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Variations in Sulfur-Containing Eight-Membered Ring Conformations of Hydrogen-Bonded and Non-Hydrogen-Bonded Cyclic Phosphates and Octahedrally Coordinated Cyclic Pentaoxyphosphoranes[1,2]

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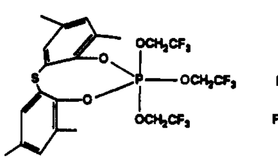
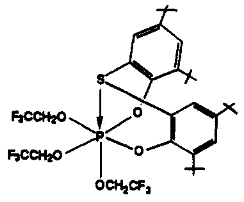
Treatment of tris(2,2,2-trifluoroethyl) phosphite with 2,2′-thiobis(4-methyl-6-*tert*-butylphenol) led to the monocyclic pentaoxyphosphorane $S[(t\text{-Bu})MeC_6H_2O]_2P(OCH_2CF_3)_3$ (**1**), by oxidative addition and to the cyclic phosphates, $S[(tert\text{-Bu})MeC_6H_2O]_2P(O)OCH_2CF_3$ (**2**) and $S[(t\text{-Bu})MeC_6H_2O]_2P(O)OCH_2CF_3{\cdot}S[(t\text{-Bu})MeC_6H_2OH]_2$ (**3**) by hydrolysis reactions. Each contained the same eight-membered ring with a sulfur atom bridging the aromatic components. X-ray analysis of **1** revealed a distorted octahedral geometry due to the presence of sulfur entering the coordination sphere. X-ray analysis showed a "free cyclic" phosphate formulation for **2** and a hydrogen bonded form for **3** as a result of the presence of an additional molecule of diol. ^1H, ^{19}F, and ^{31}P solution NMR spectra indicated the presence of non-hydrogen bonded forms for both **2** and **3**. The ring conformational variation found for **1**–**3** and related members indicates that steric properties of ring substituents and the type of bridging group, S and CH_2, act as important determinants accounting for the structural changes encountered from trigonal bipyramidal geometries with diequatorial and axial–equatorial ring placements to octahedral forms. Cyclic oxyphosphorane **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.120(2)$ Å, $b = 18.179(5)$ Å, $c = 17.034(3)$ Å, $\beta = 104.86(2)°$, and $Z = 4$. Cyclic phosphate **2** crystallizes in the monoclinic space group $C2/c$ with $a = 28.425(5)$ Å, $b = 11.807(2)$ Å, $c = 16.434(3)$ Å, $\beta = 108.89(1)°$, and $Z = 8$. Cyclic phosphate **3** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.180(2)$ Å, $b = 10.963(3)$ Å, $c = 23.709(6)$ Å, $\alpha = 81.31(2)°$, $\beta = 87.38(2)°$, $\gamma = 87.71(2)°$, and $Z = 2$. The final conventional unweighted residuals are 0.060 (**1**), 0.040 (**2**), and 0.072 (**3**).

Introduction

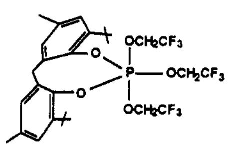
In our recent studies[3–5] of the inclusion of a sulfur-bridged eight-membered ring in pentaoxyphosphoranes, both penta- and hexacoordinated molecules are formed. These geometries are represented by a trigonal bipyramid (TBP) and an octahedron, respectively. The latter is formed as a result of P–S coordination. As the ring substituents are varied from methyl groups in A to *tert*-butyl groups for B, the structure goes from TBP to an octahedral representation.[3] Here the acyclic ligands are trifluoroethoxy groups (references are shown as superscripts). When methylene replaces sulfur as the bridging group in the cyclic component, alteration in the ring substituents from methyl and *tert*-butyl for C to the unsubstituted ring in D, causes the structure to go from a TBP with the ring in diequatorial sites (e–e),[3,6] as in A, to a TBP with the ring located in axial–equatorial positions (a–e).[3]



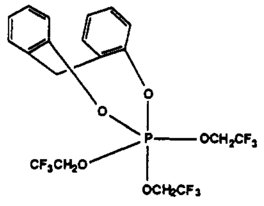
A[3]



B[3]

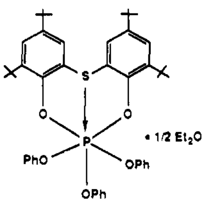


C[3,6]

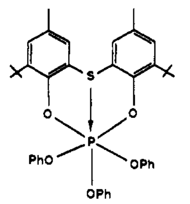


D[3]

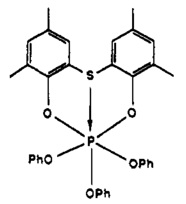
In a study of a series of related pentaoxyphosphoranes containing the less electronegative phenoxy ligands, the ring substituents were systematically varied from *tert*-butyl to methyl, E-G.[5] X-ray analysis showed hexacoordinated structures for all three derivatives. The presence of the less electronegative OPh groups which would have a reduced tendency toward apical occupancy in a TBP compared to OCH_2CF_3 groups has been advanced as a rationale for the lack of a TBP structure in this series.[5]



E[5]



F[5]



G[5]

Since the energy balance between these two structures, represented by A and B, must not be great, we have extended the present study to complete the series with OCH_2CF_3 analogous to that obtained with OPh groups, E–G. Thus the ring composition displayed for F was used to obtain **1** to ascertain if the resultant structural form would be TBP pentacoordinate or octahedral hexacoordinate.

[●] Abstract published in *Advance ACS Abstracts,* September 1, 1993.

(1) (a) Pentacoordinated Molecules. 97. (b) Part 96: Holmes, R. R.; Prakasha, T. K. *Phosphorus Sulfur and Silicon* **1993**, *80*, 1.

(2) Presented in part at the 205th National Meeting of the American Chemical Society, Denver, CO, March, 1993; INOR 99.

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(5) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 2690.

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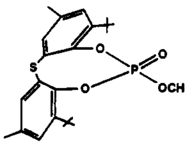
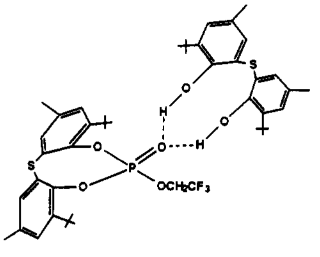
During the course of the investigation, considerable difficulty was encountered in obtaining **1** from the reaction of (2,2,2-trifluoroethyl) phosphite and 2,2′-thiobis(4-methyl-6-*tert*-butylphenol). It was found that hydrolysis was taking place, leading to the interesting cyclic phosphate products, **2** and **3**.



2



3

All three were characterized by ^{1}H, ^{19}F, and ^{31}P NMR spectroscopy and had their structures determined by X-ray studies. With these variations in ring environments from a hydrogen-bonded diol formation in **3** to three types of coordinated forms, i.e., in hydrogen-bonded and non-hydrogen-bonded phosphates, **3** and **2**, respectively, and in a pentaoxyphosphorane, **1**, it became of interest to compare their ring conformational properties as well as the structural features referred to above.

