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The Crystal and Molecular Structure of *cis*-4,6-Dimethyl-2-oxo-2-triphenylmethyl-1,3,2-dioxaphosphorinan

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Crystals of *cis*-4,6-dimethyl-2-oxo-2-triphenylmethyl-1,3,2-dioxaphosphorinan, $C_{24}H_{25}PO_3$, are monoclinic, $a=16{\cdot}21$ (2), $b=8{\cdot}40$ (1), $c=16{\cdot}61$ (2) Å, $\beta=118{\cdot}0(1)^\circ$, space group *Cc* with $Z=4$. The intensities of 1312 independent reflexions above background were collected by counter methods and refined to $R=0{\cdot}085$. The structure determination shows the 1,3,2-dioxaphosphorinan ring to have a 'half-chair' conformation, considerably different from that found in related structures. The bond distances in the molecule are unexceptional.

Introduction

Since 2-oxo-1,3,2-dioxaphosphorinans tend to be crystalline solids, a systematic study of the effect of substituent groups on the conformation of the ring can be carried out by X-ray diffraction. The ring conformations of six such compounds, containing unsubstituted, 5-substituted, or 5,5-disubstituted 2-oxo-1,3,2-dioxaphosphorinans, have been studied by X-ray diffraction. All these structures contain rings with distorted chair conformations. Other studies of substituted rings of this type have been made using n.m.r. and dipole moments (Edmundson, 1969). We report here the crystal and molecular structure of *cis*-4,6-dimethyl-2-oxo-2-triphenylmethyl-1,3,2-dioxaphosphorinan. The present analysis was undertaken for two main reasons. Firstly, the triphenyl group is a much larger substituent than any yet studied, and it was expected that this would markedly affect the ring conformation adopted. Secondly, no structural data are available on 2-methoxy-*cis*-4,6-dimethyl-1,3,2-dioxaphosphorinan, the precursor phosphite (liquid at room temperature) of the present compound. This work should enable the solution chemistry of this phosphite to be inferred. A preliminary report of this work has been published (Drew, Rodgers, White & Verkade, 1971).

Experimental

cis-4,6-Dimethyl-2-oxo-2-triphenylmethyl-1,3,2-dioxophosphorinan was prepared as described previously (Drew *et al.*, 1971). Crystal data: $C_{24}H_{25}PO_3$, M.W.: 392·44, monoclinic, $a=16{\cdot}21$ (2), $b=8{\cdot}40$ (1), $c=16{\cdot}61$ (2) Å, $\beta=118{\cdot}01$ (10)°, $U=1997{\cdot}7$ Å^3, $D_m=1{\cdot}31$ (2) (by flotation), $D_c=1{\cdot}29$, $Z=4$, $F(000)=832$. Systematic absences for hkl, $h+k=2n+1$, for $h0l$, $l=2n+1$. Space-group was confirmed as *Cc* by the structure determination.

Mo $K\alpha$ radiation, $\lambda=0{\cdot}7107$ Å, $\mu(\text{Mo }K\alpha)=1{\cdot}69$ cm^{-1}.

Diffraction intensities were measured with a General Electric XRD-5 apparatus equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Zirconium-filtered molybdenum radiation was used at 40 kV and 20 mA. The stationary-crystal stationary-counter method was used with a 4° take-off angle and counting time 10 sec. Individual backgrounds were taken for all reflexions. Several standard reflexions were measured during the course of the experiment, but no significant change in intensity was detected. A crystal of approximate size, 0·3 × 0·2 × 0·2 mm, was mounted with the *b* axis parallel to the instrument axis in a thin-walled 0·2 mm diameter capillary. 1783 independent reflexions were measured with $2\theta<50^\circ$. The standard deviation $\sigma(I)$ of these reflexions was taken as $[I+2E+(0{\cdot}03I)^2]^{1/2}$, where E is the background of the reflexion. The 1312 reflexions with $I>\sigma(I)$ were used in the subsequent refinement. Absorption and extinction corrections were not applied.

