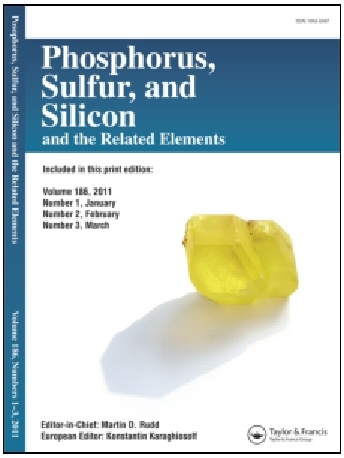

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The Effect of Trifluoroethoxy Groups on the Structures of Eight-Membered Ring-Containing Cyclic Phosphites[1]

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The Effect of Trifluoroethoxy Groups on the Structures of Eight-Membered Ring-Containing Cyclic Phosphites[1]

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*New phosphites **1–4** were synthesized from phosphorus trichloride and an appropriate diphenol followed by the addition of trifluoroethanol in the presence of triethylamine. These phosphites are to serve as precursors in the syntheses of biorelated hypervalent phosphoranes.* ^1H, ^{19}F, *and* ^{31}P *NMR spectra were recorded. X-ray analysis of **3** and **4** revealed that the sulfur-containing eight-membered ring was in a syn conformation that a allowed a sulfur donor interaction to the phosphorus atom, whereas for phosphite **2**, the eight membered sulfonyl containing ring was in an* anti *conformation that did not allow a donor interaction to phosphorus from the oxygen atom of the sulfonyl group. Structural comparisons are made with related cyclic phosphites and phosphates having donor atoms in eight-membered rings.*

Keywords Cyclic phosphites; phosphorus-sulfur donor interactions; trifluoroethoxy groups; X-ray crystallography

INTRODUCTION

Earlier our efforts concentrated on the donor interaction of sulfur, oxygen, and nitrogen to phosphorus in a variety of coordination states as found in phosphoranes, phosphites, and phosphates.[2,3] In sulfonyl-containing phosphoranes, the ease with which phosphorus can transform from five coordination to six coordination was discovered.[4,5] In phosphites containing pentafluorophenoxy groups, unusually strong donor interactions were present.[6] The present study delineates the

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syntheses of trifluoroethoxy-containing phosphites **1–4** and the crystal structures of **2–4**. These cyclic phosphates are to serve as precursors for the formation of biorelated hypervalent phosphoranes in an extension of our recent work in this area.[7] The varying geometries of **2–4** and their degree of donor interaction at phosphorus are compared with other phosphites, phosphates, and phosphoranes that have similar donor atoms.

EXPERIMENTAL

2,2′-methylene-bis(4-methyl,6-tert-butylphenol) (Aldrich) was used as supplied, whereas trifluoroethanol (Fluka) was dried over molecular sieves (4 Å, flame-dried under vacuum). Phosphorus trichloride (Aldrich) was distilled prior to use, and triethylamine (Aldrich) was distilled over potassium hydroxide pellets. Thiobis(4-methyl,6-tert-butylphenol)[8] and sulfonylbis(4-methyl,6-tert-butylphenol)[9] were synthesized according to our earlier methods. Solvents were purified according to standard procedures.[10] All reactions were carried out in an argon atmosphere. Solution NMR spectra were recorded on a Bruker Avance-400 (^{1}H and ^{31}P at 400.1 and 162.0 MHz, respectively) or Bruker DPX300 FT NMR (^{19}F at 282.4 MHz) spectrometer. Solution phosphorus NMR spectra were recorded in a sweep-off mode. Chemical shifts are reported in ppm, downfield positive, and relative to tetramethylsilane for ^{1}H and $CFCl_3$ for ^{19}F NMR and 85% H_3PO_4 for ^{31}P NMR. All were recorded at around 23°C. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory (Amherst, Massachusetts).

Syntheses

$CH_2[Me,Bu^t\text{-}C_6H_2O]_2P(OCH_2CF_3)$ (1)

Methylene-bis(4-methyl,6-tert-butylphenol) (7.80 g, 23 mmol) and phosphorus trichloride (2.00 mL, 23 mmol) were stirred in dichloromethane (100 mL). Triethylamine (9.60 mL, 69 mmol) in dichloromethane (50 mL) was added dropwise over a period of 15 min, and the solution was stirred further for 2 h. Trifluoroethanol (1.70 mL, 23 mmol) was added, and the reaction mixture stirred for an additional 24 h. The solvent was removed, and the residue was extracted with ether (120 mL) and filtered. Heptane (20 mL) was added, and the solution was left under an argon flow to obtain a powdery solid. The solid was filtered, washed with heptane (3 × 10 mL), and dried. Yield 4.10 g (38%). M.p. 141–143°C. ^{31}P NMR (CH_2Cl_2): 125.6.^{19}F NMR($CDCl_3$): −75.12

