Square Pyramidal Phosphorus. *X*-Ray Analysis of the 1,3,2-Dioxaphospholans from Hexafluoroacetone and Phosphetans

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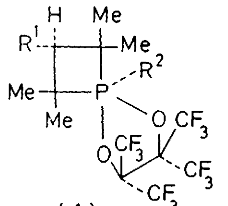
Summary *X*-Ray crystal structure determinations of two 1,3,2-dioxaphospholans formed from hexafluoroacetone and 1-*p*-bromophenylphosphetans reveal square pyramidal geometry about phosphorus.

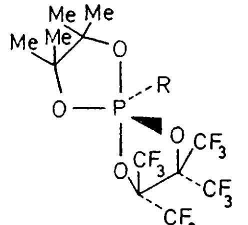
We have previously reported[1] on the variable temperature ^{19}F n.m.r. of the 1,3,2-dioxaphospholans (**1**; R^1 = H and Me), formed from hexafluoroacetone and a series of 1-substituted phosphetans, and explained the results in terms of Berry pseudorotation (BPR) processes and the varying apicophilicities of the substituents R^2. In view of the continuing uncertainty over the precise details of ligand reorganisation processes in phosphoranes[2] we thought it prudent to look more closely at the geometry of these adducts and now report on the *X*-ray structure analyses of the 1,3,2-dioxaphospholans (**1a**) and (**1b**).



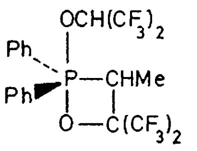
(1)

a ; R^1= H ; R^2= *p* - Br·C_6H_4

b ; R^1= *cis* – Me ; R^2= *p* – Br·C_6H_4



(2)



(3)

Crystal data: (**1a**) $C_{19}H_{18}BrF_{12}O_2P$, $M = 617{\cdot}2$, monoclinic, $a = 9{\cdot}95$, $b = 17{\cdot}06$, $c = 15{\cdot}36$ Å, $\beta = 119{\cdot}2°$, $U = 2275$ Å^3, $Z = 4$, $D_c = 1{\cdot}80$, space group $P2_1/c$. (**1b**) $C_{20}H_{20}BrF_{12}O_2P$, $M = 631{\cdot}3$, orthorhombic, $a = 30{\cdot}16$, $b = 31{\cdot}31$, $c = 10{\cdot}23$ Å, $U = 9660$ Å^3, $Z = 16$, $D_c = 1{\cdot}74$, space group *Aba*2 from the structure analysis.

Reflections with $I > 3\sigma I$ were used in the analysis from data collected using Mo-K_α radiation and graphite monochromator on an automated Stoe diffractometer. The final *R*-values are 0·091 (1122 reflections) for (**1a**) and 0·079 (1358 reflections) for (**1b**), using anisotropic temperature factors for the phosphorus, fluorine, and bromine atoms.

The molecular geometry of (**1a**) is displayed in the Figure. Crystals of (**1b**) contain two independent molecules having slight conformational differences, but the environment about phosphorus in both molecules is the same as found in (**1a**). Bond angles about phosphorus for the three molecules are given in the Table. In contrast to all previously recorded structures for five-co-ordinate phosphorus, (**1a**) and (**1b**) are essentially square-pyramidal.† This is particularly apparent from angles O(1)–P–C(9) and O(2)–P–C(7), which would be 120° and 180° respectively in a trigonal bipyramidal molecule, and from the similarity of the four angles from the apical *p*-bromophenyl carbon to the other atoms. The range observed (99—113°) for these

