

Aminopyrazine*

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Abstract. $C_4H_5N_3$, $P2_1/c$, monoclinic, $a=6.286$ (3), $b=10.238$ (2), $c=7.370$ (2) Å, $\beta=93.08$ (3)°, M.W. 95.11, $Z=4$, $D_m=1.30$, $D_x=1.306$ g cm⁻³. The amino nitrogen-to-ring carbon distance is unusually short, 1.341 (1) Å, consistent with a high degree of conjugation. The ¹⁴N nuclear quadrupole resonance frequencies are also reported and these show clear differences in the charge distributions at the *ortho* and *meta* ring N atoms.

Introduction. The electronic structure of aminopyrazine is of interest because the conjugation of the amino group with the ring can be monitored both at the *ortho* and *meta* ring N using ¹⁴N nuclear quadrupole resonance (n.q.r.). Aminopyrazine is one of a number of simple amino N heterocycles in which the amino n.q.r. lines anomalously increase in frequency with increasing temperature (Chao, 1975; Scheinbeim, 1975). The crystal structure was undertaken to aid in the analysis of the n.q.r. results and to compare the amino-ring bond lengths with those in 2- and 3-aminopyridine (Chao, Schempp & Rosenstein, 1975).

Single crystals were prepared by evaporating an acetone solution to dryness. Preliminary unit-cell constants were determined from oscillation and Weissenberg photographs, with the crystal mounted along [100] and [010]. Systematic absences $0k0$ for $k=2n+1$ and $h0l$ for $l=2n+1$ determined the space group as $P2_1/c$.

A crystal approximately $0.2 \times 0.2 \times 0.3$ mm was selected for data collection and sealed in a capillary tube to prevent sublimation. Intensity data were measured on a four-circle computer-controlled Nonius CAD-4 diffractometer using graphite-monochromated Cu $K\alpha$ radiation ($\lambda=1.5418$ Å). Integrated intensities for 980 independent reflections were measured in the range $\theta \leq 75^\circ$ with the $\theta/2\theta$ scan method. There were 187 reflections with integrated intensity less than $2\sigma(I)$, and these were assigned intensities $\sigma(I)/2$ and given zero weight during the refinement. No corrections were made for absorption or extinction.

The structure was solved by direct methods, using the phase extension and tangent refinement programs *DP-3* and *DP-5* (Hall, 1967). The atomic parameters were refined by the full matrix least-squares method (Shiono, 1970) with anisotropic temperature factors for the non-hydrogen atoms and isotropic ones for the H atoms. The quantity minimized was $\sum w(|F_m| - |F_c|)^2$ with $w=1/\sigma^2$, where σ is the standard deviation of the structure factor from counting statistics (Shiono, 1971). The atomic scattering factors for C and N were taken from Cromer & Waber (1965), while those for H were from Stewart, Davidson & Simpson (1965). The final $R(\sum |F_m| - |F_c| / \sum |F_m|)$ is 0.045 for all reflections.† The final positional and thermal parameters, with their estimated standard deviations, are listed in Table 1,

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† A list of structure factors has been deposited with the British Library Division as Supplementary Publication No. SUP 31334 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.

