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Isomeric *N*-(iodophenyl)nitrophthalimides: interplay of C—H···O hydrogen bonds, iodo···nitro and iodo···carbonyl interactions, and aromatic π···π stacking interactions

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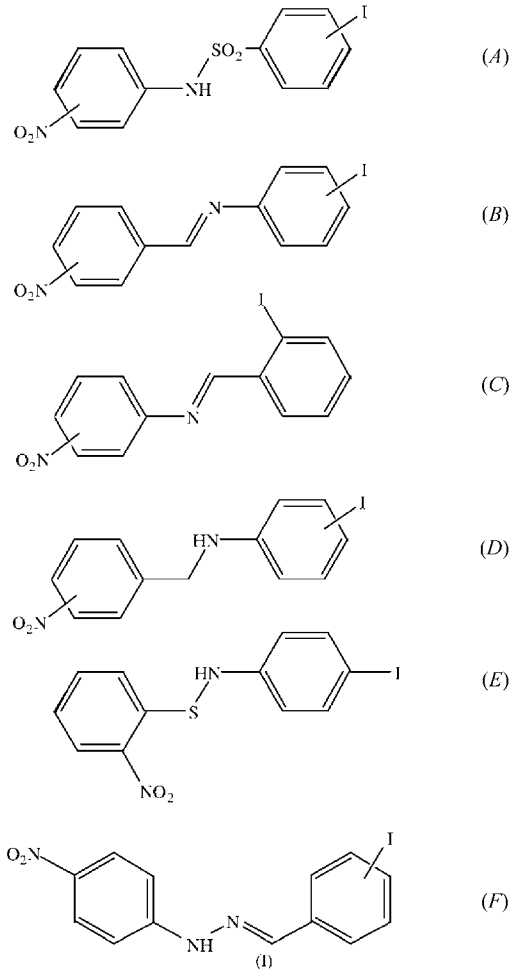
The six isomeric *N*-(iodophenyl)nitrophthalimides, $C_{14}H_7IN_2O_4$, have been synthesized and the structures of five of them are reported. In *N*-(4-iodophenyl)-4-nitrophthalimide [(I), orthorhombic $P2_12_12_1$] the molecules are linked into sheets by a combination of four independent C—H···O hydrogen bonds, but I···O interactions are absent. The isomers *N*-(3-iodophenyl)-4-nitrophthalimide [(II), monoclinic $P2_1/c$] and *N*-(2-iodophenyl)-4-nitrophthalimide [(III), monoclinic $P2_1/n$] both form sheets, but in (II) the molecules are linked by a combination of one two-centre iodo···nitro interaction and one C—H···O hydrogen bond into sheets containing $R_4^4(30)$ rings, while in (III) they are linked by an iodo···carbonyl interaction and a C—H···O hydrogen bond into sheets or $R_4^4(26)$ rings. Three-dimensional supramolecular structures are formed in both *N*-(4-iodophenyl)-3-nitrophthalimide [(IV), monoclinic $P2_1/n$] and *N*-(3-iodophenyl)-3-nitrophthalimide [(V), orthorhombic, $P2_12_12_1$]. In (IV) the molecules are linked by a three-centre iodo···nitro interaction, three C—H···O hydrogen bonds and an aromatic π···π stacking interaction, but the framework in (V) is generated by a two-centre iodo···nitro interaction and only two C—H···O hydrogen bonds: aromatic π···π stacking interactions are absent from (V).

1. Introduction

In the course of our continuing investigation of the interplay between hard and soft hydrogen bonds (Braga *et al.*, 1995; Desiraju & Steiner, 1999), aromatic π···π stacking interactions and iodo···nitro interactions in simple bis-arene systems, we have studied the supramolecular structures of an extensive series of iodoaryl–nitroaryl compounds, many in several isomeric forms, including examples of sulfonamides [(*A*), see Scheme 1; Kelly *et al.*, 2002], benzylideneanilines [(*B*) Glidewell, Howie *et al.*, 2002, and (*C*) Wardell *et al.*, 2002], benzylanilines [(*D*) Glidewell, Low *et al.*, 2002; Glidewell, Low, Skakle, Wardell & Wardell, 2004], benzenesulfanylanilines [(*E*) Glidewell *et al.*, 2003*a*], and phenylhydrazones [(*F*) Glidewell *et al.*, 2003*b*, 2004*a*].

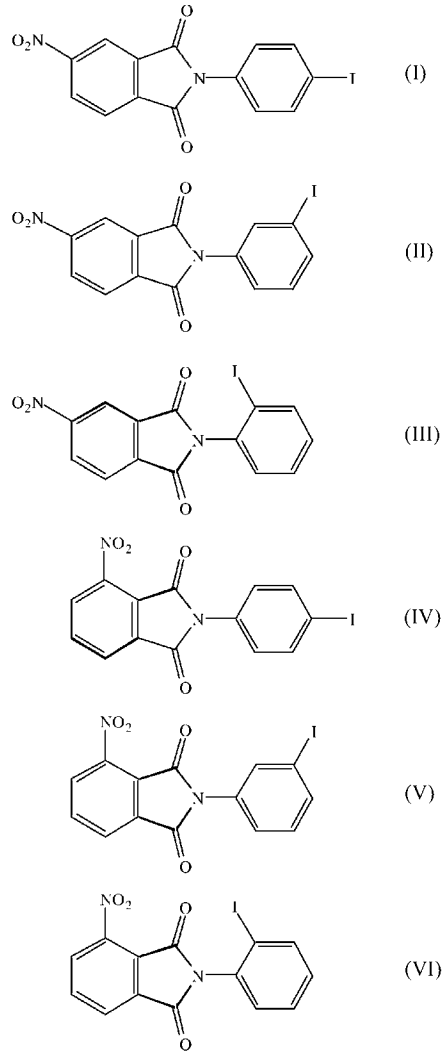
For types (*A*), (*B*) and (*D*) we have been able to study an extended series of isomeric compounds, including four isomeric iodoarene–nitroarenesulfonamides (*A*), eight isomeric nitrobenzylidene–iodoanilines (*B*) and six isomeric iodo-*N*-(nitrobenzyl)anilines (*D*). Isomeric compounds of type (*A*) can form molecular ladders built from N—H···O(nitro) and C—H···O hydrogen bonds and iodo···sulfonyl interactions; chains of edge-fused rings built from N—H···O=S hydrogen bonds and iodo···nitro interactions, which are further linked into sheets by C—H···O hydrogen bonds; and three-dimensional frameworks built

from C—H···O hydrogen bonds and iodo···nitro interactions from which, surprisingly, N—H···O hydrogen bonds are wholly absent. The isomers of type (*B*) can crystallize as



Scheme 1

isolated molecules with no direction-specific interactions between them; they can form simple chains built from C—H···O hydrogen bonds which may, in some cases only, be further linked by aromatic $\pi\cdots\pi$ stacking interactions; and different combinations of C—H···O hydrogen bonds and iodo···nitro interactions can generate either sheets of three-dimensional framework structures. Isomeric molecules of type (*D*) can be linked into simple chains by C—H···O hydrogen bonds; into molecular ladders by a combination of N—H···O and C—H···O hydrogen bonds and iodo···nitro and aromatic $\pi\cdots\pi$ stacking interactions; into sheets either by the combination of C—H···O and N—H···π(arene) hydrogen bonds and aromatic $\pi\cdots\pi$ stacking interactions or by the combination of N—H···O, C—H···O and C—H···π(arene) hydrogen bonds; or, finally, into three-dimensional frameworks containing multiple direction-specific interactions which sometimes include and sometimes exclude N—H···O hydrogen bonds. It is important to note that, within each series of isomers, no two compounds manifest the same selection of direction-specific intermolecular interactions and, again within each series, no one structure is readily predictable from a knowledge of all the others. With these observations in mind, we have now extended this study to isomeric examples of a more rigid system, namely the isomeric *N*-(iodophenyl)nitrophthalimides (I)–(VI) (see Scheme 2).