Experimental Section

Chemicals were obtained from Aldrich, Fisher Scientific, Eastman, or Fluka and used without further purification. Solvents were of HPLC grade (Fisher Scientific). Further purification was done according to standard procedures.[7]

^{1}H, ^{19}F, and ^{13}P NMR spectra were recorded on a Varian 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[8] (CDCl$_3$) at −18.0 ppm and are referenced to 85% H$_3$PO$_4$ with negative shifts upfield. All NMR spectra were obtained at 23 °C.

Tris(2,2,2-trifluoroethyl) phosphite was purchased from Aldrich. The sulfur-bridged diol, 2,2-thiobis(4-methyl-6-*tert*-butylphenol)[5] and *N*-chlorodiisopropylamine[9] were prepared by literature procedures. All the reactions were carried out in a dry dinitrogen atmosphere using standard Schlenk-type glassware.[10]

Syntheses. [Thiobis(4-methyl-6-*tert*-butyl-*o*-phenylene)dioxy)]tris(2,2,2-trifluoroethoxy)phosphorane, S[(*t*-Bu)MeC$_6$H$_2$O]$_2$P(OCH$_2$CF$_3$)$_3$ (1). To a mixture of tris(2,2,2-trifluoroethyl) phosphite (2 mL, 2.97 g, 9.06 mmol) and 2,2′-thiobis(4-methyl-6-*tert*-butylphenol) (3.25 g, 9.06 mmol) in 100 mL of diethyl ether maintained at −70 °C, was added dropwise a solution of freshly distilled *N*-chlorodiisopropylamine (1.60 mL, 1.47 g, 10.9 mmol) in diethyl ether (150 mL) over a period of 10–15 min. The reaction was brought gradually to 25 °C and stirred at this temperature for 56 h. After the filtration, the filtrate was concentrated by passing a slow stream of nitrogen over the solution. The resulting residue was extracted with a solution of ether and hexane (40 mL of each). Colorless crystals of **1** were obtained by a slow evaporation of the solution with use of a stream of nitrogen, mp 132 °C (yield 4.70 g, 76%). ^{1}H NMR (toluene-*d*$_8$, ppm): 1.40 (s, 18H, C(CH$_3$)$_3$), 1.96 (s, 6H, CH$_3$), 4.10 (m, 2H, OCH$_2$CF$_3$), 4.28 (m, 2H, OCH$_2$CF$_3$), 4.69 (m, 2H, OCH$_2$CF$_3$), 7.00–7.20 (m, 4H, H(Ar)). ^{19}F NMR (toluene-*d*$_8$, ppm): −75.40 (t, 3F, OCH$_2$CF$_3$), −75.14 (t, 6F, OCH$_2$CF$_3$). ^{31}P NMR (CDCl$_3$, ppm): −82.25. Anal. Calcd for C$_{28}$H$_{34}$F$_9$O$_5$SP: C, 49.12; H, 4.97. Found: C, 48.93; H, 5.16.

Table I. Crystallographic Data for Compounds **1–3**

	1	**2**	**3**
formula	C$_{28}$H$_{34}$O$_5$SF$_9$P	C$_{24}$H$_{30}$O$_4$SF$_3$P	C$_{46}$H$_{60}$O$_6$S$_2$F$_3$P
fw	684.60	502.54	861.08
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a, Å	11.120(2)	28.425(5)	9.180(2)
b, Å	18.179(5)	11.807(2)	10.963(3)
c, Å	17.034(3)	16.434(3)	23.709(6)
α, deg			81.31(2)
β, deg	104.86(2)	108.89(1)	87.38(2)
γ, deg			87.71(2)
V, Å^3	3328(2)	5218(3)	2355(2)
Z	4	8	2
T, °C	23 [illegible] 2	23 ± 2	23 ± 2
λ, Å	0.710 73	0.710 73	0.710 73
D_{calc}, g cm^{-3}	1.366	1.279	1.214
μ, cm^{-1}	2.211	2.244	1.946
R^a	0.060	0.040	0.072
$R_w{}^a$	0.078	0.057	0.098

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

[Thiobis(4-methyl-6-*tert*-butyl-*o*-phenylene)dioxy](2,2,2-trifluoroethoxy)phosphine Oxide, S[(*t*-Bu)MeC$_6$H$_2$O]$_2$P(O)OCH$_2$CF$_3$(2). To a mixture of tris(2,2,2-trifluoroethyl) phosphite (2.0 mL, 2.97 g, 9.06 mmol) and 2,2′-thiobis(4-methyl-6-*tert*-butylphenol (3.25 g, 9.06 mmol) in 100 mL of diethyl ether maintained at −70 °C was added dropwise a solution of *N*-chlorodiisopropylamine (1.60 mL, 1.47 g, 10.9 mmol) in diethyl ether (20 mL) over a period of 10–15 min. The reaction was brought gradually to 25 °C and stirred at this temperature for 46 h. After the filtration, the filtrate was concentrated by passing a slow stream of nitrogen over the solution to give the phosphine oxide (**2**), mp 200–202 °C (yield 1.36 g, 30%). ^{1}H NMR (CDCl$_3$, ppm): 1.37 (s, 18H, C(CH$_3$)$_3$), 2.29 (s, 6H, CH$_3$), 4.67 (m, 2H, OCH$_2$CF$_3$), 7.15–7.40 (m, 4H, H(Ar)). ^{19}F NMR (CDCl$_3$, ppm): −75.44 (t, OCH$_2$CF$_3$). ^{31}P NMR (CDCl$_3$, ppm): −13.20. Anal. Calcd for C$_{24}$H$_{30}$F$_3$O$_4$SP: C, 57.3; H, 5.9. Found: C, 56.3; H, 6.0.

[Thiobis(4-methyl-6-*tert*-butyl-*o*-phenylene)dioxy](2,2,2-trifluoroethoxy)phosphine Oxide-2,2′-Thiobis(4-methyl-6-*tert*-butylphenol), S[(*t*-Bu)MeC$_6$H$_2$O]$_2$P(O)OCH$_2$CF$_3$·S[(*t*-Bu)MeC$_6$H$_2$OH]$_2$ (3). Quantities used were as follows: tris(2,2,2-trifluoroethyl) phosphite, 2 mL, 2.97 g, 9.06 mmol; 2,2′-thiobis(4-methyl-6-*tert*-butylphenol), 6.50 g, 18.12 mmol; *N*-chlorodiisopropylamine, 3.20 mL, 2.95 g, 21.7 mmol; and diethyl ether, 250 mL. A procedure similar to that used for the synthesis of **2** was followed here, except that the reaction time was 90 h. Colorless crystals of **3** were obtained from a solution of ether and hexane (40 mL:60 mL); dec pt 120 °C, without melting (yield 2.0 g, 26%). ^{1}H NMR (CDCl$_3$, ppm): 1.38 (s, 18H, C(CH$_3$)$_3$), 1.40 (s, 18H, C(CH$_3$)$_3$), 2.19 (s, 6H, CH$_3$), 2.29 (s, 6H, CH$_3$), 4.70 (m, 2H, OCH$_2$CF$_3$), 6.60 (br, 2H, OH), 7.0–7.4 (m, 8H, H(Ar)). ^{19}F NMR (CDCl$_3$, ppm): −75.5 (t, ^3J(HF) = 9.2 Hz). ^{31}P NMR (CDCl$_3$, ppm): −13.20. Anal. Calcd for C$_{46}$H$_{60}$F$_3$O$_6$S$_2$P: C, 64.18; H, 6.97. Found: C, 64.00; H, 7.20.

