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An X-ray and NQR Study of 4-Aminopyridine and Related Aromatic Amines*

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4-Aminopyridine, $C_5H_6N_2$, crystallizes in the orthorhombic space group $P2_12_12_1$, with $Z = 4$, $a = 5{\cdot}573$ (3), $b = 7{\cdot}319$ (4), $c = 12{\cdot}121$ (4) Å. The N(amino)–C(ring) length is 1·363 (3) Å and the dihedral angle between the plane of the amino group and the pyridine ring is about 22°. Comparisons are made with the structures of other amino-heterocycles, including 2- and 3-aminopyridine, and it is shown that both the amino–ring dihedral angles and the degree of pucker at the amino N are linearly correlated with the amino–ring bond lengths. Similarly, the π-electron densities on the ring N atoms and the lone-pair electron populations on the amino N atoms, as determined by nuclear quadrupole resonance data, are linearly related to the C–NH_2 bond lengths.

Introduction

The aminopyridines form an isomeric family of simple, highly conjugated heterocyclic compounds with the molecular formula $C_5H_6N_2$. These compounds have received intensive theoretical study (Konishi, Kato & Yonezawa, 1970) because they contain a small number of atoms and provide model systems for larger molecules. A number of their physical properties, *e.g.* their ^{14}N nuclear quadrupole resonance (NQR) frequencies (Ikeda, Onda, Nakamura & Kubo, 1968; Marino, Guibé & Bray, 1968), ^{14}N NMR chemical shifts (Witanowski & Janszewski, 1969), dipole moments (Barassin & Lumbroso, 1961), and electronic absorption spectra (Gavini, Gamba & Bellobono, 1967), have also been measured. However, until now the crystal structures have not been available. We have reported the crystal structures of 2-aminopyridine (2APd) and 3-aminopyridine (3APd) previously (Chao, Schempp & Rosenstein, 1975*a*,*b*, 1976*a*), as well as two closely related molecules: aminopyrazine (APz) (Chao, Schempp & Rosenstein, 1976*b*), and 2-aminopyrimidine (2APm) (Scheinbeim & Schempp, 1976).

Experimental

4-Aminopyridine (4APd) crystallizes from ethanol in the form of almost colorless, chunky parallelepipeds. A single crystal with approximate dimensions 0·2 × 0·2 × 0·3 mm was sealed in a capillary to prevent sublimation. From indexed Weissenberg photographs, the systematic absences, $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd, uniquely determined the space group to be $P2_12_12_1$. The crystal data for 4APd are given in Table 1.

Intensity data were measured on a Nonius CAD-4 computer-controlled four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation (λ = 1·5418 Å). Integrated intensities for 685 independent reflections ($\theta \leq 75°$) were collected in the $\theta/2\theta$ mode; 90 of these with integrated intensities less than $2\sigma(I)$ were assigned intensities $I = \sigma(I)/2$ and given zero weight in the refinement. No corrections were made for absorption or extinction. The structure was solved by applying direct methods to all reflections with $|E| > 1{\cdot}5$ (*MULTAN*: Germain, Main & Woolfson, 1971). H atom positions were obtained from a difference Fourier synthesis, calculated after several cycles of refinement with isotropic thermal parameters for the C and N atoms.

The atomic parameters were refined by the full-matrix least-squares method (Shiono, 1970) with anisotropic thermal parameters for C and N and isotropic temperature factors for H. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F)$ derived from counting statistics (Shiono, 1971), and with the atomic scattering factors of Cromer & Waber (1965) for N and C and those of Stewart, Davidson & Simpson (1965) for H. The final $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ was 0·049 for all reflections.† The atomic parameters are

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32294 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Crystal data for* 4-*aminopyridine*

a	5·573 (3) Å	D_m	1·28 g cm^{-3}
b	7·319 (4)	D_x	1·269
c	12·121 (4)	Z	4
Space group	$P2_12_12_1$		

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given in Table 2 and the bond lengths and angles are shown in Fig. 1.

Molecular geometry and crystal packing

The 4-aminopyridine molecule in the solid has the expected amino form. The ring atoms are coplanar and lie (with standard deviations of 0·01 Å) on the least-squares plane given by $-2{\cdot}836x + 5{\cdot}931y - 3{\cdot}519z = 0{\cdot}982$ Å (Fig. 2). The amino N also lies in this plane (0·007 Å), but the amino H atoms H(7*A*) and H(7*B*) are significantly below the plane (0·20 and 0·17 Å respectively). The dihedral angle between the NH_2 group and the ring plane is 22°.