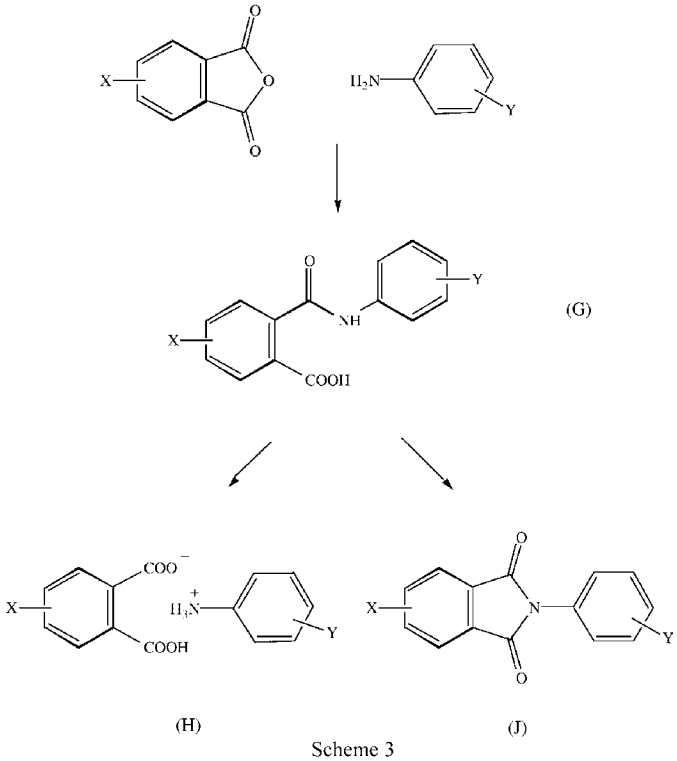


Scheme 2

These compounds have been selected for study for two reasons. Firstly, because hard hydrogen bonds are excluded, so that the only plausible direction-specific intermolecular interactions are C—H···O hydrogen bonds, albeit with two possible types of acceptor O, carbonyl and nitro; I···O interactions, again with the same two types of acceptor; and aromatic $\pi\cdots\pi$ stacking interactions. Secondly, because the molecular frameworks have only a single degree of torsional freedom, about the *N*-aryl bond, so restraining somewhat the range of possible intermolecular contacts.

N-Arylphthalimides are formed in a very general reaction between phthalic anhydrides and anilines. The primary intermediate in such a reaction is an acid of type (*G*), see Scheme 3; hydrolysis of (*G*) can give an anilinium salt (*H*) or, alter-

natively, loss of water from (*G*) can give the *N*-arylphthalimide (*J*). We have recently reported the supramolecular structures of representative examples of type (*G*) (Glidewell *et al.*, 2004*b*) and (*H*) (Glidewell *et al.*, 2003*c*), while the six isomeric compounds (I)–(VI) discussed in this paper are representative of form (*J*).



Scheme 3

2. Experimental

2.1. Synthesis

Finely ground intimate mixtures containing equimolar quantities of a nitrophthalic anhydride and the appropriate iodoaniline were heated, in the absence of solvent, until the evolution of water had ceased. The resulting solids were cooled and then heated in acetone containing activated charcoal for 10 min. These solutions were filtered, the solvent was removed from the filtrate and the resulting solids were then recrystallized to give pure samples of the compounds (I)–(VI). The solvents employed, m.p.s and ν(CO) values (cm^{-1}) in KBr discs are as follows: For (I): ethyl acetate, 493–394 K, 1776w and 1723s; for (II): butanone, 549–553 K, 1780w, 1771w and 1717s; for (III): 1,2-dichloroethane, 444–446 K, 1783m and 1728s,br; for (IV): ethanol, 461–463 K, 1780m, 1724s and 1698sh; for (V): ethanol, 524–526 K, 1783m, 1731s and 1720s; for (VI): acetone, 432–433 K, 1784m and 1731s,br. Crystals of (I)–(V) suitable for single-crystal X-ray diffraction were selected directly from the prepared samples. Despite many attempts using a wide range of solvents, no suitable crystals of (VI) could be obtained.

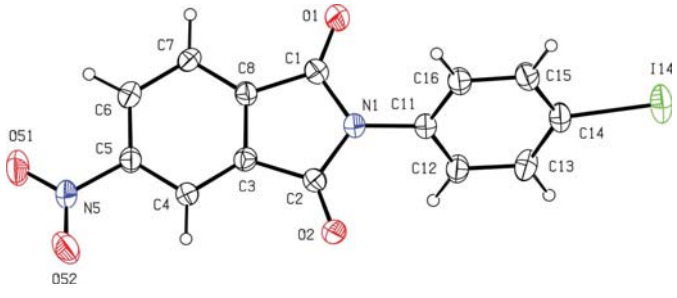


Figure 1
A molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

2.2. Data collection, structure solution and refinement

Details of cell data, data collection and structure solution and refinement are summarized in Table 1 (Blessing, 1995, 1997; Bruker, 1998, 2000; Ferguson, 1999; McArdle, 2003; Nonius, 1997; Otwinowski & Minor, 1997; Sheldrick, 1997). The space groups for (I)–(V) were all assigned uniquely from the systematic absences. The structures were all solved by direct methods using *SHELXS*97 (Sheldrick, 1997) and refined on F^2 with all data using *SHELXL*97 (Sheldrick, 1997). A weighting scheme based upon $P = (F_o^2 + 2F_c^2)/3$ was employed in order to reduce statistical bias (Wilson, 1976). All H atoms were located from difference maps and all were included in the refinements as riding atoms, with C—H distances 0.93 Å at 291 (2) K and 0.95 Å at 120 (2) K, and with U_{iso}(H) = 1.2U_{eq}(C). The molecules all lie in general positions and are all fully ordered. For (I) and (V) the correct enantiomorph was selected using the Flack parameter (Flack, 1983): the final values were −0.02 (3) and −0.03 (2), respectively.

Supramolecular analyses were made and the diagrams were prepared with the aid of *PLATON* (Spek, 2003). Figs. 1–16 show the independent components of (I)–(V) with the atom-labelling schemes and aspects of their supramolecular structures. The dihedral angles are given in Table 2, details of the hydrogen bonding are in Table 3 and details of the intermolecular I···O contacts are in Table 4.[1]

3. Results and discussion

3.1. Molecular conformations

The molecular conformations are defined by two dihedral angles, that between the *N*-phenyl ring and the heterocyclic ring, and that between the nitro group and the carbocyclic ring of the phthalimido unit (Table 2). The dihedral angle between the two ring planes varies over a rather wide range, between 40.2 (2) and 82.0 (2)°. For comparison, the corresponding angle in the unsubstituted *N*-phenylphthalimide [CSD (Allen, 2002) refcode ZZZAWJ10; Magomedova *et al.*, 1981] itself is 58.2° (no s.u.s were quoted). It may be noted here that the

