

3,5-Dichloro-6-methylpyridin-2-amine

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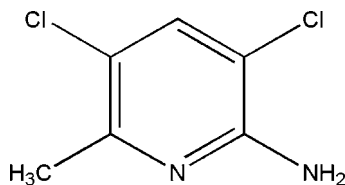
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.001$ Å; R factor = 0.024; wR factor = 0.071; data-to-parameter ratio = 33.0.

In the title compound, $\text{C}_6\text{H}_6\text{Cl}_2\text{N}_2$, intramolecular $\text{N}-\text{H}\cdots\text{Cl}$ and $\text{C}-\text{H}\cdots\text{Cl}$ contacts generate five-membered rings, producing $S(5)$ ring motifs. Pairs of intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds link neighbouring molecules into dimers with $R_2^2(8)$ ring motifs. In the crystal structure, these dimers are connected by $\text{N}-\text{H}\cdots\text{Cl}$ interactions and are packed into columns.

Related literature

For details of hydrogen-bond motifs, see: Bernstein *et al.* (1995). For related literature and applications see, for example: Goswami & Maity (2007); Taylor *et al.* (1989); Taylor & Ray (1988); Beer *et al.* (1993); Goswami *et al.* (2000, 2005); Fun *et al.* (2008).



Experimental

Crystal data

$\text{C}_6\text{H}_6\text{Cl}_2\text{N}_2$
 $M_r = 177.03$
 Monoclinic, $P2_1/n$
 $a = 12.7670$ (3) Å
 $b = 3.8037$ (1) Å
 $c = 15.4129$ (3) Å
 $\beta = 104.990$ (1)°

$V = 723.01$ (3) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.81$ mm⁻¹
 $T = 100.0$ (1) K
 $0.45 \times 0.31 \times 0.28$ mm

Data collection

Bruker SMART APEXII CCD
 area-detector diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 2005)
 $T_{\min} = 0.711$, $T_{\max} = 0.803$

26531 measured reflections
 3795 independent reflections
 3485 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.071$
 $S = 1.11$
 3795 reflections

115 parameters
 All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 0.61$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.42$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2N1}\cdots\text{N1}^i$	0.869 (15)	2.168 (15)	3.0320 (9)	172.8 (13)
$\text{N2}-\text{H1N1}\cdots\text{Cl2}$	0.828 (14)	2.603 (14)	3.0156 (7)	112.3 (12)
$\text{C6}-\text{H6A}\cdots\text{Cl1}$	1.02 (2)	2.67 (2)	3.1318 (9)	108.0 (14)
$\text{N2}-\text{H1N1}\cdots\text{Cl2}^{ii}$	0.828 (14)	2.900 (14)	3.6758 (7)	156.9 (13)

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2343).

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supplementary materials

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3,5-Dichloro-6-methylpyridin-2-amine

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Comment

The halogen substituted π -depleted heteroaromatics (*e.g.* pterin, quinoxaline, naphthyridine, or pyridine derivatives) are important intermediates in modern organic chemistry (Goswami & Maity 2007; Taylor *et al.* 1989; Taylor & Ray 1988; Beer *et al.* 1993), *e.g.* they are used as precursors for pharmacologically active compounds. These are also versatile compounds in manifold synthesis of artificial receptors for molecular recognition (Goswami *et al.* 2000, 2005; Fun *et al.* 2008).

In the title compound (I), Fig. 1, intramolecular N—H \cdots Cl and C—H \cdots Cl contacts generate five-membered rings, producing *S*(5) ring motifs (Bernstein *et al.*, 1995). Pairs of intermolecular N—H \cdots N hydrogen bonds link molecules into dimers with a $R^2_2(8)$ ring motif (Table 1). In the crystal structure, these dimers are connected by N—H \cdots Cl interactions and are packed into columns along the *b* axis, Fig. 2.

Experimental

Phosphorus oxychloride (POCl₃) (15 ml) was added to 2-amino-6-methylpyridine (2 g, 0.019 mmol) and the mixture was refluxed at 383 K for 16 h. Excess POCl₃ was distilled off. The solid residue was neutralized using KOH solution in an ice bath and a saturated NaHCO₃ solution was added. The solid residue was filtered off, extracted with CHCl₃, the solution was dried over anhydrous Na₂SO₄ and then concentrated under vacuum. The crude product was purified by column chromatography using silica gel with 20% ethyl acetate in petroleum ether as eluant to afford (I) (2.14 g, 65%) as a colourless crystalline solid, mp. 404–407 K.

Refinement

All hydrogen atoms were located from a difference Fourier map and refined freely; range of C-H distances: 0.924 (7) to 1.02 (2) Å. See Table 1 for N-H distances.

Figures

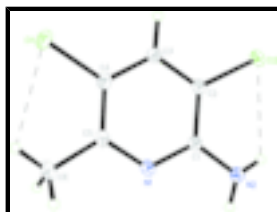


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids and the atomic numbering. Dashed lines show intramolecular hydrogen bonds.

