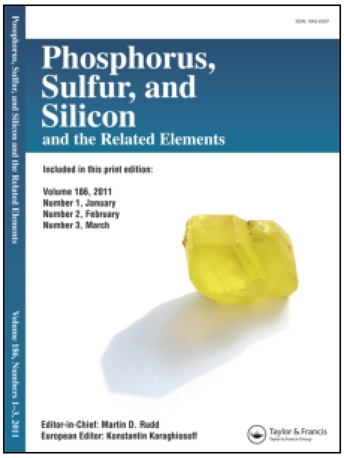


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

INFLUENCE OF PHOSPHORUS-SULFUR BONDING IN THE FORMATION OF OCTAHEDRALLY COORDINATED CYCLIC PENTAOXYPHOSPHORANES

T. K. Prakasha[a]; Roberta O. Day[a]; Robert R. Holmes[a]
[a] Department of Chemistry, University of Massachusetts, Amherst, Massachusetts

To cite this Article Prakasha, T. K. , Day, Roberta O. and Holmes, Robert R.(1995) 'INFLUENCE OF PHOSPHORUS-SULFUR BONDING IN THE FORMATION OF OCTAHEDRALLY COORDINATED CYCLIC PENTAOXYPHOSPHORANES', Phosphorus, Sulfur, and Silicon and the Related Elements, 100: 1, 149 — 161

To link to this Article: DOI: 10.1080/10426509508037706

URL: http://dx.doi.org/10.1080/10426509508037706

Phosphorus, Sulfur, and Silicon, 1995, Vol. 100, pp. 149–161
Reprints available directly from the publisher
Photocopying permitted by license only

INFLUENCE OF PHOSPHORUS–SULFUR BONDING IN THE FORMATION OF OCTAHEDRALLY COORDINATED CYCLIC PENTAOXYPHOSPHORANES[1,2]

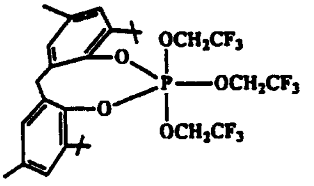
T. K. PRAKASHA, ROBERTA O. DAY and ROBERT R. HOLMES*
Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

(Received October 16, 1992)

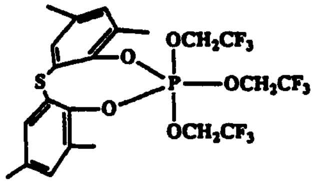
Formation of new pentaoxyphosphorane $X[R_1R_2C_6H_2O]_2P(OPh)_3$ (X = S, R_1 = R_2 = *t*-Bu for **1**; X = S, R_1 = *t*-Bu, R_2 = Me for **2**; X = S, R_1 = R_2 = Me for **3**; X = CH_2, R_1 = R_2 = *t*-Bu for **4**) containing sulfur-bridged eight-membered rings was achieved by oxidative addition reactions of triphenyl phosphite with diols in the presence of *N*-chlorodiisopropylamine in yields ranging from 70 to 80%. **1** contains 0.5 mol of Et_2O of crystallization. X-ray analysis of **1–3** revealed molecular structures having varying degrees of P–S bond formation, which results in distorted octahedral configurations. The P–S distances, 2.880(1) (**3**), 2.744(2) (**2**), and 2.640(2) Å (**1**), when included in a series with those of related cyclic oxyphosphoranes studied earlier, showed a uniform decrease which parallels a structural coordinate measuring the formation of an octahedron from a square pyramid, i.e., a trajectory proceeding from five- to six-coordinated phosphorus. The decrease in P–S distance along the series is attributable to an increase of electronic factors supplied by the alkyl substituents on the eight-membered ring, *t*-Bu > Me, and the electron-withdrawing ability of the appendent ligands, $(OC_6H_4)_2 > OCH_2CF_3 > OPh$. ^1H and ^{31}P solution-state NMR data are also reported. The structures of **1–3** contrast with that for an analogous derivative $S(Me_2C_6H_2O)_2P(OCH_2CF_3)_3$ (**B**), having the same sulfur-containing eight-membered ring which resides in a trigonal bipyramid with the ring located diequatorially and possessing no P–S bond (P–S = 3.504(3) Å). The results have important mechanistic implications for enzyme hydrolysis of phosphates at active sites having interacting sulfur residues. Oxyphosphorane **1** crystallizes in the triclinic space group $P\bar{1}$ with a = 9.696(3) Å, b = 10.814(2) Å, c = 22.113(3) Å, α = 82.62(1)°, β = 85.38(2)°, γ = 88.08(2)°, and Z = 2. Oxyphosphorane **2** crystallizes in the monoclinic space group $P2_1/n$ with a = 12.853(3) Å, b = 15.484(4) Å, c = 19.081(6) Å, β = 108.70(2)°, and Z = 4. Oxyphosphorane **3** crystallizes in the triclinic space group $P\bar{1}$ with a = 8.757(2) Å, b = 10.047(1) Å, c = 17.614(3) Å, α = 103.88°, β = 100.69(2)°, γ = 92.65(2)°, and Z = 2. The final conventional unweighted residuals are 0.056 (**1**), 0.031 (**2**), and 0.032 (**3**).

