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Crystal structure of 4-chloro-2-iodoaniline

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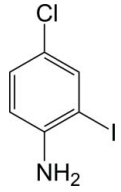
In the crystal structure of the title compound, C_6H_5ClIN, the amino group engages in N—H···N hydrogen bonding, creating [100] chains. A Cl···I contact is observed [3.7850 (16) Å]. The parallel planes of neigbouring molecules reveal highly offset π-stacking characterized by a centroid–centroid distance of 4.154 (1), a centroid-to-plane distance of 3.553 (3) and ring-offset slippage of 2.151 (6) Å.

Keywords: crystal structure; halogen–halogen interaction; aniline; π-stacking.

CCDC reference: 1015344

1. Related literature

For the synthesis and vibrational spectroscopic analysis of 4-chloro-2-iodoaniline, see: Hoque *et al.* (2013). For the dehalogenation of dihalogenated anilines in human liver microsomes, see: Zhang *et al.* (2011). For the crystal structures of related monohalogenated anilines, see: Trotter *et al.* (1966); Parkin *et al.* (2005) and of dihalogenated anilines, see: Xu *et al.* (2008). For halogen–halogen interactions, see: Pedireddi *et al.* (1994) and for π-stacking, see: Lueckheide *et al.* (2013). For van der Waals radii, see: Bondi (1964).



2. Experimental

2.1. Crystal data

C_6H_5ClIN
M_r = 253.46
Orthorhombic, $P2_12_12_1$
a = 4.1538 (4) Å
b = 11.3685 (11) Å
c = 15.8550 (16) Å
V = 748.71 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.54 mm^{-1}
T = 125 K
0.20 × 0.10 × 0.05 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.56, T_{max} = 0.81
11850 measured reflections
2281 independent reflections
2007 reflections with $I > 2\sigma(I)$
R_{int} = 0.066

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.053
S = 1.02
2281 reflections
88 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.96 e Å^{-3}
$\Delta\rho_{min}$ = −1.03 e Å^{-3}
Absolute structure: Flack x determined using 742 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.03 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2···N1^{ii}	0.90 (2)	2.28 (3)	3.142 (6)	161 (5)

Symmetry code: (ii) $x-\frac{1}{2}, -y+\frac{5}{2}, -z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *SHELXTL2014* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL2014*, *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2006).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: JJ2191).

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supporting information

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Crystal structure of 4-chloro-2-iodoaniline

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S1. Structural commentary

Dihalogenated anilines such as the title compound exhibit different toxicities depending on the identity, number and substitution pattern of the halogens on the aniline ring, and the mechanism of halogen activiation in differently substituted dihalogenated anilines by glutathione has been studied using human liver microsomes (Zhang *et al.*, 2011). The title compound may be synthesized using selective *ortho*-iodination of 4-chloroaniline (Hoque *et al.*, 2013). The C—Cl and C—I bond lengths of 1.755 (6) Å and 2.101 (5) Å in the title compound (Fig. 1) are similar to those found in the corresponding mono-substituted anilines, 4-chloroaniline with C—Cl bond length 1.75 Å (Trotter *et al.*, 1966) and 2-iodoaniline with C—I bond length 2.103 (7) Å (Parkin *et al.*, 2005). Further, the C—Cl and C—I bond lengths are similar to those found in the isomer where the positions of the halides are reversed, 2-chloro-4-iodoaniline, with C—Cl bond length 1.742 (4) Å and C—I bond length 2.103 (4) Å (Xu *et al.*, 2008).

In the structure of the titular compound, cooperative intermolecular hydrogen bonding with one of the two amine protons, H2, links the molecules into a one-dimensional chain running down the crystallographic *a*-axis (Fig. 2, Table 1). The other amine proton, H1, does not engage in any significant hydrogen bonding interaction. There is also an intermolecular halogen-halogen interaction between chlorine and iodine, with a Cl···I^{i} distance of 3.7850 (16) Å (Fig. 3) which is slightly longer than the sum of the van der Waals radii of chlorine and iodine, 3.73 Å (Bondi, 1964) [symmetry code (i): x - 1/2, -y + 3/2, -z]. For a discussion of halogen···halogen interactions, see Pedireddi *et al.*, 1994. The parallel planes of neigboring aromatic molecules reveal a highly offset face-to-face π-stacking (Fig. 3) characterized by a ring centroid-to-centroid distance of 4.154 (1) Å, centroid-to-plane distance of 3.553 (3) Å, and ring-offset slippage parameter of 2.151 (6) Å (Lueckheide *et al.*, 2013).

