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# Crystal Structure of 5-Chloropyrimidin-2-one

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The crystal structure of 5-chloropyrimidin-2-one has been derived from 2287 reflections measured by counter methods. The space group is *Pbca* with 16 molecules in the unit cell. The structure was refined to $R = 0.113$ by full matrix least squares calculations. Hydrogen bonds N – H···N and interactions Cl···O link the molecules together in planar layers (010).

Substituted pyrimidin-2-ones are substances of great biological importance and it would appear to be of interest to investigate the influence of different substituents on the structure of the ring system. We have carried out X-ray crystal structure analyses of a number of such compounds.[1–3] In the present paper the structure of the 5-chloro derivative is described.

## EXPERIMENTAL. STRUCTURE ANALYSIS

Crystals were grown by slow evaporation of an ethyl acetate solution. Weissenberg diagrams showed them to be orthorhombic, with space group *Pbca*. Strong thermal diffuse scattering occurs, especially at reflections 040, 080, and 0120. Unit cell dimensions were measured on a diffractometer and found to be $a = 9.310(2)$ Å, $b = 12.611(2)$ Å, and $c = 17.261(2)$ Å. There are 16 molecules in the unit cell.

The intensity measurements were made on a crystal of dimensions about 0.3 mm, using a Picker automatic diffractometer and mono-chromatic Mo$K\alpha$ radiation. The $\omega/2\theta$ scan mode was employed (rate 1°/min). All 2769 independent reflections with $2\theta < 55°$ were measured, of which the 2287 with $I > 0$ were retained for refinement. Of these only 1482 satisfy the condition $I > 2\sigma(I)$. Corrections for absorption, extinction and thermal diffuse scattering were not applied. The atomic form factors used were those of Hanson *et al.*,[4] except for hydrogen.[5]

The structure was solved by vector methods and refined by full-matrix least squares calculations. The weighting scheme was based on standard deviations from counter statistics and 2 % fluctuations in diffractometer stability. The hydrogen atoms were assumed to have the same anisotropic temperature factor as the atom to which they are attached, and only their positional parameters were refined. The final value of $R$ is 0.113 ($R_w = 0.079$) for 2287 reflections. If those with $I < 2\sigma(I)$ are excluded $R$ drops to 0.066 ($R_w = 0.065$). The parameters obtained were not significantly different and the discussion will be based on those derived from the largest data set. They are given in Table 1.

A list of observed and calculated structure factors will be supplied by the authors on request.

The vibrations of all atoms are strongly anisotropic, with maximum amplitudes (ranging from $B = 3.1$ to 7.7 Å$^2$) in the $y$ direction. The r.m.s. difference between atomic vibration tensor components calculated from Table 1 and those derived from the rigid body model was as high as 0.0036 Å$^2$. Corrections were therefore not carried out.

The calculations were carried out on CYBER-74.[6]

## RESULTS AND DISCUSSION

*Molecular structure.* Interatomic distances and bond angles are given in Table 2. The differences between the two crystallographically independent molecules A and B are larger than to be expected from the estimated standard deviations, being as large as $6\sigma$ for the bond N1 – C6. Maximum deviations from least squares planes are 0.03 – 0.04 Å for non-hydrogen atoms, greater than usually found for pyrimidines. The structure arrived at is therefore not quite satisfactory. We believe that this is related to the fact that all atoms lie very close to planes $y = 0$ or $y = 0.25$. The intensities of about half of the reflections are nearly zero and inaccurately measured. Various refinements starting with slightly different $y$ coordinates were tried, but

*Table 1.* Positional ($\times 10^5$ for non-hydrogens, $\times 10^4$ for hydrogens) and thermal ($\times 10^5$) parameters with estimated standard deviations. The temperature factor is exp $[-(B11h^2+B22k^2+B33l^2+B12hk+B13hl+B23kl)]$.

