

Supramolecular structures of three isomeric (*E,E*)-1-(2-iodophenyl)-4-(nitrophenyl)-2,3-diaza-1,3-butadienes: changes in intermolecular interactions consequent upon changes of substituent location

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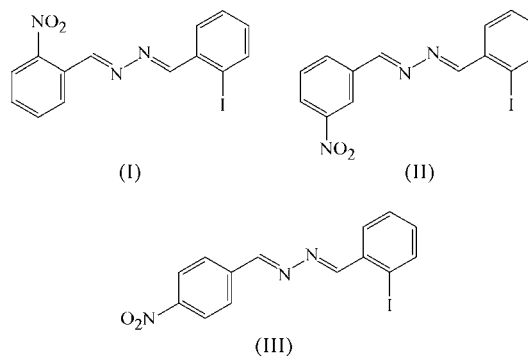
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The supramolecular structures of the three isomeric (*E,E*)-1-(2-iodophenyl)-4-(2/3/4-nitrophenyl)-2,3-diaza-1,3-butadienes, C₁₄H₁₀IN₃O₂, are compared. In the 2-nitro isomer, the molecules are disordered across centres of inversion in space group *C2/c* and are linked into chains by a two-centre iodo–nitro interaction. The molecules of the 3-nitro isomer are linked into a three-dimensional framework by a combination of C–H···O and C–H···I hydrogen bonds and aromatic π – π stacking interactions, while molecules of the 4-nitro isomer are linked into sheets by a C–H···O hydrogen bond and a two-centre iodo–nitro interaction.

Comment

In the course of our continuing investigation of the interplay between hard and soft (Braga *et al.*, 1995; Desiraju & Steiner, 1999) hydrogen bonds, 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 (Kelly *et al.*, 2002), benzylideneanilines (Glidewell, Howie *et al.*, 2002; Wardell *et al.*, 2002), benzyanilines (Glidewell, Low *et al.*, 2002; Glidewell, Low, Skakle, Wardell & Wardell, 2004) benzenesulfanylanilines (Glidewell *et al.*, 2003a) and phenylhydrazones (Glidewell *et al.*, 2003b; Glidewell, Low, Skakle & Wardell, 2004). We have now extended this study to the isomeric (*E,E*)-1-(2-iodophenyl)-4-(2/3/4-nitrophenyl)-2,3-diaza-1,3-butadienes, and report here on the molecular and supramolecular structures of three such isomers, containing the

2-nitrophenyl, 3-nitrophenyl, or 4-nitrophenyl substituents, compounds (I)–(III), respectively (Figs. 1–3).



The crystallization characteristics of the three isomers (I)–(III) are all different, with (I) crystallizing in *C2/c* with $Z' = \frac{1}{2}$, and a value of $Z' = 1$ for each of isomers (II) and (III), in space groups $P\bar{1}$ and *C2/c*, respectively. However, the intramolecular geometries are all fairly similar. The central –CH=N–N=CH– fragment is strictly planar in isomer (I) and approximately so in isomers (II) and (III), and the substituents at each of the C=N bonds adopt *E* configurations. The independent aryl rings are all twisted slightly away from this plane, to the greatest extent in (I) and the least in (III), as shown by the relevant torsion angles (Tables 1, 2 and 4). In addition, the nitro groups are all rotated away from the planes

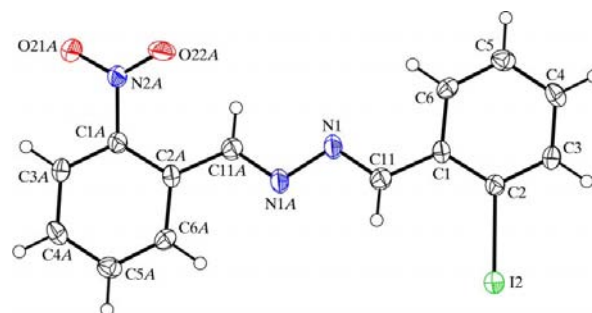


Figure 1

The molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, only one orientation of the molecule is shown. Atoms marked A are at the symmetry position (1 – x, 1 – y, 1 – z).