INTRODUCTION

We have reported the first examples of pentaoxyphosphoranes containing a diequatorial ring orientation in a trigonal bipyramid,[3,4] in contrast to the more usual axial–equatorial ring placement.[5–11] This structural variation was found by X-ray analysis of the monocyclic derivatives A[3] and B,[4] which possess eight-membered



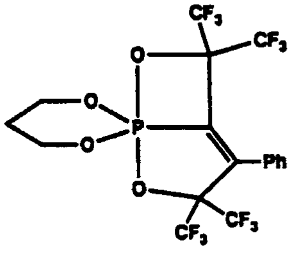
A



B

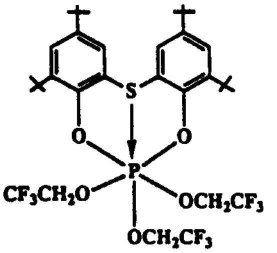
Reprinted with permission from J. Am. Chem. Soc., 115, 2690 (1993). Copyright 1993 American Chemical Society.

rings with methylene and sulfur bridges, respectively, between two aromatic components. No example with diequatorial ring placement has been reported thus far for a pentaoxyphosphorane having a smaller size ring, although Bentrude and coworkers[12] have discovered a tetraoxyphosphorane in a constrained polycyclic derivative with a saturated six-membered ring so oriented, i.e., C. The structural and conformational flexibility indicated for eight-membered rings compared to smaller rings in pentaoxyphosphoranes has been the subject of an earlier report.[4]

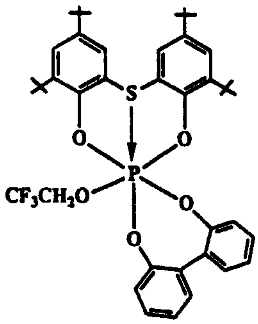


C

In the study of additional pentaoxyphosphoranes containing the sulfur-bridged eight-membered-ring system, yet a new structural variation was found. The formation of phosphorus–sulfur bonding in different degrees led to octahedral coordination at phosphorus D[4] and E.[13] The P–S distance here, 2.504(3) Å for D and 2.373(5) Å for E, contrasts with the much longer P–S distance of 3.504(3) Å found for B. The sum of the covalent radii for P and S is reported as 2.14 Å,[14] while the van der Waals sum is 3.75 Å.[15]

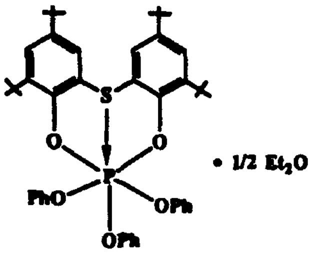


D

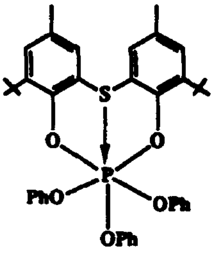


E

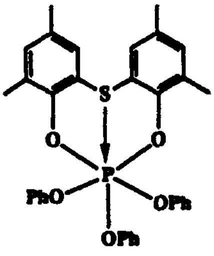
To explore this interesting coordination further, we synthesized a series of new cyclic pentaoxyphosphoranes having the sulfur-bridging eight-membered ring depicted in B, D, and E. Phenoxy groups completed the coordination sphere. These remained constant in the members **1**–**3**, while the ring substituents varied in the number of methyl and *tert*-butyl attachments. The latter variation was designed to ascertain their influence on coordination geometry and ring conformation. For comparison, pentaoxyphosphorane **4**, analogous to **1** but containing a methylene bridge in place of sulfur, was synthesized.



1



2



3

The X-ray structures of **1**–**3** are reported here. All three show P–S coordination, the degree of which varies from member to member. ^{1}H and ^{31}P NMR data also are obtained on solutions of **1**–**4**. The results of this study when included with previous structural results of the pentaoxyphosphoranes B,[4] D,[4] and E[13] provide a unique series showing a continuous variation in P–S bonding interpretable in terms of electronic factors.

EXPERIMENTAL

Reagents and Procedures. 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.[16]

^{1}H and ^{13}P NMR spectra were recorded on a Varian XL 300 FT-NMR spectrometer. ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane. Chemical shifts for ^{31}P NMR spectra were obtained by setting triphenyl phosphate[17] ($CDCl_3$) at −18.0 ppm and are referenced to 85% H_3PO_4 with negative shifts upfield. All NMR spectra were obtained at 23 °C.

Triphenyl phosphite was purchased from Eastman Kodak Co. 2,2′-Methylenebis(4,6-di-*tert*-butylphenol),[18] 2,2′-thiobis(4,6-di-*tert*-butylphenol),[19] 2,2′-thiobis(4,6-dimethylphenol),[20] and *N*-chlorodiisopropylamine[21] were prepared by literature procedures. All the reactions were carried out in a dry nitrogen atmosphere using standard Schlenk-type glassware.[22]

Syntheses. [2,2′-Methylenebis(4,6-di-tert-butylphenoxy)]triphenoxyphosphorane, $CH_2[(t\text{-}Bu)_2C_6H_2O](OPh)_3$ (**4**). To a mixture of triphenyl phosphite (2.00 mL, 2.37 g, 7.63 mmol) and 2,2′-methylenebis(4,6-di-*tert*-butylphenol) (3.24 g, 7.63 mmol) in diethyl ether (100 mL) maintained at −70 °C was added dropwise a solution of *n*-chlorodiisopropylamine (1.40 mL, 9.16 mmol) in diethyl ether (30 mL) over a period of 20 min with continuous stirring. The reaction mixture was gradually brought to 25 °C and stirred at this temperature for 95 h. The amine hydrochloride was filtered off and the filtrate concentrated under reduced pressure. The resulting residue was extracted with a 1:2 mixture (30:60 mL) of diethyl ether and hexane. Colorless crystals of **4** were obtained by passing a slow stream of nitrogen over the solution; mp 225 °C dec (yield 4.19 g, 75.0%). ^{1}H NMR (toluene-d_8): 1.48 (s, 18 H, $C(CH_3)_3$), 1.72 (s, 18 H, $C(CH_3)_3$), 3.38 (d, 1 H, CH_2), 4.42 (d, 1 H, CH_2), 6.20–7.80 (m, 19 H, Ar). ^{31}P NMR (toluene-d_8): −83.81. Anal. Calcd for $C_{47}H_{57}O_5P$: C, 77.04; H, 7.78. Found: C, 77.33; H, 7.98.

