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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### INTERCONVERSION OF COMPOUNDS WITH PENTA-AND HEXACOORDINATE PHOSPHORUS. CRYSTAL AND MOLECULAR STRUCTURE OF THE TRIALKYLAMMONIUM

### HEXAOXYPHOSPHORIDE, $[(\text{PO}_6)(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_4)(\text{CF}_3\text{C}=\text{CCF}_3)]^+[(\text{C}_2\text{H}_5)_3\text{NH}]^-$

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# INTERCONVERSION OF COMPOUNDS WITH PENTA- AND HEXACOORDINATE PHOSPHORUS. CRYSTAL AND MOLECULAR STRUCTURE OF THE TRIALKYLAMMONIUM HEXAOXYPHOSPHORIDE, $[(\text{PO}_6)(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_4)(\text{CF}_3\text{C}=\text{CCF}_3)]^-[(\text{C}_2\text{H}_5)_3\text{NH}]^+$

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(Received August 19, 1978)

The structure of triethylammonium diphenoxy-o-phenylenedioxy-1,2-bistrifluoromethylethylenedioxyphosphoride, a compound with hexacoordinate phosphorus obtained by addition of triethylammonium phenoxide to the pentacoordinate phosphorus precursor, has been determined by x-ray crystallographic methods. The compound crystallizes from ether in space group  $P2_1/n$  of the monoclinic system. There are four formula units,  $(\text{C}_{22}\text{H}_{14}\text{O}_6\text{F}_6\text{P})^-(\text{NC}_2\text{H}_5)_3^+$  in the unit cell ( $Z = 4$ ), with one ion-pair constituting the asymmetric unit of the crystal. The cell dimensions are  $a = 10.787(5)$ ,  $b = 16.604(6)$ ,  $c = 16.668(4)$  Å;  $\beta = 102.84^\circ(3)$ ;  $D_{\text{calc}} = 1.415 \text{ g cm}^{-3}$ ,  $D_{\text{meas}} = 1.412 \text{ g cm}^{-3}$  ( $25^\circ$ ). Data were obtained on a CAD4 automatic diffractometer; 5310 unique non-zero reflections were collected with  $\theta \leq 75^\circ$  using  $(\theta-2\theta)$  scan, with a scan width of  $1.0^\circ$ . The phosphorus and oxygen atoms were located using the MULTAN program. All other non-hydrogen atoms were found in subsequent iterations of partial-structure phased Fourier maps. The structure was refined by full-matrix least-squares techniques to a final  $R_w$  value of 7.5% on F based on 4855 independent reflections. The phosphorus atom is hexacoordinate and at the center of a nearly regular octahedron, with the two phenoxy groups *cis* to each other. The two P—O (exocyclic) bonds are shorter (ave. 1.656(4) Å) than the four P—O (endocyclic) bonds (ave. 1.711(4) Å). The positively charged nitrogen is closer to two of the uncharged oxygen ligands (3.000 and 3.108(6) Å) than to the negatively charged phosphorus (4.063(6) Å) within the formula unit. The changes in molecular parameters when an oxyphosphoride is derived from an oxyphosphorane by addition of a sixth oxy-ligand are discussed.

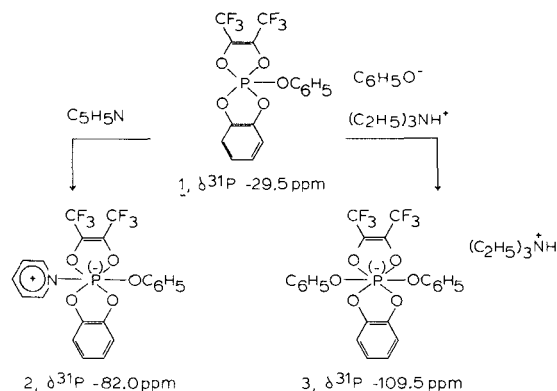
In 1968, Ramirez and coworkers<sup>2</sup> postulated that nucleophilic displacements at the P(5)<sup>3</sup> atom of *stable* oxyphosphoranes<sup>4</sup> occurred via P(6) intermediates. This hypothesis has been subsequently invoked by several investigators to interpret related types of phenomena.<sup>5-9</sup>

