The Crystal and Molecular Structure of 2,3-Benzo-5-phenyl-7-methyl-1,4-dioxa-5-phospha(P^V)-spiro[4.4]non-7-ene, $(C_6H_4O_2)P(C_6H_5)(C_5H_8)$[1]

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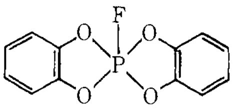
Abstract: Single crystal x-ray diffraction analysis of 2,3-benzo-5-phenyl-7-methyl-1,4-dioxa-5-phospha(P^V)spiro[4.4]non-7-ene, $(C_6H_4O_2)P(C_6H_5)(C_5H_8)$, revealed an orthorhombic system with $a = 8.210$ (1), $b = 11.466$ (5), and $c = 15.848$ (4) Å, $Z = 4$, and space group *Pnma*. The statistical appearance of either one or the other of the two enantiomeric forms in equivalent sites of the crystal resulted in a disordered structure. Refinement gave a pentacoordinate geometry close to a square pyramid with an average axial-basal angle of 103.8° and an average cis basal angle of 86.7°. The observation of the square pyramidal structure is consistent with the poor axiophilicity associated with a carbon atom in a trigonal bipyramidal environment. Comparison among related structures reveals the importance of decreasing ring size and increasing ring unsaturation as factors favoring the appearance of a square pyramidal conformation relative to a trigonal bipyramidal one.

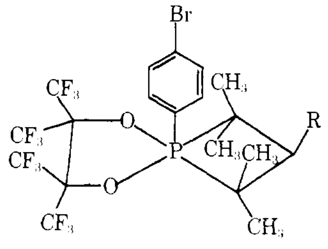
A variety of heterocyclic phosphorane systems have now been studied in which the geometry bears some degree of distortion between a trigonal bipyramid, TP, and square or rectangular pyramid, SP (RP).[3-13] It has been shown[14] that the distortion in each case closely follows the Berry coordinate[15] governing intramolecular exchange phenomena among nonrigid pentacoordinate phosphorus molecules.[16] For example, the structure[3c] of the fluorodioxaphosphole, $(C_6H_4O_2)_2PF$ (I),



I

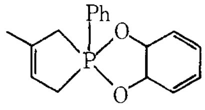
is about 65% along the TP-RP coordinate[14] toward the RP. Normally fluorine, because of its high electronegativity,[17] is positioned at an axial site in a TP framework. However, the presence of the unsaturated ring system in I, as found with a number of other examples, where the axial position is occupied by one of the following groups, Ph,[1b] adamantyl,[12b] CH_3,[3b] or OPh,[6] leads to the stabilization of the RP geometry.[14,18] This ring constraint then counters the electronegativity effect for fluorine.

In related dioxaphospholans II, containing a four- and a five-membered saturated ring system, again structures close to RPs are observed.[19] Apparently enhanced ring constraints, due to the four-membered ring, and an additional factor, the presence of ring carbon atoms, may account for the observed geometries. If instead a trigonal bipyramid structure were obtained, it would have to result at the expense of locating the weakly electronegative ring carbon atom at an axial site. In the absence of special constraints, the axial positions of a TP are occupied by the most electronegative ligands.[17]



II, R = H, CH_3

It is of interest to ascertain the structural consequences of introducing two five-membered rings containing the same set of atoms directly attached to phosphorus as that in II. Lessening the ring strain appears conducive to a tendency toward TP formation.[14,18] However, if the rings are maintained unsaturated, a factor which appears to favor the SP (RP),[14,18] the balance between these factors may result in a geometry which is still primarily SP (RP). Accordingly, we have undertaken the x-ray diffraction study of the unsaturated phosphorane III, having a composition intermediate in character between I and II.



III

Experimental Section

Preparation of III. Crystals of 2,3-benzo-5-phenyl-7-methyl-1,4-dioxa-5-phospha(P^V)spiro[4.4]non-7-ene, $(C_6H_4O_2)P(C_6H_5)(C_5H_8)$, were obtained by the addition of isoprene to 2-phenyl-1,3,2-benzodioxaphosphole in ether solution according to the preparation of Wieber and Hoos.[20] Recrystallization from ether produced transparent needles. Because of the hygroscopic character of the compound, the x-ray study was carried out on needles enclosed in thin-walled glass capillaries. Anal. Calcd for $C_{17}H_{17}O_2P$: C, 71.83; H, 5.98; P, 10.91. Found: C, 70.55; H, 5.96; P, 10.54.