Table 1. Atomic parameters in aminopyrazine

Positional parameters are given as fractional coordinates. Anisotropic thermal parameters are given according to the expression $T = \exp(-\sum \beta_{ij} h_i h_j)$ and isotropic thermal parameters according to the expression $T = \exp(B \sin^2 \theta / \lambda^2)$. Estimated standard deviations given in parentheses refer to the last significant figures in parameter values. Carbon and nitrogen positional and thermal parameters are $\times 10^4$, hydrogen positional parameters are $\times 10^3$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	
N(1)	677 (1)	-1731 (1)	4274 (1)	216 (2)	91 (1)	202 (2)	-14 (1)	52 (2)	-12 (1)	
C(2)	2451 (1)	-1189 (1)	3719 (1)	195 (3)	83 (1)	162 (2)	-1 (1)	21 (2)	-2 (1)	
C(3)	4125 (2)	-1990 (1)	3118 (2)	216 (3)	90 (1)	207 (2)	6 (1)	47 (2)	-8 (1)	
N(4)	3998 (1)	-3268 (1)	3077 (1)	319 (3)	95 (1)	223 (2)	17 (1)	56 (2)	-18 (1)	
C(5)	2193 (2)	-3799 (1)	3641 (2)	384 (4)	82 (1)	253 (3)	-12 (2)	89 (3)	-17 (1)	
C(6)	583 (2)	-3035 (1)	4229 (2)	310 (3)	95 (1)	231 (3)	-38 (2)	84 (2)	-13 (1)	
N(7)	2637 (1)	117 (1)	3764 (1)	225 (2)	80 (1)	310 (3)	3 (1)	89 (2)	6 (1)	
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>		
H(3)	546 (2)	-160 (1)	278 (2)	5.5 (3)	H(7A)	162 (2)	55 (1)	426 (2)	5.1 (3)	
H(5)	209 (2)	-474 (2)	357 (2)	5.0 (3)	H(7B)	376 (2)	49 (1)	330 (2)	6.6 (3)	
H(6)	-77 (2)	-344 (1)	460 (2)	4.5 (3)						

and Fig. 1 shows the interatomic bond distances and angles along with the atomic numbering scheme.

Discussion. The aminopyrazine molecule in the solid has the amino configuration with the NH_2 group attached to a planar pyrazine ring. The least-squares plane of the ring is given by $2.234x - 0.420y + 6.732z = 3.102 \text{ \AA}$ (where x, y, z are fractional coordinates of the crystal axes) with a standard deviation of 0.002 \AA (Fig. 2). The amino N is slightly above (0.016 \AA) this plane, one of the amino hydrogens $\text{H}(7A)$ is substantially above (0.101 \AA), and another amino hydrogen $\text{H}(7B)$ lies somewhat below (-0.067 \AA). The angle between the plane of the pyrazine ring and the plane of the NH_2 groups is 6° . $\text{N}(1)\text{--C}(2)$ and $\text{N}(1)\text{--C}(6)$ differ only slightly, 1.330 and 1.336 \AA , but $\text{N}(4)\text{--C}(3)$ and $\text{N}(4)\text{--C}(5)$ are significantly different (1.311 and 1.344 \AA). The two CNC bond angles of the ring are equal in terms of their e.s.d.'s and about 1.4° larger than the CNC angle in pyrazine (Wheatley, 1957).

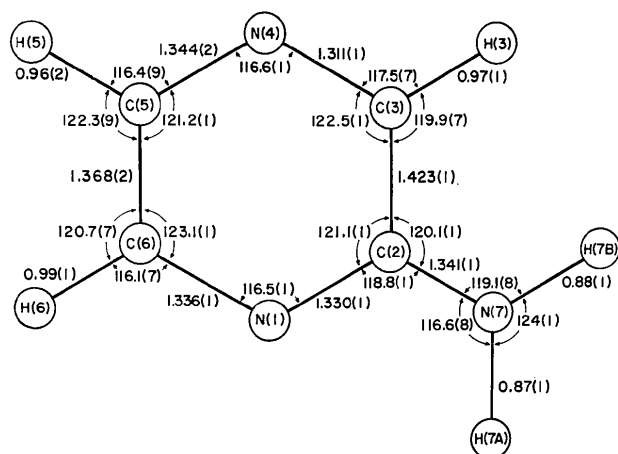


Fig. 1. Bond lengths (\AA) and angles ($^\circ$) and atomic numbering in aminopyrazine. The corresponding e.s.d.'s given in parentheses refer to the last decimal positions.

