

2-Iodoaniline at 100 K

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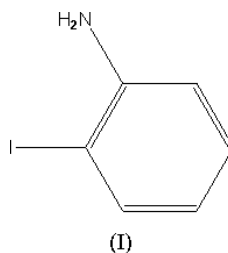
Key indicators

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) \AA , $\text{I}\cdots\text{I}$ interactions of 3.7986 (15) \AA and $\text{C}-\text{H}\cdots\pi$ contact distances of 2.53 \AA .

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).

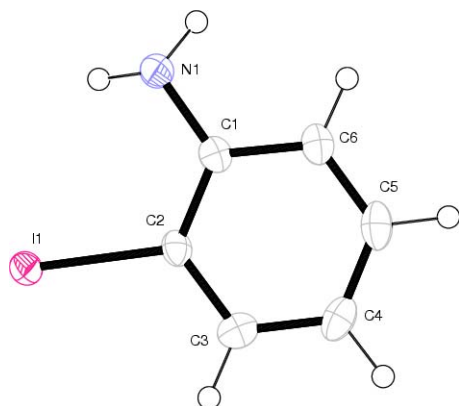


The geometry of the amino N atom (N1) in the crystal structure of (I) is observed to be slightly pyramidal in character (Fig. 1), with the sum of the angles around N1 equal to about 347°, similar to the value observed in the gas-phase electron diffraction structure of 2-fluoroaniline (Csákvái & Hargittai, 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 $\text{N1}\cdots\text{N1}^i$ separation of 3.161 (14) Å, an $\text{H11}\cdots\text{N1}^i$ distance of 2.31 (11) Å and an $\text{N1}-\text{H11}\cdots\text{N1}^i$ 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 $\text{N}\cdots\text{N}$ distance is 3.150 (11) Å.

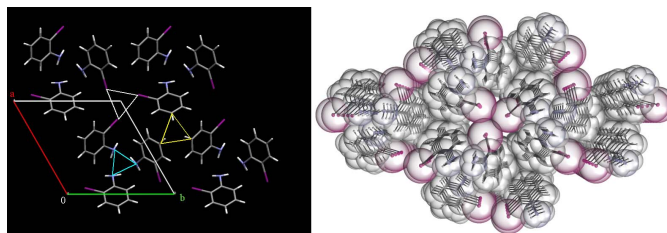
Overall, the crystal packing of (I) can be described in terms of three distinct helices (Fig. 2), one kept together via these weak $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, another involving $\text{I}\cdots\text{I}$ interactions and the third formed by $\text{C}-\text{H}\cdots\pi$ interactions. Each molecule in the structure is involved in all three types of helices (Fig. 2). The I atoms form an infinite chain via $\text{I1}\cdots\text{I1}^{ii}$ interactions, with an $\text{I1}\cdots\text{I1}^{ii}$ 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 $\text{I}\cdots\text{I}$ interactions with $\text{I}\cdots\text{I}$ distances of 3.7820 (6) and 3.9241 (6) Å. The third helix of $\text{C}-\text{H}\cdots\pi$ interactions involves the $\text{C5}-\text{H51}$ bond oriented in the approximate direction of the $\text{C3}-\text{H31}$ bond in the molecule related by symmetry position $(1-y, x-y, -\frac{1}{3}+z)$, with $\text{H51}\cdots\text{H31}$ and $\text{H51}\cdots\text{C3}$ 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

$\text{C}_6\text{H}_6\text{IN}$	Mo $K\alpha$ radiation
$M_r = 219.02$	Cell parameters from 4867 reflections
Trigonal, $P3_2$	
$a = 11.2952(8)$ Å	$\theta = 0-32^\circ$
$c = 4.5325(4)$ Å	$\mu = 4.69$ mm $^{-1}$
$V = 500.79(7)$ Å 3	$T = 100$ K
$Z = 3$	Needle, colourless
$D_x = 2.179$ Mg m $^{-3}$	$0.50 \times 0.10 \times 0.10$ 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 $\text{I}\cdots\text{I}$ contacts in white and the $\text{C}-\text{H}\cdots\pi$ 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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.104$
 $\theta_{\max} = 31.9^\circ$
 $h = -16 \rightarrow 16$
 $k = -16 \rightarrow 15$
 $l = -6 \rightarrow 6$

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

Table 1

Selected geometric parameters (Å, °).

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

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Altomare, A., Cascarano, G., Giacovazzo G., Guagliardi A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M. K., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.
- Casas, J. M., Falvello, L. R., Fornies, J. & Martin, A. (1996). *Inorg. Chem.* **35**, 56–62.
- Csákvái, E. & Hargittai, I. (1992). *J. Phys. Chem.* **96**, 5837–5842.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Ferguson, G., Low, J. N., Penner, G. H. & Wardell, J. L. (1998). *Acta Cryst.* **C54**, 1974–1977.
- Flack H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gray, L. & Jones, P. G. (2002). *Z. Naturforsch. Teil B*, **57**, 61–72.
- Nonius (2001). *COLLECT*. 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.
- Spek, A. L. (1998) *PLATON*. University of Utrecht, The Netherlands.
- Tanaka, M., Matsui, H., Mizoguchi, J. & Kashino, S. (1994). *Bull. Chem. Soc. Jpn.* **67**, 1572–1579.

