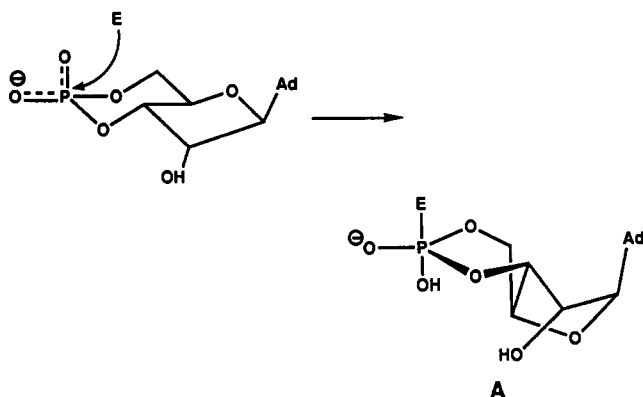
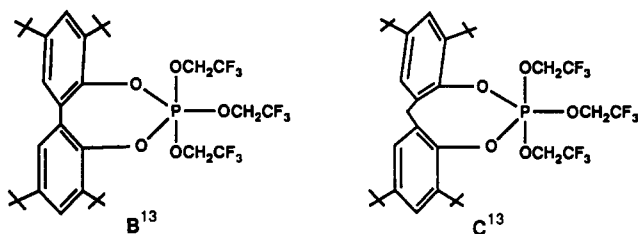


A New Structural Form for a Pentaoxyphosphorane. Diequatorial Ring Formation in a Trigonal Bipyramid¹

Previous studies²⁻⁸ of structural preferences of cyclic pentaoxyphosphoranes have led to trigonal bipyramidal geometries with the ring systems, which varied from five- to eight-membered, occupying axial-equatorial positions. Although inferences in mechanistic studies of reactions of cyclic phosphates and variable-temperature NMR studies of ligand-exchange behavior of oxyphosphoranes support intermediates with diequatorial ring placement, no X-ray investigations have yielded this structural form. For example, the activation of protein kinases by *c*-AMP has been proposed^{9,10} to result from attack by a functional group of the enzyme to yield a covalent complex, A. Diequatorial ring



formation has also been proposed^{11,12} in the course of hydrolysis of epimeric phosphorinanes. Only in the case of a NMR study by Denney and co-workers¹³ of monocyclic pentaoxyphosphoranes containing seven- and eight-membered rings has it been concluded that these rings reside in diequatorial positions.¹⁴ This is indicated to occur in the ground state at reduced temperature where pseudorotation has stopped, e.g., in formulations B and C, respectively.



- (1) (a) Pentacoordinated Molecules. 90. This communication is dedicated to Professor H. C. Brown, Purdue University, on the occasion of his 80th birthday. (b) Part 89: Hans, J.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1991**, *30*, 3928.
- (2) Kumara Swamy, K. C.; Burton, S. D.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *J. Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *53*, 437.
- (3) Schomburg, D.; Hacklin, H.; Rösenthaller, G.-V. *Phosphorus Sulfur Relat. Elem.* **1988**, *35*, 241.
- (4) Kumara Swamy, K. C.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6095.
- (5) Burton, S. D.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6104.
- (6) Holmes, R. R.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O. *Inorg. Chem.* **1991**, *30*, 1052.
- (7) Yu, J. H.; Sopchik, A. E.; Arif, A. M.; Bentrude, W. G. *J. Org. Chem.* **1990**, *55*, 3444.
- (8) Yu, J. H.; Arif, A. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1990**, *112*, 7451.
- (9) van Ool, P. J. J. M.; Buck, H. M. *Eur. J. Biochem.* **1982**, *121*, 329.
- (10) van Ool, P. J. J. M.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 79.
- (11) (a) Gorenstein, D. G.; Rowell, R.; Findley, J. J. *Am. Chem. Soc.* **1980**, *102*, 5077. (b) Rowell, R.; Gorenstein, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 5894.
- (12) Gorenstein, D. G. *Chem. Rev.* **1987**, *87*, 1047.
- (13) Abdou, W. M.; Denney, D. B.; Denney, D. Z.; Pastor, S. D. *Phosphorus Sulfur Relat. Elem.* **1985**, *22*, 99.

