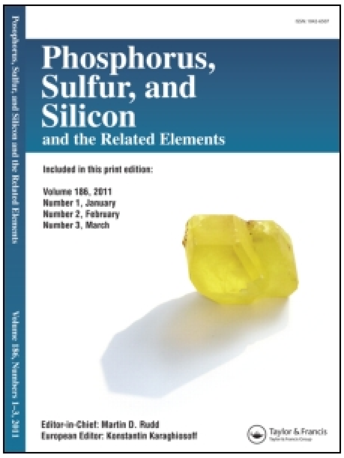

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DIEQUATORIAL AND AXIAL-EQUATORIAL ORIENTATIONS OF EIGHT-MEMBERED RINGS IN MONOCYCLIC PENTAOXYPHOSPHORANES CONTAINING TRIFLUOROETHOXY GROUPS

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DIEQUATORIAL AND AXIAL-EQUATORIAL ORIENTATIONS OF EIGHT-MEMBERED RINGS IN MONOCYCLIC PENTAOXYPHOSPHORANES CONTAINING TRIFLUOROETHOXY GROUPS[1]

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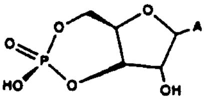
(Received January 17, 1991)

Reaction of $(CF_3CH_2O)_3P$ with diols yielded new monocyclic pentaoxyphosphoranes with eight-membered ring systems containing methylene or sulfur bridges. Trigonal-bipyramid (TBP) geometries were shown to be present by X-ray analysis for $CH_2(C_6H_4O)_2P(OCH_2CF_3)_3$ (**2**) and $S(Me_2C_6H_2O)_2P(OCH_2CF_3)_3$ (**3**) with the ring in **2** located in axial-equatorial (a–e) positions and the ring in **3** in diequatorial (e–e) sites. These structures are compared with the first pentaoxyphosphorane derivative to exhibit a diequatorial ring in a TBP, $CH_2[Me(t\text{-}Bu)C_6H_2O]_2P(OCH_2CF_3)_3$ (**1**), recently prepared in our laboratory. A pseudooctahedral structure was revealed by X-ray analysis for $S[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)_3$ (**4**). ^1H, ^{31}P, and ^{19}F solution NMR data indicated rapid intramolecular ligand exchange for **2** and **3** at room temperature. In contrast, NMR data on **1** and **4**, which contained *tert*-butyl groups, did not indicate exchange behavior. Here, retention of the basic solid-state TBP in solution was consistent with the observed spectra. Comparison of solid-state ^{31}P NMR spectra with solution ^{31}P NMR data of **3** and **4** suggested retention of their basic solid-state geometries in solution. Comparisons with related pentaoxyphosphoranes having six- and seven-membered rings suggest that seven- and eight-membered rings are more easily accommodated in diequatorial positions compared to positioning saturated six-membered rings in this location of a TBP. Oxyphosphorane **2** crystallizes in the triclinic space group $P\bar{1}$ with a = 9.712 (2) Å, b = 11.039 (3) Å, c = 12.521 (2) Å, α = 97.48 (2)°, β = 111.77 (1)°, γ = 110.56 (2)°, and Z = 2. Derivative **3** crystallizes in the triclinic space group $P\bar{1}$ with a = 9.245 (2) Å, b = 12.464 (2) Å, c = 12.891 (2) Å, α = 76.77 (1)°, β = 74.69 (2)°, γ = 70.60 (1)°, and Z = 2. Oxyphosphorane **4** crystallizes in the triclinic space group $P\bar{1}$ with a = 11.202 (2) Å, b = 11.307 (4) Å, c = 16.372 (8) Å, α = 99.66 (3)°, β = 94.39 (3)°, γ = 103.42 (2)°, and Z = 2. The final conventional unweighted residuals are 0.050 (**2**), 0.075 (**3**), and 0.076 (**4**).

INTRODUCTION

Considerable interest has developed recently in establishing whether it is possible to isolate pentaoxyphosphoranes with six-membered ring systems in diequatorial sites (e–e) as well as in axial–equatorial sites (a–e) of a trigonal-bipyramid (TBP) geometry.[2] This interest stems from the role of these pentacoordinated phosphorus compounds as intermediates or activated states postulated to exist in reaction mechanisms,[3–6] particularly in enzymatic reactions involving c-AMP.[7-11] Various



c-AMP

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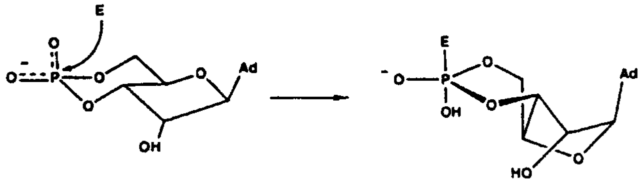
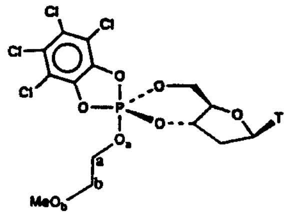
mechanisms have been advanced suggesting axial–equatorial placement of the six-membered ring in the hydrolysis of c-AMP catalyzed by c-AMP phosphodiesterase,[9] whereas in the activation of protein kinases by c-AMP, diequatorial placement of the cyclophosphate ring has been proposed[9,12] to result from attack by a functional group of the enzyme yielding a covalent complex. However, despite a variety of studies, no unambiguous structural characterization of a pentaoxyphosphorane with a diequatorial six-membered ring system has been found. Broeders et al.[13] have reported the presence of such a ring orientation in equilibrium with an a–e isomer deduced from ^{1}H NMR data on the cyclic phosphorane A.

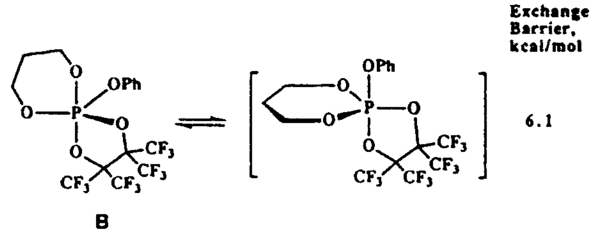




A

Both NMR data on activation energies for ligand exchange and ab initio calculations have yielded an estimate of the energy difference for these two positional arrangements for saturated six-membered ring systems of pentaoxyphosphoranes. The activation energy obtained from ^{19}F NMR data by Trippett[14] on the bicyclic derivative **B** gave an exchange barrier of 6.1 kcal/mol in close agreement of ~7

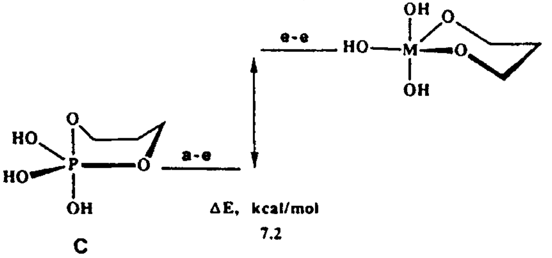
Ligand Exchange Barriers from ^{19}F NMR



B

Ab-Initio Calculation - Six-Membered Ring

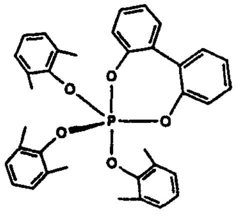
3-21G* Basis Set



C

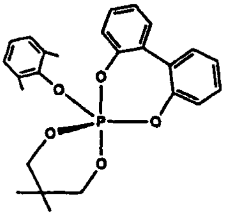
kcal/mol from theoretical calculations[15] of the energy difference of the model phosphorane system C, indicating that the e–e orientation is less stable than the a–e structure by this amount. Despite this relatively small energy difference and the inclusion of electronegativity,[16] hydrogen bonding,[17,18] and steric and ring strain factors[19–23] designed to enhance ring formation in a TBP structure, no example of an e–e structure for a six-membered ring in a pentaoxyphosphorane has appeared.