Data Collection. Preliminary precession and Weissenberg photographs indicated an orthorhombic system (Laue symmetry, *mmm*). The observed systematic absences of $hk0$ ($h = 2n + 1$) and $0kl$ ($k + l = 2n + 1$) were consistent with either $Pn2_1a$ or *Pnma* space groups.

For data collection, a colorless crystal of approximate dimensions 0.35 × 0.50 × 0.50 mm was mounted on an Enraf-Nonius CAD-4 Kappa diffractometer. The crystal b axis was aligned nearly parallel with the instrument ϕ axis. System parameters and treatment of intensity data were identical with that already described.[1b]

The unit cell dimensions resulting from least-squares refinement of the observed 2θ values of 11 high-order reflections are $a = 8.210$ (1), $b = 11.466$ (5), $c = 15.848$ (4) Å. The observed density of 1.263 g cm^{-3}, determined by the flotation method in a carbon tetrachloride-benzene mixture, agreed well with the calculated value of 1.265 g cm^{-3} based on four molecules per unit cell. The linear absorption coefficient found for Mo Kα ($\lambda = 0.7093$ Å) was 1.86 cm^{-1}. Crystal deterioration was monitored by measuring an intensity control reflection ($4\bar{3}7$) and three orientation control reflections ($\bar{1}\bar{4}11$; $\bar{4}57$; and 624) after every 50 reflections. No significant deviation from the average value of any of the control reflections was observed.

The intensities of 2270 independent reflections (excluding systematic absences) with $0.0605 \leqslant \sin\theta/\lambda_{Mo} \leqslant 0.6990$ were measured by the θ-2θ scan technique with a scan range of $0.8 + 0.2 (\tan\theta)°$ centered about the average peak position using Zr-filtered Mo Kα radiation. A total of 1615 reflections were treated as observed (for unobserved reflections $F_o{}^c = [(1/Lp)(0.01)\sigma(I)]^{1/2}$), i.e., with an

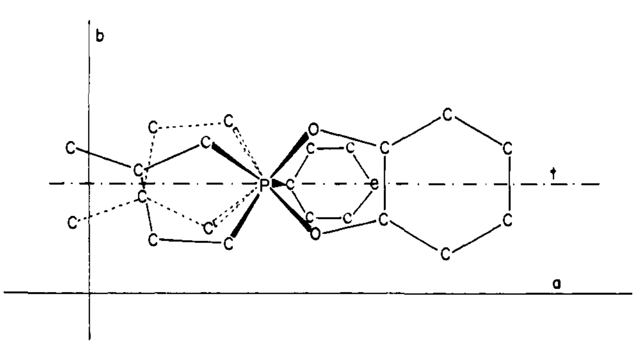


Figure 1. Schematic representation of $(C_6H_4O_2)P(C_6H_5)(C_5H_8)$ illustrating structural disorder resulting from the random placement of enantiomeric forms at the same location in the unit cell (greatly exaggerated). View is along the *c* direction. The mirror plane parallel to (010) is indicated by the dot-dash line.

Table I. Atomic Fractional Coordinates for $(C_6H_4O_2)P(C_6H_5)(C_5H_8)$ and Their Standard Deviations

Atom[a]	*x*	*y*	*z*
P	0.4026 (1)	0.2500 (0)	0.0306 (1)
O(2)	0.5188 (3)	0.3528 (2)	0.0823 (1)
C(1)	0.2282 (12)	0.3477 (10)	0.0230 (6)
C(2)	0.2564 (17)	0.1143 (12)	0.0340 (10)
C(3)	0.4916 (4)	0.2500 (0)	−0.0737 (2)
C(5)	0.6538 (3)	0.3097 (2)	0.1197 (1)
C(7)	0.7750 (5)	0.3717 (3)	0.1580 (2)
C(9)	0.9000 (4)	0.3101 (4)	0.1959 (2)
C(10)	0.1132 (13)	0.1618 (7)	−0.0179 (7)
C(11)	0.0967 (11)	0.2784 (6)	−0.0205 (6)
C(13)	0.5293 (4)	0.3530 (3)	−0.1134 (2)
C(15)	0.6000 (5)	0.3515 (4)	−0.1931 (2)
C(16)	0.6356 (7)	0.2500 (0)	−0.2315 (3)
C(17)	−0.0403 (8)	0.3442 (7)	−0.0616 (5)
H(7)	0.7774 (44)	0.4549 (30)	0.1547 (22)
H(9)	1.0002 (49)	0.3518 (29)	0.2190 (22)
H(13)	0.4993 (42)	0.4193 (31)	−0.0895 (20)
H(15)	0.6547 (47)	0.4339 (37)	−0.2133 (21)
H(16)	0.7111 (88)	0.2500 (0)	−0.2773 (44)