[2,2′-Thiobis(4,6-di-tert-butylphenoxy)]triphenoxyphosphorane, $S[(t\text{-}Bu)_2C_6H_2O](OPh)_3 \cdot {}^1/_2Et_2O$ (**1**). Quantities used were as follows: triphenyl phosphite, 2.00 mL, 2.37 g, 7.63 mmol; 2,2′-thiobis(4,6-di-*tert*-butylphenol), 3.37 g, 7.63 mmol; *n*-chlorodiisopropylamine, 1.40 mL, 1.24 g, 9.16 mmol; diethyl ether, 200 mL. A procedure similar to the synthesis of **4** was followed. Colorless crystals of **1** were obtained by concentrating the solution (30:75 mL of diethyl ether/hexane) by passing a slow stream of nitrogen over the solution; mp 174–175 °C (yield 4.06 g, 71.0%). ^{1}H NMR (toluene-d_8): 1.18 (s, 18 H, $C(CH_3)_3$), 1.43 (s, 18 H, $C(CH_3)_3$), 6.80–7.80 (m, 19 H, Ar). ^{31}P NMR (toluene-d_8): −82.6. Anal. Calcd for $C_{46}H_{55}O_5SP \cdot {}^1/_2C_4H_{10}O$: C, 73.2; H, 7.60. Found: C, 72.81; H, 7.70.

2,2′-Thiobis(4-methyl-6-tert-butylphenol) (**5**). To a mixture of 2-*tert*-butyl-4-methylphenol (164.3 g, 1.00 mol) and anhydrous zinc chloride (1.00 g, 7.5 mmol) in 350 mL of Skelly F (bp 35–60 °C) was added dropwise a solution of sulfur dichloride (31.8 mL, 55.0 g, 0.500 mol) in 100 mL of Skelly F at 0 to −5 °C. The resultant solution was stirred at room temperature for 17 h. The solution was filtered to remove a small quantity of black material. Subsequent evaporation of solvent gave light yellow crystals of the new compound, 2,2′-thiobis(4-methyl-6-*tert*-butylphenol), mp 79–81 °C (yield 116.3 g, 65.0%). ^{1}H NMR ($CDCl_3$): 1.40 (s, 18 H, $C(CH_3)_3$), 2.20 (s, 6 H, CH_3), 6.60 (s, 2 H, OH), 7.00 (d, 4 H, Ar). Anal. Calcd for $C_{22}H_{30}O_2S$: C, 73.74; H, 8.38. Found: C, 74.10; H, 8.68.

[2,2′-Thiobis(4-methyl-6-tert-butylphenoxy)]triphenoxyphosphorane, $S[(t\text{-}Bu)MeC_6H_2O]_2P(OPh)_3$ (**2**). Quantities used were as follows: triphenyl phosphite, 2.00 mL, 2.37 g, 7.63 mmol; 2,2′-thiobis(4-methyl-6-*tert*-butylphenol), 2.73 g, 7.63 mmol; *n*-chlorodiisopropylamine, 1.40 mL, 9.16 mmol; diethyl ether, 200 mL. A procedure similar to the synthesis of **4** was followed. Colorless crystals of **2** were obtained by concentrating a solution of a 1:3 mixture (40:120 mL) of diethyl ether and hexane; mp 195–196 °C (yield 3.96 g, 78.0%). ^{1}H NMR (toluene-d_8): 1.43 (s, 18 H, $C(CH_3)_3$), 1.95 (s, 6 H, CH_3), 6.80–7.80 (m, 19 H, Ar). ^{31}P NMR (toluene-d_8): −81.86. Anal. Calcd for $C_{40}H_{43}O_5SP$: C, 72.06; H, 6.46. Found: C, 71.77; H, 6.50.

[2,2′-Thiobis(4,6-dimethylphenoxy)]triphenoxyphosphorane, $S[Me_2C_6H_2O]_2P(OPh)_3$ (**3**). Quantities used were as follows: triphenyl phosphite, 2.00 mL, 2.37 g, 7.63 mmol; 2,2′-thiobis(4,6-dimethylphenol), 2.09 g, 7.63 mmol; *N*-chlorodiisopropylamine, 1.35 mL, 9.16 mmol; diethyl ether, 200 mL. A procedure similar to the synthesis of **4** was followed (except that the reaction time was only 70 h). Colorless crystals of **3** were obtained from a 1:2 mixture (30:60 mL) of diethyl ether and hexane; mp 155–156 °C (yield 3.50 g, 79.0%). ^{1}H NMR (toluene-d_8): 1.81 (s, 6 H, CH_3), 1.94 (s, 6 H, CH_3), 6.60–7.60 (m, 19 H, Ar). ^{31}P NMR (toluene-d_8): −81.16. Anal. Calcd for $C_{34}H_{31}O_5SP$: C, 70.10; H, 5.33. Found: C, 69.65; H, 5.39.

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.[23a]

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 $3° \leq 2\theta_{Mo\,K\bar{\alpha}} \leq 43°$. For **2** and **3**, empirical absorption corrections based on ψ scans were applied (relative transmission factors on I from 0.9526 to 0.9977 for **2** and from 0.9631 to 0.9994 for **3**). The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least-squares.[23b] All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs. Crystallographic data are summaried in Table I.

