Inorg. Chem. **1995,** *34,* 1243−1247

Structural Preferences of Bicyclic Pentaoxyphosphoranes with Eight-Membered Rings[1]

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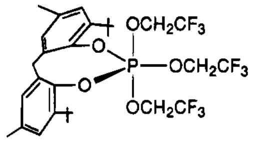
Received September 20, 1994[®]

Oxidative addition reactions of the eight-membered cyclic phosphite $CH_2[(t\text{-}Bu)_2C_6H_2O]_2POCH_2CF_3$ (**8**) with 1,2-dicarbonyl compounds yielded the new bicyclic pentaoxyphosphoranes $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)(O_2C_6Cl_4)$ (**1**), $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)(O_2C_2Ph_2)$ (**2**), and $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)[O_2C_6H_2(t\text{-}Bu)_2]$ (**3**). They were characterized by ^1H and ^{31}P NMR. ^{31}P chemical shifts of **1**−**3** correlate with previous data showing characteristic downfield shifts for bicyclic pentaoxyphosphoranes relative to monocyclic members. An X-ray study of **2** revealed the eight-membered ring in diequatorial positions of a trigonal bipyramid (TBP) with the five-membered ring situated at axial−equatorial sites. This represents the first crystallographic evidence showing rings occupying the two different sets of positions of a TBP for a pentaoxyphosphorane. **2** crystallizes in the orthorhombic space group $Pna2_1$ with $a = 20.211(4)$ Å, $b = 10.479(1)$ Å, $c = 19.784(3)$ Å, and $Z = 4$. The final conventional unweighted residual is 0.061.

Introduction

Recent X-ray studies of pentaoxyphosphoranes have provided numerous derivatives containing six- and seven-membered rings[2−10] for comparison with the well-studied oxyphosphoranes having five-membered rings.[11] Both monocyclic[4,6,8] and bicyclic[2,3,5−10] members have been synthesized and shown to have trigonal bipyramidal (TBP) structures. On the basis of the X-ray studies, the rings invariably occupy axial−equatorial (a−e) positions of the TBP.

Extension of these studies to oxyphosphoranes with eight-membered rings has yielded more structural diversity.[4,12−16] Monocyclic derivatives **4**[12,13] and **5**[13] illustrate this. In **4**, the ring is located in diequatorial sites (e−e) while in **5**, the ring enters into hexacoordination when a bridging sulfur atom replaces a methylene group. Earlier, a variable temperature NMR study by Denney and co-workers[17] supported diequatorial ring placement in a pentaoxy derivative analogous to **4**. Pentacoordinated bicyclic derivatives possessing an eight-membered ring are more rare.[7,14,18,19] For these pentaoxy derivatives, X-ray structural characterization has been achieved only for the spirocyclic phosphorane **6**.[14] Similar to **5**, the compound is hexacoordinated in an octahedral configuration.



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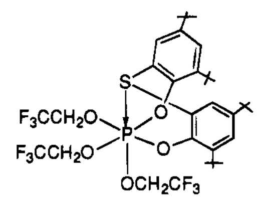

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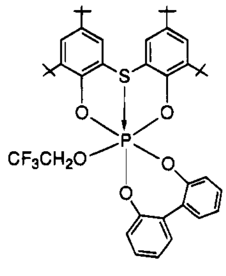

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The present study centers on the synthesis and NMR characterization of further bicyclic pentaoxyphosphoranes (**1**−**3**) containing a common eight-membered ring and a five-membered ring varying in composition.

In the absence of sulfur-induced coordination, the possibility arises that the eight-membered ring would occupy (e−e) sites of a TBP while the five-membered ring would be situated in their usual position at (a−e) sites. However, our structural study of this type of eight-membered ring in the monocyclic derivative **7** shows it to be in (a−e) sites of a TBP.[13] Hence, even in the

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[®] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

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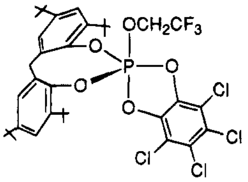

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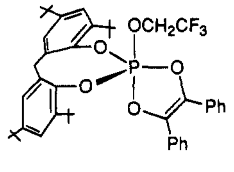

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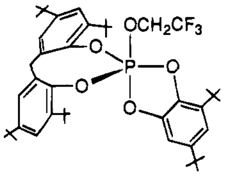

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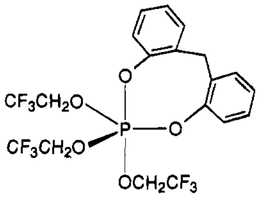
absence of hexacoordination, (a−e) or (e−e) site occupancy of the eight-membered ring in a TBP is possible.



