Crystal and Molecular Structure of Bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl) Oxide

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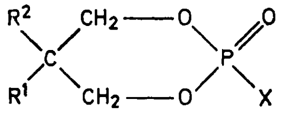
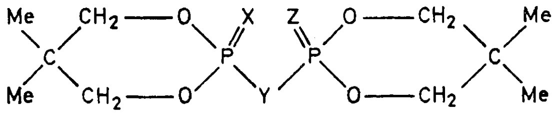
The title compound (IIe) crystallises in the orthorhombic space group *Pbca*, with $a = 26.70(2)$, $b = 9.858(8)$, $c = 11.38(1)$ Å, and $Z = 8$. The structure has been solved by direct statistical methods and refined by least-squares to R 9.2% for 1 429 observed reflections. Each dioxaphosphorinane ring has a chair conformation with the phosphoryl oxygen in the equatorial position.

CRYSTAL structures derived by *X*-ray diffraction techniques have been reported [1] for the compounds (I; a—e). In the solid state the ring conformation of each of these compounds is a distorted chair with the phosphoryl group equatorial. Solutions of 2-oxo-1,3,2-dioxaphosphorinanes (I) have also been investigated by n.m.r. and dipole-moment techniques, the results showing that in solution the conformations of these compounds are not so clearly defined as in the solid state. N.m.r. coupling constants observed [2] for (Ie) *trans* show that at —54 °C the chair form with the t-butyl group equatorial predominates, while at 35 °C the values are consistent with the presence of another conformation in which the ring has flipped at the phosphorus end of the molecule. Katritzky,[3] from a re-analysis of n.m.r. data for 2,5,5-trisubstituted-2-oxo-1,3,2-dioxaphosphorinanes originally presented by Edmunson,[4] suggests that where X in (I) is a secondary- or tertiary-alkyl group it predominantly takes up an equatorial position, whilst a primary alkyl group is almost equally axial and equatorial. Katritzky [3] has also discussed the n.m.r. parameters (ABX analysis) of compounds (II; a—d), suggesting that in solution these compounds exist mainly with the linking group Y in the equatorial position. The n.m.r. parameters of (IIe) [5] (ABX analysis) show that this compound exists almost entirely in one chair conformation. N.m.r. parameters of compounds (II) have not been determined for compounds of known geometry and are not, at present, diagnostic of the configuration at the phosphorus atom. Accordingly we have obtained the *X*-ray crystal and molecular structure of bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl) oxide, (IIe).


(I)

a; $R^1 = R^2 = H$, X = OH
b; $R^1 = R^2 =$ Me, X = OH (monohydrate)
c; $R^1 = R^2 = H$, X = OPh
d; $R^1 =$ Me, $R^2 = CH_2Br$, X = Br (isomer with CH_2Br *cis* to P=O)
e; $R^1 = Bu^t$, $R^2 = H$, X = Me (isomer with H *cis* to P=O)


(II)

a; X = Z = O, Y = S
b; X = Y = O, Z = S
c; X = Z = S, Y = Se - Se
d; X = Z = Se, Y = S - S
e; X = Z = Y = O

EXPERIMENTAL

The compound was prepared by the method of ref. 6. Crystals (m.p. 188—192 °C; lit.[6] 188—190 °C) from ethyl acetate, were well-formed white diamond-shaped plates, showing faces of the forms {100} and {011}, with (100) predominant.

Crystal Data.—$C_{10}H_{20}O_7P_2$, $M = 314.2$, Orthorhombic, $a = 26.70(2)$, $b = 9.858(8)$, $c = 11.38(1)$ Å, $U = 2\,995$ Å^3, $D_m = 1.38$, $Z = 8$, $D_c = 1.39$ g cm^{-3}, $F(000) = 1\,328$. Space group *Pbca* (D_{2h}^{15}, No. 61) from systematic absences: $0kl$, $h0l$, $hk0$ for k, l, $h = 2n + 1$ respectively. Cu-K_α (nickel-filtered) radiation, $\lambda = 1.541\,8$ Å; μ(Cu-K_α) = 28.3 cm^{-1}.

