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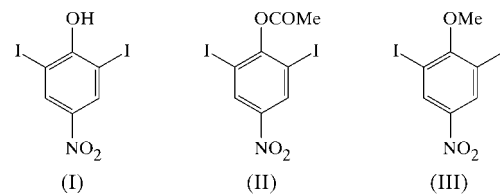
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In 2,6-diiodo-4-nitrophenol, $C_6H_3I_2NO_3$, the molecules are linked, by an $O-H\cdots O$ hydrogen bond and two iodo–nitro interactions, into sheets, which are further linked into a three-dimensional framework by aromatic π – π -stacking interactions.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



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.

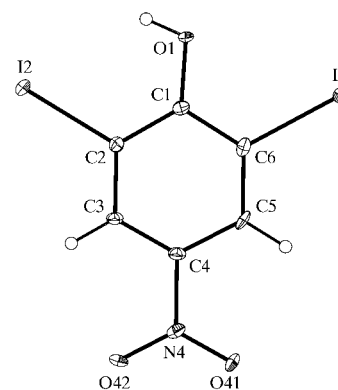


Figure 1

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

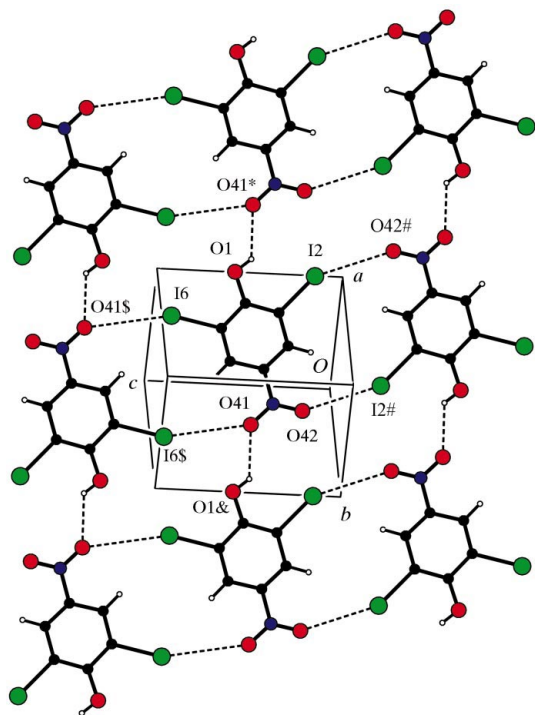


Figure 2
Part of the crystal structure of (I), showing the formation of a (110) sheet containing four distinct centrosymmetric rings. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign (\$) or ampersand (&) are at the symmetry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

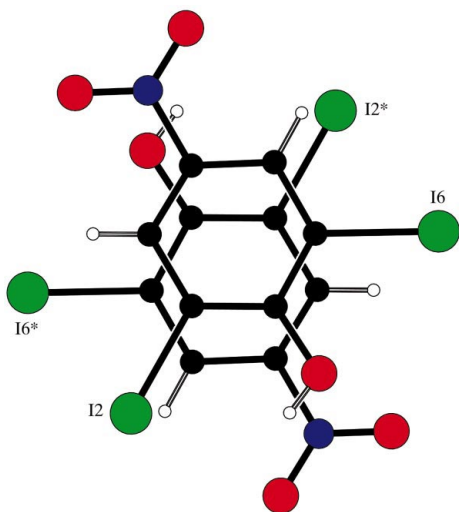


Figure 3
Part of the crystal structure of (I), showing the π - π -stacking interaction. Atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 1-z)$.

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 $I2 \cdots O4$ 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 $(\frac{3}{4}, 0, z)$. 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 $R_4^+(20)$

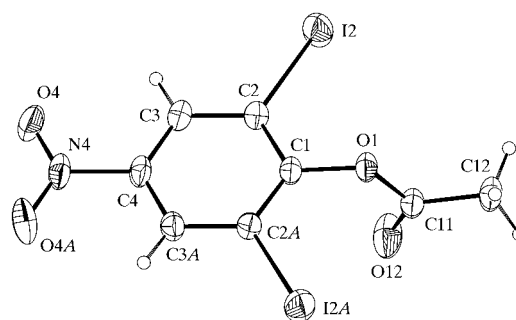


Figure 4
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms with the suffix A are at the symmetry position $(x, 1-y, z)$. For the sake of clarity, only one set of H atoms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

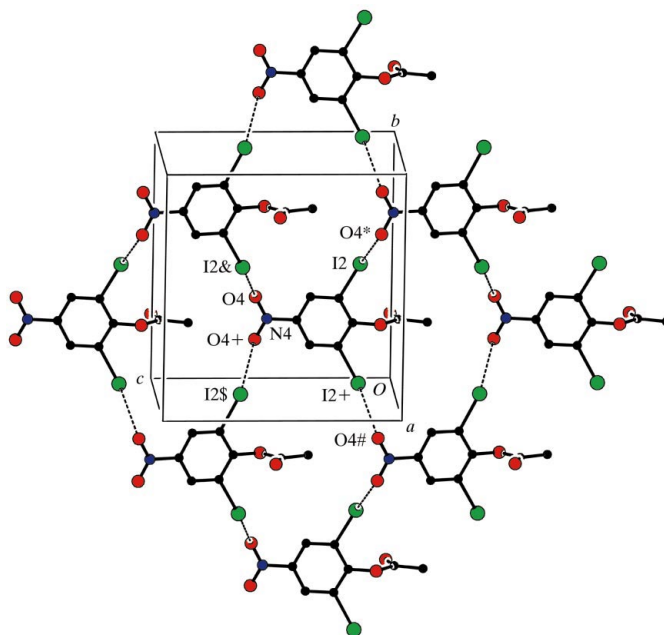


Figure 5
Part of the crystal structure of (II), showing the formation of a (100) sheet of $R_4^+(20)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with a plus sign (+), asterisk (*), hash (#), dollar sign (\$) or ampersand (&) are at the symmetry positions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

