THREE-, FOUR-, AND FIVE-COORDINATE CYCLIC PHOSPHITES, PHOSPHONATES, AND PHOSPHONIUM SALTS CONTAINING SULFURYL GROUP

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THREE-, FOUR-, AND FIVE-COORDINATE CYCLIC PHOSPHITES, PHOSPHONATES, AND PHOSPHONIUM SALTS CONTAINING SULFURYL GROUPS[1]

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Reaction of the sulfuryl diphenol $O_2S[(t\text{-Bu})MeC_6H_2OH]_2$ (10) with phosphorus trihalides in the presence of amines yielded the phosphites $O_2S[(t\text{-Bu})MeC_6H_2O]_2PR$ where R = Cl for 1 and R = Br for 2. Treatment of 1 with 2,6-dimethylphenol in a halide displacement reaction gave 3 (R = OXyl). In a similar diol reaction with $O_2S[Me_2C_6H_2OH]_2$ (11), the hydrogen-phosphonate $O_2S[Me_2C_6H_2O]_2P(O)H$ (5) formed. A related hydrogenphosphonate $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(O)H$ (4) was obtained by hydrolysis of either 1 or 2. The phosphonium bromide salt $O_2S[(t\text{-Bu})MeC_6H_2O]_2PPhBr^+Br^-$ (7) formed from the bromination of the phenylphosphonite derivative $O_2S[(t\text{-Bu})MeC_6H_2O]_2PPh$ (9), the hydrolysis of which yielded the phosphonate $O_2S[(t\text{-Bu})MeC_6H_2O]_2P(O)Ph$ (6). A related phosphonium bromide $O_2S[(t\text{-Bu})MeC_6H_2O]_2PBr_2^+Br^-$ (8) was prepared by the reaction of the diphenol 10 with PBr_3 in the presence of N-bromodiisopropylamine. All of the cyclic phosphorus derivatives 1–8 were characterized by x-ray studies and NMR measurements. All of the compounds lack donor-acceptor interaction that is potentially available via the oxygen atom of the sulfuryl group present as part of the ring system except for 4. For 4, the structure is pentacoordinated with a displacement from a tetrahedral geometry toward a trigonal bipyramid, The ring conformation is a *syn* twist-boat whereas the others lacking donor coordination reside in an *anti* chair-like ring arrangement. Solution ^{31}P NMR chemical shifts are in appropriate ranges indicating retention of the coordination geometry that was found in the solid state. Weak P-Br bond strength is suggested to account for formation of the phosphonium bromides 7and 8 which contrasts with the hexacoordinate structure obtained previously for an analogous chlorophosphorane. Comparisons with similar formulations of cyclic phosphites and phosphates having ring sulfur atoms show that there is a preponderance of donor-acceptor interactions involving sulfur compared to that experienced with the sulfuryl group.

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INTRODUCTION

Formation of higher coordinated phosphorus compounds due to Lewis acid-base interactions caused by oxygen, nitrogen, and sulfur donor atoms is a current interest to us.[2-20] Chart 1 shows representative examples. By obtaining precise information on structural changes encountered, as well as their energies, as a result of such interactions for a variety of phosphorus states, it has become possible to form a proper basis that will allow the refinement of models for nucleophilic displacement reactions, e.g., those that occur during reactions at active sites of phosphoryl transfer enzymes.[2,21] These studies[2-20] have been assisted by VT NMR measurements demonstrating ligand exchange behavior and by equilibrium studies showing the existence of isomeric forms in solution,[2,11,13] especially between five- and six-coordinte representations.

In the present study, we concentrate attention on the oxygen atom of the sulfuryl group in its capacity to interact with phosphorus in phosphites, **1–3**, hydrogenphosphonates **4** and **5**, a phosphonate, **6,** and with phosphonium salts, **7–8**. It is instructive to examine a variety of phosphorus compounds to learn the extent of oxygen atom coordination in comparison with analogous compounds undergoing sulfur atom coordination. In all of these compounds, the sulfuryl group is present as part of the same type of ring system (Chart 2). The solid state structures of **1–8** are reported as well as ^1H and ^{31}P solution NMR measurements.

EXPERIMENTAL

Phosphorus trichloride, phosphorus tribromide, 2,6-dimethylphenol, and bromine were obtained from Aldrich and used as supplied. Triethylamine was distilled over KOH pellets. The sulfuryl diphenol compounds, $O_2S[(t\text{-}Bu)MeC_6H_2OH]_2$ (**10**) and $O_2S[Me_2C_6H_2OH]_2$ (**11**),[22] the phenylphosphonite derivative, $O_2S[(t\text{-}Bu)MeC_6H_2O]_2PPh$ (**9**),[11] and N-bromodiisopropylamine[23] were synthesized according to literature methods. Solvents were purified according to standard procedures.[24] Light petroleum (88–99°C) is referred to as Skelly-C. All the reactions were carried out in a dry nitrogen atmosphere. Proton NMR spectra were recorded
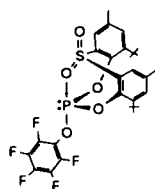
P–OSO = 2.652(5)Å, 46% TBP
^{31}P, 132.0

A [3b]
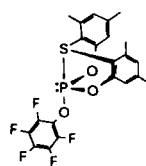
P-S = 2.940(4)Å, 46% TBP
^{31}P, 124.6

B [3a]
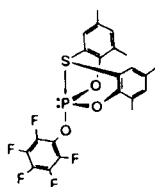
P–S = 2.828(2)Å; 54% TBP
^{31}P, 136.8

C [3b]
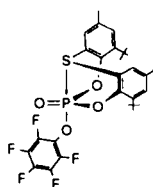
P–S = 3.085(2)Å, 37% TBP
^{31}P, -24.0

D [3b]
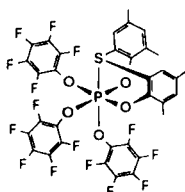
P-S = 2.389(5), 82% octa
^{31}P, -93.0

E [3b]
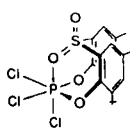
P-OSO = 1.878(4)Å, 84% octa
^{31}P, -147

F [3a]
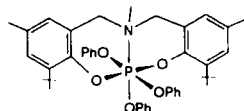
P–N = 2.143(3)Å; 73.4% octa
^{31}P, -136.1

G [4]

P–O = 2.788(6)Å, 37% TBP
^{31}P, 161.7 [31]

H [5]

CHART 1

P-OSO = 3.54(2)Å
^{31}P. 148

1

2 (R = Br) P-OSO = 3.539(7)Å, ^{31}P. 154.8
3 (R = Oxyl) P-OSO = 3.565(3)Å, ^{31}P. 134.0