S2. Synthesis and crystallization

Crystalline 4-Chloro-2-iodoaniline (I) was purchased from Aldrich Chemical Company, USA.

S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and refined using a riding model at C–H = 0.95 Å and U_{iso}(H) = 1.2 × U_{eq}(C) of the aryl C-atoms. The hydrogen atoms on nitrogen were located in the difference map and refined semifreely with the help of a distance restraint, d(N—H) 0.90 (2) Å and U_{iso}(H) = 1.2 × U_{eq}(N). The extinction parameter (EXTI) refined to zero and was removed from the refinement.

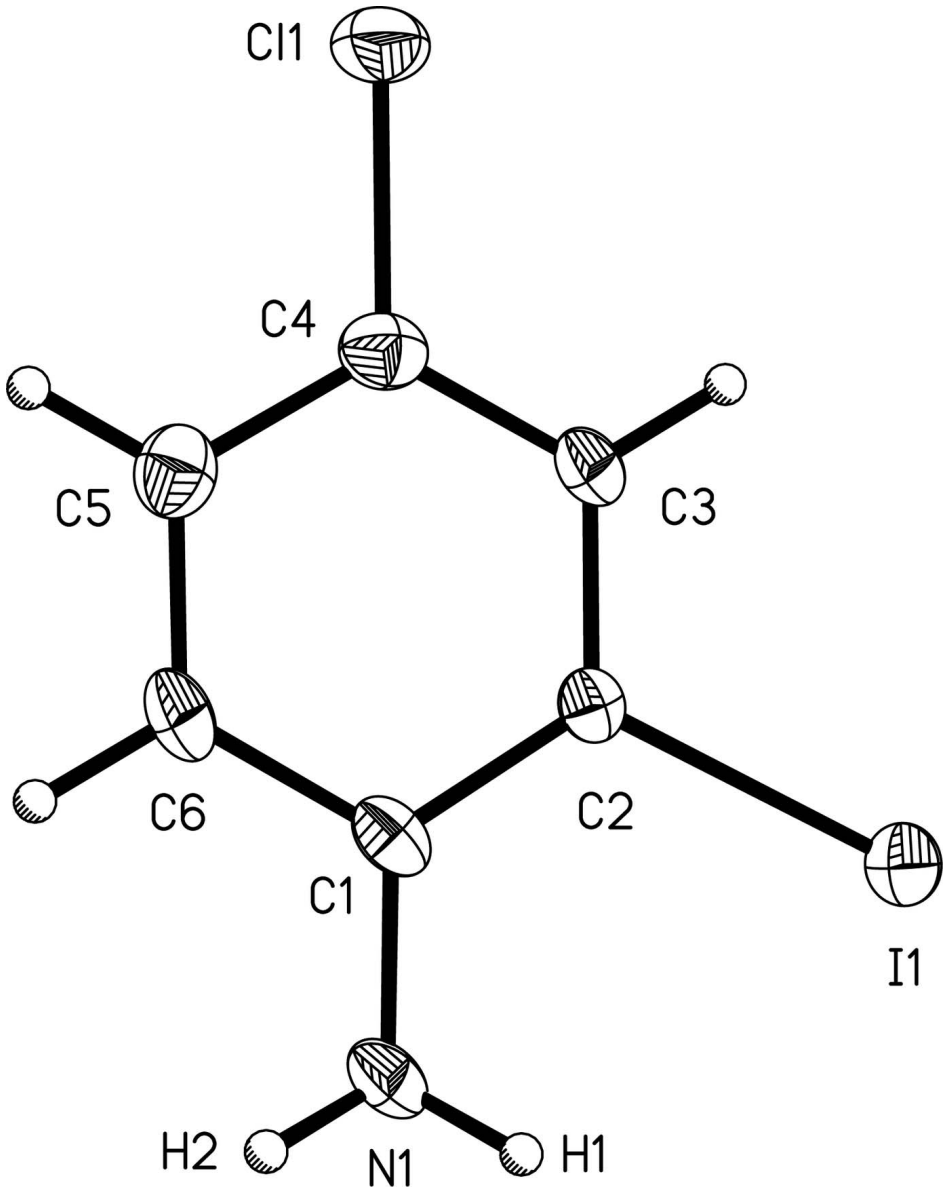

Figure 1

A view of title compound, with atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

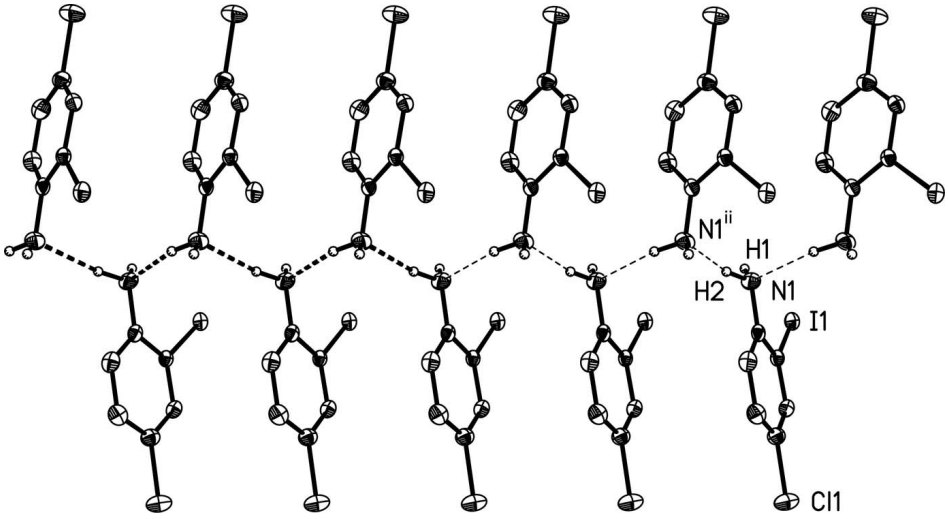

Figure 2

A view of the hydrogen bonding in 4-Chloro-2-iodoaniline forming a chain parallel to the crystallographic *a*-axis. Displacement ellipsoids are shown at the 50% probability level; hydrogen atoms on carbon removed for clarity. For symmetry code (ii), see Table 1.

