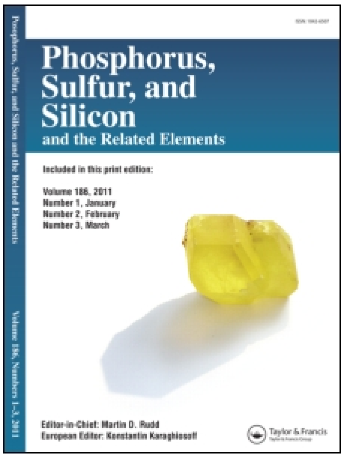

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The crystal structures of phosphoranes **8** and **10** have been determined. Phosphorane **8** crystallizes in a monoclinic space group $P2_1/c$ with a = 10.664 (1) Å, b = 12.782 (2) Å, c = 18.121 (1) Å, β = 91.67 (1)°, and Z = 4. Phosphorane **10** crystallizes in a monoclinic space group $P2_1/n$ with Z = 4, a = 7.014 (1) Å, b = 34.019 (7) Å, c = 9.022 (3) Å, and β = 111.24 (2)°. Phosphoranes **8** and **10**, with phosphorus included in a bicyclic ring system, feature a distorted trigonal-bipyramidal (TBP) local geometry about phosphorus. Determined were apical bond angles: O—P—O, 162.5 (1)° (**8**) and 163.3 (1)° (**10**) and equatorial bond angles: O—P—O, 107.7 (1)° (**8**) and 112.7 (1)° (**10**). These results suggest that compression of the equatorial O—P—O bond angle in the six-membered ring of **8** and related phosphoranes to allow pucker of the ring to assume a chair conformation may occur more easily than when phosphorus is not also part of the bicyclic ring system of **8** and **10**.

Key words: Phosphoranes, X-ray structure, trigonal bipyramid, NMR spectra.

INTRODUCTION

As analogs of the possible intermediates of the enzymic hydrolysis of adenosine 3′,5′-monophosphate (cAMP), 1,3,2-dioxaphosphorinanes containing five-coordinate phosphorus have attracted much recent study.[1] In most cases, the six-membered ring has been found to be attached to phosphorus in apical-equatorial fashion (e.g. **1**–**3**). Even apicophilic substituents such as $(CF_3)_2CHO$ and C_6F_5O are forced to occupy the equatorial position in deference to apical ring oxygen. The conformation of the six-membered ring is generally not in a chair conformation but in a twist or boat form. As first pointed out by Trippett,[2] who predicted that such a conformation should be populated, only in the latter conformation do the *2p* orbital lone pair electrons on equatorial ring oxygen lie very nearly in the equatorial plane where they are available for stabilizing back-bonding to phosphorus.[3] Relief of steric repulsions on chair to twist/boat conversion also has been postulated.[1f] However, in a few cases,[4] e.g., **2**,[1m] the six-membered ring is seen to be in a chair form. Thus, the difference in energy between chair and twist or boat forms may be small.

MNDO calculations on model structure **4** with the equatorial bond angles fixed at 120° assigned a somewhat higher energy (~4 kcal/mol) to the conformer with

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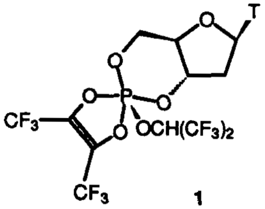
†This paper is dedicated to Professor Dr. Reinhard Schmutzler on the occasion of his 60th birthday.



