JLW thank CNPq and FAPERJ for financial support.

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