(t, $^3J_{FCCH}$ = 8.4 Hz). ^{1}H NMR(CDCl$_3$): 1.39 (s, 18H, Bu^t), 2.29 (s, 6H, aryl-CH$_3$), 3.38 (d, $^2J_{HCH}$ = 12.8, 1H, CH$_2$), 4.25 (dd, $^2J_{HCH}$ = 12.8, J_{PH} = 3.0 Hz, 1H, CH$_2$), 4.72 (qd, $^3J_{FCCH}$ = 8.4, $^3J_{POCH}$ = 5.1 Hz, 2H, POCH$_2$CF$_3$), 7.04 (s, 2H, aryl-H) , 7.10 (s, 2H, aryl-H). Anal. calcd. for $C_{25}H_{32}O_3F_3P$: C, 64.09; H, 6.88. Found: C, 64.35; H, 7.07.

$O_2S[Me,Bu^t\text{-}C_6H_2O]_2P(OCH_2CF_3)$ (2)

Sulfonyl-bis(4-methyl,6-tert-butylphenol) (8.95 g, 23 mmol) and phosphorus trichloride (2.00 mL, 23 mmol) were stirred in dichloromethane (100 mL). Triethylamine (6.40 mL, 15.5 mmol) in dichloromethane (50 mL) was added dropwise over a period of 30 min, and the solution was stirred further for 3 h. Trifluoroethanol (1.70 mL, 23 mmol) and triethylamine (3.20 mL, 7.8 mmol) were added, and the reaction mixture was stirred for an additional 24 h. The solvent was removed, and the residue was extracted with ether (150 mL) and filtered. The solvent was removed from the ether solution, and the residue was crystallized from dichloromethane-heptane (50:50 mL). The crystalline solid was filtered, washed with heptane (25 mL), and dried. Yield 4.50 g (38%). M.p. 231–233°C. ^{31}P NMR (CH$_2$Cl$_2$): 124.5.^{19}F NMR(CDCl$_3$): −74.93 (t, $^3J_{FCCH}$ = 8.3 Hz). ^{1}H NMR(CDCl$_3$): 1.40 (s, 18H, Bu^t), 2.23 (s, 6H, aryl-CH$_3$), 4.79 (qd, $^3J_{FCCH}$ = 8.4, $^3J_{POCH}$ = 5.4 Hz, 2H, POCH$_2$CF$_3$), 7.42 (d, 2.0 Hz, 2H, aryl-H), 7.75 (d, 2.0 Hz, 2H, aryl-H). Anal. calcd. for $C_{24}H_{30}O_5F_3PS$: C, 55.59; H, 5.83. Found: C, 55.27; H, 5.94.

$S[Me,Bu^t\text{-}C_6H_2O]_2P(OCH_2CF_3)$ (3)

Thio-bis(4-methyl,6-tert-butylphenol) (8.20 g, 23 mmol) and phosphorus trichloride (2.00 mL, 23 mmol) were stirred in dichloromethane (100 mL). Triethylamine (9.60 mL, 69 mmol) in dichloromethane (50 mL) was added dropwise over a period of 40 min, and the solution was stirred further for 3 h. Trifluoroethanol (1.70 mL, 23 mmol) was added, and the reaction mixture stirred for an additional 24 h. The solvent was removed, and the residue was extracted with ether (150 mL) and filtered. Heptane (40 mL) was added, and the solution was left under an argon flow to obtain a crystalline solid with an oily product. The solid was separated by decanting off the solution and washing with heptane (20 mL). This crude solid was recrystallized from heptane-dichloromethane (40:40 mL). Yield 5.20 g (47%). M.p. 106–108°C. ^{31}P NMR (CH$_2$Cl$_2$): 144.0 (q, $^4J_{POCCF}$ = 8.0 Hz). ^{19}F NMR(CDCl$_3$): −75.67 (q, $^3J_{FCCH}$ = $^4J_{POCCF}$ = 8.2 Hz).^{1}H NMR(CDCl$_3$): 1.36 (s, 18H, Bu^t), 2.26 (s, 6H, aryl-CH$_3$), 4.40 (quintuplet, $^3J_{FCCH}$ = $^3J_{POCH}$ = 8.5 Hz, 2H, POCH$_2$CF$_3$), 7.10 (d, 2.0 Hz, 2H, aryl-H) , 7.31 (d, 2.0 Hz, 2H, aryl-H). Anal. calcd. for $C_{24}H_{30}O_3F_3PS$: C, 59.25; H, 6.22. Found: C, 59.31; H, 6.26.

