Molecular Structure of 1,4-Dioxa-5-phenyl-6,6,7,8,8-pentamethyl-5λ⁵-phosphaspiro[3.4]octane. Structural Preferences of Four-Membered Rings in Phosphoranes[1]

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Reaction of 1-phenyl-1,1-difluoro-2,2,3,4,4-pentamethylphosphetane with 1,2-bis(trimethylsiloxy)ethane resulted in a high yield of 1,4-dioxa-5-phenyl-6,6,7,8,8-pentamethyl-5λ⁵-phosphaspiro[3.4]octane (IV). A crystal structure determination revealed a geometry for IV only slightly displaced from a square pyramid. The compound crystallizes in the monoclinic system, space group $P2_1/n$, with lattice constants $a = 13.595$ (2) Å, $b = 8.187$ (3) Å, $c = 14.257$ (3) Å, $\beta = 100.83$ (2)°, $V = 1558.7$ (5) Å^3, and $Z = 4$. Data were collected on an automated Enraf-Nonius CAD 4 diffractometer to a maximum $2\theta_{Mo\,K\alpha} = 55°$. The structure was refined by full-matrix least squares to a final R value of 0.046 and a weighted R of 0.053 for 1736 reflections with $I > 2\sigma(I)$. The diagonal O–P–C bond angles are 152.6 (2) and 148.4 (2)°. The four bond angles between the apical phenyl group and the basal ligands are 99.4 (2) and 101.0 (2)° for the C–P–O angles and 107.6 (2) and 110.4 (2)° for the C–P–C angles. Retention of the structure in solution is indicated by the similarity in the solid- and solution-state Raman spectra. On the basis of comparisons among related compounds, it is concluded that the presence of a four-membered ring containing like carbon atoms directly attached to phosphorus in spiro derivatives leads to a preference for the square pyramid owing to a reduction of ring strain as well as the reluctance of a saturated carbon atom to assume an axial position in a trigonal-bipyramidal framework.

Introduction

Recently, X-ray crystal structure determinations of a variety of spirocyclic phosphoranes containing five-membered rings revealed geometries near the idealized rectangular pyramid.[2-12] The structural displacement of all of these derivatives is along the Berry coordinate.[13] For example, I[9] and II[11] have

R = H, Cl

I

II
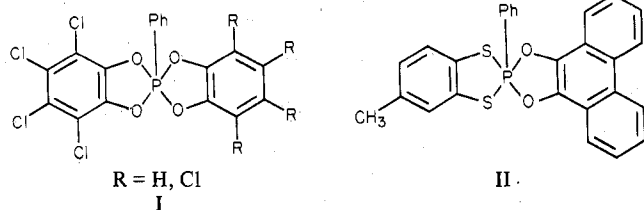
structures most closely approximating the rectangular pyramid as measured by the dihedral-angle method.[13] For cyclic derivatives containing a four-membered ring, this structural form has been reported only for the phospholane III.[14]

R = H, cis CH₃

III
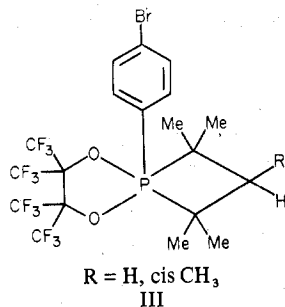
Considering the importance of cyclic five-coordinate intermediates in ligand-reorganization processes and in reaction mechanisms,[15] we continued our studies to probe factors important in preferentially stabilizing the square-pyramidal geometry involving phosphoranes with four-membered rings. In particular, replacement of the trifluoromethyl groups in III by protons would allow the assessment of possible electronic and steric effects. Accordingly, we report the preparation of the new spirocyclic IV and the determination of its crystal structure by X-ray diffraction.

IV
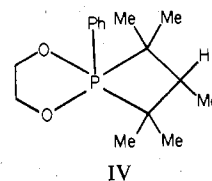
Experimental Section

NMR Spectra. Proton spectra were taken on a Perkin-Elmer R12A spectrometer. Phosphorus-31 and fluorine-19 spectra were recorded using a Varian HA-100 spectrometer. Chemical shifts are reported in ppm and coupling constants in Hz.

Raman Spectra. Solid- and solution-state Raman spectra were recorded on a Cary 82 laser Raman spectrophotometer equipped with a Coherent Radiation Model 52B argon ion laser. The spectra were measured at ambient temperature with a laser output of 100 mW at 5145 Å.

Reagents and Synthesis. All reactions were conducted either under vacuum or in a dry nitrogen or argon atmosphere. Solvents and reagents were purified and dried by standard procedures.[16] The reported melting points are uncorrected.

1-Phenyl-2,2,3,4,4-pentamethylphosphetane 1-Oxide, V. This compound was prepared by the method of Cremer and Chorvat.[17] No attempts were made to separate the resulting mixture of cis and trans isomers, mp 120–121 °C, after sublimation.

