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Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

## Crystal and Molecular Structure of the Spirophosphorane $(C_6H_4O_2)_2PCl$

RICHARD K. BROWN<sup>2</sup> and ROBERT R. HOLMES\*

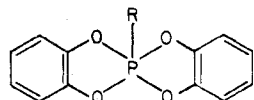
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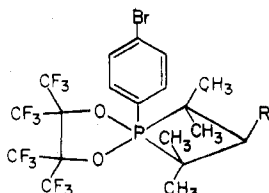
The crystal structure of 2-chloro-2,2'-spiobis(1,3,2-benzodioxaphosphole),  $(C_6H_4O_2)_2PCl$ , has been determined by single-crystal x-ray diffraction analysis. The compound crystallizes in the monoclinic space group,  $P2_1/n$ , with cell constants  $a = 6.748$  (6) Å,  $b = 12.638$  (8) Å,  $c = 14.229$  (9) Å,  $\beta = 76.19$  (5)°, and  $Z = 4$ . The molecule contains a noncrystallographic twofold axis about the P-Cl bond. With reference to the Berry coordinate, the geometry about phosphorus is 72% displaced from a trigonal bipyramid (TP) toward a rectangular pyramid (RP). Pertinent features of the molecule are the diagonal O-P-O angles, 162.9 (1)° and 149.8 (1)°, and the four bond angles between the axial chlorine atom and the basal P-O bonds, 105.0 (1), 98.3 (1), 98.8 (1), and 105.3 (1)°. The differences in the basal P-O bond lengths, 1.643 (3) and 1.640 (3) vs. 1.657 (3) and 1.662 (3) Å, are indicative of small residual trigonal-bipyramidal character. The phosphorus atom is 0.338 Å out of the mean plane of the four oxygen atoms toward the axial chlorine atom. The structure is discussed with respect to its position in the series of related substances,  $(C_6H_4O_2)_2PR$  ( $R = F, Cl, Ph, adamantyl, CH_3, \text{ and } OPh$ ), and comparisons are made with the structures of  $(CF_3)_2PCl_3$  and  $(CF_3)_3PCl_2$ .

### Introduction

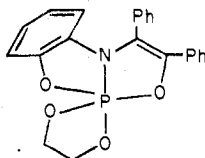
Interesting five-coordinate cyclic phosphorane structures have recently been established by x-ray crystallography.<sup>3-19</sup> Among these are I-VI shown below. The conformations of



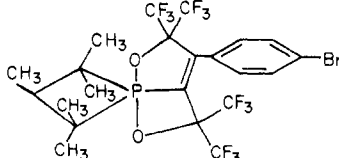
I, R = Me,<sup>4b</sup> OPh,<sup>8</sup> Ad,<sup>16</sup> Ph,<sup>5</sup> Fe<sup>4c</sup> (Ad = adamantyl)



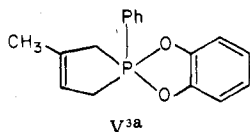
II,<sup>19</sup> R = H, CH<sub>3</sub>



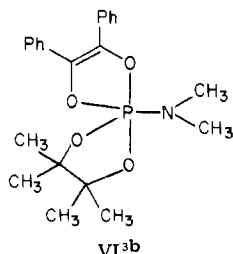
III<sup>15</sup>



IV<sup>18</sup>



V<sup>3a</sup>



VI<sup>3b</sup>

I, II, and V show relatively modest structural deviations from a rectangular pyramid (RP) while the conformations of III, IV, and VI are best viewed in terms of some degree of structural variation from the idealized trigonal bipyramid (TP).<sup>20a</sup> For the five-membered cyclic derivatives, the Berry coordinate<sup>21</sup> accurately reflects the type of structural distortion encountered.<sup>20</sup>

Factors important in influencing the observed structural variations have been discussed<sup>20,22</sup> and serve in an initial attempt to reproduce some of these structures via conformational minimization techniques<sup>1b,23</sup> based on a well-parameterized molecular mechanics model.<sup>1b,23,24</sup> The success in this attempt has led to the application of the computer simulation method to quantitatively delineate the course of the action of ribonuclease on nucleic acid substrates.<sup>25</sup> The latter are postulated to hydrolytically break down by way of phosphorane intermediates.<sup>26</sup>

Examination of the ligand construction for the derivatives I-VI suggests factors that appear dominant in determining the structures of cyclic phosphoranones. Neither carbon or nitrogen, due to the low electronegativity<sup>27</sup> of the former and high equatorial  $\pi$ -bonding characteristics<sup>28</sup> of the latter, prefers to reside in axial positions of a TP. Such factors contribute as structural determinants in II, IV, and V.<sup>22</sup> The presence of ring unsaturation and electron delocalization contribute as factors determining the structures of derivatives of I. Increased ligand electronegativity in III compared to IV and ring constraints of III relative to VI serve to establish the resulting structure of III. When VI is compared to members of I, the influence of ring unsaturation appears contributory in stabilizing the RP.<sup>22</sup>

It is important to assess the comparative role of each of the factors influencing the geometries of cyclic phosphoranones in

order to gain insight into the structural determinants for analogous transition states that are proposed in many reaction mechanisms<sup>29</sup> of four-coordinate phosphorus. Toward this goal, we report here the single-crystal analysis of the chloro derivative of I (R = Cl).

