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Hydrogen-bonded chains of rings in 3-iodobenzaldehyde 2,4-dinitrophenylhydrazone and 4-iodobenzaldehyde 2,4-dinitrophenylhydrazone, and a three-dimensional framework in 4-iodobenzaldehyde 4-nitrophenylhydrazone generated by the combination of N—H···O and C—H···O hydrogen bonds with iodo–nitro interactions

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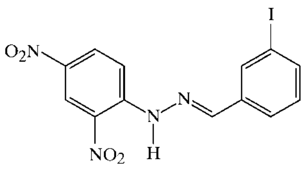
Molecules of 3- and 4-iodobenzaldehyde 2,4-dinitrophenylhydrazone, $C_{13}H_9IN_4O_4$, are both effectively planar. In the crystal structure of each compound, molecules are linked by a combination of $N-H\cdots O$ and $C-H\cdots O$ hydrogen bonds into complex chains of rings, containing four and three different ring motifs, respectively; neither compound contains any iodo–nitro interactions. In 3-iodobenzaldehyde 4-nitrophenylhydrazone, $C_{13}H_{10}IN_3O_2$, where the iodinated aryl ring is disordered over two sets of sites, the hydrogen bonds generate a chain of rings, while two independent $I\cdots O$ interactions generate a three-dimensional framework.

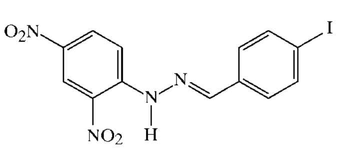
Comment

We report here the molecular and supramolecular structures of the title compounds, (I)–(III), and we compare their supramolecular behaviours with those of the related compounds (IV) and (V) which we reported recently (Glidewell *et al.*, 2003). In no two of these compounds does the interplay of hard and soft hydrogen bonds with iodo–nitro interactions generate the same pattern of supramolecular aggregation.

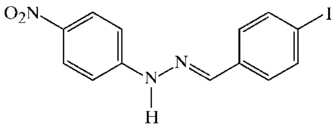
The molecules of (I)–(III) are all nearly planar, as shown by the key torsion angles (Tables 1, 3 and 5); the sole exception concerns the minor orientation of the iodinated ring in (III). The bond distances and interbond angles present no unusual features, and the principal structural interest lies in the intermolecular interactions and their consequences.



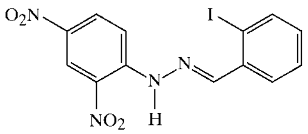
(I)



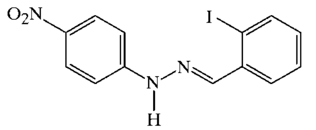
(II)



(III)



(IV)



(V)

Although the isomeric compounds (I) and (II) both crystallize in space group *C*2/*c*, they have very different unit-cell dimensions (see *Experimental*). However, we will discuss the supramolecular structures of these two compounds together, as they have a number of features in common.

There are neither iodo–nitro interactions nor aromatic π–π stacking interactions in the structures of (I) and (II), and $N-H\cdots\pi_{\rm arene}$ and $C-H\cdots\pi_{\rm arene}$ hydrogen bonds are also absent from both. Instead, the supramolecular structure of both compounds is determined by a three-centre $N-H\cdots(O)_2$ hydrogen bond, augmented by two-centre $C-H\cdots O$ hydrogen bonds (Tables 2 and 4). While the effect of the three-centre interaction is identical in (I) and (II), the effect of the $C-H\cdots O$ hydrogen bonds is different in the two compounds, and it is this difference that generates their different overall structures. In both compounds, however, the dominant $C-H\cdots O$ hydrogen bond involves the C—H bond that lies between the two nitro groups and which may therefore be expected to be the most acidic C—H bond in the molecule.

