belle 5 zeigen. Aus ihnen errechnen sich bei ausgezeichneter Konsistenz nach dem von Altona, Geise & Romers (1968) angegebenen Verfahren Puckering-Parameter φ_m von zweimal 48° und Pseudorotations-Phasen Δ von +15 und +14°. Die Konformationen liegen damit, wie auch aus der Berechnung von besten Ebenen durch verschiedene Teile der Fünfringe folgt, zwischen einer idealen Halbsesselform mit der zweizähligen Achse durch C(16) ($\Delta_{\text{theor.}} = 0°$) und einer idealen Briefumschlagform mit der Spiegelebene durch C(13) ($\Delta_{\text{theor.}} = +36°$).

Tabelle 5. *Torsionswinkel*

	Molekül	
ε-Lactamringe:	1	2
C(2)—N——C(3)-C(4)	−2°	−6°
C(1)—C(2)—N——C(3)	+39	+42
C(5)—C(4)—C(3)-N	+30	+30
C(10)-C(1)—C(2)-N	−86	−86
C(10)-C(5)—C(4)-C(3)	−75	−73
C(5)—C(10)-C(1)-C(2)	+45	+46
C(1)—C(10)-C(5)-C(4)	+39	+37
Fünfringe:	1	2
C(17)-C(13)-C(14)-C(15)	+49°	+49°
C(13)-C(14)-C(15)-C(16)	−36	−36
C(14)-C(15)-C(16)-C(17)	+8	+9
C(15)-C(16)-C(17)-C(13)	+21	+21
C(16)-C(17)-C(13)-C(14)	−42	−42

Fig. 4 zeigt einen Ausschnitt aus der Kristallstruktur. Beide Moleküle bilden durch Wasserstoffbrücken NH···O (N···O-Abstände 2,99 und 2,93 Å) von einander getrennte eindimensional unbegrenzte Verbände um die beiden verschiedenen Arten von Schraubenachsen parallel zur *a*-Achse.

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The Crystal and Molecular Structure of 5,5-Dimethyl-2-chloro-2-oxo-1,3,2-dioxaphosphorinane

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The title compound ($C_5H_{10}O_3PCl$) crystallizes in the orthorhombic system, $a = 13{\cdot}06_2$, $b = 11{\cdot}15_5$, $c = 11{\cdot}87_9$ Å (with an e.s.d., of 0·01 Å), space group *Pbca*, and $Z = 8$, at room temperature with $D_x = 1{\cdot}416$ g.cm^{-3} and $D_m = 1{\cdot}407$ g.cm^{-3}. Integrated precession photographs were taken at -40 ± 3 °C, from which 831 (354 unique) reflection data were obtained. The structure was solved from a three-dimensional Patterson map and refined using full-matrix least-squares analysis to a final R of 0·100. The phosphorinane ring has a partially flattened chair conformation, with the chlorine atom in the axial position. The P–Cl distance for tetrahedrally coordinated phosphorus is 2·004 (7) Å.

Introduction

Ring systems containing phosphorus occur in nucleic acids and are involved as intermediates in a number of biological reaction sequences. The chemical reactivity and conformation of these compounds have recently become the subjects of intensive study (Edmundson, 1964; Edmundson, 1965; Edmundson & Mitchell, 1970; Kainosho, Nakamura & Tsuboi, 1969). Of particular interest are the unsubstituted and 5,5-disubstituted 2-oxo-1,3,2,-dioxaphosphorinanes. The present study is a three-dimensional single-crystal X-ray diffraction investigation of 5,5-dimethyl-2-chloro-2-oxo-1,3,2-dioxaphosphorinane (hereafter referred to as POCL).

Experimental

A sample of POCL (m.p. 105-106 °C) was kindly supplied by R. S. Edmundson. The crystals used in this investigation were recrystallized from warm carbon tetrachloride. They were sealed in thin-walled capillary tubes and data were collected at -40 ± 3 °C, because POCL was found to react slowly with water vapor in the atmosphere.

Crystal data

Lattice constants for POCL were determined from precession photographs at room temperature and at -40 ± 3 °C using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). The films were calibrated by superimposing powder patterns of α-SiO_2, obtained with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å), on the POCL photographs. The estimated standard deviations (e.s.d.'s) are 0·01 Å. The density of POCL was determined by measuring the density of a solution of carbon tetrachloride and isopropyl alcohol in which a crystal of POCL just floated. Systematically absent reflexions were: *h*0*l*, *l* odd; *hk*0, *h* odd; 0*kl*, *k* odd. Crystal data are listed in Table 1.