X-ray Experimental Section

All X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite monochromated molybdenum radiation. Details of the experimental procedures have been described previously.[11]

Crystals were mounted in thin-walled glass capillaries which were sealed as a precaution against moisture sensitivity. Data were collected using the θ–2θ scan mode with $3° \leq 2\theta_{\text{Mo K}\bar{\alpha}} \leq 43°$. The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least-squares techniques.[12] All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs. Crystallographic data are summarized in Table I.

X-ray Study for S[(*t*-Bu)MeC$_6$H$_2$O]$_2$P(OCH$_2$CF$_3$)$_3$ (1). The colorless irregular approximately-cubic crystal used for the study was cut from a polycrystalline mass and had approximate dimensions of 0.45 × 0.50 × 0.55 mm. A total of 3823 independent reflections (+*h*, +*k*, ±*l*) were measured. Five standard reflections monitored after every 6000 s of exposure time showed serious, but reasonably isotropic, degradation of the crystal. A linear decay correction was applied (correction factors from 1.000 04 to 1.355 57 on *I*). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as fixed isotropic scatterers (ideal positions or regularized difference Fourier

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(7) (a) Riddick, J. A.; Bunger, W. B., Eds. Organic Solvents. In *Physical Methods in Organic Chemistry*; Weissberger, Wiley Interscience: New York, 1970, Vol. II. (b) Vogel, A. I. *Textbook of Practical Organic Chemistry*; Lingman: London, 1978.

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(12) The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$.

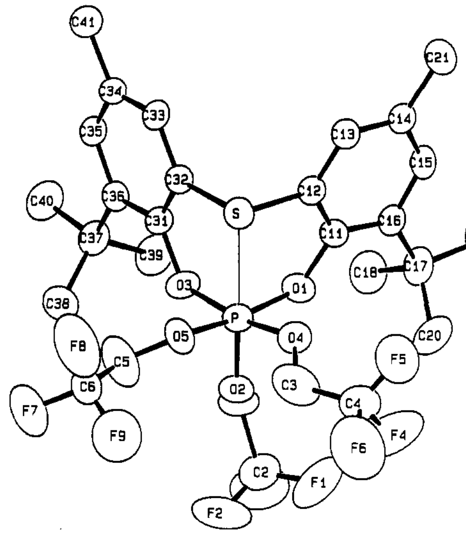


Figure 1. ORTEP plot of $S[(t\text{-}Bu)MeC_6H_2O]_2P(OCH_2CF_3)_3$ (**1**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

positions for methyl group H atoms). The final refinement was based on the 2229 reflections with $I \geq 3\sigma_I$.

X-ray Study for $S[(t\text{-}Bu)MeC_6H_2O]_2P(O)OCH_2CF_3$(2). The colorless crystal used for the study was cut from a highly-striated lath and had dimensions of 0.40 × 0.43 × 0.50 mm. A total of 2987 independent reflections ($+h, +k, \pm l$) were measured. An absorption correction based on ψ scans was applied (relative transmission factors from 0.9813 to 0.9998 on I). Refinement carried out as for compound **1** was based on 2256 observed reflections.

X-ray Study for $S[(t\text{-}Bu)MeC_6H_2O]_2P(O)OCH_2CF_3{\cdot}S[(t\text{-}Bu)MeC_6H_2OH]_2$ (3). The colorless crystal used for the study was cut from a larger plate and had approximate dimensions of 0.25 × 0.38 × 0.50 mm. A total of 5404 independent reflections ($+h, \pm k, \pm l$) were measured. During solution of the structure it became apparent that the CF_3 group was disordered. This disorder was described as well as possible with six atoms in partial occupancies. These six atoms were refined isotropically, while the rest of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the four *t*-Bu groups and aromatic hydrogen atoms were included in the refinement as fixed isotropic scatterers in ideal positions. Hydrogen atoms of the four methyl groups appeared to be rotationally disordered and were omitted from the refinement. The two hydroxyl hydrogen atoms (H5 and H6) appeared clearly on a difference Fourier synthesis and were included, fixed in these positions, as isotropic scatterers. The final refinement was based on the 3278 reflections with $I \geq 3\sigma_I$.

Results

The atom labeling schemes for **1** and **2** are given in the ORTEP plots of Figures 1 and 2, while the atom labeling scheme for **3** is given in Figures 3 and 4. Selected distances and angles for **1**–**3** are given in Tables II–IV, respectively, while selected atomic coordinates are given in Tables VIII–X. For all three compounds, complete tabulations of atomic coordinates, anisotropic thermal parameters, distances and angles, and hydrogen atom parameters are provided as supplementary material.

Discussion

Synthesis and Basic Structure. The reactions leading to the cyclic phosphates **2** and **3** differed in two respects: in the mole ratio of the phosphite and diol reactants used, being 1:1 for the formation of **2**, and 1:2 for **3**, respectively, and also in the reaction time, which was 46 h for **2**. It was lengthened to 90 h for **3**. The elemental analysis indicated that the products were phosphates. A ^{31}P chemical shift of −13.20 ppm for each, in the tetracoordinate region, confirmed the phosphate formulation. Thus, **2** and **3** formed as a result of hydrolysis apparently due to moisture in the *N*-chlorodiisopropylamine used to take up hydrogen chloride.

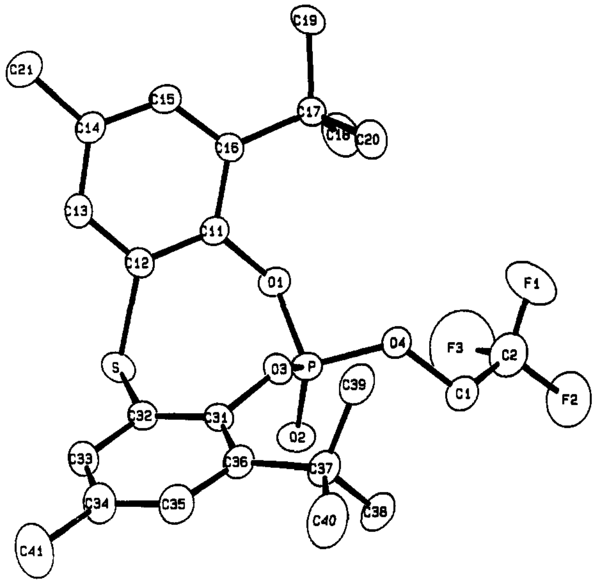
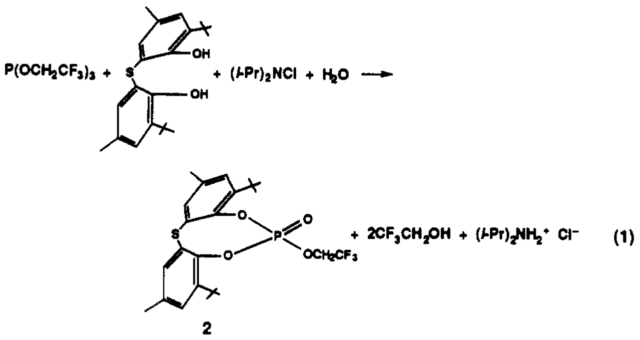


