Table 4. *Least-squares planes defined by the benzene rings referred to the cell axes*

$J=1$ $3\cdot889X-4\cdot193Y+7\cdot105Z=3\cdot639$
$J=2$ $5\cdot079X+9\cdot583Y-4\cdot700Z=5\cdot589$
$J=3$ $4\cdot573X+9\cdot943Y-3\cdot692Z=6\cdot765$

X, Y, Z are fractional coordinates

Displacements of atoms from planes

	$J=1$	$J=2$	$J=3$
C(J1)	0·003 Å	−0·002 Å	−0·006 Å
C(J2)	0·007	0·001	0·002
C(J3)	−0·008	0·000	0·003
C(J4)	−0·001	0·001	−0·004
C(J5)	0·011	−0·001	−0·000
C(J6)	−0·011	0·001	0·005
C(J7)	−0·062	0·023	0·050
C(J8)	−0·025	−0·093	0·115
O(J1)	0·021	−0·010	−0·034
N(J1)	−0·173	0·153	0·033
Cu	−0·239	0·368	−0·109

The molecules appear to interact through NH---O hydrogen bonds, the two unique bonds being N(11)–H(11)---O(21) (N–O distance, 3·04 Å, N–H–O angle, 176°) and N(31)–H(31)---O(11) at $1-x$, $1-y$, $1-z$ (N–O distance, 3·07 Å; N–H–O angle, 179°). No other intermolecular contact distances are unusual.

References

ALEXANDER, L. E. & SMITH, G. S. (1964). *Acta Cryst.* **17**, 1195.
BAKER, E. N., HALL, D. & WATERS, T. N. (1966). *J. Chem. Soc.* p. 680.
CROMER, D. & WABER, J. (1965). *Acta Cryst.* **18**, 104.
GHILARDI, C. A. & LINGAFELTER, E. C. (1970). *Acta Cryst.* B**26**, 1807.
KILBOURN, B. T., POWELL, H. M. & DARBYSHIRE, J. A. C. (1963). *Proc. Chem. Soc.* p. 207.
LINGAFELTER, E. C. & BRAUN, R. L. (1966). *J. Amer. Chem. Soc.* **88**, 2951.
STEWART, J. M. (1964). *Crystal Structure Calculation System for the IBM* 709, 7090, 7094 *Computers.* Technical Report TR-64-6, Computer Science Center, Univ. of Maryland and Research Computer Laboratory, Univ. of Washington.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
STEWART, J. M. & LINGAFELTER, E. C. (1959). *Acta Cryst.* **12**, 842.
WATERS, T. N. & HALL, D. (1959). *J. Chem. Soc.* p. 1200.

Hydrogen Bond Studies. XLVII. The Crystal Structure of the Intermolecular Complex 2-Pyridone: 6-Chloro-2-hydroxypyridine

BY JAN ALMLÖF, ÅKE KVICK AND IVAR OLOVSSON

Institute of Chemistry, University of Uppsala, S-75121 Uppsala, Sweden

The crystal structure of a 1:1 complex between 2-pyridone and 6-chloro-2-hydroxypyridine has been determined from three-dimensional X-ray diffraction data recorded on a Stoë–Philips two-circle Weissenberg diffractometer. The crystals are monoclinic, space group $C2/c$, with eight formula units in a cell of dimensions $a=10\cdot012$, $b=10\cdot999$, $c=19\cdot840$ Å, $\beta=105\cdot74°$. The pyridone molecule occurs in the keto form, the chlorohydroxypyridine in the enol form. The hydrogen atoms have been located from a difference synthesis, and their coordinates allowed to vary in the final cycles of refinement. The molecules are linked to form dimers by O–H$\cdots$O(2·57 Å) and N–H$\cdots$N(2·90 Å) hydrogen bonds. No hydrogen bonding occurs between individual dimers. Semi-empirical molecular orbital calculations for the dimer and the monomers have also been carred out, and the results of these compared.

Introduction

This work is part of a systematic investigation of hydrogen bonding in simple organic compounds which can serve as model substances for biologically important molecules. The structure of 2-pyridone (denoted by P) has been studied earlier by Penfold (1953), and that of 6-chloro-2-hydroxypyridine (ClP) by Kvick & Olovsson (1968).

