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2-Aminopyridine*

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Abstract. $C_5H_6N_2$, monoclinic, $P2_1/c$, $a=11{\cdot}709$ (4), $b=5{\cdot}673$ (6), $c=7{\cdot}594$ (6) Å, $\beta=95{\cdot}55$ (4)°, M.W. 94·12, $Z=4$, $D_m=1{\cdot}24$, $D_x=1{\cdot}248$ g cm^{-3}. The molecules form hydrogen-bonded dimers in centrosymmetrically related pairs *via* N(7)–H(7*A*)···N′(1) hydrogen bonding [3·071 (7) Å]; the dimers stack along **b**. Charge densities on each atom site and dipole moments are derived from an INDO calculation.

Introduction. ^{14}N nuclear quadrupole resonance (n.q.r.) studies of amino heterocyclic compounds have revealed frequency shifts and unusual temperature-dependent effects which appear to be connected with conjugation and hydrogen bonding (Chao, 1975; Scheinbeim, 1975). In order to clarify how n.q.r. data may be related to structural and chemical details, we have undertaken a series of X-ray structure analyses on aminopyridines, aminopyrimidines, and aminopyrazines.

Colorless, plate-shaped crystals of 2-aminopyridine were grown by slow evaporation from an ether solution. A single crystal with approximate dimensions 0·3 × 0·3 × 0·4 mm was selected and sealed in a capillary tube to prevent sublimation. From indexed Weissenberg photographs, the systematic absences *h*0*l* for *l* odd and 0*k*0 for *k* odd uniquely determined the space group to be $P2_1/c$. Three-dimensional integrated intensity data were collected on a Nonius CAD-4 computer-controlled four-circle diffractometer using graphite-monochromated Cu *Kα* radiation ($\lambda=1{\cdot}5418$ Å). Integrated intensities for 1027 independent reflections were collected with the $\theta/2\theta$ scan method in the range $\theta\le75°$, which yielded 241 reflections with integrated intensity less than $2\sigma(I)$. These were assigned intensity $I=\sigma(I)/2$, and were given zero weight during the refinement. No corrections were made for absorption or extinction.

The structure was solved by studying the Patterson–Harker section $(U,\frac{1}{2},W)$ and lines $(0,V,\frac{1}{2})$ and confirmed by multiple minimum functions calculated with a Patterson multiple superposition program, *MINJ* (Abola, 1973). All H atom positions were obtained from a difference Fourier synthesis, calculated after several cycles of refinement had been made for the heavy atom (C, N) isotropic thermal parameters. Refinement of the atomic parameters (Table 1) was carried out by full-matrix least-squares methods using anisotropic temperature factors for the non-hydrogen atoms and isotropic factors for the H atoms. The atomic scattering factors used were those of Cromer & Waber (1965) for N and C, and of Stewart, Davidson & Simpson (1965) for H. The function minimized was $\sum w(|F_o|-|F_c|)^2$, with $w=1/\sigma^2(F_o)$ derived from counting statistics (Shiono, 1971). The seven strongest reflections showed large ratios of F_c/F_o, and were given zero weight. The final $R=\sum(|F_o|-|F_c|)/|F_o|$ gave 0·068

Table 1. *Atomic parameters for 2-aminopyridine*

Positional parameters are given as fractions of the lattice translation. Thermal parameters are given according to the expression $T=\exp\,(-\sum_i\sum_j\beta_{ij}h_ih_j)$, and isotropic temperature factors to the expression $T=\exp\,(-B\sin^2\theta/\lambda^2)$. Estimated standard deviations given in parentheses refer to the least significant figure in parameter values. N and C positional and thermal parameters × 10^4; H positional parameters × 10^3. H thermal parameters are in Å^2.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	−1531 (1)	5663 (2)	4867 (2)	69 (1)	256 (4)	171 (2)	−3 (1)	1 (1)	−27 (2)
C(2)	−1730 (1)	3669 (3)	3928 (2)	74 (1)	243 (5)	137 (3)	−8 (2)	4 (1)	−3 (3)
C(3)	−2840 (1)	3044 (3)	3211 (2)	81 (1)	293 (6)	155 (3)	−37 (2)	−1 (1)	−8 (3)
C(4)	−3730 (1)	4507 (3)	3485 (2)	66 (1)	438 (6)	177 (3)	−24 (2)	−4 (2)	40 (3)
C(5)	−3534 (1)	6564 (3)	4436 (2)	72 (1)	370 (5)	188 (3)	27 (2)	14 (2)	34 (3)
C(6)	−2431 (1)	7054 (3)	5089 (2)	81 (2)	258 (4)	174 (3)	10 (2)	13 (2)	−3 (3)
N(7)	−810 (1)	2289 (3)	3736 (2)	84 (1)	348 (5)	284 (4)	22 (2)	−3 (2)	−126 (4)

	x	y	z	B		x	y	z	B
H(3)	−293 (2)	159 (3)	257 (2)	4·4 (4)	H(6)	−224 (1)	853 (3)	582 (2)	4·8 (3)
H(4)	−452 (2)	414 (3)	299 (2)	5·8 (4)	H(7*A*)	−11 (2)	281 (3)	403 (3)	6·8 (5)
H(5)	−413 (2)	768 (3)	464 (3)	6·4 (4)	H(7*B*)	−88 (2)	105 (4)	302 (2)	5·2 (4)