X-ray Study for $S[(t\text{-}Bu)_2C_6H_2O]_2(OPh)_3 \cdot {}^1/_2Et_2O$ (**1**). The crystal used for the study was cut from a large colorless plate and had dimensions of 0.25 × 0.45 × 0.50 mm. A total of 5216 independent reflections $(+h, \pm k, \pm l)$ was measured. The 53 independent non-hydrogen atoms of the phosphorane were refined anisotropically. Although thermal parameters were large for the pendant carbon atoms of the *tert*-butyl groups bound to C14 and C34, it was not possible to resolve more than one set of positions for these atoms. The 55 independent hydrogen atoms of the phosphorane were included in the refinement as fixed isotropic scatterers in ideal positions. The ether of solvation is disordered about an inversion center and poorly defined. Therefore non-hydrogen atoms from this moiety were refined isotropically and hydrogen atoms were omitted from the refinement.

X-ray Study for $S(t\text{-}BuMeC_6H_4O)_2P(OPh)_3$ (**2**). The colorless thin lath-shaped crystal used for the study had dimensions of 0.10 × 0.25 × 0.75 mm. A total of 4139 independent reflections $(+h, +k, \pm l)$ was

TABLE I

Crystallographic Data for Compounds 1–3

	1	2	3
formula	$C_{46}H_{55}O_5SP \cdot {}^1/_2C_4H_{10}O$	$C_{40}H_{43}O_5SP$	$C_{34}H_{31}O_5SP$
fw	788.048	666.824	582.661
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$(No. 2)	$P2_1/n$ (alternative No. 14)	$P\bar{1}$ (No. 2)
a, Å	9.696(3)	12.853(3)	8.757(2)
b, Å	10.814(2)	15.484(4)	10.047(1)
c, Å	22.113(3)	19.081(6)	17.614(3)
α, deg	82.62(1)		103.88(1)
β, deg	85.38(2)	108.70(2)	100.69(2)
γ, deg	88.08(2)		92.65(2)
V, Å^3	2291 (1)	3597(3)	1472(1)
Z	2	4	2
T, °C	23 ± 2	23 ± 2	23 ± 2
λ, Å	0.710 73	0.710 73	0.710 73
D_{calc}, g cm^{-3}	1.142	1.231	1.315
μ, cm^{-1}	1.427	1.694	1.973
$R(F_o)^a$	0.056	0.031	0.032
$R_w(F_o)^a$	0.076	0.043	0.047

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

measured. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included as fixed isotropic scatterers (ideal positions or regularized difference Fourier positions for the methyl group hydrogen atoms).

X-ray Study for $S(Me_2C_6H_2O)_2P(OPh)_3$ (**3**). The colorless crystal used for the X-ray study was a slightly irregular brick cut to approximate dimensions of 0.35 × 0.40 × 0.45 mm. A total of 3361 independent reflections ($+h, \pm k, \pm l$) was measured. Refinement was conduced in the same manner as described for **2**.

RESULTS

The atom-labeling schemes for **1**–**3** are given in the ORTEP plots of Figures 1–3, respectively. Important distances and angles are given in Table II. 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 percursor diol **5**, which represents a new compound, was prepared by treating 2-*tert*-butyl-4-methylphenol in a coupling reaction with sulfur dichloride in the presence of anhydrous zinc chloride as a catalyst (eq 1).

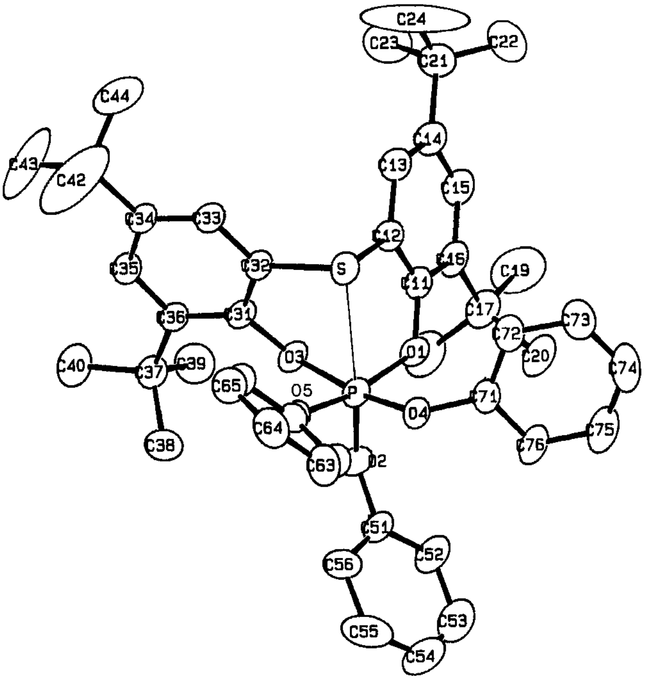


FIGURE 1 ORTEP plot of $S[(t\text{-Bu})_2C_6H_2O]_2P(OPh)_3$ from **1** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and atoms of the ether of solvation are omitted for clarity.

