Crystal and Molecular Structure of a Five-Membered Cyclic Unsaturated Pyrophosphate, $P_2O_7C_8H_{12}$

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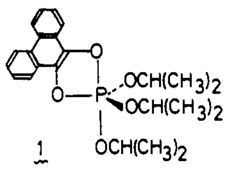
Abstract: The crystal and molecular structure of a new type of five-membered cyclic unsaturated pyrophosphate [acetoinenediol cyclopyrophosphate ($P_2O_7C_8H_{12}$)] was solved by X-ray crystallographic techniques. There are two independent molecules (A and B) in the asymmetric unit; the bond distances and angles are very similar in both molecules, which differ mainly in the dihedral angles (75 vs. 69°) between the two planes each containing the atoms O═P—O of the O═P—O—P═O system. The unsaturated five-membered rings are planar and are irregular pentagons (average value of endocyclic O—P—O angle = 98.3°). The two PO_4 groups of the pyrophosphate have virtually the same geometry, which is that of a distorted tetrahedron, with three angles smaller, and three angles larger than 109.5°. This feature is related to the high reactivity and the preservation of the rings in the reactions of the pyrophosphates with alcohols. The compound crystallizes in space group $P2_1/c$ of the monoclinic system with eight molecules in a cell of dimensions a = 12.589 (14), b = 7.833 (8), c = 26.495 (25) Å, β = 103.22 (3)°. The observed and calculated densities are 1.48 (1) and 1.47 g cm^{-3}, respectively. Data were obtained on a computer-controlled four-circle diffractometer. The structure has been refined by least-squares techniques to a final R factor on F of 6.6% based on 2472 observations above background.

The five-membered cyclic unsaturated pentaoxyphosphorane **1** is a nearly perfect trigonal bipyramid about the phosphorus atom (D_{3h} symmetry), with the ring in an apico-equatorial skeletallaaal position, according to X-ray crystallographic analysis.[2] By analogy, and from the correspondence of NMR and ir spectral data, a similar geometry has been ascribed to the related pentaoxyphosphorane[3,4] **2**.



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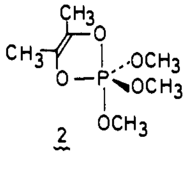

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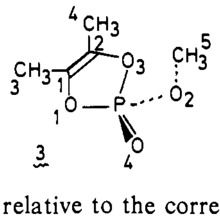
The reaction of the phosphorane **2** with 1 mol equiv of water in aprotic solvents,[5] or with acetyl bromide in acetonitrile solution,[6] yields the cyclic phosphotriester **3**. X-Ray crystallographic analysis shows that the ring in the ester **3** is planar[7] and is an irregular pentagon with a 98.5° O(1)-P-O(3) bond angle. The PO_4 group has the geometry of a distorted tetrahedron, with two of the six O-P-O angles smaller and two larger than 109.5°. These features have been related to the extraordinary reactivity of this enediol cyclophosphate **3** toward alcohols ROH, under the assumption that the nucleophilic displacements proceed *via a pentaoxyphosphorane intermediate*[7,8] **4**. While the phosphate loses



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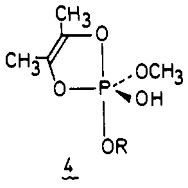

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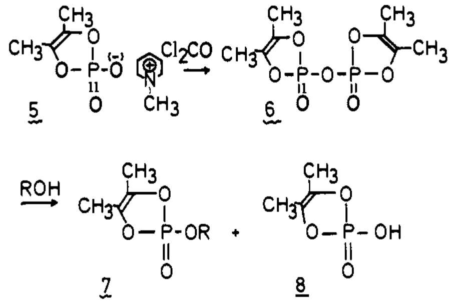
stability relative to the corresponding compounds in which the phosphorus is not part of the ring, the reverse is true for the oxyphosphorane intermediate **4** since there is a great deal of intramolecular crowding in oxyphosphoranes,[2,8] and their stability is increased by the presence of planar rings which minimize the steric crowding about the phosphorus.

The cyclic phosphate **3** reacts with pyridine to form the salt **5**, which can, in turn, be transformed into a new type of



pyrophosphate,[9] **6**. The latter (**6**) is a powerful phosphorylating reagent for alcohols and phenols. These displacements proceed with preservation of both rings and yield the corresponding cyclic ester **7** and acid **8** in equimolar amounts.[9]

This paper describes the crystal and molecular structure of the pyrophosphate **6** and compares the data with those for the related ester **3**.