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for all reflections and 0·037 for those reflections with non-zero weight.*

Discussion. The pyridine ring atoms are coplanar; the equation of the plane is $-2{\cdot}637x-2{\cdot}787y+6{\cdot}525z=1{\cdot}998$ Å with standard deviation 0·004 Å. The deviations of the atoms from this plane are shown in Fig. 1. The sum of the bond angles at the amino N atom is 357·3°, which indicates that the amino N is close to a planar sp^2 configuration. The angle between the plane of the ring and the plane determined by the NH_2 group is 15°. The amino N is, however, virtually coplanar with the ring (0·016 Å), but the amino H atoms lie 0·122 and 0·089 Å away from that plane on the same side of it. It is interesting to note that a recent microwave study of 2-aminopyridine (Kydd & Mills, 1972) has shown that in the free molecule, the amino-to-ring angle is almost two times larger (31·6°) than in the solid.

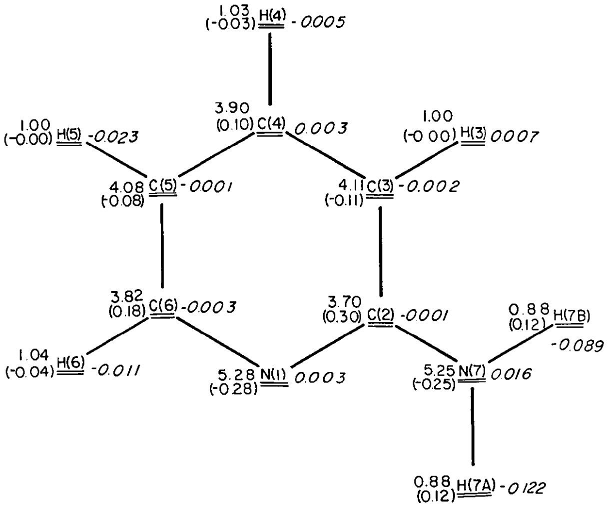

Fig. 1. Distances (Å) from the least-squares plane through the pyridine ring (italic numbers), and the total valence charge in electron units of each atom by INDO calculation. The numbers shown in parentheses are net charges on each atom (positive value means electron deficit; negative means electron excess).

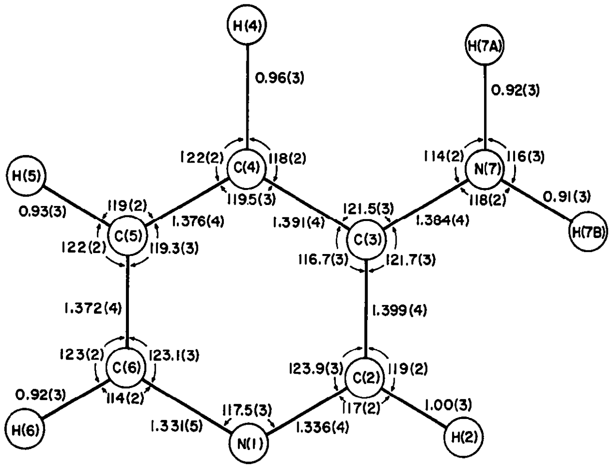

Fig. 2. Bond distances (Å) and angles (°) in 2-aminopyridine. Corresponding e.s.d.'s given in parentheses refer to the last digit.

The bond lengths and angles are shown in Fig. 2. The molecular configuration is quite similar to that of the 2-aminopyridine molecule in the 2:1 complex of 2-aminopyridine with 5,5-diethylbarbituric acid (Hsu & Craven, 1974), except that in the complex the N(1)–C(2) and N(1)–C(6) bonds are more unequal and the amino group in the complex is somewhat more pyramidal. The amino nitrogen-to-ring bond length N(7)–C(2) in 2-aminopyridine is only 1·351 (2) Å, and is almost as short as the N–C distances within the ring (1·340 and 1·345 Å), all of the three distances being well within the 1·43 Å given for the N–C single bond covalent radius (Kennard *et al.*, 1972). This suggests a considerable degree of double-bond character between N(7) and C(2) due to conjugation with the ring.