[a] Atoms are named to agree with Figure 2.

intensity greater than $0.01\sigma(I)$. Corrections for Lorentz and polarization effects were applied but no absorption corrections were made because of the small linear absorption coefficient.

Structure Determination and Refinement. Computations were carried out on a CDC 6600 computer using programming techniques, atom scattering factors, and the agreement factors, R and R_w, as cited.[1b] Initial coordinates for the phosphorus atom were derived from a Patterson map. Application of the program MULTAN in space group $Pn2_1a$ resulted in 64 sets of phase relationships based on the 350 reflections having the largest E values. Convergence on a single solution indicated the position of all nonhydrogen atoms except the methyl carbon atom (19 of the 20 nonhydrogen atoms in the asymmetric unit) and showed a near square pyramidal geometry. However, the C(10)-C(11) double bond had a length of approximately 0.7 Å. A structure factor calculation followed by a Fourier synthesis, introducing all the nonhydrogen atom positions indicated by MULTAN, showed the presence of a mirror plane (under the assumed space group $Pn2_1a$) and revealed the methyl carbon atom as well as its mirror image. Neither the C(17)-C(11) nor the C(17)-C(10) distances, however, were reasonable.

At this point, it was obvious that a crystal disorder was present in which molecules were randomly replaced by their enantiomer at the same lattice position. The positioning of the enantiomers is such that the phosphorus and oxygen atoms, as well as the benzo and phenyl rings of each, practically coincide. The methyl substituted ring, though distorted, is superimposed on the corresponding ring of its enantiomers (Figure 1). Thus, a mirror parallel to (010) is indicated and suggests refinement in the space group $Pnma$ rather than $Pn2_1a$ as a preferred course.

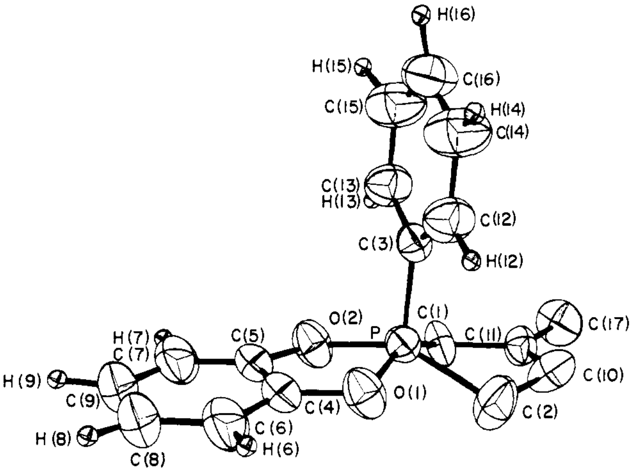


Figure 2. Molecular structure of $(C_6H_4O_2)P(C_6H_5)(C_5H_8)$. Thermal ellipsoids are shown at the 50% probability level for nonhydrogen atoms. Hydrogen atoms are represented by spheres of arbitrary radius. C. K. Johnson's ORTEP program, ORNL-3794 (1965), Oak Ridge National Laboratory.

