

marginally longer than the O...N distance of 2.742 (3) Å found in 6-chloro-2-hydroxypyridine. The bond is effectively linear with an O-H...N angle of 170 (8)°. It is to be noted that this compound as well as the 6-chloro-2-hydroxypyridine molecule (Kvick & Olovsson, 1968; Almlöf, Kvick & Olovsson, 1971) is found in the enol form. This contrasts to the keto forms found in the crystal structures of 2-pyridone (Almlöf, Kvick & Olovsson, 1971) and 5-chloro-2-pyridone (Kvick & Booles, 1972). The preference for the enol forms in the α -halogenated compounds can be explained by the electron-withdrawing properties of the halogen atoms (Katritzky, Rowe & Roy, 1967).

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Hydrogen Bond Studies. CI. A Neutron Diffraction Study of 2-Amino-5-chloropyridine*

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A neutron diffraction study of 2-amino-5-chloropyridine has been carried out. Intensities of 2631 reflexions were measured at the Brookhaven National Laboratory High Flux Beam Reactor and were used in subsequent refinements of the structure to an $R(F^2)$ of 0.060. The molecules link *via* N–H...N hydrogen bonds [H...N 2.051 (3) Å] to produce centrosymmetric, cyclic dimers which, in turn, pack in a herring-bone formation. Information on the asphericity of the electron-cloud distribution has been obtained by the X–N technique using previous X-ray data and the present neutron data. Valence electron accumulation in the middle of covalent bonds and in expected lone-pair electron regions is found. The bond distances between heavy atoms are determined to a precision of 0.001 Å; the corresponding value for heavy atom–hydrogen atom bond lengths is 0.003 Å or better.

Introduction

A neutron diffraction study of 2-amino-5-chloropyridine has been carried out in order to determine

precise H atom positions and to examine the hydrogen-bonding scheme in the crystal. The X-ray structure determination of 2-amino-5-chloropyridine has been reported earlier by Kvick & Backéus (1974), and the atomic parameters determined by neutron diffraction were used together with the X-ray data to produce X–N difference-Fourier syntheses. Information on the asphericity of the electron-cloud distribution around

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the atomic nuclei can thus be obtained. The theory of X-N syntheses has been given by Coppens (1974), and a comparison of the X-N technique with *ab initio* calculations has been reported by Almlöf, Kvik & Thomas (1974). This work is part of a series of systematic studies of model compounds for biologically important molecules presently being undertaken at the Institute of Chemistry, University of Uppsala.

Crystal data

2-Amino-5-chloropyridine, $C_5H_5N(NH_2)Cl$. F.W. 128.562. Monoclinic, $a=13.4370$ (6), $b=5.7963$ (5), $c=7.5123$ (6) Å, $\beta=105.512$ (6)°, $V=563.78$ Å³ at 24°C. $Z=4$, $D_x=1.514$ g cm⁻³. Space group $P2_1/c$ (Kvik & Backéus, 1974).

Experimental

Crystals of 2-amino-5-chloropyridine suitable for neutron diffraction were grown from chloroform. A rhombohedral crystal bounded by seven faces of the forms {100}, {011} and {001}, and with a volume of 11.64 mm³, was used for the data collection.

Neutron diffraction data were collected at room temperature (+24°C) on an automated four-circle diffractometer at the Brookhaven National Laboratory High Flux Beam Reactor using the Multiple Spectrometer Control System (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & van Norton, 1966).

Intensities of Bragg reflexions were measured by the $\theta/2\theta$ step-scan technique. The scan length was varied according to the formula: $\Delta 2\theta = k(1 + 8 \tan \theta)^\circ$ with $k=1.2$ out to $d^*=0.5$ and $k=1.4$ for the remaining data; the step size was chosen to give approximately 40 points in each scan. Data were collected over a complete hemisphere of reciprocal space out to $\sin \theta/\lambda = 0.664$ Å⁻¹ ($\lambda=1.0147$ Å). Two standard reflexions were measured at regular intervals to provide a check on the crystal and electronic stability. The variations observed in the intensities did not call for any corrective measures.