P-OSO = 3.007(2)Å; 23% TBP
^{31}P. -1.6

4

P-OSO = 3.533(2)Å
^{31}P. -8.1

5

P-OSO = 3.475(8)Å
^{31}P. 8.5

6

P-OSO = 3.29(2)Å
^{31}P. 46.8

7

P-OSO = 3.37(12)Å
^{31}P. -16.5

8
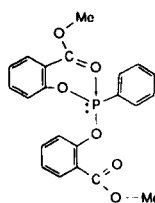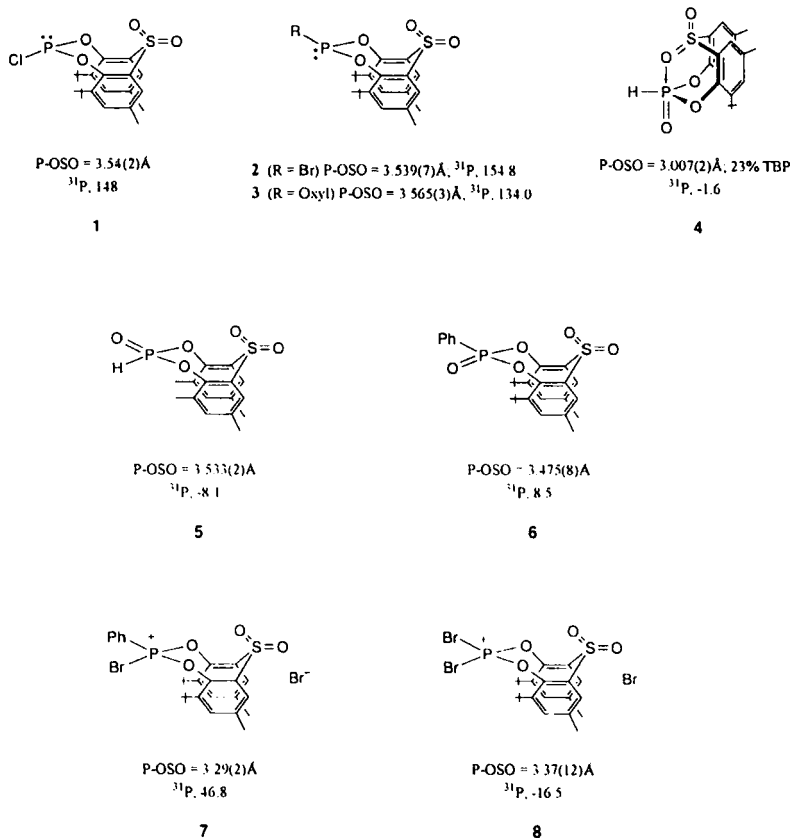
CHART 2

on a Bruker AC200 FT-NMR spectrometer and the phosphorus-31 NMR spectra were recorded on a Bruker MSL300 FT-NMR spectrometer. All ^{1}H NMR spectra were recorded in $CDCl_3$ and all the ^{31}P NMR spectra were recorded in CH_2Cl_2 in a sweep-off mode, unless mentioned otherwise. Chemical shifts are reported in ppm, downfield positive, relative to tetramethylsilane for ^{1}H or 85% H_3PO_4 for ^{31}P. All spectra were recorded at around 23°C. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses

Sulfurylbis(4-methyl-6-t-butylphenyl)chlorophosphite, $O_2S[(t\text{-}Bu)MeC_6H_2O]_2PCl$ (1)

To a solution of phosphorus trichloride (1.00 mL, 11.5 mmol) and sulfuryldiphenol (10) (4.50 g, 11.5 mmol) in ether (200 mL) was added a solution of triethylamine (3.20 mL, 23.0 mmol) in ether (100 mL) with stirring over 1 h. The solution was stirred for a further period of 4 h and filtered. Solvent was removed and the residue recrystallized from a hexane-dichloromethane mixture (1:1, 100 mL) to obtain the product which was a microcrystalline solid that was moisture sensitive. Yield 3.5 g (67%), mp 203–208°C. ^{31}H NMR: 1.44 (s, 18 H, Bu-t), 2.38 (s, 6 H, Me), 7.45 (d, 2.2 Hz, 2 H, aryl), 7.73 (d, 2.2 Hz, 2 H, aryl). ^{31}P NMR (ether): 148.0. Anal. Calcd for $C_{22}H_{28}O_4ClPS$: C, 58.08; H, 6.20. Found: C, 57.96; H, 6.20. Repeated attempts to obtain better crystals for the x-ray study resulted in crystals of the hydrolyzed product, sulfurylbis(4-methyl,6-t-butylphenyl)hydrogenphosphonate, $O_2S[(t\text{-}Bu)MeC_6H_2O]_2P(O)H$ (4).

Sulfurylbis(4-methyl-6-t-butylphenyl)bromophosphite, $O_2S[(t\text{-}Bu)MeC_6H_2O]_2PBr$ (2)

The procedure was similar to the synthesis of 1. The quantities used were: phosphorus tribromide (1.00 mL, 10.5 mmol), sulfuryldiphenol (10) (4.15 g, 10.6 mmol) and triethylamine (3.00 mL, 21.5 mmol). Yield 4.0 g (76%), mp 194–199°C. ^{1}H NMR: 1.47 (s, 18 H, Bu-t), 2.38 (s, 6 H, Me), 7.49 (s, br, 2 H, aryl), 7.77 (d, 2.2 Hz, 2 H, aryl). ^{31}P NMR: 154.8. Anal. Calcd for $C_{22}H_{28}O_4BrPS$: C, 52.91; H, 5.65. Found: C, 53.95; H, 6.02. This compound is also highly air-sensitive and the ^{31}P NMR showed the formation of the hydrolyzed product (at −1.6 ppm with $J_{P\text{-}H} = 794$ Hz). The proton NMR spectrum also showed the formation of the hydrolyzed product (4): 1.45 (s, 18 H, But), 2.38 (s, 6 H, Me), 7.44 (d, 2.2 Hz, 2 H, aryl), 7.70 (d, 1 H, $J_{P\text{-}H}$ 774 Hz, P-H), 7.73 (d, 2.2 Hz, 2 H, aryl).

Sulfurylbis(4-methyl-6-t-butylphenyl)(2,6-dimethylphenyl)phosphite, $O_2S[(t\text{-}Bu)MeC_6H_2O]_2P(OXyl)$ (3)

A solution of 2,2′-sulfurylbis(4-methyl-6-t-butylphenol) (4.47 g, 11.5 mmol) and phosphorus trichloride (1.00 mL, 11.5 mmol) in diethyl

ether (450 mL) was cooled to 0°C. Triethylamine (3.20 mL, 22.9 mmol) in diethyl ether (50 mL) was added dropwise and the mixture stirred for 24 h and then filtered. 2,6-Dimethylphenol (1.40 g, 11.5 mmol) and triethylamine (1.60 mL, 11.5 mmol) in diethyl ether (50 mL) were added dropwise to the filtrate and stirring was continued for a further 24 h. The mixture was then filtered and the colorless solution left under a flow of nitrogen. The resultant solid was dissolved in CH_2Cl_2 (80 mL) after which Skelly-C (50 mL) was added. Concentration under a nitrogen flow produced colorless crystals of the product. Yield 1.7 g (27%), mp 247°C. ^1H NMR: 1.22 (s, 18 H, Bu-*t*), 2.35 (s, 6 H, CH_3), 2.50 (s, 6 H, CH_3), 6.95–7.79 (m, 7 H, Ar(H)). ^{31}P NMR: 134.0. Anal. Calcd for $C_{30}H_{37}O_5SP$: C, 66.67; H, 6.85. Found: C, 67.08; H, 7.11.

Sulfurylbis(4,6-dimethylphenyl)hydrogenphosphonate, $O_2S[Me_2C_6H_2O]_2P(O)H$ (5)

To a solution of phosphorus trichloride (1.00 mL, 11.5 mmol) and sulfuryldiphenol (11) (3.50 g, 11.4 mmol) in ether (200 mL) was added a solution of triethylamine (3.20 mL, 23.0 mmol) in ether (100 mL) with stirring over 1 h. The solution was stirred for a further period of 20 h and then methyl salicylate (1.50 mL, 11.6 mmol) and triethylamine (1.60 mL, 11.5 mmol) was added and stirred for a further 24 h. The solution was then filtered and left under a nitrogen flow. It formed a powdery solid. The ^{31}P NMR of the solid showed the presence of the expected methyl salicylate derivative at 123.2 ppm but repeated attempts to obtain single crystals resulted in hydrolysis and only crystals of the hydrolyzed phosphite 5 were obtained. ^{31}P NMR: −7.8 (J_{P-H}= 776 Hz).

