(20) W. S. Sheldrick, personal communication.

(21) M. Eisenhut, R. Schmutzler, and W. S. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 144 (1973), and personal communication.

(22) This column is simply obtained by noting which observed angles fall outside the range of the values of the respective angles traversed between the idealized TP and SP (RP) structures (Figure 3), measuring the number of degrees that each fall outside the range, taking their sum, and multiplying by two.

(23) Nine dihedral angles are given based on the idealized TP geometry in Figure 3(a). Additional dihedral angles arise for actual structures but are not common to the idealized structures being used for comparison.

(24) (a) A. Rauk, L. C. Allen, and K. Mislow, *J. Am. Chem. Soc.*, **94,** 3035 (1972); (b) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *ibid.*, **94**, 3047 (1972); (c) L. S. Bartell and V. Plato, *ibid.*, **95**, 3097 (1973); (d) A. Strich and A. Veillard, *ibid.*, **95**, 5574 (1973).

(25) (a) R. R. Holmes, *Acc. Chem. Res.*, **5**, 296 (1972); (b) R. R. Holmes, L. S. Couch, and C. J. Hora, Jr., *J. Chem. Soc., Chem. Commun.*, 197 (1974).

(26) L. S. Bernstein, J. J. Kim, K. S. Pitzer, S. Abramowitz, and I. Levin, 30th Symposium on Molecular Structure and Spectroscopy. The Ohio State University, Columbus, Ohio, June 1975, Abstract No. TA6; L. S. Bernstein, S. Abramowitz, and I. W. Levin, *J. Chem. Phys.*, **64**, 3228 (1976); L. S. Bernstein, J. J. Kim, K. S. Pitzer, S. Abramowitz, and I. W. Levin, *ibid.*, **62**, 3671 (1975).

(27) (a) L. S. Bartell, *Inorg. Chem.*, **9**, 1594 (1970); (b) K. W. Hansen and L. S. Bartell, *ibid.*, **4**, 1775 (1965); (c) L. S. Bartell and K. W. Hansen, *ibid.*, **4**, 1777 (1965); (d) F. B. Clippard, Jr., and L. S. Bartell, *ibid.*, **9**, 805 (1970); (e) W. J. Adams and L. S. Bartell, *J. Mol. Struct.*, **8**, 23 (1971); (f) H. Yow and L. S. Bartell, *ibid.*, **15**, 209 (1973).

(28) (a) J. E. Griffiths, R. P. Carter, Jr., and R. R. Holmes, *J. Chem. Phys.*, **41**, 863 (1964); (b) I. W. Levin, *ibid.*, **50**, 1031 (1969); (c) F. A. Miller and R. J. Capwell, *Spectrochim. Acta, Part A*, **27**, 125 (1971); (d) I. W. Levin, *J. Mol. Spectrosc.*, **33**, 61 (1970).

(29) As previously cited[7,25a] electron-pair repulsion considerations, with reference to the idealized SP in Figure 3(b), suggest a correspondence in bond properties between the basal bonds of the SP and axial bonds of the TP. Thus, the more electronegative ligands would prefer the basal positions of the SP and small-membered rings would locate in a *cis*-basal rather than a basal-axial pair. The latter correspondence for the SP follows from the element and strain rules for the TP.[30]

(30) (a) F. H. Westheimer, *Acc. Chem. Res.*, **1**, 70 (1968); (b) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); (c) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

(31) J. A. Howard, D. R. Russell, and S. Trippett, *J. Chem. Soc., Chem. Commun.*, 856 (1973).

(32) A. Schmidpeter, J. Luber, D. Schomburg, and W. S. Sheldrick, *Chem. Ber.*, in press.

(33) M.-Ul-Haque, C. N. Caughlan, F. Ramirez, J. F. Pilot, and C. P. Smith, *J. Am. Chem. Soc.*, **93**, 5229 (1971).

(34) K. Mislow, *Acc. Chem. Res.*, **3**, 321 (1970).

(35) (a) D. Gorenstein and F. H. Westheimer, *J. Am. Chem. Soc.*, **92**, 634 (1970); (b) D. Gorenstein, *ibid.*, **92**, 644 (1970).

(36) F. Ramirez, *Acc. Chem. Res.*, **1**, 168 (1968).

The Crystal and Molecular Structure of the Spirophosphorane $(C_6H_4O_2)_2PC_6H_5$[1]

Richard K. Brown[2] and Robert R. Holmes*

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003. *Received September 20, 1976*

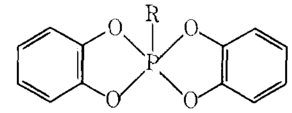
Abstract: The crystal structure of 2-phenyl-2,2′-spirobis(1,3,2-benzodioxaphosphole), $(C_6H_4O_2)_2PC_6H_5$, has been determined by single crystal x-ray diffraction analysis. The compound crystallizes in the monoclinic space group $P2_1/c$ with cell constants $a = 6.663$ (7), $b = 17.182$ (6), $c = 13.301$ (5) Å, $\beta = 88.78$ (7)°, $Z = 4$. It has a noncrystallographic twofold axis. The geometry about phosphorus is near rectangular pyramidal (RP). The structural deviations from an idealized RP are along the Berry ligand exchange coordinate. Pertinent features of the molecule are the diagonal O–P–O angles, 160.0 (2) and 145.4 (2)°, and the four bond angles between the axial phenyl group and the basal P–O bonds, 108.5 (2), 100.0 (2), 100.0 (2), 106.1 (2)°. The differences in the basal P–O bond lengths, 1.650 (4) and 1.655 (4) vs. 1.682 (4) and 1.691 (4) Å, are indicative of a small residual trigonal bipyramidal character. The phosphorus atom is 0.39 Å out of the mean plane of the four oxygen atoms toward the axial phenyl group.

