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4-Bromo-2-chloroaniline

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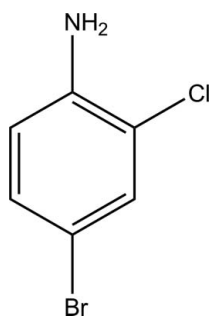
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.033; wR factor = 0.081; data-to-parameter ratio = 20.6.

The title compound, $\text{C}_6\text{H}_5\text{BrClN}$, is almost planar (r.m.s. deviation = 0.018 Å). In the crystal, molecules are linked by intermolecular $\text{N}-\text{H}\cdots\text{N}$ and weak $\text{N}-\text{H}\cdots\text{Br}$ hydrogen bonds, generating sheets.

Related literature

For background to halogentaed aromatic compounds, see: Katritzky *et al.* (1994). For related structures, see: Cox (2001); Parkin *et al.* (2005); Ng (2005); Ferguson *et al.* (1998). For the synthesis, see: Ault & Kraig (1966).



Experimental

Crystal data

 $\text{C}_6\text{H}_5\text{BrClN}$ $M_r = 206.47$ Orthorhombic, $P2_12_12_1$ $a = 10.965$ (4) Å $b = 15.814$ (6) Å $c = 4.0232$ (15) Å $V = 697.7$ (4) Å³ $Z = 4$ Mo $K\alpha$ radiation
 $\mu = 6.17$ mm⁻¹ $T = 298$ K
 $0.7 \times 0.19 \times 0.15$ mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\min} = 0.254$, $T_{\max} = 0.396$

5799 measured reflections
1710 independent reflections
1333 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.081$
 $S = 0.99$
1710 reflections
83 parameters
H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.48$ e Å⁻³
Absolute structure: Flack (1983),
511 Friedel pairs
Flack parameter: 0.035 (15)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1B}\cdots\text{Br1}^{\text{i}}$	0.86	3.04	3.719 (3)	137
$\text{N1}-\text{H1A}\cdots\text{N1}^{\text{ii}}$	0.86	2.34	3.172 (4)	164

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5285).

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supporting information

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4-Bromo-2-chloroaniline

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S1. Comment

Halogenated aromatic compounds is an important class of intermediates for the synthesis of bio-active substances such as antibacterial, antioxidizing, antiviral agents (e.g. Katritzky *et al.*, 1994). Despite their simple structures, the X-ray structures of halogenated aniline compounds periodically were reported, such as 2,5-dichloroaniline (Cox, 2001), 2-iodoaniline (Parkin *et al.*, 2005) and 5-chloro-2-nitroaniline (Ng, 2005). We now report the title compound, (I).

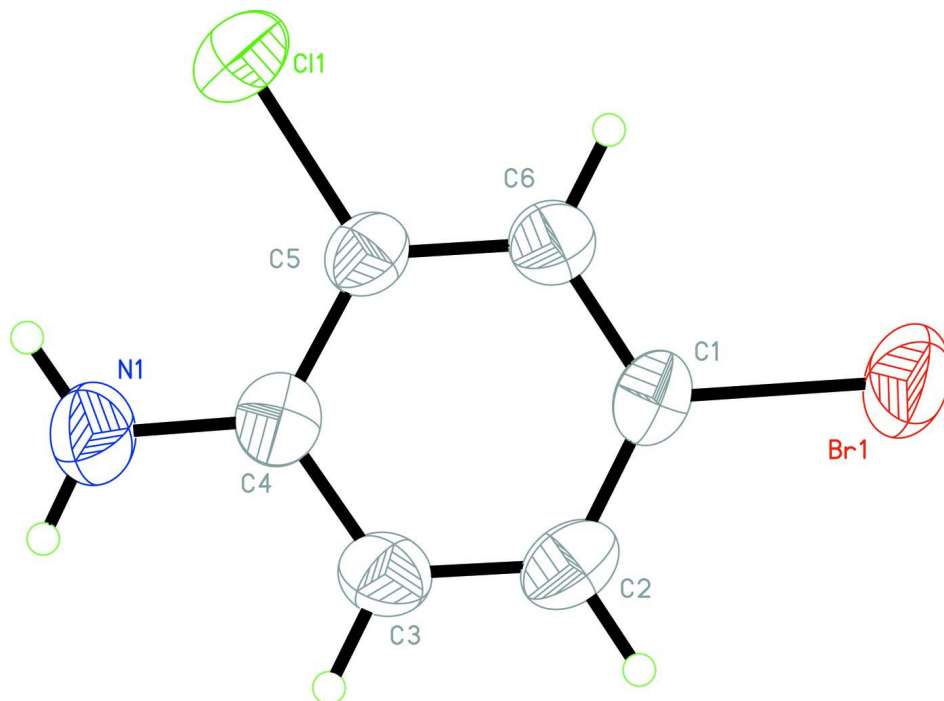
The packing of molecules in the crystal structure is stabilized and linked into a two-dimensional texture by intermolecular N—H \cdots N and N—H \cdots Br hydrogen bonds. The N \cdots N distance is 3.172 (4) Å in hydrogen bond N—H \cdots N, which are similar to that observed in 2,4-dibromo-6-chloroaniline (Ferguson *et al.*, 1998), 3.150 (11) Å and 2-iodoaniline (Parkin *et al.*, 2005), 3.161 (14) Å.