In the calculation of structure factors, atomic scattering factors for P, O, C, H were taken from *International Tables for X-ray Crystallography* (1962). The isotropic temperature factor was defined as

$$\exp\left(-B\sin^2\theta/\lambda^2\right);$$

the anisotropic thermal parameters used have the form:

$$\exp\left(-0{\cdot}25\sum_i\sum_j h_ih_jb_ib_jB_{ij}\right),\quad i,j=1,2,3$$

where b_i is the ith reciprocal cell length. Calculations were made with the ATLAS computer at Didcot, Berkshire. We used the X-ray 63 system of programs compiled by J. M. Stewart and D. High and amended for that machine by J. Baldwin. We used our own phase determining program (Drew, Templeton & Zalkin, 1969) on the Elliott 4130 at this University.

Structure analysis and refinement

The data were placed on an absolute scale, and normalized structure-factor magnitudes, $|E_{hkl}|$ were derived. The structure was solved using the symbolic addition procedure for non-centrosymmetric structures (Karle & Karle, 1966). 139 reflexions with $|E_{hkl}|>1{\cdot}52$ were used in the determination. The choice of the origin-determining pair of reflexions $h_1k_1l_1$ and $h_2k_2l_2$ in space group *Cc* is restrictive (Allen & Trotter, 1971), requiring that $h_1l_2-h_2l_1=\pm1$. A starting set of reflexions, including two origin-determining reflexions and three others whose phases were assigned symbols, were used in computed application of the tangent formula (Karle & Hauptman, 1956). An *E* map calculated from the most consistent set of phases gave eight peaks consistent with the possible structure; these positions were refined by full-matrix least squares to an *R* of 0·37. The remainder of the structure was found by Fourier syntheses. The 19 non-methyl hydrogen atoms were positioned, with the appropriate geometry, at 1·075 Å from the carbon atoms to which they were bonded. Each hydrogen atom was given the temperature factor of the appropriate carbon atom and included in the structure factor summation but not refined. These positions coincided with positive areas in the difference Fourier map. The positions of the six methyl hydrogens could not be unambiguously located in the difference Fourier and were not included. The structure was then refined (phosphorus, oxygen, non-phenyl carbons anisotropically, phenyl carbons isotropically) to an *R* of 0·085 for the 1312 observed reflexions. A weighting scheme was chosen to give average values of $w\Delta^2$ for groups of reflexions independent of the value of $|F_o|$ or $\sin\theta/\lambda$. This was $\sqrt{w}=xy$, with $x=1$ if $\sin\theta>0{\cdot}21$ and otherwise $x=\sin\theta/0{\cdot}21$ and with $y=1$ if $F_o<30$, otherwise $y=30/F_o$.

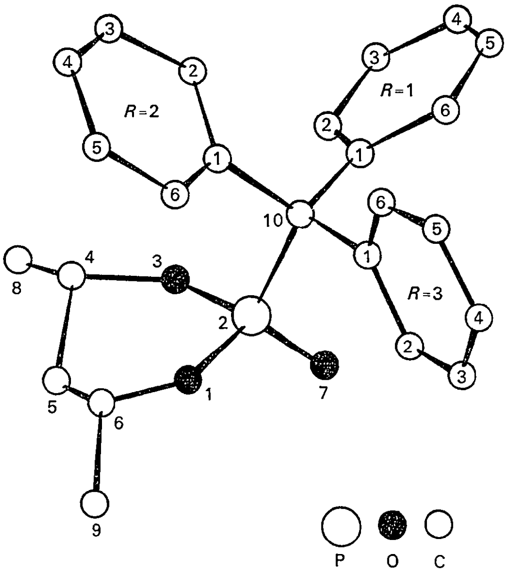


Fig. 1 The structure of *cis*-4,6-dimethyl-2-oxotriphenylmethyl-1,3,2-dioxaphosphorinan.

In the final cycle of refinement, no shift was $>0{\cdot}050\sigma$. The 471 reflexions with $I<\sigma(I)$ showed no large discrepancies and the final difference Fourier map no significant peaks. The final lists of positional coordinates and thermal parameters, together with their standard deviations, are given in Tables 1 and 2. The bond distances and angles are given in Table 3. Benzene ring atoms are numbered C(*Rn*), where *R* is the ring number 1, 2, 3 and *n* the atom number (1–6). The postulated hydrogen atom positions are given in Table 4. The final observed and calculated structure factors are given in Table 5.

