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Crystal and Molecular Structures of Symmetrical Dioxadiazaspirophosphoranes Containing Phosphorus–Hydrogen Bonds[1]

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Single-crystal X-ray diffraction analyses of the spirophosphoranes, $(OCH_2CH_2NH)_2PH$ (III) and $(OC_6H_4NH)_2PH$ (IV), resulting from the reactions of tris(dimethylamino)phosphine with ethanolamine and *o*-aminophenol, respectively, revealed trigonal-bipyramidal structures distorted approximately 25% along the Berry exchange coordinate toward an idealized rectangular pyramid. III crystallizes in the monoclinic space group $C2/c$ with $a = 10.118$ (5) Å, $b = 7.765$ (2) Å, $c = 10.381$ (5) Å, and $\beta = 121.69$ (5)° and has a crystallographic twofold axis along the P–H bond. IV crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.382$ (5) Å, $b = 10.625$ (5) Å, $c = 9.475$ (4) Å, and $\beta = 92.45$ (4)° and has an approximate twofold axis along the P–H bond. The pertinent parameters of III, P–H = 1.49 (6) Å, P–O_{ax} = 1.710 (2) Å, P–N_{eq} = 1.640 (3) Å, and the angle N_{eq}–P–N_{eq} = 130.8 (1)°, compare with similar parameters of IV, P–O_{ax} = 1.727 (2) and 1.735 (2) Å, P–N_{eq} = 1.653 (2) and 1.655 (3) Å, and the angle N_{eq}–P–N_{eq} = 121.8 (1)°. The large N_{eq}–P–N_{eq} angle in III is mainly accounted for by favorable positioning of intermolecular N–H---O hydrogen bonding tending to open the angle whereas in IV, the positions of the neighboring oxygen atoms tend to close the angle.

Introduction

Ring constraints and relative ligand electronegativity provide two of the most important factors responsible for the appearance of geometries between an idealized trigonal bipyramid (TP) and a square or rectangular pyramid (SP, RP) for pentacoordinate phosphorus compounds.[3] Unsaturation in small-membered rings containing oxygen ligands, as in some catechol derivatives,[4-7] I, leads to geometries nearer the RP than the TP. However, when R = H, a near TP is encountered.[4c] Substitution of sulfur for oxygen in the latter (when R = CH_3) produces structural changes[8] tending toward the TP. All acyclic derivatives of five-coordinate phosphorus, thus far examined, have near-TP geometries.[9]
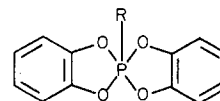
R = F,[4a] CH_3,[4b] adamantyl,[5] Ph,[6] OPh[7]

I

Recently we have shown[10a] that structural distortions between the TP and SP (RP) adhere closely to the Berry exchange coordinate[11] and that quantitative interpretation of structural variations is achievable by computer modeling.[10b]

The presence of ring heteroatoms directly attached to phosphorus provides a means of investigating the relative

effects of ring constraints and ligand electronegativity. In the dioxadiazaspirophosphorane II, X-ray diffraction by Newton


II
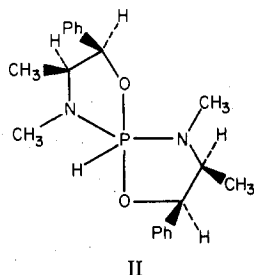
et al.[12] showed a near-TP structure with the apical oxygen atoms bent toward the assumed equatorial P–H bond and a near-"normal" N_{eq}–P–N_{eq} angle of 123°. In a preliminary report,[13] we have shown that the X-ray structure of the related unsubstituted phosphorane III is likewise a near TP. In this

III
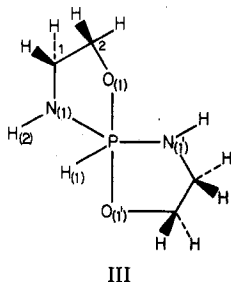
case the apical atoms were tilted away from the equatorial P–H bond and exhibited an unusually large N_{eq}–P–N_{eq} angle, 130.8 (1)°.

Hydrido derivatives in general have been little investigated. In order to extend the interpretation of geometrical effects with this class of five-coordinate phosphorus compounds, we have chosen the hydridospirophosphorane IV for study. It affords

IV
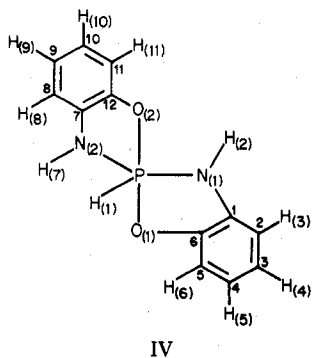
the opportunity for intermolecular hydrogen bonding, in contrast to II and, in addition, allows an assessment of unsaturation as a structural influence in heteroring systems of phosphorus. Accordingly, the single-crystal X-ray structure of IV was carried out and is reported here as well as the details of the X-ray structure of III.

