organic compounds

2,6-Diiodo-4-nitrophenol, 2,6-diiodo-4-nitrophenyl acetate and 2,6-diiodo-4-nitroanisole: interplay of hydrogen bonds, iodo–nitro interactions and aromatic π–π-stacking interactions to give supramolecular structures in one, two and three dimensions

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In 2,6-diiodo-4-nitrophenol, $C_6H_3I_2NO_3$, the molecules are linked, by an O—H···O hydrogen bond and two iodo–nitro interactions, into sheets, which are further linked into a three-dimensional framework by aromatic π–π-stacking interactions. The molecules of 2,6-diiodo-4-nitrophenyl acetate, $C_8H_5I_2NO_4$, lie across a mirror plane in space group *Pnma*, with the acetyl group on the mirror, and they are linked by a single iodo–nitro interaction to form isolated sheets. The molecules of 2,6-diiodo-4-nitroanisole, $C_7H_5I_2NO_3$, are linked into isolated chains by a single two-centre iodo–nitro interaction.

Comment

We have recently reported the molecular and supramolecular structures of several iodonitroanilines, unsubstituted at N (Garden *et al.*, 2002). In these compounds, the supramolecular aggregation is dominated by a combination of N—H···O hydrogen bonds, iodo–nitro interactions and aromatic π–π-stacking interactions, to give either two- or three-dimensional structures. The title compounds, 2,6-diiodo-4-nitrophenol, (I), 2,6-diiodo-4-nitrophenyl acetate, (II), and 2,6-diiodo-4-nitroanisole, (III), have been designed to reduce the scope for formation of hard (Braga *et al.*, 1995) hydrogen bonds, while

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retaining the other potential intermolecular interactions, in that (I) has an OH group in place of the NH_2 group in simple anilines, allowing the molecule to act as only a single donor in such bonds, while (II) and (III) have no scope at all for the formation of hard hydrogen bonds.
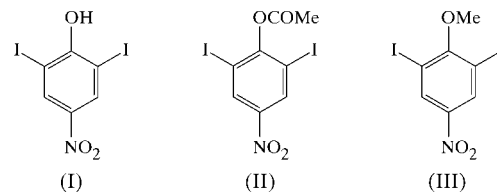
In compound (I) (Fig. 1), a combination of O—H···O hydrogen bonds and two independent iodo–nitro interactions links the molecules into sheets, and these sheets are weakly linked by aromatic π–π-stacking interactions to form a continuous three-dimensional structure. The phenolic atom O1 acts as a hydrogen-bond donor to nitro atom O41 at $(1 + x, y − 1, z)$ (Table 2), so generating by translation a $C(8)$ chain (Bernstein *et al.*, 1995) running parallel to the [1$\bar{1}$0] direction. Chains of this type are linked into sheets by the iodo–nitro interactions, which involve both I atoms and both nitro O atoms. Atoms I2 and I6 participate in iodo–nitro interactions with nitro atoms O42 and O41, respectively [I2···O42^i 3.326 (4) Å and C2—I2···O42^i 152.2 (2)°, and I6···O41^{ii} 3.552 (4) Å and C6—I6···O41^{ii} 157.9 (2)°; symmetry codes: (i) $1 − x, 1 − y, −z$; (ii) $−x, 1 − y, 2 − z$], so generating centrosymmetric $R_2^2(12)$ rings centred at $(\frac{1}{2},0,0)$ and $(0,0,1)$, respectively. The combination of these two motifs generates a chain of fused rings running parallel to the [10$\bar{2}$] direction, while the combination of this chain with the hydrogen-bonded chain along [1$\bar{1}$0] generates a (221) sheet in which there are four distinct types of ring, all centrosymmetric (Fig. 2).

