

à la délocalisation de s'étendre sur le système π du carbonyle [Fig. 4(c)]. L'excès de densité électronique dans la liaison axiale C(1)–O(1) est réparti sur trois liaisons, et par suite, sa modification de longueur n'est plus perceptible.

On a publié récemment la structure d'un glucoside d'énol, le *trans-O- β -D-glucopyranosylméthylacétoacétone* (Ruble & Jeffrey, 1974). Dans ce cas également, on n'observe pas le raccourcissement prévu de la liaison C(1)–O(1). L'explication donnée est essentiellement la même que la nôtre: un système conjugué permet une délocalisation poussée de l'excès de densité électronique dans la liaison C(1)–O(1). Notre travail montre qu'on peut déjà observer ce phénomène avec une aglycone très simple: le groupement *O*-acétyle.

Conclusion

Le tétra-*O*-acétyl- α -D-lyxopyranose cristallise avec la conformation *C* 1 (D), majoritaire en solution. Le

groupement *O*-acétyle sur C(1) est alors en position axiale. La structure de la région C(5)–O(5)–C(1)–O(1)–C(6)–O(6) est compatible avec la délocalisation électronique invoquée dans la théorie de l'effet anomérique.

Références

- CORFIELD, P. W. R., MOKREN, J. D., DURETTE, P. L. & HORTON, D. (1972). *Carbohydr. Res.* **23**, 158–162.
 DAVID, S., EISENSTEIN, O., HEHRE, W. G., SALEM, L. & HOFFMANN, R. (1973). *J. Amer. Chem. Soc.* **95**, 3806–3807.
 DURETTE, P. L. & HORTON, D. (1971). *J. Org. Chem.* **36**, 2658–2669.
 GUIBÉ, L., AUGÉ, J., DAVID, S. & EISENSTEIN, O. (1973). *J. Chem. Phys.* **58**, 5579–5583.
 HERPIN, P., FAMERY, R., AUGÉ, J., DAVID, S. & GUIBÉ, L. (1976). *Acta Cryst.* **B32**, 209–215.
 JEFFREY, G. A., POPLÉ, J. A. & RADOM, L. (1974). *Carbohydr. Res.* **38**, 81–95.
 RUBLE, J. & JEFFREY, G. A. (1974). *Carbohydr. Res.* **38**, 61–69.

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Hydrogen Bond Studies. XCIX. The Crystal and Molecular Structure of 6-Bromo-2-hydroxypyridine

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The crystal and molecular structure of 6-bromo-2-hydroxypyridine, C_5H_3NBrOH , has been determined from four-circle X-ray diffractometer data, with Mo $K\alpha$ radiation. The crystals are monoclinic, space group *C2/c*, with eight formula units in a cell of dimensions $a = 14.916$ (1), $b = 4.025$ (1), $c = 20.132$ (2) Å, $\beta = 106.02$ (1)°. The H atoms were located in a difference Fourier synthesis and full-matrix least-squares refinement based on *F* gave a final $R(F) = 0.037$. The molecules occur in the enol form and are linked to produce cyclic dimers *via* two O–H...N hydrogen bonds [2.757 (4) Å].

Introduction

This work is a part of a systematic investigation of hydrogen bonding in simple organic compounds which can serve as model substances for biologically important molecules. The crystal structure of 6-chloro-2-hydroxypyridine, the addition compound 6-chloro-2-hydroxypyridine–2-pyridone and 5-chloro-2-pyridone have been reported by Kvick & Olovsson (1968), Almlöf, Kvick & Olovsson (1971) and Kvick & Booles (1972). The structure determination of 6-bromo-2-hydroxypyridine, C_5H_3NBrOH , based on single-crystal X-ray diffractometer data collected at room temperature is presented in this paper. Further investigations of related compounds are in progress at this Institute.

A summary of the tautomerism of substituted 2-hydroxypyridines has been given by Kvick (1974).

Crystal data

6-Bromo-2-hydroxypyridine, C_5H_3NBrOH . F.W. 173.997. Monoclinic $a = 14.916$ (1),* $b = 4.025$ (1), $c = 20.132$ (2) Å, $\beta = 106.02^\circ$ (1), $V = 1161.78$ Å³ at +24°C, $Z = 8$, $D_x = 1.989$ g cm⁻³. Space group *C2/c*. The cell dimensions were determined from powder photographs taken with a Guinier–Hägg powder camera at +24°C with monochromated Cu $K\alpha_1$ radiation ($\lambda = 1.54051$ Å). Silicon ($a_{Si} = 5.43054$ Å) was used as an internal

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

standard. 35 reflexions were used in a least-squares procedure to obtain the cell constants.