Experimental Section

Data Collection for III. Crystals of 1,6-dioxa-4,9-diaza-5-λ^5-phosphaspiro[4.4]nonane, $(OCH_2CH_2NH)_2PH$, III, were obtained from the reaction of ethanolamine with $[(CH_3)_2N]_3P$ in benzene solution.[14] Recrystallization from benzene gave colorless crystals suitable for data collection. A needle of dimensions 0.9 × 0.05 × 0.05 mm was chosen for the X-ray study.

Preliminary photographic work using Cu Kα radiation indicated a monoclinic system (C-centered). Systematic absences in the Weissenberg and precession photographs, hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, indicated either space group $C2/c$ or Cc.

The crystal was transferred to an Enraf-Nonius CAD-3 diffractometer, with the crystal c axis aligned parallel to the instrument ϕ axis. The unit cell dimensions and orientation matrix were obtained by the least-squares refinement of the angular settings for 16 reflections having $16° < 2\theta_{Mo K\alpha} < 48°$. The cell constants are $a = 10.118$ (5) Å, $b = 7.765$ (2) Å, $c = 10.381$ (5) Å, and $\beta = 121.69$ (5)°. The calculated density ($Z = 4$) is 1.437 g/cm³ for $V = 693.9$ Å³. The density, measured by flotation in aqueous KI, was 1.430 g/cm³.

Intensity data were collected to a maximum θ of 25° with Zr-filtered Mo radiation ($\lambda_{K\alpha_1}$ 0.709 26 Å, $\lambda_{K\alpha_2}$ 0.713 54 Å) using the θ–2θ scan technique. Each reflection was scanned up to a maximum of four times, the number of which was determined by a preset intensity value. Instrumental and crystal stabilities were monitored every 50 reflections by using a control reflection (314). No significant deviation from its average intensity was found.

A total of 564 reflections was collected in the region $\pm h,+k,+l$. The net intensity of each reflection, I, is defined as

$$I = [P - (B_1 + B_2)](FF/n_s)$$

where P is the total peak count, B_1 and B_2 are the stationary left and right background counts, respectively, each measured for half the total scan time, FF is the attenuation factor for the filter used, and n_s is equal to the number of scans.

The standard deviation is defined as

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

where C is a factor to account for random errors other than those arising from counting statistics. A value of 0.045 was assigned as the value for C.[15] Because of the rather low linear absorption coefficient for III (3.23 cm⁻¹), no absorption corrections were made. Corrections for Lorentz and polarization effects were made. Reflections for which the intensity, I, was less than $0.1\sigma(I)$, were assigned a value of $F = [(1/Lp)(0.10\sigma(I))]^{1/2}$, where Lp is the Lorentz–polarization factor.

Structure Solution and Refinement for III. A Patterson map yielded coordinates for the phosphorus atom and suggested the space group $[C2/c$-$C_{2h}^6]$.[16] This choice of space group was substantiated by all following stages of refinement. Initial coordinates for the remaining four nonhydrogen atoms of the asymmetric unit were obtained from a Fourier synthesis phased on the phosphorus atom. Isotropic unit-weighted full-matrix least-squares refinement[17] of the parameters for the five nonhydrogen atoms of the asymmetric unit and a scale factor gave a conventional unweighted residual, $R = \sum||F_o| - |F_c||/\sum|F_o|$, of 0.156 for the 564 independent reflections.

In this and in all subsequent refinement, the atomic form factors used for nonhydrogen atoms were taken from the tabulation by Cromer and Waber[18] and for hydrogen atoms from Stewart et al.[19] A difference Fourier calculation at this point gave initial coordinates for the six hydrogen atoms of the asymmetric unit. The last cycles of refinement (anisotropic for nonhydrogen atoms and isotropic for hydrogen atoms) employed variable weights, $w^{1/2} = 2LpF_o/\sigma(I)$, and gave $R = 0.062$ and a weighted residual, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, of 0.070 for 564 reflections. During the last cycle of refinement no parameter shifted by more than $0.06\sigma(p)$, where $\sigma(p)$ is the least-squares estimate of the error for the parameter in question. A final difference Fourier synthesis (564 reflections) had a maximum density of 0.14 e/Å³.

Computations were done on a CDC 6600 computer (Model Cyber 74-18) using Zalkin's Fourier program FORDAP, Prewitt's full-matrix least-squares program SFLS, Johnson's thermal ellipsoid plot program[20] ORTEP, and several locally written programs.

