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X-ray Structural Studies of Spirophosphoranes Differing in Ring Atom Composition[1]

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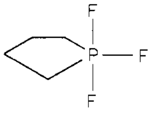
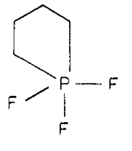
Single-crystal X-ray analysis of 2,3-benzo-5-phenyl-1,4-dioxa-5λ^5-phosphaspiro[4.4]non-7-ene, $(C_6H_4O_2)P(C_6H_5)(C_4H_6)$, V, and 2,3,5,7,8-pentaphenyl-1,4,6,9-tetraoxa-5λ^5-phosphaspiro[4.4]nona-2,7-diene, $(C_{14}H_{10}O_2)_2P(C_6H_5)$, VI, revealed pentacoordinate geometries appearing along the low-energy axial–equatorial bending coordinate connecting ideal trigonal-bipyramidal and rectangular-pyramidal conformations. The structures are displaced 82 and 86%, respectively, along the coordinate toward the rectangular pyramid. Data for both compounds were collected on an Enraf-Nonius CAD4 automated diffractometer by using Mo $K\bar{\alpha}$ radiation. V crystallizes in the monoclinic space group $P2_1$, with $a = 6.204$ (8) Å, $b = 7.194$ (4) Å, $c = 17.063$ (8) Å, $\beta = 118.81$ (5)°, and $Z = 2$. Full-matrix least-squares refinement led to $R = 0.047$ and $R_W = 0.050$ for the 1797 reflections having $I \geq 3\sigma_I$ and $6° < 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 70°$. VI crystallizes in the triclinic space group $P\bar{1}$, with $a = 9.920$ (4) Å, $b = 11.417$ (5) Å, $c = 13.628$ (6) Å, $\alpha = 77.33$ (4)°, $\beta = 75.93$ (3)°, $\gamma = 63.59$ (3)°, and $Z = 2$. Full-matrix least-squares refinement led to $R = 0.040$ and $R_W = 0.050$ for the 3696 reflections having $I \geq 2.5\sigma_I$ and $3° \leq 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 52°$. The electronegativity "rule" posed for trigonal bipyramids is modified for spirocyclics. When a conflict arises between the ring-strain and electronegativity rules, as in V, then an isomeric conversion along the low-energy trigonal bipyramid–square (or rectangular) pyramidal pathway normally occurs.

Introduction

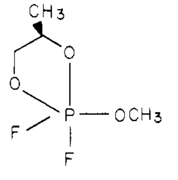
When conformational preferences for trigonal-bipyramidal molecules are discussed, two generalizations regarding the positioning of ligands prevail, the "element effect", which positions the most electronegative group at apical sites,[3] and the "ring-strain" rule, which states that four- and five-membered rings locate preferentially in apical-equatorial sites rather than in diequatorial positions.[4] Application of these two generalizations to monocyclic phosphoranes is usually straightforward, except when the two rules set up a competition for ligand sites. For example, $(CH_2)_4PF_3$ is assigned the structure[3] I rather than II based on NMR data, whereas, when the disparity in ligand electronegativity is not as great as that between C and F, as in III, the strain rule appears to dominate.[5]



I

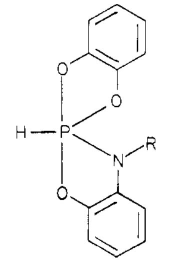


II

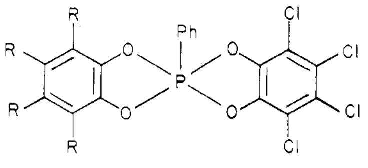


III

We have found that spirophosphoranes are more versatile in structural form than monocyclic derivatives forming a continuous series[6,7] between the ideal trigonal bipyramid (e.g., IVa[1b]) and an ideal rectangular pyramid (e.g., IVb[8]). In this regard, it is of interest to define the range over which particular preference rules operate within a given structural type as well as between structural types.

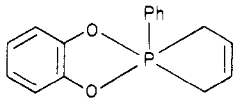


IVa, R = H, CH_3

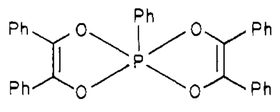


IVb, R = H, Cl

Here, we choose for study the unsaturated spirophosphoranes V and VI containing a common unique ligand but differing in the directly bonded ring atom attached to phosphorus in one of the cyclic components, similar to that in I and III. The determination of their X-ray conformations should provide further discrimination in the role of the directly bonded ring heteroatom as a structural determinant and possibly add a broader significance to the preference rules when dealing with spirocyclic phosphoranes.



V



VI

Experimental Section

Preparation of V. Crystals of 2,3-benzo-5-phenyl-1,4-dioxa-5λ^5-phosphaspiro[4.4]non-7-ene, $(C_6H_4O_2)P(C_6H_5)(C_4H_6)$, were obtained by the addition of cooled 1,3-butadiene to an ether solution of *o*-phenylene phenylphosphonite[9] according to the preparation of Razumova, Bagrov, and Petrov.[10] Colorless crystals resulted which were very sensitive to air, completely decomposing after several hours exposure; mp (uncor) 129 °C (lit.[10] 127–129 °C).

Preparation of VI. Crystals of 2,3,5,7,8-pentaphenyl-1,4,6,9-tetraoxa-5λ^5-phosphaspiro[4.4]nona-2,7-diene, $(C_{14}H_{10}O_2)_2P(C_6H_5)$, were prepared by adding dichlorophenylphosphine to a suspension of zinc dust and benzil in THF essentially as described by Schmidt et al.[11] Recrystallization from toluene yielded colorless crystals; mp (uncor) 227–229 °C (lit.[11] 216–218 °C).

Space Group Determination and Data Collection for V. Preliminary precession and Weissenberg photographs indicated monoclinic ($2/m$) symmetry, the absences $0k0$ ($k = 2n + 1$) being consistent with either space group $P2_1$ or $P2_1/m$. A well-formed crystal, having dimensions 0.50 mm × 0.45 mm × 0.10 mm, was mounted in a sealed thin-walled glass capillary for data collection and transferred to an Enraf-Nonius CAD4 automated diffractometer employing Zr-filtered molybdenum radiation (normal-focus tube, $\lambda K\alpha_1$ 0.709 26 Å, $\lambda K\alpha_2$ 0.713 54 Å). The lattice constants as determined by the least-squares refinement of the diffraction geometry for 13 reflections having $12° < 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} < 37°$ are $a = 6.204$ (8) Å, $b = 7.194$ (4) Å, $c = 17.063$ (8) Å, and $\beta = 118.81$ (5)°. A unit cell content of two molecules gives a calculated density of 1.345 g/cm³, in agreement with the value of 1.33 (2) g/cm³ as measured by flotation in a carbon tetrachloride–benzene mixture. Since it seemed unlikely that the molecule had perfect C_s symmetry, the space group $P2_1$-C_2^2 [12] was chosen. This choice was confirmed by all subsequent stages of solution and refinement.

