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2-Aminopyrimidine*

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Abstract. 2-Aminopyrimidine ($C_4H_5N_3$), orthorhombic, *Pcab*, $a=5{\cdot}709$ (2), $b=10{\cdot}917$ (2), $c=15{\cdot}103$ (2) Å, M.W. 95·11, $Z=8$, $D_x=1{\cdot}342$ g cm^{-3}. The amino-nitrogen to ring-carbon N(2)–C(2) distance is particularly short, 1·342 (2) Å, indicating significantly greater conjugation than in 2-aminopyridine where this distance is 1·351 (2) Å. The structure contains centrosymmetrically related hydrogen-bonded dimer-like pairs separated by hydrophobic regions.

Introduction. The crystal structure of 2-aminopyrimidine was studied to determine the nature of the intermolecular hydrogen bonds and their relationship to the observed anomalous positive temperature dependence of the amino nitrogen nuclear quadrupole resonance (n.q.r.) frequencies (Scheinbeim, 1975). It is also interesting to compare the effect on the amino-ring bond length of two *ortho* N atoms with the case of only a single N atom in 2-aminopyridine (Chao, Schempp & Rosenstein, 1975*a*).

Suitable crystals of 2-aminopyrimidine were obtained by sublimation at room temperature by placing a few grams of the commercial powder in a round-bottomed flask connected to a vacuum pump. After several hours, colorless crystals in the form of hexagonal prisms with dimensions on the order of 0·5 mm grew on the upper walls of the flask. A crystal approximately 0·25 × 0·25 × 0·3 mm was selected and sealed in a capillary to prevent sublimation.

Unit-cell dimensions were obtained at room temperature with a Nonius CAD-4 four-circle computer-controlled diffractometer. Intensity data for 970 reflections ($\sin\theta/\lambda \le 0{\cdot}63$) were collected with a $\theta/2\theta$ scan and graphite-monochromated Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å). There were 211 reflections with integrated intensity less than $2\sigma(I)$ and these were given zero weight in the refinement. The systematic absences $0kl$, $l\neq 2n$, $h0l$, $h\neq 2n$, $hk0$, $k\neq 2n$, $h00$, $h\neq 2n$, $0k0$, $k\neq 2n$, $00l$, $l\neq 2n$ uniquely determined the space group *Pcab*. No corrections were made for absorption or extinction.

The structure was solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1971) based on the 128 reflections with $E\ge 1{\cdot}6$. The resulting E map showed the location of all the non-hydrogen atoms. Isotropic full-matrix least-squares refinement followed by anisotropic refinement and a difference Fourier produced the H atom positions. Two more cycles of anisotropic refinement (isotropic for hydrogen thermal parameters) resulted in a final R value of 0·048 ($R=\sum||F_m|-|F_c||/\sum|F_m|$). The quantity minimized in the refinement was $\sum w||F_m|-|F_c||^2$, with $w=1/\sigma^2$ determined by the counting statistics.† The atomic scattering factors of Cromer & Waber (1965) were used for N and C, and of Stewart, Davidson & Simpson (1965) for H. The final positional and thermal parameters are listed in Table 1.

Discussion. (*a*) *Molecular geometry*. Fig. 1 shows the bond distances and angles and the atomic numbering. When corrected for rigid-body motion (Schomaker & Trueblood, 1968), the bond distances become about 0·009 Å longer (Table 2).

The internal ring angles in 2-aminopyrimidine depart noticeably from 120°. The two CNC angles, 116·2 and 115·7°, are close to the values observed in

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† A list of measured and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31413 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic parameters and their e.s.d.'s for* 2-*aminopyrimidine*