In both compounds (Figs. 1 and 2), hydrazone atom N2 acts as a donor in a three-centre hydrogen bond in which the two acceptors are, firstly, atom O21 in the same molecule at (x, y, z), giving rise to an $S(6)$ motif (Bernstein *et al.*, 1995), and secondly, atom O21 in the molecule at $(1 - x, 1 - y, 1 - z)$, producing a centrosymmetric dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, which contains an unusual sequence of three fused rings with graph-set descriptor $S(6)R_2^2(4)S(6)$ (Fig. 3). In both compounds, these dimeric aggregates are linked into chains by a single $C-H\cdots O$ hydrogen bond, but in (I), the chain is generated by

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translation, while in (II), it is generated by the action of a twofold rotation axis.

In (I), atom C13 in the molecule at (*x*, *y*, *z*), which is a component of the dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, acts as a hydrogen-bond donor to nitro atom O41 in the molecule at $(1 - x, -2 - y, 1 - z)$, which is a component of the dimer centred at $(\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$, so forming an $R^2_2(10)$ motif (Fig. 3). Propagation of this single interaction by inversion and translation then generates a chain of rings running parallel to the [010] direction. This chain is further reinforced, albeit rather weakly, by a second C—H···O hydrogen bond, in which atom C5 at (*x*, *y*, *z*) acts as a donor to nitro atom O42 in the molecule at $(x, -1 + y, z)$, which is a component of the dimer centred at $(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$, so completing the formation of a continuous chain of edge-fused rings containing four different types of ring, namely $S(6)$, $R^2_2(4)$, $R^2_2(10)$ and $R^3_3(16)$ (Fig. 3). This nearly planar structure can alternatively be regarded as a multiply perforated ribbon.

In (II), by contrast, atom C13 in the molecule at (*x*, *y*, *z*), itself a component of the $R^2_2(4)$ dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, acts as a hydrogen-bond donor to nitro atom O41 in the molecule at $(1 - x, y, \frac{1}{2} - z)$, which is a component of the dimer centred at $(\frac{1}{2}, \frac{1}{2}, 0)$. In turn, atom C13 at $(1 - x, y, \frac{1}{2} - z)$ acts as a donor to atom O4 at (*x*, *y*, *z*), so that the $R^2_2(10)$ motif in this compound is generated by the twofold rotation axis along $(\frac{1}{2}, y, \frac{1}{4})$. Propagation of this single C—H···O hydrogen bond then generates, by rotation and inversion, a deeply folded chain of rings running parallel to the [001] direction and containing three distinct types of ring (Fig. 4). The iodophenyl ring plays no part in the supramolecular aggregation.