In an effort to evaluate the influence of these factors more widely, we have initiated a study employing larger ring systems. From the limited amount of information on larger rings in oxyphosphoranes,[1b,19,20] ring strain effects do not appear to be greater than that in saturated six-membered rings. Due to the greater conformational flexibility expected for seven- and eight-membered rings, ring strain in diequatorial orientations of a TBP may even be less than that for six-membered ring systems. There are four examples of these larger rings in pentaoxyphosphoranes whose X-ray structures are known. They are shown here as derivatives D,[20] E,[19], F,[20] and G.[1b] An analogous spirocyclic derivative to G, derivative H,[1b] but containing the eight-membered ring depicted for F in place of the seven-membered ring, showed an exchange barrier for the process, a–e $\rightleftharpoons$ e–e, of 12.9 kcal/mol[1b] similar to that found for E and G.



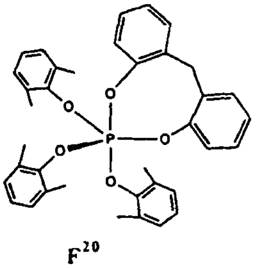
D[20]

(a-e) $\rightleftharpoons$ (e-a)
$\Delta G^{\ddagger} = 14.2$ kcal/mol



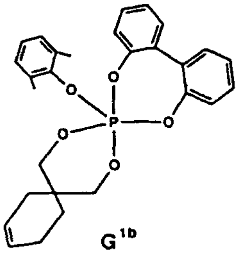
E[19]

(a-e) $\rightleftharpoons$ (e-e)
$\Delta G^{\ddagger} = 11.5$ kcal/mol



F[20]

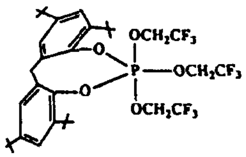
(a-e) $\rightleftharpoons$ (e-a)
$\Delta G^{\ddagger} = 12.1$ kcal/mol



G[1b]

(a-e) $\rightleftharpoons$ (e-e)
$\Delta G^{\ddagger} = 12.2$ kcal/mol

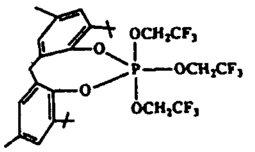
A recent X-ray study from our laboratory[24] agreed with the conclusion of Denney and co-workers[25] that diequatorial ring formation exists in cyclic derivatives containing eight-membered rings and trifluorethoxy groups. Variable-temperature solution NMR data obtained by Denney et al.[25] indicated a diequatorial structural form for I. We determined the X-ray structure of the related derivative I[24] and found, for the first time, a ring positioned diequatorially in a TBP geometry of a pentaoxyphosphorane.



1[25]

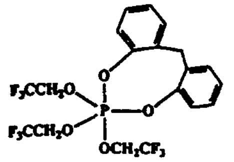
(e-e) ⇌ (e-a)

ΔG‡ = 15.4 kcal/mol

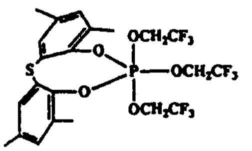


1[24]

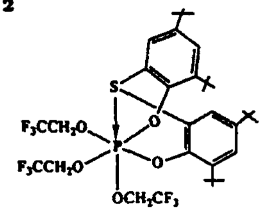
Encouraging as this is, no rationale presents itself to understand the basis of the finding. To attempt to do so, we report a related derivative here that was synthesized with the bulky *tert*-butyl groups removed from the eight-membered ring, derivative **2**, and ones that had a sulfur atom inserted in place of the bridging methylene group of the ring system, derivatives **3** and **4**. The last two pentaoxyphosphoranes differed in having ring methyl and ring *tert*-butyl groups, respectively, as a variation. Thus, ring, steric, and electronegativity effects are varied in these derivatives, all containing the same basic eight-membered-ring arrangement. X-ray and NMR investigations of these cyclic phosphoranes **2**–**4** were carried out to determine structural variations in the solid and solution phases and to compare these features with similar information obtained earlier for **1**.



2



3



4

RESULTS

The molecular geometry, excluding the trifluoroethyl groups, for **2** is shown in the ORTEP plot of Figure 2, while selected distances and angles appear in Table II. The corresponding information for **3** and **4** is given in Figures 3 and 4 and in Tables III and IV. For comparison, the corresponding information for **1** is given in Figure 1 and in Table I. Selected atomic coordinates are listed in Tables V–VII for **2**–**4**, respectively. For compounds **2**–**4**, ORTEP plots showing thermal ellipsoids for all non-hydrogen atoms and tables of atomic coordinates, thermal parameters, bond lengths and angles, and hydrogen atom parameters are provided as supplementary material.

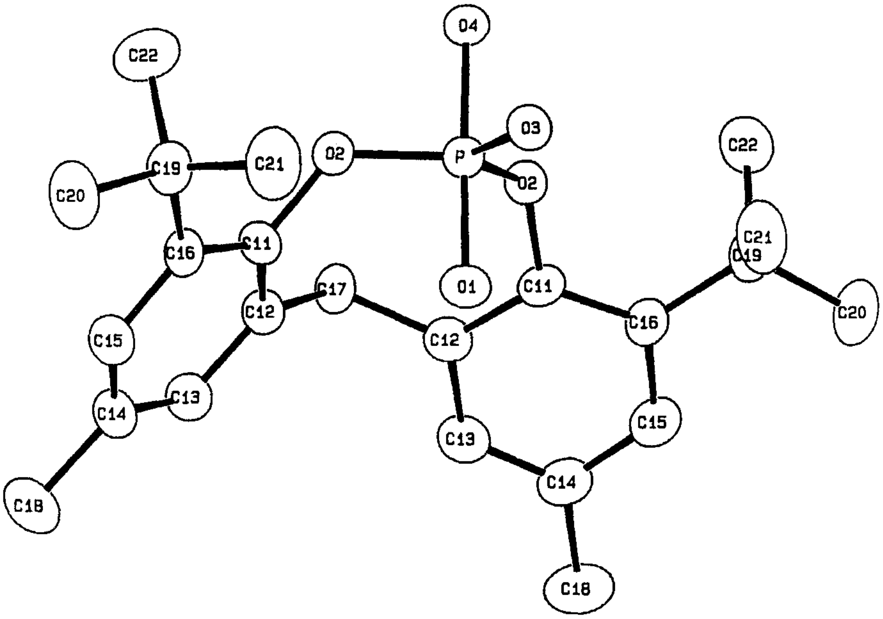


FIGURE 1 ORTEP plot of $CH_2[(t\text{-}Bu)MeC_6H_2O]_2P(OCH_2CF_3)_3$ (**1**) with thermal ellipsoids at the 30% probability level. Atoms with the same label are related by a crystallographic mirror plane. Atoms of the trifluoroethyl groups and hydrogen atoms are omitted for clarity.

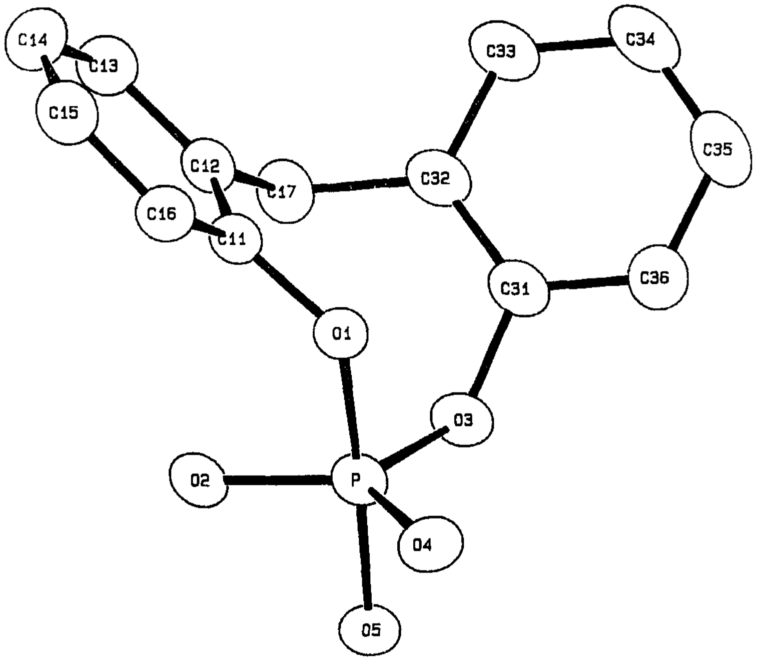


FIGURE 2 ORTEP plot of $CH_2(C_6H_4O)_2P(OCH_2CF_3)_3$ (**2**) with thermal ellipsoids at the 30% probability level. Atoms of the trifluoroethyl groups and hydrogen atoms are omitted for clarity.