---

* Part XLVI in this series appeared in *J. Chem. Phys.* (1971), **54**, 127.

Experimental

The melting point diagram for the binary system P–ClP was determined in order to investigate the existence of intermediate phases. Commercial P and ClP were purified by repeated recrystallization from ethanol and benzene, respectively. Small amounts of the components were weighed carefully and were then mixed. The mixtures were sealed in glass tubes and were then melted to obtain as homogenous samples as possible. The melting-point interval for each sample was determined, and the endpoints of the interval

were plotted against the composition of the sample.

The resulting phase diagram is shown in Fig. 1. A metastable modification of P (melting point 97 °C) is well established, and its structure determination is now in progress. The existence of an incongruently melting 1:1 addition compound is rather obvious, and there also seems to be one more addition compound in the system.

It was decided to start an investigation of the 1:1 addition compound. After several attempts using different solvents, crystals of the appropriate compound were obtained as irregular prisms from an equimolar solution of P and ClP in 50% benzene and 50% ethanol.

The cell dimensions were determined by least-squares from 31 reflexions measured from powder photographs taken with a Guinier–Hägg camera using Cu $K\alpha_1$ radiation ($\lambda = 1.54051$ Å) and silicon as an internal standard ($a_{Si} = 5.43054$ Å).

The diffraction symmetry $2/m$ and systematic absences hkl, $h+k$ odd, $h0l$, l odd on Weissenberg photographs for $l=0$ and $l=1$ suggested the space group Cc or $C2/c$. Crystallographic and physical data are given in Table 1.

Table 1. *Crystallographic and physical data*

	$C_5H_5NO:C_5H_3NClOH$
F.W.	224.64
Space group	$C2/c$
a	10.012 (3) Å
b	10.999 (4)
c	19.840 (5)
β	105.74 (2)°
V	2123 Å³
D_x	1.403 g.cm⁻³
Z	8
m.p.	64.5 °C
μ	24.9 cm⁻¹

The intensity data were collected on an automatic Stoë–Philips two-circle Weissenberg diffractometer, using unfiltered Cu $K\alpha$ radiation and an ω–2θ scan. A crystal of dimensions $0.25 \times 0.14 \times 0.09$ mm, elongated along the c axis, was used for collecting the data. The crystal was mounted in a glass capillary (wall thickness 0.029 mm) to prevent sublimation of the volatile ClP component during the experiment.

1809 independent reflexions for layers $0 \le l \le 17$ in the range $5° < 2\theta < 140°$ were measured. The equivalent sets $hk0$ and $\bar{h}k0$ were collected, and the mean values of

the intensities were used. 476 reflexions had an intensity less than the standard deviation, as estimated from the counting statistics, and these were given zero weight in all refinements.

The data were corrected for background and for Lorentz, polarization, absorption and secondary extinction effects. The crystal shape was defined by seven rational crystal boundary planes in the calculation of the absorption and extinction corrections. A small correction was also applied to account for absorption in the capillary walls. The linear absorption coefficient used for glass was 102 cm⁻¹.

During the experiment, three reference reflexions were measured at regular intervals. Their intensities decreased linearly with exposure time, reaching only 80% of their initial values at the end of the experiment. The measured intensities were corrected for this effect.

Determination of the structure

An overall temperature factor and a scale factor were determined with Wilson's (1949) method using all data. Normalized structure amplitudes $|E|$ were calculated according to Hauptman & Karle (1953). The statistical distribution of the $|E|$'s, compared with theoretical values for centric and acentric cases (Karle, Dragonette & Brenner, 1965) gave strong evidence for
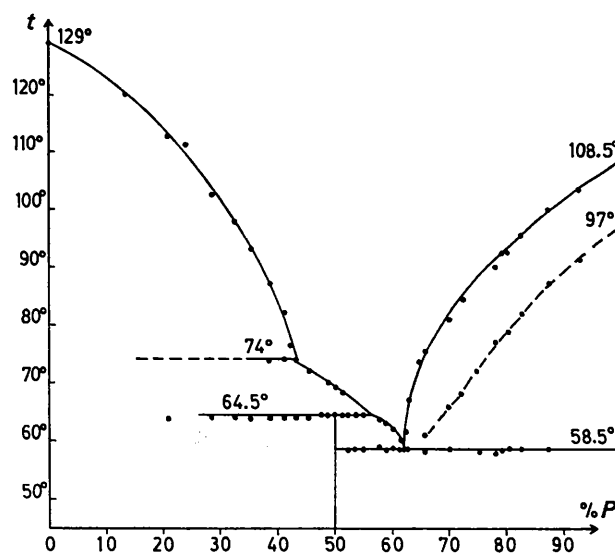

Fig. 1. The phase diagram for the binary system P–ClP.

