

4-Chlorobenzothioamide

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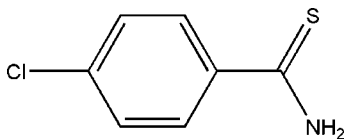
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.037; wR factor = 0.105; data-to-parameter ratio = 20.9.

In the title compound, $\text{C}_7\text{H}_6\text{ClNS}$, the dihedral angle between the aromatic ring and the thioamide fragment is 28.1 (2)°. The structure features a π -stacking interaction between the aromatic rings with a slight offset of the rings, giving a centroid-centroid separation of 3.7942 (2) Å. There are intermolecular hydrogen-bonding interactions between the amino group and the S atoms.

Related literature

For the uses of thioamides, see: Akhtar *et al.* (2006, 2007, 2008); Jagodzinski (2003); Lebana *et al.* (2008). For the biological activity of thioamides, see: Wei *et al.* (2006). For the synthesis of thioamides, see: Bauer & Kuhlein (1985); Cava & Levinson (1985); Manaka & Sato (2005). For a comparable structure, see: Jian *et al.* (2006).



Experimental

Crystal data

$\text{C}_7\text{H}_6\text{ClNS}$

$M_r = 171.64$

Monoclinic, $P2_1/c$

$a = 8.1592$ (4) Å

$b = 9.0934$ (5) Å

$c = 10.8915$ (6) Å

$\beta = 100.113$ (10)°

$V = 795.54$ (7) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 0.66$ mm⁻¹

$T = 296$ K

$0.40 \times 0.36 \times 0.18$ mm

Data collection

Bruker APEXII CCD
diffractometer

Absorption correction: multi-scan
(*SADABS*; Bruker, 2008)

$T_{\min} = 0.778$, $T_{\max} = 0.889$

6337 measured reflections

1901 independent reflections

1667 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.105$

$S = 1.06$

1901 reflections

91 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.33$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1A}\cdots\text{S1}^{\text{i}}$	0.86	2.64	3.3769 (15)	145
$\text{N1}-\text{H1B}\cdots\text{S1}^{\text{ii}}$	0.86	2.63	3.4527 (15)	160

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2933).

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supplementary materials

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4-Chlorobenzothioamide

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Comment

Thioamides are important precursors/intermediates in the synthesis of various heterocycles (Jagodzinski *et al.*, 2003). Besides being used as synthetic intermediates, they exhibit numerous biological activities (Wei *et al.*, 2006). In addition, thioamides have found use as important ligands in coordination chemistry (Lebana *et al.*, 2008). Several methods for their synthesis have been published involving the uses of Lawesson's reagent (Cava *et al.*, 1985) and phosphorus pentasulphide (Bauer *et al.*, 1985). The title compound, 4-chlorobenzothioamide was synthesized in continuation of our previous work on the synthesis and biological screenings of five membered heterocycles (Akhtar *et al.*, 2006, 2007, 2008). In this article the crystal structure of 4-chlorobenzothioamide is being reported. The title compound was synthesized by treating 4-chlorobenzonitrile with 70% sodium hydrogen sulfide hydrate and magnesium chloride hexahydrate in dimethylformamide (Manaka & Sato, 2005) as an intermediate for the synthesis of thiazoles.

The hydrogen bonding interactions between the nitrogen and sulfur atoms are in the range of those seen in *p*-trifluoromethylbenzothioamide where the corresponding interactions are between 3.3735 Å and 3.5133 Å (Jian *et al.*, 2006).

Experimental

4-Chlorobenzonitrile (14.5 mmol) was added to a slurry of sodium hydrogen sulfide hydrate (70%, 29 mmol) and magnesium chloride hexahydrate (14.5 mmol) in DMF (40 mL) and the mixture stirred at room temperature for 2 h. The resulting green slurry was poured into water (100 mL) and the precipitated solid collected by filtration. The product obtained was resuspended in 1 N HCl (50 ml), stirred for another 30 min, filtered and washed with excess of water. The recrystallization of the residue from chloroform afforded the crystals of the title compound suitable for X-ray analysis.

Refinement

The hydrogen atoms were placed in geometrically idealized positions of 0.93 Å (aromatic C—H) and 0.86 Å (amide N—H) and constrained to ride on the parent atom with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$.

