Reagents", R. E. Sievers, Ed., Academic Press, New York, N.Y., 1973, pp 143–158.
(4) J. D. Roberts, "Nuclear Magnetic Resonance", McGraw-Hill, New York, N.Y., 1959, p 63.
(5) T. P. Forrest, D. L. Hooper, and S. Ray, *J. Am. Chem. Soc.*, **96**, 4286 (1974).
(6) I. M. Armitage, L. D. Hall, A. G. Marshall, and L. G. Werbelow in ref 3, pp 322–323.
(7) Program written by G. D. Smith, Montana State University.
(8) M. R. Willcott, III, and R. E. Davis in ref 3, pp 159–169.
(9) For all PDIGM calculations, coordinates of all conformations were taken so that the oxygen atom and the four carbon atoms of the tetrahydrofuran ring were superposed in all conformations. Comparison of any two *R* factors is a comparison of the goodness of fit for two different positions for the substituents on the four nonfused carbon atoms of the six-membered ring.
(10) We applied the Hamilton *R*-ratio tests[11] to observed *R* factors in the following way. The conformation or mix of conformations with the lowest *R* factor was deemed the "best fit conformation". Any other conformation or mix of conformations was considered a "restrained conformation" with the number of protons unable to assume the "best fit conformation" defining the number of restrained parameters (*b*). Further, the number of experimental observations (*n*) was taken as the number of observed NMR peaks used in the calculation of slopes and the number of parameters (*p*) was taken as the number of protons in the molecule. The observed *R*-ratio, $R_{rest}/R_{best\ fit}$, was compared to the calculated *R*-ratio values, $R_{b,n-p,\alpha}$, which have to be exceeded to reject the hypothesis that the two conformations are indistinguishable. The confidence level at which the hypothesis is rejected is $(1 - \alpha) \times 100\%$. Values of $R_{b,n-p,\alpha}$, were taken from Hamilton[12] or calculated by the relation

$$R_{b,n-p,\alpha} = [(b/n - p)F_\alpha + 1]^{1/2}$$

as given by Hamilton.[11]

For **1a,** $n = 25$, $p = 12$, $b = 6$. The conformational mix of 94% *open,* 16% *folded* with the lowest *R* factor is not significantly different from the totally *open* conformation but is significantly different from any conformational mix of 75% or less *open* form at the 90% confidence level. The stipled area in Figure 1 shows the limits of the 90% level.
(11) W. C. Hamilton, "Statistics in Physical Science", Ronald Press, New York, N.Y., 1964, pp 157–162.
(12) Reference 11, pp 216–222.
(13) F. Johnson, *Chem. Rev.*, **68,** 375 (1968).
(14) D. H. Wertz and N. L. Allinger, *Tetrahedron,* **30,** 1579 (1974).
(15) For **1b** $n = 30$, $p = 16$, $b = 10$. The 60%:40% conformational mix is significantly different from conformational mixes of 90% *open* or greater and 35% *open* and less at the 90% confidence level. The stipled area of Figure 1 shows the limits of the 90% level.
(16) R. E. R. Craig, A. C. Craig, and G. D. Smith, *Tetrahedron Lett.*, 1189 (1975).
(17) (a) K. L. Servis, D. J. Bowler, and C. Ishii, *J. Am. Chem. Soc.*, **97,** 73 (1975); (b) K. L. Servis and D. J. Bowler, *ibid.*, **97,** 81 (1975).
(18) J. Wolinsky and M. Senyek, *J. Org. Chem.*, **33,** 3950 (1968).
(19) P. Wilder, Jr., and C. V. A. Drinnan, *ibid.*, **39,** 414 (1974).
(20) For **2** $n = 25$, $p = 20$, $b = 6$.
(21) I. D. Blackburne, A. R. Katritzky, and Y. Takeuchi, *J. Am. Chem. Soc.*, **96,** 682 (1974).
(22) The compounds used in this study were prepared by established literature procedures, with physical and spectral data in agreement: **1a,** ref 1; **1b,** A. P. Krapcho and B. P. Mundy, *J. Heterocycl. Chem.*, **2,** 355 (1965); **2,** ref 13; **3,** B. P. Mundy, *Org. Prep. Proced. Int.*, **7,** 21 (1975).

Crystal and Molecular Structure of a Spirobicyclic Pentaoxyphosphorane, $(PO_5)(C_6H_4)_2(C_6H_5)$

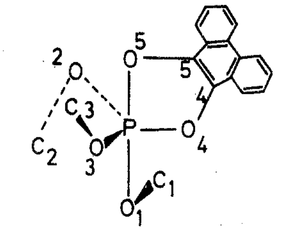
Raghupathy Sarma,*[1a] Fausto Ramirez,*[1b] and James F. Marecek[1b]

Biochemistry and Chemistry Departments of the State University of New York at Stony Brook, Stony Brook, New York 11794

Received July 15, 1975

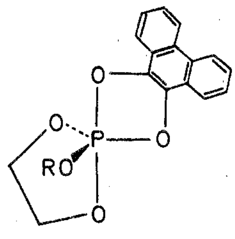
The crystal and molecular structure of a monoclinic form of spirodicatecholphenoxyphosphorane was determined by single-crystal x-ray diffraction techniques. The space group is $P2_{1/c}$ with four molecules in a unit cell of dimensions $a = 6.910$ Å, $b = 15.305$ Å, $c = 14.779$ Å, $\beta = 88.5°$. The final *R* factor for 2840 independent reflections is 8.7%. The molecular structure does not correspond to an ideal or a "slightly distorted" trigonal bipyramid or tetragonal (square) pyramid. It is suggested that the phosphorus and its five oxygen ligands have the skeletal geometry of a 15°-turnstile rotation configuration.

Compounds with five oxygen ligands covalently bonded to phosphorus, e.g., the trimethyl phosphite–phenanthrenequinone adduct 1, have been extensively studied from structural[2] and synthetic[3] points of view. The geometry around the phosphorus in the analogous pentaoxyphosphorane 2 is TBP,[4] as established by x-ray crystallography,[5] which revealed also the existence of severe crowding around the central atom. It was suggested[5] that the relatively planar ring minimizes the crowding and contributes to the stability of this type of compound.



