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# Secondary interactions in 1-iodo-3-nitrobenzene and 1-iodo-3,5-dinitrobenzene

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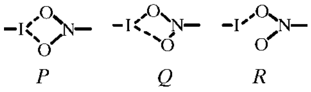
The crystal packing of 1-iodo-3-nitrobenzene, $C_6H_4INO_2$, is formed by planar molecules which are linked by I$\cdots$I and $NO_2\cdots NO_2$ interactions. In the case of 1-iodo-3,5-dinitrobenzene, $C_6H_3IN_2O_4$, the $NO_2$ groups are not exactly coplanar with the benzene ring and the molecules form sheets linked by $NO_2\cdots NO_2$ interactions. In contrast with 4-iodonitrobenzene, the crystal structures of both title compounds do not form highly symmetrical I$\cdots NO_2$ intermolecular interactions.

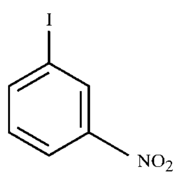
## Comment

In this communication, we report the crystal structures of two iodo-substituted nitrobenzenes. A comparison with related iodo-substituted nitrobenzenes shows that the different possibilities of I$\cdots NO_2$ interactions depend on the substitution pattern of the nitro and iodo groups in the benzene ring. Recently, Desiraju *et al.* (1993) observed that halogen atoms, presumably due to their polarizabilities, may form symmetrical (*P*) and unsymmetrical (*Q* and *R*) recognition motifs with nitro groups; the *Scheme* below illustrates these types of iodo$\cdots$nitro intermolecular interactions.

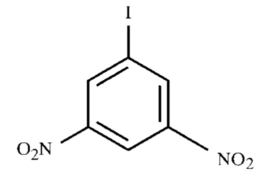


In the structures of 4-iodonitrobenzene, (I) (Thalladi *et al.*, 1996), and the 1:1 complex of 1,4-dinitrobenzene with 1,4-diiodobenzene (Allen *et al.*, 1994), there are linear ribbon patterns linked exclusively *via* symmetrical iodo$\cdots$nitro motifs (*P*). These motifs are formed from two convergent polarization-induced I$\cdots$O interactions. As part of a continuing study of intermolecular interactions in such compounds, we have investigated compounds containing 3-iodonitrobenzene substitution patterns and have determined the crystal structures of 1-iodo-3-nitrobenzene, (II), and 1-iodo-3,5-dinitrobenzene, (III).

A search of the spring 2002 release of the Cambridge Structural Database (CSD: Allen, 2002) for structures containing 3-iodonitrobenzene substitution patterns revealed only a few compounds containing additional groups on the aromatic system.



(II)



(III)

The molecular structure of (II) is shown in Fig. 1(*a*), with the associated distances and angles of special interest given in Table 1. The C—I [2.095 (7) Å] and N—O [1.224 (8) and 1.242 (8) Å] distances are in good agreement with the values reported for (I) [C—I = 2.097 (5) Å, and N—O = 1.2242 (6) and 1.232 (6) Å; Thalladi *et al.*, 1996]. The planar molecules are linked into zigzag chains *via* I$\cdots$I$^{i}$ interactions of