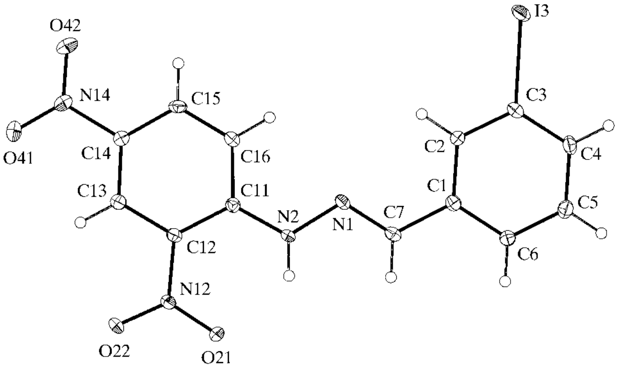

Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

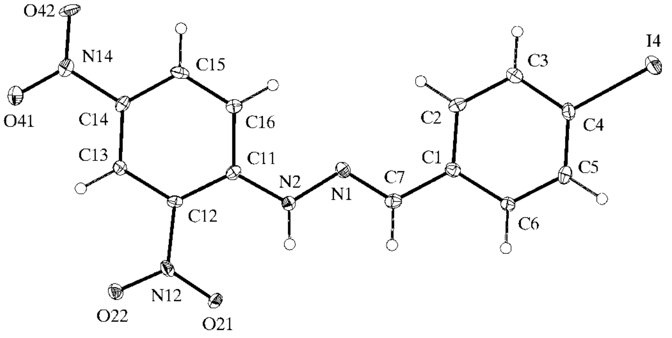

Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

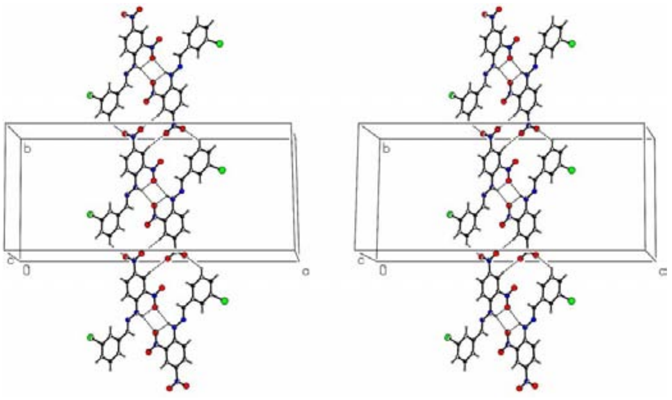

Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a continuous chain of edge-fused rings running along [010].

The supramolecular structures of (I) and (II) (Figs. 3 and 4) may be contrasted with that of the isomeric 2-iodobenzaldehyde 2,4-dinitrophenylhydrazone, (IV) (Glidewell *et al.*, 2003). In the crystal structure of (IV), the whole molecule is disordered over two sets of sites; for the major orientation, there are no direction-specific interactions between the molecules, while for the minor orientation, a single C—H···O hydrogen bond generates centrosymmetric $R^2_2(10)$ dimers. As in (I) and (II), it is the C—H bond between the two nitro groups that is involved.

In (III), the molecules (Fig. 5) are linked into a zigzag chain of rings by means of a co-operative combination of N—H···O and C—H···O hydrogen bonds (Table 6). Hydrazone atom N2 and aryl atom C16 in the molecule at (*x*, *y*, *z*) act as hydrogen-bond donors to nitro atoms O42 and O41, respectively, in the molecule at $(1 + x, 1 - y, -\frac{1}{2} + z)$, so producing a

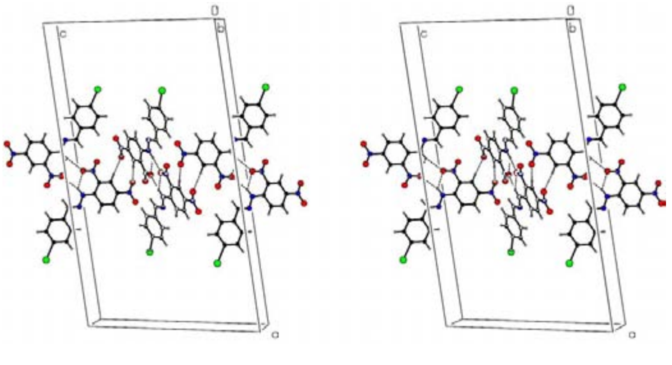

Figure 4
A stereoview of part of the crystal structure of (II), showing the formation of a chain of rings running along [001].

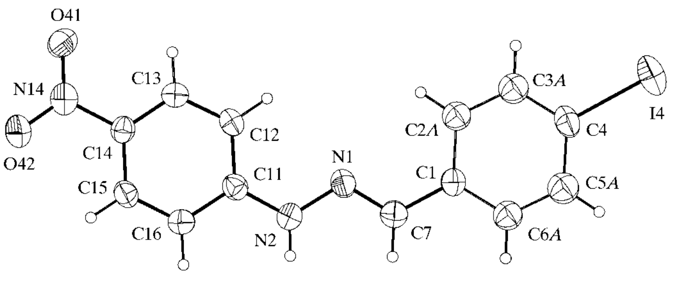

Figure 5
The molecule of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, only the major orientation of the disordered aryl ring (C1–C6) is shown.