Figure 2. ORTEP plot of $S[(t\text{-}Bu)MeC_6H_2O]_2P(O)OCH_2CF_3$ (**2**), with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Yields were in the range 25–30%. The reaction is shown for the synthesis of **2**, eq 1.



However, with rigorous exclusion of moisture using $(i\text{-}Pr)_2NCl$ that was freshly distilled over molecular sieves, the same reactants in a mole ratio of 1:1, which were heated for 56 h in the presence of *N*-chlorodiisopropylamine, yielded the cyclic pentaoxyphosphorane **1** in 76% yield. The ^{31}P chemical shift of −82.2 ppm in the higher valent region confirmed that the desired product was obtained. The reaction followed the course previously used to prepare members of this class of hypervalent compounds, that of oxidative addition of a phosphite with a diol.[3–6]

Although the ^{31}P NMR spectra showed only one signal for **2** and **3**, in each case at −13.20 ppm, the ^1H NMR solution data and microanalysis confirmed the formation of two different compounds. Subsequent X-ray analysis agreed with this interpretation and established the structure of **2** and **3** as the cyclic phosphates depicted in the Introduction with **3** having an additional mole of the eight-membered ring diol hydrogen bonded to the phosphoryl oxygen atom of the phosphate moiety.

The fact that identical ^{31}P signals were obtained for **2** and **3** implies that in solution, the hydrogen bonded ring component is dissociated from the cyclic phosphate for **3**. The ^1H NMR spectra for **3** is a composite of the proton spectra for **2** and the spectrum expected for the eight-membered ring diol. The broad signal at 6.60 ppm is assigned to the hydroxyl protons of the diol. Each phosphate exhibits one ^{19}F signal at −75.5 ppm in agreement with the above interpretation.

For the cyclic oxyphosphorane **1**, the ^1H NMR spectrum exhibited the same general shifts for the aromatic ring attachment as did **2** and **3**. However, three different signals, 4.10, 4.28, and

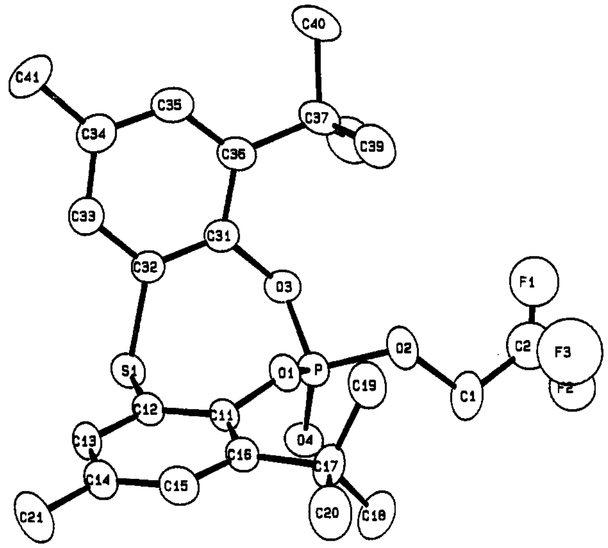


Figure 3. ORTEP plot of the S[(*t*-Bu)MeC$_6$H$_2$O]$_2$P(O)OCH$_2$CF$_3$ fragment in **3** with thermal ellipsoids at the 30% probability level. Only one set of positions for the disordered CF$_3$ group is shown. Hydrogen atoms are omitted for clarity.

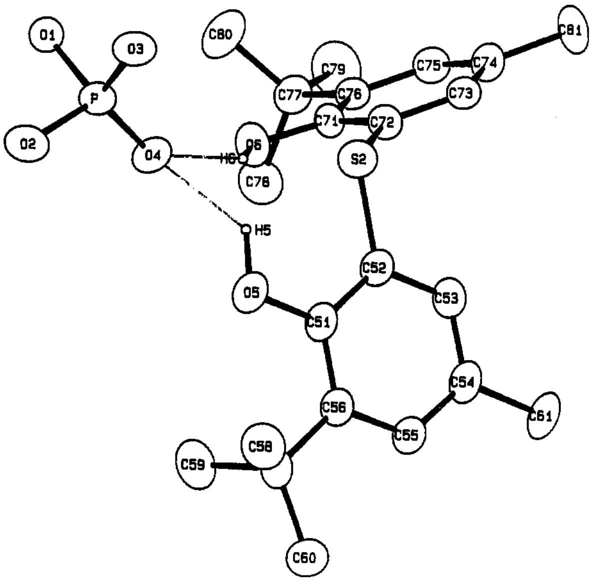


Figure 4. ORTEP plot of the S[(*t*-Bu)MeC$_6$H$_2$OH]$_2$ fragment in **3** with thermal ellipsoids at the 30% probability level. Hydrogen atoms, except for those of the hydroxyl groups which are shown as spheres of arbitrary radius, are omitted for clarity. The PO$_4$ fragment is included to show the hydrogen-bonding interactions (narrow lines).

4.69 ppm, in equal intensities, were present for the CH$_2$ protons, indicating three different OCH$_2$CF$_3$ groups. The ^{19}F pattern showed two resonances, at −75.14 and −75.40 ppm with a relative intensity of 2:1, respectively. Both the ^{1}H and ^{19}F spectra are equally consistent with a TBP structure or an octahedral representation formed as a result of P–S coordination. It is possible that the lack of agreement between the proton and fluorine spectra in this region is due to the closeness of two of the fluorine resonances.

As we observed previously, the ^{31}P chemical shift is a useful but not definitive criterion for distinguishing between five- and six-coordinated phosphorus compounds containing a core unit of SPO$_5$ bonds.[1b] We have noted that inclusion of sulfur in the coordination sphere exerts a marked downfield shift which may counterbalance the effect of an increase in coordination number.[3] For comparable formulations, for example, the ^{31}P shift for TBP **A** is −77.30 ppm[3] while that for octahedral **B** is −82.44 ppm.[3] The latter compares with −82.2 ppm for **1**. Thus, the ^{31}P shift for **1** is closer to that exhibited by the octahedral form for **B**.