| ATOM | x | y | z | B11 | B22 | B33 | B12 | B13 | B23 |
|---|---|---|---|---|---|---|---|---|---|
| CL A | -322( 9) | 24992(14) | -1369( 6) | 987( 12) | 982( 12) | 168( 3) | 428( 27) | 6( 9) | -28( 15) |
| N1 A | -18329(27) | 24575(48) | 28746(17) | 583( 29) | 788( 29) | 284( 9) | 317( 68) | 153( 27) | -257( 44) |
| N3 A | 14714(27) | 24612(35) | 19917(17) | 693( 30) | 692( 26) | 237( 10) | 116( 65) | -72( 28) | 76( 43) |
| C2 A | 2784(39) | 24832(46) | 24552(28) | 634( 42) | 569( 47) | 214( 13) | 353( 92) | -41( 29) | 31( 45) |
| C4 A | 13441(33) | 24625(49) | 12475(19) | 468( 35) | 689( 31) | 222( 11) | 271( 88) | 59( 30) | -55( 51) |
| C5 A | 318(32) | 24731(42) | 8558(19) | 631( 36) | 588( 30) | 157( 10) | -9( 83) | 27( 28) | 62( 52) |
| C6 A | -11692(33) | 24797(48) | 13038(18) | 476( 33) | 698( 32) | 208( 10) | 164( 83) | -97( 30) | -66( 56) |
| O2 A | 3316(31) | 24128(40) | 31541(15) | 1259( 39) | 1198( 37) | 173( 9) | 765( 73) | -14( 30) | 83( 44) |
| CL B | 25787(11) | 565(17) | -1263( 6) | 1866( 13) | 978( 14) | 175( 3) | -28( 19) | 23( 12) | -13( 18) |
| N1 B | 36181(30) | 375(34) | 28879(18) | 641( 33) | 626( 33) | 199( 11) | 214( 68) | -53( 30) | -73( 37) |
| N3 B | 18630(31) | -944(35) | 20186(19) | 692( 33) | 810( 36) | 225( 12) | -251( 62) | 121( 31) | -28( 48) |
| C2 B | 23021(40) | -597(46) | 24785(19) | 731( 48) | 421( 40) | 199( 13) | -144( 88) | 25( 35) | 88( 42) |
| C4 B | 11761(37) | -824(44) | 12614(23) | 569( 40) | 734( 47) | 263( 15) | -235( 85) | -5( 40) | -319( 53) |
| C5 B | 25851(39) | -92(49) | 8748(19) | 691( 38) | 679( 36) | 184( 10) | -1( 57) | 16( 42) | -457( 60) |
| C6 B | 37288(36) | 833(42) | 13012(22) | 615( 39) | 628( 43) | 213( 13) | 232( 84) | 78( 38) | -293( 47) |
| O2 B | 22468(30) | -248(41) | 31758(16) | 1162( 42) | 1199( 37) | 197( 9) | 282( 74) | 127( 32) | 79( 44) |
| H4 A | 2851(36) | 2481(36) | 1618(28) | | | | | | |
| H6 A | -2071(36) | 2434(36) | 1122(19) | | | | | | |
| H4 B | 284(37) | -287(34) | 1806(22) | | | | | | |
| H6 B | 4827(36) | 66(31) | 1129(22) | | | | | | |
| H1 A | -1713(35) | 2427(36) | 2418(21) | | | | | | |
| H1 B | 4783(38) | -16(32) | 2455(28) | | | | | | |

*Table 2.* Bond lengths (Å) and bond angles (°). Prime denotes an atom in a neighboring molecule.