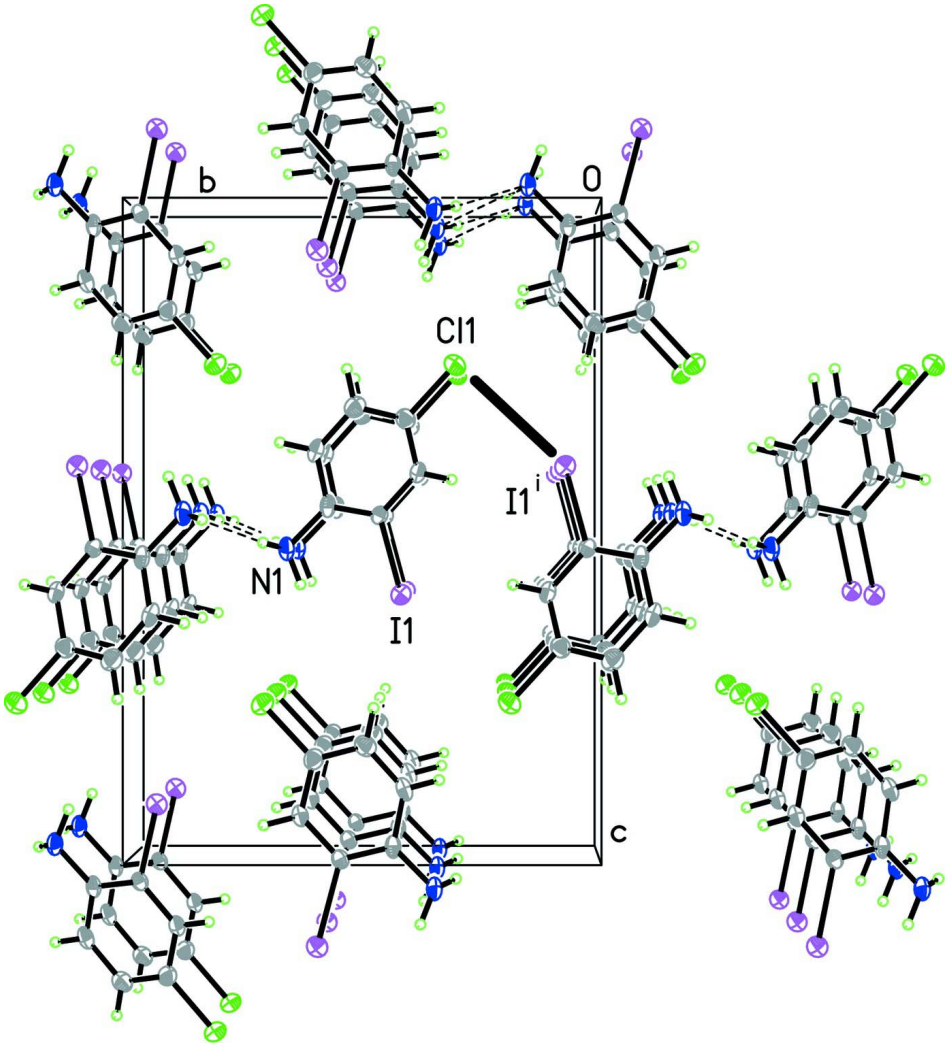

Figure 3

A view of the offset face-to-face π-stacking and Cl···I^{i} contact (thick solid line) in the packing of 4-Chloro-2-iodoaniline. Displacement ellipsoids are shown at the 50% probability level. Symmetry code (i): x - 1/2, -y + 3/2, -z.

4-Chloro-2-iodoaniline

Crystal data

C_6H_5ClIN
M_r = 253.46
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 4.1538 (4) Å
b = 11.3685 (11) Å
c = 15.8550 (16) Å
V = 748.71 (13) Å^3
Z = 4
F(000) = 472
D_x = 2.249 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5580 reflections
θ = 2.2–30.3°
μ = 4.54 mm^{-1}
T = 125 K
Plate, colourless
0.20 × 0.10 × 0.05 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.56, T_{max} = 0.81
11850 measured reflections
2281 independent reflections
2007 reflections with $I > 2\sigma(I)$
R_{int} = 0.066
θ_{max} = 30.5°, θ_{min} = 2.2°
$h = -5 \rightarrow 5$
$k = -16 \rightarrow 16$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.053
S = 1.02
2281 reflections
88 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0156P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.96 e Å^{-3}
$\Delta\rho_{min}$ = −1.03 e Å^{-3}
Absolute structure: Flack x determined using 742 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.03 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refined as a 2-component inversion twin.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	1.19309 (8)	0.92075 (3)	−0.09588 (2)	0.02161 (9)