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Crystal data

C_6H_6IN	$D_x = 2.179 \text{ Mg m}^{-3}$
$M_r = 219.02$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Trigonal, $P3_2$	Cell parameters from 16755 reflections
Hall symbol: P 32	$\theta = 0\text{--}32^\circ$
$a = 11.2952 (8) \text{ \AA}$	$\mu = 4.69 \text{ mm}^{-1}$
$c = 4.5325 (4) \text{ \AA}$	$T = 100 \text{ K}$
$V = 500.79 (7) \text{ \AA}^3$	Needle, colourless
$Z = 3$	$0.50 \times 0.10 \times 0.10 \text{ mm}$
$F(000) = 306$	

Data collection

Nonius KappaCCD area-detector diffractometer	2174 independent reflections
Graphite monochromator	1959 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.104$
Absorption correction: multi-scan (MULABS in PLATON; Spek, 1998)	$\theta_{\text{max}} = 31.9^\circ$, $\theta_{\text{min}} = 2.1^\circ$
$T_{\text{min}} = 0.385$, $T_{\text{max}} = 0.626$	$h = -16 \rightarrow 16$
4867 measured reflections	$k = -16 \rightarrow 15$
	$l = -6 \rightarrow 6$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.048$	$w = 1/[\sigma^2(F^2) + 0.07 + 1.39p]$
$wR(F^2) = 0.124$	where $p = [\max(F_o^2, 0) + 2F_c^2]/3$
$S = 1.00$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2174 reflections	$\Delta\rho_{\text{max}} = 1.4 \text{ e \AA}^{-3}$
80 parameters	$\Delta\rho_{\text{min}} = -2.0 \text{ e \AA}^{-3}$
3 restraints	Absolute structure: Flack (1983), 1032 Friedel pairs
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: 0.03 (8)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.3281 (7)	-0.1940 (7)	0.8337 (15)	0.0237
I1	0.13684 (5)	-0.06459 (5)	0.6472 (5)	0.0232
C1	0.3972 (8)	-0.0834 (8)	0.6404 (15)	0.0209

C2	0.3350 (8)	-0.0147 (8)	0.5157 (17)	0.0216
C3	0.4047 (9)	0.0911 (8)	0.3077 (16)	0.0260
C4	0.5396 (9)	0.1303 (9)	0.2276 (19)	0.0297
C5	0.6015 (9)	0.0634 (10)	0.354 (2)	0.0317
C6	0.5335 (8)	-0.0418 (8)	0.5565 (18)	0.0252
H11	0.392 (9)	-0.211 (12)	0.91 (3)	0.0294*
H12	0.261 (9)	-0.195 (12)	0.94 (2)	0.0294*
H31	0.3585	0.1382	0.2174	0.0319*
H41	0.5904	0.2055	0.0817	0.0352*
H51	0.6979	0.0917	0.2993	0.0409*
H61	0.5808	-0.0885	0.6432	0.0314*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.022 (3)	0.026 (3)	0.024 (3)	0.012 (3)	-0.001 (2)	0.002 (2)
I1	0.0221 (2)	0.0236 (2)	0.0265 (2)	0.01328 (19)	0.00161 (18)	0.00084 (18)
C1	0.023 (3)	0.021 (3)	0.020 (3)	0.012 (3)	-0.001 (2)	-0.007 (2)
C2	0.021 (3)	0.023 (3)	0.024 (3)	0.013 (3)	0.003 (3)	-0.003 (3)
C3	0.033 (4)	0.020 (3)	0.023 (4)	0.012 (3)	-0.001 (3)	-0.003 (3)
C4	0.030 (4)	0.026 (4)	0.025 (4)	0.008 (3)	0.008 (3)	-0.002 (3)
C5	0.024 (4)	0.035 (4)	0.034 (4)	0.013 (3)	0.006 (3)	-0.008 (3)
C6	0.021 (3)	0.024 (3)	0.029 (4)	0.010 (3)	0.000 (3)	-0.007 (3)

Geometric parameters (Å, °)

N1—C1	1.401 (11)	C3—C4	1.406 (13)
N1—H11	0.90 (5)	C3—H31	1.000
N1—H12	0.89 (5)	C4—C5	1.384 (15)
I1—C2	2.103 (7)	C4—H41	1.000
C1—C2	1.400 (11)	C5—C6	1.390 (13)
C1—C6	1.419 (11)	C5—H51	1.000
C2—C3	1.413 (11)	C6—H61	1.000
C1—N1—H11	106 (8)	C4—C3—H31	119.938
C1—N1—H12	116 (7)	C3—C4—C5	119.0 (8)
H11—N1—H12	124 (11)	C3—C4—H41	120.571
N1—C1—C2	122.5 (7)	C5—C4—H41	120.401
N1—C1—C6	119.4 (7)	C4—C5—C6	121.7 (8)
C2—C1—C6	118.0 (7)	C4—C5—H51	119.318
C1—C2—I1	119.9 (6)	C6—C5—H51	118.950
C1—C2—C3	121.1 (7)	C1—C6—C5	120.3 (8)
I1—C2—C3	119.0 (6)	C1—C6—H61	119.835
C2—C3—C4	119.8 (8)	C5—C6—H61	119.860
C2—C3—H31	120.298		