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Triclinic and orthorhombic polymorphs of 2-iodo-4-nitroaniline: interplay of hydrogen bonds, nitro···I interactions and aromatic π–π-stacking interactions

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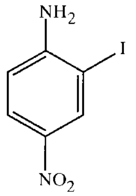
In the triclinic polymorph of 2-iodo-4-nitroaniline, $C_6H_5IN_2O_2$, space group $P\overline{1}$, the molecules are linked by paired N—H···O hydrogen bonds into $C(8)[R_2^2(6)]$ chains of rings. These chains are linked into sheets by nitro···I interactions, and the sheets are pairwise linked by aromatic π–π-stacking interactions. In the orthorhombic polymorph, space group *Pbca*, the molecules are linked by single N—H···O hydrogen bonds into spiral $C(8)$ chains; the chains are linked by nitro···O interactions into sheets, each of which is linked to its two immediate neighbours by aromatic π–π-stacking interactions, so producing a continuous three-dimensional structure.

Comment

Molecules of 4-nitroanilines generally act as double donors of hydrogen bonds and as double acceptors, such that each molecule is linked to four other molecules by N—H···O hydrogen bonds. Thus, for example, unsubstituted 4-nitroaniline itself [Cambridge Structural Database (CSD; Allen & Kennard, 1993) refcode NANILI02 (Tonogaki *et al.*, 1993)] forms sheets in the form of (4,4)-nets (Batten & Robson, 1998) built from a single type of $R_4^4(22)$ ring (Bernstein *et al.*, 1995). Similar (4,4)-nets, albeit containing successively larger rings, are found in the structures of the extended 4-nitroaniline analogues 4-$H_2NC_4H_4$–$(C{\equiv}C)_n$–$C_6H_4NO_2$-4′ (n = 0–3) [CSD refcodes KEFLEM (n = 0), KEFLOW (n = 1), KEFLUC (n = 2) and KEFMAJ (n = 3); Graham *et al.*, 1989)]. By contrast, 2-methyl-4-nitroaniline forms a continuous three-dimensional framework, in which each molecule is again linked to four other molecules (Ferguson *et al.*, 2001).

Aromatic nitro groups also form robust supramolecular synthons with iodo-aromatics, as for example in 4-iodoaniline (CSD refcode ZONYIK; Thalladi *et al.*, 1996) and 4-iodo-4′-nitrobiphenyl (CSD refcode RAYCID01; Masciocchi *et al.*, 1998), as well as in the adducts of *p*-dinitrobenzene with *p*-diiodobenzene (CSD refcode YESZEB; Allen *et al.*, 1994) and with 4-iodocinnamic acid (CSD refcode ZONYOQ; Thalladi *et al.*, 1996). In all of these species, the shortest I···O distances are very much less than the sum of the van der Waals radii (3.50 Å; Bondi, 1964), while the associated C—I···O angles lie in the range 150–170°.

As part of a continuing study of supramolecular aggregation in substituted nitroanilines (Wardell *et al.*, 2000; Cannon *et al.*, 2001; Ferguson *et al.*, 2001; Glidewell *et al.*, 2001), we have now investigated the interplay of N—H···O hydrogen bonding and nitro···I interactions in 2-iodo-4-nitroaniline ($C_6H_5IN_2O_2$), where we have obtained two polymorphs, a triclinic form, (I*a*), in space group $P\overline{1}$, and an orthorhombic form, (I*b*), in space group *Pbca*. Both forms have $Z' = 1$ and their crystal structures exhibit a combination of N—H···O hydrogen bonds, nitro···I interactions and aromatic π–π-stacking interactions.