Experimental

Crystals of 6-bromo-2-hydroxypyridine suitable for data collection were grown from chloroform. A prismatic crystal bounded by eight faces of the forms {010}, {121}, {001}, {301}, and {101} and having a maximum edge length of 0.47 mm was mounted in a glass capillary to prevent sublimation during the data collection.

The diffraction data were collected at room temperature (+24°C) on an automated Stoe-Philips four-circle diffractometer using Mo radiation. An $\omega/2\theta$ scan technique was used to obtain the intensities. Automatic attenuator filter selection made it possible to reduce the count rate in the detector by a ratio of up to 8:1. This, in combination with automatic scan-speed selection ($\times 1$, $\times 2$ or $\times 4$), resulted in a maximum relative scale factor of 32. Three standard reflexions measured at regular intervals during the experiment showed only those variations expected from counting statistics. No rescaling of the data was therefore necessary. In all, 3320 reflexions were measured with $\sin \theta/\lambda < 0.648 \text{ \AA}^{-1}$. This set included some equivalent reflexions which were averaged together after absorption correction. Removal of reflexions of zero intensity due to space-group extinction left a total of 1514 reflexions. 499 of these had $I < 3\sigma(I)$.

The data were corrected for background, Lorentz, polarization and absorption effects with the program *DATAPH* (Coppens, Leiserowitz & Rabinovich, 1965). The linear absorption coefficient for Mo $K\alpha$ radiation is 81.13 cm^{-1} . The crystal shape was represented by eight rational boundary planes; a grid of 216 sampling points was used in the Gaussian integration method. The volume of the crystal was 0.021 mm^3 .

Structure determination and refinement

The structure was solved by Patterson methods. The normalized structure factor amplitudes ($|E|$) were calculated according to the method of Hauptman & Karle (1953). The distribution of the $|E|$'s gave evidence for a centrosymmetric structure and accordingly the space group $C2/c$ was chosen. The choice was later confirmed by the successful refinement in this space group.

Preliminary atomic coordinates for the Br atom were obtained from a Patterson synthesis. A subsequent difference synthesis revealed the positions of the remaining heavy atoms.

The atomic coordinates and a scale factor were refined in the least-squares program *UPALS* (Lundgren, 1974). The quantity minimized in all least-squares refinements was $\sum w[|F_o| - |F_c|]^2$. The reflexions were weighted according to the formula:

$$w^{-1} = \sigma_c^2(F^2)/4F^2 + (kF)^2 = \sigma^2(F)$$

with $k=0.08$ in the final cycles of refinements and σ_c based on counting statistics. The quantity kF was introduced to allow for uncertainties not arising from counting statistics. The heavy atoms were refined for a few cycles with isotropic temperature factors. Two cycles of anisotropic refinement were followed by a subsequent Fourier difference synthesis which revealed the H atom positions. The validity of the H atom positions was confirmed from chemical considerations. The electron density at the H atom positions varied between 0.3 and 0.6 e \AA^{-3} with the hydrogen-bonding atom H(2) occurring at the lowest value. In the final cycles of refinement one scale factor, the atomic coordinates for all atoms, anisotropic thermal parameters for the heavy atoms and isotropic temperature factors for the H atoms and one isotropic secondary extinction parameter (in all 90 parameters) were allowed to vary. 1015 reflections had non-zero weight. The final shifts were all smaller than 0.2σ . The refinement converged at: $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.037$, $R = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2} = 0.061$. The atomic parameters from the final refinement are given in Tables 1 and 2.*

Table 1. Atomic coordinates with standard deviations in parentheses ($\times 10^5$)

	x	y	z
Br	37990 (3)	69134 (17)	17276 (3)
O	12406 (23)	15241 (95)	-1247 (17)
N	23372 (21)	41154 (89)	7470 (16)
C(2)	14486 (28)	31624 (105)	4712 (21)
C(3)	7467 (29)	37438 (112)	7910 (22)
C(4)	9769 (30)	54943 (137)	13958 (22)
C(5)	18896 (33)	64807 (106)	16967 (24)
C(6)	25303 (26)	57224 (110)	13485 (19)
H(2)	177 (6)	146 (18)	-30 (4)
H(3)	11 (4)	304 (11)	60 (3)
H(4)	50 (4)	614 (15)	164 (3)
H(5)	207 (4)	765 (12)	211 (3)

The values for the H atoms are $\times 10^5$.