Table 1. *Crystal data for 5,5-dimethyl-2-chloro-2-oxo*-1,3,2-*dioxaphosphoriane*

Formula: $C_5H_{10}O_3PCl$
Formula weight: 184·56 (based on C–12)
System: orthorhombic
Space group: *Pbca* (No. 61)
Lattice constants (Å):

	22 ± 2 °C	-40 ± 3 °C
a	$13{\cdot}06_2$	$13{\cdot}06_2$
b	$11{\cdot}15_5$	$11{\cdot}08_2$
c	$11{\cdot}87_9$	$11{\cdot}76_4$

$Z = 8$
$D_x = 1{\cdot}416$ g.cm^{-3}
$D_m = 1{\cdot}407$ g.cm^{-3}

Data collection

A crystal, approximately $0{\cdot}5 \times 0{\cdot}5 \times 0{\cdot}8$ mm, was mounted on a glass fiber along c^* and shaped with a swab dipped in benzene until it approximated a sphere of diameter 0·5 mm. The mounted crystal was then covered with a thin-walled glass capillary tube.

Timed, integrated precession photographs (maximum exposure of 18 hours) were taken of the *hKl* (*K*=0–4), *Hkl* (*H*=0–4), *hhl*, *h*,(*h*–1),*l*, and *h*,(*h*–2),*l* layers using Zr-filtered Mo $K\alpha$ radiation. The relative intensities of 831 reflections (half of each *Hkl* and *hKl* photograph and the complete *hhl* set) were measured with an Enraf–Nonius manual microdensitometer. The data for each layer were scaled and converted to $|F^2|$ by the application of the proper Lp factor. All reflections were put on a common scale using the Hamilton–Rollett–Sparks (1965) method of interlayer scaling, resulting in 354 unique reflections, which were then adjusted to an absolute scale by means of a Wilson plot. The linear absorption coefficient of POCL for Mo $K\alpha$ radiation is 5·84 and $\mu R = 0{\cdot}15$; no absorption corrections were made. Standard crystallographic programs modified for use on the Brookhaven computer were used in solving and refining this structure.

The structure was solved by determining the coordinates of the chlorine and phosphorus atoms from a Patterson map. These were used to calculate structure factors; all the remaining atoms were located on a Fourier map after two iterations. The positional and thermal parameters were refined with five cycles of full-matrix least-squares methods, using an Evans (1961) weighting scheme and the form factors which will appear in Volume IV of *International Tables for X-ray Crystallography* (1972). At this stage the original 831 (nonunique) reflexion data were used in the least-squares refinement, with each reflection, whether duplicate or not, weighted according to the above scheme. Anisotropic temperature factors for Cl and P were included, and the refinement continued until $R = 0{\cdot}110$ and $R_w = 0{\cdot}089$, where $R = \sum|F_o - F_c|/\sum|F_o|$ and $R_w = [\sum w|F_o| - |F_c|^2/\sum w|F_o|^2]^{\frac{1}{2}}$.

Just before the final least-squares refinement of the positional and thermal parameters, the positions of the

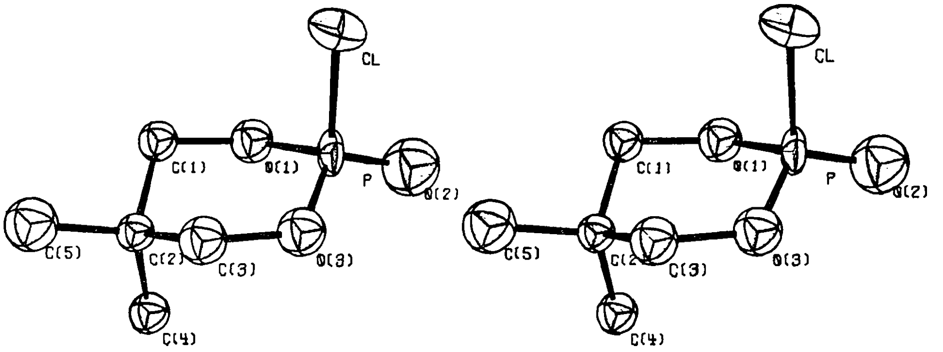


Fig. 1. Stereoview of the POCL molecule,

hydrogen atoms attached to C(1), C(3), C(4), and C(5) were calculated with a program (*HYGEN*) which utilized the fixed 'heavy' atom positions to locate the hydrogen atoms in positions reasonably free of steric hindrance. The positions of these hydrogen atoms were used in the final least-squares refinement with an assigned isotropic temperature factor of 4·5. Neither the positional nor the thermal parameters of the hydrogen atoms were varied. The final least-squares refinement used 64 parameters (13 scale factors, 30 positional parameters, 20 thermal parameters, and one isotropic extinction factor). The final discrepancy factors were $R=$

