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Hydrogen Bond Studies. LXV.* The Crystal Structure of 5-Chloro-2-pyridone, C_5H_4NOCl

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The crystal and molecular structure of 5-chloro-2-pyridone, C_5H_4NOCl, has been determined from four-circle X-ray diffractometer data, using Mo K radiation. The crystals are monoclinic, space group $C2/c$, with eight formula units in a cell of dimensions $a=13{\cdot}509$ (2), $b=8{\cdot}887$ (2), $c=12{\cdot}158$ (1) Å, $\beta=127{\cdot}396$ (7)°. The hydrogen atoms have been located from a difference Fourier synthesis and full-matrix least-squares refinement based on F^2 gave a final $R(F^2)=0{\cdot}071$ [$R(F)=0{\cdot}049$]. The molecules occur in the keto form and are linked to produce dimers *via* two N–H···O hydrogen bonds [2·796 (3) Å].

Introduction

This work forms part of a systematic investigation of hydrogen bonding in simple organic compounds that can serve as model substances for biologically important molecules. The structures of 6-chloro-2-hydroxypyridine (denoted by 6-ClPy) and the addition compound 6-chloro-2-hydroxypyridine:pyridone (denoted by 6-ClPy:Py) have been reported earlier by Kvick & Olovsson (1968) and Almlöf, Kvick & Olovsson (1971). Here we present the crystal structure of 5-chloro-2-pyridone, C_5H_4NOCl. Further investigations of related compounds are in progress at this Institute.

Experimental

Commercial 5-chloro-2-aminopyridine was used to synthesize 5-chloro-2-pyridone according to the method given by Tschitschibabin & Jegorow (1928). The product was recrystallized several times from chloroform. The final needle-shaped crystals had a melting point in the range 167·0–167·5°C.

The diffraction symmetry and systematic absences suggested one of the monoclinic space groups Cc or $C2/c$ (Nos. 9 and 15, *International Tables for X-ray Crystallography*, 1952).

The cell dimensions were determined from powder photographs taken with a Guinier–Hägg powder camera at +24°C with monochromated Cr $K\alpha_1$ radiation ($\lambda=2{\cdot}28962$ Å). CoP_3 ($a=7{\cdot}7073$ Å) was used as internal standard. Eighteen reflexions were used in a least-squares procedure to obtain the cell constants (Table 1).

Table 1. *Crystallographic and physical data*

5-Chloro-2-pyridone, C_5H_4NOCl	
F.W.	129·547
Space group	$C2/c$
a	= 13·509 (2) Å*
b	= 8·887 (2)
c	= 12·158 (1)
β	= 127·396 (7)°
U	= 1159·48 Å^3
D_x	= 1·484 g.cm^{-3}
Z	= 8
M.p.	167·0–167·5°C
μ	= 5·47 cm^{-1}

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

A crystal of dimensions 0·22×0·25×0·31 mm was mounted in a glass capillary (wall thickness about 0·02 mm) to prevent sublimation during the experiment. The data collection from this crystal was carried out at approximately +24°C using a PDP8/I-controlled four-circle Stoe X-ray diffractometer using graphite monochromated molybdenum radiation ($\lambda=0{\cdot}7107$ Å). An ω–2θ scan technique was used to obtain the intensities. Automatic 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 (×1, ×2 or ×4), resulted in a maximum absolute internal scale factor of 32. Two standard reflexions measured at regular intervals showed only expected variations from counting statistics during the experiment, and no scaling of the data was employed. 2354 reflexions in the range $2°\le 2\theta \le 55°$ were measured. This set included the equivalent sets hkl and $h\bar{k}l$ which were averaged together after absorption corrections giving 1027 independent reflexions. 306 of these had $I<2\sigma(I)$ and were considered as unobserved reflexions.

The data were corrected for background, Lorentz, polarization and absorption effects using the program *DATAPH*. A correction for monochromator polarization was also included. The polarization corrections were done according to the formula:

$$p=\frac{1+\cos^2 2\theta_M \cos^2 2\theta}{1+\cos^2 2\theta_M} \quad \text{with } \theta_M=6{\cdot}1°$$

and θ was the scattering angle for the measured reflexion. The linear absorption coefficient for Mo $K\alpha$ radiation was calculated to be 5·47 cm^{-1}. Crystal data are given in Table 1.

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Structure determination and refinement

The structure was solved by direct methods. An overall scale factor and an overall temperature factor were obtained by the method of Wilson (1942) using all data. The statistical distribution of the $|E|$ values is compared with the theoretical values expected for centric and acentric structures (Table 2). The theoretical values used are those given by Karle, Dragonette & Brenner (1965). The comparison gave an indication of a centric structure, and the space group $C2/c$ was thus chosen. The choice was later confirmed by the successful refinement in this space group.