The fluoro derivative of I appears structurally<sup>4c</sup> at one end of the series (toward the TP) while the methyl derivative<sup>4b</sup> appears at the opposite end (near the idealized RP).<sup>20a</sup> More extensive comparisons in this series are possible if the structure of the chloro derivative is obtained. Further, it is of interest to compare structural observations on the chloro derivative with the recently reported TP structures for the acyclic perfluorophosphoranes, (CF<sub>3</sub>)<sub>2</sub>PCl<sub>3</sub> and (CF<sub>3</sub>)<sub>3</sub>PCl<sub>2</sub>, obtained by electron diffraction.<sup>30</sup> Thus, the structural influence of the cyclic system in I may be ascertained.

### Experimental Section

**Preparation.** Samples of 2-chloro-2,2'-spirobis(1,3,2-benzodioxaphosphole), I (R = Cl), were prepared by a previously reported method.<sup>31</sup> It was necessary to thoroughly dry all solvents and carry out all manipulations under a dry nitrogen atmosphere. Under normal conditions the complex was found to disproportionate within minutes when exposed to the air. Crystals of the compound suitable for x-ray analysis were obtained by recrystallization from hot benzene. Anal. Calcd for C<sub>12</sub>H<sub>8</sub>O<sub>4</sub>PCl: C, 51.00; H, 2.85; P, 10.96; Cl, 12.54. Found: C, 51.41; H, 3.04; P, 10.56; Cl, 12.92.

**Collection of X-Ray Diffraction Data.** A well-formed transparent crystal of dimensions 0.20 × 0.20 × 0.45 mm was mounted in a glass capillary roughly along the crystal needle axis. As the compound is extremely hygroscopic, it was necessary to do the mounting under a nitrogen atmosphere and to dry the capillary in vacuo over P<sub>2</sub>O<sub>5</sub>.

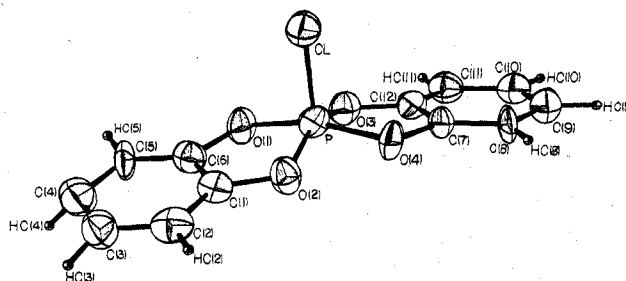
Photographic studies using Weissenberg and precession methods gave approximate unit cell dimensions, showed 2/m Laue symmetry, and indicated the absences 0k0 for k = 2n + 1 and h0l for h + l = 2n + 1. These absences are consistent with the space group P2<sub>1</sub>/n, an alternative setting for P2<sub>1</sub>/c. The crystal was transferred to the Enraf-Nonius CAD-4 diffractometer and accurate unit cell parameters were obtained by refinement of the setting angles of 15 high-order (2θ > 35°) reflections.<sup>32</sup> During data collection each reflection was measured twice. If the two net intensity values were not within 2σ, the reflection was remeasured and tested again. This test was carried out a maximum of three times before the reflection was rejected. Corrections for Lorentz and polarization effects were made. Details of the experimental conditions for data collection are listed in Table I.

**Structure Solution and Refinement.** Initial fractional coordinates for all nonhydrogen atoms were obtained using the direct methods program MULTAN.<sup>33</sup> Isotropic refinement of the coordinates led to R = 0.181 and R<sub>w</sub> = 0.233 for the 1109 reflections with F<sub>o</sub> > 3σF<sub>o</sub>. The form of the least-squares agreement indices as used in Prewitt's<sup>34</sup> SFLS-5 full-matrix least-squares routine is listed in Table I. Conversion to anisotropic refinement and variable weights, w<sup>1/2</sup> = 2LpF<sub>o</sub>/σ(I), led to R = 0.080 and R<sub>w</sub> = 0.108. At this stage of refinement, examination of a difference electron density map yielded positions for the eight independent hydrogen atoms. Further anisotropic refinement of all nonhydrogen atoms and isotropic refinement of all hydrogen atoms led to the agreement indices shown in Table I (D) for the 1343 reflections with F<sub>o</sub> > σF<sub>o</sub>. No unusual or significant trends were observed in the analysis of Σw(|F<sub>o</sub>| - |F<sub>c</sub>|)<sup>2</sup> as a function of |F<sub>o</sub>|, (sin θ)/λ, or the various classes of Miller indices.<sup>35</sup> The largest shift in any variable during the last cycle of refinement was 0.12 times its estimated standard deviation. A final difference Fourier map indicated no peaks larger than 0.9 e/Å<sup>3</sup>, about 25% of the height of a peak for a typical carbon atom.

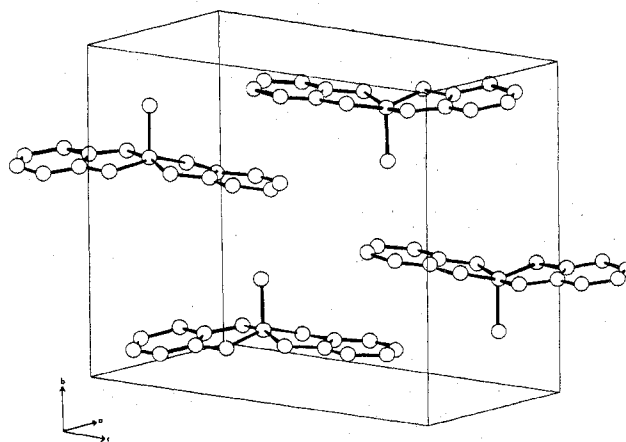
### Results and Discussion

The positional and thermal parameters from the final cycle of least-squares refinement for I (R = Cl) are presented in Tables II and III, respectively. Bond lengths and angles are listed in Table IV and Figure 1 shows the molecular geometry. The unit cell arrangement is displayed in Figure 2. There are no short intermolecular distances.