The amino–ring, N(7)–C(4), bond length [1·363 (3) Å] is about midway between the corresponding bond lengths in 2APd [1·351 (2) Å] and 3APd [1·384 (4) Å] and thus reflects a double-bond character between that of the 2- and 3-isomers (Chao, Schempp & Rosenstein, 1975*a*,*b*, 1976*a*). The ring angle at C(4) in 4APd is 116·4 (2)°, 2° smaller than the angle in pyridine (Sørensen, Mahler & Rastrup-Andersen, 1974) and 3·6° smaller than in 4-cyanopyridine (Liang, Sparrow & Sommerville, 1971). This decrease in ring angle at the point of substitution is related to the shortness of the C(4)–NH_2 bond (see below) in agreement with the observation that electron-releasing groups decrease the endocyclic angles in benzenoid rings (Domenicano, Vaciago & Coulson, 1975). The short C(4)–NH_2 bond and decreased angle at C(4) are also associated with a slight lengthening of the adjacent C(4)–C(3) and C(4)–C(5) bond lengths; their average length is 1·403 (3) Å, which is about 0·01 Å longer than in pyridine, 1·392 (1) Å (Sørensen, Mahler & Rastrup-Andersen, 1974). Similar decreases in the ring angle

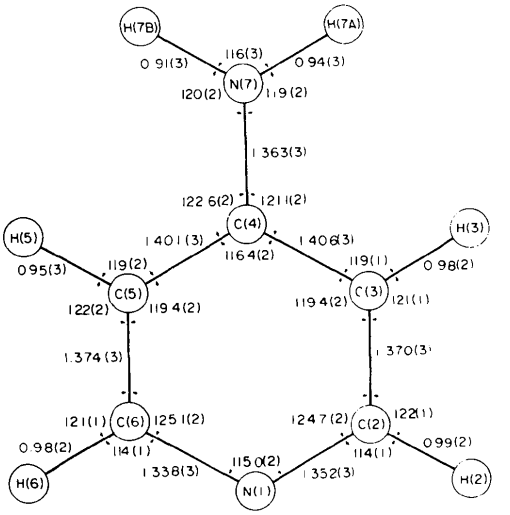


Fig. 1. Bond distances (Å), bond angles (°) and atomic numbering in 4-aminopyridine. The corresponding e.s.d.'s given in parentheses refer to the last digit.

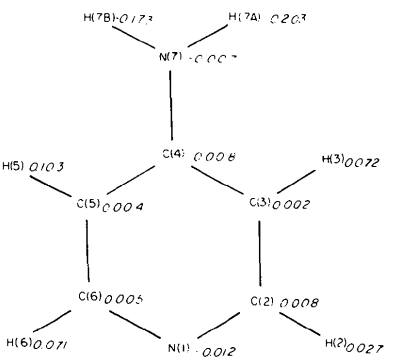


Fig. 2. Displacements (Å) from the least-squares plane through the pyridine ring in 4-aminopyridine.

Table 2. *Atomic parameters for 4-aminopyridine*

Positional parameters are given as fractions of the lattice translation. Anisotropic thermal parameters (Å²) are given according to the expression $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$, and isotropic temperature factors according to the expression $T = \exp(-B \sin^2\theta/\lambda^2)$. Estimated standard deviations given in parentheses refer to the least significant figures in parameter values. N and C positional and thermal parameters are $\times 10^4$; all H parameters are $\times 10^3$.

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	2921 (3)	4589 (3)	2625 (1)	552 (9)	562 (8)	491 (7)	−2 (8)	34 (7)	36 (9)
C(2)	3671 (4)	5516 (3)	3526 (2)	469 (9)	494 (11)	580 (15)	−62 (10)	10 (7)	63 (9)
C(3)	2502 (4)	5536 (3)	4520 (2)	481 (11)	459 (8)	484 (7)	−87 (10)	−65 (10)	4 (9)
C(4)	345 (3)	4559 (2)	4639 (1)	436 (8)	350 (8)	447 (7)	12 (8)	−27 (7)	36 (9)
C(5)	−479 (4)	3629 (3)	3702 (2)	453 (9)	431 (8)	506 (7)	−39 (10)	−51 (10)	9 (9)
C(6)	843 (4)	3696 (3)	2747 (2)	560 (5)	480 (8)	454 (7)	−4 (10)	−55 (10)	−4 (9)
N(7)	−874 (4)	4556 (3)	5614 (2)	610 (9)	692 (8)	491 (7)	−126 (10)	72 (7)	−22 (9)

	x	*y*	*z*	*B*		*x*	*y*	*z*	*B*
H(2)	518 (4)	620 (3)	341 (2)	56 (5)	H(6)	25 (4)	312 (3)	207 (2)	52 (5)
H(3)	308 (4)	629 (3)	513 (2)	53 (6)	H(7*A*)	−19 (6)	510 (5)	622 (2)	114 (11)
H(5)	−201 (5)	308 (4)	372 (2)	57 (6)	H(7*B*)	−210 (5)	375 (4)	572 (2)	73 (8)

and increases in the ring bond lengths adjacent to the point of substitution are also seen in 2APd, 2APm and APz where the ring–amino bonds are quite short. However, in 3APd, where this bond is longer, the effect is much less pronounced.

