

Isomeric *N*-(iodophenyl)nitrobenzamides form different three-dimensional framework structures

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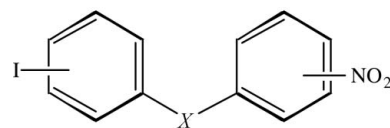
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The isomeric *N*-(iodophenyl)nitrobenzamides, C₁₃H₉IN₂O₃, all form different three-dimensional framework structures. Molecules of *N*-(2-iodophenyl)-3-nitrobenzamide (II) are linked by a combination of N—H···O and C—H···O hydrogen bonds and a two-centre iodo···carbonyl interaction. The supramolecular structure of *N*-(2-iodophenyl)-4-nitrobenzamide (III) is built from one N—H···O and two C—H···O hydrogen bonds, but short I···O contacts are absent from the structure. In *N*-(3-iodophenyl)-2-nitrobenzamide (IV), which crystallizes with *Z'* = 2 in space group *P*2₁, the structure contains two N—H···O hydrogen bonds, four C—H···O hydrogen bonds, two two-centre iodo···nitro interactions and an aromatic π ··· π stacking interaction. The structure of *N*-(3-iodophenyl)-3-nitrobenzamide (V) contains one N—H···O hydrogen bond and three C—H···O hydrogen bonds, together with a two-centre iodo···nitro interaction and an aromatic π ··· π stacking interaction, while in *N*-(3-iodophenyl)-4-nitrobenzamide (VI), the combination of one N—H···O hydrogen bond and two C—H···O hydrogen bonds is augmented not only by a two-centre iodo···nitro interaction and an aromatic π ··· π stacking interaction, but also by a dipolar carbonyl···carbonyl interaction. In the supramolecular structure of *N*-(4-iodophenyl)-4-nitrobenzamide (IX), which crystallizes with *Z'* = 2 in space group *P*1̄, there are two N—H···O hydrogen bonds, four C—H···O hydrogen bonds and two three-centre iodo···nitro interactions.

1. Introduction

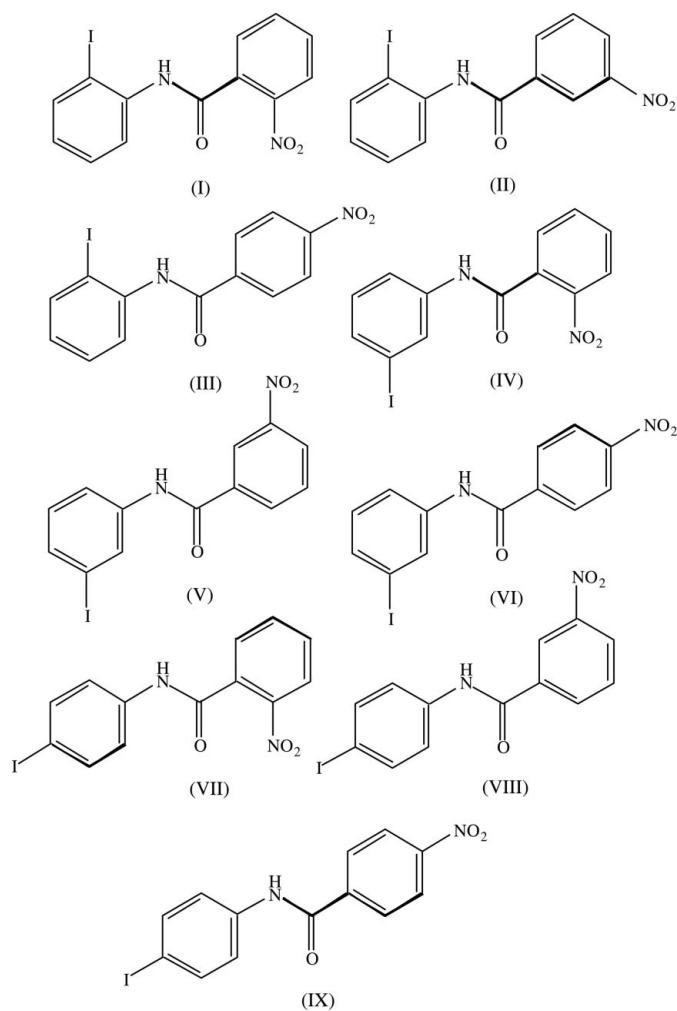
As part of a general study of the interplay of hydrogen bonds, iodo···nitro interactions and aromatic π ··· π stacking interactions in aromatic systems containing both iodo and nitro substituents, we have recently reported the molecular and supramolecular structures of a range of diaryl species (see Scheme 1) containing a variety of spacer units *X*, including the two isomeric series of arenesulfonamides (*A*) and (*B*) (Kelly *et al.*, 2002), the two isomeric series of Schiff-base imines (*C*)



- (A) *X* = -SO₂-NH-
- (B) *X* = -NH-SO₂-
- (C) *X* = -CH=N-
- (D) *X* = -N=CH-
- (E) *X* = -NH-CH₂-
- (F) *X* = -NH-CO-
- (G) *X* = -CH=N-N=CH-

(Wardell *et al.*, 2002) and (*D*) (Glidewell, Howie *et al.*, 2002; Ferguson *et al.*, 2005), benzylanilines (*E*) (Glidewell, Low *et al.*, 2002, 2004), a single example of a benzamide (*F*) (Wardell *et al.*, 2005), and 2,3-diazabutadienes (*G*) (Glidewell, Low, Skakle & Wardell, 2005; Low *et al.*, 2006).

In the case of the Schiff-base imines of type (*D*), we were able to study the supramolecular aggregation modes in eight of the possible nine isomers (Glidewell, Howie *et al.*, 2002); in the benzylaniline series (*E*) we were able to study the structures of six of the possible nine isomers (Glidewell, Low *et al.*, 2002, 2004); and in the diazabutadiene series (*G*), we have been able to study four of the six possible isomers (Glidewell, Low, Skakle & Wardell, 2005<; Low *et al.*, 2006). In each of these series, the interplay of the various weak intermolecular interactions is such that neither the supramolecular structure nor even the range of interactions involved can readily be predicted for any single example from a detailed knowledge of all the rest of the series. With this in mind, we have now expanded our preliminary study (Wardell *et al.*, 2005) of the benzamide series (*F*) to incorporate a total of seven isomers of this series, compounds (I)–(VI) and (IX).



This series of isomers offers, within a fairly compact molecular constitution, a wide variety of potential intermolecular interactions; these include N–H···O and C–H···O hydrogen bonds, in each of which the acceptor could be either a carbonyl O or a nitro O atom; N–H··· π (arene) and C–H··· π (arene) hydrogen bonds; iodo···carbonyl and iodo···nitro interactions, of which the latter could be of either

two-centre or three-centre type; aromatic π ··· π stacking interactions; and dipolar carbonyl···carbonyl and nitro···nitro interactions.

2. Experimental

2.1. Synthesis

For the preparation of compounds (II)–(IX), equimolar quantities of the appropriate nitrobenzoyl chloride and the appropriate iodoaniline (2 mmol of each component) were dissolved in chloroform (50 cm³), and these mixtures were heated under reflux for 1 h. After cooling the mixtures, the solvent was removed under reduced pressure, and the resulting products were recrystallized from ethanol, yielding the pure compounds (II)–(IX): m.p. (II) 441–443 K, (III) 469–471 K (decomposes), (IV) 431–432 K, (V) 450–452 K, (VI) 471–472 K, (VII) 426–427 K, (VIII) 464–466 K, (IX) > 510 K. IR (KBr disk, cm⁻¹): (II) 3249, 1658, 1639, 1587, 1522, 1343; (III) 3278, 1654, 1586, 1522, 1353; (IV) 3378, 3321, 1680, 1648, 1582, 1524, 1347; (V) 3309, 1656, 1589, 1521, 1346; (VI) 3298, 1645, 1587, 1525, 1346; (VII) 3281, 1655, 1574, 1525, 1347; (VIII) 3409, 1677, 1587, 1516, 1344; (IX) 3290, 1652, 1585, 1510, 1349. Crystals of isomers (II)–(VI) suitable for single-crystal X-ray diffraction were grown from solutions in ethanol; suitable crystals of isomer (IX) could not be obtained in this way, but were grown from a solution in acetone. Repeated attempts were made to obtain adequate crystals of isomers (VII) and (VIII), and for both isomers crystallization was attempted from each of acetone, acetonitrile, chloroform, ethanol, methanol and various ethanol–water mixtures, all without success.

2.2. Data collection, structure solution and refinement

Diffraction data for isomers (II)–(VI) were collected at 120 (2) K using a Nonius KappaCCD diffractometer; in all these cases graphite-monochromated Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) was employed. Data for isomer (IX) were collected at 120 (2) K on Daresbury SRS Station 9.8 (Cernik *et al.*, 1997; Clegg, 2000) using a Bruker SMART APEXII diffractometer and synchrotron radiation ($\lambda = 0.6712 \text{ \AA}$). Other details of cell data, data collection and refinement are summarized in Table 1, together with details of the software employed (Bruker, 2001, 2003; Ferguson, 1999; Hoof, 1999; McArdle, 2003; Otwinowski & Minor, 1997; Sheldrick, 1997; Sheldrick, 2003). For isomer (VIII) no usable diffraction data could be obtained even using synchrotron radiation.