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Table I. Atomic Coordinates for $(C_6H_4O_2)P(C_6H_5)(C_4H_6)$, V[a]

atom[b]	10^4x	10^4y	10^4z
P	4467 (1)	6693[c]	2293 (1)
O1	6721 (2)	7762 (2)	2101 (1)
O2	2377 (2)	8057 (3)	1449 (1)
C1	6453 (5)	4599 (4)	2626 (2)
C2	5272 (6)	3325 (4)	3000 (2)
C3	2942 (5)	3615 (3)	2725 (2)
C4	1837 (5)	5166 (4)	2092 (2)
1C1	5122 (3)	7892 (3)	3320 (1)
1C2	3267 (4)	8622 (3)	3451 (2)
1C3	3815 (6)	9552 (4)	4238 (2)
1C4	6197 (7)	9713 (5)	4903 (2)
1C5	8058 (6)	8991 (5)	4783 (2)
1C6	7535 (4)	8084 (4)	3998 (1)
2C1	5886 (3)	9263 (3)	1550 (1)
2C2	7225 (4)	10475 (3)	1329 (1)
2C3	5929 (4)	11845 (5)	698 (1)
2C4	3424 (4)	11993 (4)	316 (1)
2C5	2089 (4)	10774 (4)	547 (1)
2C6	3349 (3)	9422 (3)	1162 (1)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Atoms are labeled in agreement with Figure 1. [c] Fixed.

Data were collected by using the θ–2θ scan mode with a θ scan range of $(0.7 + 0.2 \tan \theta)^\circ$ centered about the calculated Mo K$\bar{\alpha}$ peak position. The scan range was actually extended an extra 25% on either side of the aforementioned limits for the measurement of background radiation. The scan rates varied from 0.56 to 4.0°/min, the rate to be used for each reflection having been determined by a prescan. The intensity, I, for each reflection is then given by $I = (\mathrm{FF}/S)(P - 2(B1 + B2))$, where P is the number of counts accumulated during the peak scan, $B1$ and $B2$ are the left and right background counts, S is an integer which is inversely proportional to the scan rate, and FF is either unity or a multiplier to account for the occasional attenuation of the diffracted beam. The standard deviations in the intensities, σ_I, were computed as $\sigma_I^2 = (\mathrm{FF}^2/S^2)(P + 4(B1 + B2)) + 0.002I^2$. A total of 3111 independent reflections having $6° < 2\theta_{\mathrm{Mo\,K}\bar{\alpha}} < 70°$ were measured in the region $+h,+k,\pm l$. Five standard reflections monitored after every 50 reflections gave no indication of crystal deterioration or loss of alignment. No correction was made for absorption ($\mu_{\mathrm{Mo\,K}\bar{\alpha}} = 0.205\ \mathrm{mm}^{-1}$) and the intensities were reduced to relative amplitudes, F_o, by means of standard Lorentz and polarization corrections.

Solution and Refinement for V. Initial coordinates for 15 of the 19 independent nonhydrogen atoms were obtained by direct methods (MULTAN). Initial coordinates for the remaining four independent nonhydrogen atoms were obtained by standard Fourier difference techniques. Isotropic unit-weighted full-matrix least-squares refinement[13] of the structural parameters for the 19 independent nonhydrogen atoms and a scale factor gave a conventional residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.128 and a weighted residual $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$ of 0.218 for the 744 reflections having $I \geq \sigma_I$ and $(\sin \theta)/\lambda \leq 0.52$. A comparison of F_o with F_c at this point suggested that two strong low-order reflections (01$\bar{3}$, 100) were suffering from extinction, and they were removed from the data set. Anisotropic refinement then led to $R = 0.066$ and $R_w = 0.074$. Initial coordinates for the 15 independent hydrogen atoms were then inferred from the required geometry of the molecule. Subsequent refinement, including the hydrogen atoms as isotropic contributions and employing variable weights ($w^{1/2} = 2LpF_o/\sigma_I$), led to the final values of $R = 0.047$, $R_w = 0.050$,[14a] and GOF[14b] = 1.320 for the 1797 reflections having $I \geq 3\sigma_I$ and $6° \leq 2\theta_{\mathrm{Mo\,K}\bar{\alpha}} \leq 70°$. During the final cycle of refinement the largest shift in any parameter was less than 0.02 times its estimated standard deviation. A final difference Fourier synthesis showed a maximum density of 0.36 e/Å^3.

Space Group Determination and Data Collection for VI. The conditions for data collection and reduction were the same as described for V, unless otherwise noted. Preliminary precession and Weissenberg photographs indicated triclinic symmetry, consistent with space groups $P1$ and $P\bar{1}$. A well-formed crystal, having dimensions 0.30 mm × 0.35 mm × 0.60 mm, was mounted in a sealed thin-walled glass capillary for data collection. The lattice constants as determined by the least-squares refinement of the diffraction geometry for 15 reflections having $20.8° \leq 2\theta_{\mathrm{Mo\,K}\bar{\alpha}} \leq 28.5°$ are $a = 9.920$ (4) Å, $b = 11.417$ (5) Å, $c = 13.628$ (6) Å, $\alpha = 77.33$ (4)°, $\beta = 75.93$ (3)°, and $\gamma = 63.59$ (3)°. A unit cell content of two molecules gives a calculated density of 1.320 g/cm^3 in agreement with the observed value of 1.34 (2) g/cm^3. The space group $P\bar{1}$-C_i^1[15] was chosen on the assumption that there would be one molecule in the asymmetric unit. This choice was confirmed by all subsequent stages of solution and refinement.

Data were collected as for V, except that the θ scan range was $(0.8 + 0.2 \tan \theta)^\circ$ and the scan speeds varied from 0.61 to 4.0 °/min. A total of 5219 independent reflections having $3° \leq 2\theta_{\mathrm{Mo\,K}\bar{\alpha}} \leq 52°$ were measured in the region $+h,\pm k,\pm l$. Eight standard reflections, monitored at 100-reflection intervals, gave no indication of crystal deterioration or loss of alignment. No correction was made for absorption ($\mu_{\mathrm{Mo\,K}\bar{\alpha}} = 0.148\ \mathrm{mm}^{-1}$).

Solution and Refinement for VI. Initial coordinates for 31 of the 39 independent nonhydrogen atoms were obtained by direct methods (MULTAN). Initial coordinates for the remaining eight independent nonhydrogen atoms were obtained by using standard Fourier difference techniques. The conditions for refinement were the same as stated for V. Isotropic unit-weighted full-matrix least-squares refinement[13] of the structural parameters for the 39 independent nonhydrogen atoms and a scale factor led to $R = 0.124$ and $R_w = 0.189$ for the 1577 reflections having $I \geq 3\sigma_I$ and $(\sin \theta)/\lambda \leq 0.52$.

Anisotropic refinement gave $R = 0.059$ and $R_w = 0.069$. Initial coordinates for the 25 independent hydrogen atoms were then inferred from the required geometry of the molecule. Subsequent refinement,

Table II. Thermal Parameters in $(C_6H_4O_2)P(C_6H_5)(C_4H_6)$, V[a]