It is interesting that the ring departs from the nominal C_{2v} symmetry, as is particularly evident near the ring N where the N(1)–C(2) and N(1)–C(6) bond lengths, 1·352 (3) and 1·338 (3) Å, differ by 0·014 Å. This distortion may be due to the hydrogen bonding involving N(1) (Fig. 3).

Only one of the amino H atoms, H(7*A*), participates in hydrogen bonding; the N(7)···N′(1) ($\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$) distance is 3·007 Å with a N–H···N′ angle of 169°. This hydrogen-bond distance is 0·05 to 0·10 Å shorter than those found in similar amino-heterocycles, *e.g.* 2- and 3APd, APz and 2APm. The hydrogen bonds link the 4APd molecules head-to-tail forming zigzag chains parallel to **c**; these chains are stacked antiparallel along **b** (Fig. 3). Adjacent molecules in the same chain are related by the screw axis and are oriented at an angle of 146° to each other.

Comparisons among the aminopyridines

The differences in the amino–ring bond lengths (depending on whether the amino group is situated *ortho*, *meta*, or *para* to the ring N) suggest variations in the degree of conjugation, and indeed there are several features in the geometries of the aminopyridines which vary in a regular way with the amino–ring bond lengths. For example, one can see that the longer the C–NH_2 bond length, the more the amino group departs from the ring plane. This correlation between the dihedral angles and the amino–ring bond lengths is shown in Fig. 4. The C–NH_2 bond lengths increase overall by 0·051 Å in the series 2APd, 4APd, 3APd and aniline (Lister, Tyler, Høg & Larsen, 1974) while the dihedral angle increases about 22·5°, giving a slope of about 4·4°/0·01 Å. The trend continues with aminopyrazine (Chao, Schempp & Rosenstein, 1976*b*) which has the shortest amino bond length [1·341(1) Å] and is nearly planar, although 2-aminopyrimidine (2APm) (Scheinbeim & Schempp, 1976), which also has two ring N atoms, does not fit the linear relationship. In addition, it can be seen that the three bonds about the N atom are non-planar to varying degrees, as indicated by the fact that the sum of the three bond angles around the N (Σ) departs from 360°. Fig. 5 shows the correlation of these differences (360° − Σ) with the amino–ring bond lengths.

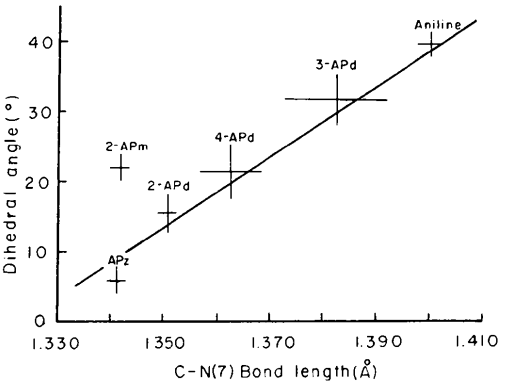


Fig. 4. Plot showing correlation of the dihedral angle between the ring and NH_2 planes *vs* the C–N(amino) bond length. The least-squares straight line was fitted without including the 2APm point.

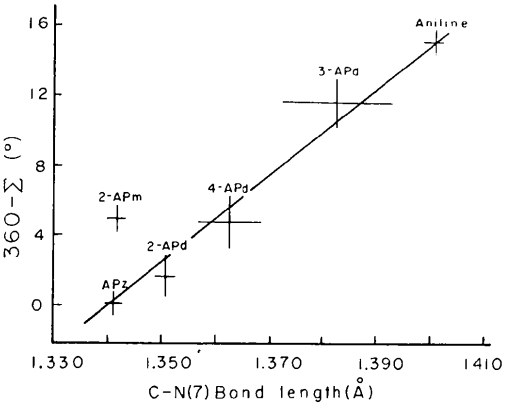


Fig 5. Plot showing the correlation of the deviation from planarity (pucker) of the amino group *vs* the C–NH_2 bond length; Σ is the sum of the bond angles around the amino N. The least-squares straight line was fitted without including the 2APm point.

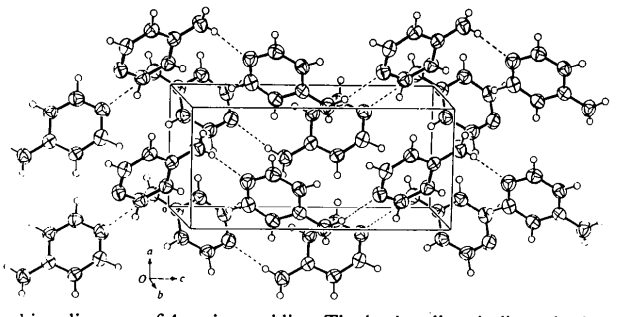
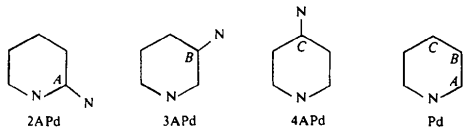


Fig. 3. Packing diagram of 4-aminopyridine. The broken lines indicate hydrogen bonds.