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Experimental Section

Phosphorus trichloride, trifluoroethanol, tetrachloro-1,2-benzoquinone, benzil, and 3,5-di-*tert*-butylquinone were purchased from Aldrich. {[2,2′-Methylenebis((4,6-di-*tert*-butylphenyl)oxy)](2,2,2-trifluoroethoxy)-phosphine}[17] (**8**), and *N*-chlorodiisopropylamine[20] were prepared by literature methods. Solvents were of HPLC grade (Fisher Scientific). Further purification was done according to standard procedures.[21] All the reactions were carried out in a dry nitrogen atmosphere using standard Schlenk-type glassware.[22] Melting points are uncorrected.

^1H, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker MSL 300 FT-NMR spectrometer. ^1H and ^{19}F chemical shifts are reported in ppm relative to tetramethylsilane and fluorotrichloromethane (external), respectively. Chemical shifts for ^{31}P NMR spectra were obtained by setting triphenyl phosphate ($CDCl_3$) at −18.0 ppm[23] and are referenced to 85% H_3PO_4 with negative shifts upfield. All NMR spectra were obtained at 23 °C.

Syntheses. [2,2′-Methylenebis((4,6-di-*tert*-butylphenyl)oxy)](2,2,2-trifluoroethoxy)phosphine, $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)$ (8), prepared by a literature procedure,[17] had the following NMR parameters: ^{31}P NMR ($CDCl_3$) 125.20 (s) (lit.[17] 125.90 ppm); ^{19}F NMR ($CDCl_3$) −75.1 (t, 3 F, OCH_2CF_3).

[2,2′-Methylenebis((4,6-di-*tert*-butylphenyl)oxy)](1,2,3,4-tetrachlorophenylene-5,6-dioxy)(2,2,2-trifluoroethoxy)phosphorane, $CH_2[(t\text{-}Bu)_2(C_6H_2O)]_2P(OCH_2CF_3)(O_2C_6Cl_4)$ (1). A neat mixture of 0.500 g (0.905 mmol) of phosphite **8** and 0.223 g (0.905 mmol) of tetrachloro-1,2-benzoquinone was stirred under a nitrogen atmosphere at 180 °C for 1 h. The reaction was cooled to room temperature and extracted with a 1:1 mixture of diethyl ether (25 mL) and hexane (25 mL) to yield 0.60 g (83%) of phosphorane **1**. It formed as a white precipitate upon refrigeration: mp 215 °C. ^1H NMR ($CDCl_3$): 1.17 (s, 18 H, $C(CH_3)_3$), 1.25 (s, 18 H, $C(CH_3)_3$), 3.85 (br, 1 H, CH_2), 4.57 (br, 1 H, CH_2), 4.75 (m, 2 H, OCH_2CF_3), 7.10−7.25 (m, 4 H, H(Ar)). ^{31}P NMR ($CDCl_3$): −54.13 (s). Anal. Calcd for $C_{37}H_{44}F_3Cl_4O_5P$: C, 55.64; H, 5.51. Found: C, 55.35; H, 5.32.

Table 1. Crystallographic Data for Compound **2**

formula: $C_{45}H_{54}O_5F_3P$	fw: 762.898
cryst syst: orthorhombic	space group: $Pna2_1$ (No. 33)
a = 20.211 (4) Å	T = 23 ± 2 °C
b = 10.479 (1) Å	λ = 0.71073 Å
c = 19.784 (3) Å	D_{calc} = 1.209 g/cm^3
μ = 1.166 cm^{-1}	R^a = 0.061
V = 4190 (2) Å^3	R_w = 0.078
Z = 4	

