

(COT)₂·2THF and KPu(COT)₂·2THF presents the possibility that the crystal field model originally proposed⁸ for the actinide(IV)–COT compounds could be applied to the actinide(III)–COT compounds to predict their magnetic properties. In this model, the Np³⁺ ion ($J = 4$) in KNp(COT)₂·2THF would have $J_z = 0$ in a magnetic field and thus would be diamagnetic, analogous to Pu⁴⁺ in Pu(COT)₂. The experimental magnetic susceptibility shows a nonmagnetic ground state and two higher magnetically degenerate levels at ~ 5 and ~ 15 cm⁻¹. In general, this conforms to the predicted ordering of the levels of $J_z = 0$ as the lowest level and $J_z = \pm 1$ and $J_z = \pm 2$ as the next levels. Further, the magnetic susceptibility is greater for the $J_z = \pm 2$ level than for $J_z = \pm 1$. The TIP observed for the lowest level can be accounted for by either weak second-order crystal fields or the magnetic field mixing the $J_z = 0$ wave functions with $J_z = \pm 1$ wave functions. The MO model of Hayes and Edelstein¹² predicts $J_z = 0$, $J_z = \pm 1$, and $J_z = \pm 2$ for the three lowest levels of the isoelectronic Pu⁴⁺ ion in Pu(COT)₂, with the magnetic susceptibilities of 0, 1.47, and 1.35 BM, respectively. Adjustments of this calculation for Np³⁺ might lead to a reasonable fit with experimental results.

Although it is not yet necessary to discard the crystal field model,^{8,12} this model assumes no mixing of J states by the crystal field and small intermediate coupling. Neither of these assumptions is strictly true for the Np³⁺ ion, as comparison of measured and calculated magnetic susceptibilities for Cs₂NaNpCl₆ in-

(12) R. G. Hayes and N. Edelstein, *J. Amer. Chem. Soc.*, **94**, 8688 (1972).

dicates.¹³ The predicted ordering of crystal field levels from first-order wave functions¹³ for a $J = 4$ ion in an eightfold cubic O site also predicts a nonmagnetic Γ_1 lowest level with Γ_4 and Γ_5 triplet levels higher in energy.¹⁴ Considering the environment of anion in a D_{8d} site not too different from an O site also yields a qualitative agreement with experiment.

The magnetic susceptibility of Pu³⁺ in KPu(COT)₂·2THF, $\mu_{\text{eff}} = 1.25$ BM, agrees with the free ion moment for Pu³⁺ with intermediate coupling taken into account.¹⁵ However, it is difficult to rationalize three crystal field levels below 70°K for Np³⁺ in KNp(COT)₂·2THF and a KPu(COT)₂·2THF magnetic susceptibility that implies all crystal field levels for Pu³⁺ are below 2.2°K. It appears probable that there is an accidental agreement between the magnetic susceptibility of the ground crystal field level and the free ion value. Further experimental and theoretical studies are considered necessary to explain the properties of these compounds adequately.

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Crystal and Molecular Structure of a Dioxadiazaspirophosphorane Derived from (–)-Ephedrine

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Abstract: The structural analysis of a spirophosphorane produced in the reaction between (–)-ephedrine and tris(dimethylamino)phosphine has been carried out *via* single-crystal X-ray diffraction analysis. Crystals of the spirophosphorane are orthorhombic with $a = 14.101$ (3), $b = 6.797$ (1), and $c = 20.394$ (4) Å and space group $P2_12_1$. The molecules contain an approximate noncrystallographic twofold axis parallel to the P–H bond. The phosphorus geometry is essentially trigonal bipyramidal, and the nitrogen and attached atoms are coplanar.

Various spirophosphoranes containing P–H bonds have been synthesized by reaction of the 2-dimethylamino derivatives of 1,3,2-dioxo- or oxazaphospholanes with diols or β -amino alcohols.² Symmetrical

dioxadiazaspirophosphoranes can be synthesized directly from the amino alcohol hydrochlorides and tris(dimethylamino)phosphine.³ The formation of the spirophosphorane presumably occurs *via* initial formation of the trivalent phosphite derivative followed by cyclization. When (–)-ephedrine⁴ (I) is used as the β -

(1) (a) University of Georgia. (b) Laboratoire de Chimie Physique II, Université Paul Sabatier.

(2) R. Burgada, D. Houalla, and R. Wolf, *C. R. Acad. Sci.*, **264**, 356 (1967); M. Sanchez, R. Wolf, R. Burgada, and F. Mathis, *Bull. Soc. Chim. Fr.*, **773** (1968); M. Sanchez, J. F. Brazier, D. Houalla, and R. Wolf, *ibid.*, **3930** (1967); M. Sanchez, L. Beslier, and R. Wolf, *ibid.*, **2778** (1969); M. Sanchez, L. Beslier, J. Roussel, and R. Wolf, *ibid.*, **3053** (1969); J. Ferekh, J. F. Brazier, A. Munoz, and R. Wolf, *C. R. Acad. Sci.*, **270**, 865 (1970).

