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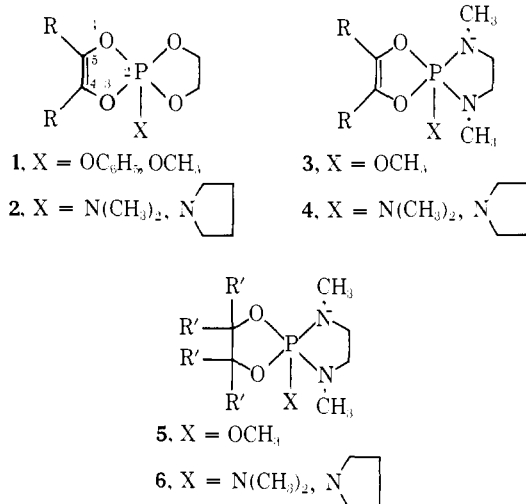
Crystal and Molecular Structure of Oxyphosphoranes. 9.¹ The Spiropentaoxyphosphorane, (PO₅)(CF₃C=CCF₃)(C₆H₄)(C₆H₅)

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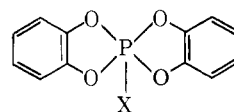
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Abstract: 2-Phenoxy-2,2-*o*-phenylenedioxy-4,5-bis(trifluoromethyl)-2,2-dihydro-1,3,2-dioxaphospholene (**12**) crystallizes from hexane in the triclinic system, space group $P\bar{1}$. There are two molecules, C₁₆H₉O₅PF₆, in the unit cell ($Z = 2$) 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 α) 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 phosphoramidites with α -diketones, *o*-quinones, monoketones, or monoaldehydes. The geometry around the phosphorus in these compounds has not been established by physical methods.⁹



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 = OC₆H₅
 8, X = F
 9, X = CH₃

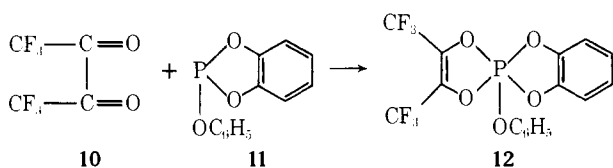
Considerable interest has been aroused by the finding that the geometry around phosphorus in compounds of this type, **8**,¹⁴ **9**,¹⁵ and **7**,^{3b} does not resemble that of the regular TBP,¹⁶ which has been observed in other types of acyclic and monocyclic oxyphosphoranes,¹⁷ by x-ray crystallography. The skeletal geometries of spirophosphoranes **8** and **9** have been described in terms of the regular TP¹⁶ (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 configuration¹⁶ was applied to a description of the geometry of spiropentaoxyphosphorane **7**.^{1b,17,25}

Table I. Atomic Coordinates ($\times 10^4$ for Nonhydrogen, $\times 10^3$ for Hydrogen Atoms) and Thermal Parameters ($\times 10^3$ for Anisotropic Atoms) for Compound **12**^{a-c}

