

A chain of edge-fused rings generated by the combination of an N—H···O hydrogen bond and an iodo–nitro interaction in 2-iodobenzaldehyde 4-nitrophenylhydrazone versus disordered and effectively isolated molecules in 2-iodobenzaldehyde 2,4-dinitrophenylhydrazone

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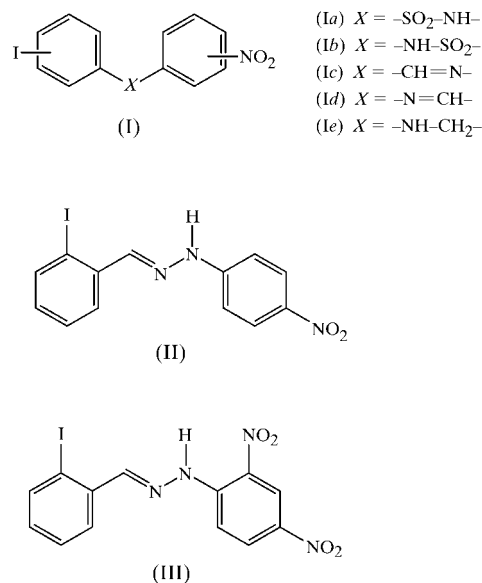
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Molecules of 2-iodobenzaldehyde 4-nitrophenylhydrazone, C₁₃H₁₀IN₃O₂, are effectively planar and are linked by an N—H···O hydrogen bond [H···O = 2.04 Å, N···O = 2.905 (6) Å and N—H···O = 166°] and a two-centre iodo–nitro interaction [I···O = 3.361 (4) Å] into a chain of edge-fused R₃³(18) rings. There are no direction-specific interactions between adjacent chains. Molecules of 2-iodobenzaldehyde 2,4-dinitrophenylhydrazone, C₁₃H₉IN₄O₄, are disordered over two orientations with occupancies of 0.681 (5) and 0.319 (5). In the major orientation, there are no direction-specific intermolecular interactions, while for the minor form, a single C—H···O hydrogen bond generates centrosymmetric dimers.

Comment

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 (I) (see *Scheme*) containing a variety of spacer units, X, namely arennesulfonamides (Ia) and (Ib) (Kelly *et al.*, 2002), Schiff base imines (Ic) (Wardell *et al.*, 2002) and (Id) (Glidewell, Howie *et al.*, 2002), and two isomeric benzylanilines (Ie) (Glidewell, Low *et al.*, 2002). Here we report the structure of two analogous compounds containing the –CH=N–NH– linker unit, namely 2-iodobenzaldehyde 4-nitrophenylhydrazone, (II),

and 2-iodobenzaldehyde 2,4-dinitrophenylhydrazone, (III), which exhibit radically different patterns of supramolecular aggregation.



Molecules of (II) are essentially planar (Fig. 1), as demonstrated by the torsion angles (Table 1) that define the orientations of the rings relative to the central linked unit. The only significant deviation from complete planarity is the 5.9 (3)° twist of the nitro group out of the plane of the aryl ring C11–C16.

The molecules are linked into molecular ladders by the combination of a single N—H···O hydrogen bond (Table 2) and a single two-centre iodo–nitro interaction. Atom I22 in the molecule at (x, y, z) forms an iodo–nitro interaction with atom O42 in the molecule at (x, 2 + y, 1 + z) [I···Oⁱⁱ = 3.361 (4) Å, C—I···Oⁱⁱ = 146.5 (2)° and I···Oⁱⁱ–Nⁱⁱ = 146.9 (3)°; symmetry code: (ii) x, 2 + y, 1 + z], so generating by translation a C(12) chain (Starbuck *et al.*, 1999) running parallel to the [021] direction. At the same time, amino atom N1 at (x, y, z) acts as hydrogen-bond donor to O41 at ($\frac{3}{2} - x, 1 + y, \frac{1}{2} + z$), while N1 at ($\frac{3}{2} - x, 1 + y, \frac{1}{2} + z$) in turn acts as donor to O41 at (x, 2 + y, 1 + z), so producing a C(8) chain parallel to [021] and generated by the c-glide plane at $x = \frac{3}{4}$. The combination of these two motifs generates a molecular ladder (Fig. 2) in which two C(12) iodo–nitro chains act as the uprights while the N—H···O hydrogen bonds act as the rungs. Alternatively, this substructure may be described as a chain of edge-fused R₃³(18) rings.

