Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

4-Iodo-*N*-(2-nitrophenylsulfanyl)-aniline: π-stacked sheets generated by a combination of N—H$\cdots$O and C—H$\cdots$O hydrogen bonds

Christopher Glidewell,[a]* John N. Low,[b] Janet M. S. Skakle[b] and James L. Wardell[c]

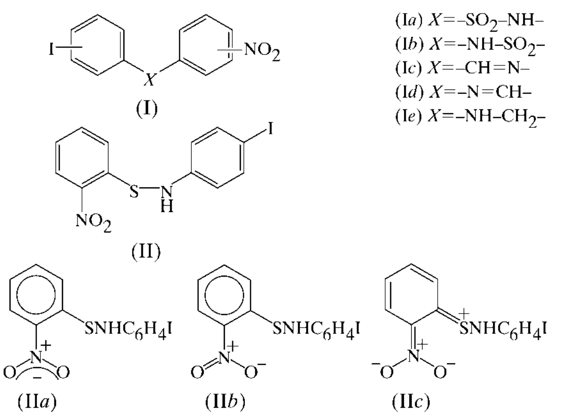
[a]School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [c]Instituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil
Correspondence e-mail: cg@st-andrews.ac.uk

Received 6 January 2003
Accepted 7 January 2003
Online 11 February 2003

Molecules of the title compound, $C_{12}H_9IN_2O_2S$, are linked by one N—H$\cdots$O hydrogen bond [H$\cdots$O = 2.16 Å, N$\cdots$O = 2.935 (4) Å and N—H$\cdots$O 147°] and two C—H$\cdots$O hydrogen bonds [H$\cdots$O both 2.49 Å, C$\cdots$O = 3.231 (5) and 3.220 (5) Å, and C—H$\cdots$O = 135 and 134°] into sheets which themselves are weakly linked by an aromatic π–π-stacking interaction between iodinated rings in centrosymmetrically related molecules. There are no iodo–nitro interactions.

Comment

As part of a general study of the interplay of hydrogen bonds, iodo–nitro interactions and aromatic π–π-stacking interactions in aromatic systems containing both iodo and nitro substituents, we have recently reported the molecular and supramolecular structures of a range of diaryl species (I) (see *Scheme*) containing a variety of spacer units *X*, *viz*. arenesulfonamides (I*a*) and (I*b*) (Kelly *et al.*, 2002), Schiff base imines (I*c*) (Wardell *et al.*, 2002) and (I*d*) (Glidewell, Howie *et al.*, 2002), and two isomeric benzylanilines (I*e*) (Glidewell, Low *et al.*, 2002). We report here the structure of an analogous compound, 4-iodo-*N*-(2-nitrophenylsulfanyl)aniline, (II), containing the –NH–S– linker unit.



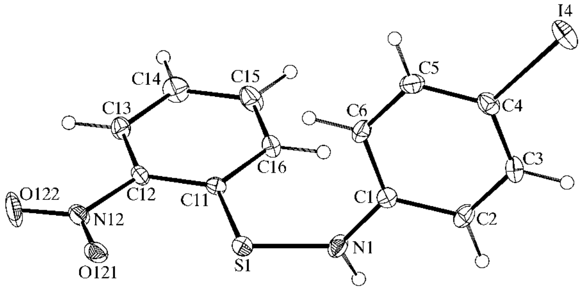


Figure 1
The molecule of (II), showing the atom-labelling scheme and displacement ellipsoids at the 30% probability level.

The conformation of compound (II) (Fig. 1) is dominated by the C1—N1—S1—C11 torsion angle (Table 1), which in turn is determined primarily by the nearly orthogonal lone-pair orbitals on atoms N1 and S1; this conformation minimizes the overlap and resonance integrals between the two occupied orbitals in question. By contrast, the C1–C6 and C11–C16 rings show only small twists away from the S1/N1/C1 and N1/S1/C11 planes, respectively, while the nitro group likewise shows only a small twist away from the C11–C16 plane; the dihedral angle between the C12-nitro and C11–C16 planes is only 5.5 (2)°.

