University IBM 370/165 computers with programs written by Dr G. M. Sheldrick (Cambridge University). The diagram was drawn with *ORTEP* (Johnson, 1965).

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Bis(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl) Oxide

By M. Bukowska-Strzyżewska and W. Dobrowolska

Institute of General Chemistry, Technical University, 36 Żwirki, 90-924 Łódź, Poland

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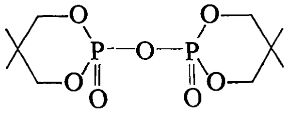
Abstract. $C_{10}H_{20}O_7P_2$, orthorhombic, *Pbca*, $a = 26{\cdot}88$ (2), $b = 9{\cdot}99$ (1), $c = 11{\cdot}13$ (1) Å; $V = 2988{\cdot}8$ Å^3; $M_r = 314{\cdot}22$; $D_x = 1{\cdot}39$, $D_m = 1{\cdot}39$ g cm^{-3}; $Z = 8$; $F(000) = 1328{\cdot}0$; $\lambda(\text{Cu }K\alpha) = 1{\cdot}5418$ Å; $\mu r(\text{Cu }K\alpha) = 0{\cdot}6$. The structure was solved by direct methods and refined by least-squares methods with anisotropic temperature factors to an *R* value of 0·121 for 1179 observed reflections. The symmetry of the bicyclic molecules is C_1. The conformation around the bridge bonds P—O—P is staggered. The two structurally independent dioxaphosphorinane rings have partially flattened chair conformations with the double-bonded O atom in an equatorial and the linking O atom in an axial position. An analysis of the causes of the flattening observed in the 1,3,2-dioxaphosphorinane rings was carried out and the structural results are compared with those for bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl) sulphide.

Introduction. We are studying several structures of bicyclic organic pyro- and thiopyrophosphates (Bukowska-Strzyżewska, Dobrowolska, Michalski, Młotkowska & Skoweranda, 1976; Bukowska-Strzyżewska, Michalski, Młotkowska & Skoweranda, 1976).

The organic phosphates have a special interest because they are the components of many biologically important molecules such as nucleic acids and some enzymes or vitamins, performing an essential function in important life processes.

Crystals of the title compound have been prepared by B. Młotkowska and crystallized by us from an ethyl acetate solution.



A preliminary report on this work has been published elsewhere (Bukowska-Strzyżewska & Dobrowolska, 1976).

Equi-inclination Weissenberg film data were collected with the multiple-film technique on the 0 to 8 layers around both the *b* and *c* crystal axes. The intensities were visually estimated with a calibrated intensity scale. In total, 1179 reflections were collected. No absorption correction was made.

The structure was solved by direct methods using the *SIGMA* 2 and *PHASE* programs of the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) on an

Table 1. *Final atomic positions* (×10^4) *with e.s.d.'s in parentheses*

	x	*y*	*z*
P(2)	1194 (1)	4589 (3)	325 (4)
P(12)	1178 (1)	7530 (4)	−74 (4)
O(1)	623 (4)	4332 (9)	277 (9)
O(11)	1710 (3)	7871 (8)	−499 (9)
O(2)	1448 (5)	4208 (11)	−719 (12)
O(12)	814 (4)	7459 (13)	−1002 (11)
O(3)	1383 (4)	3879 (9)	1470 (10)
O(13)	1072 (3)	8566 (10)	918 (10)
O(4)	1253 (4)	6176 (8)	691 (11)
C(4)	1091 (6)	3978 (16)	2546 (16)
C(14)	1459 (6)	8868 (16)	1777 (14)
C(5)	562 (6)	3529 (14)	2294 (15)
C(15)	1945 (5)	9299 (13)	1182 (13)
C(6)	339 (6)	4436 (17)	1375 (15)
C(16)	2109 (5)	8166 (16)	339 (17)
C(7)	515 (6)	2009 (15)	1949 (16)
C(17)	1863 (8)	10621 (15)	471 (17)
C(8)	243 (9)	3758 (20)	3452 (17)
C(18)	2346 (7)	9526 (22)	2135 (17)

IBM-360 computer. The positional and anisotropic thermal parameters were refined by the full-matrix least-squares method. The final R value for all the observed reflections was 0·121. H atoms were ignored. Form factors for neutral atoms were taken from Doyle & Turner (1968).