Table II. Selected Distances (Å) and Angles (deg) for S[(*t*-Bu)MeC$_6$H$_2$O]$_2$P(OCH$_2$CF$_3$)$_3$ (**1**)

	Distances		
P–S	2.363(2)	P–O5	1.656(5)
P–O1	1.698(5)	S–P	2.363(2)
P–O2	1.615(4)	S–C12	1.755(6)
P–O3	1.694(4)	S–C32	1.759(5)
P–O4	1.638(4)		
	Angles		
S–P–O1	86.4(2)	O2–P–O3	92.0(2)
S–P–O2	179.3(2)	O2–P–O4	96.9(2)
S–P–O3	87.6(2)	O2–P–O5	95.1(2)
S–P–O4	83.5(2)	O3–P–O4	170.4(2)
S–P–O5	84.3(2)	O3–P–O5	92.0(2)
O1–P–O2	94.2(2)	O4–P–O5	90.9(2)
O1–P–O3	88.4(2)	P–S–C12	92.6(2)
O1–P–O4	87.3(2)	P–S–C32	92.8(2)
O1–P–O5	170.7(2)	C12–S–C32	102.3(3)
P–O1–C11	123.5(4)	P–O2–C1	127.8(5)
P–O3–C31	124.4(3)	P–O4–C3	129.7(5)
P–O3–C5	123.3(4)		

Table III. Selected Distances (Å) and Angles (deg) for S[(*t*-Bu)MeC$_6$H$_2$O]$_2$P(O)CH$_2$CF$_3$ (**2**)

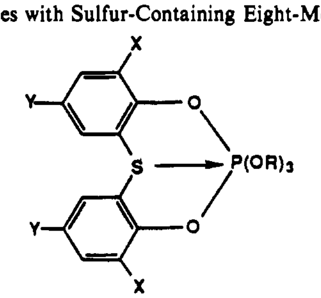
	Distances		
P–O1	1.572(2)	P–O4	1.576(2)
P–O2	1.446(3)	S–C12	1.772(3)
P–O3	1.571(2)	S–C32	1.780(3)
C11–C12	1.401(4)	P–S	3.163(1)
C31–C32	1.385(4)		
	Angles		
O1–P–O2	117.9(1)	O2–P–O4	113.7(1)
O1–P–O3	104.7(1)	O3–P–O4	100.7(1)
O1–P–O4	98.6(1)	C12–S–C32	104.8(2)
O2–P–O3	118.3(1)	P–O1–C11	129.9(2)
P–O3–C31	129.0(2)	P–O4–C1	124.1(3)
O1–C11–C12	120.1(3)	O3–C31–C32	119.0(2)
C11–C12–S	121.0(2)	C31–C32–S	123.3(2)

Table IV. Selected Distances (Å) and Angles (deg) for S[(*t*-Bu)MeC$_6$H$_2$O]$_2$P(O)CH$_2$CF$_3$·S[(*t*-Bu)MeC$_6$H$_2$OH]$_2$ (**3**)

	Distances		
S1–P	3.120(3)	S1–C12	1.781(8)
P–O1	1.556(5)	S1–C32	1.773(8)
P–O2	1.572(6)	S2–C52	1.782(7)
P–O3	1.581(6)	S2–C72	1.772(8)
P–O4	1.449(5)	O3–C31	1.403(9)
O1–C11	1.408(9)	C11–C12	1.38(1)
C31–C32	1.38(1)	O1–O3	2.506(7)
O4–O5	2.896(7)	O5–O6	4.159(8)
O4–O6	2.963(7)	O4–H5	2.061
		O4–H6	2.013
	Angles		
O1–P–O2	99.2(3)	O2–P–O4	112.7(3)
O1–P–O3	106.0(3)	O3–P–O4	117.2(3)
O1–P–O4	119.0(3)	C12–S1–C32	103.0(3)
O2–P–O3	99.5(3)	C52–S2–C72	103.5(3)
P–O1–C11	133.0(4)	P–O2–C1	123.9(6)
P–O3–C31	130.0(5)	O3–C31–C32	119.3(6)
O1–C11–C12	118.7(6)	C31–C32–S1	122.0(6)
C11–C12–S1	121.9(6)	O5–C51–C52	120.4(6)
C51–C52–S2	118.8(5)	O6–C71–C72	119.9(6)
C71–C72–S2	121.0(5)	P–O4–O5	131.0(3)
		P–O4–O6	134.7(3)

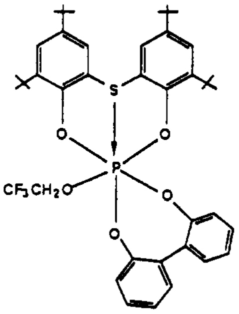
Subsequent X-ray analysis revealed that **1** has a distorted octahedral structure close to that described for **B**[3] in the Introduction. The P–S distance of 2.362(2) Å is the shortest so far observed for this class of hexacoordinated phosphorus compounds (Table V) and approaches the sum of the single bond covalent radii of 2.14 Å. The conformation of the eight-membered ring (Figure 5a) is nearly symmetrical *syn*; that is both phosphorus and sulfur are on the same side of the plane defined by the rest

Table V. Selected Parameters for Pentaoxyphosphoranes with Sulfur-Containing Eight-Membered Rings



	X	Y	R	% octa[a]	P–S, Å	O–P–O, deg[b]	C–S–C, deg
G[5]	Me	Me	Ph	44.1	2.880(1)	89.1(1)	100.2(1)
F[5]	*t*-Bu	Me	Ph	56.8	2.744(2)	89.0(1)	99.1(2)
E[5]	*t*-Bu	*t*-Bu	Ph	60.8	2.640(2)	88.7(2)	100.4(2)
B[3]	*t*-Bu	*t*-Bu	CH_2CF_3	64.5	2.504(3)	89.6(3)	102.9(4)
1	*t*-Bu	Me	CH_2CF_3	69.4	2.362(2)	88.4(2)	102.3(3)
H[4,c]	*t*-Bu	*t*-Bu	CH_2CF_3,[e]	70.8	2.373(5)	88.3(4)	103.7(5)
A[3,d]	Me	Me	CH_3CF_3		3.504(3)	117.5(3)	103.4(4)

[a] Percent displacement from an ideal square pyramid (as defined in the text) to an octahedron. [b] Values for O–P–O ring angle. [c] **H** is a bicyclic derivative.[4]



[d] **A** has the ring (e–e) in a TBP with a nonbonding P–S distance. [e] 2,2′-biphenylene.