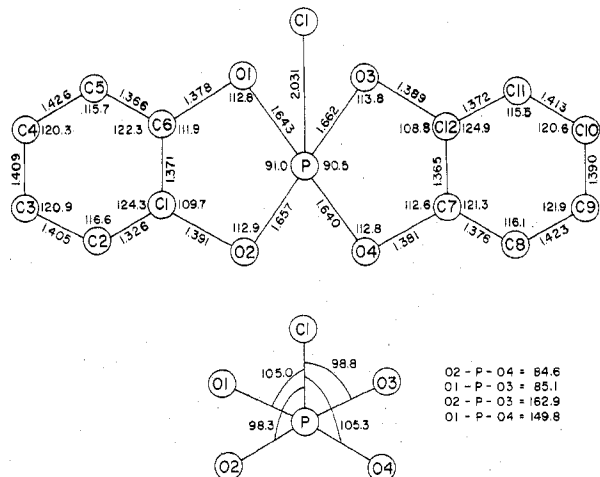
The molecular geometry is grossly represented as a RP evident from the principal bond parameters displayed in Figure



**Figure 1.** Molecular structure of (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)<sub>2</sub>PCl. Thermal ellipsoids of nonhydrogen atoms are shown at the 50% probability level. For clarity, the hydrogen atoms are represented as spheres of radius 0.30 Å. (C. K. Johnson's ORTEP program, Report ORNL-3794, Oak Ridge National Laboratory, 1965.)



**Figure 2.** Molecular packing diagram of (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)<sub>2</sub>PCl.



**Figure 3.** Schematic diagram of (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)<sub>2</sub>PCl illustrating bond parameters (distances, Å; angles, deg).

3. The four "catechol" oxygen atoms form an approximate base of a RP as the least-squares plane I listed in Table V indicates. The four oxygen atoms which make up the rectangular base show the nonbonded distances listed in Table VI, O(1)-O(2) close to O(3)-O(4) and O(1)-O(3) close to O(2)-O(4). The average values of the sides of the rectangle are 2.23 and 2.35 Å.

The unique axial position occupied by the chlorine atom makes angles with the four basal oxygen atoms centered at 101.9°, near that for an idealized RP.<sup>20a</sup> The degree to which these latter angles differ from each other is a measure of structural distortion from the idealized RP.

As reflected in the trans basal angles, O(2)-P-O(3) (162.9 (1)°) and O(1)-P-O(4) (149.8 (1)°), which would be 180 and

**Table I.** Experimental Details of the X-Ray Diffraction Study of  $(C_6H_4O_2)_2PCl$ 

(A) Crystal Parameters at Ambient Temperature<sup>a</sup>  
 $a = 6.748$  (6) Å Vol = 1178 (1) Å<sup>3</sup>  
 $b = 12.638$  (8) Å  $Z = 4$   
 $c = 14.229$  (9) Å Mol wt = 282.62  
 $\beta = 76.19$  (5)°  $\rho$ (calcd) = 1.594 g cm<sup>-3</sup>  
Space group,  $P2_1/n$ <sup>b</sup>  $\rho$ (obsd)<sup>c</sup> = 1.59 (2) g cm<sup>-3</sup>

(B) Measurement of Intensity Data  
Instrument:<sup>d</sup> Enraf-Nonius low-circle CAD-4 diffractometer controlled by a PDP8/e computer  
Radiation: Mo K (Zr-filtered)  $\lambda_{K\alpha_1} = 0.70926$  Å,  $\lambda_{K\alpha_2} = 0.71354$  Å  
Takeoff angle: 1.75 (5)°  
Reflections measd: 1571 in the region  $+h, +k, \pm l$  having  $2^\circ \leq 2\theta \leq 50^\circ$   
Crystal orientation: aligned approximately along [100]  
Scan range:  $\Delta(2\theta) = (0.8 + 0.5 \tan \theta)^\circ$  centered about the average peak position  
Scan type: coupled  $\theta$ - $2\theta$   
Standard reflections: intensity control (464); orientation control ( $282, \bar{2}82, 282$ ) measured every 50 reflections; no significant deviation from average was observed

(C) Treatment of Intensity Data  
Conversion to  $I$  and  $(I)$ :  $I = [P - 2(B_1 + B_2)](FF/n_s)^e$   
 $P$  = total count,  $B$  = background  
 $\sigma(I) = [(P + 4(B_1 + B_2))(FF^2/n_s) + (cI)^2]^{1/2}$   
 $c = 0.070$  (a parameter to account for instrumental error)<sup>3e</sup>

(D) Agreement Indices of Least-Squares Refinement  
 $n$  (no. of variables) = 195  
 $m/n$  (overdetermination ratio) = 8.0  
 $S = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}, 1.419$   
 $R = [\sum |F_o| - |F_c| / \sum |F_o|], 0.049$   
 $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}, 0.054$