S2. Experimental

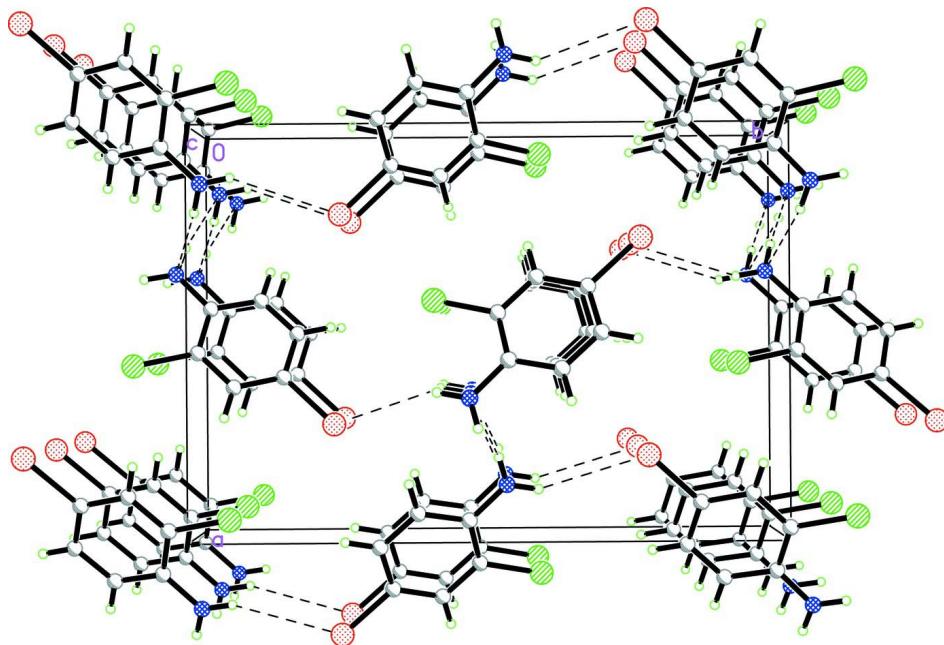
The title compound was prepared according to a previously reported method (Ault & Kraig, 1966). Colourless needles of (I) were obtained by slow evaporation of a petroleum ether solution.

S3. Refinement

The hydrogen atoms were positioned geometrically, with C—H = 0.93, 0.98, 0.97 and 0.96 Å for phenyl, methine, methylene and methyl H atoms, respectively, and were included in the refinement in the riding model approximation. The displacement parameters of methyl H atoms were set to $1.5U_{eq}(C)$, while those of other H atoms were set to $1.2U_{eq}(C)$. In the absence of significant anomalous scattering effects, Friedel pairs were merged.

**Figure 1**

The molecular structure of (I) showing 50% probability displacement ellipsoids.

**Figure 2**

The packing of (I), viewed down the *c* axis. N—H...N and N—H...Br hydrogen bond interactions are shown as dashed lines.

4-Bromo-2-chloroaniline

Crystal data

C₆H₅BrClN $M_r = 206.47$ Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

 $a = 10.965$ (4) Å $b = 15.814$ (6) Å $c = 4.0232$ (15) Å $V = 697.7$ (4) Å³ $Z = 4$ $F(000) = 424$ $D_x = 1.965$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1199 reflections

 $\theta = 2.3$ – 29.8° $\mu = 6.17$ mm⁻¹ $T = 298$ K

Needle, colourless

 $0.7 \times 0.19 \times 0.15$ mm

Data collection

Bruker SMART CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scan

Absorption correction: multi-scan

(SADABS; Bruker, 2001)

 $T_{\min} = 0.254$, $T_{\max} = 0.396$

5799 measured reflections

1710 independent reflections

1333 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.044$ $\theta_{\max} = 29.8^\circ$, $\theta_{\min} = 2.3^\circ$ $h = -14 \rightarrow 14$ $k = -20 \rightarrow 21$ $l = -5 \rightarrow 5$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.033$ $wR(F^2) = 0.081$ $S = 0.99$