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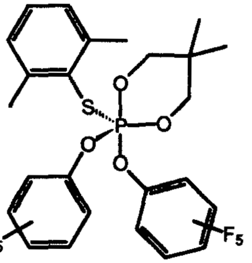

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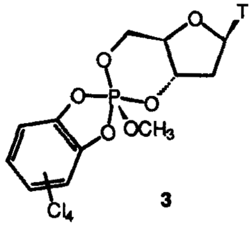

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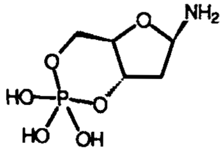

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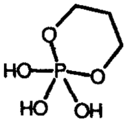
diequatorial attachment of the six-membered ring compared to its apical-equatorial counterpart.[1g] The conformation of the diequatorial six-membered ring, resulting from this approach, was a half-chair; while the apical-equatorial ring was in a twist form. Very recent *ab initio* calculations for **5** place the diequatorially attached 1,3,2-dioxaphosphorinane ring 8.7 kcal/mol higher in energy than the apical-equatorial, boat-form six-membered ring.[5]



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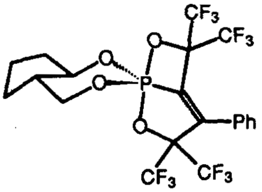

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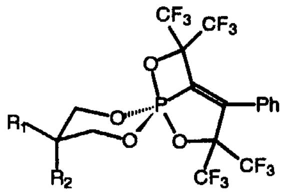
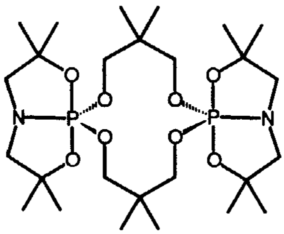
Recently, several 1,3,2-dioxaphosphorinanes with the six-membered ring constrained to be attached diequatorially to five-coordinate phosphorus have been reported, e.g. **6** (and its diastereomer)[1r] and **7**.[1n] All feature a *chair-form* six-membered ring containing a phosphorus atom with distorted trigonal bipyramidal geometry in which the apical P—O bond in the four-membered ring is tilted away from the equatorial plane. The equatorial bond angles O—P—O *within the ring* of **6** and **7** were seen to be contracted from 120° to 108°. Thus, it is not necessary that the equatorial bond angles of such rings be 120° which the NMDO calculations suggest[1g] would impart to the ring a half chair conformation rather than the chair form seen for **6** and **7**. A chair-like pucker about phosphorus was seen as well for the 12-membered ring phosphorane **9** ($\angle$O—P—O = 110.5°).[1q]



7 $R_1 = R_2 = H$
8 R_1 = *tert*-butyl, $R_2 = H$



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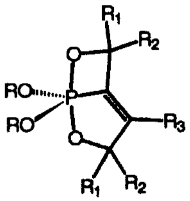
Thus, an important issue to be raised is whether the equatorial bond angles about TBP phosphorus are in general flexible enough to readily accommodate chair-like diequatorially attached rings. Alternatively, the bicyclic ring system of **6**, **7**, and **9** may predispose the equatorial bond angles to be considerably less than 120°. Hence, phosphorane **10**, in which the methoxy substituents can assume an O—P—O bond angle free on any effects of inclusion in a six- or 12-membered ring, was selected for study.

Pudovik *et al.* have prepared a series of bicyclic compounds,[6] including **10–12**. However, to our knowledge, although the X-ray crystal structures of **11** and **12** have been published, crystallographic data, bond angles and bond distances, have not appeared. We report here an X-ray crystallographic study of **10** as well as **8** which is closely related to **6** and **7**.



10 $R = CH_3$, $R_1 = R_2 = CF_3$, $R_3 = Ph$

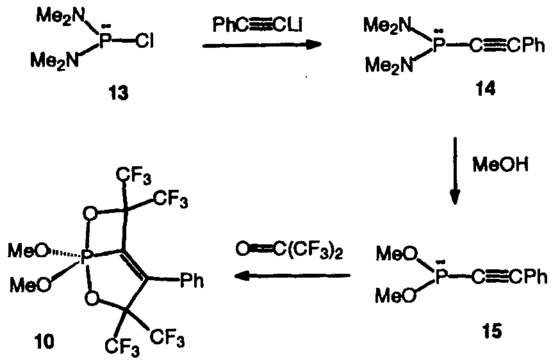
11 $R = R_1 = R_3 = CH_3$, $R_2 = CO_2CH_3$

