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## The Crystal and Molecular Structure of 2-Oxo-2-phenoxy-4*H*-1,3,2-benzodioxaphosphorin

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2-Oxo-2-phenoxy-4*H*-1,3,2-benzodioxaphosphorin, C<sub>13</sub>H<sub>11</sub>O<sub>4</sub>P, crystallizes in the orthorhombic system, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *Z* = 4. The unit-cell dimensions are *a* = 7.563 (2), *b* = 27.554 (4), *c* = 5.835 (1) Å. The structure was solved by direct methods and refined by full-matrix least-squares calculations with anisotropic thermal parameters (isotropic for H atoms) to a final *R* value of 0.045 for 1429 reflexions collected by means of a single-crystal diffractometer. The dioxaphosphorin ring is midway between a half-chair and sofa conformation with the phenoxy group in the axial position.

### Introduction

The present study is a continuation of a series of investigations into the conformations of 1,3,2-dioxaphosphorinane systems (Galdecki & Karolak-Wojciechowska, 1971; Galdecki & Karolak-Wojciechowska, 1973; Cameron, Galdecki & Karolak-Wojciechowska, 1976). Many structures of this type have been studied now, including 2-oxo-2-phenoxy-1,3,2-dioxaphosphorinane (Geise, 1967). However, no molecule having a double bond in the 1,3,2-dioxaphosphorinane ring has been investigated. Such a ring should have a slightly different conformation.

### Experimental

The crystals of 2-oxo-2-phenoxy-4*H*-1,3,2-benzodioxaphosphorin (abbreviated to PBDP) were crystallized from ligroin with benzene at room temperature in the form of plates. Weissenberg photographs showed the crystal system to be orthorhombic. Systematic absences indicated the non-centrosymmetric space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. 1429 independent reflexions were collected on a CAD-4 diffractometer from a crystal shaped into a sphere of diameter 0.3 mm (Cu radiation). The density of the crystals was determined by flotation in KI solution.

### Crystal data

C<sub>13</sub>H<sub>11</sub>O<sub>4</sub>P, *M<sub>r</sub>* = 262.2, *F*(000) = 544. Orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (*D*<sub>2</sub><sup>h</sup>; No. 19) with *a* = 7.563 (2), *b* = 27.554 (4) and *c* = 5.835 (1) Å; *V* = 1216.2 Å<sup>3</sup>; *Z* = 4. *D<sub>m</sub>* = 1.44, *D<sub>x</sub>* = 1.432 g cm<sup>-3</sup>; *μ*(Cu *Kα*) = 20.41 cm<sup>-1</sup>.

The phases of 200 reflexions were determined by means of *MULTAN* (Germain, Main & Woolfson, 1971). Table 1 shows the reflexions selected for the

Table 1. Phase assignment for specifying the origin, and other reflexions contained in the starting set

Set	<i>h k l</i>	<i>E<sub>hkl</sub></i>	Phase	
37	6 0 2	2.07	0	Determined from Σ <sub>1</sub> relationships
1	0,20,3	3.65	0	} Specifying the origin
2	5,19,0	3.19	π/2	
3	4,21,0	2.77	0	
4	2 5 7	2.68		} Other reflexions in starting set
15	4,14,1	2.29		
40	4 4 1	2.01		
Figures of merit		<i>M<sub>abs</sub></i>	<i>ψ</i> <sub>0</sub>	<i>R<sub>Karic</sub></i> COMBINED FOM
Maximum value		1.2474	617.2	49.07 2.072
Minimum value		0.8481	496.6	33.85 0.2821

starting set. After analysis of the figures of merit for 30 out of 32 solutions we decided to accept the phases of sets 15 and 40. The next use of *MULTAN* included in the starting set one extra reflexion ( $E_{257} = 2.68$ ), whose phase was not previously determined. This produced two solutions. The  $E$  map based on the 'better' set of phases with  $M_{\text{abs}} = 1.2244$  (1.0304 for 'worse' one),  $R_{\text{Karle}} = 28.01$  (34.36) and COMBINED FOM = 2.000 (1.000) showed all but one of the non-hydrogen atoms. The map did not contain any other high peaks. The position of the missing C(13) atom was calculated through the assumed symmetry of the benzene ring to which this atom belongs. This model of the PBDP molecule for which  $R = 32\%$  was directly refined by the method of least squares. The calculations were processed using the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). The structure was refined by the full-matrix least-squares program *CRYLSQ* with isotropic (six cycles) and anisotropic (five cycles) temperature factors until  $R_w \{[\sum w(F_o - F_c)^2 / \sum F_o^2]^{1/2}\}$  reached 0.062 and  $R \{[\sum |F_o - F_c| / \sum F_o]\}$ , 0.046. H positions were found from a difference Fourier map ( $R = 0.068$ ) and refined with isotropic temperature factors in one additional cycle. The final conventional  $R$  factor was 0.045 ( $R_w = 0.058$ ) excluding unobserved reflexions. The weighting scheme applied was  $w = \sigma^{-1}$  and 233 reflexions with  $F_o \leq 3\sigma$  were not used in the refinement.