| Distance | Mol. A | Mol. B | Angle | Mol. A | Mol. B |
|---|---|---|---|---|---|
| Cl–C5 | 1.715(3) | 1.730(3) | Cl–C5–C6 | 122.7(3) | 120.5(3) |
| C5–C6 | 1.358(4) | 1.361(5) | Cl–C5–C4 | 120.9(2) | 120.5(3) |
| C6–N1 | 1.338(4) | 1.364(5) | C5–C6–N1 | 119.2(3) | 117.9(3) |
| N1–C2 | 1.388(4) | 1.391(5) | C6–N1–C2 | 123.7(3) | 123.2(3) |
| C2–N3 | 1.371(4) | 1.393(5) | N1–C2–N3 | 115.7(3) | 117.5(3) |
| N3–C4 | 1.290(4) | 1.311(5) | C2–N3–C4 | 120.5(3) | 119.4(3) |
| C4–C5 | 1.397(4) | 1.409(5) | N3–C4–C5 | 124.2(3) | 123.0(3) |
| C2–O2 | 1.207(4) | 1.219(4) | C4–C5–C6 | 116.4(3) | 118.9(3) |
| N1–H | 0.86 | 1.20 | N1–C2–O2 | 120.6(4) | 120.6(4) |
| C4–H | 0.78 | 1.02 | N3–C2–O2 | 123.3(4) | 121.7(4) |
| C6–H | 0.90 | 1.07 | C5–Cl···O2′ | 171.4(2) | 176.2(2) |
| Cl···O2′ | 2.971(3) | 2.936(3) | C2–O2···Cl′ | 171.0(3) | 173.6(3) |
| N1···N3′ | 2.828(4) | 2.761(4) | | | |

it appears that the least squares refinements do not lead unequivocally to the correct deviations from $y=0$ or 0.25. Details in the structure will therefore not be discussed and we do not consider the differences between molecules A and B real.

In Fig. 1 the molecular structure is compared with those of pyrimidin-2-one [1] and 5-fluoropyrimidin-2-one.[3] The external bonding of the chlorine compound is quite different from that of the others but this hardly influences the bonds at the substituted atom C5. The greatest difference between the fluorine and chlorine derivative occurs in the bond C5–C6, which is found to be shortened by 0.016 Å by fluorine substitution and elongated by 0.014 Å by chlorine substitution. Although of doubtful significance, these effects are in general agreement with the view that both halogens withdraw electrons from the ring, but that only fluorine backdonates electrons to the $\pi$-system.[6]

The C=O bond is slightly shorter in the chloro-derivative than in the other two compounds. This is presumably related to the differences in intermolecular bonding.

*Crystal structure.* The crystal consists of nearly planar layers of molecules parallel to the *ac* plane. The distance between layers is $b/4=3.15$ Å. The hydrogen bonding is not of the N–H···O type usually found in pyrimidin-2-ones, the molecules being linked together in planar ribbons along *a* by N1–H···N3 hydrogen bonds of lengths 2.828 Å (A) and 2.761 Å (B) (Fig. 2). The ribbons appear to be held together mainly by a Cl···O interaction, this distance being 2.971 Å and 2.936 Å in layers of molecules A and B,

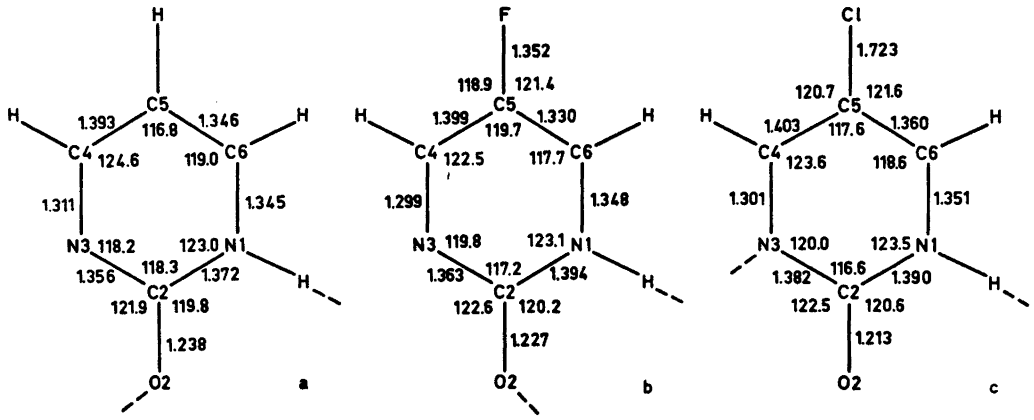


*Fig. 1.* Bond lengths and angles (uncorrected values) in (a) pyrimidin-2-one, (b) 5-fluoropyrimidin-2-one and (c) 5-chloropyrimidin-2-one (mean value of mols. A and B). E.s.d.'s are 0.003 – 0.005 Å in bond lengths and 0.2 – 0.4° in the angles.