$S[Bu^t_2\text{-}C_6H_2O]_2P(OCH_2CF_3)$ (4)

Phosphite **4** was prepared as reported earlier.[11] The following NMR data showed additional couplings between phosphorus and fluorine compared to that previously reported. ^{31}P NMR (CH_2Cl_2): 143.0 (q, $^4J_{POCCF} = 7.7$ Hz). ^{19}F NMR($CDCl_3$): −75.62 (q, $^3J_{FCCH} = {}^4J_{POCCF} = 8.2$ Hz).

X-ray Studies

The X-ray crystallographic studies were performed using a Nonius KappaCCD diffractometer and graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). Data were collected at 293 K, $\theta_{\mathrm{MoK}\alpha} \leq 25°$. All of the data were included in the refinement. Structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least squares. Refinements were based on F^2, and computations were performed on a 2.6 GHz Pentium 4 computer using SHELXS-86 for a solution[12] and SHELXL-97 for refinement.[13] All of the non-hydrogen atoms were refined anisotropically. The crystal lattice of **3** had two independent molecules in each asymmetric unit. In **4**, one of the t-butyl groups and the trifluoroethyl group were disordered, and they were refined at the isotropic level in two positions with 2:1 and 1:1 occupancy ratio, respectively. All hydrogen atoms were included in the refinement as isotropic scatterers riding in either ideal positions or with torsional refinement (in the case of methyl hydrogen atoms) on the bonded atoms. The final agreement factors were based on the reflections with $I \geq 2\sigma_I$.

Crystallographic data (excluding structure factors) for all structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary material. The publication numbers are CCDC 603516-603518. Copies of the data can be obtained free of charge from the CCDC website (http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Crystallographic data are summarized in Table I. The atom-labeling schemes for **2–4** are given in the ORTEP plots of Figures 1–3, respectively. These figures were made using ORTEP-III for Windows program.[14] The hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 50% probability level. Selected bond parameters are given in Tables II–IV.

Syntheses

The new phosphites were synthesized by adding phosphorus trichloride to a solution of an appropriate diphenol and triethylamine, followed by

TABLE I Crystallographic Data for Compounds 2–4

Compound	**2**	**3**	**4**
Formula	$C_{24}H_{30}F_3O_3PS$	$C_{24}H_{30}F_3O_5PS$	$C_{30}H_{42}F_3O_3PS$
Formula weight	486.51	518.51	570.67
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
Crystal size, mm	0.75 × 0.60 × 0.50	0.75 × 0.25 × 0.10	0.90 × 0.70 × 0.65
a (Å)	14.2033(3)	9.46930(10)	11.3226(2)
b (Å)	10.1165(2)	14.9483(3)	18.4607(4)
c (Å)	18.1218(4)	18.2531(4)	15.3111(3)
α (°)	90.00	91.7936(8)	90.00
β (°)	97.5362(9)	90.3189(13)	90.0453(12)
γ (°)	90.00	99.8095(12)	90.00
V (Å^3)	2581.39(9)	2544.55(8)	3200.37(11)
Z	4	4	4
D_{calc} (g/cm^3)	1.252	1.353	1.184
$\mu_{MoK\alpha}$ (cm^{-1})	2.31	2.44	1.96
Total reflns	4513	8947	5620
Reflns with $I > 2\sigma_I$	3683	6508	4307
R^a	0.0403	0.0990	0.0986
R_w^b	0.1052	0.2533	0.2716

$^aR = \Sigma||F_o|-|F_c||/\Sigma|Fo|$

$^bR_w(F_o^2) = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4\}^{1/2}$.

