Inorg. Chem. **1992**, *31*, 3391–3397

Conformational Variation of Sulfur-Bridged Eight-Membered Rings in Four-, Five-, and Six-Coordinated Oxygen-Ligated Phosphorus Compounds[1]

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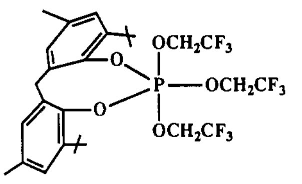
Received April 27, 1992

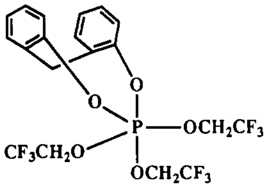
Reaction of the eight-membered sulfur-containing cyclic phosphine, $[(t\text{-Bu})_4C_{12}H_4SO_2]POCH_2CF_3$ (**1**) with phenols yielded the phosphate $[(t\text{-Bu})_4C_{12}H_4SO_2]P(O)OCH_2CF_3$ (**2**) and the pentaoxyphosphorane $[(t\text{-Bu})_4C_{12}H_4SO_2]P(C_{12}H_8O_2)OCH_2CF_3$ (**3**). Two crystalline modifications of **2** were obtained, an anti (**2a**) and a syn (**2s**) form. Due to P–S bond formation, **3** resulted as a pseudooctahedral structure. The conformation of the eight-membered ring varied in all three structures. When compared with related structures containing this basic ring system, a high degree of conformational flexibility is apparent with coordination geometries at phosphorus extending from 4 to 6. Achievement of diequatorial ring orientation in trigonal bipyramids observed for some pentaoxyphosphoranes containing eight-membered rings and the lack of this orientation with six- and seven-membered rings in analogous structures is attributed to the greater conformational flexibility of the eight-membered rings, particularly their ability to maximize ring $P–O_{eq}$ π bonding. Phosphate **2a** crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.608$ (3) Å, $b = 16.085$ (6) Å, $c = 22.772$ (3) Å, $\beta = 100.57$ (2)°, and $Z = 4$. Phosphate **2s** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.517$ (3) Å, $b = 13.229$ (3) Å, $c = 13.244$ (3) Å, $\alpha = 83.20$ (2)°, $\beta = 78.52$ (2)°, $\gamma = 77.56$ (2)°, and $Z = 2$. Phosphorane **3** crystallizes in the orthorhombic space group *Pbca* with $a = 16.186$ (5) Å, $b = 18.701$ (5) Å, $c = 27.113$ (7) Å, and $Z = 8$. The final conventional unweighted residuals are 0.062 (**2a**), 0.041 (**2s**), and 0.078 (**3**).

Introduction

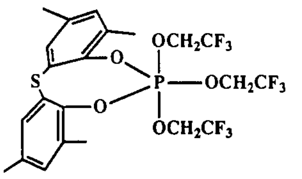
Compared to six-[2] and seven-[3]membered ring systems in pentaoxyphosphoranes, eight-membered[1b,4] rings have shown a high degree of conformational and structural flexibility. Derivatives A[1b,4] and C[1b] have provided the first examples of diequatorial (e–e) ring placement in trigonal-bipyramidal (TBP) geometries of pentaoxyphosphoranes, as demonstrated by X-ray analysis. An analogous but less substituted member, B,[1b] exhibited the more conventional axial–equatorial (a–e) ring arrangement similar to all previous six-[2,5-13] and seven-membered[3,6,7] rings in pentaoxyphosphoranes studied by X-ray diffraction. By way of contrast, the geometry of phosphorane D[1b] may be described as a distorted octahedron containing a P–S bond.



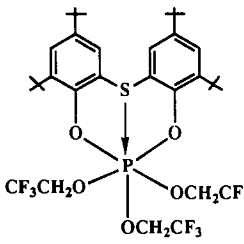
A[1b,4]



B[1b]



C[1b]



D[1b]

We suggested[1b] that the greater conformational flexibility apparent for eight-membered rings, compared to saturated six- and seven-membered ones, enhances the ability of eight-membered rings to form (e–e) formations for pentaoxyphosphoranes. Only in the case of the tetraoxyphosphorane E in the constrained polycyclic system, isolated by Bentrude and co-workers,[14] has an X-ray study[14] shown the six-membered ring to reside in (e–e) sites of a TBP.

To ascertain the uniqueness of the eight-membered ring conformations associated with the pentaoxyphosphoranes, A–D,[1b] we have extended our investigations of the same sulfur-bridged eight-membered ring present in D. In contrast to our previous studies[1b,4] in which A–D were formed by reaction of the acyclic phosphite $(CF_3CH_2O)_3P$ with diols, we incorporate the eight-membered ring in the cyclic phosphine **1** and explore its reaction with 2,6-dimethylphenol and 2,2′-biphenol. Instead of formation of the expected phosphorane F, the formation of the phosphate **2** resulted with the former reactant. Oxyphosphorane **3** was obtained with the latter phenol. In a related reaction of

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[1] (a) Pentacoordinated Molecules. 93. (b) Part 92: Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 1913.

[2] Holmes, R. R.; Day, R. O.; Deiters, J. A.; Kumara Swamy, K. C.; Holmes, J. M.; Hans, J.; Burton, S. D.; Prakasha, T. K. *Phosphorus Chemistry in America 1991*; ACS Symposium Series; American Chemical Society: Washington, DC (see also references cited therein) in press.

[3] Hans, J.; Day, R. O.; Howe, L.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 1279.

[4] Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 725.

[5] Kumara Swamy, K. C.; Burton, S. D.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *Phosphorus, Sulfur Silicon* **1990**, *53*, 437 and references cited therein.

[6] Kumara Swamy, K. C.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6095.

[7] Burton, S. D.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6104.

[8] Holmes, R. R.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O. *Inorg. Chem.* **1991**, *30*, 1052.

[9] (a) Yu, J. H.; Sopchik, A. E.; Arif, A. M.; Bentrude, W. G. *J. Org. Chem.* **1990**, *55*, 3444. (b) Yu, H.; Arif, A. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1990**, *112*, 7451.

[10] Schomburg, D.; Hacklin, H.; Röschenthaler, G.-V. *Phosphorus Sulfur* **1988**, *35*, 241.

[11] Day, R. O.; Kumara Swamy, K. C.; Fairchild, L.; Holmes, J. M.; Holmes, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 1627.

[12] Hans, J.; Day, R. O.; Howe, L.; Holmes, R. R. *Inorg. Chem.* **1991**, *30*, 3132.

[13] Hans, J.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1991**, *30*, 3928.

[14] Huang, Y.; Arif, A. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1991**, *113*, 7800.

