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2-Iodoaniline at 100 K

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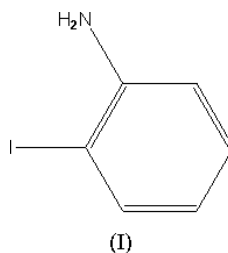
Key indicators

Single-crystal X-ray study
T = 100 K
Mean $\sigma(\text{C}-\text{C}) = 0.013 \text{ \AA}$
R factor = 0.048
wR factor = 0.124
Data-to-parameter ratio = 27.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the crystal structure of the title compound, $\text{C}_6\text{H}_6\text{IN}$, each 2-iodoaniline molecule forms part of three extended helices. Each helix exhibits a different intermolecular interaction, *viz.* weak $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds with an $\text{H}\cdots\text{N}$ distance of 2.31 (11) Å , $\text{I}\cdots\text{I}$ interactions of 3.7986 (15) Å and $\text{C}-\text{H}\cdots\pi$ contact distances of 2.53 Å .

Comment

Despite their simple structure and ready availability, few crystal structures of molecular complexes involving 2-haloanilines have been previously determined, with only eight examples in version 5.25 of the Cambridge Structural Database (CSD; Allen, 2002). In addition, the molecular structure of 2-fluoroaniline has been investigated by gas-phase electron diffraction (Csákvái & Hargittai, 1992). Four of these crystal structures contain 2-iodoaniline or the protonated 2-iodoanilinium cation. In one study (CSD refcode ZOJYAY; Casas *et al.*, 1996), the iodoaniline acts as a chelating ligand to a Pt metal centre (coordinated through the N and I atoms), whereas in the other three, the iodoaniline is in protonated ionic complexes, one as the halide salt, 2-iodoanilinium iodide (CSD refcode UFAJIU; Gray & Jones, 2002), and perhaps most notably in two polymorphs of 2-iodoanilinium picrate (CSD refcodes ZEDPON and ZEDPON01; Tanaka *et al.*, 1994). The structure of the title compound, (I), presented in this paper is thus the first example to be published of a crystal structure of the non-coordinated neutral compound, a fact that can probably be attributed to the low melting points of this family of materials (2-iodoaniline melts just above room temperature).

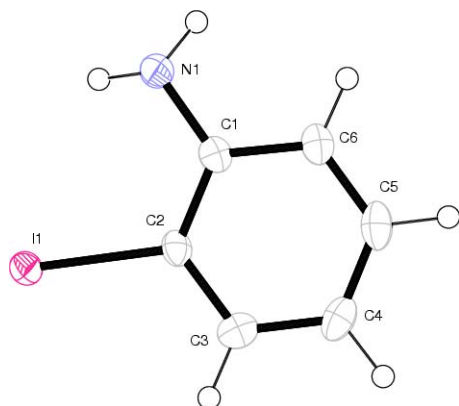


The geometry of the amino N atom (N1) in the crystal structure of (I) is observed to be slightly pyramidal in character (Fig. 1), with the sum of the angles around N1 equal to about 347°, similar to the value observed in the gas-phase electron diffraction structure of 2-fluoroaniline (Csákvái & Hargittai, 1992). Although there is obviously a large uncertainty in these values because of the presence of the I atom, the non-planarity of N1 is reasonable in terms of the hydrogen-bonding network observed within the crystal

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Figure 1

A view of (I), showing the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level.

structure. The amino groups form a hydrogen-bonded chain, with an $N1 \cdots N1^i$ separation of 3.161 (14) Å, an $H11 \cdots N1^i$ distance of 2.31 (11) Å and an $N1-H11 \cdots N1^i$ angle of $157 (10)^\circ$ [symmetry code: (i) $1 - x + y, -x, \frac{1}{3} + z$]. Although this is a rather weak interaction, it is comparable with the similar hydrogen bond that is observed in 2,4-dibromo-6-chloroaniline (Ferguson *et al.*, 1998), where the $N \cdots N$ distance is 3.150 (11) Å.