Background corrections were made by a method (Lehmann & Larsen, 1974) which separates the peak and the background in such a way that $\sigma(I)/I$ is minimized. I is the integrated intensity and $\sigma(I)$ its e.s.d. based on counting statistics. Squared structure amplitudes were obtained as $F_o^2 = I \sin 2\theta$ and were corrected for absorption by the Gaussian integration method using a grid of 216 points. The crystal shape was represented by the seven rational boundary planes. The linear absorption coefficient was calculated assuming the incoherent scattering cross section for H to be 40 barns and using the values of true absorption cross sections for coherent scattering of Cl, C, N and H tabulated in *International Tables for X-ray Crystallog-*

† Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digits.

raphy (1962). The transmission factors fall in the range, 0.689 to 0.753 ($\mu=1.580$ cm⁻¹).

3035 observed intensities were measured. The observed F_o^2 values for each standard reflexion were averaged together but symmetry-related reflexions were not since anisotropic extinction was found to be present. Removal of systematically absent reflexions left 2631 observations upon which to base the least-squares refinements.

Structure refinement

The starting parameters for refinement of the structure of 2-amino-5-chloropyridine were the final parameters from the X-ray analysis by Kvik & Backéus (1974). The structure was refined with the full-matrix least-squares program *CLINUS*. The function minimized was $\sum w(F_o^2 - |F_c|^2)^2$. Each reflexion was assigned a weight w , inversely proportional to the estimated variance of the observation:

$$w^{-1} = \sigma_c^2(F_o^2) + (kF_o^2)^2 = \sigma^2(F_o^2)$$

where $\sigma_c(F_o^2)$ is based on counting statistics and $k=0.02$ in the final cycles of refinement. The standard deviation of an observation of unit weight was:

$$S = [\sum w(F_o^2 - |F_c|^2)^2 / (m - n)]^{1/2} = 1.13$$

where m is the total number of observations and n is the number of parameters varied.

Table 1. *Atomic coordinates and neutron scattering lengths*

Parameters from the present neutron study are found on the first line followed by the parameters from the X-ray study on the second line.

	b ($\times 10^{-12}$ cm)	x ($\times 10^5$)	y ($\times 10^5$)	z ($\times 10^5$)
Cl	0.9584	7764 (5) 7757 (3)	18376 (12) 18353 (8)	36227 (10) 36218 (7)
N(1)	0.9314 (27)	36245 (5) 36268 (9)	43255 (10) 43245 (24)	46963 (9) 46955 (18)
N(2)	0.9304 (33)	44123 (7) 44093 (14)	76689 (16) 76662 (35)	60247 (12) 60237 (29)
C(2)	0.6626	35434 (7) 35415 (12)	63721 (15) 63717 (27)	54789 (12) 54771 (21)
C(3)	0.6626	25910 (7) 25907 (13)	71625 (15) 71564 (28)	57049 (13) 57005 (22)
C(4)	0.6626	17255 (7) 17319 (12)	58036 (15) 58020 (29)	51081 (12) 51096 (22)
C(5)	0.6626	18256 (6) 18287 (11)	36653 (14) 36715 (26)	43232 (12) 43269 (21)
C(6)	0.6626	27800 (6) 27797 (11)	30051 (14) 30083 (26)	41380 (12) 41387 (22)
		x ($\times 10^4$)	y ($\times 10^4$)	z ($\times 10^4$)
H(1)	-0.3723	5065 (2) 4930 (18)	7081 (4) 7151 (42)	5760 (3) 5821 (30)
H(2)	-0.3723	4405 (2) 4441 (18)	9128 (5) 8913 (48)	6680 (4) 6604 (30)
H(3)	-0.3723	2542 (2) 2575 (13)	8838 (3) 8651 (33)	6325 (3) 6244 (24)
H(4)	-0.3723	987 (2) 1081 (17)	6379 (4) 6317 (40)	5263 (3) 5238 (28)
H(6)	-0.3723	2875 (2) 2862 (14)	1347 (3) 1544 (33)	3518 (3) 3566 (24)

In the final cycles of refinement 39 positional and 78 anisotropic thermal parameters, one scale factor, six anisotropic secondary extinction components and the neutron scattering lengths for the two N atoms were refined. In order not to bias the refinement all reflexions, even those with $F_o^2 < 0$, were included in the refinement. The final agreement indices are: $R = \sum |F_o^2 - |F_c|^2| / \sum |F_o|^2 = 0.060$ and $R_w = [\sum w |F_o^2 - |F_c|^2|^2 / \sum w F_o^4]^{1/2} = 0.062$.