The [021] ladder lies in the domain 0.47 < x < 1.03. Related to this ladder by the action of the 2₁ screw axes is a second chain, which runs parallel to [0 $\bar{2}$ 1] and lies in the domain –0.03 < x < 0.53. There are no direction-specific interactions between adjacent chains. In particular, there are no C—H···O or C—H··· π (arene) hydrogen bonds and no aromatic π – π -stacking interactions.

Molecules of (III) exhibit orientational disorder (Figs. 3 and 4), with two orientations that have occupancies of 0.681 (5)

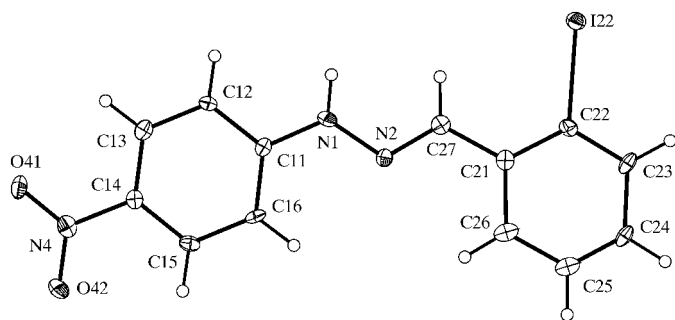


Figure 1
The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

and 0.319 (5). These orientations are related to one another approximately *via* a rotation about the line $N1 \cdots I22$. In both orientations, the molecules are nearly planar, as typified by the torsion angles for the major form (Table 3). In contrast to the supramolecular aggregation in (II), there are neither intermolecular $N-H \cdots O$ hydrogen bonds nor iodo–nitro interactions in (III). In each orientation there is an intramolecular $N-H \cdots O$ hydrogen bond (Table 4), but for most of the intermolecular $C-H \cdots O$ contacts the $H \cdots O$ distances are not significantly shorter than the sum of the van der Waals radii, and so these bonds are not structurally significant. The

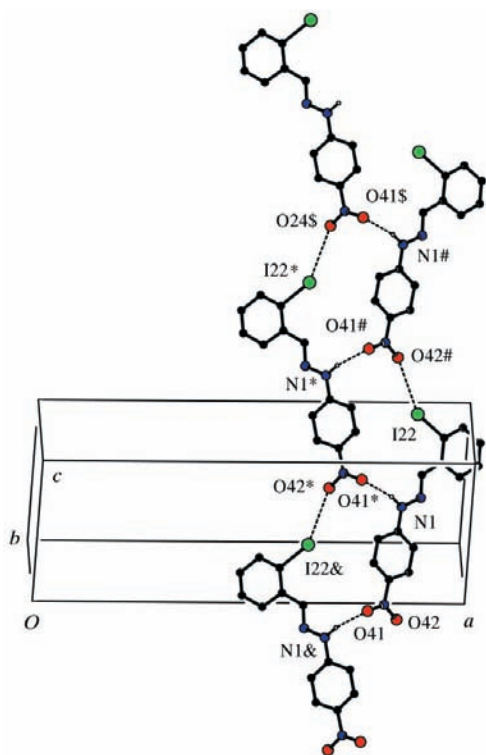
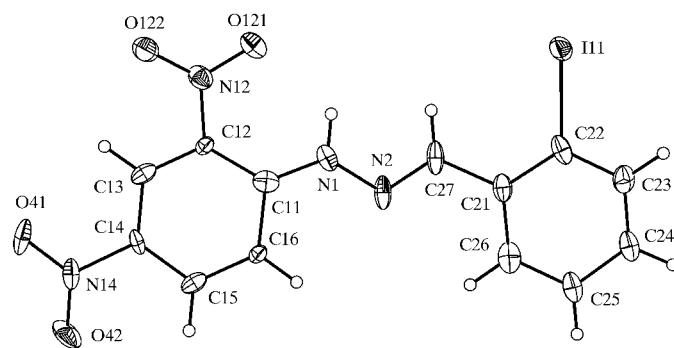
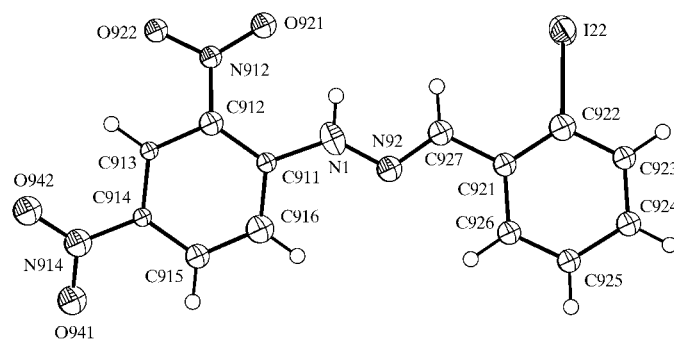