The structures of cyclic phosphoranes are especially interesting because they serve as models for transition states in many reaction mechanisms of four-coordinate phosphorus.[3] For example, the mode of hydrolysis of cyclic phosphates[3,4] and phosphonium salts,[3] the enzymatic cleavage of ribonucleic acids by ribonucleases,[5] and the chain elongation mechanism of DNA and RNA replication[6] depend intimately on the detailed structural principles developed from studies on isolatable phosphoranes.

It has recently become apparent[7] that most structural distortions of cyclic phosphoranes can be understood in terms of low angle bending force constants associated with the Berry coordinate[8] governing intramolecular ligand exchange[3a] and that the appearance of structures at specific points along the coordinate is primarily determined by a competition between factors resulting from the ligand construction which influence the energy difference between the idealized trigonal bipyramidal (TP) and square or rectangular pyramidal SP (RP) framework.

An intimate knowledge of the steric and electronic factors which determine the extent of structural glide along the TP–SP (RP) pathway is needed to quantitatively assess the structural makeup of proposed transition states and their influence in establishing specific reaction mechanisms.

Spirophosphoranes containing two catechol residues and a variety of different ligands in the fifth position offer a suitable series on which to test postulates concerning molecular properties leading to the stabilization of the SP (RP) geometry.[9] Previously studied members I have structures[10–12] which fall toward the idealized RP form.



R = F, CH_3, OPh, adamantyl

I

The presence of a phenyl group at the fifth position offers the interesting possibility of ascertaining the influence of going from an sp^3 to an sp^2 type carbon atom as well as judging the influence of comparative steric effects of the phenyl and phenoxy groups on the catechol ring system.

Experimental Section

Preparation. Samples of 2-phenyl-2,2′-spirobis(1,3,2-benzodioxaphosphole) were prepared by the direct interaction of 2 molar equiv of catechol in ether with 1 molar equiv of dichlorophenylphosphine at ambient temperature for 1 h.[13] Removal of the solvent resulted in a microcrystalline product. Crystals of the compound suitable for a detailed x-ray structure analysis were obtained by recrystallization from methylene chloride. Anal. Calcd for $C_{18}H_{13}O_4P$: C, 66.67; H, 4.04; P, 9.56. Found: C, 66.66; H, 4.40; P, 9.84; mp 181 °C (lit.[13c] 181 °C).

Data Collection. Preliminary precession and Weissenberg photographs recorded using Cu Kα radiation indicated the monoclinic system (Laue symmetry $2/m$), the absences $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, being consistent with space group $P2_1/c$. A well-formed crystal having dimensions 0.25 × 0.25 × 0.50 mm was chosen for data collection. The crystal was mounted on an Enraf-Nonius CAD 4 diffractometer with the crystal a axis nearly parallel with the instrument ϕ axis. The source to crystal and crystal to detector aperture distances are 21.7 and 17.3 cm, respectively. Zirconium filtered Mo radiation at an instrument takeoff angle of 6.5° was used for all measurements, the incident beam collimator being 0.8 mm in diameter. Unit cell dimensions, obtained by least-squares refinement of the observed 2θ values of 15 high-order reflections centered using the program SETANG,[14] are $a = 6.663$ (7), $b = 17.182$ (6), $c = 13.301$ (5) Å, $\beta = 88.78$ (7)°.[15] The observations were made at room temperature and are based on an assumed wavelength for Mo Kα_l of 0.7093 Å. The observed density of 1.40 (2) g/cm^3, determined by the flotation method in a carbon tetrachloride-benzene mixture, is in good agreement with the calculated value of 1.415 g/cm^3 for four molecules per unit cell.

Integrated diffraction data were collected using the θ-2θ scan technique, with a scan range of $(0.8 + 0.5 \tan \theta)°$ centered about the average peak position. The scan rate was variable from 4°/min to 0.61°/min, the actual value being determined by a preset intensity value and a preliminary prescan for each reflection. A scintillation counter equipped with a pulse height selector, set for a 95% window centered on the Mo Kα peak, was used to measure the data. The receiving aperture diameter was reduced to 2 mm and the manual slit height set at 4 mm. For strong reflections with count rates exceeding 50 000 counts/s, an attenuation filter of nickel foil with a filter factor (FF) of 4.60 (5) was automatically inserted. Crystal deterioration was monitored by measuring an intensity control reflection (043) after every 50 reflections. System stability was also monitored after every 50 reflections by the measurement of three orientation control reflections (400, 084, and 133). No significant deviations from the average value of any of the control reflections were observed. At each end of the 2θ scan, background counts were taken for one quarter of the total scan time. The net intensity of each reflection, I, is defined as

$$I = [P - 2(B_1 + B_2)](\mathrm{FF}/n_s)$$

where P is the total peak count, B_1 and B_2 are the stationary left and right background counts, FF is the attenuation factor for the nickel foil filter when it is inserted, and n_s is related to the scan time. The intensity data were assigned standard deviations according to the formula

$$\sigma(I) = [(P + 2(B_1 + B_2))(\mathrm{FF}/n_s)^2 + (cI)^2]^{1/2}$$

where c is a factor to account for random errors other than those due to counting statistics. A value of 0.045 was assigned to c.[16]