Figures

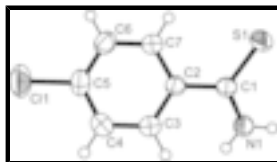


Fig. 1. Molecular structure of 4-chlorobenzothioamide showing displacement ellipsoids at the 50% probability level (for non-H atoms).



Fig. 2. Packing diagram of 4-chlorobenzothioamide as viewed down the *b* axis. Displacement ellipsoids are shown at the 50% probability level (for non-H atoms).

4-Chlorobenzothioamide

Crystal data

C_7H_6ClNS	$F_{000} = 352$
$M_r = 171.64$	$D_x = 1.433 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
Hall symbol: -P 2ybc	$\lambda = 0.71073 \text{ \AA}$
$a = 8.1592 (4) \text{ \AA}$	Cell parameters from 3894 reflections
$b = 9.0934 (5) \text{ \AA}$	$\theta = 2.5\text{--}28.5^\circ$
$c = 10.8915 (6) \text{ \AA}$	$\mu = 0.66 \text{ mm}^{-1}$
$\beta = 100.1130 (10)^\circ$	$T = 296 \text{ K}$
$V = 795.54 (7) \text{ \AA}^3$	Block, yellow
$Z = 4$	$0.40 \times 0.36 \times 0.18 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	1901 independent reflections
Radiation source: fine-focus sealed tube	1667 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.017$
$T = 296 \text{ K}$	$\theta_{\text{max}} = 28.5^\circ$
φ and ω scans	$\theta_{\text{min}} = 2.9^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2008)	$h = -10 \rightarrow 10$
$T_{\text{min}} = 0.778$, $T_{\text{max}} = 0.889$	$k = -12 \rightarrow 12$
6337 measured reflections	$l = -9 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.037$	H-atom parameters constrained
$wR(F^2) = 0.105$	$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 0.2817P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
1901 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
91 parameters	$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$

Primary atom site location: structure-invariant direct methods Extinction correction: none

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. 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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.08443 (7)	0.15260 (5)	0.36191 (4)	0.05425 (18)
Cl1	0.41127 (8)	0.84764 (5)	0.55354 (7)	0.0767 (2)
N1	0.1431 (2)	0.16063 (15)	0.60516 (12)	0.0479 (4)
H1A	0.1776	0.2025	0.6758	0.058*
H1B	0.1046	0.0724	0.6028	0.058*
C1	0.14913 (18)	0.23175 (17)	0.50045 (13)	0.0367 (3)
C2	0.21721 (18)	0.38334 (16)	0.51285 (13)	0.0346 (3)
C7	0.16710 (19)	0.48716 (18)	0.41971 (14)	0.0402 (3)
H7A	0.0925	0.4603	0.3485	0.048*
C5	0.3367 (2)	0.66844 (17)	0.53788 (18)	0.0466 (4)
C6	0.2270 (2)	0.62963 (18)	0.43192 (17)	0.0462 (4)
H6A	0.1937	0.6984	0.3693	0.055*
C3	0.3294 (2)	0.42569 (19)	0.61821 (15)	0.0448 (4)
H3A	0.3647	0.3573	0.6808	0.054*
C4	0.3893 (2)	0.5685 (2)	0.63118 (17)	0.0515 (4)
H4A	0.4641	0.5963	0.7020	0.062*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0851 (4)	0.0495 (3)	0.0281 (2)	-0.0239 (2)	0.0096 (2)	-0.00374 (15)
Cl1	0.0841 (4)	0.0399 (3)	0.1008 (5)	-0.0176 (2)	0.0012 (3)	-0.0009 (2)
N1	0.0790 (10)	0.0363 (7)	0.0299 (7)	-0.0104 (6)	0.0134 (6)	-0.0014 (5)
C1	0.0449 (7)	0.0369 (7)	0.0291 (7)	-0.0020 (6)	0.0091 (6)	-0.0005 (5)
C2	0.0393 (7)	0.0345 (7)	0.0307 (7)	-0.0002 (5)	0.0085 (5)	-0.0002 (5)
C7	0.0438 (7)	0.0415 (8)	0.0341 (8)	0.0001 (6)	0.0030 (6)	0.0029 (6)
C5	0.0457 (8)	0.0337 (7)	0.0604 (11)	-0.0048 (6)	0.0095 (7)	-0.0024 (7)
C6	0.0489 (8)	0.0383 (8)	0.0504 (10)	0.0020 (7)	0.0056 (7)	0.0095 (7)
C3	0.0520 (9)	0.0422 (8)	0.0374 (8)	-0.0029 (7)	-0.0002 (6)	0.0040 (6)
C4	0.0539 (9)	0.0483 (9)	0.0477 (10)	-0.0087 (7)	-0.0036 (7)	-0.0042 (7)