<sup>a</sup> Derived standard unit cell:  $P2_1/c$  ( $C_2h^5$ ; No. 14);  $a = 6.748$ ,  $b = 12.638$ ,  $c = 17.151$  Å;  $\beta = 126.36^\circ$ ;  $Z = 4$ . <sup>b</sup>  $P2_1/n$  is a non-standard setting for space group  $P2_1/c$  and has the equipoints  $\pm(x, y, z)$  and  $\pm(1/2 + x, 1/2 - y, 1/2 + z)$ . <sup>c</sup> Density as determined by the flotation method in a carbon tetrachloride-benzene mixture. <sup>d</sup> Experimental details of this instrument have been previously described.<sup>3</sup> <sup>e</sup>  $FF$  is the filter factor used to bring intensity values on the same scale when the filter is inserted, and  $n_s$  is a factor to account for the variability of scan speeds.

**Table II.** Atomic Coordinates for  $(C_6H_4O_2)_2PCl$  with Standard Deviations in Parentheses

Atom	x	y	z
P	0.3404 (2)	0.1633 (1)	0.3801 (1)
Cl	0.3335 (1)	0.3237 (1)	0.3790 (1)
O(1)	0.5550 (3)	0.1331 (1)	0.4093 (2)
O(2)	0.2101 (3)	0.1444 (1)	0.4933 (1)
O(3)	0.4709 (3)	0.1432 (1)	0.2667 (1)
O(4)	0.1292 (3)	0.1259 (1)	0.3519 (2)
C(1)	0.3348 (5)	0.1366 (2)	0.5580 (3)
C(2)	0.2726 (6)	0.1338 (2)	0.6538 (3)
C(3)	0.4246 (7)	0.1229 (2)	0.7053 (3)
C(4)	0.6318 (7)	0.1143 (2)	0.6565 (4)
C(5)	0.6904 (8)	0.1175 (2)	0.5533 (3)
C(6)	0.5347 (6)	0.1289 (2)	0.5079 (3)
C(7)	0.1505 (5)	0.1165 (2)	0.2532 (3)
C(8)	-0.0040 (8)	0.0989 (2)	0.2072 (3)
C(9)	0.0551 (7)	0.0927 (3)	0.1044 (4)
C(10)	0.2574 (8)	0.1031 (2)	0.0536 (3)
C(11)	0.4127 (6)	0.1208 (2)	0.1032 (3)
C(12)	0.3483 (5)	0.1272 (2)	0.2022 (3)
HC(2)	0.117 (6)	0.140 (2)	0.684 (2)
HC(3)	0.405 (7)	0.118 (2)	0.778 (3)
HC(4)	0.747 (7)	0.102 (3)	0.695 (3)
HC(5)	0.847 (6)	0.108 (2)	0.513 (3)
HC(8)	-0.140 (7)	0.091 (3)	0.242 (3)
HC(9)	-0.044 (7)	0.068 (3)	0.068 (3)
HC(10)	0.292 (8)	0.057 (3)	0.001 (4)
HC(11)	0.564 (6)	0.132 (2)	0.064 (3)

**Table III.** Thermal Parameters for  $(C_6H_4O_2)_2PCl$  with Standard Deviations in Parentheses

Atom	$B_{11}^a$ or $B_{iso}^b$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
P	2.4 (1)	3.6 (1)	3.0 (1)	0.0 (2)	-0.1 (1)	0.1 (1)
Cl	5.3 (1)	3.6 (1)	3.7 (1)	0.2 (2)	-0.6 (1)	0.0 (1)
O(1)	2.9 (1)	4.5 (2)	3.3 (2)	0.0 (2)	-0.4 (1)	0.0 (1)
O(2)	3.0 (1)	5.2 (2)	2.9 (2)	-0.2 (2)	-0.5 (1)	-0.3 (1)
O(3)	2.8 (1)	5.1 (2)	2.5 (2)	0.0 (2)	0.1 (1)	-0.1 (1)
O(4)	2.9 (1)	5.5 (2)	1.9 (2)	0.0 (2)	0.1 (1)	0.6 (1)
C(1)	3.7 (2)	3.4 (2)	2.3 (3)	-0.1 (2)	-1.4 (2)	0.3 (1)
C(2)	5.3 (3)	4.9 (2)	1.5 (3)	0.1 (2)	-1.2 (2)	0.0 (2)
C(3)	6.4 (3)	4.3 (2)	3.4 (3)	-0.2 (2)	-1.2 (2)	0.0 (2)
C(4)	5.3 (3)	3.8 (2)	4.4 (3)	-0.6 (2)	-0.9 (3)	-0.1 (2)
C(5)	3.7 (3)	3.9 (2)	4.3 (3)	-0.2 (2)	-1.3 (2)	-0.1 (2)
C(6)	2.8 (2)	3.5 (2)	3.0 (3)	-0.1 (2)	-0.4 (2)	-0.1 (2)
C(7)	2.4 (2)	3.4 (2)	3.7 (3)	0.4 (2)	-0.8 (2)	-0.1 (1)
C(8)	4.1 (3)	3.8 (2)	5.5 (3)	0.3 (2)	-1.5 (2)	0.1 (2)
C(9)	6.3 (3)	4.4 (2)	3.9 (3)	0.3 (2)	-1.7 (3)	-0.6 (2)
C(10)	6.2 (3)	4.7 (2)	4.6 (3)	0.5 (1)	-2.0 (3)	-0.6 (2)
C(11)	5.4 (3)	5.0 (2)	1.6 (3)	0.6 (2)	-0.7 (2)	-0.2 (2)
C(12)	3.4 (2)	3.4 (2)	3.7 (3)	0.2 (2)	-1.6 (2)	0.0 (2)
HC(2)	7.0 (11)					
HC(3)	9.0 (14)					
HC(4)	9.3 (15)					
HC(5)	7.3 (11)					
HC(8)	7.1 (12)					
HC(9)	10.0 (15)					
HC(10)	14.4 (19)					
HC(11)	8.2 (11)					