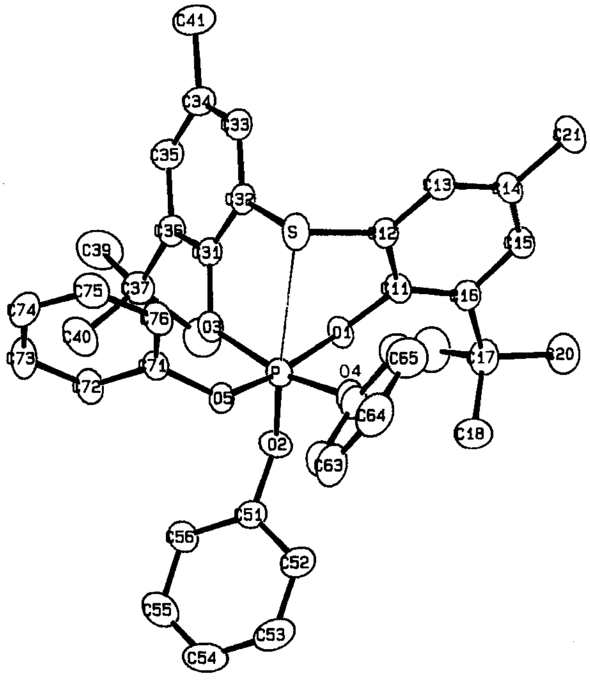
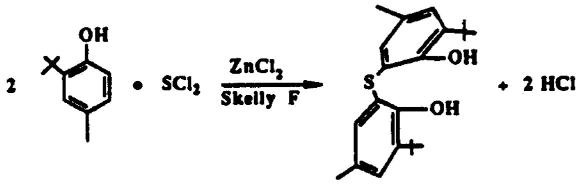


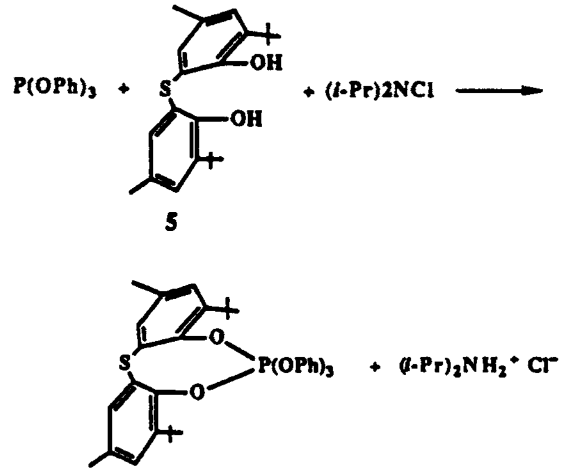
FIGURE 2 ORTEP plot of $S(t\text{-BuMeC}_6H_2O)_2P(OPh)_3$ (**2**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.



(1)

5

This preparation follows an earlier reported procedure[19] that was used to obtain the analogous diol needed for the synthesis of **1**. Oxidative addition reactions of triphenyl phosphite with the appropriate diol in the presence of *N*-chlorodiisopropylamine then lead to the desired pentaoxyphosphoranes, **1**–**4**, in good yield (70–80%). This process is illustrated in eq 2 for the formation of **2**.



(2)

2

All of the resulting compounds are sensitive to chlorine-containing solvents. For example, they decompose rapidly in $CDCl_3$ solution, giving multiple peaks in the ^{31}P NMR spectrum. By contrast, single resonances are obtained in toluene-d_8 solution with the ^{31}P chemical shifts, −84 to −81 ppm, in the five-coordinate region. NMR studies of the previous compounds showed they behaved well in $CDCl_3$ solution, all giving single ^{31}P resonances: e.g., −78.8 ppm for A,[3] −77.3 ppm for B,[4] −82.4 ppm for D,[4] and −69.3 ppm for E.[13] These values compare with ^{31}P chemical shifts obtained in toluene-d_8 for **1** (−82.6 ppm), **2** (−81.9 ppm), and **3** (−81.2 ppm).

The basic structures of the sulfur-containing-ring derivatives **1**–**3** are distorted octahedral arrangements resulting from the presence of phosphorus–sulfur interactions. Schematic diagrams presented in the Introduction for each illustrate this coordination geometry. The fact that the ^{31}P NMR shifts for the truly pentacoordinated members A and B are not particularly different from those for the hexacoordinated members (**1**–**3**, D, and E) suggests that the P–S "bonding" in the latter group of compounds may not be sufficiently strong, i.e., close enough to the covalent value, to significantly influence the ^{31}P chemical shift. However, more pertinent, as we have shown, is the presence of P–S binding in the coordination

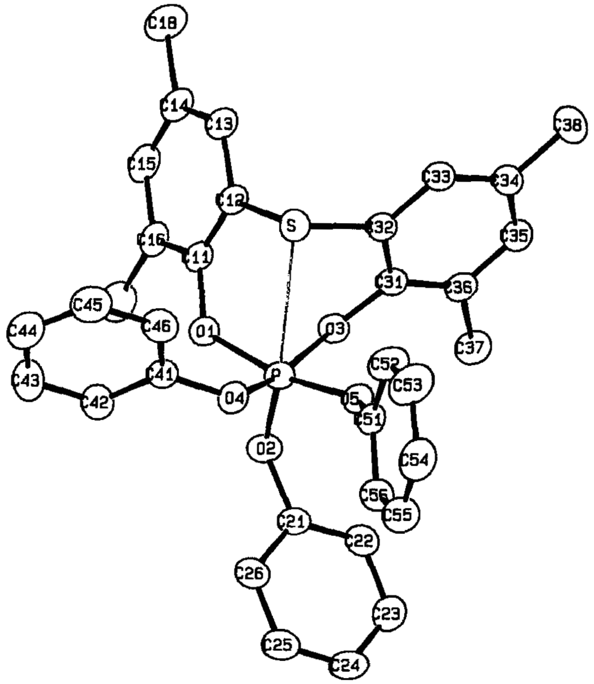


FIGURE 3 ORTEP plot of $S(Me_2C_6H_2O)_2P(OPh)_3$ (**3**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

sphere which causes a marked deshielding effect.[24] Even in hexacoordinated cyclic phosphorus compounds containing a PO_6 or PO_5N arrangement, the ^{31}P chemical shifts lie in the range from −80 to −110 ppm,[25] not too far from the values reported here. Data in the literature do not appear to be available for cyclic derivatives with PO_5S bonding for comparison here.