A total of 3097 independent reflections with $0.0582 \leqslant (\sin \theta)/\lambda \leqslant 0.6170$ were measured. The 2686 reflections with an intensity greater than $0.1\sigma(I)$ were treated as observed. For unobserved reflections $F_o = [(1/Lp)(0.10)(\sigma I)]^{1/2}$, where Lp is the Lorentz-polarization factor. Because of the very small linear absorption coefficient ($\mu_{\mathrm{Mo}} = 1.68$ cm^{-1}) no corrections were applied for absorption. Corrections for Lorentz and polarization effects were made.

Table I. Atomic Coordinates for $(C_6H_4O_2)_2PC_6H_5$ with Standard Deviations in Parentheses

Atom	x	y	z
P	0.2064 (2)	0.5081 (1)	0.2859 (1)
O(1)	0.4383 (4)	0.5392 (1)	0.3008 (2)
O(2)	0.1392 (4)	0.5972 (2)	0.2465 (2)
O(3)	0.2775 (4)	0.4357 (2)	0.3639 (2)
O(4)	−0.0236 (4)	0.5054 (2)	0.3352 (2)
C(1)	−0.0558 (7)	0.4427 (2)	0.3970 (4)
C(2)	−0.2412 (7)	0.4223 (3)	0.4408 (4)
C(3)	−0.2415 (7)	0.3570 (3)	0.5026 (4)
C(4)	−0.0592 (9)	0.3153 (3)	0.5195 (4)
C(5)	0.1236 (7)	0.3384 (3)	0.4747 (4)
C(6)	0.1151 (7)	0.4022 (3)	0.4135 (3)
C(7)	0.2958 (6)	0.6478 (3)	0.2377 (3)
C(8)	0.2878 (7)	0.7245 (3)	0.2083 (4)
C(9)	0.4693 (9)	0.7668 (3)	0.2124 (4)
C(10)	0.6458 (8)	0.7327 (3)	0.2481 (4)
C(11)	0.6507 (7)	0.6539 (3)	0.2772 (4)
C(12)	0.4710 (7)	0.6146 (3)	0.2703 (3)
C(13)	0.1966 (9)	0.4561 (3)	0.1709 (4)
C(14)	0.3680 (11)	0.4353 (4)	0.1211 (6)
C(15)	0.3556 (15)	0.3948 (5)	0.0244 (7)
C(16)	0.1670 (21)	0.3782 (4)	−0.0115 (6)
C(17)	−0.0085 (16)	0.3991 (5)	0.0410 (7)
C(18)	0.0084 (11)	0.4379 (4)	0.1311 (5)
C2H[a]	−0.346 (3)	0.454 (1)	0.429 (2)
C3H	−0.371 (3)	0.340 (1)	0.541 (2)
C4H	−0.062 (5)	0.273 (1)	0.563 (2)
C5H	0.231 (3)	0.314 (1)	0.485 (2)
C8H	0.171 (3)	0.750 (1)	0.187 (2)
C9H	0.461 (3)	0.821 (1)	0.199 (2)
C10H	0.746 (4)	0.764 (2)	0.246 (2)
C11H	0.766 (3)	0.631 (1)	0.297 (2)
C14H	0.520 (5)	0.449 (3)	0.146 (3)
C15H	0.425 (6)	0.379 (3)	0.023 (3)
C16H	0.176 (6)	0.368 (3)	−0.070 (3)
C17H	−0.156 (6)	0.365 (3)	−0.004 (2)
C18H	−0.122 (6)	0.464 (3)	0.181 (2)

[a] Hydrogen atoms carry the name of the carbon atoms to which they are bonded.

Structure Solution and Refinement. Computations were carried out on a CDC 6600 computer (Model Cyber 74-18) using local modifications of the direct methods program, MULTAN, by Main, Germain, and Woolfson,[17] Zalkin's FORDAP Fourier program, Prewitt's SFLS5 full-matrix least-squares routine, and several locally written programs. Preliminary fractional coordinates for the phosphorus and four oxygen atoms were obtained from the program MULTAN using 2000 phase relationships from the 350 reflections with the largest E values. MULTAN is a phase-permutation computer program which incorporates a weighted tangent formula.[17] One electron density map, phased on the phosphorus and oxygen atoms, was sufficient to locate all nonhydrogen atoms. The scattering factors for all nonhydrogen atoms were taken from the tabulation by Cromer and Waber[18] and those for hydrogen were taken from the tabulation by Stewart et al.[19] The agreement factors are defined in the usual manner as

$$R = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|)$$

and

$$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$$

In all least-squares refinements, the quantity minimized was

$$\Sigma w(|F_o| - |F_c|)^2$$

the weights w being evaluated as

$$w^{1/2} = 2LpF_o/\sigma(I)$$

After one cycle of isotropic unit weight least-squares refinement, allowing all 23 nonhydrogen atoms and one overall scale factor to vary, the values of R and R_w were 0.399 and 0.303, respectively. Assignment of anisotropic thermal parameters and two further cycles of least-squares refinement led to values of $R = 0.146$ and $R_w = 0.107$. A difference electron density map revealed the positions of the 13 independent hydrogen atoms. Further anisotropic variable weight refinement of the nonhydrogen atoms and isotropic refinement of the hydrogen atoms led to final values of $R = 0.083$ and $R_w = 0.073$. All of the above R values are based on the use of all 3097 independent reflections. In the last stage of refinement the largest shift in any parameter was less than 0.2 times the estimated standard deviation. The positional and thermal parameters from the final cycle of least-squares refinement are presented in Tables I and II.