Positional parameters are given as fractional coordinates $\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms. E.s.d.'s given in parentheses refer to the least significant digit of the parameter value. Thermal parameters for the non-hydrogen atoms ($\times 10^4$) are given by the expression: $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$, and for the H atoms by the expression $T=\exp(-2B\sin^2\theta/\lambda^2)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	706 (2)	1140 (1)	3482 (1)	284 (5)	57 (1)	38 (1)	16 (1)	−9 (1)	1 (1)
C(2)	2333 (3)	646 (1)	4022 (1)	257 (5)	60 (1)	32 (1)	12 (2)	4 (1)	2 (1)
N(2)	4088 (2)	1374 (1)	4292 (1)	311 (5)	68 (1)	53 (1)	−21 (2)	33 (2)	8 (1)
N(3)	2318 (2)	−515 (1)	4327 (1)	275 (5)	61 (1)	41 (1)	4 (2)	−5 (1)	3 (1)
C(4)	575 (3)	−1217 (1)	4036 (1)	333 (7)	66 (1)	42 (1)	−14 (2)	2 (2)	2 (1)
C(5)	−1111 (3)	−824 (1)	3456 (1)	304 (7)	91 (1)	44 (1)	−34 (2)	−10 (2)	−2 (1)
C(6)	−974 (3)	387 (1)	3204 (1)	272 (6)	93 (1)	38 (1)	12 (2)	−12 (2)	0 (1)

Table 1 (*cont.*)

	x	y	z	B (Å^2)
H(N2)	432 (2)	208 (1)	395 (1)	4·4 (3)
H′(N2)	534 (3)	107 (1)	465 (1)	4·0 (3)
H(C4)	57 (2)	−207 (1)	429 (1)	4·0 (3)
H(C5)	−243 (3)	−139 (1)	320 (1)	5·2 (4)
H(C6)	−221 (3)	79 (1)	283 (1)	3·8 (3)

Table 2. *Bond lengths* (Å) *and angles* (°) *in* 2-*aminopyrimidine*

Estimated standard deviations are given in parentheses. The atomic numbering is shown in Fig. 1. Square brackets contain bond distances corrected for rigid body motion.

N(1)–C(2)	1·348 (2) [1·357]	N(1)—C(2)–N(3)	125·2 (1)
C(2)–N(2)	1·342 (2) [1·350]	N(1)—C(2)–N(2)	117·5 (1)
C(2)–N(3)	1·349 (2) [1·358]	N(3)—C(2)–N(2)	117·2 (1)
N(3)–C(4)	1·331 (2) [1·339]	C(2)—N(2)–H(N2)	115 (1)
C(4)–C(5)	1·370 (2) [1·379]	C(2)—N(2)–H′(N2)	121 (1)
C(5)–C(6)	1·379 (2) [1·388]	H(N2)–N(2)–H′(N2)	119 (1)
C(6)–N(1)	1·331 (2) [1·338]	C(2)—N(3)–C(4)	115·7 (1)
N(2)–H(N2)	0·94 (2)	C(2)—N(1)–C(6)	116·2 (1)
N(2)–H′(N2)	0·96 (2)	N(3)—C(4)–C(5)	123·8 (1)
C(4)–H(C4)	1·01 (1)	C(4)—C(5)–C(6)	115·9 (1)
C(5)–H(C5)	1·05 (2)	C(5)—C(6)–N(1)	123·1 (1)
C(6)–H(C6)	1·00 (1)		

Hydrogen bonds:

i	j	k	D_{ik}	$\angle_{jik}$
N(2)	H(N2)····	N(1)^{ii}	3·117 (2)	12·9 (2)
N(2)	H′(N2)···	N(3)^{i}	3·073 (2)	8·4 (9)

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

pyrimidine, 115·2 and 115·1° (Wheatley, 1960), but the ring N(1)–C(2)–N(3) angle, 125·2°, is 3° less than the 128·2° observed in pyrimidine. This decrease is probably due to the strong conjugation between the amino group and the ring, which results in an amino nitrogen-to-ring carbon N(2)–C(2) distance of only 1·342 (2) Å, comparable to the average ring C–N distance in nitrogen heterocycles, 1·339 (5) Å (*Interatomic Distances and Configuration in Molecules and Ions*, 1965). A similarly short ring-C to amino-N bond distance is found in aminopyrazine [1·341 (1) Å] (Chao, Schempp & Rosenstein, 1976), but in 2-aminopyridine (Chao, Schemp & Rosenstein, 1975*a*) this distance is 1·351 (2) Å, *i.e.*, about 0·01 Å longer. The greater conjugation in 2-aminopyrimidine relative to 2-aminopyridine had been noted previously by ^{14}N n.q.r. measurements which showed a significantly smaller coupling constant (and therefore a smaller π orbital occupation number) for the amino nitrogen in the pyrimidine (Schempp & Bray, 1971).

