

2-Iodo-6-methoxy-4-nitroaniline: tripartite ribbons built from N—H...O hydrogen bonds and iodo–nitro inter- actions are π -stacked into sheets

Simon J. Garden,^a Christopher Glidewell,^{b*} John N. Low,^c
Janet M. S. Skakle^c and James L. Wardell^d

^aInstituto de Química, Departamento de Química Orgânica, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil, ^bSchool of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland, ^cDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and ^dInstituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil
Correspondence e-mail: cg@st-andrews.ac.uk

Received 6 January 2005

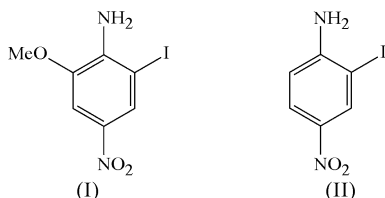
Accepted 7 January 2005

Online 12 February 2005

Molecules of the title compound, C₇H₇IN₂O₃, are linked by pairs of N—H...O hydrogen bonds into C(8)C(8)[R₂²(6)] chains of rings, and antiparallel pairs of such chains are linked by a two-centre iodo–nitro interaction into tripartite ribbons. A single aromatic π – π stacking interaction links the ribbons into sheets.

Comment

We report here the molecular and supramolecular structure of the title compound, (I) (Fig. 1), which we compare with the simpler analogue 2-iodo-4-nitroaniline, (II) (McWilliam *et al.*, 2001).



While the bond distances in (I) are generally similar to those found in both the triclinic and orthorhombic polymorphs of (II), denoted herein as (IIa) and (IIb), respectively, the molecular aggregation in (I) and (IIa) shows both similarities and differences. In compound (I), the molecules are linked into chains by pairs of N—H...O hydrogen bonds (Table 1). Amino atom N1 in the molecule at (x, y, z) acts as hydrogen-bond donor, *via* atoms H11 and H12, respectively, to the nitro atoms O1 and O2 in the molecule at $(x - 1, y, z - 1)$, so generating by translation a C(8)C(8)[R₂²(6)] chain of rings (Bernstein *et al.*, 1995) running parallel to the [101] direction (Fig. 2). Within the R₂²(6) rings, the O...H angles are both 111°

and the sum of the internal angles is 716°, so that this ring is effectively 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.

Two such chains, related to one another by inversion and hence antiparallel, pass through each unit cell, and antiparallel pairs of chains are linked into a tripartite ribbon by a single two-centre iodo–nitro interaction [I2...O1ⁱ = 3.385 (3) Å, C2—I2...O1ⁱ = 154.2 (2)°; symmetry code: (i) 1 - x, 2 - y, 2 - z]. In the central strip of this ribbon, centrosymmetric R₂²(12) rings (Starbuck *et al.*, 1999), built up only from I...O interactions, alternate with centrosymmetric R₂²(12) rings, built up from both I...O interactions and N—H...O hydrogen bonds (Fig. 2). In addition, while the iodo substituents are all located in the interior of the ribbon, the methoxy substituents all lie on the outer edges of the ribbon.

These ribbons along [101] are linked into sheets by a single aromatic π – π stacking interaction. The aryl rings in the molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ are strictly parallel, with an interplanar spacing of 3.321 (2) Å; the ring-centroid separation is 3.497 (2) Å, with a corresponding offset of 1.095 (2) Å. Propagation of this interaction by inversion then links each [101] ribbon to the two adjacent ribbons along the [011] direction, so linking the ribbons into ($\bar{1}11$) sheets (Fig. 3).