TABLE II Selected Bond Lengths [Å] and Angles [deg] for 2

P(1)-O(1)	1.642(4)	P(1)-O(2)	1.636(5)
P(1)-O(3)	1.605(5)		
O(1)-P(1)-O(2)	102.5(2)	O(1)-P(1)-O(3)	96.4(3)
O(2)-P(1)-O(3)	96.5(3)	O(4)-S(1)-O(5)	118.4(3)
C(7)-S(1)-C(6)	106.1(3)	C(1)-O(1)-P(1)	121.7(4)
C(12)-O(2)-P(1)	122.5(4)	C(15)-O(3)-P(1)	121.9(5)

TABLE III Selected Dond Lengths [Å] and Angles [deg] for 3

P-O(1)	1.637(1)	P-O(2)	1.642(1)
P-O(3)	1.648(1)	P-S	2.9129(7)
O(1)-P-O(2)	97.70(7)	O(1)-P-O(3)	94.72(7)
O(2)-P-O(3)	94.64(7)	O(1)-P-S	77.02(5)
O(2)-P-S	77.86(5)	O(3)-P-S	167.81(6)
C(1)-O(1)-P	127.0(1)	C(12)-O(2)-P	124.1(1)
C(15)-O(3)-P	118.1(1)		

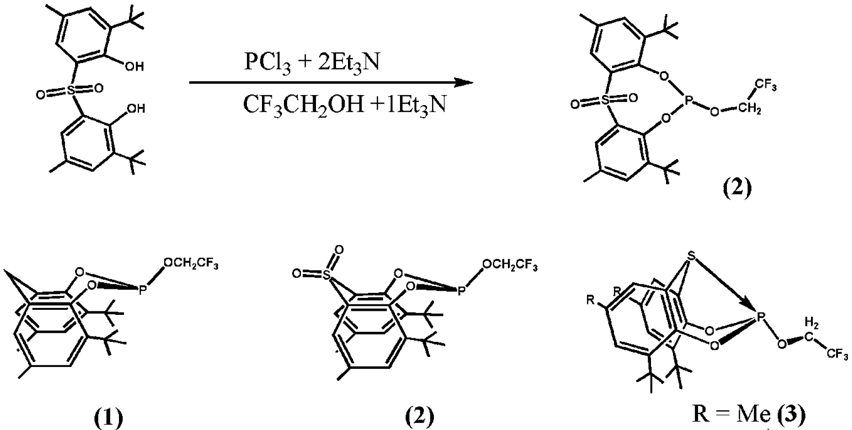
TABLE IV Selected Bond Lengths [Å] and Angles [deg] for 4

P-O(1)	1.626(3)	P-O(2)	1.622(4)
P-O(3)	1.666(5)	P-S	2.891(2)
O(1)-P-O(2)	100.5(2)	O(1)-P-O(3)	92.3(2)
O(2)-P-O(3)	91.8(2)	O(2)-P-S	78.6(1)
O(1)-P-S	78.2(1)	O(3)-P-S	164.8(2)
C(7)-S-C(6)	102.6(2)	C(1)-O(1)-P	131.1(3)
C(12)-O(2)-P	129.1(3)	C(17A)-O(3)-P	126(1)
C(17B)-O(3)-P	114(1)		

the addition of trifluoroethanol and triethylamine. The formation of **2** is shown in Scheme 1. The formation of **1** results from the use of a methylene bridged diphenol, and **3** was obtained by using a sulfur-bridged diphenol (Scheme 1). This reverse addition (that is, instead of the addition of the diphenol and triethylamine to a phosphorus trichloride solution as done previously[11]), seems to have resulted in a lower yield. Despite the presence of bulky groups, these phosphites were fairly sensitive to water in solution.

Earlier Studies

Earlier studies have shown that there are several possible structures for this type of cyclic phosphites with an eight-membered ring. The ring can be in a *syn* or *anti* form and the acyclic substituent can be

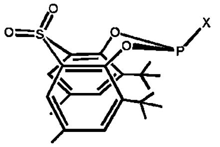


(2)

(1) **(2)**

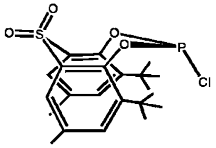
R = Me **(3)**
R = Bu^t **(4)**

SCHEME 1

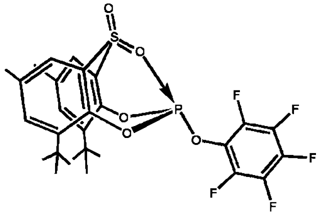


X = Br
X = OC_6H_3-2,6-Me_2

(**A**: anti-equatorial)[17]



(**B**: anti-axial)[17]



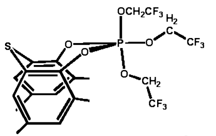
P--O = 2.652(5) Å

(**C**: syn-axial)[6a]