Sulfurylbis(4-methyl-6-t-butylphenoxy)phenylbromophosphonium bromide, $O_2S[(t-Bu)MeC_6H_2O]_2PPhBr^+ Br^-$ (7)

To a solution of the phenylphosphonite (9) (2.75 g, 5.54 mmol) in dichloromethane (70 mL) was added liquid bromine in drops with stirring until a faint yellow color remained (0.30 mL, 5.8 mmol). After overnight, Skelly-C (5 mL) was added and the solution left under a nitrogen flow. An extremely sensitive crystalline solid formed. The solution fumed on exposure to air. The ^{31}P NMR of the solution showed that the major component was the phosphonium ion at 46.8 ppm (~80%) with the remainder attrib-

uted to the hydrolysed phosphonate, $O_2S[(t-Bu)MeC_6H_2O]_2P(O)Ph$ (**6**) appearing at 8.5 ppm. Due to the extreme sensitivity of the compound to moisture and the presence of loosely bound dichloromethane molecules, only a reduced set of x-ray data was obtained and no further characterization could be carried out. Further attempts to obtain crystals from a higher boiling solvent (dichloroethane) were not successful and only the hydrolyzed phosphate crystals (**6**) were obtained.

Sulfurylbis(4-methyl-6-t-butylphenoxy)dibromophosphonium bromide, $O_2S[(t-Bu)MeC_6H_2O]_2PBr_2{}^+ Br^-$ (8)

To a solution of phosphorus tribromide (1.00 mL, 10.5 mmol) and the sulfuryldiphenol (**10**) (4.10 g, 10.5 mmol) in dichloromethane (100 mL) was added N-bromodiisopropylamine (1.5 mL) with stirring. It formed a precipitate immediately which was left under a flow of nitrogen to get a mixture of crystalline material. The amine hydrobromide could not be separated due to similar solubilities of the components. The mixture contained amine hydrobromide (white crystals), the expected phosphorane or phosphonium ion **8** (red-brown crystals, similar to **7**) and also the bromo phosphite **2** (white crystals). The latter probably formed due to the presence of amine in the N-bromodiisopropylamine. The red-brown crystals showed a ^{31}P NMR shift of −16.5 ppm. One of the crystals was used for the x-ray study.

X-ray Studies

The x-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Details of the experimental procedures have been described previously.[25]

The colorless crystals were mounted in thin-walled glass capillaries which were sealed to protect the crystals from the atmosphere as a precaution. Data were collected at 23 ± 2°C using the θ-2θ scan mode with 3° ≤ $2\theta_{MoK\alpha}$ ≤ 43° for **1** and **4–6**. For **2** and **3** the theta range was 1.5–22° whereas for **7** it was only 2–16° and for **8**, 7–22°. No corrections were made for absorption except for the data for **2** which was corrected using psi data ($T_{min}/T_{max} = 0.94$). All of the data were included in the refine-

ment except for 1and **8**, where all non-positive data were omitted. The 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 486/66 computer using SHELXS-86 for solution[26] and SHELXL-93 for refinement.[27] All the non-hydrogen atoms were refined anisotropically except for **1** and **8**, where only P, S, Cl/Br were refined anisotropically. Hydrogen atoms attached to phosphorus in **4** and **5** were located from difference Fourier syntheses and refined isotropically. Other hydrogens 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 carbon atoms. The final agreement factors are based on the reflections with $I \geq 2\sigma_I$. Crystallographic data are summarized in Table I.

In the crystal of **1** there was a dichloromethane molecule with disordered chlorines. The chlorines were assigned three positions with equal occupancy. Since the data were very weak, except that for the second row elements, all other atoms were refined isotropically and no hydrogens were included in the calculations. In the crystal for **2**, also a badly disordered dichloromethane molecule was present. It was refined with five positions for the chlorines with equal occupancy and the hydrogens on the solvent were not included. The crystal for **7** decayed during the data collection and only partial data were obtained. Psi data could not be collected. There were two molar equivalents of the dichloromethane molecule which were well behaved and their hydrogens were fixed in calculated positions. The crystal of **6** had a dichloroethane ($ClCH_2CH_2Cl$) molecule with only the carbons disordered. Here the hydrogens were not included in the calculations. The crystals of **8** decayed very rapidly (43% within the 900 data). No further suitable crystal could be found. The decay was highly anisotropic but only an average isotropic decay correction was applied. No psi data were collected and hence no correction was made for absorption. Still the structure was solved with the available data (only 40% of the expected total data). The hydrogen atoms were not included in the calculations. The weak high decay and high absorption data did not allow higher accuracy during the structure refinement. Only the P, S, and Br atoms were refined anisotropically. However, the gross structure of the phosphorus moiety was reliably determined.

TABLE I Crystallographic Data for Compounds **1–8**

ound	1	2	3	4
	$C_{22}H_{28}ClO_4PS \cdot$ CH_2Cl_2	$C_{22}H_{28}BrO_4PS \cdot$ CH_2Cl_2	$C_{30}H_{37}O_5PS$	$C_{22}H_{29}O_5PS$
ight	539.8	584.3	540.6	436.5
em	orthorhombic	monoclinic	monoclinic	monoclinic
	$P2_12_12_1$	$P2_1/n$	$C2/c$	$P2_1/c$
mm	---	1.00×0.85×0.85	1.00×0.55×0.50	1.00×0.55×0.50
	10.288(8)	9.389(2)	26.705(4)	9.588(3)
	14.412(10)	21.344(3)	9.550(2)	9.225(2)
	17.67(2)	14.101(7)	23.782(4)	25.634(6)
	90	90	90	90
	90	107.29(3)	108.16(1)	92.50(2)
	90	90	90	90
	2620(4)	2698(2)	5763(2)	2265(1)
	4	4	8	4
	1.369	1.438	1.246	1.280
	5.17	18.84	2.04	2.43
	1735	3292	3507	2590
$I>2\sigma_I$	553	1948	2655	2199
	0.1461	0.0768	0.0438	0.0392
	0.2909	0.1897	0.1129	0.1021

ound	5	6	7	8
	$C_{16}H_{17}O_5PS$	$C_{28}H_{33}O_5PS. C_2H_4Cl_2$	$C_{28}H_{33}BrO_4PS.Br. 2CH_2Cl_2$	$C_{22}H_{28}O_4Br_2PS.Br. 2CH_2$
ight	352.3	611.5	826.2	829.1
em	orthorhombic	triclinic	monoclinic	monoclinic
	Pbca	$P\bar{1}$	$P2_1/m$	C2/m
mm	1.00×0.55×0.45	1.00×0.75×0.75	---	0.40×0.35×0.30
	9.280(3)	11.302(4)	9.080(3)	19.60(1)
	15.316(3)	11.374(5)	22.114(4)	15.151(6)
	23.626(4)	13.322(5)	9.942(4)	14.07(2)
	90	91.41(3)	90	90
	90	106.67(3)	110.88(4)	120.3(1)
	90	101.53(3)	90	90
	3358(1)	1601(1)	1865(1)	3608(6)
	8	2	2	4
	1.394	1.268	1.471	1.526
	3.09	3.53	25.90	37.79
	1921	3676	1328	895
$I>2\sigma_I$	1537	2219	1038	359
	0.0361	0.1016	0.1000	0.1446
	0.0939	0.2692	0.2528	0.3086

$_o| - |F_c| |/\Sigma|Fo|$
$= \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4\}1/2$

RESULTS AND DISCUSSION

Selected bond parameters are given in Tables II–IX. The atom labeling schemes for **1–8** are given in the ORTEX[28] plots of Figures 1–8. The thermal ellipsoids are shown at the 40% probability level and all hydrogens are omitted for clarity.