For isomers (II) and (VI) the space groups $P2_1/c$ and $P2_1/n$, respectively, were uniquely assigned from the systematic absences; crystals of isomer (IX) are triclinic and the space group $P\bar{1}$ was selected, and subsequently confirmed by the successful structure analysis. For each of (III)–(V) the systematic absences provided a choice of space groups: Pc or $P2/c$ for isomer (III), $P2_1$ or $P2_1/m$ for isomer (IV), and Cc or $C2/c$ for isomer (V). The space groups Pc , $P2_1$ and Cc , respectively, were selected, and confirmed by the subsequent structure analyses.

Table 1
Experimental details.

	(II)	(III)	(IV)	(V)	(VI)	(IX)
Crystal data						
Chemical formula	C ₁₃ H ₉ IN ₂ O ₃	C ₁₃ H ₉ IN ₂ O ₃	C ₁₃ H ₉ IN ₂ O ₃	C ₁₃ H ₉ IN ₂ O ₃	C ₁₃ H ₉ IN ₂ O ₃	C ₁₃ H ₉ IN ₂ O ₃
<i>M_r</i>	368.12	368.12	368.12	368.12	368.12	368.12
Cell setting, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Monoclinic, <i>P</i> <i>c</i>	Monoclinic, <i>P</i> 2 ₁	Monoclinic, <i>C</i> <i>c</i>	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	120 (2)	120 (2)	120 (2)	120 (2)	120 (2)	120 (2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.1804 (3), 7.5099 (2), 13.8849 (3)	10.0528 (3), 4.8703 (10), 13.5719 (3)	11.0552 (3), 8.9521 (2), 12.8921 (3)	13.8494 (4), 10.0495 (3), 9.4203 (3)	7.4798 (2), 14.0889 (7), 11.8138 (6)	5.1047 (3), 15.3015 (9), 16.4806 (9)
α , β , γ (°)	90.00, 111.1634 (12), 90.00	90.00, 109.9452 (17), 90.00	90.00, 96.3899 (10), 90.00	90.00, 105.2353 (16), 90.00	90.00, 93.259 (3), 90.00	95.356 (2), 95.498 (2), 91.150 (2)
<i>V</i> (Å ³)	1281.68 (5)	624.63 (13)	1267.97 (5)	1265.03 (7)	1242.95 (9)	1275.23 (13)
<i>Z</i>	4	2	4	4	4	4
<i>D_x</i> (Mg m ⁻³)	1.908	1.957	1.928	1.933	1.967	1.917
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Synchrotron
μ (mm ⁻¹)	2.50	2.57	2.53	2.54	2.58	2.52
Crystal form, colour	Plate, colourless	Plate, brown	Plate, colourless	Block, brown	Needle, brown	Needle, colourless
Crystal size (mm)	0.50 × 0.10 × 0.02	0.42 × 0.30 × 0.08	0.40 × 0.20 × 0.08	0.46 × 0.34 × 0.16	0.48 × 0.09 × 0.07	0.09 × 0.04 × 0.02
Data collection						
Diffractometer	Bruker–Nonius KappaCCD	Bruker–Nonius KappaCCD	Bruker–Nonius KappaCCD	Bruker–Nonius KappaCCD	Bruker–Nonius KappaCCD	Bruker SMART APEXII CCD
Data collection method	φ and ω scans	φ and ω scans	φ and ω scans	φ and ω scans	φ and ω scans	Fine-slice ω scans
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
<i>T_{min}</i>	0.368	0.412	0.431	0.376	0.370	0.805
<i>T_{max}</i>	0.952	0.821	0.823	0.666	0.840	0.951
No. of measured, independent and observed reflections	15 482, 2942, 2549	10 157, 2767, 2624	16 241, 5672, 5506	7022, 2797, 2752	13 030, 2843, 2529	13 690, 7348, 6485
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>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)
<i>R_{int}</i>	0.038	0.026	0.024	0.023	0.060	0.020
θ_{\max} (°)	27.6	27.5	27.5	27.5	27.6	28.7
Refinement						
Refinement on <i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	<i>F</i> ² 0.025, 0.062, 1.07	<i>F</i> ² 0.019, 0.048, 1.21	<i>F</i> ² 0.020, 0.046, 1.11	<i>F</i> ² 0.018, 0.053, 1.24	<i>F</i> ² 0.084, 0.286, 1.17	<i>F</i> ² 0.029, 0.074, 1.04
No. of reflections	2942	2767	5672	2797	2843	7348
No. of parameters	172	173	344	172	161	337
H-atom treatment	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 0.5883P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.022P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0177P)^2 + 0.1391P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0227P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1676P)^2 + 25.4085P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.6363P]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.001	<0.0001	0.001	<0.0001	<0.0001	0.002
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.58, -0.98	0.67, -0.62	0.66, -0.80	0.56, -1.09	3.92, -2.57	0.91, -1.02
Extinction method	None	<i>SHELXL97</i>	<i>SHELXL97</i>	None	None	None
Extinction coefficient	–	0.0225 (11)	0.0075 (3)	–	–	–
Absolute structure	–	Flack (1983), 1328 Friedel pairs	Flack (1983), 2565 Friedel pairs	Flack (1983), 1349 Friedel pairs	–	–
Flack parameter	–	-0.006 (17)	-0.008 (11)	0.013 (17)	–	–

Computer programs used: *COLLECT* (Hooft, 1999), *APEX2* (Bruker, 2003), *DENZO* (Otwinowski & Minor, 1997), *SAINT* (Bruker, 2001), *OSCAIL* (McArdle, 2003), *SHELXS97* (Sheldrick, 1997), *SHELXL97* (Sheldrick, 1997), *PLATON* (Spek, 2003), *PRPKAPPA* (Ferguson, 1999), *SADABS* (Sheldrick, 2003).

The structures were solved by direct methods and refined with all data on *F*². A weighting scheme based on $P = (F_o^2 + 2F_c^2)/3$ was employed in order to reduce statistical bias

(Wilson, 1976). All H atoms were located from difference maps and then treated as riding atoms with C–H distances of 0.95 Å and N–H distances of 0.88–0.90 Å, and with *U*_{iso}(H) =

Table 2

Selected torsion angles (°).

(a) Isomers with $Z' = 1$.

Parameter	(I)†	(II)	(III)	(V)	(VI)
C11–C17–N1–C21	–173.38 (16)	–169.3 (2)	–165.0 (3)	175.5 (2)	177.2 (10)
C12–C11–C17–N1	76.1 (2)	–169.8 (2)	26.8 (4)	–25.2 (4)	167.6 (10)
C22–C21–N1–C17	–143.98 (19)	116.5 (3)	138.7 (3)	25.7 (4)	18.3 (18)

(b) Isomers with $Z' = 2$.

Parameter	(IV)	(IX)
C11–C17–N11–C21	–177.8 (3)	177.53 (18)
C31–C37–N31–C41	–170.2 (2)	–179.62 (18)
C12–C11–C17–N11	96.5 (3)	–144.7 (2)
C32–C31–C37–N31	71.4 (4)	146.52 (19)
C22–C21–N11–C17	–13.2 (4)	–27.9 (3)
C42–C41–N31–C37	31.1 (4)	–38.8 (3)

† Data for compound (I) are taken from Wardell *et al.* (2005).

1.2U_{eq}(C,N). The correct absolute configuration for the molecules in the crystal of isomer (IV) selected for data collection was determined by means of the Flack (1983) parameter; for isomers (III) and (V) the correct orientations of the structures with respect to the polar axis directions were established by means of their Flack parameters. For compound (VI), *PLATON* (Spek, 2003) indicated the presence of non-merohedral twinning, and the refined twin fractions were 0.323 (4) and 0.677 (4).

Supramolecular analyses were made and the diagrams were prepared with the aid of *PLATON* (Spek, 2003). Details of molecular conformations are given in Table 2, details of hydrogen-bond dimensions are given in Table 3, and details of short I··O interactions are given in Table 4.¹ Figs. 1–6 show the molecular components, with the atom-labelling schemes, and Figs. 7–12 show aspects of the supramolecular structures.

3. Results and discussion

3.1. Molecular conformations

In each isomer (Figs. 1–6) the central amidic portion adopts a nearly planar *trans* conformation, as shown by the C11–C17–N1–C21 torsion angles in the isomers (I)–(III), (V) and (VI) having $Z' = 1$, and the corresponding angles C11–C17–N11–C21 and C31–C37–N31–C41 for the isomers (IV) and (IX) having $Z' = 2$ (Table 2). However, the two independent torsion angles defining the orientation of the two aryl rings relative to the central amide group show a very wide range of values, such that none of the molecular skeletons even approaches planarity. In addition, the nitro groups make modest non-zero dihedral angles with the adjacent aryl rings,

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM5035). Services for accessing these data are described at the back of the journal.