The two correlations together demonstrate that as conjugation with the ring increases and the amino–ring bond length shortens, the amino group is drawn into a more nearly sp^2 configuration, as expected. It is interesting that these correlations are observed in the presence of a variety of different hydrogen-bonding schemes (Fig. 6) involving the amino groups as donors and the ring N atoms as acceptors. It is not possible to decide, of course, whether conjugation determines the geometry, which is then little affected by the hydrogen bonding, or whether the hydrogen bonding plays a significant role in determining the geometry, in which case the degree of conjugation follows as a consequence. Comparative studies of the free-molecule geometries by microwave techniques could resolve this question.

Another interesting feature concerns the angles *A*, *B* and *C* in 2APd, 3APd, 4APd and Pd. If we take pyridine as a reference and subtract its bond angles from the corresponding angles in the aminopyridines, the results are 2·2, 2·0 and 1·8° in 2APd, 4APd and 3APd respectively, and these decreases in the ring angles also correlate well with the corresponding bond lengths of the C–NH_2 bonds. However, the e.s.d.'s of the angles are about 0·3° and therefore this correlation cannot be considered firmly established.



Although the ring N–C bond lengths in the aminopyridines vary from as short as 1·331 Å in 3APd to as long as 1·352 Å in 4APd, they give an average value of 1·340 Å which is close to the C–N bond length in pyridine, 1·338 (1) Å; thus, it appears that 1·340 Å can be taken as representative of typical C–N aromatic bond lengths.

All three compounds have the amino groups acting as H donors and the ring N atoms as H acceptors. Fig. 6 shows the configuration of the hydrogen bonding; aminopyrazine is included for comparison. One interesting feature is that neither the N···N nor the N···H directions are along the bisectors of the CNC angles, which is the direction usually assumed to be the lone-pair position. However, the sums of the CNC′, CN···N and C′N···N′ angles (Fig. 6) are near 360°, and this is also true for the sums of the CNC′, CN···H′ and C′N···H angles, which indicates that the five atoms [C(1), C(6), N(1), N(7), H(7*A*) or C(3), C(5), N(4), N(7), H(7*B*)] are coplanar. This in turn implies that the lone pair of the ring N is at least coplanar with the plane of the ring.

The bond lengths after correction for thermal motion are given in Table 3 (Schomaker & Trueblood, 1968; Wood, 1973). The correlations shown in Figs. 4 and 5 are not changed by using the corrected C–N(7) bond lengths, although the slopes become somewhat steeper.

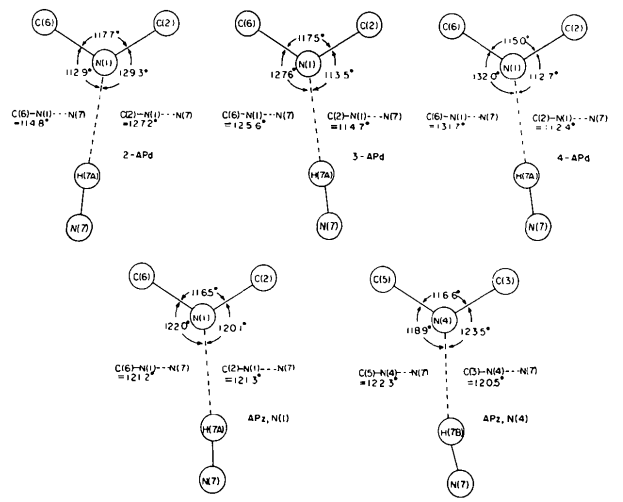


Fig. 6. The hydrogen-bonding configuration in the three aminopyridines and aminopyrazine.

Nuclear quadrupole resonance

NQR studies of aminopyridines have previously been carried out by two different groups, but only the ring N atoms were discussed to any extent, partly because the molecular structures were unknown. Marino, Guibé & Bray (1968) found that the amino group acts as a strong π-electron donor, and, in addition, appears to behave as a weak σ-electron donor. Ikeda, Onda, Nakamura & Kubo (1968) found that the NQR results did not compare satisfactorily with molecular-orbital calculations.