(I)

In the triclinic polymorph, (I*a*), the planar molecules (Fig. 1*a*) are linked into chains by an uncommon synthon comprising pairs of N—H···O hydrogen bonds. The two N—H bonds in the molecule at (x, y, z) form hydrogen bonds (Table 1) with the two O atoms in the molecule at (x, $1 + y$, $-1 + z$), so producing by translation a $C(8)[R_2^2(6)]$ chain of rings (Bernstein *et al.*, 1995) running parallel to the $[01\overline{1}]$ direction (Fig. 2). The N—H···O hydrogen bonding in (I*a*) is thus wholly different from that normally found in 4-nitroanilines. In the $R_2^2(6)$ ring, the N—O···H angles are 111 and 110°, and the sum of the internal angles is 360° within experimental uncertainly, so that this ring is planar. The chain of rings can thus be regarded as a continuous sequence of planar hexagonal rings in which the covalently bonded aryl rings alternate with hydrogen-bonded rings of almost the same size. In this connection, Desiraju (1995) has already drawn attention to the importance of ring size and shape, as opposed to ring composition, as an important factor in crystal engineering and molecular recognition. There are two $C(8)[R_2^2(6)]$ chains of rings passing through each unit cell, related by the centres of inversion and thus running antiparallel to one another. A combination of nitro···I interactions and aromatic π–π-stacking interactions links these chains into sheets and it is convenient to consider these interactions in turn.

There is a very short intermolecular I···O contact [I···O2^{i} 3.266 (5) Å, C—I···O2^{i} 154.5 (2)° and I···O2^{i}—N4^{i} 154.1 (4)°; symmetry code (i) $-1 + x$, $1 + y$, $-1 + z$], which serves to link parallel chains of the same polarity into two-dimensional sheets parallel to (011), in which the $R_2^2(6)$ rings described above alternate with larger rings (Fig. 2). If the graph-set notation generally employed for hydrogen-bonded motifs is extended to other directed but non-covalent interactions (Starbuck *et al.*, 1999), these larger rings may be described as being of $R_4^4(20)$ type. The shortest intermolecular I$\cdots$O distance involving the other O atom [I$\cdots$O1$^{\rm ii}$ 3.494 (5) Å; symmetry code: (ii) $-x$, $2-y$, $1-z$] is not significantly shorter than the sum of the van der Waals radii, and is thus not regarded as structurally significant. Two (011) sheets pass through each unit cell, and these sheets are themselves linked into pairs by aromatic π–π-stacking interactions. Molecules at (x, y, z) and ($1-x$, $2-y$, $1-z$) are linked by a π–π interaction; the interplanar spacing is 3.451 (3) Å and the centroid offset is 0.747 (3) Å.

In the orthorhombic polymorph (I*b*), (Fig. 1*b*), the dihedral angle between the aryl ring and the C—NO$_2$ plane is 11.1 (5)°. The hydrogen bonding differs from that in (I*a*) in that the molecules of (I*b*) act as single donors and as single acceptors of hydrogen bonds, so that simple *C*(8) chains are formed rather than chains of rings, as in (I*a*), or the sheets commonly found in 4-nitroanilines and their analogues. Amino N1 at (x, y, z) acts as hydrogen-bond donor to O1 at ($1-x$, $-\frac{1}{2}+y$,

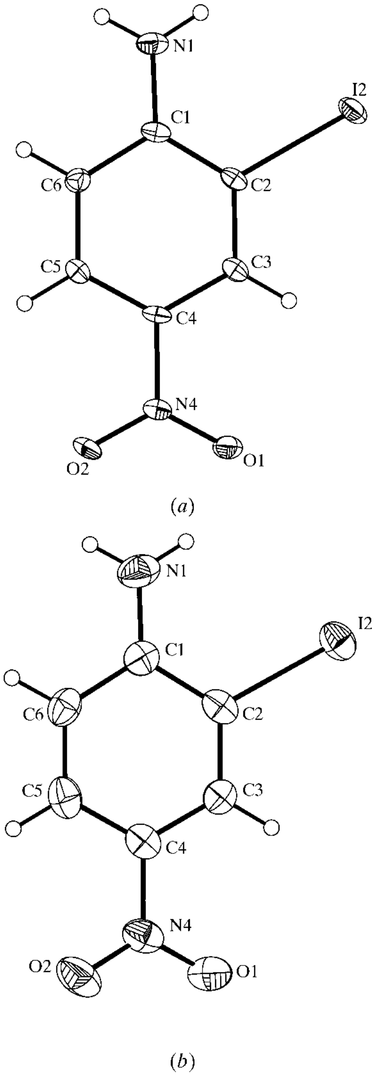


Figure 1
The asymmetric unit of 2-iodo-4-nitroaniline, showing the atom-labelling scheme (*a*) in the triclinic polymorph (I*a*) and (*b*) in the orthorhombic polymorph (I*b*). Displacement ellipsoids are drawn at the 30% probability level.