Initial *X*-ray studies were by use of Stöe precession-retigraph and Weissenberg cameras. Cell dimensions were obtained from diffractometer measurements of 2θ values for axial reflections. Intensity data were collected for a crystal of dimensions *ca.* 0.20 × 0.25 × 0.25 mm, mounted with the *b* axis vertical, on a General Electric XRD 6 diffractometer equipped with a manual goniometer, pulse-height analyser, and scintillation counter. The stationary-crystal–stationary-counter method of intensity estimation

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[1] (*a*) Mazhar-ul-Haque, C. N. Caughlan, and W. L. Moats, *J. Org. Chem.*, 1970, **35**, 1446; (*b*) W. Murayama and M. Kainosho, *Bull. Chem. Soc. Japan*, 1969, **42**, 1819; (*c*) H. J. Geise, *Rec. Trav. chim.*, 1967, **86**, 362; (*d*) T. A. Beireke, *Acta Cryst.*, 1969, **B25**, 413; (*e*) Mazhar-ul-Haque, C. N. Caughlan, J. H. Hargis, and W. G. Bentrude, *J. Chem. Soc.* (*A*), 1970, 1786.

[2] W. G. Bentrude and J. H. Hargis, *Chem. Comm.*, 1969, 1113.

[3] A. R. Katritzky, M. R. Nesbit, J. Michalsky, Z. Tulimowski, and A. Zwierzak, *J. Chem. Soc.* (*B*), 1970, 140.

[4] K. D. Bartle, R. S. Edmunson, and D. W. Jones, *Tetrahedron*, 1967, **23**, 1701.

[5] D. S. Rycroft and R. F. M. White, unpublished results.

[6] W. Stec and A. Zwierzak, *Canad. J. Chem.*, 1967, **45**, 2513.

was used throughout,[7] with a 4° take-off angle and a counting time of 10 s. Backgrounds for all but the strongest reflections were taken from a graph prepared by measuring individual backgrounds at $(2\theta_{hl} + 1)°$ for some 300 reflections over the range of 2θ used. The (004) reflection was used as a reference reflection to check on crystal stability. No significant alteration in the measured intensity was observed during the data collection. Reflections were corrected for Lorentz and polarisation effects, but not for absorption. Of 1 534 data with $2\theta \leqslant 90°$ measured, 1 429 were considered observed.

Structure Solution and Refinement.—The structure was solved by direct statistical methods based on those of Karle and Karle [8] and numerous refs. cited therein. Data were put on an absolute scale and a set of normalised structure factors (E values) calculated by means of a Wilson plot.[9] The origin-defining phases, together with three symbolic ones, were chosen from 202 reflections with $E > 1.5$. Application of the symbolic-addition procedure, using the argument $\sigma_3\sigma_2^{-\frac{3}{2}}Eh\sum_{k}E_kE_{h-k}$ to calculate the sign probabilities, gave unambiguously the signs of all 202 reflections. An E map computed with these reflections revealed clearly the positions of all the non-hydrogen atoms of the molecule. A structure-factor calculation at this stage gave R 32%. Structure refinement was by least-squares using the block-diagonal approximation and weighting scheme $\sqrt{w} = F^*/F_o$ for $|F_o| > F^*$ and $\sqrt{w} = F_o/F^*$ for $|F_o| < F^*$ with $F^* = 35$ electrons. Unobserved reflections, after ref. 10, were computed throughout but excluded from the refinement. In the early refinement stage, reflections were also excluded from the least squares if $\Delta F/|F_o| > 3R$. Four cycles of isotropic refinement of positional and thermal parameters gave R 12% and two further cycles of anisotropic refinement reduced R to 10.5%. A difference Fourier at this stage gave only partial evidence for 12 of the hydrogen atoms at their expected positions, the remainder being introduced at calculated positions assuming C–H 1.05 Å. Three further cycles of refinement, with heavy atoms vibrating anisotropically and hydrogen atoms isotropically, gave a final stationary R of 9.2% for the 1 429 observed reflections and 9.8% for the 1 534 recorded. Final parameter shifts were $< 0.2\,\sigma$. Tables 1 and 2 list the final atomic co-ordinates and isotropic thermal parameters. Final observed and calculated structure factors, anisotropic thermal parameters, and initial phases for sign determination are listed in Supplementary Publication No. SUP 21815 (3 pp., 1 microfiche).*