Table 2. *Positional and thermal parameters for* POCL

The β_{ij}'s are used in the expression:

$$\exp-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\,.$$

All positional and thermal parameters are multiplied by 10^4; e.s.d.'s are in parentheses. B for the hydrogen atoms was fixed at 4·5.

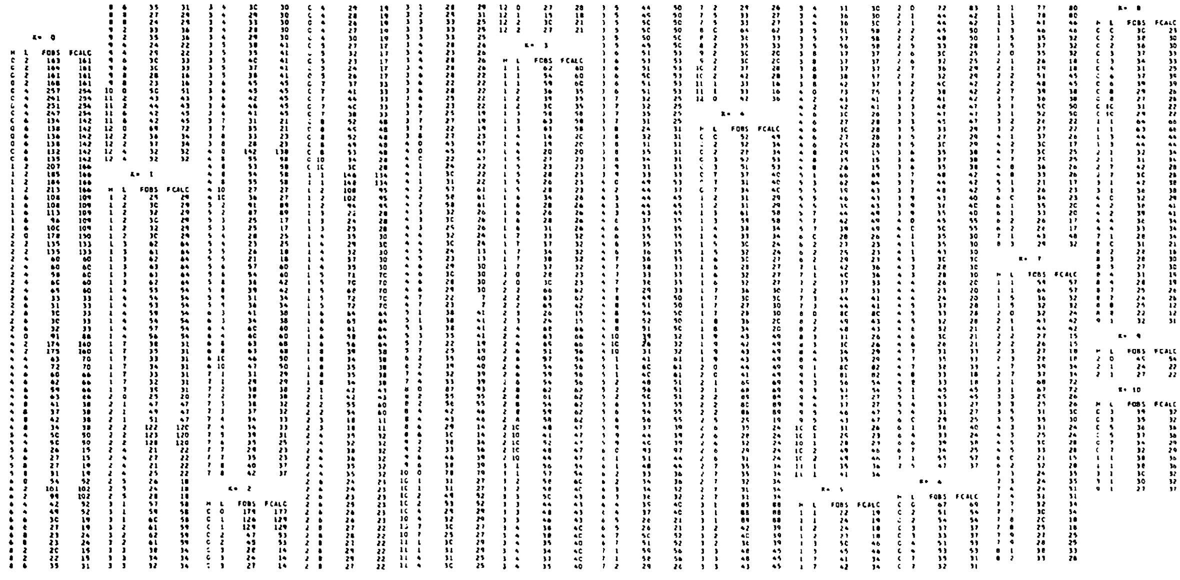
(*a*) Positional parameters and isotropic temperature factors

	x	y	z	B
Cl	8619 (4)	4315 (5)	4980 (5)	–
P	8010 (4)	2765 (5)	5482 (4)	–
O(1)	6921 (10)	2762 (10)	4993 (8)	3·17 (25)
O(2)	8595 (12)	1778 (12)	5144 (11)	5·59 (36)
O(3)	7872 (8)	2919 (11)	6748 (8)	3·57 (28)
C(1)	6178 (15)	3620 (16)	5440 (15)	3·04 (44)
C(2)	6056 (12)	3512 (15)	6726 (14)	1·64 (41)
C(3)	7127 (14)	3753 (17)	7258 (15)	3·64 (47)
C(4)	5676 (12)	2266 (17)	7099 (13)	3·19 (42)
C(5)	5317 (15)	4486 (17)	7157 (14)	4·65 (52)
C(1)H1	5520	3469	5085	
C(1)H2	6403	4431	5259	
C(3)H1	7095	3622	8072	
C(3)H2	7330	4579	7106	
C(4)	5613	2249	7920	
C(4)H2	5000	2051	6712	
C(4)H3	6146	1597	6811	
C(5)H1	5233	4426	7942	
C(5)H2	5560	5323	6887	
C(5)H3	4631	4423	6712	