Further evidence for the strong conjugation in 2-aminopyrimidine is found in the n.q.r data for the ring N atoms. The asymmetry parameter in pyrimidine (Schempp & Bray, 1967) is 0·386 while in 2-aminopyrimidine it falls to $\sim$0·05. The asymmetry parameters in these cases are a measure of the difference between the nitrogen σ and π bond occupancies, and thus the ring N atoms in 2-aminopyrimidine have much higher π orbital occupation numbers than those in pyrimidine.

In spite of the evident strong amino–ring conjugation in 2-aminopyrimidine, the dihedral angle between the plane of the amino group $(-0{\cdot}316a+0{\cdot}506b+0{\cdot}766c=5{\cdot}063)$ and the least-squares plane of the ring $(-0{\cdot}562a+0{\cdot}271b+0{\cdot}781c=4{\cdot}207)$ is about 22°. In 2-aminopyridine, the corresponding angle is about 7° smaller (15°) (Chao, Schempp & Rosenstein, 1975*a*), which might appear to provide a better geometry for conjugation in the pyridine. Nevertheless, the presence of two electrophilic ring N atoms in 2-aminopyrimidine is evidently more than sufficient to ensure a larger $p\pi$–$p\pi$ interaction than in 2-aminopyridine. Passing to the limit of no ring N atom at all, aniline should display considerably less conjugation. The C–N bond distance, 1·402 Å [microwave determination by Lister, Tyler, Høg & Larsen (1974)] indeed agrees with this expectation, being fully 0·06 Å longer than the corresponding C–N(amino) bond distance in 2-aminopyrimidine. In the case of aniline, the angle between the amino group and the plane of the ring is large, 37·5°. In 2-aminopyridine and 2-aminopyrimidine there is no simple relationship between the n.q.r and bond shortening evidence for conjugation and the amino–ring dihedral angle. This seems to favor an argument given by Dewar (1969) that the existence of considerable $p\pi$

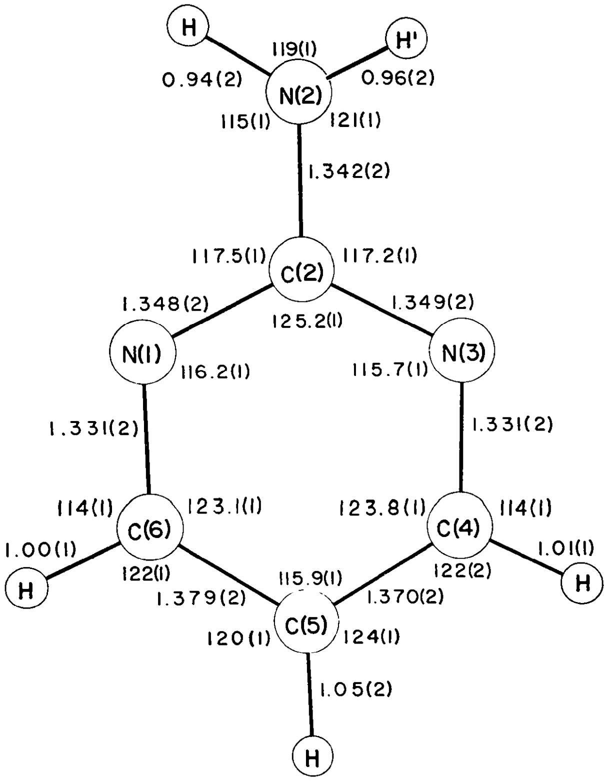

Fig. 1. Bond distances (Å) and angles (°), and atomic numbering in 2-aminopyrimidine.