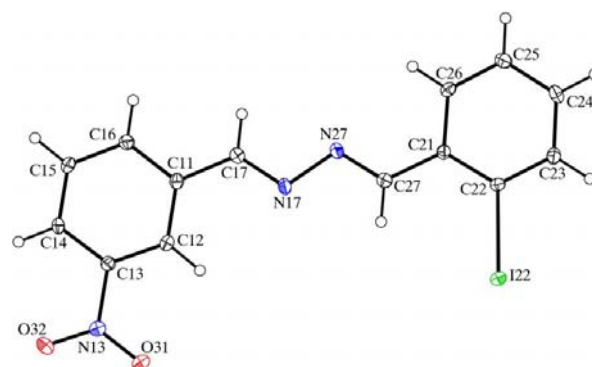


Figure 2

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

of the adjacent aryl rings, to the greatest extent in (I) and the least in (II). Corresponding bond lengths and angles are all very similar for the three isomers and there are no unusual values. In isomer (I), the population of the iodo site was found to exceed that of the nitro sites, with occupancy factors of 0.559 (3) and 0.441 (3), respectively. We conclude that some reorganization of substituted aryl groups has occurred, either during the synthesis of (I) or during its crystallization, such that a small proportion of (*E,E*)-1,4-bis(2-iodophenyl)-2,3-diaza-1,3-butadiene has co-crystallized with (I).

The molecules of compound (I) (Fig. 1) lie across inversion centres in space group $C2/c$, with the iodo and nitro substituents disordered; the reference molecule was selected as that lying across $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The paucity of direction-specific intermolecular interactions in (I) is striking: there are no intermolecular hydrogen bonds of any kind and no aromatic π - π stacking interactions are present. However, atom I2 at (x, y, z) can make two possible contacts, with either another I2 or with nitro atom O21, both at $(1-x, y, \frac{3}{2}-z)$, i.e. both components of the molecule of (I) centred across $(\frac{1}{2}, \frac{1}{2}, 1)$, and with dimensions $I \cdots I^i = 3.247 (2) \text{ \AA}$ and $C-I \cdots I^i = 163.3 (2)^\circ$, and

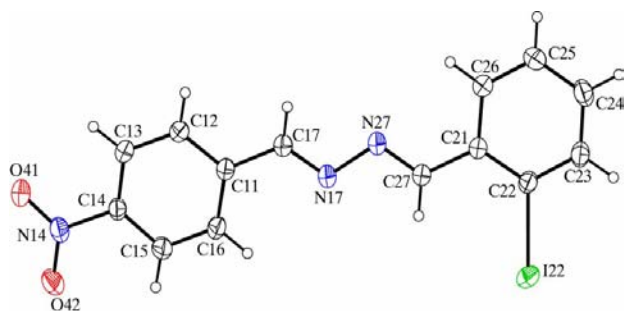


Figure 3
The molecule of compound (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

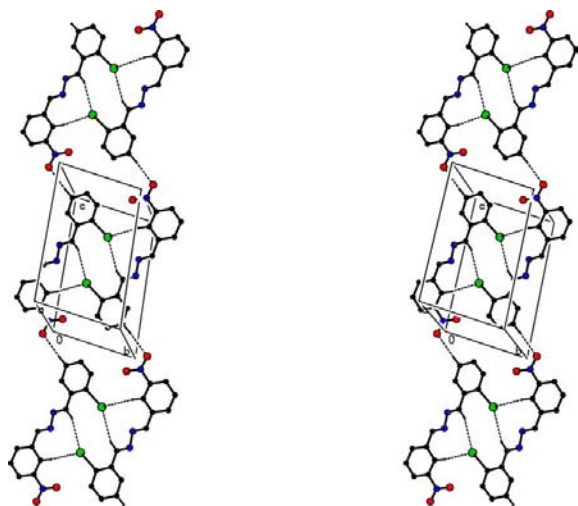


Figure 4
Stereoview of part of the crystal structure of compound (II), showing the formation of a hydrogen-bonded chain of edge-fused rings along [101]. For the sake of clarity, H atoms not involved in the hydrogen bonds shown have been omitted.