The final positional parameters are listed in Table 1.* mations. In both rings the bridge atom O(4) takes an

Discussion. A view of the molecule projected along the z axis is shown in Fig. 1(*a*) and a view projected along the axis perpendicular to the P—O—P plane in Fig. 1(*b*).

Intramolecular bond lengths and valency angles are shown in Fig. 2. The estimated standard deviations have the following mean values: P—O 0·011, C—O 0·020, C—C 0·022 Å. The mean standard deviations for the angles are: O—P—O 0·63, P—O—P 0·83, P—O—C 0·93 and C—C—C 1·29°.

The molecule has C_1 symmetry despite a fully symmetric molecular formula and the lack of strong intermolecular interactions. The angle between the bridge bonds P(2)—O(4) and P(12)—O(4) is 132°. A distinct variation in the lengths of these bonds is observed: O(4)—P(2) = 1·647 (10), O(4)—P(12) = 1·612 (10) Å. The two structurally independent dioxaphosphorinane rings have deformed chair conformations. In both rings the bridge atom O(4) takes an axial position. The flattening of the rings is illustrated in Fig. 3.

The conformations about the bridge bonds in the pyrophosphate groups are approximately staggered; the torsion angles O(12)—P(12)—O(4)—P(2) and O(2)—P(2)—O(4)—P(12) are 30·9 and 50·6.

The packing of the molecules in the crystal is shown in Fig. 4.

The conformation of the molecules and the configuration of the bonds on the P atoms are analogous to those in the structure of bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl) sulphide (Bukowska-Strzyżewska, Michalski, Młotkowska & Skoweranda, 1976).

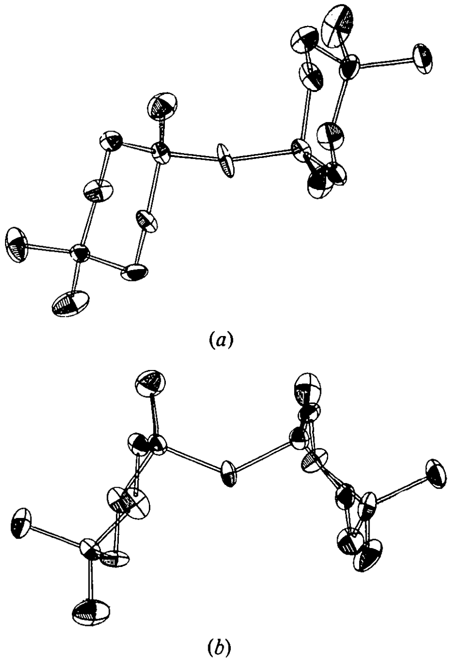


Fig. 1. (*a*) The molecule projected along the z axis. (*b*) The molecule projected along the axis perpendicular to the P—O—P plane.

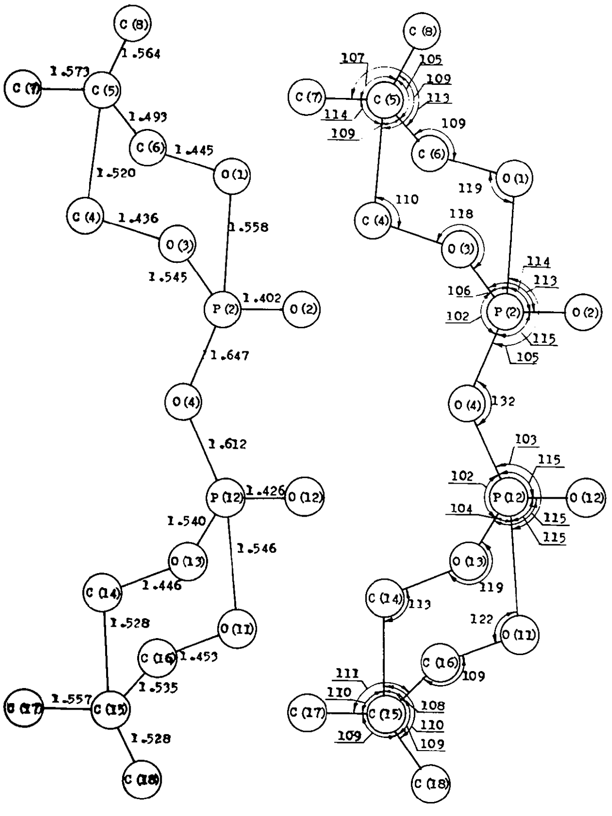


Fig. 2. Intramolecular bond lengths (Å) and angles (°).