Data Collection for IV. Crystals of 1,6-dioxa-4,9-diaza-2,3,7,8-dibenzo-5λ^5-phosphaspiro[4.4]nona-2,7-diene, $(OC_6H_4NH)_2PH$, IV, were prepared according to Sanchez[21] from the reaction of o-aminophenol with $[(CH_3)_2N]_3P$ in benzene solution.[22] Recrystallization from benzene and drying under vacuum at 130 °C yields colorless plates (mp 160 °C). A well-formed crystal of dimensions 0.625 × 0.125 × 0.850 mm was used in the X-ray analysis.

Preliminary precession and Weissenberg photographs recorded using Cu Kα radiation indicated the monoclinic system (Laue symmetry $2/m$). Systematic absences ($h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$), later confirmed in data collection, led to the space group $[P2_1/c$-$C_{2h}^5]$.[23]

The crystal was mounted on an Enraf-Nonius CAD-4 diffractometer with the crystal c axis aligned nearly parallel to the instrument axis. Zirconium-filtered Mo radiation ($\lambda_{K\alpha_1}$ 0.709 26 Å, $\lambda_{K\alpha_2}$ 0.713 54 Å) at a takeoff angle of 3.5° was used. The unit cell dimensions,

Table I. Atomic Coordinates for $(OCH_2CH_2NH)_2PH$ (III) with Standard Deviations in Parentheses

atom	x	y	z
P	0.0000	0.0950 (1)	0.2500
N(1)	0.1341 (3)	0.0070 (4)	0.4095 (3)
C(1)	0.2869 (4)	−0.0169 (6)	0.4353 (4)
C(2)	0.2832 (4)	0.0902 (6)	0.3121 (4)
O(1)	0.1279 (3)	0.0894 (3)	0.1895 (2)
H(1)	0.0000 (0)	0.287 (8)	0.2500 (0)
H(2)	0.118 (5)	−0.008 (5)	0.476 (5)
H(3)	0.366 (5)	0.022 (5)	0.534 (5)
H(4)	0.306 (4)	−0.135 (6)	0.426 (4)
H(5)	0.330 (4)	0.213 (5)	0.358 (4)
H(6)	0.360 (7)	0.055 (7)	0.282 (7)
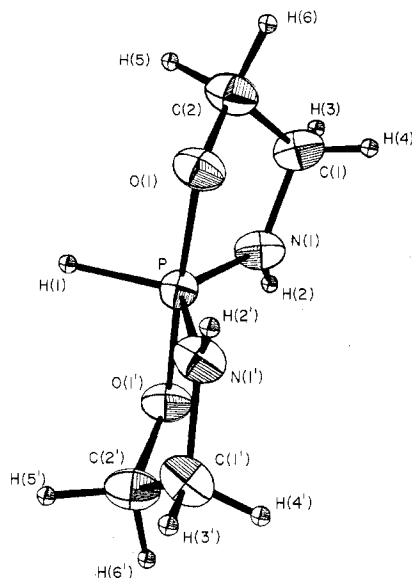
Figure 1. ORTEP[20] drawing of a molecule of $(OCH_2CH_2NH)_2PH$, III. Thermal ellipsoids are represented at the 50% probability level for nonhydrogen atoms. Hydrogen atoms are represented by spheres of arbitrary radius.

obtained by least-squares refinement of 14 accurately centered high-angle reflections, are $a = 11.382$ (5) Å, $b = 10.625$ (5) Å, $c = 9.475$ (4) Å, and $\beta = 92.45$ (4)°. The calculated density based on $Z = 4$ is 1.428 g/cm³ for $V = 1144.8$ Å³. The density measured by flotation in aqueous KI was 1.416 g/cm³.

Intensity data were recorded to a maximum θ of 30° using the θ–2θ scan technique (scan range of 0.8 + 0.5 tan θ degrees centered about the average peak position). The actual scan width used was extended an extra 25% on each side of the calculated limits for the measurement of background intensity. Variable scan rates from 4 to 0.4°/min were used, the actual value for each reflection depending on a prescan. Crystal stability was monitored every 50 reflections by measuring an intensity control reflection ($\bar{4}25$). Instrument stability was also monitored by measuring three orientation control reflections after every 50 reflections. No deviations greater than 3.3% from the intensity control reflection were encountered.