Table VI. P–O Distances (Å) in Cyclic Hexacoordinated Pentaoxyphosphoranes

	P–O (ring)	P–O, acyclic (*cis* to P–S)	P–O, acyclic (*trans* to P–S)
1	1.698(5)	1.638(4)	1.615(4)
	1.694(4)	1.656(5)	
B[3]	1.681(5)	1.663(7)	1.640(7)
	1.684(6)	1.649(6)	
E[5]	1.676(3)	1.649(3)	1.613(3)
	1.689(3)	1.652(3)	
F[5]	1.681(3)	1.655(2)	1.612(3)
	1.673(2)	1.634(3)	
G[5]	1.656(2)	1.643(2)	1.597(2)
	1.680(1)	1.644(2)	
Av[a]	1.681(3)	1.648(4)	1.615(2)
H[4,b]	1.699(8)[c]	1.655(8)	1.630(8)[d,e]
	1.711(8)[c]		
	1.661(8)[d,f]		

[a] The average values excluded P–O distances for **H**. [b] **H** is a bicyclic derivative. See footnote *c* to Table V. [c] These P–O distances refer to the eight-membered ring of **H**. [d] These distances refer to P–O bonds of the seven-membered ring of **H**. [e] This P–O ring bond is *trans* to the P–S bond. [f] This P–O ring bond is *cis* to the P–S bond.

of the ring atoms, with a pseudo mirror plane passing through the phosphorus and sulfur atoms.

As before,[3–5] if we neglect the position of the sulfur atom, the five remaining oxygen atoms of **1** are located in a square pyramidal (SP) arrangement with the phosphorus atom displaced from the base defined by O1, O4, O5, and O3 toward the remaining apical oxygen atom O2 where O2 is situated *trans* to sulfur. The four atoms which form the basal plane are coplanar to within the limits of the error, ±0.003(4) Å, with the phosphorus atom displaced from this plane by a distance of 0.132(2) Å in a direction toward the apical O2 atom.

We have found that the geometry of this class of cyclic oxyphosphoranes lies along a trajectory connecting a SP with an octahedron. The displacement toward the octahedron is 69.4% for **1** and varies over the range of 44% to 71% for the compounds studied so far (Table V). A fairly linear correlation is found between a decrease in the P–S distance and the approach of the phosphorus atom to the basal plane of the SP.

In the calculation of the percent displacement from a square pyramid toward an octahedron, Table V, an average P–O distance over this class of cyclic pentaoxyphosphoranes was used, 1.665 Å (Table VI), to obtain the distance of the phosphorus atom from the basal plane of "ideal" square pyramid, 0.431 Å. In general, for phosphoranes,[13,14] as with other main group elements assuming this geometrical form, the *trans* basal angle is 150.[15]

The values of P–O bond lengths for hexacoordinated pentaoxyphosphoranes with sulfur containing eight-membered ring systems (Table VI) follow the order P–O (ring) > P–O (acyclic, *cis* to P–S) > P–O (acyclic, *trans* to P–S). This is the order expected. Due to P–S coordination, ring strain is expected in forming two five-membered rings causing a bond lengthening effect. Here the average distance is 1.681 Å for the P–O bonds in the eight-membered rings. For comparison, structure **A**, which lacks P–S coordination and contains this ring system, has P–O ring bond distances of 1.614 and 1.620 Å.[3] Although the ring for **A** is positioned diequatorially in a TBP of lower coordination number, the equatorial P–O bond to the OCH_2CF_3 ligand has a similar value, 1.620 Å, thus supporting little strain for the ring in **A**. The seven-membered ring in the bicyclic hexacoordinated phosphorane, **H**, which contains the eight-membered ring with P–S coordination, also exhibits a shorter distance.[4] The P–O ring bond of the seven-membered ring *cis* to the P–S linkage is 1.661 Å in length. This compares with 1.699 and 1.711 Å for related P–O bonds of the eight-membered ring.

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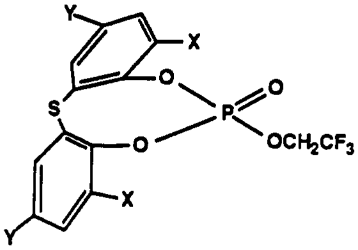
(13) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **99**, 3318 (1977).

(14) Holmes, R. R. *Pentacoordinated Phosphorus—Structure and Spectroscopy, Vol. 1*, ACS Monograph 175, American Chemical Society: Washington, DC, 1980.

(15) R. R. Holmes. Five-Coordinated Structures. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed., John Wiley and Sons: New York, 1984; Vol. 32, pp 119–235.

Table VII. Selected Distance and Angle Parameters for Phosphates with Sulfur-Containing Eight-Membered Rings



	X	Y		P–O, Å P–O, Å ring	acyclic	P–S, Å	O–P–O, deg ring	C–S–C, deg
I$_a$[4]	*t*-Bu	*t*-Bu	*anti*	1.578(8) 1.581(8)	1.545(9)	3.499(5)	107.1(5)	106.3(6)
I$_s$[4]	*t*-Bu	*t*-Bu	*syn*	1.579(2) 1.574(2)	1.582(2)	3.166(1)	104.0(1)	104.1(1)
2	*t*-Bu	Me	*syn*	1.572(2) 1.571(2)	1.576(2)	3.163(1)	104.7(1)	104.8(2)
3	*t*-Bu	Me	*syn*	1.556(5) 1.581(6)	1.572(6)	3.120(3)	106.0(3)	103.0(3)
			av	1.574(4)	1.569(5)	3.150(3)[a]	104.9(3)[a]	104.0(3)[a]

[a] The average values exclude the phosphate with the *anti* ring from **I**$_a$.

Table VIII. Selected Atomic Coordinates in Crystalline $S(t\text{-}BuMeC_6H_2O)_2P(OCH_2CF_3)_3$ (**1**)[a]

atom[b]	*x*	*y*	*z*	B_{equiv},[c] Å^2
S	0.6385(2)	0.10426(9)	1.00395(9)	5.03(4)
P	0.6633(2)	0.1779(1)	1.1213(1)	5.19(4)
O1	0.7617(4)	0.2299(2)	1.0831(2)	5.7(1)
O2	0.6799(4)	0.2273(2)	1.2022(2)	6.3(1)
O3	0.7859(4)	0.1239(2)	1.1661(2)	5.2(1)
O4	0.5491(4)	0.2253(2)	1.0637(3)	6.7(1)
O5	0.5633(4)	0.1196(2)	1.1446(2)	6.4(1)
C1	0.7889(7)	0.2556(4)	0.2512(4)	7.9(2)
C3	0.4394(8)	0.2410(6)	1.0743(5)	12.6(3)
C5	0.5842(8)	0.0846(5)	1.2181(5)	10.2(3)
C11	0.7658(5)	0.2276(3)	1.0040(3)	4.5(1)
C12	0.7124(5)	0.1692(3)	0.9561(3)	4.5(1)
C31	0.8262(5)	0.0653(3)	1.1294(3)	4.4(1)
C32	0.7623(5)	0.0459(3)	1.0509(3)	4.4(1)