Table 2. *Statistical distribution of the normalized structure amplitudes $|E|$, compared with theoretical values*

	Experimental	Theoretical Centric	Acentric
Number of reflexions with $|E| > 3.0$	9(0.4%)	6(0.3%)	0(0.01%)
Number of reflexions with $|E| > 2.0$	91(4.4%)	95(4.5%)	38(1.8%)
Number of reflexions with $|E| > 1.0$	691(33%)	680(32%)	790(37%)
$< |E| >$	0.79	0.80	0.89
$< |E|^2 >$	1.00	1.00	1.00
$< |E|^2 - 1 >$	0.95	0.97	0.74

Table 3. *Observed and calculated structure factors*

The three columns are, in order; l, $10 \cdot |F_o|$, $10 \cdot |F_c|$. Reflexions not included in the refinement are indicated by *.

a centrosymmetric structure (*cf.* Table 2). Accordingly the space group $C2/c$ was chosen. The choice was later confirmed by the successful refinement of the structure in this space group.

The 263 reflexions with $|E| > 1.5$ were used as input to a multi-solution program for sign determination by iterative application of Sayre's equation. The calculation of one of the 16 solutions converged much faster than the others, and also the signs of the individual terms in Sayre's equation showed the best consistency. It appeared later that all 263 signs in this solution had been correctly determined. A Fourier synthesis using these signs for the E values showed 19 large peaks. From a knowledge of the geometry of the molecules the peaks corresponding to the 15 heavy atoms could easily be recognized.

Atomic coordinates, isotropic temperature factors and an overall scale factor were now refined in two cycles of full-matrix least-squares refinement. The conventional discrepancy index $R = \sum ||F_o| - |F_c||/\sum |F_o|$ was at this stage 0·13 excluding zero weight data. Two more cycles with anisotropic temperature factors lowered R to 0·07. An $(F_o - F_c)$ Fourier synthesis, using only data with $\sin \theta/\lambda < 0.4$ Å^{-1}, showed the sites of the nine hydrogen atoms quite clearly. The heights of the 'noise' peaks were all less than half the height of the lowest hydrogen peak.

Refinement of the scale factor, all atomic coordinates, anisotropic temperature factors for the heavy atoms and isotropic for hydrogen lowered R to 0·055. The weighted R value $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$ at this stage was 0·066. The total number of parameters varied was 172.

A small correction for secondary extinction was now applied in accordance with Zachariasen's (1967) formula. Further refinement of all atoms gave finally $R = 0.048$, $R_w = 0.052$.

The final shifts in the parameters were all less than one tenth of their corresponding standard deviations, as estimated from the least-squares matrix in the final cycle of refinement. Observed and calculated structure factors are listed in Table 3.

A weight analysis indicated a satisfactory weighting scheme in the final cycle of refinement, where the weights used were $w = (156 + |F| + 0.02|F|^2 + 0.0006|F|^3)^{-1}$.

The scattering factors used were those given in *International Tables for X-ray Crystallography* (1962) for Cl, O, N and C and the spherical scattering factor for hydrogen proposed by Stewart, Davidson & Simpson (1965).