Table 1. *Final atomic coordinates* (× 10^4) *and isotropic thermal parameters with estimated standard deviations in parentheses*

	x	*y*	*z*	*B*
O(1)	0845 (11)	0747 (19)	0810 (11)	*
P(2)	0000†	1635 (6)	0000†	*
O(3)	−0618 (11)	0260 (19)	−0643 (10)	*
C(4)	−0512 (16)	−1424 (30)	−0453 (17)	*
C(5)	0539 (17)	−1789 (30)	0006 (17)	*
C(6)	1051 (16)	−0926 (27)	0912 (15)	*
O(7)	0292 (12)	2801 (22)	−0475 (11)	*
C(8)	−1028 (20)	−2271 (35)	−1355 (18)	*
C(9)	2112 (18)	−1076 (36)	1337 (20)	*
C(10)	−0680 (13)	2536 (23)	0526 (13)	*
C(11)	−1479 (12)	3579 (22)	−0213 (12)	2·9 (3)
C(12)	−2007 (16)	3011 (28)	−1104 (16)	4·5 (4)
C(13)	−2787 (19)	3853 (32)	−1710 (17)	5·1 (5)
C(14)	−3040 (17)	5227 (30)	−1469 (17)	4·8 (5)
C(15)	−2498 (16)	5848 (28)	−0614 (16)	4·5 (4)
C(16)	−1728 (15)	5021 (25)	0001 (14)	3·8 (4)
C(21)	−1100 (13)	1156 (23)	0830 (13)	3·2 (3)
C(22)	−2016 (14)	0672 (24)	0372 (14)	3·7 (4)
C(23)	−2364 (17)	−0567 (24)	0671 (17)	4·9 (5)
C(24)	−1788 (18)	−1359 (33)	1460 (18)	5·3 (5)
C(25)	−0851 (19)	−0924 (31)	1953 (17)	5·1 (5)
C(26)	−0513 (15)	0348 (26)	1629 (14)	3·9 (4)
C(31)	−0044 (12)	3571 (22)	1336 (18)	3·0 (3)
C(32)	0798 (16)	4243 (28)	1427 (15)	4·2 (4)
C(33)	1334 (19)	5203 (33)	2181 (19)	5·5 (5)
C(34)	1099 (19)	5460 (33)	2839 (18)	5·4 (5)
C(35)	0246 (17)	4868 (30)	2759 (16)	4·9 (5)
C(36)	−0297 (15)	3899 (26)	2007 (15)	4·0 (4)

* Anisotropic temperature factors used for these atoms.
† P(2) used to define the origin in the *xz* plane.

Table 2. *Final anisotropic thermal parameters, with standard deviations in parentheses*

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	3·6 (6)	4·6 (7)	4·2 (7)	0·2 (6)	1·1 (6)	−0·5 (7)
P(2)	3·4 (2)	3·8 (2)	3·2 (2)	0·3 (2)	1·8 (2)	0·2 (2)
O(3)	4·5 (7)	4·7 (7)	3·4 (6)	0·7 (7)	1·5 (6)	−0·5 (7)
C(4)	4·4 (11)	4·2 (12)	4·8 (10)	0·6 (10)	2·7 (11)	0·0 (11)
C(5)	5·3 (12)	4·7 (10)	5·0 (11)	1·6 (11)	3·0 (12)	0·6 (10)
C(6)	4·6 (12)	4·1 (11)	4·1 (11)	0·9 (11)	2·2 (11)	0·4 (10)
O(7)	5·4 (8)	6·3 (9)	4·5 (9)	−0·4 (8)	2·8 (8)	0·7 (8)
C(8)	6·5 (13)	5·2 (13)	5·1 (12)	−0·3 (12)	1·6 (13)	−1·5 (13)
C(9)	4·6 (12)	6·7 (14)	6·5 (12)	2·1 (12)	2·7 (13)	0·8 (13)
C(10)	3·0 (8)	3·5 (9)	2·9 (10)	−0·3 (10)	1·4 (10)	−0·0 (9)

Table 3. *Bond distances and angles, with estimated standard deviations in parentheses*

