

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

3-Chloropyridin-2-amine

Zhi-Nan Hu,^a Hui-Bin Yang,^b Huan Luo^b and Bin Li^{b*}

^aDepartment of Chemistry, Liaoning University, Shenyang 110036, People's Republic of China, and ^bAgrochemicals Division, Shenyang Research Institute of Chemical Industry, Shenyang 110021, People's Republic of China
Correspondence e-mail: libin1@sinochem.com

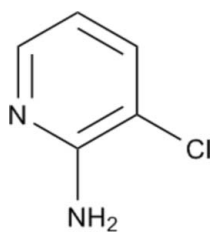
Received 2 April 2011; accepted 11 April 2011

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.059; wR factor = 0.182; data-to-parameter ratio = 14.5.

In the title compound, $\text{C}_5\text{H}_5\text{ClN}_2$, a by-product in the synthesis of ethyl 2-(3-chloropyridin-2-yl)-5-oxopyrazolidine-3-carboxylate, the amine groups form intermolecular hydrogen-bonding associations with pyridine N-atom acceptors, giving centrosymmetric cyclic dimers. Short intermolecular $\text{Cl}\cdots\text{Cl}$ interactions [3.278 (3) Å] also occur.

Related literature

The title compound was isolated as a by-product in the preparation of ethyl 2-(3-chloropyridin-2-yl)-5-oxopyrazolidine-3-carboxylate, an intermediate in the synthesis of the insecticide chlorantraniliprole (systematic name 3-bromo-*N*-[4-chloro-2-methyl-6-[(methylamino)carbonyl]phenyl]-1-(3-chloro-2-pyridinyl)-1*H*-pyrazole-5-carboxamide), see: Lahm *et al.* (2005). For related structures, see: Chao *et al.* (1975); Anagnostis & Turnbull (1998); Hemamalini & Fun (2010).



Experimental

Crystal data

$\text{C}_5\text{H}_5\text{ClN}_2$
 $M_r = 128.56$
Monoclinic, $P2_1/c$
 $a = 11.149$ (8) Å
 $b = 5.453$ (4) Å
 $c = 9.844$ (7) Å
 $\beta = 90.581$ (12)°
 $V = 598.5$ (7) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.52$ mm⁻¹
 $T = 296$ K
 $0.38 \times 0.32 \times 0.22$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\min} = 0.827$, $T_{\max} = 0.894$
2778 measured reflections
1057 independent reflections
867 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.182$
 $S = 1.05$
1057 reflections
73 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.57$ e Å⁻³
 $\Delta\rho_{\min} = -0.31$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2A}\cdots\text{N1}^i$	0.86	2.22	3.051 (5)	162

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2107).

References

- Anagnostis, J. & Turnbull, M. M. (1998). *Acta Cryst.* **C54**, 681–683.
Bruker (2001). SMART, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Chao, M., Schemp, E. & Rosenstein, R. D. (1975). *Acta Cryst.* **B31**, 2922–2924.
Hemamalini, M. & Fun, H.-K. (2010). *Acta Cryst.* **E66**, o1416–o1417.
Lahm, G. P., Selby, T. P. & Freudenberger, J. H. (2005). *Bioorg. Med. Chem. Lett.* **15**, 4898–4906.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

Acta Cryst. (2011). E67, o1138 [doi:10.1107/S1600536811013432]