Description of the structure

The structure is shown in Fig. 2. The atomic parameters are presented in Tables 4 and 5. The average estimated standard deviations in the atomic positions are 0·001 Å for chlorine, 0·003 Å for oxygen, nitrogen and carbon, and 0·04 Å for hydrogen.
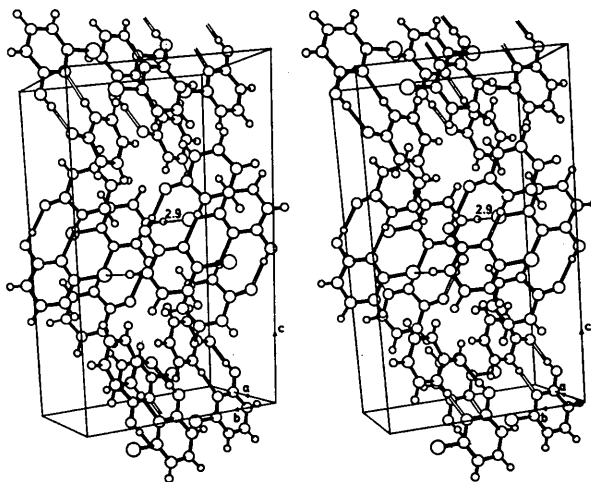

Fig. 2. A stereoscopic pair of drawings showing the packing of the structure. Covalent bonds are filled, hydrogen bonds are open. The shortest contact between individual dimers is also shown.
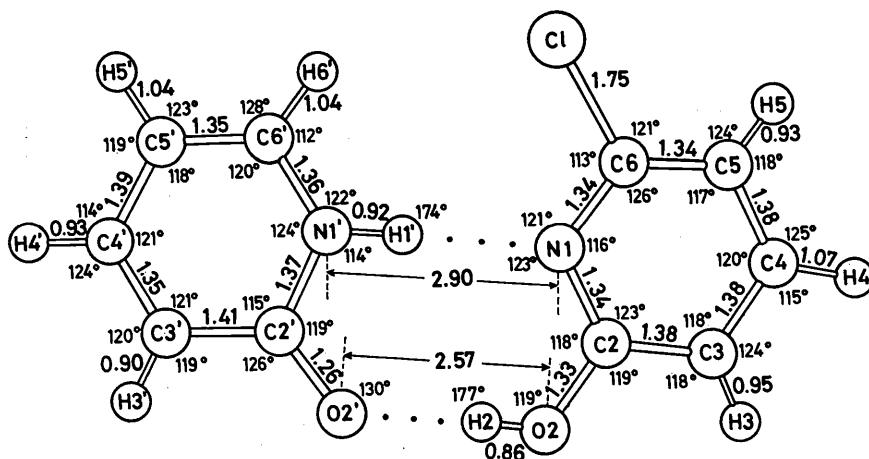

Fig. 3. Bond distances and angles. The values are not corrected for thermal motion.

Table 4. *Atomic coordinates* × 10⁴, *in the case of hydrogen* × 10³

	x/a	y/b	z/c
N(1)	3486 (3)	812 (2)	5091 (1)
C(2)	2956 (3)	−305 (3)	5093 (2)
C(3)	3208 (4)	−1023 (4)	5682 (2)
C(4)	4018 (4)	−549 (4)	6300 (2)
C(5)	4572 (4)	604 (4)	6309 (2)
C(6)	4273 (3)	1218 (3)	5705 (2)
O(2)	2144 (3)	−728 (2)	4493 (2)
Cl	4945 (1)	2668 (1)	5654 (1)
H(2)	202 (4)	−29 (4)	412 (2)
H(3)	279 (4)	−181 (4)	564 (2)
H(4)	416 (4)	−113 (3)	675 (2)
H(5)	512 (3)	−91 (3)	673 (2)
N(1′)	3175 (3)	2128 (2)	3789 (2)
C(2′)	2300 (4)	1513 (3)	3243 (2)
C(3′)	2153 (4)	2018 (4)	2577 (2)
C(4′)	2869 (4)	3016 (4)	2490 (2)
C(5′)	3759 (4)	3602 (3)	3059 (2)
C(6′)	3891 (4)	3138 (3)	3705 (2)
O(2′)	1710 (3)	561 (2)	3374 (1)
H(1′)	328 (4)	177 (3)	422 (2)
H(3′)	156 (5)	167 (4)	220 (2)
H(4′)	279 (4)	339 (4)	206 (3)
H(5′)	433 (4)	434 (4)	297 (2)
H(6′)	443 (4)	351 (4)	418 (2)

also indirectly confirmed by the differences between the C(2)–O(2) and C(2′)–O(2′) distances, 1·33 and 1·26 Å, and between the C(2)–N(1)–C(6) and C(2′)–N(1′)–C(6′) angles, 116° and 124°, respectively.

Table 6. *Bond lengths*

(a) Covalent bonds.