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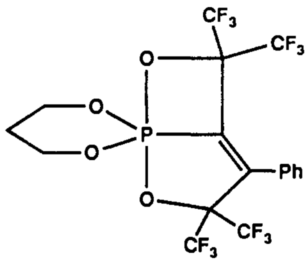
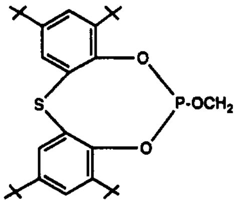


E[14]



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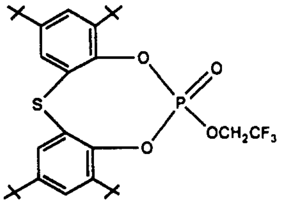
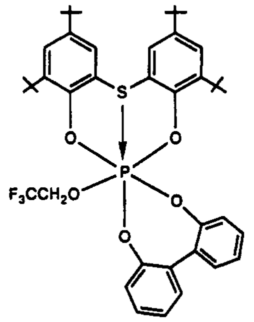
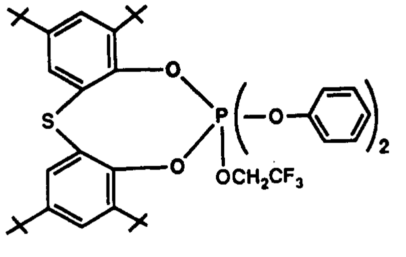


2

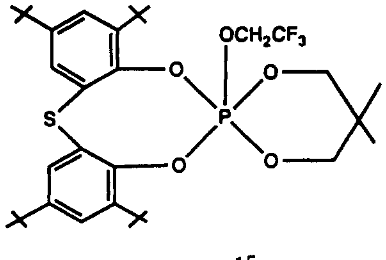


3

1 with 2,2-dimethyl-1,3-propanediol, phosphate 2 was again produced but as an impurity with the major product being the formation of oxyphosphorane G.[15]



F



G[15]

Subsequent X-ray analysis reported here reveals the isolation of two crystalline forms of 2. The eight-membered ring is found to exist in an anti (**2a**) and a syn (**2b**) conformation, each of which differs from that found for 3.

Experimental Section

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.[16] Melting points are uncorrected. 2,2′-Thiobis(4,6-di-*tert*-butylphenol)[17] and *N*-chlorodiisopropylamine[18] were prepared by literature methods. All the reactions were carried out in a dry nitrogen atmosphere using standard Schlenk-type glassware.[19]

^{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[20] and are referenced to 85% H_3PO_4 with negative shifts upfield. All NMR spectra were obtained at 23 °C unless otherwise stated.

Syntheses. [2,2′-Thiobis(4,6-di-*tert*-butylphenyleneoxy)-*O,O′*](2,2,2-trifluoroethoxy)phosphine, [(*t*-Bu)$_4$C$_{12}$H$_4$SO$_2$]POCH$_2$CF$_3$ (1).[21] To a solution of 13.37 g (0.0974 mol, 8.50 mL) of phosphorus trichloride in 100 mL of toluene at 0.4 °C was added dropwise a solution of 44.20 g (0.0998 mol) of 2,2′-thiobis(4,6-di-*tert*-butylphenol) and 20.24 g (0.2000 mol, 27.80 mL) of triethylamine in 200 mL of diethyl ether. The reaction mixture was stirred at room temperature for 28 h. To the reaction mixture at 0.4 °C was added dropwise 10.0 g (0.101 mol, 7.30 mL) of 2,2,2-trifluoroethanol and 10.12 g (0.1000 mol, 13.90 mL) of triethylamine in 25 mL of diethyl ether. Stirring was continued at room temperature for 28 h. After the removal of triethylamine hydrochloride by filtration, the filtrate was concentrated under reduced pressure. The resulting compound (**1**) was crystallized from a 1:1 mixture of diethyl ether (150 mL) and hexane (150 mL), mp 202–204 °C (yield 45.6 g, 82.0%).

^{1}H NMR (toluene-d_8, ppm): 1.17 (s, 18 H, $C(CH_3)_3$), 1.49 (s, 18 H, $C(CH_3)_3$), 4.02 (m, 2 H, OCH_2CF_3), 6.90–7.70 (4 H, H(Ar)). ^{19}F NMR (toluene-d_8, ppm): −75.2 (m). ^{31}P NMR (toluene-d_8, ppm): 145.5. Anal. Calcd for $C_{30}H_{42}F_3O_3SP$: C, 63.16; H, 7.37; S, 5.62. Found: C, 63.16; H, 7.48; S, 5.97.

[2,2′-Thiobis(4,6-di-*tert*-butylphenyleneoxy)-*O,O′*](2,2,2-trifluoroethoxy)phosphine Oxide, [(*t*-Bu)$_4$C$_{12}$H$_4$SO$_2$]P(O)OCH$_2$CF$_3$ (2). In an attempt to prepare the monocyclic phosphorane F, the following reaction was carried out.

To a mixture of [2,2′-thiobis(4,6-di-*tert*-butylphenyleneoxy)-*O,O′*]-(2,2,2-trifluoroethoxy)phosphine (**1**) (1.00 g, 0.001 75 mol) and 2,6-dimethylphenol (0.430 g, 0.003 50 mol) in diethyl ether (100 mL) maintained at −70 °C was added dropwise a solution of *N*-chlorodiisopropylamine (0.300 mL, 0.276 g, 0.002 04 mol) in diethyl ether (20 mL) over a period of 10 min with continued stirring. The reaction was brought to 25 °C and stirred at this temperature for 24 h. After filtration, the filtrate was concentrated to 25 mL and to it 25 mL of hexane was added. The solvent mixture was then concentrated by passing a slow stream of nitrogen over it. Instead of the expected monocyclic phosphorane, F, the corresponding phosphine oxide **2** was obtained, mp 197 °C (yield 0.510 g, 49.7%). ^{1}H NMR ($CDCl_3$, ppm): 1.30 (s, 18 H, $C(CH_3)_3$), 1.40 (s, 18 H, $C(CH_3)_3$, 4.62 (m, 2 H, OCH_2CF_3), 7.38 (s, 2 H, H(Ar)), 7.52 (s, 2 H, H(Ar)). ^{19}F NMR ($CDCl_3$, ppm): −75.4 (t). ^{31}P NMR ($CDCl_3$, ppm): −13.36. Anal. Calcd for $C_{30}H_{42}F_3O_4SP$: C, 61.42; H, 7.22; S, 5.46. Found: C, 61.57; H, 7.26; S, 6.03.

[2,2′-Thiobis(4,6-*tert*-butylphenyleneoxy)-*O,O′*](biphenylene-2,2′-dioxy)(2,2,2-trifluoroethoxy)phosphorane, [(*t*-Bu)$_4$C$_{12}$H$_4$SO$_2$]-P(C$_{12}$H$_8$O$_2$)OCH$_2$CF$_3$ (3). The synthesis of **3** closely followed the procedure used for **2**. Quantities used were as follows: [2,2′-Thiobis-(4,6-di-*tert*-butylphenyleneoxy)-*O,O′*](2,2,2-trifluoroethoxy)phosphine (**1**) (1.00 g, 0.001 75 mol), 2.2′-biphenol (0.326 g, 0.001 75 mol), *N*-chlorodiisopropylamine (0.300 mL, 0.276 g, 0.002 04 mol), and diethyl ether (200 mL). Colorless crystals of **3** were obtained by concentrating a solution of a 1:3 mixture (30:90 mL) of dichloromethane and hexane, mp 242 °C (yield 1.117 g, 84.6%).