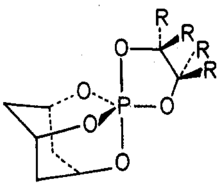
1 $C_1,C_2C_3 \equiv CH_3$; $\delta^{31}P = +44.7$ ppm
2 $C_1,C_2,C_3 \equiv$ iso-C_3H_7; $\delta^{31}P = +48.6$ ppm
3 $C_1,C_2,C_3 \equiv C_6H_5$; $\delta^{31}P = +58.6$ ppm

Spirobicyclic pentaoxyphosphoranes, e.g., 4 and 5, are also known, and are relatively stable.[6] The introduction of an additional five-membered ring into the monocyclic pentaoxyphosphoranes is accompanied by a significant displacement of the ^{31}P NMR chemical shift toward lower magnetic field, i.e., by a decrease in the shielding of the P nucleus by electrons, cf. 4 vs. 1 and 5 vs. 3. This effect could reflect significant differences in molecular structure between spirobicyclic and monocyclic pentaoxyphosphoranes, but there are no x-ray data on the molecular structure of 4 and 5. Six-membered rings do not cause this effect.[6,7]

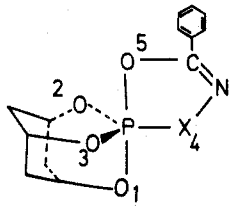


4 $R = CH_3$; $\delta^{31}P = +23.0$ ppm
5 $R = C_6H_5$; $\delta^{31}P = +27.0$ ppm

There seems to be a tendency toward the TBP geometry in five-coordinate phosphorus, as there is in five-coordinate antimony.[8] Although there are as yet no x-ray crystallographic data for the caged polycyclic pentaoxyphosphorane[9,10] **6**, the molecular structures of the two analogous compounds **7** and **8** are known.[11,12] The skeletal geometry about the P atom is close to TBP in **7** and **8**, but there are significant distortions in them from ideal D_{3h} symmetry, e.g., O(2)–P–O(3) = 106° and O(5)–P–X(4) = 84° in **7** and **8**, while O(1)–P–O(5) = 170° in **7** and 168° in **8**. It was suggested[11,12] that the molecules of phosphoranes **7** and **8**, in their ground state in the crystal, have geometries which begin to resemble those of TR configurations.[4,13] If so, when those molecules are placed in solution, they are able to undergo relatively rapid intramolecular permutational isomerization, since they require relatively little energy to reach the barrier configuration of the TR mechanism.[13]



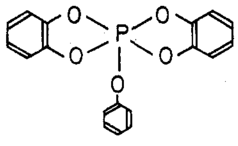
6 $R = CF_3$; $\delta^{31}P = +42.4$ ppm



7 $X = NC_6H_5$; $\delta^{31}P = +56.8$ ppm

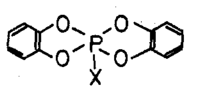
8 $X = C(CF_3)_2$; $\delta^{31}P = +17.9$ ppm

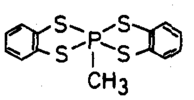
The purpose of this investigation was to ascertain the effect exerted on the *static stereochemistry of a pentaoxyphosphorane* by the presence of two five-membered rings in the spiro configuration. The molecule chosen was the spirodicatecholphenoxyphosphorane,[6b] **9**.



9 $\delta^{31}P = +30.2$ ppm

The results of x-ray crystallographic analysis of a number of spirobicyclic phosphoranes having combinations of P–O and P–C[14] (**10**), P–O and P–F[14] (**11**), P–S and P–C[15] (**12**), and P–O, P–S, and P–C[16] bonds have been interpreted in terms of more or less distorted TP[4] skeletal geometries.[17a]





10 $X = CH_3$

11 $X = F$

12

The TP geometry has also been suggested from x-ray data for certain spirodioxatricarbophosphoranes with four- and five-membered rings;[18] in contrast, some monocyclic dioxatricarbophosphoranes with a four-membered ring have slightly distorted TBP configuration.[19] Unfortunately, the effect of the spirobicyclic feature on the skeletal geometry of phosphoranes is obscured in these examples[14–16,18] by the circumstance that they have quite different "ligand subset symmetry",[13,20] i.e., the equatorial and the apical subsets of ligands cannot be made up of the same element, and electronic, as well as steric, factors may contribute to the striking differences in molecular geometry in these cases.

Several examples of phosphoranes with P–C bonds, and with certain combinations of P–C and P–O bonds, are known to have slightly distorted TBP geometries according to x-ray crystallography.[21–28]

Experimental Section

Preparation of Spirodicatecholphenoxyphosphorane (9). This substance was prepared as described.[6b] The crystals for x-ray analysis were obtained from a mixture of benzene and hexane at 20°; they had mp 108–110° and $\delta^{31}P$ +30.0 ppm vs. H_3PO_4 (CH_2Cl_2 solution).

Crystal Data. Compound **9**: $C_{18}H_{13}O_5P$; monoclinic; $P2_{1/c}$; $a = 6.910 \pm 0.01$ Å, $b = 15.305 \pm 0.01$ Å, $c = 14.779 \pm 0.01$ Å, $\beta = 88.5°$; $Z = 4$; d calcd = 1.445 g/cm^3; d meas = 1.437 g/cm^3.

Data Collection and Structure Determination. The crystals were extremely sensitive to atmospheric moisture and dissolved readily during exposure. This was prevented by sealing the crystal in a capillary tube filled with a small amount of P_2O_5 at one end of the tube. The crystal used for data collection had dimensions 0.7 × 0.4 × 0.4 mm.

Intensity data were collected using a computer controlled CAD4 automatic diffractometer using Cu Kα (1.542 Å) radiation. Nearly 3000 reflections were collected using θ–2θ scan with a scan width of 1.2°. Four reflections were measured periodically to monitor any crystal deterioration. No such effects were observed during the entire data collection. Ninety-six separate measurements were made for each scan; the first 16 and the last 16 measurements were summed to provide the background measurements for each reflection. There were approximately 2840 reflections with $|F_0|^2 > 2\sigma(|F_0|^2)$ with σ estimated from counting statistics.

Since the crystal was sealed inside a capillary tube, an empirical absorption correction was applied;[29] this correction was determined by performing an azimuth scan for a reflection occurring at a χ value of approximately 90°. The variation in intensity of such a reflection for the different azimuth angles is dependent on the thickness of the crystal traversed by the incident and the reflected beams and this variation is used to calculate the transmission factor for the crystal for all the other reflections. The transmission factor varied from a value of 1.00 to approximately 1.30 during the azimuth scan.

Structure amplitudes derived in the usual way were used in calculating a sharpened Patterson map, which was used in deducing the position of the phosphorus atom. Remaining atoms were located from a series of structure factors followed by weighted Fourier syntheses calculated using $w|F_N|\exp\alpha$ as coefficients, where the weighting factor $w = \tanh(|F_N||F_P|/\Sigma f_{Qj}^2)$;[30] $|F_N|$ is the observed structure amplitude, $|F_P|$ is the contribution from the known atoms, and Qj corresponds to the unknown atoms. The structure was refined by full matrix least squares, minimizing the function $\Sigma w(\Delta F)^2$. The weighting scheme used was of the form $w = 1/(a + |F_0| + c|F_0|^2)$ where a and c were of the order of $2F_{min}$ and $2/F_{max}$, respectively.[31] The atomic scattering factors for all the nonhydrogen atoms were taken from a standard source. The final least-squares cycle was performed with anisotropic temperature parameters for all the nonhydrogen atoms. No attempt was made to locate the positions of the hydrogen atoms. Refinement was stopped with an R value of 8.7% for 2840 reflections. A final difference Fourier synthesis $\rho_{obsd} - \rho_{calcd}$ was calculated. The maximum electron density in this synthesis was 0.383 e/A^3, indicating that no atoms other than hydrogen remain to be located. The final positional and thermal parameters are given in Table I. The observed and calculated structure factors are given in Table II.