	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
P	3887 (3)	7148 (1)	6542 (1)	4.11 (6)	4.99 (8)	4.28 (6)	1.12 (5)	0.88 (5)	-0.85 (5)
O(1)	4018 (7)	6293 (4)	5578 (4)	3.53 (16)	6.45 (24)	4.70 (19)	1.17 (17)	0.16 (15)	-2.06 (19)
O(2)	1235 (7)	7248 (4)	6036 (4)	3.12 (15)	7.13 (22)	4.75 (20)	1.43 (15)	0.56 (16)	-1.80 (19)
O(3)	5441 (8)	8169 (4)	6056 (4)	5.12 (19)	4.60 (23)	5.20 (20)	0.12 (17)	1.57 (17)	-1.30 (18)
O(4)	5416 (8)	6319 (4)	7420 (4)	5.42 (19)	6.05 (24)	3.55 (18)	1.75 (18)	0.15 (15)	-0.24 (17)
O(5)	3410 (7)	7749 (4)	7678 (4)	4.72 (17)	6.22 (24)	3.45 (18)	1.52 (18)	0.86 (16)	-0.95 (18)
C(1)	2135 (11)	6217 (6)	4712 (6)	4.60 (26)	5.43 (30)	4.04 (28)	0.79 (23)	0.50 (24)	-0.75 (24)
C(2)	521 (11)	6788 (7)	4999 (6)	4.16 (24)	5.41 (39)	3.72 (26)	0.44 (25)	1.05 (22)	-0.18 (27)
C(3)	6334 (12)	9166 (6)	6581 (6)	5.59 (29)	4.46 (35)	4.26 (28)	1.05 (26)	1.12 (24)	-0.17 (26)
C(4)	5908 (12)	6670 (7)	8502 (6)	5.37 (30)	6.93 (36)	3.65 (31)	0.86 (27)	0.19 (25)	-1.05 (27)
C(5)	4763 (12)	7464 (6)	8667 (6)	5.53 (29)	5.58 (37)	3.70 (30)	0.88 (28)	0.99 (27)	-1.25 (28)
C(6)	-1523 (11)	6845 (8)	4292 (7)	3.14 (25)	8.70 (48)	5.75 (35)	0.92 (29)	0.50 (25)	-0.21 (33)
C(7)	-1874 (13)	6303 (8)	3265 (7)	4.68 (31)	8.41 (52)	4.25 (31)	0.90 (33)	-0.25 (26)	-0.36 (34)
C(8)	-255 (14)	5749 (8)	3028 (7)	5.77 (35)	7.06 (45)	4.05 (33)	-0.38 (32)	0.31 (29)	-1.93 (32)
C(9)	1800 (12)	5675 (7)	3741 (6)	5.21 (30)	5.12 (41)	4.64 (29)	0.87 (29)	1.02 (25)	-1.24 (28)
C(10)	8528 (13)	9254 (8)	7133 (8)	4.28 (30)	6.02 (48)	8.78 (50)	0.78 (31)	0.83 (34)	-1.83 (41)
C(11)	9458 (17)	10286 (9)	7620 (9)	5.59 (42)	10.40 (54)	10.26 (56)	-0.43 (39)	1.50 (42)	-4.56 (51)
C(12)	8244 (18)	11103 (8)	7583 (10)	8.79 (51)	7.79 (46)	7.62 (54)	-0.77 (41)	2.60 (48)	-2.05 (42)
C(13)	6000 (20)	11007 (8)	7003 (9)	12.09 (60)	5.14 (40)	7.79 (54)	2.76 (45)	3.32 (54)	0.12 (39)
C(14)	5050 (15)	9996 (8)	6521 (8)	6.49 (38)	7.44 (42)	7.19 (43)	2.55 (36)	0.91 (35)	-0.32 (36)
C(15)	4721 (15)	8156 (10)	9622 (7)	5.41 (37)	14.39 (71)	4.37 (33)	1.74 (43)	-0.47 (29)	-2.87 (41)
C(16)	7678 (16)	6099 (9)	9251 (8)	7.59 (41)	7.81 (55)	5.41 (38)	2.55 (43)	0.21 (34)	0.05 (40)
F(151)	3008 (14)	8582 (8)	9537 (7)	15.53 (42)	21.99 (46)	10.08 (33)	10.58 (58)	-0.98 (37)	-8.82 (50)
F(152)	4599 (18)	7501 (8)	10552 (5)	29.00 (75)	12.16 (51)	5.18 (27)	8.06 (58)	4.76 (43)	0.03 (31)
F(153)	6394 (17)	8799 (7)	9903 (10)	15.31 (56)	20.60 (50)	18.23 (49)	-7.52 (45)	7.64 (58)	-15.04 (78)
F(161)	9599 (10)	6249 (7)	8873 (6)	5.62 (23)	14.64 (48)	10.57 (37)	3.43 (30)	0.28 (24)	-1.35 (36)
F(162)	7110 (14)	4985 (7)	9272 (7)	10.74 (41)	10.25 (40)	14.16 (53)	2.97 (35)	-0.37 (36)	4.05 (40)
F(163)	8101 (13)	6391 (9)	10280 (5)	13.88 (40)	18.86 (68)	5.17 (27)	8.50 (55)	-2.05 (26)	-1.61 (37)
	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>B</i>					
H(6)	-275	728	445	5.0					
H(7)	-331	633	274	6.0					
H(8)	-52	537	227	5.0					
H(9)	305	526	362	5.0					
H(10)	945	867	712	5.0					
H(11)	1108	1031	802	9.0					
H(12)	893	1179	803	7.0					
H(13)	500	1164	682	7.0					
H(14)	341	993	611	6.0					

^a Numbers in parentheses are estimated standard deviations in the least significant digits. ^b Anisotropic thermal parameters are of the form $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*}b^{*} + 2B_{13}hla^{*}c^{*} + 2B_{23}klb^{*}c^{*})]$. ^c Isotropic hydrogen thermal parameters are in \AA^2 .

This paper reports the x-ray crystallographic analysis of a spirophosphorane, **12**, which combines the structural features of the two types of compounds, **1** and **7**, previously synthesized. The incorporation of one catechol bidentate ligand into the 1,3,2-dioxaphospholene ring is achieved by reaction of hexafluorobiacetyl (**10**) with phenyl *o*-phenylene phosphite.²⁶



Experimental Section

Preparation of 2-Phenoxy-2,2-*o*-phenylenedioxy-4,5-bis(trifluoromethyl)-2,2-dihydro-1,3,2-dioxaphospholene (12). The compound was prepared as described.²⁶ The crystals for x-ray analysis were obtained by dissolving 600 mg of the substance in 6 mL of hot hexane and allowing the solution to cool to 21 °C undisturbed: mp 85–86 °C; $\delta^3\text{B} + 29.5$ ppm vs. H_3PO_4 0; $\delta^{19}\text{F} - 12.9$ ppm vs. CF_3COOH 0 (both at 25 °C in CH_2Cl_2 solution).

