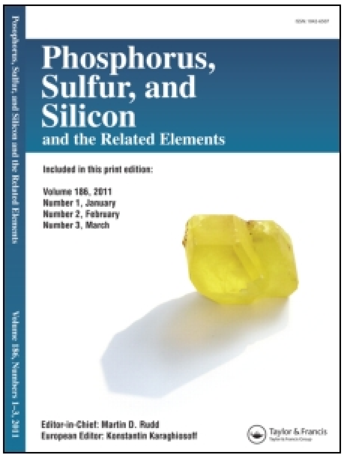

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CYCLIC OXYPHOSPHORANES. ^{31}P CHEMICAL SHIFT CORRELATIONS

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CYCLIC OXYPHOSPHORANES. ^{31}P CHEMICAL SHIFT CORRELATIONS

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Recent X-ray structures and solution NMR behavior of cyclic oxyphosphoranes are reviewed followed by a presentation of ^{31}P NMR chemical shift data for monocyclic and bicyclic oxyphosphoranes with rings varying from six- to eight-membered. Effects caused by the presence of the number of rings, the ring size, the variation in ring hetero atoms, and the electronegativity of attached nonring substituents, are correlated with structural and bonding features, particularly with changes in P—O π bonding. The formation of hexacoordinated phosphorus brought about by the introduction of sulfur into ring arrangements is deemed to be a potentially important consideration for enzyme-phosphate action at active sites where sulfur residues may be present.

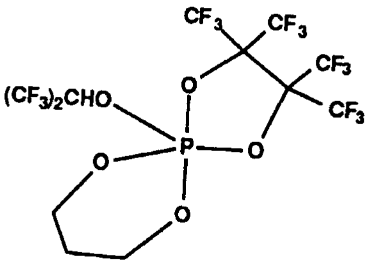
Key words: Pentacoordinate phosphorus; cyclic oxyphosphoranes; hexacoordinate phosphorus; ^{31}P NMR chemical shifts; X-ray structures.

INTRODUCTION

A relatively new area of hypervalent phosphorus chemistry concerns the formation of cyclic pentaoxyphosphoranes containing ring sizes varying from six- to eight-membered.[1,2] A study of this area, particularly the pentacoordinated state, has important applications in delineating pathways of nucleophilic displacement reactions of tetracoordinated phosphorus.[3] Recent chemical and structural studies relative to the use of oxyphosphorane models for cyclic adenosine monophosphate, cAMP, action with phosphodiesterases and protein kinases have been described.[1,4–14] What is presented here is a review of pertinent structural aspects of oxyphosphorane chemistry followed by a correlation of ^{31}P chemical shifts of this class of compounds useful in the interpretation of ring and substituent variations.

X-RAY STUDIES

Previous studies[15] have mostly centered on five-membered rings. It was only as recently as 1988 that Dr. Schomberg *et al.*[16] reported the first structural study of a pentaoxyphosphorane having a six-membered ring. A bicyclic derivative was studied by X-ray diffraction and found to have the rings located in axial-equatorial (a–e) sites of a trigonal bipyramid.



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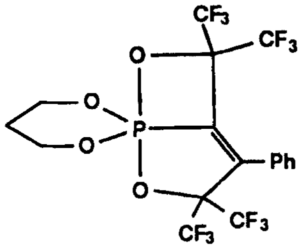
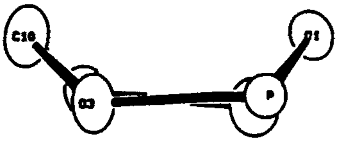
Since then we have carried out X-ray and NMR studies[2,17–21] of a variety of cyclic oxyphosphoranes containing ring sizes from five- to eight-membered in an attempt to learn structural and conformational preferences as ring size varies and to understand what the important factors are that may induce structural and conformational changes.

Of the members studied thus far, no example has been found for a pentaoxyphosphorane where a six-membered ring occupies diequatorial positions (e–e) of a trigonal bipyramid based on X-ray studies, although Bentrude and coworkers[22] found this ring orientation for a tetraoxyphosphorane having a constrained polycyclic system.

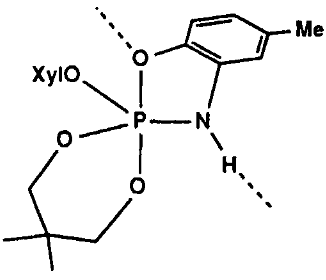


Outside of this example, X-ray analysis has shown that all such rings occupy axial-equatorial (a–e) sites of a TBP.[13,14,17–21] For saturated six-membered rings, the ring conformation is normally a boat arrangement with the axial oxygen atom at the prow and the opposite methylene group at the stern.[2]



However, introduction of intermolecular hydrogen bonding possibilities as described below yields chair conformations as well.[21,23]

In an effort to induce diequatorial ring formation, hydrogen bonding was introduced as a constraint on the system in the preparation of a series of tetraoxyphosphoranes containing an imino function.[21,23] Some representative examples are displayed here from Reference 23.