P(2)–O(1)	1·585 (14) Å	O(1)–P(2)–O(3)	104·6 (8)°
P(2)–O(3)	1·572 (15)	O(1)–P(2)–O(7)	113·7 (9)
P(2)–O(7)	1·469 (21)	O(1)–P(2)–C(10)	105·1 (9)
P(2)–C(10)	1·860 (25)	O(3)–P(2)–O(7)	112·8 (9)
O(1)–C(6)	1·44 (3)	O(3)–P(2)–C(10)	106·8 (9)
O(3)–C(4)	1·44 (3)	O(7)–P(2)–C(10)	113·1 (11)
C(4)–C(5)	1·54 (3)	C(6)–O(1)–P(2)	128·4 (12)
C(5)–C(6)	1·52 (3)	C(4)–O(3)–P(2)	126·9 (12)
C(4)–C(8)	1·51 (3)	C(4)–C(5)–C(6)	111·0 (24)
C(6)–C(9)	1·53 (3)	C(9)–C(6)–C(5)	113·0 (25)
		C(9)–C(6)–O(1)	106·5 (20)
C(5)–C(4)–C(8)	111·6 (25)°	O(1)–C(6)–C(5)	111·2 (17)
C(5)–C(4)–O(3)	107·1 (20)		
O(3)–C(4)–C(8)	107·1 (19)		

	Ring 1	Ring 2	Ring 3
C(10)–C(*R*1)	1·57 (2) Å	1·54 (3) Å	1·53 (3) Å
C(*R*1)–C(*R*2)	1·40 (3)	1·38 (3)	1·42 (3)
C(*R*2)–C(*R*3)	1·39 (3)	1·38 (3)	1·40 (3)
C(*R*3)–C(*R*4)	1·35 (4)	1·37 (4)	1·34 (5)
C(*R*4)–C(*R*5)	1·37 (3)	1·40 (4)	1·42 (4)
C(*R*5)–C(*R*6)	1·37 (3)	1·42 (3)	1·40 (3)
C(*R*6)–C(*R*1)	1·37 (3)	1·39 (3)	1·39 (4)
P(2)—C(10)–C(*R*1)	108·3 (15)°	107·2 (14)°	110·0 (15)°
C(10)–C(*R*1)–C(*R*2)	120·5 (18)	124·5 (16)	122·6 (21)
C(10)–C(*R*1)–C(*R*6)	121·6 (16)	118·2 (17)	119·4 (19)
C(*R*2)–C(*R*1)–C(*R*6)	117·7 (17)	117·3 (21)	117·9 (18)
C(*R*1)–C(*R*2)–C(*R*3)	119·4 (24)	122·7 (18)	119·3 (24)
C(*R*2)–C(*R*3)–C(*R*4)	121·6 (22)	119·9 (22)	122·1 (29)
C(*R*3)–C(*R*4)–C(*R*5)	119·7 (21)	119·9 (28)	120·4 (24)
C(*R*4)–C(*R*5)–C(*R*6)	119·5 (23)	118·9 (21)	117·7 (28)
C(*R*5)–C(*R*6)–C(*R*1)	121·9 (23)	121·2 (19)	122·3 (24)