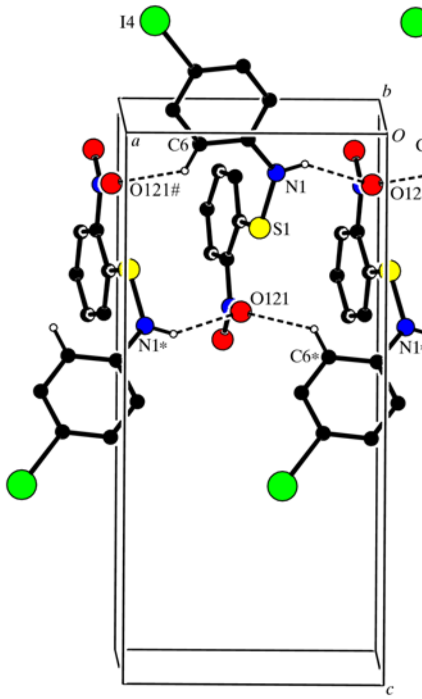


Figure 2
Part of the crystal structure of (II), showing the formation of a chain of edge-fused $R_2^2(16)$ rings along [100]. For the sake of clarity, H atoms not involved in the hydrogen-bonding motifs shown have been omitted. Atoms marked with an asterisk (*), hash (#) or ampersand (&) are at the symmetry positions $(-\frac{1}{2}+x, y, \frac{1}{2}-z)$, $(\frac{1}{2}-x, y, \frac{1}{2}-z)$ and $(-1+x, y, z)$, respectively.

DOI: 10.1107/S0108270103000775

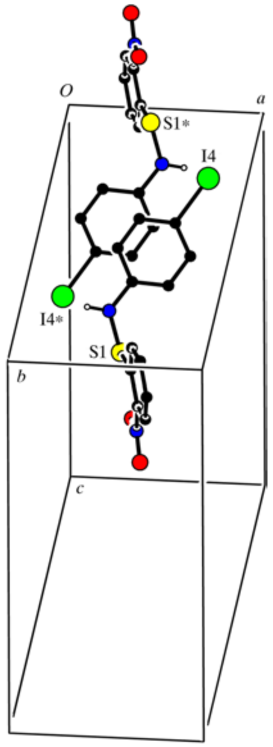


Figure 3
Part of the crystal structure of (II), showing the π–π-stacking interaction. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, -z)$.

The bond distances N1—C1 and N1—S1 are respectively long and short for their types (Allen *et al.*, 1987), and while C12—N12 is short for its type, the N—O bonds are both long. There is evidence of some quinonoid bond fixation in the nitrated C11–C16 aryl ring, and we note that N12—O121 is somewhat longer than N12—O122. Taken together, these observations suggest that forms (II*a*)–(II*c*) are all significant contributors to the overall molecular–electronic structure.

Consistent with form (II*c*), the internal C—C—C bond angles at atoms C11 and C12 show marked deviations from a value of 120° (Table 1), in a sense indicative of the electron-donor action of the –S—NHAr substituent (Ar is aryl) and the electron-acceptor behaviour of the nitro group (Domenicano & Murray-Rust, 1979); the exocyclic angles at atom C11 are suggestive of a repulsive non-bonded interaction between S1 and O121.

The supramolecular aggregation of (II) is dominated by N—H···O and C—H···O hydrogen bonds, augmented by weak aromatic π–π-stacking interactions. It is perhaps surprising that there are no iodo–nitro interactions; nor are there any C—H···π(arene) interactions. The principal direction-specific intermolecular interaction is the N—H···O hydrogen bond (Table 2). The amino atom N1 in the molecule at (x, y, z) acts as donor to nitro atom O121 in the molecule at $(-\frac{1}{2} + x, y, \frac{1}{2} - z)$, so producing a $C(7)$ chain running parallel to the [100] direction and generated by the *a*-glide plane at $z = \frac{1}{4}$. The action of this hydrogen bond is reinforced by that of a C—H···O hydrogen bond; C6 at (x, y, z) acts as donor to O121 at $(\frac{1}{2} + x, y, \frac{1}{2} - z)$, producing a $C(9)$ chain and generated by the same *a*-glide plane. The combination of these two chains generates a chain of edge-fused $R_2^2(16)$ rings (Fig. 2).

