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2-Iodo-*N*-(3-nitrobenzyl)aniline and 3-iodo-*N*-(3-nitrobenzyl)aniline exhibit entirely different patterns of supramolecular aggregation

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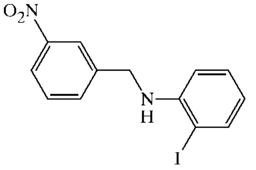
In 2-iodo-*N*-(3-nitrobenzyl)aniline, $C_{13}H_{11}IN_2O_2$, the molecules are linked into a three-dimensional structure by a combination of C—H⋯O hydrogen bonds, iodo–nitro interactions and aromatic π–π-stacking interactions, but N—H⋯O and C—H⋯π(arene) hydrogen bonds are absent. In the isomeric 3-iodo-*N*-(3-nitrobenzyl)aniline, a two-dimensional array is generated by a combination of N—H⋯O, C—H⋯O and C—H⋯π(arene) hydrogen bonds, but iodo–nitro interactions and aromatic π–π-stacking interactions are both absent.

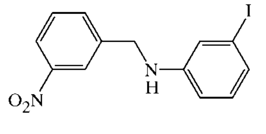
Comment

We have recently reported (Glidewell *et al.*, 2002) the molecular and supramolecular structures of eight isomeric nitrobenzylidene–iodoanilines, $O_2NC_6H_4CH{=}NC_6H_4I$, all of which manifest different combinations of C—H⋯O hydrogen bonds, iodo–nitro interactions and aromatic π–π-stacking interactions, giving supramolecular structures in zero, one, two or three dimensions. Here, we report the structures of two representative iodo-*N*-(nitrobenzyl)anilines, namely compounds (I) and (II), of general formula $O_2NC_6H_4CH_2NH$-C_6H_4I, in which N—H⋯O hydrogen bonds can occur, in addition to all of the interactions noted above.

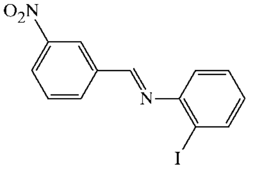
The bond lengths and inter-bond angles in (I) and (II) show no unusual features, but the molecular conformations are markedly different. If the C1—N1—C17 fragment is taken as a reference plane, it is clear from the torsion angles (Tables 1 and 3; Figs. 1 and 4) that the location of the iodo and nitro substituents is entirely different in (I) and (II). Since the overall conformations are dependent on largely unhindered rotations about single bonds in the C1—N1—C17—C11 unit, it is likely that the observed conformations are determined primarily by direction-specific intermolecular interactions of various types, the manifestation of which differs significantly between the two structures.



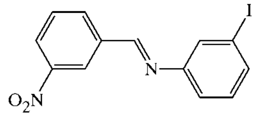
(I)



(II)



(III)



(IV)

In the supramolecular structure of compound (I) (Fig. 1), there are, surprisingly, no N—H⋯O hydrogen bonds. Instead, the structure is determined by a combination of weak C—H⋯O hydrogen bonds, iodo–nitro interactions and aromatic π-π-stacking interactions. Atom C4 in the iodinated ring of the molecule at (x, y, z) acts as a hydrogen-bond donor to atom O131 in the molecule at ($1 - x, 1 - y, 1 - z$) (Table 2), so generating a cyclic centrosymmetric motif (Fig. 2). Atom I2 in the molecule at (x, y, z) forms a weak two-centre iodo–nitro interaction with atom O131^{ii}, with I⋯O^{ii} = 3.517 (2) Å, C—I⋯O^{ii} = 158.12 (7)° and I⋯O^{ii}—N^{ii} = 101.4 (2)° [symmetry code: (ii) $x, y, z - 1$]. The combination of these two interactions generates a molecular ladder, or a chain of edge-fused rings, running parallel to the [001] direction, with hydrogen-bonded $R_2^2(24)$ rings centred at $(\frac{1}{2},\frac{1}{2},\frac{1}{2}+n)$ (n is zero or integer), and $R_4^2(12)$ rings containing both hydrogen bonds and I⋯O interactions (Bernstein *et al.*, 1995; Starbuck *et al.*, 1999) centred at $(\frac{1}{2},\frac{1}{2},n)$ (n is zero or integer) (Fig. 2).