^{31}P NMR chemical shifts obtained earlier for B and D in the solid state indicate that the X-ray structures are retained in solution.[4] For B, which has a diequatorial ring orientation, the ^{31}P chemical shift in the solid state is −74.7 ppm. This value is close to that in $CDCl_3$ solution, −77.3 ppm. For the distorted octahedral structure D, the ^{31}P shifts are −82.9 ppm (solid state) and −82.4 ppm ($CDCl_3$ solution), nearly identical values. The maintenance of the integrity of the solid-state structure in solution is further supported by a similar conclusion of Maciel and co-workers,[26] who compared ^{31}P chemical shifts of a more extensive range of phosphoranes and found that they did not differ substantially from one another in the solid and solution states.

The structures of **1**–**3** contrast with those of A[3] and B[4] which are trigonal pyramidal. B has the same ring system as **3** but contains OCH_2CF_3 groups in place of OPh groups. One might speculate that the more electronegative OCH_2CF_3 ligands show a greater tendency to occupy the preferred axial sites of a trigonal bipyramid and thus support the formation of the structure obtained for B. Evidence that OCH_2CF_3 is more electronegative than OPh is available from the greater deshielding for OCH_2CF_3 apparent from ^{31}P shifts of $MeN[P(OCH_2CF_3)_2]_2$ (149.9

TABLE II

Selected Distances (Å) and Angles (deg) for $S[(t\text{-}Bu)_2C_6H_2O]_2P(OPh)_3 \cdot {}^1/_2Et_2O$ (**1**), $S(t\text{-}BuMeC_6H_2O)_2P(OPh)_3$ (**2**), and $S(Me_2C_6H_2O)_2P(OPh)_3$ (**3**)[a]

Distances

	1	**2**	**3**
S-C12	1.765(5)	1.775(4)	1.771(3)
P-S	2.640(2)	2.744(2)	2.880(1)
P-O1	1.676(3)	1.681(3)	1.656(2)
P-O2	1.613(3)	1.612(3)	1.597(2)
S-C32	1.767(4)	1.780(3)	1.770(2)
P-O3	1.689(3)	1.673(2)	1.680(1)
P-O4	1.649(3)	1.655(2)	1.643(2)
P-O5	1.652(3)	1.634(3)	1.644(2)

Angles

	1	**2**	**3**
S-P-O1	82.4(1)	76.70(9)	77.16(7)
S-P-O2	168.5(1)	165.8(1)	165.83(7)
S-P-O3	79.0(1)	79.19(9)	74.45(6)
S-P-O4	89.9(1)	85.6(1)	87.21(7)
S-P-O5	85.3(1)	92.78(9)	88.00(6)
O1-P-O2	93.2(2)	90.4(1)	91.7(1)
O1-P-O3	88.7(2)	89.0(1)	89.11(8)
O1-P-O4	90.5(2)	88.6(1)	91.18(9)
P-S-C12	87.8(2)	85.8(1)	84.08(9)
O1-P-O5	167.7(2)	169.4(1)	165.16(9)
O2-P-O3	90.3(2)	95.0(1)	96.94(9)
O2-P-O4	100.8(2)	100.1(1)	101.92(9)
O2-P-O5	98.9(2)	100.2(1)	102.93(9)
O3-P-O4	168.9(2)	164.8(1)	161.1(1)
O3-P-O5	88.8(2)	90.4(1)	86.62(8)
O4-P-O5	89.6(2)	89.3(1)	88.31(9)
C12-S—C32	100.4(2)	99.1(2)	100.2(1)
P-S—C32	88.0(2)	86.7(1)	83.73(8)

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figures 1-3 for **1**-**3**, respectively.

ppm) relative to $MeN[P(OPh)_2]_2$ (135.1 ppm) and of $PhN[P(OCH_2CF_3)_2]_2$ (140.3 ppm) relative to $PhN[P(OPh)_2]_2$ (127.7 ppm).[27]

Structural Details

(A) Coordination Geometry. Viewed as pentaoxyphosphoranes, all three compounds, **1**-**3**, can be described as having rectangular pyramidal geometry about the phosphorus atom with atoms O1, O3, O4, and O5 defining the basal plane and atom O2 in the apical position. For **1**, the atoms of the basal plane are coplanar to within ±0.008(3) Å, while the phosphorus atom is displaced from this plane by a distance of 0.169(1) Å in a direction toward the apical O2. For **2**, these values are ±0.034(2) and ±0.186(1) Å, while the values for **3** are ±0.030(2) and ±0.241(1) Å. In all cases, the trans basal angles (ranging from 161.1(1) to 169.4(1)°) are larger

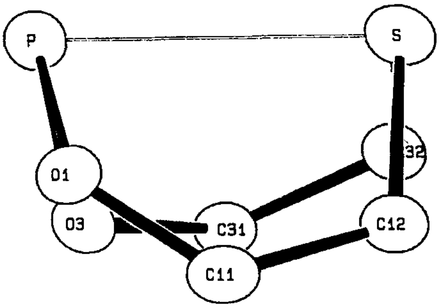


FIGURE 4 ORTEP plots showing the conformation of the eight-membered ring in **1**. This plot is very similar to those for **2** and **3**.

than would be expected for rectangular pyramids involving phosphorus, where the usual value is on the order of 150°. The enlargement of the trans basal angles is undoubtedly due to a bonding interaction with the sulfur atom trans to the apical O2 (S–P–O2 angles ranging from 165.8(1) to 168.5(1)°).