Since the molecular structures are now known, it is possible to construct sp^2-like wave functions (Table 4)

Table 3. *Bond lengths* (Å) *after correction for thermal motion*

	APz	2APd	3APd	4APd
N(1)–C(2)	1·340	1·357	1·345	1·363
C(2)–C(3)	1·433	1·419	1·411	1·378
C(3)–C(4)	–	1·376	1·402	1·416
C(4)–C(5)	–	1·393	1·385	1·412
C(5)–C(6)	1·377	1·380	1·384	1·382
C(6)–N(1)	1·345	1·351	1·342	1·348
C(2)–N(7)	1·350	1·362	–	–
C(3)–N(7)	–	–	1·394	–
C(4)–N(7)	–	–	–	1·371
C(3)–N(4)	1·320	–	–	–
N(4)–C(5)	1·355	–	–	–
$\bar{\sigma}$[a]	0·001	0·002	0·004	0·003

[a] Mean standard deviations from the refinements prior to the rigid-body analyses.

for the ring N atoms and apply the Townes and Dailey theory (Schempp & Bray, 1970) for the ring nuclear quadrupole coupling constant, e^2qQ, and the asymmetry parameter, η, in terms of the bond populations (Schempp, 1968; Sauer, 1972):

$$\frac{e^2qQ}{e^2q_pQ} = \alpha = (1-\zeta^2)(n_l - n_\sigma) + \tfrac{1}{2}(n_\sigma - n_\pi), \quad (1)$$

$$\alpha\eta = \tfrac{3}{2}(n_\sigma - n_\pi). \quad (2)$$

Here e^2qQ is the experimental coupling constant, and the coupling constant per p electron, e^2q_pQ, is taken to be 8·4 MHz (Schempp & Bray, 1970); n_l and n_σ are the lone-pair and N–C σ-bond populations respectively; n_π is the π-bond population, and $\zeta = \cot\gamma$, where 2γ is the ring CNC angle (Table 4). The z principal axis of the electric field gradient (EFG) tensor is taken in the lone-pair direction, assumed along the bisector of the CNC angle, and the y axis is perpendicular to the ring plane (Schempp & Bray, 1970; Lucken, 1969). If the lone-pair population n_l is taken as 2, these equations can be solved for n_σ and n_π with the experimental values for α and η. The results are given in Table 5(*A*), where the values in parentheses assume ideal 120° sp^2 hybridization (*i.e.* $\zeta = 0.5774$).

Table 4. *Orbital wave functions, bond types, and occupation numbers of the ring nitrogens in aminopyridines and aminopyrazine*

$\zeta = \cot\gamma$, where 2γ is the CNC bond angle.

Bond type	Valence-bond wave function	Occupation number
σ	$\psi_1 = \frac{1}{\sqrt{2}}\left[(1-\zeta^2)^{1/2}s - \zeta p_z + p_y\right]$	n_σ
σ	$\psi_2 = \frac{1}{\sqrt{2}}\left[(1-\zeta^2)^{1/2}s - \zeta p_z - p_y\right]$	n_σ
Lone pair	$\psi_3 = \zeta s + (1-\zeta^2)^{1/2}p_z$	n_l
π	$\psi_4 = p_x$	n_π

Similarly, we can write for the amino N atoms

$$\frac{e^2qQ}{e^2q_pQ} = \alpha = (n_l - n_C)\zeta - (1 + \gamma\zeta - \tfrac{2}{3}\gamma)(n_H - n_C), \quad (3)$$

$$\alpha\eta = \tfrac{3}{2}(n_H - n_C)\gamma, \quad (4)$$

where $\cos(\mathrm{NHN}) = \gamma\zeta/(2-\gamma\zeta)$, $\cos(\mathrm{CNH}) = \{\gamma(1-\gamma)/(2-\gamma\zeta)[1-\zeta(1-\gamma)]\}^{1/2}$, n_C and n_H represent the N–C and N–H σ-bond populations, and, as before, n_l is the lone-pair population, this time in a π orbital. For ideal 120° hybridization, $\zeta = 1$ and $\gamma = \frac{2}{3}$, whereas for ideal sp^3 hybridization, $\zeta = \frac{3}{4}$ and $\gamma = \frac{2}{3}$ (Sauer, 1972).

Table 5. *The* ^{14}N *quadrupole coupling constants, asymmetry parameters, hybridization parameters and electron orbital populations of aminopyridines and several similar compounds at* 77 K

(*A*) Ring nitrogen (n_π is the π-electron population and n_σ is the average σ electron population in the N–C bonding orbitals; n_l is the assumed lone-pair population).

e^2q_pQ is 8·4 MHz; $\Delta = n_l + 2n_\sigma + n_\pi - 5$ is the total electron excess. Values shown in parentheses assume a pure sp^2 configuration.