Table II. Thermal Parameters for $(C_6H_4O_2)_2PC_6H_5$ with Standard Deviations in Parentheses

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	0.0175 (3)	0.0030 (1)	0.0062 (1)	0.0011 (1)	−0.0006 (1)	0.0002 (1)
O(1)	0.0168 (8)	0.0038 (1)	0.0079 (2)	0.0013 (3)	−0.0003 (3)	0.0006 (1)
O(2)	0.0197 (8)	0.0034 (1)	0.0084 (2)	0.0003 (3)	−0.0031 (4)	0.0010 (1)
O(3)	0.0170 (8)	0.0038 (1)	0.0079 (2)	0.0015 (3)	0.0004 (4)	0.0012 (1)
O(4)	0.0157 (8)	0.0038 (1)	0.0082 (2)	0.0012 (3)	−0.0004 (3)	0.0006 (2)
C(1)	0.0214 (14)	0.0026 (2)	0.0059 (3)	−0.0019 (4)	−0.0071 (6)	0.0005 (2)
C(2)	0.0238 (13)	0.0043 (2)	0.0060 (3)	−0.0021 (4)	0.0008 (6)	−0.0008 (2)
C(3)	0.0298 (15)	0.0044 (2)	0.0048 (4)	−0.0010 (5)	0.0002 (6)	−0.0004 (2)
C(4)	0.0320 (18)	0.0043 (2)	0.0067 (4)	−0.0012 (5)	−0.0005 (7)	−0.0003 (2)
C(5)	0.0288 (15)	0.0038 (2)	0.0055 (4)	−0.0002 (5)	0.0004 (6)	0.0010 (2)
C(6)	0.0163 (13)	0.0037 (2)	0.0051 (3)	0.0002 (4)	0.0010 (5)	−0.0007 (2)
C(7)	0.0180 (13)	0.0035 (2)	0.0052 (3)	−0.0003 (4)	0.0002 (5)	0.0003 (2)
C(8)	0.0293 (14)	0.0037 (2)	0.0081 (4)	−0.0020 (5)	0.0001 (6)	0.0013 (3)
C(9)	0.0287 (17)	0.0049 (2)	0.0077 (5)	−0.0010 (5)	−0.0005 (7)	0.0007 (3)
C(10)	0.0261 (17)	0.0044 (2)	0.0079 (4)	0.0011 (5)	0.0006 (7)	0.0009 (3)
C(11)	0.0193 (14)	0.0047 (2)	0.0077 (4)	−0.0018 (5)	0.0024 (6)	0.0007 (2)
C(12)	0.0224 (14)	0.0027 (2)	0.0055 (4)	0.0012 (5)	0.0007 (6)	0.0006 (2)
C(13)	0.0355 (18)	0.0032 (2)	0.0066 (4)	−0.0000 (5)	0.0018 (7)	−0.0002 (2)
C(14)	0.0608 (27)	0.0076 (4)	0.0099 (6)	−0.0012 (8)	0.0065 (9)	−0.0018 (4)
C(15)	0.0638 (36)	0.0090 (5)	0.0115 (8)	−0.0022 (10)	0.0090 (14)	−0.0031 (5)
C(16)	0.0965 (51)	0.0058 (4)	0.0075 (6)	−0.0024 (12)	0.0024 (15)	−0.0013 (4)
C(17)	0.0768 (42)	0.0095 (5)	0.0123 (7)	−0.0021 (11)	−0.0060 (15)	−0.0045 (5)
C(18)	0.0518 (27)	0.0073 (4)	0.0097 (6)	0.0006 (8)	−0.0064 (10)	−0.0036 (4)
C2H[b]	3.8 (7)	C11H	4.8 (9)			
C3H	7.6 (9)	C14H	11.0 (9)			
C4H	6.9 (9)	C15H	14.7 (10)			
C5H	4.8 (7)	C16H	12.0 (12)			
C8H	6.4 (8)	C17H	13.4 (9)			
C9H	5.6 (9)	C18H	12.8 (9)			
C10H	5.3 (9)					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] For all hydrogen atoms the temperature factors are thermal Bs in Å^2.