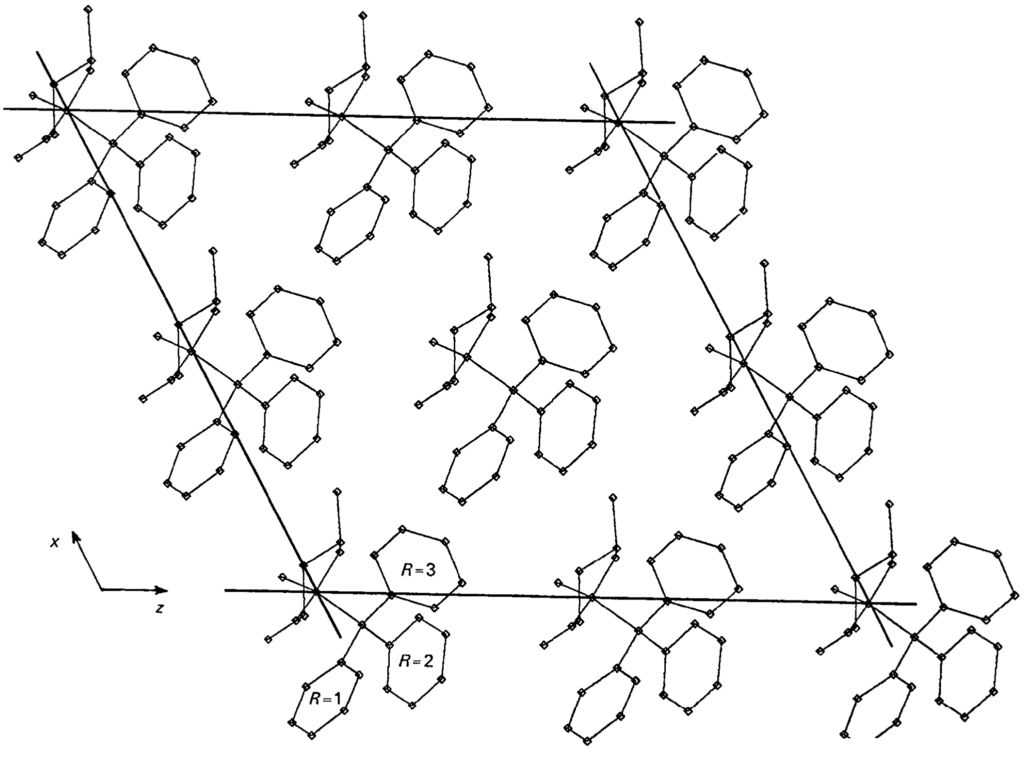


Fig. 2. The *b* projection of the unit cell of (VII).

Table 4. *Hydrogen atom positions* ($\times 10^4$)

	x	y	z
H(4)	−0795	−1734	−0004
H(5-1)	0819	−1408	−0435
H(5-2)	0643	−3048	0121
H(6)	0838	−1418	1384
H(12)	−1809	1933	−1315
H(13)	−3201	3395	−2388
H(14)	−3665	5834	−1944
H(15)	−2675	6975	−0429
H(16)	−1311	5510	0669
H(22)	−2483	1288	−0243
H(23)	−3086	−0909	0285
H(24)	−2060	−2314	1698
H(25)	−0390	−1545	2568
H(26)	0207	0696	2009
H(32)	1021	4016	0922
H(33)	1960	5744	2232
H(34)	1559	6141	3432
H(35)	0024	5148	3258
H(36)	−0932	3395	1948

Discussion of the structure

A view of the molecule, showing the atomic numbering scheme, bond distances and the conformation of the 2-oxo-1,3,2-dioxaphosphorinan entity is shown in Fig. 1. The crystal structures of six molecules containing this ring have been determined. These are listed in Table 6. In molecules (I) to (VI) inclusive, the conformation of the rings is a distorted chair with atoms O(1), C(6), C(4), O(3) planar and with atoms P(2), C(5) being on opposite sides of that plane [designated as plane (i)]. The ring conformation can best be described by the two dihedral angles which plane (i) makes with plane (ii) containing atoms O(1), P(2), O(3) and plane (iii) containing atoms C(4), C(5), C(6). Data on all seven compounds is given in Table 6.

In the present structure, molecule (VII), atoms O(1), C(6), C(4), O(3) have deviations from the least-squares plane (see Table 7) of −0·07, 0·07, −0·07, 0·07 Å respectively. These deviations are greater than those found in (I) to (VI) which are all planar within experimental error. In the present structure, the deviations of atoms P(2) and C(5) from plane (i) are −0·03 and 0·69 Å respectively. Thus the conformation of the ring can be described as a 'half-chair', five of its atoms lying in an approximate plane. The dihedral angles between planes (i) and (ii) are approximately the same in all seven structures, ranging between 51·2 and 54·9°. The dihedral angles between planes (i) and (iii) vary considerably and it has been shown by Haque, Caughlan, Hargis & Bertrude (1970), in a discussion of (I) to (IV), that these angles decrease as the size of the 2-axial group X increases ($CPh_3 > Me$, $Ph > Br$, $OPh > OH$). The reason given is that steric repulsion between X and the axial methylene hydrogens on C(4) and C(6) can be relieved by flattening the phosphorus end of the ring thus decreasing the dihedral angle. For (I) to (VI), this is a relatively small effect, angles ranging between 32·6° (for $X = Ph$) to 41·8° (for $X = OH$). For (VII) with $X = CPh_3$, the angle is 3·7°, a large difference from the mean which can only be accounted for by steric repulsion.