The aromatic ring of (I) forms a close π···π contact with that at $(1 − x, 1 − y, 1 − z)$ (Fig. 3); the interplanar spacing between parallel rings is 3.379 (4) Å, the centroid separation is 3.493 (4) Å and the centroid offset is 0.886 (4) Å. In this manner, each (221) sheet (Fig. 2) is linked to the two adjacent sheets, so generating a continuous framework in three dimensions.
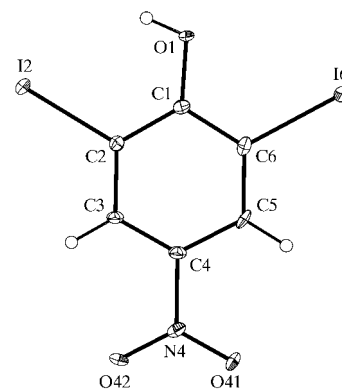
Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

Molecules of compound (II) lie across the mirror planes in space group *Pnma* (Fig. 4). The non-H atoms of the acetate group all lie on the mirror plane (chosen for the sake of convenience as that at $y = \frac{1}{4}$ for the reference molecule), so that the plane of the acetate group is orthogonal to the aromatic ring. The methyl group was modelled using six H-atom sites, each with occupancy 0.5. The crystal structure
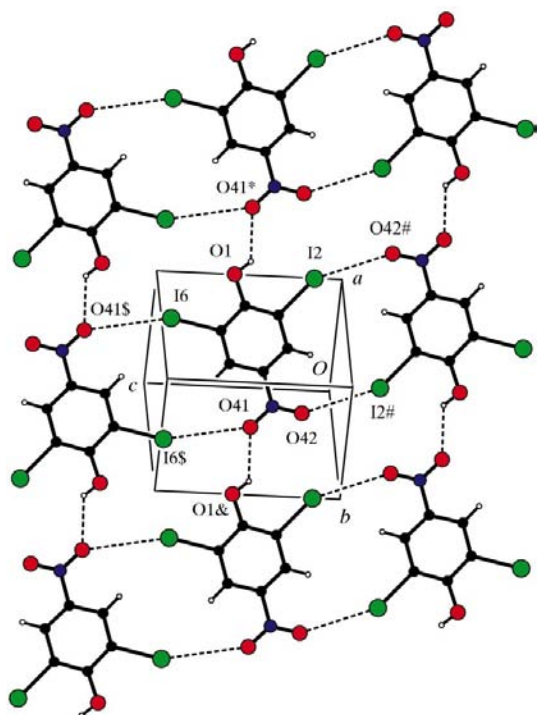

Figure 2
Part of the crystal structure of (I), showing the formation of a (110) sheet containing four distinct centrosymmetric rings. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions $(1 + x, y - 1, z)$, $(1 - x, 1 - y, -z)$, $(-x, 1 - y, 2 - z)$ and $(x - 1, 1 + y, z)$, respectively.
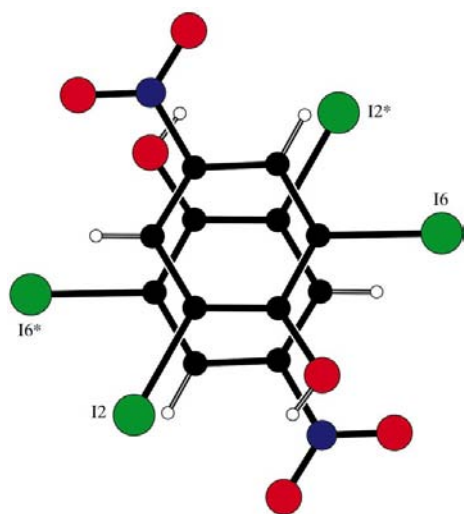

Figure 3
Part of the crystal structure of (I), showing the π–π-stacking interaction. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

exhibits neither C—H···O hydrogen bonds nor aromatic π–π-stacking interactions. Instead, the single short iodo–nitro interaction generates a simple and elegant sheet structure (Fig. 5).