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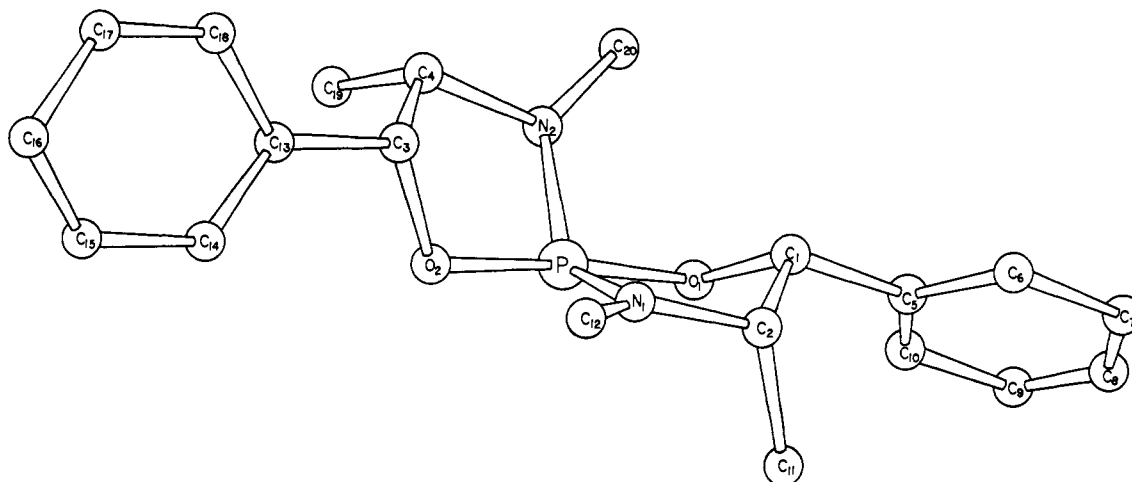
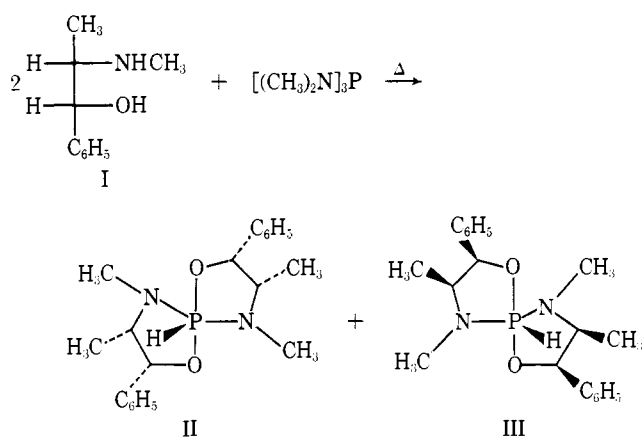


Figure 1. A projection of a molecule of III onto the ac plane. The numbering scheme used in the analysis is indicated in the diagram.



amino alcohol, the spirophosphoranes produced are diastereoisomers II and III that differ only in the sense of chirality at phosphorus.⁵ In benzene, II and III are interconverted by epimerization at phosphorus and the relative amounts of the diastereomers change with temperature.⁶ Slow crystallization from benzene produces a single isomeric phosphorane.

An X-ray structural analysis of the crystalline product obtained from benzene has been carried out and the structure of this isomer identified as III. In addition to the elucidation of the stereochemistry of this isomer, the X-ray study is the first structural analysis of a saturated phosphorane. We now report the details of this study.

Experimental Section

Suitable needle crystals of the spirophosphorane III were obtained by recrystallization from benzene. Initial precession photographs revealed an orthorhombic system mounted along the b axis; the direction of elongation and systematic absences uniquely established the space group as $P2_12_12_1$. The sample was transferred to an Enraf-Nonius CAD-3 automated diffractometer. The reported cell dimensions and orientation matrix were obtained from 15 accurately centered reflections near $\theta = 30^\circ$. Intensity data were collected to a maximum θ of 65° using Ni-filtered Cu $K\alpha$ radiation (λ 1.54180 Å) and ω - 2θ scan technique. In all, 1729 intensity measurements were recorded of which 1375 were unique and

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considered to be above background.⁷ The intensities were corrected for Lorentz-polarization effects⁸ but not for absorption.

Crystal Data. Molecular formula, $C_{20}H_{27}O_2N_2P$; molecular weight, 358.42; linear absorption coefficient (μ), 13.56 cm^{-1} (Cu $K\alpha$); crystal dimensions, $0.5 \times 0.3 \times 0.2 \text{ mm}$; space group, $P2_12_12_1$ (absences $h00, h = 2n + 1$; $0k0, k = 2n + 1$; $00l, l = 2n + 1$); cell constants, $a = 14.101(3)$, $b = 6.797(1)$, $c = 20.394(4)$ Å; $V = 1954.6 \text{ Å}^3$; calculated density, 1.218 g/cm^3 assuming $Z = 4$.