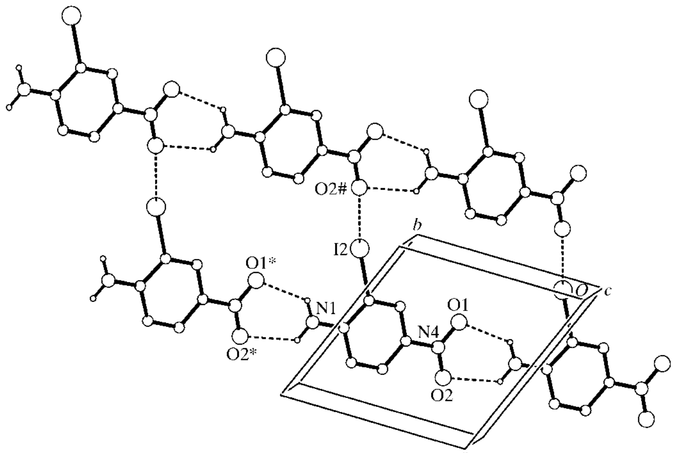


Figure 2
Part of the crystal structure of the triclinic polymorph, (I*a*), showing $C(8)[R_2^2(6)]$ chains of rings linked by nitro$\cdots$I interactions into a (011) sheet. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions (x, $1+y$, $-1+z$) and ($-1+x$, $1+y$, $-1+z$), respectively.

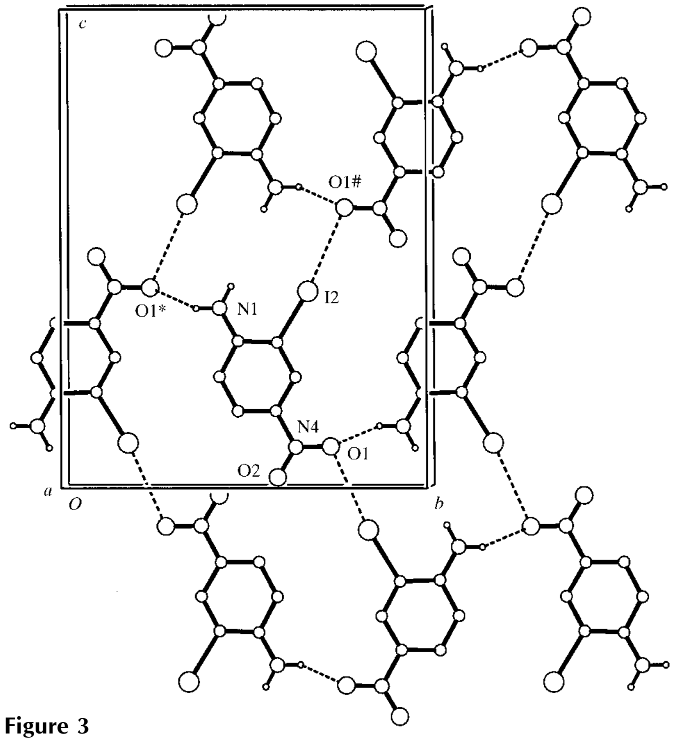


Figure 3
Part of the crystal structure of the orthorhombic polymorph, (I*b*), showing the linking of *C*(8) spiral chains parallel to [010] into a (100) sheet of $R_4^2(12)$ and $R_4^4(28)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions ($1-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$) and (x, $\frac{3}{2}-y$, $\frac{1}{2}+z$), respectively.