The net intensity of each reflection, I, is calculated as $I = (FF/n_s)[P - 2(B_1 + B_2)]$, where P is the total scan count, B_1 and B_2 are the left and right background counts, FF is a factor for an attenuator when it was inserted (unity otherwise), and n_s is inversely related to the scan rate. The intensity data were assigned standard deviations $\sigma(I) = [(P + 2(B_1 + B_2))(FF/n_s^2) + (CI)^2]^{1/2}$, where C had a value of 0.045 to account for instrument instability.

A total of 1834 independent reflections was measured in the region $+h,+k,\pm l$ of which 663 were treated as unobserved ($I < \sigma(I)$) in the least-squares refinement. Despite the low linear absorption coefficient (2.39 cm⁻¹), absorption corrections ranging from 1.07 to 1.14 were made because of the flat platelet used. Corrections for Lorentz and polarization effects were also made. Reflections for which I was less than $0.1\sigma(I)$ were assigned values as for III.

Structure Solution and Refinement for IV. Computations were carried out using programs, atom scattering factors, weights, and agreement factors R and R_w as cited for III. The coordinates for the phosphorus atom and the 16 other nonhydrogen atom positions were obtained by direct methods on the basis of the program MULTAN.[24,25] Isotropic refinement of the parameters for the 17 unique nonhydrogen atoms and a scale factor using unit weights yielded values of R and R_w of 0.147 and 0.154, respectively. Anisotropic refinement using variable weights led to values of $R = 0.129$ and $R_w = 0.089$. Coordinates for 11 hydrogen atoms of the asymmetric unit were obtained partially from a difference Fourier map calculated at this point and partially by calculation. Because the hydrogen atom positions did not all refine satisfactorily, they were fixed at the positions given in Table V, part B.

The final cycles of anisotropic refinement (variable weights) of the nonhydrogen atoms with fixed parameters for the hydrogen atoms gave values of $R = 0.039$ and $R_w = 0.037$ for the 1171 reflections having $I > \sigma(I)$ and $2\theta_{MoK\bar{\alpha}} < 60°$. During the last cycle of refinement, no parameter shifted by as much as $0.04\sigma(p)$ where $\sigma(p)$ is the least-squares estimate of the error for the parameter in question. A structure factor calculation using the final parameters from above but including the weak data (1834 reflections total) gave $R = 0.075$ and $R_w = 0.040$. A final difference Fourier synthesis based on these 1834 reflections had a maximum density of 0.51 e/Å³.

Results and Discussion

The positional and thermal parameters of III are given in Tables I and II, respectively. Bond lengths and angles are recorded in Table III and the molecular geometry is shown via an ORTEP plot[20] in Figure 1. Analogous data are presented in Tables IV–VI for the spirophosphorane IV. Figure 2 shows the corresponding molecular geometry for IV. Phosphorane III contains a crystallographic twofold axis lying along the equatorial P–H bond while IV contains a noncrystallographic approximate twofold axis lying along the P–H bond. The principal bond parameters for III and IV are illustrated in Figures 3 and 4, respectively.

As mentioned in the Introduction, the spirophosphorane III is a near TP. The same is found for the dibenzo derivative IV. On the basis of the sum of the differences of the dihedral angles from polytopal faces (calculated from the observed angles at phosphorus and unit bond vectors compared to those for the idealized TP and RP[10a]), structure III is estimated to be displaced 25% from the TP to the RP. By the same method structure IV is found distorted by a similar amount.

Table II. Thermal Parameters for $(OCH_2CH_2NH)_2PH$ (III) with Standard Deviations in Parentheses

atom	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	0.0127 (2)	0.0140 (2)	0.0075 (2)	0.0000	0.0055 (1)	0.0000
N(1)	0.0136 (4)	0.0247 (8)	0.0090 (4)	0.0031 (4)	0.0065 (3)	0.0024 (4)
C(1)	0.0138 (6)	0.0256 (10)	0.0092 (5)	0.0031 (5)	0.0051 (4)	−0.0007 (5)
C(2)	0.0124 (5)	0.0286 (10)	0.0122 (5)	−0.0017 (6)	0.0066 (4)	−0.0016 (5)
O(1)	0.0123 (4)	0.0253 (5)	0.0096 (3)	−0.0020 (3)	0.0063 (3)	−0.0008 (3)

atom	$B,{}^b$ Å²	atom	B, Å²	atom	B, Å²
H(1)	6.8 (1.5)	H(3)	4.0 (7)	H(5)	4.2 (7)
H(2)	4.1 (8)	H(4)	5.0 (9)	H(6)	8.3 (1.3)

^{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 B's in Å².