$I \cdots O^i = 3.312 (8) \text{ \AA}$ and $C-I \cdots O^i = 167.1 (2)^\circ$ [symmetry code: (i) $1-x, y, \frac{3}{2}-z$]. It is convenient to consider first the possible consequences of these interactions in pure (I), and then to consider the effects of the co-crystallized diiodo compound. If adjacent molecules of (I) along [001] are consistently aligned in a head-to-tail fashion, then the iodo-nitro interaction generates a $C(11)$ chain (Starbuck *et al.*, 1999) along [001]. If, however, adjacent molecules are aligned in a head-to-head fashion, the $I \cdots I$ contact can only link the molecules together in pairs.

The angular properties of this $C-I \cdots I$ interaction are admirably consistent with generalizations proposed (Ramassubbu *et al.*, 1986) from the results of database analysis, namely that in structures where $X \cdots X$ distances ($X =$ halogen) are significantly less than the van der Waals sum, the observed $C-X \cdots X$ angles are clustered either around 180° or around 90° . These authors also note that, in such interactions,

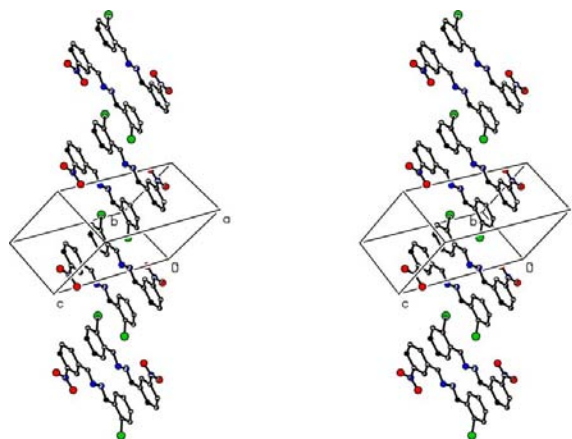


Figure 5
Stereoview of part of the crystal structure of compound (II), showing the formation of a π -stacked chain of hydrogen-bonded dimers along [110]. For the sake of clarity, H atoms not involved in the hydrogen bonds shown have been omitted.

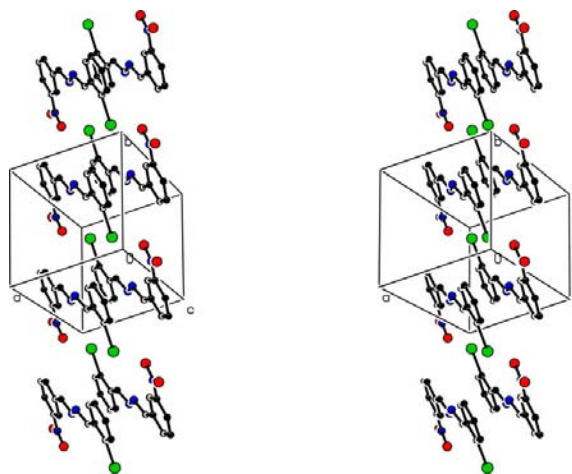


Figure 6
Stereoview of part of the crystal structure of compound (II), showing the formation of a π -stacked chain of hydrogen-bonded dimers along [010]. For the sake of clarity, H atoms not involved in the hydrogen bonds shown have been omitted.