supplementary materials

Geometric parameters (\AA , $^\circ$)

S1—C1	1.6714 (15)	C7—C6	1.383 (2)
C11—C5	1.7374 (16)	C7—H7A	0.9300
N1—C1	1.3195 (19)	C5—C4	1.375 (3)
N1—H1A	0.8600	C5—C6	1.376 (3)
N1—H1B	0.8600	C6—H6A	0.9300
C1—C2	1.483 (2)	C3—C4	1.386 (2)
C2—C3	1.391 (2)	C3—H3A	0.9300
C2—C7	1.393 (2)	C4—H4A	0.9300
C1—N1—H1A	120.0	C4—C5—C6	121.55 (15)
C1—N1—H1B	120.0	C4—C5—C11	119.26 (14)
H1A—N1—H1B	120.0	C6—C5—C11	119.19 (14)
N1—C1—C2	116.55 (13)	C5—C6—C7	119.19 (15)
N1—C1—S1	121.02 (12)	C5—C6—H6A	120.4
C2—C1—S1	122.42 (11)	C7—C6—H6A	120.4
C3—C2—C7	118.65 (14)	C4—C3—C2	120.85 (15)
C3—C2—C1	120.94 (14)	C4—C3—H3A	119.6
C7—C2—C1	120.40 (13)	C2—C3—H3A	119.6
C6—C7—C2	120.74 (15)	C5—C4—C3	119.02 (15)
C6—C7—H7A	119.6	C5—C4—H4A	120.5
C2—C7—H7A	119.6	C3—C4—H4A	120.5
S1—C1—C2—C7	28.1 (2)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots S1 ⁱ	0.86	2.64	3.3769 (15)	145
N1—H1B \cdots S1 ⁱⁱ	0.86	2.63	3.4527 (15)	160

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

Fig. 1

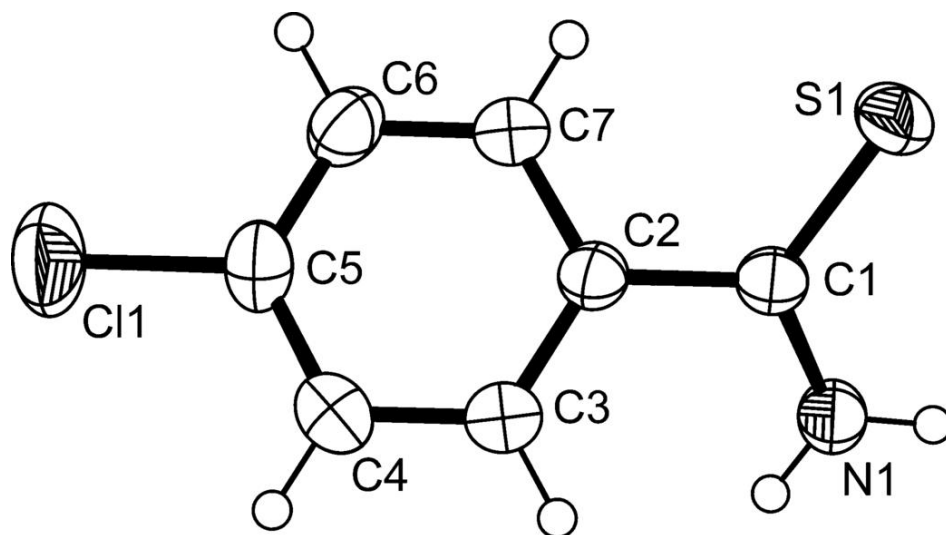


Fig. 2