ClP molecule		P molecule	
N(1)–C(2)	1·338 (4) Å	N(1′)–C(2′)	1·373 (4) Å
C(2)–C(3)	1·377 (6)	C(2′)–C(3′)	1·405 (6)
C(3)–C(4)	1·376 (6)	C(3′)–C(4′)	1·347 (6)
C(4)–C(5)	1·382 (6)	C(4′)–C(5′)	1·392 (6)
C(5)–C(6)	1·337 (6)	C(5′)–C(6′)	1·352 (6)
C(6)–N(1)	1·336 (4)	C(6′)–N(1′)	1·357 (4)
C(2)–O(2)	1·330 (5)	C(2′)–O(2′)	1·262 (4)
O(2)–H(2)	0·86 (4)	N(1′)–H(1′)	0·92 (4)
C(3)–H(3)	0·95 (4)	C(3′)–H(3′)	0·90 (5)
C(4)–H(4)	1·07 (4)	C(4′)–H(4′)	0·93 (5)
C(5)–H(5)	0·93 (4)	C(5′)–H(5′)	1·04 (4)
C(6)–Cl	1·745 (3)	C(6′)–H(6′)	1·04 (4)

(b) Hydrogen bonds.

N(1)···N(1′)	2·904 (4) Å
O(2)···O(2′)	2·570 (4)

Bond distances and angles, together with their e.s.d.'s, are given in Tables 6 and 7 and are shown in Fig. 3. The uncertainties in the cell dimensions have been taken into account in the estimation of the standard deviations. The proposed hydrogen assignment, with the P molecule in keto form and the ClP in enol form, is quite evident from the difference maps. It is

The molecules are linked to form dimers by O–H···O and N–H···N hydrogen bonds with bond lengths 2·570 (4) and 2·904 (3) Å (values in parenthesis denote e.s.d.'s in the least significant digits here and throughout this paper).

The planes of the molecules in the dimer make an angle of 13·6° with one another. The closest contact

Table 5. *Thermal parameters*

Anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11} - \ldots - hk\beta_{12} - \ldots)]$. The β values given have been multiplied by 10⁴.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	109 (3)	90 (2)	33 (1)	2 (4)	26 (3)	−1 (2)
C(2)	110 (4)	94 (3)	40 (1)	−23 (6)	27 (4)	5 (3)
C(3)	139 (5)	117 (4)	41 (2)	−19 (7)	36 (4)	29 (4)
C(4)	145 (5)	143 (5)	43 (2)	16 (8)	41 (4)	36 (4)
C(5)	132 (5)	147 (5)	33 (1)	4 (8)	19 (4)	1 (4)
C(6)	106 (4)	103 (3)	31 (1)	−8 (5)	30 (3)	−3 (3)
O(2)	189 (4)	101 (3)	43 (1)	−89 (5)	−10 (3)	7 (3)
Cl	158 (1)	110 (1)	43 (1)	−73 (2)	24 (1)	−24 (1)
N(1′)	124 (3)	85 (2)	31 (1)	−13 (5)	23 (3)	2 (3)
C(2′)	118 (4)	89 (3)	36 (2)	13 (6)	23 (3)	−8 (3)
C(3′)	178 (6)	109 (4)	36 (2)	−7 (7)	17 (5)	5 (4)
C(4′)	179 (6)	121 (4)	39 (2)	31 (8)	55 (5)	31 (4)
C(5′)	154 (5)	100 (4)	51 (2)	5 (7)	59 (5)	19 (4)
C(6′)	133 (5)	91 (3)	42 (2)	−13 (6)	35 (4)	7 (4)
O(2′)	174 (4)	101 (2)	35 (1)	−63 (5)	21 (3)	−13 (2)

	B
H(2)	7·8 (11) Å²
H(3)	7·5 (10)
H(4)	6·4 (9)
H(5)	4·8 (8)
H(1′)	5·8 (9)
H(3′)	8·6 (13)
H(4′)	8·2 (12)
H(5′)	6·6 (9)
H(6′)	5·6 (8)

between individual dimers is between Cl and H(3), 2·91 Å, whereas the sum of the corresponding van der Waals radii is about 3·00 Å. If the C(3)–H(3) bond length is set to the reasonable value 1·08 Å, the Cl· · ·H distance decreases to 2·84 Å.