$X \cdots X$ distances are commonly observed *ca* 0.5 Å below the conventional van der Waals sum of 3.90 Å for I \cdots I (Bondi, 1964). The short I \cdots I contact distance here is well below the van der Waals sum, even allowing for the polar flattening effect (Nyburg & Faerman, 1985), and may point to an avoidance of such I \cdots I contacts wherever possible. Such avoidance is readily achieved by the head-to-tail alignment of the molecules of (I) within an [001] chain, so that disorder of the molecules is correlated in one direction. This neither implies nor requires any correlation between adjacent [001] chains. Such short contacts can be avoided, even when a molecule of the diiodo analogue is present; such a molecule can readily form two iodo–nitro interactions, one at each I atom. Each such diiodo molecule would, in these circumstances, simply effect a reversal in the polarity of a chain formed by molecules of (I). Overall, therefore, we conclude that molecules of (I) are linked into [001] chains by a two-centre iodo–nitro interaction, with no short I \cdots I contacts.

The molecules of compound (II) (Fig. 2) are linked into a three-dimensional framework by a combination of C–H \cdots O and C–H \cdots I hydrogen bonds and two independent aromatic π – π stacking interactions. The hydrogen bonds together generate a one-dimensional substructure, and each of the stacking interactions in combination with the C–H \cdots I hydrogen bonds independently generates a further one-dimensional substructure. Accordingly, the formation of the framework is most readily analysed and discussed in terms of these three simple substructures.

Aryl atom C12 and methine atom C27 in the molecule at (x, y, z) both act as hydrogen-bond donors to iodine I22 in the molecule at $(1 - x, 1 - y, 1 - z)$, thereby generating a centrosymmetric dimer characterized by an array of three edge-fused $[R_2^1(9)][R_2^2(10)][R_2^1(9)]$ rings (Bernstein *et al.*, 1995), centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 4). These complex dimers are

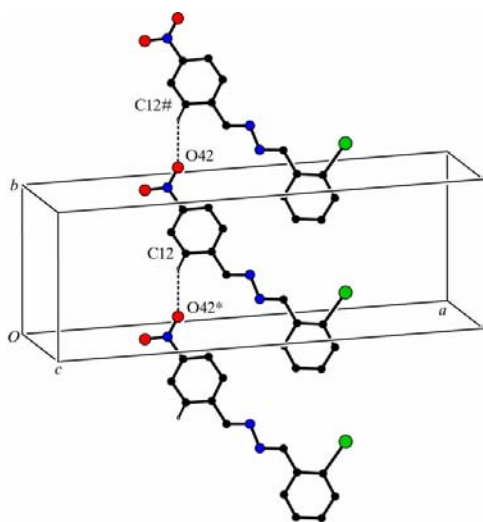


Figure 7
Part of the crystal structure of compound (III), showing the formation of a hydrogen-bonded chain along [010]. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, y - 1, z)$ and $(x, 1 + y, z)$, respectively.

themselves linked by a further hydrogen bond, of the C–H \cdots O type: the aryl atom C25 in the molecule at (x, y, z) acts as donor to nitro atom O32 in the molecule at $(1 + x, y, 1 + z)$, so forming a C(13) chain running parallel to the [101] direction. Propagation of this hydrogen bond by translation and inversion then links the dimers into a [101] ribbon, in the form of a chain of edge-fused rings, with $R_4^1(22)$ rings centred at $(n, \frac{1}{2}, n)$ ($n = \text{zero or integer}$), alternating with $R_2^2(10)$ rings centred at $(\frac{1}{2} + n, \frac{1}{2}, \frac{1}{2} + n)$ ($n = \text{zero or integer}$), with the $R_2^1(9)$ rings on the two edges of the ribbon (Fig. 4).

The dimers generated by the C–H \cdots I hydrogen bonds in (II) are also linked by two independent π – π stacking interactions to form two further one-dimensional substructures. The first of these involves the centrosymmetric pair of molecules at (x, y, z) and $(-x, -y, 1 - z)$, which are components of the dimers centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$, respectively. The nitrated ring at (x, y, z) and the iodinated ring at $(-x, -y, 1 - z)$ are nearly parallel, with a dihedral angle between their planes of only 2.3 (2)°. The interplanar spacing is *ca* 3.47 Å and the ring-centroid separation is 3.767 (2) Å, corresponding to a near-ideal centroid offset of *ca* 1.47 Å. Propagation of this interaction by inversion then links the hydrogen-bonded dimers into a π -stacked chain running parallel to the [110] direction (Fig. 5).