Each of the two symmetry-related I atoms in (II) participates in a two-centre iodo–nitro interaction with the O4 atoms at $(\frac{1}{2} - x, 1 - y, z - \frac{1}{2})$ and $(\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2})$, respectively, with I2···O4 3.323 (3) Å and C—I···O4 140.8 (2)°. Propagation of these interactions produces two $C(6)$ chain motifs running parallel to the [001] direction and generated by the 2_1 screw axes along $(\frac{1}{4}, \frac{1}{2}, z)$ and $(\frac{1}{4}, 0, z)$. The combination of these two symmetry-related motifs and their propagation by the space group generates a (100) sheet in the form of a (4,4) net (Batten & Robson, 1998) built from a single type of $R_4^4(20)$
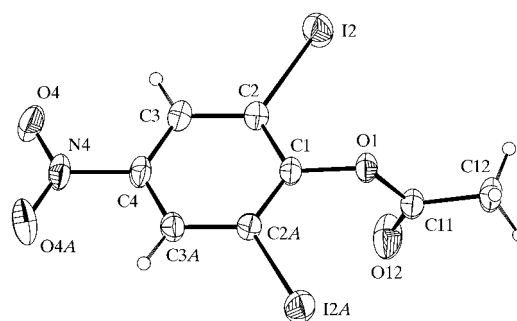

Figure 4
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms with the suffix *A* are at the symmetry position $(x, 1 - y, z)$. For the sake of clarity, only one set of H atoms bonded to C12 is shown.
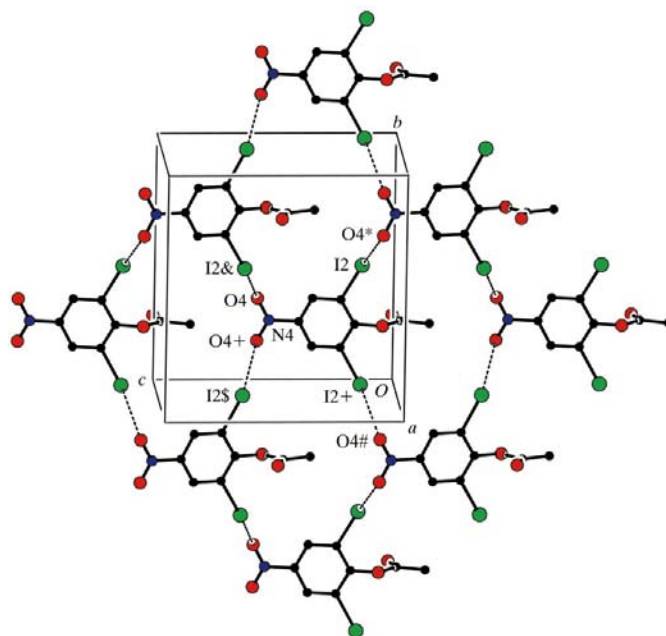

Figure 5
Part of the crystal structure of (II), showing the formation of a (100) sheet of $R_4^4(20)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with a plus sign (+), asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions $(x, \frac{1}{2} - y, z)$, $(\frac{1}{2} - x, 1 - y, z - \frac{1}{2})$, $(\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2})$, $(\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z)$ and $(\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$, respectively.

ring. The central space in each ring is occupied by an acetate group.

In compound (III) (Fig. 6), neither C—H···O hydrogen bonds nor aromatic π–π-stacking interactions are present in the crystal structure. The molecules are linked into chains by an iodo–nitro interaction involving only one of the two I atoms and only one of the nitro O atoms. Atom I2 in the molecule at (x, y, z) forms a very short I···O contact with nitro atom O42 in the molecule at $(\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2})$ [I2···O42^{iv}

2.992 (3) Å and C2—I2···O42^{iv} 171.3 (2)°; symmetry code: (iv) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$], and propagation of this interaction leads to the formation of a chain running parallel to the $[10\bar{1}]$ direction, generated by the n glide plane at $y = \frac{1}{4}$ (Fig. 7).