3-Chloropyridin-2-amine

Zhi-Nan Hu, Hui-Bin Yang, Huan Luo and Bin Li

S1. Comment

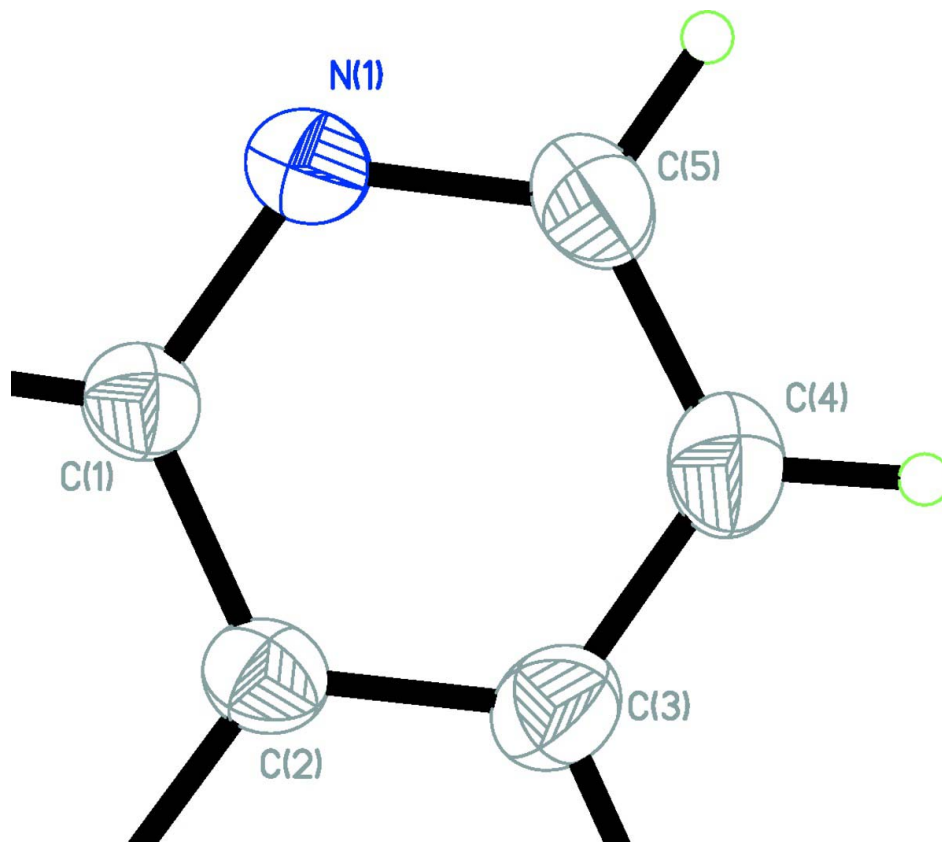
The structures of salts of the halo-substituted aminopyridine, such as 2-amino-5-chloropyridine-fumaric acid (Hemamalini & Fun, 2010), 2-amino-3,5-dichloropyridinium chloride monohydrate (Anagnostis & Turnbull, 1998), are known but the the structure of 2-amino-3-chloropyridine is not known. This compound, C₅H₅Cl₁N₂ (I) was isolated as a by-product in the preparation of ethyl 2-(3-chloropyridin-2-yl)-5-oxopyrazolidine-3-carboxylate, an important intermediate in the synthesis of the insecticide chlorantraniliprole (3-bromo-N-[4-chloro-2-methyl-6-[(methylamino)carbonyl]phenyl]-1-(3-chloro-2-pyridinyl)-1H-pyrazole-5-carboxamide) (Lahm *et al.*, 2005). In the structure of (I) (Fig. 1), intermolecular amine N—H \cdots N_{pyridine} hydrogen-bonding interactions (Table 1) give centrosymmetric cyclic dimers (Fig. 2), similar to those found in the structure of 2-aminopyridine (Chao *et al.*, 1975). In (I) there is an intramolecular N—H \cdots Cl interaction [3.001 (3) Å] while in the crystal structure there are also short Cl \cdots Clⁱⁱ interactions [3.278 (3) Å] [symmetry code: (ii) -x + 2, -y, -z + 1].

