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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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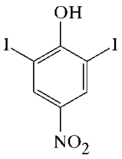
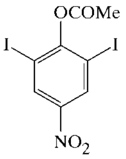
In 2,6-diiodo-4-nitrophenol, $C_6H_3I_2NO_3$, the molecules are linked, by an O—H$\cdots$O hydrogen bond and two iodo–nitro interactions, into sheets, which are further linked into a three-dimensional framework by aromatic π–π-stacking interactions. The molecules of 2,6-diiodo-4-nitrophenyl acetate, $C_8H_5I_2NO_4$, 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

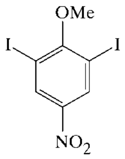
We have recently reported the molecular and supramolecular structures of several iodonitroanilines, unsubstituted at N (Garden *et al.*, 2002). In these compounds, the supramolecular aggregation is dominated by a combination of N—H$\cdots$O hydrogen bonds, iodo–nitro interactions and aromatic π–π-stacking 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 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.



(I)



(II)



(III)

In compound (I) (Fig. 1), a combination of O—H$\cdots$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$\cdots$O42^{i} 3.326 (4) Å and C2—I2$\cdots$O42^{i} 152.2 (2)°, and I6$\cdots$O41^{ii} 3.552 (4) Å and C6—I6$\cdots$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 $\pi\cdots\pi$ 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.

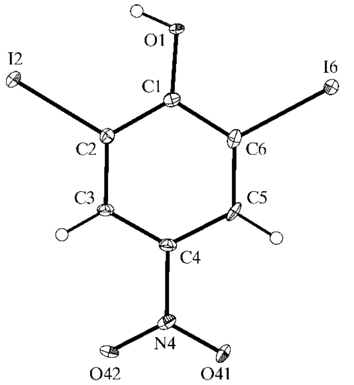


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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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 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 $R_4^4(20)$

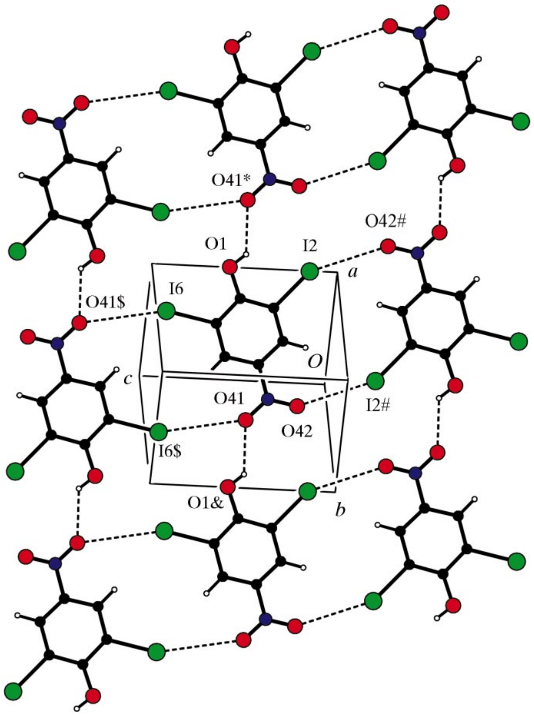

Figure 2
Part of the crystal structure of (I), showing the formation of a (110) sheet containing four distinct centrosymmetric rings. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry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

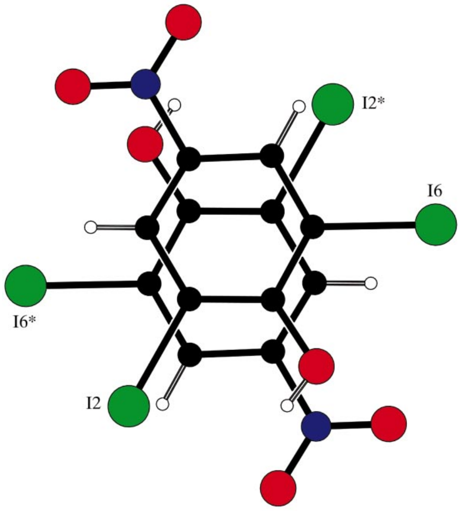

Figure 3
Part of the crystal structure of (I), showing the π–π-stacking interaction. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

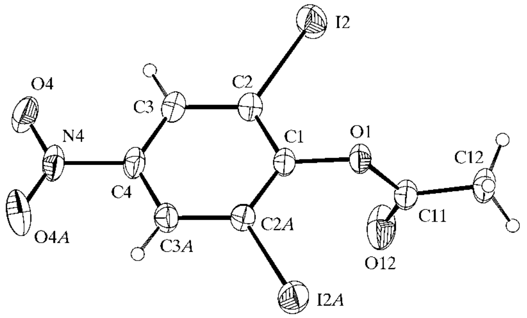

Figure 4
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms with the suffix *A* are at the symmetry position $(x, 1 - y, z)$. For the sake of clarity, only one set of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

