

## 4-Iodo-2-methyl-5-nitroaniline exhibits neither strong hydrogen bonding nor intermolecular I...nitro interactions

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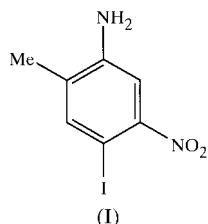
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In the title compound, C<sub>7</sub>H<sub>7</sub>IN<sub>2</sub>O<sub>2</sub>, the O atoms of the nitro group are disordered over two sets of sites and there is evidence that the intramolecular I...nitro interaction is repulsive. In the crystal structure, there are neither strong hydrogen bonds, nor intermolecular I...nitro interactions, nor aromatic  $\pi$ - $\pi$ -stacking interactions.

### Comment

In nitroanilines, the supramolecular structure is generally dominated by the effects of N—H...O hydrogen bonds (Ploug-Sørensen & Andersen, 1986; Tonogaki *et al.*, 1993; Ellena *et al.*, 1999; Cannon *et al.*, 2001; Ferguson *et al.*, 2001). When an iodo substituent is introduced, as in 2-iodo-4-nitroaniline, which crystallizes in two polymorphic forms (McWilliam *et al.*, 2001), the supramolecular structures of both polymorphs are determined by the interplay of N—H...O hydrogen bonds, I...nitro interactions and aromatic  $\pi$ - $\pi$ -stacking interactions. Pursuing this theme, we have now investigated the analogous compound 4-iodo-2-methyl-5-nitroaniline, (I), whose structure proves to consist of essentially isolated molecules.



In molecules of (I) (Fig. 1), the nitro group O atoms are disordered over two pairs of sites, *i.e.* O1A/O2A and

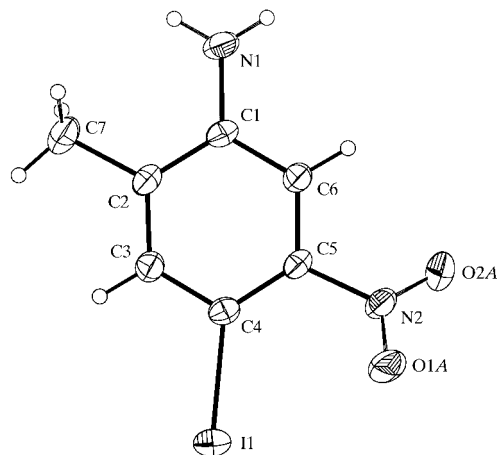
O1B/O2B, with equal occupancies. For both orientations, the nitro group is twisted significantly out of the plane of the adjacent arene ring (Table 1), suggesting that the intramolecular I...nitro interaction may be repulsive. Consistent with this, the exocyclic bond angles at C4 and C5 (Fig. 1) differ significantly from 120°; in particular, the angles I1—C4—C3 and N2—C5—C6 are both less than 116°, consistent with I...nitro repulsion. The N2—C5—C4 angle is smaller than I1—C4—C5, but these values are to some extent constrained by the internal C—C—C angles, whose values, in turn, are controlled by the electronic properties of the *ipso* substituents (Domenicano & Murray-Rust, 1979). The C—NH<sub>2</sub> and C—NO<sub>2</sub> distances in (I) (Table 1) are both very much longer than the corresponding distances in 2-iodo-4-nitroaniline (McWilliam *et al.*, 2001), but they are in fact fairly typical of those in simple 3-nitroanilines (Ploug-Sørensen & Andersen, 1986; Ellena *et al.*, 1999; Cannon *et al.*, 2001); the C—I distance in (I) is unexceptional and there is no evidence from the bond distances as a whole for any electronic delocalization between substituents.

Examples of arene structures with an iodo substituent adjacent to nitro groups are uncommon. However, in 2,4,6-trinitroiodobenzene [Cambridge Structural Database (CSD; Allen & Kennard, 1993) refcode ITNOBE01 (Weiss *et al.*, 1999)], where the molecules lie across twofold rotation axes in space group *P*<sub>4</sub><sub>3</sub><sub>2</sub><sub>1</sub><sub>2</sub>, the two exocyclic angles for the 2-nitro group, *viz.* 119.8 (6)° adjacent to I and 116.6 (6)° remote from I, are consistent with I...O<sub>2</sub>N repulsion. Moreover, while the 4-nitro group is almost coplanar with the arene ring, the 2-nitro group is twisted out of the ring plane by *ca* 75°.

Intermolecular I...nitro interactions are generally regarded as being attractive, and indeed, they are major determinants of the supramolecular aggregation in a number of systems (Allen *et al.*, 1994; Thalladi *et al.*, 1996; Masciocchi *et al.*, 1998; Ranganathan & Pedireddi, 1998; McWilliam *et al.*, 2001). In such cases, the C—I...O angles for three-centre I...O<sub>2</sub>N interactions are typically in the range 145–165°, while in two-centre I...O(nitro) interactions, the C—I...O angles often exceed 170°. By contrast, the intramolecular I...O interactions in (I) have C—I...O angles of 63.3 (2) (to O1A) and 65.1 (2)° (to O1B); likewise in ITNOBE01 (Weiss *et al.*, 1999), where the intermolecular C—I...O angle is 161.1 (2)°, the corresponding intramolecular angle is only 61.4 (2)°. Both the I and nitro N atoms are positively polarized, while the nitro O atom is negatively polarized. In intermolecular I...nitro interactions, the difference between the I...N and I...O distances usually exceeds 1.0 Å, allowing the attractive I...O interaction to dominate, while in (I), this difference is no more than 0.5 Å even for the shortest I...O distance, with no O atom interposed between I and N.