Semi-empirical molecular orbital calculations have been carried out for the dimer and the monomers, using the method of 'complete neglect of differential overlap' (CNDO; Pople, Santry & Segal, 1965; Pople & Segal, 1965). It appears from the calculations that the gross charge on H(3) is positive (cf. Fig. 4). Some kind of interaction between Cl and H(3) clearly exists, but it is doubtful whether it should be interpreted as a C–H· · ·Cl hydrogen bond, especially since the angle is rather unfavourable for such a situation.

The molecules become slightly polarized when dimers are formed (cf. Fig. 4 and Table 8) and this may be relevant to the hydrogen bonding situation. Regarding the atoms as point charges, the gain in classical electrostatic energy when dimers P–ClP are formed can be expressed as $E = -\sum Q_i Q_j / R_{ij}$. In this expression Q_i and Q_j denote the gross charges on atoms i and j, R_{ij} is the internuclear distance and the summation is to be taken over all atoms i in P and all atoms j in ClP. Using the charges given in Table 8, E was calculated to be 8·3 kcal/mole for polarized molecules and 5·1 kcal/mole for unpolarized molecules.

The C–C distances are unusually short in both molecules. The mean distance is 1·37 Å, and some values are in the range 1·33–1·35 Å. From the calculated π-bond orders the bond lengths can be estimated from various semi-empirical relationships suggested by

several authors, e.g. Lofthus (1959). In general, the estimated C–C bond lengths are 0·02–0·03 Å longer than the experimental values, whereas the C–N distances are in good agreement with experiment (cf. Fig. 5). Calculations on the ClP–ClP dimer gave essentially the same result. One possible reason for this
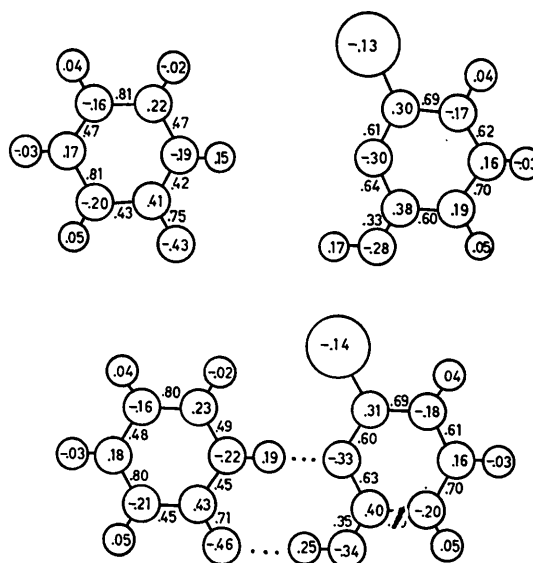

Fig. 4. Gross atomic charges and π-bond orders: (a) for the monomers, (b) for the dimer. The orientation is the same as in Fig. 3.

Table 7. Bond angles

(a) Covalent bonds.

Cl P molecule	Angles	P molecule	Angles
C(6)–N(1)–C(2)	116·2 (3)°	C(6')–N(3')–C(2')	123·5 (3)°
N(1)–C(2)–O(2)	117·7 (3)	N(1')–C(2')–O(2')	118·8 (3)
N(1)–C(2)–C(3)	123·2 (3)	N(1')–C(2')–C(3')	115·4 (3)
O(2)–C(2)–C(3)	119·1 (3)	O(2')–C(2')–C(3')	125·9 (3)
C(2)–C(3)–C(4)	117·9 (4)	C(2')–C(3')–C(4')	121·3 (4)
C(3)–C(4)–C(5)	119·8 (4)	C(3')–C(4')–C(5')	121·4 (4)
C(4)–C(5)–C(6)	117·5 (4)	C(4')–C(5')–C(6')	118·0 (4)
C(5)–C(6)–N(1)	125·5 (3)	C(5')–C(6')–N(1')	120·5 (6)
C(2)–C(3)–H(3)	118 (2)	C(2')–C(3')–H(3')	119 (3)
C(4)–C(3)–H(3)	124 (2)	C(4')–C(3')–H(3')	120 (3)
C(3)–C(4)–H(4)	115 (2)	C(3')–C(4')–H(4')	124 (3)
C(5)–C(4)–H(4)	125 (2)	C(5')–C(4')–H(4')	114 (3)
C(4)–C(5)–H(5)	118 (2)	C(4')–C(5')–H(5')	119 (2)
C(6)–C(5)–H(5)	124 (2)	C(6')–C(5')–H(5')	123 (2)
C(5)–C(6)–Cl	121·2 (3)	C(5')–C(6')–H(6')	128 (2)
N(1)–C(6)–Cl	113·2 (2)	N(1')–C(6')–H(6')	112 (2)
C(2)–O(2)–H(2)	119 (3)	C(2')–N(1')–H(1')	114 (2)
		C(6)'–N(1')–H(1')	122 (2)