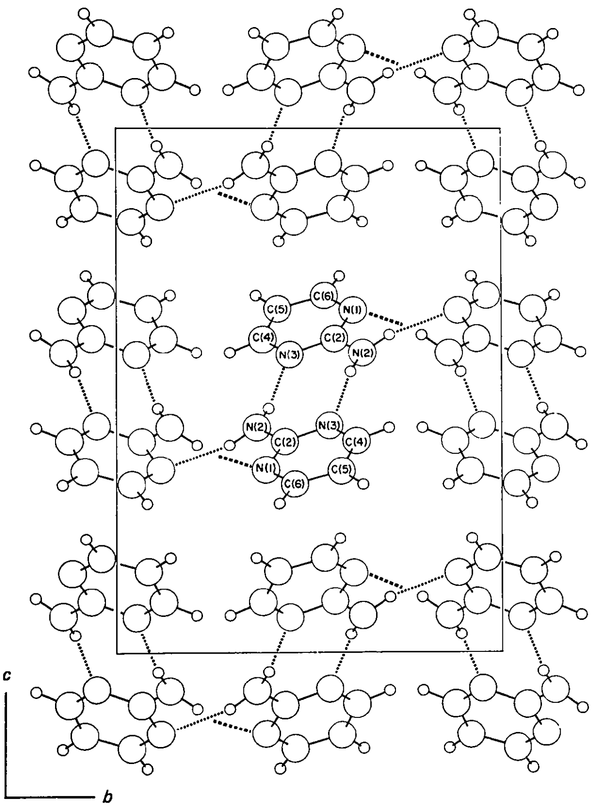

Fig. 2. Projection of the structure of 2-aminopyrimidine down **a**, showing the N(2)–H′(N2)N$\cdots$(3)^{i} dimeric hydrogen bonds and the N(2)–H(N2)$\cdots$N(1)^{ii} bridges between the dimers.

interaction does not imply or require close coplanarity of the amino group with the ring.

The ring atoms deviate slightly from the least-squares plane resulting in a shallow boat conformation. C(6) and N(3) are essentially on the plane (+0·002 and +0·004 Å), N(1) and C(4) are above (+0·014 and +0·013 Å), whereas C(2) and C(5) are below (−0·017 and −0·015 Å). While this departure from planarity is not great, it is somewhat larger than observed in aminopyrazine (Chao, Schempp & Rosenstein, 1976) and in 2-, 3-, and 4-aminopyridine (Chao, Schempp & Rosenstein, 1975*a*, *b*), where the maximum deviation of a ring atom rarely exceeds 0·008 Å. Pyrimidine itself is highly planar, the maximum displacement being 0·004 Å for C(2). The amino nitrogen N(2) is significantly below the plane (−0·047 Å).

According to Domenicano, Vaciago & Coulson (1975), the shortening of the C(2)–N(2) bond distance caused by conjugation produces an increase in *s* character in the carbon C(2)–N(2) σ orbital, thus increasing the *p* character of the two C(2) ring orbitals and leading to a consequent decrease in the N(1)–C(2)–N(3) angle. The C(2)–N(1) and C(2)–N(3) bonds should then be longer than the corresponding C–N bonds in pyrimidine owing to the increased *p* character in these orbitals. The average C(2) to ring nitrogen bond distance in 2-aminopyrimidine is 1·349 (2) Å (1·358 Å when corrected for thermal motion), and in pyrimidine the corresponding C–N bond length averages 1·315 (7) Å (1·335 Å when corrected for thermal motion). The difference of 0·02 Å illustrates the expected increase.

(*b*) *Hydrogen bonding*. The structure contains two crystallographically non-equivalent hydrogen bonds. The first, N(2)–H′(N2)$\cdots$N(3)^{i}, together with its centrosymmetrically-related mate, connects two molecules forming a dimeric unit shown in Fig. 2 (i denotes the symmetry operation $-x, -y, -z$). The N(2)$\cdots$N(3)^{i} distance is 3·073 (2) Å and the H′(N2)–N(2)$\cdots$N(3)^{i} angle is 8·4 (9)°. A similarly hydrogen-bonded dimer is observed in the structure of 2-amino-4,6-dichloropyrimidine (Clews & Cochran, 1948) and in one of the tautomeric base pairs in the structure of isocytosine (Sharma & McConnell, 1965).

The second hydrogen bond, N(2)–H(N2)$\cdots$N(1)^{ii} forms bridges between dimer pairs (ii denotes the symmetry operation $\frac{1}{2}+x, \frac{1}{2}-y, z$), resulting in regions of three-dimensionally hydrogen-bonded dimers separated by hydrophobic regions (Fig. 2). The N(2)$\cdots$N(1)^{ii} distance is 3·117 (2) Å and the H(N2)–N(2)$\cdots$N(1)^{ii} angle is 12·9 (9)°. The hydrogen-bonding scheme is shown in Fig. 2, a projection of the structure down **a**. Hydrogen-bond distances and angles are listed in Table 2.

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