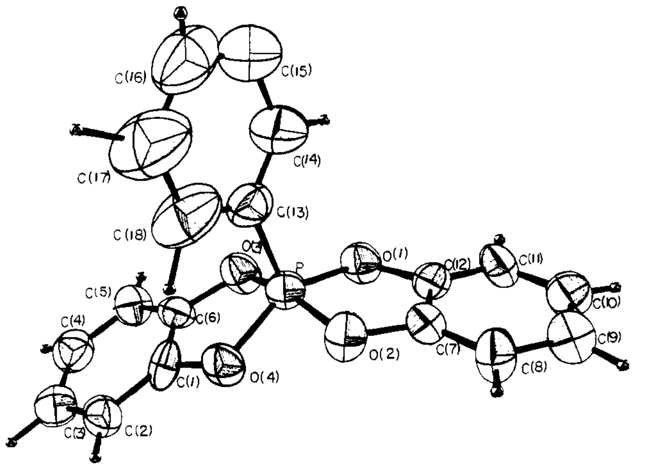


Figure 1. ORTEP drawing of a molecule of $(C_6H_4O_2)_2PC_6H_5$ with thermal ellipsoids at the 50% probability level for nonhydrogen atoms. Hydrogen atoms are represented by spheres of arbitrary radius.

Results and Discussion

Structure and Bonding. Bond lengths and angles for $(C_6H_4O_2)_2PC_6H_5$ are listed in Table III, and its structure is displayed in Figure 1.[20] Placement of the molecules in the unit cell is shown in Figure 2. There are no short intermolecular distances.

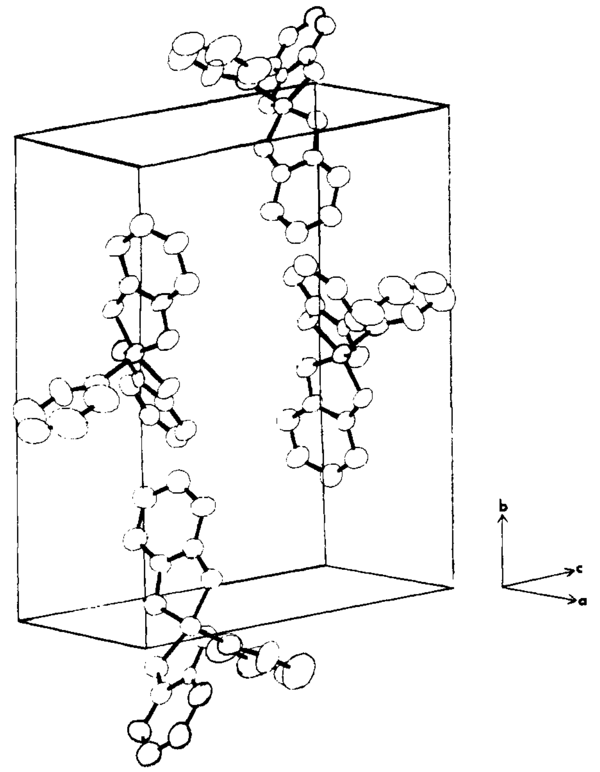


Figure 2. Unit cell ORTEP drawing of $(C_6H_4O_2)_2PC_6H_5$.

The molecular geometry is best viewed in relation to an idealized RP. From a quantitative assessment[7] of structural distortions of cyclic phosphoranes, the present catechol derivative is calculated to be 72% along the Berry exchange coordinate[8] toward the idealized RP based on the dihedral angle method (cf. Figure 7 of ref 7). If angular changes at phosphorus are considered (cf. Figure 5 of ref 7), the result is only slightly modified, 76%.