Table III. Bond Distances (Å) and Angles (deg) in
$(OCH_2CH_2NH)_2PH$ (III)

Distances

P-N(1)	1.640 (3)	N(1)-H(2)	0.80 (4)
P-O(1)	1.710 (2)	C(1)-H(3)	0.96 (4)
N(1)-C(1)	1.436 (5)	C(1)-H(4)	0.95 (4)
C(1)-C(2)	1.509 (5)	C(2)-H(5)	1.06 (4)
C(2)-O(1)	1.410 (4)	C(2)-H(6)	1.02 (6)
P-H(1)	1.49 (6)		

Angles

O(1)-P-O(1')	177.1 (1)	P-N(1)-C(1)	118.8 (2)
N(1)-P-N(1')	130.8 (1)	P-N(1)-H(2)	120 (3)
N(1)-P-O(1)	88.6 (1)	C(1)-N(1)-H(2)	121 (3)
O(1)-P-N(1')	90.2 (1)	N(1)-C(1)-C(2)	103.0 (3)
O(1)-P-H(1)	91 (1)	C(1)-C(2)-O(1)	106.4 (3)
N(1)-P-H(1)	115 (1)	C(2)-O(1)-P	111.6 (2)
N(1)-C(1)-H(3)	112 (2)	C(1)-C(2)-H(5)	108 (2)
N(1)-C(1)-H(4)	111 (2)	C(1)-C(2)-H(6)	115 (3)
H(4)-C(1)-H(3)	108 (3)	H(5)-C(2)-H(6)	98 (4)
H(3)-C(1)-C(2)	111 (2)	H(5)-C(2)-O(1)	116 (2)
H(4)-C(1)-C(2)	111 (2)	H(6)-C(2)-O(1)	113 (3)

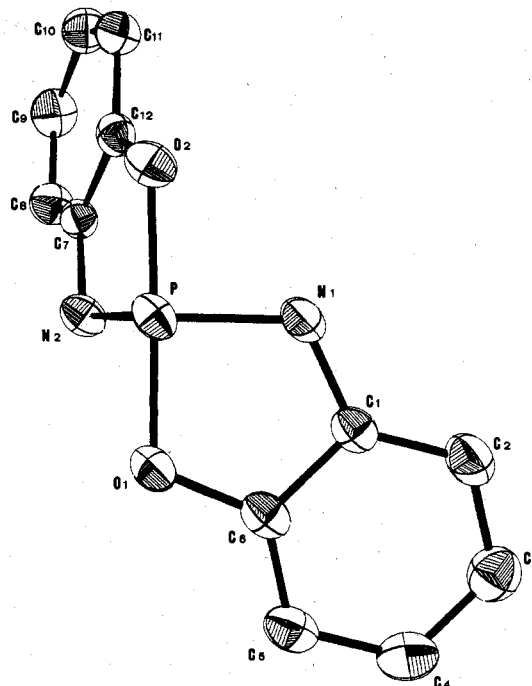**Table IV.** Atomic Coordinates for $(OC_6H_4NH)_2PH$ (IV) with Standard Deviations in Parentheses

atom	x	y	z
P	0.1137 (1)	0.7386 (1)	0.7616 (1)
N(1)	0.0223 (2)	0.6255 (2)	0.7090 (3)
N(2)	0.2295 (2)	0.7770 (2)	0.6709 (3)
O(1)	0.0267 (2)	0.8459 (2)	0.6685 (2)
O(2)	0.2018 (2)	0.6352 (2)	0.8603 (2)
C(1)	-0.0668 (3)	0.6606 (3)	0.6114 (3)
C(2)	-0.1488 (3)	0.5886 (3)	0.5382 (4)
C(3)	-0.2261 (3)	0.6475 (4)	0.4416 (4)
C(4)	-0.2210 (3)	0.7757 (4)	0.4200 (4)
C(5)	-0.1375 (3)	0.8490 (3)	0.4930 (4)
C(6)	-0.0618 (3)	0.7897 (3)	0.5884 (3)
C(7)	0.3269 (3)	0.6963 (3)	0.6908 (3)
C(8)	0.4270 (3)	0.6893 (3)	0.6159 (4)
C(9)	0.5111 (3)	0.6005 (4)	0.6595 (4)
C(10)	0.4925 (3)	0.5206 (3)	0.7705 (4)
C(11)	0.3904 (3)	0.5266 (3)	0.8438 (3)
C(12)	0.3080 (3)	0.6147 (3)	0.8010 (3)