Experimental Section

Preparation of 2-Oxo-2-(2′-oxo-4′,5′-dimethyl-2′,2′-dihydro-1′,3′,2′-dioxaphospholenyl)oxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene (6) or Acetoinenediol Cyclopyrophosphate. The following procedure is an improvement of the previous[9] synthesis of pyrophosphate **6**. Freshly distilled acetyl bromide (20 ml) was added to a stirred solution of **2,2,2-trimethoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene**[4] (**2**) (230 g, 1.1 mol) in anhydrous acetonitrile (700 ml). The remaining acetyl bromide (76 ml, total of 1.2 mol) was added at a rate which kept the solution at a temperature of 60° (ca. 1 hr). The solution was stirred for 45 min, the solvent was evaporated, and the residue was distilled to yield **2-oxo-2-methoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene**[5,7] (**3**, 160 g, 90% of the theory). A solution of the phosphotriester (**3**, 74.0 g, 0.45 mol) and pyridine (125 ml, 1.5 mol) in benzene (500 ml) was refluxed for 7 hr, with stirring, under anhydrous conditions. The mixture was cooled to 20°, and the solid was decanted off with suitable protection against moisture, washed with benzene (ca. 2 l.), and dried; the *N*-methylpyridinium salt[9] (**5**, 105 g) was obtained in 95% of the theory. A solution of phosgene, (Cl_2CO, 25 ml, 0.37 mol) in benzene (60 ml) was dropped (30 min) into a stirred suspension of the salt (**5**, 102 g, 0.42 mol) in benzene (600 ml) at 0°. The mixture was stirred at 0° for 1 hr, was brought to 20°, and was filtered to remove *N*-methylpyridinium

Table I. Positional and Thermal Parameters (×10^4) for Nonhydrogen Atoms[a, b]

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P(1)	2298(1)	3219(1)	533(1)	60(1)	168(1)	16(1)	−10(1)	10(1)	−8(1)
P(2)	2764(1)	1463(1)	−338(1)	60(1)	190(1)	15(1)	−9(1)	5(1)	−9(1)
P(11)	2648(1)	412(1)	2150(1)	65(1)	172(1)	16(1)	−5(1)	6(1)	4(1)
P(12)	2228(1)	−1348(1)	3039(1)	64(1)	188(1)	14(1)	15(1)	5(1)	2(1)
O(1)	2057(2)	−210(2)	−364(1)	69(2)	193(3)	14(1)	−4(2)	3(1)	0(1)
O(2)	2412(2)	1973(2)	−929(1)	88(2)	204(3)	15(1)	−19(2)	7(1)	0(1)
O(3)	3286(2)	4507(2)	691(1)	49(2)	200(3)	20(1)	−19(2)	7(1)	−13(1)
O(4)	1325(2)	4507(2)	541(1)	57(2)	186(3)	24(1)	−22(2)	14(1)	−11(1)
O(5)	3906(2)	1334(3)	−100(1)	72(2)	355(5)	23(1)	6(3)	−2(1)	−26(1)
O(6)	2341(2)	1648(2)	826(1)	105(2)	188(3)	21(1)	−5(2)	14(1)	4(1)
O(7)	2151(1)	2873(2)	−67(1)	65(2)	177(3)	15(1)	−6(2)	5(1)	−6(1)
O(11)	1684(2)	1736(2)	1997(1)	54(2)	150(3)	16(1)	−14(2)	5(1)	−1(1)
O(12)	3624(2)	1663(3)	2145(1)	59(2)	216(4)	21(1)	12(2)	8(1)	4(1)
O(13)	3028(2)	−2934(2)	3103(1)	77(2)	180(3)	15(1)	23(2)	7(1)	0(1)
O(14)	2516(2)	−728(2)	3621(1)	71(2)	224(3)	16(1)	37(2)	10(1)	1(1)
O(15)	2584(2)	−1183(2)	1868(1)	149(3)	173(3)	19(1)	9(3)	16(1)	−4(1)
O(16)	1092(2)	−1654(3)	2788(1)	72(2)	287(4)	20(1)	7(2)	−1(1)	7(1)
O(17)	2791(2)	97(2)	2764(1)	76(2)	183(3)	16(1)	−6(2)	4(1)	8(1)
C(1)	1334(2)	−338(4)	−865(1)	55(2)	238(6)	15(1)	−28(3)	−2(1)	−18(2)
C(2)	1528(3)	879(3)	−1176(1)	86(3)	197(4)	14(1)	7(3)	11(1)	−6(1)
C(3)	2842(3)	6214(3)	705(1)	85(4)	155(4)	15(1)	−24(3)	15(1)	−8(1)
C(4)	1760(3)	6167(4)	629(1)	55(3)	187(4)	14(1)	−19(3)	10(1)	−4(1)
C(5)	556(3)	−1712(5)	−934(2)	83(3)	297(8)	32(1)	−10(4)	9(1)	−23(2)
C(6)	1038(3)	1295(6)	−1722(1)	124(4)	385(9)	16(1)	10(5)	4(1)	−3(2)
C(7)	3664(2)	7563(4)	832(1)	80(3)	214(5)	17(1)	−34(4)	8(1)	−9(1)
C(8)	968(2)	7574(4)	632(1)	79(3)	187(4)	25(1)	−9(3)	18(1)	−10(1)
C(11)	2137(2)	3407(3)	2000(1)	49(3)	164(4)	12(1)	11(3)	6(1)	0(1)
C(12)	3211(3)	3367(3)	2072(1)	67(3)	150(4)	16(1)	17(3)	13(1)	2(1)
C(13)	3712(2)	−2915(3)	3618(1)	51(2)	213(5)	13(1)	4(3)	5(1)	8(1)
C(14)	3423(2)	−1717(4)	3894(1)	62(2)	212(5)	16(1)	29(3)	12(1)	4(1)
C(15)	1308(2)	4795(4)	1884(1)	55(2)	200(5)	17(1)	16(3)	5(1)	6(1)
C(16)	4034(3)	4729(4)	2113(1)	69(3)	260(6)	26(1)	−6(4)	16(1)	0(1)
C(17)	4532(3)	−4263(4)	3734(1)	92(3)	286(6)	22(1)	59(4)	17(1)	16(2)
C(18)	3846(3)	−1215(5)	4445(1)	81(3)	347(8)	20(1)	26(5)	4(1)	6(2)