Discussion

Molecular Structure of 9. The interatomic distances[32] and bond angles and their standard deviations are listed in Table III. Some intramolecular distances between nonbonded atoms are collected in Table IV. Equations of least-squares planes, and deviations of certain atoms from these

Table I

A. Atomic Coordinates and Their Standard Deviations (in Parentheses)

Atom	*X*	*Y*	*Z*
P	0.0817 (2)	0.3153 (0)	0.4739 (0)
O1	−0.1440 (7)	0.3530 (3)	0.4841 (2)
O2	0.1522 (7)	0.4036 (3)	0.4159 (3)
O3	0.0619 (7)	0.2426 (3)	0.3972 (3)
O4	0.0236 (7)	0.2650 (3)	0.5708 (2)
O5	0.3157 (7)	0.3046 (3)	0.4904 (2)
C1	−0.1759 (11)	0.4233 (4)	0.4254 (4)
C2	−0.0010 (11)	0.4507 (4)	0.3878 (4)
C3	−0.1027 (12)	0.1896 (4)	0.3906 (4)
C4	0.1828 (11)	0.2262 (4)	0.6065 (4)
C5	0.3540 (11)	0.2470 (4)	0.5617 (4)
C6	0.0078 (13)	0.5217 (5)	0.3267 (5)
C7	−0.1708 (14)	0.5596 (5)	0.3071 (5)
C8	−0.3497 (14)	0.5309 (5)	0.3469 (5)
C9	−0.3548 (12)	0.4582 (5)	0.4092 (5)
C10	−0.0976 (16)	0.1061 (5)	0.4297 (6)
C11	−0.2661 (18)	0.0542 (6)	0.4212 (7)
C12	−0.4275 (17)	0.0804 (6)	0.3770 (6)
C13	−0.4252 (16)	0.1634 (6)	0.3384 (6)
C14	−0.2603 (14)	0.2183 (5)	0.3447 (6)
C15	0.5321 (12)	0.2183 (5)	0.5854 (5)
C16	0.5336 (13)	0.1609 (5)	0.6623 (5)
C17	0.3594 (14)	0.1404 (5)	0.7095 (5)
C18	0.1783 (13)	0.1718 (5)	0.6846 (4)

B. Thermal Parameters

Atom	B11	B22	B33	B23	B13	B12
P	0.0194	0.0038	0.0030	−0.0020	0.0041	0.0002
O1	0.0213	0.0051	0.0035	−0.0002	0.0035	0.0018
O2	0.0219	0.0041	0.0041	−0.0014	0.0040	0.0016
O3	0.0259	0.0050	0.0035	−0.0023	0.0052	−0.0017
O4	0.0233	0.0043	0.0033	−0.0008	0.0051	0.0009
O5	0.0219	0.0050	0.0036	−0.0022	0.0024	0.0023
C1	0.0258	0.0037	0.0031	−0.0006	0.0013	−0.0010
C2	0.0237	0.0037	0.0037	−0.0016	0.0030	−0.0003
C3	0.0285	0.0042	0.0032	−0.0005	0.0033	−0.0014
C4	0.0240	0.0035	0.0033	−0.0010	0.0026	−0.0003
C5	0.0250	0.0036	0.0033	−0.0021	0.0029	0.0003
C6	0.0298	0.0040	0.0047	−0.0002	0.0019	0.0005
C7	0.0329	0.0042	0.0053	0.0002	0.0002	−0.0008
C8	0.0329	0.0042	0.0054	0.0012	−0.0028	−0.0015
C9	0.0274	0.0045	0.0042	0.0015	0.0001	−0.0012
C10	0.0422	0.0038	0.0063	0.0021	−0.0043	0.0002
C11	0.0528	0.0038	0.0074	−0.0047	−0.0053	0.0003
C12	0.0446	0.0047	0.0069	−0.0045	−0.0034	−0.0016
C13	0.0394	0.0051	0.0071	−0.0029	−0.0069	−0.0021
C14	0.0341	0.0043	0.0058	−0.0019	−0.0079	−0.0006
C15	0.0240	0.0050	0.0043	−0.0012	0.0003	0.0002
C16	0.0305	0.0044	0.0044	−0.0020	−0.0004	−0.0002
C17	0.0344	0.0043	0.0041	0.0010	0.0006	0.0001
C18	0.0330	0.0046	0.0034	0.0008	0.0035	0.0008

Table III

Bond Distances and Angles in Spirodicatecholphenoxyphosphorane (9)

A. In PO_5 Group

Bond angles, deg		Bond distances, Å	
O(1)–P–O(5)	160.02 (2.3)	P–O(1)	1.666 (10)
O(2)–P–O(4)	151.36 (2.1)	P–O(2)	1.666 (10)
O(3)–P–O(4)	105.37 (1.0)	P–O(4)	1.666 (10)
O(2)–P–O(3)	103.26 (1.0)	P–O(5)	1.650 (10)
O(1)–P–O(3)	101.99 (1.0)	P–O(3)	1.597 (10)
O(3)–P–O(5)	97.98 (0.9)		
O(4)–P–O(5)	92.38 (0.8)		
O(1)–P–O(2)	91.47 (0.8)		
O(2)–P–O(5)	83.25 (0.8)		
O(1)–P–O(4)	83.04 (0.8)		

B. In the Phenoxy Ligand (Ring B)

Bond angles, deg		Bond distances, Å	
P–O(3)–C(3)	122.51 (1.8)	O(3)–C(3)	1.403 (17)
O(3)–C(3)–C(14)	120.37 (2.6)		
O(3)–C(3)–C(10)	117.95 (2.5)		

X	*Y*	*Z*	<*XYZ*, deg	*D*(X–Y), Å	*D*(Y–Z), Å
C(3)	C(10)	C(11)	116.35 (3.0)	1.403 (23)	1.418 (28)
C(10)	C(11)	C(12)	124.07 (3.8)	1.418 (28)	1.368 (28)
C(11)	C(12)	C(13)	117.56 (3.5)	1.368 (28)	1.392
C(12)	C(13)	C(14)	120.86 (3.4)	1.392 (27)	1.421 (26)
C(13)	C(14)	C(3)	119.48 (3.1)	1.421 (26)	1.371 (22)
C(14)	C(3)	C(10)	121.65 (3.1)	1.371 (22)	1.403 (23)