The structure was solved by the heavy atom method⁹ using P coordinates of 0.03, 0.10, and 0.14 located by means of a Patterson map.¹⁰ The first electron density map provided positional parameters for eight additional atoms, and subsequent electron density maps revealed the remaining nonhydrogen atoms. The R value for the 25 unrefined atomic positions was 0.25. Isotropic refinement¹¹ of all positional parameters and temperature factors reduced R to 0.13. Anisotropic refinement of the molecule was initially done in stages, first on one-half of the molecule then the other, because of program limitations. A final anisotropic refinement of all parameters with weights of $1/\sigma_{F_o}^2$ was performed using UGALS.¹² The final conventional unweighted R value was 0.095. A difference map at this stage revealed peaks corresponding to several H atoms including the H bound to P, but refinement of these atomic positions was not successful. Other than peaks attributed to H, the difference map was essentially featureless. The positional parameters and anisotropic temperature factors obtained from the last cycle of refinement are listed in Table I. A projection of the molecule onto the ac plane showing the numbering scheme used in the analysis is seen in Figure 1.

Results and Discussion

The molecules of III contain an approximate non-crystallographic twofold axis parallel to the presumed

(7) Peaks for which $I \leq 1.5(I + B_r + B_l)^{1/2}$ were excluded from the final data set and were considered unobserved.

(8) Corrections were made using program DIFCOR, a Fortran program for the IBM-360 used for CAD-3 Lorentz-polarization corrections: M. G. Newton, University of Georgia.

(9) J. M. Robertson, *Pure Appl. Chem.*, 9, 179 (1964).

(10) Fourier maps were calculated using FORDAP, written by A. Zalkin, Lawrence Radiation Laboratory, Livermore, Calif.

(11) The full-matrix, least-squares program (UCLALS) used in refinement was written by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood and modified by M. G. Newton for the IBM 360.

(12) The standard deviation of F_o, σ_{F_o} , was estimated from

$$\sigma_{F_o} = \frac{1}{2} \sqrt{\frac{f_i}{S_i L p} \frac{I + B_r + B_l + (\nu I_r)^2}{I_r}}$$

where f_i = filter factor for the attenuation filter used in the measurement, S_i = the total number of scans made in the measurement, Lp = Lorentz-polarization factor, I = total intensity including backgrounds, B_r = right background, B_l = left background, $I_r = I - B_l - B_r$, and ν = instrumental stability constant.

(13) UGALS, an IBM-360 Fortran program for full-matrix least-squares refinement written by C. J. Finder and M. G. Newton, University of Georgia. The program will refine as many as 350 parameters. The core requirement is variable and adjusts automatically to the number of parameters being refined.

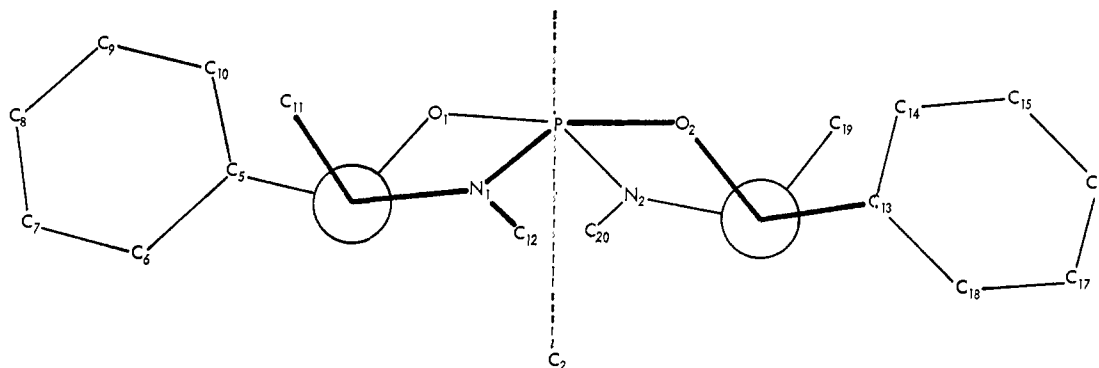


Figure 2. A Newman projection of III viewed down the C_1 - C_2 and C_3 - C_4 bonds. The approximate twofold axis is illustrated.