From the position of the methyl carbon atom, rough positions of the carbon atoms C(11) and C(10) were computed to give suitable C(10)-C(11) double bond and C(17)-C(11) bond lengths. Introduction of these positions in a structure factor calculation with assigned scaling factors of 0.5 for C(17), C(10), and C(11) placed C(1) and C(2) in nonsymmetric positions. Based on the latter estimated positions for C(1) and C(2), with an occupation factor of 0.5 assigned to each of these atoms, anisotropic refinement of all independent nonhydrogen atoms led to values of $R = 0.142$ and $R_w = 0.115$ for 2251 reflections having $|F_o - |F_c|| < 10\sigma(F_o)$. A difference electron density map revealed the positions of the five independent hydrogen atoms attached to either the phenyl or benzo rings. Isotropic refinement of the hydrogen atoms and anisotropic refinement of the nonhydrogen atoms for one cycle gave $R = 0.133$ and $R_w = 0.108$ for 2258 reflections. The parameters for the hydrogen atoms were not permitted to vary during the last cycles of refinements. The final cycle of full matrix least-squares anisotropic refinement for nonhydrogen atoms, with the hydrogen atoms fixed, gave values of $R = 0.130$ and $R_w = 0.106$ for 2258 reflections having $|F_o - |F_c|| < 10\sigma(F_o)$. Owing to the disorder present, the positions of the other hydrogen atoms were not located. In the last stage of refinement, the largest shift in any parameter was less than 0.35 times the estimated standard deviation.

Results and Discussion

The positional and thermal parameters for III are presented in Tables I and II, respectively. The molecular geometry is shown in Figure 2 and bond distances and angles are presented in Table III. The packing arrangement in the unit cell is illustrated in Figure 3.

The basic structural features conform closely to a square pyramid with the rings comprising the basal system and the phenyl substituent, the axial position. The trans basal angles, O(1)-P-C(1) = 152.5° and O(2)-P-C(2) = 150.0°, are nearly equal and midway between the 120 and 180° angles exhibited by a TP conformation. As measured by the sum of dihedral angles connecting polytopal faces (discussed elsewhere[14]), the structure of III is approximately 94% along the TP-SP coordinate toward the SP. The average axial-basal angle is 103.8° and the average cis basal angle is 86.7°. Corresponding values for an idealized SP are 105 and 86°.[14]

The main deviation from an idealized SP is expressed by the unequal cis basal angles, O(2)-P-C(1) = 92.6° and C(2)-P-O(1) = 77.5°. Probably this difference is a result of a packing effect caused by the methyl group and its asymmetric placement on the five-membered carbon containing ring. The presence of the larger angle, 92.7°, on the same side of the ring as the methyl substitution is consistent with this view. To

Table II. Anisotropic Thermal Parameters for $(C_6H_4O_2)P(C_6H_5)(C_5H_8)$ with Standard Deviations in Parentheses

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	1.26 (1)	0.84 (1)	0.31 (0)	0.00 (0)	−0.04 (1)	0.00 (0)
O(2)	2.20 (4)	0.68 (2)	0.45 (1)	0.13 (2)	−0.30 (2)	−0.08 (1)
C(1)	1.01 (12)	1.15 (10)	0.38 (3)	0.30 (8)	−0.17 (5)	−0.33 (4)
C(2)	1.64 (16)	1.34 (13)	0.89 (6)	−0.41 (11)	−0.61 (7)	−0.56 (6)
C(3)	1.29 (6)	0.64 (3)	0.31 (1)	0.00 (0)	−0.09 (2)	0.00 (0)
C(5)	1.61 (4)	0.85 (2)	0.28 (1)	−0.06 (3)	−0.08 (2)	−0.02 (1)
C(7)	2.88 (8)	1.28 (4)	0.45 (1)	−0.71 (5)	−0.34 (3)	0.00 (2)
C(9)	1.97 (6)	2.36 (6)	0.46 (1)	−0.62 (5)	−0.31 (3)	0.04 (2)
C(10)	1.55 (13)	0.89 (9)	0.66 (4)	−0.06 (10)	0.16 (6)	0.19 (6)
C(11)	1.11 (7)	0.84 (14)	0.40 (2)	0.00 (8)	−0.05 (3)	−0.10 (4)
C(13)	2.24 (6)	0.78 (3)	0.48 (1)	−0.02 (3)	0.09 (2)	0.08 (2)
C(15)	2.87 (8)	1.47 (4)	0.55 (2)	−0.22 (5)	0.18 (3)	0.34 (2)
C(16)	2.31 (11)	1.91 (8)	0.38 (2)	0.00 (0)	0.15 (4)	0.00 (0)
C(17)	1.36 (9)	1.54 (8)	0.62 (3)	0.49 (7)	−0.05 (5)	0.00 (4)
H(7)	6.56[b]	H(13)	5.38			
H(9)	9.50	H(15)	10.22			
		H(16)	11.15			

[a] The temperature factor is defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The β_{ij} are multiplied by 100. [b] For all hydrogen atoms the temperature factors are thermal *B*s in Å^2.