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

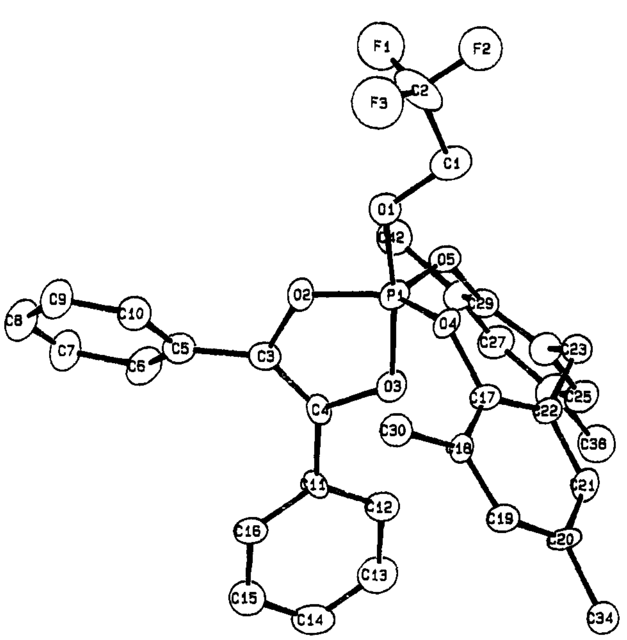

Figure 1. ORTEP plot of $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)(O_2C_2Ph_2)$, **2**, with thermal ellipsoids at the 30% probability level. The terminal carbon atoms of the four *t*-Bu groups (C31, C32, and C33 bonded to C30, etc.) and all hydrogen atoms are omitted for clarity.

[2,2′-Methylenebis((4,6-di-*tert*-butylphenyl)oxy)](1,2-diphenylethylene-1,2-dioxy)(2,2,2-trifluoroethoxy)phosphorane, $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)(O_2C_2Ph_2)$ (2). The procedure for the synthesis of **1** was followed here. The quantities used were as follows: 0.500 g (0.905 mmol) of **8**; 0.190 g (0.905 mmol) of benzil. Yield: 0.634 g (92%). Mp 218−220 °C. ^1H NMR ($CDCl_3$): 1.15 (s, 18 H, $C(CH_3)_3$), 1.25 (s, 18 H, $C(CH_3)_3$), 3.90 (br, 1 H, CH_2), 4.60 (br, 1 H, CH_2), 4.75 (m, 2 H, OCH_2CF_3), 6.30−7.60 (m, 14 H, H(Ar)). ^{31}P NMR ($CDCl_3$): −57.96. Anal. Calcd for $C_{45}H_{54}F_3O_5P$: C, 70.87; H, 7.09. Found: C, 70.45; H, 6.01.

[2,2′-Methylenebis((4,6-di-*tert*-butylphenyl)oxy)](3,5-di-*tert*-butyl-1,2-phenylenedioxy)(2,2,2-trifluoroethoxy)phosphorane, $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)[O_2C_6H_2(t\text{-}Bu)_2]$ (3). The procedure for the synthesis of **1** was followed here. The quantities used were as follows: 0.500 g (0.905 mmol) of **8**; 0.181 g (0.905 mmol) of 3,5-di-*tert*-butylquinone. Yield: 0.609 g (87%). Mp 245 °C. ^1H NMR ($CDCl_3$): 1.10−1.35 (multiplet, 54 H, $C(CH_3)_3$), 3.65 (d, 1 H, $^2J_{(HH)}$ = 13.50 Hz, CH_2), 4.45 (dd, 1 H, $^2J_{(HH)}$ = 13.50 Hz, CH_2), 4.65 (m, 2 H, OCH_2CF_3), 6.60−7.40 (multiplet, 6 H, H(Ar)). ^{31}P NMR ($CDCl_3$): −54.53. Anal. Calcd for $C_{45}H_{65}F_3O_5P$: C, 69.85; H, 8.40. Found: C, 70.20; H, 8.75. X-ray Crystallographic Study for Compound 2

The X-ray crystallographic study was done using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation. Details of the experimental procedures have been described previously.[24]