TABLE II Bond lengths [Å] and angles [deg] for **1**

P-O(2)	1.51(3)	S-O(3)	1.47(2)
P-O(1)	1.63(2)	S-C(7)	1.79(3)
P-Cl	1.82(2)	S-C(6)	1.81(3)
P-O(3)	3.54(2)	O(1)-C(1)	1.33(4)
S-O(4)	1.41(2)	O(2)-C(12)	1.52(4)
O(2)-P-O(1)	100.6(11)	O(4)-S-C(6)	109(2)
O(2)-P-Cl	110.2(12)	O(3)-S-C(6)	107(2)
O(1)-P-Cl	103.6(12)	C(7)-S-C(6)	105.7(14)
O(4)-S-O(3)	121.0(12)	C(1)-O(1)-P	126(3)
O(4)-S-C(7)	104(2)	P-O(2)-C(12)	126(2)
O(3)-S-C(7)	110(2)		

TABLE III Bond lengths [Å] and angles [deg] for **2**

P-O(2)	1.618(7)	S-O(4)	1.430(8)
P-O(1)	1.629(7)	S-C(7)	1.775(10)
P-Br	2.207(3)	S-C(6)	1.784(9)
P-O(3)	3.539(7)	O(1)-C(1)	1.391(11)
S-O(3)	1.418(8)	O(2)-C(12)	1.396(12)
O(2)-P-O-(1)	103.4(3)	O(3)-S-C(6)	109.1(4)
O(2)-P-Br	96.5(3)	O(4)-S-C(6)	105.2(4)
O(1)-P-Br	95.8(3)	C(7)-S-C(6)	107.5(4)
O(3)-S-O(4)	118.9(5)	C(1)-O(1)-P	116.5(6)
O(3)-S-C(7)	109.7(4)	C(12)-O(2)-P	118.4(6)
O(4)-S-C(7)	105.8(4)		

TABLE IV Bond lengths [Å] and angles [deg] for **3**

P-O(3)	1.601(3)	S-C(7)	1.782(3)
P-O(1)	1.635(2)	S-C(6)	1.783(3)
P-O(2)	1.640(2)	O(1)-C(1)	1.396(4)
S-O(4)	1.427(3)	O(2)-C(12)	1.407(4)
S-O(5)	1.433(3)	O(3)-C(13)	1.385(5)

P-O(4)	3.565(3)		
O(3)-P-O(1)	92.55(13)	O(4)-S-C(6)	110.0(2)
O(3)-P-O(2)	98.55(13)	Ȯ(5)-S-C(6)	105.3(2)
O(1)-P-O(2)	104.09(12)	C(7)-S-C(6)	107.4(2)
O(4)-S-O(5)	118.3(2)	C(1)-O(1)-P	119.6(2)
O(4)-S-C(7)	109.3(2)	C(12)-O(2)-P	122.0(2)
O(5)-S-C(7)	105.9(2)	C(13)-O(3)-P	131.2(2)

TABLE V Bond lengths [Å] and angles [deg] for **4**

P-O(3)	1.542(3)	S-C(6)	1.778(3)
P-O(1)	1.584(2)	S-C(7)	1.781(3)
P-O(2)	1.588(2)	O(1)-C(1)	1.401(3)
S-O(4)	1.430(2)	O(2)-C(12)	1.397(3)
S-O(5)	1.432(2)	P-O(4) 3.007(2)	
O(4)-S-O(5)	118.3(2)	O(3)-P-O(1)	112.25(13)
O(4)-S-C(6)	109.03(14)	O(3)-P-O(2)	111.38(14)
O(5)-S-C(6)	107.18(14)	O(1)-P-O(2)	102.27(11)
O(4)-S-C(7)	108.44(14)	C(1)-O(1)-P	127.2(2)
O(5)-S-C(7)	106.24(14)	C(12)-O(2)-P	128.3(2)
C(6)-S-C(7)	107.08(13)	O(4)-P-O(3)	159.7(1)

TABLE VI Bond lengths [Å] and angles [deg] for **5**

P-O(3)	1.445(3)	S-O(5)	1.430(2)
P-O(1)	1.579(2)	S-C(7)	1.776(3)
P-O(2)	1.590(2)	S-C(6)	1.781(3)
P-O(4)	3.533(2)	O(1)-C(1)	1.407(4)
S-O(4)	1.428(2)	O(2)-C(12)	1.402(4)
O(3)-P-O(1)	115.60(14)	O(4)-S-C(6)	110.73(14)
O(3)-P-O(2)	114.23(14)	O(5)-S-C(6)	106.87(14)
O(1)-P-O(2)	105.81(12)	C(7)-S-C(6)	101.96(14)
O(4)-S-O(5)	118.74(14)	C(1)-O(1)-P	123.2(2)
O(4)-S-C(7)	110.18(14)	C(12)-O(2)-P	124.7(2)
O(5)-S-C(7)	107.0(2)		

TABLE VII Bond lengths [A] and angles [deg] for **6**

P-O(3)	1.445(8)	S-O(5)	1.422(8)
P-O(1)	1.587(7)	S-C(6)	1.769(11)
P-O(2)	1.587(7)	S-C(7)	1.774(10)
P-C(13)	1.783(11)	O(1)-C(1)	1.426(12)

S-O(4)	1.418(8)	O(2)-C(12)	1.415(12)
P-O(4)	3.475(8)		
O(3)-P-O(1)	113.8(4)	O(4)-S-C(6)	110.4(5)
O(3)-P-O(2)	113.8(4)	O(5)-S-C(6)	106.2(5)
O(1)-P-O(2)	106.6(4)	O(4)-S-C(7)	110.3(5)
O(3)-P-C(13)	119.9(5)	O(5)-S-C(7)	105.9(5)
O(1)-P-C(13)	100.4(4)	C(6)-S-C(7)	105.1(5)
O(2)-P-C(13)	100.4(4)	C(1)-O(1)-P	121.8(6)
O(4)-S-O(5)	118.1(5)	C(12)-O(2)-P	121.7(6)

TABLE VIII Bond lengths [A] and angles [deg] for **7**

Br(2)-P	2.125(8)	S-O(3)	1.41(2)
P-O(1)	1.55(2)	S-O(2)	1.46(2)
P-C(7)	1.77(3)	S-C(6)	1.78(3)
P-O(2)	3.29(2)	O(1)-C(1)	1.37(3)
O(1)-P-O(1) #1	113.3(10)	O(3)-S-C(6)	107.7(12)
O(1)-P-C(7)	102.9(8)	O(2)-S-C(6)	108.2(11)
O(1)-P-Br(2)	109.2(5)	C(6)-S-C(6) #1	105.7(13)
C(7)-P-Br(2)	119.3(10)	C(1)-O(1)-P	124.5(13)
O(3)-S-O(2)	118.6(12)		

Symmetry transformation used to generate equivalent atoms: #1 x, -y+3/2, z

TABLE IX Bond lengths [Å] and angles [deg] for **8**

P-O(1)	1.73(5)	S-O(3)	1.35(14)
P-Br(1)	2.09(4)	S-O(2)	1.36(7)
P-Br(2)	2.11(2)	S-C(6)	1.59(8)
P-O(2)	3.37(12)	O(1)-C(1)	1.13(7)
O(1) #1-P-O(1)	108(4)	O(3)-S-C(6)	108(3)
O(1)-P-Br(1)	109(2)	O(2)-S-C(6)	112(4)
O(1)-P-Br(2)	109(1)	C(6) #1-S-C(6)	101(5)
Br(1)-P-Br(2)	114(2)	C(1)-O(1)-P	109(4)
O(3)-S-O(2)	116(5)	S-O(2)-P	83(4)