atom[b]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	2.42 (2)	2.54 (2)	2.14 (2)	−0.01 (2)	1.03 (1)	0.23 (2)
O1	2.5 (1)	3.9 (1)	3.7 (1)	0.7 (1)	1.7 (1)	1.3 (1)
O2	2.3 (1)	4.3 (1)	2.8 (1)	−0.1 (1)	0.9 (1)	1.0 (1)
C1	4.1 (1)	3.0 (1)	4.3 (1)	0.6 (1)	2.2 (1)	−0.1 (1)
C2	5.9 (1)	2.6 (1)	4.4 (1)	0.1 (1)	2.5 (1)	0.6 (1)
C3	4.9 (1)	2.7 (1)	4.6 (1)	−0.8 (1)	2.4 (1)	0.0 (1)
C4	3.4 (1)	3.8 (1)	4.1 (1)	−1.1 (1)	1.3 (1)	0.3 (1)
1C1	3.1 (1)	2.1 (1)	2.4 (1)	0.1 (1)	1.4 (1)	0.3 (1)
1C2	3.6 (1)	3.1 (1)	3.9 (1)	0.3 (1)	2.2 (1)	0.4 (1)
1C3	7.0 (2)	3.4 (1)	5.7 (1)	0.0 (1)	4.8 (1)	−0.4 (1)
1C4	8.2 (2)	3.6 (1)	3.7 (1)	−1.1 (1)	3.3 (1)	−1.1 (1)
1C5	5.7 (1)	4.9 (1)	3.3 (1)	−0.7 (1)	1.0 (1)	−0.8 (1)
1C6	3.4 (1)	3.7 (1)	3.2 (1)	0.2 (1)	1.0 (1)	−0.6 (1)
2C1	2.5 (1)	3.0 (1)	2.3 (1)	0.2 (1)	1.3 (1)	0.1 (1)
2C2	3.0 (1)	3.5 (1)	3.4 (1)	−0.1 (1)	1.9 (1)	0.1 (1)
2C3	4.7 (1)	3.2 (1)	3.9 (1)	−0.2 (1)	2.8 (1)	0.6 (1)
2C4	4.6 (1)	3.2 (1)	3.5 (1)	0.9 (1)	1.9 (1)	1.3 (1)
2C5	2.9 (1)	4.3 (1)	3.0 (1)	0.6 (1)	1.1 (1)	1.1 (1)
2C6	2.6 (1)	3.4 (1)	2.1 (1)	0.0 (1)	1.1 (1)	0.1 (1)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. Anisotropic temperature factors used during refinement 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} given above in Å^2 are related to the dimensionless β_{ij} as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Atoms are labeled in agreement with Figure 1.

Table III. Refined Parameters for Hydrogen Atoms in $(C_6H_4O_2)P(C_6H_5)(C_4H_6)$, V[a]

atom[a]	10^3x	10^3y	10^3z	B_{iso}, Å^2
1H2	161 (5)	860 (5)	299 (2)	5 (1)
1H3	247 (5)	998 (5)	430 (2)	5 (1)
1H4	651 (5)	1042 (5)	545 (2)	5 (1)
1H5	962 (5)	898 (4)	519 (2)	5 (1)
1H6	877 (5)	753 (5)	397 (2)	5 (1)
2H2	893 (4)	1030 (4)	152 (1)	3 (1)
2H3	672 (4)	1262 (5)	54 (2)	4 (1)
2H4	268 (4)	1283 (4)	−6 (2)	4 (1)
2H5	44 (5)	1083 (4)	28 (1)	3 (1)
AH1	817 (5)	483 (5)	303 (2)	5 (1)
BH1	631 (5)	401 (5)	208 (2)	5 (1)
H2	611 (4)	237 (4)	339 (2)	4 (1)
H3	206 (4)	296 (4)	296 (2)	4 (1)
AH4	109 (5)	465 (6)	148 (2)	6 (1)
BH4	46 (6)	588 (6)	209 (2)	6 (1)

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

Table IV. Bond Lengths (Å) and Angles (deg) in $(C_6H_4O_2)P(C_6H_5)(C_4H_6)$, V[a]

Lengths

P-O1	1.760 (1)	2C4-2C5	1.388 (4)
P-C4	1.857 (3)	2C5-2C6	1.366 (3)
P-O2	1.709 (1)	2C6-2C1	1.387 (3)
P-C1	1.853 (3)	1C2-1H2	0.95 (3)
P-1C1	1.814 (2)	1C3-1H3	0.94 (3)
O1-2C1	1.359 (3)	1C4-1H4	0.99 (3)
O2-2C6	1.361 (3)	1C5-1H5	0.88 (3)
C1-C2	1.496 (4)	1C6-1H6	0.88 (3)
C2-C3	1.304 (4)	2C2-2H2	0.96 (2)
C3-C4	1.472 (4)	2C3-2H3	0.87 (3)
1C1-1C2	1.378 (3)	2C4-2H4	0.84 (3)
1C2-1C3	1.387 (4)	2C5-2H5	0.90 (2)
1C3-1C4	1.367 (5)	C1-AH1	0.97 (3)
1C4-1C5	1.368 (5)	C1-BH1	0.99 (3)
1C5-1C6	1.382 (4)	C2-H2	0.92 (3)
1C6-1C1	1.389 (3)	C3-H3	0.94 (3)
2C1-2C2	1.376 (3)	C4-AH4	1.00 (3)
2C2-2C3	1.394 (4)	C4-BH4	1.00 (3)
2C3-2C4	1.369 (3)		

Angles

O1-P-C4	158.6 (1)	1C1-1C2-1H2	122 (2)
C1-P-O2	148.0 (1)	1C1-1C2-1C3	120.4 (2)
O1-P-1C1	98.3 (1)	1H2-1C2-1C3	118 (2)
1C1-P-C4	103.1 (1)	1C2-1C3-1H3	116 (2)
O2-P-1C1	105.5 (1)	1C2-1C3-1C4	120.5 (3)
C1-P-1C1	106.5 (1)	1H3-1C3-1C4	123 (2)
O1-P-O2	86.6 (1)	1C3-1C4-1H4	118 (2)
C1-P-C4	88.4 (1)	1C3-1C4-1C5	119.7 (3)
C1-P-O1	86.7 (1)	1H4-1C4-1C5	123 (2)
O2-P-C4	86.7 (1)	1C4-1C5-1H5	125 (2)
P-O1-2C1	113.8 (1)	1C4-1C5-1C6	120.2 (3)
P-O2-2C6	115.5 (1)	1H5-1C5-1C6	114 (2)
P-C1-AH1	115 (2)	1C1-1C6-1H6	122 (2)
P-C1-BH1	108 (2)	1C1-1C6-1C5	120.7 (2)
P-C1-C2	103.8 (2)	1H6-1C6-1C5	117 (2)
AH1-C1-BH1	108 (3)	O1-2C1-2C2	127.8 (2)
AH1-C1-C2	113 (2)	O1-2C1-2C6	111.2 (2)
BH1-C1-C2	108 (2)	2C2-2C1-2C6	120.9 (2)
C1-C2-H2	123 (2)	2C1-2C2-2H2	122 (1)
C1-C2-C3	115.7 (2)	2C1-2C2-2C3	117.3 (2)
H2-C2-C3	122 (2)	2H2-2C2-2C3	120 (2)
C2-C3-H3	123 (2)	2C2-2C3-2H3	119 (2)
C2-C3-C4	115.5 (2)	2C2-2C3-2C4	121.5 (3)
H3-C3-C4	122 (2)	2H3-2C3-2C4	119 (2)
P-C4-AH4	110 (2)	2C3-2C4-2H4	120 (2)
P-C4-BH4	112 (2)	2C3-2C4-2C5	120.7 (3)
P-C4-C3	104.8 (2)	2H4-2C4-2C5	119 (2)
AH4-C4-BH4	104 (3)	2C4-2C5-2H5	121 (2)
AH4-C4-C3	108 (2)	2C4-2C5-2C6	118.0 (2)
BH4-C4-C3	119 (2)	2H5-2C5-2C6	121 (2)
P-1C1-1C2	121.5 (2)	O2-2C6-2C5	126.9 (2)
P-1C1-1C6	120.1 (2)	O2-2C6-2C1	111.5 (2)
1C2-1C1-1C6	118.4 (2)	2C5-2C6-2C1	121.5 (2)

[a] Footnotes *a* and *b* to Table I apply.