The scattering factors for P, O and C were those of Doyle & Turner (1968) and those in *International Tables for X-ray Crystallography* (1962) for H atoms. All calculations were carried out on an IBM-370 computer. The illustrations were prepared by *ORTEP* (Johnson, 1965).\*

## Results and discussion

The final positional parameters are listed in Table 2. A view of the molecule of PBDP and the numbering system, not consistent with the chemical numbering, are shown in Fig. 1. Intramolecular bond lengths and angles are shown in Tables 3 and 4.

The 4*H*-1,3,2-dioxaphosphorin ring is more flattened at the C than at the P, quite contrary to the dioxaphosphorinanes which have already been investigated. This flattening results from the presence of the condensed benzene ring and the partly double character of the C(4)–C(5) bond (1.374 Å). Table 5 lists torsion angles in the 4*H*-1,3,2-dioxaphosphorin ring of PBDP in comparison with those for the ideal half-chair conformation, in the cyclohexene ring (Chiang & Bauer, 1969) and in steroid systems with one double

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32965 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Atomic coordinates ( $\times 10^4$ ) with e.s.d.'s in parentheses

	$x$	$y$	$z$
P	1623 (1)	3959 (1)	341 (2)
O(1)	2140 (5)	3888 (1)	-2025 (5)
O(2)	1909 (4)	4481 (1)	1253 (5)
O(3)	-396 (3)	3850 (1)	760 (5)
O(4)	2637 (3)	3651 (1)	2188 (4)
C(4)	-1272 (5)	4048 (1)	2672 (6)
C(5)	-513 (5)	4401 (1)	4009 (6)
C(6)	-1478 (8)	4576 (2)	5887 (8)
C(7)	-3151 (7)	4388 (2)	6342 (9)
C(8)	-3885 (6)	4038 (2)	4962 (8)
C(9)	-2942 (5)	3866 (1)	3094 (8)
C(10)	1316 (6)	4589 (1)	3596 (9)
C(11)	2664 (5)	3140 (1)	2231 (6)
C(12)	3457 (5)	2888 (1)	467 (7)
C(13)	3495 (6)	2382 (1)	622 (7)
C(14)	2772 (6)	2147 (1)	2488 (8)
C(15)	1963 (6)	2410 (1)	4237 (8)
C(16)	1923 (5)	2922 (1)	4124 (6)
H(6)	4137 (58)	163 (15)	3019 (90)
H(7)	1242 (85)	494 (17)	2209 (95)
H(8)	4726 (57)	3920 (13)	5099 (67)
H(9)	-3352 (65)	3612 (13)	2064 (87)
H(10)	2470 (66)	4472 (17)	4363 (81)
H(11)	1091 (70)	4973 (15)	3927 (86)
H(12)	3947 (85)	3058 (20)	-681 (103)
H(13)	4217 (61)	2221 (14)	-219 (73)
H(14)	2847 (65)	1746 (16)	2522 (102)
H(15)	1135 (72)	2197 (15)	5398 (78)
H(16)	1063 (74)	3165 (17)	5313 (95)

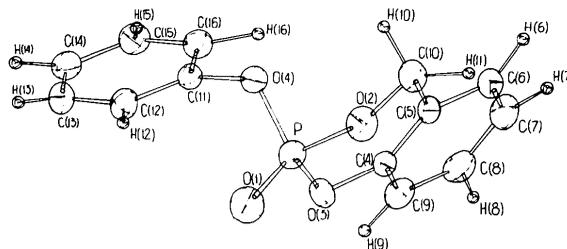


Fig. 1. The view of the PBDP molecule and numbering of atoms. The thermal ellipsoids have been scaled to include 40% probability.