$C(6)C(8)[R^2_2(8)]$ chain of rings running parallel to the $[20\bar{1}]$ direction and generated by the *c*-glide plane at $y = \frac{1}{2}$ (Fig. 6). A second such chain, related to the first by the C-centring operation, is generated by the *c*-glide plane at $y = 0$, but there are neither $X-\text{H}\cdots\pi_{\text{arene}}$ hydrogen bonds (X = C or N) nor aromatic π–π stacking interactions between or within the chains.

There are, however, two long two-centre iodo–nitro interactions between the molecules. Atom I4 in the molecule at (x, y, z) makes contacts with nitro atom O41 in the molecule at $(\frac{3}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$ [I···O = 3.537 (4) Å and C—I···O = 142.9 (2)°] and with nitro atom O42 in the molecule at $(\frac{3}{2}+x, -\frac{1}{2}+y, z)$ [I···O = 3.525 (4) Å and C—I···O = 140.4 (2)°]. If these two interactions are regarded as structurally significant then it is a straightforward matter to show that they generate a continuous three-dimensional structure, independent of the contribution of the hydrogen bonding. The two I···O interactions individually generate $C(14)$ chains (Starbuck *et al.*, 1999) running parallel to the $[30\bar{1}]$ and $[3\bar{1}0]$ directions, respectively (Fig. 7). In addition, the action of the glide planes generates chains running parallel to the [310] direction. Finally, the combination of the two interactions together generates a chain running parallel to the [010] direction (Fig. 7). Atom I4 in the molecule at $(\frac{3}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$ makes an I···O contact with atom O42 at $(3+x, 1-y, -\frac{1}{2}+z)$, while atom O41 in this molecule at $(3+x, 1-y, -\frac{1}{2}+z)$ makes an I···O contact with atom I4 in the molecule at $(\frac{3}{2}+x, \frac{1}{2}+y, z)$, which is in turn linked directly to the molecule at $(x, 1+y, z)$, so generating a $C^2_2(28)$ chain parallel to [010] (Fig. 7). The combination of the [010], [310], $[3\bar{1}0]$ and $[30\bar{1}]$ iodo–nitro chains is sufficient to generate a three-dimensional framework.

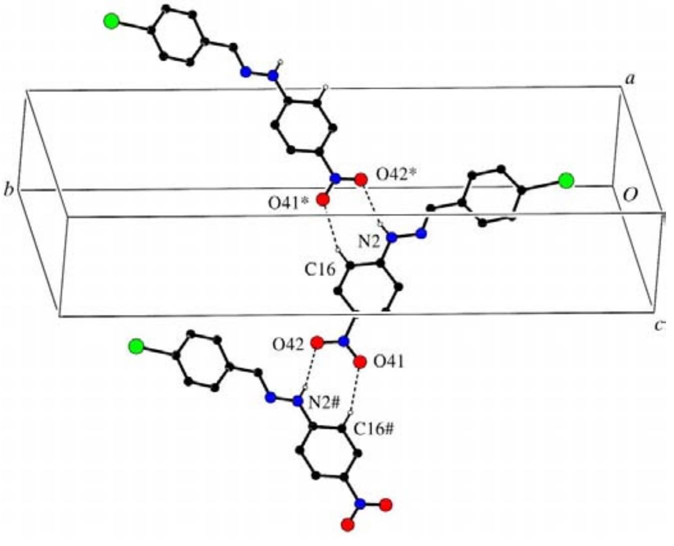

Figure 6
Part of the crystal structure of (III), showing the formation of a hydrogen-bonded chain of rings along $[20\bar{1}]$. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(1+x, 1-y, -\frac{1}{2}+z)$ and $(-1+x, 1-y, \frac{1}{2}+z)$, respectively.