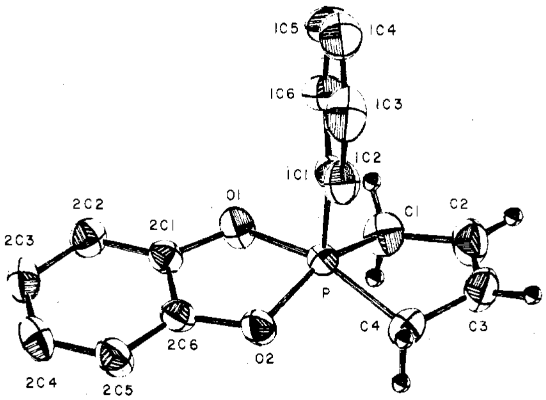


Figure 1. ORTEP plot of the molecular geometry of $(C_6H_4O_2)P(C_6H_5)(C_4H_6)$, V, with thermal ellipsoids at the 50% probability level.

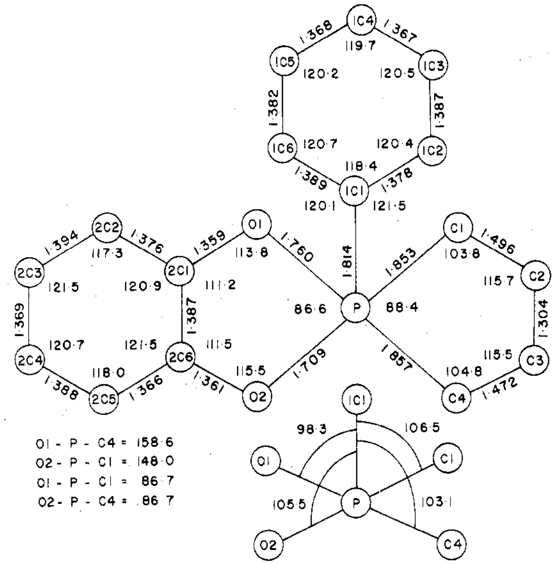


Figure 2. Schematic drawing of $(C_6H_4O_2)P(C_6H_5)(C_4H_6)$, V, showing selected bond distances (Å) and angles (deg).

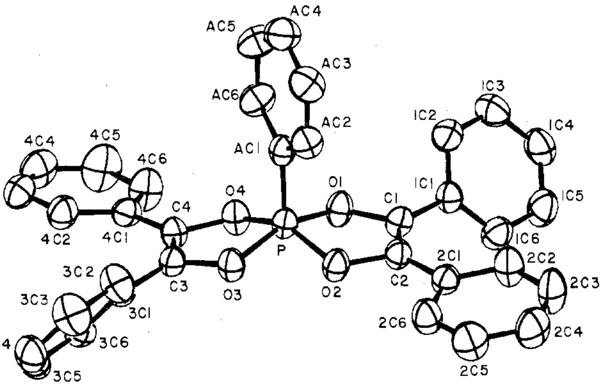


Figure 3. ORTEP plot of the molecular geometry of $(C_{14}H_{10}O_2)_2P(C_6H_5)$, VI, with thermal ellipsoids at the 50% probability level.

including the hydrogen atoms as isotropic contributions and using variable weights, led to the final values of $R = 0.040$, $R_w = 0.050$, and GOF[16] = 1.469 for the 3696 reflections having $I \geq 2.5\sigma_I$ and $3° \leq 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 52°$. During the final cycle of refinement, the largest shift in any parameter was less than 0.01 times its estimated standard deviation. A final difference Fourier synthesis showed a maximum density of 0.27 e/Å^3.

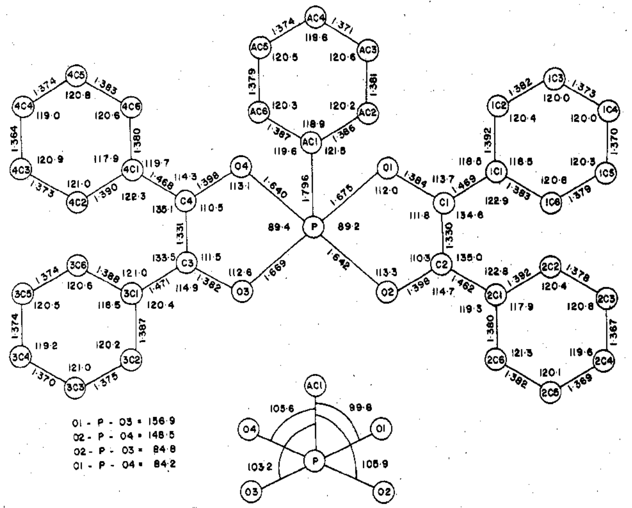


Figure 4. Schematic drawing of $(C_{14}H_{10}O_2)_2P(C_6H_5)$, VI, showing selected bond distances (Å) and angles (deg).

Table V. Atomic Coordinates for $(C_{14}H_{10}O_2)_2P(C_6H_5)$, VI[a]

atom[b]	10^4x	10^4y	10^4z
P	2044 (1)	7061 (1)	4565 (1)
O1	2261 (2)	6276 (1)	3596 (1)
O2	2226 (2)	8286 (1)	3736 (1)
O3	2577 (2)	7639 (1)	5358 (1)
O4	2858 (2)	5567 (1)	5152 (1)
C1	2047 (3)	7116 (2)	2690 (2)
C2	2028 (3)	8268 (2)	2759 (2)
C3	3050 (3)	6733 (2)	6198 (2)
C4	3175 (3)	5553 (2)	6100 (2)
1C1	1883 (3)	6549 (2)	1880 (2)
1C2	817 (3)	6007 (3)	2096 (2)
1C3	654 (3)	5431 (3)	1364 (2)
1C4	1545 (3)	5393 (3)	417 (2)
1C5	2605 (3)	5915 (3)	198 (2)
1C6	2780 (3)	6485 (3)	925 (2)
2C1	1837 (3)	9484 (2)	2064 (2)
2C2	1432 (3)	9712 (3)	1108 (2)
2C3	1251 (4)	10883 (3)	487 (2)
2C4	1459 (4)	11843 (3)	797 (2)
2C5	1849 (4)	11639 (3)	1737 (2)
2C6	2029 (3)	10469 (3)	2366 (2)
3C1	3387 (3)	7236 (2)	6973 (2)
3C2	2394 (3)	8454 (2)	7285 (2)
3C3	2751 (4)	8951 (3)	7971 (2)
3C4	4080 (3)	8255 (3)	8361 (2)
3C5	5074 (3)	7049 (3)	8053 (2)
3C6	4739 (3)	6543 (2)	7363 (2)
4C1	3505 (3)	4288 (2)	6762 (2)
4C2	3550 (3)	4158 (2)	7792 (2)
4C3	3820 (3)	2970 (3)	8397 (2)
4C4	4018 (3)	1891 (3)	8007 (2)
4C5	3960 (4)	2005 (3)	6992 (2)
4C6	3714 (3)	3191 (2)	6370 (2)
AC1	31 (3)	7572 (2)	5008 (2)
AC2	−990 (3)	8879 (2)	4845 (2)
AC3	−2538 (3)	9235 (3)	5155 (2)
AC4	−3084 (3)	8304 (3)	5628 (2)
AC5	−2080 (3)	7006 (3)	5792 (2)
AC6	−530 (3)	6636 (2)	5485 (2)

[a] See footnote *a* to Table I. [b] Atoms are labeled to agree with Figure 3.

Computations were done on a CDC 6600 computer (Model Cyber 74-18) by using 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, and several locally written programs.