Both substituted methyl groups on C(4) and C(6) are equatorial but while C(8) is in the plane formed by atoms C(4), C(5), C(6), atom C(9) is 0·18 Å from that plane. We find no reason for this latter deviation from a consideration of intramolecular distances as the two methyl groups are bent away from the phenyl rings.

Table 5. *Observed and calculated structure factors* ($\times 1{\cdot}0$)

Unobserved reflexions are not included
Adjacent columns are for h, F_o and F_c.

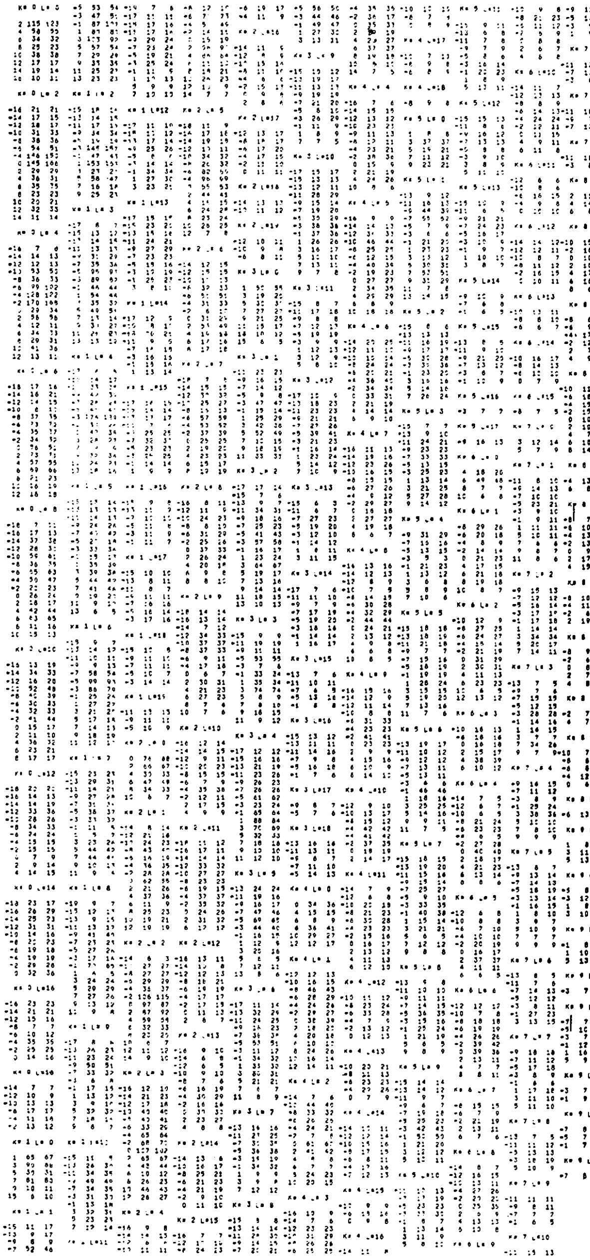
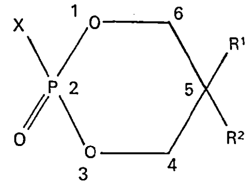


Table 6. *Comparison of conformations of* 2-*oxo*-1,3,2-*dioxaphosphorinan rings in assorted molecules*



Molecule	R^1	R^2	X	Angle* (*a*)	Angle* (*b*)
(I)	H	H	OH	54·2°	40·4°
(II)	H	H	OPh	53·1	36·5
(III)	Me	CH_2Br	Br	52·5	36·7
(IV)	t-butyl	H	Me	54·9	33·5
(V)	Me	Me	Ph	51·2	32·6
(VI)	Me	Me	OH	54·7	41·8
(VII)	H	H	CPh_3	53·3	3·7

* Angle *a* is the dihedral angle between planes (i) and (ii) and angle *b* that between planes (i) and (iii). Planes contain the following atoms: (i) O(1), C(6), C(4), O(3); (ii) C(4), C(5), C(6); (iii) O(1), P(2), O(3).

References: (I) Haque, Caughlan, Hargis & Bentrude (1970), (II) Geiss (1967), (III) Beineke (1969), (IV) Haque, Caughlan & Moats (1970), (V) Killean, Lawrence & Magennis (1971), (VI) Murayama & Mainosho (1969), (VII) This work.