$\frac{1}{2} - z$), while N1 at ($1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$) in turn acts as donor to O1 at ($x, -1 + y, z$); hence a $C(8)$ spiral is generated around the 2_1 screw axis along ($\frac{1}{2}, y, \frac{1}{4}$) (Fig. 3). Four such chains run through each unit cell, one around each of the 2_1 axes parallel to [010]; two lie in the domain $0.30 < x < 0.70$, and the other two lie in the domain $0.80 < x < 1.20$.

Within each of these domains, the chains are linked into sheets by nitro$\cdots$I interactions [I$\cdots$O1^{iii} 3.153 (7) Å, C—I$\cdots$O1^{iii} 171.5 (3)° and I$\cdots$O1^{iii}—N4^{iii} 112.6 (5)°; symmetry code: (iii) $x, \frac{3}{2} - y, \frac{1}{2} + z$] and propagation of this interaction generates sheets parallel to (100) built from alternating $R_4^2(12)$ and $R_4^4(28)$ rings (Fig. 3). As in the triclinic polymorph, only one O atom forms I$\cdots$O contacts shorter than the sum of the van der Waals radii. There are two (100) sheets passing through each unit cell, and each sheet is linked to its two immediate neighbours by aromatic π–π-stacking interactions (Fig. 4), so generating a continuous three-dimensional structure. The aryl ring at (x, y, z) is a component of the (100) sheet in the domain $0.30 < x < 0.70$; this ring forms π–π interactions with the rings at ($\frac{1}{2} + x, y, \frac{1}{2} - z$) and ($-\frac{1}{2} + x, y, \frac{1}{2} - z$), which are components of the sheets in the domains $0.80 < x < 1.20$ and $-0.20 < x < 0.20$, respectively. These rings are not all parallel by symmetry, but the interplanar angles are only *ca* 2.0°, with interplanar spacings of *ca* 3.56 Å and centroid offsets of *ca* 1.21 Å.

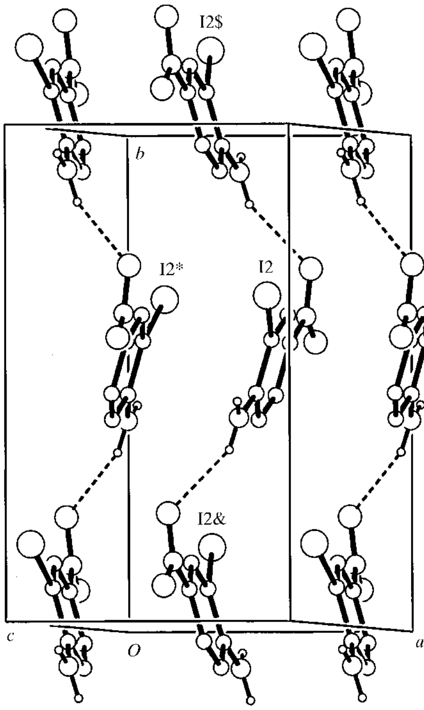


Figure 4
Part of the crystal structure of (I*b*) showing the linking of (100) sheets by means of aromatic π–π-stacking interactions. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions ($-\frac{1}{2} + x, y, \frac{1}{2} - z$), ($\frac{1}{2} + x, y, \frac{1}{2} - z$), ($1 - x, \frac{1}{2} + y, \frac{1}{2} - z$) and ($1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$), respectively.

The C—I distances in (I*a*) and (I*b*) are 2.098 (5) and 2.087 (8) Å, respectively; the other bond lengths and angles show no unexpected features.