[a] Anisotropic thermal parameters are in the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits.

chloride; the latter was washed with benzene, and the washings were added to the filtrate. The combined benzene solution was concentrated to ca. 200 ml [at 30° (30 mm)] and filtered to remove the last traces of the chloride. The filtrate was evaporated, and the residue was recrystallized from methylene chloride-hexane to give a first (43 g) and a second (14 g) crop of the pyrophosphate[9] 6 (95% of the theory). The crystals of 6 used in the X-ray analysis were obtained from methylene chloride-hexane and had: mp 85-86°; $\delta^{31}P = +1.5$ ppm to high field of $H_3PO_4 = 0$ (in CH_2Cl_2); τ 8.02 ppm vs. $(CH_3)_4Si = 10$ (in $CDCl_3$).

Crystal Data. $P_2O_7C_8H_{12}$: monoclinic; $P2_1/c$; $a = 12.589$ (14), $b = 7.833$ (8), $c = 26.495$ (25) Å, $\cos\beta = -0.2287$ (5); ($\lambda_{MoK\alpha_1} = 0.7093$ Å at 21°); $Z = 8$ (two molecules per asymmetric unit); $D_{calcd} = 1.47$ g cm^{-3}, D_{meas} (by flotation in benzene-diiodomethane) = 1.48 (1) g cm^{-3}; μ(Mo Kα) = 7.88 cm^{-1}.

Data Collection and Structure Refinement. Precession and Weissenberg photographs of the ($hk0$), ($hk1$), ($0kl$), ($1kl$), and ($h0l$) zones showed systematic absences ($h0l$) for l odd and ($0k0$) for k odd, implying space group $C_{2h}{}^5 = P2_1/c$. The cell dimensions were determined by a least-squares fit of the observed 2θ angles for 21 reflections centered automatically on a four-circle diffractometer.

Intensity data were collected from an almost colorless crystal of approximate hexagonal prismatic habit and dimensions 0.1 × 0.05 × 0.2 mm. Crystals of this material decompose rapidly in air, and thus the data crystal oriented along b* (the prism axis) was sealed in a glass capillary where it remained stable over the course of the data collection. Data were obtained on a computer-controlled Picker four-circle diffractometer[10] using Mo Kα radiation monochromatized by reflection from the (002) plane of a highly oriented pyrolytic graphite monochromator. One independent set of data was collected for 2θ(Mo Kα) < 60°. The 3800 observations gave 2472 independent reflections with $F_o{}^2 > 3\sigma_{count}(F_o{}^2)$ with $\sigma(F_o{}^2)$ being based on Poisson counting statistics. The intensities of two standard reflections were measured periodically and were found to have fallen off to 66% of their original values by the end of data collection. This decrease in intensity was uniform over the exposure time, and the individual intensities were scaled to the zero time standards. Data were collected by the θ–2θ step scans using a scan width $\Delta 2\theta = 1.40(1 + \tan\theta)$ and a step size $\delta 2\theta$ of 0.02°. The center of the scan range was set at the Bragg angle calculated for 0.7104 Å. Background was measured as the average of the first and last five points of the scan. The take-off angle was 2.7°, and pulse height–pulse shape discrimination system was used.

Table II. Calculated Hydrogen Atom Positions (×10^4)[a]

Atom	X	Y	Z
H-5a	626	−2391	−620
H-5b	−253	−1293	−1056
H-5c	590	−2499	−1244
H-6a	1372	2255	−1836
H-6b	1089	227	−1964
H-6c	199	1395	−1799
H-7a	4385	7112	863
H-7b	3497	8555	579
H-7c	3608	8178	1176
H-8a	234	7136	568
H-8b	1141	8262	982
H-8c	1031	8550	380
H-15a	588	4369	1849
H-15b	1487	5711	2183
H-15c	1395	5535	1579
H-16a	4749	4237	2167
H-16b	3871	5452	1768
H-16c	3963	5629	2372
H-17a	4563	−4928	3429
H-17b	5321	−3765	3892
H-17c	4447	−5019	4035
H-18a	3454	−269	4542
H-18b	3864	−2234	4699
H-18c	4686	−944	4528

[a] Hydrogen atom H-5 is attached to C-5. All were assigned a B of 5.5 Å^2 in the structure factor calculation.