1710 reflections

83 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from

neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0374P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.008$ $\Delta\rho_{\max} = 0.33$ e Å⁻³ $\Delta\rho_{\min} = -0.48$ e Å⁻³

Extinction correction: SHELXTL (Sheldrick,

2008), $F_c^* = kF_c[1 + 0.001xFe^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.246 (8)

Absolute structure: Flack (1983), 511 Friedel

pairs

Absolute structure parameter: 0.035 (15)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.28337 (3)	0.74386 (2)	0.51936 (10)	0.0646 (2)

Cl1	0.42519 (8)	0.41363 (5)	0.4648 (3)	0.0588 (3)
C1	0.3957 (3)	0.65802 (18)	0.6258 (8)	0.0432 (7)
C2	0.4999 (3)	0.6770 (2)	0.7973 (9)	0.0494 (8)
H2A	0.5151	0.7322	0.8656	0.059*
C3	0.5812 (3)	0.6145 (2)	0.8673 (9)	0.0456 (8)
H3A	0.6518	0.6276	0.9846	0.055*
C4	0.5613 (3)	0.5320 (2)	0.7681 (8)	0.0428 (8)
C5	0.4548 (3)	0.51544 (19)	0.5957 (8)	0.0395 (7)
C6	0.3728 (2)	0.57746 (17)	0.5249 (7)	0.0431 (7)
H6A	0.3018	0.5649	0.4087	0.052*
N1	0.6464 (2)	0.47087 (18)	0.8346 (8)	0.0565 (8)
H1A	0.7124	0.4838	0.9383	0.068*
H1B	0.6338	0.4196	0.7726	0.068*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0770 (3)	0.0451 (2)	0.0717 (3)	0.01789 (15)	-0.0064 (2)	0.0025 (2)
Cl1	0.0638 (5)	0.0349 (4)	0.0776 (6)	-0.0034 (3)	-0.0023 (5)	-0.0047 (5)
C1	0.0509 (17)	0.0347 (16)	0.0438 (16)	0.0061 (14)	0.0043 (14)	0.0027 (13)
C2	0.0582 (18)	0.0357 (18)	0.054 (2)	-0.0081 (15)	0.0075 (16)	-0.0027 (15)
C3	0.0368 (15)	0.0481 (19)	0.0520 (18)	-0.0064 (14)	-0.0002 (14)	-0.0008 (15)
C4	0.0399 (16)	0.0430 (18)	0.0455 (18)	0.0005 (14)	0.0086 (14)	0.0040 (13)
C5	0.0416 (15)	0.0344 (15)	0.0424 (16)	-0.0028 (12)	0.0053 (13)	0.0012 (12)
C6	0.0424 (14)	0.0406 (15)	0.0461 (16)	-0.0022 (12)	-0.0007 (16)	0.0016 (16)
N1	0.0434 (15)	0.0500 (17)	0.076 (2)	0.0101 (13)	-0.0015 (15)	0.0006 (15)

Geometric parameters (Å, °)

Br1—C1	1.883 (3)	C3—H3A	0.9300
Cl1—C5	1.725 (3)	C4—N1	1.369 (4)
C1—C6	1.361 (4)	C4—C5	1.383 (4)
C1—C2	1.368 (5)	C5—C6	1.361 (4)
C2—C3	1.361 (5)	C6—H6A	0.9300
C2—H2A	0.9300	N1—H1A	0.8600
C3—C4	1.382 (4)	N1—H1B	0.8600
C6—C1—C2	120.7 (3)	C3—C4—C5	117.1 (3)
C6—C1—Br1	119.1 (2)	C6—C5—C4	121.8 (3)
C2—C1—Br1	120.2 (2)	C6—C5—Cl1	119.0 (2)
C3—C2—C1	119.4 (3)	C4—C5—Cl1	119.2 (2)
C3—C2—H2A	120.3	C1—C6—C5	119.4 (3)
C1—C2—H2A	120.3	C1—C6—H6A	120.3
C2—C3—C4	121.6 (3)	C5—C6—H6A	120.3
C2—C3—H3A	119.2	C4—N1—H1A	120.0
C4—C3—H3A	119.2	C4—N1—H1B	120.0
N1—C4—C3	120.2 (3)	H1A—N1—H1B	120.0
N1—C4—C5	122.7 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1B \cdots Br1 ⁱ	0.86	3.04	3.719 (3)	137
N1—H1A \cdots N1 ⁱⁱ	0.86	2.34	3.172 (4)	164

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