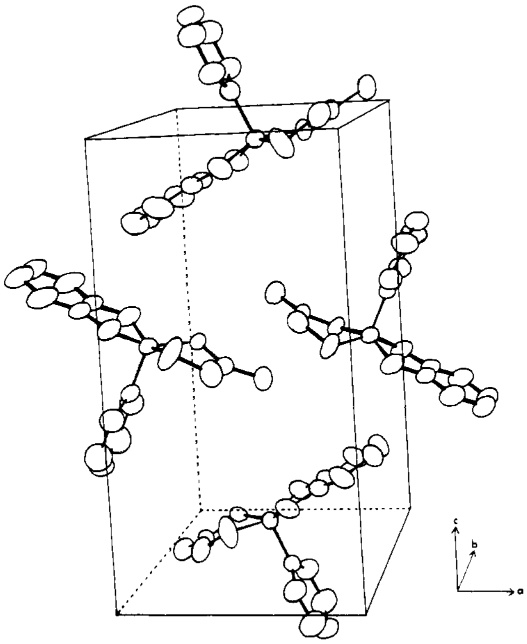


Figure 3. Unit cell ORTEP drawing of $(C_6H_4O_2)P(C_6H_5)(C_5H_8)$.

clarify this point, we are studying the structures of related members, symmetrically substituted.

Comparison of structural details between III and the dioxaphospholan[19] II shows a great deal of similarity, including the orientation of the phenyl rings and their comparative P-C phenyl bond distances. The P-C bond distances in the unsaturated five-membered ring of III, 1.97 and 1.82 Å, compare with 1.96 and 1.89 Å in the more strained four-membered ring of II. In the latter phosphorane, it is apparent that residual axial TP character is associated with the longer P-C bond length and residual equatorial TP character with the shorter P-C length. This is borne out by a comparison of P-O bond lengths in II. The latter type of comparison cannot be made for III since the "catechol" ring system is located symmetrically with respect to a crystallographic mirror plane and the P-O bond lengths were determined to be the same.

The alternation in bond angles around the basal rings is similar to that discussed[1b] for the catechol derivative IV (R = Ph). This shows up as a compression of the benzo ring with smaller angles at C(6) and C(7) relative to C(4) and C(5). This variation is present also in related derivatives.[3,6,12b]

Table III. Bond Distances (Å) and Angles (deg) and Their Standard Deviations (in Parentheses) for $(C_6H_4O_2)P(C_6H_5)$-(C_5H_8)

Distances			
P-O(2)	1.724 (2)	C(8)-C(9)	1.379 (9)
P-C(1)	1.822 (11)	C(10)-C(11)	1.345 (11)
P-C(2)	1.966 (14)	C(11)-C(17)	1.503 (11)
P-C(3)	1.807 (4)	C(13)-C(15)	1.390 (5)
O(2)-C(5)	1.351 (3)	C(15)-C(16)	1.346 (5)
C(1)-C(11)	1.502 (13)	C(7)-H(7)	0.96 (3)
C(2)-C(10)	1.534 (18)	C(9)-H(9)	1.02 (4)
C(3)-C(13)	1.374 (4)	C(13)-H(13)	0.88 (4)
C(4)-C(5)	1.369 (6)	C(15)-H(15)	1.09 (4)
C(5)-C(7)	1.365 (5)	C(16)-H(16)	0.95 (7)
C(7)-C(9)	1.384 (5)		
Angles			
O(2)-P-C(3)	102.2 (1)	C(4)-C(5)-O(2)	111.5 (2)
C(1)-P-C(3)	104.9 (3)	C(1)-C(11)-C(10)	116.0 (7)
C(2)-P-C(3)	105.8 (4)	C(11)-C(10)-C(2)	116.5 (9)
O(1)-P-O(2)	83.3 (1)	C(4)-C(5)-C(7)	121.4 (2)
O(2)-P-C(1)	92.6 (4)	C(5)-C(7)-C(9)	117.9 (3)
C(1)-P-C(2)	90.5 (5)	C(7)-C(9)-C(8)	120.7 (3)
C(2)-P-O(1)	77.5 (4)	C(1)-C(11)-C(17)	118.0 (7)
O(1)-P-C(1)	152.5 (4)	C(17)-C(11)-C(10)	126.0 (8)
O(2)-P-C(2)	150.0 (4)	C(12)-C(3)-C(13)	118.6 (2)
P-O(2)-C(5)	114.4 (2)	C(3)-C(13)-C(15)	119.9 (3)
P-C(1)-C(11)	105.6 (7)	C(13)-C(15)-C(16)	120.9 (3)
P-C(2)-C(10)	99.9 (8)	C(14)-C(16)-C(15)	119.7 (3)