Structure factors were derived in the usual way; no absorption

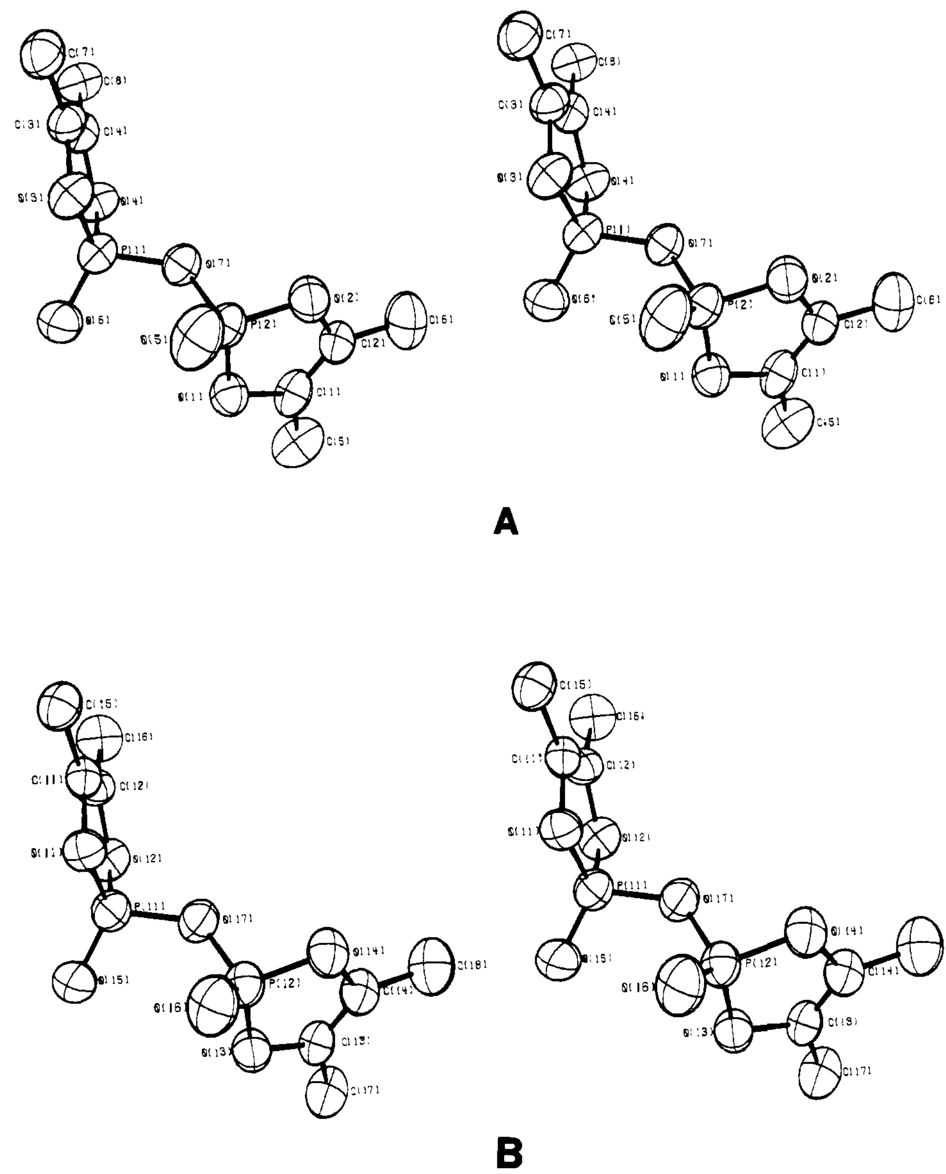


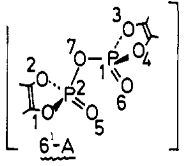
Figure 1. A stereoscopic drawing of the two independent isolated molecules of $P_2O_7C_8H_{12}$. The 50% probability vibrational ellipsoids are shown.

correction was necessary. The Sayre[11] equation was used according to Long's[12] method to compute an E map which revealed the positions of all nonhydrogen atoms. The structure was refined isotropically by full-matrix least-squares, minimizing the function $\Sigma w\Delta^2$ with $\Delta = |F_o| - |F_c|$ with weights $w = 4F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = \sigma_{\text{count}}^2(I) + (0.04F^2)^2$. The atomic scattering factors for all nonhydrogen atoms were taken from a standard source,[13] while that for hydrogen atoms was the best spherically averaged value of Stewart et al.[14] In view of the number of parameters to be refined (34 nonhydrogen atoms and 307 variables if all atoms are refined anisotropically), block-diagonal methods were used in final least-squares cycles. In alternate cycles, all atoms of one of the two molecules in the asymmetric unit were allowed anisotropic motion while parameters of the second molecule were fixed and vice versa. The hydrogen atom positions were fixed in idealized locations with fixed bond lengths of 0.98 Å and an isotropic thermal parameter $B = 5.5$ Å^2. The final values of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = \{[\Sigma w||F_o| - |F_c||^2]/\Sigma w|F_o^2|\}^{1/2}$ were 0.066 and 0.090, respectively,[15] and the error in an observation of unit weight was 2.48. The maximum density in a final difference electron density synthesis was 0.39 electrons Å^{-3}, approximately 10% of the height of a carbon atom. The final parameters are presented in Tables I and II and the structure amplitudes as $10|F_o|$ and $10|F_c|$ in Table III.[16]

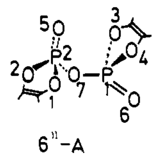
Discussion of Results

In the crystals of the pyrophosphate **6**, there are two independent molecules, A and B, in the asymmetric unit. Figure 1 shows the structure and the numbering system for the atoms in the two molecules. Vibrational thermal elipsoids for the atoms are also displayed in Figure 1. The unit cell contents are shown in Figure 2. The relevant interatomic distances and bond angles and their standard deviations were calculated from the positional parameters in Tables I and II and the correlation matrix and are presented in Table IV. Some significant dihedral angles between planes are given in Table V. The least-square planes are described in Table VI.