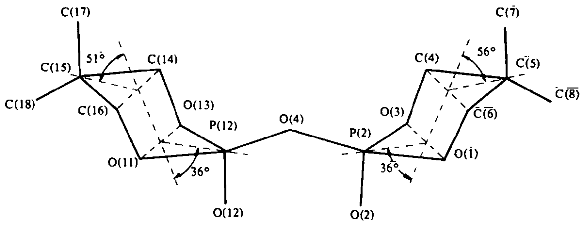


Fig. 3. The flattening of the rings.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33122 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

They differ in that the oxide molecule has a lower symmetry than the sulphide (C_1 and C_2 respectively), the P—O—P bridge angle (132°) is greater than the P—S—P (102°), there is a different distribution of π bonds within the P_2O_7 and P_2O_6S groups, and there is less flattening of the phosphorus parts of the rings in the structure of the oxide in comparison with that of the sulphide.

In both compounds the configuration of the bonds on the P atoms is opposite to that predicted by Katritzky, Nesbit, Michalski, Tulimowski & Zwierzak (1970) with the bridge atom (oxygen or sulphur) in the equatorial position.

The distributions of the π bonds in both condensed PO_4 tetrahedra are somewhat different (see Table 2). The bond orders were obtained from Cruickshank (1961).

The contribution of the π bonds to the bridge bonds is minimal [the order of the π bond for P(2)—O(4) and P(12)—O(4) is 0·3 and 0·2 respectively]. The atoms O(2) and O(12) instead are linked to the P atoms by means of almost double bonds. The orders of these π bonds may be estimated as 0·9 and 0·8 respectively. The P—O bond orders in the ring are about 1·5.

The values given in Fig. 2 imply a considerable deformation of the angles between the bonds in the PO_4 tetrahedra. Their mean values in the two tetrahedra, 109·3 and 109·2°, are almost exactly equal to the tetrahedral angle. The deformation of the tetrahedral angles is caused by the variation of the π bonds in the individual P—O bonds and thus by the different lengths of these bonds. All the O—P—O angles formed between the short P(2)—O(2), P(12)—O(12) bonds and the other P—O bonds are greater than the tetrahedral value and range from 113·5 to 115·3°. The angles between the longer P—O bonds are smaller than tetrahedral and range from 102·0 to 106·1°. The observed flattening of the rings is caused by the presence of the hetero-atoms in the ring and by the steric interaction between the axial substituent at the P atom and the axial H atoms in the 4,6 positions of the ring.

Table 2. *The distribution of the π bonds within condensed tetrahedra of* PO_4

	Bond length	π-bond order		Bond length	π-bond order
P(2)—O(1)	1·558 Å	0·4	P(12)—O(11)	1·546 Å	0·5
P(2)—O(2)	1·402	0·9	P(12)—O(12)	1·426	0·8
P(2)—O(3)	1·545	0·5	P(12)—O(13)	1·540	0·5
P(2)—O(4)	1·647	0·2	P(12)—O(4)	1·612	0·3

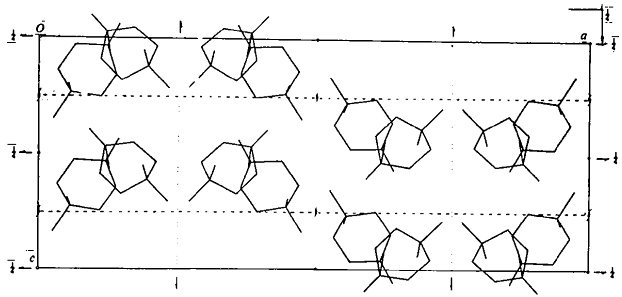

Fig. 4. The packing of the molecules in the crystal, projected along **b**.

Structures containing 1,3,2-dioxaphosphorinane rings reported thus far indicate that the dihedral angle of the chair in the phosphorus part ranges from 31 to 46° whereas in cyclohexane it is 55°.

When the double-bonded atom is an axial substituent at the P atom then the flattening is of the order 43·9–45·7° (Dutasta, Grand & Robert, 1974; Bartczak, Christensen, Kinas & Stec, 1975).