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(15) Prakasha, T. K.; Day, R. O.; Holmes, R. R. Unpublished work.

(16) (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.

(17) Pastor, S. D.; Spivack, J. D.; Steinhuebel, L. P. *J. Heterocycl. Chem.* **1984**, *21*, 1285.

(18) Bock, H.; Kompa, K. L. *Chem. Ber.* **1966**, *99*, 1347.

(19) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(20) Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Wiley: New York, 1976; p 82.

(21) Abdou, W. M.; Mahran, M. R. *Phosphorus Sulfur* **1986**, *26*, 119. The authors report a preparation of **1** describing it as a viscous oil, boiling at 110–115 °C at 0.05 mm. A ^{31}P chemical shift of 130.3 ppm (in $CDCl_3$) was reported which is considerably different from our value of 145.5 ppm (in toluene-d_8). Our compound is crystalline and melts at 202–204 °C.

Table I. Crystallographic Data for Compounds **2a**, **2s**, and **3**

compd	**2a**	**2s**	**3**
formula	$C_{30}H_{42}O_4F_3SP$	$C_{30}H_{42}O_4F_3SP$	$C_{42}H_{50}O_5F_3SP$
fw	586.700	586.700	754.897
cryst syst	monoclinic	triclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)
a, Å	9.608 (3)	9.517 (3)	16.186 (5)
b, Å	16.085 (6)	13.229 (3)	18.701 (5)
c, Å	22.772 (3)	13.244 (3)	27.113 (7)
α, deg		83.20 (2)	
β, deg	100.57 (2)	78.52 (2)	
γ, deg		77.56 (2)	
V, Å^3	3460 (3)	1591 (1)	8207 (7)
Z	4	2	8
T, °C	23 ± 2	23 ± 2	23 ± 2
λ, Å	0.710 73	0.710 73	0.710 73
D_{calc}, g cm^{-3}	1.126	1.225	1.222
μ, cm^{-1}	1.775	1.931	1.656
$R(F_o)^a$	0.062	0.041	0.078
$R_w(F_o)^a$	0.072	0.059	0.084

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

^1H NMR ($CDCl_3$, ppm): 1.20–1.58 (m, 36 H, $C(CH_3)_3$), 3.96 (m, 2 H, OCH_2CF_3), 7.26–7.52 (m, 12 H, H(Ar)). ^{31}P NMR ($CDCl_3$, ppm): –69.3. Anal. Calcd for $C_{42}H_{50}F_3O_5SP$: C, 67.10; H, 6.65. Found: C, 66.89; H, 6.71.

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.[22] Crystals were mounted in thin-walled glass capillaries which were sealed with a flame as a protection against moisture. Data were collected using the θ–2θ scan mode with $3° \leq 2\theta_{Mo\ K\bar{\alpha}} \leq 43°$. No corrections were made for absorption. The structures were solved by use of direct methods and were refined by full-matrix least squares.[23]

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 *anti*-[(*t*-Bu)$_4$C$_{12}$H$_4$SO$_2$]P(O)OCH$_2$CF$_3$ (2a). Only very small platelike crystals of **2a** which diffracted weakly were available for the X-ray study. The colorless crystal used had approximate dimensions of 0.08 × 0.23 × 0.26 mm. A total of 3946 independent reflections was measured ($+h,+k,\pm l$). Large thermal parameters for the fluorine atoms of the CF_3 group suggested disorder in this region of the molecule, but it was not possible to resolve more than one set of positions for these atoms. The final refinement (non-hydrogen atoms anisotropic; hydrogen atoms fixed isotropic in ideal positions) was based on 1175 reflections with $I > 3\sigma_I$. The maximum density on a final difference Fourier synthesis (0.498 e/Å^3) was in the vicinity of the CF_3 group.

X-ray Study for *syn*-[(*t*-Bu)$_4$C$_{12}$H$_4$SO$_2$]P(O)OCH$_2$CF$_3$ (2s). The colorless crystal used for the study was cut from a fused mass of crystals with rhomboidal faces and had dimensions of 0.40 × 0.45 × 0.50 mm. A total of 3629 independent reflections ($+h,\pm k,\pm l$) was measured. Two sets of positions were found for the three pendant atoms of the *t*-Bu group bound to C34 (rotational disorder). The final refinement as described for **2a**, but omitting the hydrogen atoms of the disordered *t*-Bu group, was based on 2929 reflections with $I \geq 3\sigma_I$. The maximum density on a final difference Fourier synthesis was 0.334 e/Å^3.

X-ray Study for [(*t*-Bu)$_4$C$_{12}$H$_4$SO$_2$]P(C$_{12}$H$_8$O$_2$)OCH$_2$CF$_3$ (3). The colorless crystal used for the study was cut from a mostly opaque polycrystalline mass with transparent regions and was roughly a triangular prism with edges of 0.5 mm and a height of 0.55 mm. A total of 4710 independent reflections ($+h,+k,+l$) was measured. During data collection an isotropic decrease in the intensities of the four standard reflections was observed. A linear decay correction was applied (from 1.000 to 1.351 on *I*). As in the case of **2s**, two sets of positions were found for the three pendant atoms of the *t*-Bu group bound to C34. Disorder was also apparent in the trifluoroethyl group (wagging disorder), which was modeled by including two positions for F2. The final refinement (disordered non-hydrogen atoms isotropic, remaining non-hydrogen atoms anisotropic, hydrogen atoms as described for **2s**) was based on 2038 reflections with $I > 3\sigma_I$. The maximum density on a final difference Fourier synthesis (0.591 e/Å^3) was in the vicinity of the disordered CF_3 group.

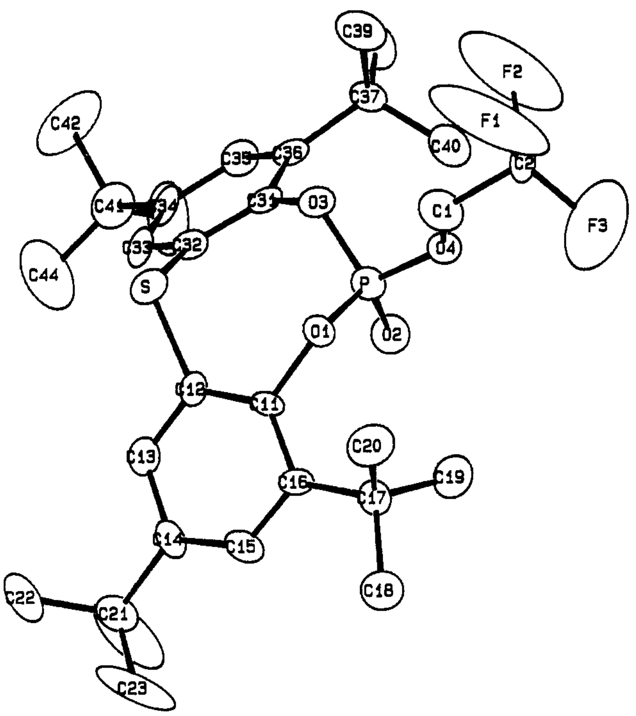

Figure 1. ORTEP plot of *anti*-[(*t*-Bu)$_4$C$_{12}$H$_4$SO$_2$]P(O)OCH$_2$CF$_3$ (**2a**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table II. Selected Atomic Coordinates in Crystalline *anti*-[(*t*-Bu)$_4$C$_{12}$H$_4$SO$_2$]P(O)OCH$_2$CF$_3$ (**2a**)[a]