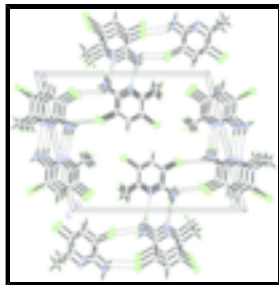


Fig. 2. The crystal packing for (I), showing dimers with $R^2_2(8)$ motifs and stacking of the dimers into columns along the b -axis. Intermolecular interactions are drawn as dashed lines.

3,5-Dichloro-6-methylpyridin-2-amine

Crystal data

$C_6H_6Cl_2N_2$

$M_r = 177.03$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2yn$

$a = 12.7670$ (3) Å

$b = 3.8037$ (1) Å

$c = 15.4129$ (3) Å

$\beta = 104.990$ (1)°

$V = 723.01$ (3) Å³

$Z = 4$

$F_{000} = 360$

$D_x = 1.626$ Mg m⁻³

Melting point: 404 K

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 9896 reflections

$\theta = 2.4$ – 40.3 °

$\mu = 0.81$ mm⁻¹

$T = 100.0$ (1) K

Block, colourless

$0.45 \times 0.31 \times 0.28$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100.0$ (1) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2005)

$T_{\min} = 0.711$, $T_{\max} = 0.803$

26531 measured reflections

3795 independent reflections

3485 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\text{max}} = 37.5$ °

$\theta_{\text{min}} = 2.4$ °

$h = -21 \rightarrow 21$

$k = -6 \rightarrow 6$

$l = -26 \rightarrow 26$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.071$

$S = 1.11$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 0.1631P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

3795 reflections $\Delta\rho_{\max} = 0.61 \text{ e } \text{\AA}^{-3}$
 115 parameters $\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$
 Primary atom site location: structure-invariant direct methods Extinction correction: none

Special details

Experimental. The low-temperature data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.116608 (15)	0.89761 (5)	0.117299 (12)	0.01973 (5)
C12	0.150078 (13)	0.32687 (5)	-0.194719 (10)	0.01603 (4)
N1	0.36956 (5)	0.65340 (16)	0.02268 (4)	0.01455 (9)
N2	0.38950 (5)	0.41291 (19)	-0.10983 (4)	0.01738 (11)
H2N1	0.4571 (12)	0.379 (4)	-0.0819 (9)	0.027 (3)*
H1N1	0.3607 (11)	0.284 (4)	-0.1526 (9)	0.025 (3)*
C1	0.32310 (5)	0.51854 (18)	-0.05855 (4)	0.01322 (10)
C2	0.20904 (5)	0.49965 (17)	-0.08923 (4)	0.01321 (10)
C3	0.14544 (5)	0.61633 (18)	-0.03563 (4)	0.01465 (10)
H3	0.0672 (10)	0.605 (3)	-0.0583 (8)	0.022 (3)*
C4	0.19660 (5)	0.75331 (18)	0.04856 (4)	0.01450 (10)
C5	0.30903 (5)	0.77194 (18)	0.07629 (4)	0.01437 (10)
C6	0.37037 (7)	0.9165 (2)	0.16549 (5)	0.02130 (13)
H6C	0.4268 (13)	1.055 (5)	0.1579 (11)	0.041 (4)*
H6B	0.4079 (16)	0.744 (5)	0.2083 (12)	0.061 (5)*
H6A	0.3222 (16)	1.071 (6)	0.1929 (13)	0.065 (6)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.02170 (8)	0.02155 (8)	0.01862 (8)	0.00364 (6)	0.01006 (6)	-0.00108 (5)
C12	0.01665 (7)	0.01786 (7)	0.01167 (7)	-0.00132 (5)	0.00022 (5)	-0.00081 (5)
N1	0.0143 (2)	0.0174 (2)	0.0113 (2)	-0.00002 (17)	0.00219 (17)	-0.00112 (17)
N2	0.0146 (2)	0.0247 (3)	0.0127 (2)	0.00163 (19)	0.00317 (18)	-0.00292 (19)
C1	0.0136 (2)	0.0146 (2)	0.0110 (2)	0.00045 (18)	0.00251 (18)	0.00056 (18)
C2	0.0140 (2)	0.0139 (2)	0.0108 (2)	-0.00021 (18)	0.00163 (17)	0.00039 (18)
C3	0.0143 (2)	0.0153 (2)	0.0142 (2)	0.00085 (19)	0.00352 (19)	0.0011 (2)

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C4	0.0168 (2)	0.0140 (2)	0.0137 (2)	0.0020 (2)	0.00586 (19)	0.00056 (19)
C5	0.0172 (2)	0.0141 (2)	0.0117 (2)	0.00022 (19)	0.00350 (19)	-0.00028 (19)
C6	0.0264 (3)	0.0224 (3)	0.0135 (3)	-0.0011 (3)	0.0023 (2)	-0.0044 (2)

Geometric parameters (Å, °)