Nucleophilic displacements at the P(4) atom of phosphonium salts and of some types of phosphate esters proceed via *transient* oxyphosphorane intermediates,<sup>10-14</sup> and it is conceivable that P(6) intermediates may also be involved in reactions of P(4) compounds under certain conditions.<sup>15,16</sup> This concept has been utilized in several recent studies involving different types of P(4) compounds.<sup>17-21</sup>

The present investigation was undertaken in an effort to correlate the molecular structure of the *stable* oxyphosphorane,<sup>22</sup> **1**, with that of the related oxyphosphoride,<sup>23</sup> **3**. The latter is obtained by addition of triethylammonium phenoxide to the oxyphosphorane **1** in solution. The ion-pair oxyphosphoride,

**3**, is somewhat more stable than the zwitterion analog, **2**, which is formed when pyridine is added to the same P(5) precursor **1**.<sup>23</sup> In this series of compounds, both P(5) and P(6) structures generate single crystals suitable for analysis by x-ray crystallographic methods.<sup>22</sup> A correlation of molecular parameters among interconvertible oxyphosphorane-oxyphosphoride pairs should provide valuable insight into the stereoelectronic properties of these two valence states of phosphorus. In solution, such interconversions, e.g.  $\text{RP}(\text{OC}_6\text{H}_5)_4 + \text{C}_6\text{H}_5\text{O}^- \rightleftharpoons \text{RP}(\text{OC}_6\text{H}_5)_5$  have been detected also by means of NMR spectroscopy.<sup>24</sup>

The first example of a crystalline oxyphosphoride, namely, triethylammonium *tris*-o-phenylenephosphoride, was isolated by Allcock in 1964.<sup>25</sup> Further work by Allcock and his coworkers<sup>26</sup> led to the elucidation of this structure by x-ray crystallographic methods.<sup>27</sup> A relatively large number of oxyphosphorides have been reported in recent



years,<sup>28–41</sup> and in most cases, the main criterion for the assignment of the P(6) structure has been the relatively effective shielding of the corresponding  $^{31}P$  nucleus by electrons, as reflected by the high-field displacement of the nmr signal relative to that of the usual P(4) reference compound.<sup>42</sup> Carbo-phosphorides<sup>43–46</sup> and halophosphorides<sup>47–53</sup> have also been extensively investigated.

## EXPERIMENTAL

**Preparation of triethylammonium diphenoxy-*o*-phenylenedioxy-1,2-bis(trifluoromethylethenylenedioxy)phosphoride (3)** Compound 3 was prepared from the reaction of phenoxy-*o*-phenylenedioxy-1,2-bis(trifluoromethylethenylenedioxy)phosphorane (or 2-phenoxy-2,2-phenylenedioxy-4,5-bis(trifluoromethyl-2,2-dihydro-1,3,2-dioxaphospholene) (1) with 1 mol equiv of phenol and triethylamine in ether solution at 0°, by the procedure described.<sup>23</sup> The crystals for x-ray analysis were obtained from diethyl ether at 0°, directly from the reaction mixture; they had mp 119–121°, and  $\delta^{31}P$  -109.5 ppm<sup>42</sup> in a freshly prepared, nearly saturated  $CD_2Cl_2$  solution (*ca.* 1 M).

**Crystal data** Compound 3,  $(C_{22}H_{14}O_6F_6P)^-(NC_2H_5)_3^+$ : monoclinic;  $P2_1/n$ ;  $a = 10.787(5)$ ,  $b = 16.604(6)$ ,  $c = 16.668(4)$  Å;  $\beta = 102.84^\circ(3)$ ;  $V = 2911$  Å<sup>3</sup>;  $Z = 4$  (one formula unit per asymmetric unit);  $D_{calc} = 1.415$  g cm<sup>-3</sup>,  $D_{meas} = 1.412$  g cm<sup>-3</sup>, by flotation in bromoform-1,2-dichloroethane, at 25°.