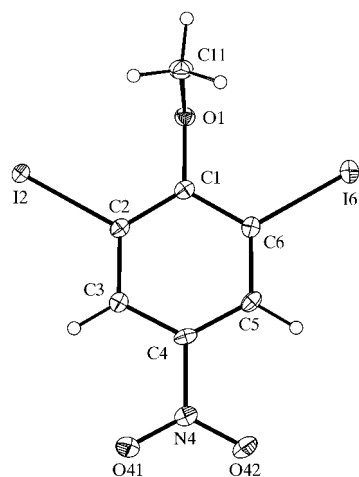


Figure 6
The molecule of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

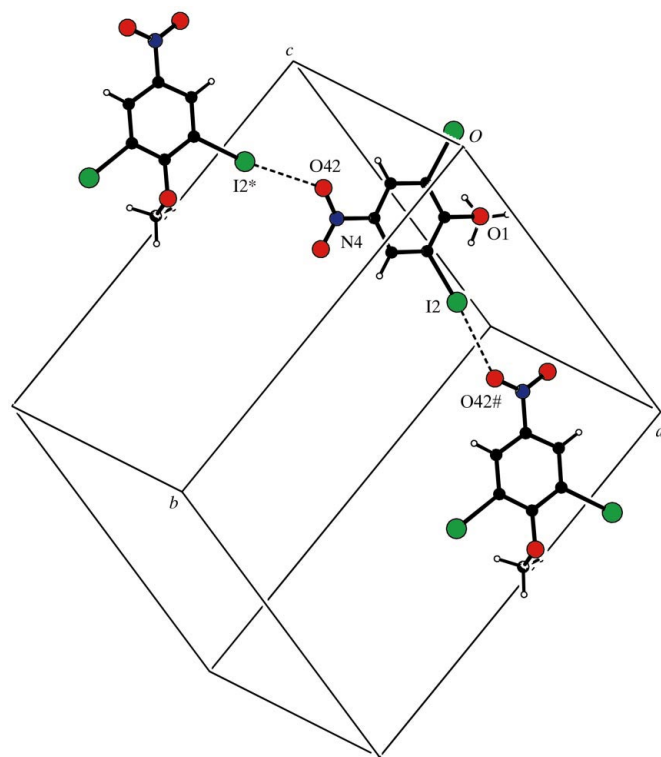


Figure 7
Part of the crystal structure of (III), showing the formation of a chain along [101]. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2})$, respectively.

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 [101] 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).

Experimental

Compound (I) was obtained by reaction of 4-nitrophenol with K[ICl₂] 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

C₆H₃I₂NO₃
M_r = 390.89
 Triclinic, $P\bar{1}$
a = 7.9749 (2) Å
b = 8.0952 (3) Å
c = 8.1395 (3) Å
 α = 69.3082 (18)°
 β = 66.657 (2)°
 γ = 67.3547 (15)°
V = 432.59 (3) Å³

Z = 2
D_x = 3.001 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 1850 reflections
 θ = 2.9–27.4°
 μ = 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_{min} = 0.297, *T_{max}* = 0.700
 4596 measured reflections

1850 independent reflections
 1735 reflections with $I > 2\sigma(I)$
R_{int} = 0.091
 θ_{\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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.35 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.57 \text{ e } \text{Å}^{-3}$

Table 1

Selected torsion angles (°) for (I).

C3—C4—N4—O41	−178.5 (6)	C3—C4—N4—O42	1.1 (8)
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Table 2

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

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

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

Compound (II)

Crystal data

C₈H₅I₂NO₄
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) Å³
Z = 4
D_x = 2.453 Mg m⁻³

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

Refinement

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

Mo *K*α radiation
 Cell parameters from 2206 reflections
 θ = 2.4–32.6°
 μ = 5.36 mm⁻¹
T = 292 (2) K
 Block, colourless
 0.50 × 0.23 × 0.12 mm
 2206 independent reflections
 1555 reflections with *I* > 2σ(*I*)
R_{int} = 0.044
 θ_{max} = 32.6°
h = -12 → 12
k = -17 → 18
l = -17 → 15

$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2 + 0.8851P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 1.20 e Å⁻³
 Δρ_{min} = -0.41 e Å⁻³
 Extinction correction: *SHELXL97* (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

C₇H₅I₂NO₃
M_r = 404.92
 Monoclinic, *C2/c*
a = 15.2372 (3) Å
b = 16.2672 (4) Å
c = 8.3262 (2) Å
 β = 99.2039 (15)°
V = 2037.22 (8) Å³
Z = 8

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

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.033
wR (*F*²) = 0.077
S = 1.07
 2312 reflections
 119 parameters

D_x = 2.640 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 2312 reflections
 θ = 2.9–27.5°
 μ = 6.15 mm⁻¹
T = 120 (2) K
 Block, yellow
 0.10 × 0.05 × 0.03 mm
 2312 independent reflections
 2068 reflections with *I* > 2σ(*I*)
R_{int} = 0.056
 θ_{max} = 27.5°
h = -19 → 19
k = -21 → 18
l = -10 → 10

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0371P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 1.42 e Å⁻³
 Δρ_{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 *Pn2₁a* (= *Pna2₁*) 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: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); 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: TR1033). Services for accessing these data are described at the back of the journal.

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