C11—C4	1.7396 (7)	C2—C3	1.3733 (9)
C12—C2	1.7346 (6)	C3—C4	1.3941 (9)
N1—C1	1.3409 (8)	C3—H3	0.970 (13)
N1—C5	1.3468 (9)	C4—C5	1.3894 (10)
N2—C1	1.3607 (9)	C5—C6	1.4996 (10)
N2—H2N1	0.869 (14)	C6—H6C	0.924 (17)
N2—H1N1	0.828 (14)	C6—H6B	0.96 (2)
C1—C2	1.4118 (9)	C6—H6A	1.02 (2)
C1—N1—C5	121.03 (6)	C5—C4—C3	120.23 (6)
C1—N2—H2N1	116.4 (9)	C5—C4—C11	121.27 (5)
C1—N2—H1N1	115.0 (9)	C3—C4—C11	118.50 (5)
H2N1—N2—H1N1	119.1 (13)	N1—C5—C4	120.35 (6)
N1—C1—N2	117.62 (6)	N1—C5—C6	116.03 (6)
N1—C1—C2	120.07 (6)	C4—C5—C6	123.62 (6)
N2—C1—C2	122.28 (6)	C5—C6—H6C	109.4 (10)
C3—C2—C1	120.08 (6)	C5—C6—H6B	115.3 (11)
C3—C2—C12	120.37 (5)	H6C—C6—H6B	102.0 (15)
C1—C2—C12	119.55 (5)	C5—C6—H6A	111.3 (11)
C2—C3—C4	118.24 (6)	H6C—C6—H6A	107.2 (15)
C2—C3—H3	118.9 (7)	H6B—C6—H6A	110.8 (14)
C4—C3—H3	122.8 (7)		
C5—N1—C1—N2	178.27 (6)	C2—C3—C4—C5	0.46 (10)
C5—N1—C1—C2	0.13 (10)	C2—C3—C4—C11	-179.37 (5)
N1—C1—C2—C3	-0.61 (10)	C1—N1—C5—C4	0.64 (10)
N2—C1—C2—C3	-178.66 (7)	C1—N1—C5—C6	179.98 (6)
N1—C1—C2—C12	179.63 (5)	C3—C4—C5—N1	-0.94 (10)
N2—C1—C2—C12	1.58 (9)	C11—C4—C5—N1	178.89 (5)
C1—C2—C3—C4	0.29 (10)	C3—C4—C5—C6	179.77 (7)
C12—C2—C3—C4	-179.95 (5)	C11—C4—C5—C6	-0.40 (10)

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>
N2—H2N1 \cdots N1 ⁱ	0.869 (15)	2.168 (15)	3.0320 (9)	172.8 (13)
N2—H1N1 \cdots C12	0.828 (14)	2.603 (14)	3.0156 (7)	112.3 (12)
C6—H6A \cdots C11	1.02 (2)	2.67 (2)	3.1318 (9)	108.0 (14)
N2—H1N1 \cdots C12 ⁱⁱ	0.828 (14)	2.900 (14)	3.6758 (7)	156.9 (13)

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

Fig. 1

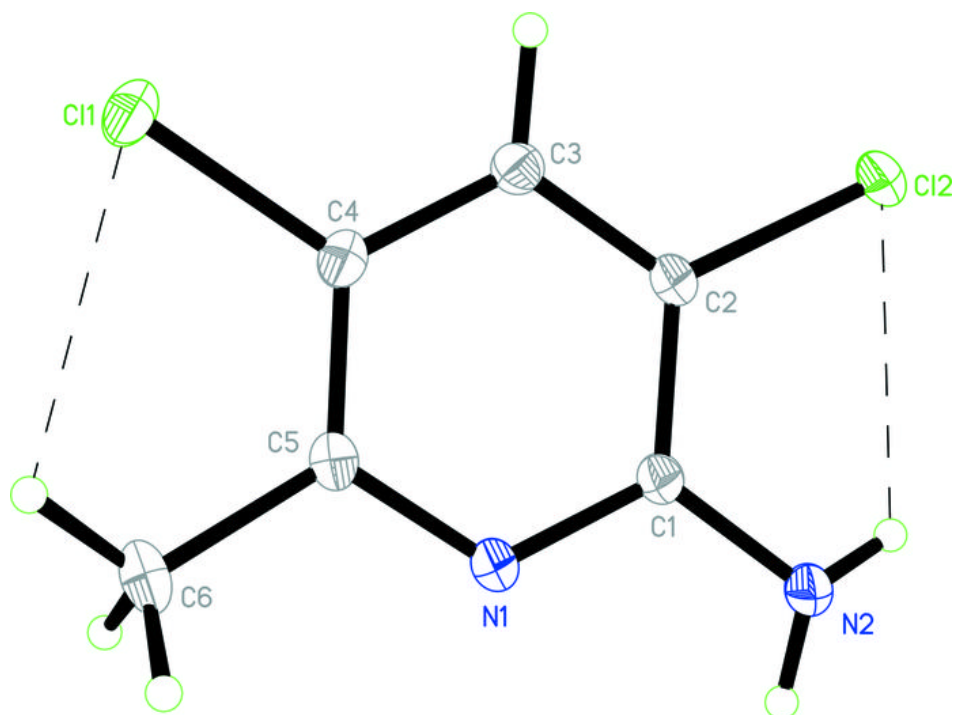


Fig. 2