The discussion of the data is facilitated by an examination of formula **6′**-A which represents one of the hypothetical conformations in which the five atoms of the anhydride group, O═P—O—P═O, lie in the plane of the paper. The actual conformations of molecules A and B in the crystal approach those shown in formula **6″**-A, which is obtained from **6′**-A by appropriate rotations about the bonds P(1)-O(7) and P(2)-O(7) for molecule A (and P(12)-O(17) and P(11)-O(17) for molecule B).



6′-A



6″-A

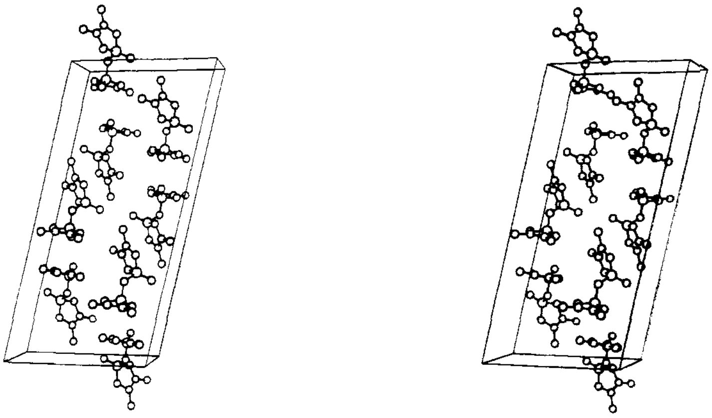


Figure 2. A stereoscopic drawing of four asymmetric units (eight molecules) whose central oxygen atoms all lie within the same unit cell. View approximately along b and c is vertical.

Table IV. Bond Distances (Å) and Angles (Deg)

Molecule A		Molecule B	
P(1)–O(3)	1.582(2)[a]	P(11)–O(11)	1.578(2)
P(1)–O(4)	1.590(2)	P(11)–O(12)	1.574(2)
P(1)–O(6)	1.449(2)	P(11)–O(15)	1.449(2)
P(1)–O(7)	1.582(2)	P(11)–O(17)	1.612(2)
P(2)–O(1)	1.577(2)	P(12)–O(13)	1.583(2)
P(2)–O(2)	1.580(2)	P(12)–O(14)	1.577(2)
P(2)–O(5)	1.435(2)	P(12)–O(16)	1.453(2)
P(2)–O(7)	1.608(2)	P(12)–O(17)	1.598(2)
O(1)–C(1)	1.432(3)	O(11)–C(11)	1.427(3)
O(2)–C(2)	1.438(3)	O(12)–C(12)	1.429(3)
O(3)–C(3)	1.454(3)	O(13)–C(13)	1.437(3)
O(4)–C(4)	1.410(3)	O(14)–C(14)	1.436(3)
C(1)–C(2)	1.319(4)	C(11)–C(12)	1.322(4)
C(1)–C(5)	1.438(4)	C(11)–C(15)	1.490(4)
C(2)–C(6)	1.473(4)	C(12)–C(16)	1.474(4)
C(3)–C(4)	1.330(4)	C(13)–C(14)	1.301(4)
C(3)–C(7)	1.464(4)	C(13)–C(17)	1.459(4)
C(4)–C(8)	1.488(4)	C(14)–C(18)	1.476(4)
P(1)–O(7)–P(2)	127.5(1)	P(11)–O(17)–P(12)	127.6(1)
O(3)–P(1)–O(4)	98.9(1)	O(11)–P(11)–O(12)	98.3(1)
O(3)–P(1)–O(6)	118.0(1)	O(11)–P(11)–O(15)	119.0(1)
O(3)–P(1)–O(7)	106.2(1)	O(11)–P(11)–O(17)	105.2(1)
O(4)–P(1)–O(6)	117.8(1)	O(12)–P(11)–O(15)	118.9(1)
O(4)–P(1)–O(7)	102.0(1)	O(12)–P(11)–O(17)	101.3(1)
O(6)–P(1)–O(7)	112.0(1)	O(15)–P(11)–O(17)	111.7(1)
O(1)–P(2)–O(2)	98.0(1)	O(13)–P(12)–O(14)	97.9(1)
O(1)–P(2)–O(5)	117.4(1)	O(13)–P(12)–O(16)	117.1(1)
O(1)–P(2)–O(7)	105.4(1)	O(13)–P(12)–O(17)	105.5(1)
O(2)–P(2)–O(5)	118.7(1)	O(14)–P(12)–O(16)	118.7(1)
O(2)–P(2)–O(7)	102.4(1)	O(14)–P(12)–O(17)	101.6(1)
O(5)–P(2)–O(7)	112.8(1)	O(16)–P(12)–O(17)	113.6(1)
P(2)–O(1)–C(1)	109.4(2)	P(11)–O(11)–C(11)	108.5(2)
P(2)–O(2)–C(2)	108.2(2)	P(11)–O(12)–C(12)	108.8(2)
P(1)–O(3)–C(3)	108.0(2)	P(12)–O(13)–C(13)	108.8(2)
P(1)–O(4)–C(4)	108.4(2)	P(12)–O(14)–C(14)	108.3(2)
O(1)–C(1)–C(2)	111.1(2)	O(11)–C(11)–C(12)	112.0(3)
O(1)–C(1)–C(5)	116.1(3)	O(11)–C(11)–C(15)	114.0(2)
C(2)–C(1)–C(5)	132.8(3)	C(12)–C(11)–C(15)	133.8(3)
O(2)–C(2)–C(1)	112.4(2)	O(12)–C(12)–C(11)	111.7(2)
O(2)–C(2)–C(6)	114.9(2)	O(12)–C(12)–C(16)	116.0(3)
C(1)–C(2)–C(6)	132.6(3)	C(11)–C(12)–C(16)	132.2(3)
O(3)–C(3)–C(4)	110.9(2)	O(13)–C(13)–C(14)	111.4(2)
O(3)–C(3)–C(7)	114.4(3)	O(13)–C(13)–C(17)	115.7(2)
C(4)–C(3)–C(7)	134.5(3)	C(14)–C(13)–C(17)	132.8(3)
O(4)–C(4)–C(3)	113.4(3)	O(14)–C(14)–C(13)	112.9(3)
O(4)–C(4)–C(8)	116.6(3)	O(14)–C(14)–C(18)	115.2(2)
C(3)–C(4)–C(8)	130.0(3)	C(13)–C(14)–C(18)	131.9(3)