TABLE 1

Final fractional atomic co-ordinates for the non-hydrogen atoms ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x	y	z
O(1)	1 064(2)	1 425(6)	4 105(6)
P(2)	1 181(1)	2 471(3)	5 074(2)
O(3)	1 712(2)	2 129(6)	5 523(5)
C(4)	2 101(3)	1 814(10)	4 648(10)
C(5)	1 935(3)	710(8)	3 809(8)
C(6)	1 461(3)	1 084(10)	3 217(8)
C(7)	1 869(4)	−647(9)	4 537(10)
C(8)	2 335(4)	557(12)	2 837(10)
O(9)	800(2)	2 549(7)	6 001(6)
O(10)	1 250(2)	3 841(6)	4 334(6)
O(11)	1 394(2)	6 128(7)	3 522(6)
P(12)	1 194(1)	5 403(3)	4 673(2)
O(13)	631(2)	5 674(6)	4 726(5)
C(14)	338(3)	5 563(9)	3 632(8)
C(15)	555(3)	6 462(9)	2 677(8)
C(16)	1 084(4)	6 061(9)	2 482(9)
C(17)	522(4)	7 980(9)	3 048(9)
C(18)	257(5)	6 221(12)	1 544(10)
O(19)	1 464(3)	5 801(7)	5 759(7)

TABLE 2

Final fractional atomic co-ordinates for hydrogen atoms ($\times 10^3$) and isotropic thermal parameters, with estimated standard deviations in parentheses

Atom	x	y	z	B_{iso}/Å^2
H(4,1)	216(3)	259(8)	415(7)	3.2(10)
H(4,2)	241(3)	154(9)	509(7)	5.5(12)
H(6,1)	136(3)	50(9)	281(8)	3.3(11)
H(6,2)	153(3)	196(9)	276(8)	2.9(10)
H(14,1)	32(3)	462(9)	335(8)	2.8(10)
H(14,2)	−5(3)	589(8)	371(8)	3.9(12)
H(16,1)	129(3)	666(9)	194(8)	5.6(11)
H(16,2)	108(3)	516(9)	216(9)	3.9(10)
H(7,1)	218(3)	−103(8)	473(9)	8.7(14)
H(7,2)	155(3)	−108(9)	440(9)	7.3(13)
H(7,3)	182(3)	28(9)	490(8)	11.5(17)
H(8,1)	240(3)	146(9)	310(8)	10.8(14)
H(8,2)	226(3)	−32(9)	310(8)	9.4(14)
H(8,3)	259(3)	44(9)	225(9)	10.5(15)
H(17,1)	85(3)	832(9)	323(8)	9.0(15)
H(17,2)	16(3)	825(9)	290(9)	8.1(13)
H(17,3)	49(3)	703(9)	317(9)	8.2(14)
H(18,1)	−6(3)	614(9)	190(8)	8.9(13)
H(18,2)	−2(3)	692(9)	159(8)	9.3(14)
H(18,3)	31(3)	586(9)	82(8)	9.5(14)

Mean C–H 1.01 Å. The number before the comma in the atom designation refers to the atom to which the hydrogen atom is attached.

DISCUSSION

In the solid state each six-membered ring is in a chair configuration with the phosphoryl oxygen equatorial.

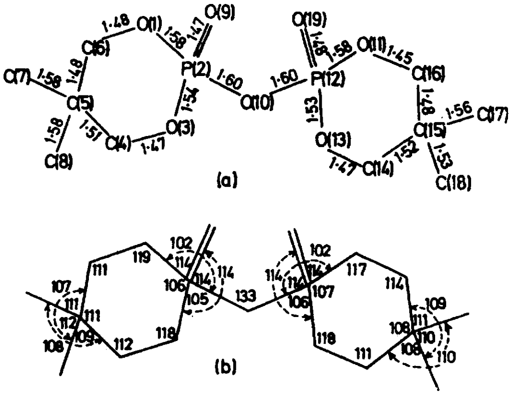

FIGURE 1 (a) Atom numbering and intramolecular bond distances (Å) for (IIe); estimated standard deviations 0.01 Å. (b) Intramolecular bond angles (°)

Intramolecular bond distances and angles and atom numbering are given in Figures 1 (a) and (b) and Table 3,

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-sized copies.)