Table 2. *Statistical distribution of the normalized structure amplitudes* (E) *compared with theoretical values*

	Experimental	Centrosymmetric	Non-centrosymmetric
$\langle \lvert E\rvert^2\rangle$	1·00	1·00	1·00
$\langle \lvert E^2-1\rvert\rangle$	1·099	0·968	0·736
$\langle \lvert E\rvert\rangle$	0·749	0·798	0·886
$\lvert E\rvert>3$ %	1·36	0·3	0·01
$\lvert E\rvert>2$ %	4·9	5·0	1·8
$\lvert E\rvert>1$ %	24·9	32·0	37·0

146 reflexions with $|E|>1\cdot5$ from a primitive cell were used as input to a multi-solution program (Long, 1965) for sign determination by iterative application of Sayre's formula. Two types of iterations were used. In one type, newly determined signs were immediately used in the determination of other signs, and in the other, the new signs were not used until the next cycle. The first procedure failed to give the correct solution. The more conservative approach, however, gave among its 16 solutions the correct one; it had the second highest consistency index (0·96). It later appeared that 142 of the 146 signs had been correctly determined. The solution with the highest consistency index (0·99) and fastest convergence failed to give a useful E map. Atomic coordinates from the correct E map and a scale factor were refined in a least-squares refinement using the program *LINUS*. The quantity minimized in all least-squares refinements was:

$$\sum w[|F_o^2|-|F_c^2|]^2.$$

The reflexions were weighted according to the formula:

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

with $k=0\cdot05$ in the final cycles of refinement and σ_c based on counting statistics. The quantity kF^2 was included to take account of other random errors not arising from counting statistics. The heavy atoms were refined for a few cycles using isotropic temperature factors and the refinement converged at $R(F^2)=0\cdot25$. A few cycles of anisotropic refinement and a subsequent Fourier difference synthesis using data with $\sin\theta/\lambda<0\cdot5$ Å^{-1} then revealed the hydrogen atom positions. The hydrogen peaks varied between 0·41 and 0·54 e.Å^{-3}. The highest spurious peak had a height of 0·23 e.Å^{-3}. The validity of the hydrogen positions were confirmed from chemical considerations. 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 hydrogen atoms (89 parameters in all) were allowed to vary. 694 reflexions had non-zero weight. The final shifts were all smaller than $0\cdot1\sigma$. The refinement converged at:

$$R(F^2)=\sum ||F_o^2|-|F_c^2||/\sum |F_o^2|=0\cdot071$$
$$R_w(F^2)=[\sum w(|F_o^2|-|F_c^2|)^2/\sum w|F_o^4|]^{1/2}=0\cdot102$$

corresponding to a conventional $R(F)$ based on F of 0·049. Excluded from the refinement in the final cycles were one strong and 26 weak reflexions. The 26 reflexions had $|F_o^2-F_c^2|/\sigma(F^2)>4\cdot0$ and were affected by non-random errors, caused by electronic disturbances in the counting chain. The exclusion of these reflexions did not significantly change the refined values of the parameters. Refinement of isotropic extinction showed that the very strong $22\bar{1}$ reflexion was the only one seriously affected by secondary extinction. It was also affected by other errors due to its large intensity. The extinction correction was thus unsatisfactory, resulting in over-correction of other reflexions in the data. It was therefore decided to remove the $22\bar{1}$ reflexion from the final refinement, and to make no isotropic extinction correction. The 306 reflexions with I smaller than $2\sigma(I)$ mentioned earlier were also left out of the refinement. Only five of the latter had $|F_o-F_c|/\sigma(F)>3\cdot0$ and only one, $20\bar{8}>4\cdot0$. The reflexion $20\bar{8}$ was, owing to a mechanical failure, measured with a lead filter introduced in the X-ray beam and hence had a measured intensity of zero counts. The atomic parameters from the final cycle of refinement are given in Tables 3 and 4. Observed and calculated structure factor amplitudes are listed in Table 5.