Table I. Final Fractional Coordinates and Anisotropic Temperature Factors^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	0.4704 (2)	0.5961 (5)	0.1395 (2)	0.0047 (2)	0.0268 (8)	0.0031 (1)	-0.0006 (7)	0.0007 (3)	0.0008 (6)
O ₁	0.3655 (5)	0.7173 (10)	0.1445 (4)	0.0059 (5)	0.0278 (20)	0.0035 (3)	0.0031 (18)	0.0014 (6)	-0.0006 (15)
O ₂	0.5771 (4)	0.04785 (11)	0.1392 (4)	0.0043 (4)	0.0335 (23)	0.0035 (3)	-0.0010 (17)	-0.0015 (6)	0.0025 (15)
N ₁	0.4128 (6)	0.3868 (15)	0.1581 (5)	0.0051 (5)	0.0267 (26)	0.0038 (4)	-0.0013 (23)	0.0018 (7)	0.0009 (18)
N ₂	0.4902 (6)	0.6723 (14)	0.0614 (4)	0.0069 (6)	0.0297 (31)	0.0034 (3)	-0.0006 (24)	0.0013 (8)	0.0000 (16)
C ₁	0.2874 (7)	0.5914 (17)	0.1311 (6)	0.0035 (6)	0.0238 (29)	0.0045 (4)	-0.0030 (26)	0.0014 (9)	0.0007 (23)
C ₂	0.3091 (7)	0.4066 (18)	0.1705 (5)	0.0035 (6)	0.0275 (32)	0.0034 (4)	-0.0015 (27)	0.0004 (8)	0.0037 (21)
C ₃	0.6070 (8)	0.4268 (19)	0.0736 (5)	0.0059 (7)	0.0346 (38)	0.0022 (3)	0.0023 (32)	0.0019 (9)	0.0003 (21)
C ₄	0.5867 (7)	0.6205 (18)	0.0344 (6)	0.0034 (6)	0.0299 (36)	0.0038 (4)	0.0020 (26)	0.0011 (8)	-0.0001 (22)
C ₅	0.1952 (8)	0.6991 (20)	0.1512 (6)	0.0044 (7)	0.0322 (37)	0.0034 (4)	0.0026 (27)	0.0000 (9)	0.0040 (23)
C ₆	0.1089 (8)	0.6018 (23)	0.1381 (6)	0.0053 (7)	0.0520 (46)	0.0035 (4)	0.0036 (38)	-0.0005 (11)	0.0027 (32)
C ₇	0.0235 (10)	0.7039 (28)	0.1580 (7)	0.0063 (9)	0.0580 (62)	0.0037 (5)	0.0054 (43)	0.0000 (11)	0.0057 (31)
C ₈	0.0279 (12)	0.8850 (28)	0.1877 (7)	0.0092 (11)	0.0413 (52)	0.0045 (5)	0.0143 (49)	0.0036 (14)	0.0050 (31)
C ₉	0.1094 (10)	0.9786 (22)	0.2007 (7)	0.0059 (8)	0.0367 (46)	0.0061 (6)	0.0017 (37)	0.0021 (13)	0.0040 (28)
C ₁₀	0.1956 (9)	0.8829 (20)	0.1819 (6)	0.0069 (8)	0.0244 (35)	0.0044 (5)	0.0014 (33)	0.0027 (11)	0.0009 (22)
C ₁₁	0.2908 (8)	0.4171 (20)	0.2457 (5)	0.0066 (7)	0.0421 (43)	0.0027 (4)	0.0018 (38)	0.0018 (9)	0.0008 (23)
C ₁₂	0.4504 (9)	0.1866 (18)	0.1678 (6)	0.0081 (9)	0.0262 (35)	0.0044 (4)	0.0122 (31)	0.0021 (10)	0.0042 (22)
C ₁₃	0.7079 (7)	0.3640 (17)	0.0758 (6)	0.0039 (6)	0.0273 (34)	0.0031 (4)	0.0022 (26)	-0.0004 (9)	0.0010 (20)
C ₁₄	0.7616 (9)	0.3500 (18)	0.1333 (6)	0.0088 (9)	0.0343 (40)	0.0031 (4)	0.0055 (34)	-0.0007 (12)	-0.0027 (24)
C ₁₅	0.8576 (9)	0.2761 (21)	0.1341 (8)	0.0068 (9)	0.0363 (42)	0.0057 (6)	0.0118 (35)	0.0006 (13)	-0.0001 (32)
C ₁₆	0.8989 (8)	0.2187 (20)	0.0739 (8)	0.0057 (8)	0.0298 (38)	0.0056 (5)	0.0048 (32)	0.0009 (12)	-0.0021 (28)
C ₁₇	0.8461 (8)	0.2297 (21)	0.0143 (7)	0.0047 (7)	0.0286 (37)	0.0060 (6)	-0.0043 (31)	0.0008 (11)	-0.0010 (27)
C ₁₈	0.7510 (9)	0.3053 (20)	0.0158 (6)	0.0085 (9)	0.0340 (40)	0.0035 (4)	-0.0111 (35)	0.0011 (11)	-0.0029 (24)
C ₁₉	0.6597 (8)	0.7849 (20)	0.0436 (6)	0.0051 (7)	0.0310 (40)	0.0053 (5)	-0.0124 (30)	0.0014 (10)	0.0007 (25)
C ₂₀	0.4327 (7)	0.8041 (19)	0.0199 (6)	0.0054 (7)	0.0352 (40)	0.0045 (5)	0.0091 (30)	-0.0001 (9)	0.0093 (25)

^a Anisotropic temperature factors (β_{ij}) have the form $h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}$.