The most surprising aspect of the structure of (I) is the absence of significant intermolecular interactions. The shortest intermolecular N—H...O contact (Table 2) has H...O and N...O distances of 2.51 and 3.325 (9) Å, respectively, both far too long for this contact to be regarded as a significant N—H...O hydrogen bond; there are no intermolecular I...O contacts less than 3.60 Å and there are no aromatic  $\pi$ - $\pi$ -

stacking interactions. The crystal structure of (I) thus differs in all respects from those of the polymorphs of 2-iodo-4-nitroaniline (McWilliam *et al.*, 2001). Contrasts of this kind provide continuing challenges to attempts at the prediction from first principles of the crystal structures of simple molecular compounds (Lommerse *et al.*, 2000).



**Figure 1**  
The molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For clarity, only one orientation of the nitro group is shown.

## Experimental

To an aqueous solution of  $K[ICl_2]$  (60 ml,  $0.67 \text{ mol dm}^{-3}$ ) (Larsen *et al.*, 1956; Garden *et al.*, 2001) was added rapidly a warm solution of 2-methyl-5-nitroaniline (3.00 g, 20 mmol) in methanol (40 ml). The reaction mixture was stirred at room temperature for 2 h. The solid product was collected, washed with water and air dried. Preparative thin-layer chromatography on silica using  $CHCl_3$  as eluent yielded two components, namely 2,4-diiodo-6-methyl-3-nitroaniline (more mobile) and 4-iodo-2-methyl-5-nitroaniline, (I) (less mobile), in a molar ratio of 1:1.2. Crystals of (I) (m.p. 377–379 K) suitable for single-crystal X-ray diffraction were grown from a solution in ethanol. NMR (p.p.m.):  $\delta_H$  2.12 (s, 3H,  $CH_3$ ), 3.88 (s, br, 2H,  $NH_2$ ), 7.22 (s, 1H, aromatic), 7.60 (s, 1H, aromatic);  $\delta_C$  16.9 ( $CH_3$ ), 70.7, 111.2, 129.0, 142.6, 145.4 and 150.8 (aromatic).

### Crystal data

$C_7H_7IN_2O_2$	$D_x = 2.073 \text{ Mg m}^{-3}$
$M_r = 278.05$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2552 reflections
$a = 13.5264 (7) \text{ \AA}$	$\theta = 1.7\text{--}30.8^\circ$
$b = 4.2773 (2) \text{ \AA}$	$\mu = 3.56 \text{ mm}^{-1}$
$c = 16.3725 (8) \text{ \AA}$	$T = 150 (2) \text{ K}$
$\beta = 109.835 (1)^\circ$	Needle, yellow
$V = 891.06 (8) \text{ \AA}^3$	$0.30 \times 0.05 \times 0.05 \text{ mm}$
$Z = 4$	

### Data collection

Nonius KappaCCD diffractometer	2552 independent reflections
$\varphi$ scans, and $\omega$ scans with $\kappa$ offsets	2243 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan ( <i>DENZO-SMN</i> ; Otwinowski & Minor, 1997)	$R_{int} = 0.021$
$T_{min} = 0.415$ , $T_{max} = 0.842$	$\theta_{max} = 30.8^\circ$
7521 measured reflections	$h = -17 \rightarrow 19$
	$k = -6 \rightarrow 6$
	$l = -23 \rightarrow 11$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 1.2042P]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.086$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.06$	$\Delta\rho_{max} = 1.65 \text{ e \AA}^{-3}$
2552 reflections	$\Delta\rho_{min} = -0.88 \text{ e \AA}^{-3}$
129 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

C1—C2	1.405 (5)	C4—I1	2.095 (3)
C2—C3	1.382 (5)	C1—N1	1.388 (4)
C3—C4	1.387 (4)	C5—N2	1.472 (4)
C4—C5	1.396 (4)	N2—O1A	1.202 (9)
C5—C6	1.382 (5)	N2—O1B	1.208 (8)
C6—C1	1.401 (4)	N2—O2A	1.250 (8)
C2—C7	1.510 (4)	N2—O2B	1.217 (8)
I1—C4—C3	115.9 (2)	N2—C5—C6	115.8 (3)
I1—C4—C5	127.3 (2)	N2—C5—C4	122.4 (3)
C4—C5—N2—O1A	−32.5 (7)	C4—C5—N2—O1B	11.2 (8)
C4—C5—N2—O2A	142.2 (5)	C4—C5—N2—O2B	−162.1 (6)

**Table 2**

Short intermolecular contacts ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H12 \cdots O1B^i$	0.86	2.51	3.325 (9)	158
$N1-H12 \cdots O1A^i$	0.86	2.65	3.406 (9)	148
$N1-H11 \cdots N1^ii$	0.86	2.38	3.174 (5)	153

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

Compound (I) crystallized in the monoclinic system; space group  $P2_1/n$  was uniquely assigned from the systematic absences. H atoms were treated as riding, with C—H distances of 0.93  $\text{\AA}$  for aromatic H atoms and 0.96  $\text{\AA}$  for methyl H atoms, and an N—H distance of 0.86  $\text{\AA}$ .

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); 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: GG1080). Services for accessing these data are described at the back of the journal.

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