Cl1	1.0100 (4)	0.80636 (12)	0.24943 (10)	0.0322 (3)
N1	0.8012 (13)	1.1528 (4)	−0.0258 (3)	0.0236 (9)
H1	0.795 (14)	1.124 (5)	−0.0783 (19)	0.028*
H2	0.625 (10)	1.196 (4)	−0.017 (4)	0.028*
C1	0.8463 (11)	1.0685 (4)	0.0375 (3)	0.0187 (10)
C2	1.0139 (12)	0.9638 (4)	0.0242 (3)	0.0167 (10)
C3	1.0695 (12)	0.8840 (4)	0.0886 (3)	0.0190 (10)
H3	1.1867	0.8136	0.0784	0.023*
C4	0.9513 (13)	0.9087 (5)	0.1680 (3)	0.0233 (11)
C5	0.7803 (14)	1.0111 (5)	0.1839 (4)	0.0255 (12)
H5	0.6977	1.0266	0.2387	0.031*
C6	0.7316 (12)	1.0906 (4)	0.1191 (3)	0.0228 (11)
H6	0.6182	1.1615	0.1301	0.027*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01729 (14)	0.02359 (15)	0.02395 (16)	0.00030 (14)	0.00153 (14)	−0.00153 (15)
Cl1	0.0468 (9)	0.0259 (7)	0.0238 (7)	0.0013 (7)	−0.0056 (6)	0.0049 (6)
N1	0.027 (2)	0.0132 (19)	0.031 (3)	0.003 (2)	−0.001 (3)	0.0002 (18)
C1	0.014 (2)	0.013 (2)	0.029 (3)	−0.002 (2)	−0.003 (2)	−0.001 (2)
C2	0.015 (3)	0.016 (2)	0.019 (3)	−0.0008 (19)	−0.001 (2)	−0.002 (2)
C3	0.018 (2)	0.014 (2)	0.024 (3)	0.0009 (18)	−0.003 (2)	−0.003 (2)
C4	0.025 (3)	0.021 (3)	0.024 (3)	−0.003 (3)	−0.004 (2)	0.002 (2)
C5	0.026 (3)	0.026 (3)	0.025 (3)	−0.003 (2)	0.001 (2)	−0.004 (2)
C6	0.023 (3)	0.015 (2)	0.030 (3)	0.002 (2)	−0.001 (2)	−0.007 (2)