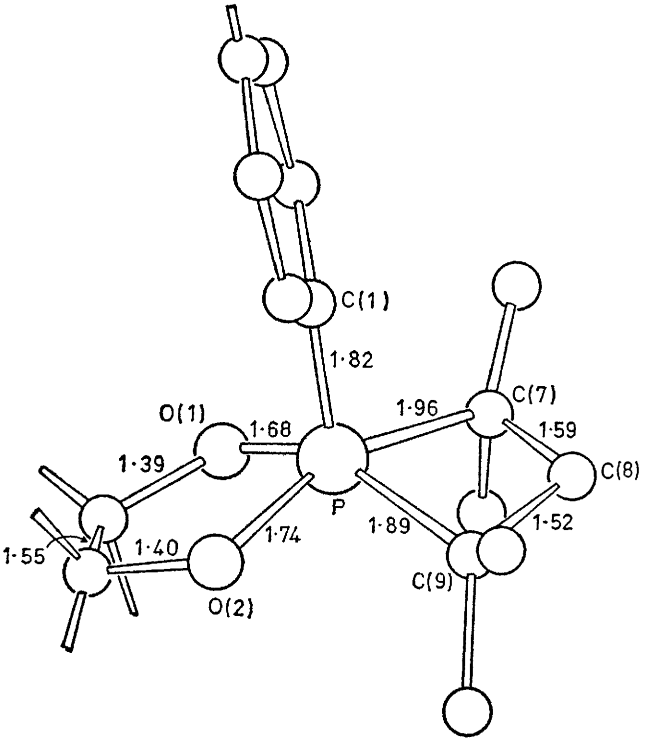


Figure. Molecular geometry of $P(C_6H_4Br)(C_3F_6O)_2(C_7H_{14})$. CF_3 groups and the Br atom have been omitted. Bond lengths (Å) have e.s.d.s ±0·02 Å for P–O and P–C, and ±0·03 Å for other bonds shown.

Table. Bond angles and e.s.d.s (°) about the phosphorus atom in the two phospholans (**1a**) and (**1b**)

Angle	(**1a**)	(**1b**)	
C(1)–P–C(7)	105·6(8)	105·7(1·1)	104·4(1·0)
C(1)–P–C(9)	110·7(7)	112·6(1·2)	110·0(1·0)
C(1)-P–O(1)	101·6(6)	100·6(9)	100·5(9)
C(1)–P–O(2)	100·0(6)	99·6(8)	99·4(7)
C(7)–P–C(9)	78·1(9)	75·9(1·4)	80·7(1·3)
O(1)–P–O(2)	85·0(6)	86·2(9)	86·1(8)
C(7)–P–O(1)	92·7(8)	92·3(1·2)	92·3(1·1)
C(9)–P–O(2)	90·3(8)	91·5(1·1	88·7(1·0)
C(7)–P–O(2)	154·2(7)	154·5(1·2)	156·1(1·0)
C(9)–P–O(1)	147·7(8)	146·6(1·2)	149·5(1·0)

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† Distortion towards square pyramidal geometry has been reported, *e.g.* M. Eisenhut, R. Schmutzler, and W. S. Sheldrick, *J.C.S. Chem. Comm.*, 1973, 144.

angles spans the value of 104·1° calculated from an electrostatic model of five-co-ordination which minimises the repulsion between five charges on a sphere constrained to C_{4v} symmetry.[3] The highest symmetry possible for (**1a**) and (**1b**), C_s, is only approximately attained judging from the angles in the Table. The departure of the overall geometry of (**1a**) and (**1b**) from that of a trigonal bipyramid towards a square pyramid is perhaps even more marked than is found for pentaphenylantimony,[4] which hitherto is the only example of square pyramidal geometry for a Group VA element. Comparable bond lengths within the three independent molecules do not differ significantly, and fall within the ranges observed in related molecules, although the P–C(7) and P–C(9) distances are unusually long.

In contrast to (**1a**) and (**1b**), both of the spirophosphoranes (**2**; R = SPh) and (**2**; R = p-O·C_6H_4·Br) derived from hexafluoroacetone have trigonal bipyramidal geometry[5] and the 1,2-oxaphosphetan (**3**) is essentially trigonal bipyramidal.[6] Apparently the particular combination of both a four- and a five-membered ring is necessary before square pyramidal geometry becomes the more stable.

These results do not affect our interpretation of the variable temperature ^{19}F n.m.r. spectra of the phosphetan–hexafluoroacetone adducts.[1] The square pyramidal conformation adopted corresponds to the transition state which would normally be assumed for BPR between topomeric trigonal bipyramids having the four-membered ring apical–equatorial. Presumably in this particular system the square pyramidal conformation is of slightly lower energy than the related trigonal bipyramids. The high barrier to equivalence of all the CF_3 groups must still involve traversing a trigonal bipyramid having the four-membered ring diequatorial.

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