**Data collection and structure determination.** The crystals were sensitive to atmospheric moisture and were sealed inside a capillary tube in an argon atmosphere. Intensity data were collected using a computer controlled ENRAF–NONIUS CAD4 automatic diffractometer using nickel filtered  $CuK\alpha$  ( $\lambda = 1.542$  Å) radiation. A  $(\theta-2\theta)$  scan was used with a scan width of 1° and a scan speed of 1.5°/min. Approximately 5310 unique non-zero reflections with  $\theta \leq 75^\circ$  were measured from one crystal. Of these, about 450 reflections were eliminated as they had their intensities less than or equal to  $2\sigma$  as measured from counting statistics. The remaining 4860 reflections were used in the structure analysis.

Since the crystal was sealed inside a capillary tube an empirical absorption correction was applied; this correction<sup>54</sup> was determined by performing an azimuth scan for a reflection occurring on the diffractometer at a  $\chi$  value of nearly 90°. The

variation in intensity of this reflection with the azimuth angle 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 all other reflections. For the crystal used in the above data collection the transmission factor varied from a value of 1.00 to 1.40 during a scan of 180°.

The structure amplitudes derived in the usual way after correction for Lorentz polarization, and absorption factors, were used to calculate a sharpened Patterson map. The Patterson map indicated the position of the phosphorus atom unambiguously. The phases of 499 reflections with  $E$  value greater than 1.2, calculated using the MULTAN program of Main *et al.*<sup>55</sup> were used to independently confirm the above position of phosphorus and also to indicate the positions of the six oxygen atoms in the molecule. The remaining atoms of the structure were determined in successive Fourier maps calculated with phases from the partial structures. All the non-hydrogen atoms were refined using the full matrix least squares program of L. W. Finger described in NBS Technical Note 854. The function minimized was  $\sum \omega(\Delta F)^2$  with weights derived from  $\sigma(I)$  through  $\omega = 1/\sigma^2(F)$ . The refinement was carried to an  $R_w$  factor of 7.5% for 4855 reflections. A final difference electron density map showed no significant, non-hydrogen atom electron density. The final parameters are presented in Table VI (see paragraph concerning supplementary material at the end of this paper).

## DISCUSSION OF RESULTS

**Molecular structure of the trialkylammonium hexaoxyphosphoride 3** Figure 1 illustrates the formula unit of the compound, and Figure 2 shows

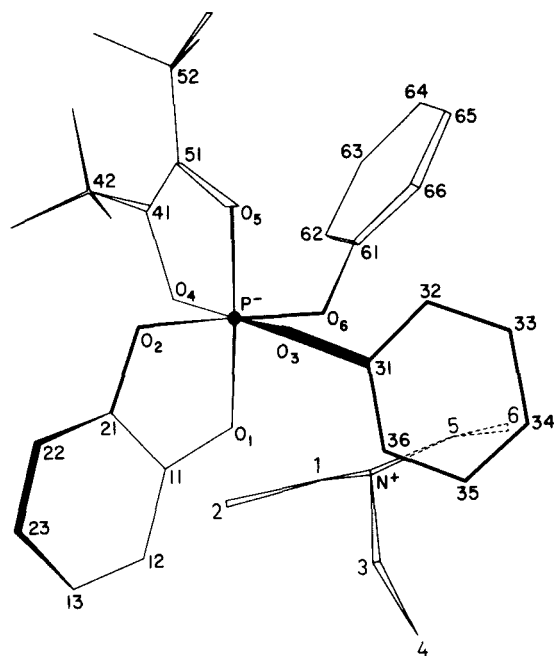


FIGURE 1 Computer generated drawing of a molecule of compound 3.