Table 3. *Atomic coordinates with standard deviations in parentheses* ($\times 10^4$)

The values for hydrogen atoms are $\times 10^3$.

	x	y	z
Cl	4150 (1)	3575 (1)	10625 (1)
O	994 (2)	4199 (2)	4674 (2)
N	1358 (2)	4468 (3)	6744 (2)
C(2)	1723 (2)	4039 (3)	5960 (3)
C(3)	2954 (3)	3441 (3)	6724 (3)
C(4)	3676 (3)	3307 (3)	8108 (3)
C(5)	3224 (3)	3758 (3)	8836 (3)
C(6)	2069 (3)	4325 (3)	8139 (3)
H(1)	54 (2)	486 (3)	625 (2)
H(3)	323 (3)	316 (3)	615 (3)
H(4)	451 (3)	288 (3)	864 (3)
H(6)	171 (3)	473 (3)	853 (3)

The atomic scattering factors used for the heavy atoms were those given in *International Tables for X-ray Crystallography* (1962). The spherical scattering factors for hydrogen atoms proposed by Stewart, Davidson & Simpson (1965) were used.

The calculations were performed on the CDC 3600

Table 4. *Thermal parameters with estimated standard deviations* ($\times 10^4$)

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

Heavy atoms	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	147 (1)	290 (2)	116 (1)	28 (1)	49 (1)	25 (1)
O	84 (2)	246 (4)	118 (3)	8 (2)	59 (2)	− 7 (2)
N	78 (2)	196 (4)	122 (3)	8 (2)	60 (2)	− 4 (3)
C(2)	78 (3)	164 (5)	125 (3)	− 7 (3)	61 (3)	−11 (3)
C(3)	91 (3)	215 (6)	145 (4)	11 (3)	71 (3)	−13 (4)
C(4)	88 (3)	178 (5)	147 (4)	12 (3)	52 (3)	− 7 (4)
C(5)	100 (3)	169 (5)	111 (3)	4 (3)	49 (3)	8 (3)
C(6)	102 (3)	199 (5)	122 (4)	5 (3)	69 (3)	− 1 (4)

Hydrogen atoms	B (Å^2)
H(1)	4·7 (6)
H(3)	6·5 (7)
H(4)	6·1 (7)
H(6)	5·5 (7)

in Uppsala using programs briefly described by Jönsson & Liminga (1971). Smaller calculations were performed using the departmental IBM 1800 computer.

Description of the structure

The 5-chloro-2-pyridone molecules occur in the keto form, in contrast to 6-ClPy, and are linked to form dimers *via* pairs of N–H···O hydrogen bonds [2·796 (3) Å]. The two molecules of the dimer are related by a centre of symmetry and are each planar and parallel to one another (Table 6). Fig. 1 shows a stereoscopic view of the structure approximately along the **b** direction. All illustrations in this paper were prepared using the plotting program *ORTEP.*

Table 5. *Observed and calculated structure factors*

The four columns are, in order, the indices k and l, $10|F_o|$ and $10|F_c|$. A negative value for F_o marks reflexions deleted from the least-squares refinement.

Table 6. *Deviations of the atoms from the least-squares plane through the six heavy atoms in the ring*

The primed atoms belong to the second molecule in the dimer.

	Deviation (Å)
N	−0·006 (3)
C(2)	0·006 (3)
C(3)	−0·001 (3)
C(4)	−0·003 (3)
C(5)	0·001 (3)
C(6)	0·006 (3)
H(1)	0·006 (26)
O	0·010 (2)
H(3)	−0·024 (30)
H(4)	0·018 (30)
H(6)	−0·062 (30)
Cl	0·009 (1)
N′	−0·125 (3)
C′(2)	−0·137 (3)
C′(3)	−0·131 (3)
C′(4)	−0·128 (3)
C′(5)	−0·132 (3)
C′(6)	−0·137 (3)

The root-mean-square (r.m.s.) vibrational amplitudes along the principal axes are given in Table 7.

Table 7. *The root-mean-square components R_i* (Å) *of thermal displacement of the atoms along the ellipsoid axes* ($\times 10^3$)

	R_1	R_2	R_3
Cl	226 (1)	333 (1)	355 (1)
O	219 (3)	238 (3)	316 (3)
N	207 (3)	242 (3)	282 (3)
C(2)	208 (4)	241 (4)	261 (4)
C(3)	221 (4)	259 (4)	302 (4)
C(4)	223 (4)	261 (4)	303 (4)
C(5)	222 (4)	261 (4)	276 (4)
C(6)	236 (4)	243 (4)	283 (4)

The packing in the structure

The packing in the structure is illustrated in Figs. 1 and 2. Fig. 2 is a view along the planes of the dimers. From consideration of the sum of the van der Waals radii of the various atoms (Pauling, 1960), the closest contacts between individual dimers are O···H(6) 2·33 Å, and O···H(4) 2·44 Å. There are no other intermolecular distances shorter than the sum of van der Waals radii. As can be seen from Fig. 1, the distance O···H(6) is between dimers of different orientation.