Crystal Data. Compound **12**: $\text{C}_{16}\text{H}_9\text{O}_5\text{PF}_6$; triclinic; $P\bar{1}$; $a = 6.105$ (3), $b = 12.130$ (8), $c = 12.037$ (10) \AA ; $\alpha = 85.35$ (6), $\beta = 101.00$ (6), $\gamma = 98.54$ (6)°; $Z = 2$.

Data Collection and Structure Determination. The crystals were extremely sensitive to atmospheric moisture and decomposed within a few minutes when exposed to air. Crystals were handled under a constant flow of argon and sealed in glass capillaries. Intensity data were collected on a $P\bar{1}$ diffractometer using Cu $K\alpha$ radiation by $\theta/2\theta$ scan technique. Four different crystals were necessary to collect the data, since the crystals deteriorated rapidly. The data sets were averaged, and of 3130 unique reflections 1706 had $|F_o|^2 > 2\sigma(|F_o|^2)$. Neither absorption nor extinction corrections were applied. The structure was solved by direct methods using the program MULTAN²⁷ and refined by full-matrix least squares to an R value of 14.7%. The positions of hydrogen atoms were calculated but not refined. The final positional and thermal parameters are given in Table I. The observed and calculated structure factors are available as supplementary material.

Results

The atoms in compound **12** are numbered as shown in Figure 1, which includes the bond distances and angles. Some intramolecular nonbonded distances are given in Table II. Equations of least-squares planes, the deviations of certain atoms from the planes, and the dihedral angles between planes are collected in Tables III and IV. An isolated molecule is shown in Figure 2.

The data disclose that the geometry around the phosphorus in **12** does not resemble that of an ideal TBP with D_{3h} sym-

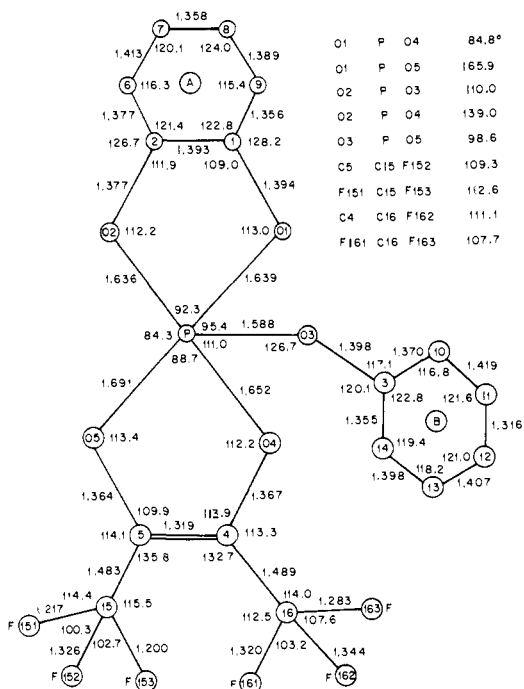


Figure 1. Numbering system, and bond distances and angles in spirooxyphosphorane **12**. The esd's for phosphorus bond distances are 0.005 Å, and for bond angles 0.3°; for C–O bond distances 0.009 Å, bond angles 0.4°; for benzene ring, bond distances 0.010 Å, bond angles 0.7°; for trifluoromethyl groups, bond distances 0.012 Å, bond angles 0.9°.

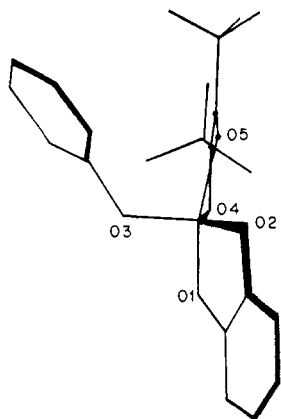


Figure 2. Computer-generated drawing of the molecule of the spirooxyphosphorane **12**. Note deviations from ideal skeletal TP geometry disclosed by the twisted spirobicyclo system.

Table II. Selected Intramolecular Nonbonded Distances Å in Compound **12**

O(1) ... O(4)	2.220	P ... C(4)	2.511
O(2) ... O(5)	2.234	P ... C(1)	2.533
O(4) ... O(5)	2.338	P ... C(5)	2.560
C(10) ... O(3)	2.360	O(2) ... O(3)	2.640
O(1) ... O(2)	2.362	O(3) ... O(4)	2.671
C(14) ... O(3)	2.386	P ... C(3)	2.670
O(1) ... O(3)	2.387	C(3) ... O(5)	2.740
O(3) ... O(5)	2.487	C(14) ... O(5)	3.078
P ... C(2)	2.504	O(2) ... O(4)	3.080

metry. Figure 3-I shows the placement of the oxygen ligands of **12** on a hypothetical TBP skeleton, with O(4) and O(5) of the phospholene ring, and O(1) and O(2) of the benzophospholene ring, occupying apical–equatorial positions for reasons