TABLE I

Main interatomic distances (Å) and angles (deg) within the formula unit of compound 3

(i) Bond distances <sup>a</sup>			
P—O(1)	1.686	O(1)—C(11)	1.380
P—O(2)	1.721	O(2)—C(21)	1.365
P—O(3)	1.653	O(3)—C(31)	1.391
P—O(4)	1.736	O(4)—C(41)	1.364
P—O(5)	1.703	O(5)—C(51)	1.329
P—O(6)	1.660	O(6)—C(61)	1.410
C(11)—C(21)	1.375	C(31)—C(32)	1.372
C(11)—C(12)	1.403	C(32)—C(33)	1.408
C(12)—C(13)	1.362	C(33)—C(34)	1.448
C(21)—C(22)	1.374	C(34)—C(35)	1.364
C(22)—C(23)	1.379	C(35)—C(36)	1.388
C(23)—C(13)	1.423	C(36)—C(31)	1.372
C(41)—C(42)	1.446	C(61)—C(62)	1.369
C(41)—C(51)	1.319	C(62)—C(63)	1.419
C(42)—F(41)	1.232	C(63)—C(64)	1.413
C(42)—F(42)	1.307	C(64)—C(65)	1.368
C(43)—F(43)	1.296	C(65)—C(66)	1.452
C(51)—C(52)	1.421	C(66)—C(61)	1.407
C(52)—F(51)	1.280		
C(52)—F(52)	1.306		
C(52)—F(53)	1.334		
N—C(1N)	1.490	C(1N)—C(2N)	1.491
N—C(3N)	1.524	C(3N)—C(4N)	1.489
N—C(5N)	1.507	C(5N)—C(6N)	1.575
(ii) Interionic Distance			
P <sup>−</sup> N <sup>+</sup> 4.063			
(iii) Nonbonded Distances 3.8 Å			
O(1)⋯O(6)	2.259 ( <i>cis</i> minimum)	O(2)⋯O(6)	3.380 ( <i>trans</i> minimum)
O(5)⋯O(6)	2.484 ( <i>cis</i> maximum)	O(1)⋯O(5)	3.386 ( <i>trans</i> maximum)
N⋯O(6)	3.000	N⋯C(61)	3.641
N⋯O(1)	3.108	N⋯C(66)	3.708
(iv) Bond Angles			
O(1)—P—O(2)	91.3	O(3)—P—O(6)	93.4
O(1)—P—O(3)	95.0	O(4)—P—O(5)	88.5
O(1)—P—O(4)	87.3	O(4)—P—O(6)	91.4
O(1)—P—O(5)	175.8	O(5)—P—O(6)	95.2
O(1)—P—O(6)	84.9	P—O(1)—C(11)	111.5
O(2)—P—O(3)	87.1	P—O(2)—C(21)	111.4
O(2)—P—O(4)	88.2	P—O(3)—C(31)	129.1
O(2)—P—O(5)	88.5	P—O(4)—C(41)	110.3
O(2)—P—O(6)	176.3	P—O(5)—C(51)	113.1
O(3)—P—O(4)	174.8	P—O(6)—C(61)	124.7
O(3)—P—O(5)	89.1		

<sup>a</sup> The esd's for P—O, O—C, C—C, C—F, and C—N are 0.004, 0.008, 0.013, 0.010, and 0.011 Å, respectively; for P<sup>−</sup>N<sup>+</sup>, 0.006 Å; for all bond angles, 0.3°.

the contents of one unit cell. The interatomic distances and bond angles within the formula unit are listed in Table I. Some distances between atoms in adjacent formula units are given in Table II. Equations of least-squares planes, and deviations of certain atoms from these planes are presented in

Table III, and dihedral angles formed by pairs of these planes are shown in Table IV.

The asymmetric unit of the crystal of compound **3** consists of one oxyphosphoride anion and one trialkylammonium cation, with this ion-pair constituting a discrete "molecule". The distance between

TABLE II  
Distances  $< 3.5$  Å between atoms in adjacent formula units (FU)<sup>a</sup>