[a] The least-squares derived estimated standard deviations are low because of blocking of the matrix with the loss of some correlation effects. The tabulated errors should therefore be increased by a factor of 2 or 3.

Table V. Some Dihedral Angles between Planes Defined by Three Atoms

Plane 1	Plane 2	Angle, deg
	Molecule A	
O(5),P(2),O(7)	O(6),P(1),O(7)	75.1(1)
P(1),O(7),P(2)	O(5),P(2),O(7)	42.3(2)
P(1),O(7),P(2)	O(6),P(1),O(7)	43.3(2)
	Molecule B	
O(15),P(11),O(17)	O(16),P(12),O(17)	69.5(1)
P(12),O(17),P(11)	O(15),P(11),O(17)	38.3(2)
P(12),O(17),P(11)	O(16),P(12),O(17)	40.6(2)

Table VI. Equations of Best Least-Squares Planes and Deviations of Individual Atoms from Planarity (Å)

1. P(2), O(1), O(2), C(1), C(2)
$9.970x - 4.402y - 10.953z = 2.489$
P(2), −0.01; O(1), 0.05; O(2), 0.06; C(1), −0.06; C(2), −0.06
2. P(2), O(1), O(2), C(1), C(2), C(5), C(6)
$9.815x - 4.479y - 11.312z = 2.453$
P(2), −0.01; O(1), 0.07; O(2), 0.08; C(1), −0.01; C(2), −0.02; C(5), −0.08; C(6), −0.07
3. P(1), O(3), O(4), C(3), C(4)
$-1.958x - 1.240y + 26.092z = 0.547$
P(1), 0.00; O(3), 0.05; O(4), 0.05; C(3), −0.03; C(4), −0.02
4. P(1), O(3), O(4), C(3), C(4), C(7), C(8)
$-1.957x - 1.203y + 26.111z = 0.560$
P(1), 0.00; O(3), 0.06; O(4), 0.05; C(3), −0.02; C(4), −0.01; C(7), −0.02; C(8), −0.01
5. P(11), O(11), O(12), C(11), C(12)
$-2.042x + 1.087y + 26.180z = 5.127$
P(11), 0.01; O(11), −0.05; O(12), −0.07; C(11), 0.04; C(12), 0.01
6. P(11), O(11), O(12), C(11), C(12), C(15), C(16)
$-2.098x + 1.002y + 26.227z = 5.116$
P(11), 0.01; O(11), −0.06; O(12), −0.08; C(11), 0.02; C(12), −0.02; C(15), 0.03; C(16), 0.05
7. P(12), O(13), O(14), C(13), C(14)
$9.564x + 4.733y - 10.796z = -1.795$
P(12), 0.01; O(13), −0.05; O(14), −0.05; C(13), 0.06; C(14), 0.05
8. P(12), O(13), O(14), C(13), C(14), C(17), C(18)
$9.487x + 4.746y - 11.144z = -1.925$
P(12), 0.01; O(13), −0.05; O(14), −0.07; C(13), 0.03; C(14), 0.01; C(17), −0.02; C(18), −0.01

The two independent molecules (A and B) in the asymmetric unit are related by a pseudocenter of symmetry (at $\frac{1}{4}$, $\frac{1}{8}$, and $\frac{3}{8}$), which is at a nonrational position in the $P2_1/c$ space group. A comparison of bond distances and angles (Table IV) shows relatively good agreement between A and B, within experimental error. On the other hand, as shown in Table V, the dihedral angle (75°) formed by the two planes which contain the three-atom systems O=P—O- in molecule A is significantly different from the corresponding dihedral angle (69°) in molecule B. Table V also shows the torsion angles associated with the two phosphoryl groups, (5)O=P(2) and (6)O=P(1) and the P—O—P plane, in molecule A (42 and 43°); the corresponding torsion angles in molecule B are 38 and 41°. The P—O—P bond angles are virtually the same in molecules A and B (average value = 127.6°).