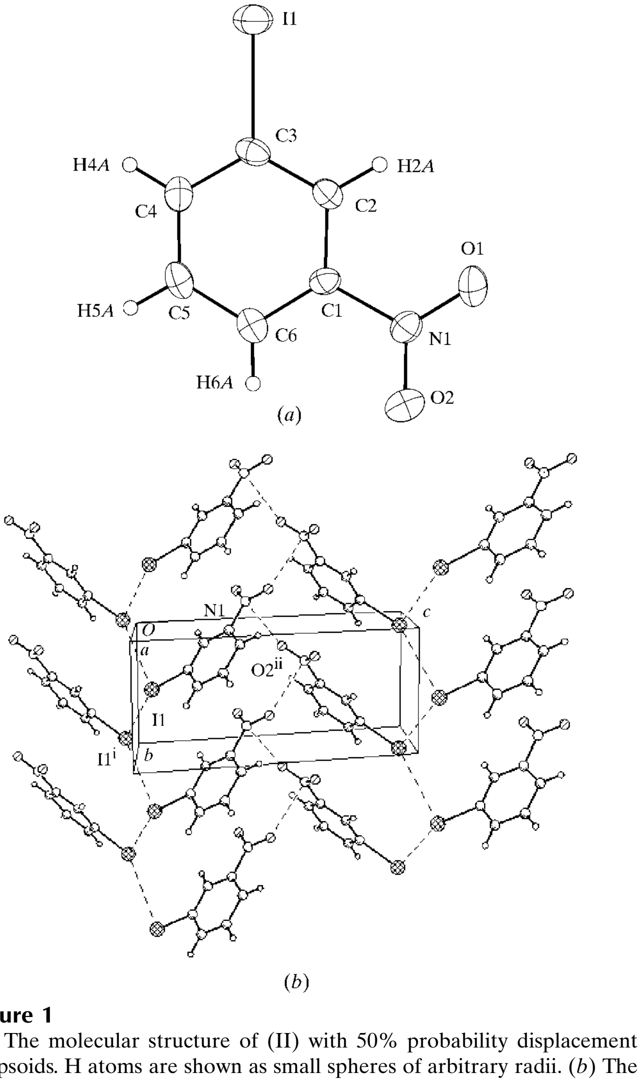


**Figure 1**
(*a*) The molecular structure of (II) with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. (*b*) The crystal packing of (II) [symmetry codes: (i) $-x, \frac{1}{2}+y, -z$; (ii) $1-x, \frac{1}{2}+y, 1-z$].

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3.990 (7) Å [Fig. 1*b*; symmetry code: (i) $-x, \frac{1}{2}+y, -z$]. A similar pattern of I···I zigzag chains has also been observed for 1,2-diiodo-4-nitro-5-(*n*-butylamino)benzene (Senskey *et al.*, 1995). The overall network is formed using additional $NO_2\cdots NO_2$ interactions, with $O_2N1\cdots O2^{ii}NO$ = 2.928 (12) Å [symmetry code: (ii) $1-x, \frac{1}{2}+y, 1-z$]. These distances are within the acceptable limits described in the literature for 1,2,4-trinitrobenzene (Laerdahl *et al.*, 1998). In contrast with the crystal structures of (I) and related compounds, the lack of iodo···nitro interactions in (II) is surprising.

In an attempt to engineer a two-dimensional network with highly symmetrical *P* motifs, we looked to iodo-substituted nitrobenzene with additional nitro groups on the ring and determined the structure of 3-iodo-1,5-dinitrobenzene, (III). The molecular structure of (III) is shown in Fig. 2(*a*), with the associated dimensions given in Table 2. The C—I and N—O distances are in good agreement with the structures of (I) and (II). Neither $NO_2$ group is exactly coplanar with the benzene ring; the angles between the least-squares planes of the nitro groups and the benzene ring are 13 and 21°. The crystal packing of (III) can be described as a periodical arrangement of two nearly parallel sheets of molecules (Fig. 2*b*), and two such sheets are linked by $NO_2\cdots NO_2$ interactions, with $N1\cdots O1^{v}$ = 2.944 (7) Å and $N1\cdots O3^{iv}$ = 3.009 (7) Å [symmetry codes: (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (v) $-x, y, \frac{3}{2}-z$]. Each sheet forms $I\cdots NO_2$ interactions, with $I1\cdots O2^{iii}$ 3.206 (3) Å [symmetry code: (iii) $x, 2-y, -\frac{1}{2}+z$], which conforms to the *R* type of motif, with only one of the two nitro O atoms in contact with an I atom. The presence of one iodo and two nitro groups is still not sufficient to engineer crystal packings containing symmetrical *P* motifs as building blocks.