1-Phenyl-1,1-difluoro-2,2,3,4,4-pentamethylphosphetane, VI. To a heavy-walled glass tube, flamed out and filled with argon, the phosphetane oxide V (11.5 g, 48 mmol) was added under argon. Sulfur tetrafluoride (6.2 g, 57 mmol) was condensed at −196 °C onto the phosphetane V contained in the tube via a conventional vaccum line. The tube was sealed under vacuum and allowed to warm up overnight from −70 to 0 °C. A colorless liquid formed. The tube was opened under vacuum and the volatile components removed. After the tube was vented with argon, the viscous liquid that remained was transferred via a long-needled syringe into a small distillation flask. Distillation gave the phosphetane VI as a colorless liquid, bp 73–75 °C (0.05 mm) (9.6 g, 77.5%). Solidification occurs on placement in the refrigerator. ^{19}F NMR (CFCl₃): δ 58 ($^1J_{PF}$ = 904 (d)). ^{31}P NMR (H₃PO₄): δ 2.87 ($^1J_{PF}$ = 908 (t)). ^{1}H NMR (internal Me₄Si): δ$_{CH_3}$ 0.7 (3 H, dd), 1.2 (6 H, d, $^3J_{HP}$ = 33.3), 1.3 (6 H, d, $^3J_{HP}$ = 30), δ$_H$ 1.7 (1 H, m), δ$_{Ph}$ 7.1–7.95 (5 H, m). Anal. Calcd for C₁₄H₂₁F₂P: C, 65.14; H, 8.2; P, 11.99. Found: C, 64.93; H, 8.1; P, 12.21.

1,4-Dioxa-5-phenyl-6,6,7,8,8-pentamethyl-5λ⁵-phosphaspiro[3.4]-octane, IV. Phosphetane VI (3.68 g, 14 mmol) and 1,2-bis(trimethylsiloxy)ethane (3.26 g, 15.2 mmol) were syringed into a heavy-walled glass tube which had been dried by flaming and filled

with argon. After the tube was sealed under vacuum, it was heated at 60 °C for 2 h. A viscous substance formed which crystallized on cooling to room temperature. The tube was opened and argon admitted. The crystals were dissolved in 7 mL of ether and were transferred via a long-needled syringe into a small ampule. White crystals of IV, which formed on cooling, were recrystallized three times from ether and dried under vacuum, mp 62–64 °C (3.5 g, 91%). Crystals of IV are hygroscopic but can be handled in air for short periods. The compound is easily soluble in common organic solvents. ^{31}P NMR (benzene-d_6, H_3PO_4): δ 14.14. ^{1}H NMR (internal Me$_4$Si): δ_{CH_3} 0.7 (3 H, dd), 1.2 (6 H, d, $^3J_{PH}$ = 28.9), 1.49 (6 H, d, $^3J_{PH}$ = 24.4), δ_{CH_2} 3.31 (4 H, m), δ_{Ph} 7.05–8.0 (5 H, m).

Anal. Calcd for $C_{16}H_{25}O_2P$: C, 68.55; H, 8.99; P, 11.05. Found: C, 68.24; H, 8.86; P, 11.30.

Collection of Intensity Data. A crystal of the spirocyclic IV of dimensions 0.72 × 0.46 × 0.24 mm was sealed in a 0.5-mm glass capillary (Glaskapillaren). Diffraction data were collected at room temperature (22 ± 1 °C) with an Enraf-Nonius CAD4 diffractometer controlled by a PDP8/E computer. Zirconium-filtered Mo Kᾱ (normal-focus tube) radiation ($\lambda_{K\alpha^1}$ 0.709 26 Å, $\lambda_{K\alpha^2}$ 0.713 54 Å) at a takeoff angle of 3.5° was used. The crystal was optically centered, and unit cell constants and an orientation matrix were determined from the angular settings of 15 well-centered high-order ($2\theta_{Mo K\alpha}$ > 20.5°) reflections. From the observed Laue symmetry ($2/m$) and systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, the space group was uniquely determined as $P2_1/n$ [alternate setting of $P2_1/c$, C_{2h}^5; No. 14].[18] The lattice constants are a = 13.595 (2) Å, b = 8.187 (3) Å, c = 14.257 (3) Å, β = 100.83 (2)°, and V = 1558.7 (5) Å^3. The density of 1.233 g/cm^3 as determined by flotation in aqueous KI is in agreement with the value of 1.246 g/cm^3 calculated for 4 formula units/unit cell.

Intensity data were collected using the ω–2θ scan technique with the ω scan width being determined from the formula $(A + B \tan \theta)°$, where A = 0.80° and B = 0.20, centered about the average peak position. The scan rate was variable from 4.02 to 0.37°/min, the actual value being determined from a preset intensity value and a preliminary prescan for each reflection. The source-to-crystal and crystal-to-detector aperture distances were 21.7 and 17.3 cm, respectively. The incident-beam collimator was 1.3 mm in diameter while the counter aperture height was 4 mm and its width was determined from the formula (1.80 + 0.20 tan θ) mm. Five control reflections (623, 55$\bar{1}$, 50$\bar{9}$, 606, 640) measured after every 100 reflections gave no indication of crystal deterioration.