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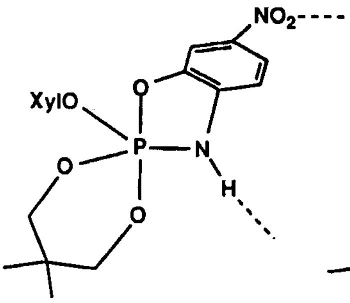

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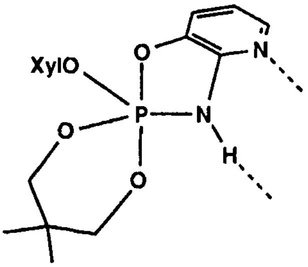
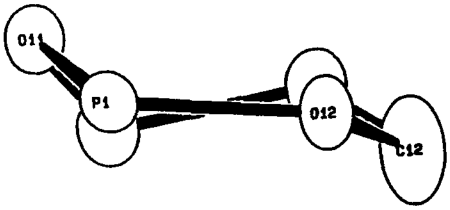
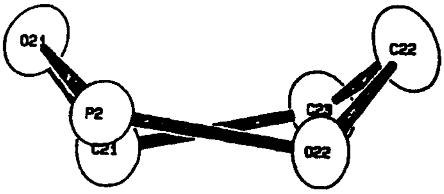
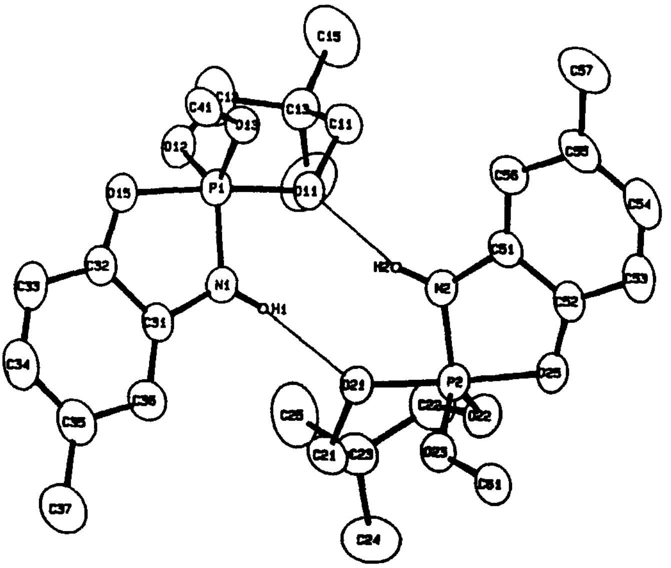


24

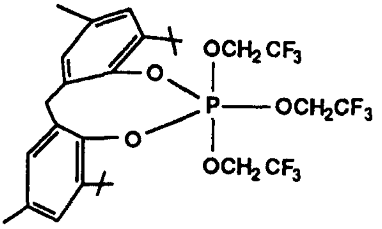
X-ray studies showed the formation of chair conformations for the phosphorinane rings situated in the usual (a–e) orientation. For **20** and **24**, hydrogen bonded dimers formed. For **20**, one six-membered ring was in a chair form and the other was in a boat conformation. This is shown here along with an ORTEP drawing. A chair form also was present in **23**. Here the hydrogen bonding occurred intermolecularly and gave a chain arrangement of phosphorane units. The dimer for **24** had both six-membered rings in twisted chair conformations.







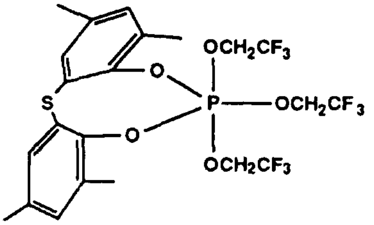
However, if one employs an eight-membered ring, diequatorial site occupancy has been observed for a pentaoxyphosphorane in a TBP geometry.[24] Apparently the greater flexibility in this larger ring allows this to occur.



38

Activation energies for intramolecular ligand exchange where a ground state TBP geometry with an (a–e) ring orientation is postulated to transgress a barrier state with the ring occupying (e–e) sites have been obtained from variable temperature NMR of these nonrigid cyclic phosphoranes.[2,18–21,25] Depending on ring size and substituent make-up, values in the range of 7–11 kcal/mol are obtained. These results are supported by *ab-initio* calculations for saturated six-membered rings in pentaoxyphosphoranes.[26] Thus, the (e–e) ring geometry is within the realm of possibility experimentally for seven- and six-membered ring sizes as well. This feature deserves additional exploration.

When a sulfur bridge atom is introduced into an eight-membered ring, additional structural possibilities arise. Besides (e–e) ring formation in a TBP, an octahedral geometry arises in certain pentaoxyphosphoranes as a consequence of P—S "bonding."[27–29] In the monocyclic phosphorus systems, **41**[27] and **47**,[27] changing the ring substituents from Me to *t*-Bu results in the X-ray structure going from pentacoordinate for **41** with an (e–e) ring orientation of a TBP to hexacoordinate for **47** as a result of sulfur moving into the coordination sphere.[27] In the former, the ring is in a chair form and the P—S distance is 3.50 Å (near the Van der Waals' sum) which decreases to 2.504 Å in the resulting octahedral structure of the latter derivative. Here the ring is in a row-boat conformation.