Experimental

A solution of 4-nitroaniline (20 mmol) in methanol (40 ml) was added rapidly to an aqueous solution of K[ICl$_2$] (60 ml, 0.67 mol dm^{-3}) at room temperature (Larsen *et al.*, 1956; Garden *et al.*, 2001). The reaction mixture was stirred at room temperature for 2 h, and then filtered to remove the product. The product was washed with water and allowed to dry in air. After recrystallization from ethanol, the product had a melting point of 385–387 K. NMR (CDCl$_3$): δ_H 4.84 (2H, *br s*, NH$_2$), 6.66 (1H, *d*, J = 9.2 Hz, H-6), 8.00 (1H, *dd*, J = 2.4, 8.9 Hz, H-5), 8.51 p.p.m. (*d*, J = 2.4 Hz, H-3); δ_C 81.6 (C-2), 113.3 (C-6), 126.7 (C-5), 136.5 (C-3), 140.2 (C-4), 153.4 p.p.m. (C-1). Crystals suitable for single-crystal X-ray diffraction were obtained from an ethanol solution. Samples of the two polymorphs were isolated manually at ambient temperature.

Compound (I*a*)

Crystal data

$C_6H_5IN_2O_2$
M_r = 264.02
Triclinic, $P\overline{1}$
a = 7.1647 (4) Å
b = 7.9572 (4) Å
c = 8.0489 (5) Å
α = 67.905 (3)°
β = 86.956 (3)°
γ = 65.744 (2)°
V = 384.84 (4) Å^3
Z = 2
D_x = 2.278 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1728 reflections
θ = 3.1–27.5°
μ = 4.11 mm^{-1}
T = 150 (2) K
Needle, yellow
0.28 × 0.08 × 0.03 mm

Data collection

KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.393, T_{max} = 0.887
4602 measured reflections
1728 independent reflections
1556 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 27.5°
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.120
S = 1.09
1728 reflections
100 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2 + 1.2313P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.77 e Å^{-3} (0.96 Å from I2)
$\Delta\rho_{min}$ = −2.14 e Å^{-3} (0.83 Å from I2)

Table 1
Hydrogen-bonding geometry (Å, °) for (I*a*).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H11$\cdots$O1^i	0.88	2.35	2.994 (7)	130
N1—H12$\cdots$O2^i	0.88	2.40	3.000 (8)	126

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

Compound (I*b*)

Crystal data

$C_6H_5IN_2O_2$
M_r = 264.02
Orthorhombic, *Pbca*
a = 7.4215 (5) Å
b = 12.6755 (9) Å
c = 16.4638 (11) Å
V = 1548.77 (18) Å^3
Z = 8
D_x = 2.265 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2339 reflections
θ = 2.5–31.1°
μ = 4.08 mm^{-1}
T = 296 (2) K
Plate, yellow
0.20 × 0.20 × 0.03 mm

Data collection

Bruker SMART 1000 CCD-detector diffractometer
φ–ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{\min} = 0.495$, $T_{\max} = 0.887$
12391 measured reflections
2339 independent reflections
1109 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.089$
$\theta_{\max} = 31.1°$
$h = -10 \rightarrow 10$
$k = -17 \rightarrow 14$
$l = -22 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.180$
$S = 0.96$
2339 reflections
100 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0943P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 2.20$ e Å^{-3} (0.91 Å from I2)
$\Delta\rho_{\min} = -1.21$ e Å^{-3} (0.90 Å from I2)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H11$\cdots$O1$^{\rm i}$	0.86	2.31	3.085 (11)	150

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

Polymorph (I*a*) is triclinic; space group $P\overline{1}$ was chosen and confirmed by the successful structure solution and refinement. Polymorph (I*b*) is orthorhombic; space group *Pbca* was uniquely assigned from the systematic absences. All H atoms were treated as riding atoms with N—H distances of 0.86 or 0.88 Å and C—H distances of 0.93 or 0.95 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997) for compound (I*a*), *SMART* (Bruker, 1999) for compound (I*b*); cell refinement and data reduction: *DENZO–SMN* (Otwinowski & Minor, 1997) for compound (I*a*), *SAINT* (Bruker, 1999) for compound (I*b*). For both 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, 2001); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

X-ray data for (I*a*) were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, using a Nonius KappaCCD diffractometer, and for (I*b*) at the University of Aberdeen using a Bruker SMART CCD diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1480). Services for accessing these data are described at the back of the journal.

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