SCHEME 2

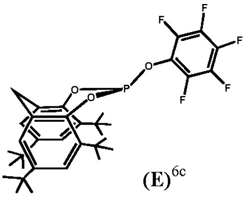
in a pseudo-axial or pseudo-equatorial orientation. Scheme 2 shows the three forms observed[6a,17] (a pseudo-equatorial orientation for a *syn* ring is not known). Though the example shows only the sulfonyl system, similar forms are known for other systems with bridging units, such as CH_2 or S in place of the SO_2 group.[6b,c]

From Scheme 3 one can easily see that the nature of the structure depends on the electronic and steric factors present at the eight-membered ring and on the type of acyclic substituent. For example, in the phosphorane **D**,[15] the ring maintains an *anti* conformation with no donor interaction between phosphorus and sulfur. However, phosphites of the same system with pentafluorophenoxy groups show a syn ring conformation with a P-S donor interaction, even when no steric effect is present. This is seen in **F**,[6c] where there are only hydrogen atoms close to the phenoxy

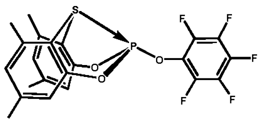


P--S = 3.504(3) Å

(**D**)[15]

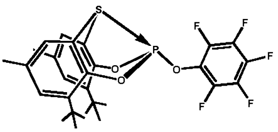


(**E**)[6c]



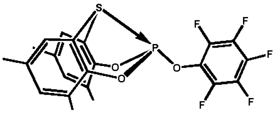
P--S = 2.940(4) Å

(**F**)[6c]



P--S = 2.876(2) Å

(**G**)[6b]



P--S = 2.828(2) Å

(**H**)[6a]

SCHEME 3

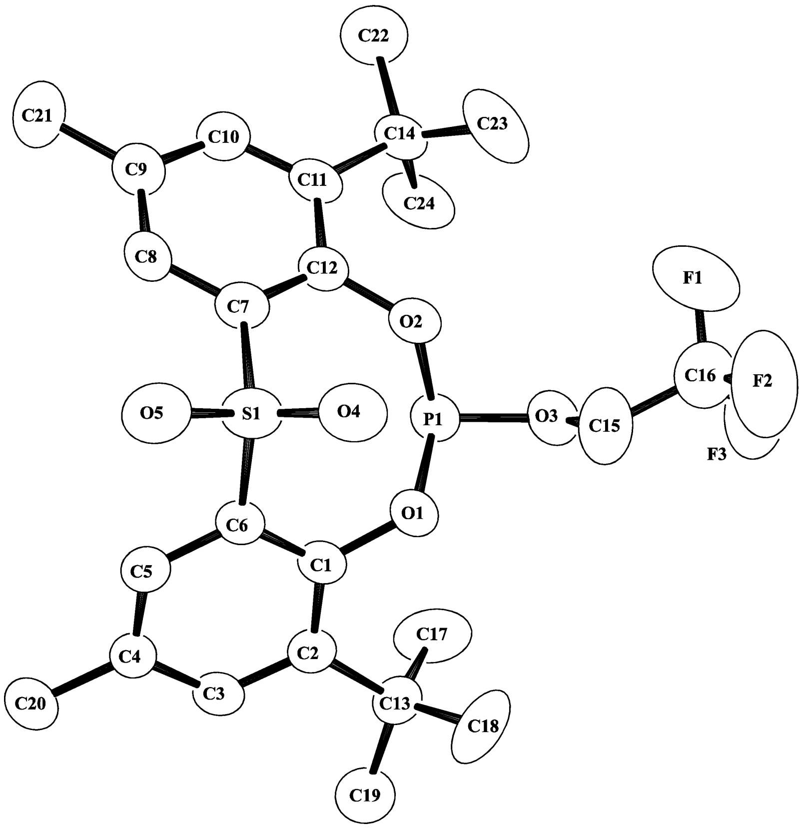


FIGURE 1 ORTEP diagram of **2** (hydrogen atoms are omitted for clarity).

oxygen of the eight-membered ring. Despite the lack of any steric effect at all, the ring assumes a syn conformation with donor interaction. The electron-withdrawing effect of the pentafluorophenyl group appears to be the controlling feature in this case and that of **G**[6b] and **H**.[6a] The nature of the interaction is confirmed when the non-donor CH_2 group was used (**E**).[6c] In the phosphite **E**, even in the presence of bulky tert-butyl groups, the ring maintained an *anti* conformation. This suggests that only when donor interaction is possible, e.g., when electronic effects are present, will the ring goes to a syn conformation in phosphites.