Results and Discussion

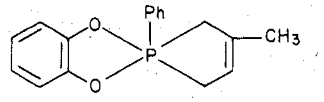
The refined positional and thermal parameters for the nonhydrogen atoms of the spirocyclic phosphorane $(C_6H_4O_2)P(C_6H_5)(C_4H_6)$, V, containing a butadiene moiety, are given in Tables I and II, respectively, while the refined parameters for the hydrogen atoms are given in Table III. Figure 1 shows the molecular geometry of V as well as the atom labeling scheme. Bond lengths and angles for V are listed in Table IV, and Figure 2 summarizes pictorially the principal nonhydrogen atom bond parameters. Analogous data are presented in Tables V–VIII for the pentaphenyl spirocyclic $(C_{14}H_{10}O_2)_2P(C_6H_5)$, VI. Figure 3 displays the molecular geometry of VI and pertinent bond parameters are schematically shown in Figure 4.

The extent of structural distortion present in V and VI is similar, and both structures may be regarded as located at a point not too far from an idealized rectangular pyramid (RP) along the coordinate connecting the latter idealized configuration with the trigonal bipyramid (TP). The phenyl substituent in each occupies the apical position with the spirocyclic system comprising the basal network. Indicative of the RP character, the trans-basal angles, O1–P–C4 = 158.6 (1)° and O2–P–C1 = 148.0 (1)° for V and O1–P–O3 = 156.9 (1)° and O2–P–O4 = 148.5 (1)° for VI, are within 5.3 and 3.2°, respectively, of their average values.

The basal atoms in V show an average deviation from a least-squares plane of 0.077 Å (plane 1, Table IX). Of course, this deviation from planarity is less for VI, 0.056 Å (plane 1, Table X), since VI contains all four atoms directly bonded to phosphorus which are of the same kind. In an ideal RP, these four atoms are strictly planar, whereas in the ideal TP, the average deviation is 0.25 Å. Comparison of the nonbonded distances O1–O2 with O3–O4 and O1–O4 with O2–O3 (Table XI) shows a near RP.

A more quantitative approach, as measured by the sum of the dihedral angles from polytopal faces based on unit bond distances,[6] shows that the structure of V is 82% along the TP–RP coordinate toward the RP; for VI, this value is 86%.[7,17] Close adherence to the TP–RP coordinate is evident by comparing the dihedral angle (δ_i) sums $\sum_i|\delta_i(\mathrm{C}) - \delta_i(\mathrm{TP})|$ and $R - \sum_i|\delta_i(\mathrm{C}) - \delta_i(\mathrm{RP})|$, where $R = \sum_i|\delta_i(\mathrm{TP}) - \delta_i(\mathrm{RP})| = 217.7°$.[6] These sums are each 178.6° for V and 186.8° each for VI.[17] Their equality shows that the structural distortions are directly on the TP–RP coordinate. Evidence that the C_{2v} constraint of the Berry coordinate[18] is adhered to for V is seen from the closeness of the value of dihedral angle between planes 2 and 3 (Table IX), 89.4°, compared to the required 90°. For VI, the value of this angle is 87.4° (Table X).

One reason for carrying out the X-ray study of V was that the X-ray analysis of the related derivative containing a ring methyl substituent showed disorder which produced a pseudo mirror plane bisecting the two five-membered rings.[19] The final R value was 0.130 compared to 0.047 for V, and the structure deviated somewhat from the TP–RP coordinate. The structure of V had no such disorder and fell directly on the TP–RP coordinate. Hence, the bond parameters for V for this structural type should be used in preference to those from the disordered derivative.



The fact that the butadiene derivative V is not too far displaced from an ideal rectangular pyramid suggests the operation of the electronegativity rule[3] posed for trigonal bipyramids. The energy required to place a ring carbon atom in an axial orientation of a TP apparently is more than compensated by traversing the low–energy axial–equatorial bending coordinate (TP–RP) to reach a near RP.[20]

We know from previous studies[1b,21] that substitution of one

Table VI. Thermal Parameters in $(C_{14}H_{10}O_2)_2P(C_6H_5)$, VI[a]

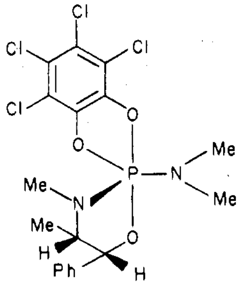
atom[b]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	4.09 (3)	2.41 (2)	2.45 (2)	−1.51 (2)	−0.63 (2)	−0.27 (2)
O1	5.4 (1)	2.9 (1)	2.7 (1)	−1.7 (1)	−0.8 (1)	−0.4 (1)
O2	5.2 (1)	3.2 (1)	2.7 (1)	−2.3 (1)	−0.9 (1)	0.0 (1)
O3	5.1 (1)	3.0 (1)	3.0 (1)	−2.0 (1)	−1.2 (1)	−0.2 (1)
O4	5.1 (1)	2.7 (1)	3.2 (1)	−1.5 (1)	−1.3 (1)	−0.3 (1)
C1	3.8 (1)	3.2 (1)	2.7 (1)	−1.5 (1)	−0.4 (1)	−0.3 (1)
C2	3.9 (1)	3.4 (1)	2.6 (1)	−1.8 (1)	−0.6 (1)	−0.4 (1)
C3	3.7 (1)	2.9 (1)	2.7 (1)	−1.4 (1)	−0.7 (1)	−0.1 (1)
C4	3.7 (1)	3.1 (1)	2.8 (1)	−1.3 (1)	−0.8 (1)	−0.5 (1)
1C1	4.0 (1)	2.8 (1)	2.9 (1)	−1.4 (1)	−0.9 (1)	−0.2 (1)
1C2	4.8 (1)	5.0 (1)	3.5 (1)	−2.6 (1)	−0.5 (1)	−0.5 (1)
1C3	5.5 (1)	5.6 (1)	5.2 (1)	−3.3 (1)	−1.6 (1)	−0.5 (1)
1C4	5.9 (1)	4.7 (1)	4.2 (1)	−2.4 (1)	−1.8 (1)	−0.9 (1)
1C5	6.3 (2)	5.5 (1)	3.1 (1)	−2.9 (1)	−0.3 (1)	−1.1 (1)
1C6	5.2 (1)	4.5 (1)	3.4 (1)	−2.8 (1)	−0.2 (1)	−0.8 (1)
2C1	3.7 (1)	3.3 (1)	3.0 (1)	−1.6 (1)	−0.6 (1)	−0.2 (1)
2C2	6.8 (2)	3.9 (1)	3.8 (1)	−2.3 (1)	−1.8 (1)	0.0 (1)
2C3	8.5 (2)	4.8 (1)	3.8 (1)	−2.8 (1)	−2.4 (1)	0.8 (1)
2C4	8.0 (2)	4.2 (1)	5.1 (1)	−3.2 (1)	−2.2 (1)	1.4 (1)
2C5	8.4 (2)	4.4 (1)	6.0 (2)	−3.9 (1)	−2.8 (1)	0.9 (1)
2C6	6.6 (2)	4.1 (1)	4.1 (1)	−3.0 (1)	−2.0 (1)	0.4 (1)
3C1	3.8 (1)	3.1 (1)	2.6 (1)	−1.7 (1)	−0.5 (1)	−0.2 (1)
3C2	4.8 (1)	3.8 (1)	4.6 (1)	−1.0 (1)	−1.4 (1)	−1.3 (1)
3C3	6.5 (2)	4.1 (1)	5.6 (1)	−1.4 (1)	−1.2 (1)	−2.2 (1)
3C4	6.7 (2)	5.1 (1)	4.0 (1)	−3.3 (1)	−1.6 (1)	−0.7 (1)
3C5	5.0 (1)	4.7 (1)	4.3 (1)	−2.6 (1)	−1.9 (1)	0.3 (1)
3C6	3.6 (1)	3.2 (1)	3.9 (1)	−1.6 (1)	−0.7 (1)	−0.2 (1)
4C1	3.3 (1)	2.9 (1)	3.4 (1)	−1.3 (1)	−0.7 (1)	−0.2 (1)
4C2	5.9 (1)	4.1 (1)	3.6 (1)	−2.9 (1)	−1.0 (1)	0.1 (1)
4C3	5.8 (1)	4.9 (1)	4.0 (1)	−3.0 (1)	−1.3 (1)	0.9 (1)
4C4	6.2 (2)	3.6 (1)	5.7 (2)	−2.0 (1)	−1.3 (1)	1.1 (1)
4C5	9.2 (2)	3.1 (1)	6.1 (2)	−2.3 (1)	−1.4 (1)	−0.4 (1)
4C6	7.4 (2)	3.2 (1)	4.3 (1)	−1.9 (1)	−1.2 (1)	−0.5 (1)
AC1	4.2 (1)	3.0 (1)	2.7 (1)	−1.7 (1)	−0.8 (1)	−0.5 (1)
AC2	4.6 (1)	3.1 (1)	4.1 (1)	−1.7 (1)	−1.2 (1)	−0.1 (1)
AC3	4.4 (1)	3.9 (1)	5.4 (1)	−1.2 (1)	−1.4 (1)	−0.5 (1)
AC4	4.3 (1)	5.5 (1)	5.1 (1)	−2.3 (1)	−0.6 (1)	−0.8 (1)
AC5	5.4 (1)	4.6 (1)	5.8 (1)	−3.0 (1)	0.1 (1)	−0.3 (1)
AC6	4.8 (1)	3.3 (1)	4.7 (1)	−1.9 (1)	−0.3 (1)	−0.2 (1)