Table 3

Hydrogen-bond parameters (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A	Motif	Direction
(II)						
N1–H1···O17 ⁱ	0.88	2.16	2.950 (3)	149	C(4)	[010]
C23–H23···O31 ⁱⁱ	0.95	2.45	3.385 (4)	169	C(11)	[100]
(III)						
N1–H1···O17 ⁱⁱⁱ	0.88	2.07	2.920 (3)	164	C(4)	[010]
C24–H24···O42 ^{iv}	0.95	2.34	3.175 (5)	147	C(13)	[201]
C26–H26···Cg1 ^{v†}	0.95	2.95	3.800 (3)	149	–	[001]
(IV)						
N11–H11···O17 ^{vi}	0.88	2.28	2.977 (3)	137	C(4)	[010]
N31–H31···O37 ^{vii}	0.88	2.01	2.863 (3)	162	C(4)	[010]
C14–H14···O321 ^{viii}	0.95	2.48	3.244 (4)	137	C ₂ ² (7)	[010]
C15–H15···O322	0.95	2.41	3.245 (4)	147	D	–
C16–H16···O121 ^{ix}	0.95	2.55	3.416 (4)	151	C(6)	[010]
C35–H35···O122 ^{ix}	0.95	2.44	3.251 (5)	143	C ₂ ² (14)	[110]
(V)						
N1–H1···O17 ^v	0.88	2.08	2.937 (3)	165	C(4)	[001]
C12–H12···O17 ^v	0.95	2.48	3.266 (4)	140	C(5)	[001]
C24–H24···O31 ^x	0.95	2.48	3.371 (4)	157	C(12)	[101]
C26–H26···O17 ^v	0.95	2.51	3.256 (5)	136	C(6)	[001]
(VI)						
N1–H1···O41 ^{xi}	0.88	2.33	3.191 (13)	167	C(9)	[101]
C16–H16···O41 ^{xi}	0.95	2.40	3.291 (14)	155	C(6)	[101]
C24–H24···O17 ^{xiii}	0.95	2.36	3.192 (15)	147	C(8)	[101]
(IX)						
N11–H11···O17 ⁱⁱ	0.90	2.06	2.936 (2)	163	C(4)	[100]
N31–H31···O37 ^{xiii}	0.90	2.04	2.915 (2)	164	C(4)	[100]
C13–H13···O141 ^{xiv}	0.95	2.41	3.233 (4)	145	R ₂ ² (10)	–
C15–H15···O342	0.95	2.40	3.305 (4)	159	D	–
C33–H33···O341 ^{xv}	0.95	2.50	3.231 (3)	134	R ₂ ² (10)	–
C35–H35···O142	0.95	2.36	3.254 (3)	157	D	–

† Cg1 is the centroid of ring C11–C16. Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 + x, y, z$; (iii) $x, -1 + y, z$; (iv) $1 + x, 1 - y, -\frac{1}{2} + z$; (v) $x, 1 - y, -\frac{1}{2} + z$; (vi) $1 - x, \frac{1}{2} + y, 1 - z$; (vii) $-x, -\frac{1}{2} + y, -z$; (viii) $1 - x, -\frac{1}{2} + y, -z$; (ix) $-1 + x, 1 + y, z$; (x) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (xi) $-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$; (xii) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (xiii) $-1 + x, y, z$; (xiv) $-x, 1 - y, 1 - z$; (xv) $3 - x, -y, 1 - z$.

Table 4

Geometric parameters (Å, °) for I··O contacts.

C–I··O	C–I	I··O	C–I··O	Motif	Direction
(II)					
C22–I22···O17 ⁱ	2.101 (2)	3.069 (2)	175.6 (2)	C(6)	[001]
(IV)					
C23–I23···O37 ⁱⁱ	2.103 (3)	3.164 (2)	173.7 (2)	C ₂ ² (16)	[011]
C43–I43···O17 ⁱⁱⁱ	2.108 (3)	3.233 (2)	166.6 (2)	C ₂ ² (16)	[011]
(V)					
C23–I23···O32 ^{iv}	2.103 (4)	3.190 (3)	160.5 (2)	C(11)	[112]
(VI)					
C23–I23···O42 ^v	2.106 (11)	3.243 (8)	157.7 (3)	C(12)	[010]
(IX)					
C24–I24···O141 ^{vi}	2.095 (2)	3.438 (2)	155.4 (2)	C(13)	[001]
C24–I24···O142 ^{vi}	2.095 (2)	3.394 (2)	167.5 (2)	C(13)	[001]
C44–I44···O341 ^{vii}	2.096 (2)	3.512 (2)	154.6 (2)	C(13)	[001]
C44–I44···O342 ^{vii}	2.096 (2)	3.368 (2)	166.1 (2)	C(13)	[001]

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

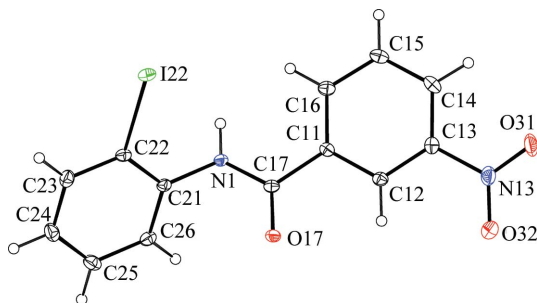


Figure 1
A molecule of isomer (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

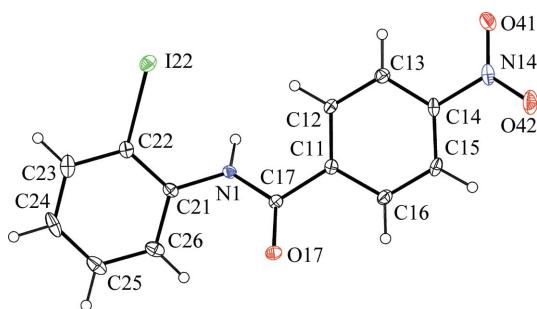


Figure 2
A molecule of isomer (III) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

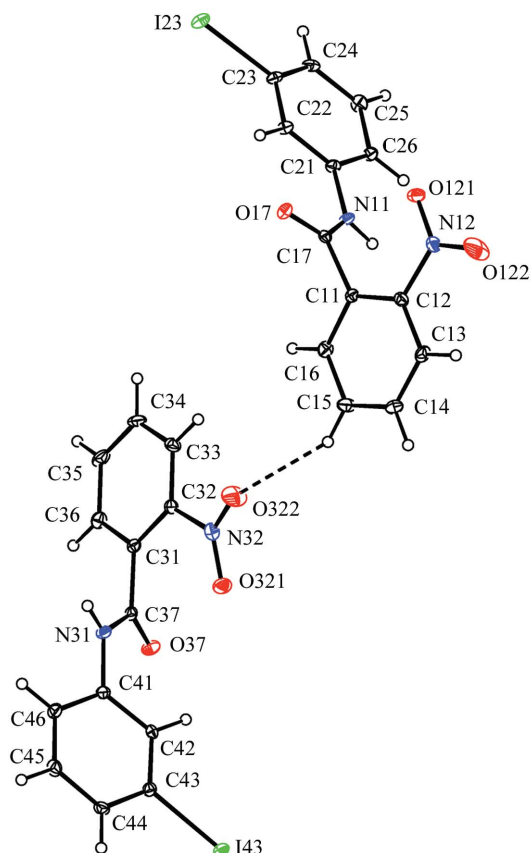


Figure 3
The two independent molecules in isomer (IV) showing the atom-labelling scheme and the C—H...O hydrogen bond within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

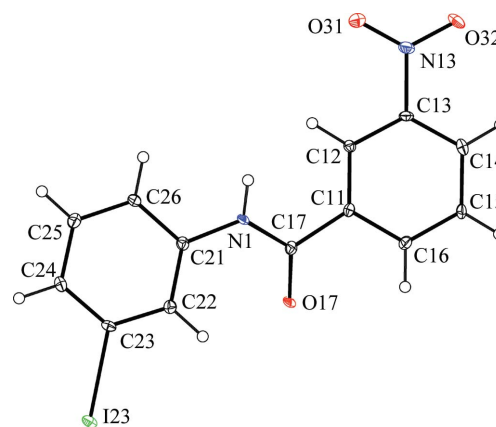


Figure 4
A molecule of isomer (V) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

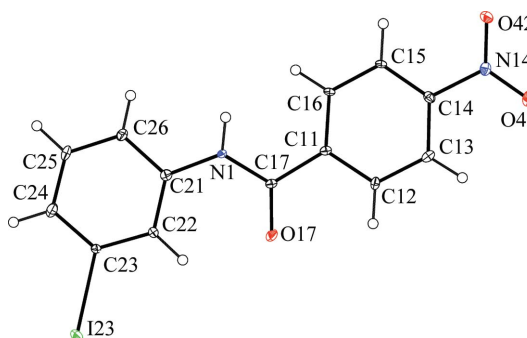


Figure 5
A molecule of isomer (VI) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

ranging from 1.4 (2)° in isomer (IV) to 16.1 (2)° in isomer (III).