The total actual scan width used was extended an extra 25% on each side of the calculated scan width for the measurement of background intensity. The net intensity of each reflection, I, is then defined as

$$I = [P - 2(B_1 + B_2)](1/n_s)$$

where P is the peak scan count, B_1 and B_2 are the left and right background counts, and n_s is inversely related to the scan rate. The intensity data were assigned standard deviations according to the formula

$$\sigma(I) = [(P + 4(B_1 + B_2))(1/n_s) + (CI)^2]^{1/2}$$

where C is a factor to account for random errors other than those due to counting statistics. A value of 0.045 was assigned to C. Corrections to the intensity data due to Lorentz–polarization effects were made. Because of the very small linear absorption coefficient ($\mu_{Mo K\alpha}$ = 1.81 cm^{-1}), no corrections were applied for absorption. A total of 3585 independent reflections were measured with 1° ≤ $2\theta_{Mo K\alpha}$ ≤ 55° in the region +h,+k,±l. The 3170 reflections with an intensity greater than 0.1$\sigma(I)$ were treated as observed. For the 415 "unobserved" reflections F_o = $[(1/Lp)(0.10\ \sigma(I))]^{1/2}$, where Lp is the Lorentz–polarization factor.

Solution and Refinement of the Structure. Initial coordinates for the 19 nonhydrogen atoms comprising the asymmetric unit were obtained by direct methods (MULTAN). Unit-weighted isotropic full-matrix least-squares refinement[19] of the parameters for these 19 atoms and a scale factor gave a conventional unweighted residual, R = $\sum||F_o| - |F_c||/\sum|F_o|$, of 0.181 and a conventional weighted residual, R_w = $\{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, of 0.256 for the 1257 reflections having 1° ≤ $2\theta_{Mo K\alpha}$ ≤ 43° and $I > 2\sigma(I)$. Unit-weighted anisotropic refinement gave R = 0.163 and R_w = 0.243 for the same 1257 reflections. The initial coordinates for the 15 methyl hydrogen
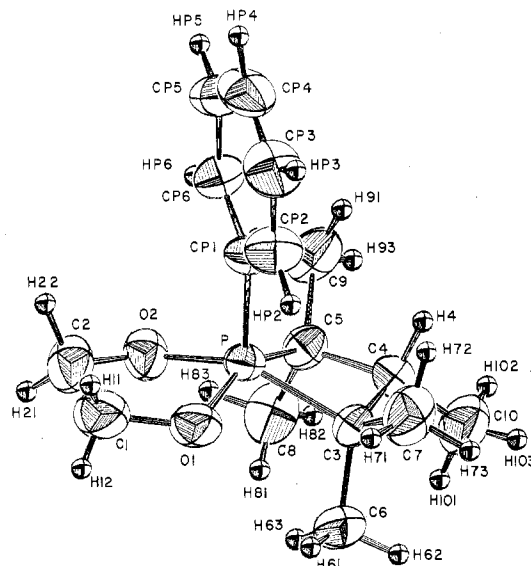

Figure 1. ORTEP plot of $P(C_6H_5)(CH_2O)_2(C_8H_{16})$ with thermal ellipsoids at the 50% probability level for nonhydrogen atoms. Hydrogen atoms are represented by spheres of arbitrary radius.

Table I. Atomic Coordinates^a in Crystalline $P(C_6H_5)(CH_2O)_2(C_8H_{16})$

atom^b	10^4x	10^4y	10^4z
P	2439 (1)	6378 (2)	4257 (1)
O(1)	3260 (3)	7866 (4)	4681 (3)
O(2)	3208 (3)	5786 (4)	3541 (2)
C(1)	4253 (5)	7576 (8)	4548 (5)
C(2)	4229 (4)	6185 (9)	3874 (4)
C(3)	1365 (4)	7728 (6)	4454 (4)
C(4)	612 (4)	6456 (7)	3942 (4)
C(5)	1319 (4)	5545 (6)	3383 (3)
C(6)	1364 (4)	9355 (7)	3906 (4)
C(7)	1206 (5)	8139 (8)	5457 (4)
C(8)	1281 (4)	6184 (8)	2367 (4)
C(9)	1095 (4)	3716 (7)	3315 (4)
C(10)	−391 (5)	7042 (8)	3402 (5)
CP(1)	2749 (4)	4908 (6)	5226 (3)
CP(2)	2914 (4)	5399 (7)	6180 (4)
CP(3)	3190 (5)	4275 (9)	6905 (4)
CP(4)	3311 (5)	2663 (9)	6705 (5)
CP(5)	3189 (4)	2158 (7)	5781 (5)
CP(6)	2913 (4)	3276 (7)	5040 (4)

^{a} Numbers in parentheses are the estimated standard deviations in the last significant figure. ^{b} Atoms labeled to agree with Figure 1.

atoms of the asymmetric unit were taken from a difference Fourier synthesis based on the above. Initial coordinates for the 10 remaining methylene and phenyl hydrogen atoms of the asymmetric unit were inferred from the required geometry of the molecule. A comparison of F_o's with F_c's suggested that 13 low-order reflections were being severely effected by extinction, and they were removed from the data set.

Further unit-weighted refinement of the atomic parameters for the 44 atoms of the asymmetric unit (anisotropic for nonhydrogen atoms, isotropic for hydrogen atoms) included the high-angle data and gave R = 0.046 and R_w = 0.053 for the 1736 reflections having $I > 2\sigma(I)$. The final cycles of refinement using experimental weights, $w^{1/2}$ = $2LpF_o/\sigma(I)$, gave R = 0.053, R_w = 0.055, and S (goodness of fit) = 1.001 for the 2192 reflections having $I > \sigma(I)$ and 1° ≤ $2\theta_{Mo K\alpha}$ ≤ 55°. The goodness of fit S = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observations and N_v represents the number of variables.