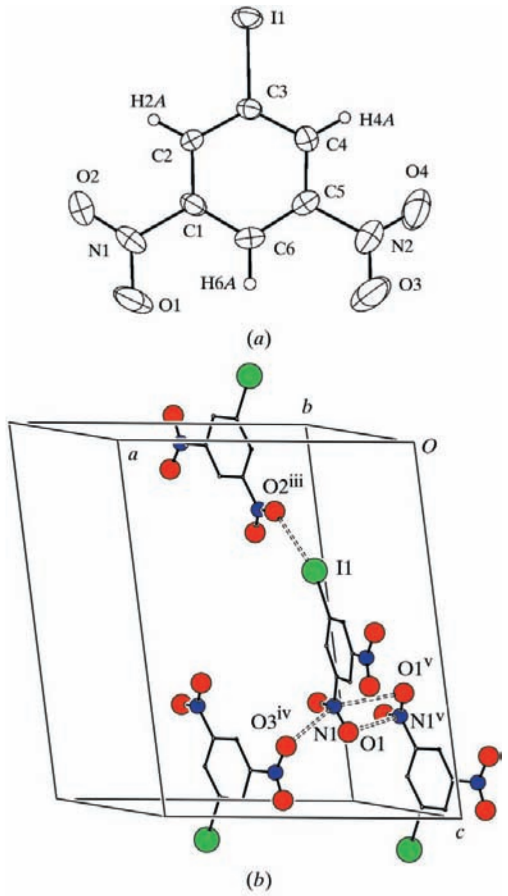

**Figure 2**
(a) The molecular structure of (III) with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. (*b*) The crystal packing of (III), showing the I···O and N···O interactions [symmetry codes: (iii) $x, 2-y, -\frac{1}{2}+z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (v) $-x, y, \frac{3}{2}-z$.]

In contrast, the higher-substituted compound 2-iodo-1,3,5-trinitrobenzene, (IV) (Weiss *et al.*, 1999), forms planes using $I\cdots NO_2$ *P* motifs and these planes are linked by $NO_2\cdots NO_2$ interactions. The *P* motifs are generated by the nitro and iodo groups arranged in *para* positions. A comparison of selected N—O, N—C and C—I bond lengths and angles in compounds (I)–(IV) shows no significant differences to explain the presence of these different intermolecular interactions.

We have compared these structures with related iodo-substituted nitrobenzenes containing additional substituents, such as I (Garden *et al.*, 2002), $NH_2$ (McWilliam *et al.*, 2001), NH*R* (Senskey *et al.*, 1995) and OH (Garden *et al.*, 2002). In these crystal packings, we only observed the $I\cdots NO_2$ interactions of the type *P* motif if the nitro and iodo groups were arranged in *para* positions. Fundamental organic chemistry suggests that there is a reactivity difference between *meta*- and *para*-substituted benzene rings, based on electronic arguments. In this case, however, additional substitution in the *ortho* or *meta* position has no effect; it is only those complexes with I in the *para* position which display the *P*-type motif of crystal packing. Allen *et al.* (1997) combined a CSD search and an *ab initio* orbital study of the geometrical parameters of halogen···nitro supramolecular synthons. These indicated that halogen···nitro interactions decrease in strength in the order Cl > Br > I, and that the frequency of formation of higher symmetrical motifs decreases in the same order. To understand if there is a relationship between the role of the substitution pattern on the benzene ring backbone and the different types of intermolecular interactions, we will investigate other supramolecular synthons in the future.

## Experimental

Commercially available (Aldrich) 1-iodo-3-nitrobenzene, (II), and 1-iodo-3,5-dinitro-benzene, (III), were heated separately in acetone until most of the solid had dissolved. Crystals suitable for X-ray diffraction analysis were obtained by slow cooling of solutions in acetone containing a few drops of heptane.

### Compound (II)

*Crystal data*

$C_6H_4INO_2$
$M_r$ = 249.00
Monoclinic, $P2_1$
$a$ = 5.977 (3) Å
$b$ = 5.224 (3) Å
$c$ = 11.972 (6) Å
$\beta$ = 104.383 (10)°
$V$ = 362.1 (3) Å$^3$
$Z$ = 2
$D_x$ = 2.284 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 102 reflections
$\theta$ = 5.0–17.0°
$\mu$ = 4.36 mm$^{-1}$
$T$ = 213 (2) K
Needle, colourless
0.3 × 0.1 × 0.1 mm

*Data collection*

Bruker SMART 1000 CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan [*SADABS* (Sheldrick, 1996; Blessing, 1995)]
$T_{\min} = 0.599$, $T_{\max} = 0.647$
2423 measured reflections