Figure 2
Part of the crystal structure of (II), showing the formation of a molecular ladder along [021]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign (\$) or ampersand (&) are at the symmetry positions $(\frac{3}{2} - x, 1 + y, \frac{1}{2} + z)$, $(x, 2 + y, 1 + z)$, $(\frac{3}{2} - x, 3 + y, \frac{3}{2} + z)$ and $(\frac{3}{2} - x, -1 + y, -\frac{1}{2} + z)$, respectively.



(a)



(b)

Figure 3
The (a) major and (b) minor orientations of (III), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 30% probability level.

sole exception occurs for the minor orientation, where centrosymmetrically related molecules are linked into a dimer *via* an $R_2^2(10)$ motif (Fig. 5). For the major orientation, however, the structure must be regarded as being comprised of isolated molecules.

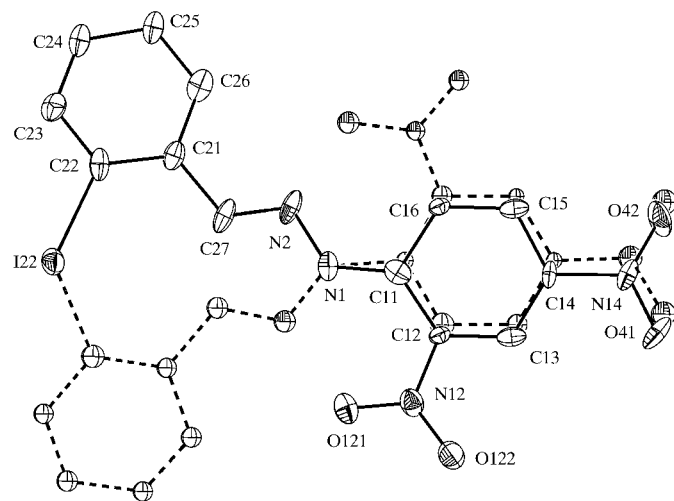


Figure 4
Part of the crystal structure of (III), showing the overlap of the major (full lines) and minor (broken lines) orientations. For the sake of clarity, H atoms have been omitted.

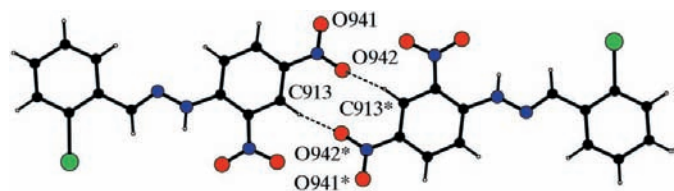


Figure 5
Part of the crystal structure of (III), showing the centrosymmetric $R_2^2(10)$ dimer formed by the minor form. Atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 2-z)$.

The occurrence of an iodo–nitro interaction in (II) may be compared with the absence of such an interaction not only in (III) but also in those analogues of types (Ic) and (Id) where the iodo substituent is in a 2-position (Wardell *et al.*, 2002; Glidewell, Howie *et al.*, 2002). Similarly, the absence of aromatic π – π -stacking interactions from the structures of (II) and (III) may be compared with the case of 4-nitrobenzylidene-2'-iodoaniline, which is of the type (Id) but has the same disposition of substituents as in (II). In 4-nitrobenzylidene-2'-iodoaniline, such interactions link hydrogen-bonded chains into sheets. Clearly, the qualitative prediction of which of the possible weak supramolecular interactions will be significant in compounds of these general types is far from straightforward.

Experimental

For each of (II) and (III), a finely powdered mixture of the aldehyde and the appropriate phenylhydrazine (1:1 molar ratio) was gently heated on a hot-plate until effervescence ceased. The mixtures were cooled and crystallized from ethanol.