Symmetry transformations used to generate equivalent atoms: #1 x, -y, z

Syntheses

Scheme 1 illustrates the synthetic methods used to obtain the products **1–8**. Sulfuryldiphenol **10** and **11** were the most prevalent starting materials. The diphenol **10** was used along with Et$_3$N to initiate reactions with
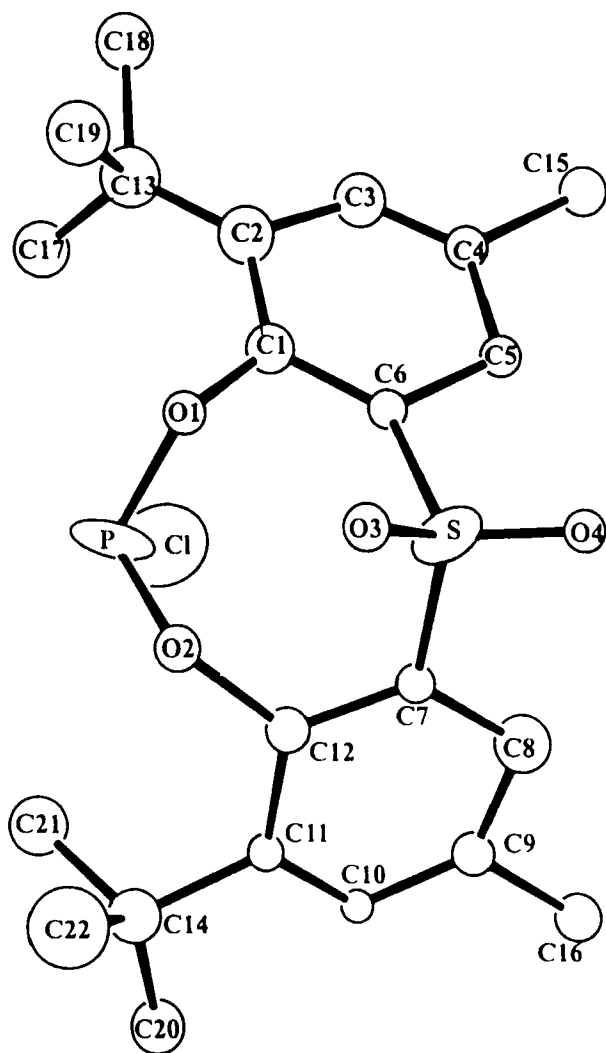
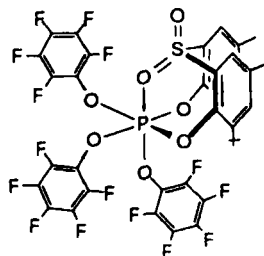FIGURE 1 ORTEX diagram of the chloro phosphite **1**

phosphorus trihalides to prepare the phosphites **1–3**. Reaction of **1** with 2,6-dimethylphenol led to **3**. Due to the high air sensitivity of **1** and **2**, hydrolysis occurred to give the hydrogenphosphonate **4**. In a similar reaction sequence leading to the formation of **4**, the diphenol **11** as a starting

reagent yielded the hydrogenphosphonate **5**. The phosphonium bromide salt **7** was obtained from the bromination of the phenylphosphonite **9**. Due to its extreme sensitivity to hydrolysis, crystals of the phenylphosphonate **6**resulted. In an attempt to prepare a bromine containing phosphorane analogous to **F** in Chart 1, the reaction of the diphenol **10** with PBr$_3$ in the presence of N-bromodiisopropylamine was conducted. However, the phosphonium bromide salt **8** formed instead in an unseparable mixture. The product formed as red-brown crystals.

Structural Descriptions

All of the compounds lack donor-acceptor interactions except **4** (Chart 2). For **4**, the ring is in a twisted boat *syn* conformation (Figure 4), whereas in the absence of donor coordination, the ring has an *anti* chair-like conformation. A typical orientation of this ring form is seen in Figure 7 for phosphonium bromide **7**.

The phosphites **1–3** have the same composition other than the variation in the **R** group. It is known that the similarly composed phosphite **A** (Chart 1) undergoes Lewis acid-base coordination[3b] where the R group is pentafluorophenoxy. It might reasonably be expected that coordination from the oxygen atom of the sulfuryl group would occur for **1** which has been shown to have an electronegativity comparable to the pentafluorophenoxy ligand.[3a] Thus **F** in Chart 1 with chlorine substituents is displaced 84% toward an octahedral geometry[29] as a result of sulfuryl oxygen atom coordination.[3a] This same degree of geometrical displacement is found for the analogous oxyphosphorane **I**[11] containing three pentafluorophenoxy ligands in place of chlorine atoms.
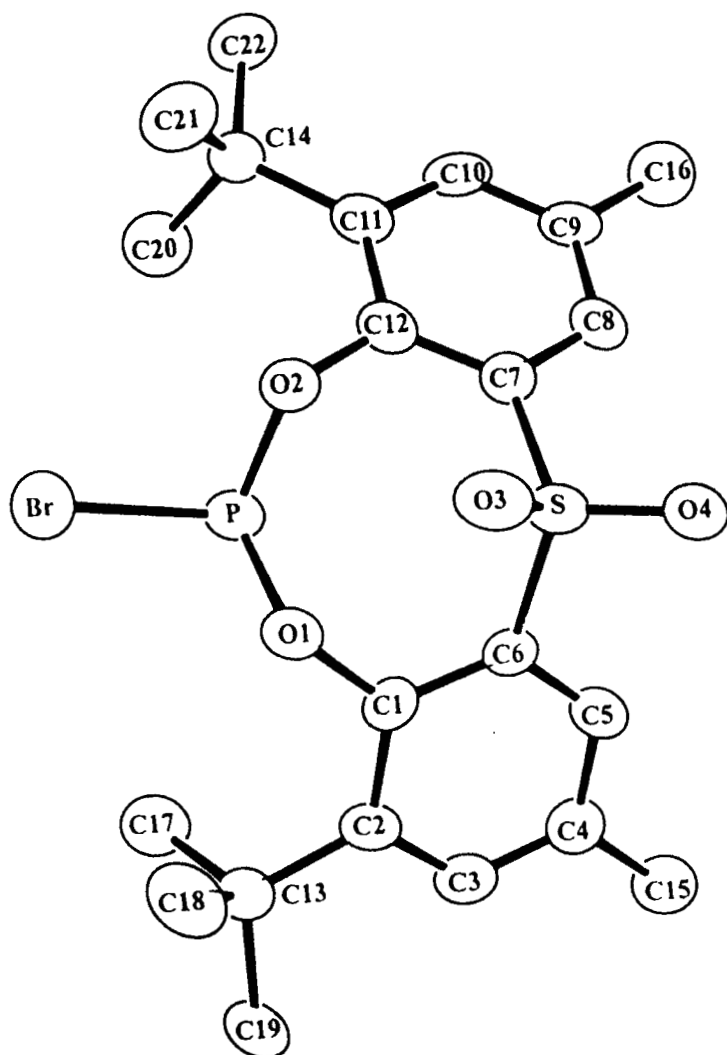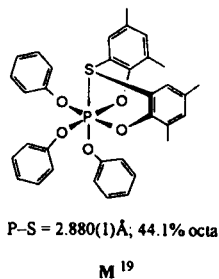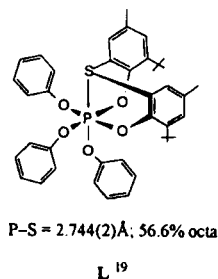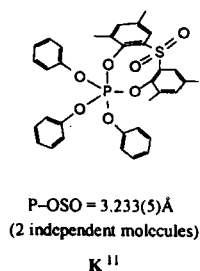