The formation of the ribbon in (I) (Fig. 2) may be contrasted with the formation of sheets in (IIa). The very same hydrogen-bonded motif occurs in (IIa), generating a chain of rings, again by translation, although along the [011] direction. However, the iodo–nitro interaction in (IIa), the dimensions of which are very similar to that in (I), links parallel hydrogen-bonded chains related by translation, so forming an (011) sheet containing just a single type of R₄⁴(20) ring between the hydrogen-bonded chains. The (011) sheets in (IIa) are linked

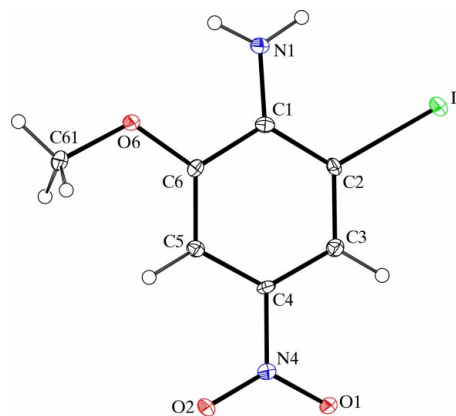


Figure 1

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.

into pairs by a centrosymmetric π - π stacking interaction. The different modes of the I...O linking of the hydrogen-bonded chains, by inversion in (I) and by translation in (IIa), is most plausibly ascribed to the presence of the methoxy substituent in (I). The continuous linking of hydrogen-bonded chains by translation is prevented in (I) simply by the steric bulk of the methoxy substituent, whereas linking in pairs by inversion is readily accomplished when the methoxy substituents are located on the outer edges of the ribbon.

By contrast, in the orthorhombic polymorph of (II), denoted here as (IIb), a single N—H...O hydrogen bond and a two-centre iodo–nitro interaction suffice to generate sheets of alternating $R_4^2(12)$ and $R_4^1(28)$ rings, which are themselves

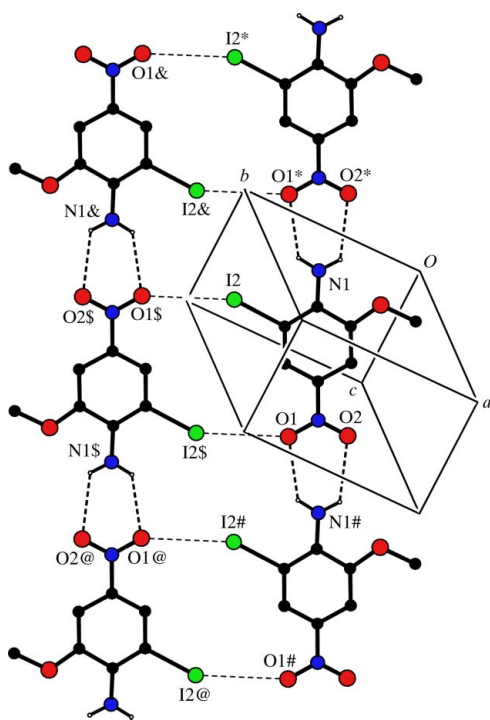


Figure 2 Part of the crystal structure of (I), showing the formation of a ribbon along [101]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign (\$), ampersand (&) or 'at' sign (@) are at the symmetry positions $(x - 1, y, z - 1)$, $(1 + x, y, 1 + z)$, $(1 - x, 2 - y, 2 - z)$, $(-x, 2 - y, 1 - z)$ and $(2 - x, 2 - y, 3 - z)$, respectively.

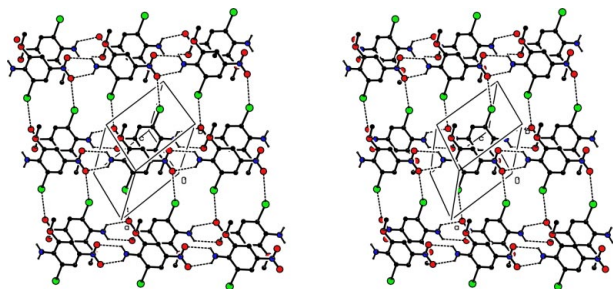


Figure 3 A stereoview of part of the crystal structure of (I), showing the π -stacking of the [101] ribbons to form a $(\bar{1}11)$ sheet. For the sake of clarity, H atoms bonded to C atoms have been omitted.

linked into a three-dimensional framework structure by means of a single π - π stacking interaction (McWilliam *et al.*, 2001).