The colorless crystal used for the study was cut to dimensions of 0.28 × 0.38 × 0.50 mm and mounted inside of a thin walled glass capillary tube which was then sealed as a precaution against moisture sensitivity. Data were collected using the $\theta-2\theta$ scan mode with $3° \le 2\theta_{MoK\bar{\alpha}} \le 43°$. Intensities were observed to decrease dramatically at

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Table 2. Selected Atomic Coordinates in Crystalline $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)(O_2C_2Ph_2)$, **2**[a]

atom[b]	*x*	*y*	*z*	B_{equiv},[c] Å^2
P1	0.2966(1)	0.0426(3)	0.118	3.54(5)
O1	0.2272(3)	0.0478(7)	0.1593(3)	4.4(2)
O2	0.2566(3)	−0.0467(7)	0.0670(3)	3.9(1)
O3	0.3648(3)	0.0218(7)	0.0698(3)	3.9(1)
O4	0.3335(3)	−0.0095(6)	0.1851(3)	3.4(1)
O5	0.2986(3)	0.1952(6)	0.1112(3)	3.6(1)
C1	0.2203(5)	0.118(1)	0.2199(6)	6.2(3)
C3	0.2894(5)	−0.079(1)	0.0074(5)	3.7(2)
C4	0.3530(5)	−0.039(1)	0.0103(4)	3.2(2)
C17	0.4030(4)	−0.031(1)	0.1920(5)	3.5(2)
C18	0.4246(4)	−0.1559(9)	0.2033(5)	2.9(2)
C19	0.4925(5)	−0.1687(9)	0.2104(6)	3.9(2)
C20	0.5382(4)	−0.0664(9)	0.2068(5)	3.2(2)
C21	0.5125(4)	0.0528(9)	0.1989(5)	3.3(2)
C22	0.4436(4)	0.0741(9)	0.1932(5)	3.0(2)
C23	0.4162(5)	0.209(1)	0.1891(5)	3.8(2)
C24	0.4099(4)	0.2728(9)	0.1201(5)	3.5(2)
C25	0.4641(5)	0.3393(9)	0.0931(6)	4.2(3)
C26	0.4572(5)	0.404(1)	0.0310(6)	4.7(3)
C27	0.3963(5)	0.403(1)	0.0001(5)	4.7(3)
C28	0.3423(5)	0.340(1)	0.0244(5)	3.6(2)
C29	0.3518(4)	0.2696(9)	0.0842(5)	3.4(2)

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

Table 3. Selected Distances (Å) and Angles (deg) for $CH_2[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)(O_2C_2Ph_2)$, **2**[a]

	Bond Distances		
P1−O1	1.622(7)	O1−C1	1.41(1)
P1−O2	1.600(7)	O2−C3	1.39(1)
P1−O3	1.693(6)	O3−C4	1.36(1)
P1−O4	1.613(6)	O4−C17	1.43(1)
P1−O5	1.605(7)	O5−C29	1.43(1)
C17−C22	1.37(1)	C22−C23	1.52(1)
C3−C4	1.35(1)	C23−C24	1.52(1)
C3−C5	1.48(1)	C24−C25	1.40(1)
		C24−C29	1.37(1)
	Bond Angles		
O1−P1−O2	84.2(3)	P1−O1−C1	121.9(6)
O1−P1−O3	172.7(4)	P1−O2−C3	115.9(5)
O1−P1−O4	90.1(3)	P1−O3−C4	114.0(5)
O1−P1−O5	91.8(4)	P1−O4−C17	125.8(6)
O2−P1−O3	88.7(3)	P1−O5−C29	126.4(6)
O2−P1−O4	123.8(4)	O3−C4−C3	110.4(8)
O2−P1−O5	122.6(3)	O2−C3−C4	110.0(8)
O3−P1−O4	92.5(3)	O4−C17−C22	117.8(8)
O3−P1−O5	93.4(4)	C17−C22−C23	121.7(8)
O4−P1−O5	113.4(4)	C22−C23−C24	119.0(8)
C23−C24−C29	121.6(8)	O5−C29−C24	117.6(8)

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

higher θ values. A total of 2497 independent reflections ($+h$, $+k$, $+l$) was measured. No corrections were made for absorption.

