

## Crystal Structures of the Hydrochlorides of Pyrimidine and Pyrimidin-2-one

SVEN FURBERG and JOHAN B. AAS

Department of Chemistry, University of Oslo, Oslo 3, Norway

The crystal structures of the hydrochlorides of pyrimidine and pyrimidin-2-one have been derived from counter measurements and refined to  $R=0.030$  and  $0.047$ , respectively. Standard deviations in bond distances lie in the range  $0.003-0.004$  Å. The main effect of protonation in both compounds is to increase the ring angle at the nitrogen atom by  $6^\circ$ . The ions are linked together by  $N-H \dots Cl^-$  hydrogen bonds of lengths  $3.00-3.06$  Å. There are also several close  $(CH) \dots Cl^-$  contacts with  $H \dots Cl^-$  distances in the range  $2.6-2.9$  Å.

Continuing our investigations of the structure of pyrimidine derivatives <sup>1,2</sup> we have determined the crystal structures of the hydrochlorides of pyrimidine (P.HCl) and pyrimidin-2-one (P-2-one.HCl). The main purpose of the work is to establish the effect of protonation on the molecular structure of the simplest pyrimidines.

### EXPERIMENTAL. STRUCTURE ANALYSIS

The compounds were prepared by mixing pyrimidine and pyrimidin-2-one with equivalent amounts of hydrochloric acid in alcoholic solution and recrystallized from alcohol. The space groups were derived from Weissenberg diagrams and unit cell dimensions measured on a diffractometer. The densities were measured by flotation.

Recrystallization of P.HCl ( $C_4H_4N_2.HCl$ ) yielded thin hygroscopic plates (100) elongated along  $b$ . They had to be kept in glass capillaries during the X-ray exposures. Systematic absences correspond to space groups  $Cmca$  or  $C2ca$ , of which the former was chosen, being strongly favoured by the intensity statistics. Unit cell dimensions are  $a=6.747(1)$  Å,  $b=9.222(1)$  Å,  $c=18.651(2)$  Å. The density was found to be  $1.35$  g/cm<sup>3</sup> and there are eight

molecules in the unit cell. All atoms must lie in mirror planes.

P-2-one.HCl ( $C_4H_4N_2O.HCl$ ) was obtained as stable needles elongated along  $b$ . The space group is  $Pbca$ , with unit cell dimensions  $a=10.204(1)$  Å,  $b=9.180(1)$  Å and  $c=12.898(2)$  Å. The density is  $1.46$  g/cm<sup>3</sup> and there are eight formula units per cell.

The intensity measurements were made on crystals of dimensions  $0.2-0.4$  mm, using an automatic diffractometer and monochromatic  $MoK\alpha$  radiation. The  $\omega/2\theta$  scan mode was employed. Reflections with  $2\theta < 65^\circ$  and  $I > 2\sigma$  ( $I$ ) were measured, 700 for P.HCl and 1183 for P-2-one.HCl. The intensities were scaled on the basis of measurements of three standard reflections. Corrections for absorption and extinction were not applied. The atomic form factors were those of Hanson *et al.*,<sup>3</sup> except for hydrogen.<sup>4</sup>

The structures were 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. Anisotropic temperature factors were applied to the non-hydrogen atoms, isotropic ones to the hydrogen atoms. The final value of  $R$  was  $0.030$  ( $R_w=0.038$ ) for P.HCl and  $0.047$  ( $R_w=0.047$ ) for P-2-one.HCl. The parameters are given in Tables 1 and 2.

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

The cations were assumed to be rigid bodies. The r.m.s. difference between the atomic vibration tensor components calculated from Tables 1 and 2 and those derived from the model was  $0.0007$  Å<sup>2</sup> for P.H<sup>+</sup> and  $0.0016$  Å<sup>2</sup> for P-2-one.H<sup>+</sup>. Librational corrections to the bond lengths were derived (Table 3). Fig. 1 shows the thermal ellipsoids.

The calculations were carried out on CYBER-74.<sup>4</sup>

Table 1. Positional ( $\times 10^5$  for non-hydrogens,  $\times 10^4$  for hydrogens) and thermal ( $\times 10^5$ ) parameters for P.HCl. E.s.d.'s in parenthesis. The temperature factor is  $\exp[-B11h^2 + B22k^2 + B33l^2 + B12hk + B13hl + B23kl]$ .