The trifluoroethoxy group is somewhat less bulky than aryloxy groups and has moisture repelling fluorines. Hence, they were synthesized in order to be used as a starting material for the synthesis of biorelevant phosphoranes with better solubility and stability (to be reported in an additional study elsewhere). The trifluoroethoxy group

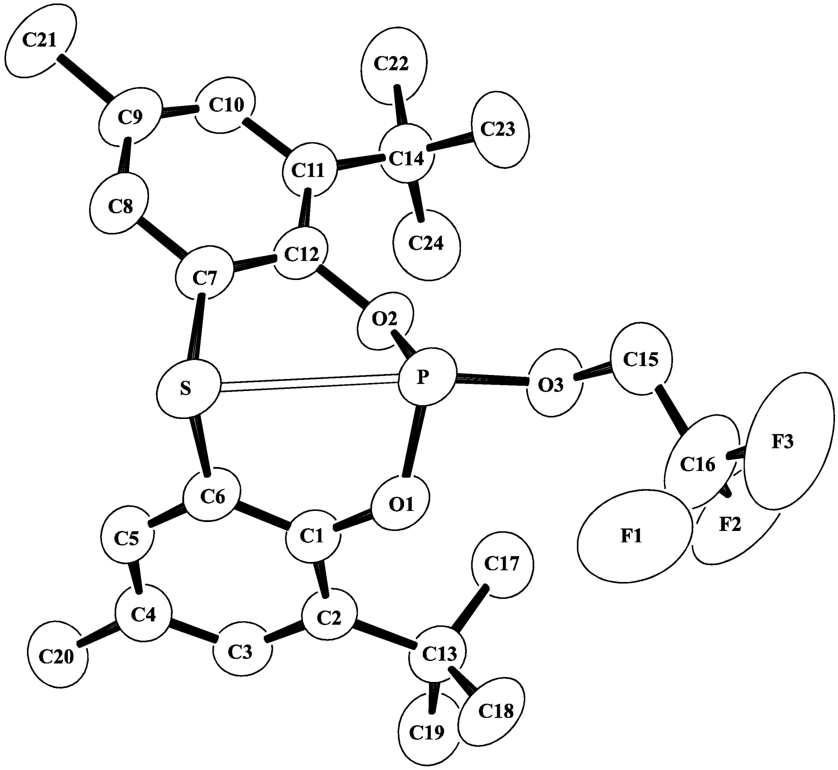
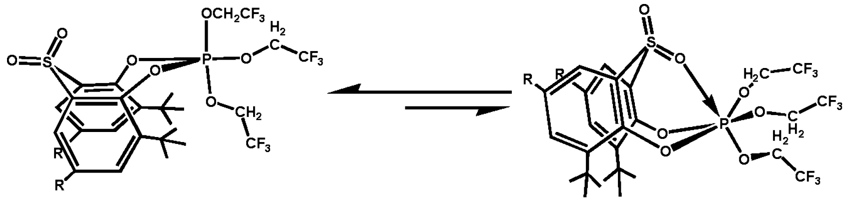


FIGURE 2 ORTEP diagram of **3** (hydrogen atoms are omitted for clarity).

has proven to be a unique group in that it forms phosphoranes, which lack donor interaction (as seen in **D**[15]), or leads to equilibrium between penta (**I**)- and hexa (**J**)-coordinated phosphoranes (Scheme 4).[16] Hence, phosphites with trifluoroethoxy groups were interesting to study to



X-ray Structures:
R = Me or Bu^t

(I)

(Based on
solution NMR data)

(J)