(b) Hydrogen bonds.

	Angles
N(1)· · · ·H(1')–N(1')	174 (3)°
H(1')· · ·N(1) –C(2)	123 (1)
H(1)'· · ·N(1) –C(6)	121 (1)
O(2')· · ·H(2) –O(2)	177 (4)
H(2)· · · ·O(2')–C(2')	130 (1)

Table 8. *Gross atomic charges in atomic units*

	ClP monomer	ClP dimer		P monomer	P dimer
N(1)	−0·299	−0·335	N(1')	−0·195	−0·220
C(2)	0·376	0·399	C(2')	0·413	0·434
C(3)	−0·191	−0·204	C(3')	−0·201	−0·211
C(4)	0·157	0·164	C(4')	0·170	0·181
C(5)	−0·170	−0·180	C(5')	−0·157	−0·161
C(6)	0·303	0·310	C(6')	0·220	0·228
O(2)	−0·278	−0·344	O(2')	−0·434	−0·460
H(2)	0·172	0·251	H(1')	0·147	0·187
H(3)	0·045	0·048	H(3')	0·052	0·055
H(4)	−0·025	−0·029	H(4')	−0·029	−0·029
H(5)	0·040	0·040	H(5')	0·037	0·040
Cl	−0·129	−0·145	H(6')	−0·025	−0·018

discrepancy would be the approximations used in the CNDO calculation scheme. The method was therefore tested for different compounds for which accurate molecular dimensions are known, *e.g.* benzene and pyridine. However, the results were all in good agreement with experimental values (*cf.* Fig. 5).

It would thus be natural to assume that the short apparent C–C distances are due to a rigid-body thermal motion of the dimer. Such a motion would have minor effects on bonds close to the center of mass of the dimer, and would hence be well compatible with the observed discrepancies.

Fig. 5. Bond lengths in Å plotted against bond orders: (*a*) C–C bonds, (*b*) C–N bonds. Results of some test calculations with the same program and the curves supplied by Lofthus are given for comparison.

The thermal parameters are not particularly consistent with this assumption, however. On the other hand, the thermal parameters may have been affected by various types of systematic errors, especially since the corrections for radiation damage and for absorption in the capillary walls are rather uncertain.

The question of the unusually short bond lengths can not be fully answered from the present investigation. We believe, however, that if more accurate data were obtained, an analysis of the thermal parameters in terms of a rigid-body motion would give a definitive answer to this problem.

The aromatic ring in *P* is slightly non-planar. The carbon atom C(2'), to which the oxygen atom is attached, is 0·02 Å out of the plane defined by the other atoms in the ring (*cf.* Table 9). The ring in ClP is planar within experimental error. The Cl and O atoms deviate significantly from the planes of the corresponding molecules, and in these cases the deviations are 0·04–0·06 Å.
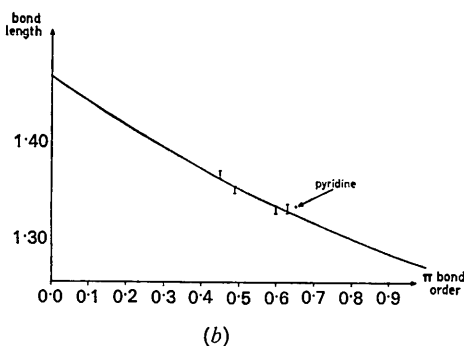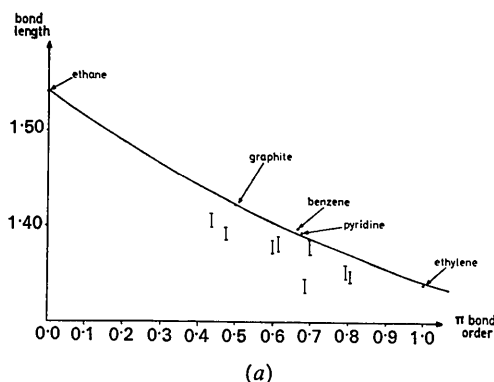
Table 9. *Deviations of the atoms from the least-squares planes through the aromatic rings*

