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 $\pi$–$\pi$-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

Simon J. Garden, Fernanda R. da Cunha, James L. Wardell, Janet M. S. Skakle, John N. Low† and Christopher Gidewell‡

In 2,6-diiodo-4-nitrophenol, C₆H₃I₂NO₃, 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, C₈H₅I₂NO₄, 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, C₇H₅I₂NO₃, 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 hydrogen bonds, while retaining the other potential intermolecular interactions, in that (I) has an OH group in place of the NH₂ 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 0 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. The combination of these two motifs generates a chain of fused rings running parallel to the [1 0 2] direction, while the combination of this chain with the hydrogen-bonded chain along [1 0 0] generates a (2 2 1) 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 (2 2 1) 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 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 \( \pi-\pi \)-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 \( C-I \cdots O4 \) 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 \( (\frac{1}{2}, \frac{1}{2}, z) \) and \( (\frac{1}{2}, 0, z) \). 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 \( \pi-\pi \)-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 \((1 - y, 1 - z)\). 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 \((x, 1 - y, z)\), \((\frac{1}{2} - x, 1 - y, z - \frac{1}{2})\), \((\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2})\), \((\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2})\) 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 \(\left(\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}\right)\). [I2···O42]

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**

\[C_6H_3I_2NO_3, \text{Z} = 2, \quad D_x = 2.904 \text{ Mg m}^{-3}\]

Triclinic, \(PT\)

\(a = 7.9749(2) \text{ Å}, \quad b = 8.0952(3) \text{ Å}, \quad c = 8.1395(3) \text{ Å}\) and \(a = 69.3082(18)°, \quad \beta = 66.657(2)°, \quad y = 67.3547(15)°\) respectively.

Cell parameters from 1850 reflections

\(V = 432.59(3) \text{ Å}^3, \quad \rho = 1.57 \text{ e Å}^{-3}\) and \(\Delta \rho_{\text{max}} = 1.57 \text{ e Å}^{-3}\)

### Data collection

Nonius KappaCCD area-detector diffractometer

\(\psi\) scans, and \(\omega\) scans with \(\kappa\) offsets

Absorption correction: multi-scan \(\Delta\rho_{\text{max}} = 2.9–27.4°\)

Absorption correction: multi-scan \(\theta = 120(2) \text{ K}\)

### 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

#### Table 1

<table>
<thead>
<tr>
<th>C3--C4--N4--O41</th>
<th>178.5 (6)</th>
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<tbody>
<tr>
<td>C3--C4--N4--O42</td>
<td>178.5 (6)</td>
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</table>

#### Table 2

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

\(D-H\cdots A\)  \(D-H\)  \(H\cdots A\)  \(D\cdots A\)  \(D-H\cdots A\)

| O1---H1`1···O41  | 0.84  | 2.20  | 2.808 (6) | 129 |

Symmetry code: (i) \(1 + x, y, z\).
### Compound (II)

**Crystal data**

\[
\begin{align*}
C_6H_5NO_3 & : M_r = 164.12 \\
 & : \text{Monoclinic, } \text{C}2/c \\
 & : a = 8.1267 (3) \text{ Å} \\
 & : b = 16.2672 (4) \text{ Å} \\
 & : c = 8.3262 (2) \text{ Å} \\
 & : \beta = 99.2039 (15)^\circ \\
 & : V = 2037.22 (8) \text{ Å}^3 \\
 & : Z = 8 \\
D_0 & = 1.87 \text{ Mg m}^{-3} \\
\end{align*}
\]

Mo Kα radiation

Cell parameters from 2206 reflections

\[\theta = 2.4−32.6^\circ\]

\[\mu = 1.07 \text{ mm}^{-1}\]

\[T = 292 (2) \text{ K}\]

Block, colourless

0.50 × 0.23 × 0.12 mm

**Data collection**

Bruker SMART 1000 CCD area-detector diffractometer

2206 independent reflections

1555 reflections with \(I > 2\sigma(I)\)

\(\theta_{\text{max}} = 32.6^\circ\)

\(h = -12 \rightarrow 12\)

\(k = -17 \rightarrow 18\)

\(l = -17 \rightarrow 15\)

**Refinement**

Refinement on \(F^2\)

\[wR(F^2) = 0.041\]

\[S = 1.04\]

2206 reflections

81 parameters

H-atom parameters constrained

**Table 3**

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<th>C3—C4—N4—O4</th>
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<th>−92.6 (3)</th>
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</thead>
</table>

Symmetry code: (i) x, y, z.

### Compound (III)

**Crystal data**

\[
\begin{align*}
C_6H_5NO_3 & : M_r = 164.12 \\
 & : \text{Monoclinic, } \text{C}2/c \\
 & : a = 8.3262 (2) \text{ Å} \\
 & : b = 16.2672 (4) \text{ Å} \\
 & : c = 8.1267 (3) \text{ Å} \\
 & : \beta = 99.2039 (15)^\circ \\
 & : V = 2037.22 (8) \text{ Å}^3 \\
 & : Z = 8 \\
D_0 & = 1.87 \text{ Mg m}^{-3} \\
\end{align*}
\]

Mo Kα radiation

Cell parameters from 2312 reflections

\[\theta = 2.9−27.5^\circ\]

\[\mu = 6.15 \text{ mm}^{-1}\]

\[T = 120 (2) \text{ K}\]

Block, yellow

0.10 × 0.05 × 0.03 mm

**Data collection**

Nonius KappaCCD area-detector diffractometer

2312 independent reflections

2068 reflections with \(I > 2\sigma(I)\)

\(\theta_{\text{max}} = 27.5^\circ\)

\(h = -19 \rightarrow 19\)

\(k = -21 \rightarrow 18\)

\(l = -10 \rightarrow 10\)

**Refinement**

Refinement on \(F^2\)

\[wR(F^2) = 0.033\]

\[S = 1.07\]

2312 reflections

119 parameters

H-atom parameters constrained

**Table 4**

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<td>173.0 (4)</td>
<td>C6—C1—O1—C11</td>
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### References