C. In Five-Membered Ring Fused to Ring A

Bond angles, deg		Bond distances, Å	
O(1)–P–O(2)	91.47 (0.8)		
P–O(2)–C(2)	111.66 (1.4)	O(2)–C(2)	1.355 (17)
O(2)–C(2)–C(1)	113.41 (2.1)	O(1)–C(1)	1.403 (16)
C(2)–C(1)–O(1)	109.34 (1.8)	C(1)–C(2)	1.382 (19)
C(1)–O(1)–P	111.83 (1.4)		
O(1)–C(1)–C(9)	124.24 (2.0)		
O(2)–C(2)–C(6)	125.74 (1.8)		

D. In Ring A

X	*Y*	*Z*	<*XYZ*, deg	*D*(X–Y), Å	*D*(Y–Z), Å
C(1)	C(2)	C(6)	120.83 (2.7)	1.382 (19)	1.413 (21)
C(2)	C(6)	C(7)	115.31 (2.6)	1.413 (21)	1.401 (21)
C(6)	C(7)	C(8)	123.13 (3.1)	1.401 (21)	1.424 (23)
C(7)	C(8)	C(9)	120.47 (2.9)	1.424 (23)	1.444 (23)
C(8)	C(9)	C(1)	113.84 (2.5)	1.444 (23)	1.374 (21)
C(9)	C(1)	C(2)	126.40 (2.9)	1.374 (21)	1.382 (19)

E. In Five-Membered Ring Fused to Ring C

Bond angles, deg		Bond distances, Å	
O(4)–P–O(5)	92.38 (0.8)	O(4)–C(4)	1.368 (17)
P–O(4)–C(4)	110.76 (1.4)	O(5)–C(5)	1.405 (17)
O(4)–C(4)–C(5)	113.78 (2.0)	C(4)–C(5)	1.377 (19)
C(4)–C(5)–O(5)	109.21 (1.8)		
C(5)–O(5)–P	112.23 (1.4)		
O(4)–C(4)–C(18)	124.48 (2.1)		
O(5)–C(5)–C(15)	125.81 (1.8)		

F. In Ring C

X	*Y*	*Z*	<*XYZ*, deg	*D*(X–Y), Å	*D*(Y–Z), Å
C(4)	C(5)	C(15)	124.92 (2.9)	1.377 (19)	1.361 (21)
C(5)	C(15)	C(16)	115.25 (2.5)	1.361 (21)	1.437 (23)
C(15)	C(16)	C(17)	120.21 (2.9)	1.437 (23)	1.410 (23)
C(16)	C(17)	C(18)	123.44 (3.1)	1.410 (23)	1.399 (23)
C(17)	C(18)	C(4)	114.47 (2.5)	1.399 (23)	1.423 (21)
C(18)	C(4)	C(5)	121.67 (2.6)	1.423 (21)	1.377 (19)

planes, are given in Table V. The dihedral angles formed by pairs of these planes are shown in Table VI.

The data in Tables III–VI demonstrate that the skeletal geometry about the phosphorus atom in the spiropentaoxyphosphorane **9** does not resemble a regular TBP, or even a reasonably distorted TBP. This is brought out by Figure 1, which is a drawing of the molecule of **9** generated by computer from the experimental data, and by formula I, Figure 2, which is the hypothetical ideal TBP arrangement of the P05 group. In formula I, the five-membered rings formed by the phosphorus atom and the two catechol bidentate ligands, A and C, are placed in apical-equatorial skeletal positions in accordance with previous observations[5] in the related system **2**.

A superficial examination of the data suggests, at first, the skeletal geometry of a regular TP for compound **9**. However, a more detailed analysis reveals significant deviations from ideal TP symmetry. This is shown in Figure 3 and in the hypothetical ideal TP arrangement of the P05 group, namely, formula II,[33,34] Figure 2. This question will be discussed in the next sections.

Table IV
Intramolecular Nonbonded Distances
$\leqslant 3.5$ Å in Compound 9

O(2)–O(5)	2.203 (14)	O(1)–O(3)	2.536 (14)
O(1)–O(4)	2.208 (13)	O(2)–O(3)	2.559 (14)
O(1)–O(2)	2.386 (14)	O(3)–O(4)	2.595 (14)
O(4)–O(5)	2.392 (13)	O(2)–O(4)	3.228 (13)
O(3)–O(5)	2.450 (14)	O(1)–O(5)	3.265 (13)
C(3)–O(1)	2.868 (17)	C(1)–O(3)	3.238 (17)
C(3)–O(4)	3.051 (17)	C(4)–O(3)	3.236 (17)
C(5)–O(3)	3.202 (17)	C(2)–O(5)	3.502 (17)
C(2)–O(3)	3.218 (17)	C(4)–O(1)	3.515 (17)
C(14)–O(3)	2.406 (20)	C(14)–O(1)	3.038 (20)
C(10)–O(3)	2.404 (21)		
P–C(4)	2.502 (14)	P–C(3)	2.632 (14)
P–C(2)	2.506 (14)	P–C(14)	3.417 (17)
P–C(5)	2.539 (14)	P–C(10)	3.501 (19)
P–C(1)	2.546 (14)		

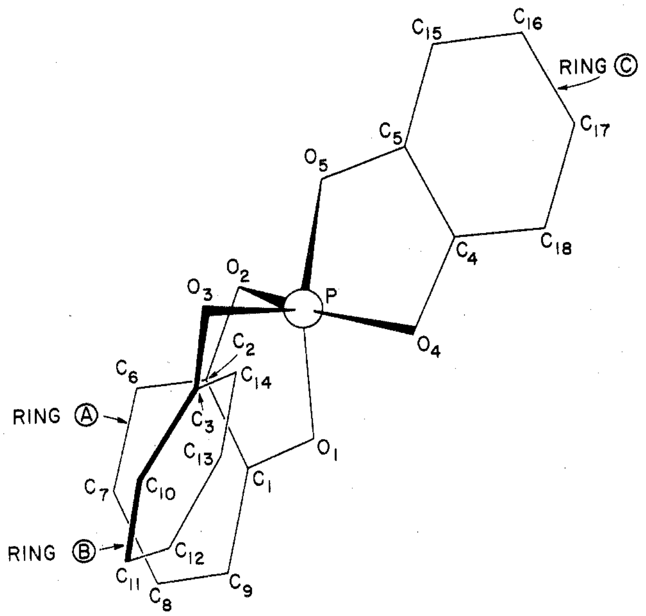


Figure 1. Computer-generated drawing of one molecule of spirodicatecholphenoxyphosphorane (**9**), emphasizing the deviations from the ideal skeletal TBP geometry. Best least-squares plane is P, O(2), O(3), O(4).

It is suggested that the skeletal geometry of the molecules of **9** in the crystal resembles that of a *15°-TR configuration*.[13,20,38] The TR mechanism was advanced as a dynamic concept (see Figure 4), but it appears that in certain phosphoranes, including a "homophosphorane" such as **9**, the TR configuration represents the best compromise between the tendency of the phosphorus to become TBP, the strain present in both rings, and the various steric requirements associated with the bond angles, the interatomic distances, and the intramolecular nonbonded distances.