	e^2qQ (MHz)	η	$\zeta = \cot\gamma$ (0·5774)	n_π	n_σ	n_l	Δ	Reference
2APd	3·746	0·035	0·6044	1·30 (1·33)	1·29 (1·34)	2	0·88 (1·01)	(*a*)
3APd	4·497	0·390	0·6068	1·12 (1·16)	1·26 (1·30)	2	0·64 (0·76)	(*a*)
4APd	3·781	0·085	0·6371	1·24 (1·32)	1·26 (1·34)	2	0·76 (1·00)	(*a*)
Pd	4·585	0·396	0·6135	1·10 (1·15)	1·24 (1·29)	2	0·58 (0·73)	(*b*)
APz N(1)	3·883	0·086	0·6188	1·25 (1·31)	1·27 (1·33)	2	0·79 (0·97)	(*c*)
APz N(4)	4·707	0·513	0·6176	1·06 (1·11)	1·25 (1·30)	2	0·56 (0·71)	(*c*)
Pz	4·858	0·536	0·6371	1·02 (1·08)	1·23 (1·29)	2	0·48 (0·66)	(*d*)
2APm	3·734	0·049	0·6255	1·27 (1·33)	1·28 (1·34)	2	0·83 (1·01)	(*e*)
Pm	4·436	0·386	0·6352	1·09 (1·17)	1·23 (1·31)	2	0·55 (0·79)	(*d*)

(*B*) Amino nitrogen (n_H, n_C and n_l are the electron populations of the N–H, N–C, and lone-pair orbitals). Values in parentheses refer to pure sp^3 hybrids.

	e^2qQ (MHz)	η	$\zeta^* = \cot\gamma$ (1·0)	γ^* (0·6667)	$n_H - n_C$	$n_l - n_C$	n_l†	Reference
2APd	3·550	0·346	0·9865	0·6330	0·15 (0·15)	0·53 (0·52)	1·78	(*a*)
3APd	3·709	0·384	0·9143	0·6667	0·17 (0·17)	0·60 (0·56)	1·85	(*a*)
4APd	3·506	0·385	0·9586	0·6312	0·17 (0·16)	0·55 (0·52)	1·80	(*a*)
APz	3·317	0·408	0·9967	0·7196	0·15 (0·16)	0·49 (0·50)	1·74	(*c*)
Aniline	3·933	0·269	0·8905	0·6314	0·13 (0·13)	0·62 (0·55)	1·87	(*f*)
2APm	3·270	0·406	0·9656	0·6763	0·16 (0·16)	0·51 (0·50)	1·76	(*e*)

(*a*) Marino, Guibé & Bray (1968). (*b*) Guibé (1962). (*c*) Chao, Schempp & Rosenstein (1976*b*). (*d*) Schempp & Bray (1967). (*e*) Schempp & Bray (1971). (*f*) Yim, Whitehead & Lo (1968).

* The C–N–H(7*A*) and C–N–H(7*B*) angles are assumed to be equal to their average values.

† $n_C = 1.25\,e$ is assumed.

One cannot assume $n_l = 2$ here since conjugation effects are important, and hence one can only solve the equations for the quantities $(n_H - n_C)$ and $(n_l - n_C)$, as shown in Table 5(*B*). The sp^3-like wave functions for the amino N are given in Table 6.

The data in Table 5(*A*) confirm that the amino group in the *ortho* and *para* positions is a significant electron donor to the ring N; this is most evident in the observation that n_π at the ring N in 2- and 4APd is about 0·15 *e* larger than in unsubstituted pyridine. As expected for a *meta* substituent, the value for n_π in 3APd does not differ much from that in pyridine, nor does n_π for the *meta* N [N(4)] in APz differ much from that in pyrazine. It can also be observed that the σ-bond population, n_σ, is relatively constant, as has been found in other NQR studies of substituted pyridines (Schempp & Bray, 1970). The overall electron charge excess, Δ, at the ring N thus increases from 0·06 to 0·33 *e* over that in pyridine as a result of strong π and weak σ donation from the amino group.*

It can be seen that taking account of the angular correction, ξ, generally leads to smaller and perhaps somewhat more realistic values for the bond populations and the electron excess. In addition, when the angular term is included, the π-electron densities on the ring N atoms correlate very well with the amino–ring bond lengths, whereas this regularity is absent if idealized 120° bonds are assumed.

Fig. 7 shows a plot of the increase of n_π in the aminopyridines over n_π in unsubstituted pyridine [*i.e.* $\Delta n_\pi = (n_\pi)_{APd} - (n_\pi)_{Pd}$] *vs* the amino–ring bond lengths. As the amino–ring bond length decreases, the π-orbital occupancy of the ring N increases, exactly as expected from increased double-bond character: the slope of the line gives an increase of 0·05 electron units for every 0·01 Å decrease in bond length. Aminopyrazine and 2-aminopyrimidine can also be added to the graph by plotting $\Delta n_\pi = [(n_\pi)_{N(1)} + (n_\pi)_{N(2)}]_{amino} - 2(n_\pi)_{unsub.}$, *i.e.* the total increase in π charge density at both N atoms. Interestingly, the point for APz falls nearly on the line, whereas 2APm is sharply off, and this behavior mirrors the situations in Figs. 4 and 5.