1797 independent reflections
1584 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\max} = 30°$
$h = -8 \rightarrow 7$
$k = -7 \rightarrow 7$
$l = -16 \rightarrow 14$

*Refinement*

Refinement on $F^2$
$R(F) = 0.046$
$wR(F^2) = 0.112$
$S = 1.03$
1797 reflections
91 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.94$ e Å$^{-3}$
$\Delta\rho_{\min} = -1.11$ e Å$^{-3}$
Absolute structure: Flack (1983) and Bernardinelli & Flack (1985)
Flack parameter = 0.09 (6)

**Table 1**
Selected geometric parameters (Å, °) for (II).

| | | | |
|---|---|---|---|
| I1—C3 | 2.095 (7) | O1—N1 | 1.224 (8) |
| C1—N1 | 1.465 (12) | N1—O2 | 1.242 (8) |
| | | | |
| C2—C1—N1 | 117.0 (6) | O2—N1—C1 | 117.9 (5) |
| C6—C1—N1 | 119.3 (6) | C2—C3—I1 | 119.4 (5) |
| O1—N1—O2 | 123.4 (6) | C4—C3—I1 | 119.0 (5) |
| O1—N1—C1 | 118.6 (5) | | |

## Compound (III)

*Crystal data*

$C_6H_3IN_2O_4$
$M_r = 294.00$
Monoclinic, $C2/c$
$a = 13.842$ (9) Å
$b = 8.164$ (5) Å
$c = 15.288$ (9) Å
$\beta = 101.766$ (12)°
$V = 1691.2$ (18) Å$^3$
$Z = 8$

$D_x = 2.309$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 53 reflections
$\theta = 3.4$–$17.6°$
$\mu = 3.77$ mm$^{-1}$
$T = 213$ (2) K
Needle, colourless
$0.4 \times 0.2 \times 0.2$ mm

*Data collection*

Bruker SMART 1000 CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan [*SADABS* (Sheldrick, 1996; Blessing, 1995)]
$T_{\min} = 0.421$, $T_{\max} = 0.470$
6318 measured reflections

2404 independent reflections
1927 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 30°$
$h = -19 \rightarrow 19$
$k = -11 \rightarrow 8$
$l = -21 \rightarrow 21$

*Refinement*

Refinement on $F^2$
$R(F) = 0.037$
$wR(F^2) = 0.084$
$S = 1.07$
2404 reflections
118 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0103P)^2 + 2.3695P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.93$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.99$ e Å$^{-3}$

**Table 2**
Selected geometric parameters (Å, °) for (III).

| | | | |
|---|---|---|---|
| I1—C3 | 2.094 (3) | O3—N2 | 1.215 (5) |
| O1—N1 | 1.225 (5) | N2—O4 | 1.213 (5) |
| C1—N1 | 1.470 (5) | N2—C5 | 1.473 (5) |
| N1—O2 | 1.207 (6) | | |
| | | | |
| C6—C1—N1 | 118.6 (3) | O1—N1—C1 | 117.1 (4) |
| C2—C1—N1 | 117.9 (3) | O4—N2—O3 | 124.1 (4) |
| C4—C3—I1 | 120.3 (2) | O4—N2—C5 | 118.1 (4) |
| C2—C3—I1 | 118.4 (3) | O3—N2—C5 | 117.7 (4) |
| O2—N1—O1 | 125.1 (4) | C6—C5—N2 | 118.1 (3) |
| O2—N1—C1 | 117.8 (3) | C4—C5—N2 | 118.1 (3) |

For compound (II), the Friedel pairs were not merged, owing to the determination of the absolute structure by refining the Flack (1983) parameter. The number of Friedel pairs measured was 625. For both compounds, H atoms were treated as riding, with C—H distances of 0.94 Å.

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Siemens, 1996); program(s) used to refine structure: *SHELXTL*. For compound (II), molecular graphics: *SHELXTL*. For compound (III), molecular graphics: *SHELXTL* and *ORTEP*-3 (Farrugia, 1997). For both compounds, software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1017). Services for accessing these data are described at the back of the journal.

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