Compound (II)

Crystal data

$C_{13}H_{10}IN_3O_2$
 $M_r = 367.14$
Orthorhombic, $Pca2_1$
 $a = 24.0858$ (11) Å
 $b = 5.0699$ (2) Å
 $c = 10.5080$ (4) Å
 $V = 1283.16$ (9) Å³
 $Z = 4$
 $D_x = 1.900$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 2800 reflections
 $\theta = 3.4$ – 27.4°
 $\mu = 2.50$ mm⁻¹
 $T = 120$ (2) K
Plate, red
 $0.32 \times 0.08 \times 0.06$ mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
Absorption correction: multi-scan
DENZO-SMN (Otwinowski & Minor, 1997)
 $T_{\min} = 0.502$, $T_{\max} = 0.865$
8490 measured reflections

2800 independent reflections
2082 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.063$
 $\theta_{\text{max}} = 27.4^\circ$
 $h = -31 \rightarrow 27$
 $k = -6 \rightarrow 6$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.080$
 $S = 1.02$
2800 reflections
160 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0298P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 1.20$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.47$ e Å⁻³
Absolute structure: Flack (1983),
1259 Friedel pairs
Flack parameter = -0.08 (4)

Table 1
Selected torsion angles ($^\circ$) for (II).

C11–N1–N2–C27	178.4 (5)	C22–C21–C27–N2	–179.0 (5)
N1–N2–C27–C21	179.1 (5)	C13–C14–N4–O41	–5.8 (8)
C12–C11–N1–N2	178.6 (5)	C13–C14–N4–O42	174.1 (5)

Table 2
Hydrogen-bonding geometry (Å, $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1 \cdots O41 ⁱ	0.88	2.04	2.905 (6)	166

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

Compound (III)

Crystal data

$C_{13}H_9IN_4O_4$
 $M_r = 412.14$
Triclinic, $P\bar{1}$
 $a = 7.8890$ (5) Å
 $b = 8.1405$ (6) Å
 $c = 12.1760$ (10) Å
 $\alpha = 83.876$ (4) $^\circ$
 $\beta = 83.679$ (4) $^\circ$
 $\gamma = 63.151$ (3) $^\circ$
 $V = 691.98$ (9) Å³

$Z = 2$
 $D_x = 1.978$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 2924 reflections
 $\theta = 1.7$ – 27.4°
 $\mu = 2.34$ mm⁻¹
 $T = 120$ (2) K
Plate, orange
 $0.08 \times 0.06 \times 0.01$ mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
Absorption correction: multi-scan
DENZO-SMN (Otwinowski & Minor, 1997)
 $T_{\min} = 0.835$, $T_{\max} = 0.977$
7346 measured reflections

2924 independent reflections
2187 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.054$
 $\theta_{\text{max}} = 27.4^\circ$
 $h = -10 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.132$
 $S = 1.07$
2924 reflections
243 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0694P)^2 + 0.0755P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.84$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.88$ e Å⁻³

Table 3
Selected torsion angles ($^\circ$) for (III).

N1–N2–C27–C21	–179.6 (7)	N2–C27–C21–C22	–178.2 (7)
C11–N1–N2–C27	–171.0 (10)	C11–C12–N12–O121	6.1 (14)
N2–N1–C11–C12	–178.0 (9)	C13–C14–N14–O41	–10.0 (2)

Table 4
Hydrogen-bonding geometry (Å, $^\circ$) for (III).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1 \cdots O121	0.88	2.06	2.677 (9)	126
N1–H91 \cdots O921	0.88	2.07	2.716 (13)	130
C16–H16 \cdots O122 ⁱ	0.95	2.58	3.301 (18)	133
C23–H23 \cdots O41 ⁱⁱ	0.95	2.59	3.438 (18)	149
C913–H913 \cdots O942 ⁱⁱⁱ	0.95	2.35	3.21 (3)	150
C916–H916 \cdots O922 ^{iv}	0.95	2.60	3.34 (3)	136

Symmetry codes: (i) $1+x, y, z$; (ii) $1+x, y-1, z-1$; (iii) $1-x, 1-y, 2-z$; (iv) $x-1, y, z$.

Compound (II) is orthorhombic and the systematic absences permitted $Pca2_1$ and $Pcam$ (= $Pbcm$) as possible space groups. $Pca2_1$ was chosen and confirmed by the analysis. Compound (III) is triclinic; space group $P\bar{1}$ was selected and confirmed by the structure analysis. In (III), sites N1 and I22 are common to both orientations. In the minor orientation, the nitrated C911–C916 ring was treated as a rigid hexagon, and all non-H atoms in this orientation were refined isotropically. DFIX constraints were applied to the nitro group centred on atom N914. 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 both compounds, data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1609). Services for accessing these data are described at the back of the journal.

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