The amino N atoms have not been thoroughly analyzed in previous NQR work (Marino, Guibé & Bray, 1968; Schempp & Bray, 1971; Chao, Schempp & Rosenstein, 1976*b*; Yim, Whitehead & Lo, 1968), in part because the geometries of the amino groups have

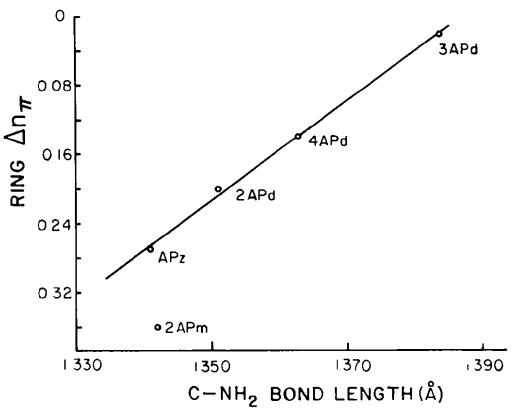


Fig. 7. Plot of the increase in the *ring* nitrogen π population, Δn_π, *vs* the C–NH_2 bond length; Δn_π is derived from the NQR data and is given in units of the electron charge. The line represents a least-squares fit to the points, omitting 2APm. The ordinate has been inverted to show similarities with Figs. 4, 5 and 8; hence a decrease in the C–NH_2 length gives an increased Δn_π on the ring N.

* It may be pointed out that equation 2 is based on the assumption that $n_\sigma > n_\pi$, as has generally been found to be the case in pyridines (Schempp & Bray, 1970). This accords with smaller values for η as n_π is increased by π-electron donating groups. However, if n_π increases too much, η passes through zero, corresponding to an interchange of the *x* and *y* axes of the EFG tensor; η is then taken as negative in equation 2. This is probably the case in 2APd where the conjugation is particularly strong. Evidence that $n_\pi > n_\sigma$ in 2APD is found in the temperature dependence of the NQR lines which show that $\alpha\eta$ for 2APd is a decreasing function of temperature (Chao, 1975). Hence, the data in Table 5(*a*) assume $n_\pi > n_\sigma$ in the case of 2APd. Since $|\eta|$ is small, this assumption does not affect the value of n_π.

Table 6. *Orbital wave functions, bond types and occupation numbers for the amino nitrogens in aminopyridines and aminopyrazines*

γ and ζ are hybridization parameters. $\cos\widehat{NHN} = \gamma\zeta/(2-\gamma\zeta)$, $\cos\widehat{CHN} = -[\gamma(1-\gamma)/\{(2-\gamma\zeta)[1-\zeta(1-\gamma)]\}]^{1/2}$ (Sauer, 1972). For simplicity, we have assumed that both CNH angles are equal and the two N–H bonds are equivalent.

Bond type	Valence-bond wave function	Occupation number
σ	$\psi_{NH} = \left[\frac{\gamma\zeta}{2}\right]^{1/2} s - \left[\frac{\gamma(1-\zeta)}{2}\right]^{1/2} p_z - \left[\frac{(1-\gamma)}{2}\right]^{1/2} p_x - \left[\frac{1}{2}\right]^{1/2} p_y$	n_H
σ	$\psi_{NH} = \left[\frac{\gamma\zeta}{2}\right]^{1/2} s - \left[\frac{\gamma(1-\zeta)}{2}\right]^{1/2} p_z - \left[\frac{(1-\gamma)}{2}\right]^{1/2} p_x + \left[\frac{1}{2}\right]^{1/2} p_y$	n_H
σ	$\psi_{NC} = [\zeta(1-\gamma)]^{1/2} s - [(1-\zeta)(1-\gamma)]^{1/2} p_z + \gamma^{1/2} p_x$	n_C
π	$\psi_l = (1-\zeta)^{1/2} s + \zeta^{1/2} p_z$	n_l

not been known. We can now carry out an analysis in the spirit of the discussion of the ring N atoms using equations 3 and 4. To avoid dealing with the lone-pair occupancy, about which it would be unwise to make *a priori* assumptions, we deal with the quantities $(n_H - n_C)$ and $(n_l - n_C)$ for the amino N atoms, where the former is the difference between the N–H and N–C σ populations and the latter is the difference between the lone-pair and the N–C populations. The data given in Table 5(*B*) shows that $n_H - n_C$ is relatively constant while $n_l - n_C$ varies from a low of 0·49 *e* for highly conjugated APz to a maximum of 0·62 *e* for weakly conjugated aniline. In fact, a plot of $(n_l - n_C)$ *vs* the amino–ring bond length shows another good linear correlation (Fig. 8) when the sp^3-model hybrids are corrected for angular distortions. If the n_C σ-bond population is assumed relatively constant, as is likely, then Fig. 8 represents the variation of the amino lone-pair population, and shows, as expected, that bond shortening, and hence increased conjugation, leads to smaller π-densities on the amino N. If the n_C σ-bond population is estimated at 1·25 *e* (Schempp & Chao, 1976), the amino lone-pair densities lie between 1·74 *e* for APz and 1·87 *e* for aniline.