[7] R. Bonnett, M. B. Hursthouse, and S. Neidle, *J.C.S. Perkin II*, 1972, 902.

[8] I. L. Karle and J. Karle, *Acta Cryst.*, 1966, **21**, 849.

[9] A. J. C. Wilson, *Acta Cryst.*, 1949, **2**, 318.

[10] A. J. Dunning and B. E. Vand, *Acta Cryst.*, 1969, **15**, 1092.

and are similar to those found for other cyclic phosphorus esters. Table 4 lists the results of a least-squares planes analysis for (IIe). As with other cyclic esters, there is distortion from the ideal chair so that each ring shows a general flattening. The dihedral angles between the planes O(1), O(3), C(4), C(6) and O(1), P(2), O(3), and O(11), O(13), C(14), C(16) and O(11), P(12), O(13) are 37.0 and 35.4° respectively [*cf.* (Ia) 40.4, (Ic) 36.5, (Id) 36.7, and (Ie) 33.5°] rather than the 60° expected for an ideal chair. The dihedral angles between the planes C(4)—(6) and O(1), O(3), C(4), C(6), and C(14)—C(16) and O(11), O(13), C(14), C(16) are 50.1 and 51.3° respectively [*cf.* (Ia) 54.2, (Ic) 53.1, (Id) 52.5, and (Ie) 54.9°]. Mazhar-ul-Haque *et al.*[1a] have suggested that 1,3-steric repulsion between X, the axial group at phosphorus, and the axial methylene hydrogens is relieved by flattening the phosphorus end of the ring. Steric strain involving the axial substituent at phosphorus may also be relieved by bending the P–X bond away from the methylene hydrogens, thereby reducing the O=P–X bond angle. In (IIe) the O(9)–P(2)–O(10) and O(19)–P(12)–O(10) angles of 114.3° can be compared with the corresponding angle[1e] for compounds (I), which decreases in the order X = OH (116.6°), PhO (113.7°), Br (111.5°), and Me (108.7°). The variations produced by –OH, –OPh, and $-O-P-O-CH_2-CMe_2-CH_2-O$ are all very similar and are probably largely determined by interactions arising from the oxygen atom in these groups which is directly bonded to phosphorus. If this is indeed the case, there may be a contribution from electrostatic repulsion between lone-pair electrons of the cyclic and exocyclic oxygen atoms in addition to the 1,3-steric interaction.

TABLE 3

Intramolecular bond angles (°), with estimated standard deviations in parentheses

O(9)–P(2)–O(10)	114.3(4)	O(19)–P(12)–O(10)	114.3(4)
O(1)–P(2)–O(9)	114.0(4)	O(11)–P(12)–O(19)	113.8(4)
O(3)–P(2)–O(10)	104.7(4)	O(13)–P(12)–O(10)	105.6(4)
O(1)–P(2)–O(10)	102.2(4)	O(11)–P(12)–O(10)	101.8(4)
O(3)–P(2)–O(9)	114.3(4)	O(13)–P(12)–O(19)	113.6(4)
O(1)–P(2)–O(3)	106.0(4)	O(11)–P(12)–O(13)	106.7(4)
P(2)–O(3)–C(4)	118.2(6)	P(12)–O(13)–C(14)	117.7(5)
O(3)–C(4)–C(5)	111.7(8)	O(13)–C(14)–C(15)	111.0(8)
C(4)–C(5)–C(6)	111.0(8)	C(14)–C(15)–C(16)	108.3(7)
C(4)–C(5)–C(8)	108.6(8)	C(14)–C(15)–C(18)	108.3(8)
C(8)–C(5)–C(7)	111.6(8)	C(18)–C(15)–C(17)	110.3(8)
C(7)–C(5)–C(6)	110.6(8)	C(17)–C(15)–C(16)	110.5(8)
C(8)–C(5)–C(6)	106.9(8)	C(18)–C(15)–C(16)	109.1(8)
C(4)–C(5)–C(7)	108.1(8)	C(14)–C(15)–C(17)	110.3(7)
C(5)–C(6)–O(1)	110.7(7)	C(15)–C(16)–O(11)	114.3(8)
C(6)–O(1)–P(2)	119.1(5)	C(16)–O(11)–P(12)	117.4(6)
P(2)–O(10)–P(12)	132.6(4)		