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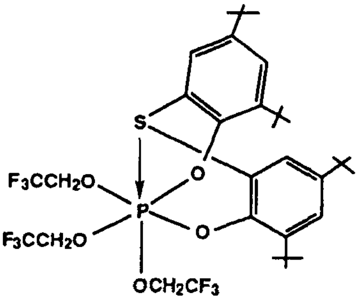
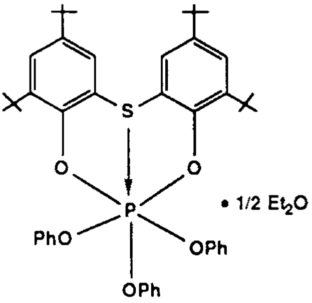


47

In fact, a series of pentaoxyphosphoranes containing such rings has been found whose structures show in incremental variation from the TBP to the octahedron.[28,29] This is the first representation of such a series showing a continuous variation between five- and six-coordinated cyclic pentaoxyphosphorus compounds.



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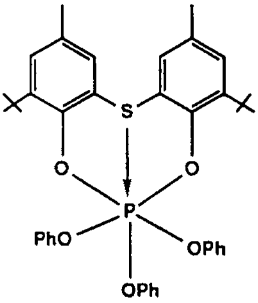

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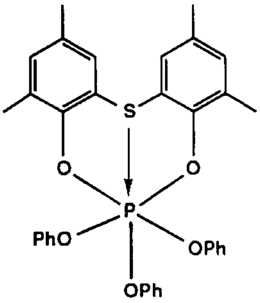

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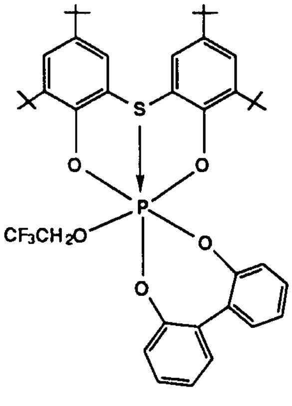
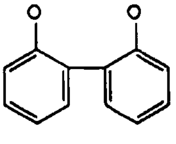


52

A graphical representation of this geometrical transformation[29] is shown here where the displacment of phosphorus from the mean plane of four attached oxygen atoms (that are considered to comprise the base of a square pyramid SP) is toward the remaining apical oxygen atom (which is *trans* to the approaching sulfur atom). This displacement is represented as a function of the P—S distance for the compounds listed in Table I. The decrease in P—S distance along the series has been attributed[29] 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 pendent ligands,



$> OCH_2CF_3 > OPh$

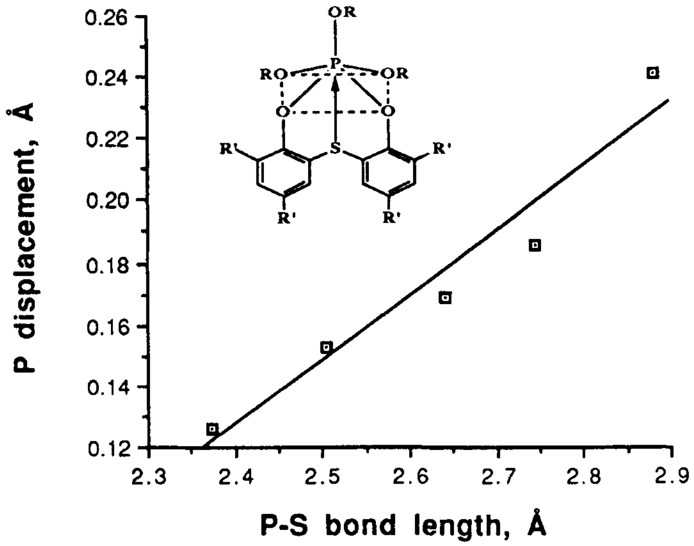


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TABLE I

Comparison of bond parameters for P—S coordination in cyclic pentaoxyphosphoranes

compd.[a]	P-S, Å	P-O, Å (*trans* to P-S)	δ (^{31}P), ppm	P displacement, Å	% O_h [b]
41[27]	3.504(3)		-77.30		
51[29]	2.880(1)	1.597(2)	-81.16	0.241(1)	44.1
50[29]	2.744(2)	1.612(3)	-81.86	0.186(1)	56.8
49[29]	2.640(2)	1.613(3)	-82.60	0.169(1)	60.8
47[27]	2.504(3)	1.640(7)	-82.44	0.153(2)	64.5
52[28]	2.373(5)	1.630(8)	-69.3[c]	0.126(3)	70.8

[a] The coordination geometry at phosphorus for **41** which lacks P—S coordination is five, that for the others containing P—S coordination is betweeen five and six. References are shown as superscripts.

[b] % O_h is the % displacement from the SP geometry (with an O—P—O *trans* basal angle of 150°) toward an octahedron. For the latter O—P—O angle, the P atom would be 0.431 Å from the base of the SP.

[c] All the above derivatives here are monocyclic, whereas **52** is bicyclic (Table X). As discussed in the text, ^{31}P shifts for bicyclics are appreciably downfield from monocyclics.