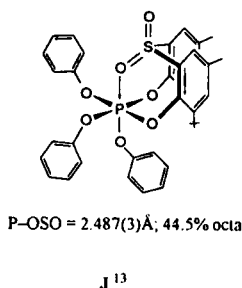P-OSO = 1.936(7)Å; 82% octa

I[11]

FIGURE 2 ORTEX diagram of the bromo phosphite **2**

In comparing the phosphoryl containing hydrogenphosphonates **4** and **5**, which differ only in the aromatic substituents of the ring system, **4** exhibits weak P-O coordination whereas **5** has the ring in a chair-like conformation and lacks any P-O interaction (Chart 2). It has been observed that in ring

systems like these that have methyl substituents, the tendency is toward reduced donor action compared to the same type of ring system when present with *t*-butyl groups attached to the aromatic component, for example, compare $\mathbf{J}^{13}$ with $\mathbf{K}^{11}$ or $\mathbf{L}^{19}$ with $\mathbf{M}.^{19}$ The *t*-butyl groups can supply an increased nucleophilicity to the ring containing donor atom.[19] In addition, the larger *t*-butyl group may introduce a steric interaction[17] that is favorable in supporting the donor-acceptor behavior.

P–OSO = 2.487(3)Å; 44.5% octa

J [13]

P–OSO = 3.233(5)Å
(2 independent molecules)

K [11]

P–S = 2.744(2)Å; 56.6% octa

L [19]

P–S = 2.880(1)Å; 44.1% octa

M [19]

Although these observations apply to oxyphosphoranes, it might be expected to hold true for the lower coordinate state of phosphorus in **4** and **5**.

Like **5**, phosphonate **6** lacks P-O donor interaction. For all of the compounds **1–3**, **5**, and **6** the P-OSO distance lies in a narrow range 3.48Å-3.57Å, well outside the sum of the van der Waals' radii of 3.35 Å.[30]

Somewhat surprisingly, both **7** and **8** which exist as phosphonium bromide salts, lack any donor-acceptor tendency. Both structures have their rings in *anti* chair-like conformations. The presence of a formal positive charge should increase the electrophilicity at the phosphorus center. However, the P-OSO distances 3.29(2)Å for **7** and 3.37(12)Å for **8**, are approx-
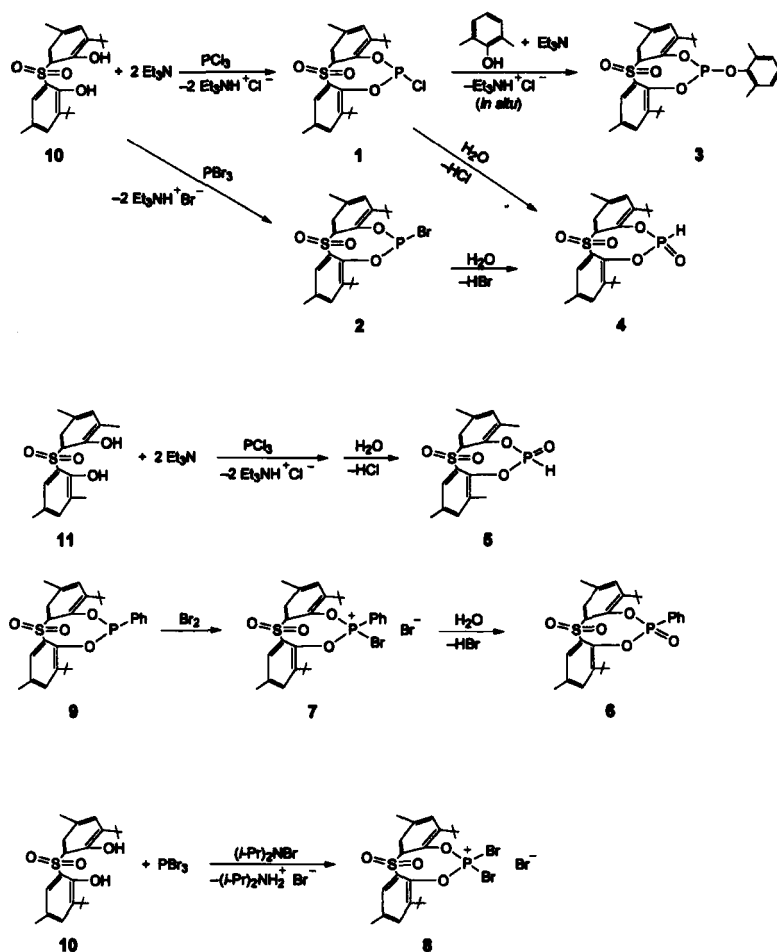
SCHEME 1

imately 0.2Å shorter than those for **1–3, 5,** and **6** but still very close to the van der Waals' sum.

Formation of the phosphonium salts for **7** and **8** is most likely a result of a low P-Br bond energy, 264 kJ/mol (for PBr$_3$).[31] The analogous composition with three chlorine atoms instead of bromine resides as a phosphorane **F**[3a] in an octahedral geometry (Chart 1). The P-Cl bond energy is 326 kJ/mol (for PCl$_3$).[31]
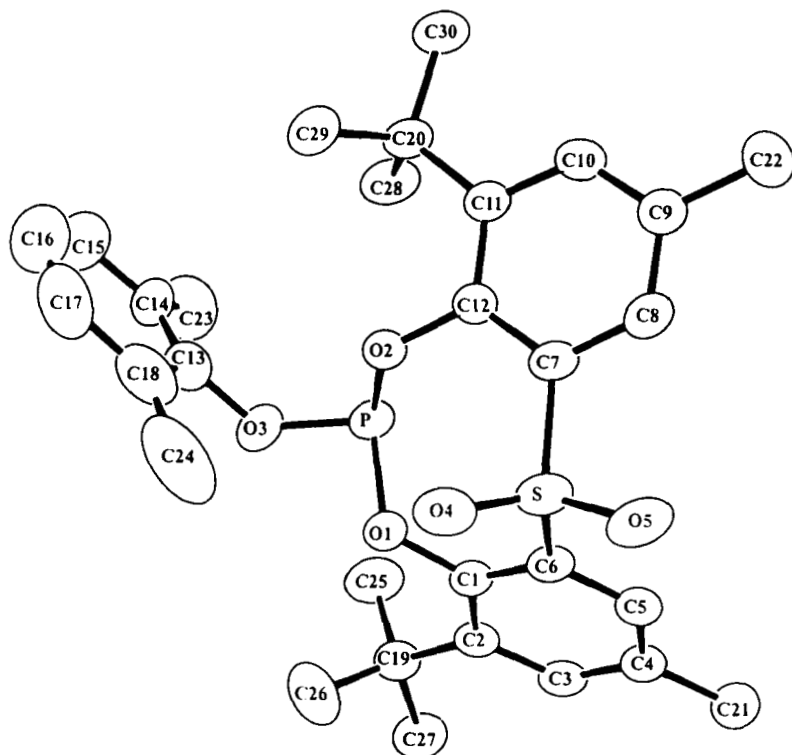
FIGURE 3 ORTEX diagram of the xylyloxy phosphite **3**

Solution NMR

The ^{1}H and ^{31}P NMR spectra of **1–8** indicate that the coordination geometries are retained in solution. The ^{31}P spectra are representative of the respective coordination types. For the phosphites **1–3**, the ^{31}P shifts are downfield in the range 134–155 ppm (Chart 2). On an increase in coordination number, the phosphoryl containing compounds **4–6** have ^{31}P shifts between −8.1 to 8.5 ppm, whereas that for the phosphonium salts **7** and **8** are at 46.8 ppm and −16.5 ppm, respectively.