Pertinent structural features which allow this conclusion are

Table III. Bond Distances (Å) and Angles (deg) in $(C_6H_4O_2)_2PC_6H_5$

Distances			
P-O(1)	1.650 (4)	C(13)-C(14)	1.358 (11)
P-O(2)	1.682 (4)	C(14)-C(15)	1.469 (13)
P-O(3)	1.691 (4)	C(15)-C(16)	1.380 (18)
P-O(4)	1.655 (4)	C(16)-C(17)	1.395 (17)
P-C(13)	1.775 (6)	C(17)-C(18)	1.379 (13)
O(1)-C(12)	1.374 (6)	C(18)-C(13)	1.407 (11)
O(2)-C(7)	1.360 (6)	C(2)-C2H	0.98 (4)
O(3)-C(6)	1.371 (6)	C(3)-C3H	1.08 (6)
O(4)-C(1)	1.370 (6)	C(4)-C4H	0.96 (4)
C(1)-C(2)	1.399 (8)	C(5)-C5H	0.89 (5)
C(2)-C(3)	1.391 (8)	C(8)-C8H	0.98 (4)
C(3)-C(4)	1.432 (8)	C(9)-C9H	0.98 (4)
C(4)-C(5)	1.403 (9)	C(10)-C10H	0.90 (5)
C(5)-C(6)	1.367 (7)	C(11)-C11H	0.94 (5)
C(6)-C(1)	1.357 (8)	C(14)-C14H	1.07 (7)
C(7)-C(8)	1.378 (8)	C(15)-C15H	0.96 (8)
C(8)-C(9)	1.410 (9)	C(16)-C16H	0.96 (9)
C(9)-C(10)	1.405 (9)	C(17)-C17H	1.08 (8)
C(10)-C(11)	1.413 (9)	C(18)-C18H	1.08 (8)
C(11)-C(12)	1.376 (8)		
C(12)-C(7)	1.378 (8)		
Angles			
C(13)-P-O(1)	108.5 (2)	C(1)-C(2)-C(3)	116.0 (5)
C(13)-P-O(2)	100.0 (2)	C(2)-C(3)-C(4)	120.6 (6)
C(13)-P-O(3)	100.0 (2)	C(3)-C(4)-C(5)	121.4 (5)
C(13)-P-O(4)	106.1 (2)	C(4)-C(5)-C(6)	115.7 (5)
O(1)-P-O(2)	90.0 (2)	C(5)-C(6)-C(1)	123.5 (5)
O(3)-P-O(4)	89.9 (2)	C(6)-C(1)-C(2)	122.8 (5)
O(1)-P-O(4)	145.4 (2)	C(7)-C(8)-C(9)	116.5 (5)
O(2)-P-O(3)	160.0 (2)	C(8)-C(9)-C(10)	121.4 (6)
O(1)-P-O(3)	84.0 (2)	C(9)-C(10)-C(11)	121.1 (6)
O(2)-P-O(4)	84.2 (2)	C(10)-C(11)-C(12)	115.3 (5)
P-O(1)-C(12)	114.3 (3)	C(11)-C(12)-C(7)	124.2 (5)
P-O(2)-C(7)	113.5 (3)	C(12)-C(7)-C(8)	121.5 (5)
P-O(3)-C(6)	116.6 (3)	C(13)-C(14)-C(15)	119.0 (7)
P-O(4)-C(1)	113.1 (3)	C(14)-C(15)-C(16)	118.4 (8)
P-C(13)-C(14)	120.5 (6)	C(15)-C(16)-C(17)	122.0 (8)
P-C(13)-C(18)	119.1 (6)	C(16)-C(17)-C(18)	118.4 (9)
O(1)-C(12)-C(7)	110.7 (4)	C(17)-C(18)-C(13)	121.8 (8)
C(12)-C(7)-O(2)	111.2 (4)	C(18)-C(13)-C(14)	120.4 (6)
O(3)-C(6)-C(1)	110.8 (5)		
C(6)-C(1)-O(4)	112.3 (5)		

readily seen from the data in Table III. The four "catechol" oxygen atoms form an approximate base of a RP with the unique axial position occupied by the phenyl group. The base lengths are O(1)-O(2) = 2.359 (5); O(3)-O(4) = 2.363 (5); O(1)-O(3) = 2.230 (5); and O(2)-O(4) = 2.223 (5) Å. The four angles formed by the latter group to the basal oxygen atoms of the spirocyclic system average about 104°, near that for an idealized RP.

More detailed examination reveals the extent of structural change toward the idealized TP. The least-squares plane 1 of Table IV shows the trans basal oxygen atoms, O(1) and O(4), below and the other trans basal pair, O(2) and O(3), above the plane. A negative direction is upward in Figure 1, toward the phenyl substituent. Consistent with this, the trans basal angles are 145.4 (2) and 160.0 (2)°, respectively. Thus, residual equatorial character of a TP is indicated for the P-O(1) and P-O(4) bonds associated with the smaller phosphorus angle. Likewise the bonds P-O(2) and P-O(3), associated with the larger angle at phosphorus, have residual axial TP character.

The same effect shows up in the bond distance values, P-O(1) and P-O(4), with shorter lengths as expected for residual equatorial character, 1.650 (4) and 1.655 (4) Å, respectively, while the bonds having residual axial TP character, P-O(2) and P-O(3), show longer bond distances, 1.682 (4) and 1.691 (4) Å, respectively. Further, the four basal oxygen atoms make angles at phosphorus to the phenyl carbon with one pair centered at 100.0 (2)°, the pair of oxygen atoms which have residual axial character of a TP, and the other pair centered at a large angle, 107 (2)°, consistent with residual equatorial character of a TP.

As mentioned in the introduction, several catechol derivatives I have now been subjected to x-ray analyses.[10-12] The resulting structures bear a close resemblance to one another but do appear at different points[7] along a TP-RP distortion coordinate governed by a local C_{2v} constraint. The order[7] toward the idealized RP, including the phenyl derivative reported here, is F (65), Ph (72), adamantyl (73), CH_3 (82), and OPh (88). The numbers in parentheses indicate the percentage of the Berry coordinate traversed. Both increased steric interactions and reduced electronegativity associated with the axial ligand R are conducive to the formation of a RP, the former by steric repulsion of the axial group and ligands in the basal plane (in a TP, two of these ligands would be at 90°), the latter by an enhancement in electron pair repulsion between the axial group and basal ligands.[7,9]

In terms of the trend in electronegativity, F > Ph > CH_3, these groups are positioned correctly relative to each other

Table IV. Atom Distances from Least-Squares Planes (Å)[a]

	Plane				
	I[b]	II	III	IV	V
P		−0.003	−0.001	−0.112	−0.112
O(1)	0.100		0.001		0.118
O(2)	−0.102	0.003		0.174	0.172
O(3)	−0.096	0.003		0.161	0.162
O(4)	0.098		0.001	−0.117	
C(13)		0.000	0.001		

Plane									
VI		VII		VIII		IX		X	
C(1)	0.001	C(7)	0.003	C(13)	−0.003	P	−0.011	P	−0.005
C(2)	0.005	C(8)	0.006	C(14)	0.006	O(3)	0.068	O(1)	0.026
C(3)	−0.006	C(9)	0.014	C(15)	−0.005	C(6)	−0.077	C(12)	−0.026
C(4)	0.000	C(10)	0.011	C(16)	−0.002	C(1)	−0.071	C(7)	−0.036
C(5)	0.006	C(11)	−0.001	C(17)	0.005	O(4)	0.065	O(2)	0.031
C(6)	−0.006	C(12)	−0.005	C(18)	0.000				

[a] The weighting scheme used was, for the *i*th atom, $w_i = (a\sigma_x b\sigma_y c\sigma_z)^{-2/3}$. [b] The phosphorus atom is located 0.392 Å out of the mean plane of the four basal oxygen atoms toward the phenyl group.