The range of molecular conformations in the crystalline state indicates that the direction-specific intermolecular forces, in particular the hydrogen bonds and the iodo...oxygen interactions, are capable of overcoming the rotational barriers associated with the bonds linking the rings to the central spacer unit. Despite the marked non-planarity, it is still possible to identify in each isomer two distinct edges of the elongated molecules, while the 4- and 4'-positions can be regarded as forming the ends of the molecules. Where neither the iodo nor the nitro substituent occupies a 4- or 4'-site, the ring orientations are such that in isomers (I), (II) and (V) these substituents are on opposite edges of the molecule, while in isomer (IV) they are on the same edge. Since in each of these isomers the rings are involved in direction-specific intermolecular interactions, it may be concluded that the sum of the resultant forces in any isomer can overcome the two independent intramolecular rotational barriers constraining the orientations of the aryl rings relative to the central amide spacer unit.

3.2. Supramolecular structures

3.2.1. Isomer (I), *N*-(2-iodophenyl)-2-nitrobenzamide. The molecules of (I) are linked into a three-dimensional structure,

which was described (Wardell *et al.*, 2005) in terms of three simple one-dimensional sub-structures built, respectively, from an N—H···O hydrogen bond, a combination of a C—H···O hydrogen bond and a two-centre iodo···nitro interaction, and a C—H··· π (arene) hydrogen bond, and running, respectively, along the [100], [010] and [001] directions.

3.2.2. Isomer (II), *N*-(2-iodophenyl)-3-nitrobenzamide. The molecules of isomer (II) (Fig. 1) are linked into sheets by a combination of two hydrogen bonds, one each of N—H···O and C—H···O types (Table 3), and the hydrogen-bonded sheets are linked into a three-dimensional framework structure by a single two-centre iodo···carbonyl interaction (Table 4).

Atom N1 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the amidic atom O17 in the molecule at $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, so forming a $C(4)$ (Bernstein *et al.*, 1995) chain typical of carboxamides, running parallel to the [010] direction and generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{1}{2})$. In addition, atom C23 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the nitro atom O31 in the molecule at $(1 + x, y, z)$, so

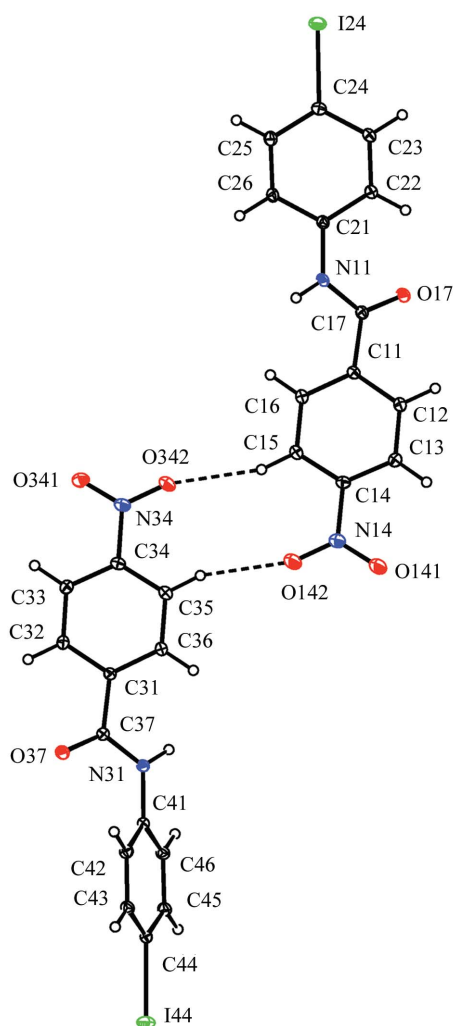


Figure 6
The two independent molecules of isomer (IX) showing the atom-labelling scheme and the hydrogen bonds within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

generating by translation a $C(11)$ chain running parallel to the [100] direction. The combination of the $C(4)$ and $C(11)$ chains along [010] and [100], respectively, then generates a (001) sheet in the form of a (4,4)-net built from a single type of $R_4^4(28)$ ring (Fig. 7*a*).

Adjacent sheets are linked by the iodo···carbonyl interaction (Table 3). Atom I22 in the molecule at (x, y, z) , which lies in the (001) sheet generated by the screw axes at $z = \frac{1}{4}$, makes a short two-centre contact with the amidic atom O17 in the molecule at $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$, which forms part of the (001) sheet generated by the screw axes at $z = -\frac{1}{4}$. Propagation of this interaction forms a $C(6)$ (Starbuck *et al.*, 1999) chain running parallel to the [001] direction and generated by the c -glide plane at $y = \frac{1}{4}$ (Fig. 7*b*). The combination of the (001) hydrogen-bonded sheets and the [001] iodo···carbonyl chain is sufficient to generate a continuous framework structure.

3.2.3. Isomer (III), *N*-(2-iodophenyl)-4-nitrobenzamide. The molecules of isomer (III) (Fig. 2) are linked into a three-

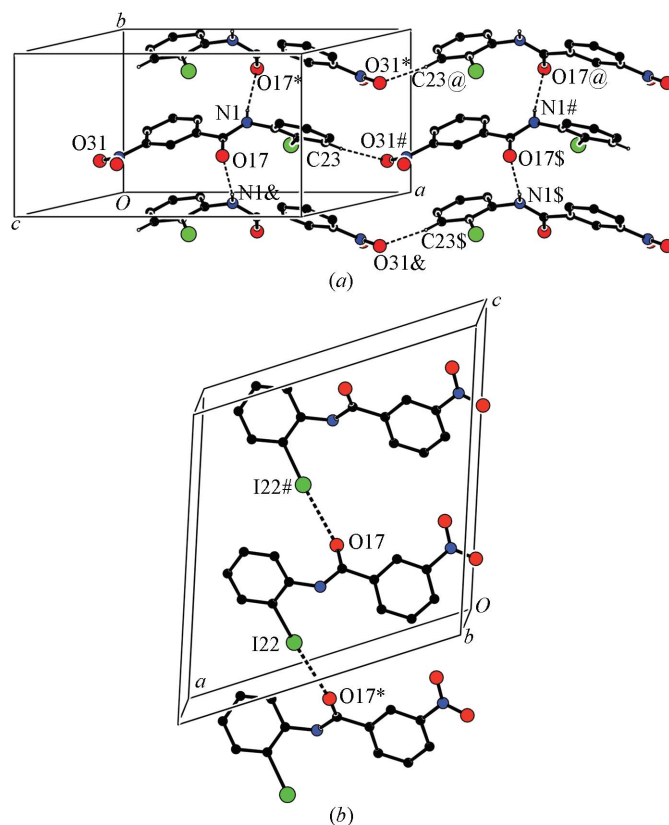


Figure 7
(*a*) Part of the crystal structure of isomer (II) showing the formation of a sheet of $R_4^4(28)$ rings parallel to (001) generated by the N—H···O and C—H···O hydrogen bonds. For the sake of clarity, the H atoms not involved in the motifs shown have been omitted. The atoms marked with an asterisk (*), a hash (#), a dollar sign (\$), an ampersand (&) or an '@' sign (@) are at the symmetry positions $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, $(1 + x, y, z)$, $(2 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ and $(2 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, respectively. (*b*) Part of the crystal structure of isomer (II) showing the formation of the $C(6)$ iodo···carbonyl chain along [001]. For the sake of clarity, all of the H atoms have been omitted. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(x, \frac{1}{2} - y, \frac{1}{2} + z)$, respectively.

dimensional framework by three hydrogen bonds, one each of N—H···O, C—H···O and C—H··· π (arene) types (Table 3), and the formation of the framework can readily be analysed in terms of three one-dimensional sub-structures, each containing just a single type of hydrogen bond.