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM5022). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	(I)	(II)	(III)	(IV)	(V)
Crystal data					
Chemical formula	$C_{14}H_7IN_2O_4$	$C_{14}H_7IN_2O_4$	$C_{14}H_7IN_2O_4$	$C_{14}H_7IN_2O_4$	$C_{14}H_7IN_2O_4$
M_r	394.12	394.12	394.12	394.12	394.12
Cell setting, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Orthorhombic, $P2_12_12_1$
a, b, c (Å)	4.1092 (1), 6.7843 (1), 48.6775 (10)	7.9592 (9), 6.5708 (7), 25.648 (3)	13.4591 (6), 7.6018 (3), 14.7086 (7)	7.52380 (10), 22.6556 (5), 7.92010 (10)	6.8070 (1), 13.0955 (2), 14.8369 (3)
β (°)	90.00	97.960 (3)	110.592 (1)	107.3824 (16)	90.00
V (Å^3)	1357.03 (5)	1328.4 (3)	1408.74 (11)	1288.38 (4)	1322.58 (4)
Z	4	4	4	4	4
D_x (Mg m^{-3})	1.929	1.971	1.858	2.032	1.979
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	3015	4808	5040	2918	2984
θ range (°)	3.0–27.5	2.6–32.6	2.5–32.5	3.0–27.5	3.1–27.5
μ (mm^{-1})	2.38	2.43	2.29	2.50	2.44
Temperature (K)	298 (2)	291 (2)	291 (2)	120 (2)	120 (2)
Crystal form, colour	Plate, yellow	Plate, brown	Block, orange	Block, colourless	Block, colourless
Crystal size (mm)	0.28 × 0.04 × 0.03	0.29 × 0.11 × 0.02	0.40 × 0.32 × 0.30	0.40 × 0.25 × 0.20	0.50 × 0.40 × 0.40
Data collection					
Diffractometer	Kappa-CCD	Bruker SMART 1000CCD area detector	Bruker SMART 1000CCD area detector	Kappa-CCD	Kappa-CCD
Data collection method	φ and ω scans with κ offsets	φ and ω scans	φ and ω scans	φ and ω scans with κ offsets	φ and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{min}	0.749	0.539	0.424	0.412	0.319
T_{max}	0.936	0.953	0.503	0.602	0.376
No. of measured, independent and observed reflections	9768, 3015, 2760	13 842, 4808, 1564	14 517, 5040, 3064	7971, 2918, 2724	8214, 2984, 2880
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.070	0.086	0.017	0.039	0.038
θ_{max} (°)	27.5	32.6	32.5	27.5	27.5
Range of h, k, l	$-3 \Rightarrow h \Rightarrow 5$ $-8 \Rightarrow k \Rightarrow 8$ $-63 \Rightarrow l \Rightarrow 62$	$-11 \Rightarrow h \Rightarrow 12$ $-6 \Rightarrow k \Rightarrow 9$ $-36 \Rightarrow l \Rightarrow 38$	$-20 \Rightarrow h \Rightarrow 20$ $-11 \Rightarrow k \Rightarrow 11$ $-18 \Rightarrow l \Rightarrow 22$	$-9 \Rightarrow h \Rightarrow 9$ $-29 \Rightarrow k \Rightarrow 27$ $-10 \Rightarrow l \Rightarrow 10$	$-8 \Rightarrow h \Rightarrow 8$ $-15 \Rightarrow k \Rightarrow 17$ $-17 \Rightarrow l \Rightarrow 19$
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.119, 1.21	0.049, 0.097, 0.77	0.043, 0.134, 1.03	0.022, 0.052, 1.09	0.025, 0.054, 1.06
No. of reflections	3015	4808	5040	2918	2984
No. of parameters	190	190	190	190	190
H-atom treatment	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.2598P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.032P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0607P)^2 + 0.5997P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0071P)^2 + 1.5414P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0224P)^2 + 0.3484P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.0001	<0.0001	<0.0001	0.003	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.63	0.70, −0.35	1.02, −0.58	0.45, −0.68	0.33, −0.75
Absolute structure	Flack (1983), 1917 Friedel pairs	–	–	–	Flack (1983), 1266 Friedel pairs
Flack parameter	−0.02 (3)	–	–	–	−0.028 (17)

structure of *N*-phenylphthalimide contains no direction-specific intermolecular interactions of any kind: C—H···N, C—H···O and C—H···π(arene) hydrogen bonds and aromatic $\pi\cdots\pi$ stacking interactions are all absent. Hence, it is not necessarily appropriate to attempt a detailed interpretation of the variation in the inter-ring dihedral angle in terms of direction-specific intermolecular forces.

For a nitro group bonded directly to an aromatic ring, the minimum energy conformation for the isolated molecules is expected to be fully planar, as for the archetypal compound nitrobenzene. In gaseous nitrobenzene, the barrier to rotation of the nitro group around the C—N bond is modest: determinations based on microwave spectroscopy, Raman spectroscopy and electron diffraction broadly concur in estimating this barrier at around 15 kJ mol^{-1} (Domenicano *et al.*, 1990). Thus, the minimum-energy planar conformation of nitroarenes can readily be perturbed, for example, by hydrogen bonds or I···O interactions involving the nitro O atoms. In

Table 2
Dihedral angles (°).

For (I)–(III) n = 5, for (IV) and (V) n = 4.

	(N1,C1,C2,C3,C8)^(C11–C16)	(Cn,Nn,On1,On2)^(C3–C8)
(I)	61.1 (3)	8.9 (3)
(II)	51.7 (2)	12.8 (3)
(III)	82.0 (2)	7.7 (2)
(IV)	40.2 (2)	34.8 (2)
(V)	48.1 (2)	30.6 (2)

(I)–(V) the twist angles of the nitro groups appear to fall into two groups: in (I)–(III) the twist does not exceed 13°, while for both (IV) and (V) it exceeds 30° (Table 2). In the first of these groups, nitro O atoms participate in C—H···O hydrogen bonds in (I) and in iodo···nitro interactions in (II) (see below, §3.3), but in neither of these interactions in (III): of the second group, the nitro O atoms participate in iodo···nitro interaction in both (IV) and (V), but in C—H···O hydrogen bonds only in (IV). Again, it is difficult to discern any pattern in the intermolecular interactions which can provide a convincing interpretation of the conformational characteristics.

One consequence of these conformations is that all the molecules are chiral, although this chirality has no chemical significance. Compounds (II), (III) and (IV) all crystallize in centrosymmetric space groups containing equal numbers of the two enantiomeric molecular forms, but for (I) and (V), which both crystallize in the space group $P2_12_12_1$, a given crystal contains only one enantiomorph. Thus, these two compounds are possible examples of conglomerate crystallization (Bernal & Cetrullo, 1990).

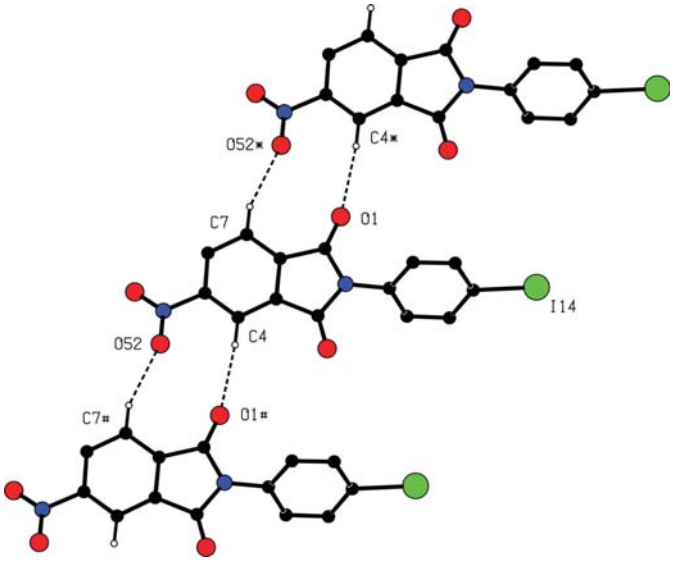


Figure 2
Part of the crystal structure of (I) showing the formation of a chain of rings along [1$\bar{1}$0]. For the sake of clarity, the H atoms not involved in the motifs shown have been omitted, as has the unit-cell box. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-1+x, 1+y, z)$ and $(1+x, -1+y, z)$, respectively.