P-H bond as illustrated in Figure 2. Tables II, III, and IV of bond lengths, bond angles, and selected dihedral

Table II. Bond Lengths (Å)^a

P-O ₁	1.697 (8)	P-O ₂	1.703 (7)
P-N ₁	1.681 (10)	P-N ₂	1.698 (10)
O ₁ -C ₁	1.421 (13)	O ₂ -C ₃	1.447 (14)
N ₁ -C ₂	1.490 (13)	N ₂ -C ₄	1.509 (14)
N ₁ -C ₁₂	1.474 (16)	N ₂ -C ₂₀	1.476 (15)
C ₁ -C ₂	1.522 (17)	C ₃ -C ₄	1.567 (18)
C ₁ -C ₅	1.548 (15)	C ₃ -C ₁₃	1.486 (15)
C ₂ -C ₁₁	1.557 (15)	C ₄ -C ₁₉	1.531 (17)
C ₅ -C ₆	1.410 (17)	C ₁₃ -C ₁₈	1.423 (17)
C ₅ -C ₁₀	1.397 (19)	C ₁₃ -C ₁₄	1.398 (17)
C ₆ -C ₇	1.449 (20)	C ₁₇ -C ₁₈	1.436 (18)
C ₇ -C ₈	1.373 (26)	C ₁₆ -C ₁₇	1.427 (20)
C ₈ -C ₉	1.340 (22)	C ₁₅ -C ₁₆	1.413 (21)
C ₉ -C ₁₀	1.431 (19)	C ₁₄ -C ₁₅	1.444 (17)

^a Bond distances have not been corrected for thermal motion. The estimated standard deviations do not contain cell constant errors.

Table III. Bond Angles (deg)

O ₁ -P-O ₂	176.6 (4)	N ₁ -P-N ₂	123.3 (5)
O ₁ -P-N ₁	88.6 (4)	O ₂ -P-N ₂	89.7 (4)
O ₁ -P-N ₂	92.9 (4)	O ₂ -P-N ₁	91.8 (4)
P-O ₁ -C ₁	111.8 (6)	P-O ₂ -C ₃	112.0 (6)
P-N ₁ -C ₂	115.9 (8)	P-N ₂ -C ₄	114.8 (7)
P-N ₁ -C ₁₂	129.6 (7)	P-N ₂ -C ₂₀	129.3 (7)
C ₂ -N ₁ -C ₁₂	114.4 (9)	C ₄ -N ₂ -C ₂₀	115.3 (9)
O ₁ -C ₁ -C ₂	103.9 (8)	O ₂ -C ₃ -C ₄	102.4 (9)
O ₁ -C ₁ -C ₅	108.4 (9)	O ₂ -C ₃ -C ₁₃	108.7 (9)
C ₂ -C ₁ -C ₅	114.9 (9)	C ₄ -C ₃ -C ₁₃	115.6 (9)
N ₁ -C ₂ -C ₁	100.5 (8)	N ₂ -C ₄ -C ₃	100.1 (8)
N ₁ -C ₂ -C ₁₁	109.6 (8)	N ₂ -C ₄ -C ₁₉	113.0 (10)
C ₁ -C ₂ -C ₁₁	116.6 (10)	C ₃ -C ₄ -C ₁₉	115.3 (9)
C ₁ -C ₂ -C ₅	116.9 (11)	C ₃ -C ₄ -C ₁₃	117.6 (10)
C ₁ -C ₅ -C ₁₀	122.5 (10)	C ₃ -C ₁₃ -C ₁₄	124.3 (10)
C ₆ -C ₅ -C ₁₀	120.6 (11)	C ₁₄ -C ₁₃ -C ₁₈	118.0 (10)
C ₄ -C ₆ -C ₇	116.1 (13)	C ₁₃ -C ₁₈ -C ₁₇	121.2 (11)
C ₆ -C ₇ -C ₈	121.0 (14)	C ₁₆ -C ₁₇ -C ₁₈	119.1 (12)
C ₇ -C ₈ -C ₉	123.5 (15)	C ₁₅ -C ₁₆ -C ₁₇	120.7 (11)
C ₈ -C ₉ -C ₁₀	117.4 (14)	C ₁₄ -C ₁₅ -C ₁₆	118.2 (13)
C ₅ -C ₁₀ -C ₉	121.5 (12)	C ₁₃ -C ₁₄ -C ₁₅	122.7 (12)

angles, respectively, are arranged to allow quick comparisons of structure parameters related by the twofold axis. Values in the left-hand column of the tables

are accompanied by the symmetry-related counterpart in the right-hand column. As can be seen from the tables, values of symmetry equivalent parameters are in reasonable agreement.