The second stacking interaction involves the centrosymmetric pair of molecules at (x, y, z) and $(1 - x, -y, 1 - z)$,

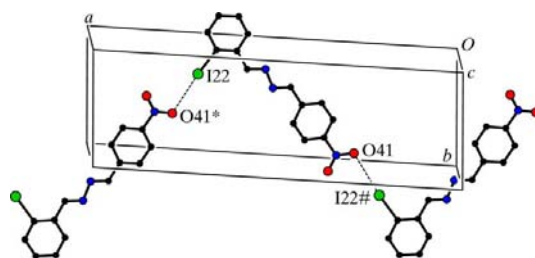


Figure 8
Part of the crystal structure of compound (III), showing the formation of an iodo–nitro chain along [101]. For the sake of clarity, H atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$ and $(x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2})$, respectively.

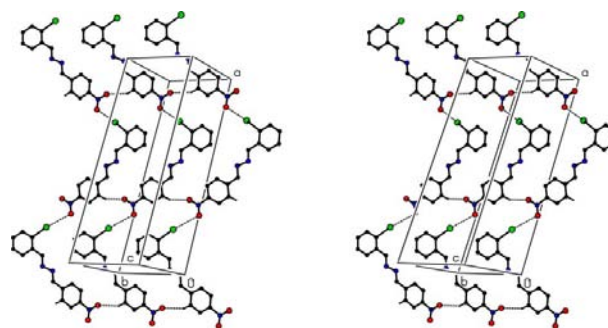


Figure 9
Stereoview of part of the crystal structure of compound (III), showing the formation of a (101) sheet. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

components of hydrogen-bonded dimers centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$. Again, the adjacent ring planes make a dihedral angle of $2.3 (2)^\circ$, but now the interplanar spacing is *ca* 3.42 Å, with a ring-centroid separation of 3.725 (2) Å, giving a ring-centroid offset of *ca* 1.48 Å. Propagation of this interaction then generates a chain of dimers along [010] (Fig. 6). The combination of the independent chains along [101], [110] and [010] is sufficient to link all of the molecules of (II) into a single three-dimensional framework. It is notable, however, that iodo–nitro interactions are absent from the structure of (II).

The molecules of compound (III) (Fig. 3) are linked into sheets by a combination of a rather weak C–H...O hydrogen bond and a two-centre iodo–nitro interaction, and again it is convenient to consider the effect of each of these interactions in turn. Aryl atom C12 in the molecule at (x, y, z) acts as hydrogen-bond donor to nitro atom O42 in the molecule at $(x, y - 1, z)$, so generating by translation a *C*(6) chain running parallel to the [010] direction (Fig. 7); eight chains of this type pass through each unit cell. In addition, atom I22 in the molecule at (x, y, z) forms a nearly linear two-centre I...O interaction with nitro atom O41 in the molecule at $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$, with dimensions I...Oⁱ = 3.362 (2) Å, C–I...Oⁱ = 171.62 (6)° and I...Oⁱ–Nⁱ = 113.6 (2)° [symmetry code: (i) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$]. In this way, a *C*(13) (Starbuck *et al.*, 1999) chain is formed running parallel to the [101] direction and generated by the *n*-glide plane at $y = \frac{3}{4}$ (Fig. 8). The combination of the [010] and [101] chains generates a (10 $\bar{1}$) sheet in the form of a (4,4)-net built from a single type of *R*₄⁴(32) ring (Fig. 9). Four sheets of this type pass through each unit cell, but there are no direction-specific interactions between adjacent sheets. In particular, C–H... π (arene) hydrogen bonds and aromatic π – π stacking interactions are absent from the structure of (III).