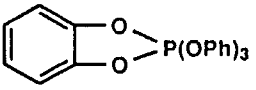
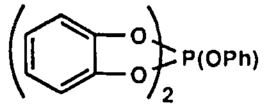
^{31}P NMR STUDIES

Pentacoordination. We assume that the integrity of the solid state structures, obtained by X-ray analysis, are retained in solution. There is no evidence to the contrary. Earlier Maciel and coworkers[30] showed that ^{31}P chemical shifts obtained on solid state and solution samples did not differ substantially from each other over a range of pentacoordinated phosphorus compounds. For pentaoxyphosphoranes, the ^{31}P chemical shift varied from -85 to -25 ppm while the largest solid to solution shift was only 4 ppm. It was concluded that the structures of the compounds involved did not vary significantly between the solid and solution phase. We have noted the same finding[27] for **41** having a TBP structure and **47** which approaches octahedral. For **41** 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 **47**, the ^{31}P shifts are -82.9 ppm (solid state) and -82.4 ppm ($CDCl_3$ solution), nearly identical values.[27]

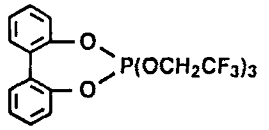
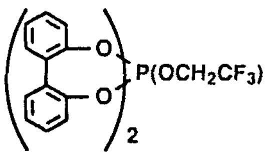
Presented here is a summary of ^{31}P chemical shifts for cyclic oxyphosphoranes selected to illustrate effects caused by the presence of the number of rings, the ring size, the variation in ring hetero atoms, and the electronegativity of attached nonring substituents. In general, ^{31}P chemical shifts for pentaoxyphosphoranes range from $+10$ to -90 ppm with respect to 85% H_3PO_4.[31] For the following, it is understood that chemical shifts (δ) are in ppm.

Tables II and III contain ^{31}P shift data for monocyclic and bicyclic oxyphosphoranes that possess six-membered rings, respectively. Tables IV–VII provide the respective chemical shift data for monocyclic and bicyclic oxyphosphoranes that have seven-membered and eight-membered rings. In all of these tables, the rings are located (a–e) based on X-ray analysis which was performed for most of the entries. The only exceptions are **38**[24,27] and **41**[27] in Table VI where X-ray studies have shown the eight-membered rings to be positioned at (e–e) sites. The ^{31}P shift does not seem to be influenced by the ring location, cf. entries **38** (e–e) with **39** (a–e) in Table VI where they differ from each other only in a ring substituent replacment of a methyl group by a *t*-butyl group. This results in a chemical shift change form -78.80 to -78.50.

Ramirez and coworkers[32] noted sometime ago that a deshielding effect was apparent along the series of pentaoxyphosphoranes going from acyclic $P(OPh)_5$ ($\delta = -88.70$), to monocyclic


(δ = -60.80), to bicyclic

(δ = -30.2)

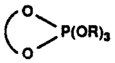
as the number of five-membered catecholate rings increased in the TBP structure. The deshielding effect was attributed to reduced π back-bonding from oxygen to phosphorus as a result of "steric inhibition" of p—d π bonding attributed to the presence of the five-membered rings. We find this same deshielding effect manifests itself with more flexible six-, seven-, and eight-membered rings as one goes from monocyclic to bicyclic forms. For example, going from

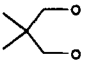
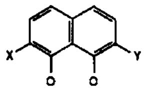
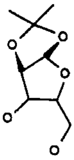
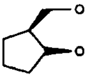
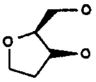
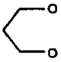

(30) to

(34)

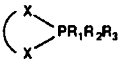
the ^{31}P chemical shift changes from -63.10[37] to -47.34,[38] respectively.

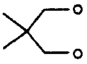
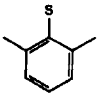
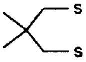
TABLE II

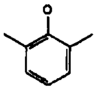
^{31}P chemical shifts (δ) for monocyclic oxyphosphoranes with six-membered rings[a]



No.[b]	Ring	OR	δ, ppm
1[19]		OXyl	-77.45
2[19]	 X = Y = H X = Y = Cl X = H, Y = Cl	OXyl	-88.17 -88.32 -88.55
3[19]	 (*cis*-fused)	OXyl	-80.00
4[7]	 (*trans*-fused)	OMe	-68.00
5[7]	 (*trans*-fused)	OMe	-67.90
6[33]		OEt	-72.0



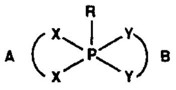
No.[b]	Ring	R$_1$	R$_2$	R$_3$	δ, ppm
7[34]		OC$_6$F$_5$	OC$_6$F$_5$		-44.71
8[34]		OC$_6$F$_5$	OC$_6$F$_5$	OXyl	-15.96

a. For Tables II-VII, OXyl refers to 

b. References are listed as supercripts.

TABLE III

^{31}P chemical shifts (δ) for bicyclic oxyphosphoranes with a six-membered ring (A) and another varying in ring size from five- through to six-membered (B)