The data in Table 5(*A*) assume for simplicity a lone-pair population of 2 on the ring N atoms. As long as this population is constant, a different value for n_l affects n_π and n_σ only by an additive constant; if $n_l = 1{\cdot}8$, n_π and n_σ are each smaller by 0·2 *e* and Δ by 0·8 *e*. ASMO-SCF valence-electron calculations with assumed molecular geometries for the aminopyridines have given ring-N lone-pair populations near 1·7 *e* and amino-nitrogen π populations near 1·9 *e* (Konishi, Kato & Yonezawa, 1970). With $e^2q_pQ = 8{\cdot}4$ MHz, n_l cannot be much smaller than 1·9 if values of $n_\pi < 1{\cdot}0$ are to be avoided. But since n_l and e^2q_nQ cannot be assigned with certainty, little emphasis can be placed on the absolute values for n_π, n_σ and Δ. However, differences in the values between one compound and another ought to be reliable. The fact that the NQR-derived data follow the same pattern as the crystallographic–geometric correlations provides satisfying evidence for the validity of the NQR analysis.

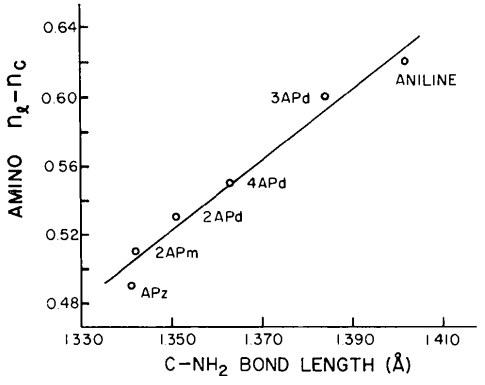


Fig. 8. Plot showing the decrease in $(n_l - n_C)$ for the *amino* N as the C–NH$_2$ bond length becomes shorter; n_l and n_C are the amino-N lone pair and N–C σ populations respectively. If n_C may be considered constant, the line reflects the change in the amino π population. The least-squares line was fitted to all points.

Previous work has shown that the ring π-electron population is linearly related to the Cl^{35} NQR frequency in the monochloropyridines and is also correlated with the π-electron loss of the CN group in monocyanopyridines (Schempp & Bray, 1968). Since the ring π population and the amino π population are each linearly related to the C–NH$_2$ bond length, they are obviously correlated with each other in the monoaminopyridines.

It is interesting to note, however, that the NQR correlations occur in the presence of a notable variety of different hydrogen-bonding schemes. In the electron donor–acceptor model of hydrogen bonding, which has been strongly supported by Ratajczak & Orville-Thomas (1973), the lone-pair population of the acceptor ring N will be smaller than two and will vary with the hydrogen-bond strength. In the amino heterocycles discussed here, all the N–H···N angles lie within 3° of 170°, but the N–H···N distances vary from 3·007 Å in 4APd to 3·123 Å in 3APd. There are no direct correlations of these distances with the NQR data, and thus the lone-pair population appears sensibly constant and independent of the hydrogen-bond strength. Although there is also no correlation of the hydrogen-bond parameters with the molecular geometries, it is still unclear whether the requirements of conjugation primarily determine the amino configuration or whether the hydrogen bonding modifies the amino geometry and thus helps to establish the degree of conjugation. The former appears more probable.

We also note that ^{14}N NMR chemical shifts in solution have been measured for the ring N atoms (68, 88, 105 and 128 ppm for pyridine, 3APd, 4APd and 2APd respectively) and the amino N atoms (330, 328, 321, and 313 ppm for alinine, 3APd, 4APd and 2APd respectively) (Witanowski & Janszewski, 1969), and these also scale approximately with the amino–ring bond lengths and the NQR-derived π populations. The chemical shifts reflect the overall electron density at the nucleus and thus lend support to the NQR analysis.

Although there have been a number of attempts in the past to correlate NQR data with crystallographic measurements, few of these have so far been successful, and it can be noted that there are no simple correlations of the quadrupole coupling constants and asymmetry parameters themselves with the crystallographic data. However, comparisons of the two purely crystallographic correlations in Figs. 4 and 5 with the NQR-derived correlations of Figs. 7 and 8 show remarkable qualitative similarities and also make good

chemical sense. We are therefore confident that all four correlations are meaningful and are scarcely likely to be accidental. The latter correlations also demonstrate the importance of having good crystallographic data and of using the true bond angles in the NQR analysis.

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