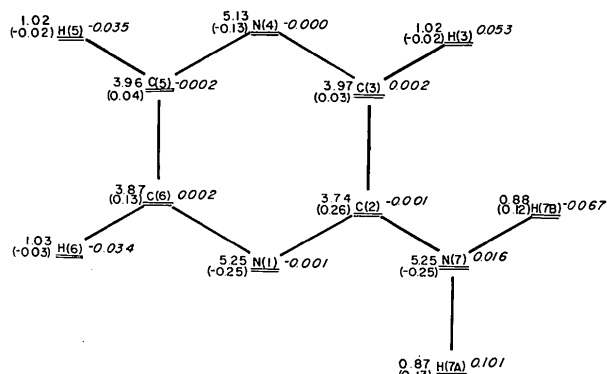


Fig. 2. Displacements (\AA) from the least-squares plane through the pyrazine ring (italic numbers), and the total valence charge in electron units of each atom by INDO. The numbers shown in parentheses are net charges on each atom (a positive value means electron deficit; negative means electron excess).

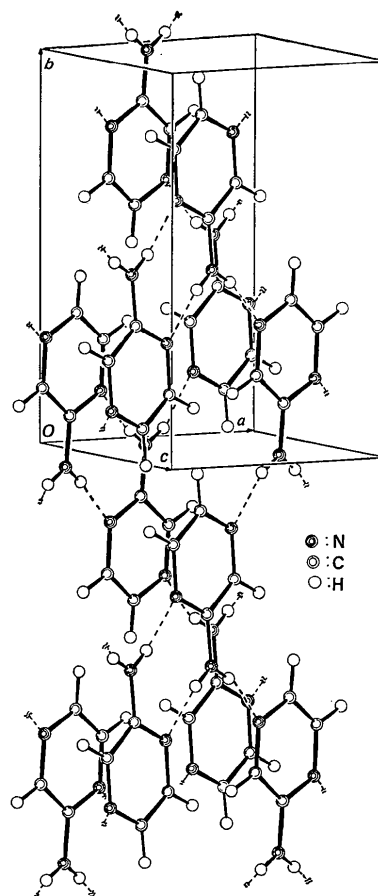


Fig. 3. Packing diagram of aminopyrazine. The dotted lines are hydrogen bonds.

The high degree of conjugation expected in aminopyrazine is confirmed by the very short amino-ring $\text{N}(7)\text{--C}(2)$ distance, 1.341 \AA . This is much shorter than the amino-ring distances in 2-aminopyridine, 1.351 \AA , and 3-aminopyridine, 1.384 \AA (Chao, Schempp & Rosenstein, 1975), and is very close to the value in 2-aminopyrimidine, 1.342 \AA (Scheinbeim & Schempp, 1976). In 2-amino-3-chloropyrazine the amino bond length is noticeably longer, 1.366 \AA (Morrow & Huddle, 1972).

The crystal structure contains hydrogen-bonded dimers and zigzag chains (Figs. 3 and 4) which use all the H atoms capable of hydrogen bonding. The hydrogen-bonded dimers are related by centrosymmetry, and thus the two molecules of the dimer are parallel to each other; the perpendicular distance between the parallel planes is 0.52 \AA . Similar pairs of centrosymmetrically related hydrogen bonds are found in several complexes of biological interest, for example, guanine hydrochloride monohydrate II and isocytosine (Voet & Rich, 1970 and references therein). $\text{H}(7A)$ is involved in the dimeric hydrogen bond $\text{N}(7)\text{--H}(7A)\cdots\text{N}'(1)$ ($-x, -y, 1-z$) with N--N $3.080(3) \text{ \AA}$ and

\angle NHN 173 (1)°. The other amino hydrogen, H(7B), is hydrogen bonded to N(4) ($1-x, \frac{1}{2}+y, \frac{1}{2}-z$) with N(7)-H(7B)···N(4) 3.060 (2) Å and \angle NHN 167 (1)°. This hydrogen bond links the molecules head-to-tail to form zigzag chains parallel to **b**. Adjacent molecules in the same chain are not parallel to each other, but are tilted about 4.7°.