ATOM	X	Y	Z	B	B11	B22	B33	B12	B13	B23
CL	0(0)	26506(5)	8185(3)		3132(16)	1338(7)	203(1)	0(0)	0(0)	-64(4)
N1	0(0)	75413(16)	7084(8)		2685(42)	1348(21)	192(4)	0(0)	0(0)	-91(17)
N3	0(0)	65428(24)	19223(10)		5914(84)	1738(39)	276(6)	0(0)	0(0)	393(22)
C2	0(0)	64246(23)	12187(12)		4338(81)	1147(27)	316(7)	0(0)	0(0)	32(2)
C4	0(0)	78776(29)	21862(13)		4367(81)	2252(42)	197(6)	0(0)	0(0)	-108(25)
C5	0(0)	98766(27)	17626(12)		4697(98)	1496(31)	389(7)	0(0)	0(0)	-410(23)
C6	0(0)	88651(24)	18427(12)		4197(78)	1176(24)	284(6)	0(0)	0(0)	81(2)
H1	0(0)	7305(20)	343(18)	5,1(,5)						
H2	0(0)	5514(28)	1004(14)	6,2(,6)						
H4	0(0)	7928(28)	2693(18)	7,7(,7)						
H5	0(0)	81(27)	1956(15)	8,2(,7)						
H6	0(0)	9543(29)	728(12)	5,4(,6)						

Table 2. Parameters for P-2-one.HCl. Given as in Table 1.

ATOM	X	Y	Z	B	B11	B22	B33	B12	B13	B23
CL	21498(6)	4898(6)	11199(5)		897(6)	1819(7)	938(6)	419(11)	-565(9)	-492(18)
N1	53619(20)	36127(21)	40547(18)		883(19)	939(22)	652(15)	-293(36)	-181(27)	-187(29)
N3	48446(19)	17873(22)	46735(16)		746(18)	1168(24)	508(13)	-93(36)	239(25)	64(31)
O2	55568(18)	28867(23)	57275(14)		1846(28)	2488(39)	538(11)	-296(45)	-223(26)	-292(34)
C2	58403(21)	27561(24)	48917(18)		669(18)	1231(38)	518(15)	78(41)	73(38)	-246(36)
C4	34448(23)	16958(28)	37698(20)		733(21)	1245(38)	665(17)	-328(45)	95(34)	-414(48)
C5	37982(26)	25781(33)	29615(21)		1117(29)	1958(43)	589(17)	-719(65)	-327(37)	78(48)
C6	47773(27)	35337(38)	31488(21)		1187(28)	1418(35)	635(18)	-463(54)	-168(38)	438(44)
H1	6854(34)	4228(32)	4128(21)	5,1(,7)						
H3	3794(38)	1196(34)	5172(24)	6,6(,8)						
H4	2738(27)	971(38)	3782(18)	4,7(,6)						
H5	3371(26)	2488(28)	2327(21)	4,7(,6)						
H6	5894(27)	4184(38)	2617(22)	5,9(,7)						

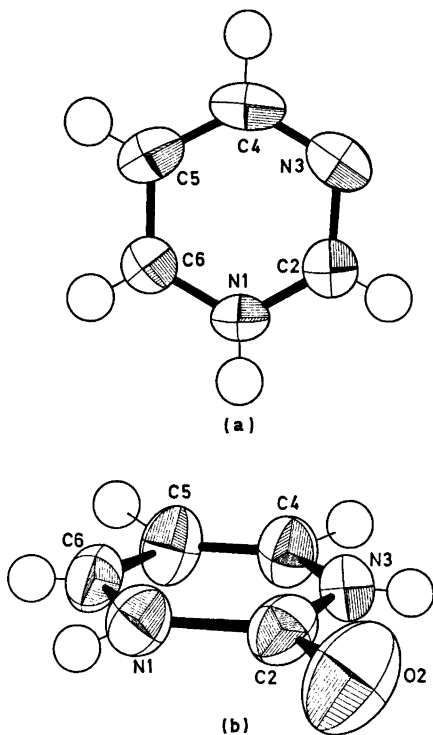


Fig. 1. Thermal ellipsoids plotted at 50% level. (a) P.H<sup>+</sup> viewed along *x*. (b) P-2-one.H<sup>+</sup> viewed along *y*.

## RESULTS AND DISCUSSION

*The structure of the cations.* The bond lengths (uncorrected and corrected values) and angles in the cations P.H<sup>+</sup> and P-2-one.H<sup>+</sup> are given in Table 3. For comparison the (corrected) values reported for pyrimidine<sup>6</sup> and pyrimidine-2-one<sup>8</sup> are also included.

It is seen that the main structural effect of protonation is to increase substantially the ring angle at the protonated nitrogen atom (N1 in P.H<sup>+</sup> and N3 in P-2-one.H<sup>+</sup>). This is in agreement with earlier evidence that bonding of an extraannular atom to a ring nitrogen atom causes the ring angle to increase.<sup>7</sup> The angle is increased by 5.8° in P.H<sup>+</sup> and by 5.9° in P-2-one.H<sup>+</sup>. The interior angles adjacent to the site of addition are correspondingly adjusted.