During the last cycle of refinement, the largest shift for a non-hydrogen parameter was 0.05$\sigma(p)$, while the largest shift for a hydrogen parameter was 0.15$\sigma(p)$, where $\sigma(p)$ is the least-squares estimate of the error for the parameter in question. A final difference Fourier synthesis (2192 reflections) showed a maximum density of 0.39 e/Å^3. A structure factor calculation based on the final refined

Table II. Anisotropic Thermal Parameters in Crystalline $P(C_6H_5)(CH_2O)_2(C_8H_{16})$

atom[b]	anisotropic parameters, $Å^{2a}$						equiv[c] isotropic B
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	
P	3.5 (1)	2.6 (1)	2.8 (1)	0.0 (1)	0.7 (1)	0.2 (1)	2.9
O(1)	4.6 (2)	3.3 (2)	6.6 (2)	−0.5 (2)	0.6 (2)	0.1 (2)	4.7
O(2)	4.1 (2)	5.6 (2)	3.5 (2)	0.4 (2)	1.1 (1)	0.7 (2)	4.2
C(1)	4.6 (3)	4.7 (3)	8.8 (4)	−0.5 (3)	0.3 (3)	1.3 (3)	5.7
C(2)	4.0 (3)	7.6 (4)	4.9 (3)	1.2 (3)	0.9 (2)	1.8 (3)	5.1
C(3)	3.8 (2)	3.0 (2)	4.0 (2)	0.5 (2)	1.3 (2)	−0.3 (2)	3.4
C(4)	3.7 (2)	3.5 (2)	4.6 (3)	−0.2 (2)	1.3 (2)	0.6 (2)	3.8
C(5)	3.8 (2)	3.4 (2)	3.6 (2)	0.3 (2)	0.5 (2)	−0.5 (2)	3.6
C(6)	5.2 (3)	3.1 (3)	6.8 (3)	0.3 (2)	1.3 (3)	0.2 (3)	4.8
C(7)	6.6 (4)	6.4 (4)	5.0 (3)	1.3 (3)	2.3 (3)	−0.9 (3)	5.5
C(8)	5.4 (3)	7.4 (4)	3.7 (3)	0.9 (3)	0.2 (2)	−0.5 (3)	5.3
C(9)	4.6 (3)	4.1 (3)	7.5 (4)	0.1 (3)	−0.4 (3)	−1.8 (3)	5.1
C(10)	4.1 (3)	6.2 (4)	8.4 (4)	0.8 (3)	0.6 (3)	−0.1 (3)	5.9
CP(1)	4.4 (3)	3.1 (3)	3.0 (2)	0.0 (2)	0.5 (2)	0.3 (2)	3.4
CP(2)	5.9 (3)	4.5 (3)	3.5 (3)	−0.1 (3)	0.3 (2)	0.1 (2)	4.6
CP(3)	6.0 (4)	7.4 (4)	3.5 (3)	0.0 (3)	0.2 (2)	1.1 (3)	5.3
CP(4)	5.1 (3)	6.5 (4)	5.2 (3)	−0.3 (3)	−0.1 (3)	2.9 (3)	5.1
CP(5)	5.3 (3)	3.7 (3)	6.4 (4)	0.0 (2)	0.0 (3)	1.4 (3)	4.9
CP(6)	4.7 (3)	3.7 (3)	4.1 (3)	0.6 (2)	0.4 (2)	0.4 (2)	4.1

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; the B_{ij} in $Å^2$ are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Atoms are labeled in agreement with Figure 1. [c] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Refined Parameters for Hydrogen Atoms in Crystalline $P(C_6H_5)(CH_2O)_2(C_8H_{16})$

atom[a]	coordinates[a]			isotropic thermal parameter B, $Å^2$
	10^3x	10^3y	10^3z	
H(4)	46 (3)	569 (4)	442 (3)	3 (1)
H(11)	467 (4)	741 (6)	521 (3)	6 (1)
H(12)	445 (4)	852 (7)	438 (4)	7 (1)
H(21)	449 (4)	636 (7)	332 (4)	8 (2)
H(22)	460 (3)	520 (6)	417 (3)	6 (1)
H(61)	190 (4)	998 (7)	428 (4)	7 (1)
H(62)	71 (4)	985 (7)	387 (4)	8 (1)
H(63)	159 (4)	922 (6)	331 (4)	6 (1)
H(71)	181 (4)	878 (6)	578 (3)	6 (1)
H(72)	112 (4)	715 (6)	584 (3)	5 (1)
H(73)	54 (5)	880 (7)	542 (4)	8 (2)
H(81)	146 (4)	727 (7)	234 (4)	7 (1)
H(82)	63 (3)	597 (5)	196 (3)	5 (1)
H(83)	185 (4)	560 (6)	212 (3)	6 (1)
H(91)	104 (4)	324 (6)	396 (4)	7 (1)
H(92)	155 (4)	318 (6)	301 (3)	5 (1)
H(93)	45 (4)	353 (7)	287 (4)	7 (1)
H(101)	−31 (4)	778 (7)	287 (4)	6 (1)
H(102)	−82 (4)	613 (7)	314 (4)	7 (1)
H(103)	−78 (4)	758 (7)	380 (4)	7 (1)
HP(2)	285 (4)	654 (6)	631 (3)	6 (1)
HP(3)	324 (4)	470 (7)	755 (4)	8 (2)
HP(4)	358 (4)	188 (7)	721 (4)	8 (2)
HP(5)	327 (4)	105 (6)	560 (3)	5 (1)
HP(6)	289 (4)	287 (6)	441 (3)	6 (1)

[a] See footnotes *a* and *b* to Table I.

parameters but incorporating the weak data (3572 reflections total) gave $R = 0.075$ and $R_w = 0.056$, while the difference Fourier synthesis based on this set showed a maximum density of 0.53 e/$Å^3$.