The five-membered rings are very nearly planar and have normal geometry in molecules A and B. The average of the C-O bond distances is 1.433 (12) Å; the mean C-C length is 1.470 (17) Å; and the mean C=C bond length is 1.318 (13) Å. The rings are irregular pentagons, with an average value of 98.3° for the endocyclic O-P-O bond angle. These features are also found in the related ester **3**.[7] A small endocyclic O-P-O angle has been observed in saturated five-membered cyclic phosphates by Steitz and Lipscomb,[17] and by Newton, Cox and Bertrand.[18]

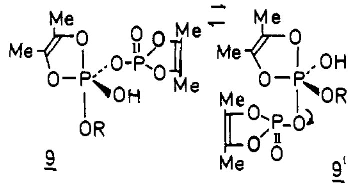
The two methyl groups attached to the sp^2 carbons of the rings seem to repel each other since the average value of the CH_3-C-C bond angles is 132.5°, while the average of the CH_3-C-O bond angles is 115.3°. This type of methyl-methyl repulsion is also observed[7] in the ester **3**.

The phosphoryl bonds, P=O, are significantly shorter [average bond distance, 1.447 (8) Å] than the other P—O bonds [average length, 1.587 (12) Å]. The value reported[7] for the P=O bond of ester **3** is 1.38 Å.

Probably, the most interesting feature of the structure of the pyrophosphate **6** pertains to the geometry of the PO_4 groups. Table VII lists the six O-P-O angles associated with each of the two PO_4 groups in **6**-A; the related bond angles in both groups are the same within experimental error, and the average value of the pair is used to compute the deviation from the regular tetrahedral angle. The corresponding deviations for the ester **3**[7] are included in Table VII. The main deviation from the tetrahedron resides in the endocyclic O-P-O bond angle (−11°). The angles formed by the exocyclic anhydride O(7), the phosphorus, and the ring oxygens, O(4) or O(2), and O(3) or O(1) are somewhat smaller than the tetrahedral angle (deviations are −7 and −4°, respectively); the trend is less marked in ester **3** (−2 and 0°). The angles formed by the phosphoryl oxygen, O(6) or O(5), the phosphorus, and the ring oxygens are significantly larger than the tetrahedral value (+9, +8°); the same trend is seen in ester **3** (+7, +6°). The angle of the phosphoryl oxygen, the phosphorus, and the anhydride oxygen, O(7), is close to tetrahedral in both **6** and **3**.

Table VII suggests that the transformation of the pyrophosphate **6** into the oxyphosphorane **9** by addition of the nucleophile ROH might be relatively easy. The necessary contractions of the bond angles amount to −49°, which represents a net economy of 8° relative to the formation of the oxyphosphorane from a regular tetrahedral PO_4 (−49 vs. −57°). The required expansion of the bond angles amounts to +24°, or a net economy of 9° relative to the ideal case (24 vs. 33°). Note the corresponding angle deformations in the ester **3**.

These structural factors may contribute to the high degree of reactivity of the phosphorus atom of the pyrophosphate **6**, and of the ester **3**, toward alcohols. The pyrophosphate **6** is significantly more reactive than the ester **3**, and this could be related to the electronic, as well as the steric, differences between the ligands in the corresponding systems: **6** → **9**, and **3** → **4**. The cyclic phosphate ligand in **9** is a relatively strong electron-withdrawing group, and this should contribute toward its apicophilicity,[19,20] i.e., its tendency to occupy the apical skeletal position of the trigonal bipyramid. A permutational isomerization, **9** → **9′**, possibly by the turnstile rotation mechanism[19,20] with the ring as the turnstile pair, places the phosphate ligand in the apical position, from which it can depart to give the observed products of the displacement with ring-preservation: **6** + ROH → **7** + **8**.



9 9′

Table VII. Deviations from Regular Tetrahedron in PO_4 Group. Bond Angle Deformations in the Transformation of PO_4 Group into Oxyphosphorane[a]

Bond angle	Deviation[c] from 109.5°, deg	Angle deformation,[a] deg	
	Cyclopyrophosphate[b] (**6**, Molecule A)		
O(3)–P(1)–O(4) O(1)–P(2)–O(2)	−11	−9	−49
O(7)–P(1)–O(4) O(7)–P(2)–O(2)	−7	−12	
O(6)–P(1)–O(4) O(5)–P(2)–O(2)	+9	−28	
O(6)–P(1)–O(3) O(5)–P(2)–O(1)	+8	+2	+24
O(6)–P(1)–O(7) O(5)–P(2)–O(7)	+3	+8	
O(7)–P(1)–O(3) O(7)–P(2)–O(1)	−4	+14	
	Cyclophosphate[d] (**3**)		
O(3)–P–O(1)	−11	−8	−51
O(2)–P–O(1)	−2	−17	
O(4)–P–O(1)	+7	−26	
O(4)–P–O(3)	+6	+5	+27
O(4)–P–O(2)	0	+11	
O(2)–P–O(3)	0	+11	