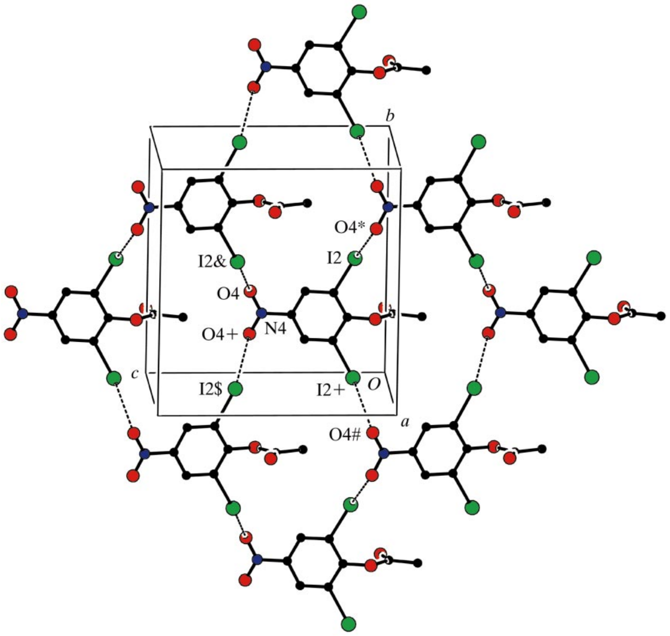

Figure 5
Part of the crystal structure of (II), showing the formation of a (100) sheet of $R_4^4(20)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with a plus sign (+), asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions $(x, \frac{1}{2} - y, z)$, $(\frac{1}{2} - x, 1 - y, z - \frac{1}{2})$, $(\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2})$, $(\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z)$ 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$^{\rm iv}$ 2.992 (3) Å and C2—I2···O42$^{\rm iv}$ 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$\overline{1}$] direction, generated by the n glide plane at $y = \frac{1}{4}$ (Fig. 7).

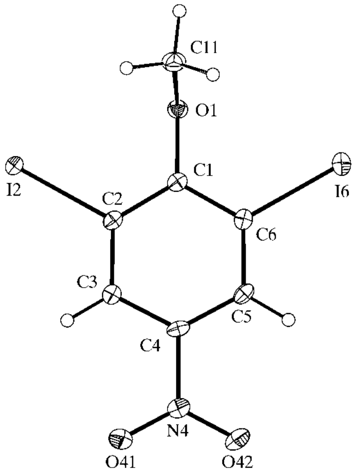

Figure 6
The molecule of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

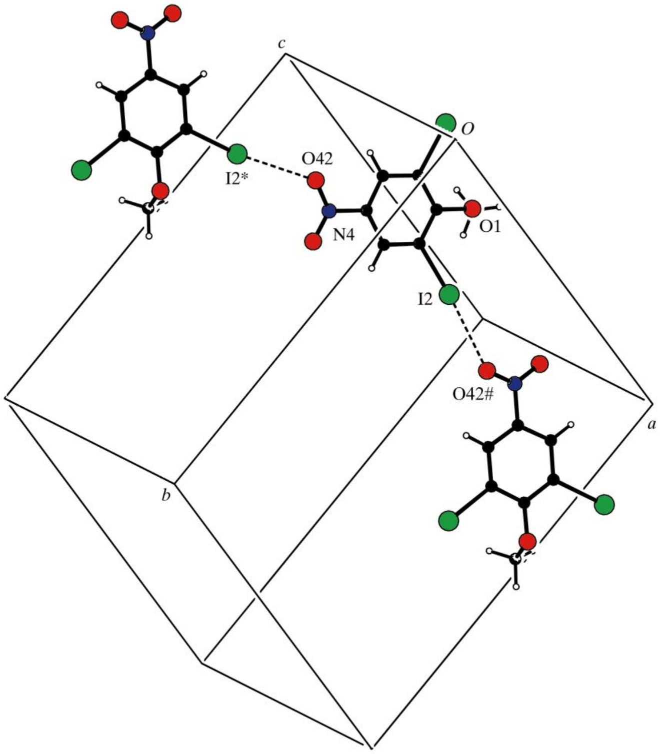

Figure 7
Part of the crystal structure of (III), showing the formation of a chain along [10$\overline{1}$]. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions ($x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$) and ($\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$), respectively.

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).

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

$C_6H_3I_2NO_3$
$M_r = 390.89$
Triclinic, $P\overline{1}$
$a = 7.9749$ (2) Å
$b = 8.0952$ (3) Å
$c = 8.1395$ (3) Å
$\alpha = 69.3082$ (18)°
$\beta = 66.657$ (2)°
$\gamma = 67.3547$ (15)°
$V = 432.59$ (3) Å^3
$Z = 2$
$D_x = 3.001$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1850 reflections
$\theta = 2.9$–27.4°
$\mu = 7.24$ mm^{-1}
$T = 120$ (2) K
Block, yellow
0.15 × 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)
$T_{\rm min} = 0.297$, $T_{\rm max} = 0.700$
4596 measured reflections
1850 independent reflections
1735 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.091$
$\theta_{\rm max} = 27.4$°
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 10$

Refinement

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

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$^{\rm i}$	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 × 0.23 × 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 $I > 2\sigma(I)$
$R_{\rm int} = 0.044$
$\theta_{\max} = 32.6°$
$h = -12 \rightarrow 12$
$k = -17 \rightarrow 18$
$l = -17 \rightarrow 15$

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$^{\rm i}$	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 × 0.05 × 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 $I > 2\sigma(I)$
$R_{\rm int} = 0.056$
$\theta_{\max} = 27.5°$
$h = -19 \rightarrow 19$
$k = -21 \rightarrow 18$
$l = -10 \rightarrow 10$

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 $P\overline{1}$ 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).

The X-ray data for (I) and (III) were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. The data for (II) were collected at the University of Aberdeen, Scotland. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. SJG, FRC and JLW thank CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1033). Services for accessing these data are described at the back of the journal.

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