When the axial substituent is bonded to the P atom by means of a nearly single bond the flattening of the ring increases and the dihedral angle of the chair in the phosphorus part of the ring decreases to 41·8–3·7° (Murayama & Kainosho, 1969; Rodgers, White & Verkade, 1971; Grand, Martin, Robert & Tordjman, 1975; Bartczak, Christensen, Kinas & Stec, 1976; Beineke, 1969; Grand & Robert, 1975; Silver & Rudman, 1972; Cameron, Gałdecki & Karolak-Wojciechowska, 1976; Cameron, Karolak-Wojciechowska & Zwierzak, 1977; Haque, Caughlan, Hargis & Bentrude, 1970; Bukowska-Strzyżewska, Michalski, Młotkowska & Skoweranda, 1976; Drew & Rodgers, 1972).

The double bond P=*R* in the axial position causes the opening of the tetrahedral angles *R*=P—O(1) and *R*=P—O(3) in the RPO_3 groups and thus causes the increase in the distances between *R* and the axial H atoms in the 4,6 positions of the ring.

The repulsion causing the flattening of the ring is then reduced and the deformation observed is basically the result of the presence of hetero-atoms in the ring. The reverse situation takes place when, as in the examined structure, the double bond P=O adopts the horizontal position. Then the angles *R*—P—O(1) and *R*—P—O(3) between the axial substituent *R* and the O atoms in the rings must be smaller than tetrahedral. This reduces the distance between *R* and the axial H atoms in the 4,6 positions, resulting in a greater flattening of the ring.

The degree of deformation of the 1,3,2-dioxaphosphorinane ring is thus determined by the following factors: (1) The configuration of the substituents on the P atoms. (2) The distribution of the π bonds within the PO_4 tetrahedron. (3) The size of the axial substituent.

The last factor causes greater flattening of the rings in the sulphide structure in comparison with the oxide structure (the dihedral angles of the chair in its phosphorus part are 36 and 31° for the two structures respectively).

In the oxide structure the arrangement of the bonds within the two condensed tetrahedra is considerably different from that in single (uncondensed) rings. This is the first reported structure in which the O atom axial in relation to the ring is bonded to the P atom by almost a single bond.

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N,*N'*-Ethylenebis(salicylideneimine)

BY N. BRESCIANI PAHOR, M. CALLIGARIS, G. NARDIN AND L. RANDACCIO

Istituto di Chimica, Università di Trieste, 34127 *Trieste, Italy*

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Abstract. $C_{16}H_{16}N_2O_2$, $M_r = 268\cdot3$, monoclinic, $P2_1/c$, $a = 6\cdot094$ (6), $b = 7\cdot567$ (6), $c = 30\cdot68$ (2) Å, $\beta = 97\cdot87$ (5)°, $U = 1401\cdot4$ Å^3; $D_c = 1\cdot271$ g cm^{-3}, $Z = 4$; $\mu = 6\cdot69$ cm^{-1} (Cu $K\alpha$). Direct methods were used to determine the structure from three-dimensional X-ray data. Block-diagonal-matrix least-squares refinement, based on 1262 independent reflexions, converged with R at 0·035. The molecules, approximately centrosymmetric, are in the enoliminic form with intramolecular hydrogen bonds.

Introduction. Intensity data were collected on a Siemens diffractometer by the θ–2θ scan technique with Cu $K\alpha$ radiation ($\lambda = 1\cdot5418$ Å). 2503 independent reflexions were measured in the region $2\theta \leq 60°$ and 1262 with $I > 3\sigma(I)$ were corrected for the Lorentz and polarization effects. No corrections for absorption ($\mu R = 0\cdot7$) or extinction were applied. The scattering factors were those of Moore (1963). A set of 211 E values greater than 2·08 were then used in the direct-methods program of Germain, Main & Woolfson (1971). An E map calculated from one of the best solutions clearly revealed all the non-hydrogen atoms, which were then refined by block-diagonal-matrix least squares, allowing finally for anisotropic thermal motion. The calculated positions of the H atoms well fitted the electron density peaks on the subsequent difference Fourier map. The two H atoms involved in the hydrogen bonds were located directly from the difference map. The final anisotropic refinement, in