[a] See footnote *a* to Table II. [b] See footnote *b* to Table V.

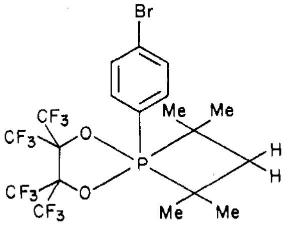
Table VII. Refined Parameters for Hydrogen Atoms in $(C_{14}H_{10}O_2)_2P(C_6H_5)$, VI[a]

atom[b]	10^3x	10^3y	10^3z	B_{iso}, Å^2
1H2	23 (3)	602 (2)	274 (2)	5.1 (6)
1H3	−7 (3)	504 (2)	150 (2)	5.3 (6)
1H4	142 (3)	502 (2)	−12 (2)	5.1 (6)
1H5	323 (3)	585 (3)	−39 (2)	5.8 (6)
1H6	355 (3)	682 (2)	79 (2)	4.8 (6)
2H2	122 (3)	907 (3)	91 (2)	6.2 (7)
2H3	95 (3)	1104 (2)	−19 (2)	5.1 (6)
2H4	135 (3)	1261 (3)	39 (2)	7.7 (8)
2H5	196 (3)	1226 (3)	201 (2)	7.3 (8)
2H6	229 (3)	1032 (2)	307 (2)	5.2 (6)
3H2	146 (3)	900 (2)	698 (2)	5.3 (6)
3H3	205 (3)	981 (3)	814 (2)	6.9 (7)
3H4	427 (3)	859 (2)	885 (2)	5.0 (6)
3H5	599 (3)	656 (2)	835 (2)	5.3 (6)
3H6	543 (2)	572 (2)	715 (2)	3.1 (4)
4H2	338 (3)	492 (3)	810 (2)	5.8 (6)
4H3	384 (3)	287 (3)	914 (2)	5.6 (6)
4H4	418 (3)	110 (3)	843 (2)	5.4 (6)
4H5	413 (3)	132 (3)	670 (2)	8.8 (9)
4H6	370 (3)	326 (3)	565 (2)	5.6 (6)
AH2	−58 (3)	955 (2)	448 (2)	4.8 (6)
AH3	−323 (3)	1010 (2)	506 (2)	5.5 (6)
AH4	−415 (3)	854 (2)	583 (2)	4.1 (5)
AH5	−246 (3)	641 (3)	609 (2)	7.7 (8)
AH6	17 (2)	572 (2)	561 (2)	4.2 (5)

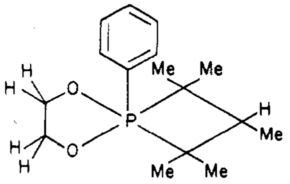
[a] See footnote *a* to Table I. [b] See footnote *b* to Table V.



VII



VIII



IX

or more ring oxygen atoms in the type of spirocyclic system present in VI with nitrogen atoms (which have a strong preference for equatorial sites of a TP owing to enhanced p–d π bonding) results in a dramatic shift along the TP–RP coordinate toward the TP; cf. VI, 86% displaced from the ideal TP, with VII,[22] 19% displaced[7] (based on actual bond lengths), or IVa,[1b] 11% (R = H) and 5.5% (R = CH_3) displaced from the TP. It should be pointed out, however, that the presence of a saturated five-membered ring in VII[6,23–25] and the presence of an equatorial nonring proton in IVa[1b] are conducive to the formation of a TP. The competing influence of these factors

Table VIII. Bond Lengths (Å) and Angles (deg) in $(C_{14}H_{10}O_2)_2P(C_6H_5)$, VI[a]

Lengths

P-O1	1.675 (2)	1C4-1C5	1.370 (4)	4C3-4C4	1.364 (4)	2C5-2H5	0.93 (3)
P-O3	1.669 (2)	1C5-1C6	1.379 (4)	4C4-4C5	1.374 (4)	2C6-2H6	1.01 (2)
P-O2	1.642 (2)	1C6-1C1	1.383 (3)	4C5-4C6	1.383 (4)	3C2-3H2	0.99 (3)
P-O4	1.640 (2)	2C1-2C2	1.392 (3)	4C6-4C1	1.380 (3)	3C3-3H3	0.95 (3)
P-AC1	1.796 (2)	2C2-2C3	1.378 (4)	AC1-AC2	1.386 (3)	3C4-3H4	0.93 (3)
O1-C1	1.384 (3)	2C3-2C4	1.367 (4)	AC2-AC3	1.381 (4)	3C5-3H5	0.97 (3)
O2-C2	1.398 (3)	2C4-2C5	1.369 (4)	AC3-AC4	1.371 (4)	3C6-3H6	0.94 (3)
O3-C3	1.382 (3)	2C5-2C6	1.382 (4)	AC4-AC5	1.374 (4)	4C2-4H2	0.98 (3)
O4-C4	1.398 (3)	2C6-2C1	1.380 (3)	AC5-AC6	1.379 (4)	4C3-4H3	0.99 (3)
C1-C2	1.330 (3)	3C1-3C2	1.387 (3)	AC6-AC1	1.387 (3)	4C4-4H4	0.93 (3)
C3-C4	1.331 (3)	3C2-3C3	1.375 (4)	1C2-1H2	0.93 (2)	4C5-4H5	0.89 (3)
C1-1C1	1.469 (3)	3C3-3C4	1.370 (4)	1C3-1H3	0.97 (2)	4C6-4H6	0.97 (3)
C2-2C1	1.462 (3)	3C4-3C5	1.374 (4)	1C4-1H4	0.98 (2)	AC2-AH2	1.00 (2)
C3-3C1	1.471 (3)	3C5-3C6	1.374 (3)	1C5-1H5	0.88 (3)	AC3-AH3	0.92 (3)
C4-4C1	1.468 (3)	3C6-3C1	1.388 (3)	1C6-1H6	0.96 (2)	AC4-AH4	0.95 (2)
1C1-1C2	1.392 (3)	4C1-4C2	1.390 (3)	2C2-2H2	0.96 (3)	AC5-AH5	0.90 (3)
1C2-1C3	1.382 (4)	4C2-4C3	1.373 (4)	2C3-2H3	0.99 (2)	AC6-AH6	0.97 (2)
1C3-1C4	1.373 (4)			2C4-2H4	0.91 (3)		