The atomic scattering factors used were those given by Hanson, Herman, Lea & Skillman (1964), except for the H atoms for which spherical scattering factors given by Stewart, Davidson & Simpson (1965) were preferred. The anomalous scattering factors for the Br atom were taken from Cromer (1965) with the values $\Delta f' = -0.21$ and $\Delta f'' = 2.68$.

The calculations were performed on the CDC 3600 and IBM 370/155 computers in Uppsala. Smaller calculations were performed on the departmental IBM 1800 computer.

Description and discussion of the structure

The 6-bromo-2-hydroxypyridine molecules exist in the enol form and are linked to produce cyclic dimers *via*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31331 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

pairs of O—H...N hydrogen bonds [2.757 (4) Å]. The two molecules in the dimer are related to each other by a centre of symmetry and are both planar and parallel to each other (see Table 4). Fig. 1 gives a stereoscopic view of the structure. All illustrations in this paper have been prepared with the plotting program ORTEP-II (Johnson, 1965). The r.m.s. vibrational amplitudes along the principal axes are given in Table 5.

Packing arrangements

The hydrogen-bonded dimeric units are related by the *c* glide planes. Two sets of such units are thus

formed (Fig. 1) with an angle of 59.6° between their respective planes. Each of the sets consists of infinite stacks of parallel dimers in the *b* direction with a stacking distance of 3.49 Å. The molecules thus form a herring-bone pattern in projection along the *a* axis.

Except for the hydrogen-bond distances there are no intermolecular contacts shorter than the sum of the van der Waals radii (Pauling, 1960). The shortest contacts between the dimeric units are: Br(*x*, *y*, *z*)...H(4) ($\frac{1}{2} + x, \frac{1}{2} + y, z$) of 3.10 (6) Å, O(*x*, *y*, *z*)...H(3) ($-x, -y, -z$) of 2.70 (5) Å and C(5) (*x*, *y*, *z*)...H(5) ($\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$) of 2.92 (5) Å.

Table 2. Thermal parameters with estimated standard deviations ($\times 10^5$)

The anisotropic thermal parameters are of the form $\exp(-\beta_{11}h^2 - \dots - 2\beta_{12}hk \dots)$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	480 (4)	9391 (54)	357 (2)	-587 (7)	119 (2)	-452 (5)
O	392 (15)	11920 (338)	294 (9)	-267 (55)	107 (9)	-519 (42)
N	388 (15)	6269 (212)	253 (8)	67 (47)	94 (9)	33 (35)
C(2)	363 (18)	6809 (274)	241 (10)	95 (54)	76 (11)	106 (41)
C(3)	390 (19)	7302 (318)	275 (10)	86 (57)	130 (11)	221 (44)
C(4)	454 (20)	8088 (325)	303 (12)	280 (70)	168 (12)	88 (52)
C(5)	507 (22)	6174 (290)	273 (11)	33 (59)	124 (12)	-8 (44)
C(6)	421 (18)	5736 (232)	248 (10)	-74 (57)	109 (10)	125 (41)

	B (Å ²)
H(2)	7.8 (1.7)
H(3)	3.9 (1.0)
H(4)	5.5 (1.2)
H(5)	3.9 (1.0)