<sup>a</sup> The form of the anisotropic thermal ellipsoid is given by  $\exp[-\sum_i \sum_j h_i h_j r_i^* r_j^* B_{ij}] / 4$  with  $i, j = 1, 2, 3$ , where  $r_i^*$  is the  $i$ th reciprocal axis. <sup>b</sup> For all hydrogen atoms the temperature factors are isotropic  $B$ 's in Å<sup>2</sup>.

**Table IV.** Bond Distances (Å) and Angles (deg) for  $(C_6H_4O_2)_2PCl$ <sup>a</sup>

Distances			
P-Cl	2.031 (1)	C(7)-C(8)	1.376 (8)
P-O(1)	1.643 (3)	C(8)-C(9)	1.423 (7)
P-O(2)	1.657 (3)	C(9)-C(10)	1.390 (7)
P-O(3)	1.662 (3)	C(10)-C(11)	1.413 (7)
P-O(4)	1.640 (3)	C(11)-C(12)	1.372 (5)
O(1)-C(6)	1.378 (5)	C(12)-C(7)	1.365 (5)
O(2)-C(1)	1.391 (6)	C(2)-HC(2)	1.04 (4)
O(3)-C(12)	1.389 (5)	C(3)-HC(3)	1.02 (4)
O(4)-C(7)	1.381 (6)	C(4)-HC(4)	1.07 (4)
C(1)-C(2)	1.326 (8)	C(5)-HC(5)	1.08 (4)
C(2)-C(3)	1.402 (6)	C(8)-HC(8)	0.94 (4)
C(3)-C(4)	1.409 (7)	C(9)-HC(9)	0.98 (5)
C(4)-C(5)	1.426 (7)	C(10)-HC(10)	0.94 (5)
C(5)-C(6)	1.366 (6)	C(11)-HC(11)	1.05 (4)
C(6)-C(1)	1.371 (5)		
Angles			
Cl-P-O(1)	105.0 (1)	O(4)-C(7)-C(8)	126.2 (4)
Cl-P-O(2)	98.3 (1)	O(3)-C(12)-C(7)	108.8 (3)
Cl-P-O(3)	98.8 (1)	O(4)-C(7)-C(12)	112.6 (3)
Cl-P-O(4)	105.3 (1)	P-O(3)-C(12)	113.8 (2)
O(1)-P-O(2)	91.0 (1)	P-O(4)-C(7)	112.8 (2)
O(3)-P-O(4)	90.5 (1)	C(1)-C(2)-C(3)	116.6 (4)
O(1)-P-O(3)	85.1 (1)	C(2)-C(3)-C(4)	120.9 (4)
O(2)-P-O(4)	84.6 (1)	C(3)-C(4)-C(5)	120.3 (5)
O(1)-P-O(4)	149.8 (1)	C(4)-C(5)-C(6)	115.7 (4)
O(2)-P-O(3)	162.9 (1)	C(5)-C(6)-C(1)	122.3 (4)
O(1)-C(6)-C(5)	125.8 (3)	C(6)-C(1)-C(2)	124.3 (4)
O(2)-C(1)-C(2)	126.0 (4)	C(7)-C(8)-C(9)	116.1 (4)
P-O(1)-C(6)	112.8 (2)	C(8)-C(9)-C(10)	121.9 (5)
P-O(2)-C(1)	112.9 (2)	C(9)-C(10)-C(11)	120.6 (5)
O(1)-C(6)-C(1)	111.9 (3)	C(10)-C(11)-C(12)	115.5 (3)
O(2)-C(1)-C(6)	109.7 (4)	C(11)-C(12)-C(7)	124.9 (3)
O(3)-C(12)-C(11)	126.4 (3)	C(12)-C(7)-C(8)	121.3 (3)

<sup>a</sup> Standard deviations in parentheses.

120° in a TP or both equal at 150° in an idealized RP, the observed geometry is considerably displaced toward the RP. Correspondingly, the P-O bond lengths vary according to the

Table V. Atom Distances from Least-Squares Planes (Å)

	Plane <sup>a</sup>				
	I <sup>b</sup>	II	III	IV	V
P		0.003	-0.001	-0.098	0.101
O(1)	0.091		0.001		0.078
O(2)	-0.090	-0.004		0.139	-0.140
O(3)	-0.090	-0.004		0.138	-0.140
O(4)	0.091		0.001	-0.079	
Cl		0.000	0.000		

	Plane <sup>a</sup>			
	VI	VII	VIII	IX
C(1)	0.001	C(7) 0.001	P 0.013	P -0.012
C(2)	-0.003	C(8) 0.002	O(1) -0.084	O(3) 0.070
C(3)	0.004	C(9) -0.003	C(6) 0.079	C(12) -0.091
C(4)	-0.001	C(10) 0.001	C(1) 0.101	C(7) -0.073
C(5)	-0.001	C(11) 0.004	O(2) -0.077	O(4) 0.077
C(6)	0.001	C(12) -0.004		

<sup>a</sup> The form of the least-squares plane is  $lX + mY + nZ + d = 0$  where  $X, Y, Z$  are orthogonal coordinates. The weights used were for the  $i$ th atom  $w_i = (a\sigma_x b\sigma_y c\sigma_z)^{1/3}$ . <sup>b</sup> The phosphorus atom is located 0.338 Å out of the mean plane of the four basal oxygen atoms toward the chlorine atom.