Figure 2. Molecular structure (ORTEP[20] drawing) of $(OC_6H_4NH)_2PH$, IV. Thermal ellipsoids are shown at the 50% probability level.
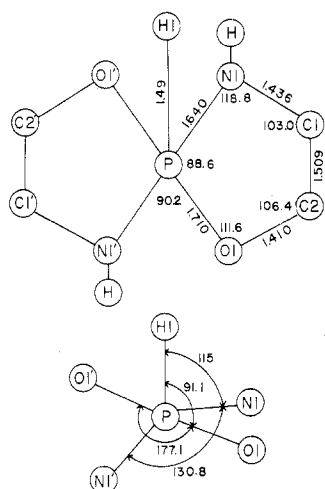
The structural distortion for III has been shown[10a] to be along the Berry exchange coordinate.[11] This is further evident from the value of the dihedral angle of 89.1° formed by the planes P-N(1)-N(1')-H(1) and P-O(1)-O(1')-H(1), which intersect along the crystallographic twofold axis. This dihedral angle is in the range expected, 90-85.9°, if the distortions that are followed for angle variations are along the coordinate leading to the idealized RP. The average deviation of atom positions from planes I and II which are strictly followed for an idealized TP is 0.035 Å (Table VII).

Similarly, the atom positions for the least-squares planes of the dibenzo derivative IV, given in Table VIII, show an even

Table V

A. Thermal Parameters for $(OC_6H_4NH)_2PH$ (IV) with Standard Deviations in Parentheses

atom	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	0.0088 (1)	0.0059 (1)	0.0099 (1)	-0.0001 (1)	0.0021 (1)	-0.0003 (1)
N(1)	0.0086 (3)	0.0055 (3)	0.0136 (4)	-0.0004 (2)	0.0010 (3)	0.0008 (2)
N(2)	0.0090 (3)	0.0076 (3)	0.0119 (4)	-0.0005 (2)	0.0020 (2)	0.0021 (2)
O(1)	0.0085 (2)	0.0059 (2)	0.0146 (4)	0.0002 (2)	0.0003 (2)	0.0000 (2)
O(2)	0.0094 (2)	0.0081 (2)	0.0114 (3)	0.0003 (2)	0.0020 (2)	0.0015 (2)
C(1)	0.0074 (3)	0.0068 (3)	0.0108 (5)	0.0003 (3)	0.0023 (3)	-0.0003 (3)
C(2)	0.0101 (4)	0.0073 (3)	0.0165 (6)	-0.0005 (3)	0.0016 (4)	-0.0007 (4)
C(3)	0.0092 (4)	0.0123 (5)	0.0144 (6)	-0.0005 (3)	-0.0001 (4)	-0.0020 (4)
C(4)	0.0096 (4)	0.0128 (5)	0.0136 (6)	0.0027 (3)	0.0008 (4)	0.0000 (4)
C(5)	0.0094 (4)	0.0081 (4)	0.0147 (6)	0.0017 (3)	0.0024 (4)	0.0010 (4)
C(6)	0.0080 (3)	0.0070 (4)	0.0113 (5)	0.0008 (3)	0.0033 (3)	0.0000 (3)
C(7)	0.0073 (3)	0.0073 (3)	0.0102 (5)	-0.0007 (2)	0.0003 (3)	0.0001 (3)
C(8)	0.0086 (4)	0.0106 (4)	0.0141 (6)	-0.0002 (3)	0.0018 (4)	0.0015 (4)
C(9)	0.0082 (4)	0.0137 (5)	0.0175 (7)	-0.0002 (3)	0.0031 (4)	-0.0005 (4)
C(10)	0.0089 (4)	0.0107 (4)	0.0181 (7)	0.0012 (3)	-0.0008 (4)	-0.0003 (4)
C(11)	0.0099 (4)	0.0088 (4)	0.0126 (5)	0.0001 (3)	-0.0003 (4)	0.0009 (3)
C(12)	0.0083 (4)	0.0072 (3)	0.0094 (5)	-0.0008 (3)	0.0005 (3)	-0.0012 (3)

B. Fixed Hydrogen Atom Coordinates for $(OC_6H_4NH)_2PH$ (IV)[b]

atom	x	y	z	atom	x	y	z
H(1)	0.090	0.801	0.873	H(7)	0.223	0.819	0.607
H(2)	0.032	0.557	0.739	H(8)	0.438	0.745	0.535
H(3)	-0.153	0.506	0.554	H(9)	0.581	0.597	0.612
H(4)	-0.291	0.601	0.398	H(10)	0.557	0.461	0.803
H(5)	-0.277	0.818	0.355	H(11)	0.376	0.472	0.919
H(6)	-0.128	0.938	0.471				

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 The isotropic thermal parameter, B, was fixed at 5.0 Å^2 for all hydrogen atoms.