Atom in FU 1	Atom in FU 2	Distance, Å	Symmetry operation
F(42)	F(43)	2.978	$-x + 1, -y + 1, -z$
F(41)	F(43)	3.048	$-x + 1, -y + 1, -z$
F(43)	F(43)	3.316	$-x + 1, -y + 1, -z$
O(2)	C(1N)	3.339	$1/2 + x, 1/2 - y + 1, 1/2 + z$
F(51)	C(3N)	3.380	$x + 1, y, z$
O(3)	C(4N)	3.395	$1/2 + x, 1/2 - y + 1, 1/2 + z$
F(41)	F(42)	3.401	$-x + 1, -y + 1, -z$
C(42)	F(43)	3.438	$-x + 1, -y + 1, -z$
F(53)	C(5N)	3.462	$1/2 + x, 1/2 - y + 1, 1/2 + z$
C(33)	F(42)	3.479	$1/2 - x, 1/2 + y, 1/2 - z$

<sup>a</sup> P(I)  $\cdots$  N(III) is 5.074 Å, where Roman numerals refer to formulas shown in Figure 2.

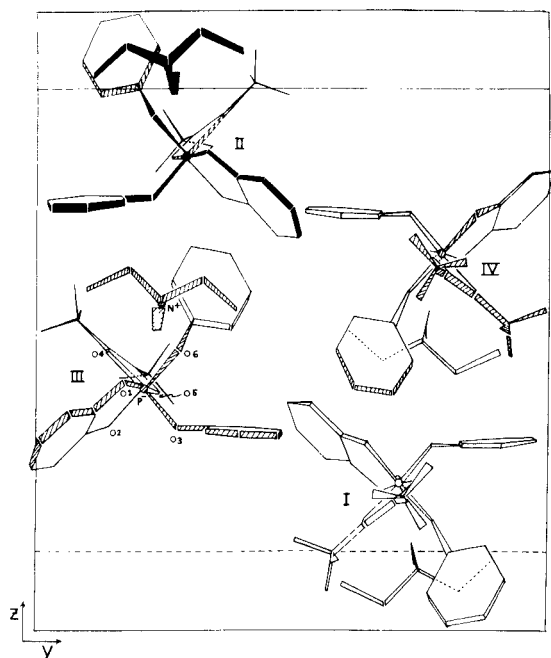


FIGURE 2 Packing of the formula units (ion-pairs) in compound 3. The view is perpendicular to the  $y$ - $z$  plane.

the anion and the cation in the ion-pair is 4.063 Å, while the cation is only 3.000 and 3.108 Å from closest neighbors within the formula units, namely, the phenoxy O(6) and the endocyclic O(1) atoms, respectively.

The P(6) atom is at the center of a nearly regular octahedron, with the two phenoxy groups in *cis* or vicinal positions, and the two five-membered dioxaphospholene rings orthogonal to each other.

TABLE III

Coefficients  $A, B, C, D$  of the equation to plane,  $AX + BY + CZ - D = 0$ , where  $X, Y, Z$  are coordinates relative to orthogonal axes. Deviations in Å of individual atoms from planes; root mean square deviations in parentheses

Plane 1:	O(1), O(2), O(5), O(6) (0.028) -0.449; 0.647; 0.616; 8.494 P = 0.038
Plane 2:	O(1), O(3), O(4), O(5) (0.033) -0.023; 0.689; -0.724; 6.296 P = 0.036
Plane 3:	O(2), O(3), O(4), O(6) (0.043) 0.903; 0.360; 0.234; 5.961 P, 0.011
Plane 4:	P, O(1), O(2), C(11), C(21) (0.015) -0.462; 0.650; 0.603; 8.500
Plane 5:	C(31), C(32), C(33), C(34), C(35), C(36) (0.012) -0.182; -0.058; 0.982; 2.490 O(3) = 0.113
Plane 6:	P, O(4), O(5) (0.0) -0.005; 0.664; -0.748; 5.993
Plane 7:	O(4), O(5), C(41), C(42), C(51), C(52) (0.015) 0.098; 0.628; -0.772; 5.774
Plane 8:	C(61), C(62), C(63), C(64), C(65), C(66) (0.011) -0.705; 0.448; -0.549; 4.224 O(6) = 0.100

TABLE IV

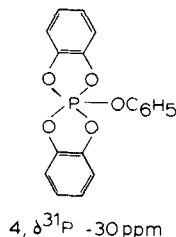
Dihedral angles for least squares planes<sup>a</sup>

Plane 1–Plane 2	89.37°
Plane 1–Plane 3	91.63°
Plane 2–Plane 3	86.70°
Plane 6–Plane 7	6.42°

<sup>a</sup> The planes are defined in Table III. The dihedral angles,  $\theta$ , are expressed as  $\leq 90^\circ$ .