In TR, the five ligands of I ≡ a move as a pair, which is made up of the ligands of catechol C, O(4), O(5), and as a trio, which consists of the exocyclic ligand O(3) plus the ligands of catechol A, O(1), O(2).[35] The diequatorial angle of the trio, O(2)–P–O(3), contracts from 120° to 90° to give b. The pair tilts 9° in the plane P, O(1), O(4), O(5), toward the apical ligand of the trio, O(1), to give c, which is conveniently represented by the Newman projection d. The pair rotates (or twists) against the trio in opposite directions, with the pair-equatorial O(4) moving toward the trio-equatorial O(3) that will remain equatorial in the newly formed TBP.[36] *The ideal 15°-TR configuration is depicted in formula e.* Further rotation leads to the 30°-TR, f, and the

Table V
Least-Squares Planes[a]

A. Deviations from the Planes of All Atoms Included in the Plane Calculation

1. P, O(2), O(3), O(4)
$0.9601X - 0.2578Y + 0.1080Z = 0.2382$; P, −0.003; O(2), 0.001; O(3), 0.001; O(4), 0.001
2. P, O(1), O(3), O(5)
$-0.1803X - 0.6852Y + 0.7057Z = 1.4922$; P, 0.006; O(1), −0.003; O(3), −0.001; O(5), −0.003
3. P, O(1), O(2), O(5)
$0.1164X + 0.5978Y + 0.7931Z = 8.7139$; P, −0.188; O(1), 0.095; O(2), −0.006; O(5), 0.096
4. P, O(1), O(4), O(5)
$0.1653X + 0.7838Y + 0.5986Z = 8.2901$; P, −0.192; O(1), 0.093; O(4), 0.002; O(5), 0.094
5. O(1), O(2), O(4), O(5)
$0.1425X + 0.6996Y + 0.7002Z = 8.7355$; O(1), −0.062; O(2), 0.062; O(4), 0.062; O(5), −0.062
6. P, O(1), O(2), C(1), C(2)
$0.1792X + 0.5700Y + 0.8019Z = 8.5871$; P, −0.087; O(1), 0.084; O(2), 0.079; C(1), −0.042; C(2), 0.035
7. C(1), C(2), C(6), C(7), C(8), C(9)
$0.1287X + 0.6352Y + 0.7616Z = 8.7661$; C(1), 0.001; C(2), −0.002; C(6), 0.005; C(7), −0.007; C(8), 0.005; C(9), −0.002
8. P, O(4), O(5), C(4), C(5)
$0.0879X + 0.8220Y + 0.5627Z = 8.0472$; P, −0.075; O(4), 0.066; O(5), 0.071; C(4), −0.027; C(5), −0.036
9. C(4), C(5), C(15), C(16), C(17), C(18)
$0.1255X + 0.7968Y + 0.5911Z = 8.2530$; C(4), −0.010; C(5), −0.001; C(15), 0.012; C(16), −0.012; C(17), 0.002; C(18), 0.009
10. C(3), C(10), C(11), C(12), C(13), C(14)
$-0.3570X + 0.3822Y + 0.8523Z = 6.2170$; C(3), 0.009; C(10), −0.006; C(11), 0.006; C(12), 0.002; C(13), 0.001; C(14), 0.006
11. O(3), C(3), C(10), C(14)
$-0.3573X + 0.3822Y + 0.8522Z = 6.2143$; O(3), 0.011; C(3), 0.011; C(10), −0.004; C(14), −0.004

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

12. O(2), O(3), O(4)
Same as plane 1
P, −0.004
13. O(1), O(3), O(5)
Same as plane 2
P, 0.008
14. O(1), O(2), O(5)
$0.1283X + 0.6453Y + 0.7531Z = 8.769$; P, −0.286
15. O(1), O(4), O(5)
$0.1559X + 0.7497Y + 0.6432Z = 8.5252$; P, 0.287
16. O(2), O(4), O(5)
$0.2150X + 0.6763Y + 0.7046Z = 8.768$; P, 0.410
17. O(1), O(2), O(4)
$0.0693X + 0.7190Y + 0.6915Z = 8.775$; P, −0.411
18. O(1), O(2), O(3)
$0.5022X - 0.2224Y + 0.8357Z = 4.372$; P, 0.784
19. O(3), O(4), O(5)
$-0.3699X + 0.9168Y - 0.1508Z = 2.303$; P, 0.787
20. O(1), O(3), O(4)
$0.7617X + 0.6474Y = 0.0284Z = 2.783$; P, 0.816
21. O(2), O(3), O(5)
$-0.6327X + 0.0757Y + 0.7707Z = 4.433$; P, 0.852
5. O(1), O(2), O(4), O(5)
$0.1425X + 0.6996Y + 0.7002Z = 8.7355$: P, −0.350

C. Three-Atom Planes for Calculation of Dihedral Angles

22. P, O(3), C(3)
$0.4292X - 0.6753Y + 0.5998Z = 1.2637$
23. P, O(1), O(2)
$0.2516X + 0.4551Y + 0.8541Z = 8.3659$
24. P, O(1), O(4)
$0.3421X + 0.7887Y + 0.5108Z = 7.6400$
25. P, O(2), O(5)
$-0.0693X + 0.5511Y + 0.8316Z = 8.4295$
26. P, O(4), O(5)
$0.0170X + 0.8788Y + 0.4769Z = 7.5925$

[a] X, Y, and Z are in orthogonal coordinates with deviations of the individual atoms from the planes given in Å.

Table VI
Some Dihedral Angles Between Planes[a]

Plane a	Plane b	Angle, deg	Plane a	Plane b	Angle, deg
1	2	85	19	1	53
1	3	88	18	5	60
1	4	89	21	5	60
2	3	83	19	5	61
2	4	82	20	5	57
3	4	16	18	17	63
2	5	88	18	20	78
1	5	89	17	20	60
6	8	21	21	16	63
8	24	15	21	19	79
6	25	14	16	19	64
11	22	84	18	21	72
1	22	49	18	19	59
2	22	36	18	20	78
6	7	5	20	19	72
8	9	3	17	16	9
7	17	7	21	19	79
9	17	8	21	20	63
7	8	3	19	20	72
9	4	2	14	15	9
7	1	88	23	26	36
9	1	89	24	25	33
18	1	51	23	5	18
17	1	87	23	5	17
20	1	56	26	5	18
21	1	57	24	5	17
16	1	84			

[a] The planes are defined in Table V. The dihedral angles, θ, are expressed as $\leqslant 90°$. To visualize these angles in terms of Figures 1–5, use θ or $180° - \theta$.