In the simplest of the three sub-structures, atom N1 in the molecule at (x, y, z) acts as a hydrogen-bond donor to amidic atom O17 in the molecule at $(x, -1 + y, z)$, so generating by translation the $C(4)$ chain motif characteristic of carboxamides, here running parallel to the $[010]$ direction. The second sub-structure is generated by the C—H···O hydrogen bond; atom C24 in the molecule at (x, y, z) acts as a donor to the nitro atom O42 in the molecule at $(1 - x, 1 - y, -\frac{1}{2} + z)$, so forming a $C(13)$ chain running parallel to the $[20\bar{1}]$ direction and generated by the c -glide plane at $y = \frac{1}{2}$. The combination of

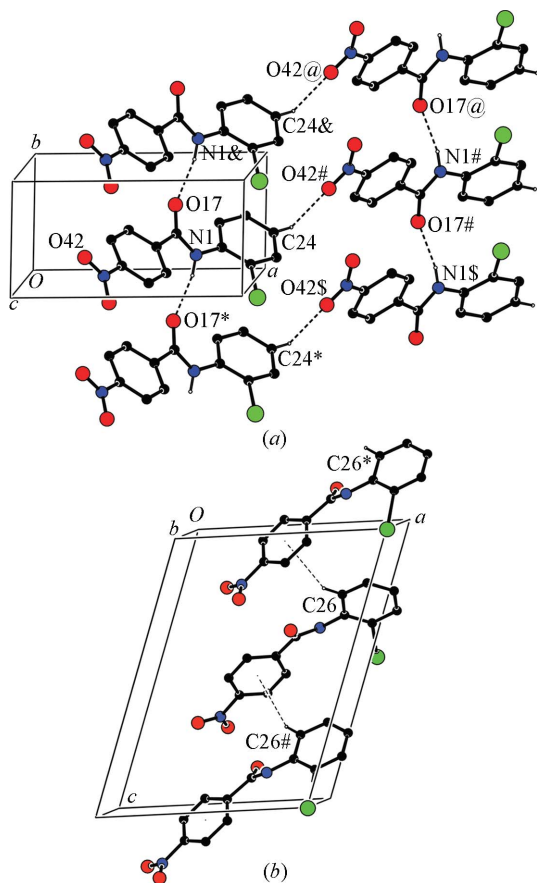


Figure 8

(a) Part of the crystal structure of isomer (III) showing the formation of a sheet of $R_4^1(32)$ rings parallel to $(10\bar{2})$ generated by the N—H···O and C—H···O hydrogen bonds. For the sake of clarity, the H atoms not involved in the motifs shown have been omitted. The atoms marked with an asterisk (*), a hash (#), a dollar sign (\$), an ampersand (&) or an 'at' sign (@) are at the symmetry positions $(x, -1 + y, z)$, $(1 + x, 1 - y, -\frac{1}{2} + z)$, $(1 + x, -y, -\frac{1}{2} + z)$, $(x, 1 + y, z)$ and $(1 + x, 2 - y, -\frac{1}{2} + z)$, respectively. (b) Part of the crystal structure of isomer (III) showing the formation of a chain along $[001]$ generated by the C—H··· π (arene) hydrogen bond. 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 $(x, 1 - y, -\frac{1}{2} + z)$ and $(x, 1 - y, \frac{1}{2} + z)$, respectively.

the $C(4)$ and $C(13)$ chains generates a $(10\bar{2})$ sheet in the form of a $(4,4)$ -net built from a single type of $R_4^1(32)$ ring (Fig. 8a). In the final sub-structure, atom C26 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the aryl ring C11–C16 of the molecule at $(x, 1 - y, -\frac{1}{2} + z)$, so producing a chain running parallel to the $[001]$ direction, again generated by the c -glide plane at $y = \frac{1}{2}$ (Fig. 8b). The combination of all three of the one-dimensional sub-structures then generates a three-dimensional framework structure.

3.2.4. Isomer (IV), *N*-(3-iodophenyl)-2-nitrobenzamide. Isomer (IV) crystallizes with $Z' = 2$ in space group $P2_1$, and the molecules are linked into a three-dimensional framework of considerable complexity by means of two N—H···O hydrogen bonds, four C—H···O hydrogen bonds (Table 3), two iodo···nitro interactions, both of two-centre type (Table 4), and a single aromatic π ··· π stacking interaction; C—H··· π (arene) hydrogen bonds are, however, absent.

The asymmetric unit (Fig. 3) was selected to contain the C—H···O hydrogen bond with the shortest H···O distance, and there are thus seven independent interactions linking these two-molecule aggregates. Each of the independent molecules, type 1 containing N11 and type 2 containing N31, forms a $C(4)$ chain running parallel to the $[010]$ direction and containing a single type of N—H···O hydrogen bond (Table 3). The chain of type 1 molecules is generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{1}{2})$, while the chain of type 2 molecules is generated by the 2_1 screw axis along $(0, y, 0)$. The formation of the type 1 chain is weakly augmented by an aromatic π ··· π stacking interaction. The nitrated ring C11–C16 of the type 1 molecule at (x, y, z) and the iodinated ring C21–C26 of the type 1 molecule at $(1 - x, -\frac{1}{2} + y, 1 - z)$ are inclined to one another at only $5.1(2)^\circ$: the corresponding ring-centroid separation is $3.735(2)$ Å with an interplanar spacing of ca 3.40 Å and a ring offset of ca 1.55 Å.

In combination with the C—H···O hydrogen bond within the asymmetric unit, the two $C(4)$ chains generate a $(10\bar{1})$ sheet containing a single type of $R_6^6(34)$ ring (Fig. 9a). The $(10\bar{1})$ sheets are linked to form the overall three-dimensional framework by two readily identifiable and rather simple one-dimensional sub-structures, one built from two C—H···O hydrogen bonds, and the other built from two iodo···carbonyl interactions.

Atom C35 in the type 2 molecule at (x, y, z) acts as a hydrogen-bond donor to the nitro atom O122 in the type 1 molecule at $(-1 + x, 1 + y, z)$: in combination with the C—H···O hydrogen bond within the asymmetric unit, this interaction then generates by translation a $C_2^2(14)$ chain running parallel to the $[1\bar{1}0]$ direction (Fig. 9b). Finally, atoms I23 and I43 in the aggregate at (x, y, z) form nearly linear two-centre contacts with, respectively, the carbonyl atoms O37 at $(x, -1 + y, 1 + z)$ and O17 at $(x, 1 + y, -1 + z)$ which, in combination with the C—H···O hydrogen bond within the asymmetric unit, generates by translation a $C_2^2(16)C_2^2(16)[R_2^2(14)]$ chain of rings running parallel to the $[01\bar{1}]$ direction (Fig. 9c). Either of these chain motifs is sufficient to link adjacent $(10\bar{1})$ sheets into a single three-dimensional framework.

3.2.5. Isomer (V), *N*-(3-iodophenyl)-3-nitrobenzamide. In the supramolecular structure of isomer (V) (Fig. 4), which is three-dimensional, it is possible to identify four independent one-dimensional sub-structures: one is built from an N—H···O hydrogen bond, augmented by two C—H···O hydrogen bonds, where all three interactions utilize a single acceptor (Table 3); another is built from just a single C—H···O hydrogen bond (Table 3); a third sub-structure is built from a two-centre iodo···nitro interaction (Table 4); finally, there is a one-dimensional sub-structure built from an aromatic π ··· π stacking interaction.

Atoms N1, C12 and C26 in the molecule at (x, y, z) all act as hydrogen-bond donors to the amidic atom O17 in the molecule at $(x, 1 - y, -\frac{1}{2} + z)$. These hydrogen bonds individually give rise to chains of $C(4)$, $C(5)$ and $C(6)$ types, respectively, all running parallel to the $[001]$ direction and generated by the c -glide plane at $y = \frac{1}{2}$; together they generate a $C(4)C(5)C(6)[R_2^1(6)][R_2^1(7)]$ chain of rings (Fig. 10a). The remaining C—H···O hydrogen bond (Table 2) generates a simple chain motif; atom C24 in the molecule at (x, y, z) acts as

a donor to the nitro atom O31 in the molecule at $(-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, so forming a $C(12)$ chain running parallel to the $[10\bar{1}]$ direction and generated by the n -glide plane at $y = \frac{1}{4}$ (Fig. 10b).

The iodo···nitro interaction (Table 4) likewise generates a simple chain. Atom I23 in the molecule at (x, y, z) forms a two-centre contact with the nitro atom O32 in the molecule at $(-\frac{1}{2} + x, -\frac{1}{2} + y, 1 + z)$, so generating by translation a $C(11)$ chain running parallel to the $[11\bar{2}]$ direction (Fig. 10c). Finally, the nitrated ring C11–C16 in the molecule at (x, y, z) and the iodinated ring C21–C26 in the molecule at $(\frac{1}{2} + x, \frac{1}{2} + y, z)$ are almost parallel, with a dihedral angle between them of only $2.5(2)^\circ$. The corresponding ring-centroid separation is $3.858(2)$ Å and the interplanar spacing is *ca* 3.48 Å, corresponding to a ring offset of *ca* 1.66 Å. Propagation by translation of this stacking interaction then generates a π -stacked chain running parallel to the $[110]$ direction (Fig. 10d). The combination of $[001]$, $[10\bar{1}]$, $[11\bar{2}]$ and $[110]$ chains suffices to generate a complex three-dimensional framework.