Geometric parameters (Å, º)

I1—C2	2.101 (5)	C2—C3	1.386 (7)
Cl1—C4	1.755 (6)	C3—C4	1.380 (7)
Cl1—I1^{i}	3.7850 (16)	C3—H3	0.95
N1—C1	1.400 (7)	C4—C5	1.387 (8)
N1—H1	0.90 (2)	C5—C6	1.383 (7)
N1—H2	0.90 (2)	C5—H5	0.95
C1—C2	1.395 (7)	C6—H6	0.95
C1—C6	1.402 (7)		
Cl1···I1^{i}	3.7850 (16)		
C4—Cl1—I1^{i}	86.03 (18)	C4—C3—H3	120.7
C1—N1—H1	115 (4)	C2—C3—H3	120.7
C1—N1—H2	112 (4)	C3—C4—C5	121.3 (5)
H1—N1—H2	109 (5)	C3—C4—Cl1	119.1 (4)
C2—C1—N1	122.9 (5)	C5—C4—Cl1	119.6 (4)
C2—C1—C6	117.5 (5)	C6—C5—C4	119.2 (5)
N1—C1—C6	119.5 (5)	C6—C5—H5	120.4
C3—C2—C1	122.0 (5)	C4—C5—H5	120.4
C3—C2—I1	117.2 (4)	C5—C6—C1	121.3 (5)
C1—C2—I1	120.8 (4)	C5—C6—H6	119.4
C4—C3—C2	118.7 (5)	C1—C6—H6	119.4
N1—C1—C2—C3	176.8 (5)	I1^{i}—Cl1—C4—C3	−49.3 (4)
C6—C1—C2—C3	−0.5 (7)	I1^{i}—Cl1—C4—C5	129.0 (4)
N1—C1—C2—I1	−3.3 (7)	C3—C4—C5—C6	−0.9 (8)
C6—C1—C2—I1	179.4 (4)	Cl1—C4—C5—C6	−179.2 (4)
C1—C2—C3—C4	0.8 (8)	C4—C5—C6—C1	1.2 (8)
I1—C2—C3—C4	−179.1 (4)	C2—C1—C6—C5	−0.5 (7)
C2—C3—C4—C5	−0.1 (8)	N1—C1—C6—C5	−177.9 (5)
C2—C3—C4—Cl1	178.2 (4)		

Symmetry code: (i) $x-1/2, -y+3/2, -z$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2···N1^{ii}	0.90 (2)	2.28 (3)	3.142 (6)	161 (5)

Symmetry code: (ii) $x-1/2, -y+5/2, -z$.