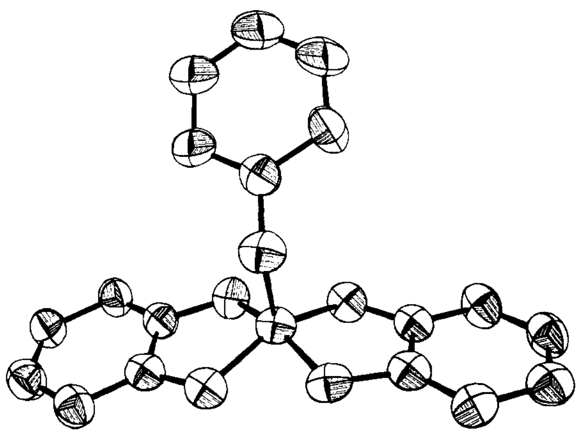


Figure 3. ORTEP plot of the molecular geometry of $(C_6H_4O_2)_2POC_6H_5$. The thermal ellipsoids are shown at the 50% probability level.

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

Planes[a]	Angle	Planes[a]	Angle
II, VIII	74.4	VI, IX	4.9
III, VIII	12.6	VII, X	5.6
II, III	86.9	IX, X	35.1

[a] Planes as defined in Table IV.

along the TP-RP coordinate. In terms of steric effects, the OPh group is correctly positioned in the series, closest to the RP. The phenyl bonded to oxygen, due to the angle at the oxygen atom, has a number of nonbonded contacts with the basal oxygen atoms, centered near 3.0 Å, and is rather symmetrically placed between the two "catechol" rings[11] as the ORTEP plot[20] in Figure 3 indicates.

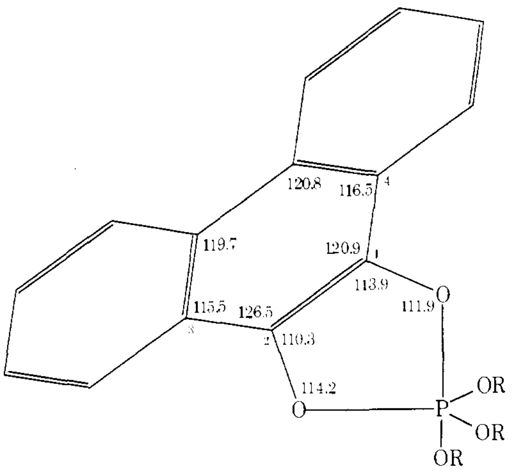
The position of the adamantyl moiety, which appears to exert a steric effect at least as large as the OPh group, is not easily rationalized at present. As the structural data indicate,[12] the single C-C bonds of the adamantyl group, near the "catechol" ring systems, are somewhat elongated as is the P-C bond, 1.838 Å. The latter value compares with 1.775 and 1.777 Å for the two independent molecules present in the methyl derivative,[10b] and 1.775 (6) Å for the P-C bond in the phenyl derivative.

Most of the other bond distances and angles in the phenyl derivative under study here follow a pattern similar to that in related catechol compounds.[10-12] The smaller angles in the six-membered portions of the basal rings at C(2), C(5), C(8), and C(11), near 116 (1)°, complement the larger angles at C(1), C(6), C(7), and C(12), respectively, centered at 123 (2)°, and are similar to those observed in related derivatives.[10-12] These angle variations are more pronounced in a TP. For example, in the phenanthrenequinone II[21] and the amino bicyclic III[22] structures, which closely follow the TP-SP coordinate (being 16 and 35%, respectively, along the coordinate[7]), the effect is enhanced at the ring carbon atoms labeled C(2) compared to those labeled C(1).

No doubt, these subtle angle alternations are again a manifestation of secondary effects associated with the considerable difference in axial vs. equatorial bonding in a TP. Since the basal bonds of an idealized RP are intermediate in character between the two types of bonds in a TP,[7,9] ring systems such as these under discussion, I-III, exhibit more of an averaging of the angle variations as the RP structure is approached. In structure III,[22] the saturated five-membered ring, which can reduce ring strain as a result of ring puckering compared to an unsaturated ring, shows less variation in bond angles and distances centered at the ring carbon atoms.