The corresponding conventional $R(F)$ is 0.033 if the 937 reflexions with $F_o^2 < 3\sigma_c(F_o^2)$ are excluded from the calculations.

Three different trial models were used to correct for the secondary extinction. The corrections used were those appropriate for isotropic extinction, secondary extinction for type I crystals, and secondary extinction for type II crystals. A physical interpretation of the extinction parameters is given by Coppens & Hamilton (1970). In the present case the mosaic-spread-dominated type I model gave R indices considerably lower than for the remaining two models. Consequently anisotropic extinction parameters for a type I crystal were refined in the last cycles of refinements. The refinements were based on a non-averaged data set since the extinction components are not equal for the equivalent forms of a reflexion.

The neutron scattering factors were taken to be $\bar{b}_{Cl} =$

0.9584, $\bar{b}_C = 0.6626$ and $\bar{b}_H = -0.3723$ (all $\times 10^{-12}$) cm (Shull, 1971). The values for the N atoms were obtained from the refinement and are listed in Table 1. It is reassuring that the individual scattering lengths for the N atoms were determined to be nearly identical although no constraints were included in the refinement. The scattering lengths for the N atoms were refined because several recent refinements have indicated that values lower than $\bar{b}_N = 0.94$ (Bacon, 1972) should be used (Kvick, Koetzle, Thomas & Takusagawa, 1974).

The refined atomic parameters and scattering lengths are given in Table 1 and the refined anisotropic thermal and extinction parameters in Table 2. The scale factor used in the calculation of the X-N difference synthesis was obtained from one cycle of least-squares refinement using the X-ray data, the atomic parameters from the neutron study and spherical X-ray scattering factors.

The calculations were carried out on the CDC 6600 computers at Brookhaven National Laboratory and on the IBM 370/155 and 1800 computers in Uppsala.

Comparison of neutron and X-ray parameters

Atomic positional and thermal parameters from the neutron and X-ray studies are compared in Tables 1 and 2. As expected a close agreement is generally found

Table 2. Anisotropic thermal ($\times 10^5$) and extinction ($\times 10^2$) parameters

The parameters from the neutron study are followed on the second line by the parameters from the X-ray refinement. The anisotropic thermal parameters are of the form $\exp\{-\beta_{11}h^2 + \dots 2\beta_{12}hk + \dots\}$.

Thermal parameters

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	392 (4)	2934 (25)	2287 (18)	-194 (7)	272 (7)	-402 (14)
	391 (2)	2930 (15)	2412 (11)	-204 (4)	248 (3)	-394 (9)
N(1)	354 (4)	2082 (21)	1740 (17)	-6 (6)	239 (6)	-257 (13)
	379 (7)	2200 (38)	1778 (27)	15 (13)	211 (11)	-137 (26)
N(2)	537 (7)	3241 (35)	2859 (24)	-464 (10)	466 (9)	-1206 (21)
	562 (10)	3380 (59)	3108 (48)	-453 (21)	491 (18)	-1382 (44)
C(2)	412 (5)	2045 (27)	1422 (19)	-87 (9)	236 (8)	-171 (17)
	446 (8)	2144 (45)	1451 (28)	-83 (16)	210 (12)	-49 (28)
C(3)	490 (6)	1896 (29)	1578 (19)	50 (9)	341 (9)	-194 (18)
	535 (9)	1971 (45)	1571 (30)	43 (17)	323 (14)	-139 (29)
C(4)	405 (6)	2101 (27)	1562 (20)	119 (9)	307 (8)	-10 (18)
	439 (9)	2301 (45)	1610 (30)	157 (16)	312 (13)	158 (31)
C(5)	336 (5)	2012 (26)	1358 (18)	15 (8)	188 (7)	24 (16)
	360 (7)	2101 (42)	1424 (26)	-22 (15)	166 (11)	135 (27)
C(6)	353 (5)	1821 (27)	1543 (19)	27 (9)	211 (8)	-190 (17)
	402 (7)	1934 (41)	1528 (28)	46 (15)	202 (12)	-130 (29)
H(1)*	543 (14)	3666 (77)	2750 (55)	-354 (25)	370 (23)	-445 (47)
	4.3 (5)					
H(2)	853 (19)	3803 (90)	3821 (72)	-446 (32)	441 (29)	-1578 (69)
	5.1 (6)					
H(3)	874 (16)	2678 (66)	3071 (57)	-19 (25)	684 (25)	-1016 (47)
	3.0 (4)					
H(4)	567 (13)	3718 (71)	3303 (61)	256 (25)	607 (23)	-434 (51)
	4.7 (5)					
H(6)	628 (13)	2581 (62)	2999 (54)	-45 (22)	466 (22)	-919 (44)
	2.8 (4)					

* The second line for hydrogen atoms represents the isotropic thermal parameter B .