S2. Experimental

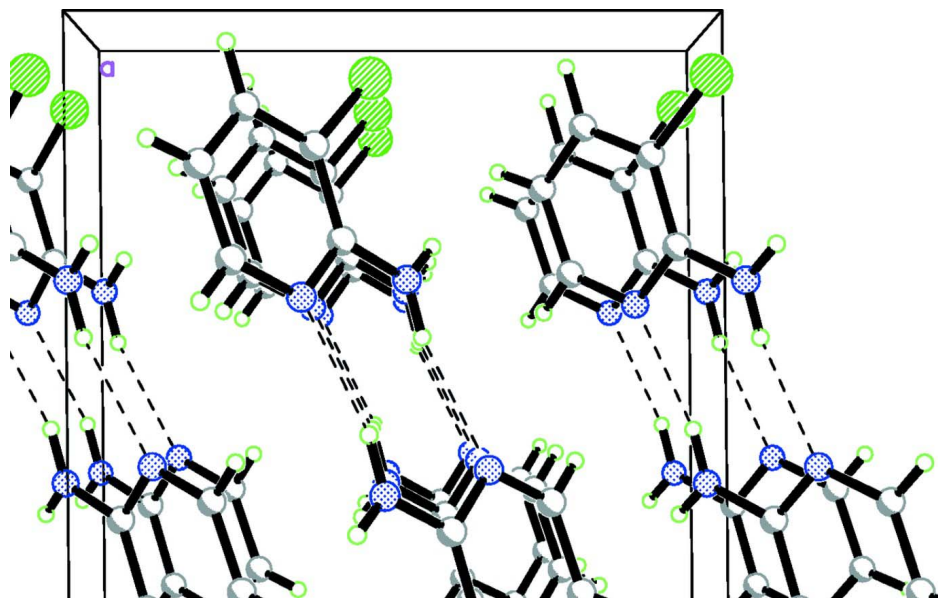
Sodium ethoxide (3.48 g, 50.4 mmol) and 150 ml of absolute ethanol was heated to reflux, after wich 6.80 g (47.4 mmol) of 3-chloro-2-hydrazinylpyridine was added and the mixture was allowed to reflux for 5 minutes. The slurry was then treated dropwise with 9.79 g (56.9 mmol) of diethyl maleate over a period of 5 minutes and the resulting solution was held at reflux for 10 minutes. After cooling to 338 K, the reaction mixture was treated with 5.0 ml (87.3 mmol) of glacial acetic acid. The mixture was diluted with 60 ml water and then cooled to room temperature, giving a precipitate which was isolated *via* filtration, and separated by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:5). The title compound was obtained as a yellow solid (0.60 g, 8%) and recrystallized from dichloromethane to afford colorless single crystals suitable for X-ray diffraction. Anal.: Calc. for C₅H₅Cl₁N₂: C, 46.47; H, 3.84; Cl, 27.96; N, 21.85%. Found: C, 46.71; H, 3.99; Cl, 27.58; N, 21.79. ¹H NMR(CDCl₃): 5.02(s,2H, NH₂), 6.62(dd,1H, pyridine-H), 7.48(dd, 1H, pyridine-H), 7.98 (dd, 1H, pyridine-H).

S3. Refinement

Although all H atoms were visible in difference maps, they were placed in geometrically calculated positions, with N—H and C—H = 0.86 and 0.93 Å respectively, and included in the final refinement in the riding model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

**Figure 1**

The molecular structure of (I), showing atom numbering scheme and 30% probability displacement ellipsoids.

**Figure 2**

The packing of (I) in the unit cell viewed down *b*, showing hydrogen-bonding interactions as dashed lines.

3-Chloropyridin-2-amine

Crystal data

C₅H₅ClN₂ $M_r = 128.56$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 11.149 (8) \text{ \AA}$ $b = 5.453 (4) \text{ \AA}$ $c = 9.844 (7) \text{ \AA}$ $\beta = 90.581 (12)^\circ$ $V = 598.5 (7) \text{ \AA}^3$ $Z = 4$ $F(000) = 264$ $D_x = 1.427 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1473 reflections

 $\theta = 3.7\text{--}27.2^\circ$ $\mu = 0.52 \text{ mm}^{-1}$ $T = 296 \text{ K}$

Block, yellow

 $0.38 \times 0.32 \times 0.22 \text{ mm}$

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scansAbsorption correction: multi-scan
(*SADABS*; Bruker, 2001) $T_{\min} = 0.827$, $T_{\max} = 0.894$

2778 measured reflections

1057 independent reflections

867 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.048$ $\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 1.8^\circ$ $h = -13 \rightarrow 11$ $k = -6 \rightarrow 6$ $l = -8 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.059$ $wR(F^2) = 0.182$ $S = 1.05$

1057 reflections

73 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.1147P)^2 + 0.2179P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.57 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.31 \text{ e \AA}^{-3}$