Table 3
Hydrogen-bonding geometry and short intermolecular contacts (Å, °).

D—H···A	H···A	D···A	D—H···A	Motif	Direction
(I)					
C4—H4···O1^{i}	2.61	3.531 (6)	171	C(6)	[1$\bar{1}$0]
C6—H6···O51^{ii}	2.50	3.219 (7)	134	C(5)	[010]
C7—H7···O52^{iii}	2.46	3.342 (8)	159	C(6)	[1$\bar{1}$0]
C15—H15···O2^{iv}	2.61	3.211 (6)	123	C(7)	[010]
(II)					
C16—H16···O2^{iv}	2.47	3.181 (6)	133	C(7)	[001]
(III)					
C7—H7···O2^{v}	2.60	3.449 (4)	152	C(6)	[101]
(IV)					
C6—H6···O2^{vi}	2.57	3.177 (3)	122	C(7)	[001]
C12—H12···O41^{vii}	2.56	3.487 (3)	166	C(9)	[101]
C16—H16···O1^{viii}	2.54	3.484 (3)	170	R_2^2(12)	–
(V)					
C6—H6···O2^{ix}	2.44	3.064 (3)	123	C(7)	[001]
C16-H16···O2^{x}	2.44	3.204 (3)	138	C(6)	[100]

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

3.2. Supramolecular structures

3.2.1. Hydrogen-bond dimensions. The question of whether an intermolecular C—H···O contact should or should not be

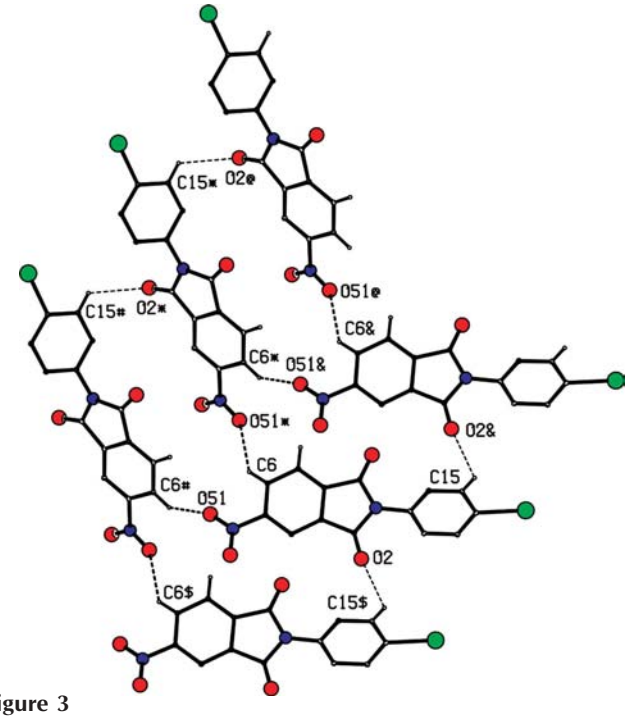


Figure 3
Part of the crystal structure of (I) showing the formation of a $C(5)C(7)[R_3^3(22)]$ chain of edge-fused rings along [010]. For the sake of clarity, the H atoms not involved in the motifs shown are omitted, as is the unit-cell outline. The atoms marked with an asterisk (*), a hash (#), a dollar sign ($), an ampersand (&) or an at sign (@) are at the symmetry positions $(1-x, \frac{1}{2}+y, \frac{3}{2}-z)$, $(1-x, -\frac{1}{2}+y, \frac{3}{2}-z)$, $(x, -1+y, z)$, $(x, 1+y, z)$ and $(1-x, \frac{3}{2}+y, \frac{3}{2}-z)$, respectively.

Table 4
Geometry of iodo···nitro and iodo···carbonyl interactions (Å, °).

	I···O	C—I···O	I···O—N/C	Motif	Direction
(II)					
C13—I13···O51^{i}	3.443 (4)	152.5 (2)	104.1 (3)	*C*(11)	[001]
(III)					
C12—I12···O1^{ii}	3.269 (2)	153.4 (2)	142.8 (2)	*C*(6)	[010]
(IV)					
C14—I14···O41^{iii}	3.451 (2)	154.92 (7)	97.4 (2)	*C*(11)	[010]
C14—I14···O42^{iii}	3.416 (2)	166.64 (7)	99.2 (2)	*C*(11)	[010]
(V)					
C13—I13···O42^{iv}	3.385 (2)	155.08 (8)	107.4 (2)	*C*(10)	[010]

Symmetry codes: (i) $x, -\frac{1}{2}-y, -\frac{1}{2}+z$; (ii) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{5}{2}-z$; (iv) $-x, \frac{1}{2}+y, \frac{3}{2}-z$.

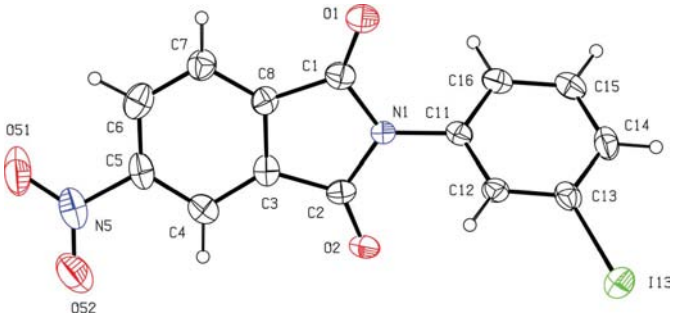


Figure 4
A molecule of (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

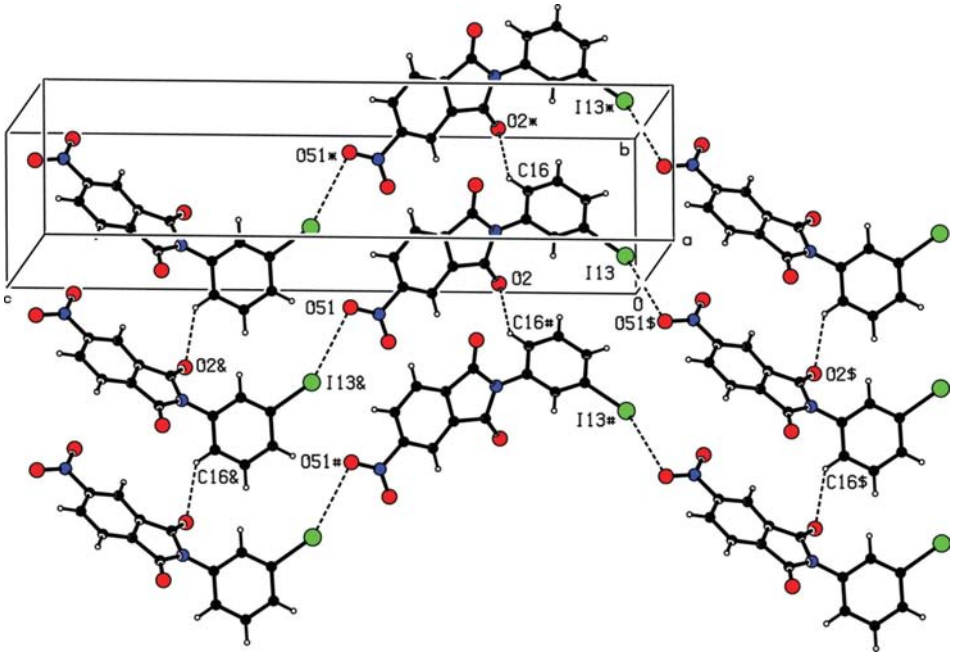


Figure 5
Part of the crystal structure of (II) showing the formation of a (100) sheet of $R_4^4(30)$ rings by a combination of [010] and [001] chains. The atoms marked with an asterisk (*), a hash (#), a dollar sign ($) or an ampersand (&) are at the symmetry positions $(x, 1+y, z)$, $(x, -1+y, z)$, $(x, -\frac{1}{2}-y, -\frac{1}{2}+z)$ and $(x, -\frac{1}{2}-y, \frac{1}{2}+z)$, respectively.

