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).

Fig. 3. The packing diagram of the dimers.

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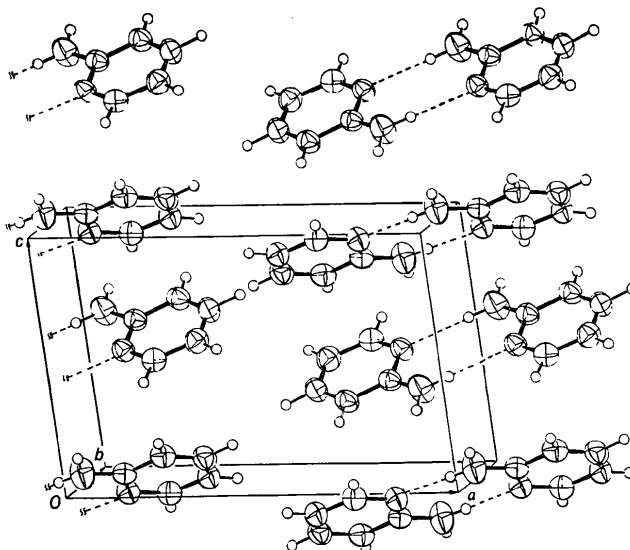MARINO, R., GUIBÉ, L. & BRAY, P. J. (1968). J. Chem. Phys. 49, 5104–5107.

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3-Aminopyridine*

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Abstract. $C_5H_6N_2$, monoclinic, Cc, $a=6\cdot186$ (4), $b=15\cdot298$ (6), $c=5\cdot713$ (3) Å, $\beta=110\cdot54$ (2)°, M.W. 94·12, $Z=4$, $D_m=1\cdot24$ (flotation in carbon tetrachloride and hexane mixture), $D_x=1\cdot246$ g cm^{-3}. The molecules are joined head-to-tail via very weak N–H$\cdots$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 ×

0·3 mm was selected and sealed in a capillary tube to avoid sublimation. From indexed Weissenberg photographs, the systematic absences for *hkl*, *h* + *k* odd, for
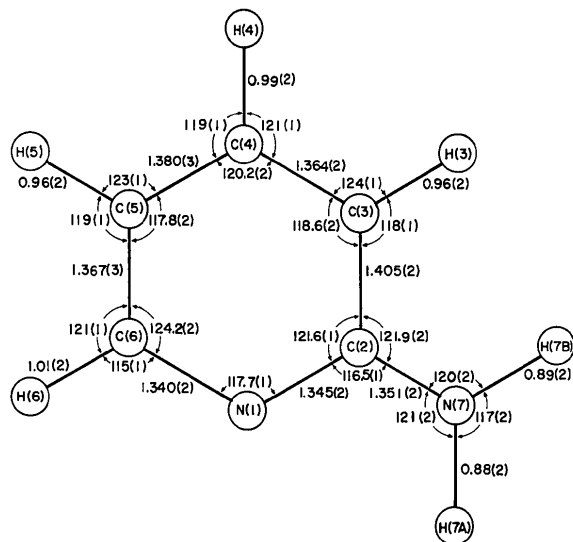

Fig. 1. Bond lengths (Å) and angles (°) in 3-aminopyridine. Corresponding e.s.d.'s given in parentheses refer to the last digit.
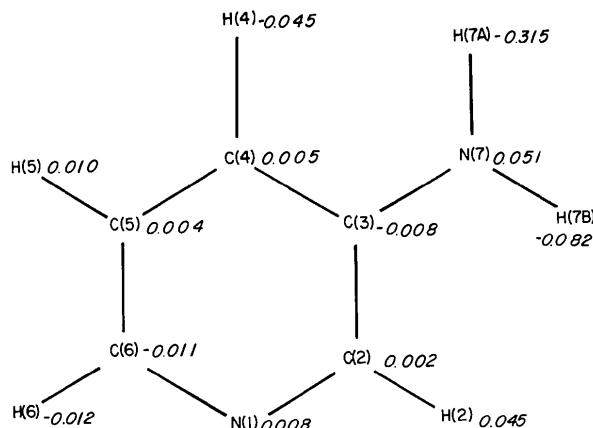

Fig. 2. Displacements (Å) from the least-squares plane through the pyridine ring.

h0l, *l* odd, and for 0*k*0, *k* odd, give the permissible space groups *Cc* and *C2/c*. The statistical distribution of *E* values indicated the non-centrosymmetric alternative, *Cc*.