Atoms denoted by * were not included in the calculations of the planes. Since C(2') was significantly out of plane 2, it was not included in the final calculation of the plane.

Plane 1. ClP

Atom	Deviation from the plane	deviation / e.s.d.
N(1)	0·003 Å	1·0
C(2)	0·000	0·0
C(3)	0·004	0·9
C(4)	−0·005	1·0
C(5)	−0·002	0·5
C(6)	0·002	0·5
Cl*	0·041	41
O(2)*	−0·039	13
H(2)*	−0·007	0·2
H(3)*	−0·006	0·2
H(4)*	−0·023	0·6
H(5)*	−0·059	1·7
H(1')*	0·282	–
N(1')*	0·306	–
O(2')*	0·011	–

Table 9 (cont.)

Plane 2. P

Atom	Deviation from the plane	$\dfrac{\text{deviation}}{\text{e.s.d.}}$
N(1′)	0·002 Å	0·5
C(2′)*	0·021	6·2
C(3′)	−0·002	0·6
C(4′)	0·002	0·5
C(5′)	0·000	0·0
C(6′)	−0·002	0·5
O(2′)*	0·062	26
H(1′)*	0·051	1·4
H(3′)*	−0·028	0·0
H(4′)*	0·030	0·7
H(5′)*	−0·046	1·2
H(6′)*	−0·101	2·8
H(2)*	0·341	–
O(2)*	0·516	–
N(1)*	0·203	–

The geometry of the Cl*P* molecule is very similar to that obtained by Kvick & Olovsson for pure Cl*P*. As in the present case, the molecules occur in the enol form and are linked to form dimers by hydrogen bonds. The pairing in that case is caused by O–H···N hydrogen bonds. Except for the C(5)–C(6) distance, which is 0·024 (7) Å shorter in the present case, neither distances nor angles differ significantly in the two determinations.

In the crystal structure of pure *P* (Penfold, 1953) the molecules are linked by hydrogen bonds to form infinite chains. The accuracy of this determination is comparatively low, but in general the molecular dimensions are significantly different from those in the present determination. The metastable modification probably contains dimers *P–P*, and it will accordingly be of greater interest for a comparison of molecular dimensions.

All calculations were carried out on the CDC3600 computer in Uppsala. The Wilson plot and the calculation of normalized structure amplitudes were performed using the programs XDATA and EFACT from the program library at the Brookhaven National Laboratory. The structure was solved with a program for sign determination written by Long (1965). The MO-LCAO calculations were carried out with a local modification of the program CNDO/3, originally written by Rolf Manne, University of Uppsala. All other calculations were performed with programs described by Nahringbauer (1967) and Liminga (1967).

References

HAUPTMAN, H. & KARLE, J. (1953). *Acta Cryst.* **6**, 136.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
KARLE, I. L., DRAGONETTE, K. S. & BRENNER, S. A. (1965). *Acta Cryst.* **19**, 713.
KVICK, Å. & OLOVSSON, I. (1968). *Ark. Kemi*, **30**, 71.
LIMINGA, R. (1967). *Acta Chem. Scand.* **21**, 1206.
LOFTHUS, A. (1959). *Mol. Phys.* **2**, 367.
LONG, R. E. (1965). Doctoral dissertation, Univ. of California at Los Angeles.
NAHRINGBAUER, I. (1967). *Acta Cryst.* **23**, 956.
PENFOLD, B. R. (1953). *Acta Cryst.* **6**, 591.
POPLE, J. A., SANTRY, D. P. & SÉGAL, G. A. (1965). *J. Chem. Phys.* **43**, S129.
POPLE, J. A. & SÉGAL, G. A. (1965). *J. Chem. Phys.* **43**, S136.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558.