atom[b]	*x*	*y*	*z*	B_{equiv},[c] Å^2
S	0.8507 (4)	–0.0021 (3)	0.1505 (2)	4.66 (9)
P	0.5467 (4)	0.0083 (2)	0.2145 (2)	3.86 (8)
O1	0.5344 (7)	0.0127 (5)	0.1446 (3)	3.4 (2)
O2	0.5365 (9)	–0.0749 (5)	0.2392 (4)	4.4 (2)
O3	0.6854 (8)	0.0572 (5)	0.2431 (3)	3.8 (2)
O4	0.4279 (8)	0.0680 (5)	0.2252 (4)	4.1 (2)
C11	0.576 (1)	–0.0596 (8)	0.1130 (5)	3.2 (3)
C12	0.717 (1)	–0.0738 (8)	0.1175 (5)	3.2 (3)
C13	0.759 (1)	–0.1421 (8)	0.0887 (5)	3.8 (4)
C14	0.658 (1)	–0.1955 (8)	0.0545 (5)	4.0 (3)
C15	0.518 (1)	–0.1712 (8)	0.0491 (5)	4.1 (4)
C16	0.468 (1)	–0.1036 (8)	0.0767 (5)	3.3 (3)
C31	0.811 (1)	0.0124 (8)	0.2676 (5)	3.4 (3)
C32	0.888 (1)	–0.0253 (7)	0.2287 (5)	3.5 (3)
C33	1.009 (1)	–0.0733 (9)	0.2513 (6)	3.8 (3)
C34	1.051 (1)	–0.0831 (9)	0.3123 (5)	3.9 (4)
C35	0.973 (1)	–0.0395 (9)	0.3492 (5)	4.2 (4)
C36	0.855 (1)	0.0090 (8)	0.3298 (5)	3.7 (3)

[a] Numbers in parentheses are estimated standard deviatioins. [b] Atomis are labeled to agree with Figure 1. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Results

The atom-labeling scheme for **2a** is shown in the ORTEP plot of Figure 1. Selected atomic coordinates and selected distances and angles are given in Tables II and III, respectively. The corresponding informtion for **2s** is given in Figure 2 and in Tables IV and V, while for **3** the information is given in Figures 3 and 5 and in Tables VI and VII. Further results of the crystallographic studies are provided as supplementary material.

Discussion

Syntheses. Phosphate **2** was obtained by two different routes which gave products whose crystalline forms differed. Reaction of the cyclic phosphine **1** with 2 mol of 2,6-dimethylphenol in the

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(22) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.
(23) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$.

Table III. Selected Distances (Å) and Angles (deg) for *anti*-$[(t\text{-Bu})_4C_{12}H_4SO_2]P(O)OCH_2CF_3]$ (**2a**)[a]

	Distances		
S–C12	1.79 (1)	P–O4	1.545 (9)
S–C32	1.79 (1)	O1–C11	1.46 (1)
P–O1	1.578 (8)	O3–C31	1.43 (1)
P–O2	1.461 (9)	O4–C1	1.46 (2)
P–O3	1.581 (8)	C11–C12	1.35 (2)
		C31–C32	1.39 (2)
	Angles		
C12–S–C32	106.3 (6)	O2–P–O4	113.9 (5)
O1–P–O2	115.6 (5)	O3–P–O4	102.6 (5)
O1–P–O3	107.1 (5)	P–O1–C11	119.0 (7)
O1–P–O4	102.2 (4)	P–O3–C31	119.9 (7)
O2–P–O3	114.1 (5)	P–O4–C1	124.9 (9)
O1–C11–C12	117.3 (9)	O3–C31–C32	118.7 (9)
S–C12–C11	124 (1)	S–C32–C31	120.6 (9)

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

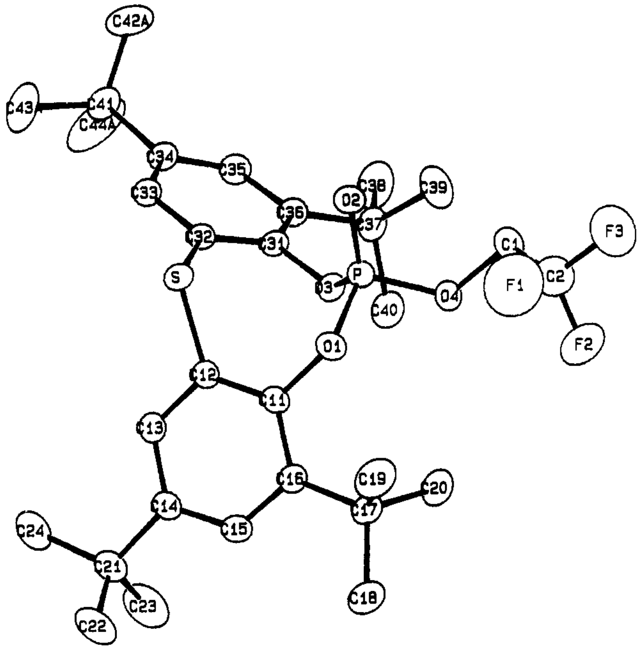
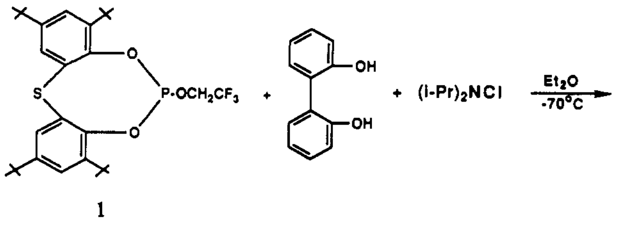


Figure 2. ORTEP plot of *syn*-$[(t\text{-Bu})_4C_{12}H_4SO_2]P(O)OCH_2CF_3$ (**2s**) with thermal ellipsoids at the 30% probability level. Only one set of positions for disordered atoms is shown, and hydrogen atoms are omitted for clarity.

presence of *N*-chlorodiisopropylamine led to an oxidation process yielding the anti form of the tetracoordinate phosphate, **2a** (49.7% yield), instead of the expected pentacoordinated derivative, F. Apparently, moisture in the hygroscopic phenol compound was responsible for the oxidation. In other work[15] involving a similar reaction of **1** with 2,2-dimethyl-1,3-propanediol, the expected spirocyclic phosphorane, G,[15] formed, but in addition, a small amount of crystalline impurity reported here yielded the syn form of the phosphate, **2s**, as shown by X-ray analysis.

With the use of 2,2′-biphenol, the above reaction scheme involving **1** proceeded as expected to give the pentaoxyphosphorane **3** in 85% yield, eq 1.