Experimental

An equimolar mixture of 2-iodobenzaldehyde and the appropriate nitrobenzaldehyde hydrazone (3 mmol of each) in methanol (20 ml) was heated under reflux for 30 min, cooled and then left at room temperature. The precipitate from each reaction was collected after 24 h and recrystallized from 1,2-dichloroethane. While pure samples of compounds (II) (m.p. 458–460 K) and (III) (m.p. 490–491 K) were obtained in this way from 3- and 4-nitrobenzaldehyde hydrazones, respectively, the X-ray analysis showed that the product (m.p. 471–473 K) obtained using 2-nitrobenzaldehyde hydrazone was, in fact, compound (I) co-crystallized with some (*E,E*)-1,4-bis(2-iodophenyl)-2,3-diaza-1,3-butadiene, despite the sharp melting point.

Compound (I)

Crystal data

$C_{14}H_{10}I_{1.12}N_{2.88}O_{1.76}$
 $M_r = 388.69$
 Monoclinic, *C*2/*c*
 $a = 15.3033 (8) \text{ \AA}$
 $b = 3.7952 (3) \text{ \AA}$
 $c = 23.3097 (16) \text{ \AA}$
 $\beta = 97.836 (4)^\circ$
 $V = 1341.16 (16) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.925 \text{ Mg m}^{-3}$
 Mo *K* α radiation
 Cell parameters from 1482 reflections
 $\theta = 3.0\text{--}27.4^\circ$
 $\mu = 2.66 \text{ mm}^{-1}$
 $T = 120 (2) \text{ K}$
 Block, colourless
 $0.08 \times 0.06 \times 0.04 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
 $T_{\min} = 0.815, T_{\max} = 0.901$
 6403 measured reflections
 1482 independent reflections

1156 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.066$
 $\theta_{\max} = 27.4^\circ$
 $h = -19 \rightarrow 19$
 $k = -4 \rightarrow 4$
 $l = -30 \rightarrow 30$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.100$
 $S = 1.07$
 1482 reflections
 104 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0232P)^2 + 8.8667P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.91 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.82 \text{ e \AA}^{-3}$

Table 1

Selected torsion angles ($^\circ$) for (I).

N1 ⁱ –N1–C7–C1	–179.5 (5)	C1–C2–N2–O21	–154.3 (7)
N1–C7–C1–C2	–165.9 (4)		

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

Compound (II)

Crystal data

$C_{14}H_{10}IN_3O_2$
 $M_r = 379.15$
 Triclinic, *P* $\bar{1}$
 $a = 7.2969 (3) \text{ \AA}$
 $b = 7.3235 (3) \text{ \AA}$
 $c = 13.7939 (6) \text{ \AA}$
 $\alpha = 97.405 (2)^\circ$
 $\beta = 100.410 (2)^\circ$
 $\gamma = 107.590 (3)^\circ$
 $V = 677.73 (5) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.858 \text{ Mg m}^{-3}$

Mo *K* α radiation
 Cell parameters from 3120 reflections
 $\theta = 3.0\text{--}27.6^\circ$
 $\mu = 2.37 \text{ mm}^{-1}$
 $T = 120 (2) \text{ K}$
 Plate, yellow
 $0.20 \times 0.12 \times 0.05 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
 $T_{\min} = 0.649, T_{\max} = 0.891$
 13 382 measured reflections
 3120 independent reflections

2909 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\max} = 27.6^\circ$
 $h = -9 \rightarrow 9$
 $k = -9 \rightarrow 9$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.085$
 $S = 1.28$
 3120 reflections
 181 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 0.3339P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.06 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.04 \text{ e \AA}^{-3}$

Table 2

Selected torsion angles ($^\circ$) for (II).