Table VI. Some Intramolecular Nonbonded Distances (Å)

O(1)-O(2)	2.353 (4)	O(2)-O(3)	3.283 (6)
O(3)-O(4)	2.344 (4)	Cl-O(1)	2.923 (3)
O(1)-O(3)	2.235 (5)	Cl-O(2)	2.800 (2)
O(2)-O(4)	2.219 (5)	Cl-O(3)	2.815 (2)
O(1)-O(4)	3.170 (6)	Cl-O(4)	2.928 (4)

Table VII. Some Dihedral Angles between Least-Squares Planes (deg)

Planes <sup>a</sup>	Angle
II, III	87.0
VI, VIII	6.7
VII, IX	6.7
VIII, IX	26.6

<sup>a</sup> Planes as defined in Table V.

expected residual TP character. Residual equatorial character of a TP is indicated for the shorter P-O(1) and P-O(4) bonds associated with the smaller O-P-O angle. Likewise, the longer bonds, P-O(2) and P-O(3), associated with the larger O-P-O angle, are a manifestation of residual axial TP character.

In terms of the least-squares planes of Table V, while plane I which is a defining plane for a RP, planes IV and V define an ideal TP. The latter are seen to be less closely followed than plane I. The close adherence of the atoms to planes II and III indicates that the structural distortions for the chloro derivative are along the Berry coordinate.<sup>21</sup> For structural distortions following a local  $C_{2v}$  constraint between idealized TP and RP representations, a dihedral angle between planes II and III in the range 90-85.9° is expected. The observed value here is 87.0° (Table VII).

If the dihedral angles from connecting polyhedral faces are computed (Table VIII) and compared with those of various idealized arrangements, as we have done previously for other structures of this class,<sup>20</sup> the structure of the chloro derivative is found to lie directly on the Berry coordinate at a point 71.6% displaced from the idealized TP toward the idealized RP. The portion of the graph showing this effect for the derivatives of I is given in Figure 4.

It is seen that the chloro derivative is positioned near the phenyl derivative. In line with the discussion given previously<sup>20a</sup> about the ordering in this series along the Berry coordinate, the appearance of the chloro derivative between the fluoro and phenyl is in accord with the electronegativity trend  $F > Cl > Ph > CH_3$ . However, on this basis a greater

Table VIII. Dihedral Angles ( $\delta$ ) for (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)<sub>2</sub>PCl, deg<sup>a</sup>

Edge <sup>b</sup>	$\delta$ (TP)	$\delta$ (C)	$\delta$ (RP)
45	101.5	110.4	117.6
25	101.5	112.1	119.3
14	101.5	112.1	119.3
12	101.5	111.0	117.6
35	101.5	84.4	76.9
13	101.5	84.3	76.9
23	53.1	73.5	76.9
34	53.1	74.4	76.9
24	53.1	12.6	0.0
$\Sigma_i  \delta_i(C) - \delta_i(TP) $		156.1	
$\Sigma_i  \delta_i(C) - \delta_i(RP) $		61.7	
$R - \Sigma_i  \delta_i(C) - \delta_i(RP) $		156.2 <sup>c</sup>	

<sup>a</sup> For purposes of comparison with a similar tabulation of dihedral angles for other compounds,<sup>20a</sup> the atom numbering scheme shown above is used, where the subscripts 1 and 5 refer to axial atoms in the connecting trigonal bipyramid obtained along the Berry path. <sup>b</sup> The number pairs refer to the common edge connecting the two triangular faces whose normals give the dihedral angle. <sup>c</sup>  $R = \Sigma_i |\delta_i(TP) - \delta_i(RP)| = 217.9^\circ$ . This value represents the sum of dihedral angle changes on going from the idealized TP to the RP. With reference to the figure shown above, the angles in the RP are  $\angle 1,2 = 4,5 = 90^\circ$ ,  $\angle 2,5 = 1,4 = 82.3^\circ$ ,  $\angle 2,4 = 1,5 = 150^\circ$ , and  $\angle 1,3 = 2,3 = 4,3 = 5,3 = 105^\circ$ .