$3 + (i\text{-}Pr)_2NH_2^+\ Cl^-$ (1)

Table IV. Selected Atomic Coordinates in Crystalline *syn*-$[(t\text{-Bu})_4C_{12}H_4SO_2]P(O)OCH_2CF_3]$ (**2s**)[a]

atom[b]	*x*	*y*	*z*	B_{equiv},[c] Å^2
S	0.47274 (8)	0.11924 (6)	0.54575 (5)	3.45 (2)
P	0.13200 (8)	0.12535 (6)	0.60431 (5)	3.18 (2)
O1	0.1899 (2)	0.1509 (1)	0.7002 (1)	3.45 (4)
O2	0.1745 (2)	0.0204 (1)	0.5741 (2)	4.15 (5)
O3	0.1606 (2)	0.2169 (1)	0.5205 (1)	3.16 (4)
O4	−0.0384 (2)	0.1596 (1)	0.6425 (2)	3.86 (5)
C11	0.2777 (3)	0.2239 (2)	0.7006 (2)	3.02 (6)
C12	0.4041 (3)	0.2228 (2)	0.6274 (2)	3.14 (6)
C13	0.4882 (3)	0.2974 (2)	0.6256 (2)	3.53 (7)
C14	0.4499 (3)	0.3708 (2)	0.6967 (2)	3.65 (7)
C15	0.3249 (3)	0.3657 (2)	0.7722 (2)	3.78 (7)
C16	0.2353 (3)	0.2939 (2)	0.7779 (2)	3.28 (6)
C31	0.2614 (3)	0.2085 (2)	0.4262 (2)	3.07 (6)
C32	0.4087 (3)	0.1677 (2)	0.4289 (2)	3.01 (6)
C33	0.5077 (3)	0.1568 (2)	0.3374 (2)	3.37 (6)
C34	0.4630 (3)	0.1890 (2)	0.2432 (2)	3.51 (7)
C35	0.3157 (3)	0.2355 (2)	0.2452 (2)	3.77 (7)
C36	0.2113 (3)	0.2469 (2)	0.3348 (2)	3.25 (6)

[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 V. Selected Distances (Å) and Angles (deg) for *syn*-$[(t\text{-Bu})_4C_{12}H_4SO_2]P(O)OCH_2CF_3$ (**2s**)[a]

	Distances		
S–C12	1.776 (3)	P–O4	1.582 (2)
S–C32	1.774 (3)	O1–C11	1.407 (4)
P–O1	1.579 (2)	O3–C31	1.415 (3)
P–O2	1.441 (2)	O4–C1	1.428 (4)
P–O3	1.574 (2)	C11–C12	1.385 (3)
P–S	3.166 (1)	C31–C32	1.396 (4)
	Angles		
C12–S–C32	104.1 (1)	O2–P–O4	113.2 (1)
O1–P–O2	117.7 (1)	O3–P–O4	100.5 (1)
O1–P–O3	104.0 (1)	P–O1–C11	126.6 (2)
O1–P–O4	99.9 (1)	P–O3–C31	126.1 (2)
O2–P–O3	118.7 (1)	P–O4–C1	122.3 (2)
O1–C11–C12	119.6 (2)	O3–C31–C32	118.9 (2)
S–C12–C11	121.1 (2)	S–C32–C31	122.4 (2)

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

The ^{31}P NMR solution-state spectra shows resonances supporting the progression of coordination from 3 for the cyclic phosphine **1** (145.5 ppm in toluene-d_8) to 4 for the phosphate **2** (−13.4 ppm in $CDCl_3$) to 5 for the oxyphosphorane **3** (−69.3 ppm in $CDCl_3$). Most likely, the coordination geometry at phosphorus is retained on going from the solid state to solution. However, no information is obtained on what ring conformations prevail in solution compared to what was observed from the X-ray studies as described below.

Structures and Ring Conformations. Four-coordinated phosphate **2** was found in two crystalline modifications in which the solid-state conformations of the eight-membered ring differ. In the monoclinic form, **2a**, the ring has an anti or chairlike conformation (Figure 4a); i.e., with respect to the rest of the ring atoms, the sulfur atom is tipped away from the phosphorus atom. The sulfur atom is also tipped toward the trifluoroethoxy group (Figure 1). In this form the molecule has a pseudomirror plane (excluding the trifluoroethyl group) which passes through P, S, O2, and O4. It could therefore be called symmetrical anti.

In the triclinic form, **2s**, the ring has a twisted boatlike conformation in which the phosphorus and sulfur atoms are syn (Figure 4b) and in which the sulfur atom is tipped away from the trifluoroethoxy group (Figure 2). The ring could also be described as a very twisted tub: atoms C11, C12, O3, and C31 are coplanar to within ± 0.021 (3) Å. Atoms P, O1, S, and C32 are displaced from this plane in the same direction by distances of 1.211 (1), 0.953 (2), 1.249 (1), and 0.544 (2) Å, respectively. This form could be referred to as twist syn.

The ideal molecular symmetry would be C_s for either form, and there is no reason to believe that the two forms would not

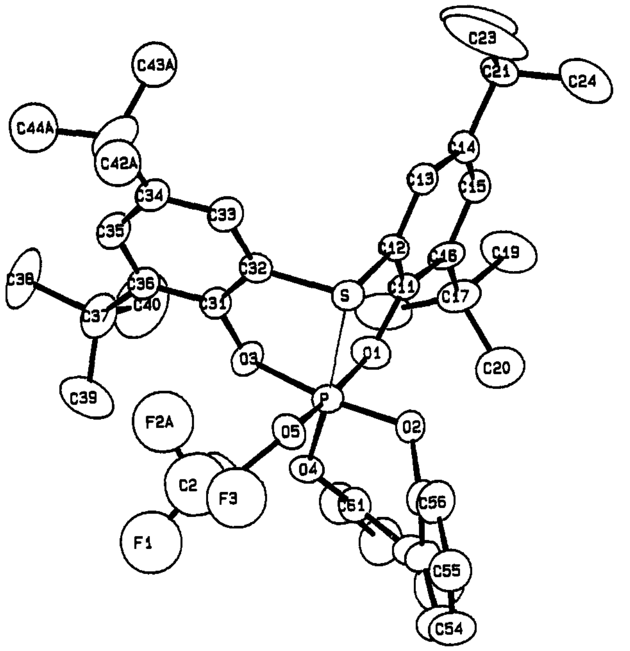


Figure 3. ORTEP plot of $[(t\text{-Bu})_4C_{12}H_4SO_2]P(C_{12}H_8O_2)OCH_2CF_3$ (**3**) with thermal ellipsoids at the 40% probability level. Only one set of positions for disordered atoms is shown and hydrogen atoms are omitted for clarity.