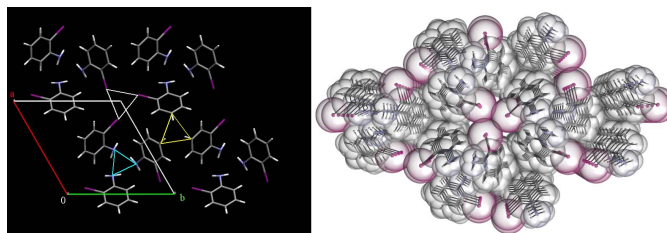
Overall, the crystal packing of (I) can be described in terms of three distinct helices (Fig. 2), one kept together via these weak $N-H \cdots N$ hydrogen bonds, another involving $I \cdots I$ interactions and the third formed by $C-H \cdots \pi$ interactions. Each molecule in the structure is involved in all three types of helices (Fig. 2). The I atoms form an infinite chain via $I1 \cdots I1^{ii}$ interactions, with an $I1 \cdots I1^{ii}$ distance of 3.7986 (15) Å [symmetry code: (ii) $-y, x-y, -\frac{1}{3} + z$]. These interactions are similar to those reported by Gray & Jones (2002) in their structure of 3-iodoanilinium iodide, containing two crystallographically unique $I \cdots I$ interactions with $I \cdots I$ distances of 3.7820 (6) and 3.9241 (6) Å. The third helix of $C-H \cdots \pi$ interactions involves the $C5-H51$ bond oriented in the approximate direction of the $C3-H31$ bond in the molecule related by symmetry position $(1 - y, x - y, -\frac{1}{3} + z)$, with $H51 \cdots H31$ and $H51 \cdots C3$ distances of 2.53 and 2.86 Å, respectively.

Experimental

2-Iodoaniline (98%) was obtained from Aldrich. A quantity (0.4 g) of the compound was purified by recrystallization from benzene. Colourless needle crystals of (I) were grown by heating the solution until all the precipitated material was redissolved, and then allowing the solution to cool slowly to room temperature.

Crystal data

C_6H_6IN	Mo $K\alpha$ radiation
$M_r = 219.02$	Cell parameters from 4867 reflections
Trigonal, $P3_2$	
$a = 11.2952 (8) \text{ \AA}$	$\theta = 0-32^\circ$
$c = 4.5325 (4) \text{ \AA}$	$\mu = 4.69 \text{ mm}^{-1}$
$V = 500.79 (7) \text{ \AA}^3$	$T = 100 \text{ K}$
$Z = 3$	Needle, colourless
$D_x = 2.179 \text{ Mg m}^{-3}$	$0.50 \times 0.10 \times 0.10 \text{ mm}$


Figure 2

Packing diagrams for (I), viewed down the c axis. The three helices observed in the crystal packing are indicated on the left, with the weak amine-amine hydrogen bond highlighted in blue, the $I \cdots I$ contacts in white and the $C-H \cdots \pi$ interactions in yellow.

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*MULABS* in *PLATON*; Spek, 1998)
 $T_{\min} = 0.385$, $T_{\max} = 0.626$
 4867 measured reflections

2174 independent reflections
 1959 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.104$
 $\theta_{\text{max}} = 31.9^\circ$
 $h = -16 \rightarrow 16$
 $k = -16 \rightarrow 15$
 $l = -6 \rightarrow 6$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.124$
 $S = 1.00$
 2174 reflections
 80 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F^2) + 0.07 + 1.39P]$
 where $P = [\max(F_o^2, 0) + 2F_c^2]/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.4 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -2.0 \text{ e \AA}^{-3}$
 Extinction correction: none
 Absolute structure: Flack (1983), 1032 Friedel pairs
 Flack parameter: 0.03 (8)

Table 1

Selected geometric parameters (Å, °).

$N1-C1$	1.401 (11)	$C2-C3$	1.413 (11)
$I1-C2$	2.103 (7)	$C3-C4$	1.406 (13)
$C1-C2$	1.400 (11)	$C4-C5$	1.384 (15)
$C1-C6$	1.419 (11)	$C5-C6$	1.390 (13)
$N1-C1-C2$	122.5 (7)	$I1-C2-C3$	119.0 (6)
$N1-C1-C6$	119.4 (7)	$C2-C3-C4$	119.8 (8)
$C2-C1-C6$	118.0 (7)	$C3-C4-C5$	119.0 (8)
$C1-C2-I1$	119.9 (6)	$C4-C5-C6$	121.7 (8)
$C1-C2-C3$	121.1 (7)	$C1-C6-C5$	120.3 (8)

All H atoms were positioned geometrically. Those bound to C atoms were refined as riding groups, while those bound to N atoms were refined, with the $N-H$ bond length restrained to 0.90 (1) Å. Although the value of R_{int} is rather high for this structure (0.104), as are the minimum and maximum difference densities. The positions of the minimum and maximum difference electron densities are at (0.806, 0.861, 0.167) and (0.407, 0.280, -0.008), respectively.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP3* (Farrugia, 1997) and *MERCURY* (Version 1.3; Bruno *et al.*, 2002); software used to prepare material for publication: *CRYSTALS*.

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