Thus, there is no intramolecular contact between C(8), C(9) and the benzene rings less than 4·6 Å. On steric grounds then, one would expect 4,6 equatorial substitution to have little effect on ring conformation. This cannot be substantiated from the available structural data although a comparison of (I) and (VI) leads to the conclusion that 5,5′ disubstitution has no significant effect on ring conformation. Therefore, it seems reasonable to compare the conformation of the ring in the present compound, which is 4,6 disubstituted, with the ring conformations in (I) to (VI) which are either non-substituted, 5-monosubstituted or 5,5′-disubstituted.

Table 7. *Deviations of atoms from the least-squares planes* $Ax+By+Cz=D$, *where x, y, z are the crystallographic fractional coordinates*

		Plane 1		Plane 2
	A	−13·56		−6·67
	B	0·01		−6·58
	C	14·56		10·04
	D	−0·03		0·82
Atoms	C(6)	0·07 Å	C(5)	0·00 Å
	C(4)	−0·07	C(6)	0·00
	O(3)	0·07	C(4)	0·00
	O(1)	−0·07	C(8)	0·00*
	P(2)	−0·03*	C(9)	0·18*
	C(5)	0·69*		

* Atom given zero weight in the calculation of the plane.

In (VII), benzene ring ($R=2$) is closest to the axial hydrogens H(4) and H(6) placed (see Table 4) in tetrahedral positions 1·075 Å from the central carbon atoms. The benzene ring ($R=2$) is not orientated symmetrically with respect to the 2-oxo-1,3,2-dioxaphosphorinan ring, the angle between the ring and the plane containing atoms C(10), P(2), O(7) being 74·1°. The ring is thus twisted away from H(4) towards H(6). H(4) has no close contacts with atoms in any phenyl ring, the minimum distance being 4·7 Å. However H(6) is 2·83 Å from C(26) and 3·31 Å from C(25) [also 2·5 Å from H(26)], distances which are comparable with the sum of the appropriate van der Waals radii (C: 2·0, H: 1·2 Å; Pauling, 1960). Any twist in the ring to a distorted chair conformation would decrease these contact distances and therefore it appears probable that these steric effects are the cause of the present conformation of the ring. There are no intramolecular contacts between the other benzene rings ($R=1,3$) and C(4), C(6) under 4·3 Å.

Intermolecular contacts less than 3·75 Å between non-hydrogen atoms are listed in Table 8. There are no abnormally short distances and it can be assumed that intermolecular forces have only minimal effect on the conformation of the 1,3,2-dioxaphosphorinan ring. In Table 8, it is noticeable that the shortest contacts are between substituted groups on the ring O(7), C(8), C(9) and carbon atoms in the phenyl rings. This mode of packing is illustrated by the unit cell diagram in Fig. 2 which shows the *b* projection.

Table 8. *Intermolecular distances less than* 3·75 Å

Roman numerals as superscripts refer to atoms in the following equivalent positions relative to the reference molecule at (x,y,z)

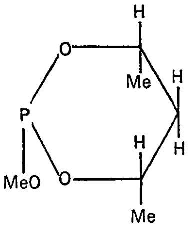
(i)	$\frac{1}{2}+x,\ \frac{1}{2}+y,\ z$	(iv)	$x,\ 1+y,\ z$
(ii)	$\frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$	(v)	$x,\ 1-y,\ \frac{1}{2}+z$
(iii)	$\frac{1}{2}+x,\ y-\frac{1}{2},\ z$	(vi)	$x,\ -y,\ \frac{1}{2}+z$

$O(7)$–$C(23^{i})$	3·62 Å	$C(15)$–$C(23^{iv})$	3·64 Å
$O(1)$–$C(13^{ii})$	3·66	$C(16)$–$C(8^{iv})$	3·73
$C(9)$–$C(13^{ii})$	3·68	$C(35)$–$O(7^{v})$	3·50
$C(9)$–$C(16^{iii})$	3·64	$C(36)$–$C(8^{vi})$	3·70
$C(15)$–$C(8^{iv})$	3·53	$C(35)$–$C(8^{vi})$	3·75