As for the effect of protonation on bond lengths a comparison of P-2-one and P-2-one.H<sup>+</sup> shows that significant changes occur in this case. Ring bonds adjacent to the protonated atom N3 increase in length by about 0.02 Å, whereas C4–C5 becomes shorter by 0.036 Å and C6–N1 by 0.020 Å. In fact, P-2-one.H<sup>+</sup> has very nearly *mm* symmetry. Protonation of cytosine produces similar changes both in angles and bonds.<sup>8</sup> On the other hand there are no clearly significant differences in

Table 3. Bond lengths (Å) and angles (°) for P.H<sup>+</sup> and P-2-one.H<sup>+</sup> with estimated standard deviations. E.s.d.'s in bond lengths for P are 0.007–0.008 Å, for P-2-one 0.003–0.004 Å.

	P.H <sup>+</sup> Uncorr.	P.H <sup>+</sup> Corr.	P Corr.	P-2-one.H <sup>+</sup> Uncorr.	P-2-one.H <sup>+</sup> Corr.	P-2-one Corr.
N1–C2	1.306(3)	1.331	1.33	1.375(3)	1.387	1.384
C2–N3	1.317(3)	1.333	1.34	1.379(3)	1.387	1.367
N3–C4	1.326(3)	1.348	1.35	1.330(3)	1.341	1.320
C4–C5	1.359(4)	1.384	1.41	1.358(4)	1.367	1.403
C5–C6	1.357(3)	1.373	1.38	1.355(4)	1.361	1.355
C6–N1	1.310(3)	1.331	1.36	1.324(3)	1.333	1.353
C2–O2				1.203(3)	1.208	1.244
N1–H1	0.84(3)			0.90(3)		
C2–H2	0.93(3)					
C4–H4	0.95(3)			0.98(3)		
C5–H5	0.97(3)			0.93(3)		
C6–H6	0.87(3)			0.96(3)		
N3–H3				0.88(3)		
N1–C2–N3	123.2(0.2)		128.2	112.6(0.2)		118.3
C2–N3–C4	116.6(0.2)		115.1	124.1(0.2)		118.2
N3–C4–C5	122.7(0.2)		122.5	120.9(0.2)		124.6
C4–C5–C6	117.3(0.2)		116.3	116.8(0.3)		116.8
C5–C6–N1	119.5(0.2)		122.7	121.4(0.3)		119.0
C6–N1–C2	120.9(0.2)		115.2	124.1(0.2)		123.0
N1–C2–O2				123.7(0.2)		119.8
N3–C2–O2				123.7(0.2)		121.9

bond lengths between pyrimidine and its hydrochloride. The relatively low accuracy of the pyrimidine analysis, and the thermal effects, make, however, a meaningful comparison difficult. The *mm* symmetry of pyrimidine is lost on protonation and the two ring bonds at N1 become equal, 1.331 Å.

The oxygen atom is engaged in hydrogen bonding in P-2-one, but not in P-2-one.H<sup>+</sup> and the C=O bond is accordingly shorter in the latter case.

The cation P.H<sup>+</sup> is planar by space group requirement. Some of the atoms in P-2-one.H<sup>+</sup> are significantly (up to 0.014 Å) displaced from the least squares plane and this cation is slightly curved in the crystal in the same manner as P-2-one.<sup>2</sup>

**Crystal structures.** The cations are linked to the chlorine ions by N–H...Cl<sup>−</sup> hydrogen bonds. There is one such bond of length 3.002 Å in P.HCl, two in P-2-one.HCl, of lengths 3.043 and 3.064 Å, respectively. The bonds lie approximately in the pyrimidine planes and are nearly linear, the N–H...Cl<sup>−</sup> angles being 165–171°. They are shorter than "normal" N–H...Cl<sup>−</sup> bonds (3.1–3.2 Å) but longer