Table 3. Bond lengths (Å) with e.s.d.'s in parentheses

P–O(1)	1.448 (3)	C(13)–C(14)	1.380 (4)
P–O(2)	1.549 (2)	C(14)–C(15)	1.393 (3)
P–O(3)	1.575 (2)	C(15)–C(16)	1.414 (3)
P–O(4)	1.571 (3)	C(16)–C(11)	1.376 (5)
O(2)–C(10)	1.470 (2)		
O(3)–C(4)	1.407 (2)	H(6)–C(6)	1.069 (48)
C(4)–C(5)	1.374 (4)	H(7)–C(7)	1.017 (28)
C(5)–C(6)	1.402 (2)	H(8)–C(8)	1.103 (18)
C(5)–C(10)	1.496 (8)	H(9)–C(9)	0.972 (25)
C(6)–C(7)	1.392 (3)	H(10)–C(10)	1.032 (13)
C(7)–C(8)	1.374 (4)	H(11)–C(10)	1.089 (16)
C(8)–C(9)	1.387 (3)	H(12)–C(12)	0.898 (24)
C(9)–C(4)	1.381 (4)	H(13)–C(13)	0.859 (34)
O(4)–C(11)	1.409 (2)	H(14)–C(14)	1.108 (14)
C(11)–C(12)	1.379 (3)	H(15)–C(15)	1.093 (12)
C(12)–C(13)	1.396 (2)	H(16)–C(16)	1.163 (47)

Table 4. Valency angles ( $^{\circ}$ ) for non-hydrogen atoms with *e.s.d.*'s in parentheses

O(1)–P–O(2)	114.5 (1)	C(5)–C(6)–C(7)	119.6 (12)
O(1)–P–O(3)	112.6 (2)	C(6)–C(7)–C(8)	121.1 (3)
O(1)–P–O(4)	116.8 (6)	C(7)–C(8)–C(9)	119.6 (4)
O(2)–P–O(3)	105.0 (2)	C(8)–C(9)–C(4)	119.1 (11)
O(2)–P–O(4)	101.4 (8)	C(9)–C(4)–C(5)	122.6 (9)
O(3)–P–O(4)	105.3 (5)	P–O(4)–C(11)	123.9 (11)
P–O(2)–C(10)	117.7 (4)	O(4)–C(11)–C(16)	116.4 (30)
P–O(3)–C(4)	120.4 (4)	O(4)–C(11)–C(12)	119.8 (24)
O(2)–C(10)–C(5)	111.3 (6)	C(11)–C(12)–C(13)	117.6 (32)
O(3)–C(4)–C(9)	115.6 (4)	C(12)–C(13)–C(14)	120.8 (18)
O(3)–C(4)–C(5)	121.9 (8)	C(13)–C(14)–C(15)	120.5 (27)
C(4)–C(5)–C(6)	118.1 (12)	C(14)–C(15)–C(16)	119.6 (19)
C(4)–C(5)–C(10)	122.6 (13)	C(15)–C(16)–C(11)	117.7 (35)
C(6)–C(5)–C(10)	119.3 (18)	C(16)–C(11)–C(12)	123.8 (30)

bond in the six-membered rings (*Terpenoids and Steroids*, 1974; Duax & Norton, 1975). The 4H-1,3,2-dioxaphosphorin ring has a conformation intermediate between P,O(2) half-chair and O(2) sofa. Pseudo mirror and twofold symmetry is present with asymmetry parameters (Duax & Norton, 1975)  $\Delta C_s^4 = 9.95$  and  $\Delta C_2^{4,5} = 11.37$ . The average dihedral angle in this ring is  $27.51^{\circ}$ . The torsion angle O(2)–P–O(3)–C(4), equal to  $-33.18^{\circ}$ , differs from the mean values ( $40 \sim 60^{\circ}$ ) occurring in steroid systems with a similar conformation (*Terpenoids and Steroids*, 1974). Flattening of the ring is accompanied by increase of the valency angles at the O atoms in comparison with those at C(*sp*<sup>3</sup>). The increase in the O valency angles is revealed by the decrease of the torsion angles C(10)–O(2)–P–O(3) and O(2)–P–O(3)–C(4) and by the difference between P–O(3)–C(4)=C(5) and C(4)=C(5)–C(10)–O(2) torsion angles (Table 5).

The dihedral angle between plane (i) defined by the atoms O(2), P, O(3) and plane (ii) [O(2), O(3), C(4) and C(5)] is  $32.0^{\circ}$ . Because of this deformation of the dioxaphosphorin ring, atom C(10) is significantly out of plane (ii), by about  $0.3 \text{ \AA}$  and for this reason it has not been taken into account in the calculation of this least-squares plane. The dihedral angles between plane (iii) calculated from atoms C(4), C(5) and C(10) and the previously defined planes are  $10.2^{\circ}$  (ii) and  $27.4^{\circ}$  (i) (Table 6). As a further consequence of the presence of