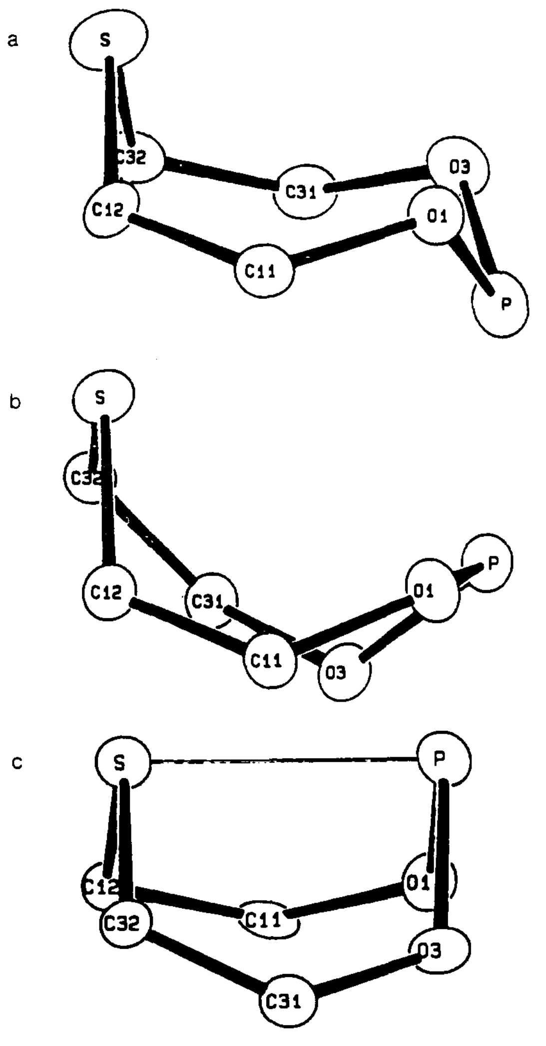


Figure 4. ORTEP plots showing the conformation of the eight-membered ring in (a) compound **2a**, (b) compound **2s**, and (c) compound **3**.

interconvert in solution. A recent X-ray study by Reddy et al.[24] of the cyclic phosphate H, containing an eight-membered ring quite analogous to the ring we are studying with a methylene bridge in place of sulfur, reports a boatlike conformation for the dioxaphosphocin ring, similar to that in the syn phosphate **2s**. It is suggested from an NMR analysis[24] that a boat conformation is retained in solution. The ^{31}P NMR signal of H at −15.00 ppm compares closely with that for **2**, −13.36 ppm, both in $CDCl_3$.

The pentaoxyphosphorane **3** contains the same ligand which forms the eight-membered ring in the phosphate, **2**, but it is present in yet another conformation (Figure 4c). This boatlike confor-

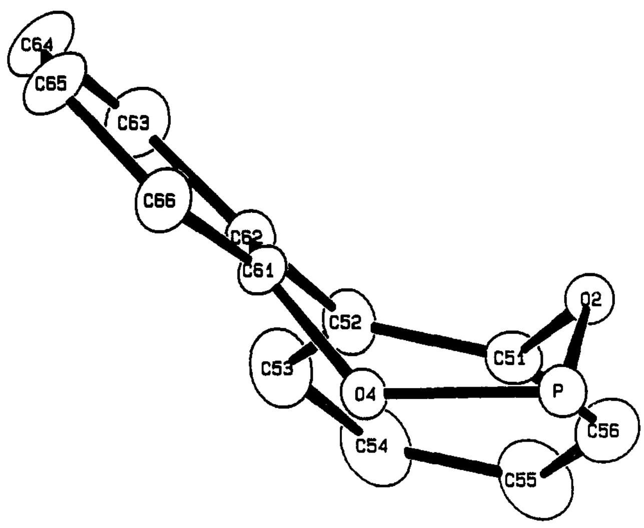


Figure 5. ORTEP plot showing the conformation of the seven-membered ring in compound **3**, as well as the atom labeling for the fused phenyl rings.

Table VI. Selected Atomic Coordinates in Crystalline $[(t\text{-Bu})_4C_{12}H_4SO_2]P(C_{12}H_8O_2)OCH_2CF_3$ (**3**)[a]

atom[b]	x	y	z	B_{equiv},[c] Å^2
S	0.4674 (2)	0.1847 (2)	0.0745 (1)	2.98 (6)
P	0.4142 (2)	0.0911 (2)	0.1244 (1)	3.19 (7)
O1	0.3189 (5)	0.1139 (4)	0.1034 (3)	3.6 (2)
O2	0.4226 (5)	0.0397 (4)	0.0747 (3)	3.1 (2)
O3	0.4025 (5)	0.1536 (4)	0.1700 (3)	3.6 (2)
O4	0.3795 (5)	0.0306 (4)	0.1624 (3)	3.4 (2)
O5	0.5130 (4)	0.0801 (4)	0.1382 (3)	3.4 (2)
C1	0.5413 (9)	0.055 (1)	0.1844 (5)	7.7 (5)
C11	0.3062 (7)	0.1640 (6)	0.0673 (4)	2.9 (3)
C12	0.3696 (7)	0.2081 (6)	0.0515 (4)	2.4 (3)
C13	0.3581 (7)	0.2616 (6)	0.0175 (4)	2.9 (3)
C14	0.2810 (7)	0.2724 (6)	−0.0024 (4)	2.9 (3)
C15	0.2169 (7)	0.2283 (6)	0.0133 (4)	3.5 (3)
C16	0.2246 (7)	0.1737 (6)	0.0481 (4)	3.0 (3)
C31	0.4436 (6)	0.2180 (6)	0.1690 (4)	2.8 (3)
C32	0.4799 (7)	0.2408 (6)	0.1263 (4)	2.9 (3)
C33	0.5253 (7)	0.3028 (6)	0.1241 (5)	3.7 (3)
C34	0.5357 (8)	0.3448 (6)	0.1659 (5)	3.9 (3)
C35	0.4946 (8)	0.3213 (7)	0.2086 (5)	4.3 (3)
C36	0.4462 (7)	0.2599 (6)	0.2114 (5)	3.6 (3)
C51	0.4668 (8)	−0.0257 (6)	0.0763 (4)	3.6 (3)
C52	0.4271 (9)	−0.0836 (7)	0.0978 (5)	4.3 (3)
C53	0.468 (1)	−0.1483 (7)	0.0954 (5)	5.9 (4)
C54	0.545 (1)	−0.1524 (7)	0.0723 (6)	6.3 (4)
C55	0.5827 (9)	−0.0954 (8)	0.0516 (5)	5.8 (4)
C56	0.5415 (9)	−0.0303 (7)	0.0526 (5)	4.9 (3)
C61	0.3217 (7)	−0.0220 (7)	0.1516 (5)	3.4 (3)
C62	0.3452 (8)	−0.0791 (6)	0.1214 (5)	3.7 (3)
C63	0.287 (1)	−0.1310 (7)	0.1167 (5)	5.7 (4)
C64	0.210 (1)	−0.1277 (9)	0.1398 (6)	7.7 (4)
C65	0.1919 (9)	−0.0727 (8)	0.1692 (6)	6.0 (4)
C66	0.2491 (9)	−0.0205 (8)	0.1759 (5)	4.7 (3)

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

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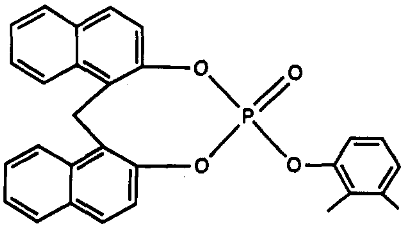
(24) Reddy, C. D.; Reddy, R. S.; Reddy, M. S.; Krishnaiah, M.; Berlin, K. D.; Sunthankar, P. *Phosphorus, Sulfur Silicon* **1991**, *62*, 1.