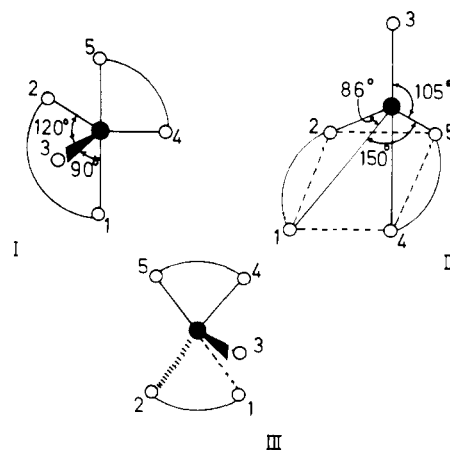


Figure 3. I, ideal TBP. II, ideal TP. III, general representation of irregular ("non-TBP") phosphoranes; P and ligand pair (4,5) are on the plane of the paper and ligands of trio (3,1,2) are on successive planes parallel to it.

Table III. Least-Squares Planes in Compound **12**

A. Coefficients, *A*, *B*, *C*, *D*, of the Equation of Plane, $Ax + By + Cz + D = 0$, and Deviation in Å of Individual Atoms from Planes; *x*, *y*, and *z* Are Relative to the Orthogonal Axes.

Plane 1: P–O(2)–O(3)–O(4)	–0.275; 0.579; 0.768; –11.254
O(2) = 0.003; O(3) = 0.002; O(4) = 0.003; P = –0.008	
Plane 2: P–O(1)–O(2)–O(5)	0.320; 0.819; –0.477; –3.417
O(1) = –0.069; O(2) = 0.003; O(5) = –0.067; P = 0.134	
Plane 3: P–O(1)–O(3)–O(5)	0.775; –0.285; 0.565; –1.490
O(1) = 0.006; O(3) = 0.002; O(5) = 0.006; P = –0.014	
Plane 4: P–O(1)–O(4)–O(5)	0.744; 0.650; –0.157; –4.195
O(1) = –0.066; O(4) = 0.006; O(5) = –0.064; P = 0.123	
Plane 5: O(1)–O(2)–O(4)–O(5)	0.551; 0.765; –0.333; –3.697
O(1) = 0.186; O(2) = –0.184; O(4) = –0.188; O(5) = 0.186; P = 0.389	
Plane 6: P–O(4)–O(5)–C(4)–C(5)	0.722; 0.675; –0.155; –4.491
O(4) = –0.080; O(5) = –0.071; C(4) = 0.044; C(5) = 0.029; P = 0.078	
Plane 7: P–O(1)–O(2)–C(1)–C(2)	0.333; 0.794; –0.509; <i>D</i> = –2.999
O(1) = –0.064; O(2) = –0.064; C(1) = 0.029; C(2) = 0.030; P = 0.069	

B. ^a Deviations from the Planes of the Phosphorus Atom That Is Not Included in the Plane Calculation

Plane 12	O(1)–O(2)–O(3)	P = 0.762
Plane 13	O(1)–O(2)–O(4)	P = 0.554
Plane 14	O(1)–O(3)–O(4)	P = –0.797
Plane 15	O(1)–O(2)–O(5)	P = 0.203
Plane 16	O(1)–O(4)–O(5)	P = 0.191
Plane 17	O(2)–O(3)–O(5)	P = –0.793
Plane 18	O(2)–O(4)–O(5)	P = 0.568
Plane 19	O(3)–O(4)–O(5)	P = –0.764

^a Planes numbered 8–11 are three-atom planes defined in Table IV for calculation of dihedral angles.

previously discussed.^{3,25} The differences between ideal and observed bond angles in **12** are summarized in Table V. The corresponding values for the three related spirophosphoranes **7–9** and for the nearly regular TBP **13**¹⁷ and **14**²⁸ are included in Table V.

Other noteworthy features of the molecular structure of **12** are: (1) The endocyclic P–O–C angles have comparable values

Table IV. Some Dihedral Angles^a in Compound **12**

Plane a	Atoms	Plane b	Atoms	Angle, deg
6	P-O(4)-O(5)-C(4)-C(5)	9	P-O(1)-O(4)	9.3 (15) ^b
7	P-O(1)-O(2)-C(1)-C(2)	10	P-O(2)-O(5)	10.0 (14)
1	P-O(2)-O(3)-O(4)	2	P-O(1)-O(2)-O(5)	88.9 (88)
1	P-O(2)-O(3)-O(4)	3	P-O(1)-O(3)-O(5)	86.8 (85)
1	P-O(2)-O(3)-O(4)	4	P-O(1)-O(4)-O(5)	87.1 (89)
2	P-O(1)-O(2)-O(5)	3	P-O(1)-O(3)-O(5)	104.5 (97)
2	P-O(1)-O(2)-O(5)	4	P-O(1)-O(4)-O(5)	32.3 (16)
3	P-O(1)-O(3)-O(5)	4	P-O(1)-O(4)-O(5)	72.4 (82)
3	P-O(1)-O(3)-O(5)	5	O(1)-O(2)-O(4)-O(5)	88.8 (88)
5	O(1)-O(2)-O(4)-O(5)	12	O(1)-O(2)-O(3)	117.1 (120)
5	O(1)-O(2)-O(4)-O(5)	14	O(1)-O(3)-O(4)	60.4 (57)
5	O(1)-O(2)-O(4)-O(5)	17	O(2)-O(3)-O(5)	59.5 (60)
5	O(1)-O(2)-O(4)-O(5)	19	O(3)-O(4)-O(5)	59.7 (61)
6	P-O(4)-O(5)-C(4)-C(5)	7	P-O(1)-O(2)-C(1)-C(2)	31.3 (21)