Computations were done on a CDC 6600 computer (Model Cyber 74-18) using several locally written programs and the following: the direct methods program MULTAN by Main, Germain, and Woolfson; Zalkin's Fourier program, FORDAP; Prewitt's full-matrix least-squares program, SFLS; Johnson's thermal ellipsoid plot program, ORTEP.

Results and Discussion

Figure 1 shows the molecular geometry as well as the atom-labeling scheme. The refined positional and thermal parameters for the nonhydrogen atoms are given in Tables I and II, respectively, while the refined parameters for the hydrogen atoms are given in Table III. Bond lengths and angles for nonhydrogen atoms are tabulated in Tables IV and

Table IV. Bond Lengths[b] (A) and Selected Nonbonded Intramolecular Distances in (A) in Crystalline $P(C_6H_5)(CH_2O)_2(C_8H_{16})$

Bond Lengths			
P–O(1)[a,c]	1.686 (4)	C(3)–C(6)	1.545 (8)
P–O(2)	1.664 (4)	C(5)–C(8)	1.532 (7)
P–C(3)	1.894 (5)	C(3)–C(7)	1.524 (8)
P–C(5)	1.904 (5)	C(5)–C(9)	1.527 (7)
P–CP(1)	1.821 (5)	C(4)–C(10)	1.512 (8)
O(2)–C(2)	1.418 (7)	CP(1)–CP(2)	1.395 (7)
O(1)–C(1)	1.418 (7)	CP(1)–CP(6)	1.389 (7)
C(1)–C(2)	1.487 (9)	CP(3)–CP(4)	1.367 (11)
C(3)–C(4)	1.545 (7)	CP(4)–CP(5)	1.362 (10)
C(5)–C(4)	1.550 (7)	CP(5)–CP(6)	1.395 (8)
		CP(2)–CP(3)	1.382 (9)

Nonbonded Distances			
CP(1)–C(3)	3.050 (7)	C(3)–O(1)	2.538 (6)
CP(1)–C(5)	3.006 (7)	C(5)–O(2)	2.543 (6)
CP(1)–O(1)	2.675 (6)	O(1)–O(2)	2.346 (5)
CP(1)–O(2)	2.691 (6)	C(3)–C(5)	2.344 (7)

[a] Atoms named to agree with Figure 1. [b] The number in parentheses following each entry is the estimated standard deviation in the last significant figure. [c] The bracketed parameters are those related by a pseudo mirror plane.

V and are summarized pictorially in Figure 2. The C–H bond lengths averaged 0.97 (4) Å with maximum and average deviations from this value of 0.08 and 0.03 Å, respectively. A tabulation of bond lengths and angles involving hydrogen atoms is available as supplementary material.

The molecular geometry about phosphorus can be best described as a rectangular pyramid (RP) with the base formed by atoms O(1), O(2), C(3), and C(5) which are coplanar to within ±0.03 Å (Table VI, plane I) and show the nonbonded distances given in Table IV. The distance of 2.346 (5) Å between O(1) and O(2) is close to the C(3)–C(5) distance of 2.344 (7) Å, and the distance of 2.543 (6) Å between O(2) and C(5) is close to the O(1)–C(3) distance of 2.538 (6) Å. The average values of the sides of the rectangles are 2.345 and 2.541 Å.

The unique apical position occupied by CP(1) forms angles about phosphorus with the four basal atoms that are within 5.6° of the value of 105° for the idealized RP or square pyramid (SP), while the two trans basal angles are within 2.6° of 150° expected for the idealized model.[13]

Also consistent with the description as an RP is the pseudo mirror plane defined by atoms P, CP(1), CP(4), C(4), and
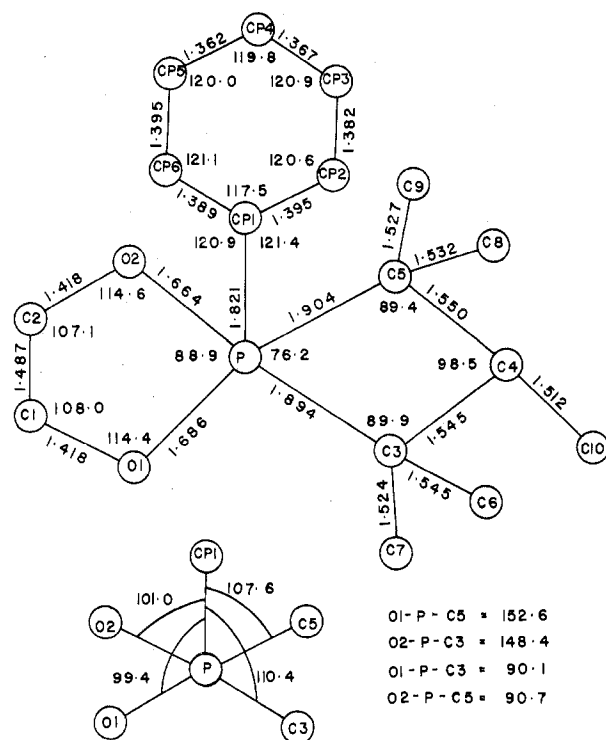
Figure 2. Schematic drawing of $P(C_6H_5)(CH_2O)_2(C_8H_{16})$ showing selected bond distances (Å) and angles (deg).

