Boat Conformation of a Perhydro-1,3,2-Oxazaphosphorine Ring Containing Five-co-ordinate Phosphorus: *X*-Ray Crystal and Molecular Structures of 2,2-Bis-(*p*-bromophenoxy)-2-dimethylamino-4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxaphosph(v)olan and 5-*p*-Bromophenoxy-10-methyl-2,2,3,3-tetrakis-trifluoromethyl-1,4,6-trioxa-10-aza-5-phosphaspiro[4.5]decane

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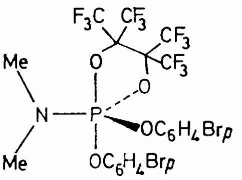
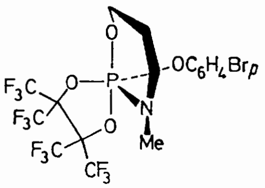
Summary The preference for the equatorial plane of the lone-pair of nitrogen attached to trigonal bipyramidal phosphorus(v) is demonstrated in the molecular geometries, determined by *X*-ray crystallography, of 2,2-bis-*p*-bromophenoxy-2-dimethylamino-4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxaphosph(v)olan and of 5-*p*-bromophenoxy-10-methyl-2,2,3,3-tetrakistrifluoromethyl-1,4,6-trioxa-10-aza-5-phosphaspiro[4.5]decane where the perhydro-oxazaphosphorine ring adopts a boat conformation.

A preference for the equatorial plane of lone-pairs on equatorial heteroatoms attached directly to phosphorus in trigonal bipyramidal (tbp) phosphoranes is supported by both calculation[1] and experiment.[2] We have ascribed an important role to this effect in determining the considerable preference of five-membered rings, containing hereroatoms directly bonded to phosphorus, for an apical–equatorial as opposed to a diequatorial position in tbp five-co-ordinate phosphoranes.[3] We now report the first *X*-ray analysis of a stable phosphorane showing clearly this preferred orientation in the case of an acyclic equatorial nitrogen and explore the consequences of the effect on the preferred conformations of phosphoranes containing six-membered rings with heteroatoms attached to phosphorus.



(1)



(2)

A single crystal *X*-ray analysis carried out on the dimethylaminophosphorane (**1**) confirmed that its geometry is essentially as depicted. The nitrogen is almost coplanar with its attached atoms (within 0·11 Å), and occupies an equatorial site of a slightly distorted trigonal bipyramid. The dihedral angle between the nitrogen plane and the tbp equatorial plane is 81°; the nitrogen lone-pair is therefore within 10° of its predicted orientation.

Crystal data: $C_{20}H_{14}Br_2F_{12}NO_4P$, $M = 751$, triclinic, $a = 21{\cdot}62$, $b = 8{\cdot}07$, $c = 8{\cdot}02$ Å, $\alpha = 76{\cdot}1$, $\beta = 102{\cdot}3$, $\gamma = 90{\cdot}8°$, $U = 1326$ Å^3, $Z = 2$, $D_c = 1{\cdot}88$ g cm^{-3}, space group $P\bar{1}$ assumed. 1169 Reflexion intensities measured by a Stoe Weissenberg diffractometer (λ for Mo-$K_\alpha = 0{\cdot}7107$ Å) have refined to $R = 0{\cdot}064$ using anisotropic thermal parameters for Br, F, and P, with phenyl rings treated as rigid groups.

Examination, using Dreiding models and sp^2 hydridised O, N, and S atoms, of 1,3,2-diheterophosphorinan rings in tbp phosphoranes shows that only in a boat ring occupying an apical–equatorial position is it possible for the lone-pair on the equatorial heteroatom to be in the favoured equatorial plane. This lone-pair effect is so large (*ca.* 10 kcal mol^{-1} with N and S and perhaps 5 kcal mol^{-1} with O[3]) that it might be expected to over-ride the normal preference of the six-membered ring for a chair conformation. We therefore carried out a single crystal *X*-ray analysis on the phosphorane (**2**) containing a perhydro-1,3,2-oxazaphosphorine ring.