Two of these molecular ladders pass through each unit cell, and each ladder is linked to its four immediate neighbours by means of aromatic π–π-stacking interactions, so linking all of

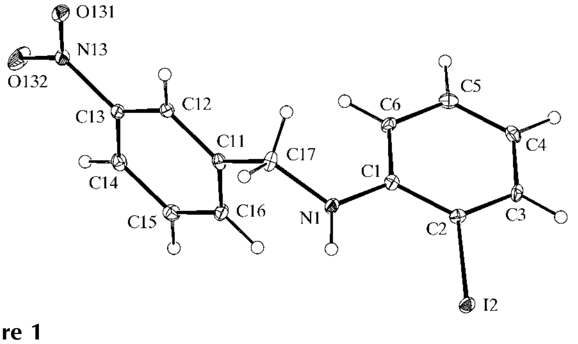


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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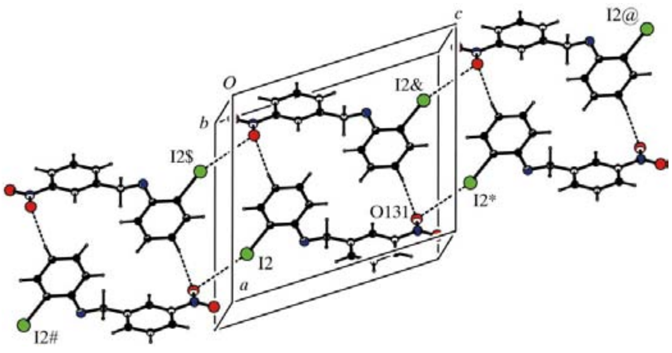

Figure 2
Part of the crystal structure of (I), showing the formation of a molecular ladder along [001]. Atoms marked with an asterisk (*), hash (#), dollar sign ($), ampersand (&) or 'at' sign (@) are at the symmetry positions $(x, y, 1 + z)$, $(x, y, z - 1)$, $(1 - x, 1 - y, -z)$, $(1 - x, 1 - y, 1 - z)$ and $(1 - x, 1 - y, 2 - z)$, respectively.

the ladders into a single three-dimensional continuum. The nitrated ring of the molecule at (x, y, z) forms a π–π-stacking interaction with the iodinated ring of the molecule at $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$ (Fig. 3), where the interplanar angle is 5.3°, the centroid separation is 3.696 (2) Å and the interplanar spacing is *ca* 3.42 Å, corresponding to a centroid offset of *ca* 1.40 Å (Fig. 3). The molecules at (x, y, z) and $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$ form part of the ladders along $(\frac{1}{2},\frac{1}{2},z)$ and $(1,1,z)$, respectively. Propagation of the π–π-stacking interaction by the *n*-glide plane links the ladder along $(\frac{1}{2},\frac{1}{2},z)$ to that at $(0,1,z)$, while the action of the centres of inversion links the $(\frac{1}{2},\frac{1}{2},z)$ ladder to those along $(0,0,z)$ and $(1,0,z)$ also. Hence, each ladder is linked to four others, forming a continuously linked bundle.

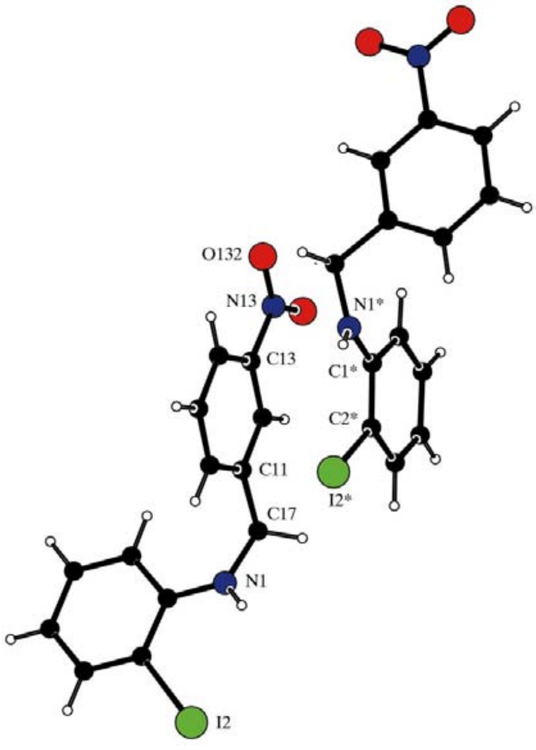

Figure 3
Part of the crystal structure of (I), showing the aromatic π–π-stacking interaction between rings of different types. For the sake of clarity, the unit-cell box has been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$.