Table V. Bond Angles[b] (deg) for Nonhydrogen Atoms in Crystalline $P(C_6H_5)(CH_2O)_2(C_8H_{16})$

CP(1)-P-C(3)[a,c]	110.4 (2)	P-CP(1)-CP(2)	121.4 (4)
CP(1)-P-C(5)	107.6 (2)	P-CP(1)-CP(6)	120.9 (4)
CP(1)-P-O(1)	99.4 (2)	CP(6)-CP(1)-CP(2)	117.5 (4)
CP(1)-P-O(2)	101.0 (2)	CP(1)-CP(2)-CP(3)	120.6 (5)
O(1)-P-C(3)	90.1 (2)	CP(1)-CP(6)-CP(5)	121.1 (5)
O(2)-P-C(5)	90.7 (2)	CP(2)-CP(3)-CP(4)	120.9 (6)
O(1)-P-O(2)	88.9 (2)	CP(6)-CP(5)-CP(4)	120.0 (6)
C(3)-P-C(5)	76.2 (2)	CP(3)-CP(4)-CP(5)	119.8 (6)
O(1)-P-C(5)	152.6 (2)	P-C(3)-C(7)	121.2 (4)
O(2)-P-C(3)	148.4 (2)	P-C(5)-C(9)	121.2 (4)
P-O(1)-C(1)	114.4 (4)	P-C(3)-C(6)	110.8 (3)
P-O(2)-C(2)	114.6 (3)	P-C(5)-C(8)	112.1 (4)
O(1)-C(1)-C(2)	108.0 (5)	C(4)-C(3)-C(7)	113.2 (4)
O(2)-C(2)-C(1)	107.1 (5)	C(4)-C(5)-C(9)	111.7 (4)
P-C(3)-C(4)	89.9 (3)	C(4)-C(3)-C(6)	113.9 (4)
P-C(5)-C(4)	89.4 (3)	C(4)-C(5)-C(8)	114.0 (4)
C(3)-C(4)-C(5)	98.5 (4)	C(6)-C(3)-C(7)	107.3 (4)
C(3)-C(4)-C(10)	118.7 (5)	C(8)-C(5)-C(9)	107.7 (4)
C(5)-C(4)-C(10)	118.6 (5)		

a–c See footnotes to Table IV.

C(10) which are coplanar to within ±0.01 Å (plane VI, Table VI). For perfect C_s molecular symmetry, the phenyl group must be at right angles to the mirror plane. The dihedral angle between the least-squares mean plane through the phenyl group atoms (plane VII, Table VI) and the least-squares plane through the atoms defining the pseudo mirror plane is 90.5° (Table VI). The extent to which the molecular geometry deviates from C_s symmetry can be seen in the bond lengths and angles (Figure 2) and is consonant with residual trigonal-bipyramidal (TP) character. Residual trigonal-bipyramidal character is evident in the slight elongation of "axial" bonds P–O(1) and P–C(5) and corresponding larger trans basal angle compared to the respective bond lengths and trans basal angle for the "equatorial" bonds P–O(2) and P–C(3). This is a very small difference since the structure is displaced about 87% from the trigonal bipyramid toward the square pyramid (Table VII).

The discrepancy between the values of 198.0° for $\sum_i |\delta_i(C)$

$- \delta_i(TP)|$ and 181.2° for $S - \sum_i |\delta_i(C) - \delta_i(SP)|$ listed in Table VII shows that the distortion is not exactly along the Berry coordinate. A similar discrepancy was also determined in the related phospholane III giving, respectively, 187.7 and 176.7° for the terms above. This may be largely due to the constraints on the molecular geometry imposed by the four-membered ring.

Although there are no short intermolecular contacts, it is of interest to see if there are indications of structural change on going to the solution state. Raman spectra are shown in Figure 3 for the solid state and for solutions in CS_2 and CCl_4. Where comparisons can be made, the spectra coincide in line frequency. Qualitatively, the relative intensities of the lines are, in general, comparable from spectrum to spectrum. Thus, the spectra indicate that no substantial change in structure takes place on going from the solid state of IV to the solution state.

Comparison of the structural parameters of III and IV shows they are remarkably similar. The percent displacement along the Berry coordinate for III is about 84%, slightly less than that for IV (Table VII). The major difference is found in the C(1)–C(2) bond length and what corresponds to the "axial" bond character of P–O(1) and P–C(5). These bond lengths are approximately 0.06 Å longer in III.[14] The longer C(1)–C(2) bond length in III (1.55 (3) Å) probably arises from a repulsion between attached CF_3 groups. In IV these four CF_3 groups have been replaced by protons. A secondary effect due to the electron-withdrawing property of the CF_3 group may produce the lengthening in the P–O(1) and P–C(5) bonds increasing the amount of residual axial character of these bonds in III relative to those of IV. The orientation of the phenyl substituent and the P–CP(1) bond lengths are much the same in each of these derivatives. Thus, no evidence is given to support steric repulsions between the CF_3 groups and the phenyl group.