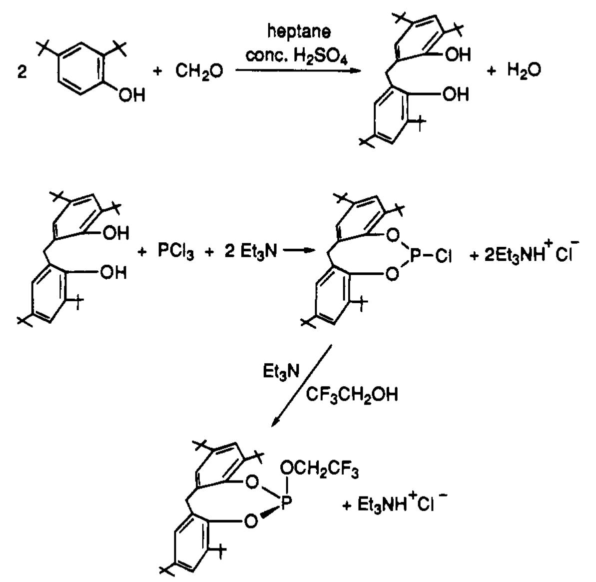
The structure was solved by use of direct methods and difference Fourier techniques and was refined by full-matrix least-squares methods.[25] Due to the paucity of data, fluorine atoms and the terminal carbon atoms of the *t*-Bu groups were refined isotropically, while the remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as fixed isotropic scatterers in ideal positions. The final refinement was based on the 1747 reflections with $I \geq 3\sigma_I$.

Crystallographic data are summarized in Table 1.

Results

The atom-labeling scheme and the molecular geometry for **2** are shown in the ORTEP plot of Figure 1, while selected atomic coordinates are given in Table 2 and selected distances and angles are given in Table 3. Atomic coordinates, anisotropic thermal parameters, complete distances and angles, and hydrogen atom parameters are provided as supplementary material.

Scheme 1



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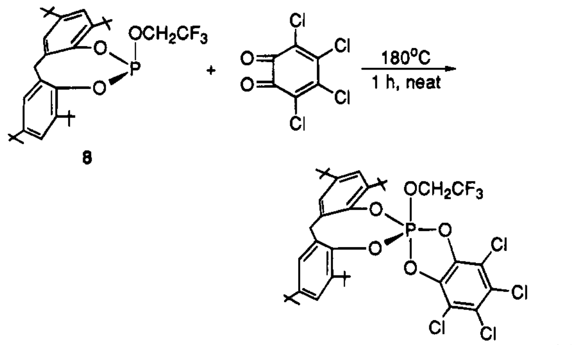
Discussion

Synthesis. The preparation of cyclic phosphite, **8**, was achieved in 41% yield by following the procedure of Denney and co-workers conducted at 5 °C[17] (Scheme 1).

The ^{31}P resonance at 125.20 ppm confirms the tricoordinate structure for the phosphite.

The new bicyclic pentaoxyphosphoranes **1**−**3** were prepared by the oxidative addition of a quinone to the cyclic phosphite **8** in yields of 83−92%. A typical reaction is illustrated for **1** (eq 1).



1 (1)

Structural Features. The ^{31}P NMR chemical shifts of −54.13 ppm (**1**), −57.96 ppm (**2**), and −54.53 ppm (**3**), all in $CDCl_3$, indicated the presence of pentacoordinated structures in solution. The molecular geometry of **2** around the phosphorus atom can be referred to as a trigonal bipyramid (TBP) with the surprising occurrence that the rings occupy the two different sets of positions (Figure 1). Previously, for bicyclic pentaoxyphosphoranes, X-ray results showed that the rings spanned only axial−equatorial sites.[2−10,26−28] In **2**, the five-membered ring occupies an (a−e) set of positions while the eight-membered ring is situated in (e−e) sites. As pointed out in the Introduction, this same type of eight-membered ring with varying substitution

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[25] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$.

[26] Reference 11, Chapter 2.