Angles

O1-P-O3	156.9 (1)	1C1-1C2-1H2	119 (2)	2H5-2C5-2C6	116 (2)	4C2-4C3-4C4	120.9 (3)
O2-P-O4	148.5 (1)	1C1-1C2-1C3	120.4 (2)	2C1-2C6-2H6	118 (1)	4H3-4C3-4C4	117 (2)
O1-P-AC1	99.8 (1)	1H2-1C2-1C3	120 (2)	2C1-2C6-2C5	121.3 (3)	4C3-4C4-4H4	120 (2)
O3-P-AC1	103.2 (1)	1C2-1C3-1H3	122 (2)	2H6-2C6-2C5	121 (1)	4C3-4C4-4C5	119.0 (3)
O2-P-AC1	105.9 (1)	1C2-1C3-1C4	120.0 (3)	C3-3C1-3C2	120.4 (2)	4H4-4C4-4C5	121 (2)
O4-P-AC1	105.6 (1)	1H3-1C3-1C4	118 (2)	C3-3C1-3C6	121.0 (2)	4C6-4C5-4H5	117 (2)
O1-P-O2	89.2 (1)	1C3-1C4-1H4	121 (2)	3C2-3C1-3C6	118.5 (2)	4C6-4C5-4C4	120.8 (3)
O3-P-O4	89.4 (1)	1C3-1C4-1C5	120.0 (3)	3C1-3C2-3H2	120 (2)	4H5-4C5-4C4	122 (2)
O1-P-O4	84.2 (1)	1H4-1C4-1C5	118 (2)	3C1-3C2-3C3	120.2 (2)	4C1-4C6-4H6	119 (2)
O2-P-O3	84.8 (1)	1C6-1C5-1H5	118 (2)	3H2-3C2-3C3	119 (2)	4C1-4C6-4C5	120.6 (3)
P-O1-C1	112.0 (1)	1C6-1C5-1C4	120.3 (3)	3C2-3C3-3H3	117 (2)	4H6-4C6-4C5	120 (2)
P-O2-C2	113.3 (1)	1H5-1C5-1C4	121 (2)	3C2-3C3-3C4	121.0 (3)	P-AC1-AC2	121.5 (2)
P-O3-C3	112.6 (1)	1C1-1C6-1H6	118 (1)	3H3-3C3-3C4	122 (2)	P-AC1-AC6	119.6 (2)
P-O4-C4	113.1 (1)	1C1-1C6-1C5	120.6 (2)	3C3-3C4-3H4	119 (2)	AC2-AC1-AC6	118.9 (2)
O1-C1-C2	111.8 (2)	1H6-1C6-1C5	121 (2)	3C3-3C4-3C5	119.2 (3)	AC1-AC2-AH2	118 (1)
O1-C1-1C1	113.7 (2)	C2-2C1-2C6	119.3 (2)	3H4-3C4-3C5	121 (2)	AC1-AC2-AC3	120.2 (2)
C2-C1-1C1	134.6 (2)	C2-2C1-2C2	122.8 (2)	3C6-3C5-3H5	121 (2)	AH2-AC2-AC3	121 (1)
O2-C2-C1	110.3 (2)	2C6-2C1-2C2	117.9 (2)	3C6-3C5-3C4	120.5 (2)	AC2-AC3-AH3	121 (2)
O2-C2-2C1	114.7 (2)	2C1-2C2-2H2	119 (2)	3H5-3C5-3C4	118 (2)	AC2-AC3-AC4	120.6 (2)
C1-C2-2C1	135.0 (2)	2C1-2C2-2C3	120.4 (2)	3C1-3C6-3H6	119 (1)	AH3-AC3-AC4	118 (2)
O3-C3-C4	111.5 (2)	2H2-2C2-2C3	120 (2)	3C1-3C6-3C5	120.6 (2)	AC3-AC4-AH4	121 (1)
O3-C3-3C1	114.9 (2)	2C2-2C3-2H3	120 (2)	3H6-3C6-3C5	120 (2)	AC3-AC4-AC5	119.6 (3)
C4-C3-3C1	133.5 (2)	2C2-2C3-2C4	120.8 (3)	C4-4C1-4C6	119.7 (2)	AH4-AC4-AC5	119 (1)
O4-C4-C3	110.5 (2)	2H3-2C3-2C4	119 (2)	C4-4C1-4C2	122.3 (2)	AC4-AC5-AH5	118 (2)
O4-C4-4C1	114.3 (2)	2C3-2C4-2H4	121 (2)	4C6-4C1-4C2	117.9 (2)	AC4-AC5-AC6	120.5 (3)
C3-C4-4C1	135.1 (2)	2C3-2C4-2C5	119.6 (3)	4C1-4C2-4H2	120 (2)	AH5-AC5-AC6	121 (2)
C1-1C1-1C6	122.9 (2)	2H4-2C4-2C5	119 (2)	4C1-4C2-4C3	121.0 (2)	AC1-AC6-AH6	119 (1)
C1-1C1-1C2	118.5 (2)	2C4-2C5-2H5	124 (2)	4H2-4C2-4C3	119 (2)	AC1-AC6-AC5	120.3 (2)
1C6-1C1-1C2	118.5 (2)	2C4-2C5-2C6	120.1 (3)	4C2-4C3-4H3	122 (2)	AH6-AC6-AC5	120 (1)

[a] Footnote *a* to Table I and footnote *b* to Table V apply.

has yet to be fully appreciated.

In spirocyclics VIII[25] and IX,[26] containing a four- and five-membered ring both of which are saturated, with a similar heteroring composition to V, again the structures are relatively close to the RP (84% displaced from the TP for VIII[6] and 87% for IX[6,26] based on actual bond lengths). Since monocyclic phosphoranes have never been found to deviate far from the TP,[7,23] these observations appear, then, to support the structural type I for $(CH_2)_4PF_3$ rather than II, in accord with inferences from an NMR study.[3]

Earlier, we calculated that monocyclic phosphoranes, containing like ring atoms bonded to phosphorus, undergo less stabilization in a square-pyramidal conformation than spirocyclics in the corresponding RP.[23] Thus, it seems likely that the increased ring-strain energy for a monocyclic in the isomeric form I is more than compensated by the energy gain for ligands oriented in compliance with the electronegativity rule[3] or, more broadly, the substituent effect.[27] For spirocyclics, the TP → RP conversion normally provides the lower energy path when the ring-strain and electronegativity "rules" conflict with each other.[6,20]

Evidence for "residual" TP character in V and VI is apparent from a comparison of bond lengths illustrated in Figures 2 and 4, respectively. The longer P–O1 and P–C4 bonds for V compared to the lengths of P–O2 and P–C1 (Figure 2) coincide with the larger of the two trans basal angles, O1–P–C4 = 158.6 (1)°. The same type of comparison holds for VI. Consequently, "axial" and "equatorial" character are indicated for the longer and shorter bond length sets, respectively.