While the polymorphs (IIa) and (IIb) crystallize concomitantly from ethanol solution (McWilliam *et al.*, 2001), we note a recent report that the thermodynamically less stable orthorhombic polymorph (IIb) can be selectively crystallized from ethanol in the presence of self-assembled monolayers of substituted mercaptobiphenyls, acting as specific templating agents (Hiremath *et al.*, 2004).

Experimental

2-Methoxy-4-nitroaniline (1.68 g, 10 mmol) was dissolved in boiling methanol (25 ml). An aqueous solution of $K[ICl_2]$ (10 ml, 2 M) (Garden *et al.*, 2001) was slowly added to the boiling solution, after which the solution was maintained under reflux for a further 20 min. The reaction mixture was cooled and diluted with water (50 ml). The resulting solid was collected by filtration, washed with water and air-dried (2.88 g, 99% yield, m.p. 427–431 K). Recrystallization from aqueous ethanol gave thin yellow plates (m.p. 430–431 K). Crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in $CHCl_3$. 1H NMR ($CDCl_3$): δ 3.96 (3H, s, OMe), 5.02 (2H, broad s, NH_2), 7.62 (1H, d, $J = 2.4$ Hz) and 8.23 (1H, d, $J = 2.4$ Hz) (aromatic); ^{13}C NMR ($CDCl_3$): δ 56.6, 78.4, 105.5, 128.2, 139.1, 144.1 and 144.5.

Crystal data

$C_7H_7IN_2O_3$
 $M_r = 294.05$
 Triclinic, $P\bar{1}$
 $a = 8.0671$ (3) Å
 $b = 8.0739$ (4) Å
 $c = 8.6212$ (5) Å
 $\alpha = 112.616$ (2)°
 $\beta = 115.060$ (3)°
 $\gamma = 93.810$ (3)°
 $V = 451.55$ (4) Å³

$Z = 2$
 $D_x = 2.163$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2061 reflections
 $\theta = 3.7$ – 27.5 °
 $\mu = 3.52$ mm⁻¹
 $T = 120$ (2) K
 Plate, yellow
 0.10 × 0.06 × 0.03 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{min} = 0.720$, $T_{max} = 0.902$
 8665 measured reflections

2061 independent reflections
 1845 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.039$
 $\theta_{max} = 27.5$ °
 $h = -9 \rightarrow 10$
 $k = -10 \rightarrow 10$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.053$
 $S = 1.00$
 2061 reflections
 119 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0279P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 1.27$ e Å⁻³
 $\Delta\rho_{min} = -0.77$ e Å⁻³

Table 1 Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H11...O1 ⁱ	0.88	2.36	3.007 (3)	130
N1—H12...O2 ⁱ	0.88	2.45	3.028 (3)	124

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

Crystals of (I) are triclinic; space group $P\bar{1}$ was selected and confirmed by the structure analysis. All H atoms were located from difference maps and then treated as riding atoms, with C—H = 0.95

(aromatic) or 0.98 Å (methyl) and N–H = 0.88 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C},\text{N})$, or $1.5U_{\text{eq}}(\text{C})$ for the methyl group.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1806). Services for accessing these data are described at the back of the journal.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.
- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- Garden, S. J., Torres, J. C., Souza Melo, S. C., Lima, A. S., Pinto, A. C. & Lima, E. L. S. (2001). *Tetrahedron Lett.* **42**, 2089–2092.
- Hiremath, R., Varney, S. W. & Swift, J. A. (2004). *Chem. Commun.* pp. 2676–2677.
- Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
- McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
- McWilliam, S. A., Skakle, J. M. S., Low, J. N., Wardell, J. L., Garden, S. J., Pinto, A. C., Torres, J. C. & Glidewell, C. (2001). *Acta Cryst.* **C57**, 942–945.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Starbuck, J., Norman, N. C. & Orpen, A. G. (1999). *New J. Chem.* **23**, 969–972.