Extinction parameters [as defined by Coppens & Hamilton (1970)]

Z'_{11}	Z'_{22}	Z'_{33}	Z'_{12}	Z'_{13}	Z'_{23}
237 (11)	62 (4)	249 (11)	-28 (5)	-182 (9)	7 (4)

between the non-hydrogen atom parameters; significant differences do arise however for some of the atoms. The H atom parameters show a characteristic disparity resulting from the asphericity of the electron distribution associated with these atoms. A tendency for higher thermal parameters in the X-ray case can be noticed.

Description and discussion of the structure

The 2-amino-5-chloropyridine molecules exist in the amino form and are linked to produce dimers *via* pairs of N-H...N hydrogen bonds [$H \cdots N = 2.051$ (3) Å]. Only *one* of the amino H atoms participates in hydrogen bonding. The two molecules of the dimer are related by a centre of symmetry and are both planar and parallel to each other. Fig. 1 gives a stereoscopic illustration of the structure.

A discussion of the packing has been given in a previous paper describing the X-ray study (Kvick & Backéus, 1974).

The molecular structure

The molecular dimensions of 2-amino-5-chloropyridine are given in Table 3 and are illustrated in Fig. 2. The only significant differences in bond distances involving non-hydrogen atoms found by neutron and X-ray techniques are present in the distances C(5)–Cl and C(3)–C(4) where the deviations are 7 and 4 e.s.d.'s respectively. The most significant difference in thermal parameters for non-hydrogen atoms also involves the Cl atom where the β_{33} thermal parameter is 6σ larger in the X-ray case. The X–N difference syntheses in planes perpendicular to the C(5)–Cl bond show two

large peaks of electron density having their maxima roughly in the plane 1.81 Å away from the C(5) position; the C(5)–Cl nuclear distance is 1.729 (3) Å. It is

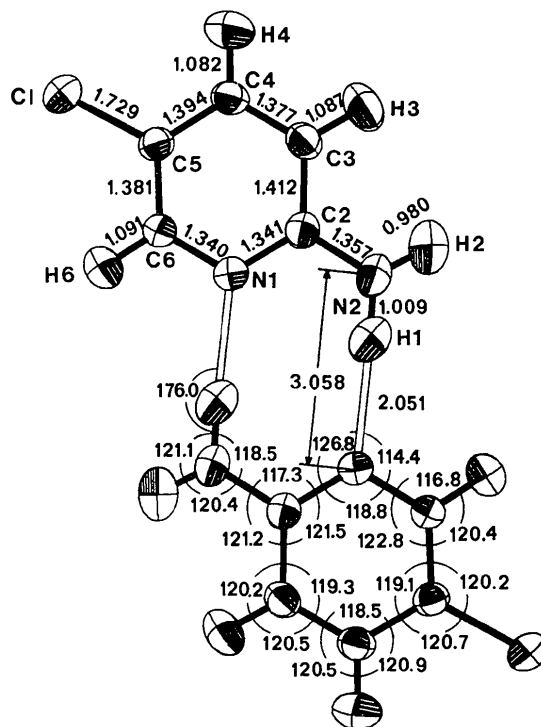


Fig. 2. Bond distances and angles. The values are not corrected for thermal motion.