3.2.6. Isomer (VI), *N*-(3-iodophenyl)-4-nitrobenzamide. The molecules of isomer (VI) (Fig. 5) are linked into sheets by

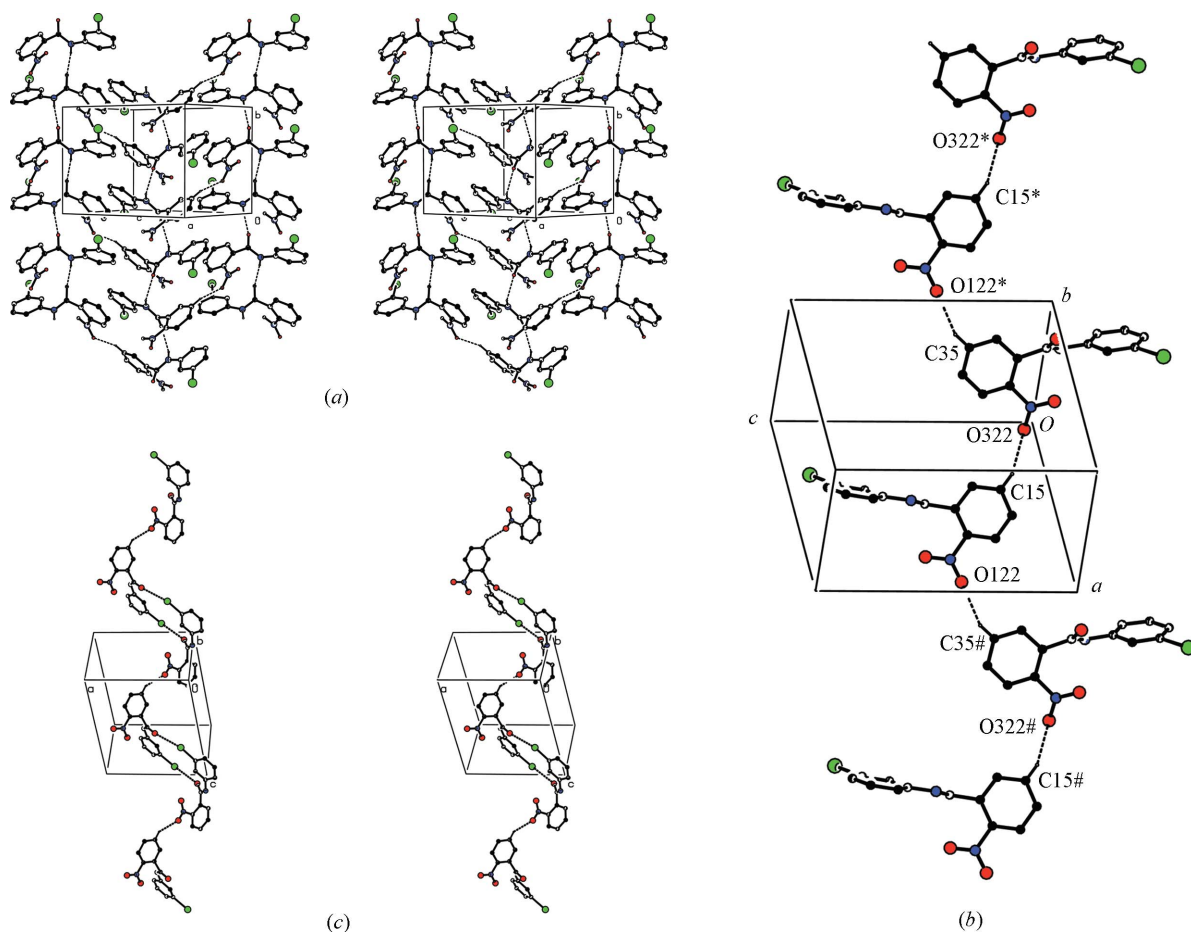


Figure 9

(a) A stereoview of part of the crystal structure of isomer (IV) showing the formation of a sheet of $R_6^c(34)$ rings parallel to $(10\bar{1})$ generated by the two N—H···O hydrogen bonds and the C—H···O hydrogen bond within the asymmetric unit. For the sake of clarity, the H atoms not involved in the motifs shown have been omitted. (b) Part of the crystal structure of isomer (IV) showing the formation of a $C_2^2(14)$ chain along $[110]$ generated by two C—H···O hydrogen bonds. 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 $(-1 + x, 1 + y, z)$ and $(1 + x, -1 + y, z)$, respectively. (c) A stereoview of part of the crystal structure of isomer (IV) showing the formation of a $C_2^2(16)C_2^2(16)[R_2^2(14)]$ chain of rings along $[011]$ generated by one C—H···O hydrogen bond and two iodo···carbonyl interactions. For the sake of clarity, the H atoms other than H15 have been omitted.

a combination of one N—H···O hydrogen bond and two C—H···O hydrogen bonds (Table 3), reinforced by a two-centre iodo···nitro interaction (Table 4), and these sheets are linked into a three-dimensional framework structure by a combination of an aromatic π ··· π stacking interaction and a dipolar carbonyl···carbonyl interaction.

Atoms N1 and C126 in the molecule at (x, y, z) both act as hydrogen-bond donors to the atom O41 in the molecule at $(-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z)$, so forming a $C(6)C(9)[R_2^1(7)]$ chain of rings running parallel to the $[101]$ direction and generated by the n -glide plane at $y = \frac{3}{4}$ (Fig. 11). At the same time, atom C24 at (x, y, z) acts as a hydrogen-bond donor to atom O17 in the molecule at $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, thus forming a simple $C(8)$

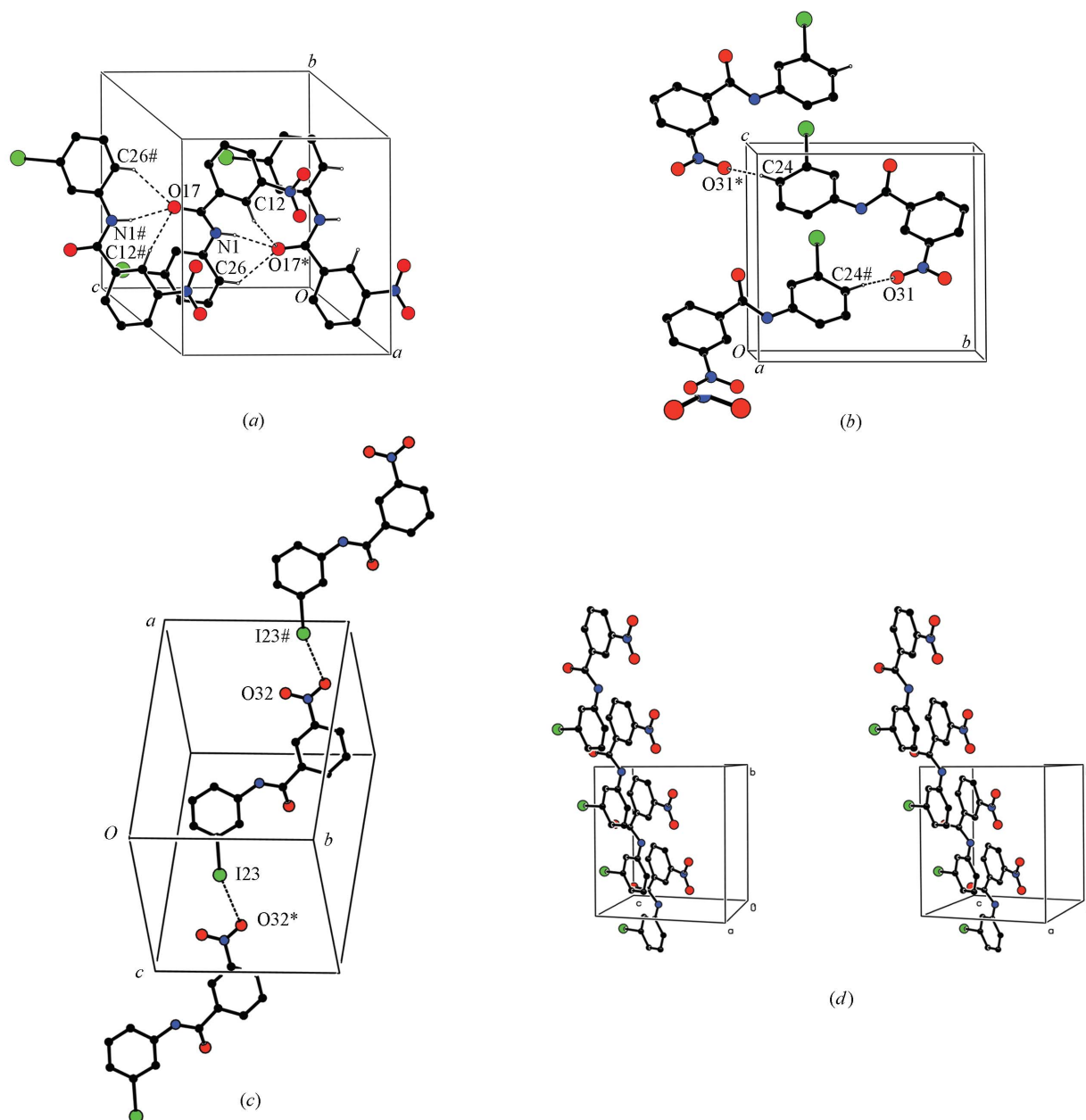


Figure 10

(a) Part of the crystal structure of isomer (V) showing the formation of a chain of rings along $[001]$ generated by one N—H···O hydrogen bond and two C—H···O hydrogen bonds. 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 $(x, 1 - y, -\frac{1}{2} + z)$ and $(x, 1 - y, \frac{1}{2} + z)$, respectively. (b). Part of the crystal structure of isomer (V) showing the formation of a $C(12)$ chain along $[101]$ generated by a single C—H···O hydrogen bond. 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 $(\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, respectively. (c) Part of the crystal structure of isomer (V) showing the formation of a $C(11)$ chain along $[112]$ generated by a two-centre iodo···nitro interaction. For the sake of clarity, all of the H atoms have been omitted. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-\frac{1}{2} + x, -\frac{1}{2} + y, 1 + z)$ and $(\frac{1}{2} + x, \frac{1}{2} + y, -1 + z)$, respectively. (d) A stereoview of part of the crystal structure of isomer (V) showing the formation of a π -stacked chain along $[110]$. For the sake of clarity, all of the H atoms have been omitted.