TABLE I

Selected Distances (Å) and Angles (deg) for $CH_2[(t\text{-}Bu)MeC_6H_2O]_2P(OCH_2CF_3)_3$ (**1**)[a]

		Distances	
P–O1	1.647 (4)	C11–C12	1.403 (6)
P–O2	1.595 (3)	C12–C17	1.516 (6)
P–O3	1.601 (4)	O2–C11	1.415 (5)
P–O4	1.659 (4)		
		Angles	
O1–P–O2	93.0 (1)	P–O2–C11	127.6 (3)
O1–P–O3	88.1 (2)	C11–C12–C17	122.2 (4)
O1–P–O4	176.1 (2)	O2–C11–C12	166.8 (4)
O2–P–O3	121.5 (1)	C12–C17–C12′	118.9 (5)
O2–P–O4	89.1 (1)		
O3–P–O4	87.9 (2)		
O2–P–O2′	116.8 (2)		

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 1.

TABLE II

Selected Distances (Å) and Angles (deg) for $CH_2(C_6H_4O)_2P(OCH_2CF_3)_3$ (**2**)[a]

		Distances	
P–O1	1.660 (3)	P–O4	1.592 (4)
P–O2	1.594 (4)	P–O5	1.654 (4)
P–O3	1.602 (4)	O1–C11	1.389 (4)
O3–C31	1.404 (7)	C11–C12	1.386 (8)
C31–C32	1.387 (7)	C17–C12	1.527 (6)
		C17–C32	1.522 (8)
		Angles	
O1–P–O2	88.9 (2)	O2–P–O4	124.7 (2)
O1–P–O3	94.9 (2)	O2–P–O5	88.9 (2)
O1–P–O4	90.1 (2)	O3–P–O4	115.2 (2)
O1–P–O5	175.6 (2)	O3–P–O5	89.5 (2)
O2–P–O3	119.9 (2)	O4–P–O5	88.1 (2)
P–O1–C11	129.7 (4)	P–O3–C31	127.7 (3)
O1–C11–C12	121.9 (3)	O3–C31–C32	120.1 (5)
C11–C12–C17	122.2 (4)	C31–C32–C17	121.9 (5)
C12–C17–C32	110.4 (5)		

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 2.

DISCUSSION

Synthesis and Basic Structures

The monocyclic pentaoxyphosphoranes **1–4** are conveniently prepared in good yields (70–80%) by oxidative addition reactions of diols to tris(2,2,2-trifluoroethyl)-phosphite (eq 1). All the monocyclic pentaoxyphosphoranes, **1–4**, are stable when stored under vacuum, otherwise hydrolysis ensues, producing an oil.

Compound **1** constitutes the first and, prior to this study, the only X-ray structure of a pentaoxyphosphorane in which the ring system spans equatorial sites in a trigonal-bipyramidal geometry. Compounds **2** and **3** are also trigonal bipyramidal

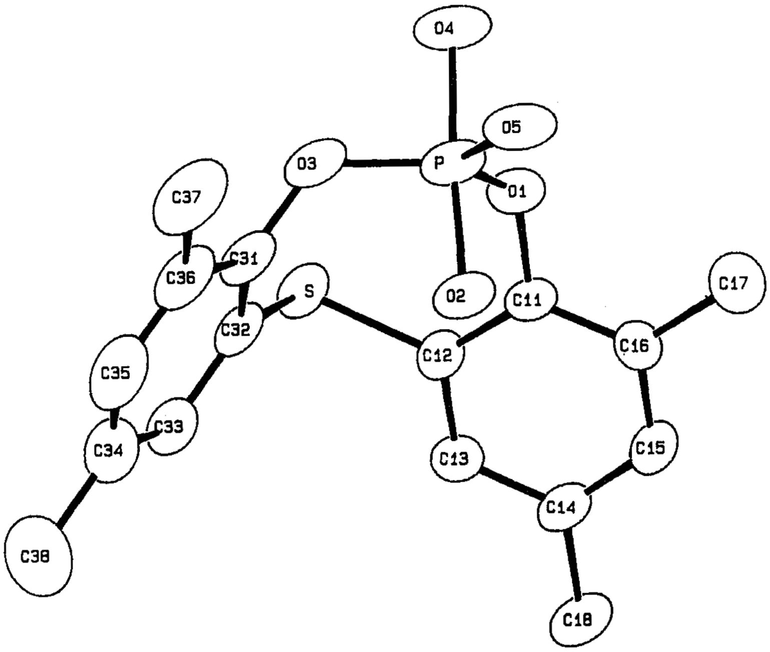


FIGURE 3 ORTEP plot of $S(Me_2C_6H_2O)_2P(OCH_2CF_3)_3$ (3) with thermal ellipsoids at the 30% probability level. Atoms of the trifluoroethyl groups and hydrogen atoms are omitted for clarity.

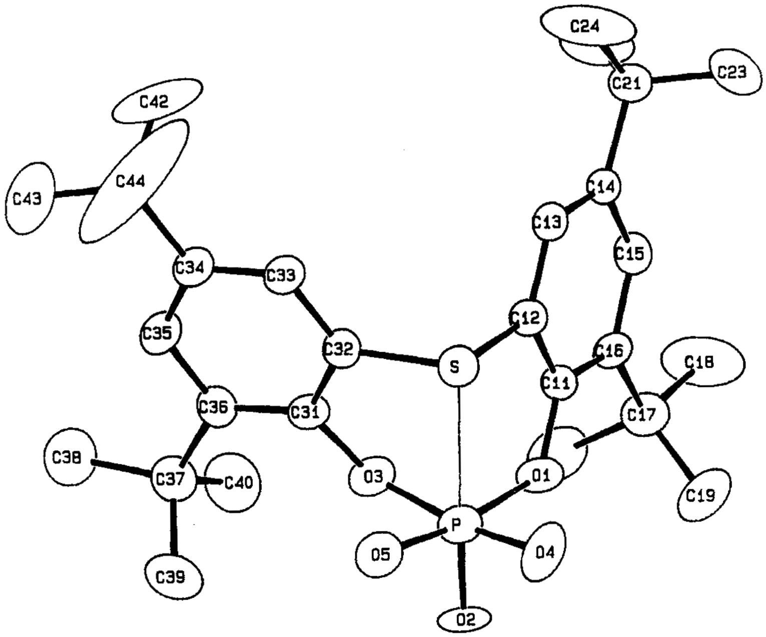
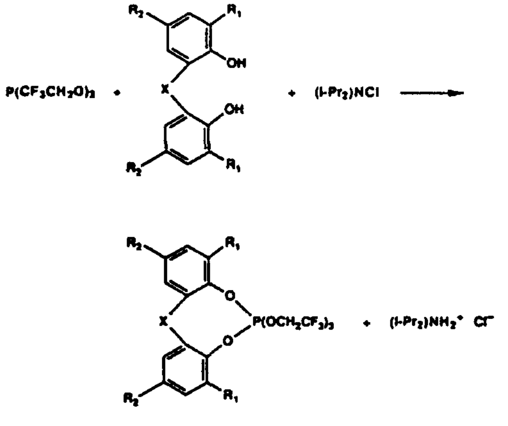


FIGURE 4 ORTEP plot $S[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)_3$ (4) with thermal ellipsoids at the 30% probability level. Atoms of the trifluoroethyl groups and hydrogen atoms are omitted for clarity.