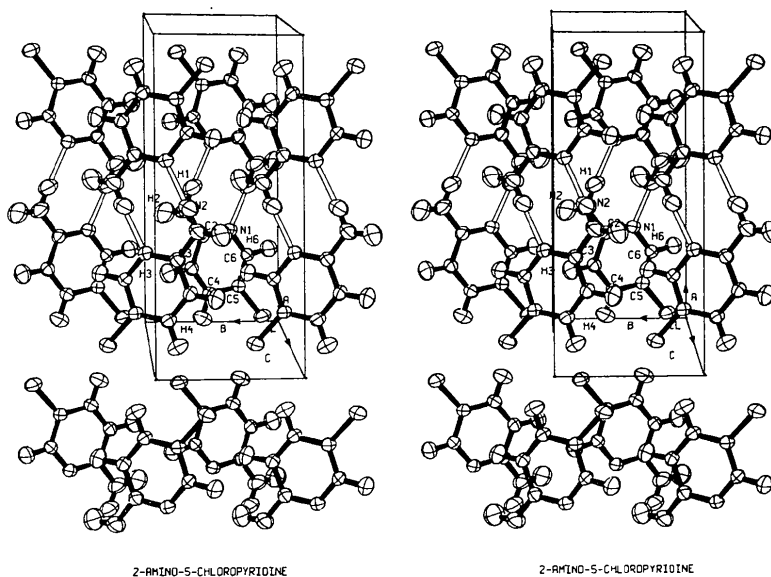


Fig. 1. Stereoscopic illustration of the crystal structure of 2-amino-5-chloropyridine. Covalent bonds are filled and hydrogen bonds are open. The thermal ellipsoids are scaled to enclose 50% probability.

possible that the difference in the C(5)–Cl distance is associated with a hybridization giving lone-pair electrons in these regions. However, caution must be used in the interpretation of X–N syntheses in the vicinity of atoms heavier than the first row elements. The spherical atomic scattering factors presently used for heavier atoms may well be of a quality which gives rise to artifacts in the vicinity of these atoms.

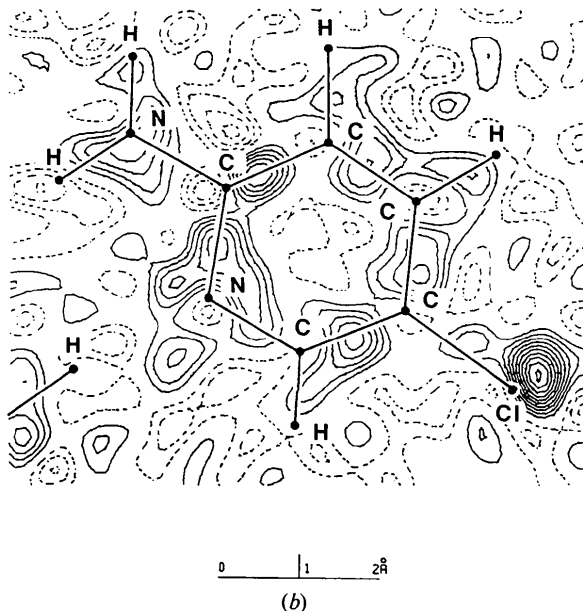
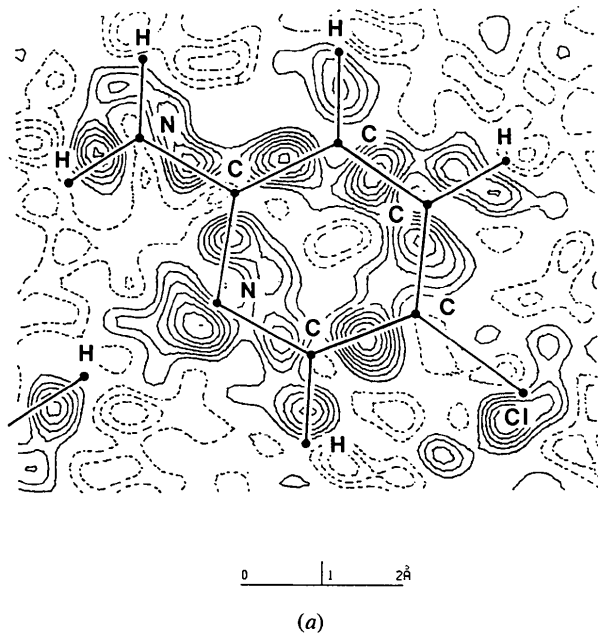


Fig. 3. X–N difference synthesis in the plane of the pyridine ring (a) and in a parallel plane 0.4 Å above the ring (b). The contours are drawn at $0.06 \text{ e } \text{Å}^{-3}$ intervals; negative regions are represented by dashed lines.

Table 3. Intramolecular bond lengths (Å) and angles (°)

(a) Distances. Values in square brackets are corrected for thermal rigid-body motion.