This structure confirms the earlier stereochemical assignment based on the presence of two nmr signals in the  $^{19}\text{F}$  nmr spectrum of a dichloromethane solution of compound **3** at  $25^\circ$ . The alternative configuration, with trans or distal phenoxy groups and both dioxaphospholene rings in one plane, would have resulted in structurally equivalent trifluoromethyl groups. The ring with the ethylenedioxy-group is slightly puckered, with the phosphorus atom in the flap of an envelope conformation.

In the oxyphosphoride anion, the two exocyclic P—O distances are shorter (ave. 1.656(4) Å) than the four endocyclic P—O distances (ave. 1.711(4) Å). This suggests a higher degree of  $p-d$   $\pi$ -bonding<sup>56</sup> involving the phosphorus atom and the lone electron pairs of the phenoxy oxygen atoms, relative to the lone pairs on endocyclic oxygens. This effect has also been observed in the precursor oxyphosphorane<sup>23</sup> **1**, and in the related oxyphosphorane **4**, for which there is structural information from x-ray crystallography.<sup>57</sup> This difference in exo- and endocyclic P—O bond distances has been attributed to a "steric inhibition of  $p-d$   $\pi$ -bonding" when the two oxygen atoms form part of a relatively small ring, such as five- and four-membered rings. The effect has been correlated to the significant departure from the regular trigonal bipyramidal geometry which is observed in oxyphosphoranes **1** and **4**, i.e., when the two small rings define a spiro-configuration with respect to the P(5) atom.<sup>58,59</sup> The effect has also been related to the decrease in the shielding of the P-nucleus by electrons, as reflected in a displacement of the  $^{31}\text{P}$  nmr chemical shift toward lower magnetic fields (i.e., a decrease in the negative value of the signal<sup>42</sup>), which is observed when one or more five-membered rings are introduced in an acyclic pentaoxyphosphorane, e.g.,  $(\text{C}_6\text{H}_5\text{O})_5\text{P}$ ,  $\delta^{31}\text{P} = -88.7$  ppm.<sup>58,59</sup>



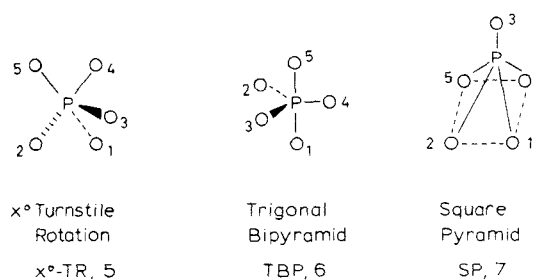
Concerning the packing of the ion-pairs in the crystal (Figure 2 and Table II), the close contacts involving atoms in adjacent formula units are of the hydrophobic-hydrophobic type. The closest approach between the anion of one formula unit and the cation of another is  $\text{P}(\text{I}) \cdots \text{N}(\text{III}) = 5.074$  Å.

TABLE V

Bond angles around the pentacoordinate phosphorus in the spiro-pentaoxyphosphorane **1**

Atoms	Angle, deg.	Atoms	Angle, deg.
O(1)—P—O(5)	169.5	O(1)—P—O(3)	95.4
O(2)—P—O(4)	139.0	O(1)—P—O(2)	92.3
O(3)—P—O(4)	111.0	O(4)—P—O(5)	88.7
O(2)—P—O(3)	110.0	O(1)—P—O(4)	84.8
O(3)—P—O(5)	98.6	O(2)—P—O(5)	84.3