^a Angles between the normals of the planes which are defined in Table IV. ^b Values in parentheses refer to the corresponding angle in spirodicatolphenoxyphosphorane (**7**), ref 1b.

Table V. Deviations from Ideal Trigonal Bipyramid (TBP) in Spirooxyphosphoranes and in Acyclic (**13**) and Monocyclic (**14**) Oxyphosphoranes

Compd Angle, deg	Deviation from, deg	12 ^a	8 ^b	7 ^c	9 ^d	13 ^e	14 ^f
O(2)-P-X(3) ^g	120	-10	-13	-17	-14	-4	-3
O(1)-P-O(5)	180	-14	-12	-20	-23	-3	-2
O(4)-P-O(5)	90	-1	+2	+2	+1	-1	-1
O(1)-P-O(4)	90	-5	-4	-7	-7	-2	-1
X(3)-P-O(4)	120	-9	-13	-15	-14	+5	-3
O(2)-P-O(4)	120	+19	+26	+31	+28	-2	+5
O(1)-P-X(3)	90	+5	+6	+12	+12	+2	+1
X(3)-P-O(5)	90	+9	+6	+8	+11	-2	-2
O(2)-P-O(5)	90	-6	-5	-7	-7	+1	+1
O(1)-P-O(2)	90	+2	+1	+1	0	+2	+3

^a Present work. ^b Spirodicatolfluorophosphorane; ref 12 and 14. ^c Spirodicatolphenoxyphosphorane; ref 1b. ^d Spirodicatolmethylphosphorane. One of two independent molecules in the asymmetric unit; the other shows similar deviations (<1.5° in all angles); ref 13 and 15. ^e Pentaphenoxyphosphorane, ref 17. ^f 2,2,2-Triisopropoxy-4,5-(2',2''-biphenylene)-2,2-dihydro-1,3,2-dioxaphospholene; ref 28. ^g X = O in **7**, **12**-**14**; X = F in **8**; X = C in **9**.

(ca. 112–113°), but the exocyclic angle P-O(2)-C(3) is larger (126.7°), reflecting the interference between phenyl ring **B** and one oxygen ligand; note the relatively short nonbonded distances O(5)⋯C(3) and O(5)⋯C(14). (2) The endocyclic O-C-C angles are similar (ca. 110°) and are constrained relative to the exocyclic angle O(3)-C(3)-C(14), 120.1°. (3) The two trifluoromethyl groups repel each other, as reflected in the angles C(4)-C(5)-C(15), 135.8°, and C(5)-C(4)-C(16), 132.7°, relative to the normal 120° for an sp² carbon.

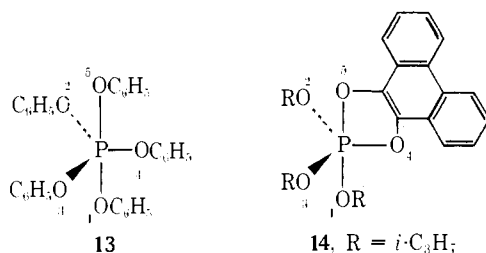
The P-O bond distances in **12** are listed in Table VI, and are compared with the corresponding distances in the spiro compounds **7**-**9**. Table VI includes bond distances for the TBP oxyphosphoranes **13** and **14**. It is apparent that the P-O bonds in **12** cannot be categorized as apical vs. equatorial, using as criterion the generalization that apical bonds are longer than

Table VI. Bond Distances (Å) in Oxyphosphoranes^a

Bond	Compd					
	12	8	7	9	13	14
P-O(1)	1.64	1.66	1.67	1.67	1.66	1.65
P-O(2)	1.64	1.63	1.67	1.66	1.60	1.59
P-O(5)	1.69	1.66	1.65	1.67	1.66	1.75
P-O(4)	1.65	1.63	1.67	1.65	1.60	1.64
P-X ^b (3)	1.59	1.55	1.60	1.78	1.60	1.60

^a Numbering scheme in Figure 3. In ideal TBP O(1),O(5) would be apical, O(2),X(3),O(4) equatorial. ^b X = O in **7**, **12**-**14**; X = F in **8**; X = C in **9**.

equatorial bonds of comparable constitutional types; this question will be discussed in the next section.