	Neutron	X-ray*
Cl—C(5)	1.729 (1) [1.735]	1.736 (1)
N(1)—C(2)	1.341 (1) [1.346]	1.342 (2)
N(1)—C(6)	1.340 (1) [1.344]	1.341 (2)
N(2)—C(2)	1.357 (1) [1.361]	1.355 (2)
N(2)—H(1)	1.009 (3) [1.014]	0.812 (24)
N(2)—H(2)	0.980 (3) [0.984]	0.839 (26)
C(2)—C(3)	1.412 (1) [1.419]	1.408 (2)
C(3)—C(4)	1.377 (1) [1.381]	1.368 (2)
C(3)—H(3)	1.087 (2) [1.092]	0.960 (19)
C(4)—C(5)	1.394 (1) [1.401]	1.389 (2)
C(4)—H(4)	1.082 (2) [1.088]	0.953 (22)
C(5)—C(6)	1.381 (1) [1.388]	1.377 (2)
C(6)—H(6)	1.091 (2) [1.096]	0.971 (19)

(b) Angles

C(2)—N(1)—C(6)	118.8 (1)	118.3 (1)
C(2)—N(2)—H(1)	118.5 (1)	117.0 (16)
C(2)—N(2)—H(2)	120.4 (1)	123.6 (16)
H(1)—N(2)—H(2)	121.1 (2)	119.3 (23)
N(1)—C(2)—N(2)	117.3 (1)	117.1 (2)
N(1)—C(2)—C(3)	121.5 (1)	121.6 (1)
N(2)—C(2)—C(3)	121.2 (1)	121.3 (2)
C(2)—C(3)—C(4)	119.3 (1)	119.3 (1)
C(2)—C(3)—H(3)	120.2 (1)	117.8 (11)
C(4)—C(3)—H(3)	120.5 (1)	122.9 (11)
C(3)—C(4)—C(5)	118.5 (1)	118.8 (1)
C(3)—C(4)—H(4)	120.5 (1)	120.3 (14)
C(5)—C(4)—H(4)	120.9 (1)	120.9 (14)
Cl—C(5)—C(4)	120.7 (1)	120.9 (1)
Cl—C(5)—C(6)	120.2 (1)	120.0 (1)
C(4)—C(5)—C(6)	119.1 (1)	119.1 (1)
N(1)—C(6)—C(5)	122.8 (1)	122.9 (1)
N(1)—C(6)—H(6)	116.8 (1)	116.6 (11)
C(5)—C(6)—H(6)	120.4 (1)	120.5 (11)

* Kvick & Backéus (1974).

The quality of the X–N syntheses in the plane of the pyridine ring appears generally to be excellent. Fig. 3 shows the results found in the plane of the ring and in a plane displaced 0.4 Å from the ring. Electron densities are found in the covalent bonds and at the expected lone-pair regions. Of particular interest is the difference of hybridization of the N atoms. The pyridine N atom is expected to have an electron lone-pair in the plane of the ring whereas the amino N atom is expected to have an electron lone-pair perpendicular to the ring. This expectation is convincingly verified in Fig. 3. The X–N syntheses also explain the well-known disparity in bond distances involving covalently attached H atoms determined by X-ray and neutron diffraction techniques. The asphericity of the electron distribution around H atoms results in apparently shorter X–H distances found by X-ray studies. The difference in H atomic positions is close to 0.13 Å in C–H bonds. In N–H and O–H bonds the difference varies considerably with the hybridization and hydrogen-bond involvement of the N–H and O–H groups. A more extensive discussion of these matters is given by Kvick (1974).

Typical systematic differences in X–H bond distances determined by X-ray and neutron diffraction are given in Table 4, which summarizes three comparative neutron and X-ray studies. Similar disparities are also found by Coppens (1974), Lundgren & Tellgren (1974), Hanson, Sieker & Jensen (1972), and Thomas (1975). The systematic difference is only present in the bond distances; the bond angles are not affected in X–H

bonds (Table 4). A similar but smaller effect exists for first row elements in a pronounced asymmetric bonding environment (Coppens, 1974).