Table VII. Selected Distances (Å) and Angles (deg) for $[(t\text{-Bu})_4C_{12}H_4SO_2]P(C_{12}H_8O_2)OCH_2CF_3$ (3)[a]

	Distances		
S–C12	1.76 (1)	P–S	2.373 (5)
S–C32	1.76 (1)	O1–C11	1.37 (1)
P–O1	1.699 (8)	O2–C51	1.42 (1)
P–O2	1.661 (8)	O3–C31	1.37 (1)
P–O3	1.711 (8)	O4–C61	1.39 (1)
P–O4	1.630 (8)	O5–C1	1.42 (2)
P–O5	1.655 (8)	C11–C12	1.38 (2)
C51–C52	1.39 (2)	C31–C32	1.37 (2)
C61–C62	1.40 (2)	C52–C62	1.47 (2)
	Angles		
P–S–C12	93.4 (4)	P–S–C32	91.5 (4)
C12–S–C32	103.7 (5)	O3–P–O4	88.8 (4)
O1–P–O2	86.9 (4)	O3–P–O5	91.7 (4)
O1–P–O3	88.3 (4)	O4–P–O5	96.0 (4)
O1–P–O4	94.2 (4)	P–O1–C11	123.2 (7)
O1–P–O5	169.8 (4)	P–O2–C51	121.1 (7)
O2–P–O3	171.9 (4)	P–O3–C31	122.1 (7)
O2–P–O4	98.0 (4)	P–O4–C61	126.2 (7)
O2–P–O5	91.8 (4)	P–O5–C1	123.6 (8)
S–P–O1	87.3 (3)	S–P–O2	86.2 (3)
S–P–O3	87.0 (3)	S–P–O4	175.5 (3)
S–P–O5	82.5 (3)	O1–C11–C12	121 (1)
S–C12–C11	114.2 (8)	O3–C31–C32	120 (1)
S–C32–C31	116.1 (8)	O2–C51–C52	117 (1)
O4–C61–C62	119 (1)	C62–C52–C51	124 (1)
		C52–C62–C61	123 (1)

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



H[24]

mation could be described as symmetrical syn; i.e., phosphorus and sulfur lie on a pseudomirror plane with respect to the rest of the atoms of the ligand (Figure 3) and are on the same side of the ring with respect to the remaining ring atoms.

The PO_5 geometry in 3 can be referred to a rectangular pyramid (RP) with O4 in the apical position. The atoms of the basal plane, O1, O2, O3, and O5, are coplanar to within ±0.024 (8) Å, with the P atom displaced from this plane by a distance of 0.126 (3) Å in a direction toward the apical O4. The trans basal angles (O2–P–O3 - 171.9 (4)° and O1–P–O5 = 169.8 (4)°) are on the order of 20° larger than would be expected for an RP involving phosphorus. This observation can be interpreted as a deformation toward octahedral geometry due to a bonding interaction between phosphorus and sulfur. The P–S distance of 2.375 (3) Å as well as the near-octahedral geometry at phosphorus and the pyramidal geometry at sulfur (Table VII), which are evident when the P–S bond is recognized, also supports P–S bond formation. Viewed in this fashion, the tridentate ligand has a facial placement in the octahedral coordination sphere of phosphorus. A *mer* placement is probably unlikely due to the tendency of tricoordinate sulfur to be found in a pyramidal geometry.

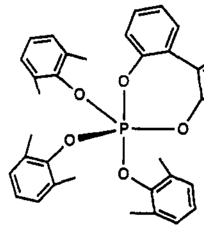
The seven-membered ring system in 3 is in a slightly twisted "row boat" conformation (Figure 5). The atoms forming the base of the boat (P, O4, C51, and C52) are coplanar to within ±0.08 (1) Å, while the "stern" atoms (C61 and C62) and the prow atom (O2) are displaced from this plane in the same direction by distances of 0.82 (1), 0.87 (1), and 0.614 (8) Å, respectively.

Ring Conformation Comparisons. The differing conformations for the eight-membered ring found in **2a**, **2s**, and **3** illustrate the flexibility of this ring system despite the constraints which are imposed by the fused aromatic rings. This ring system has also been examined[1b] in the related compounds C and D. In D the ring conformation is symmetrical syn with S→P bonding, as is found in 3. In C there is no S→P bonding to cause an octahedral deformation and the ring system spans equatorial sites of a TBP with a symmetrical anti conformation like that found in **2a**.

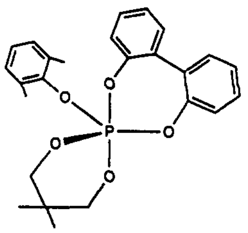
In a more quantitative vein (Table VIII), the P–S distances across the ring vary from 2.373 (5) Å (P–S bond) for 3 to 3.504 (3) Å (symmetrical anti) for C with an intermediate value of 3.166 (1) Å (twist syn) for **2s**. Variations in P–O bond lengths follow the coordination number at phosphorus: 1.578 (5) Å average for the four-coordinated phosphates, **2a** and **2s**, 1.617 (6) Å average for the five-coordinated oxyphosphorane C, and 1.694 (7) Å average for the six-coordinate derivatives, 3 and D. The largest angular variations are at phosphorus and reflect the coordination geometry. The O–P–O angles range from an average of 89.0 (4)° for octahedral coordination (3 and D) to 117.5 (3)° for the ring located diequatorially in a TBP (C) to intermediate near tetrahedral values (107.1 (5) and 104.0 (1)°) for the four-coordinated species **2a** and **2s**. There is little angular variation at sulfur where a range of only 3.4° is observed.

In the related compounds A[1b,4] and B,[1b] the sulfur atom of the eight-membered ring is replaced by a methylene group. This replacement precludes the conformation which accompanies S–P bond formation across the ring. Otherwise, the possible ring conformations appear to be the same. Diequatorial ring placement in a TBP (A) gives the symmetrical anti conformation found in **2a** and C. Axial–equatorial placement in a TBP (B) results in the twist syn conformation similar to that found in **2s**.

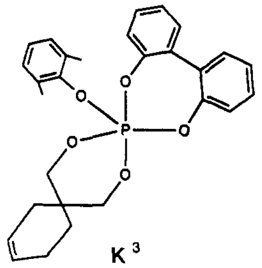
The same seven-membered ring in compound 3 which spans (a–e) sites of a TBP also has been observed occupying (a–e) sites of the trigonal-bipyramidal pentaoxyphosphoranes I, J, and K and in the phosphite L. In all these cases, the seven-membered ring is in a row boat conformation, similar to that found in 3 (Figure 5). The observation of the same conformation involving three-, five-, and six-coordinated phosphorus demonstrates the rigidity of this ring system relative to the varied conformations exhibited by the eight-membered rings in **2**, **3**, and A–D. Some geometric parameters for this ring system are given in Table IX.