[a] Numbers in parentheses are estimated standard deviation. [b] Atoms are labeled to agree with Figure 1. [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 IX. Selected Atomic Coordinates in Crystalline $S(t\text{-}BuMeC_6H_2O)_2P(O)OCH_2CF_3$ (**2**)[a]

atom[b]	*x*	*y*	*z*	B_{equiv},[c] Å^2
S	0.83635(3)	0.09026(8)	0.04482(5)	3.74(2)
P	0.89881(3)	0.21429(8)	0.21639(6)	3.60(2)
O1	0.84730(7)	0.2756(2)	0.1772(1)	3.74(5)
O2	0.93449(7)	0.2239(2)	0.1709(2)	4.70(6)
O3	0.88531(7)	0.0927(2)	0.2408(1)	3.47(5)
O4	0.91604(7)	0.2729(2)	0.3075(2)	4.76(6)
C1	0.9654(1)	0.3110(3)	0.3501(3)	5.6(1)
C11	0.7995(1)	0.2301(3)	0.1451(2)	3.10(7)
C12	0.7894(1)	0.1428(3)	0.0842(2)	2.99(7)
C31	0.8882(1)	−0.0120(3)	0.2014(2)	3.18(7)
C32	0.8635(1)	−0.0247(3)	0.1142(2)	3.36(7)

[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 $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

The remainder of the P–O distances in Table VI refer to acyclic P–O bonds that are basal (*cis* to P–S) or apical (*trans* to P–S) values with reference to a square pyramid described above. In this geometry, the basal distances are longer than apical ones for phosphorus[13,14] and other main group elements.[15] It is noted that, as expected, all the P–O distances for the hexacoordinated derivatives of Table VI are longer than those for the tetracoordinated compounds with the same ring system as listed in Table VII.

Structural Comparisons

Pentacoordinate and Hexacoordinate Forms. Approximate representations of the structures of A–D are shown here where the aromatic ring components and acyclic ligands are drawn in on ORTEP plots of the skeletal ring conformations. The ring representation for **1** is not appreciably different for **B** (*cf.* Figure 5c). The TBP structure for the cyclic oxyphosphorane A has the diequatorially oriented eight-membered ring in a chairlike conformation with a P–S distance of 3.504(3) Å.[3] By contrast, the distorted octahedral structure for **B** has the analogous ring in a boatlike conformation with a P–S distance of 2.504(3) Å.[3] By flipping the phosphorus atom from its *anti* position in A to a *syn* orientation in **B**, i.e., upward in the drawing here, the principal change is executed to convert one geometry to the other. In doing so, it is evident that bulkier groups attached to the aromatic ring at the 6-position would tend to favor the structure for **B** as this structure relieves a steric interaction with the acyclic group *trans* to the sulfur atom. The steric effect arises between the *tert*-butyl substituted on the ring and the adjacent OCH_2CF_3 ligand. The latter ligand becomes an axial ligand in the TBP of A. This offers a rationale for the structure of **1**, like **B**, that contains *tert*-butyl groups at the same 6 position on the aromatic ring. The implication is that if a compound analogous to **1** was synthesized that had the methyl and *t*-butyl groups reversed in

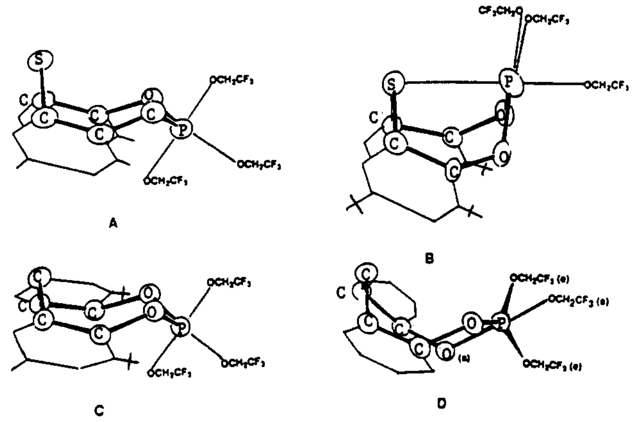


Table X. Selected Atomic Coordinates in Crystalline $S(t\text{-}BuMeC_6H_2O)_2P(O)OCH_2CF_3{\cdot}S(t\text{-}BuMeC_6H_2OH)_2$ (3)[a]

atom[b]	x	y	z	B_{equiv},[c] Å^2
S1	0.4623(2)	0.3701(2)	0.18247(8)	4.96(5)
S2	0.4240(2)	0.0919(2)	0.30527(8)	4.79(5)
P	0.7783(2)	0.2540(2)	0.18673(9)	4.51(5)
O1	0.7886(5)	0.3933(4)	0.1619(2)	4.4(1)
O2	0.9377(6)	0.2090(5)	0.1711(2)	6.3(1)
O3	0.6917(6)	0.1940(5)	0.1424(2)	5.1(1)
O4	0.7381(6)	0.2196(5)	0.2467(2)	5.3(1)
O5	0.7226(6)	−0.0201(5)	0.3169(2)	5.9(1)
O6	0.5424(5)	0.3292(5)	0.3299(2)	5.2(1)
C1	1.037(1)	0.151(1)	0.2117(5)	10.8(3)
C11	0.7159(7)	0.5007(7)	0.1760(3)	3.9(2)
C12	0.5656(8)	0.5053(7)	0.1790(3)	4.3(2)
C31	0.5997(8)	0.2494(7)	0.0995(3)	4.5(2)
C32	0.4891(8)	0.3306(7)	0.1129(3)	4.3(2)
C51	0.6332(8)	−0.0527(6)	0.3641(3)	4.2(2)
C52	0.4909(8)	−0.0053(6)	0.3664(3)	4.0(2)
C71	0.3993(7)	0.3173(7)	0.3445(3)	3.8(2)
C72	0.3278(8)	0.2127(7)	0.3345(3)	4.1(2)

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

their positions, the structure represented by **A** would be expected. This has yet to be accomplished.

When methylene groups are at the bridging position in place of sulfur in the eight-membered ring system, it is found that the unsubstituted ring present in **D** has a TBP structure[3] with the ring in a boatlike conformation, whereas *tert*-butyl substitution in the 6-position for **C** results in a TBP with the ring conformation in a chairlike *anti* orientation,[3,6] similar to **A**. One might expect, on the basis of the discussion of steric effects between structures of **A** and **B**, that **D** would have assumed the structural form of **C**. However, there are major differences to consider. For one, there is no interaction that brings the bridging methylene group close to the phosphorus atom. Hence there is no increase in coordination geometry. Also it is seen that in comparison to **C** the phosphorus atom movement for **D** is relatively slight (to a so-called half-chair conformation) in bringing about the major structural change between these two compounds. In so doing, the diequatorial ring in the TBP for **C** becomes axial–equatorial in the TBP for **D**. A further effect is the much larger angle at the bridging carbon atom compared to that when sulfur is so located.