60°-TR, g ≡ h, configurations. From i a tilt of the pair, O(5), O(4), away from O(2), and an expansion of angle O(1)–P–O(3) from 90° to 120° generates the new TBP isomer (j). It is recognized that the configuration of the molecules of **9** in solution need not be like that in the crystal, but the absence of strongly polar groups suggests that the differences may not be very significant. If so, compound **9** in solution can undergo facile permutational isomerization from a 15°-TR to a 45°-TR simply by going over a barrier that resembles the 30°-TR (f in Figure 4) and is not much higher in energy than the ground state configuration.

Molecular Parameters of Compound 9 in Relation to the TBP, TP, and TR Skeletal Geometries. A. Bond Distances. The virtual identity of the four endocyclic P–O bond lengths in **9** contrasts with the difference between the

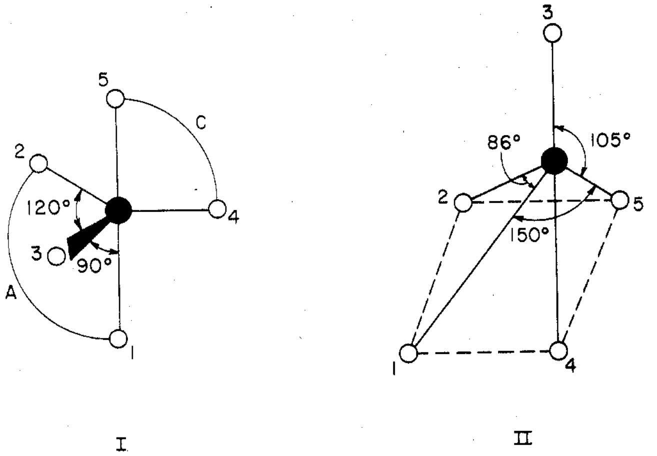


Figure 2. The five oxygen ligands of compound **9** with hypothetical ideal skeletal geometries: I = TBP; II = TP.

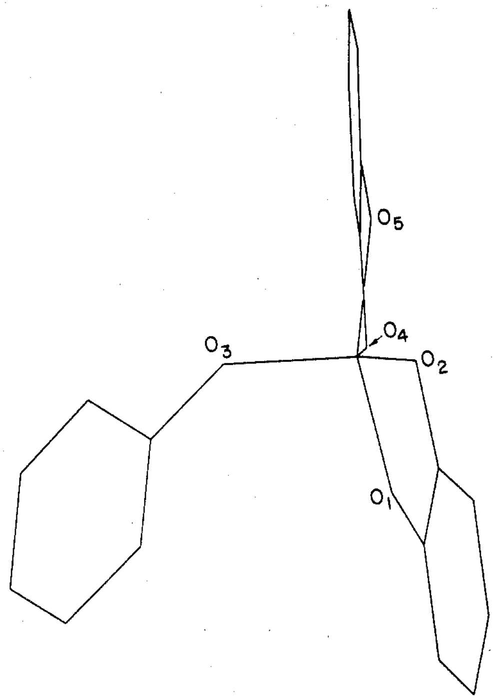


Figure 3. Computer-generated drawing of the molecule of **9** emphasizing the deviations from the ideal skeletal TP geometry. Note the twisted spirobicyclic system.

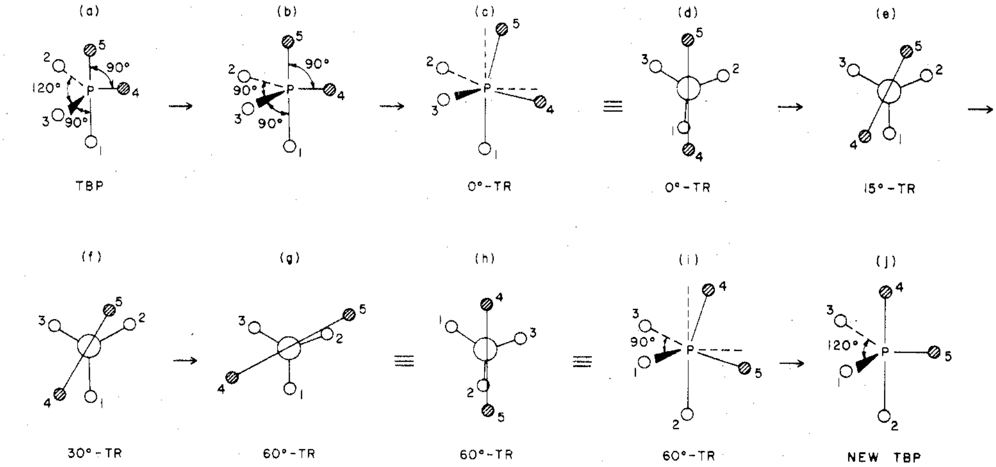


Figure 4. Permutational isomerization of an oxyphosphorane with ideal TBP skeletal symmetry by the turnstile rotation (TR). Ligand pair = O(4), O(5). Ligand trio = O(1), O(2), O(3).

Table VII
Deviations from Ideal Skeletal Symmetries in Compound 9

A. From Trigonal Bipyramid (TBP)

Bond angle	Deviation from TBP	Bond angle	Deviation from TBP
O(2)–P–O(3)	−16.7° (from 120°)	O(2)–P–O(4)	+31.4° (from 120°)
O(1)–P–O(5)	−20.0° (from 180°)	O(1)–P–O(3)	+12.0° (from 90°)
O(4)–P–O(5)	+2.4° (from 90°)	O(3)–P–O(5)	+8.0° (from 90°)
O(1)–P–O(4)	−7.0° (from 90°)	O(2)–P–O(5)	−6.7° (from 90°)
O(3)–P–O(4)	−14.6° (from 120°)	O(1)–P–O(2)	+1.5° (from 90°)

B. From Tetragonal Pyramid (TP)

Bond angle	Deviation from TP	Bond angle	Deviation from TP
O(1)–P–O(5)	+10° (from 150°)	O(3)–P–O(4)	+0.4° (from 105°)
O(2)–P–O(4)	+1.5° (from 150°)	O(1)–P–O(4)	−3.0° (from 86°)
O(3)–P–O(5)	−7.0° (from 105°)	O(2)–P–O(5)	−2.8° (from 86°)
O(1)–P–O(3)	−3.0° (from 105°)	O(1)–P–O(2)	+5.5° (from 86°)
O(2)–P–O(3)	−1.7° (from 105°)	O(4)–P–O(5)	+6.4° (from 86°)

apical and equatorial endocyclic P–O bond lengths in **2**.[5] The exocyclic P–O(3) bond in **9** is relatively short; this suggests that the catechol rings are competitors for the electrons of the oxygen atoms which can contribute to p–d π bonding in the P–O bonds. On the other hand, the corresponding oxygen electrons of the phenoxy ligand are more available for π bonding to phosphorus, which causes the relative shortening of that P–O bond.