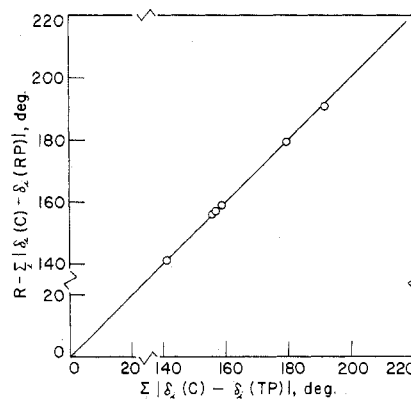
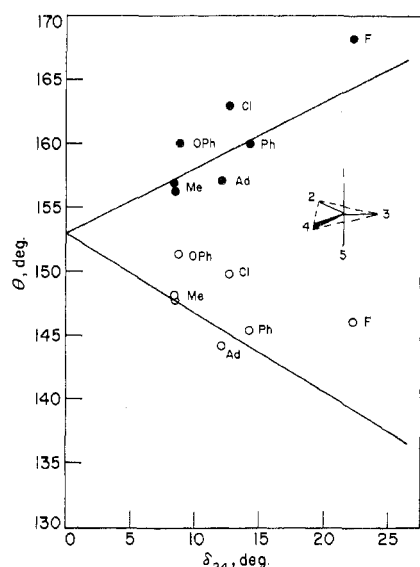


Figure 4. The sum of dihedral angles for the cyclic phosphoranes I, (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)<sub>2</sub>PR, relative to those for an idealized RP geometry vs. the same sum relative to those for a TP geometry on a common reference scale. The solid line traces the Berry exchange coordinate. From lower left to upper right, the sequence of points is R = F, Cl, Ph, adamantyl, CH<sub>3</sub>, and OPh. An idealized 30° TR structure would appear at the coordinates (223.8, 171.0).<sup>20a</sup>

separation between the positions along the distortion coordinate for the chloro and phenyl derivatives is expected.

To obtain a more satisfactory interpretation, it is necessary to probe the structural features in somewhat more detail. As discussed above, evidence of the extent of displacement along a TP-RP path is apparent in the trans O-P-O angles and their respective P-O bond distances. We have shown by graphical display<sup>20a</sup> that trends in these parameters are obtained which, in general, correlate well with the percent displacement along the distortion coordinate.

Relative to the trans angles O(2)-P-O(3) (axial type in a TP frame) and O(1)-P-O(4) (equatorial type in a TP frame) reported<sup>5</sup> for the phenyl derivative, those for the chloro derivative are increased by 2.9 (1) and 4.4 (1)°, respectively (Figure 5). The corresponding P-O bond distances show a decrease for the chloro derivative compared to those for the phenyl derivative, more so for the axial than the equatorial



**Figure 5.** Variation of the angles at phosphorus  $\theta_{15}$  (filled circles) and  $\theta_{24}$  (open circles) vs. the dihedral angle  $\delta_{24}$  for derivatives of  $(C_6H_4O_2)_2PR$  as structural distortion proceeds along the Berry coordinate (solid lines) from a RP toward a TP. Other compounds are included on the same type of graph in Figure 6 of ref 20a.

type (i.e., in a TP reference frame). The average bond length decrease is 0.027 (3) Å per P–O bond. These changes are consistent with the greater electronegativity of the chlorine atom which lessens the electron pair repulsions between the P–Cl bond and the four adjacent P–O bonds and displaces the structure toward the TP.<sup>5,20,22</sup>

For the phenyl derivative, a steric interaction also is expected, principally from nonbonded repulsions between the  $\alpha$  hydrogen atoms of the phenyl ring and the four oxygen atoms. This term appears to affect the smaller O(1)–P–O(4) angle to a slightly greater extent than the O(2)–P–O(3) as measured by vertical displacements from the corresponding angles plotted for the chloro derivative in Figure 5. This may occur indirectly via relief of ring constraints<sup>22</sup> brought about by progressive bond lengthening of P–O(2) and P–O(3) relative to P–O(1) and P–O(4) as greater TP character is assumed by the structure.

A similar comparison between the methyl and adamantyl derivatives of I, which are expected to have about the same group electronegativity, shows that they have approximately equal values for the larger trans O–P–O angle but the adamantyl derivative<sup>16</sup> has a 4° lower value for the smaller trans O–P–O angle compared to this value for the methyl derivative.<sup>4b</sup> As a result, the structure of the adamantyl derivative appears relatively displaced along the Berry coordinate toward the TP compared to the position of the methyl derivative<sup>20a</sup> (Figure 4).

However, the structure of the phenoxy derivative of I is displaced 88% toward the RP compared to 82% for the methyl derivative. The bond angle data for the phenoxy derivative<sup>8</sup> now shows that the larger trans O–P–O angle is the one being reduced. The latter angle is smaller than that for the chloro compound, while the smaller trans O–P–O angle of the phenoxy derivative is larger than that for the chloro derivative (Figure 5).

Based on the above line of reasoning, a balance is implied between the magnitude of the steric effect and the group electronegativity of the unique ligand. With the combination of a relatively high ligand electronegativity and an appreciable steric effect, the electron pair repulsion term is sufficiently relaxed to cause considerable widening of the trans O–P–O angles. However, the larger trans O–P–O angle is then more

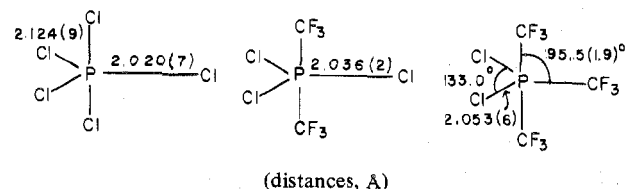
susceptible to a direct steric effect causing its reduction relative to any change in the corresponding smaller trans O–P–O angle. Ring constraints,<sup>22</sup> acting to lower the smaller trans O–P–O angle, would be less operative under these circumstances since the dominant steric effect will have caused the P–O bonds to assume more equal character. Thus, the appearance of the structure of the phenoxy phosphorane displaced along the distortion coordinate toward the RP appears reasonable.