The hydrogen bond

The 2-amino-5-chloropyridine molecules are linked to produce cyclic dimers *via* pairs of N–H...N hydrogen bonds across centres of symmetry. The N...N bond distance is 3.058 (3) Å; the H...N separation is 2.051 (3) Å and the bond is nearly linear with an N–H...N angle of 174°. An X–N synthesis in the plane of the bond is presented in Fig. 4. It is clearly seen that the positive side of H(1) points toward the electron lone-pair region of the pyridine N(1). The second H atom H(2) of the amino group is *not* involved in hydrogen bonding. The N(2)–H(2) bond distance of 0.980 (3) Å gives an indication of the bond distance for an N–H bond not involved in hydrogen bonding in

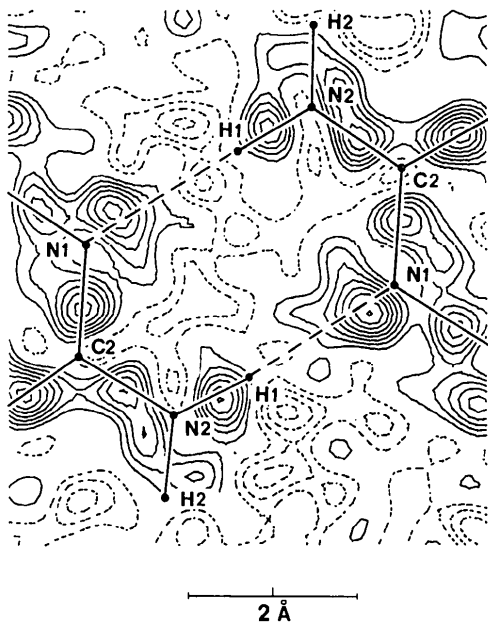


Fig. 4. X–N difference synthesis in the plane of the hydrogen bond. The contours are drawn at 0.06 e Å⁻³ intervals; negative regions are represented by dashed lines.

Table 5. The root-mean-square components R_i (Å × 10³) of thermal displacement of the atoms along the ellipsoid axes

	R_1	R_2	R_3
Cl	175 (1)	219 (1)	256 (1)
N(1)	171 (1)	183 (1)	221 (1)
N(2)	177 (1)	219 (2)	307 (1)
C(2)	177 (1)	185 (1)	203 (1)
C(3)	169 (1)	196 (1)	214 (1)
C(4)	167 (1)	195 (1)	207 (1)
C(5)	168 (1)	185 (1)	190 (1)
C(6)	167 (1)	177 (1)	206 (1)
H(1)	196 (3)	251 (3)	281 (3)
H(2)	204 (3)	278 (3)	348 (3)
H(3)	181 (3)	260 (3)	307 (3)
H(4)	186 (3)	260 (3)	301 (3)
H(6)	186 (3)	227 (2)	297 (3)

Table 4. Distances between H atom positions (Δ) and angles between X–H directions (δ) as determined from X-ray and neutron data

H_X and H_N are the H atom positions as found by X-ray and neutron diffraction, respectively.

Compound	Covalent bond	X–H _N	X–H _X	Δ	δ
2-Amino-5-chloropyridine ^{a,b}	N(2)–H(1)	1.009 (3) Å	0.812 (24) Å	0.20 (3) Å	2 (2) ^o
	N(2)–H(2)	0.980 (3)	0.839 (26)	0.15 (3)	3 (2)
	C(3)–H(3)	1.087 (2)	0.960 (19)	0.14 (2)	2 (1)
	C(4)–H(4)	1.082 (3)	0.953 (22)	0.14 (3)	0 (1)
	C(6)–H(6)	1.091 (2)	0.971 (19)	0.12 (2)	1 (1)
	Pyridine-2,3-dicarboxylic acid ^{c,d}	N(1)–H(4)	1.036 (4)	0.963 (33)	0.09 (3)
	C(4)–H(1)	1.087 (4)	0.946 (30)	0.14 (3)	1 (1)
	C(5)–H(2)	1.080 (3)	0.957 (21)	0.13 (2)	2 (1)
	C(6)–H(3)	1.095 (3)	0.988 (26)	0.13 (2)	3 (2)
α -Glycine ^{e,f}	O(3)–H(5)	1.163 (5)	1.091 (40)	0.13 (3)	5 (1)
	N–H(1)	1.054 (2)	0.996 (19)	0.07 (2)	2 (1)
	N–H(2)	1.037 (2)	0.982 (18)	0.07 (2)	2 (1)
	N–H(3)	1.025 (2)	0.959 (16)	0.07 (2)	1 (1)
	C(2)–H(4)	1.090 (2)	0.963 (16)	0.13 (2)	2 (1)
	C(2)–H(5)	1.089 (2)	0.966 (18)	0.13 (2)	3 (1)
			Δ (mean)	δ (mean)	
	N–H				2
	C–H			0.13	2