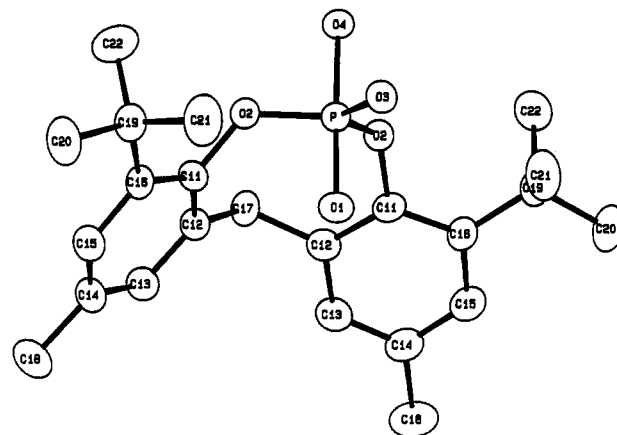
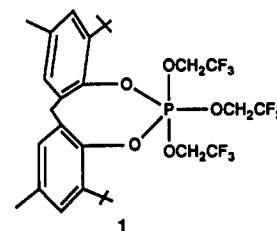


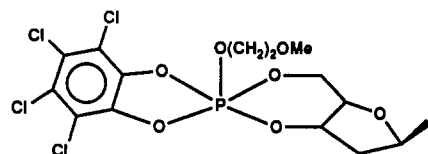
Figure 1. ORTEP plot of **1** with atoms of the trifluoroethyl groups omitted for clarity. Atoms with the same label are mirror-related ($x, y, 1/2 - z$). Bond lengths (Å): P-O1 = 1.647 (4), P-O4 = 1.659 (4), P-O2 = 1.595 (3), P-O3 = 1.601 (4). Bond angles (deg): O1-P-O4 = 176.1 (2), O2-P-O2' = 116.8 (2), O2-P-O3 = 121.5 (1), O3-P-O4 = 87.9 (2), O3-P-O1 = 88.1 (2), O2-P-O1 = 93.0 (1), O2-P-O4 = 89.1 (1), P-O2-C11 = 127.6 (3), C12-C17-C12' = 118.9 (5).

We report here the synthesis and X-ray analysis of **1**, closely related to C. **1** was synthesized by the addition of 2,2'-



methylenebis(4-methyl-6-*tert*-butylphenol) to $P(OCH_2CF_3)_3$ in the presence of *N*-chlorodiisopropylamine in ether solution.¹⁵ The geometry about the phosphorus atom is essentially trigonal bipyramidal with the eight-membered ring system diequatorially positioned ($e-e$).¹⁶ This is the first unambiguous structural

- (14) In a recent NMR study (Broeders, N. L. H. L.; Koole, L. H.; Buck, H. M. *J. Am. Chem. Soc.* **1990**, *112*, 7475), it was concluded that diequatorial ring orientation in a TBP existed in equilibrium with an axial-equatorial ring structure for



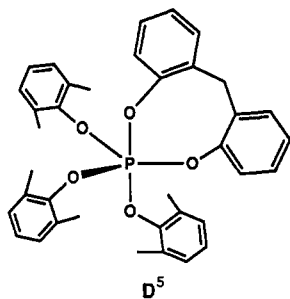
- (15) To a mixture of $P(OCH_2CF_3)_3$ (1.487 g, 4.53 mmol) and 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol) (1.54 g, 4.53 mmol) in diethyl ether at $-75^\circ C$ was added (*i*-Pr)₂NHCl (0.737 g, 5.44 mmol) in ether. The reaction was brought to room temperature, and the mixture was stirred for 40 h. The removal of (*i*-Pr)₂NHCl by filtration followed by slow evaporation of solvent gave 1.81 g of **1** (60% yield); mp 147-150 °C. Colorless crystals were obtained for an X-ray analysis by slow evaporation of a solution of **1** which consisted of a 1:2 mixture of ether and *n*-hexane. ³¹P NMR (CDCl₃, ppm): -78.8. ¹⁹F NMR (CDCl₃, ppm): -75.6 (axial OCH₂CF₃ groups), -77.1 (equatorial OCH₂CF₃ group). Anal. Calcd for C₂₉H₃₆F₉O₅P: C, 52.25; H, 5.40. Found: C, 52.17; H, 5.54. 2,2'-Methylenebis(4-methyl-6-*tert*-butylphenol) was prepared as described previously: Davis, A. R.; Sullivan, A. V. U.S. Patent 2,538,355, 1951. Davis, A. R.; Sullivan, A. V. *Chem. Abstr.* **1951**, *45*, 4086b. (*i*-Pr)₂NHCl was prepared as described previously: Bock, H.; Kompa, K. L. *Chem. Ber.* **1966**, *99*, 1347.
- (16) X-ray study: C₂₉H₃₆F₉O₅P, orthorhombic space group *Pnam* (alternate setting of *Pnma*, No. 62), $a = 19.802$ (2) Å, $b = 10.237$ (2) Å, $c = 15.818$ (3) Å, $Z = 4$, and $\mu_{MolK\alpha} = 1.670$ cm⁻¹. A total of 1923 independent reflections were measured (Enraf-Nonius CAD4 diffractometer, $2\theta \pm 2^\circ C$, graphite-monochromated Mo radiation, $\lambda(K\alpha) = 0.71073$ Å, $2\theta_{max} = 43^\circ$). The trifluoroethyl group bonded to O1 is disordered with respect to the mirror plane. Anisotropic refinement of non-hydrogen atoms with all but the two disordered H atoms included as fixed isotropic scatterers in ideal positions gave $R = 0.053$ and $R_w = 0.072$ for 1223 observed reflections ($I \geq 3\sigma$).