Examination of least-squares planes listed in Table IV shows a high degree of planarity for the "catechol" unit, plane X (average deviation, 0.014 Å) and the phenyl substituent, plane VI (0.004 Å). The phosphorus atom appears as the flap atom in the otherwise relatively planar methyl substituted five-membered ring, plane IX. It is 0.648 Å out of the latter plane toward the axial phenyl group.

Least-squares plane I is strictly followed for an idealized SP. Planes IV and V are defining planes for a TP and planes II and III of Table IV are followed by both the SP and TP. An angle between planes II and III in the range 90-85.9° is expected if structural distortions follow the local C_{2v} constraint of a Berry coordinate. This angle in the present structure is 89.7°. The

Table IV. Atom Distances from Least-Squares Planes (Å) and Some Dihedral Angles between Them (deg)

	Plane[a]				
	I	II	III	IV	V
P	(−0.432)	−0.062	0.026	−0.013	−0.080
O(1)	−0.001		0.008		−0.280
O(2)	0.000	−0.018		0.009	0.039
C(2)	0.040	0.251		0.876	0.634
C(1)	−0.039		−0.107	−0.854	
C(3)		−0.066	0.029		

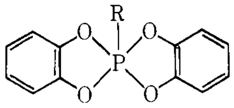
Plane[a]									
VI		VII		VIII		IX		X	
C(3)	−0.005	C(4)	−0.002	O(1)	0.000	C(1)	−0.011	O(1)	0.008
C(12)	0.007	C(5)	−0.002	O(2)	0.000	C(2)	0.052	O(2)	0.009
C(13)	0.007	C(6)	0.007	C(5)	0.000	C(10)	−0.035	C(4)	−0.029
C(14)	−0.005	C(7)	0.007	C(4)	0.00	C(11)	−0.017	C(5)	−0.029
C(15)	−0.005	C(8)	−0.005	P	(−0.273)	C(17)	0.011	C(6)	0.003
C(16)	0.000	C(9)	−0.005			P	(−0.648)	C(7)	0.003
								C(8)	0.014
								C(9)	0.014
								P	(−0.228)

Planes	Angle[b]
II, III	89.7
VII, VIII	2.9
VIII, IX	5.4

[a] Values in parentheses are distances of the phosphorus atom from the respective mean plane but said atom is not included in the calculation of the least-squares plane. The weighting scheme used was, for the ith atom, $w_i = (a\sigma_x b\sigma_y c\sigma_z)^{-2/3}$. [b] The dihedral angles are given as ≤90°.

closeness to a SP is evident from the small average deviation of atoms from plane I, 0.020 Å, compared to 0.438 and 0.258 Å for average atom deviations from planes IV and V, respectively.

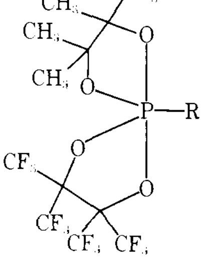
Of some interest for comparison with related cyclic derivatives are the ligand bite sizes. These are O(1)-O(2) = 2.358 (2) and C(1)-C(2) = 2.693 (17) Å for III. The O(1)-O(2) distance for III is the same as the value we reported[1b] for the bite sizes in the phenyl derivative of IV, 2.36 Å.



R = Ph, adamantyl, Me, OPh

IV

The parameters reported here for III when compared to those for the phospholan structure II[19] shows that a SP geometry is retained on going from a four- to a five-membered carbon containing ring. Introduction of unsaturation in the five-membered ring influences the formation of a SP. In other derivatives, it is noted that this factor contributes to the stabilization of the SP form. For example, the spirophosphoranes V have been reported[19] to have TP geometry. This contrasts with derivatives I[3c] and IV[1b,3b,6,12b] which tend toward SP (RP) geometries. Consistent with earlier observations,[18b] we conclude that decreasing ring size, increasing ring unsaturation, and increasing ring atom electronegativity (when all the ring atoms bonded to phosphorus are the same) are important factors favoring the appearance of a SP relative to a TP conformation.