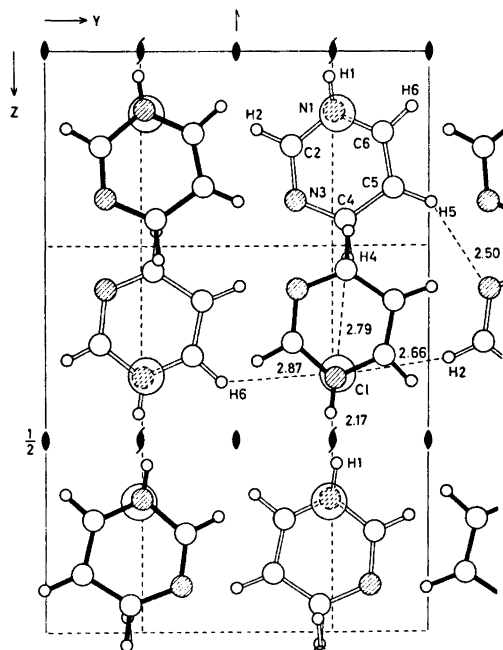


Fig. 2. The structure of P.HCl in *a* projection. Molecules at *x*=0 in open lines, at *x*=1/2 in heavy lines. Short contacts in broken lines.

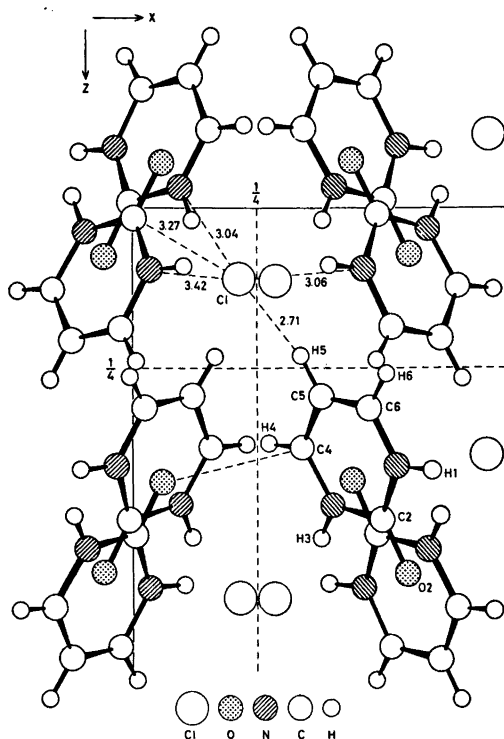


Fig. 3. The structure of P-2-one.HCl in  $b$  projection. Broken lines indicate contacts.

than, *e.g.*, that of 2.95 Å in pyridine hydrochloride.<sup>9</sup>

The general arrangement of the ions in the two crystals is shown in Figs. 2 and 3.

P.HCl has a layer structure (Fig. 2), with all atoms in mirror planes at  $x=0$  and  $x=1/2$ . Within a layer the chlorine ions have close contacts (2.6–2.9 Å) to hydrogen atoms H2, H4, and H6 in different neighbouring cations, in addition to the hydrogen bond involving H1. There is also a rather short distance (2.50 Å) between N3 and H5. The shortest inter-layer contacts (3.38 Å) are between the chlorine ions in one layer and the atoms N1 in the layers above and below. This makes the chlorine ions nearly octahedrally coordinated to atoms in six different cations. There is very little stacking overlap between the cations and the layers appear to be held together mainly by electrostatic  $N^+ \dots Cl^-$  interactions. Similar packing arrangements have been observed in several hydrohalides of nitrogen heteroaromatics.<sup>8,10</sup>

In P-2-one.HCl (Fig. 3) parallel cations inclined  $50.6^\circ$  to the  $ac$  plane stack in columns in the  $b$  direction. The shortest  $Cl^- \dots Cl^-$  distance is 4.73 Å. The chlorine ions are linked to N1 and N3 in different cations by the hydrogen bonds, which form an angle of  $88^\circ$  with one another. They also have a short contact (2.7 Å) to H5 and are at approximately van der Waals distance from C2 (3.27 Å) and N1 (3.42 Å) in other neighbouring cations. The oxygen atom is not involved in hydrogen bonding, the nearest atom in another cation being C4 at a distance of 3.04 Å.

#### REFERENCES

1. Furberg, S. and Solbakk, J. *Acta Chem. Scand. A* 28 (1974) 435.
2. Furberg, S. and Solbakk, J. *Acta Chem. Scand.* 24 (1970) 3230.
3. Hanson, H. R., Hermann, F., Lea, J. D. and Skillman, S. *Acta Crystallogr.* 17 (1964) 1040.
4. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 17 (1964) 3175.
5. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
6. Wheatley, P. J. *Acta Crystallogr.* 13 (1960) 80.
7. Singh, C. *Acta Crystallogr.* 19 (1965) 861.
8. Trus, B. L. and March, R. H. *Acta Crystallogr. B* 28 (1972) 1834.
9. Rerat, C. *Acta Crystallogr.* 15 (1962) 427.
10. Bryan, R. F. and Tomita, K. I. *Acta Crystallogr.* 15 (1962) 1174.

Received March 10, 1975.