When the phosphorus–sulfur interaction is considered, the geometry at phosphorus may be described as distorted octahedra. The P–S distances range from 2.640(2) to 2.880(1) Å as compared to the van der Waals sum of 3.75 Å[15] or the sum of the single-bond covalent radii of 2.14.[14]

(B) Ring Conformation. The conformations of the eight-membered rings for **1**–**3** are very similar to each other but somewhat different from those seen previously in the related compounds D[4] and E,[13] for which the P–S distances are somewhat shorter, 2.504(3) Å for D and 2.375(3) Å for E. Figure 4 shows this conformation for **1**. In D and E, the ring conformation was described as symmetrical syn; that is, the phosphorus and sulfur atoms were on the same side of the ring relative to the other ring atoms (syn), and there was a pseudomirror plane which contained the phosphorus and sulfur atoms such that the ring oxygen atoms were equivalent. In compounds **1**–**3**, the rings have a syn conformation, but there is a slight twist to the ring in each case which removes the pseudomirror plane. As is apparent in Figure 4, the ring oxygen atoms, O1 and O3, attached to phosphorus are not equivalent.

It is also possible to view the eight-membered-ring conformations for **1**–**3** as very twisted tubs. For compound **1**, the atoms forming the floor of the tub (O3, C31, C11, and C12) are coplanar to within ±0.111(4) Å, while P, O1, S, and C32 are displaced in the same direction from this plane by distances of 1.554(1), 0.682(3), 1.344(1), and 0.368(4) Å, respectively. For compound **3**, the corresponding numbers are ±0.084(2) Å and 1.535(1), 0.802(2), 1.327(1), and 0.396(2) Å. For compound **2**, the atoms forming the floor of the tub (O1, C11, C31, and C32) are coplanar to within ±0.106(3) Å with P, O3, S, and C12 displaced from the plane by distances of 1.561(1), 0.774(2), 1.364(1), and 0.385(4) Å, respectively.

Bond Length Comparisons and Reaction Coordinate

Table III lists pertinent data measuring the extent of P–S coordination in cyclic oxyphosphoranes. It is noted that there is a continuous decrease in the P–S distance for the compounds studied, which in general parallels an increase in the P–O bond

TABLE III

Comparison of Bond Parameters for P–S Coordination in Cyclic Pentaoxyphosphoranes

compd[a]	P–S, Å	P–O, Å (trans to P–S)	S–P–O, deg[b]	P displacement, Å[c]
B[4]	3.504(3)	*d*	*d*	
3	2.880(1)	1.597(2)	165.83(7)	0.241(1)
2	2.744(2)	1.612(3)	165.8(1)	0.186(1)
1	2.640(2)	1.613(3)	168.5(1)	0.169(1)
D[4]	2.504(3)	1.640(7)	172.2(3)	0.153(2)
E[13]	2.373(5)	1.630(8)	175.5(3)	0.126(3)

[a] The coordination geometry at phosphorus for B, which lacks P–S coordination, is five; that for the others containing P–S coordination is pseudo-six. References are shown as superscripts. 1–3 comprise this work. [b] This angle refers to the oxygen atom trans to sulfur in the hexacoordinated structure: [c] Displacement of the phosphorus atom from the base plane (defined by the four oxygen atoms cis to sulfur) of a square pyramid toward the trans oxygen atom (apical position in the square pyramid). [d] In B, with diequatorial ring placement in a trigonal bipyramid, these entries do not apply.

length that is opposite the incoming sulfur atom. The latter P–O bond lengthening is expected for a series in which the degree of hexacoordination progressively increases. Accompanying this change, the P–S–O angle involving this same trans-situated oxygen atom approaches 180°, again in agreement with the formation of an octahedral arrangement at phosphorus.

The last column of Table III lists the displacement of the phosphorus atom from a base plane of the four oxygen atoms oriented cis to sulfur where the displacement is toward the remaining oxygen atom located trans to sulfur. This displacement, which decreases in the series of cyclic pentaoxyphosphoranes given in Table III, parallels a decrease in the P–S distance and indicates the extent of geometrical conversion from a square pyramid to an octahedron as the coordination number for phosphorus changes from 5 to 6. This correlation is shown graphically in Figure 5 and represents the first such defined reaction coordinate for cyclic phosphorus compounds connecting coordination numbers 5 and 6. The percent displacement toward the octahedron is calculated to be 44.1 for **3** and progressively increases along the series 56.8 (**2**), 60.8 (**1**), 64.5 (D), and 70.8 (E).[24]

These results may have important implications for phosphates at enzyme active sites in the presence of sulfur-containing amino acid residues, e.g. in enzymes like tyrosyl-tRNA synthetase.[28] Previously, only pentacoordinated intermediates of phosphorus have received serious attention. In a preliminary study on compounds related to **1**–**3**,[29] we find that the formation of a P–S interaction catalyzes the cleavage of a P–O linkage, resulting in phosphate formation via a rapid hydrolysis process.