An additional feature of note in V is the tilting of the apical phenyl group away from the butadiene moiety. This is seen from the larger nonbonded distances, 1C1–C1 and 1C1–C4 relative to 1C1–O1 and 1C1–O2 (Table XI). The much higher displacement of the phosphorus atom from the butadiene plane (plane 6 of Table IX), 0.706 Å, compared to that from the adjoining portion of the spirocyclic system (plane 7, Table IX), 0.229 Å, also shows this effect. In the more symmetrical pentaphenyl derivative VI, the tilting of the phenyl group is hardly noticeable (cf. planes 6 and 7 of Table X and corresponding nonbonded distances in Table XI). These observations are consistent with the operation of greater electron pair repulsions in P–C bonds compared to that in P–O bonds as embodied in the VSEPR theory.[28]

Table IX

Atom Distances from Least-Squares Planes (Å) in $(C_6H_4O_2)P(C_6H_5)(C_4H_6)$, V

	plane 1	plane 2	plane 3	plane 4[a]	plane 5[a]
P	0.413[b]	0.011	0.019	0.000	0.000
O1	0.080	−0.005		0.000	
O2	−0.085		−0.014	0.000	
C1	−0.069		−0.008		0.000
C4	0.074	−0.005			0.000
1C1		−0.002	0.003		

plane 6		plane 7		plane 8		plane 9		plane 10	
C1	−0.001	O1	−0.003	1C1	−0.001	2C1	−0.002	2C1	0.027
C2	0.002	2C1	0.003	1C2	0.007	2C2	0.003	2C2	0.016
C3	−0.002	2C6	0.006	1C3	−0.009	2C3	−0.001	2C3	−0.012
C4	0.001	O2	−0.006	1C4	0.005	2C4	−0.001	2C4	−0.018
P	0.706[b]	P	0.229[b]	1C5	0.001	2C5	0.002	2C5	0.002
				1C6	−0.002	2C6	0.000	2C6	0.023
						O1	−0.081[b]	O1	−0.029
						O2	−0.051[b]	O2	−0.009

Some Dihedral Angles between Least-Squares Planes (deg)

planes	angle	planes	angle	planes	angle	planes	angle
2, 3	89.4	4, 7	10.5	5, 6	32.0	9, 10	1.0
4, 5	38.0	4, 10	8.5	3, 8	43.9		

[a] These planes are not least-squares fitted since only three nonlinear points are required to define a plane. [b] Indicates atom was *not* included in the definition of a particular least-squares plane. The phosphorus atom is directed upward toward the phenyl group in Figure 1.

Table X

Atom Distances from Least-Squares Planes (Å) in $(C_{14}H_{10}O_2)_2P(C_6H_5)$, VI

	plane 1	plane 2	plane 3	plane 4[a]	plane 5[a]
P	0.390[b]	−0.002	0.011	0.000	0.000
O1	0.048	0.001		0.000	
O2	−0.062		−0.005	0.000	
O3	0.063	0.001			0.000
O4	−0.049		−0.005		0.000
AC1		0.000	−0.002		

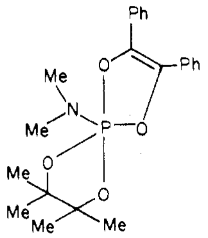
plane 6		plane 7		plane 8		plane 9		plane 10		plane 11		plane 12	
O1	−0.001	O3	0.007	1C1	−0.005	2C1	−0.005	3C1	0.003	4C1	−0.003	AC1	0.001
C1	0.001	C3	−0.008	1C2	0.001	2C2	0.002	3C2	0.000	4C2	0.007	AC2	0.000
C2	0.001	C4	−0.013	1C3	0.003	2C3	0.001	3C3	−0.003	4C3	−0.006	AC3	−0.001
O2	−0.001	O4	0.014	1C4	−0.003	2C4	−0.002	3C4	0.003	4C4	−0.000	AC4	0.001
1C1	0.014[b]	3C1	−0.133[b]	1C5	−0.001	2C5	−0.001	3C5	0.001	4C5	0.005	AC5	0.000
2C1	0.008[b]	4C1	0.111[b]	1C6	0.005	2C6	0.004	3C6	−0.004	4C6	−0.004	AC6	−0.001
P	0.335[b]	P	0.299[b]										

Some Dihedral Angles between Least-Squares Planes (deg)

planes	angle	planes	angle	planes	angle	planes	angle
2, 3	87.4	4, 5	39.2	6, 8	52.8	7, 10	46.6
4, 6	16.5	3, 12	16.5	6, 9	7.6	7, 11	11.9
5, 7	14.8						

[a] These planes are not least-squares fitted planes since only three nonlinear points are required to define a plane. [b] Indicates atom was *not* included in definition of a particular least-squares plane. The phosphorus atom is directed upward toward the apical phenyl group in Figure 3.

Other features that have been observed before for spirocyclic phosphoranes having near-RP structures[23] are also present in V and VI. These include the observance of shorter bond lengths for ring atoms attached to "axial" atoms (viewed in terms of residual TP character), 2C1–O1 and C3–C4 for V and C3–O3 and C1–O1 for VI, compared to ring atoms attached to "equatorial"-type atoms, 2C6–O2 and C2–C1 for V and C4–O4 and C2–O2 for VI. Also the compression in the benzo ring angles below 120° at 2C2 and 2C5 in V is commonly observed.[29] The interpretation of these effects has been adequately discussed.[29] In VI, the observance of exocyclic angles near 135° at C1, C2, C3, and C4 is similar to that in X at C1 and C2.[24] A steric repulsion of the phenyl groups is thought to contribute to the angle widening.[24]



X

Table XI. Selected Intramolecular Nonbonded Distances (Å)

$(C_6H_4O_2)P(C_6H_5)(C_4H_6)$, V		$(C_{14}H_{10}O_2)_2P(C_6H_5)$, VI	
O1–C4	3.554 (3)	O1–O3	3.276 (2)
O2–C1	3.424 (3)	O2–O4	3.159 (2)
O1–O2	2.378 (2)	O1–O2	2.329 (2)
C1–C4	2.585 (4)	O3–O4	2.328 (2)
O2–C4	2.449 (3)	O1–O4	2.222 (2)
O1–C1	2.481 (3)	O2–O3	2.232 (2)
1C1–O1	2.703 (2)	AC1–O1	2.657 (3)
1C1–O2	2.804 (2)	AC1–O2	2.745 (3)
1C1–C1	2.938 (3)	AC1–O3	2.717 (3)
1C1–C4	2.876 (3)	AC1–O4	2.739 (3)
1C1–2C1	3.420 (3)	AC1–C1	3.313 (3)
1C1–2C6	3.474 (3)	AC1–C2	3.366 (3)
1C1–C2	3.339 (3)	AC1–C3	3.412 (3)
1C1–C3	3.317 (3)	AC1–C4	3.408 (3)
1C2–O2	3.213 (3)	AC2–O2	3.018 (3)
1C2–C4	3.219 (4)	AC2–O3	3.365 (3)
1C6–O1	3.035 (3)	AC6–O1	3.233 (3)
1C6–C1	3.271 (4)	AC6–O4	2.974 (3)

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Registry No. V, 24901-17-5; VI, 18005-43-1.

Supplementary Material Available: A compilation of observed and calculated structure factor amplitudes for V and VI (34 pages). Ordering information is given on any current masthead page.

References and Notes

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