TABLE 4

Least-squares planes equations in the form $lX + mY + nZ + P = 0$, where X, Y, and Z are orthogonal (Å) co-ordinates in the *a*, *b*, and *c* axial directions respectively. Deviations (Å) of relevant atoms from the plane are given in square brackets

Plane (1): O(3), C(4), C(6), O(1)

$$-0.051X + 0.933Y - 0.357Z - 0.505 = 0$$

[O(3) 0.01, C(4) −0.01, C(6) 0.01, O(1) −0.01, C(5) 0.65, P(2) −0.56]

Plane (2): O(13), C(14), C(16), O(11)

$$0.194X - 0.980Y - 0.056Z - 5.434 = 0$$

[O(13) 0.01, C(14) −0.01, C(16) 0.01, O(11) −0.01, C(15) 0.68, P(12) −0.54]

Dihedral angle: (1)–(2) 154.6°.

If the chair conformation with equatorial phosphoryl groups is maintained by the compound in solution, then the low-field ^1H n.m.r. shift observed[5] for the axial methylene hydrogen atoms may indicate that the phosphorinane rings are able to rotate about the central P–O–P group so that oxygen atoms of one ring deshield the axial methylene protons of the other ring.

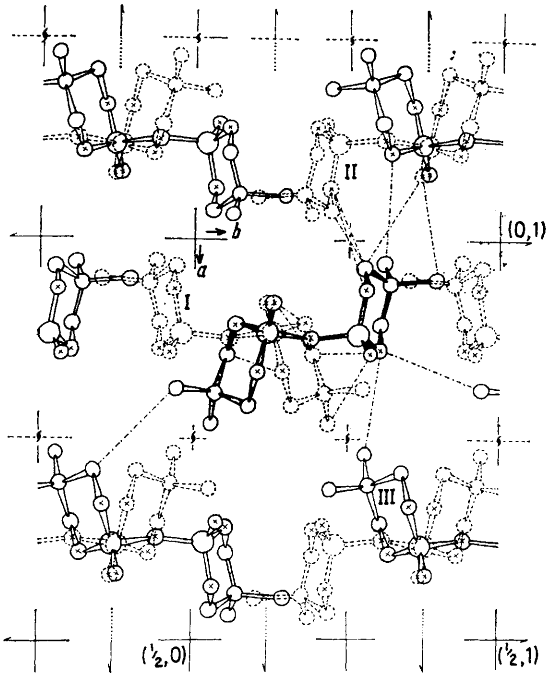

FIGURE 2 (IIe) viewed down the *c* axis. Large open circle P, small open circle C, small crossed circle O. Dashed lines indicate shortest intermolecular contacts; see Table 5 for equivalent positions

The packing of the molecules projected along [001] is presented in Figure 2, and corresponding intermolecular distances from the central molecule given in Table 5.

TABLE 5

Shortest intermolecular contact distances (Å) <3.6 Å, with estimated standard deviations in parentheses

$O(19) \cdots C(6^{I})$	3.34(1)	$O(11) \cdots C(8^{III})$	3.53(1)
$O(9) \cdots C(6^{I})$	3.36(1)	$O(19) \cdots C(8^{I})$	3.57(1)
$C(14) \cdots O(13^{II})$	3.42(1)	$C(14) \cdots O(9^{II})$	3.59(1)

Roman numeral superscripts denote the following equivalent positions with respect to the reference molecule at x, y, z:

I $x, \frac{1}{2} - y, \frac{1}{2} + z$
II $-x, 1 - y, 1 - z$
III $\frac{1}{2} - x, \frac{1}{2} + y, z$

No particularly close contacts are found, the shortest (3.34 and 3.36 Å) being between O(19) and O(9) of the central molecule at (x, y, z) and C(6) belonging to a molecule at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$.

We thank Dr. M. B. Hursthouse of Queen Mary College, University of London, for diffractometer data collection facilities, M. Potts of the City of London Polytechnic Computer Unit, and staff of the London Polytechnics Computer Unit for ICL 1905E computing facilities, Dr. F. Ahmed *et al.* for use of the N.R.C. crystallographic programs, Dr. R. S. Rycroft for the sample of (IIe), and Dr. C. J. Brown for helpful discussions.

[6/498 *Received, 12th March,* 1976]