[a] The transformation of a regular PO_4 tetrahedron into a regular PO_5 trigonal bipyramid involves the contraction of three bond angles from 109.5 to 90° (3 × (−19°) = −57°) and the expansion of three bond angles from 109.5 to 120° (3 × 11° = 33°). [b] Assuming that O(4) becomes apical when nucleophile adds to P(1), or that O(2) becomes apical when nucleophile adds to P(2). If O(3) goes apical upon attack at P(1), or O(1) goes apical upon attack at P(2), the overall contraction is −53° (net economy of 4°), and the overall expansion is +28° (net economy of 5°). [c] Based on the average of the two bond angles. The geometry of the PO_4 groups in molecules 6A and 6B are the same within experimental error. [d] Assuming that O(1) occupies the apical position in the oxyphosphorane intermediate. If O(3) goes apical, the overall contraction is −52° (or a net economy of 5°), and the overall expansion is +27° (or a net economy of 6°).

The reaction of the methyl ester **3** with alcohols yields mainly the products of ring opening[7,8] and relatively small amounts of the products of ring preservation. This difference between the cyclic pyrophosphate **6** and the cyclic ester **3** is traceable to the higher apicophilicity of the phosphate over the methoxy ligands, and to the better leaving-group character of the phosphate.[21]

Supplementary Material Available. Table III will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-5457.

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Ligand Electronegativity Effect on the Spin Distribution in Phosphoranyl Radicals[1]

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Abstract: The trimethylphosphoranyl radical Me_3PH has been identified in γ-irradiated trimethylphosphine at $-196°$ by means of its ESR spectrum consisting of an anisotropic ^{31}P doublet of isotropic ^{1}H doublets. Since this radical lacks electronegative groups which are thought to stabilize compounds and radicals of pentacoordinate phosphorus that assume trigonal bipyramidal geometry, the spin distribution is of particular interest. Comparison of the isotropic hyperfine splittings ($A_{iso}(^{31}P) = 484$ G; $A_{iso}(^{1}H) = 182$ G) with those obtained previously for alkoxyphosphoranyl radicals shows that the ^{31}P hfsc decreases monotonically on progressive substitution of the two apical alkoxy groups by alkyl or hydrogen ligands. In contrast, the large coupling to the hydrogen ligand in one apical position increases significantly when the other apical substituent is changed from an alkoxy to an alkyl group. These results indicate that the replacement of alkoxy groups by less electronegative ligands in the apical positions brings about a transfer of spin density from the orbitals of the central atom to the σ orbitals of the ligands leading to destabilization. This effect of electronegative substituents on the spin density distribution is in accord with the proposal that the half-occupied MO is largely localized along the axial three-center bond connecting the apical ligands and the central atom.

A substantial body of ESR data now exists for a wide variety of phosphoranyl radicals,[2] and this information has naturally stimulated interest in the structure of this important class of intermediates.[3,4] Although many ESR studies have subscribed to the traditional view that the unpaired electron occupied essentially an equatorial sp^2 orbital of pentacoordinate (sp^3d hybridized) phosphorus in trigonal bipyramidal geometry, new light was shed on the electronic structure of these radicals by the recent finding[3] that large spin densities often reside in the σ orbitals of the axial ligands. While this latter result is difficult to reconcile with descriptions based on directed valence-bond theory, it becomes immediately understandable in terms of MO theory which assigns the unpaired electron in these radicals to an antibonding orbital of a_1 (C_{2v}) or a' (C_s) representation.[3] This orbital may be regarded as a three-center σ^* orbital derived from the axial ligand orbitals and the symmetry-allowed 3s and 3p orbitals of the phosphorus atom.

A corollary to this MO description is that the spin density distribution between the contributing group of ligand and central atom orbitals should be sensitive to the electronegativities of the ligands in the apical (axial) sites. In particular, the progressive replacement of two apicophilic electronegative groups by alkyl or hydrogen ligands should destabilize the radical,[3,5] the anticipated effect being to increase the spin populations on the apical ligands at the expense of the phosphorus atom.

Although the ESR spectra of a number of organophosphoranyl radicals with only one electronegative ligand (alkoxy) have been documented,[6] as yet the only ESR report describing a phosphoranyl radical without any electronegative ligands concerns the parent species PH_4.[7] However, the isotropic ^{31}P and ^{1}H splittings attributed to this radical appear to be quite anomalous and the identification has been seriously questioned.[8,9] In this paper we report the ESR spectrum and spin density distribution for the trimethylphosphoranyl radical thereby completing the set of ESR parameters for the series $R_nP(OR')_{4-n}$ (n = 0-4), where R is Me or H, and R′ is Me, Et, or t-Bu. Taken in conjunction with other work, our present results are shown to provide further evidence that the unpaired electron is largely localized along the axial three-center bond connecting the apical ligands and the central atom.

Experimental Section

Samples of trimethylphosphine (Strem Chemicals Inc.) were prepared in Suprasil ESR tubes by standard high-vacuum techniques. Attempts were made to obtain single crystals by a low-temperature technique[10] but our efforts in this direction were frustrated by the apparent occurrence of a phase transition in the solid below the melting point ($-85°$) and only partially oriented samples could be obtained for studies at $-196°$. However, even the small degree of preferential orientation induced by this method proved to be valuable in locating the characteristic features of the powder ESR spectrum, as discussed below.