(1)

R_1 = *t*-Bu, R_2 = Me, X = CH_2 (1); R_1 = R_2 = H, X = CH_2 (2);
R_1 = R_2 = Me, X = S (3); R_1 = R_2 = *t*-Bu, X = S (4)

at phosphorus, but in compound **2** in which the ring system is the same as that of **1** (except that the methyl and *tert*-butyl ring substituents have been replaced by hydrogen atoms), the ring has an axial–equatorial orientation. In compound **3**, however, where the methylene bridge in the eight-membered ring has been replaced by a sulfur atom, the ring system returns to the diequatorial arrangement with a geometry very similar to that found in **1**. It is important to note that the P—S distance in **3** is 3.504 (3) Å, which can be taken to be an essentially nonbonding distance when compared to the van der Waals sum of 3.75 Å. The lack of perturbation in the O1—P—O3 angle of **3** (i.e., it is "closed down" from 120° to a value of 117.5(3)° rather than opened up as one would expect if sulfur approached phosphorus) also suggests a negligible P—S interaction.

TABLE III

Selected Distances (Å) and Angles (deg) for $S(Me_2C_6H_2O)_2P(OCH_2CF_3)_3$ (3)[a]

	Distances		
S–C12	1.790 (8)	P–O3	1.620 (5)
S–C32	1.795 (7)	P–O4	1.659 (7)
P–O1	1.614 (6)	P–O5	1.620 (5)
P–O2	1.645 (7)	O1–C11	1.40 (1)
O3–C31	1.38 (1)	C11–C12	1.37 (1)
		C31–C32	1.39 (1)
	Angles		
C12–S–C32	103.4 (4)	O2–P–O4	175.3 (3)
O1–P–O2	89.6 (3)	O2–P–O5	88.9 (3)
O1–P–O3	117.5 (3)	O3–P–O4	90.1 (3)
O1–P–O4	89.1 (3)	O3–P–O5	119.3 (3)
O1–P–O5	123.1 (3)	O4–P–O5	87.9 (3)
O2–P–O3	94.5 (3)	P–O1–C11	126.2 (4)
P–O3–C31	125.3 (6)	O1–C11–C12	120.0 (7)
O3–C31–C32	120.4 (6)	S–C12–C11	121.7 (7)
		S–C32–C31	120.8 (6)

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 3.

TABLE IV

Selected Distances (Å) and Angles (deg) for $S[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)_3$ (4)[a]

Distances			
S-P	2.504 (3)	P-O3	1.684 (6)
P-O1	1.681 (5)	P-O4	1.663 (7)
P-O2	1.640 (7)	P-O5	1.649 (6)
S-C12	1.752 (7)	S-C32	1.769 (8)
O1-C11	1.35 (1)	O3-C31	1.362 (8)
C11-C12	1.435 (9)	C31-C32	1.38 (1)
Angles			
S-P-O1	84.8 (2)	O1-P-O5	170.5 (3)
S-P-O2	172.2 (3)	O2-P-O3	93.5 (3)
S-P-O3	82.4 (2)	O2-P-O4	98.6 (4)
S-P-O4	85.7 (3)	O2-P-O5	100.5 (4)
S-P-O5	86.0 (3)	O3-P-O4	167.8 (3)
O1-P-O2	88.6 (3)	O3-P-O5	87.3 (3)
O1-P-O3	89.6 (3)	O4-P-O5	89.1 (3)
O1-P-O4	92.1 (3)	C12-S-C32	102.9 (4)
P-S-C12	91.5 (3)	P-S-C32	89.1 (3)
P-O1-C11	127.0 (4)	P-O3-C31	124.6 (5)
O1-C11-C12	119.5 (6)	O3-C31-C32	116.8 (7)
S-C12-C11	115.5 (6)	S-C32-C31	117.0 (6)

[a] Estimated standard deviations in parentheses. The atom labeling scheme is shown in Figure 4.

TABLE V

Selected Atomic Coordinates in Crystalline $CH_2(C_6H_4O)_2P(OCH_2CF_3)_3$ (2)[a]

atom[b]	x	y	z	B_{equiv},[c] Å^2
S	0.4748 (2)	0.5082 (2)	0.1823 (1)	4.30 (5)
P	0.4725 (2)	0.7265 (2)	0.1731 (2)	5.55 (6)
O1	0.5766 (5)	0.7650 (4)	0.2588 (3)	4.6 (1)
O2	0.4748 (6)	0.8735 (5)	0.1810 (4)	10.6 (2)
O3	0.3578 (5)	0.6998 (4)	0.2335 (4)	5.2 (1)
O4	0.5816 (6)	0.7204 (6)	0.1102 (4)	7.2 (2)
O5	0.3668 (6)	0.6652 (6)	0.0919 (4)	7.3 (2)
C11	0.6041 (7)	0.6886 (6)	0.3086 (4)	3.6 (2)
C12	0.5664 (7)	0.5570 (6)	0.2792 (5)	3.7 (2)
C13	0.5967 (7)	0.4764 (6)	0.3272 (5)	3.9 (2)
C14	0.6666 (6)	0.5190 (6)	0.4036 (5)	3.7 (2)
C15	0.7028 (7)	0.6500 (7)	0.4312 (5)	4.2 (2)
C16	0.6738 (7)	0.7359 (6)	0.3857 (5)	3.8 (2)
C31	0.2772 (7)	0.5878 (6)	0.2294 (5)	4.0 (2)
C32	0.3227 (7)	0.4843 (7)	0.2101 (5)	4.3 (2)
C33	0.2497 (7)	0.3628 (7)	0.2079 (5)	4.3 (2)
C34	0.1306 (7)	0.3493 (7)	0.2262 (5)	4.7 (2)
C35	0.0861 (7)	0.4552 (7)	0.2451 (5)	5.0 (2)
C36	0.1571 (7)	0.5760 (7)	0.2461 (5)	4.4 (2)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

TABLE VI

Selected Atomic Coordinates in Crystalline $S(Me_2C_6H_2O)_2P(OCH_2CF_3)_3$ (3)[a]

atom[b]	x	y	z	B_{equiv},[c] Å^2
P	0.1692 (2)	0.3792 (1)	0.7227 (1)	3.77 (3)
O1	0.3647 (3)	0.4573 (3)	0.7501 (3)	3.60 (8)
O2	0.2022 (3)	0.5005 (3)	0.8274 (3)	4.07 (9)
O3	0.0960 (4)	0.3810 (3)	0.5856 (3)	4.40 (9)
O4	0.1923 (4)	0.2466 (3)	0.7418 (3)	4.54 (9)
O5	−0.0206 (4)	0.3011 (3)	0.7062 (3)	4.47 (9)
C11	0.4763 (5)	0.5926 (4)	0.8082 (4)	3.5 (1)
C12	0.4550 (6)	0.6953 (5)	0.7612 (4)	4.1 (1)
C13	0.5799 (6)	0.8264 (5)	0.8216 (5)	5.2 (2)
C14	0.7211 (7)	0.8535 (6)	0.9242 (5)	5.9 (2)
C15	0.7397 (6)	0.7491 (6)	0.9677 (5)	5.5 (2)
C16	0.6172 (6)	0.6187 (5)	0.9110 (4)	4.4 (1)
C17	0.3017 (6)	0.6682 (5)	0.6478 (4)	4.5 (1)
C31	0.1831 (5)	0.4246 (5)	0.5194 (4)	4.2 (1)
C32	0.2770 (5)	0.5617 (5)	0.5434 (4)	4.2 (1)
C33	0.3526 (6)	0.5978 (5)	0.4690 (4)	4.9 (1)
C34	0.3308 (6)	0.5000 (6)	0.3744 (5)	5.7 (2)
C35	0.2388 (6)	0.3661 (6)	0.3527 (5)	5.9 (2)
C36	0.1612 (6)	0.3262 (6)	0.4259 (5)	5.2 (2)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