SCHEME 4

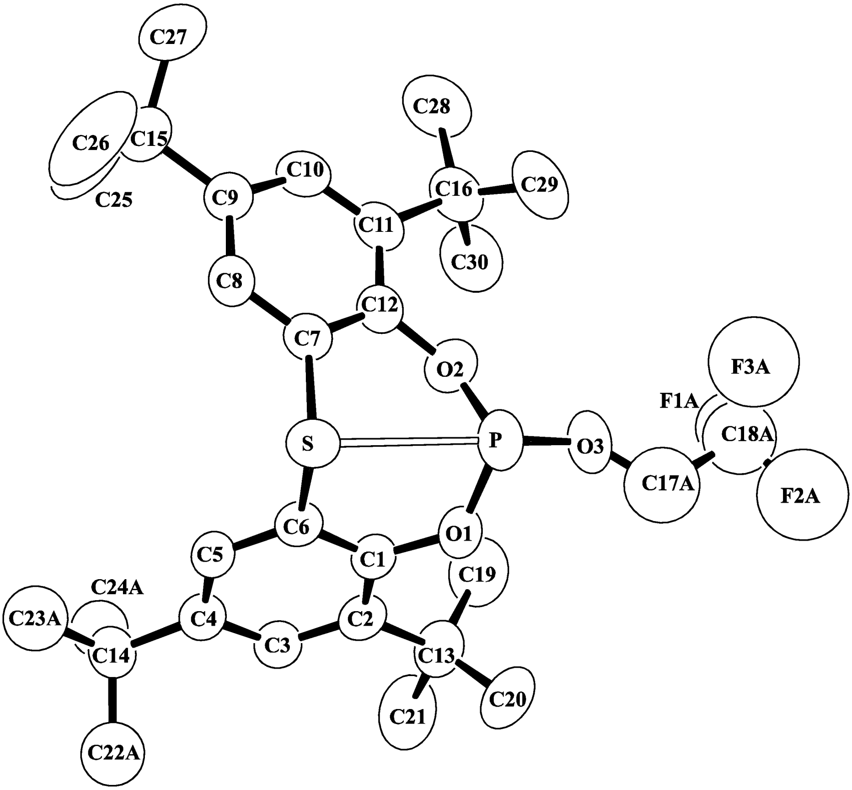


FIGURE 3 ORTEP diagram of **4** (hydrogen atoms are omitted for clarity).

determine how the donor interaction was affected by this unique group. Consequently, a study of the X-ray structures of **2–4** are reported in the following section.

Structure

The structure of phosphite **1**, shown in Scheme 1, was not determined by crystal studies but was established based on NMR comparisons discussed in the following section. It did not show any fluxional behavior or isomerism. Similar silicon compounds were found to show isomerism.[9]

The sulfonyl-containing phosphite **2** did not show any donor interaction in contrast to that observed in the pentafluorophenoxy containing phosphite **C** (Scheme 2). However, the structure of **2** is in agreement with that of other phosphites having chloro, bromo or xylyloxy groups.[17] In all of these phosphites, there was no P-O donor interaction,

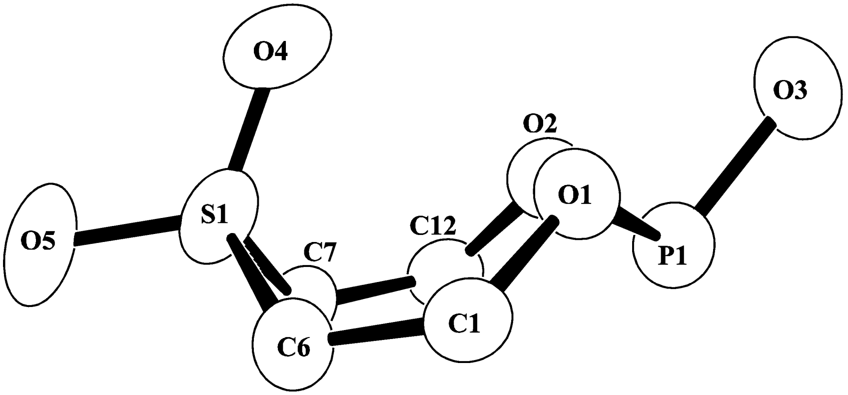


FIGURE 4 ORTEP diagram of **2** showing the eight-membered ring conformation with the orientation of substituents at phosphorus and the opposite sulfur atom.

and the eight-membered ring was in an *anti* conformation (Figure 4). A similar lack of donor interaction was observed when a very bulky α,α-dimethylbenzyl-substituted sulfonyl diphenol was used.[1]

The sulfur-containing phosphites **3** and **4** show a P-S donor interaction, and the eight-membered ring is in syn conformation (Figure 5) with the P-S distances being 2.9129(7) and 2.891(2) Å, respectively. It is in the same range as observed for pentaflourophenoxy phosphites **F–H** (Scheme 3). It appears that in the sulfur system there is little influence of the acyclic groups on donor interaction. In sharp contrast, in the SO_2 system (in phosphites **2**, **A** and **B**), the donor interaction depends very much on the electronic and steric effects of the acyclic groups. Though

