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5-Aminopyrimidine

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.001 Å
R factor = 0.039
wR factor = 0.130
Data-to-parameter ratio = 17.3

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

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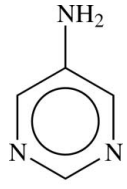
In the title compound, $C_4H_5N_3$, the nearly planar 5-aminopyrimidine molecule has twofold rotation symmetry. The crystal structure is stabilized by a hydrogen bond between the amino group and the ring N atoms, thus forming a two-dimensional network parallel to the *ab* plane.

Comment

Recently, there has been considerable interest in the use of pyrimidine (pym) as a bridging ligand for the formation of coordination polymers. Strong magnetic couplings can be mediated by μ-bonded pym ligands. One-, two- and three-dimensional structural motifs have been studied. For example, $Cu(NO_3)_2(pym)(H_2O)_2$ behaves as a uniform $S = \frac{1}{2}$ antiferromagnetic chain (Feyerherm *et al.*, 2000; Yasui *et al.*, 2001). Structurally, the complex $Cu(dca)(NO_3)(pym)(H_2O)$ (dca = dicyanamide) is two-dimensional, but magnetically it behaves as a one-dimensional chain, because the magnetic coupling through the 3-atom pym bridges is significantly stronger than that through the 5-atom dca bridges (Manson *et al.*, 2003). Examples of structurally three-dimensional materials include $Cu_3(dca)_6(pym)_2\cdot 0.75H_2O$ (Manson *et al.*, 2003) and $Cu(HCO_2)_2(pym)$ (Manson *et al.*, 2005). The former of these has a large exchange coupling constant ($J/k_B = -69.4$ K), while the latter exhibits long-range magnetic ordering below T_N = 2.8 K. Spontaneous magnetization is also observed in the three-dimensional complexes $M(dca)_2(pym)$ (M = Fe or Co), with ordering temperatures of 3.2 and 1.8 K, respectively (Kusaka *et al.*, 2000).



(I)

We are interested in increasing the dimensionality in these systems through the use of pyrimidine derivatives with hydrogen-bonding functionalities. Aminopyrimidines (apym) are one promising family that has this capability. 2-Aminopyrimidine (2-apym) has been used extensively as a ligand in coordination complexes. For example, a novel molecular tube-like structure containing monodentate 2-apym ligands and the relatively rare $\mu_{1,3,5}$ coordination mode for the dca anions has been reported for $M(dca)_2(2\text{-apym})$ (M = Co or Ni) (Jensen *et al.*, 2000). Monodentate 2-apym ligands are also found in the complex $Cu(dca)_2(2\text{-apym})_2$, which forms one-dimensional dibridged $\mu_{1,5}$-dca chains (van Albada *et al.*, 2000). When 2-apym acts as a bridging ligand, strong exchange coupling

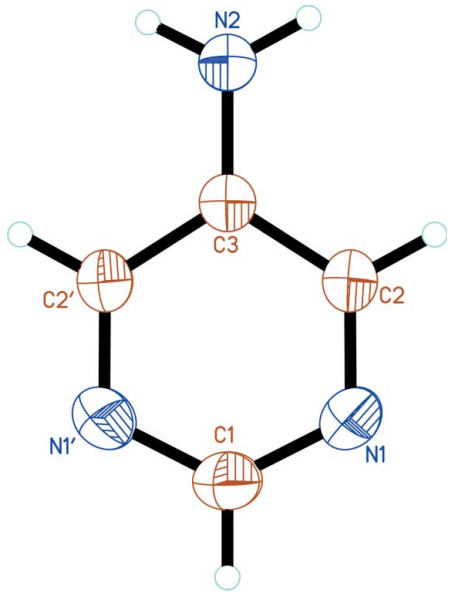


Figure 1
A view of the molecular structure of 5-aminopyrimidine, showing the atom-numbering scheme. The prime corresponds to symmetry code (i) in Table 1. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

contants can be obtained, *e.g.* in $[Cu_4(2\text{-apym})_6(\mu\text{-}OCH_3)_2(\mu\text{-}F)_3(F)_2](BF_4)$ ($J/k_B = -274$ K) (van Albada *et al.*, 2003). Another example of bridging 2-apym ligands is found in the zigzag chain structure of $Cu_2(acetate)_4(2\text{-apym})$ (Smith *et al.*, 1991; Blake *et al.*, 2002). We are aware of no coordination complexes derived from 4-apym or 5-apym. The N atoms of the 2-apym and 4-apym derivatives are more sterically hindered than the 5-apym derivative, thus making 5-apym a promising candidate for a bridging ligand. While the crystal structure of the 4-apym ligand has been published (Van Meervelt & Uytterhoeven, 2003), we report here, for the first time, that of 5-apym, *viz.* (I).