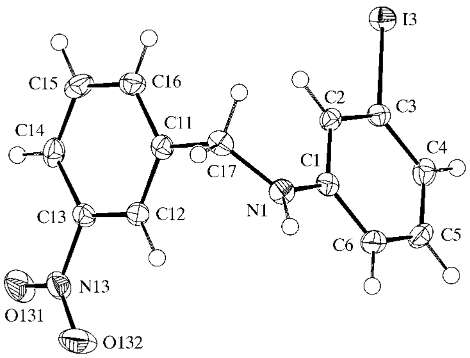

Figure 4
A view of the molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

The structure of compound (II) (Fig. 4), by contrast with that of (I), is dominated by hydrogen bonds (Table 4), while iodo–nitro interactions and aromatic π–π-stacking interactions are both absent. The amino atom N1 in the molecule at (x, y, z) acts as a hydrogen-bond donor to atom O131 in the molecule at $(\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$ and, at the same time, atom C14 at (x, y, z) acts as a hydrogen-bond donor to atom O132 at $(\frac{1}{2} - x, 1 - y, z - \frac{1}{2})$. Propagation of these two hydrogen bonds thus produces a $C(5)C(8)[R^2_2(13)]$ chain of rings (Bernstein *et al.*, 1995), running parallel to the [001] direction and generated by the 2_1 screw axis along $(\frac{1}{4},\frac{1}{2},z)$ (Fig. 5).

Four [001] chains run through each unit cell of (II) and they are linked into sheets, parallel to (010), by means of a single C—H···π(arene) hydrogen bond. Atom C15 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the iodinated ring

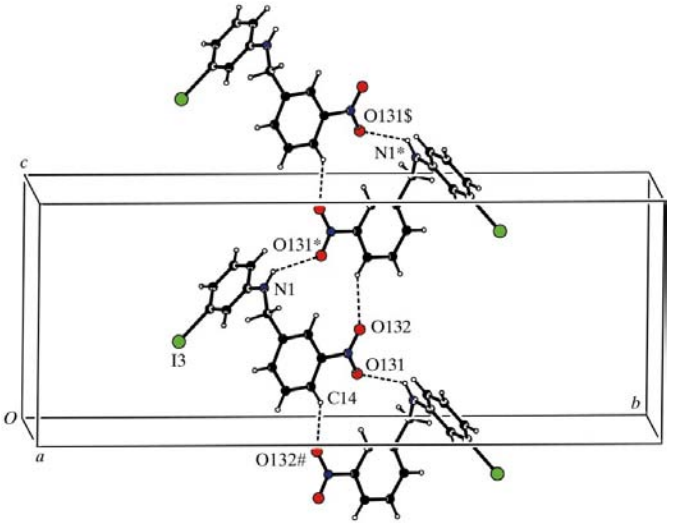

Figure 5
Part of the crystal structure of (II), showing the formation of a chain of rings along [001]. Atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions $(\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$, $(\frac{1}{2} - x, 1 - y, z - \frac{1}{2})$ and $(x, y, 1 + z)$, respectively.

C1–C6 (centroid *Cg*1, Table 4) of the molecule at ($\frac{1}{2} + x$, y, $\frac{1}{2} - z$), and propagation of this interaction produces a chain running parallel to the [100] direction, generated by the *a*-glide plane at $z = \frac{1}{4}$ (Fig. 6). The combination of the [100] and [001] chains generates the (010) sheet.

In view of the differences between compounds (I) and (II), in terms of both the overall supramolecular structures and the types of weak intermolecular interaction involved, it is of interest to compare these structures with those of analogues (III) and (IV) (see *Scheme*), from the structures of which N—H···O hydrogen bonds are precluded (Glidewell *et al.*, 2002). In compound (III), the molecules are linked into simple chains by C—H···O hydrogen bonds. Unlike (I), there are no iodo–nitro interactions in (III) and, indeed, such interactions are absent from all isomers of (III) having the iodo substituent in the 2-position. In the structure of (IV), a combination of C—H···O hydrogen bonds and iodo–nitro interactions generates molecular ladders, which are themselves linked into sheets by aromatic *π*–*π*-stacking interactions. As noted above, in the saturated analogue (II), there are neither iodo–nitro interactions nor aromatic *π*–*π*-stacking interactions. Thus, both (I) and (II) exhibit very marked differences in supramolecular aggregation from their analogues, (III) and (IV), respectively. These differences were not predicted, and they are not readily explicable.