Table VI. Bond Distances (Å) and Angles (deg) in $(OC_6H_4NH)_2PH$ (IV)

Distances

P-N(1)	1.653 (2)	P-N(2)	1.655 (3)
P-O(1)	1.727 (2)	P-O(2)	1.735 (2)
N(1)-C(1)	1.394 (4)	N(2)-C(7)	1.408 (4)
C(1)-C(2)	1.372 (5)	C(7)-C(8)	1.370 (5)
C(2)-C(3)	1.391 (5)	C(8)-C(9)	1.394 (5)
C(3)-C(4)	1.379 (5)	C(9)-C(10)	1.375 (5)
C(4)-C(5)	1.389 (5)	C(10)-C(11)	1.381 (5)
C(5)-C(6)	1.375 (5)	C(11)-C(12)	1.373 (4)
C(6)-C(1)	1.390 (4)	C(12)-C(7)	1.381 (4)
C(6)-O(1)	1.372 (4)	C(12)-O(2)	1.372 (4)

Angles

N(1)-P-N(2)	121.8 (1)	O(1)-P-O(2)	177.8 (1)
N(1)-P-O(1)	89.2 (1)	N(2)-P-O(2)	88.9 (1)
O(2)-P-N(1)	92.5 (1)	O(1)-P-N(2)	91.4 (1)
P-N(1)-C(1)	115.8 (2)	P-N(2)-C(7)	114.9 (2)
N(1)-C(1)-C(6)	109.6 (3)	N(2)-C(7)-C(12)	109.6 (2)
C(1)-C(6)-O(1)	112.1 (2)	C(7)-C(12)-O(2)	112.3 (2)
C(6)-O(1)-P	112.8 (2)	C(12)-O(2)-P	112.3 (2)
C(1)-C(2)-C(3)	118.6 (3)	C(7)-C(8)-C(9)	117.4 (3)
C(2)-C(3)-C(4)	120.8 (3)	C(8)-C(9)-C(10)	121.2 (3)
C(3)-C(4)-C(5)	120.8 (3)	C(9)-C(10)-C(11)	121.1 (3)
C(4)-C(5)-C(6)	117.8 (3)	C(10)-C(11)-C(12)	117.5 (3)
C(5)-C(6)-C(1)	121.7 (3)	C(11)-C(12)-C(7)	121.6 (3)
C(6)-C(1)-C(2)	120.2 (3)	C(12)-C(7)-C(8)	121.2 (3)

Table VII. Atom Distances (Å) from Least-Squares Planes I–IV for $(OCH_2CH_2NH)_2PH$ (III)[a]

	I	II[b]	III[b,c]		IV	
P	0.006	-0.006	P	0.001	P	-0.001
N(1)	0.064		N(1)	-0.044	N(1')	0.044
O(1)	-0.034	0.034	C(1)	0.064	C(1')	-0.064
N(1')		-0.064	O(1)	-0.011	O(1')	0.011
O(1')	-0.034	0.034	C(2)	(0.517)	C(2')	(-0.517)

[a] Values in parentheses show atom distances relative to the mean plane of concern but are not included in the calculation of the least-squares plane. [b] The displacement of atoms from plane II is required by the crystallographic twofold axis to equal the atom displacements in plane I. The same relation holds true for planes III and IV. [c] The dihedral angle between planes III and IV is 133.8°.

Table VIII. Atom Distances (Å) from Least-Squares Planes I–VI for $(OC_6H_4NH)_2PH$ (IV)[a]

	I	II	III[b]		IV[c]	
P	-0.009	-0.014				
N(1)	-0.008		N(1)	-0.002	N(2)	-0.001
O(1)	0.012	0.020	C(1)	0.009	C(7)	0.003
N(2)		-0.014	C(6)	-0.001	C(12)	-0.003
O(2)	0.012	0.019	O(1)	0.002	O(2)	0.001

	V		VI	
P	(-0.196)	P	(-0.260)	
N(1)	(-0.045)	N(2)	(0.015)	
O(1)	(-0.023)	O(2)	(-0.007)	
C(1)	0.001	C(7)	0.012	
C(2)	-0.001	C(8)	-0.012	
C(3)	-0.002	C(9)	0.004	
C(4)	0.004	C(10)	0.002	
C(5)	-0.004	C(11)	0.001	
C(6)	0.000	C(12)	-0.008	

[a] Values in parentheses show atom distances from the least-squares plane of interest but are not included in the calculation of the least-squares plane. [b] The dihedral angle between planes III and V is 1.40°. [c] The dihedral angle between planes IV and VI is 0.58°.