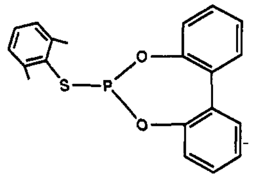
I[7]



J[6]



K[3]



L[3]

The anti conformation for the sulfur-bridged eight-membered ring has now been found in the four-coordinated phosphate, **2a**, and in diequatorial positions of the five-coordinated pentaoxyphosphorane, C,[1b] in addition to its appearance in diequatorial positions of the five-coordinated pentaoxyphosphorane A,[1b,4] where a CH_2 group has replaced the sulfur ring atom as the bridging unit. Likewise, the syn conformation of the eight-

Table VIII. Ring Geometry for the Eight-Membered Sulfur-Containing Rings in Compounds **2a**, **2s**, **3**, C, and D

compd	P coord no.	ring conformation	P–S, Å	P–O, Å	O–P–O, deg	C–S–C, deg	P–O–C, deg
C[a]	5	symmetrical anti	3.504 (3)	1.614 (6) 1.620 (5)	117.5 (3)	103.4 (4)	125.3 (6) 126.2 (4)
2a[b]	4	symmetrical anti	3.499 (5)	1.578 (8) 1.581 (8)	107.1 (5)	106.3 (6)	119.0 (7) 119.9 (7)
2s[b]	4	twist syn	3.166 (1)	1.574 (3) 1.579 (2)	104.0 (1)	104.1 (1)	126.1 (2) 126.6 (2)
D[a]	pseudo 6	symmetrical syn	2.504 (3)	1.681 (5) 1.684 (6)	89.6 (3)	102.9 (4)	124.6 (5) 127.0 (4)
3[b]	pseudo 6	symmetrical syn	2.373 (5)	1.699 (8) 1.711 (8)	88.3 (4)	103.7 (5)	122.1 (7) 123.2 (7)

[a] Reference 1b. [b] This work.

Table IX. Bond Parameters for the Seven-Membered Rings in **3**, I, J, K, and L

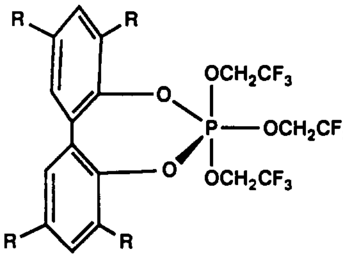
compd	P coord no.	δ_{Ph-Ph},[a] deg	P–O, Å	O–P–O, deg	P–O–C, deg
3[b]	pseudo 6	41.1 (5)	1.661 (8) 1.630 (8)	98.0 (4)	121.1 (7) 126.2 (7)
I[c]	5	35.6 (5)	1.678 (2)$_{ax}$ 1.601 (3)$_{eq}$	94.0 (1)	122.3 (2) 133.3 (2)
J[d]	5	36.2 (2)	1.685 (4)$_{ax}$ 1.616 (3)$_{eq}$	92.9 (2)	119.8 (3) 130.9 (3)
K[e]	5	41.3 (3)	1.682 (4)$_{ax}$ 1.617 (5)$_{eq}$	93.1 (2)	118.9 (4) 128.5 (4)
L[e]	3	39.6 (2)	1.635 (4) 1.632 (4)	100.0 (1)	118.5 (2) 124.1 (3)

[a] Dihedral angle between planes for the two phenyl groups as a measure of rotation out of coplanarity. [b] This work. [c] Reference 7. [d] Reference 6. [e] Reference 3.

membered ring has been observed in entirely different geometrical configurations, in the tetrahedral phosphate environment, **2s**, where the sulfur bridge is present, and in axial–equatorial positions of the trigonal-bipyramidal pentaoxyphosphorane B,[1b] where the CH_2 bridge is present. This ready accommodation of a common ring conformation in varying geometries for phosphorus, independent of the presence of sulfur as a bridging unit, emphasizes the considerable conformational flexibility of this eight-membered cyclic system. The isolation of both a syn and anti form for **2** indicates a small energy difference exists between them. However, it is still not apparent why (e–e) ring orientations in TBP structures arise for A and C compared to the (a–e) ring occupancy in a TBP found for B. It is more understandable that the pentaoxyphosphoranes **3** and D exist in pseudooctahedral structures via a P–S bond formation. Here the bulky *tert*-butyl groups of the phenyl rings situated ortho to the attached P–O bonds appear to exert a steric effect with the phosphorus atom in the anti conformation (Figure 4a). In the syn conformation (Figure 4c), as observed for **3** and D, the phosphorus atom is moved out of the way, resulting in P–S "bond" formation.

One last point to consider is the stabilization of these sulfur and methylene-bridged eight-membered rings in (e–e) sites of a TBP in contrast to the observance of only (a–e) orientations by X-ray crystallography for six-[2,5-13] and seven-membered[3,6,7] rings in pentaoxyphosphoranes. The answer, at least in part, may hinge on the ability of the more flexible eight-membered rings to orient the $P–O_{eq}–C$ ring atoms so that the dihedral angle that this grouping makes with the equatorial plane approaches 90°, the angle that would maximize the equatorial ring oxygen p orbital contribution to back-bonding with phosphorus as we noted earlier.[1b,25] This angle is 77.7 (2)° for A[1b] and 76.5 (5)° (average) for C.[1b] With a reduction in conformational flexibility implied for six- and seven-membered rings, this criterion would be difficult to meet, as pointed out by Trippett[25] for saturated six-membered rings. The resulting loss of stabilization from this effect may be sufficient to give preference to (a–e) ring orientations in TBP structures of pentaoxyphosphoranes with six- and seven-membered rings.

However, in view of a six-membered ring occupying (e–e) sites in the constrained tetraoxyphosphorane E, revealed by X-ray analysis,[14] and the solution NMR study of Denney and coworkers[26] indicating that a seven-membered ring in the pentaoxyphosphoranes M is situated (e–e), additional examples may be



M (R = t-Bu, H)

found for these smaller rings as substituent and bonding effects become more understood. This will assist in evaluating models for activated states in nucleophilic displacements, particularly in enzymatic reactions involving cyclic AMP[27-31] where both (e–e)[29,32] and (a–e)[29] orientations of a six-membered ring in TBP geometries are considered, depending on the enzyme system under consideration.

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE 88-19152) is gratefully acknowledged.

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

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(25) Trippett, S. *Pure Appl. Chem.* **1974**, *40*, 595.
(26) Abdou, W. M.; Denney, D. B.; Denney, D. Z.; Pastor, S. D. *Phosphorus Sulfur* **1985**, *22*, 99.
(27) Miller, J. P. In *Cyclic 3',5'-Nucleotides: Mechanisms of Action*; Cramer, H., Schulz, J., Eds.; John Wiley and Sons: London, 1977; pp 77–104.
(28) Jastorff, B.; Hoppe, J.; Morr, M. *Eur. J. Biochem.* **1979**, *101*, 555.
(29) van Ool, P. J. J. M.; Buck, H. M. *Eur. J. Biochem.* **1982**, *121*, 329.
(30) Mehdi, S.; Coderre, J. A.; Gerlt, J. A. *Tetrahedron* **1983**, *39*, 3483.
(31) Nelson, K. A.; Bentrude, W. G.; Setzer, W. N.; Hutchinson, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 4058 and references cited therein.
(32) van Ool, P. J. J. M.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 79.