Four of these chains pass through each unit cell and they are linked into a three-dimensional continuum by a combination of a further C—H···O hydrogen bond and a π–π-stacking interaction. Atom C16 in the molecule at (x, y, z) acts as hydrogen-bond donor to O122 in the molecule at $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$, so producing a $C(6)$ chain running parallel to [001] and generated by the *c*-glide plane at $y = \frac{3}{4}$. In this manner, the [100] chains are linked into (010) sheets, and there are two such sheets passing through each unit cell, one in the domain $\frac{1}{2} < y < 1$ and the other in the domain $0 < y < \frac{1}{2}$. Finally, the (010) sheets are weakly linked by a centrosymmetric π–π-stacking interaction; the iodinated C1–C6 rings in the molecules at (x, y, z) and $(1 - x, 1 - y, -z)$ are parallel, with an interplanar spacing of 3.341 (2) Å and a centroid–centroid separation of 3.800 (2) Å, corresponding to a centroid–centroid offset of 1.810 (2) Å (Fig. 3). These two molecules lie in the (010) sheets generated, respectively, by the *c*-glide planes at $y = \frac{3}{4}$ and $y = \frac{1}{4}$, and propagation of the interaction by the space group suffices to link together all of the (010) sheets.

Experimental

A sample of compound (II) was prepared by reaction of equimolar quantities of 2-nitrophenylsulfenyl chloride and 4-iodoaniline in dichloromethane solution, in the presence of an excess of triethylamine. Purification was by thin-layer chromatography and crystals of (II) suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in ethanol.

Crystal data

$C_{12}H_9IN_2O_2S$
$M_r = 372.18$
Orthorhombic, *Pbca*
$a = 7.4171$ (2) Å
$b = 22.1145$ (8) Å
$c = 15.7093$ (4) Å
$V = 2576.73$ (13) Å^3
$Z = 8$
$D_x = 1.919$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2928 reflections
$\theta = 3.6$–27.5°
$\mu = 2.64$ mm^{-1}
$T = 120$ (2) K
Plate, orange
0.35 × 0.20 × 0.08 mm

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.404 (5)	C11—C12	1.407 (5)
S1—N1	1.679 (3)	C12—C13	1.385 (6)
S1—C11	1.774 (4)	C13—C14	1.365 (5)
C12—N12	1.455 (5)	C14—C15	1.388 (5)
N12—O121	1.238 (4)	C15—C16	1.374 (6)
N12—O122	1.224 (4)	C16—C11	1.394 (5)
C1—N1—S1	124.9 (3)	S1—C11—C16	120.7 (3)
N1—S1—C11	101.5 (2)	C11—C12—C13	122.6 (3)
C12—C11—C16	115.8 (4)	C11—C12—N12	119.5 (4)
S1—C11—C12	123.5 (3)	C13—C12—N12	118.0 (3)
C1—N1—S1—C11	94.7 (3)	N1—S1—C11—C12	171.7 (3)
C2—C1—N1—S1	163.4 (3)	C11—C12—N12—O121	5.7 (5)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O121^{i}	0.88	2.16	2.935 (4)	147
C6—H6$\cdots$O121^{ii}	0.95	2.49	3.231 (5)	135
C16—H16$\cdots$O122^{iii}	0.95	2.49	3.220 (5)	134

Symmetry codes: (i) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (iii) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.458$, $T_{\max} = 0.817$
10 802 measured reflections
2928 independent reflections
1867 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.066$
$\theta_{\max} = 27.5°$
$h = -7 \rightarrow 9$
$k = -17 \rightarrow 28$
$l = -16 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.082$
$S = 0.97$
2928 reflections
163 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.76$ e Å^{-3}
$\Delta\rho_{\min} = -1.02$ e Å^{-3}

The space group *Pbca* was uniquely assigned from the systematic absences. H atoms were treated as riding atoms, with C—H distances of 0.95 Å and N—H distances of 0.88 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997) and *PRPKAPPA* (Ferguson, 1999).

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. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1610). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Domenicano, A. & Murray-Rust, P. (1979). *Tetrahedron Lett.* pp. 2283–2286.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Glidewell, C., Howie, R. A., Low, J. N., Skakle, J. M. S., Wardell, S. M. S. V. & Wardell, J. L. (2002). *Acta Cryst.* B**58**, 864–876.
Glidewell, C., Low, J. N., Skakle, J. M. S., Wardell, S. M. S. V. & Wardell, J. L. (2002). *Acta Cryst.* C**58**, o487–o490.
Kelly, C. J., Skakle, J. M. S., Wardell, J. L., Wardell, S. M. S. V., Low, J. N. & Glidewell, C. (2002). *Acta Cryst.* B**58**, 94–108.
Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
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). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2002). *PLATON*. Version of September 2002. Utrecht University, The Netherlands.
Wardell, J. L., Wardell, S. M. S. V., Skakle, J. M. S., Low, J. N. & Glidewell, C. (2002). *Acta Cryst.* C**58**, o428–o430.