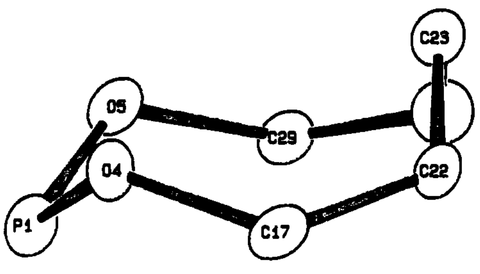
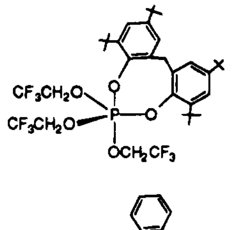
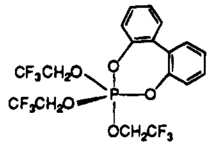
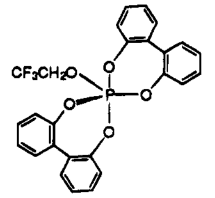


Figure 2. ORTEP plot showing the conformation of the eight-membered ring in compound **2**.

Table 4. ^{31}P Chemical Shifts (δ) for Cyclic Pentaoxyphosphoranes Containing Trifluoroethoxy Groups

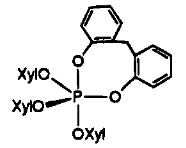
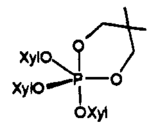
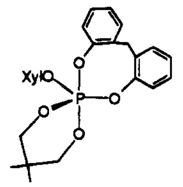
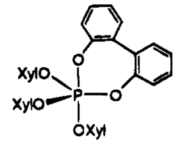
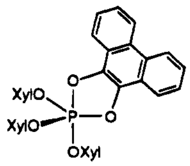
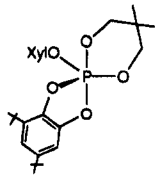
No.^{a}	Compound	δ, ppm
9[17]		−78.50
10[17]		−63.10
11[8]		−47.34

[a] References are listed as superscripts.

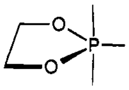
on the aromatic components has been structurally characterized in (a−e) positions of a TBP (compound 7[13]) and in (e−e) positions of a TBP (compound 4[12,13]) where both of these derivatives are monocyclic pentaoxyphosphoranes and contain the same trifluoroethoxy acyclic ligands. Hence, little energy difference is implied in moving this eight-membered ring between the two sets of positions of a TBP.

If we make a comparison with ring strain analysis reported in a previous paper,[1b] where the amount of strain for rings positioned at diequatorial sites of a TBP progressively decreased (in kcal/mol) from five- to seven-membered in the following series, then, based on our above discussion, it would appear reasonable that the (e−e) oriented eight-membered ring should have a strain value approaching 0−2 kcal/mol. These ring types occupying (a−e) positions of a TBP are deemed to be essentially strain free.[1b,29]

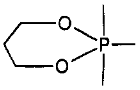
Table 5. ^{31}P Chemical Shifts (δ) for Cyclic Pentaoxyphosphoranes Containing Xylyloxy Groups

No.^{a}	Compound^b	δ, ppm
12[18]		−87.44
13[4]		−77.45
14[18]		−69.05
15[4]		−68.34
16[4]		−57.02
17[3]		−51.30

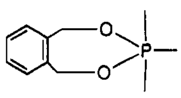
[a] References are listed as superscripts. [b] OXyl = 2,6-dimethylphenoxy.



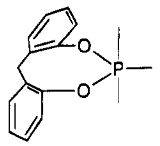
18 kcal/mol



7 kcal/mol



5 kcal/mol



0–2 kcal/mol

The same type of ring arrangement found for **2** is expected in TBP structures for **1** and **3** since they have the identical eight-membered ring and trifluoroethoxy groups with the other ring component being a five-membered one that will surely occupy (a−e) positions. As observed earlier,[13,14,28] this structural finding reinforces the greater flexibility attributed to the eight-membered ring in its structural accommodation compared to smaller ring sizes. As a result of greater ring flexibility, achievement of diequatorial ring orientation for eight-membered rings in TBP formations for some pentaoxyphosphoranes and the lack of this orientation with six- and seven-membered rings in analogous structures were associated with the ability of the eight-membered ring to maximize ring $P-O_{eq}$ π bonding.[13,14]

Structural Details for Oxyphosphorane 2. Distortions

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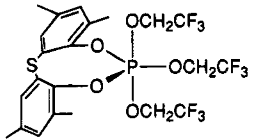
(27) Holmes, R. R.; Day, R. O.; Deiters, J. A.; Kumara Swamy, K. C.; Holmes, J. M.; Hans, J.; Burton, S. D.; Prakasha, T. K. In *Phosphorus Chemistry, Developments in American Science*; Walsh, E. N., Griffiths, E. J., Parry, R. W., Quin, L. D., Eds., ACS Symposium Series 486; American Chemical Society: Washington, DC, 1992; pp 18−40 and references cited therein.