B. Bond Angles. The O–P–O angles fall in three categories: two angles are relatively large, four are intermediate in value, and four are relatively small. The data are consistent with the TR or TP geometries, but not with the TBP configuration; see Table VII. Angle O(2)–P–O(3) is the "diequatorial angle of the trio" in the TR mechanism (Figure 4). In this interpretation angle O(2)–P–O(4) has expanded +31° from the TBP 120° as a result of the motion of O(4) toward O(3). Among the deviations from TP note the expansion of O((1)–P–O(5) and the contraction of O(3)–P–O(5).

The two endocyclic angles, O(1)–P–O(2) and O(4)–P–O(5), are quite small and suggestive of the overall ring strain associated with the spiropentaoxyphosphorane system.

C. Intramolecular Nonbonded Distances. As shown in Table IV, the O–O distances are consistent with TR or TP configurations, but not with TBP geometry.

The O–O and C–O distances disclose considerable intramolecular crowding. The placement of the phenoxy ring may be related to this feature. The estimated[37] half-thickness of the aromatic ring is 1.85 Å, and the maximum separations between O(3) and other oxygens are O(2)–O(3) = 2.56 Å and O(3)–O(4) = 2.59 Å. Models show that, in fact, ring B occupies the most favorable position to avoid interferences between ring B and the catechol rings A and C. Note also the relatively short distances C(3)–O(1) and C(14)–O(1) (the latter compared to C(10)–O(1) = 3.87 Å).

D. Least-Squares Planes and Dihedral Angles Between Them. The planarity of the catechol ring systems, A and C, is evident in planes 6–9 (Table V). Ring B is planar (plane 10) and O(3) is on that plane (plane 11). The dihedral angles formed by planes 11 and 22, and by planes 1 and 22, reveal the position of ring B.

In the regular TBP the phosphorus should be in these planes: O(2), O(3), O(4); O(1), O(2), O(5); O(1), O(3), O(5); O(1), O(4), O(5). In compound **9** this is true only for the first two planes (1 and 2 in Table V). Both TR and TP geometries can accommodate these observations. Planes 1 and 2 are nearly, but not exactly, orthogonal (Table VI).

Four oxygens define a fairly good plane (5 in Table V) as would be expected of a TP (II, Figure 2). However, note that O(1), O(5) are on one side of the plane, while O(2), O(4), are on the opposite side; these pairs would be transdibasal in the regular TP. The P is 0.350 Å from plane 5 and on the same side as O(1), O(5). These deviations from regular TP can, in fact, be seen in Figure 3. One can imagine that O(1) and O(5) have been lifted from the basal plane of the TP, toward the phosphorus. The net effect is a twist of one catechol A against the other, C.

The dihedral angle between planes 8 and 24 (Table V) is 15° (Table VI). This angles is the basis for assigning the 15°-TR configuration to the skeletal geometry of compound **9**.

Other deviations from ideal TBP and TP geometry are revealed by the positions of the phosphorus atom with respect to several three-oxygen planes (Table V), and by a number of dihedral angles given in Table VI.

It seems clear that spirobicyclic phosphoranes, not only those which have different kinds of ligands bonded to the phosphorus,[14–18] such as **10**, **11**, **12**, and **13**, but also those of the pentaoxyphosphorane type, **9**, depart drastically from the skeletal geometry of the TBP. However, whether these departures should be described in terms of "hybrids" between TP and TBP[17] or in terms of TR configurations is debatable. The fact is that a number of known phosphoranes are ideal or nearly ideal TBP, while none is an ideal or nearly ideal TP. Hence, the simplest thing is to express the deviations from ideal TBP in terms of the same type of skeletal geometry, such as the TR configuration,[38] which can accommodate all the data. With this approach, the x-ray data for a new structure can be easily sorted out. First, the ligands are placed on an ideal TBP skeleton according to the assumptions and rules of the oxyphosphorane concept, e.g., apicophilicities, placement of four-, five- and six-membered rings in appropriate skeletal positions of the ideal TBP, etc.[7,13,20] Then, the motions of the atoms on the TR mechanism are applied to the ideal TBP molecule as defined in Figure 4. Finally, the actual molecular parameters are compared with the expectations based on this treatment and the soundness of the original choice of pair–trio combination is assessed by the correspondence between the expected and the observed parameters.

Acknowledgment. We are grateful to Drs. H. J. Bernstein and L. Andrews of Brookhaven National Laboratories, Upton, N.Y., for their advice in the production of Figures 1, 3. The TR concept which guided us in the interpretation of the experimental data stems from an extended collaboration between one of us (F.R.) and Professor I. Ugi and Dr. D. Marquarding of Technische Universität, München.

Registry No.—9, 19579-02-3.