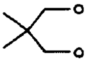
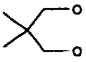
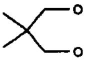
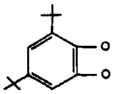
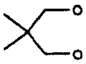
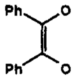
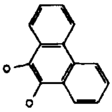
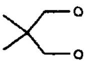
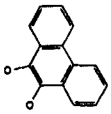
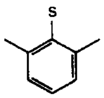
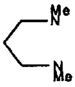
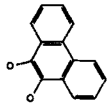
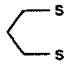
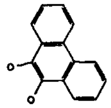
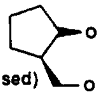
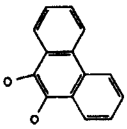
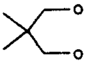
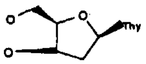
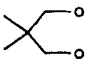
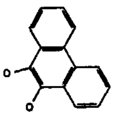
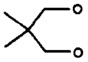
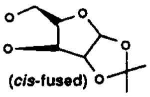
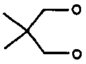
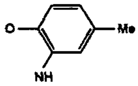
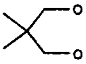
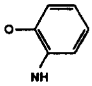
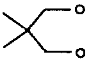
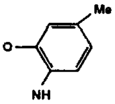
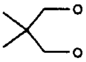
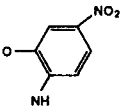
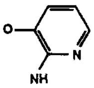
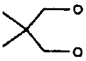
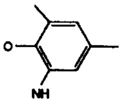
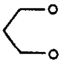
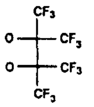
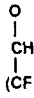
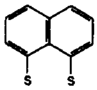
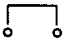
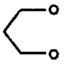
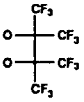
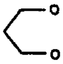
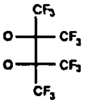
No.[a]	Ring A	Ring B	R	δ, ppm
9[18]			Ph	-49.15
10[18]			OXyl	-51.30
11[18]			OXyl	-53.55
12[20]			OXyl	-48.96
13[20]				-20.30
14[20]			OXyl	-38.91
15[17]			OXyl	3.96
16[20]	 (*trans*-fused)		OXyl	-49.01
17[2]		 (*trans* annelated thymidine)	OXyl	-69.00
18[20]			Ph	-28.36

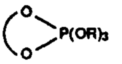
TABLE III (*Continued*)

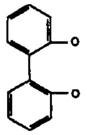
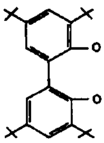
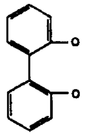
No.[a]	Ring A	Ring B	R	δ, ppm
19[20]			Ph	-52.32
20[21]			OXyl	-57.70
21[21]			OXyl	-57.90
22[21]			OXyl	-57.60
23[23]			OXyl	-59.17
24[23]			OXyl	-58.84
25[23]			OXyl	-56.88
26[35]				-50.80
27[36]			Ph	-17.6
28[35]			H	-35.75
29[35]			OMe	-47.95

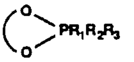
a. References are listed as supercripts.

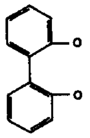
TABLE IV

^{31}P chemical shifts (δ) for monocyclic oxyphosphoranes with seven-membered rings



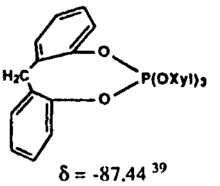
No.[a]	Ring	OR	δ, ppm
30[37]		OCH_2CF_3	-63.10
31[37]		OCH_2CF_3	-68.34
32[19]		OXyl	-68.34



No.[a]	Ring	R_1	$R_2 = R_3$	δ, ppm
33[38]		Ph	OXyl	-42.97

a. References are listed as superscripts.

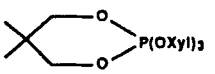
There is a variation of ^{31}P chemical shift with ring size. In the series of monocylic derivatives having (a–e) ring orientations in TBP geometries,[19,39] the deshielding lies in the order of ring size: five > seven > six > eight.



<

δ = -87.44 [39]

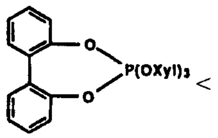
42



<

δ = -77.45 [19]

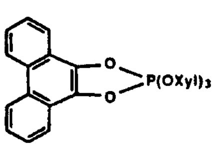
1



<

δ = -68.34 [19]

32



δ = -57.02 [19]

53

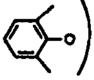
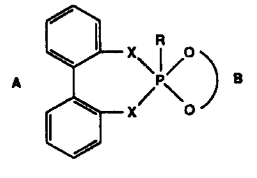
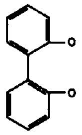
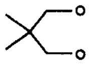
(Oxyl = )

TABLE V

^{31}P chemical shifts (δ) for bicyclic oxyphosphoranes with a seven-membered ring (A) and another varying in ring size from five- through seven-membered (B).



Ring A, X = O

No.[a]	Ring B	R	δ, ppm
34[38]		OCH_2CF_3	-47.34
35[18]		OXyl	-60.00

Ring A, X = S

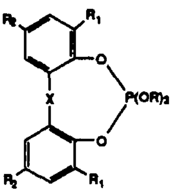
No.[a]	Ring B	R	δ, ppm
36[36]		Ph	+17.0

a. References are listed as superscripts.

This same order exists with other comparisons possible from the data in the tables. The monocyclic derivatives with seven-membered rings and OCH_2CF_3 groups, **30** and **31** (Table IV) have ^{31}P shifts of -63.10[37] and -68.34[37] which represent deshielding relative to the monocyclic derivatives with eight-membered rings and OCH_2CF_3 groups, **37**, **38**, and **39** (Table VI), where shifts are -78.33,[27] -78.80,[27] and -78.50,[37] respectively. A further comparision is possible with the bicyclic phosphoranes **27** (Table III) and **36** (Table V) having six- and seven-membered sulfur bonded rings, respectively, and common phenyl groups and five-membered rings. Here the seven-membered ring compound **36** (^{31}P = 17.0[36]) is more deshielded than the six-membered ring structure **27** (^{31}P = -17.6[36]) in line with the order expressed above. The order of deshielding for the ring sizes, five > seven > six > eight, of the types discussed is in line with ring flexibility where the eight-membered ring in a TBP is more flexible than either a six- or seven-membered ring and the five-membered ring is the least flexible. This order of ring flexibility for these compounds agrees with that reasoned from X-ray structural analyses.[27,28] This increase in ring flexibility may allow a greater P—O π bonding contribution for the large ring size. This is similar to that discussed by Ramirez and coworkers[32]