Intensity data were measured on a Nonius CAD-4 computer-controlled four-circle diffractometer, using graphite-monochromated Cu *Kα* radiation ($\lambda = 1·5418$ Å). Integrated intensities for 573 independent reflections ($\theta \leq 75°$) were collected with the $\theta/2\theta$ scan method. There were 28 reflections with integrated intensity (I) smaller than $2\sigma(I)$, and these were assigned intensities $I = \sigma(I)/2$ and given zero weight during the refinement. No corrections were made for absorption or extinction.

The structure was solved by direct methods on all reflections with $E > 1·4$, using *MULTAN* (Germain, Main & Woolfson, 1971). The full-matrix least-squares refinement, with anisotropic temperature factors for C and N and isotropic temperature factors for H minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma)^2$, σ being the standard deviation of the intensity (Shiono, 1971). H atom positions were located on a difference map. The atomic scattering factors used were those of Cromer & Waber (1965) for C and N, and of Stewart, Davidson & Simpson (1965) for H. The atomic parameters given in Table 1 correspond to a final $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0·039$ for all reflections.* Bond lengths and angles are given in Fig. 1.

Discussion. The 3-aminopyridine molecule in the solid has the amino configuration with a slightly pyramidal NH₂ group attached to the pyridine ring. The ring atoms are nearly coplanar and lie (with a standard deviation of 0·01 Å) on the least-squares plane given by $-0·796x + 13·014y - 2·468z = 4·188$ Å (Fig. 2). The amino N is slightly above this plane (0·051 Å), one of the amino H atoms [H(7*B*)] is slightly below ($-0·082$

Table 1. *Atomic parameters for 3-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. Parameters are listed × 10⁴ for C and N, × 10³ for H atoms. Isotropic temperature factors are in Å².

	x	y	z	β₁₁	β₂₂	β₃₃	β₁₂	β₁₃	β₂₃
N(1)	−1439 (5)	3725 (1)	3109 (6)	320 (6)	62 (1)	463 (10)	−16 (2)	187 (6)	−28 (2)
C(2)	630 (5)	4077 (1)	4319 (6)	348 (8)	47 (1)	361 (9)	−4 (2)	161 (7)	−7 (2)
C(3)	2501 (5)	4026 (1)	3487 (6)	258 (7)	38 (1)	324 (8)	9 (2)	82 (6)	8 (2)
C(4)	2125 (6)	3588 (1)	1245 (7)	297 (6)	47 (1)	390 (9)	4 (2)	148 (6)	−4 (2)
C(5)	1 (0)	3221 (2)	1 (0)	372 (8)	57 (1)	382 (9)	−17 (2)	150 (7)	−31 (3)
C(6)	−1712 (6)	3295 (2)	999 (6)	313 (8)	63 (1)	472 (11)	−29 (2)	138 (8)	−27 (3)
N(7)	4578 (5)	4437 (1)	4748 (6)	288 (6)	62 (1)	417 (8)	−8 (2)	93 (6)	−26 (2)

	x	y	z	B		x	y	z	B
H(2)	81 (5)	442 (2)	588 (6)	5·6 (7)	H(6)	−317 (6)	307 (2)	25 (6)	6·3 (7)
H(4)	341 (5)	353 (2)	69 (5)	4·5 (5)	H(7*A*)	584 (5)	419 (2)	450 (6)	4·5 (5)
H(5)	−24 (5)	293 (2)	−151 (8)	5·7 (7)	H(7*B*)	483 (5)	465 (2)	632 (7)	6·3 (8)

Å), and the other amino H [H(7A)] is substantially below the plane (-0.315 Å).

The angle between the plane of the ring and the plane determined by the NH_2 group is 32°, most of which is a twist about the C(3)–N(7) bond, since one of the NH vectors lies nearly in the ring plane. The sum of the bond angles about the amino N is 348.5°. In a microwave determination, the amino group in aniline was found to have a dihedral angle of 37.5° with the ring plane (Lister, Tyler, Hog & Larsen, 1974), whereas in 2- and 4-aminopyridine this angle is 15° and 21°, respectively (Chao, Schempp & Rosenstein, 1975, 1976).