The intermolecular distances and angles in compounds (I)–(III) present no unusual features. In each compound, the nitro group is almost coplanar with the adjacent aryl ring (Tables 1, 3 and 4).
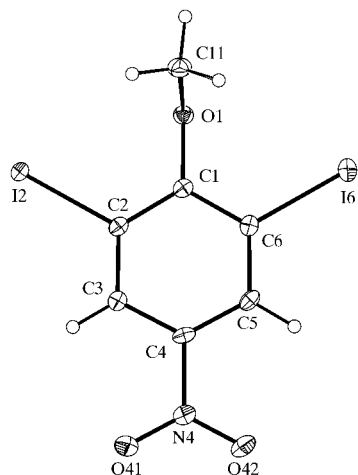

Figure 6
The molecule of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.
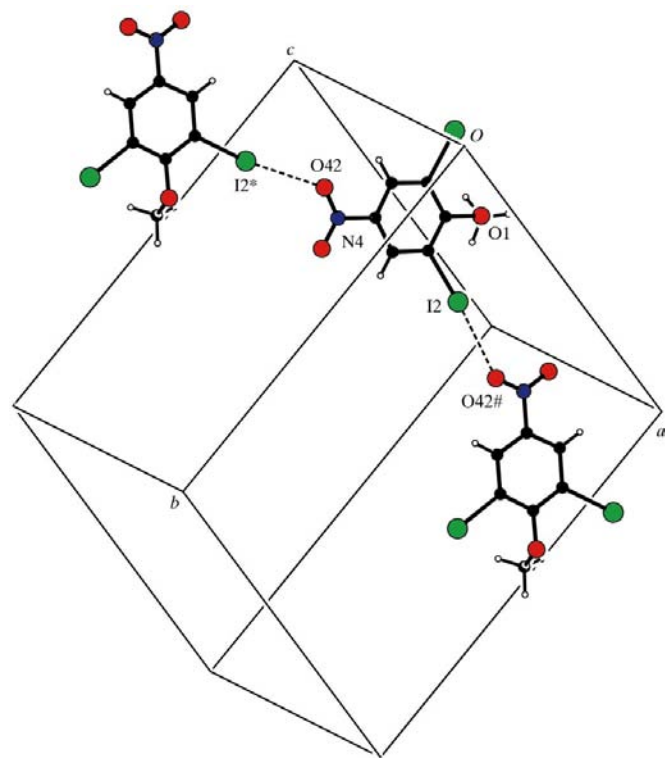
Experimental

Compound (I) was obtained by reaction of 4-nitrophenol with K[ICl$_2$] in aqueous solution (Garden *et al.*, 2001). Compounds (II) and (III) were obtained from (I) by acetylation using acetic anhydride and methylation using dimethyl sulfate, respectively. Crystals of (I)–(III) suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in ethanol [m.p. 439–441 K for (I), 409–411 K for (II) and 418–419 K for (III)].

Compound (I)

Crystal data

$C_6H_3I_2NO_3$	$Z = 2$
$M_r = 390.89$	$D_x = 3.001$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.9749$ (2) Å	Cell parameters from 1850
$b = 8.0952$ (3) Å	reflections
$c = 8.1395$ (3) Å	$\theta = 2.9$–27.4°
$\alpha = 69.3082$ (18)°	$\mu = 7.24$ mm^{-1}
$\beta = 66.657$ (2)°	$T = 120$ (2) K
$\gamma = 67.3547$ (15)°	Block, yellow
$V = 432.59$ (3) Å^3	$0.15 \times 0.10 \times 0.05$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	1850 independent reflections
φ scans, and ω scans with κ offsets	1735 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)	$R_{int} = 0.091$
	$\theta_{max} = 27.4°$
	$h = -10 \rightarrow 10$
	$k = -10 \rightarrow 10$
$T_{min} = 0.297$, $T_{max} = 0.700$	$l = -10 \rightarrow 10$
4596 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0584P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$+ 0.3136P]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.17$	$(\Delta/\sigma)_{max} < 0.001$
1850 reflections	$\Delta\rho_{max} = 1.35$ e Å^{-3}
110 parameters	$\Delta\rho_{min} = -1.57$ e Å^{-3}
H-atom parameters constrained	

Figure 7
Part of the crystal structure of (III), showing the formation of a chain along $[10\bar{1}]$. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2})$, respectively.