Usually when saturated five-membered rings are present, the structural forms assumed by spirocyclic phosphoranes are much closer to the idealized trigonal bipyramid.[13] In the present derivative IV, as well as III, containing a four-membered ring with like carbon atoms bound to phosphorus, it might be argued that a trigonal-bipyramidal structure is unlikely since it would be necessary to place a saturated ring carbon in an unfavorable axial site, in violation of the element effect.[20] However, there is NMR evidence that the latter configuration is possible. Denney and co-workers[21] detected the presence of two isomers VII at low temperature for the
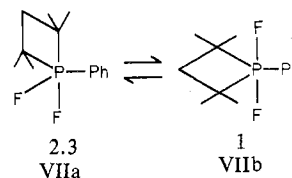
cyclic fluorophosphorane in the approximate ratio of 2.3:1. The NMR data indicated that rapid exchange occurred at ambient temperatures. The minor isomer, although consistent with the element effect, has a four-membered ring in what should be a highly strained diequatorial orientation, at least compared to the normal equatorial angle of 120°. That such a configuration is possible has been demonstrated from the X-ray analysis of the constrained cyclic[22] derivative
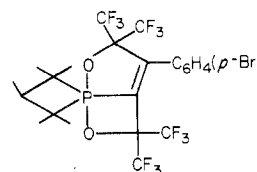
Table VI. Distances in Å from Some Least-Squares Mean Planes for $P(C_6H_5)(CH_2O)_2(C_8H_{16})^{a,b}$

	Plane								
	I	II	III	IV	V	VI	VII	VIII	IX
P	(0.440)	−0.045	0.037	0.242	0.298	−0.004	(−0.087)	0.149	0.115
O(1)	0.033	0.019		−0.132	−0.101			−0.098	−0.109
O(2)	−0.033		−0.017		−0.061			−0.180	0.155
C(1)	(0.000)							0.046	−0.161
C(2)	(0.047)							0.083	
C(3)	−0.031		−0.014	0.048					
C(4)	(0.161)					0.011			
C(5)	0.031	0.016		−0.158	−0.136				
C(6)									
C(7)									
C(8)									
C(9)									
C(10)						−0.007			
CP(1)		0.010	−0.006			0.003	0.006		
CP(2)							−0.005		
CP(3)							0.008		
CP(4)						−0.002	0.027		
CP(5)							−0.009		
CP(6)							−0.026		

[a] Some dihedral angles between planes are 90.5° (VI and VII), 79.8° (I and VII), and 86.1° (II and III). [b] Distances in parentheses are distances from least-squares planes of atoms not included in least-squares plane calculations.

Table VII. Dihedral Angles (δ) for $P(C_6H_5)(CH_2O)_2(C_8H_{16})$ (deg)[a]
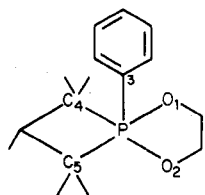
edge[b]	δ[c]	edge[b]	δ[c]
45	125.0 (122.8)	13	82.1 (82.9)
25	115.4 (116.0)	23	78.5 (80.1)
14	116.7 (117.1)	34	71.4 (69.6)
12	110.0 (113.0)	24	4.2 (4.5)
35	76.6 (74.3)		

$\sum_i |\delta_i(C) - \delta_i(TP)| = 198.0°\ (200.8°)$

$\sum_i |\delta_i(C) - \delta_i(SP)| = 36.7°\ (37.3°)$

$S^d - \sum_i |\delta_i(C) - \delta_i(SP)| = 181.2°\ (180.6°)$

av % along Berry coord = 87.0 (87.5)

[a] For purposes of comparison with other tabulations,[13] the atom-numbering scheme shown above is used, where subscripts 1 and 5 refer to axial-type atoms, 2 and 4 refer to equatorial-type atoms, and 3 refers to the equatorial-pivotal atom for a trigonal bipyramid in the Berry process. [b] The number pairs refer to the common edge connecting the two triangular faces of the coordination polyhedron of the P atom whose normals give the dihedral angle. [c] The numbers in parentheses are for a hypothetical coordination polyhedron defined by unit vectors along the bonds from the P atom to the five coordinated atoms. [d] $S = \sum_i |\delta_i(TP) - \delta_i(SP)| = 217.9°$.

Thus, the four-membered carbon-containing ring has appeared in several major pentacoordinate phosphorane orientations. On the basis of a numerical model which allows the estimation of pentacoordinate isomer energies, we calculate that isomer VIIb is approximately 2 kcal/mol higher in energy than VIIa.[20]