TABLE VI

^{31}P chemical shifts (δ) for monocyclic oxyphosphoranes with eight-membered rings



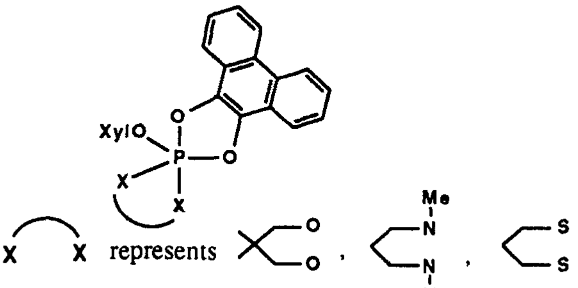
No.[a]	X	R_1	R_2	OR	δ, ppm
37[27]	CH_2	H	H	OCH_2CF_3	-78.33
38[27,b]	CH_2	*t*-Bu	Me	OCH_2CF_3	-78.80
39[37]	CH_2	*t*-Bu	*t*-Bu	OCH_2CF_3	-78.50
40[29]	CH_2	*t*-Bu	*t*-Bu	OPh	-83.81
41[27,b]	S	Me	Me	OCH_2CF_3	-77.30
42[39]	CH_2	H	H	OXyl	-87.44
43[40]	S	Me	Me	OR_1 = Ph OR_2 = OR_3 = OXyl	-73.00

a. References are listed as superscripts.

b. Ring located in (e-e) sites.

where due to the presence of five-membered rings it was proposed that P—O π bonding decreased. We prefer to call this phenomena a ring strain effect rather than "steric inhibition" of p—d π bonding, the ring strain being the least with the eight-membered ring system under discussion.

When the type of ring heteroatom is changed from O to NMe to S, a sequential deshielding effect in this order also is observed. This is evident in the series of bicyclic derivatives shown here[17,20] where a five-membered ring remains constant as the heteroatoms are varied in the attached six-membered ring.

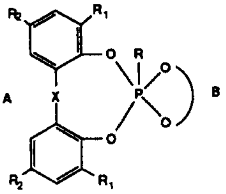


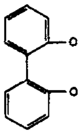
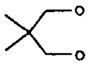
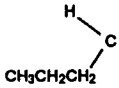
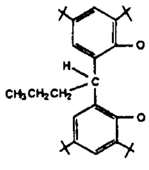
12 14 15

δ = -48.96 [20] δ = -38.91 [20] δ = +3.96 [17]

TABLE VII

^{31}P chemical shifts (δ) for bicyclic oxyphosphoranes with an eight-membered ring (A) and another varying in ring size from six- through eight-membered (B)



No.[a]	X	R_1	R_2	R	Ring B	δ, ppm
44[38]	CH_2	*t*-Bu	*t*-Bu	Ph		-43.90
45[39]	CH_2	H	H	OXyl		-69.05
46[40]		*t*-Bu	*t*-Bu	OCH_2CF_3		-11.17

a. References are listed as superscripts.

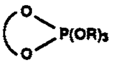
Like the deshielding due to increased number of rings,[32] the deshielding here may be attributed to a decrease in p—d π bonding where the effectiveness of such bonding lies in the order O > N > S.

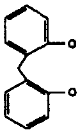
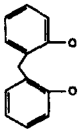
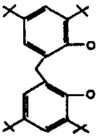
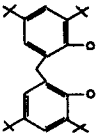
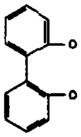
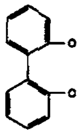
A final feature of note in discussing ^{31}P chemical shift variations of oxyphosphoranes is due to the alteration in the nature of the acyclic group attached to phosphorus. This is more readily discussed relative to Table VIII where appropriate ^{31}P data are summarized for compounds that allow this comparison to be made.

Actually, two principal factors express themselves on analysis of the chemical shift data, an electronegativity effect and a p—d π bonding effect. Comparison of the relative chemical shifts for a monocyclic oxyphosphorane where an oxygen bonding acyclic group is replaced by a more electronegative oxygen bonding acyclic group shows a deshielding of the ^{31}P shift. This is shown in Table VIII as Δ and is evident when OXyl or OPh is replaced by the more electronegative OCH_2CF_3 group. Evidence that OCH_2CF_3 is more electronegative than OPh is available from the greater deshielding when OCH_2CF_3 is present apparent from ^{31}P shifts of $MeN[P(OCH_2CF_3)_2]_2$ (149.9) relative to $MeN[P(OPh)_2]_2$ (135.1) and of $PhN[P(OCH_2CF_3)_2]_2$ (140.3) relative to $PhN[P(OPh)_2]_2$ (127.7).[41]

TABLE VIII
Substituent effects on ^{31}P chemical shifts (δ)

Monocyclic Oxyphosphoranes



No.[a]	Ring	OR	δ, ppm	Δ,[b] ppm	Ring Size
42[39]		OXyl	-87.44	---	8
37[27]		OCH_2CF_3	-78.33	9.11 (42)	8
40[29]		OPh	-83.81	---	8
39[37]		OCH_2CF_3	-78.50	5.31 (40)	8
32[19]		OXyl	-68.34	---	7
30[37]		OCH_2CF_3	-63.10	5.24 (32)	7