*Correlation of molecular parameters in the phosphoride **3** and its phosphorane precursor **1*** The bond angles around the P(5) atom in the phosphorane **1** are listed in Table V.<sup>22</sup> The geometry of the molecule from x-ray data is shown in Figure 3. The P(5) coordination polyhedron for this type of "non-trigonal bipyramidal" oxyphosphorane has been represented by formula **5**, i.e., an  $x^\circ$ -turnstile rotation configuration.<sup>59</sup> For reasons already given a convenient classification of these compounds can be made according to the value of  $x$  in  $x^\circ$ -TR, where  $x$  refers to the dihedral angle formed by plane O(1), P, O(4) and plane O(4), P, O(5). In phosphorane **1**,  $x = 9^\circ$ . The larger the value of  $x$ , the greater the departure of the P(5) coordination from trigonal bipyramidal geometry, e.g.,  $x = 15^\circ$  in the spiro-oxyphosphorane **4**, which shows an even less regular geometry than that of analog **1**. For comparison purposes, the hypothetical distribution of the five oxyphosphorane ligands on the skeletons of the regular trigonal bipyramid and the regular square pyramid are shown in formulas **6** (angles of  $180^\circ$ ,  $120^\circ$ , and  $90^\circ$ ) and **7** (angles of  $150^\circ$ ,  $105^\circ$ , and  $86^\circ$ ), respectively.



There are significant differences in the intramolecular non-bonded distances between the oxyphosphorane ligands in the  $x^\circ$ -TR, the TBP, and the SP skeletal geometries; note, for example, that ligands O(1), O(2), O(4) and O(5) are not in one plane in formula **5**, as they would be in formula **7**.

Moreover, there are significant differences in the bond distances of the five ligands of an oxyphosphorane when the configuration is of the TBP type *vs.* the non-TBP type. In the TBP oxyphosphoranes ( $x^\circ = 0$ , as defined above), the three equatorial bonds are distinctly shorter than the two apical bonds, and this has been attributed, in part, to higher degree of  $p-d$   $\pi$ -bonding when an oxy-ligand is equatorial than when it is apical.<sup>60</sup> However, in non/TBP oxyphosphoranes where  $x > 8^\circ$ , there is no longer a differentiation between equatorial and apical bonds in terms of the P—O bond distances.<sup>59</sup> With these considerations in mind, it is instructive to compare the molecular parameters of the oxyphosphorane **1** and its analogous oxyphosphoride **3**.

The phosphorane **1** (Figure 3, Table V) can be transformed into the phosphoride **3** (Figure 4, Table I) by an attack of the phenoxide ion on P(5) in line with ligands O(4) or O(2), both of which form part of five-membered rings. The O(4)-in-line attack results in the least motion of the ligands and is, therefore, the most attractive reaction path, i.e. the ligands designated as O(3) and O(6) in the phosphoride of Figure 4 correspond, respectively, to the attacking phenoxide and the phenoxide already present in the phosphorane [i.e., O(3) in Figure 3]. In both, the O(4)-in-line and the O(2)-in-line attacks, the entering phenoxide would bisect angles that involve one ring-oxygen and one phenoxide oxygen. However, the O(4)-in-line attack results, directly and with the minimum group motion, in the least crowded molecule. Note that the phenyl rings attached to O(3) and O(6) in Figure 4 are relatively uncrowded, since there is space available around

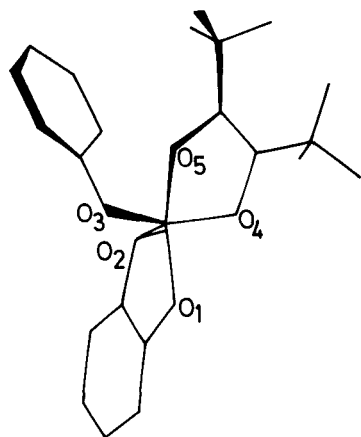


FIGURE 3 A molecule of the penta-oxyphosphorane, **1**, precursor of the trialkylammonium hexa-oxyphosphoride, **3**, from data in Ref. 22.