regarded as a hydrogen bond is often in practice a matter of judgement and preference. In Table 3 we list the results of a search for all such contacts in the compounds whose structures are described here for which the H···O distances are less than 2.65 Å and for which the C—H···O angles are above 100°: in the event no contact had a C—H···O angle less than 120°. While some of these interactions, for example that formed by the C7 atom in (I), would probably find fairly general acceptance as hydrogen bonds, others, such as that involving the C15 atom in the same compound, possibly might not. For this reason, we consider these interactions as a whole as hydrogen bonds and short intermolecular contacts. It is perhaps worth pointing out here that in (I) the two longer interactions, formed by the C4 and C15 atoms, have the effect of cooperatively reinforcing the shorter and therefore probably stronger bonds formed by the C7 and C6 atoms, respectively: it is recognized that these long interactions may, indeed, be adventitious consequences of the shorter interactions.

3.2.2. Compound (I). The supramolecular structure of (I) (Fig. 1) depends solely upon C—H···O hydrogen bonds: there are no significant I···O contacts present in the structure and C—H···π(arene) hydrogen bonds and aromatic $\pi\cdots\pi$ stacking interactions are also absent.

Atom C7 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the nitro O52 atom in the molecule at $(-1+x, 1+y, z)$, thereby generating by translation a $C(6)$ chain (Bernstein *et al.*, 1995) running parallel to the $[1\bar{1}0]$ direction. This chain is modestly reinforced by a second C—H···O interaction in which, although the H···O and C···O distances are both rather long (Table 3), the C—H···O fragment is nearly linear: the C4 atom at (x, y, z) acts as a donor to the carbonyl O1 atom in the molecule at $(1+x, -1+y, z)$, thus generating by translation a second $C(6)$ chain parallel to $[1\bar{1}0]$. The combination of the two $[1\bar{1}0]$ motifs then generates a $C(6)C(6)[R_2^2(10)]$ chain of rings (Fig. 2). This can alternatively be regarded as a molecular ladder, in which the $C(6)$ chains form the uprights and the phthalimido units provide the rungs.

A second pair of C—H···O interactions, albeit having much smaller C—H···O angles than those found in the first pair, generates a second chain of rings, this time running parallel to the [010] direction. The phthalimide C6 atom in the molecule at (x, y, z) acts as a hydrogen-bond donor to the nitro O51 atom in the molecule at $(1-x, \frac{1}{2}+y, \frac{3}{2}-z)$, thus producing a $C(5)$ chain generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{3}{4})$ (Fig. 3). This is reinforced by a second,

longer C—H···O interaction in which the phenyl C15 atom at (x, y, z) acts as a donor to the carbonyl O2 atom in the molecule at $(x, 1 + y, z)$, thus generating by translation a $C(7)$ chain. The combination of the two [010] motifs then generates a $C(5)C(7)[R_3^3(22)]$ chain of edge-fused rings. The combination of the [010] and [1$\bar{1}$0] chains generates a (001) sheet built solely from C—H···O interactions, but there are no direction-specific interactions between adjacent sheets.

3.2.3. Compound (II). The supramolecular structure of (II) (Fig. 4) is two-dimensional and it arises from a combination of two simple chain motifs generated respectively by a two-centre iodo···nitro interaction (Table 4) and a single C—H···O hydrogen bond (Table 3): there are neither C—H···π(arene) hydrogen bonds nor aromatic $\pi\cdots\pi$ stacking interactions in the structure of (II).

The I13 atom in the molecule at (x, y, z) forms a short contact with the nitro O51 atom in the molecule at $(x, -\frac{1}{2} - y, -\frac{1}{2} + z)$, thus producing a $C(11)$ chain (Starbuck *et al.*, 1999) running parallel to the [001] direction: this chain is generated by the *c*-glide plane at $y = -0.25$ and it lies in the domain $0.07 < x < 0.45$ (Fig. 5). A second antiparallel chain, related to the first by inversion, is generated by the *c*-glide plane at $y = 0.25$ and it lies in the domain $0.55 < x < 0.93$. Within each of these domains the chains are linked by the C—H···O hydrogen bond: the phenyl C16 atom in the molecule at (x, y, z) acts as a hydrogen-bond donor to the carbonyl O2 atom in the molecule at $(x, 1 + y, z)$, so generating by translation a $C(6)$ chain running parallel to the [010] direction. The combination of the [010] and [001] chains generates a (100) sheet in the form of a (4,4) net (Batten & Robson, 1998) built from a single type of $R_4^4(30)$ ring (Fig. 5). One sheet lies in each

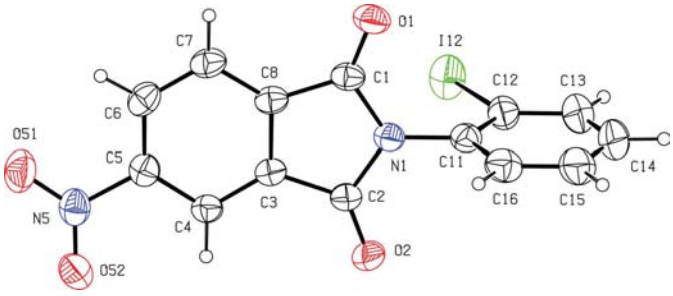


Figure 6
A molecule of (III) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

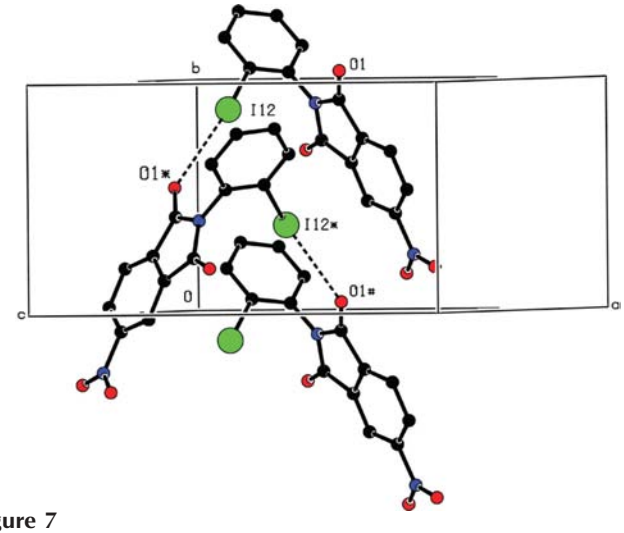


Figure 7
Part of the crystal structure of (III) showing the formation of an I···O chain along [010]. For the sake of clarity, the H atoms have been omitted. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ and $(x, -1 + y, z)$, respectively.

