Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-Amino-7-chloro-1,8-naphthyridine

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.108
Data-to-parameter ratio = 16.0

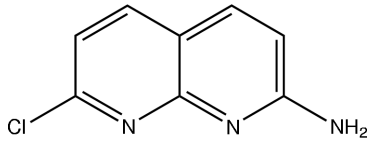
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 11 August 2004
Accepted 24 August 2004
Online 31 August 2004

The title compound, $C_8H_6ClN_3$, has been structurally characterized. Intermolecular N—H···N hydrogen bonds give rise to a dimer structure, which is further extended into a one-dimensional chain parallel to the *a* axis through *π*–*π* interactions.

Comment

In recent years, research on derivatives of 1,8-naphthyridine has been intensive because these compounds show a wide range of biological activities, such as anti-inflammatory activity (Roma *et al.*, 2000), highly selective alkylation and cleavage reagent of DNA (Nakatani, Sando, Kumasawa *et al.*, 2001; Nakatani, Sando, Yoshida & Saito, 2001; Nakatani *et al.*, 2000), molecular beacon (Smith *et al.*, 2002), and antiviral activity (Bachand *et al.*, 2002). As part of our investigation of derivatives of 1,8-naphthyridine, we report here the synthesis and crystal structure of 2-amino-7-chloro-1,8-naphthyridine, (I).



(I)

The C—N and C—C distances in (I) show no remarkable features, with C—N distances in the range 1.307 (2)–1.363 (2) Å; these are shorter than the single-bond distance of 1.480 Å and longer than the typical C=N distances of 1.280 Å, indicating partial double-bond character. This can be interpreted in terms of conjugation in the heterocycle. The title molecule acts as both hydrogen-bond donor and acceptor

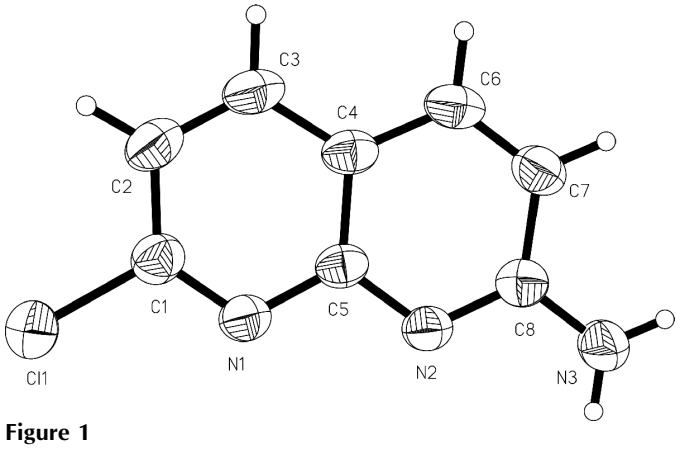


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme

to form a dimer with another molecule through N—H···N hydrogen bonds. There are π–π interactions [the centroid-to-centroid distance is 3.636 (4) Å and the perpendicular distances are 3.354 and 3.356 Å] between dimers that lead to a one-dimensional chain parallel to the *a* axis.

Experimental

The title compound, (I), was prepared using a method similar to that reported by Newkome *et al.* (1981). Malic acid (3 g, 22 mmol) and 2,6-diaminopyridine (2.2 g, 20 mmol) were ground to an intimate powder and cooled in an ice bath, and then concentrated sulfuric acid (10 ml) was added dropwise. The solution was heated at 383 K for 2–3 h, poured over ice and then made alkaline with concentrated ammonium hydroxide (pH 8). 2-Amino-7-hydroxy-1,8-naphthyridine was isolated in 92% yield. A mixture of 2-amino-7-hydroxy-1,8-naphthyridine (3.2 g, 20 mmol), phosphorus pentachloride (4.7 g, 22.5 mmol) and phosphorus oxychloride (5 ml, 54 mmol) was refluxed for 2 h, ice was carefully added and the solution was made alkaline with sodium carbonate. The precipitate was collected and recrystallized from acetone to give (I) in 70% yield. Crystals of (I) suitable for X-ray analysis were grown from an acetone solution (m.p. 452–455 K). ^{1}H NMR (500 Hz, $CDCl_3$, TMS): δ 7.86 (*d, J* = 8 Hz, 1H), 7.84 (*d, J* = 9 Hz, 1H), 7.18 (*d, J* = 8 Hz, 1H), 6.79 (*d, J* = 9 Hz, 1H), 5.50 (*s*, *br*, 2H).

Crystal data

$C_8H_6ClN_3$
M_r = 179.61
Monoclinic, $P2_1/n$
a = 6.906 (7) Å
b = 12.538 (13) Å
c = 9.099 (9) Å
β = 91.012 (17)°
V = 787.7 (14) Å^3
Z = 4
D_x = 1.515 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3155 reflections
θ = 2.8–27.2°
μ = 0.42 mm^{-1}
T = 293 (2) K
Block, orange
0.50 × 0.40 × 0.35 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.816, T_{max} = 0.866
4791 measured reflections
1749 independent reflections
1498 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 27.2°
$h = -8 \rightarrow 8$
$k = -15 \rightarrow 9$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.108
S = 1.05
1749 reflections
109 parameters
H atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2 + 0.2069P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Selected bond distances (Å).

N1—C1	1.307 (2)	C5—C4	1.418 (2)
N1—C5	1.363 (2)	C4—C3	1.398 (2)
N2—C8	1.329 (2)	C4—C6	1.418 (2)
N2—C5	1.354 (2)	C8—C7	1.435 (2)
C2—C3	1.363 (3)	C6—C7	1.344 (3)
C2—C1	1.399 (2)		

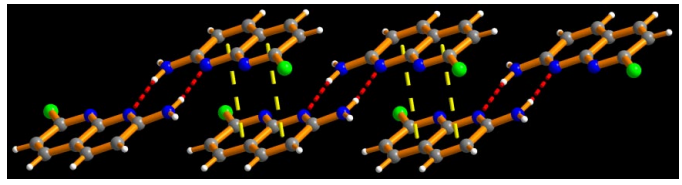


Figure 2
The one-dimensional chain formed by N—H···N hydrogen bonding (red) and π–π interactions (yellow)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···N2^{i}	0.86	2.12	2.974 (3)	172

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

H atoms were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C,N).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

This work was supported by the National Natural Science Foundation of China and the Natural Science Foundation of Guangdong Province. The authors thank Seik Weng Ng for help.

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