The 5-apym molecule lies on a twofold rotation axis. The atom-numbering scheme is shown in Fig. 1. The bond lengths and angles are typical of pyrimidines, including pym (Wheatley, 1960; Furberg *et al.*, 1979), 2-apym (Scheinbeim & Schempp, 1976; Furberg *et al.*, 1979) and 4-apym (Van Meervelt & Uytterhoeven, 2003). The ring atoms deviate only slightly from coplanarity, with atoms N1 and C2 out of the least-squares plane by 0.0022 (6) Å. By symmetry, the amino N atom lies in the plane of the pym ring. The dihedral angle between the plane of the amino group and the least-squares plane of the ring is 9.4 (17)°, signficantly smaller than the 22° angle observed in 2-apym (Scheinbeim & Schempp, 1976).

As illustrated in Fig. 2, the packing of the 5-apym molecules is stabilized by an N2—H3···N1^{i} hydrogen bond (Table 2). The hydrogen-bond network results in the formation of two-dimensional sheets parallel to the *ab* plane. The pym plane is tilted by 11.50 (6)° with respect to the ***ab*** plane. Adjacent sheets are arranged such that uniform slipped stacks of 5-apym molecules form along the $a + b$ diagonal. The 5-apym centroid–centroid distance of 3.723 Å and perpendicular separation of 3.362 Å confirm the presence of π–π interactions (Spek, 2003).

Experimental

5-Aminopyrimidine was prepared according to the literature procedure of Phillips *et al.* (1999). Single crystals suitable for X-ray diffraction were grown by recrystallization from benzene.

Crystal data

$C_4H_5N_3$
$M_r = 95.11$
Monoclinic, $C2/c$
$a = 7.5982$ (10) Å
$b = 10.1226$ (13) Å
$c = 6.8106$ (10) Å
$\beta = 118.596$ (5)°
$V = 459.93$ (11) Å^3
$Z = 4$
$D_x = 1.374$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1724 reflections
$\theta = 3.4$–29.5°
$\mu = 0.09$ mm^{-1}
$T = 298$ (2) K
Rod, colourless
0.50 × 0.22 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: integration (*XPREP* in *SHELXTL*; Sheldrick, 2001)
$T_{min} = 0.956$, $T_{max} = 0.987$
2534 measured reflections
641 independent reflections
584 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 29.5°$
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 13$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.130$
$S = 1.12$
641 reflections
37 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0723P)^2 + 0.0952P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.3298 (11)	C2—C3	1.3993 (11)
C2—N1	1.3262 (14)	C3—N2	1.3531 (17)
N1—C1—N1^{i}	125.97 (14)	C2—C3—C2^{i}	114.65 (12)
N1—C2—C3	122.97 (9)	C2—N1—C1	116.72 (9)
N2—C3—C2	122.68 (6)	C3—N2—H3	117.7 (12)
N1—C2—C3—N2	179.77 (6)	C3—C2—N1—C1	0.43 (12)
N1—C2—C3—C2^{i}	−0.23 (6)	N1^{i}—C1—N1—C2	−0.21 (6)

Symmetry code: (i) $-x, y, -z+\frac{1}{2}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H3···N1^{ii}	0.89 (2)	2.23 (2)	3.1078 (11)	170 (2)

Symmetry code: (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

H atoms on aromatic C atoms were positioned geometrically and refined with a riding model, with C—H = 0.93 Å. The amino-group H atom was located in a difference map and its position freely refined. For all H atoms, U_{iso}(H) was constrained to be 1.2 (aromatic) or 1.5 (amino) times U_{eq} of the carrier atom.

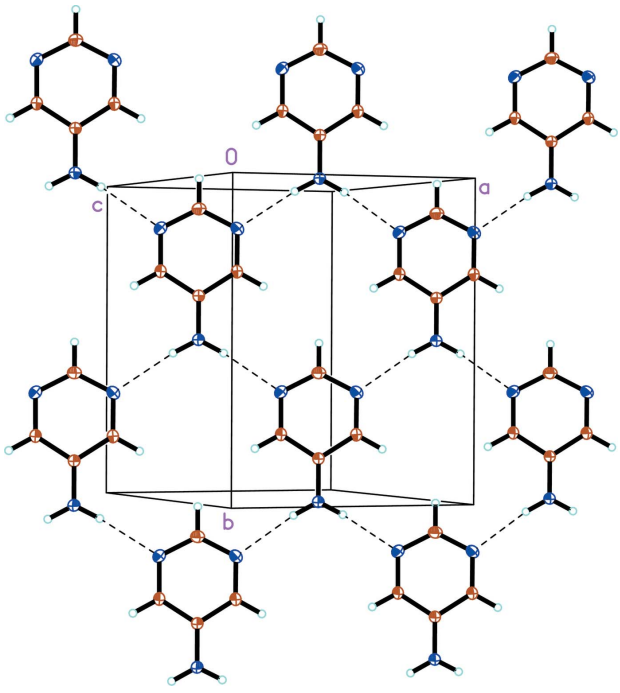


Figure 2
A packing diagram for 5-aminopyrimidine, illustrating the two-dimensional network in the *ab* plane. Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are depicted as dashed lines.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); 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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