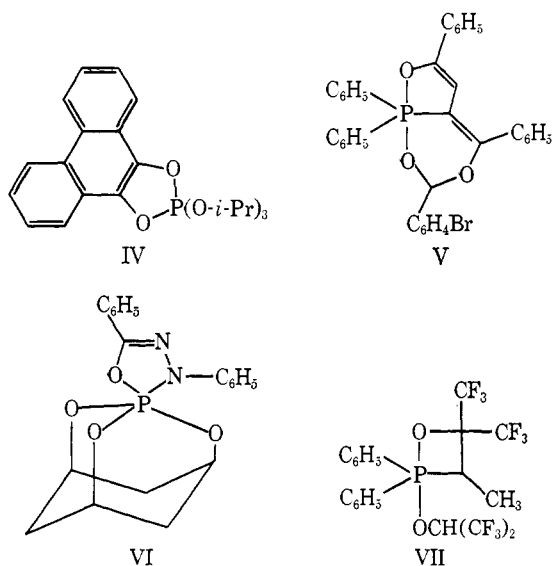
Table IV. Selected Dihedral Angles (deg)^a

Atoms I-J-K-L	Angle	Atoms I-J-K-L	Angle
N ₁ -P-O ₁ -C ₁	-26.2 (8)	N ₂ -P-O ₂ -C ₃	-25.1 (8)
N ₂ -P-O ₁ -C ₁	97.0 (8)	N ₁ -P-O ₂ -C ₃	98.2 (8)
O ₁ -P-N ₁ -C ₂	1.5 (8)	O ₂ -P-N ₂ -C ₄	-5.0 (8)
O ₁ -P-N ₁ -C ₁₂	-177 (1)	O ₂ -P-N ₂ -C ₂₀	-175 (1)
O ₂ -P-N ₁ -C ₂	175.1 (8)	O ₁ -P-N ₂ -C ₄	172.9 (8)
O ₂ -P-N ₁ -C ₁₂	1 (1)	O ₁ -P-N ₂ -C ₂₀	2 (1)
N ₂ -P-N ₁ -C ₂	-94.1 (9)	N ₁ -P-N ₂ -C ₄	-96.9 (8)
N ₂ -P-N ₁ -C ₁₂	90 (1)	N ₁ -P-N ₂ -C ₂₀	93 (1)
P-O ₁ -C ₁ -C ₂	45 (1)	P-O ₂ -C ₃ -C ₄	46 (1)
P-O ₁ -C ₁ -C ₅	167.8 (7)	P-O ₂ -C ₃ -C ₁₃	168.3 (7)
P-N ₁ -C ₂ -C ₁	25 (1)	P-N ₂ -C ₄ -C ₃	29 (1)
P-N ₁ -C ₂ -C ₁₁	-98 (1)	P-N ₂ -C ₄ -C ₁₉	-94 (1)
C ₁₂ -N ₁ -C ₂ -C ₁	-158.0 (9)	C ₂₀ -N ₂ -C ₄ -C ₃	-158.6 (9)
C ₁₂ -N ₁ -C ₂ -C ₁₁	79 (1)	C ₂₀ -N ₂ -C ₄ -C ₁₉	78 (1)
O ₁ -C ₁ -C ₂ -N ₁	-41 (1)	O ₂ -C ₃ -C ₄ -N ₂	-44 (1)
O ₁ -C ₁ -C ₂ -C ₁₁	77 (1)	O ₂ -C ₃ -C ₄ -C ₁₉	78 (1)
C ₅ -C ₁ -C ₂ -N ₁	-159 (1)	C ₁₃ -C ₃ -C ₄ -N ₂	-162 (1)
C ₅ -C ₁ -C ₂ -C ₁₁	-41 (1)	C ₁₃ -C ₃ -C ₄ -C ₁₉	-40 (1)
O ₁ -C ₁ -C ₅ -C ₆	176 (1)	O ₂ -C ₃ -C ₁₃ -C ₁₈	180 (1)
O ₁ -C ₁ -C ₅ -C ₁₀	-5 (1)	O ₂ -C ₃ -C ₁₃ -C ₁₄	3 (1)
C ₂ -C ₁ -C ₅ -C ₆	-68 (1)	C ₄ -C ₃ -C ₁₃ -C ₁₈	-66 (1)
C ₂ -C ₁ -C ₅ -C ₁₀	111 (1)	C ₄ -C ₃ -C ₁₃ -C ₁₄	117 (1)

^a The dihedral angle has a positive sign if vector K-L is clockwise from vector J-I when viewed down vector J-K and a negative sign if counterclockwise.

The phosphorus atom in III is a very slightly distorted trigonal bipyramid with the two oxygen atoms in apical positions and the nitrogen atoms in equatorial positions. This result is in agreement with the electronegativity rules,¹⁴ and similar dispositions have been observed in other pentacoordinate phosphorus compounds.¹⁵⁻¹⁸ The O-P-O angle is 3.4° smaller than the ideal 180° angle and the N-P-N angle is 3.3° larger than the ideal 120° angle. The five-membered ring O-P-N angles of 88.6 and 89.7° and the inter-ring O-P-N angles of 92.9 and 91.8° show practically insignificant deviations from an ideal 90° angle.