Discussion

Research on electron diffraction,²⁹ x-ray crystallography,^{1a,28,30} and IR, Raman, and NQR spectrometry³¹ of phosphoranes led to the assignment of TBP skeletal geometry to this type of compound. Those investigations also revealed differences between bonds connecting the phosphorus to ligands of identical or comparable constitution. Those differences have been expressed in terms of apical and equatorial bonds, e.g., O(1), O(5), and O(2), O(3), O(4), respectively, in Figure 3-1.

Bond differentiation in TBP phosphoranes has also emerged from the various models that have been used to discuss bonding in these compounds.^{25,32-41} In addition, attempts have been made to justify and to predict the placement of different ligands on the two types of skeletal positions of the TBP, in terms of element and strain rules⁴² and apicophilicity functions.⁴³⁻⁴⁶ Recently, the significant effect of equatorial or apical ligand subset symmetry⁴³ on the relative stability of phosphorane permutational isomers has been emphasized. Although the apicophilicity and related rules do not cover all the ligands that are known to occur in actual phosphoranes, the rules permit some degree of rationalization of existing data in stable (isolable) compounds. These rules are also useful in applications of the oxyphosphorane hypothesis⁴⁷⁻⁵¹ to the mechanism of displacement at four-coordinate phosphorus, since one of the assumptions in this hypothesis is the apical entry and departure of ligands into, and from, TBP phosphorane intermediates.

These considerations justify current efforts to arrive at a satisfactory description of the skeletal geometry of the "non-TBP phosphoranes", i.e., of those molecules which do not meet the bond angle and distance criteria associated with the regular TBP. A possible approach^{18,19,52} is to assume that the distortions from the TBP will follow the trends suggested by the Berry pseudorotation⁵³⁻⁵⁶ or the turnstile rotation^{25,43,57} mechanisms of intramolecular permutational isomerization of phosphoranes. The TR mechanism was introduced in connection with sterically constrained phosphoranes such as **15-17**,⁵⁸⁻⁶⁰ and is thought to be applicable also to simpler cyclic compounds,^{61,62} e.g., **14**. Early calculations²⁵ and more recent ones^{35,37,41} give a definite energetic advantage to pseudorotation over TR in acyclic phosphoranes of types PX₅. The idealized barrier configurations in these mechanisms are depicted in Figure 3-II (TP,¹⁶ C_{4v} for pseudorotation) and 3-III⁶³ (30°-TR, C_s symmetry, with the angles shown in Table VII).

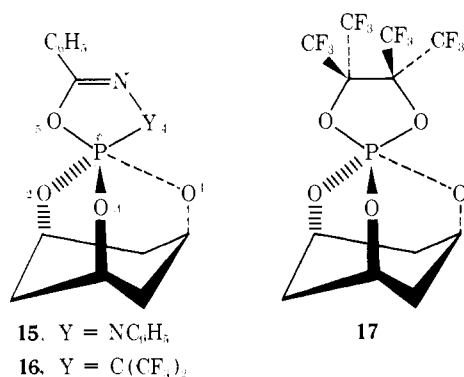


Table VII. Deviations from Ideal Tetragonal Pyramid (TP) and 30° Turnstile Rotation Configuration (30°-TR) in Spirooxyphosphoranes

Angle, deg	Deviation from, deg	Compd			
		12	8	7	9
A. From Ideal TP					
O(1)-P-O(5)	150	+16	+18	+10	+7
O(2)-P-O(4)	150	-11	-4	+1	-2
X(3)-P-O(5)	105	-6	-9	-7	+6
O(1)-P-X(3)	105	-10	-9	-3	-3
O(2)-P-X(3)	105	+5	+2	-2	+1
X(3)-P-O(4)	105	+6	+2	+1	+1
O(1)-P-O(4)	86	-1	0	-3	-3
O(2)-P-O(5)	86	-2	-2	-3	-3
O(1)-P-O(2)	86	+6	+5	+5	+4
O(4)-P-O(5)	86	+3	+6	+6	+5
B. From Ideal 30°-TR ^a					
O(1)-P-O(5)	155	+11	+13	+5	+2
O(2)-P-O(4)	155	-16	-9	-4	-7
X(3)-P-O(4)	114	-3	-7	-9	-8
X(3)-P-O(5)	114	-15	-18	-16	-3
O(2)-P-X(3)	90	+20	+17	+13	+16
O(1)-P-X(3)	90	+5	+6	+12	+12
O(1)-P-O(2)	90	+2	+1	+1	0
O(4)-P-O(5)	90	-1	+2	+2	+1
O(1)-P-O(4)	85	0	+1	-2	-2
O(2)-P-O(5)	85	-1	0	-2	-1

^a The motions of ligands in TR are discussed in ref 25. The calculated angles are approximate.