The weak P-OSO coordination for **4** giving a geometry displaced 23% toward a trigonal bipyramid (TBP)[32] is not reflected in its ^{31}P chemical shift of −1.6 ppm. The latter is typical for compounds having an increase
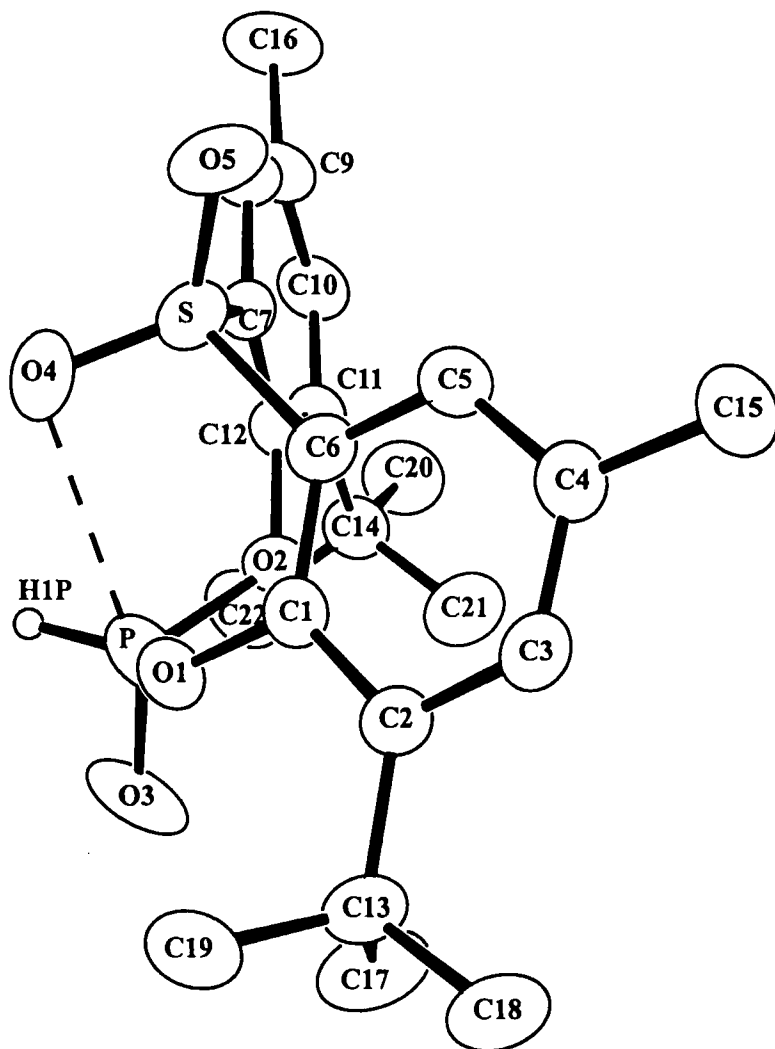
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FIGURE 4 ORTEX diagram of the hydrogenphosphonate **4**

in coordination geometry due to donor action for the more weakly coordi-
nating phosphites and phosphates.[10] Some representative ^{31}P chemical
shifts are included in Chart 1. For example, the phosphite **A** (Chart 1)
showing an appreciable displacement toward a TBP due to P-OSO donor

interaction has a ^{31}P shift of 132.0 ppm[3b] which is hardly any different for phosphite **3** (^{31}P = 134 ppm) with a xylyloxy group in place of the pentafluorophenoxy ligand. A more direct comparison is apparent between **N** and **O**. The ^{31}P shift for **N** which shows sulfur donor action is nearly the same as that for **O** which has a related composition but lacks the possibility of donor coordination.[10] A solid state value for **O** of 165.7 ppm compares with a solution value of 168.4 ppm for **N**.

N   **O**
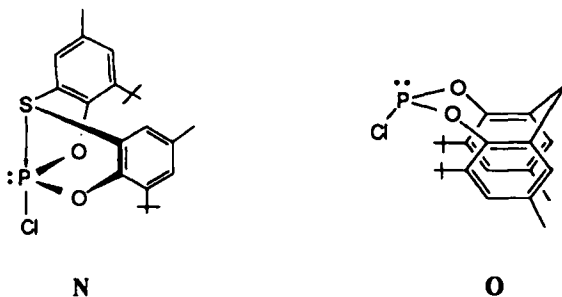
However, for the more strongly coordinating oxyphosphoranes, differences in ^{31}P are noticeable. Several oxyphosphoranes containing the sulfonyl group[11,13] as part of the cyclic system show evidence of the presence of isomers in solution from the observance of two closely spaced ^{31}P NMR signals in CDCl$_3$ solution. The ^{31}P signals for **P**[11] are −39.4 and −46.4 ppm. For **Q**,[13] they are -73.1 and −85.5 ppm.

P[11]   **Q**[13]
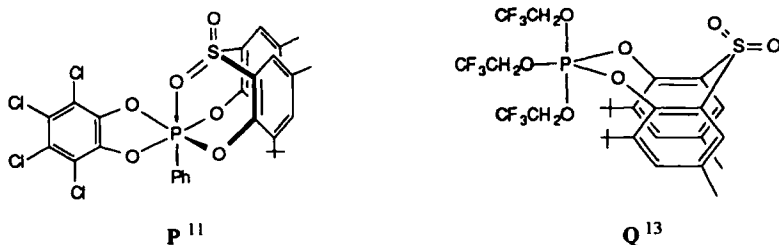
In view of the existence of trigonal bipyramidal geometries in the absence of sulfone donor action and the formation of octahedral geometries as a result of sulfone donor action, it seems most reasonable that the presence of isomers is due to these two representations.[2]
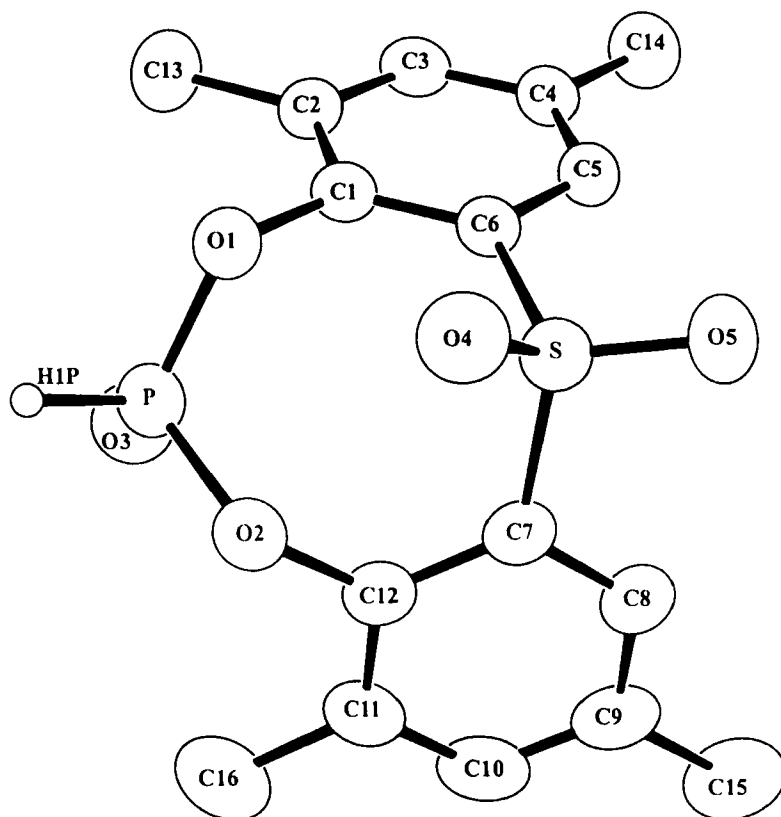
FIGURE 5 ORTEX diagram of the hydrogenphosphonate **5**