The molecules are linked together in centrosymmetric dimers *via* pairs of N(7)–H(7*A*)···N′(1) [$-x$, $1-y$, $1-z$] hydrogen bonds with a N–H···N′ angle of 171 (2)° and N···N′ distance of 3·071 Å. Only this one amino H atom participates in hydrogen bonding. The two molecules of the dimer are necessarily parallel to each other by symmetry, but they are not coplanar, the two planes being offset from each other by 0·259 Å.

The stacking of the parallel dimers forms an infinite column parallel to the symmetry axis, *i.e.*, the **b** axis (Fig. 3). Viewed along the **a** axis, the packing forms a herring-bone pattern with an angle of 58·9° between the two sets of planes, which are related by the twofold screw axis. No overlapping occurs within the stacks. Except for the N′(1)···N(7) hydrogen-bond distances, all the other intermolecular contacts are larger than the sum of the van der Waals radii. The crystal structure as a whole is similar to 2-amino-5-chloropyridine (Kvick & Backéus, 1974).

The charge density of each of the atoms in 2-aminopyridine and the dipole moment of the molecule were estimated using the INDO approximation (Pople, Beveridge & Dobosh, 1967) with the observed atomic coordinates, giving the results shown in Fig. 1. The calculated dipole moment 2·10 D agrees fairly well with the observed value 2·04 D measured in benzene solution (Barassin & Lumbroso, 1961). However, this value for the dipole moment is twice that found by microwave spectroscopy (0·96 D) by Kydd & Mills (1972), who recognized the discrepancy but referred to a self-consistent-field theory calculation (Carper & Stengl, 1970) which gave 0·999 D to substantiate their result and they then ascribed the higher value found in

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31299 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

solution to complex formation with the solvent. The ring charge distribution can be explained by a resonance structure in which the lone pair electrons of the amino N are strongly conjugated with the ring, which is consistent both with the shortened bond length between N(7) and C(2), and with the low value of the ^{14}N nuclear quadrupole coupling constant for the ring N (Marino, Guibé & Bray, 1968).

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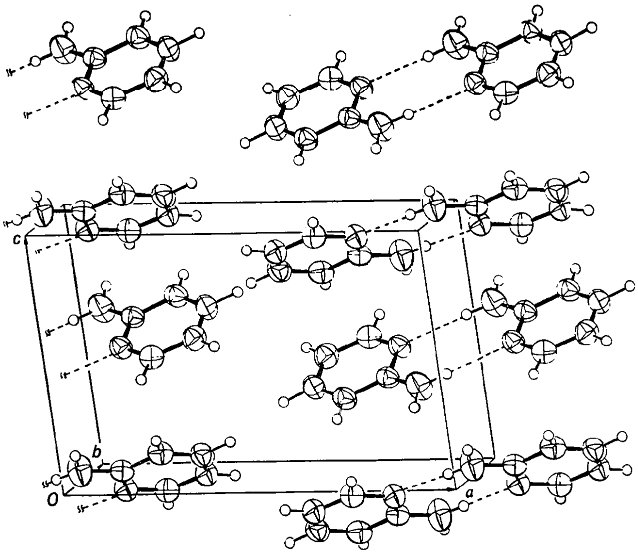

Fig. 3. The packing diagram of the dimers.

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3-Aminopyridine*

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Abstract. $C_5H_6N_2$, monoclinic, *Cc*, $a=6{\cdot}186\,(4)$, $b=15{\cdot}298\,(6)$, $c=5{\cdot}713\,(3)$ Å, $\beta=110{\cdot}54\,(2)°$, M.W. 94·12, $Z=4$, $D_m=1{\cdot}24$ (flotation in carbon tetrachloride and hexane mixture), $D_x=1{\cdot}246$ g cm^{-3}. The molecules are joined head-to-tail *via* very weak N–H···N hydrogen bonds to form infinite chains parallel to **a**. The amino group makes a dihedral angle of 32° with the least-squares plane of the ring. The amino–ring bond length is short enough (1·384 Å) to indicate significant double-bond character, but is nonetheless noticeably longer than in 2- and 4-aminopyridine.

Introduction. As indicated in the preceding paper, aminopyridines, -pyrimidines, and -pyrazines are of interest in ^{14}N n.q.r. studies because they present relatively simple cases where the chemical reasonableness of semi-empirical interpretations of n.q.r. data may be examined (Schempp & Bray, 1970). Recently we have found that the frequencies of the amino nitrogen n.q.r. lines in several compounds increase with increasing temperature, contrary to the usual situation, apparently due to the combined effects of conjugation and hydrogen bonding (Chao, 1975; Scheinbeim, 1975). The crystal structure of 3-aminopyridine was determined in conjunction with these studies.

Colorless, blade-shaped crystals of 3-aminopyridine were obtained by slow evaporation from methanol; a single crystal with approximate dimensions 0·2 × 0·2 ×

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