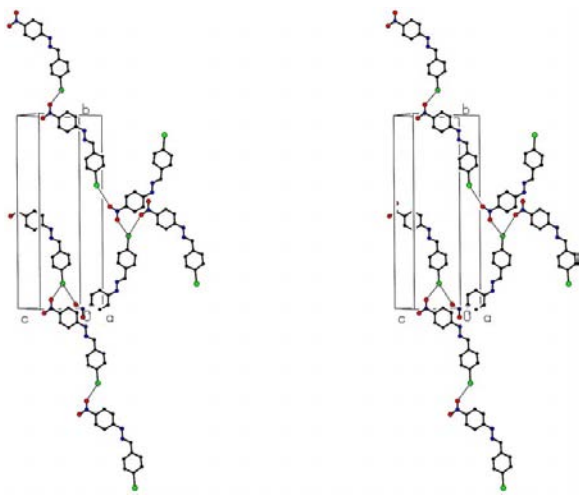

Figure 7
A stereoview of part of the crystal structure of (III), showing the formation of iodo–nitro chains along [010], $[3\bar{1}0]$ and $[30\bar{1}]$.

In 2-iodobenzaldehyde 4-nitrophenylhydrazone, (V) (Glidewell *et al.*, 2003), an isomer of (III), a combination of an N—H···O hydrogen bond and a single two-centre iodo–nitro interaction links the molecules into a chain of edge-fused $R^3_3(18)$ rings. It is unfortunate that we cannot discuss here the supramolecular structure of the further isomer 3-iodobenzaldehyde 4-nitrophenylhydrazone, but repeated attempts to prepare this compound in pure crystalline form have been unsuccessful.

Experimental

For the preparation of each of (I)–(III), a finely powdered mixture of the appropriate iodobenzaldehyde and the appropriate phenylhydrazine (1:1 molar ratio) was heated gently on a hotplate until effervescence ceased. The mixtures were cooled and recrystallized from ethanol.

Compound (I)

Crystal data

$C_{13}H_9IN_4O_4$
$M_r = 412.14$
Monoclinic, $C2/c$
$a = 30.0604\ (9)$ Å
$b = 13.5628\ (4)$ Å
$c = 7.0263\ (2)$ Å
$\beta = 101.390\ (2)^\circ$
$V = 2808.23\ (14)$ Å^3
$Z = 8$
$D_x = 1.950$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3220 reflections
$\theta = 3.0$–27.5°
$\mu = 2.31$ mm^{-1}
$T = 120\ (2)$ K
Plate, colourless
0.45 × 0.25 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.424$, $T_{\max} = 0.955$
17 244 measured reflections
3220 independent reflections
2545 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$
$\theta_{\max} = 27.5^\circ$
$h = -38 \rightarrow 38$
$k = -17 \rightarrow 15$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.070$
$S = 1.02$
3220 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 3.2981P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.77$ e Å^{-3}
$\Delta\rho_{\min} = -1.32$ e Å^{-3}

Table 1
Selected torsion angles (°) for (I).

C2—C1—C7—N1	0.7 (4)	N1—N2—C11—C12	176.9 (2)
C1—C7—N1—N2	179.6 (2)	C11—C12—N12—O21	−4.5 (4)
C7—N1—N2—C11	−172.6 (3)	C13—C14—N14—O41	4.1 (4)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O21	0.88	1.98	2.607 (3)	127
N2—H2*A*···O21$^{\rm i}$	0.88	2.45	3.289 (3)	160

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Compound (II)

Crystal data

$C_{13}H_9IN_4O_4$
$M_r = 412.14$
Monoclinic, $C2/c$
$a = 32.359\ (2)$ Å
$b = 4.6293\ (3)$ Å
$c = 18.4169\ (15)$ Å
$\beta = 97.631\ (3)^\circ$
$V = 2734.4\ (3)$ Å^3
$Z = 8$
$D_x = 2.002$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3074 reflections
$\theta = 3.2$–27.6°
$\mu = 2.37$ mm^{-1}
$T = 120\ (2)$ K
Needle, orange
0.45 × 0.04 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.416$, $T_{\max} = 0.954$
12 789 measured reflections
3074 independent reflections
1686 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.118$
$\theta_{\max} = 27.6^\circ$
$h = -41 \rightarrow 40$
$k = -5 \rightarrow 6$
$l = -23 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.087$
$S = 0.94$
3074 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0235P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.82$ e Å^{-3}
$\Delta\rho_{\min} = -1.09$ e Å^{-3}

Table 3
Selected torsion angles (°) for (II).