TABLE VII

Selected Atomic Coordinates in Crystalline $S[(t\text{-Bu})_2C_6H_2O]_2P(OCH_2CF_3)_3$ (4)[a]

atom[b]	x	y	z	B_{equiv},[c] Å^2
S	0.6173 (2)	0.1080 (2)	0.4674 (2)	4.92 (5)
P	0.7024 (3)	0.1640 (2)	0.1823 (2)	5.44 (6)
O1	0.8366 (6)	0.0823 (4)	0.2475 (4)	5.1 (1)
O2	0.7294 (6)	0.2780 (4)	0.2091 (4)	5.1 (1)
O3	0.5222 (6)	0.1900 (5)	0.2485 (4)	5.5 (1)
O4	0.6889 (7)	0.0479 (5)	0.1476 (4)	6.8 (2)
O5	0.7393 (7)	0.2145 (5)	0.0538 (4)	6.5 (2)
C11	0.8956 (9)	0.1148 (6)	0.3216 (6)	4.1 (2)
C12	0.8077 (8)	0.1295 (6)	0.4242 (6)	4.1 (2)
C13	0.8706 (9)	0.1541 (6)	0.4996 (6)	4.2 (2)
C14	1.0210 (9)	0.1655 (6)	0.4706 (7)	4.7 (2)
C15	1.1073 (9)	0.1479 (7)	0.3656 (7)	5.0 (2)
C16	1.0453 (9)	0.1248 (7)	0.2900 (6)	4.7 (2)
C31	0.4514 (9)	0.2683 (7)	0.3205 (7)	5.4 (2)
C32	0.4901 (8)	0.2452 (7)	0.4219 (7)	4.9 (2)
C33	0.419 (1)	0.3253 (8)	0.4930 (8)	6.0 (3)
C34	0.307 (1)	0.4267 (8)	0.4635 (9)	7.2 (3)
C35	0.267 (1)	0.4421 (8)	0.363 (1)	7.7 (3)
C36	0.3348 (9)	0.3663 (8)	0.2910 (8)	6.4 (3)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 4. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

The geometry at phosphorus in compound **4** is not trigonal bipyramidal. If the sulfur atom is discounted, the geometry may be referred to as a square pyramid with atom O2 in the apical position. The atoms forming the basal plane (O1, O3, O4, and O5) are coplanar to within ±0.020 (6) Å, while the phosphorus atom is displaced from this plane by a distance of 0.153 (2) Å in a direction toward the apical O2. The trans basal angles of 170.5 (3) and 167.8 (3)° are about 20° larger than the typical value for these angles in square-pyramidal phosphorus[26–28] and shows the effect of the sulfur atom which caps the basal plane. The P—S distance of 2.504 (3) Å is somewhat long compared to the sum of the covalent radii of 2.14 Å, indicating a somewhat weakened, but significant bond. When the sulfur atom is included in the coordination sphere of phosphorus, the geometry may be described as a distorted octahedron.

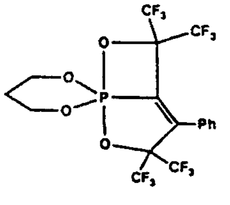
Structural Distortions, Bond Length Comparisons, and Diequatorial Ring Formation

Distortions away from the ideal TBP geometry for **2** lie on the Berry pseudorotation coordinate[29] connecting the apparent TBP with a rectangular pyramid (RP) having O3 in the apical position. By use of the dihedral angle method[26] to assess displacement, the geometry is displaced 13.4% using the actual bond distances (or 13.5% average using unit vectors) from the TBP toward the RP. For **3**, the corresponding displacement is 11.0% (also 11.0% average using unit vectors), where atom O3 is the pivotal atom.

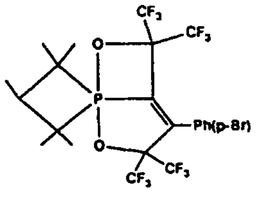
The P—O bond distances in **1–3** are similar to each other for specific structural types. The P—O_{eq} ring bonds and P—O_{eq} trifluoroethoxy bonds all have lengths in the range 1.59–1.62 Å. As expected,[30] the P—O_{ax} bond lengths to these same two groups are longer, in the range 1.65–1.67 Å. The octahedrally coordinated sulfur derivative **4** shows even somewhat longer P—O bonds. Here the P—O ring bond lengths average 1.68 Å while the P—O nonring bonds in what would be cis-basal positions of a square pyramid (with neglect of sulfur in the coordination sphere) have lengths in the range 1.65–1.66 Å. In keeping with this geometrical description, the apical P—O length is slightly shorter, 1.64 Å. The latter shortening typically is found for apical bonds relative to basal bonds in square pyramids of main-group elements.[26–28] Thus, the increase in the P—O bond lengths in **4** relative to **1–3** is in line with the expanded coordination shell brought about by the entrance of the sulfur atom.

The average P—O_{eq} bond length in **1–3** and P—O_{ax} ring bond length in **2** of 1.61 and 1.66 Å, respectively, are about 0.02 Å greater than these average distances for saturated six-membered pentaoxyphosphoranes for which P—O_{eq} = 1.59 Å and P—O_{ax} = 1.64 Å.[19,23] These slightly longer distances are similar to what was observed for D[20] and E[19] containing seven-membered rings and F[20] containing an eight-membered ring in axial–equatorial orientations in related pentaoxyphosphoranes. Since there is no large increase in the P—O_{eq} ring bond lengths for **1** and **3** that have diequatorial rings compared to this distance for **2** and D–F having axial–equatorial positioned rings, no large change in ring strain accompanying diequatorial placement is indicated, perhaps limited to a maximum of the 6–7 kcal/mol discussed in the Introduction for placing saturated six-membered rings in e–e positions relative to a–e positions in the absence of steric effects. Thus to stabilize the e–e ring orientation, the barrier to overcome in doing so must include factors other than ring strain effects.

A six-membered ring recently isolated in a tetraoxyphosphorane J by Bentrude and co-workers[31] has been shown by X-ray analysis to reside in e–e sites of a TBP.



J[31]



K[32]

Use of special ring constraints provided by the bicyclic component in this case appears operative in inducing diequatorial placement of the phosphorinane ring similar to that found earlier by Trippett[32] with this same ring system in positioning a four-membered ring diequatorially K.

For the series of compounds studied here, steric effects are indicated to play a role as well as ring alterations induced by the presence of the ring sulfur atom. The absence in **2** of the *tert*-butyl groups situated ortho to the skeletal ring structure in **1** suggests that the presence of these groups is influential in inducing the formation of the e–e ring orientation in **1** compared to the a–e form for **2**. However, in what way these steric effects may operate is not apparent.

Again, the formation of a pseudooctahedral structure for **4** may be associated in part with the presence of the *tert*-butyl substituents as a component of the eight-membered ring system. The resulting enhancement of the ability of sulfur to form a relatively strong P—S linkage in **4** is reasonable compared to the e–e ring orientation in **3** which has less bulky methyl groups in place of the *tert*-butyl groups. In this case, the P—S linkage is a very weak one. The fact that derivatives **1** and **3** provide the first examples of diequatorial ring placement in pentaoxyphosphoranes suggests that the use of the electronegative trifluoroethoxy groups with their strong preference for axial positions of a TBP geometry is a primary factor.

The above discussion on comparative P—O bond lengths for seven- and eight-membered ring systems in oxyphosphoranes indicates that diequatorial ring arrangements for seven-membered rings are equally likely to exist. Further work should establish this point. The closeness in activation energy for the ring exchange process a–c $\rightleftharpoons$ e–e for the related spirocyclics G[1b] (12.2 kcal/mol) and H[1b] (12.9 kcal/mol) containing seven- and eight-membered rings, respectively, also suggests that isolation of a structure having a seven-membered ring in diequatorial positions of a TBP should be possible. If we use 7 kcal/mol as a maximum here for diequatorial ring formation relative to axial–equatorial placement as discussed above, then a steric term of approximately 5 kcal/mol may comprise the remainder of the activation barrier in G and H.