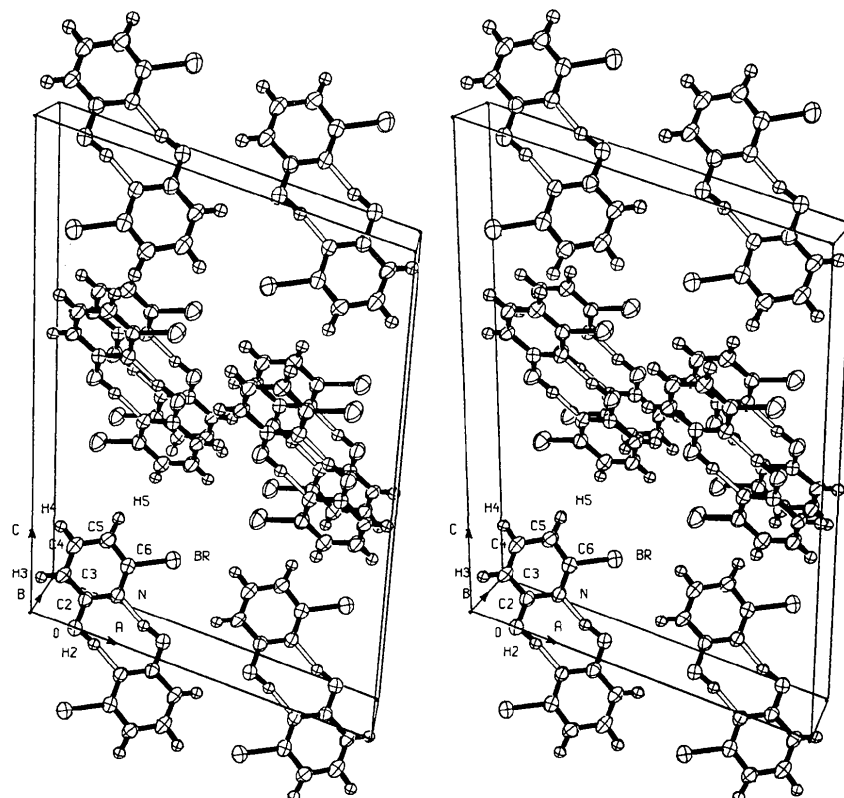


Fig. 1. A stereoscopic illustration of the crystal packing. The thermal ellipsoids are drawn at the 50% probability level. Covalent bonds are filled and hydrogen bonds are open.

Table 3. Distances (Å) and angles (°) with standard deviations in parentheses

(a) Covalent bonds

N—C(2)	1.344 (5)	N—C(2)—C(3)	122.9 (4)
C(2)—O	1.328 (5)	N—C(2)—O	118.2 (4)
C(2)—C(3)	1.392 (6)	C(3)—C(2)—O	118.9 (4)
C(3)—C(4)	1.366 (6)	C(2)—N—C(6)	117.1 (3)
C(4)—C(5)	1.387 (6)	C(2)—C(3)—C(4)	117.6 (4)
C(5)—C(6)	1.366 (6)	C(3)—C(4)—C(5)	120.8 (4)
C(6)—Br	1.897 (4)	C(4)—C(5)—C(6)	117.0 (4)
C(6)—N	1.332 (5)	C(5)—C(6)—N	124.6 (4)
		C(5)—C(6)—Br	119.9 (3)
O—H(2)	0.95 (10)	N—C(6)—Br	115.5 (3)
C(3)—H(3)	0.97 (6)	H(2)—O—C(2)	109 (5)
C(4)—H(4)	1.01 (7)	H(3)—C(3)—C(2)	123 (3)
C(5)—H(5)	0.92 (5)	H(3)—C(3)—C(4)	119 (3)
		H(4)—C(4)—C(3)	122 (3)
		H(4)—C(4)—C(5)	117 (3)
		H(5)—C(5)—C(4)	123 (4)
		H(5)—C(5)—C(6)	120 (4)

(b) Hydrogen bond

O·····N	2.757 (4)	O—H(2)···N	170 (8)
H(2)···N	1.82 (10)	C(2)—O·····N	116.1 (3)

Table 4. Deviations (Å) of the atoms from the least-squares plane through the six atoms in the ring

The primed atoms belong to the second molecule in the dimer. The equation of the least-squares plane is $-0.95310x + 3.49287y - 9.18212z = 0.52649$.

N	0.002 (3)	Br	-0.060 (1)	N'	0.215 (3)
C(2)	0.007 (4)	O	0.002 (4)	C'(2)	0.210 (4)
C(3)	-0.016 (4)	H(2)	0.090 (74)	C'(3)	0.233 (4)
C(4)	0.018 (5)	H(3)	-0.021 (48)	C'(4)	0.199 (5)
C(5)	-0.001 (4)	H(4)	0.065 (60)	C'(5)	0.218 (4)
C(6)	-0.007 (4)	H(5)	0.013 (51)	C'(6)	0.224 (4)

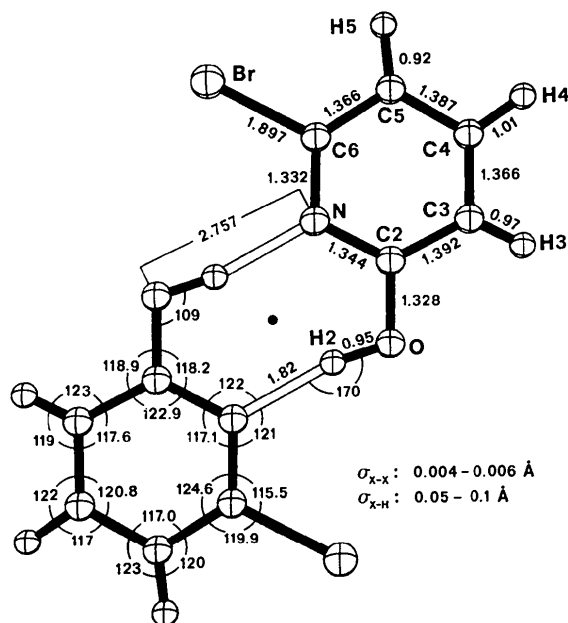


Fig. 2. Bond distances and angles. The distances have not been corrected for thermal motion.