(*b*) Anisotropic temperature factors

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	68 (5)	91 (6)	96 (5)	−13 (5)	27 (5)	33 (6)
P	27 (3)	47 (5)	67 (4)	16 (4)	12 (4)	−10 (4)

Table 3. *Structure factors for* POCL



0·100 and $R_w=0{\cdot}083$ with

$$[\textstyle\sum w(F_o-F_c)^2/(n\text{–}v)]^{\frac{1}{2}}=0{\cdot}97.$$

The isotropic extinction factor used is the one suggested by Zachariasen (1968) and treated by Coppens & Hamilton (1970). This parameter corrected for deviations between F_o and F_c that were as extreme as $F_o/F_c=0{\cdot}43$. The final value of the extinction parameter was $17{\cdot}2\times10^4$ for an average path length of 0·005 cm. The final positional and thermal parameters are listed in Table 2; structure factors are given in Table 3.

A subroutine was prepared for the Fourier program in which each reflection was stored until the following reflection was read. If the two were identical, the second reflection was rejected, otherwise it was included in the Fourier summation. In this manner only one reflection of each set of duplicate reflections was used in the Fourier summation; these are the first of each set found in Table 3. The highest electron density in the final difference Fourier synthesis (F_o-F_c) was 0·6 e.Å^{-3}, about 12% of the height of a carbon atom in this structure.

Results and discussion

In the solid state, POCL molecules exist in the chair form with the phosphorus and carbon (2) atoms above and below the plane formed by the other atoms [O(1), C(1), C(3), O(3)] in the ring (Fig. 1). The equation for the least-squares plane through these atoms is $6{\cdot}832x+8{\cdot}493y-4{\cdot}387z=4{\cdot}891$, with each atom lying within one e.s.d. of the plane (0·006 to 0·018 Å). The chlorine and carbon (4) atoms are in axial positions, while oxygen (2) and carbon (5) atoms are in the equatorial positions.

The dihedral angle between the plane formed by C(1)–C(2)–C(3) and the least-squares plane is 51·9°, while that formed between the P–O(1)–O(3) plane and the least-squares plane is 34·6°. This flattening out of the molecule has been observed in similar compounds (Kainosho *et al.*, 1969; Haque, Caughlan, Hargis & Bentrude, 1970).

Although neither the positional nor the thermal parameters of the hydrogen atoms obtained from *HYGEN* varied in the least-squares refinement, the resulting C–C and C–O interatomic distances were affected; they fell within a smaller range and were slightly shorter than those distances calculated prior to the inclusion of the hydrogen atoms. This was to be expected, inasmuch as refinement in the absence of hydrogen atoms tends to shift the carbon positions toward the hydrogen atoms. The average C–H distance after the final refinement was 0·99 Å (range 1·02 to 0·97 Å).

The observed interatomic distances and angles are found in Table 4. The P–Cl distance is shown with and without a thermal 'riding' correction (Busing & Levy, 1964).

X-ray diffraction investigations of a number of similar compounds have been reported recently: 2-oxo-2-phenoxy-1,3,2-dioxaphosphorinane (Geise, 1967), 2-

Table 4. *Significant interatomic distances and angles in POCL*

(*a*) Intramolecular distances

P–Cl	1·982 (7) Å	O(1)–C(1)	1·457 (20)
	(no 'riding' correction)	O(3)–C(3)	1·470 (20)
	2·004 (7)	C(2)–C(1)	1·526 (22)
	(with 'riding' correction)	C(2)–C(3)	1·555 (21)
P=O(2)	1·393 (14)	C(2)–C(4)	1·531 (22)
P–O(1)	1·534 (11)	C(2)–C(5)	1·522 (22)
P–O(3)	1·510 (10)		

(*b*) Intermolecular distances

O(1)*–Cl†	3·884 (10) Å	Cl†–Cl§	3·915 (7) Å
O(1)*–O(1)‡	4·889 (20)		

(*c*) Intramolecular angles around phosphorus

Cl—P–O(2)	112·0 (0·6)°	O(3)–P–Cl	104·1 (0·6)°
O(2)–P–O(1)	113·6 (0·8)	O(1)–P–Cl	105·2 (0·5)
O(1)–P–O(3)	105·0 (0·6)	O(2)–P–O(3)	115·8 (0·8)
		Average: 109·3°	

(*d*) Intramolecular angles around carbon(2)