Ring Conformations

In order to describe the conformation of the eight-membered rings, it is useful to consider the ideal molecular symmetries. Compound **1** has crystallographic C_s symmetry, where the mirror plane passes through atoms P and C17 of the eight-membered ring (Figures 1 and 5a), which also has C_s symmetry. The conformation of this ring is chairlike in that atoms C17 and P lie on opposite sides of an imaginary plane defined by the remaining six ring atoms.

The idealized molecular symmetry of both **3** and **4** is also C_s and for these two compounds the eight-membered rings have pseudomirror planes which contain both the phosphorus and the sulfur atoms (Figure 6). The conformation of the eight-membered ring in **3** is essentially the same as that found in **1**, where phosphorus and sulfur are on opposite sides of the imaginary plane defined by the remaining six ring atoms. This "anti" arrangement is in keeping with the large P—S distance of 3.504 (3) Å. In the case of **4**, however, the eight-membered ring is boatlike, where the phosphorus and the sulfur atoms are the prow and stern of the boat. This "syn" arrangement is in keeping with the shorter P—S distance of 2.504 (3) Å.

While the diequatorial ring placement in **1** and **3** permits C_s ring symmetry, the axial–equatorial ring placement in **2** causes the ring to be twisted and a mirror plane passing through P and C17 is not possible (Figure 5b). The conformation of the ring in **2** can be viewed, when compared with that of **4**, as a very twisted boat with P and C17 in prow and stern or syn positions. The conformation of the ring in **2** is essentially the same as that found in the related tris(xylyloxy) compound F[20] with the identical bidentate ligand. The latter was described as a very distorted tub. For comparison, **2** may also be described as a distorted tub. Atoms O1, C11, C31, and C32 are coplanar to within ±0.012 (6) Å. The remaining ring atoms are displaced from this plane in the same direction by distances of 1.242 (2) Å (P), 1.039 (4) Å (O3), 0.426 (6) Å (C12), and 0.983 (6) Å (C17). This description also points out the syn disposition of P and C17.

It is interesting that the dihedral angles that the P—O_{eq}—C ring atoms make with the equatorial plane for **1** and **3** containing the rings in e–e orientations are not too far from 90°, the angle that would maximize the equatorial oxygen p orbital contribution to back-bonding with phosphorus.[14] This angle is 77.7 (2)° for **1** (with reference to the P—O2—C11 ring atoms) and 76.8 (5) and 76.1 (5)° for the less symmetric structure of **3**. These values refer to the P—O3—C31 ring atoms and P—O1—C11 ring atoms, respectively. Trippett[14] concluded that saturated six-membered rings would be stabilized in a boat conformation in an a–e orientation as it is the only ring form that meets the above cited dihedral angle criteria of 90°. In general, this ring conformation has been found to be the most prevalent[2,19–23] in the absence of additional constraints, e.g., hydrogen bonding.[17,18] For **2**, with an a–e orientation of the eight-membered ring, this dihedral angle is 85.0 (4)° for the P—O3—C31 ring atoms. The dihedral angle for the acyclic equatorial OCH_2CF_3 groups varies from 74.5 (3) and 89.6 (4)° for **2** to 83.6 (7)° for **3** and to 90° for **1**, encompassing a similar range of values as found for the dihedral angles of the ring atoms.

It might be expected to be more difficult to meet this dihedral angle criterion for diequatorial ring orientations as the ring size is reduced to a six-membered one

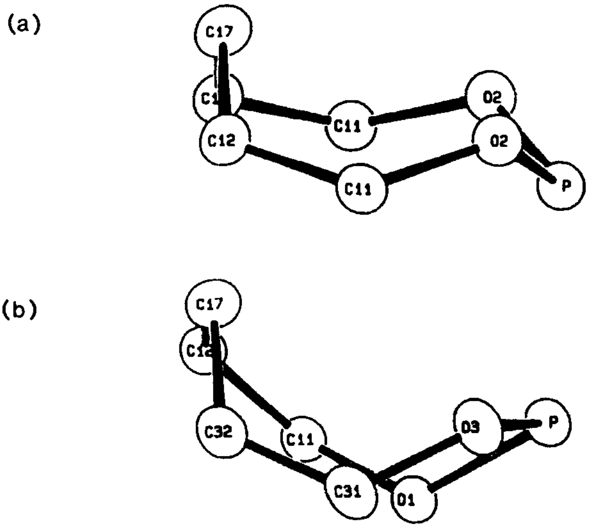


FIGURE 5 ORTEP plot showing the conformation of the eight-membered ring for (a) $CH_2[(t\text{-}Bu)MeC_6H_2O]_2P(OCH_2CF_3)_3$ (**1**) and (b) $CH_2(C_6H_4O)_2P(OCH_2CF_3)_3$ (**2**).

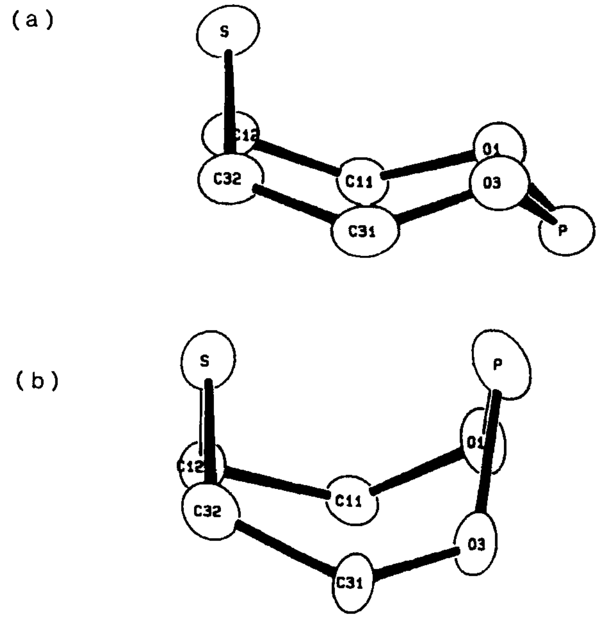


FIGURE 6 ORTEP plot showing the conformation of the eight-membered ring for (a) $S(Me_2C_6H_2O)_2$-$P(OCH_2CF_3)_3$ (**3**) and (b) $S[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)_3$ (**4**).

in a TBP due to a loss of conformational flexibility, even for a saturated one. The apparent operation of this back-bonding principle may contribute to the lack of any examples of the latter type thus far uncovered in a pentaoxyphosphorane.

NMR Behavior

^{19}F NMR spectra of **2** and **3** each show one triplet pattern showing equivalence of the CF_3 groups. The ^1H NMR patterns for **2** and **3** also exhibit one type of ethoxy proton, each giving a multiplet. These data are consistent with rapid pseudorotation which for **2** would conventionally involve a ring interchange among a–e sites[33] while the trifluoroethoxy groups likewise permute presumably via a Berry process.[29] ^{31}P chemical shifts show pentacoordination is retained in solution.

For **3**, which has the ring in diequatorial sites in the ground state (X-ray structure), the exchange process might be more complex. It could involve a Berry pseudorotational process e–e $\rightleftharpoons$ a–e which takes the ring through a square-pyramidal barrier state to a TBP with the ring located in a–e sites, or the sulfur atom might more firmly bond to phosphorus as in the pseudooctahedral structure of **4** and execute a more complex exchange process. The latter process in not speculated on in this paper. ^{31}P NMR chemical shifts which were obtained on the solid-state and $CDCl_3$ solutions for the sulfur-containing ring derivatives **3** and **4** indicate that the solid-state structures retain their coordination geometry in solution. For the e–e ring derivative **3**, the ^{31}P chemical shifts are -74.70 ppm (solid state) and -77.30 ppm ($CDCl_3$ solution), while for the pseudooctahedral structure **4**, the ^{31}P shifts are -82.94 ppm (solid state) and -82.44 ppm ($CDCl_3$ solution).