The axial P-O bond lengths previously observed in the oxyphosphoranes IV-VII range from 1.63 to 1.79 Å.



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In structure IV,¹⁵ the P-O bond length in the five-membered ring is 1.76 Å whereas the exocyclic P-O bond length is 1.63 Å. The P-O bond lengths in V¹⁶ are 1.737 and 1.786 Å for the six-membered and five-membered ring, respectively. The axial P-O bond in the adamantyl-like portion of VI¹⁷ has a length of 1.627 Å whereas the P-O bond length in the five-membered ring is 1.754 Å. In the four-membered ring phosphorane, VII,¹⁸ the ring P-O length is 1.79 Å and the exocyclic bond is 1.71 Å. There are two trends in the above data: (1) the longest axial P-O bond lengths occur in five-membered rings where the oxygen atom is joined to an unsaturated center and in highly strained systems and (2) the longer axial P-O bond is accompanied by a shorter bond in the alternate axial position. In structure III, however, the oxygen atoms are attached to a saturated carbon center in a five-membered ring and the two P-O lengths have virtually identical values of 1.697 and 1.703 Å. This result suggests that a normal P-O axial bond length is approximately 1.70 Å in the absence of the various steric and electronic factors present in IV-VII.

The two nitrogen atoms are essentially coplanar with attached atoms. In fact, the atoms P, O₁, O₂, N₁, C₂, and C₁₂ and the symmetry equivalent group P, O₁, O₂, N₂, C₄, and C₂₀ form two planar groups. These planes are easily seen in Figure 1 and the standard deviations of the atoms from the least-squares plane are listed in Table V.

Table V. Deviation of Atoms from Least-Squares Planes

Atom	Dev, Å	Atom	Dev, Å
Plane I: 0.1416X + 0.1784Y + 0.9737Z = 4.464			
N ₁	-0.032	C ₁₂	-0.007
P	-0.031	O ₁	0.004
C ₂	0.032	O ₂	0.033
Plane II: 0.4421X + 0.8146Y + 0.3756Z = 7.313			
N ₂	-0.064	C ₂₀	-0.011
P	-0.011	O ₁	0.043
C ₄	0.044	O ₂	0.000
Plane III: 0.0438X - 0.4457Y + 0.8941Z = 0.762			
C ₅	-0.002	C ₈	-0.003
C ₆	0.000	C ₉	0.001
C ₇	0.002	C ₁₀	0.001
Plane IV: 0.3424X + 0.9289Y - 0.1414Z = 5.501			
C ₁₃	-0.004	C ₁₆	0.006
C ₁₄	0.001	C ₁₇	-0.007
C ₁₅	-0.004	C ₁₈	0.007

In effect, the five-membered rings contain four coplanar atoms (P, O₁, N₁, C₂ and P, O₁, N₂, C₄) with the N-CH₃ carbon atoms also in the plane of the four ring atoms. The planarity of the nitrogen atoms suggests sp² hybridization at nitrogen and possible dπ-pπ overlap between phosphorus and nitrogen.¹⁹

The mean P-N bond length of 1.69 ± 0.01 Å in III is in reasonable agreement with the P-N bond length of 1.671 Å in VI and is somewhat longer than the mean P-N bond length of 1.644 Å observed in a diazaphosphorane, a system which also contains planar

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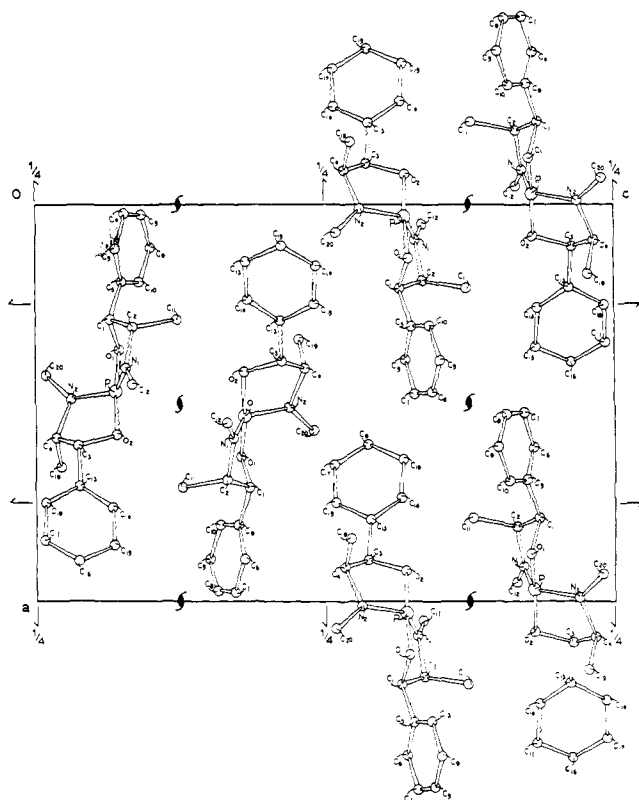


Figure 3. Unit cell packing diagram projected onto the ac plane.

nitrogen atoms. P–N bonds in cyclophosphazines are considerably shorter, e.g., 1.58 Å in $N_3P_3Cl_6$.²⁰ However, the P–N bond lengths in $P(NMe_2)_3$ ²¹ (1.70 Å) are in accord with those in III.