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. 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	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.89884 (8)	0.20978 (18)	0.46576 (10)	0.0821 (5)
N1	0.6085 (2)	0.5920 (5)	0.3676 (2)	0.0597 (7)
N2	0.6357 (3)	0.2720 (5)	0.5172 (3)	0.0716 (8)
H2A	0.5613	0.2836	0.5385	0.086*

H2B	0.6804	0.1628	0.5553	0.086*
C1	0.6825 (2)	0.4252 (5)	0.4237 (3)	0.0505 (7)
C2	0.8035 (2)	0.4167 (5)	0.3855 (3)	0.0535 (7)
C3	0.8465 (3)	0.5728 (6)	0.2897 (3)	0.0635 (8)
H3	0.9266	0.5667	0.2645	0.076*
C4	0.7692 (3)	0.7404 (7)	0.2306 (3)	0.0725 (10)
H4	0.7955	0.8481	0.1640	0.087*
C5	0.6520 (3)	0.7431 (6)	0.2735 (4)	0.0698 (9)
H5	0.6000	0.8571	0.2345	0.084*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0717 (7)	0.0833 (7)	0.0913 (8)	0.0322 (4)	0.0101 (5)	0.0145 (4)
N1	0.0545 (13)	0.0566 (14)	0.0681 (15)	0.0068 (11)	0.0018 (10)	0.0047 (11)
N2	0.0674 (16)	0.0602 (16)	0.088 (2)	0.0131 (12)	0.0194 (14)	0.0196 (13)
C1	0.0572 (14)	0.0411 (13)	0.0533 (15)	0.0036 (11)	0.0026 (11)	-0.0039 (11)
C2	0.0558 (15)	0.0510 (15)	0.0537 (15)	0.0099 (11)	0.0019 (11)	-0.0057 (12)
C3	0.0561 (15)	0.076 (2)	0.0583 (17)	-0.0019 (14)	0.0070 (13)	0.0002 (14)
C4	0.077 (2)	0.074 (2)	0.067 (2)	-0.0049 (15)	0.0047 (17)	0.0178 (15)
C5	0.073 (2)	0.0617 (19)	0.074 (2)	0.0057 (14)	-0.0054 (16)	0.0155 (15)

Geometric parameters (Å, °)

C11—C2	1.735 (3)	C2—C3	1.361 (4)
N1—C5	1.334 (4)	C3—C4	1.380 (4)
N1—C1	1.344 (4)	C3—H3	0.9300
N2—C1	1.351 (4)	C4—C5	1.378 (5)
N2—H2A	0.8600	C4—H4	0.9300
N2—H2B	0.8600	C5—H5	0.9300
C1—C2	1.405 (4)		
C5—N1—C1	118.5 (3)	C2—C3—C4	118.9 (3)
C1—N2—H2A	120.0	C2—C3—H3	120.6
C1—N2—H2B	120.0	C4—C3—H3	120.6
H2A—N2—H2B	120.0	C5—C4—C3	117.9 (3)
N1—C1—N2	117.3 (3)	C5—C4—H4	121.0
N1—C1—C2	120.0 (2)	C3—C4—H4	121.0
N2—C1—C2	122.7 (2)	N1—C5—C4	124.0 (3)
C3—C2—C1	120.7 (3)	N1—C5—H5	118.0
C3—C2—C11	120.2 (2)	C4—C5—H5	118.0
C1—C2—C11	119.0 (2)		
C5—N1—C1—N2	-179.0 (3)	C1—C2—C3—C4	0.1 (5)
C5—N1—C1—C2	1.5 (4)	C11—C2—C3—C4	-178.0 (2)
N1—C1—C2—C3	-1.3 (4)	C2—C3—C4—C5	0.9 (5)
N2—C1—C2—C3	179.2 (3)	C1—N1—C5—C4	-0.6 (5)
N1—C1—C2—C11	176.8 (2)	C3—C4—C5—N1	-0.7 (5)

N2—C1—C2—C11 -2.6 (4)

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—H2 <i>A</i> \cdots N1 ⁱ	0.86	2.22	3.051 (5)	162
N2—H2 <i>B</i> \cdots C11	0.86	2.61	3.001 (4)	109

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