Table VII gives the differences between the bond angles observed in compound **12** and those in the ideal TP and 30°-TR configurations. It is concluded that neither one of these two ideal geometries constitutes an adequate description of the molecule of **12**. For example, note the angle deviations on the assumption that O(3) is in the axial or flagpole position, while O(1), O(2), O(4), O(5) are in the basal position of the TP. The latter four ligands are not coplanar; in plane 5 (Table III), O(1) and O(5) are displaced +0.186 Å to one side, and O(2) and O(4) are displaced -0.186 Å to the opposite side of the plane, with the P atom displaced +0.389 Å toward the side of O(1) and O(2); cf. Figure 2.

Table VII includes also deviations from ideal TP and 30°-TR in the series **7-9**. From Tables V-VII it is apparent that there are certain trends in the distortions of all of these compounds from the ideal symmetries, TBP, TP, and 30°-TR, although there is considerable variation in the extent of the deviations of the corresponding bond angles among the compounds. In these phosphoranes, bonds connecting the phosphorus to constitutionally identical or related ligands cannot be classified as apical vs. equatorial according to their relative lengths.

Further analysis of the data in Tables V-VII can be made from two points of view. One is to regard the actual geometry as a "mix" of ideal TBP and TP contributions.^{18,19} The other is to consider that the actual geometry represents the accommodation of all bond angles and distances in the molecule to the electronic and steric demands of all the ligands; we have suggested^{16,17} the designation "static x°-TR configuration", or simply "x°-TR" for the result of this accommodation. The direction, but not the magnitude, of the deviations from the ideal TBP can be rationalized in terms of the TR mechanism for permutational isomerization. Since the ligands that can be introduced into stable oxyphosphoranes can vary a great deal in electronic properties and in steric constraint,^{3,9,24,43,54} it is expected that several or all the angles around the phosphorus in a given x°-TR will be different. In this approach, no attempt is made to fit the actual geometry to the ideal TP or 30°-TR,

and Table VII is not regarded as having much significance as a description of the ground state of the phosphoranes. On the other hand, Table V discloses the extent of the distortions in *actual* non-TBP phosphoranes relative to the geometry of actual TBP phosphoranes, such as **13** and **14**. Moreover, a comparison between the data in Tables V and VI shows the correlation that exists between the TBP and the non-TBP geometries, and the bond distances of the ligands in both types of compounds. The meaningful comparisons are between constitutionally identical bonds, e.g., the pairs O(1), O(2) and O(5), O(4). It appears to be fairly general that the differentiation between apical and equatorial bonds is no longer possible in these non-TBP phosphoranes; however, it is not clear how much distortion from the ideal TBP must occur before the bond differentiation is experimentally undetectable.

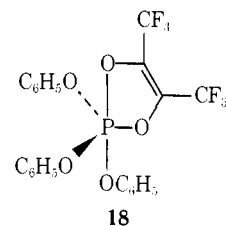
Calculations in simple PX_5 molecules suggest longer bonds for basal vs. the axial (flagpole) ligands in the ideal TP,^{35,41,64} and also longer bonds for the pair ligands vs. the trio ligands in the ideal 30°-TR. However, the relevance of these results to actual complex phosphoranes is questionable since, in fact, these molecules deviate significantly from all the ideal geometries, D_{3h} , C_{4v} , and C_s .

From Tables such as V and VI one can classify a given phosphorane as TBP (**13**, **14**), or non-TBP (**12**, 7–9). A more economical way of doing the same thing is to calculate a value for x in the x° -TR configuration, according to some definition. The TR mechanism²⁵ suggests a definition of x as the dihedral angle between certain planes. One such plane contains the phosphorus plus the trio-apical and the pair-equatorial ligands [P, O(1), O(4)]. The second plane should contain the phosphorus and both pair ligands⁶⁵ [P, O(4), O(5)]. The values of x in x° -TR in the series of compounds of Table V are **12** $\equiv 9^\circ$, **8** $\equiv 8^\circ$, **7** $\equiv 15^\circ$, and **9** $\equiv 19^\circ$. It is significant that an increase in the value of x corresponds to increasing distortion of most bond angles from those in the ideal TBP. Moreover, as x increases, so does the resemblance of the actual geometry to both the ideal TP and 30°-TR (Table VII).

Tables V–VII suggest a correlation between the magnitude of x in x° -TR and the differentiation of constitutionally equivalent bonds as apical vs. equatorial. Thus the phosphoranes with $x \geq 8^\circ$ do not allow this differentiation. It should be of interest to examine similar correlations for phosphoranes where x falls in the range $0^\circ < x < 8^\circ$.