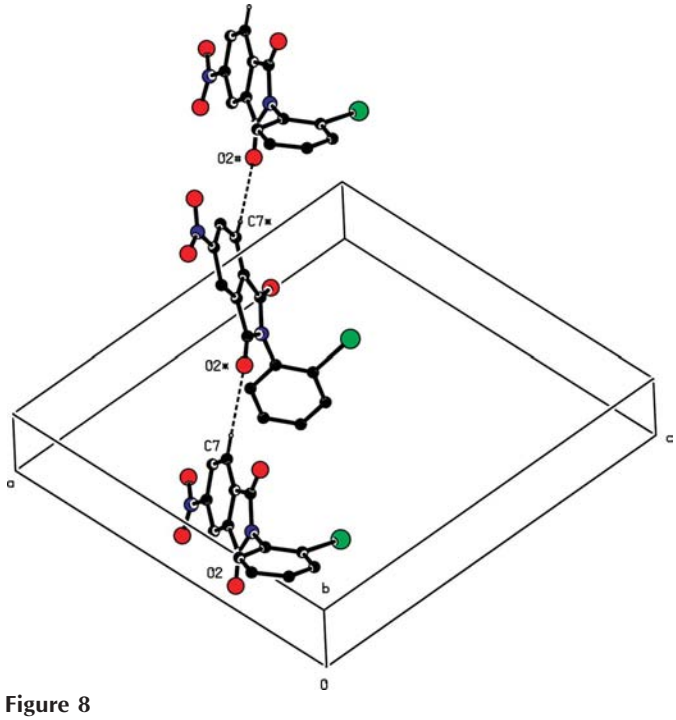


Figure 8
Part of the crystal structure of (III) showing the formation of a hydrogen-bonded chain along [101]. For the sake of clarity, the H atoms not involved in the motifs shown have been omitted. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$ and $(1 + x, y, 1 + z)$, respectively.

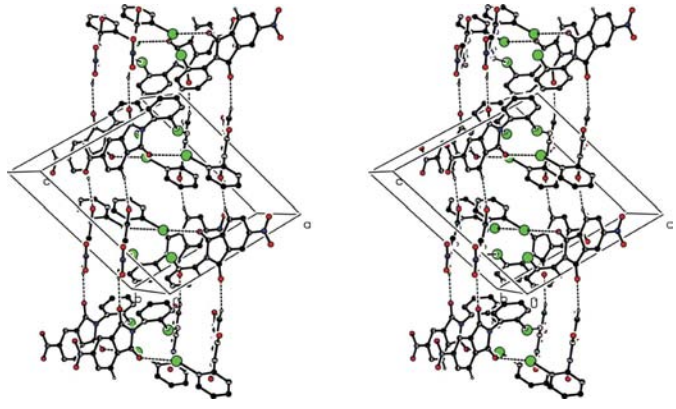


Figure 9
Stereoview of the crystal structure of (III) showing the formation of a (4,4) net parallel to (10$\bar{1}$). For the sake of clarity, the H atoms not involved in the motifs shown have been omitted.

of the domains $0.07 < x < 0.45$ and $0.55 < x < 0.93$, but there are no direction-specific interactions between adjacent sheets.

3.2.4. Compound (III). The supramolecular structure of (III) (Fig. 6) is two-dimensional. There are two significant direction-specific interactions between the molecules, an I···O interaction involving one of the carbonyl O atoms (although iodo···nitro interactions are absent) and a rather long C—H···O hydrogen bond involving the second carbonyl O atom as the acceptor. The nitro group thus plays no role whatsoever in the supramolecular aggregation.

The I12 atom in the molecule at (x, y, z) forms a short I···O contact with the carbonyl O1 atom in the molecule at $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, so forming a $C(6)$ chain (Starbuck *et al.*, 1999) running parallel to the [010] direction and generated by the 2_1 screw axis along $(\frac{1}{4}, y, \frac{1}{4})$ (Fig. 7). Two chains of this type pass through each unit cell and adjacent chains are linked by a single, rather weak C—H···O hydrogen bond. The phthalimide C7 atom in the molecule at (x, y, z) acts as a hydrogen-bond donor to the carbonyl O2 atom in the molecule at $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$, so forming a $C(6)$ chain running parallel to the [101] direction and generated by the *n*-glide plane at $y = 0.75$ (Fig. 8). The combination of the [010] and [101] chains generates a $(10\bar{1})$ sheet in the form of a (4,4) net (Batten & Robson, 1998) built from a single type of $R_4^4(26)$ ring (Fig. 9). There are no direction-specific interactions between adjacent sheets: in particular, both C—H···π(arene) hydrogen bonds and aromatic $\pi\cdots\pi$ stacking interactions are absent from the structure of (III).

3.2.5. Compound (IV). In (II) a combination of a two-centre iodo···nitro interaction and a single C—H···O hydrogen bond links the molecules into sheets, but the supramolecular structure of (IV) (Fig. 10), in contrast, is dominated by a nearly symmetrical three-centre iodo···nitro interaction and two nearly linear C—H···O hydrogen bonds. The iodo···nitro interaction generates chains, while the hydrogen bonds link all of these chains into a single three-dimensional framework. The formation of this framework is most readily considered in terms of the effect of the three intermolecular interactions taken in turn, and of their pairwise combinations.

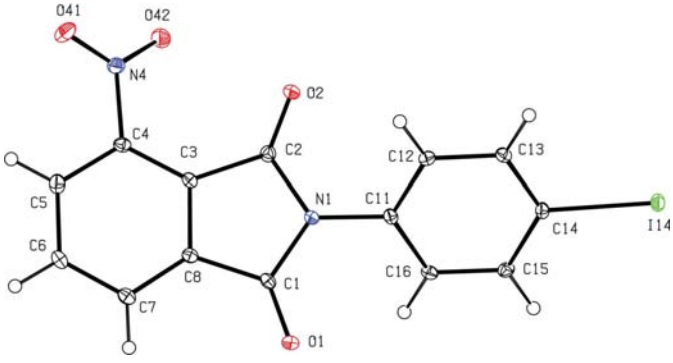


Figure 10
A molecule of (IV) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

The I14 atom in the molecule at (x, y, z) forms an essentially planar and only slightly asymmetric three-centre I···$(O)_2$ interaction with the two nitro O atoms of the molecule at $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{5}{2} - z)$. Propagation of this interaction

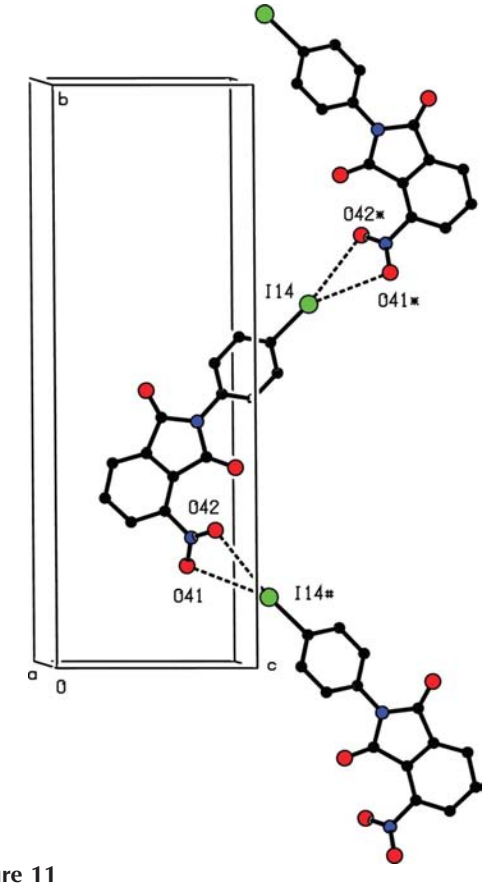


Figure 11
Part of the crystal structure of (IV) showing the formation of an I···O chain along [010]. For the sake of clarity, the H atoms have been omitted. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{5}{2} - z)$ and $(\frac{3}{2} - x, -\frac{1}{2} + y, \frac{5}{2} - z)$, respectively.