characterization of a pentaoxyphosphorane with a diequatorial ring system.

The molecule has a crystallographic mirror plane which contains atoms P, O1, O3, O4, and C17 (Figure 1). The trifluoroethyl groups bonded to O3 and O4 conform to this symmetry, while the one bonded to O1 is disordered. Distortions away from ideal trigonal bipyramidal symmetry are "anti Berry"¹⁷ in nature (O2-P-O2' closed down to 116.8 (2)° with the axial oxygen atoms tipped toward O3).

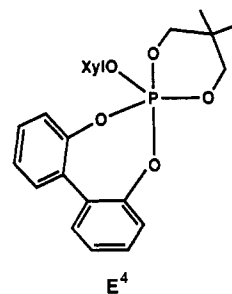
The ¹⁹F NMR spectrum of **1** at room temperature shows two different resonances in the intensity ratio of 2:1, at -75.6 and -77.1 ppm, respectively. The lower field peak is assigned to the axial and the higher field peak to equatorial trifluoroethoxy groups. Thus, the solution-state structure is in agreement with the solid-state structure in having the eight-membered ring at diequatorial sites of a TBP geometry.

The only other X-ray structural investigation of an oxyphosphorane having an eight-membered ring is D⁵ where the ring is positioned at axial-equatorial (a-e) sites. Either the elec-



tronegativity of the trifluoroethoxy group in **1** exceeds that of the xylyloxy group sufficiently to displace the ring from its preferred (a-e) orientation in D or increased steric effects encountered due to the presence of *tert*-butyl groups in **1**, or a combination of both, act to stabilize the e-e structure found for **1**. No unusual ring strain is apparent for **1** in that the equatorial P-O ring bond lengths, 1.595 (3) Å, are nearly the same as the length of the P-O bond to the equatorial trifluoroethoxy group, 1.601 (4) Å, as well

as being very close to the P-O equatorial ring bond in D, 1.60 (1) and 1.61 (1) Å (two independent molecules per unit cell). X-ray characterization of pentaoxyphosphorane E⁴ having a



seven-membered ring reveals a TBP geometry analogous to that of **1** with the ring located at axial-equatorial sites. ¹H NMR spectroscopy shows a pseudorotational process, indicating exchange via a TBP intermediate with a diequatorial ring orientation that has a barrier energy of 11.5 kcal/mol. This energy is not expected to be much different for the eight-membered ring in the TBP of **1**. Hence, it would represent the approximate energy to overcome in stabilizing the diequatorial ring structure found for **1**. Further studies of this feature are in progress as well as attempts to stabilize seven- and six-membered rings in diequatorial sites.

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Registry No. **1**, 138489-68-6; P(OCH₂CF₃)₃, 370-69-4; 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol), 119-47-1.

Supplementary Material Available: Figure S1 (ORTEP plot of the asymmetric unit of **1**) and tables of atomic coordinates, thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1** (Tables S1-S4) (8 pages); a listing of structure factors for **1** (6 pages). Ordering information is given on any current masthead page.

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(17) Berry, R. S. *J. Chem. Phys.* 1960, 32, 933.

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