(a) Kvik & Backéus (1974). (b) Present work. (c) Kvik, Koetzle, Thomas & Takusagawa (1974). (d) Kvik & Chomnilpan (1974). (e) Jönsson & Kvik (1972). (f) Almlöf, Kvik & Thomas (1974).

a case where the N atom is sp^2 hybridized. In a situation where the amino group N atom is sp^3 hybridized and both H atoms are free from hydrogen bonding the

corresponding mean value is 1.013 Å (Lehmann, Verbist, Hamilton & Koetzle, 1973). In addition to the change in hybridization, it is possible that the lower

Table 6. Observed and calculated square neutron structure factors ($\times 10^{-25}$ cm²)

The columns are k , l , F_o^2 , $|F_c^2|$, $100\sigma(F_c^2)$, where $\sigma(F_c^2)^2$ is the value used for weighting in the final least-squares refinement. All reflections included in the table were used in the refinement.

k	l	F_o^2	$ F_c^2 $	$100\sigma(F_c^2)$
1	0	1000	1000	100
2	0	1000	1000	100
3	0	1000	1000	100
4	0	1000	1000	100
5	0	1000	1000	100
6	0	1000	1000	100
7	0	1000	1000	100
8	0	1000	1000	100
9	0	1000	1000	100
10	0	1000	1000	100
11	0	1000	1000	100
12	0	1000	1000	100
13	0	1000	1000	100
14	0	1000	1000	100
15	0	1000	1000	100
16	0	1000	1000	100
17	0	1000	1000	100
18	0	1000	1000	100
19	0	1000	1000	100
20	0	1000	1000	100
21	0	1000	1000	100
22	0	1000	1000	100
23	0	1000	1000	100
24	0	1000	1000	100
25	0	1000	1000	100
26	0	1000	1000	100
27	0	1000	1000	100
28	0	1000	1000	100
29	0	1000	1000	100
30	0	1000	1000	100
31	0	1000	1000	100
32	0	1000	1000	100
33	0	1000	1000	100
34	0	1000	1000	100
35	0	1000	1000	100
36	0	1000	1000	100
37	0	1000	1000	100
38	0	1000	1000	100
39	0	1000	1000	100
40	0	1000	1000	100
41	0	1000	1000	100
42	0	1000	1000	100
43	0	1000	1000	100
44	0	1000	1000	100
45	0	1000	1000	100
46	0	1000	1000	100
47	0	1000	1000	100
48	0	1000	1000	100
49	0	1000	1000	100
50	0	1000	1000	100
51	0	1000	1000	100
52	0	1000	1000	100
53	0	1000	1000	100
54	0	1000	1000	100
55	0	1000	1000	100
56	0	1000	1000	100
57	0	1000	1000	100
58	0	1000	1000	100
59	0	1000	1000	100
60	0	1000	1000	100
61	0	1000	1000	100
62	0	1000	1000	100
63	0	1000	1000	100
64	0	1000	1000	100
65	0	1000	1000	100
66	0	1000	1000	100
67	0	1000	1000	100
68	0	1000	1000	100
69	0	1000	1000	100
70	0	1000	1000	100
71	0	1000	1000	100
72	0	1000	1000	100
73	0	1000	1000	100
74	0	1000	1000	100
75	0	1000	1000	100
76	0	1000	1000	100
77	0	1000	1000	100
78	0	1000	1000	100
79	0	1000	1000	100
80	0	1000	1000	100
81	0	1000	1000	100
82	0	1000	1000	100
83	0	1000	1000	100
84	0	1000	1000	100
85	0	1000	1000	100
86	0	1000	1000	100
87	0	1000	1000	100
88	0	1000	1000	100
89	0	1000	1000	100
90	0	1000	1000	100
91	0	1000	1000	100
92	0	1000	1000	100
93	0	1000	1000	100
94	0	1000	1000	100
95	0	1000	1000	100
96	0	1000	1000	100
97	0	1000	1000	100
98	0	1000	1000	100
99	0	1000	1000	100
100	0	1000	1000	100