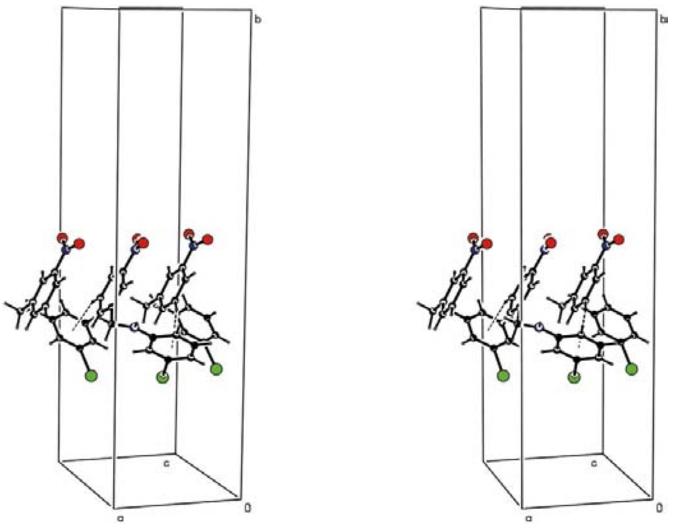

Figure 6
A stereoview of part of the crystal structure of (II), showing the formation by the C—H···*π*(arene) hydrogen bond of a chain along [100].

Experimental

Samples of (I) and (II) were prepared by reduction of the corresponding *N*-(benzylidine)anilines (III) and (IV), respectively, using a fivefold molar excess of Na(BH$_4$) in refluxing methanol for 1 h. After work-up, crystals of (I) and (II) suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in ethanol [m.p: 361–363 K for (I) and 352–353 K for (II)].

Compound (I)

Crystal data

$C_{13}H_{11}IN_2O_2$
$M_r = 354.14$
Monoclinic, $P2_1/n$
$a = 11.4056$ (3) Å
$b = 8.7364$ (3) Å
$c = 12.8357$ (5) Å
$\beta = 109.0049$ (12)°
$V = 1209.28$ (7) Å^3
$Z = 4$
$D_x = 1.945$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2744 reflections
$\theta = 3.0$–27.5°
$\mu = 2.64$ mm^{-1}
$T = 150$ (2) K
Plate, yellow
0.10 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.778$, $T_{\max} = 0.879$
9597 measured reflections
2744 independent reflections
2320 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\max} = 27.5°$
$h = -14 \rightarrow 14$
$k = -11 \rightarrow 11$
$l = -13 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.053$
$S = 1.06$
2744 reflections
163 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2)P)^2 + 0.2916P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.77$ e Å^{-3}
$\Delta\rho_{\min} = -0.71$ e Å^{-3}

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

C2—C1—N1—C17	162.8 (2)	N1—C17—C11—C12	−167.5 (2)
C1—N1—C17—C11	84.4 (3)	C12—C13—N13—O131	−0.9 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O131$^{\rm i}$	0.95	2.55	3.468 (3)	164

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

Compound (II)

Crystal data

$C_{13}H_{11}IN_2O_2$
$M_r = 354.14$
Orthorhombic, $Pbca$
$a = 7.9024$ (5) Å
$b = 28.7265$ (15) Å
$c = 11.3019$ (6) Å
$V = 2565.6$ (3) Å^3
$Z = 8$
$D_x = 1.834$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3186 reflections
$\theta = 1.4$–29.0°
$\mu = 2.49$ mm^{-1}
$T = 120$ (2) K
Lath, orange
0.35 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.632$, $T_{\max} = 0.775$
16 085 measured reflections
3186 independent reflections
2487 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 28.5°$
$h = -10 \rightarrow 10$
$k = -37 \rightarrow 37$
$l = -15 \rightarrow 15$

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

C2—C1—N1—C17	18.2 (3)	N1—C17—C11—C12	45.5 (3)
C1—N1—C17—C11	63.7 (3)	C12—C13—N13—O131	−169.3 (2)

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

*Cg*1 is the centroid of the C1–C6 ring.

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1⋯O131^{i}	0.88	2.51	3.087 (3)	124
C14—H14⋯O132^{ii}	0.95	2.52	3.364 (3)	148
C15—H15⋯*Cg*1^{iii}	0.95	2.57	3.438 (3)	151

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.083$
$S = 1.21$
3186 reflections
163 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.5158P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.49$ e Å^{-3}
$\Delta\rho_{\min} = -1.26$ e Å^{-3}

For compounds (I) and (II), the space groups $P2_1/n$ and *Pbca*, respectively, were uniquely assigned from the systematic absences. H atoms were treated as riding atoms, with C—H distances of 0.95 (aromatic) and 0.99 Å (CH_2), and N—H distances of 0.88 Å.

For compound (I), data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*. For compound (II), data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*. For both compounds, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); 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: GG1122). Services for accessing these data are described at the back of the journal.

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