The chains, which are antiparallel to each other and related by the *c*-glide, are stacked on one another along **c** so that the planes of rings overlap. No hydrogen bonds exist within the stacks and so only van der Waals interactions exist between the antiparallel chains. Each of the chains is coordinated with four other chains and cross-linked to two of the four chains by the dimeric hydrogen bonds so that the molecules form a two-dimensional sheet; these sheets are stacked on one another to form the packing unit. For each sheet there exist alternating zones of dimeric hydrogen bonds and non-dimeric hydrogen bonds. The closest contacts between the sheets are N(1) (x, y, z)···C(5) ($x, -\frac{1}{2}-y, \frac{1}{2}+z$) at 3.351 (2) Å and C(2) (x, y, z)···N(4) ($x, -\frac{1}{2}-y, \frac{1}{2}+z$) at 3.352 (2) Å. These distances between the aromatic planes are close to the interlayer separation in graphite, 3.355 Å (Trucano & Chen, 1975).

The ^{14}N n.q.r. spectrum in aminopyrazine shows six resonance lines which were matched to ν_{\pm} pairs using a selective-saturation double resonance technique (Chao, 1975). The nuclear quadrupole coupling constants $e^2qQ = \frac{2}{3}(\nu_+ + \nu_-)$ and asymmetry parameters $\eta = 3(\nu_+ - \nu_-)/(\nu_+ + \nu_-)$ are given in Table 2. The n.q.r. indicates three distinct nitrogens, one similar to that in pyrazine or pyridine, one characteristic of the ring N in 2-aminopyridine, and a strongly conjugated amino N (Schempp & Bray, 1970), which are assigned, then, to N(4), N(1), and N(7), respectively. The n.q.r. results show that the overall loss of π charge from the amino N in aminopyrazine is larger than in the mono-aminopyridines. The amino-ring bond length appears to correlate with the n.q.r.-derived π -electron gain on the ring N(1) nitrogen in the aminopyridines and aminopyrazine (Chao & Schempp, 1975).

Table 2. The ^{14}N n.q.r. frequencies ν_{\pm} , coupling constants e^2qQ , and asymmetry parameters η in aminopyrazine at 77 K

	ν_{\pm} (kHz)	e^2qQ (kHz)	η
N(1)	2996.4	3883.4	0.0864
	2828.7		
N(4)	4133.7	4707.2	0.5127
	2927.1		
N(7)	2827.6	3319.2	0.4076
	2151.2		

The charge densities on aminopyrazine were calculated by the INDO method (Pople, Beveridge & Dobosh, 1967) giving the values shown in Fig. 2. The calculated dipole moment is 1.71 D compared with the

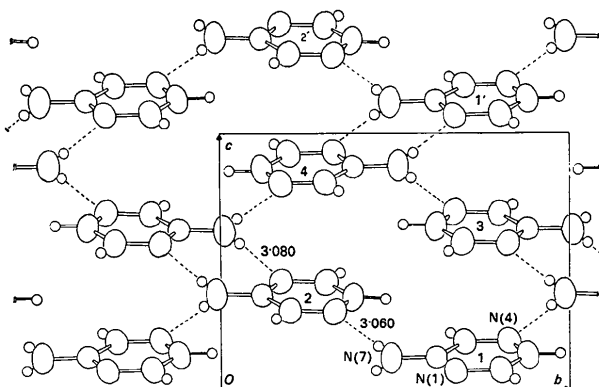


Fig. 4. One sheet of the packing unit in aminopyrazine. The symmetry code is (1) ($x, \frac{1}{2}-y, \frac{1}{2}+z$), (2) ($-x, -y, 1-z$), (3) ($x, 1+y, z$), (4) ($1-x, \frac{1}{2}+y, \frac{1}{2}-z$), (1') ($-1+x, -\frac{1}{2}-y, \frac{1}{2}+z$), (2') ($-1-x, -1-y, 1-z$).

measured value of 1.97 D (Lumbroso & Barassin, 1965). The electron excess at each N is about one-half that found from a population analysis based upon the n.q.r. parameters (Chao & Schempp, 1976).

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