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

C3—C4—N4—O41	−178.5 (6)	C3—C4—N4—O42	1.1 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O41^i	0.84	2.20	2.808 (6)	129

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

Compound (II)

Crystal data

$C_8H_5I_2NO_4$
$M_r = 432.93$
Orthorhombic, $Pnma$
$a = 8.0608 (9)$ Å
$b = 12.4501 (14)$ Å
$c = 11.6790 (13)$ Å
$V = 1172.1 (2)$ Å^3
$Z = 4$
$D_x = 2.453$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2206
  reflections
$\theta = 2.4–32.6°$
$\mu = 5.36$ mm^{-1}
$T = 292 (2)$ K
Block, colourless
$0.50 \times 0.23 \times 0.12$ mm

Data collection

Bruker SMART 1000 CCD area-
  detector diffractometer
φ and ω scans
Absorption correction: multi-scan
  (*SADABS*; Bruker, 1999)
  $T_{min} = 0.258$, $T_{max} = 0.528$
11 456 measured reflections

2206 independent reflections
1555 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 32.6°$
$h = -12 \rightarrow 12$
$k = -17 \rightarrow 18$
$l = -17 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.112$
$S = 1.04$
2206 reflections
81 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2$
  $+ 0.8851P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.20$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}
Extinction correction: *SHELXL*97
  (Sheldrick, 1997)
Extinction coefficient: 0.0321 (13)

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

C3—C4—N4—O4	1.6 (6)	C2—C1—O1—C11	−92.6 (3)
C3—C4—N4—O4^i	179.9 (4)		

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

Compound (III)

Crystal data

$C_7H_5I_2NO_3$
$M_r = 404.92$
Monoclinic, $C2/c$
$a = 15.2372 (3)$ Å
$b = 16.2672 (4)$ Å
$c = 8.3262 (2)$ Å
$\beta = 99.2039 (15)°$
$V = 2037.22 (8)$ Å^3
$Z = 8$

$D_x = 2.640$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2312
  reflections
$\theta = 2.9–27.5°$
$\mu = 6.15$ mm^{-1}
$T = 120 (2)$ K
Block, yellow
$0.10 \times 0.05 \times 0.03$ 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)
  $T_{min} = 0.530$, $T_{max} = 0.829$
7397 measured reflections

2312 independent reflections
2068 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$
$\theta_{max} = 27.5°$
$h = -19 \rightarrow 19$
$k = -21 \rightarrow 18$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.077$
$S = 1.07$
2312 reflections
119 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.42$ e Å^{-3}
$\Delta\rho_{min} = -1.65$ e Å^{-3}

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

C3—C4—N4—O41	−7.4 (5)	C2—C1—O1—C11	89.7 (5)
C3—C4—N4—O42	173.0 (4)	C6—C1—O1—C11	−94.7 (5)

Compound (I) is triclinic; space group $P\bar{1}$ was selected and confirmed by the analysis. For compound (II), the systematic absences permitted $Pnma$ and $Pn2_1a$ (= $Pna2_1$) as possible space groups; $Pnma$ was selected and confirmed by the structure analysis. For compound (III), the systematic absences permitted $C2/c$ and Cc as possible space groups; $C2/c$ was selected and confirmed by the analysis. All H atoms were located from difference maps and were treated as riding atoms, with O—H distances of 0.84 Å and C—H distances in the range 0.93–0.98 Å.

For compounds (I) and (III), 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, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*. For all three 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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