C17–N17–N27–C27	177.5 (3)	N17–C17–C11–C12	–8.9 (4)
N27–N17–C17–C11	–179.4 (3)	N27–C27–C21–C22	–171.0 (3)
N17–N27–C27–C21	–180.0 (3)	C12–C13–N13–O31	–5.3 (4)

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H...A	D—H	H...A	D...A	D—H...A
C12—H12...I22 ⁱ	0.95	3.04	3.972 (3)	168
C25—H25...O32 ⁱⁱ	0.95	2.50	3.436 (4)	167
C27—H27...I22 ⁱ	0.95	3.06	3.923 (3)	153

Symmetry codes: (i) 1 - x, 1 - y, 1 - z; (ii) x + 1, y, z + 1.

Compound (III)

Crystal data

C ₁₄ H ₁₀ I ₂ N ₃ O ₂	$D_x = 1.833 \text{ Mg m}^{-3}$
$M_r = 379.15$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 4956 reflections
$a = 27.9470 (11) \text{ \AA}$	$\theta = 2.7\text{--}32.5^\circ$
$b = 8.0563 (3) \text{ \AA}$	$\mu = 2.34 \text{ mm}^{-1}$
$c = 13.7464 (5) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 117.4250 (10)^\circ$	Plate, yellow
$V = 2747.16 (18) \text{ \AA}^3$	$0.37 \times 0.25 \times 0.06 \text{ mm}$
$Z = 8$	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	4956 independent reflections
φ and ω scans	3759 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$R_{\text{int}} = 0.024$
$T_{\text{min}} = 0.479, T_{\text{max}} = 0.873$	$\theta_{\text{max}} = 32.5^\circ$
15 927 measured reflections	$h = -42 \rightarrow 40$
	$k = -12 \rightarrow 12$
	$l = -20 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 0.5558P]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.079$	$(\Delta/\sigma)_{\text{max}} = 0.004$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.82 \text{ e \AA}^{-3}$
4956 reflections	$\Delta\rho_{\text{min}} = -0.77 \text{ e \AA}^{-3}$
181 parameters	
H-atom parameters constrained	

Table 4
Selected torsion angles (°) for (III).

C17—N17—N27—C27	172.5 (2)	N17—C17—C11—C12	-175.3 (2)
N27—N17—C17—C11	178.31 (19)	N27—C27—C21—C22	173.5 (2)
N17—N27—C27—C21	178.14 (18)	C13—C14—N14—O41	6.9 (3)

Table 5
Hydrogen-bond geometry (Å, °) for (III).

D—H...A	D—H	H...A	D...A	D—H...A
C12—H12...O42 ⁱ	0.93	2.58	3.430 (2)	153

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

For each of (I) and (III), the systematic absences permitted $C2/c$ and Cc as possible space groups. For each isomer, space group $C2/c$ was selected and confirmed by the subsequent analysis. Crystals of isomer (II) are triclinic. Space group $P\bar{1}$ was selected and confirmed by the subsequent analysis. It became apparent at an early stage in the refinement of (I) that the occupancies of the iodo and nitro substituents were not identical, as had been expected. The refined occupancy factors were 0.559 (3) for the iodo substituent and 0.441 (3) for the nitro group; when (I) was refined with these occupancies fixed at $\frac{1}{2}$, the R factors rose to $R = 0.050$ and $wR_2 = 0.133$, with unacceptable displacement parameters for the nitro N atom. All H atoms were located from difference maps and then treated as riding

atoms, with C—H distances of 0.95 Å at 120 K and 0.93 Å at 293 K, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *COLLECT* (Nonius, 1998) for (I) and (II); *SMART* (Bruker, 1998) for (III). Cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* for (I) and (II); *SAINT* (Bruker, 2000) for (III). Data reduction: *DENZO* and *COLLECT* for (I) and (II); *SAINT* (Bruker, 2000) for (III). For all three compounds, structure solution: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); structure refinement: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); publication software: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data for (I) and (II) were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. X-ray data for (III) were collected at the University of Aberdeen; the authors thank the University of Aberdeen for funding the purchase of this instrument. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1830). Services for accessing these data are described at the back of the journal.

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