Crystal data: $C_{16}H_{13}BrF_{12}NO_4P$, $M = 622$, monoclinic, $a = 26{\cdot}74$, $b = 5{\cdot}138$, $c = 38{\cdot}22$ Å, $\beta = 96{\cdot}5^\circ$, $U = 8518$ Å^3, $Z = 16$, $D_c = 1{\cdot}94$ g cm^{-3}, space group $C2/c$ from systematic absences and structure. 2422 Reflexion intensities measured by a Stoe Weissenberg diffractometer (λ for Cu-K_α = 1·5418 Å) refined to $R = 0{\cdot}118$ using anisotropic thermal parameters for Br, F, and P, with phenyl rings treated as rigid groups. The crystals deteriorate rapidly in the *X*-ray beam; two crystals were used in the data collection.

The two non-crystallographically related molecules of (**2**) have almost identical geometries; one is shown in the Figure with selected bond lengths averaged from the two molecules. Each molecule has a slightly distorted tbp geometry about the phosphorus atom. The nitrogen atom has a planar environment with the lone pair essentially in the equatorial plane. [The dihedral angles between the nitrogen planes and the P–N–O(1)–O(2) planes are 6·5 and 4° for the two molecules]. The oxazaphosphorine rings are boat-shaped with torsion angles about the C(2)–C(3) bonds of 6 and 13° for each molecule.

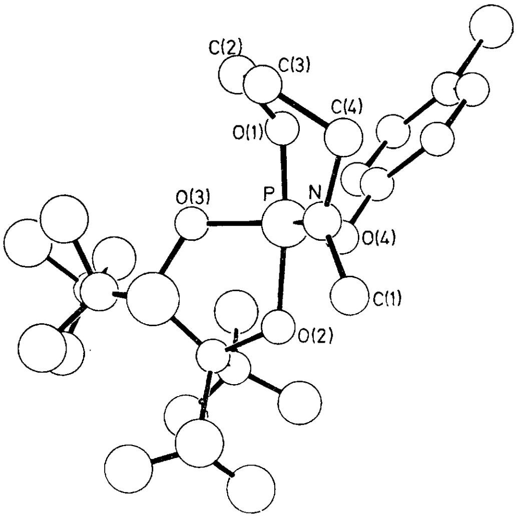


FIGURE. The molecular structure of P(OC$_6$H$_4$Br)[O$_2$C$_2$(CF$_3$)$_4$]-[O(CH$_2$)$_3$NMe], with all hydrogen atoms omitted. Average bond lengths, with e.s.d.s., for the two molecules are P–N 1·63(2), P–O(1) 1·62(1), P–O(2) 1·72(1), P–O(3) 1·64(2), P–O(4) 1·59(2), N–C(1) 1·47(3), N–C(4) 1·45(3), O(1)–C(2) 1·42(3), C(2)–C(3) 1·50(4), C(3)–C(4) 1·50(4) Å.

This striking preference for an apical–equatorial boat conformation in the five-co-ordinate state, if general for 1,3,2-diheterophosphorinan rings, is relevant to the confused situation surrounding the stereochemistry of nucleophilic substitutions at the phosphorus of 1,3,2-diheterophosphorinan 1-oxides and 1-sulphides.[4] The most stable of the possible intermediates in these substitutions will have apical–equatorial boat six-membered rings and these could be formed either from higher energy chair five-co-ordinate intermediates or by nucleophilic attack on twist–boat conformations of the original oxides or sulphides. Different investigators study compounds having different ring substituents or having the phosphorus-containing ring fused to another six-membered ring. These changes will affect the energy differences and energy barriers between the chair and boat (or twist-boat) conformations in both the four- and five-co-ordinate states and could well be the source of some of the apparent confusion.

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[2] For leading references see E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1972, **94**, 5674.

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