Table 5. The root-mean-square components R_i (Å) of thermal displacements of the atoms along the ellipsoid axes ($\times 10^3$)

	R_1	R_2	R_3
Br	203 (1)	246 (1)	305 (1)
O	199 (4)	218 (3)	326 (4)
N	199 (4)	218 (4)	228 (4)
C(2)	193 (5)	212 (4)	240 (5)
C(3)	190 (5)	218 (4)	256 (5)
C(4)	193 (5)	240 (5)	267 (5)
C(5)	218 (5)	226 (5)	234 (5)
C(6)	194 (5)	215 (4)	228 (5)

Molecular dimensions

The bond distances and angles, given in Table 3 and illustrated in Fig. 2, have been calculated with the program *ORFFE* (Busing, Martin & Levy, 1964). The standard deviations have been estimated from the errors in the atomic coordinates obtained in the form of a variance-covariance matrix from the last cycle of refinement. The effect of the errors in the cell dimensions has also been taken into account.

The pyridine ring is planar; the deviations of the heavy atoms from their least-squares plane are all less than or equal to 0.018 Å. The H and O atoms also lie in the plane whereas the Br atom is significantly out of the plane [0.060 (1) Å].

The mean C—C bond distance of 1.378 Å is in perfect agreement with that found in 6-chloro-2-hydroxypyridine (Kvick & Olovsson, 1968). The longest C—C distance is also the one closest to the O substituent. The molecular dimensions are in general in excellent agreement with the values found in 6-chloro-2-hydroxypyridine. The C—Br distance of 1.897 (4) Å is comparable with the mean value of 1.896 Å found in 2,5-dibromobenzenesulphonic acid tetrahydrate (Lundgren, 1972) and in agreement with the mean value of 1.897 Å computed from 58 C—Br distances by James & Williams (1973).

The hydrogen atom positions

The C—H distances obtained from the refined coordinates varied between 0.92 (5) and 1.01 (7) Å and the O—H distance was found to be 0.95 (10) Å. The deviations from spherical electron density for the H atoms cause shifts of the apparent X-ray H positions [see Almlöf, Kvick & Thomas (1973)]. Comparative precise X-ray and neutron studies have shown that the apparent H atom position is 0.13 Å closer to the C atom in C—H bonds than the actual nuclear position as determined by neutron diffraction (Kvick, 1974). The systematic error does, however, only affect the bond distances and not the bond angles in these bonds.

When this displacement is taken into account the C—H distances from the present analysis agree well with those from neutron diffraction studies.

The hydrogen bond

The cyclic dimers are formed *via* O—H···N hydrogen bonds. The O···N distance is 2.757 (4) Å which is

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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References

- ALMLÖF, J., KVICK, Å. & OLOVSSON, I. (1971). *Acta Cryst.* B27, 1201–1208.
- ALMLÖF, J., KVICK, Å. & THOMAS, J. O. (1973). *J. Chem. Phys.* 59, 3901–3906.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* 18, 1035–1038.
- CROMER, D. T. (1965). *Acta Cryst.* 18, 17–23.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* 17, 1040–1044.
- HAUPTMAN, H. & KARLE, J. (1953). *Acta Cryst.* 6, 136–141.
- JAMES, M. N. G. & WILLIAMS, G. J. B. (1973). *Acta Cryst.* B29, 1172–1174.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- KATRITZKY, A. R., ROWE, J. D. & ROY, S. K. (1967). *J. Chem. Soc. (B)*, pp. 758–761.
- KVICK, Å. (1974). *Acta Univ. Ups.* 322, 1–53.
- KVICK, Å. & BOOLES, S. S. (1972). *Acta Cryst.* B28, 3405–3409.
- KVICK, Å. & OLOVSSON, I. (1968). *Ark. Kem.* 30, 71–80.
- LUNDGREN, J.-O. (1972). *Acta Cryst.* B28, 475–481.
- LUNDGREN, J.-O. (1974). *Crystallographic Computer Programs*. Institute of Chemistry, Univ. of Uppsala, Sweden, UUI-C-B13-4-01.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

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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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