Structural Comparisons

From the structural results for **1–8**, in comparison with previous work, we find that **A** (Chart 1) and **4** (Chart 2) are the only phosphorus compounds in these charts that give evidence of donor action via an oxygen atom of the sulfuryl group. This contrasts with donor action for phosphites and phosphates when sulfur is used as the coordinating agent as part of the same type of ring system.[3a,3b,6,10]

Table X summarizes the degree of coordination for sulfur in contrast to that for the sulfuryl oxygen atom. In general, sulfur is a better Lewis base in this respect than the sulfuryl oxygen atom. This is seen on comparing
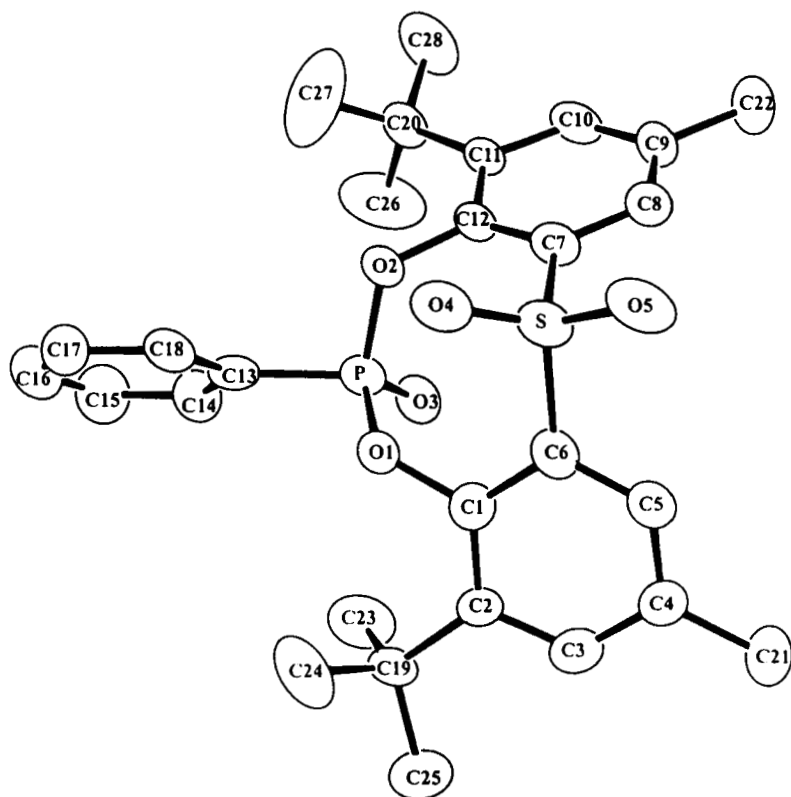
FIGURE 6 ORTEX diagram of the phenyl phosphonate **6**

the % TBP for **W** with a sulfur donor which is more greatly displaced than **A** with a sulfuryl oxygen donor atom. Although this in itself is not strong evidence, the lack of formation of donor-acceptor interactions of the P-OSO kind relative to the considerable number found showing P-S coordination provides additional evidence supporting this conclusion. Chart 2 shows some of the compounds which have been synthesized in this work that lack donor acid-base interaction. Others have been reported earlier.[3a]

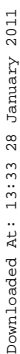FIGURE 7 ORTEX diagram of the phosphonium bromide **7**

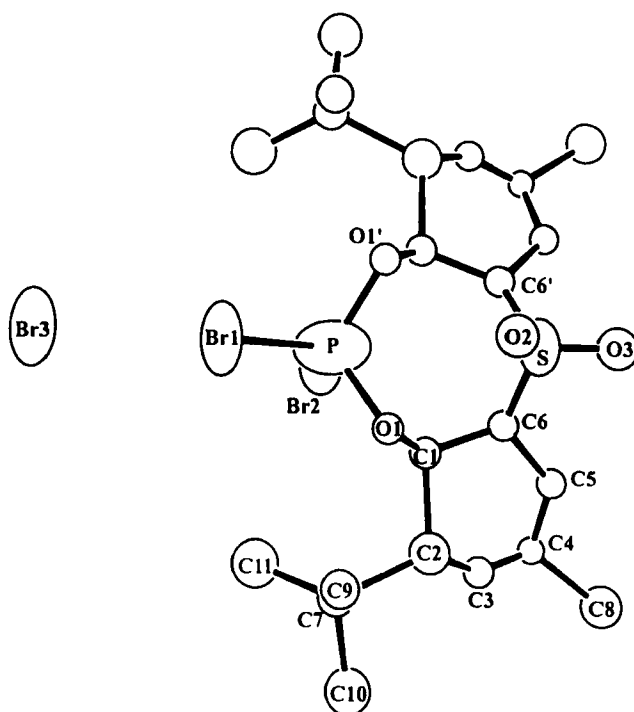FIGURE 8 ORTEX diagram of the phosphonium bromide **8**

TABLE X Donor-Acceptor Bond Distances (Å) and Bond Angles (deg) for Cyclic Phosphites and Phosphates Measuring the Degree of Trigonal Bipyramidal Coordination

compd no.[ab]	P-S	R_{ax}-P-S[c]	% TBP[d]
R	3.243(2)	160.60(8)	27
S	3.177(2)	162.9(1)	31
T	3.114(2)	167.7(1)	35
D	3.085(2)	163.7(1)	37
U	3.043(2)	172.2(1)	40
V	2.952(9)	173.3(9)	47
B	2.940(4)	162.8(5)	46
W[e]	2.876(2)	163.5(1)	51
C	2.828(2)	174.9(1)	54
X	2.816(2)	169.2(1)	55
	P-OSO	R_{ax}-P-OSO[c]	
4	3.007(2)	159.7(1)	23
A	2.652(5)	172.9(2)	46

a. Compound labels refer to the following

U [10]   W [6]   V [10] X [10]   S [10] T [10]   R [3a]
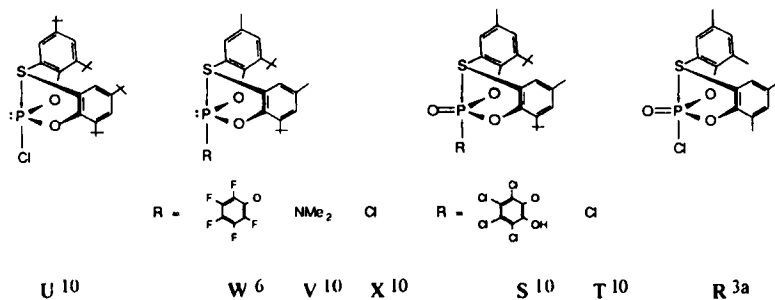
b. References are listed as superscripts below each formula. Compounds **A, B, C,** and **D** are depicted in Chart 1 while **4** appears in Chart 2.

c. With reference to a TBP with sulfur or the donor oxygen atom in an axial position and both ring oxygen atoms in equatorial positions.

d. Percent geometrical displacement from a pyramid (**A, B, C, U** and **V, W, X** or a tetrahedron **R, S, T** and **4**) toward a TBP.[32]

e. An additional coordination is present in **W** due to the weak interaction of an *ortho* fluorine atom with phosphorus. A P-F distance of 3.006(3)Å is obtained.

Acknowledgements

Crystallographic Information Available. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 135143 – CCDC 135150. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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(32) The displacement toward a TBP is calculated simply by noting how far the P-OSO distance is displaced from the sum of the van der Waals' radii $(3.35Å)^{30}$ toward the sum of the covalent radii (1.83Å). See *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Sutton, L., Ed.; Special Publication Nos. 11 and 18; The Chemical Society: London, 1958 and 1965.

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