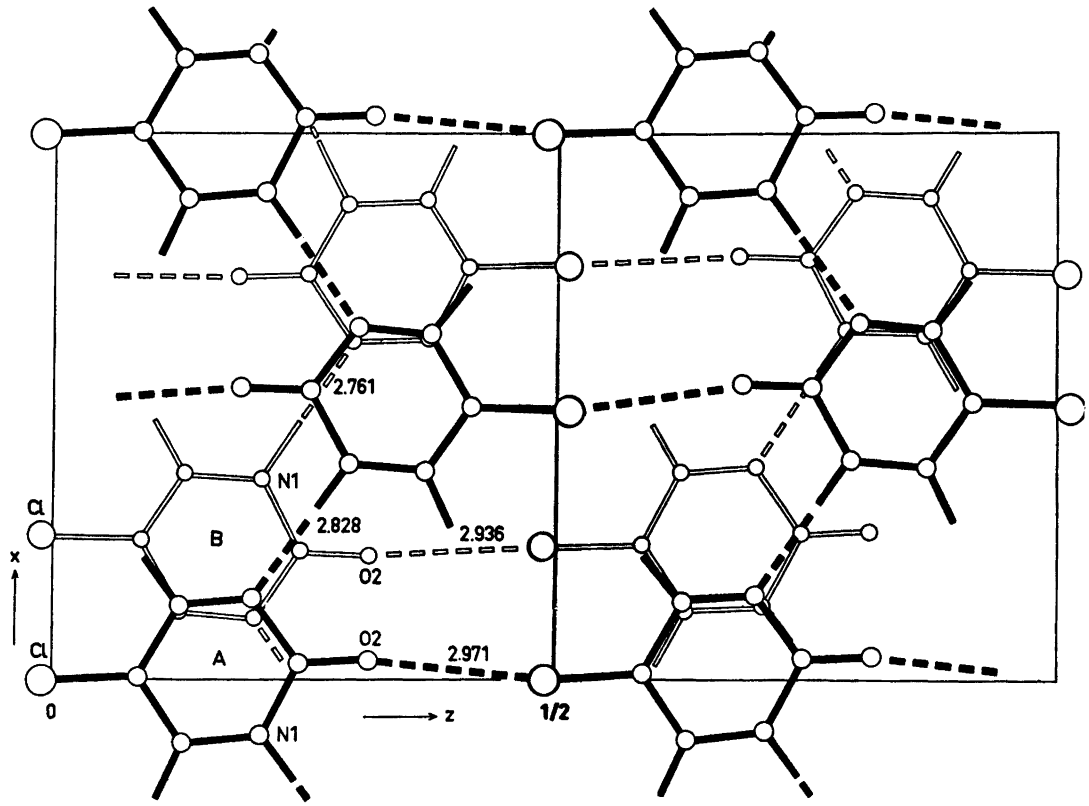


*Fig. 2.* The structure in *b* projection. One layer of A molecules (heavy lines) and one of B molecules (open lines) are shown. Hydrogen bonds and Cl···O contacts in broken lines.

respectively. This is significantly shorter than the normal van der Waals separation (3.25 Å) between chlorine and oxygen atoms. The C–Cl and C=O bonds are nearly parallel to the Cl···O direction and the interaction may possibly be classified as a charge transfer bond.[7] A similar short Cl···O contact of 2.88 Å is present in the crystal structure of *N*-chloro-succinimide.[8]

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