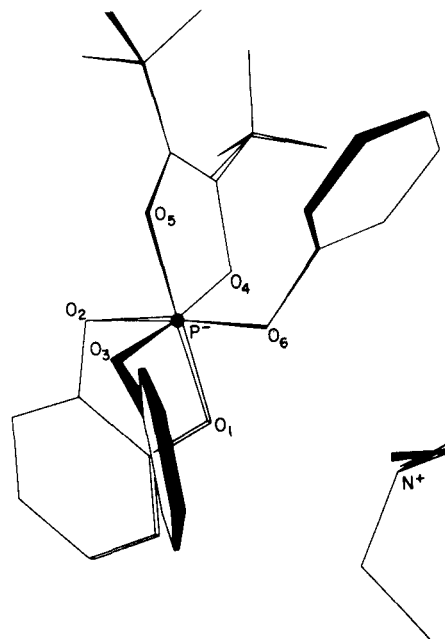


FIGURE 4 View of the hexa-oxyphosphoride ion-pair, **3**, illustrating its relationship to the penta-oxyphosphorane precursor, **1**. Ligand O(6) in Figure 4 is assumed to correspond to ligand O(3) in Figure 3 from "minimum-motion" considerations.

ligands O(1), O(6) and O(3), O(5), respectively. In the P(6) anion, the region around O(1), O(4), O(6) is relatively uncrowded and permits the closest approach of the bulky triethylammonium cation to the P-anion. This can also be seen in Figures 1 and 2, with the positive nitrogen being closest to O(6) and O(1).

Analogous steric arguments can be advanced to explain why the attacking phenoxy group does not approach the phosphorane in line with the P—O(3) axis, which would result in a different diastereoisomer. In the O(3)-in-line approach, the entering phenoxide bisects an angle defined by two ring-oxygens, which is at first sight a favorable steric situation; however, the two phenoxy-rings end up creating a more crowded phosphoride than in the alternate diastereoisomer.

**Conclusions** The stereochemistry of oxyphosphoranes, e.g. **1** (Figure 3), and oxyphosphorides, e.g., **3** (Figure 4) must be analyzed not only in terms of the geometry of the polyhedra defined by the phosphorus atom and its ligands, but also in terms of the conformation of all the groups which surround those polyhedra. The preferred overall molecular configuration of these compounds

seems to depend on both electronic and steric factors. It is suggested that the geometry of the oxyphosphorane coordination polyhedron is quite sensitive to  $p-d$   $\pi$ -bonding involving lone electron pairs on ligated oxygen atoms. Other factors being equal, the extent of this  $p-d$   $\pi$ -bonding is greater when the ligand is in a P(5) trigonal bipyramidal equatorial position than when it is in an apical position. There seems to be a steric inhibition of this  $p-d$   $\pi$ -bonding when two five-membered rings are present in a spiro-configuration in penta-oxyphosphoranes. The effect of this steric inhibition is to prevent the establishment of the trigonal bipyramidal geometry about P(5). If this steric inhibition effect is operative also in oxyphosphorides, it does not seem to affect the establishment of the octahedral geometry about P(6). The conformation of the groups around the coordination polyhedron, in both oxyphosphoranes and oxyphosphorides, seems to be largely determined by the available space around the phosphorus, and by the steric demands of the groups themselves. It is recognized that the stereochemical information on which these conclusions are based has been obtained in the crystalline state of the compounds. However, two arguments can be advanced to support the speculation that analogous stereochemistry may prevail in solutions of the oxyphosphoranes and the oxyphosphorides: (1) The type of intermolecular contacts revealed by the crystal packing; (2) the effect observed on the  $^{31}\text{P}$  nmr shifts by the introduction of rings in the oxyphosphoranes, which represent data in solution and agree with the steric inhibition of  $p-d$   $\pi$ -bonding hypothesis. The results of the investigation offer some support to the view that nucleophilic substitutions on stable oxyphosphoranes, and nucleophilic catalysis of reactions of phosphotriesters with alcohols, may involve the interconversion of P(5) and P(6) structures.

**Supplementary material available** Table VI, Fractional Coordinates and Thermal Parameters for Nonhydrogen Atoms, and Table VII, Structure Factors (31 pages). This material can be consulted by writing to the senior author.

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