Table 6. Details of the dioxaphosphorin-ring geometry

Plane	Atoms in the plane	Other atoms	Distances of the atoms from the plane ( $\text{\AA}$ )
(i)	O(2)		0.00002
	P		-0.00002
	O(3)		0.00000
		C(4)	-0.6654
		C(10)	-1.0302
		C(5)	-1.1375
(ii)	O(2)		0.01766
	O(3)		-0.03644
	C(4)		-0.05687
	C(5)		-0.03806
		C(10)	-0.2998
(iii)		P	-0.5130
	C(4)		0.00008
	C(5)		-0.00009
	C(10)		-0.00002
		O(2)	0.4570
	O(3)	0.0517	
	P	-0.1514	
	Planes	Angle between the planes ( $^{\circ}$ )	
	(i) and (ii)		32.0
	(ii) and (iii)		10.2
	(i) and (iii)		27.4

the double bond C(4)–C(5) considerable differences in P–O and O–C distances in the dioxaphosphorin ring are observed. The lengths of the P–O(2) and P–O(3) bonds are  $1.549$  and  $1.575 \text{ \AA}$ , whereas the C(10)–O(2) and C(4)–O(3) distances are  $1.470$  and  $1.407 \text{ \AA}$  respectively.

As expected, the double-bonded ( $1.448 \text{ \AA}$ ) O atom is in the equatorial and the phenoxy group in the axial position to the dioxaphosphorin ring. The mean length of the single P–O bonds in the distorted tetrahedron PO<sub>4</sub> is  $1.565 \text{ \AA}$ . The mean values of the angles O=P–O and O–P–O are  $114.6$  and  $103.9^{\circ}$ . The stronger repulsion between double-bonded and single-bonded O atoms as compared with repulsion between two single-bonded O atoms explains such a deformation.

Information on the geometry of the condensed benzene ring (B) and phenoxy group (A) is given in Table 7.

Table 5. Torsion angles ( $^{\circ}$ ) in the 4H-1,3,2-dioxaphosphorin and similar rings

	PBDP	Cyclohexene	Steroids with half-chair conformation	Steroids with intermediate conformation	Steroids with sofa conformation
P–O(3)–C(4)=C(5)	10.99	15.2	–(11 ~ 20)	–(10 ~ 30)	–(27 ~ 43)
O(3)–C(4)=C(5)–C(10)	-2.29	0	-5 ~ 5	-4 ~ 6	-5 ~ 9
C(4)–C(5)–C(10)–O(2)	19.33	15.2	–(12 ~ 23)	–(9 ~ 20)	–(3 ~ 12)
C(5)–C(10)–O(2)–P	-46.92	-44.9	43 ~ 54	40 ~ 54	15 ~ 40
C(10)–O(2)–P–O(3)	52.36	60.2	–(59 ~ 69)	–(64 ~ 65)	–(46 ~ 66)
O(2)–P–O(3)–C(4)	-33.18	-44.9	39 ~ 48	41 ~ 58	60 ~ 64

Table 7. Details of aromatic-ring geometry: phenoxy group – ring A, fused benzene – ring B

	Ring A	Ring B
Mean value of the C–C bond length (Å)	1.390	1.385
Mean value of the C–C–C angle (°)	120.0	120.0
Mean value of the C–H bond length (Å)	1.02	1.04
The distances (Å) of C atoms in aromatic rings from the least-squares ring plane		
C(11) or C(4)	–0.00097	–0.00637
C(12) or C(5)	–0.00071	0.00152
C(13) or C(6)	–0.00188	0.00395
C(14) or C(7)	0.00617	–0.00508
C(15) or C(8)	–0.00754	0.00012
C(16) or C(9)	0.00495	0.00590

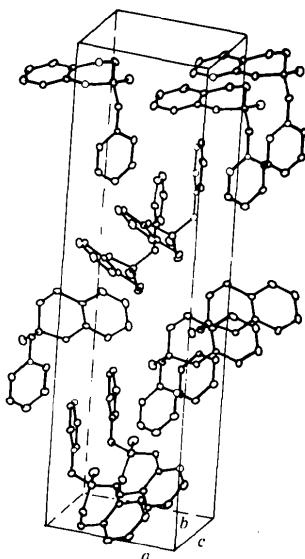


Fig. 2. The packing of molecules in the crystal.

The packing of the molecules of PBDP in the crystals is shown in Fig. 2. There are no intermolecular contacts short enough to affect the conformation of the rings. The shortest intermolecular distances (less than 3.5 Å) are listed in Table 8.

Table 8. The shortest intermolecular distances (less than 3.5 Å)

The first atom is at $x, y, z$ and the second at (i) $x, y, z - 1$ ; (ii) $x - 1, y, z$ and (iii) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$ .			
O(1)···O(4 <sup>i</sup> )	3.460	C(8)···O(4 <sup>ii</sup> )	3.267
O(1)···C(5 <sup>i</sup> )	3.374	C(9)···O(4 <sup>ii</sup> )	3.436
O(1)···C(10 <sup>i</sup> )	3.262	C(10)···O(2 <sup>iii</sup> )	3.288
O(1)···C(16 <sup>i</sup> )	3.488		

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