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

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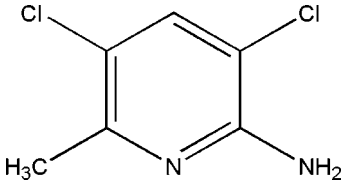
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.001 Å; R factor = 0.024; wR factor = 0.071; data-to-parameter ratio = 33.0.

In the title compound, $C_6H_6Cl_2N_2$, intramolecular N–H···Cl and C—H···Cl contacts generate five-membered rings, producing $S(5)$ ring motifs. Pairs of intermolecular N—H···N hydrogen bonds link neighbouring molecules into dimers with $R_2^2(8)$ ring motifs. In the crystal structure, these dimers are connected by N—H···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

$C_6H_6Cl_2N_2$
M_r = 177.03
Monoclinic, $P2_1/n$
a = 12.7670 (3) Å
b = 3.8037 (1) Å
c = 15.4129 (3) Å
β = 104.990 (1)°
V = 723.01 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.81 mm^{-1}
T = 100.0 (1) K
0.45 × 0.31 × 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 $I > \check{2}I$)
R_{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
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*N*1···N1^{i}	0.869 (15)	2.168 (15)	3.0320 (9)	172.8 (13)
N2—H1*N*1···Cl2	0.828 (14)	2.603 (14)	3.0156 (7)	112.3 (12)
C6—H6*A*···Cl1	1.02 (2)	2.67 (2)	3.1318 (9)	108.0 (14)
N2—H1*N*1···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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Acta Cryst. (2009). E**65**, o97 [doi:10.1107/S1600536808041366]

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

Hoong-Kun Fun, Reza Kia, Annada C. Maity, Sibaprasad Maity and Shyamaprosad Goswami

S1. 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···Cl and C—H···Cl contacts generate five-membered rings, producing *S(5)* ring motifs (Bernstein *et al.*, 1995). Pairs of intermolecular N—H···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···Cl interactions and are packed into columns along the *b* axis, Fig. 2.

S2. Experimental

Phosphorus oxychloride ($POCl_3$) (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 $POCl_3$ was distilled off. The solid residue was neutralized using KOH solution in an ice bath and a saturated $NaHCO_3$ solution was added. The solid residue was filtered off, extracted with $CHCl_3$, the solution was dried over anhydrous Na_2SO_4 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.

S3. 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.