12 $R = Et$, $R_1 = CN$, $R_2 = C(CH_3)_3$, $R_3 = Ph$

RESULTS AND DISCUSSION

Synthesis

The preparation of **8** and the study of its conformation by ^1H NMR analysis will be published elsewhere. Phosphorane **10** was prepared as shown below. Reaction of bis(dimethylamino)chlorophosphine (**13**) with lithium phenylacetylide at room temperature gave bis(dimethylamino)-2-phenylethynylphosphine (**14**) which underwent methanolysis in refluxing benzene to yield dimethoxy 2-phenylethynylphosphonite (**15**). Phosphorane **10** was prepared from the reaction of phosphonite **15** with hexafluoroacetone at low temperature,[1r] followed by recrystallization from diethyl ether/*n*-pentane:



X-ray Structural Study

X-ray crystallographic analysis of colorless, monoclinic crystals of **8** and **10** gave well-refined structures with R_w values of 4.7% (**8**) and 4.2% (**10**). ORTEP perspective views of **8** and **10** are given in Figures 1 and 2, respectively. Crystal data for **8** and **10** are recorded in Table I, while pertinent bond distances, bond angles, and torsion angles are listed in Table II.

The ORTEP drawings show the local geometry of five-coordinate phosphorus in **8** and **10** to be that of a somewhat distorted TBP. The geometries about phosphorus of structures **8** and **10** are very similar (see Table II). Atoms O(1), O(3), C(3), and P of **8** and **10** are located in the equatorial plane, as evidenced by the sum of the equatorial bond angles, 359.6° (**8**) and 359.9° (**10**). The individual angles, however, in both phosphoranes vary considerably from 120°. The apical P—O(2) bond of the five-membered ring is essentially perpendicular to the equatorial plane. (Bond angles involving O(2), P and the atoms C(3), O(1), and O(3) range 88–95°.) Incorporation of the apical atom O(4) into the four-membered ring moves the P—O(4) bond away from perpendicularity to the equatorial plane (∠O(4)—P—C(3): 74.4° (**8**), 75.0° (**10**); ∠O(2)—P—O(4): 162.5° (**8**), 163.3° (**10**)).

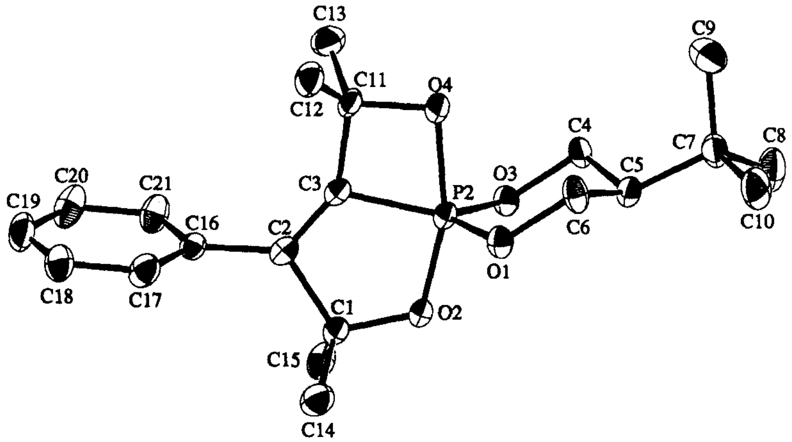


FIGURE 1 ORTEP drawing of the X-ray crystal structure of **8**.