C2—C1—C7—N1	−1.2 (9)	N1—N2—C11—C12	177.1 (5)
C1—C7—N1—N2	178.8 (5)	C11—C12—N12—O21	−7.5 (7)
C7—N1—N2—C11	176.2 (5)	C13—C14—N14—O41	4.1 (7)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O21	0.88	2.04	2.640 (5)	125
N2—H2*A*···O21$^{\rm i}$	0.88	2.56	3.353 (6)	150
C13—H13···O41$^{\rm ii}$	0.95	2.37	3.310 (6)	175

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

Compound (III)

Crystal data

$C_{13}H_{10}IN_3O_2$
$M_r = 367.14$
Monoclinic, Cc
$a = 4.9348\ (4)$ Å
$b = 27.825\ (2)$ Å
$c = 10.3893\ (9)$ Å
$\beta = 101.076\ (2)^\circ$
$V = 1399.99\ (19)$ Å^3
$Z = 4$
$D_x = 1.742$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4058 reflections
$\theta = 2.5$–32.5°
$\mu = 2.29$ mm^{-1}
$T = 291\ (2)$ K
Plate, orange
0.42 × 0.20 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.447$, $T_{\max} = 0.914$
7191 measured reflections
4058 independent reflections
1686 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\max} = 32.5^\circ$
$h = -7 \rightarrow 7$
$k = -42 \rightarrow 35$
$l = -15 \rightarrow 10$

Table 5
Selected torsion angles (°) for (III).

C2*A*—C1—C7—N1	10.4 (11)	C7—N1—N2—C11	−176.5 (5)
C2*B*—C1—C7—N1	−24.5 (11)	N1—N2—C11—C12	−7.7 (8)
C1—C7—N1—N2	176.5 (5)	C13—C14—N14—O41	−1.4 (7)

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O42$^{\rm iii}$	0.86	2.29	3.117 (7)	163
C16—H16···O41$^{\rm iii}$	0.93	2.44	3.330 (7)	159

Symmetry code: (iii) $1 + x, 1 - y, z - \frac{1}{2}$.

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.106$
$S = 0.88$
4058 reflections
169 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ e Å^{-3}
Absolute structure: Flack (1983), 1511 Friedel pairs
Flack parameter = 0.01 (3)

Crystals of (I)–(III) are all monoclinic, and for each compound the systematic absences permitted *C*2/*c* and *Cc* as possible space groups. Space group *C*2/*c* was chosen for (I) and (II), and *Cc* was chosen for (III); these selections were all confirmed by the subsequent structural analyses. In (III), the C—H units of the iodinated ring were disordered over two sets of sites having occupancies of 0.545 (12) (C*nA*; *n* = 2, 3, 5 and 6) and 0.455 (12) (C*nB*); the disordered C atoms were all refined isotropically. A data set for (III) collected at 120 (2) K provided no tractable solution, but in the 291 (2) K data set, only ~42% of the reflections are labelled as observed. All H atoms were treated as riding atoms, with C—H distances of 0.95 Å and N—H distances of 0.88 Å for (I) and (II) at 120 (2) K, and C—H distances of 0.93 Å and N—H distances of 0.86 Å for (III) at 291 (2) K. For (III), the correct orientation of the structure relative to the directions of the polar axes was established by means of the Flack (1983) parameter.

For all compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1680). Services for accessing these data are described at the back of the journal.

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