(28) Holmes, R. R.; Prakasha, T. K. *Phosphorus, Sulfur Silicon* **1993**, *80*, 1.

(29) Holmes, R. R. *Pentacoordinated Phosphorus—Reaction Mechanisms*; ACS Monograph 176; American Chemical Society: Washington, DC, 1980, Vol. II, p 36.

away from the ideal TBP geometry are "anti-Berry" in nature (O4−P−O5 closed down to 113.4(4)° with the axial oxygen atoms tipped toward O2). A similar "anti-Berry" distortion was observed in the related compound **4**,[12,13] which contains the same eight-membered diequatorial ring system ($O_{eq}-P-O_{eq} = 116.8(2)°$). In compound **9**,[13] where the ring CH_2 group is replaced by a sulfur atom, the ring $O_{eq}-P-O_{eq}$ angle of 117.5(3)° is also less than 120°. Of the three, compound **2** has the smallest ring angle at phosphorus as well as the greatest deviation from 180° in the $O_{ax}-P-O_{ax}$ angle. The latter is 172.7(4)° for **2**, 176.1(2)° for **4**, and 175.3(3)° for **9**.



9

The eight-membered ring in compound **2** is in the symmetrical *anti* conformation (Figure 2) which was also seen in compounds **4** and **9**.

The five-membered ring in **2** is nearly planar (±0.056 Å), and is approximately perpendicular to the equatorial plane (atoms P1, O2, O4, and O5 coplanar to within ±0.021 Å). The dihedral angle between the two aforementioned planes is 87.2(3)°. The dihedral angles between the $P-O_{eq}-C$ planes and the equatorial plane for **2** are 81.2(5), 80.5(6), and 80.6(5)° for the planes containing C3, C17, and C29, respectively. These values approach the value of 90° believed to maximize the oxygen p-orbital contribution to back-bonding with phosphorus.[13,30]

^{31}P NMR Chemical Shifts. The ^{31}P chemical shifts for **1**−**3** have the values −54.13, −57.96, and −54.53 ppm, respectively, all in $CDCl_3$ solution. These values may be compared to those of the series of cyclic pentaoxyphosphoranes containing acyclic trifluoroethoxy groups that are listed in Table 4 and those of a related series containing xylyloxy groups in Table 5. Due to the greater electronegativity of the OCH_2CF_3 group compared to the OXyl group, comparable formulations in Table 4 are shifted downfield from those in Table 5. Also ring effects are present. For the types of rings studied, shielding in general decreases due to the presence of ring sizes in the order eight > six > seven > five, and shielding decreases from monocyclic to bicyclic.[28] Both of these ring effects have been associated in general with reduced P−O π bonding as the ring size decreases and as ring constraints are increased going from mono- to bicyclic derivatives.[28]

The ^{31}P chemical shifts for **1**−**3** agree with this assessment. If the same amount of deshielding found on going from **10** to **11** is applied to **9**, a new value of ∼−62 ppm is estimated for a bicyclic pentaoxyphosphorane with two eight-membered rings. Recognizing that one of the rings in **1**−**3** is five-membered, a further decrease in shielding is expected. Thus, the observed ^{31}P values of **1**−**3** are in line with predicted values from related derivatives. As previously noted,[28] these ^{31}P chemical shift correlations thus provide a useful means of interpreting ring and substituent variations in cyclic pentaoxyphosphoranes.

Acknowledgment. The support of this research by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We also thank Natalia Timosheva for preparing some of the starting materials.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **2** (Tables S1−S4) (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the American Chemical Society; see any current masthead page for ordering information.

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[30] Trippett, S. *Pure Appl. Chem.* **1974**, *40*, 595.