Unlike the less encumbered phosphoranes **2** and **3** that indicate rapid ligand exchange, NMR data of **1** and **4** indicate nonexchanging structures in solution at room temperature. Like that discussed for **4**, retention of the solid-state structure in solution for **1** is demonstrated by the upfield ^{31}P chemical shift, -78.8 ppm in $CDCl_3$, reported earlier.[24] In agreement with the ^{19}F NMR spectrum[24] (in $CDCl_3$) showing two types of fluorine atom environments, one that is assigned to the axial OCH_2CF_3 groups at -75.6 ppm (6 F) and the other at a slightly higher chemical shift that is assigned to the equatorial OCH_2CF_3 at -77.1 ppm (3 F), the ^1H NMR spectrum (in $CDCl_3$) contains two multiplets assignable to axial ethoxy protons (4.50 ppm, 4 H) and equatorial ethoxy protons (3.20 ppm, 2 H). In an analogous fashion, two signals are assigned to the bridging methylene group (at 3.50 and 4.10 ppm), thus indicating their nonequivalence. Presumably, steric interactions which would be encountered with the *tert*-butyl groups during the course of an exchange process serve to inhibit this action for **1**. In the case of the pseudooctahedral structure for **4**, as discussed above, the presence of the *tert*-butyl groups apparently contribute to destabilize the TBP structure having a diequatorial ring arrangement like that in the structure of the closely analogous derivative, **3**.

For **4** in $CDCl_3$ solution, ^{19}F signals at -75.68 ppm (6 F) and -75.98 (3 F) are consistent with the *fac* arrangement of trifluoroethoxy ligands as found in the solid-state structure. As mentioned, this solid-state pseudooctahedral structural form is indicated to be retained in solution from the almost identical ^{31}P chemical shifts observed for each of these states. The ^{31}P chemical shifts for **4** are about 5 ppm upfield from the average of the ^{31}P chemical shifts for the pentacoordinated compounds **1**–**3**. Hence, the ^{31}P data for **4** in solution are consistent with the presence of a weakly bonded P—S linkage at the sixth coordination site. Again the ^1H NMR spectrum is complimentary to the ^{19}F spectrum, indicating a nonexchanging entity. However, three proton multiplets are seen in the intensity ratio of 1:1:1, which corresponds to nonequivalence of each of the ethoxy groups.

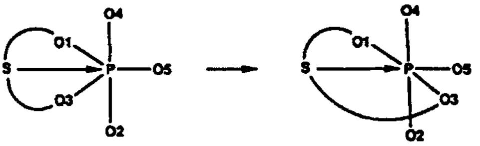
Speculation on an Interconversion Mechanism for 3 and 4

It is of interest to consider the way in which the geometries of the sulfur containing derivatives **3** and **4** might interconvert in solution. If the sulfur atom in **3** were to approach the phosphorus atom along the S → P vector (Figure 3), it would come into the coordination sphere of the phosphorus atom opposite O5, causing the O1—P—O3 angle to open up so that O1 and O3 would assume trans positions. In this case the tridentate ligand would assume a *mer* arrangement in the octahedral coordination sphere. Since the observed arrangement in **4** is *fac*, either a rearrangement of the acyclic ligands in **3** must occur simultaneously or the precursor to the octahedron has the bidentate ligand positioned axial–equatorially, as in **2**. Most likely, the *mer* arrangement is highly strained and as sulfur approaches phosphorus, ring rearrangement to a–e sites takes place giving a structural arrangement like **2** with sulfur in place of the methylene group (C17 of Figure 2). As sulfur approaches the phosphorus atom opposite O4, a simple opening up of the O2—P—O3 angle would result in a *fac* arrangement for the resulting tridentate ligand.

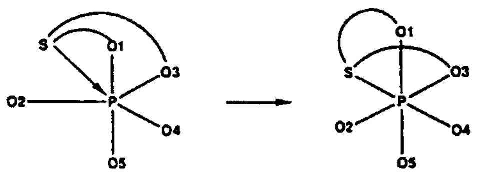
CONCLUSION

Interesting new oxyphosphoranes with eight-membered rings have been prepared exhibiting structural diversity. The first pentaoxyphosphoranes having diequatorially placed rings have been uncovered in TBP structures, **1** and **3**. Substituent modifications of the rings lead to axial–equatorial ring placement in **2** and a pseudo-hexacoordinated member, **4**. Ring sulfur to phosphorus coordination and steric effects due to *tert*-butyl groups appear to be the main factors promoting this structural versatility of ring orientation and coordination variation.

Approach of S from the diequatorial ring of 3 to P to give a *mer* structure:



Approach of S from an ax-eq ring to P to give a *fac* structure:



EXPERIMENTAL

Chemicals were obtained from Aldrich, Fisher Scientific, or Fluka and used without further purification. Solvents were of HPLC grade (Fisher Scientific). Further purification was done according to standard procedures.[34] Melting points are uncorrected.

^{1}H, ^{19}F, and ^{31}P NMR spectra were recorded on a Varian Associates XL-300 FT-NMR spectrometer. ^{1}H and ^{19}F chemical shifts are reported in ppm relative to tetramethylsilane and fluorotrichloromethane (external), respectively. Chemical shifts for ^{31}P NMR spectra were obtained by setting triphenyl phosphate ($CDCl_3$) at −18.0 ppm[35] and are referenced to 85% H_3PO_4 with negative shifts upfield. Solid-state ^{31}P NMR spectra for **3** and **4** were recorded on a Bruker 200 spectrometer and are referenced to $CaHPO_4$. All NMR spectra were obtained at 23 °C unless otherwise stated.

Tris(2,2,2-trifluoroethyl)phosphite and bis(2-hydroxyphenyl)methane were purchased from Aldrich. 2,2'-Methylenebis(4-methyl-6-*tert*-butylphenol),[36] 2,2'-thiobis(4,6-di-*tert*-butylphenol),[37] 2,2'-thiobis(4,6-dimethylphenol),[38] and *N*-chlorodiisopropylamine[39] were prepared by literature methods. All the reactions were carried out in a dry nitrogen atmosphere using standard Schlenk-type glassware.[40]

Syntheses. [2,2'-Methylenebis(o-phenyleneoxy)]tris(2,2,2-trifluoroethoxy)phosphorane, $CH_2(C_6H_4O)_2P(OCH_2CF_3)_3$ (**2**). To a mixture of tris(2,2,2-trifluoroethyl) phosphite (1.0 mL, 1.49 g, 4.53 mmol) and bis (2-hydroxyphenyl)methane (0.907 g, 4.53 mol) in diethyl ether (100 mL) maintained at −70 °C was added dropwise a solution of *N*-chlorodiisopropylamine (0.80 mL, 0.737 g, 5.44 mmol) in diethyl ether (30 mL) over a period of 20 min with continuous stirring. The reaction was brought to 25 °C and stirred at this temperature for 44 h. The amine hydrochloride was filtered and the filtrate was concentrated by passing a slow stream of nitrogen through it. Crystallization occurred after standing for 12 h and afforded **2**, mp 94–97 °C (yield 1.67 g, 70%). ^{1}H NMR ($CDCl_3$): 3.88 (s, 2 H, CH_2), 4.40 (m, 6 H, OCH_2CF_3), 6.9–7.4 (m, 8 H, *H*(Ar)). ^{19}F NMR ($CDCl_3$): −75.96(OCH_2CF_3). ^{31}P NMR($CDCl_3$): −78.33. Anal. Calcd for $C_{19}H_{16}F_9O_5P$: C, 43.34; H, 3.04. Found: C, 43.70; H, 3.19.