Since only a few P–N bond lengths have been measured, it is instructive to compare variations in P–O bond lengths in phosphites, phosphates, and oxyphosphoranes and compare with the analogous P–N bonds. The equatorial P–O bonds in IV (1.633, 1.588, 1.574 Å) and in VI (1.601, 1.590 Å) average 1.597 ± 0.006 Å which is similar in value to the mean P–O bond lengths in *trans*-methyl-*meso*-hydrobenzoin phosphite²² (1.623 ± 0.005 Å) and in triethyl and trivinyl phosphite (1.600 ± 0.006 Å).²³ Formal P–O single bonds in phosphate triesters have average lengths that are somewhat shorter (e.g., 1.574 ± 0.005 Å in *trans*-methyl-*meso*-hydrobenzoin phosphate)²² than those in phosphites and oxyphosphoranes. The axial lengths in oxyphosphoranes are the longest P–O bond types (1.70 Å). On the basis of the limited information presented, P–O bond lengths in phosphites are generally similar in value to equatorial P–O bond lengths in oxyphosphoranes. By analogy, the P–N bonds in III should be close in value to those in $P(NMe_2)_3$, and as mentioned in the preceding paragraph, this is indeed the case. Thus, P–N and P–O bond lengths in III are in accord with previously measured systems.

The three bond angles around the nitrogen atoms

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average 120.0° for N_1 and 119.8° for N_2 providing further evidence of the sp^2 hybridization. The P–N–CH₃ angles are enlarged to nearly 130° , presumably to relieve nonbonded interactions between the methyl groups on nitrogen and the oxygen atoms. The $O_1 \cdots C_{20}$ and $O_2 \cdots C_{12}$ nonbonded distances are 2.77 and 2.73 Å, respectively, compared to the van der Waals sum of 3.4 Å using 2.0 Å as the radius of the methyl group. The N–C bond distances compare favorably to values in methylamine,²⁴ *N,N*-dimethyl-*p*-nitroaniline,²⁵ and the diazaphosphocine oxide.¹⁹ All other bond distances and angles in III are in agreement with values found in other structures. Both phenyl rings display normal geometry and deviations of the ring atoms from the least-squares planes are given in Table V. The exocyclic valency angles $C_3-C_{13}-C_{14}$ and $C_1-C_5-C_{10}$ are significantly larger than the alternate exocyclic angles $C_3-C_{13}-C_{18}$ and $C_1-C_5-C_6$ possibly because of nonbonded interactions between $O_1 \cdots C_{10}$ and $O_2 \cdots C_{14}$.

Figure 2 shows a Newman projection of a molecule of III viewed down the C_1-C_2 and C_3-C_4 bonds. The conformation of the rings when viewed down the C–C bonds is twist-envelope with $O_1-C_1-C_2-N_1$ and $O_2-C_3-C_4-N_2$ dihedral angles of 41 and 44° , respectively. However, the $O_1-P-N_1-C_2$ and $O_2-P-N_2-C_4$ ring dihedral angles are small (1.5 and 5.0° , respectively), demonstrating an approximate envelope conformation with C_1 and C_3 in a flap position. Similar ring conformations have been found in methyl-*meso*-hydrobenzoin phosphite and phosphate.²²

The ring torsion angles in III are generally larger than corresponding angles measured in *trans*-methyl-*meso*-hydrobenzoin phosphate²² which have ring conformations similar to III. In III, the ring torsion angles (deg) are: O–C–C–N, -41 , 44 ; C–C–N–P, $+25$, $+29$; C–N–P–O, 1.5 , -5.0 ; N–P–O–C, -26 , -25 ; P–O–C–C, $+45$, $+46$. The average of the dihedral angle magnitude in III is 28.7° whereas the average ring dihedral angle magnitude in *meso*-hydrobenzoin phosphite and phosphate is 22.5° . Apparently, the 90° O–P–N angle in the trigonal bipyramid allows the five-membered ring and its substituents to approach a more nearly staggered arrangement than in the case of the tri- and tetracoordinated esters with larger phosphorus ring angles.

A packing diagram is shown in Figure 3. There are no unusually short intermolecular contacts. Only two intermolecular distances are less than 3.6 Å, $C_{12} \cdots O_1$, 3.44 (1) Å ($x, -1 + y, z$), and $C_{20} \cdots C_{17}$, 3.47 (2) Å ($-1/2 + x, 3/2 - y, -z$), and six less than 3.75 Å.

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Supplementary Material Available. Listings of h, k, l, F_o , and F_c 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, $24\times$ reduction, negatives) containing all 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 \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6888.

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