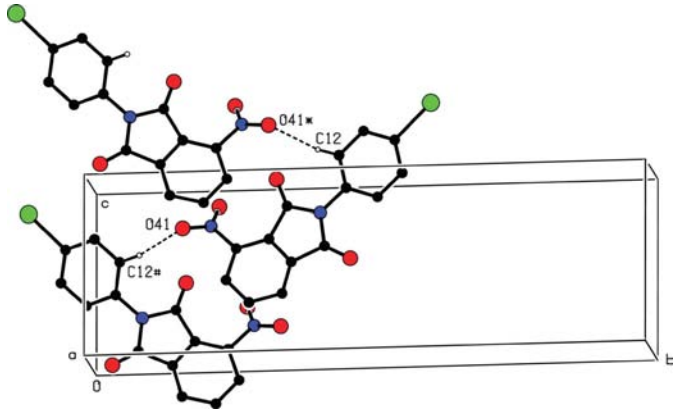


Figure 12
Part of the crystal structure of (IV) showing the formation of a hydrogen-bonded chain along [101]. For the sake of clarity, the H atoms not involved in the motif shown have been omitted. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{3}{2} + z)$, respectively.

produces a $C(11)[R_2^1(4)]$ chain of rings running parallel to the [010] direction and generated by the 2_1 screw axis along $(\frac{3}{4}, y, \frac{5}{4})$ (Fig. 11). A second such chain, antiparallel to the first and related to it by inversion, is generated by the 2_1 screw axis along $(\frac{1}{4}, -y, \frac{3}{4})$.

The phenyl C12 atom in the molecule at (x, y, z) acts as a hydrogen-bond donor to the nitro O41 atom in the molecule at $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$, while C12 at $(\frac{1}{2}, +x, \frac{1}{2}-y, \frac{1}{2}+z)$, in turn acts as a donor to O41 at $(1+x, y, 1+z)$. This hydrogen bond thus produces a simple $C(9)$ chain running parallel to the [101] direction, which is generated by the *n*-glide plane at $y = 0.25$ (Fig. 12). The combination of the [101] chain generated by the iodo···nitro interaction and the [101] chain of hydrogen bonds generates a $(10\bar{1})$ sheet in the form of a (4,4) net. Within the $(10\bar{1})$ sheet the iodo···nitro chain along $(\frac{3}{4}, y, 1.25)$ is directly linked to the two chains along $(\frac{1}{4}, -y, \frac{3}{4})$ and $(1.25, -y, 1.75)$.

In addition, the phenyl C16 atom in the molecule at (x, y, z) acts as a hydrogen-bond donor to the carbonyl O1 atom in the molecule at $(1-x, 1-y, 1-z)$, so generating a centrosymmetric $R_2^2(12)$ motif (Fig. 13): in a similar way, the C16 atom in the molecule at $(\frac{3}{2}-x, \frac{1}{2}+y, \frac{5}{2}-z)$ acts as a donor to O1 in the molecule at $(\frac{1}{2}+x, \frac{3}{2}-y, \frac{3}{2}+z)$. The molecules at (x, y, z) and $(\frac{3}{2}-x, \frac{1}{2}+y, \frac{5}{2}-z)$ both lie in the iodo···nitro chain along $(\frac{3}{4}, y, 1.25)$, whereas the molecules at $(1-x, 1-y, 1-z)$ and $(\frac{1}{2}+x, \frac{3}{2}-y, \frac{3}{2}+z)$ lie respectively in the iodo···nitro chains along $(\frac{1}{4}, -y, -\frac{1}{4})$ and $(1.25, -y, 2.75)$. Hence, the combination of the $R_2^2(12)$ hydrogen-bond motif with the iodo···nitro chains parallel to [010] generates a $(30\bar{1})$ sheet in the form of a (6,3) net.

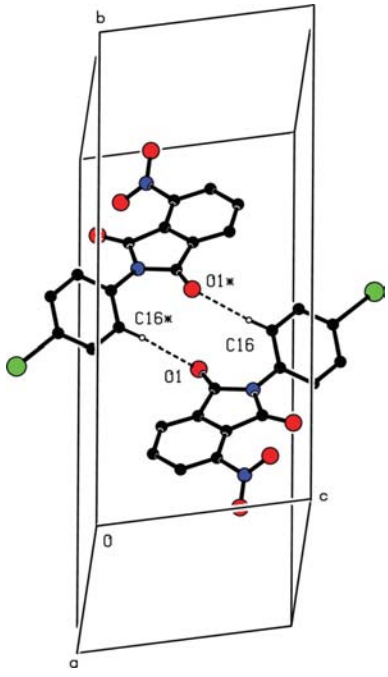


Figure 13
Part of the crystal structure of (IV) showing the formation of an $R_2^2(12)$ hydrogen-bonded dimer. For the sake of clarity, the H atoms not involved in the motif shown have been omitted. The atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 1-z)$.

Finally, the combination of the two hydrogen bonds generates a second type of $(10\bar{1})$ sheet, this time in the form of a (6,3) net, as opposed to the (4,4) net structure of the $(10\bar{1})$ sheet which involves the iodo···nitro interaction. The reference $C(9)$ chain is generated by the *n*-glide plane at $y = 0.25$ and the $R_2^2(12)$ ring serves to link this chain to two antiparallel chains, generated respectively by the *n*-glide planes at $y = -0.25$ and $y = 0.75$.

Thus, each of the three intermolecular interactions alone generates its characteristic sub-structure, one-dimensional or finite (zero-dimensional) as the case may be; each of the pairwise combinations generates a different two-dimensional sub-structure; and the combination of all three interactions generates a single three-dimensional framework which is, in fact, reinforced by a weak C—H···O interaction and a single aromatic $\pi\cdots\pi$ stacking interaction. The C6 atom in the molecule at (x, y, z) forms a weak hydrogen bond with O2 in the molecule at $(x, y, -1+z)$, so generating by translation a $C(7)$ chain running parallel to the [001] direction. In addition, the phenyl rings of the molecules at (x, y, z) and $(2-x, 1-y, 2-z)$ are parallel, with a centroid separation of 3.738 (2) Å; the interplanar spacing is 3.400 (2) Å, corresponding to a centroid offset of 1.553 (2) Å.

3.2.6. Compound (V). The three-dimensional structure of (V) (Fig. 14) is determined by two C—H···O hydrogen bonds, one of them rather weak and a two-centre iodo···nitro interaction. However, C—H···π(arene) hydrogen bonds and aromatic $\pi\cdots\pi$ stacking interactions are both absent from the structure. The construction of the three-dimensional framework is most readily analysed and described in terms of the three individual one-dimensional substructures generated by each of the individual intermolecular interactions.

The I13 atom in the molecule at (x, y, z) makes a short I···O contact with the nitro O42 atom in the molecule at $(-x, \frac{1}{2}+y, \frac{3}{2}-z)$, so producing a $C(10)$ chain running parallel to the [010] direction which is generated by the 2_1 screw axis along $(0, y, \frac{3}{4})$. A second antiparallel chain is generated by the screw axis along $(\frac{1}{2}, -y, \frac{1}{4})$.