Several factors may contribute to the establishment of the non-TBP skeletal geometry in phosphoranes, in the sense described above. These factors probably stem from differences in the electronic and steric properties of the ligands to the phosphorus, and of the atoms connected to the ligands themselves. We speculate that the drastic effect of the 5,5- and 5,4-spiro systems on the geometry could mean that the simultaneous incorporation of one P atom into two 1,3,2-dioxaphospholene rings, or a combination of a dioxaphospholene and a 1,2-oxaphosphetane ring, prevents to some extent the involvement of the electrons of the oxygens in p-d π bonding with the pentavalent phosphorus, which could decrease the tendency of the latter to adopt the TBP skeletal geometry. These differences in p-d π bonding may also account for the observation that in acyclic and monocyclic TBP oxyphosphoranes, apical P–O bonds are longer than the *corresponding* equatorial P–O bonds (more π bonding, hence higher bond order, in the latter); moreover, endocyclic P–O bonds are longer than the exocyclic P–O bonds of the same kind.²⁸ These effects may also be related to the significant decrease observed in the shielding of the P nucleus by electrons upon introduction of these types of rings into oxyphosphoranes, as suggested by displacements of the ³¹P NMR chemical shifts toward lower magnetic fields in monocyclic and spirobicyclic oxyphosphoranes.⁴⁸ The downfield displacement may reflect the steric inhibition of p-d π bonding associated with the presence of the

ring. An example is provided by the phosphorane⁶⁶ **18**, which has $\delta^{31}P + 61.8$ ppm, much larger than the value $\delta^{31}P + 29.5$



ppm for the spirobicyclic analogue **12** (both relative to $H_3PO_4 = 0$).

Supplementary Material Available: Structure factors (8 pages). Ordering information is given on any current masthead page.

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 (57) To transform an ideal TBP ground state into the ideal 30°-TR barrier configuration by single TR (ref 25), utilizing ligands O(1), O(2), O(3) as *trio*, and ligands O(4), O(5) as *pair*, and leaving equatorial ligand O(3) in the equatorial position of the new TBP, (a) contract the diequatorial angle O(2)-P-O(3) of the trio by 30° (120° → 90°); (b) tilt the pair (as a unit) 9° in the plane P, O(1), O(4), O(5), toward the apical ligand O(1) of the trio; (c) rotate (or twist) the pair against the trio in opposite directions, moving the equatorial ligand O(4) of the pair toward the equatorial ligand O(3) of the trio that is to remain equatorial upon completion of the permutational isomerization. These motions are assumed to be concerted; however, ab initio calculations suggest that, at least in the model PH₅, a sequential process, TBP → 0°-TR → 30°-TR, is favored (cf. ref 41).
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 (64) Holmes (ref 18, 19) has suggested a correspondence between the basal bonds of the TP and the apical bonds of the TBP on the basis of "electron pair repulsion considerations".
 (65) The carbon atoms of the phospholene ring, C(4), C(5), attached to the ligands, O(4), O(5) have been included with the phosphorus in plane 6 of Table IV, as well as in the corresponding planes used to calculate *x* in the series of compounds 7-9. The actual value of *x* differs somewhat if C(4), C(5) are omitted from the plane calculations, without affecting the trend noted in the series.
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Structural Effects on the Nonradiative Decay of Alkylbenzenes. The Nature of the "α-Substitution Effect"¹

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Abstract: The previously reported "α-substitution effect", whereby alkyl substituents on a carbon attached to the benzene ring increase nonradiative decay, is demonstrated to be caused by an increase in the rate of internal conversion ($S_0 \leftarrow S_1$ decay). Perdeuteration of the *tert*-butyl group in *tert*-butylbenzene has no effect on the phenomenon, thus eliminating involvement of the β C-H stretching mode in the decay process. However, molecules with β CH₃ groups oriented out of the plane of the benzene ring (cf. II and IV) have particularly high decay rates, and it is suggested that (1) β carbon-carbon bonds do participate in $S_0 \leftarrow S_1$ decay and (2) participation of these bonds is optimal when they are out of the plane. The ability of *tert*-butyl groups to facilitate aryl $S_0 \leftarrow S_1$ decay may be a general phenomenon.

Some time ago we reported² that the excited singlet lifetimes and fluorescence efficiencies of alkylbenzenes varied as a function of (at least) two structural parameters, e.g., a previously observed "xylene effect" (whereby an ortho or para arrangement of groups enhances the fluorescence efficiency (ϕ_f)) and a new "α-substitution effect" (whereby alkyl substituents on a carbon attached to the ring reduce ϕ_f). As regards the latter phenomenon, it was demonstrated that ϕ_f for monoalkylbenzenes decreases as a linear function of the number of β hydrogens; thus, *tert*-butylbenzene (nine β hydrogens) has a ϕ_f (0.032) which is 77% lower than that of toluene. In the case of *tert*-butylbenzene (and also isopropylbenzene, which has a ϕ_f 52% that of toluene), the diminution results from a sharp increase in the nonradiative decay rate

(k_d). Since this rate is the sum of internal conversion (k_{ic}) and intersystem crossing (k_{isc}), a more detailed analysis of the origin of this increase necessitated the measurement of intersystem crossing efficiencies (ϕ_{isc}). These have now been determined and are reported below, together with some observations which further bear on the nature of this enhanced decay.

Experimental Section

Instrumentation. Analyses of the 2-heptene isomer compositions were performed on a Varian Aerograph 1200 vapor phase chromatograph with a Hewlett-Packard 3380A recording integrator. UV absorbance measurements were done with 1-cm cells in a Beckman DUR coupled to a Gilford 222A photometer. Alkylbenzene emission