The amino–ring bond length C(3)–N(7) is 1.384 Å which is shorter than the 1.43 Å distance given for N–C single bonds (Kennard *et al.*, 1972), but longer than the comparable bonds in 2-aminopyridine (1.351 Å) (Chao, Schempp & Rosenstein, 1975) and 4-aminopyridine (1.363 Å) (Chao, Schempp & Rosenstein, 1976). Nonetheless, this considerable shortening of almost 0.05 Å suggests significant double-bond character in the amino-to-ring bond, and this is supported by the near coplanarity of the amino N with the ring. None of the other bond lengths and angles are unusual.

The molecules are linked to one another by a very weak N(7)–H(7A)$\cdots$N'(1) ($1+x,y,z$) hydrogen bond (3.123 Å); the angle is 167.2°. It is this amino H which lies far from the ring plane. The other amino H, H(7B), is distant [2.46 (3) Å] from the amino N'(7) ($x,1-y,\frac{1}{2}+z$) across the chain; the N(7)–N'(7) distance is 3.336 (4) Å. Although these distances are too long to be recognized as hydrogen bonds, it is interesting to note that the configuration is entirely appropriate to the existence of an interaction, since H(7B) lies nearly on the line joining N(7) to N'(7) and close to the direction of the N'(7) lone pair electrons. It seems likely that this weak interaction is responsible for the relative positions of the chains.

The molecules are joined head-to-tail by the hydrogen bonds to form infinite chains parallel to **a** (Fig. 3). Molecules in the same chain are parallel and related to each other by a translation of one unit cell along **a**. The perpendicular distance between the ring planes of adjacent molecules in the chain is 0.796 Å.

The angle between the glide-related planes of neighboring chains is 63°. Viewed along **a**, each chain is surrounded by six other chains making a herring-bone pattern (Fig. 4). It appears that the amino H(7B) plays a role in this stacking.

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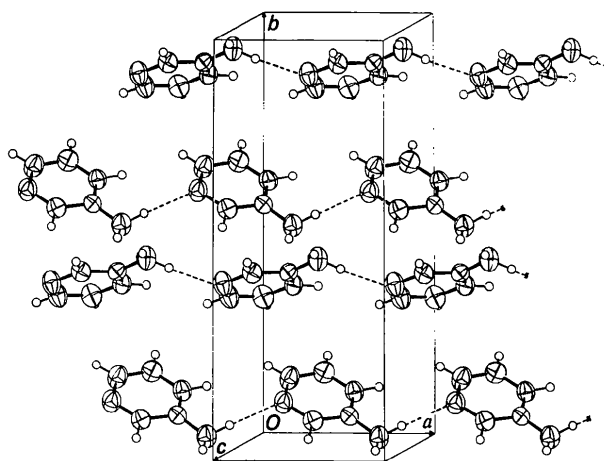
Fig. 3. Packing diagram (Johnson, 1965) of 3-aminopyridine. Dotted lines indicate hydrogen bonds.
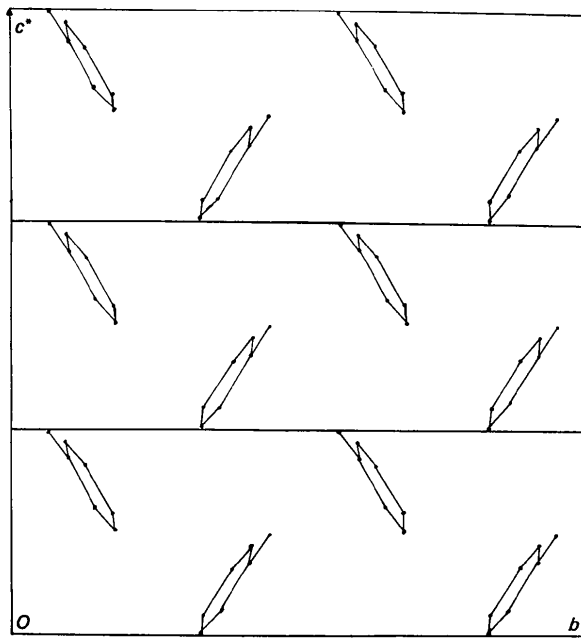

Fig. 4. Packing diagram, viewed along **a**, showing the packing of the chains.

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