Supplementary Material Available. Table II (26 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Send correspondence to this author at the Department of Biochemistry, State University of New York at Stony Brook. (b) Department of Chemistry, State University of New York. The support of this research by the National Science Foundation Grant GP-40523 is gratefully acknowledged.
(2) F. Ramirez, *Acc. Chem. Res.*, **1**, 168 (1968).
(3) F. Ramirez, *Synthesis*, 90 (1974).
(4) The following abbreviations will be used: TBP = trigonal bipyramid or trigonal bipyramidal; TP = tetragonal pyramid or tetragonal pyramidal; TR = turnstile rotation.
(5) (a) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Am. Chem. Soc.*, **87**, 127 (1965); (b) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *ibid.*, **89**, 2268 (1967).
(6) (a) F. Ramirez, M. Nagabhushanam, and C. P. Smith, *Tetrahedron*, **24**, 1785 (1968); (b) F. Ramirez, A. J. Bigler, and C. P. Smith, *ibid.*, **24**, 5041 (1968).
(7) F. Ramirez, *Bull. Soc. Chim. Fr.*, 3491 (1970).
(8) K. W. Shen, W. E. McEwen, S. J. LaPlaca, W. C. Hamilton, and A. P. Wolf, *J. Am. Chem. Soc.*, **90**, 1718 (1968).
(9) F. Ramirez, I. Ugi, S. Pfohl, E. A. Tsolis, J. F. Pilot, C. P. Smith, P. Gillespie, P. Hoffmann, and D. Marquarding, *Phosphorus*, **1**, 1 (1971).
(10) F. Ramirez, I. Ugi, F. Lin, S. Pfohl, P. Hoffmann, and D. Marquarding, *Tetrahedron*, **30**, 371 (1974).
(11) W. C. Hamilton, J. S. Ricci, Jr., F. Ramirez, L. Kramer, and P. Stern, *J. Am. Chem. Soc.*, **95**, 6335 (1973).
(12) H. L. Carrell, H. M. Berman, J. S. Ricci, Jr., W. C. Hamilton, F. Ramirez, J. F. Marecek, L. Kramer, and I. Ugi, *J. Am. Chem. Soc.*, **97**, 38 (1975).
(13) (a) P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971); (b) F. Ramirez and I. Ugi, *Adv. Phys. Org. Chem.*, **9**, 256 (1971).
(14) (a) H. Wunderlich, D. Mootz, R. Schmutzler, and M. Wieber, *Z. Naturforsch. B*, **29**, 32 (1974); (b) H. Wunderlich and D. Mootz, *Acta Crystallogr., Sect. B*, **30**, 935 (1974); (c) H. Wunderlich, *ibid.*, **30**, 939 (1974).
(15) M. Eisenhut, R. Schmutzler, and W. S. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 144 (1973).
(16) E. Duff, D. R. Russell, and S. Trippett, *Phosphorus*, **4**, 203 (1974).
(17) (a) R. R. Holmes, *J. Am. Chem. Soc.*, **96**, 4143 (1974); (b) *Acc. Chem. Res.*, **5**, 296 (1972).
(18) J. A. Howard, D. R. Russell, and S. Trippett, *J. Chem. Soc., Chem. Commun.*, 856 (1973).
(19) M. Ul-Haque, C. N. Caughlan, F. Ramirez, J. F. Pilot, and C. P. Smith, *J. Am. Chem. Soc.*, **93**, 5229 (1971).
(20) F. Ramirez and I. Ugi, *Bull. Soc. Chim. Fr.*, 453 (1974).
(21) P. J. Wheatley, *J. Chem. Soc.*, 2206 (1964).
(22) H. Hess and D. Frost, *Z. Anorg. Allg. Chem.*, **342**, 240 (1966).
(23) L. G. Hoard and R. A. Jacobson, *J. Chem. Soc. A*, 1203 (1966).
(24) J. W. Cox and E. R. Corey, *Chem. Commun.*, 123 (1967).
(25) G. Chioccola and J. J. Daly, *J. Chem. Soc. A*, 568 (1968).
(26) A. Almenningen, B. Anderson, and E. E. Artrup, *Acta Chem. Scand.*, **23**, 2179 (1969).
(27) D. D. Swank, C. N. Caughlan, F. Ramirez, and J. F. Pilot, *J. Am. Chem. Soc.*, **93**, 5236 (1971).
(28) M. J. C. Hewson, R. Schmutzler, and W. S. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 190 (1973).
(29) A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, **24**, 351 (1968).
(30) G. A. Sim, *Acta Crystallogr.*, **13**, 511 (1960).
(31) D. E. Pilling, D. W. J. Cruickshank, A. Bujosa, F. M. Lovell, and M. R. Truter in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis", Pergamon Press, Oxford, 1961, p 32.
(32) The value of 1.76 Å has been given for the pure single P–O bond: D. W. Cruickshank, *J. Chem. Soc.*, 5486 (1961).
(33) TBP formula I (Figure 2) becomes TP formula II as a result of a 30° contraction of angle O(1)–P–O(5) *in the plane P, O(1), O(3), O(5)*, and a 30° expansion of angle O(2)–P–O(4) *in the plane P, O(2), O(3), O(4)*; these two planes are orthogonal at all stages of the motions. These motions form part of the Berry pseudorotation mechanism to explain the permutational isomerization of phosphoranes having regular or slightly distorted TBP geometry (cf. ref 34).
(34) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).
(35) The choice of ligands O(1), O(2) of catechol A as the pair, and of ligand O(3) plus ligands O(4), O(5) of catechol C as the trio, provides an alternate and nearly equivalent TR mechanism for compound **9**. To visualize this alternative rotate formula a, Figure 4, 180° about bond P–O(3), and carry out a set of motions analogous to those depicted in Figure 4, using the appropriate ligands. The TR mechanisms of **9** using O(1), O(2) or O(4), O(5) as the pair generate configurations which are indistinguishable within the uncertainty in the data of Tables III–VII.
(36) To retain the apical-equatorial placement of the five-membered rings in the ideal TBP, O(4) must move toward O(3).
(37) L. Pauling, "The Nature of the Chemical Bond", 2nd ed, Cornell University Press, Ithaca, N.Y., 1948, p 189.
(38) NOTE ADDED IN PROOF. The term "static TR configuration" is a convenient designation for those phosphoranes which clearly do not resemble a TBP about the phosphorus atom. As originally conceived (ref 13), "TR configuration" had the dynamic connotation defined in Figure 4; however, this concept now seems more general and capable of providing an adequate description of the molecular geometry of certain complex phosphoranes. X-Ray analyses carried out since the submisssion of this paper have uncovered other examples of 5,5-spirobicyclic homophosphoranes (five oxygen ligands), and 5-monocyclic heterophosphoranes (two oxygen and three carbon ligands) whose geometry conform to the definition of static TR configuration.

Structural Effects on Excited State Production by Dioxetanes. 3,4-Dimethyl-3,4-diphenyldioxetane and 3-Methyl-3-phenyldioxetane

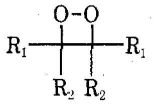
Martha A. Umbreit and Emil H. White*

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

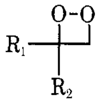
Received August 12, 1975

The preparation of 3,4-dimethyl-3,4-diphenyldioxetane (**1c**) is reported. Its activation energy for decomposition is 25 ± 1 kcal/mol, and its activation entropy is −3 ± 3 eu. The efficiency of excited triplet ketone production of **1c** is equal to that of tetramethyldioxetane (**1a**) as determined by direct comparison of dioxetane-induced dibromoanthracene emission. The efficiency of 3-methyl-3-phenyldioxetane (**2c**), determined by the same method, is less than one-third that of **1a**.

Excited triplet carbonyl products are efficiently generated in the thermal cleavage of 1,2-dioxetanes in apparent violation of spin-conservation rules.[1,2] Large differences have been observed in the yields of triplet products (in effect, the percentage of carbonyl products formed in the triplet state) from various dioxetanes,[1,3] although no explanations for this have been advanced. The efficiencies range from 30–50% for tetramethyldioxetane (**1a**) (100% corresponds to one triplet carbonyl per dioxetane[4])[1b] to 2–4% for 3,4-dimethyl-3,4-di-*n*-butyldioxetane (**1b**)[3a,5] and 3,3-dibenzyl- and 3,3-diphenyldioxetanes (**2a**[3b] and **2b**).[3c] In an effort to identify some of the basic structural factors affecting the efficiency of triplet production, we wish to report the efficiences of excited state formation of the dioxetanes **1c** and **2c** relative to **1a**.



1a, $R_1 = R_2 = Me$
b, $R_1 = Me$; $R_2 = n\text{-}Bu$
c, $R_1 = Me$; $R_2 = Ph$
d, $R_1 = H$; $R_2 = OEt$



2a, $R_1 = R_2 = CH_2Ph$
b, $R_1 = R_2 = Ph$
c, $R_1 = Me$; $R_2 = Ph$

We have prepared the new dioxetane, 3,4-dimethyl-3,4-diphenyldioxetane (**1c**), via the bromohydroperoxide, by a