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3-Chloropyridin-2-amine

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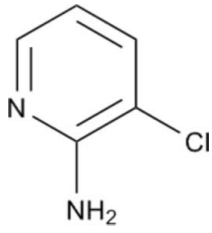
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.004 Å; R factor = 0.059; wR factor = 0.182; data-to-parameter ratio = 14.5.

In the title compound, $C_5H_5ClN_2$, 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 Cl···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

$C_5H_5ClN_2$
M_r = 128.56
Monoclinic, $P2_1/c$
a = 11.149 (8) Å
b = 5.453 (4) Å
c = 9.844 (7) Å
β = 90.581 (12)°
V = 598.5 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.52 mm^{-1}
T = 296 K
0.38 × 0.32 × 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_{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···A	D—H	H···A	D···A	D—H···A
N2—H2A···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).

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supplementary materials

Acta Cryst. (2011). E**67**, o1138 [**doi:10.1107/S1600536811013432**]

3-Chloropyridin-2-amine

Z.-N. Hu, H.-B. Yang, H. Luo and B. Li

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, $C_5H_5Cl_1N_2$ (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···$N_{pyridine}$ 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···Cl interaction [3.001 (3) Å] while in the crystal structure there are also short Cl···Cl^{ii} interactions [3.278 (3) Å] [symmetry code: (ii) -*x* + 2, -*y*, -*z* + 1].

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 recyrstallized from dichloromethane to afford colorless single crystals suitable for X-ray diffraction. Anal.: Calc. for $C_5H_5Cl_1N_2$: 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. ^{1}H NMR($CDCl_3$): 5.02(s,2*H*, NH_2), 6.62(dd,1*H*, pyridine-H), 7.48(dd, 1*H*, pyridine-H), 7.98 (dd, 1*H*, pyridine-H).

Refinement

Although all H atoms were visible in difference maps, they were placed in geometrically calculated positions, with N—H and C—H = o.86 and 0.93 Å respectively, and included in the final refinement in the riding model approximation, with U_{iso}(H) = 1.2U_{eq}(C).

Figures

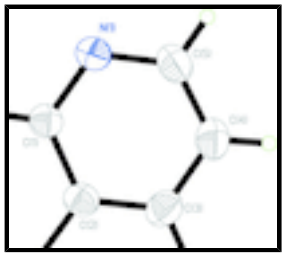

Fig. 1. The molecular structure of (I), showing atom numbering scheme and 30% probability displacement ellipsoids.

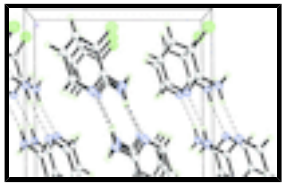

Fig. 2. The packing of (I) in ther unit cell viewed down *b*, showing hydrogen-bonding interactions as dashed lines.

3-Chloropyridin-2-amine

Crystal data

$C_5H_5ClN_2$	$F(000) = 264$
$M_r = 128.56$	$D_x = 1.427$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 1473 reflections
$a = 11.149$ (8) Å	$\theta = 3.7$–$27.2°$
$b = 5.453$ (4) Å	$\mu = 0.52$ mm^{-1}
$c = 9.844$ (7) Å	$T = 296$ K
$\beta = 90.581$ (12)°	Block, yellow
$V = 598.5$ (7) Å^3	0.38 × 0.32 × 0.22 mm
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	1057 independent reflections
Radiation source: fine-focus sealed tube	867 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.048$
φ and ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 1.8°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	$h = -13 \rightarrow 11$
$T_{min} = 0.827$, $T_{max} = 0.894$	$k = -6 \rightarrow 6$
2778 measured reflections	$l = -8 \rightarrow 11$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.059$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.182$	H-atom parameters constrained
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.1147P)^2 + 0.2179P]$ where $P = (F_o^2 + 2F_c^2)/3$
1057 reflections	$(\Delta/\sigma)_{max} < 0.001$
73 parameters	$\Delta\rho_{max} = 0.57$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.31$ e Å^{-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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{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 (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	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, °)

Cl1—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—Cl1	120.2 (2)	C4—C5—H5	118.0
C1—C2—Cl1	119.0 (2)		
C5—N1—C1—N2	−179.0 (3)	C1—C2—C3—C4	0.1 (5)
C5—N1—C1—C2	1.5 (4)	Cl1—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—Cl1	176.8 (2)	C3—C4—C5—N1	−0.7 (5)
N2—C1—C2—Cl1	−2.6 (4)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···N1^{i}	0.86	2.22	3.051 (5)	162
N2—H2B···Cl1	0.86	2.61	3.001 (4)	109

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1.

Fig. 1

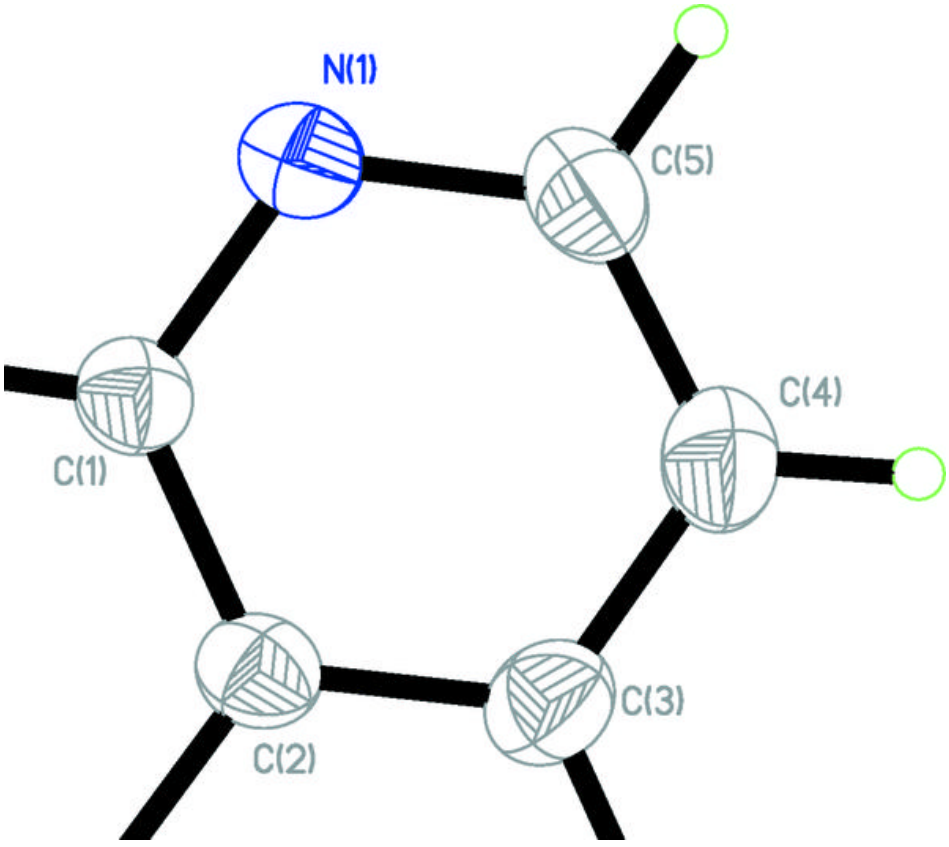

Fig. 2