Although the interpretation given above for structural distortions encountered in the series I is self-consistent, additional examples will be sought to test or modify the present proposal. Similar arguments may be formulated to interpret bond distance variations which are complementary to bond angle changes in this series of "catechol" complexes.

Most of the bond angles in the ring system of the chloro derivative follow a pattern similar to that observed for other members of the series, I. The angles at carbon atoms 2, 5, 8, and 11 (with reference to Figure 3) are invariably smaller<sup>5</sup> than 120°, while those at carbon atoms 1, 6, 7, and 12 in the six-membered rings are larger than 120°. Comparison of the phenyl and chloro members shows that the average values of the two sets of angles are the same, centered at 116° for the first-mentioned angle set and 123° for the latter set. It has been observed that these angle variations become more pronounced as the ideal TP structure is approached.<sup>5</sup>

The nearly planar character of the six-membered rings is evident from the average atom out-of-plane distance of  $\sim 0.003$  Å from the least-squares planes VI and VII of Table V. The dihedral angle that these planes make with the associated five-membered rings of the basal system is 6.7° (Table VII). The latter compares with an average value of this dihedral angle for the phenyl derivative of 5.3°.<sup>5</sup>

It is interesting to compare the P–Cl bond lengths of the chloro derivative of I with P–Cl bond lengths obtained by



electron diffraction for  $PCl_5$ ,<sup>37</sup>  $(CF_3)_2PCl_3$ ,<sup>30</sup> and  $(CF_3)_3PCl_2$ .<sup>30</sup> Although NMR studies<sup>38</sup> suggest that the  $CF_3$  groups are equatorially oriented in TP structures, the electron diffraction work<sup>30</sup> supports earlier vibrational studies<sup>39</sup> on  $CF_3PCl_4$  and  $(CF_3)_2PCl_3$  indicating that the  $CF_3$  groups appear preferentially at the axial sites of a TP conformation.

Although our data do not decide the issue, the following correspondence is noted. The P–Cl bond length in the chloro derivative of I (2.031 (1) Å) is close in value to the equatorial P–Cl bond types above. The same is true for the P–F bond length comparison between the RP conformation of I ( $R = F^{4c}$ ) and  $PF_5$ .<sup>40</sup> The former P–F bond distance, 1.546 (2) Å, compares with 1.534 (4) Å (equatorial) and 1.577 (5) Å (axial) observed for  $PF_5$ . These comparisons show evidence for the duality in bond properties between TP and RP structures which suggests that TP equatorial bonds and RP axial bonds bear a close correspondence. Similarly TP axial and RP basal bonds should form a complementary pair. The same conclusions are reached from electron pair repulsion arguments.<sup>20a,22,41</sup>

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Supplementary Material Available: A compilation of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

## Crystal and Molecular Structure of 2,2,3,3-Tetramethyl-5-dimethylamino-7,8-diphenyl-1,4,6,9-tetraoxa-5-phospha ( $P^V$ )spiro[4.4]non-7-ene, $(C_6H_{12}O_2)(C_{14}H_{10}O_2)PN(CH_3)_2^1$

JOHN S. SZOBOTA<sup>2</sup> and ROBERT R. HOLMES\*

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The crystal structure of 2,2,3,3-tetramethyl-5-dimethylamino-7,8-diphenyl-1,4,6,9-tetraoxa-5-phospha ( $P^V$ )spiro[4.4]non-7-ene,  $(C_6H_{12}O_2)(C_{14}H_{10}O_2)PN(CH_3)_2$  has been determined by single-crystal x-ray diffraction analysis. The compound crystallizes in the monoclinic space group  $P2_1/c$  with cell constants  $a = 11.379$  (3) Å,  $b = 12.646$  (4) Å,  $c = 15.848$  (4) Å,  $\beta = 102.25$  (5)°, and  $Z = 4$ . Based on the dihedral angle method, the structural deviations from an idealized trigonal bipyramid (TP) indicate that this derivative is 31% along the Berry ligand exchange coordinate toward the idealized rectangular pyramid (RP). Pertinent features of the molecule are the  $O_{ax}-P-O_{ax}$  angle, 169.7 (1)°, the  $O_{eq}-P-O_{eq}$  angle, 129.9 (1)°, the near equality of  $P-O_{eq}$  and  $P-O_{ax}$  bond lengths of the saturated ring, 1.660 (1) and 1.662 (1) Å, respectively, with the  $P-O_{eq}$  bond length of the unsaturated ring, 1.673 (1) Å, and the planar configuration of the dimethylamino group which is rotated out of the equatorial plane by a torsional angle of 62°. The direction of rotation is such that repulsions between the  $N$ -methyl groups and the methyl group on the flap carbon atom of the saturated ring are minimized.

### Introduction

From an estimation of ring strain in small-membered cyclic containing phosphoranes, the conclusion was reached that increasing ring unsaturation favors the appearance of a square or rectangular pyramid (SP, RP) compared to a trigonal bipyramid (TP).<sup>3</sup> Based on an electron pair repulsion ar-

gument, when the ring atoms directly bonded to phosphorus are of the same type, increasing atom electronegativity, as well, favors the SP(RP).<sup>3,4</sup>

We have carried out x-ray diffraction studies on the derivatives, I-V.<sup>1b,5-7</sup> These derivatives were chosen to test the generality of the above hypotheses. The present study concerns