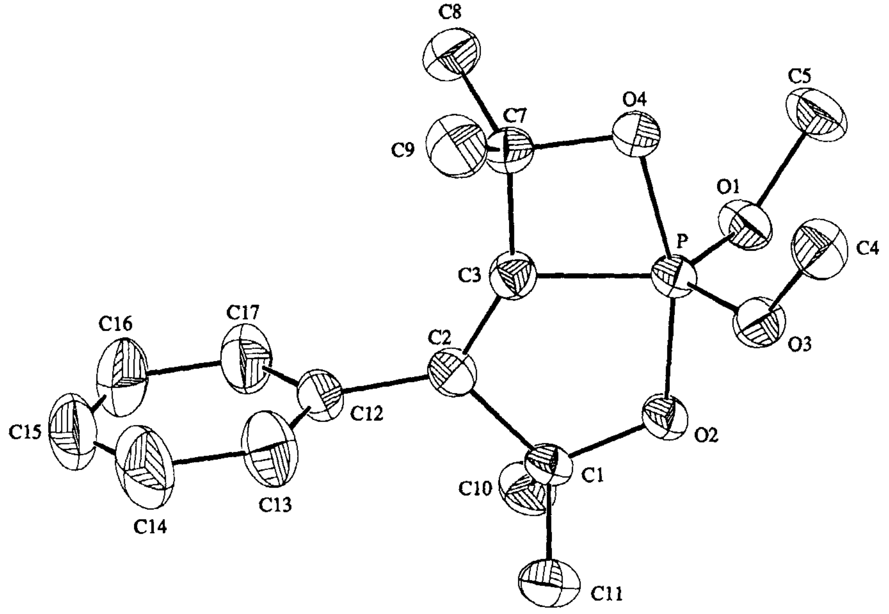


FIGURE 2 ORTEP drawing of the X-ray crystal structure of **10**.

The lengths of analogous bonds in **8** and **10** differ by no more than 0.03 Å. Significantly, *the equatorial bond angle O(1)—P—O(3) of* **10** *(112.7°) is larger than that of* **8** *by 5.0°*. The same angle for **9** is 110.5°.[1q] Evidently, this angle is readily deformable to the optimal values required for **6**–**9**. However, the decrease in the angle in question in **6**–**8** no doubt leads to some loss in stability of the bonding system about phosphorus, although the deviations from the 112.7° value found for **10** are not large. They presumably reflect a decreased energy of the six-membered ring when it is puckered about phosphorus to form the chair conformation. Presumably, a more-nearly half chair conformation, which would result if a rigid 120° O—P—O bond angle were imposed, would be of higher energy.

It should be emphasized that the equatorial O—P—O bond angle associated with phosphorane **10** is relatively small (112.7°). Perhaps this results from the presence on equatorial nitrogen of **9** and at C(3) of **6**–**8** of either an electron lone pair or a π molecular orbital suitably oriented for back-bonding to phosphorus. Nonetheless, such angles are known to vary widely in phosphoranes.[7] It may be that for other, as yet unknown, molecules with the six-membered ring diequatorially attached to phosphorus, the diequatorial O—P—O angle will be constrained to be larger than in **6**–**9** and lead to considerable flattening of the ring geometry about phosphorus. This effect also may change somewhat the free energy difference between chair and boat/twist conformations.

Finally, it should be noted that in the ORTEP structure of **10** the torsion angles C5—O1—P—O2 (−161.5°) and C(4)—O(3)—P—O(2) (173.6°) are closer to 180° than they are in **8**. When these atoms are antiperiplanar (torsion angle 180°), back-bonding from an oxygen electron lone pair to the phosphorus bonding system is

TABLE I

Crystal data for phosphoranes **8** and **10**

	compound	
	8	**10**
mol formula	$PF_{12}O_4C_{21}H_{19}$	$PO_4F_{12}C_{16}H_{11}$
mol wt	594.34	526.218
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
crystal system	monoclinic	monoclinic
cell dimensions		
a, Å	10.664 (1)	7.014 (1)
b, Å	12.782 (2)	34.019 (7)
c, Å	18.121 (1)	9.022 (3)
β, deg	91.67 (1)	111.24 (2)
V, Å^3	2469.18	2006.54
Z	4.0	4.0
D_{calcd}, g/cm^3	1.599	1.742
radiation, Å	λ (Cu) 1.54056	λ (Mo) 0.70930
2 θ range, deg.	4.00-130.00	4.00-50.00
scan technique	$\theta/2\theta$	$\theta/2\theta$
scan width, deg.	0.8000 + 0.1400 tan θ	1.0000 + 0.3500 tan θ
no. of reflections used	3984	3522
absorption coeff., cm^{-1}	21.003	2.600
data to parameter ratio	8.549	8.198
shift to error ratio	0.009	0.001
R	0.0457	0.0414
R_w	0.0473	0.0415