chain, also parallel to $[10\bar{1}]$ but this time generated by the n -glide plane at $y = \frac{1}{4}$. The combination of these two $[10\bar{1}]$ chains generates a $(10\bar{1})$ sheet (Fig. 11) which also includes a nearly linear two-centre iodo...nitro interaction between atom I23 in the molecule at (x, y, z) and atom O42 in the molecule at $(x, -1 + y, z)$ (Table 4), so forming a sheet containing three distinct types of ring, $R_2^1(7)$, $R_3^3(17)$ and $R_2^3(18)$ (Bernstein *et al.*, 1995; Starbuck *et al.*, 1999).

The nitrated ring C11–C16 in the molecule at (x, y, z) makes dihedral angles of only $2.8(2)^\circ$ with the iodinated ring C21–C26 in each of the two molecules at $(-x, 1 - y, 1 - z)$ and $(1 - x, 1 - y, 1 - z)$. The ring-centroid separations are $3.714(7)$ and $3.808(7)$ Å, respectively, and the interplanar spacings are *ca* 3.49 and 3.44 Å, corresponding to ring offsets of *ca* 1.27 and 1.63 Å. The action of the weaker of the two π stacking interactions is reinforced by an antiparallel type (II) (Allen *et al.*, 1998) dipolar interaction between the carbonyl groups in the molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, with $O \cdots C(1 - x, 1 - y, 1 - z) = 3.195(14)$ Å and $C - O \cdots C(1 - x, 1 - y, 1 - z) = 76.6(7)^\circ$. The effect of these two types of interaction is the linking of each $(10\bar{1})$ sheet to its two immediate neighbours, so forming a continuous three-dimensional structure.

3.2.7. Isomer (IX), *N*-(4-iodophenyl)-4-nitrobenzamide.

Isomer (IX) crystallizes with $Z' = 2$ in space group $P\bar{1}$; the molecules containing atoms N11 and N31 (Fig. 6) are denoted as types 1 and 2, respectively. The molecules are linked into a complex three-dimensional framework by a combination of two $N - H \cdots O$ and four $C - H \cdots O$ hydrogen bonds (Table 3) and two independent three-centre iodo...nitro interactions (Table 4).

Within the selected asymmetric unit the molecules are linked by $C - H \cdots O$ hydrogen bonds defining an $R_2^2(10)$ motif, and it is convenient to regard this compact bimolecular aggregate as the basic building block in the overall structure. The first of the one-dimensional sub-structures is built from two independent $N - H \cdots O$ hydrogen bonds. Atoms N11 and N31 at (x, y, z) acts as hydrogen-bond donors, respectively, to

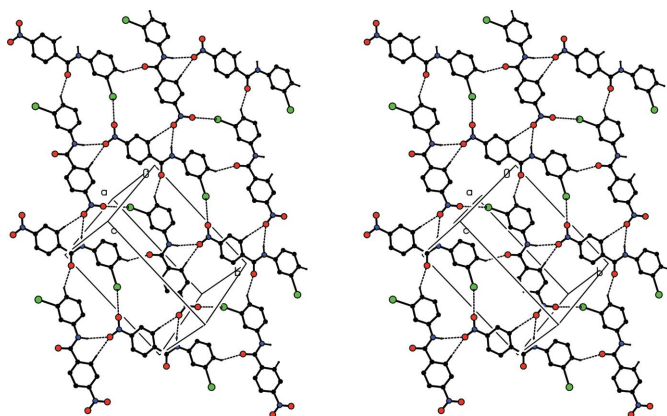


Figure 11

A stereoview of part of the crystal structure of isomer (VI) showing the formation of a hydrogen-bonded sheet parallel to $(10\bar{1})$, which is reinforced by a two-centre iodo...nitro interaction. For the sake of clarity, the H atoms not involved in the motifs shown have been omitted

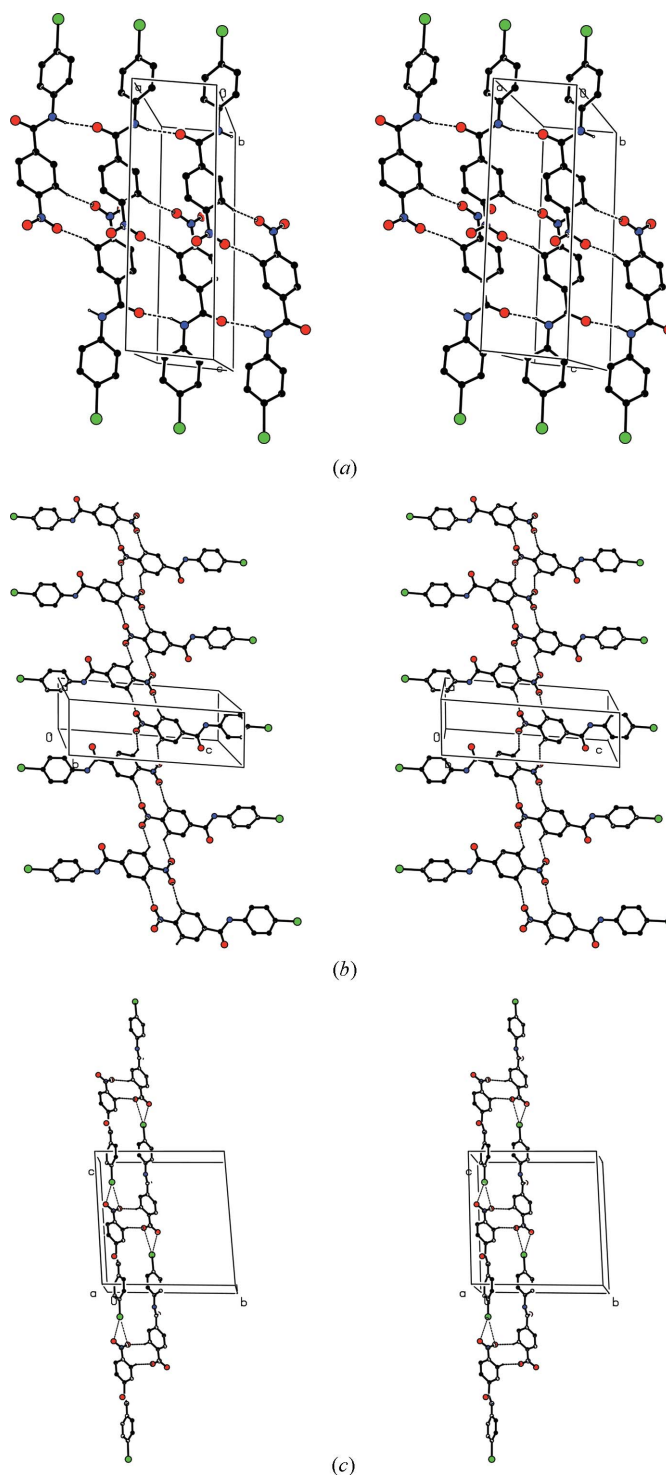


Figure 12

(a) A stereoview of part of the crystal structure of isomer (IX) showing the formation of a chain along $[100]$ comprising edge-fused $R_2^2(10)$ and $R_4^4(30)$ rings. For the sake of clarity, the H atoms not involved in the motif shown have been omitted. (b) A stereoview of part of the crystal structure of isomer (IX) showing the formation of a chain along $[310]$ containing three types of $R_2^2(10)$ ring. For the sake of clarity, the H atoms not involved in the motif shown have been omitted. (c) A stereoview of part of the crystal structure of isomer (IX) showing the formation of a chain along $[001]$ comprising edge-fused $R_2^2(10)$ and $R_4^4(24)$ rings. For the sake of clarity, the H atoms not involved in the motif shown have been omitted.

atoms O17 at $(1 + x, y, z)$ and O37 at $(-1 + x, y, z)$. These two hydrogen bonds individually generate by translation two independent antiparallel $C(4)$ chains running parallel to the $[100]$ direction, one built exclusively of type 1 molecules and the other containing only type 2 molecules. In combination with the two $C-H \cdots O$ hydrogen bonds within the asymmetric unit, the $N-H \cdots O$ hydrogen bonds generate a $[100]$ chain of edge-fused $R_2^2(10)$ and $R_4^4(30)$ rings (Fig. 12a).