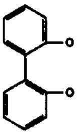
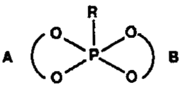
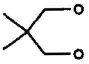
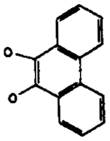
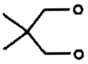
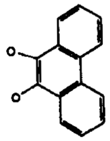
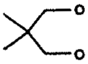
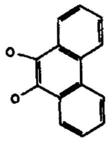
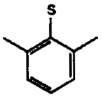
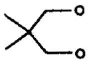
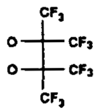
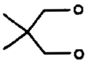
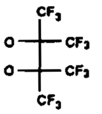
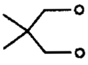
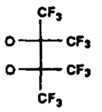
No.[a]	Ring	$R_1=R_2$	R_3	δ, ppm	Δ,[b] ppm	Ring Size
33[38]		OXyl	Ph	-42.97	25.37 (32)	7

TABLE VIII (*Continued*)

Bicyclic Oxyphosphoranes



No.[a]	Ring A	Ring B	R	δ, ppm	Δ,[b] ppm	Ring Size	
						A	B
12[20]			OXyl	-48.96	---	6	5
18[20]			Ph	-28.36	20.60 (12)	6	5
13[20]				-20.30	28.66 (12)	6	5
26[35]			$OCH(CF_3)_2$	-50.80	---	6	5
29[35]			OMe	-47.95	2.85 (26)	6	5
28[35]			H	-35.75	15.05 (26)	6	5

a. References are shown as superscripts.

b. Δ *refers to the amount of* ^{31}P *deshielding in ppm calculated with reference to the entry shown in* parenthesis.

In the monocyclic or bicyclic derivatives where an OR group is replaced by an acyclic group having no oxygen atom to bond to phosphorus, i.e., OXyl replaced by Ph or SXyl or $OCH(CF_3)_2$ replaced by a hydrogen atom, groups of lower electronegativities than the OR groups, a greater deshielding is apparent than that obtained with a change in electronegativity of the OR group as first discussed. In these instances, the loss of P—O π bonding by introduction of a ligand which does not form a P—O bond is felt to be the main reason for the deshielding effect.

The only example that counters this correlation is that for the electronegativity effect of the bicyclics, **26** vs **29**. One would expect $OCH(CF_3)_2$ in **26** to have a greater electronegativity than OCH_3 and to appear downfield relative to **29**. However, there is a small reversal in order here of about 3 ppm. A steric effect brought about by the presence of ring CF_3 groups and acyclic CF_3 groups may be responsible in this case.

It is clear from the above analysis that the greatest ^{31}P shift to low field is experienced by attachment of ligands either in ring heteroatoms or acyclic groups that are not oxygen bonding. Thus, the lowest field shifts are found for oxyphosphoranes that contain at least one bond to phosphorus that lacks an oxygen atom. Examination of Tables II–VII reveals that this occurs for derivatives that contain the acyclic groups, Ph, H, and SXyl, and for the ring components that have S or N bonded to the phosphorus atom. Table IX summarizes phosphorus compounds that have ^{31}P shifts downfield from -45. Of course, due to the general downfield shift for bicyclic compared to monocyclics, the tabulation predominates in bicyclic formulations. This screen though excludes all pentaoxyphosphoranes except for the most sterically encumbered bicyclic derivative **46**[40] which had two identical eight-membered rings with *t*-butyl substituents in addition to a bridging $CH(CH_2CH_2CH_3)$ group. However, the tetraoxyphosphoranes **9**, **19**, and **43**, each containing one phenyl group, have ^{31}P shifts upfield from -45 at -49.15,[18] -52.32[20] and -73.00,[40] respectively. Actually, the only derivative substantially out-of-line with this correlation is the monocyclic **43** which has two OXyl groups and one phenyl substituent. At least it shows a downfield shift relative to the analogous monocylic **42** which has three OXyl groups. The chemical shift for **42** is -87.44.[39]

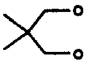
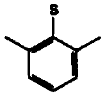
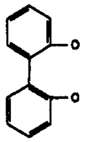
Hexacoordination. Formulas and ^{31}P shifts are summarized in Table X for hexacoordinated derivatives showing P—S interactions. Although the X-ray structures of the pentaoxyphosphorus compounds that have a sulfur-bridging eight-membered ring are displaced progressively toward an octahedron as a result of P—S coordination (44–71%, Table I), the ^{31}P chemical shift change is very modest, going from -77.30 for the five-coordinated species **41**[27] (Table VI) with the ring in an (e–e) orientation of a TBP to -82.44 for the six-coordinated derivative **47**[27] (Table X) which is displaced 65% toward an octahedron. This could be used as evidence that the strength of the P—S bond interaction is not great, although it places the chemical shift in the region cited,[31] about -80 to -110, for cyclic phosphorus compounds containing a PO_6 or PO_5N arrangement. As discussed above, the presence of P—S bonding causes a marked deshielding effect. Thus, introduction of sulfur into the coordination sphere may cause a balance between an increase in ^{31}P shift usually associated with a higher coordination number and a decrease since it is sulfur that is responsible for the increase in coordination geometry. Data in the literature do not appear to be available for cyclic derivatives with PO_5S bonding for comparison.