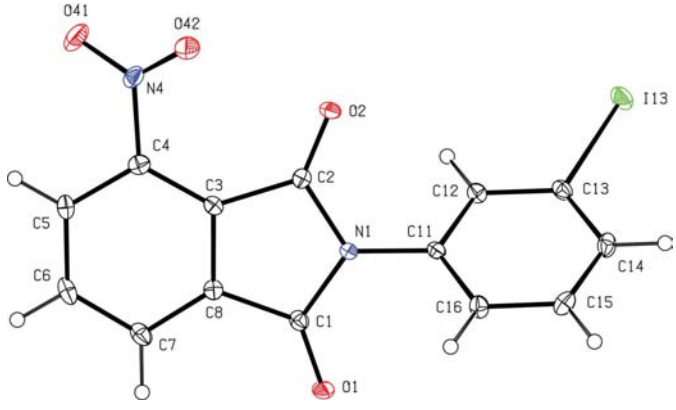


Figure 14
A molecule of (V) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

The set of $C(10)$ chains which are generated by screw axes having $y = \frac{3}{4}$ and related by translation along [100] are linked by the stronger of the two hydrogen bonds. The phenyl C16 atom in the molecule at (x, y, z) acts as a hydrogen-bond donor to the carbonyl O2 atom in the molecule at $(1 + x, y, z)$, so producing a $C(6)$ chain parallel to [100]. The combination of $C(6)$ chains parallel to [100] and $C(10)$ chains parallel to [010] generates a (001) sheet, in the form of a (4,4) net built from a single type of $R_4^4(28)$ ring (Fig. 15). Two sheets of this type pass through each unit cell, generated respectively by 2_1 axes along [010] having $y = \frac{3}{4}$ and $\frac{1}{4}$, and the successive (001) sheets are weakly linked by the second C—H···O hydrogen bond.

The phthalimide C6 atom in the molecule at (x, y, z) acts as a hydrogen-bond donor to the carbonyl O2 atom in the molecule at $(\frac{1}{2} - x, -y, -\frac{1}{2} + z)$, so forming a $C(7)$ chain running parallel to the [001] direction which is generated by the 2_1 screw axis along $(\frac{1}{4}, 0, z)$ (Fig. 16). The two molecules at (x, y, z) and $(\frac{1}{2} - x, -y, -\frac{1}{2} + z)$ lie, respectively, in the (001) sheets generated by screw axes at $y = \frac{3}{4}$ and $y = \frac{1}{4}$, and propagation of the $C(7)$ chain motif links all the (001) sheets into a continuous framework structure.

However, iodo···nitro interactions are present only in the structures of isomers (II), (IV) and (V), and only in (IV) is a three-centre I···$(O)_2$ interaction present. An iodo···carbonyl interaction occurs only in isomer (III), while there are no I···O interactions of any kind in isomer (I). Aromatic π···π stacking interactions occur only in isomer (IV) and C—H···π(arene) hydrogen bonds do not occur at all.

While none of the isomers (I)–(V) crystallizes either as an isolated molecule or with a one-dimensional supramolecular structure, the sheet structures of (I)–(III) all differ from one another, as do the two framework structures in (IV) and (V). Thus, not only do the number and identity of the types of intermolecular interaction vary, but the structural consequences of these interactions also show a wide range of behaviour. As we have noted previously (Glidewell, Low, Skakle, Wardell & Wardell, 2004), there is no correlation between the number of different types of direction-specific interaction manifest in a given structure and its overall complexity, in particular its supramolecular dimensionality.

Finally, we may note that unlike the three isomeric series (*A*), (*B*) and (*D*), all of the isomers (I)–(V) crystallize with $Z' = 1$.

3.3. General discussion of the supramolecular structures

The supramolecular analyses described above (§§3.2.2–3.2.6) for (I)–(V) show that as in the three series of isomeric compounds of types (*A*), (*B*) and (*D*) (see §1), no two isomers from (I)–(V) exhibit the same combination of direction-specific intermolecular forces. C—H···O hydrogen bonds are present in all structures (I)–(V), but the numbers of such hydrogen bonds vary from only one each in isomers (II) and (III), through two in (V) and three in (IV), to a total of four independent hydrogen bonds in isomer (I). Moreover, in isomers (II), (II) and (V) the hydrogen-bond acceptors are all carbonyl O atoms, whereas in isomers (I) and (IV) both carbonyl O and nitro O atoms are involved (Table 3).

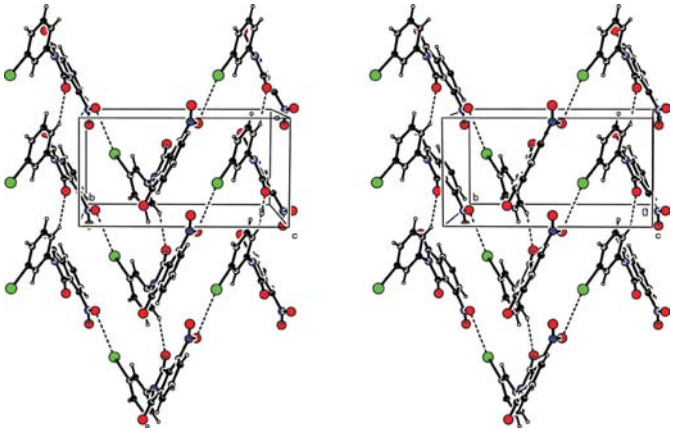


Figure 15
Stereoview of part of the crystal structure of (V) showing the formation of a (001) sheet of $R_4^4(28)$ rings by a combination of the $C(6)$ and $C(10)$ chains along [100] and [010].

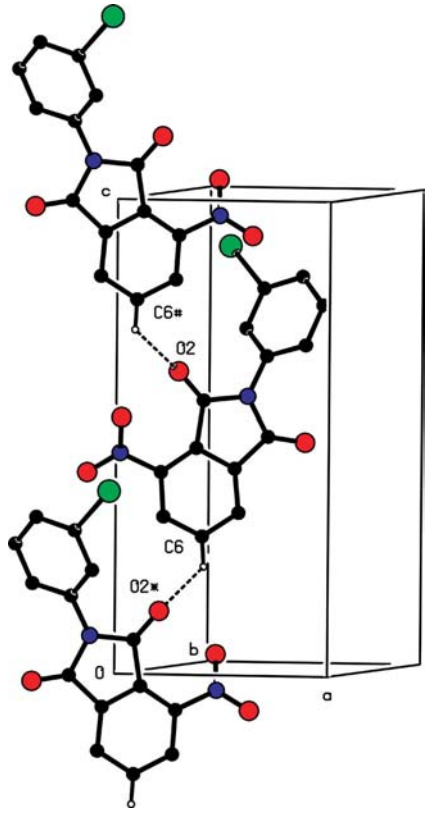


Figure 16
Part of the crystal structure of (V) showing the formation of the [001] chain which links adjacent (001) sheets. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} - x, -y, -\frac{1}{2} + z)$ and $(\frac{1}{2} - x, -y, \frac{1}{2} + z)$, respectively.

4. Concluding comments

In previous studies of the extended series of isomeric compounds, such as those of types (*A*), (*B*) and (*D*) (see Scheme 1, §1), we have found in each such series that the patterns of supramolecular aggregation are never the same in any two isomers. Moreover, where a rather large variety of direction-specific intermolecular interactions is potentially available, as in series (*A*), even the types of individual interactions present differ in every isomer studied. As with those series, so too with the present isomer series (I)–(V), where no two isomers use the same spectrum of intermolecular interactions or give similar supramolecular structures. Weak forces of the types manifest here, dependent upon molecular polarizability and polarization, are not easy to model computationally. Variations in the supramolecular aggregation behaviour within an extended series of isomeric compounds, such as those described here, provide a keen test of computational methods for crystal-structure prediction (Lommerse *et al.*, 2000; Motherwell *et al.*, 2002): the accurate prediction of behaviour across such a series of isomeric species would generate real confidence in the efficacy of the predictive methods employed.

X-ray data for (I), (IV) and (V) were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England, using a Nonius Kappa-CCD diffractometer: the authors thank the staff of the Service for all their help and advice. Data for (II) and (III) were collected at the University of Aberdeen using a Bruker SMART 1000CCD diffractometer and the authors thank the University of Aberdeen for funding the purchase of the diffractometer. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. JLW and SMSVW thank CNPq and FAPERJ for financial support.

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