As observed with phosphoranes containing five-membered rings, the presence of two such rings results in a structural form more displaced toward the square or rectangular pyramid, particularly if the rings are unsaturated.[13] In this context, it has been argued that a lower ring strain results when a ring containing like atoms bonded to phosphorus is located in equivalent cis-basal positions of a square pyramid compared to the inequivalent axial–equatorial orientation in a trigonal
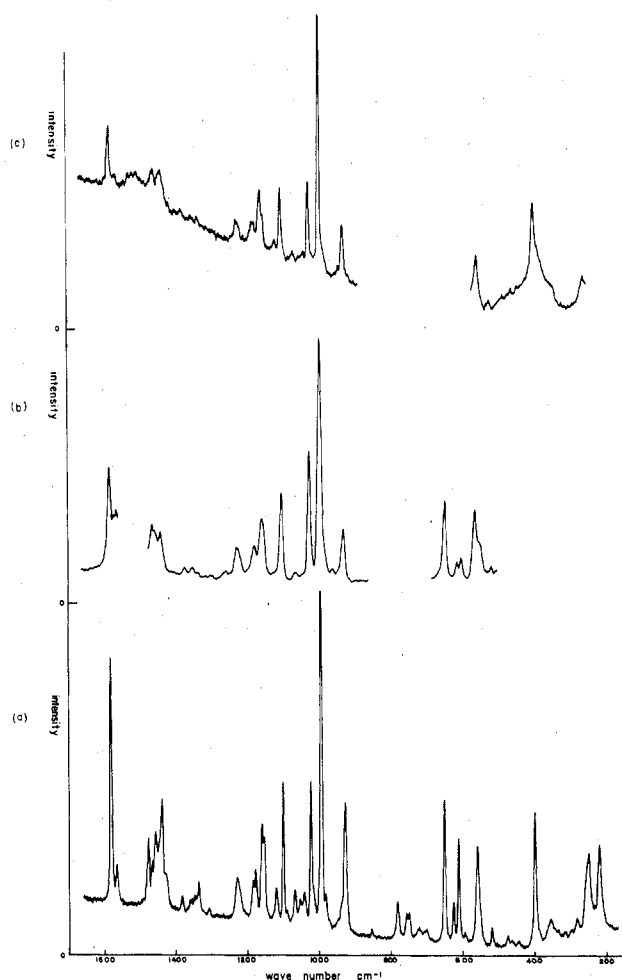

Figure 3. Laser Raman spectra of $P(C_6H_5)(CH_2O)_2(C_8H_{16})$: (a) solid, (b) CCl_4 solution, (c) CS_2 solution. Scattered radiation due to the solvents has been deleted.

bipyramid.[23] This effect also appears to act as a stabilizing influence when four-membered rings are involved, as in III and IV, especially since no appreciable steric effect is indicated between the apical phenyl substituent and the CF_3 groups in III, a factor which might act to stabilize the square-pyramidal form.[3,4,24]

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Crystal and Molecular Structures of Symmetrical Dioxadiazaspirophosphoranes Containing Phosphorus–Hydrogen Bonds[1]

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Single-crystal X-ray diffraction analyses of the spirophosphoranes, $(OCH_2CH_2NH)_2PH$ (III) and $(OC_6H_4NH)_2PH$ (IV), resulting from the reactions of tris(dimethylamino)phosphine with ethanolamine and *o*-aminophenol, respectively, revealed trigonal-bipyramidal structures distorted approximately 25% along the Berry exchange coordinate toward an idealized rectangular pyramid. III crystallizes in the monoclinic space group $C2/c$ with $a = 10.118$ (5) Å, $b = 7.765$ (2) Å, $c = 10.381$ (5) Å, and $\beta = 121.69$ (5)° and has a crystallographic twofold axis along the P–H bond. IV crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.382$ (5) Å, $b = 10.625$ (5) Å, $c = 9.475$ (4) Å, and $\beta = 92.45$ (4)° and has an approximate twofold axis along the P–H bond. The pertinent parameters of III, P–H = 1.49 (6) Å, P–O$_{ax}$ = 1.710 (2) Å, P–N$_{eq}$ = 1.640 (3) Å, and the angle N$_{eq}$–P–N$_{eq}$ = 130.8 (1)°, compare with similar parameters of IV, P–O$_{ax}$ = 1.727 (2) and 1.735 (2) Å, P–N$_{eq}$ = 1.653 (2) and 1.655 (3) Å, and the angle N$_{eq}$–P–N$_{eq}$ = 121.8 (1)°. The large N$_{eq}$–P–N$_{eq}$ angle in III is mainly accounted for by favorable positioning of intermolecular N–H---O hydrogen bonding tending to open the angle whereas in IV, the positions of the neighboring oxygen atoms tend to close the angle.

Introduction

Ring constraints and relative ligand electronegativity provide two of the most important factors responsible for the appearance of geometries between an idealized trigonal bipyramid (TP) and a square or rectangular pyramid (SP, RP) for pentacoordinate phosphorus compounds.[3] Unsaturation in small-membered rings containing oxygen ligands, as in some catechol derivatives,[4–7] I, leads to geometries nearer the RP than the TP. However, when R = H, a near TP is encountered.[4c] Substitution of sulfur for oxygen in the latter (when R = CH$_3$) produces structural changes[8] tending toward the TP. All acyclic derivatives of five-coordinate phosphorus, thus far examined, have near-TP geometries.[9]
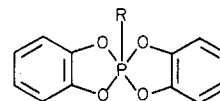
R = F,[4a] CH$_3$,[4b] adamantyl,[5] Ph,[6] OPh[7]

I

Recently we have shown[10a] that structural distortions between the TP and SP (RP) adhere closely to the Berry exchange coordinate[11] and that quantitative interpretation of structural variations is achievable by computer modeling.[10b]

The presence of ring heteroatoms directly attached to phosphorus provides a means of investigating the relative