Molecular dimensions

The bond distances and angles, given in Tables 8 and 9 and illustrated in Fig. 3, were calculated with the program *ORFFE*. The standard deviations were 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.

Table 8. *Bond lengths*

The distances are not corrected for thermal motion.

(*a*) Covalent bonds

Cl—C(5)	1·736 (3) Å
O—C(2)	1·250 (3)
N—C(2)	1·366 (3)
N—C(6)	1·356 (4)
N—H(1)	0·95 (3)
C(2)–C(3)	1·427 (4)
C(3)–C(4)	1·343 (5)
C(3)–H(3)	0·99 (3)
C(4)–C(5)	1·405 (5)
C(4)–H(4)	0·97 (3)
C(5)–C(6)	1·342 (4)
C(6)–H(6)	0·93 (3)

(*b*) Hydrogen bond

O···H(1)	1·85 (3)
N···O	2·796 (3)
N—H(1)	0·95 (3)

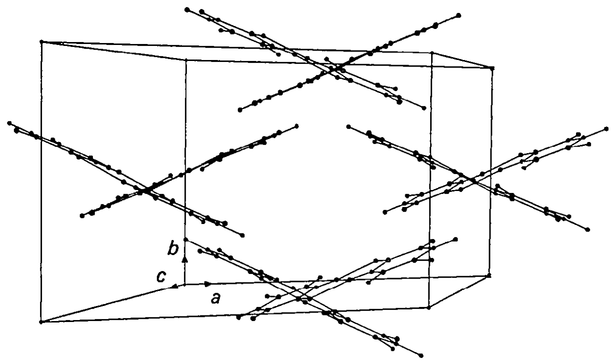

Fig. 2. Drawing showing the structure viewed along the planes of the dimers.

Table 9. *Bond angles*

(*a*) Covalent bonds

C(2)–N—C(6)	124·4 (3)°
C(2)–N—H(1)	116 (2)
C(6)–N—H(1)	119 (2)
O—C(2)–N	119·8 (2)
O—C(2)–C(3)	125·2 (3)
N—C(2)–C(3)	114·9 (3)
C(2)–C(3)–C(4)	121·3 (3)
C(2)–C(3)–H(3)	115 (2)
C(4)–C(3)–H(3)	124 (2)
C(3)–C(4)–C(5)	120·1 (3)
C(3)–C(4)–H(4)	122 (2)
C(5)–C(4)–H(4)	118 (2)
Cl—C(5)–C(4)	120·3 (2)
Cl—C(5)–C(6)	120·2 (3)
C(4)–C(5)–C(6)	119·6 (3)
N—C(6)–C(5)	119·6 (3)
N—C(6)–H(6)	114 (2)
C(5)–C(6)–H(6)	126 (2)

(*b*) Hydrogen bond

C(2)–O ·····N	123·8 (2)
C(2)–O ·····H(1)	123 (2)
N—H(1)···O	175 (2)

The molecules are planar. The deviations of the heavy atoms of the pyridine ring from the least-squares plane through the ring are all less than or equal to 0·006 Å. The chlorine and oxygen atoms are respectively 0·009 and 0·010 Å out of this plane. The deviations are listed in Table 6. As mentioned above, the two molecules of the dimer are related by a centre of symmetry and are parallel. The distance between the least-squares planes of the two molecules is 0·13 Å. The intramolecular distances are all similar to those found in the pyridone (Py) molecule of the complex 6-ClPy:Py (for notation see Introduction). The average C–C distance is 1·379 Å in the present compound and 1·374 Å in Py. From the distances in the pyridine ring it is evident that the double-bond character in the C(3)–C(4) (1·343 Å) and C(5)–C(6) (1·342 Å) bonds is very large whereas the C(2)–C(3) (1·427 Å) and C(4)–

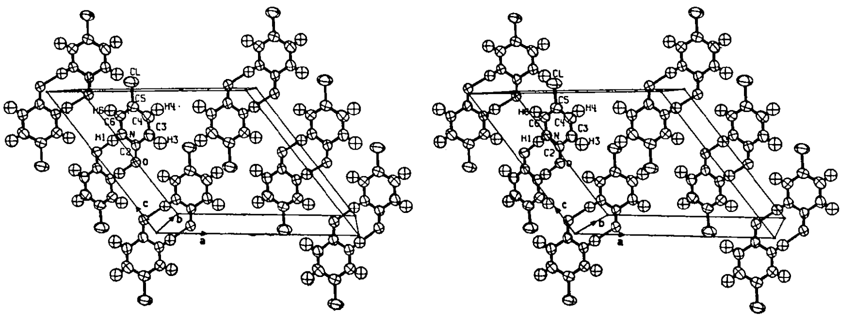

Fig. 1. Stereoscopic drawing of the crystal structure of 5-chloro-2-pyridone. The structure is viewed approximately along the *b* axis. Covalent bonds are filled and hydrogen bonds are open.