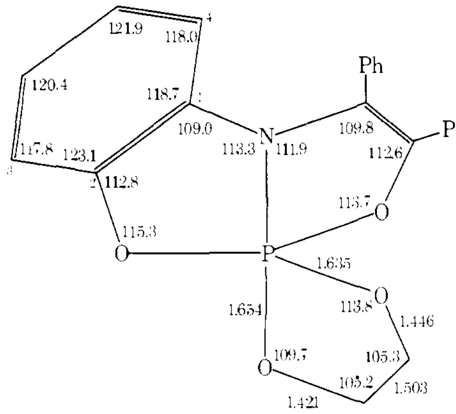
Several additional least-squares planes are included in Table IV which may be of interest for different comparisons. Planes II and III are rigorously satisfied for idealized TP and SP geometries. For strict adherence to distortions following a local C_{2v} constraint, a dihedral angle between planes II and III in the range 85.9-90.0° is expected. The observed value between the least-squares planes II and III is 86.9° (Table V). Planes IV and V, whose atoms show average distances out of these planes of 0.141 Å, would be exactly followed if the geometry were strictly TP. Plane I is a defining plane for an idealized SP (RP). Here an average out-of-plane atom distance of 0.099 Å is obtained.

As with other members of this class of cyclic phosphoranes,[10-12] the least-squares planes show very small average out-of-plane variations, ~0.005 Å for the "benzene" rings and somewhat higher average variations for the five-membered hetero rings, 0.04 Å. The dihedral angles between the least-squares planes of the fused five- and six-membered rings of the



R = *i*-Pr

II



III

distances, Å

angles, deg

basal system on the right in Figure 1 is 5.6° and for that on the left, 4.9° (Table V).

Acknowledgment. The support for this research by the National Science Foundation (MPS 74-11496) and the National Institutes of Health (GM 21466) is gratefully acknowledged as is the inclusion of funds by NSF for the purchase of an Enraf-Nonius CAD 4 diffractometer. The authors are indebted to Professor J. S. Wood for his assistance with the structure solution and refinement. We also wish to thank the University of Massachusetts Computing Center for computer time and Mr. Robert Gonter for his help with several of the locally written programs.

Supplementary Material Available: A compilation of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Pentacoordinated Molecules. 22. (b) Previous paper in this series: R. R. Holmes and J. A. Deiters, *J. Am. Chem. Soc.*, **99**, 3318 (1977).
(2) This work represents a portion of the Ph.D. Thesis of R. K. Brown, University of Massachusetts, Amherst.
(3) For recent reviews refer to (a) R. Luckenbach, "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements", Georg Thieme Verlag, Stuttgart, 1973; (b) W. E. McEwen and K. D. Berlin, Ed., "Organophosphorus Stereochemistry", Parts I and II, Dowden, Hutchinson and Ross, Stroudsburg, Pa., 1975.
(4) F. H. Westheimer, *Acc. Chem. Res.*, 1, 70 (1968).
(5) F. M. Richards and H. W. Wyckoff, "Bovine Pancreatic Ribonuclease", in "The Enzymes", Vol. IV, 3rd ed, P. D. Boyer, Ed., Academic Press, New York, N.Y., 1971, pp 647–806, and references cited therein.
(6) (a) D. L. Sloan, L. A. Loeb, and A. S. Mildvan, *J. Biol. Chem.*, **250**, 8913 (1975); (b) A. S. Mildvan, *Annu. Rev. Biochem.*, **43**, 357 (1974); (c) A. Kornberg, "DNA Synthesis", W. H. Freeman, San Francisco, Calif., 1974; (d) L. Stryer, "Biochemistry", W. H. Freeman, San Francisco, Calif., 1975, pp 574 and 603.
(7) See ref. 1b.
(8) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).
(9) (a) R. R. Holmes, *J. Am. Chem. Soc.*, **97**, 5379 (1975); (b) *ibid.*, **96**, 4143 (1974).
(10) (a) H. Wunderlich and D. Mootz, *Acta Crystallogr., Sect. B*, **30**, 935 (1974); (b) H. Wunderlich, *ibid.*, **30**, 939 (1974).
(11) R. Sarma, F. Ramirez, and J. F. Maracek, *J. Org. Chem.*, **41**, 473 (1976).
(12) W. S. Sheldrick, personal communication.
(13) (a) M. Wieber and W. R. Hoos, *Tetrahedron Lett.*, 5333 (1968); (b) *ibid.*, 4693 (1969); (c) *Monatsh. Chem.*, **101**, 776 (1970).
(14) One of a package of routines including cell refinement and data collection programs supplied by Enraf-Nonius Inc. for use with the PDP-8E computer.
(15) The unit cell for this molecule is nearly identical with that of $(C_6H_5O)P(C_6H_4O_2)_2$, which also crystallizes in space group $P2_1/c$ and has $a = 6.910$, $b = 15.305$, $c = 14.779$ Å, $\beta = 88.5°$, $Z = 4$.[11] Initially, it was thought that the two structures might be isomorphic. However, this was not the case.
(16) (a) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957); (b) R. C. G. Killean, D. F. Grant, and J. L. Lawrence, *Acta Crystallogr., Sect. B*, **25**, 374 (1969).
(17) (a) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971); (b) T. Debaerdemaeker and M. M. Woolfson, *ibid.*, **28**, 477 (1972).
(18) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(19) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(20) C. K. Johnson's program ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(21) R. D. Spratley, W. C. Hamilton, and J. Ladell, *J. Am. Chem. Soc.*, **89**, 2272 (1967).
(22) W. S. Sheldrick, personal communication; A. Schmidpeter, D. Schomburg, W. S. Sheldrick, and J. H. Weinmaier, *Angew. Chem.*, **88**, 851 (1976).