optimal.[3] As noted above, this geometry is available to the equatorial oxygen of such rings when they are bonded to phosphorus in equatorial-apical fashion. The inability of diequatorially disposed chair-form rings to be stabilized in this manner is evident from the structure of **8**.

EXPERIMENTAL

X-ray Crystallography. Crystals of dimensions 0.27 × 0.24 × 0.18 mm^3 (**8**) and 0.34 × 0.26 × 0.18 mm^3 (**10**) were mounted on glass fibers for data collection on a CAD4 diffractometer at −125°C for **8** and at ambient temperature for **10**. Cell constants were obtained from 25 reflections with $10.0° < 2\theta < 20.0°$. The space group was determined from systematic absences and subsequent least-squares refinement to be $P2_1/c$ (**8**) and $P2_1/n$ (**10**). Standard reflections showed no decay for **8** but decay (~31%) for **10** during data collection, an anisotropic decay correction was applied for **10**. Lorentz and polarization corrections, and an empirical absorption correction based on a series of ψ scans, were applied to the data. Intensities of equivalent reflections were averaged. The structure was solved by the standard direct method techniques with a SPD/VAX package. Non-hydrogen atoms were refined with anisotropic

TABLE II

Pertinent bond lengths (Å), bond angles (deg), and torsion angles (deg) for **8** and **10**[a]

atoms	compd	
	8	**10**
P-O(1)	1.571 (2)	1.561 (2)
P-O(2)	1.686 (2)	1.695 (2)
P-O(3)	1.571 (2)	1.555 (2)
P-O(4)	1.810 (2)	1.783 (2)
P-C(3)	1.772 (3)	1.777 (3)
O(1)-C(5 or 6)	1.472 (3)	1.447 (4)
O(3)-C(4)	1.466 (3)	1.447 (4)
O(1)-P-O(3)	107.7 (1)	112.7 (1)
O(1)-P-C(3)	127.8 (1)	123.1 (1)
O(1)-P-O(2)	93.9 (1)	92.0 (1)
O(1)-P-O(4)	94.9 (1)	97.3 (1)
O(2)-P-O(4)	162.5 (1)	163.3 (1)
O(2)-P-O(3)	95.4 (1)	92.2 (1)
O(2)-P-C(3)	88.3 (1)	88.3 (1)
O(3)-P-C(3)	124.1 (1)	124.1 (1)
O(4)-P-C(3)	74.4 (1)	75.0 (1)
P-O(1)-C(5 or 6)	116.5 (2)	124.8 (2)
P-O(3)-C(4)	115.8 (2)	126.9 (2)
O(2)-P-O(1)-C(5 or 6)	-142.21 (0.20)	-161.54 (0.28)
O(2)-P-O(3)-C(4)	141.63 (0.19)	173.62 (0.27)
O(4)-P-O(1)-C(5 or 6)	52.94 (0.21)	32.36 (0.29)
O(4)-P-O(3)-C(4)	-51.41 (0.19)	-20.42 (0.29)

[a] **Numbers in parentheses are estimated standard deviations in the least significant digits.**

thermal parameters. Hydrogen atoms were calculated and added to the structure factor calculations. Scattering factors[8] and $\Delta f'$ and $\Delta f''$ values[9] were taken from the literature. A more detailed description of the above procedures has been published.[1f] Crystal data, data collection, and refinement parameters are collected in Table I.