The second one-dimensional motif is built solely from $C-H \cdots O$ hydrogen bonds. Atom C13 at (x, y, z) acts as a hydrogen-bond donor to atom O141 at $(-x, 1 - y, 1 - z)$, so generating by inversion an $R_2^2(10)$ dimer of type 1 molecules centred at $(0, \frac{1}{2}, \frac{1}{2})$; similarly, atom C33 at (x, y, z) acts as a donor to atom O341 at $(3 - x, -y, 1 - z)$, generating a second centrosymmetric $R_2^2(10)$ dimer, this time containing type 2 molecules and centred at $(\frac{3}{2}, 0, \frac{1}{2})$. These motifs combine with the hydrogen bonds within the asymmetric unit to generate a chain of edge-fused rings running parallel to the $[3\bar{1}0]$ direction, and containing three distinct types of $R_2^2(10)$ ring (Fig. 12b).

The final one-dimensional sub-structure is built from two independent three-centre iodo \cdots nitro interactions, each involving just one type of molecule (Table 3). Atom I24 at (x, y, z) forms a nearly symmetrical $I \cdots (O)_2$ contact with atoms O141 and O142 at $(x, y, 1 + z)$, while atom I44 at (x, y, z) forms a similar, although less symmetrical, contact with atoms O341 and O342 at $(x, y, -1 + z)$. The individual interactions generate by translation two independent antiparallel $C(13)C(13)[R_2^1(4)]$ motifs (Starbuck *et al.*, 1999), while the two together, in combination with the hydrogen bonds within the asymmetric unit, generate a chain of edge-fused $R_2^2(10)$ and $R_4^4(24)$ rings parallel to $[001]$ (Fig. 12c).

The combination of the chains along $[100]$, $[001]$ and $[3\bar{1}0]$ suffices to generate a three-dimensional structure of considerable complexity.

3.3. General comparison of the structures

Although the isomers described here all adopt three-dimensional supramolecular structures, the range and identity of the direction-specific intermolecular forces is different in each isomer.

Taking firstly the isomers (I)–(III), (V) and (VI), which crystallize with $Z' = 1$, these all contain a single $N-H \cdots O$ hydrogen bond but, as noted above (see §3.2), this involves a carbonyl O atom as the acceptor, except in isomer (VI), where a nitro O atom acts as the acceptor. The structures of all these isomers contain $C-H \cdots O$ hydrogen bonds, one in isomer (II), two in each of (I), (III) and (VI), and three in isomer (V); while these usually have nitro O atoms as the acceptor, carbonyl O atoms participate in isomers (V) and (VI). Iodo \cdots carbonyl interactions are present only in isomer (II), while two-centre iodo \cdots nitro interactions are present in each of (I), (V) and (VI); by contrast, there are no short $I \cdots O$ contacts of any sort in isomer (III). Isomer (II) does, however, present the sole example amongst all of these isomers of $C-H \cdots \pi$ (arene) hydrogen bonding. Aromatic $\pi \cdots \pi$ stacking

interactions are present in each of the isomers (V) and (VI), but in none of the other $Z' = 1$ isomers, while dipolar carbonyl \cdots carbonyl interactions are observed only in the structure of isomer (VI).

Of the two isomers, (IV) and (IX), having $Z' = 2$, both contain two independent $N-H \cdots O$ hydrogen bonds, all with carbonyl O acceptors, and both contain four independent $C-H \cdots O$ hydrogen bonds, all with nitro O acceptors. However, the iodo \cdots nitro interactions are of two-centre type in isomer (IV), but of three-centre type in isomer (IX), while only the structure of isomer (IV) contains aromatic $\pi \cdots \pi$ stacking interactions.

Just as the range and number of distinct intermolecular interactions in any one of these isomers could not readily be predicted, even given a detailed knowledge of each of the other isomers, so too the detailed construction of the three-dimensional framework structure of any given isomer is not predictable from the structures of all of the others. Allied to this, even the crystallization characteristics show no discernible pattern; with the exception of isomers (II) and (VI), which have been analysed in two different settings of the same space group, no two of the isomers reported here adopt the same space group (Table 1), while isomer (I) crystallizes in $P2_12_12_1$ (Wardell *et al.*, 2005); of the seven isomers whose structure are now known, no fewer than four crystallize in non-centrosymmetric space groups.

4. Concluding discussion

We have found in several earlier studies of closely related series of compounds, in particular in series of geometric isomers, that every member of a given series manifests in its crystal structure a different range of direction-specific intermolecular interactions, such that no individual structure could readily be predicted even with full a knowledge of the structures of every other member of the same series (Glidewell, Howie *et al.*, 2002; Glidewell, Low *et al.*, 2002, 2004). The same conclusion must be drawn from the structures described here: neither the molecular conformations nor the supramolecular aggregation patterns are readily predictable from one isomer to another. Equally, the variations in the space groups (Table 1) from one isomer to another are not readily explicable, nor whether the space group is centrosymmetric or non-centrosymmetric, nor whether the non-centrosymmetric structures are polar or non-polar. We have suggested above (§3.1) that in the present series the direction-specific intermolecular forces are well able to overcome the intramolecular rotational barriers defining the molecular conformations; consistent with this proposition is the observation of conformational polymorphism in the related series (*D*) (Ferguson *et al.*, 2005), where the conformations are clearly determined by the intermolecular forces.

A particular puzzle is posed by the three-centre iodo \cdots nitro interaction, where a series of elegant structures containing symmetrical or nearly symmetrical three-centre interactions have been reported by others; the earlier examples serve as the archetypes for this interaction, which rapidly

came to be regarded as a robust supramolecular synthon for crystal engineering (Allen *et al.*, 1994; Thalladi *et al.*, 1996; Masciocchi *et al.*, 1998; George *et al.*, 2004). However, these reports each refer to a single geometrical isomer and these structures all happen to involve molecular components with the substituents at the distal ends, namely the 1:1 adduct of 1,4-diiodobenzene and 1,4-dinitrobenzene (Allen *et al.*, 1994), 4-iodonitrobenzene (Thalladi *et al.*, 1996), 4-iodo-4'-nitrobiphenyl (Masciocchi *et al.*, 1998) and *N*-4-iodophenyl-*N'*-4'-nitrophenylurea (George *et al.*, 2004). Likewise, we have observed this interaction in *N*-(4-iodophenylsulfonyl)-4-nitroaniline and in *N*-(4'-nitrodophenylsulfonyl)-4-iodoaniline, but not in any of the other isomers in these series; indeed, in the series (A)–(G) noted above (see §1), wherever one or other of the iodo or nitro substituents is in the 2- or 3-positions, three-centre iodo··nitro interactions are absent. Consistent with these observations, in 2,4,6-trinitroiodobenzene (picryl iodide), a three-centre interaction is formed by the 4-nitro substituent but not by the other two nitro groups (Weiss *et al.*, 1999), while in 1,2-diiodo-4-nitro-5-(butylamino)benzene, the 1-iodosubstituent participates in a three-centre iodo··nitro interaction, while the 2-iodo substituent is involved only in a two-centre iodo··nitro interaction (Senskey *et al.*, 1995). Hence, it may be that the initial acceptance of the three-centre iodo··nitro synthon owes less to its intrinsic utility than to the chance selection of the isomeric forms of the compounds used in the initial studies. On the other hand, there is a three-centre iodo··nitro interaction in *N*-(4-iodophenyl)-3-nitrophthalimide, but there are no iodo··nitro interactions at all in *N*-(4-iodophenyl)-2-nitrophthalimide (Glidewell, Low, Skakle, Wardell & Wardell, 2005). Thus, in substituted aryl systems this synthon appears to behave predictably only for specific isomeric forms, but normally to be absent for the remaining isomeric forms. Reported examples of structures that are described as having been specifically and deliberately engineered by the application of particular supramolecular synthons are often restricted to specific isomer forms of their molecular components, sometimes to a single isomer; in some of these cases there must arise at least a suspicion of an element of *post hoc* rationalization as opposed to reliable supramolecular design.

The difficulty of structure prediction appears to be entirely characteristic of the crystal structures of molecular compounds where all of the intermolecular forces are comparatively weak, but of comparable magnitudes to the rotational energy barriers associated with single bonds, so that the molecular conformations are a direct reflection of the intermolecular interactions. For this reason alone, molecular conformations computed for isolated molecules are unlikely ever to reproduce the conformations observed experimentally in the crystalline state. More disturbing is the fact that, to date, attempts to make computed predictions of the crystal and molecular structures of even rather simple compounds have met with only limited success (Lommerse *et al.*, 2000; Motherwell *et al.*, 2002; Day *et al.*, 2005). Compounds whose molecules contain internal degrees of freedom, such as rotations about single bonds, particularly where aryl rings are

connected to a semi-rigid unit, as in the examples discussed here, seem to pose particular difficulty, possibly associated with the delicate interplay of intramolecular and intermolecular forces.

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