The P–O–C angles in (VII) average to 127·7°, much larger than those found in (I) to (VI) which range between 116° [in (VI)] and 120° [in (III), (IV), (V)]. Such an increase in angle would also significantly decrease the contacts between the benzene ring atoms and the axial hydrogen atoms on C(4) and C(6). It was postulated by Haque, Caughlan, Hargis & Bentrude (1970) that steric strain involving the axial substituent X at phosphorus could also be relieved by bending the P–X bond away from the axial hydrogen atoms, thus decreasing the angle O(7)–P(2)–X. In (I) to (VII), this angle is 116·6, 113·7, 111·5, 108·7, 111·7, 117·8 and 113·1°, respectively. There is an approximate correlation between size of angle and size of X for (I) to (VI), although the angle in (VII) appears well out of sequence. It is perhaps invidious to include the latter compound for comparison of O(7)–P(2)–X angles as its ring conformation, a 'half-chair', is so different. The bond distances in (VII) are comparable with those found in other structures, the P(2)–O(1), P(2)–O(3) bonds averaging to 1·578 (15) Å and P(2)–O(7) being 1·469 (21) Å. The ring C–O and C–C bond distances are also unexceptional. The ring angles, apart from those already considered, are also similar to those found in (I) to (VI). The bond distances and angles of the atoms in the phenyl rings are within experimental error of the expected values. All three rings are planar, the maximum distances of any ring atom from the plane being 0·03 Å.

From the conformation of the present compound we can predict the probable solution stereochemistry of the precursor phosphite (VIII).

(VIII)



Firstly the methoxyl group in the phosphite (VIII) can be concluded to be *cis* to the 4,6 methyl groups if the generally accepted stereochemical course for the Michaelis–Arbuzov reaction (Kirby & Warren, 1967) is assumed to be followed here. Secondly as discussed by White, Bertrand, McEwen & Verkade (1970), values of vicinal POCH and HCCH nuclear spin–spin coupling constants for (VIII) indicate a chair-like conformation with equatorially disposed 4,6 methyl groups. Thus, the methoxy group in the phosphite (VIII) must occupy an equatorial position. This conclusion is of importance since considerable evidence has been presented which indicates a greatly preferred axial methoxy disposition in several substituted 2-methoxy-1,3,2-dioxaphosphorinans (White *et al.*, 1970; Rodgers, White & Verkade, 1970; Bentrude, Yee & Hargis, 1970].

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References

ALLEN, F. H., TROTTER, J. & ROGERS, D. (1971). *J. Chem. Soc.* (*B*) p. 166.
BEINEKE, T. A. (1969). *Acta Cryst.* **B25**, 413.
BENTRUDE, W. G., YEE, K. C. & HARGIS, J. H. (1970). Abstracts, ACS Meeting, Chicago, Illinois, ORGN 147.
DREW, M. G. B., RODGERS, J., WHITE, D. W. & VERKADE, J. G. (1971). *Chem. Commun.* p. 227.
DREW, M. G. B., TEMPLETON, D. H. & ZALKIN, A. (1969). *Acta Cryst.* **B25**, 261.
EDMUNDSON, R. S. (1969). *Tetrahedron Letters*, p. 1905.
GEISE, H. J. (1967). *Rec. Trav. chim. Pays-Bas*, **86**, 362.
HAQUE, M. U., CAUGHLAN, C. N., HARGIS, J. H. & BENTRUDE, W. G. (1970). *J. Chem. Soc.* (*A*), p. 1786.
HAQUE, M. U., CAUGHLAN, C. N. & MOATS, W. L. (1970). *J. Org. Chem.* **35**, 1446.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635.
KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.
KILLEAN, R. C. G., LAWRENCE, J. L. & MAGENNIS, I. M. (1971). *Acta Cryst.* **B26**, 189.
KIRBY, A. J. & WARREN, S. G. (1967). *The Organic Chemistry of Phosphorus*, pp. 37–45. Amsterdam: Elsevier.
MURAYAMA, W. & KAINOSHO, M. (1969). *Bull. Chem. Soc. Japan*, **42**, 1819.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
RODGERS, J., WHITE, D. W. & VERKADE, J. G. (1971). *J. Chem. Soc.* (*A*), p. 77.
WHITE, D. W., BERTRAND, R. D., MCEWEN, G. K. & VERKADE, J. G. (1970). *J. Amer. Chem. Soc.* **92**, 7125.