The same compound formula as **47** but replacement of two of the OCH_2CF_3 groups with

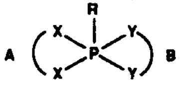
TABLE IX

Cyclic oxyphosphoranes that have ^{31}P chemical shifts downfield from −45 ppm

Monocyclic Oxyphosphoranes

No.[a]	Ring	R_1	R_2	R_3	δ, ppm
7[34]		OC_6F_5	OC_6F_5		-44.71
8[34]		OC_6F_5	OC_6F_5	OXyl	-15.96
33[38]		Ph	OXyl	OXyl	-42.97

Bicyclic Oxyphosphoranes



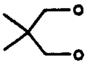
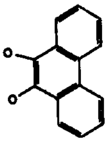
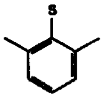
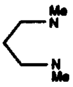
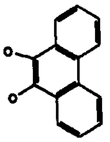
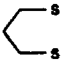
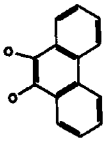
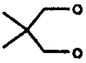
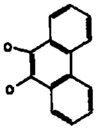
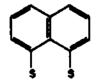
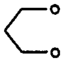
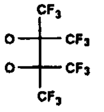
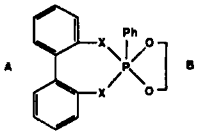
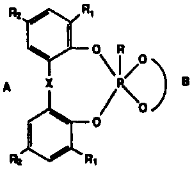
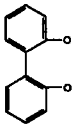
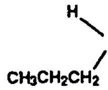
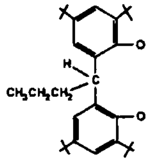
No.[a]	Ring A	Ring B	R	δ, ppm
13[20]				-20.30
14[20]			OXyl	-38.91
15[17]			OXyl	3.96
18[20]			Ph	-28.36

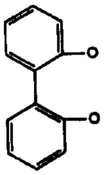
TABLE IX (*Continued*)

No.[a]	Ring A	Ring B	R	δ, ppm
27[36]			Ph	-17.6
28[35]			H	-35.75
36[36]				+17.0



No.[a]	X	R_1	R_2	R	Ring B	δ, ppm
44[38]	CH_2	*t*-Bu	*t*-Bu	Ph		-43.90
46[40]		*t*-Bu	*t*-Bu	OCH_2CF_3		-11.17

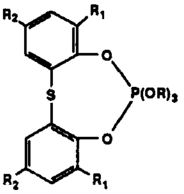
a. References are listed as superscripts.



to give a bicyclic derivative **52** (Table X) shows a deshielding effect. The chemical shift, δ, goes from −82.44 for the tris(trifluoroethoxy) derivative to −69.30 for the bicyclic.[28] This change expresses the ring deshielding effect cited above on going

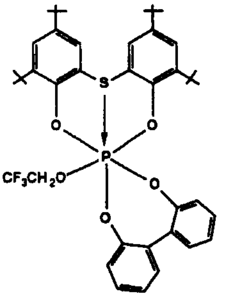
TABLE X

^{31}P chemical shifts (δ) for monocyclic pseudo octahedral phosphorus compounds with sulfur-bridging eight-membered rings[a]



No.[b]	R_1	R_2	OR	δ, ppm
47[27]	t-Bu	t-Bu	OCH_2CF_3	-82.44
48[42]	t-Bu	Me	OCH_2CF_3	-82.25
49[29]	t-Bu	t-Bu	OPh	-82.60
50[29]	t-Bu	Me	OPh	-81.86
51[29]	Me	Me	OPh	-81.16

a. One example of this ring system (R_1 = R_2 = t-Bu) in a bicyclic derivative is



52

with a chemical shift of -69.30 ppm.[28]

b. References are listed as superscripts.

from acyclic to monocyclic to bicyclic for five-coordinated derivatives. The P—S distance in the bicyclic compound **52** shortens to 2.373 Å from 2.504 in **47**, close to the 2.14 Å value for the covalent P—S bond length. Both of these compounds have large displacements toward octahedral geometries, 64.5% for **47**[27] and 70.8% for **52**[28] (Table I).

We have commented earlier,[29] that these results may have important implications for phosphates at enzyme active sites in the presence of sulfur containing amino acid residues. Previously, only pentacoordinated intermediates of phosphorus have received serious attention. On occurrence it is likely that the structural change induced by the formation of a P—S interaction during phosphate activation may be sufficient to trigger enzyme action.

CONCLUSION

We see that substituent effects in cyclic pentaoxyphosphoranes with ring sizes varying from five- to eight-membered produce quite a number of interesting stereochemical and ring conformational changes among five- and six-coordinate species. ^{31}P data indicate that the X-ray structures are retained in solution and also that ^{31}P chemical shifts are interpretable in terms of changes in shielding at the phosphorus atom brought about by electronic factors and the number of attached rings and hence should prove useful in establishing structural types for new formulations. It remains to learn what factors are conducive to the formation of a trigonal bipyramid having a six-membered ring located in diequatorial positions of a pentaoxyphosphorane. Once this is known, it may be possible to discriminate among mechanisms that have been advanced governing the interactions of cAMP at enzyme active sites.[1,4–14] The fact that sulfur interactions promote octahedral coordination suggest their importance at phosphate-enzyme active sites where sulfur may take part.

ACKNOWLEDGEMENT

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