C(1)–C(2)–C(3)	106·9 (1·4)°	C(5)–C(2)–C(1)	108·5 (1·4)°
C(3)–C(2)–C(4)	109·3 (1·4)	C(1)–C(2)–C(4)	112·9 (1·4)
C(4)–C(2)–C(5)	110·2 (1·3)	C(3)–C(2)–C(5)	108·9 (1·4)
		Average: 109·5°	

(*e*) Other intramolecular angles

P–O(3)–C(3)	123·5 (1·0)°	C(2)–C(3)–O(3)	108·9 (1·3)°
P–O(1)–C(1)	118·7 (1·0)	C(2)–C(1)–O(1)	112·1 (1·4)

* $x, \frac{1}{2}-y, \frac{1}{2}+z$
† $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$
‡ $1-x, \frac{1}{2}+y, \frac{3}{2}-z$
§ $x-\frac{1}{2}, y, \frac{3}{2}-z$

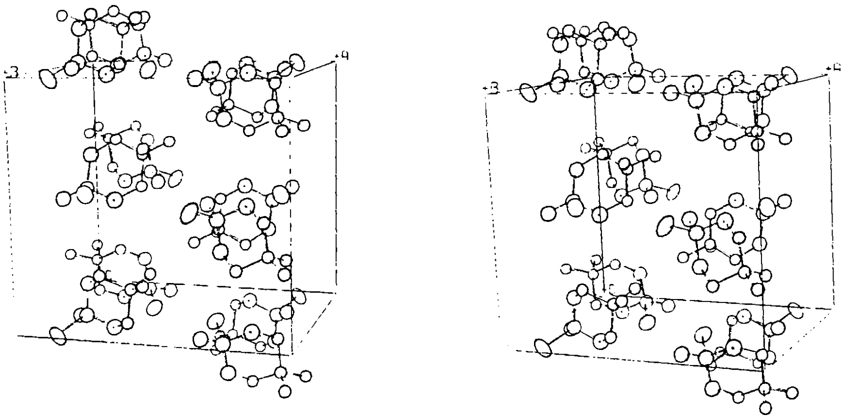


Fig. 2. POCL packing diagram, stereoview. For purposes of identification, each chlorine atom is elliptical and each oxygen(1) atom is marked with a dot.

bromo-5-bromoethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinane (Beineke, 1969), 5,5-dimethyl-2-oxo-2-hydroxy-1,3,2-dioxaphosphorinane (Murayama & Kainosho, 1969), propane-1,3-diol cyclic phosphate (Haque, Caughlan & Moats, 1970), 5-t-butyl-2-methyl-2-oxo-1,3,2-dioxaphosphorinane (Haque *et al.*, 1970). and 5,5-dimethyl-2-oxo-2-phenyl-1,3,2-dioxaphosphorinane (Killean, Lawrence & Magennis, 1970). The agreement between the bond lengths found for POCL and the average results of all similar compounds is as follows: (bond, average bond lengths, range of bond lengths, average found in POCL; all distances are in Å):

P=O: $1{\cdot}46_6$, 1·393–1·48, 1·393;
P–O: $1{\cdot}55_7$, 1·510–1·582, 1·522;
C–O: $1{\cdot}47_2$, 1·43–1·523, 1·463;
C–C: $1{\cdot}53_7$, 1·49–1·588. 1·534.

These average values and the POCL values for the C–C and C–O distances show excellent agreement. The POCL values lie within a smaller range which is to be expected from the use of *HYGEN*. The P–O distance in POCL is somewhat smaller than the average, but still within 3 e.s.d.'s. However, the P=O distance in POCL is significantly smaller than the average and has not been included in the calculation of the average P=O distance. This discrepancy is understandable, considering that the thermal motion of the oxygen atom is highly anisotropic and requires a 'riding' correction based on an anisotropic refinement of its temperature factor. The e.s.d.'s of all similar bonds are approximately the same.

The P–Cl distance of 2·004 (7) Å in POCL compares satisfactorily with the average P–Cl distance of 2·017 (2) Å in 2,2,4-trichloro-4,6,6-tris(dimethylamino)cyclotriphosphazatriene (Ahmed & Pollard, 1970), which also contains tetrahedrally substituted phosphorus atoms.

The packing diagram is shown in Fig. 2. Some of the more interesting intermolecular distances are listed in Table 4 (*b*). The atoms referred to are the chlorine and oxygen atoms lying close to the *C* face, which form a nearly planar parallelogram. All intermolecular distances are greater than the sum of the van der Waals radii of adjacent atoms, indicating the absence of any significant interactions between the POCL molecules in the solid state.

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