C(5) (1·405 Å) interactions have much smaller contributions of π bonding. The longest carbon–carbon distance is that closest to the double-bonded oxygen. The C=O distance of 1·250 (3) Å is somewhat shorter than the 1·262 (4) Å found in Py. The carbonyl bond distance depends on the hydrogen bond interaction with the oxygen atom. In Py a strong O–H···O hydrogen bond of 2·570 (4) Å brings about the increase in the C=O distance. The C–Cl distance of 1·736 (3) Å is comparable with 1·740 (3) Å in 6-ClPy.

The hydrogen atom positions

After anisotropic refinement of the heavy atoms, the hydrogen atomic coordinates were obtained from a Fourier difference synthesis. From these it is clear that H(1) is covalently bonded to the nitrogen atom and not to the oxygen atom. This is also shown indirectly by the observed angle C(2)–N–C(6) of 124·4 (3)° ,which is sensitive to the protonation of the nitrogen atom. In 6-ClPy the angle is 117·1 (2)°, and the hydrogen is attached to the oxygen atom. The hydrogen positions from the difference synthesis were refined to give carbon–hydrogen distances between 0·93 and 0·99 Å (Table 8). The mean refined C–H distance is 0·96 Å. The distances involving hydrogen atoms are incorrect because of the systematic error inherent in using nonpolarized scattering factors for the hydrogen atoms in the refinements. None of the hydrogen atoms deviate by more than 0·06 Å from the least-squares plane of the pyridine ring (Table 6). The atom H(1) is 0·06 Å out of the plane based on N, O and N′, O′ (primed atoms belong to the second molecule of the dimer).

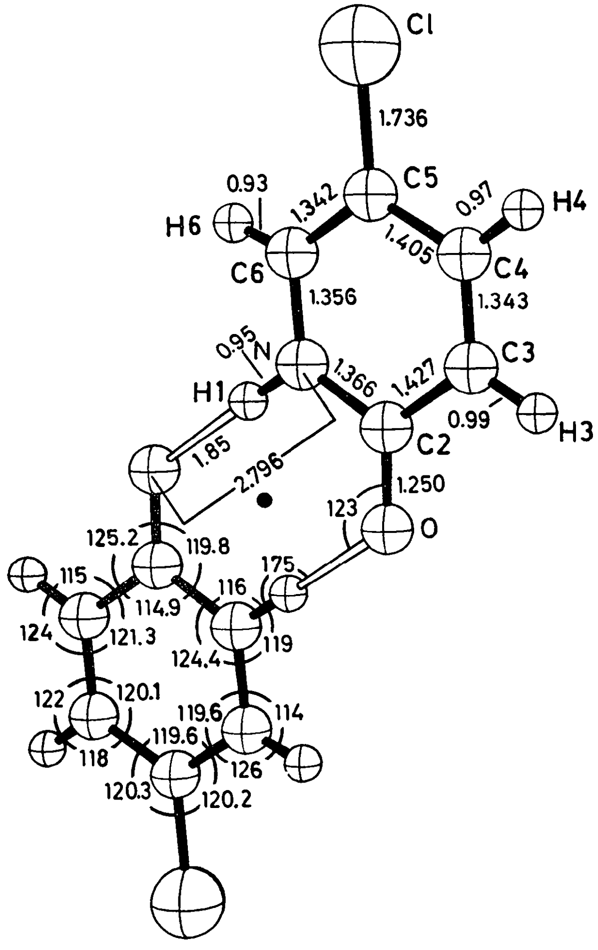

Fig. 3. Bond distances and angles. The values are not corrected for thermal motion.

The hydrogen bond

Dimers are formed by hydrogen bonding between nitrogen and oxygen atoms. The hydrogen bond is of the N–H···O type, which is common in this type of compound. The bond distance is 2·796 (3) Å. The hydrogen bond is almost linear with the N–H···O angle 175 (2)°. The O···H(1) distance is 1·85 (3) Å, and N–H(1) is 0·95 (3)° Å. The correct N–H value should be roughly 0·1 Å longer. In a recent neutron-diffraction study of α-glycine by Jönsson & Kvick (1972) an almost linear hydrogen bond of similar strength [N···O = 2·770 (1) Å, N–H···O = 169·3 (2)°] had an O···H distance of 1·728 (2) Å and an N–H distance of 1·054 (2) Å. The correct values for the present compound are probably very close to these.

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