R = SPh, p-OC_6H_4Br

V

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Supplementary Material Available: A compilation of observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

References and Notes

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Crystal and Molecular Structure of Oxyphosphoranes. 9.[1] The Spiropentaoxyphosphorane, $(PO_5)(CF_3C{=}CCF_3)(C_6H_4)(C_6H_5)$

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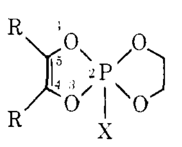
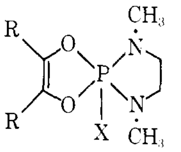
Abstract: 2-Phenoxy-2,2-*o*-phenylenedioxy-4,5-bis(trifluoromethyl)-2,2-dihydro-1,3,2-dioxaphospholene (**12**) crystallizes from hexane in the triclinic system, space group $P\bar{1}$. There are two molecules, $C_{16}H_9O_5PF_6$, in the unit cell ($Z = 2$) of dimensions $a = 6.105$ (3), $b = 12.130$ (8), $c = 12.037$ (10) Å, $\alpha = 85.35$ (6), $\beta = 101.00$ (6), $\gamma = 98.54$ (6)°. Intensities for 3130 reflections were measured on a $P\bar{1}$ diffractometer (Cu $K\alpha$) by $\theta/2\theta$ scan techniques. The structure was solved by direct methods (MULTAN program), and refined to a final R of 14.7% for 1706 reflections by full-matrix least-squares methods. Bond angles around the phosphorus atom in **12** deviate significantly from those of the ideal trigonal bipyramid (TBP), tetragonal pyramid (TP), and 30°-turnstile rotation configuration (30°-TR). Bonds connecting the phosphorus to constitutionally identical ligands in **12** cannot be classified as apical and equatorial in terms of their lengths within the accuracy of the measurements. To characterize the skeletal geometry of **12**, and of other phosphoranes with similar properties ("non-TBP phosphoranes"), the term "x°-TR configuration" is proposed. The x°-TR represents the accommodation of all bond angles and distances in the molecule to the electronic and steric demands of the ligands. The direction, but not the magnitude, of the deviations from the ideal TBP found in the actual x°-TR can be rationalized in terms of the TR mechanism for permutational isomerization of phosphoranes.

Spirophosphoranes, **1–6,** with five oxygens,[3-5] four oxygens and one nitrogen,[3-5] three oxygens and two nitrogens,[4,6] and two oxygens and three nitrogens[4,6-8] as ligands to the phosphorus have been prepared from the reaction of five-membered cyclic phosphites or phosphoroamidites with α-diketones, *o*-quinones, monoketones, or monoaldehydes. The geometry around the phosphorus in these compounds has not been established by physical methods.[9]



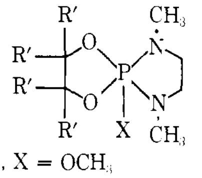
1, X = OC_6H_5, OCH_3

2, X = $N(CH_3)_2$, N



3, X = OCH_3

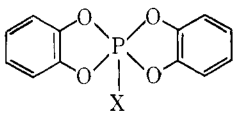
4, X = $N(CH_3)_2$, N



5, X = OCH_3

6, X = $N(CH_3)_2$, N

A second type of spirophosphorane is based on two catechol bidentate ligands[10,11] plus one additional oxygen,[11] **7,** fluorine,[12] **8,** or carbon,[13] **9,** ligand.



7, X = OC_6H_5
8, X = F
9, X = CH_3

Considerable interest has been aroused by the finding that the geometry around phosphorus in compounds of this type, **8,**[14] **9,**[15] and **7,**[1b] does not resemble that of the regular TBP,[16] which has been observed in other types of acyclic and monocyclic oxyphosphoranes,[17] by x-ray crystallography. The skeletal geometries of spirophosphoranes **8** and **9** have been described in terms of the regular TP[16] (or square pyramid), or of "mixes" of TP and TBP.[14,15,18,19] The results of x-ray analysis of other spirophosphoranes with two five-membered rings and combinations of oxygen, sulfur, and carbon ligands,[20,21] and with a four- and a five-membered ring and oxygen and carbon ligands,[22] have also been interpreted in this manner.[23,24] More recently the term static x°-TR configuration[16] was applied to a description of the geometry of spirophosphorane **7.**[1b,17,25]