For compounds **1**–**3**, D,[4] and E,[13] the P–O bond trans to sulfur is the shortest, averaging 1.618(5) Å, while the P–O bonds that are part of the sulfur-bridged eight-membered-ring system are the longest, 1.683(5) Å (average). The remaining two P–O bonds are intermediate in length with an average value of 1.650(5) Å. If one views these compounds in terms of a PO_5 square pyramid (see inset to Figure

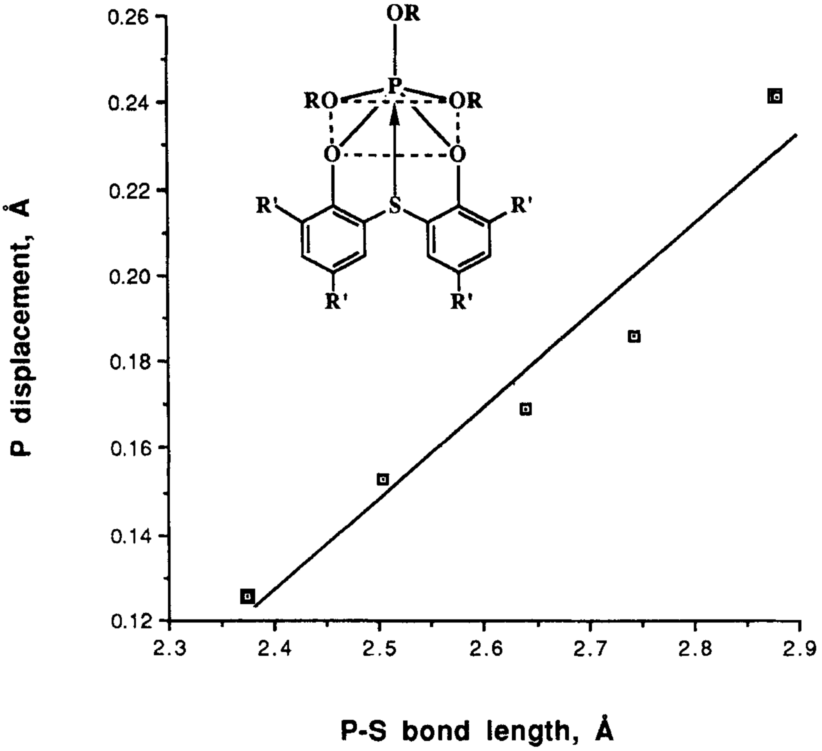


FIGURE 5 Displacement of phosphorus from the mean plane of four attached oxygen atoms considered to comprise the base of a square pyramid. The displacement is toward the remaining apical oxygen atom, which is trans to the approaching sulfur atom, as depicted in the inset. This displacement is represented as a function of the P–S distance for the compounds listed in Table III.

5), the observation of longer basal bonds compared to the apical one agrees with that expected[30] for a square pyramid containing a main group element.

It is noted that the P–S distance for **1**–**3** decreases as the total bulk of the substituents increases. However, examination of this trend with **1**, D,[4] and E,[13] which have the same eight-membered-ring systems, reveals an order of decreasing P–S distance that parallels the increasing electron delocalization ability of the remaining ligands: $(OC_6H_4)_2 > OCH_2CF_3 > OPh$. Hence, it seems reasonable that the series is under electronic control and that the order of P–S distances within the series **1**–**3** is determined by the electron-donating ability of the eight-membered-ring substituents: *t*-Bu > Me. This factor acts to strengthen the P–S linkage in **1** > **2** > **3**, in line with observations.

ACKNOWLEDGEMENT

The support of this research by the National Science Foundation (Grant CHE 91-22352) is gratefully acknowledged.

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.

REFERENCES AND NOTES

(1) (a) Pentacoordinated Molecules. 95. (b) Part 94: Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.*, in press.

(2) Presented in part at the XIIth International Conference on Phosphorus Chemistry, Toulouse, France, 1992; Abstract B-19.

(3) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 725-726.

(4) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 1913-1920.

(5) Kumara Swamy, K. C.; Burton, S. D.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *53*, 437.

(6) Schomburg, D.; Hacklin, H.; Röschenthaler, G.-V. *Phosphorus Sulfur Relat. Elem.* **1988**, *35*, 241.

(7) Kumara Swamy, K. C.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6095.

(8) Burton, S. D.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6104.

(9) Holmes, R. R.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O. *Inorg. Chem.* **1991**, *30*, 1052.

(10) Yu, J. H.; Sopchik, A. E.; Arif, A. M.; Bentrude, W. G. *J. Org. Chem.* **1990**, *55*, 3444.

(11) Yu, J. H.; Arif, A. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1990**, *112*, 7451.

(12) Huang, Y.; Arif, A. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1991**, *113*, 7800.

(13) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 3391-3397.

(14) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 224.

(15) Reference 14, p 260.

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

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

(18) Odorisio, P. A.; Pastor, S. D.; Spivack, J. D.; Bini, D.; Rodebaugh, R. K. *Phosphorus Sulfur Relat. Elem.* **1984**, *19*, 285.

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

(20) Pastor, S. D.; Denney, D. Z. *Phosphorus Sulfur Relat. Elem.* **1987**, *32*, 105.

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

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

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

(24) Holmes, R. R.; Prakasha, T. K. *Phosphorus, Sulfur Silicon Relat. Elem.*, accepted for publication.

(25) Brazier, J. F.; Lamandé, L.; Wolf, R. *Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; Tebby, J. C., Ed.; CRC Press Inc.: Boca Raton, FL, 1991; Chapter 18.

(26) Dennis, L. W.; Bartuska, V. J.; Maciel, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 230.

(27) Balakrishna, M. S.; Prakasha, T. K.; Krishnamurthy, S. S.; Siriwardane, U.; Hosmane, N. S. *J. Organomet. Chem.* **1990**, *390*, 203.

(28) Johnson, K. A.; Benkovic, S. J. Analysis of Protein Function by Mutagenesis. In *The Enzymes*, Vol. XIX, 3rd ed.; Sigman, D. S., Boyer, P. D., Eds.; Academic Press, Inc.: New York, 1990; Chapter 4, pp 177 ff.

(29) Unpublished work.

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