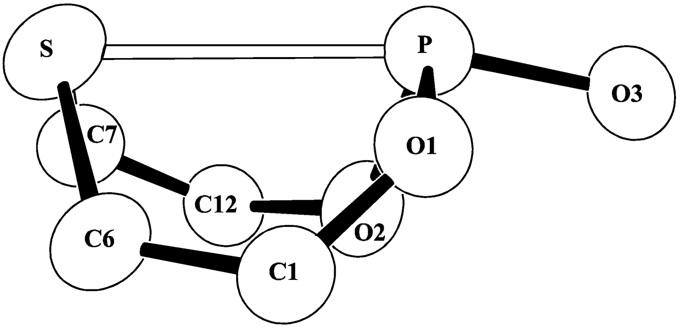
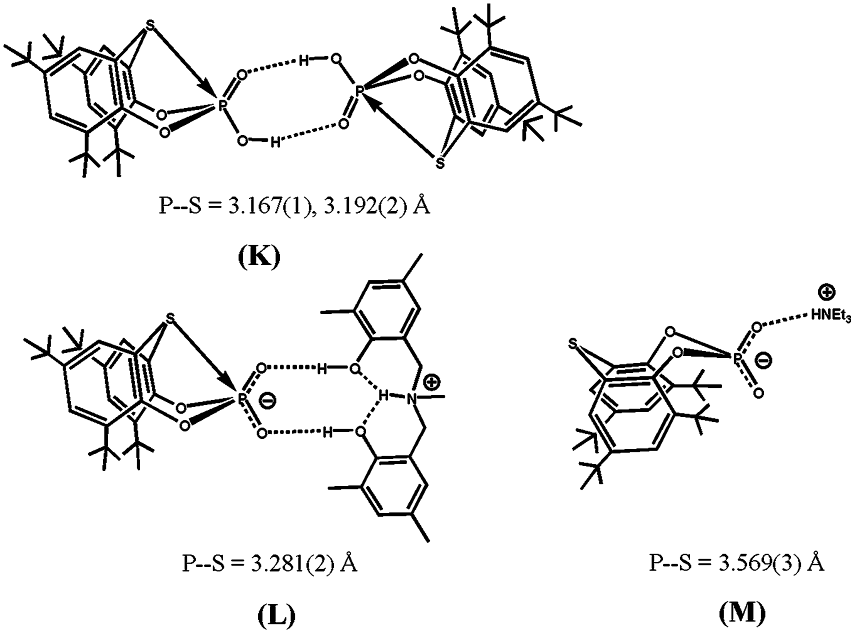


FIGURE 5 ORTEP diagram of **3** showing the eight-membered ring conformation along with the orientation of substituents at the phosphorus atom.



P--S = 3.167(1), 3.192(2) Å

(K)

P--S = 3.281(2) Å

(L)

P--S = 3.569(3) Å

(M)

SCHEME 5

phosphorane **D** does not show any P-S interaction, all other phosphites and phosphoranes with bulky tert-butyl groups invariably showed a P-S interaction.[2] We have observed a similar but weaker interaction even in phosphate **K** and anionic phosphate **L** as shown in Scheme 5, where the eight-membered ring maintained a twist-syn conformation.[18] With the use of a simpler cation, an *anti* conformation was found for the ring in the anionic phosphate **M**.[19] It has a ring conformation identical to that shown in Figure 4 for phosphite **2**, although **M** has an additional oxygen atom connected to phosphorus and a bridgehead sulfur atom instead of a sulfonyl group.

NMR

Chemical Shift Contradiction

Generally, when there is a donor interaction due to an increased electron density at phosphorus, an upfield chemical shift is expected and most often observed. However, as described in our previous article,[1] phosphites with donor interaction (144.0 and 143.0 ppm for **3** and **4**, respectively) showed a chemical shift that was downfield compared to those without any such interaction (125.6 and 124.5 ppm for **1** and **2**, respectively). This contradiction of about 18 ppm is readily explained by the fact that the phosphorus resides in between two aromatic ring currents as seen in the forms **A** and **B** (Scheme 2). This causes a shielding at phosphorus and an upfield shift, similar to the effect that has been understood in the proton NMR of a trifluoroethoxy group in phosphoranes.[5,20] In the coordinated form **C** (Scheme 2), the phosphorus moves out of this shielding region. This leads to a loss of a shielding effect and results in a downfield shift, and from this value the coordination effect moves the chemical shift to the upfield region. When the coordination is not too strong as in **3** and **4**, the chemical shift we observe is still downfield to that of the uncoordinated phosphites **1** and **2**.

As described in our previous article,[1] often phosphoranes with eight-membered rings exhibit fluxionality. However, all phosphites **1–4** showed no detectable isomerization. Interestingly, whenever there was donor interaction at phosphorus, a phosphorus–fluorine coupling was observed (in phosphites **3** and **4**). When there was no such donor interaction, no detectable phosphorus–fluorine coupling was present (as found in **1** and **2**). It is not clear whether a steric or electronic effect is involved or whether it is a manifestation of a through space interaction.

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