Spectral and Physical Data. ^{1}H and ^{13}C NMR spectra were recorded on Varian Unity-300 and XL-300 spectrometers. ^{31}P NMR spectra were determined on Varian Unity-300 or FT 80 spectrometers with full proton decoupled {^{1}H}. ^{31}P NMR chemical shifts are expressed in ppm downfield from external 85% H_3PO_4. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA. The melting point of **10** is uncorrected.

***Preparation of dimethoxy 2-phenylethynylphosphonite* (15).** A solution of bis(dimethylamino)-2-phenylethynylphosphine[1r] (1.85 g, 8.40 mmol) and methanol (0.65 g, 20.2 mmol) in 50 mL of benzene was refluxed under an argon atmosphere for 1 day. The solvent was removed by rotary evaporation. The residue was short-path distilled to give 1.3 g of a colorless liquid (6.70 mmol, 80% yield): bp 79–80°C at 0.025 mmHg (lit.[10] bp 84–85°C at 0.55 mmHg); ^{31}P NMR (121 MHz, C_6D_6, {^{1}H}) δ 136.8 (s);

^{1}H NMR (300 MHz, C_6D_6) δ 3.48 (d, $^3J_{PH}$ = 10.6 Hz, 6H, 2 CH_3), 6.87–6.92, 7.29–7.32 (m, 5H, C_6H_5); ^{13}C NMR (75 MHz, C_6D_6, {^{1}H}) δ 53.86 (d, $^2J_{PC}$ = 5.6 Hz, 2C, 2 CH_3), 89.79 (d, $^1J_{PC}$ = 47.0 Hz, 1C, P*C*), 104.53 (d, $^2J_{PC}$ = 2.7 Hz, 1C, PC*C*), 122.04 (d, $^3J_{PC}$ = 2.4 Hz, 1C, *ipso*-Ph), 129.44 (s, 2C, *m*-Ph), 132.19 (d, $^6J_{PC}$ = 2.1 Hz, 1C, *p*-Ph), 132.02 (d, $^4J_{PC}$ = 2.1 Hz, 2C, *o*-Ph).

Preparation of dimethoxy 2-phenylethynylphosphonite Hexafluoroacetone Adduct (**10**). Via the literature procedure,[1r] reaction of **15** (1.25 g, 6.44 mmol) with hexafluoroacetone (excess) in 5 mL of CH_2Cl_2 gave a white solid crude product which was recrystallized from diethyl ether/*n*-pentane at −20°C to give 1.47 g of colorless crystals (2.79 mmol, 43% yield): mp 91–92°C (lit.[6c] mp 90°C); ^{31}P NMR (121 MHz, C_6D_6, {^{1}H}) δ −9.16 (s) (lit.[6c] δ −15 (CCl_4); ^{1}H NMR (300 MHz, C_6D_6) δ 3.37 (d, $^3J_{PH}$ = 14.2 Hz, 6H, 2CH_3), 6.95–6.98, 7.13–7.16 (m, 5H, C_6H_5); ^{13}C NMR (75 MHz, C_6D_6, {^{1}H}) δ 55.20 (d, $^2J_{PC}$ = 8.2 Hz, 2C, 2CH_3), 121.09 (q, $^1J_{FC}$ = 286.5 Hz, 2C, CF_3), 121.27 (q, $^1J_{FC}$ = 286.1 Hz, 2C, CF_3), 127.33 (s, 2C, *m*-Ph), 128.07 (s, 2C, *o*-Ph), 129.93 (s, 1C, *p*-Ph), 146.23 (d, $^3J_{PC}$ = 8.5 Hz, 1C, *ipso*-Ph). The remaining signals were too weak to be assigned. Anal. Calcd for $C_{16}H_{11}F_{12}O_4P$: C, 36.52; H, 2.11. Found: C, 36.46, H, 2.11.

ACKNOWLEDGEMENT

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