[2,2'-Thiobis(4,6-dimethyl-o-phenyleneoxy)]tris(2,2,2-trifluoroethoxy)phosphorane, $S(Me_2C_6H_2O)_2P(OCH_2CF_3)_3$ (**3**). The synthesis of **3** was similar to that for **2**. The quantities of materials used were as follows: tris(2,2,2-trifluoroethyl) phosphite (2 mL, 2.97 g, 9.06 mmol), 2,2'-thiobis(4,6-dimethylphenol) (2.48 g, 9.06 mmol), *N*-chlorodiisopropylamine (1.60 mL, 1.47 g, 10.87 mmol), and diethyl ether (200 mL). Colorless crystals of **3** were obtained from a Skelly-F solution, mp 142–145 °C(yield 4.35 g, 80%). ^{1}H NMR ($CDCl_3$): 2.26 (d, 12 H, CH_3), 4.60(br, 6 H, OCH_2CF_3), 7.00 (s, 2 H, *H*(Ar)), 7.39 (s, 2 H, *H*(Ar)). ^{19}F NMR ($CDCl_3$): −76.0 (OCH_2CF_3). ^{31}P NMR ($CDCl_3$): −77.30. Solid-state ^{31}P NMR (referenced to $CaHPO_4$): −74.70. Anal. Calcd for $C_{22}H_{22}F_9O_5SP$: C, 44.00; H, 3.67. Found: C, 44.07; H, 3.75.

[2,2'-Thiobis(4,6-di-tert-butyl-o-phenyleneoxy)]tris(2,2,2,-trifluoroethoxy)phosphorane, $S[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)_3$ (**4**).[41] **4** was prepared similar to **2**. The quantities used were as follows: tris(2,2,2-trifluoroethyl) phosphite (2 mL, 2.97 g, 9.06 mmol), 2,2'-thiobis(4,6-di-*tert*-butylphenol) (4.01 g, 9.06 mmol), *N*-chlorodiisopropylamine (1.60 mL, 1.47 g, 10.87 mmol), and diethyl ether (200 mL). Colorless crystals of **4** were obtained by concentrating a solution of a 1:3 mixture (40:120 mL) of diethyl ether and hexane, mp 190–193 °C (yield 5.57 g, 80%). ^{1}H NMR ($CDCl_3$): 1.35 (s, 18 H, $C(CH_3)_3$), 1.45 (s, 18 H, $C(CH_3)_3$), 4.10 (m, 2 H, OCH_2CF_3), 4.20 (m, 2 H, OCH_2CF_3), 4.58 (m, 2 H, OCH_2CF_3), 7.30–7.50 (m, 4 H, *H*(Ar)). ^{19}F NMR ($CDCL_3$): −75.98 (t, 3 F, OCH_2CF_3), −75.68 (t, 6 F, OCH_2CF_3). ^{31}P NMR ($CDCl_3$): −82.44. Solid-state ^{31}P NMR (referenced to $CaHPO_4$): −82.94. Anal. Calcd for $C_{34}H_{46}F_9O_5SP$: C, 53.13; H, 5.99. Found: C, 53.42; H, 6.27.

[2,2'-Methylenebis(4-methyl-6-tert-butyl-o-phenyleneoxy)]tris(2,2,2-trifluoroethoxy)phosphorane, $CH_2[(t\text{-}Bu)MeC_6H_2O]_2P(OCH_2CF_3)_3$ (**1**). The synthesis was reported previously[24] as was the ^{19}F and ^{31}P NMR in $CDCl_3$ solution. The ^{1}H NMR data are reported here from a $CDCl_3$ solution: 1.30 (s, 18 H, $C(CH_3)_3$), 2.30 (s, 6 H, CH_3), 3.20 (m, 2 H, OCH_2CF_3(equatorial)), 3.50 (m, 1 H, CH_2), 4.10 (m, 1 H, CH_2), 4.50 (m, 4 H, OCH_2CF_3 (axial)), 6.9–7.30 (m, 4 H, *H*(Ar)).

X-RAY EXPERIMENTAL SECTION

All X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda_{K\bar{\alpha}}$ = 0.71073 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental procedures have been described previously.[42] Crystals were mounted in thin-walled glass capillaries which were sealed with a flame as a protection against moisture. For **3** and **4**, epoxy was used as an adhesive. For **2** this was not possible since an apparent reaction with the epoxy caused the crystals to melt slowly. The crystal used was mechanically wedged into the capillary.

Data were collected using the θ–2θ scan mode with $3° \leq 2\theta_{Mo\,K\bar{\alpha}} \leq 43°$ ($+h, \pm k, \pm l$). In all cases data collection was halted after the 36–43° shell due to the precipitous fall off in intensity with increasing scattering angle. No corrections were made for absorption. The structures were solved by use of direct methods and difference fourier techniques and were refined by full-matrix least squares.[43]

All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs.

X-ray Study for $CH_2(C_6H_4O)_2P(OCH_2CF_3)_3$ (**2**). Crystals of **2** are colorless striated sheets with internal defects. They are deliquescent and form puddles when left exposed overnight. The crystal used for the study was cut to approximate dimensions of 0.50 × 0.50 × 0.55 mm.

Crystal Data for 2: $C_{19}H_{16}F_9O_5P$, triclinic space group $P\bar{1}$ (No. 2),[44] a = 9.712 (2) Å, b = 11.039 (3) Å, c = 12.521 (2) Å, α = 97.48 (2)°, β = 111.77 (1)°, γ = 110.56 (2)°, V = 1114 (1) Å^3, Z = 2, and $\mu_{\mathrm{Mo}\,K\bar{\alpha}}$ = 2.188 cm^{-1}. A total of 2541 independent reflections was measured. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included as fixed isotropic scatterers in ideal positions. The final agreement factors[45] were R = 0.050 and R_w = 0.051 for the 1771 reflections with I $\geq 3\sigma_I$.

X-ray Study for $S(Me_2C_6H_2O)_2P(OCH_2CF_3)_3$ (**3**). Crystals of **3** are colorless, frosted, and unfaceted. The irregular crystal used for the study was cut to approximate dimensions of 0.25 × 0.50 × 0.62 mm. The crystal experienced some degradation during data collection.

Crystal Data for 3: $C_{22}H_{22}F_9O_5SP$, triclinic space group $P\bar{1}$, a = 9.245 (2) Å, b = 12.464 (2) Å, c = 12.891 (2) Å, α = 76.77 (1)°, β = 74.69 (2)°, γ = 70.60 (1)°, V = 1335.0 (5) Å^3, Z = 2 and $\mu_{\mathrm{Mo}\,K\bar{\alpha}}$ = 2.649 cm^{-1}. A total of 3057 independent reflections was measured. A linear decay correction was applied (correction factors on I from 1.000 to 1.243). The structure was refined as described for **2**, except that the methyl hydrogen atoms were in regularized difference Fourier positions. The final agreement factors[45] were R = 0.075 and R_w = 0.079 for the 2135 reflections with $I \geq 3\sigma_I$.

X-ray Study for $S[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)_3$ (**4**). Crystals of **4** are polycrystalline masses of fused plates. The platelike crystal used for the X-ray study was cut to dimensions of 0.13 × 0.50 × 0.63 mm.

Crystal Data for 4: $C_{34}H_{46}F_9O_5SP$, triclinic space group $P\bar{1}$, a = 11.202 (2) Å, b = 11.307 (4) Å, c = 16.372 (8) Å, α = 99.66 (3)°, β = 94.39 (3)°, γ = 103.42 (2)°, V = 1974 (2) Å^3, Z = 2, and $\mu_{\mathrm{Mo}\,K\bar{\alpha}}$ = 1.936 cm^{-1}. A total of 4517 independent reflections was measured. Refinement was conducted as described for **2**. Large thermal parameters for several groups of atoms (*t*-Bu or trifluoromethyl) suggested disorder, but only one set of positions for the atoms in question could be resolved. The final agreement factors[45] were R = 0.076 and R_w = 0.075 for the 2673 reflections with $I \geq 3\sigma_I$.

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Supplementary Material Available: ORTEP plots of **2–4** showing thermal ellipsoids for all non-hydrogen atoms (Figures S1–S3) and tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **2** (Tables S1–S4), **3** (Tables S5–S8), and **4** (Tables S9–S12) (30 pages); listings of observed and calculated structure factors for **2–4** (15 pages). Ordering information is given on any current masthead page.

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