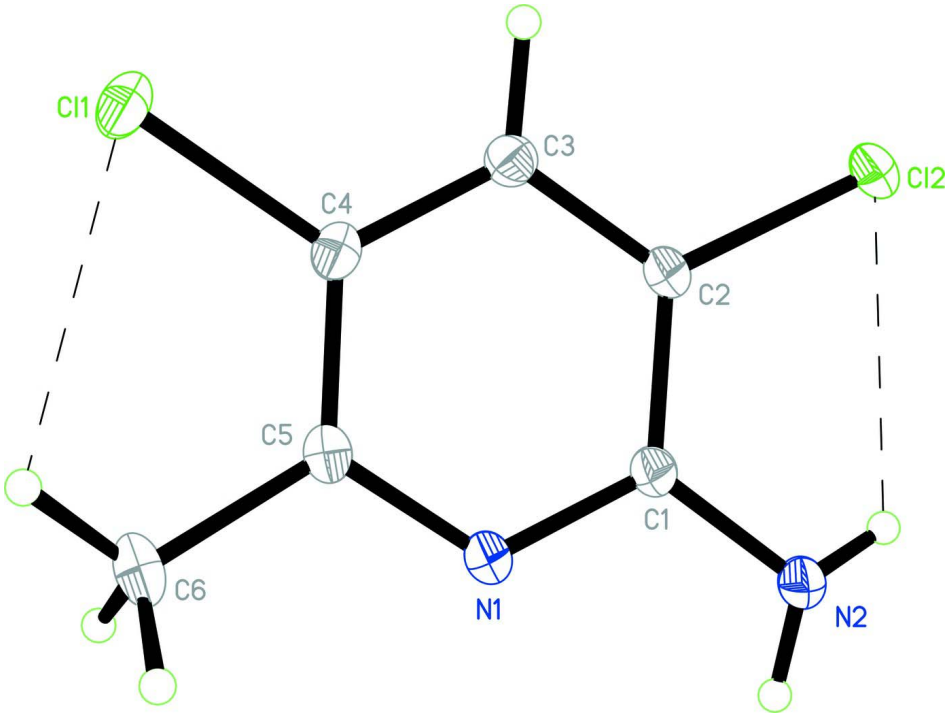

Figure 1

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

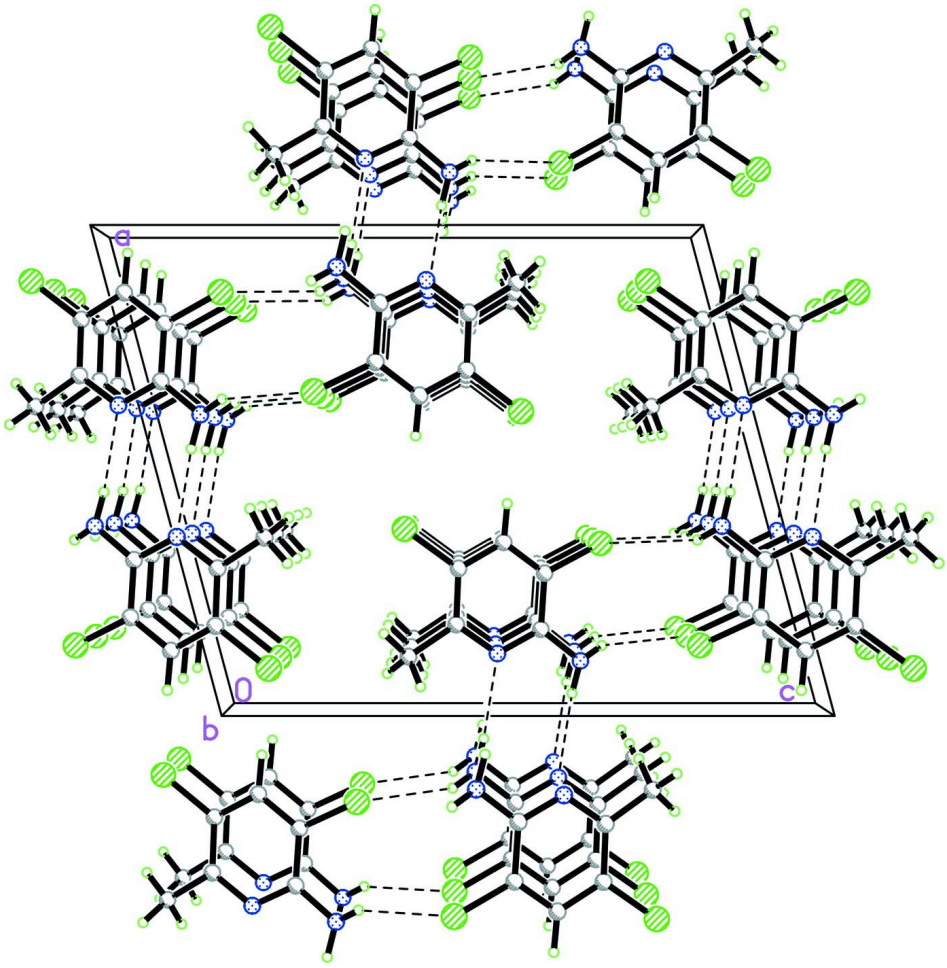

Figure 2

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
β = 104.990 (1)°
V = 723.01 (3) Å^3
Z = 4

F(000) = 360
D_x = 1.626 Mg m^{-3}
Melting point: 404 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9896 reflections
θ = 2.4–40.3°
μ = 0.81 mm^{-1}
T = 100 K
Block, colourless
0.45 × 0.31 × 0.28 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
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 $I > 2\tilde{}I$)
R_{int} = 0.026
θ_{max} = 37.5°, θ_{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
3795 reflections
115 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
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 0.1631P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.116608 (15)	0.89761 (5)	0.117299 (12)	0.01973 (5)
Cl2	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 (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02170 (8)	0.02155 (8)	0.01862 (8)	0.00364 (6)	0.01006 (6)	−0.00108 (5)
Cl2	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)
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, º)

Cl1—C4	1.7396 (7)	C2—C3	1.3733 (9)
Cl2—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—Cl1	121.27 (5)
C1—N2—H1N1	115.0 (9)	C3—C4—Cl1	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—Cl2	120.37 (5)	H6C—C6—H6B	102.0 (15)
C1—C2—Cl2	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—Cl1	−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—Cl2	179.63 (5)	C3—C4—C5—N1	−0.94 (10)
N2—C1—C2—Cl2	1.58 (9)	Cl1—C4—C5—N1	178.89 (5)
C1—C2—C3—C4	0.29 (10)	C3—C4—C5—C6	179.77 (7)

Cl2—C2—C3—C4	−179.95 (5)	Cl1—C4—C5—C6	−0.40 (10)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*N*1···N1^{i}	0.869 (15)	2.168 (15)	3.0320 (9)	172.8 (13)
N2—H1*N*1···Cl2	0.828 (14)	2.603 (14)	3.0156 (7)	112.3 (12)
C6—H6*A*···Cl1	1.02 (2)	2.67 (2)	3.1318 (9)	108.0 (14)
N2—H1*N*1···Cl2^{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.