For the sulfur bridging systems in **A** and **B**, the C–S–C angles are 103.4 and 102.9°, respectively.[3] For the methylene bridging systems in **C** and **D**, the C–C–C angles are 118.9[3,6] and 110.4°,[3] respectively. As this angle becomes larger, the aromatic rings move toward a more planar ring arrangement. The consequence of this is that the *tert*-butyl group in the 6 position moves in a direction that is out of the way of any steric interaction with the axial OCH_2CF_3 ligand in **C**. The smaller conformational ring change and the bridge angle expansion when a methylene group is present both operate to reduce the significance of a steric effect of the kind under discussion. Thus, it is difficult to predict for the phosphoranes with the methylene containing eight-membered rings which orientation is structurally favored as a result of ring substitution since the energy differences are expected to be considerably smaller than that between TBP **A** and octahedral **B**, which contains ring sulfur atoms. From the structures obtained, however, the implication is that the energy is lower for the TBP ring arrangement encountered for **D** compared to **C**.

Tetracoordinate Forms. It is of interest here to note that the same ring conformations present in **C** (which is similar to **A**) and **D** were found in the tetracoordinated cyclic phosphate, **I**.[4] Two different crystalline modifications were synthesized, a monoclinic form with the ring in an *anti* or chairlike conformation ($\mathbf{I_a}$), very similar to **C** or **A**, and a triclinic form with the ring in a *syn* or

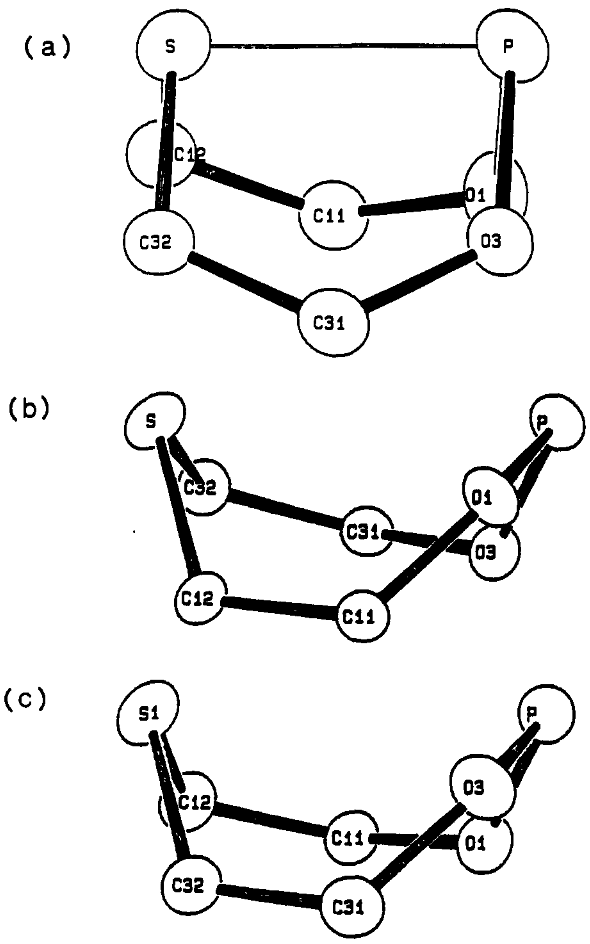
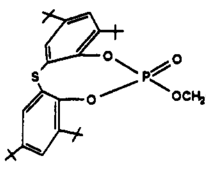
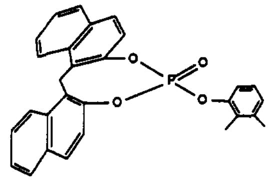


Figure 5. ORTEP plots showing the conformations of the eight-membered rings in (a) $S[(t\text{-}Bu)MeC_6H_2O]_2P(OCH_2CF_3)_3$ (**1**), (b) $S[(t\text{-}Bu)MeC_6H_2O]_2P(O)OCH_2CF_3$ (**2**), and (c) the $S[(t\text{-}Bu)MeC_6H_2O]_2P(O)OCH_2CF_3$ fragment in **3**.



I[4]



J[17]

boatlike conformation ($\mathbf{I_s}$), analogous to that for **D**.[16] Thus, packing forces are sufficient to stabilize each of these ring arrangements. However, steric requirements of the type discussed above would be less in the tetracoordinate structure. In a related cyclic phosphate, having a methylene bridge in place of sulfur, **J**, a recent X-ray study by Reddy et al.[17] revealed a boatlike conformation for the dioxaphosphocin, similar to that for the *syn* conformation of **D**.

In our present study, tetracoordinated compounds **2** and **3** contain the same cyclic phosphate composition but differ in that **3** is a cocrystal of the phosphate with the related diol. The presence of the latter diol, however, does not influence any significant conformational or structural changes since the geometry of the cyclic phosphates is very similar in the two compounds (Figures 2 and 3). The eight-membered rings are in the twist-*syn* configuration (Figures 5b and 5c) seen previously in the *syn* form of the related phosphate $\mathbf{I_s}$,[4] and as mentioned also for **D**.[3] Selected

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(16) See: Maryanoff et al. (Maryanoff, B. E.; Hutchins, R. O.; Maryanoff, C. A. *Top. Stereochem.* **1979**, *11*, 187) and references cited therein for further ring comparisons of boat and chair conformations.

(17) Reddy, C. D.; Reddy, R. S.; Reddy, M. S.; Krishnaiah, M.; Berlin, K. D.; Sunthankar, P. *Phosphorus, Sulfur, Silicon* **1991**, *62*, 1.

bond parameters included in Table VII indicate the similarity in the *syn* forms of **2**, **3**, and $\mathbf{I}_s$.

Details of Ring Conformations of 2 and 3. In **3**, the diol of co-crystallization is hydrogen bonded to the phosphoryl oxygen atom, O4, in such a way that both hydroxyl hydrogen atoms enter into an interaction with the same oxygen atom forming a 10-membered ring (Figure 4). Since the O–C–C–S–C–C–O backbone of the diol is identical to that found in the eight-membered phosphorus-containing rings in the phosphates, it is of interest to compare their geometry. There are no striking differences in any of the bond lengths or angles of the backbone. However, the O–O distance in the phosphorus-containing rings is restricted by bonding to phosphorus and has values of 2.488(3) Å for **2** and 2.506(7) Å for **3**. In the diol, this distance is much larger, 4.159(8) Å and shows a considerable ability to accommodate different "bites" or O–P–O angles. If we include pentacoordinate geometries having this ring system, we find the O–P–O angles range from 88.3° in **H** to 117.5° in **A** (Table V). The above discussion shows that the flexibility of the backbone resulting in the freedom of the ring to alter conformation is due to mostly rotational changes.

Conclusion. The incorporation of sulfur into an eight-membered ring leads to the formation of cyclic phosphates, **2** and **3**, showing no tendency for a P–S interaction. In agreement with our previous studies in this area, the same type of ring system incorporated into the pentaoxyphosphorane **1** yielded a hexacoordinated octahedral structure as a consequence of a close P–S interaction. The results suggest that phosphoryl transfer enzymes that have sulfur present at active sites may lead to the formation of hexacoordinated phosphorus species. Heretofore, only five-coordinated phosphorus has been considered.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1** (Tables S1–S4), **2** (Tables S5–S8), and **3** (Tables S9–S12) (31 pages). Ordering information is given on any current masthead page.