Figure 3. Schematic diagram of $(OCH_2CH_2NH)_2PH$, III, showing principal bond parameters (distances, Å; angles, deg).
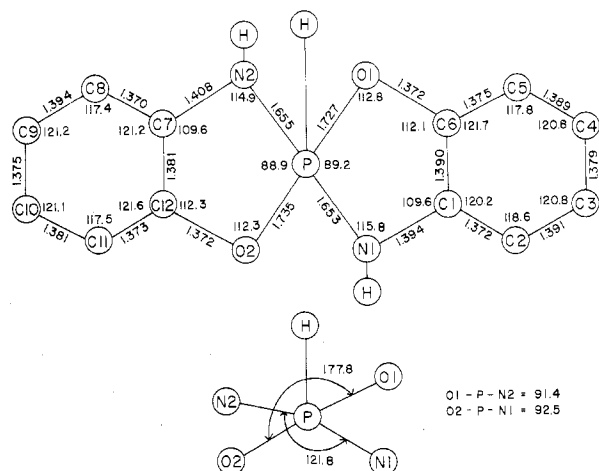
Figure 4. Schematic diagram of $(OC_6H_4NH)_2PH$, IV, showing principal bond parameters (distances, Å; angles, deg).

closer adherence for the defining planes for a TP, planes I and II here, giving average out-of-plane atom deviations of 0.010 and 0.017 Å, respectively. Although refinement did not reveal the location of the equatorial P–H bond, the angle between the O(1)–P–O(2) and N(1)–P–N(2) planes is 88.6° indicating that the P–H bond lies along an approximate C_2 axis. Thus, the local C_{2v} constraint is closely followed for the structural deviations from the ideal TP for IV.

Plane III in Table VII for the spirophosphorane III shows puckering primarily centered at C(2) which is directed toward the equatorial P–H bond as seen in Figure 1. The opposite puckering at this same flap atom in structure II[12] has been attributed[10b,13] to a more favorable orientation of the attached phenyl substituents. The effect of unsaturation on going to the dibenzo derivative IV, as seen by the least-squares planes III–VI, is to produce a high degree of planarity for all ring atoms other than the phosphorus atom (Table VIII). The latter acts as the flap atom and is located on the side of the mean planes of the rings opposite the equatorial hydrogen atom.

The most striking difference in the geometry around phosphorus between III and IV is found in the values of the N_{eq}–P–N_{eq} angle (cf. values in Tables III and VI). The widening of this angle to 130.8 (1)° for III compared to 120° for an ideal TP has been associated with intermolecular hydrogen bonding and P–N π bonding.[13] Application of a molecular-mechanics model[10b] including positioning of the specific hydrogen-bonding interactions, N–H---O, resulted in an almost 10° increase in the N_{eq}–P–N_{eq} angle compared with the angle obtained when conformational minimization was carried out without this intermolecular effect.[13] The dibenzo derivative IV shows a similar ability to hydrogen bond intermolecularly, N(1)–H---O(1) = 3.246 (4) Å and N-
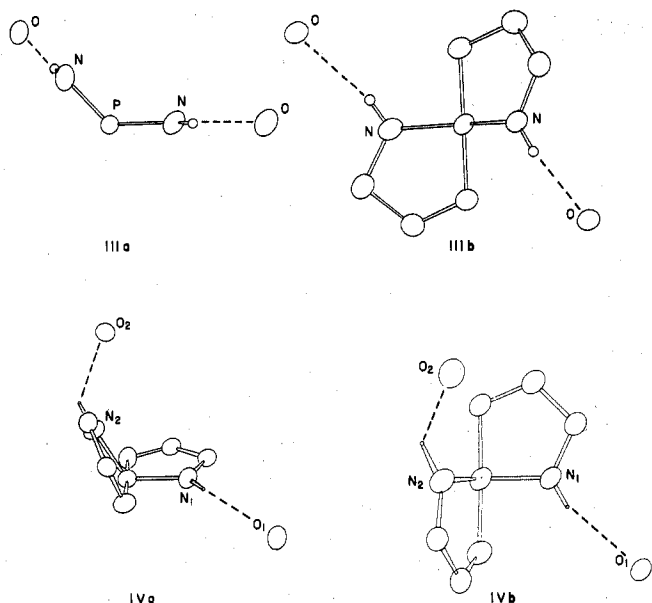
Figure 5. Partial structures illustrating intermolecular hydrogen bonding (dashed lines). (OCH$_2$CH$_2$NH)$_2$PH: IIIa, view down axial axis; IIIb, view along edge of the equatorial plane. (OC$_6$H$_4$NH)$_2$PH: IVa, view approximately down axial axis (the O(1) atom in the N(1)-H---O(1) hydrogen bond is close to lying in the P-N(1)-C(1) plane); IVb, view along edge of the equatorial plane. In all views the P-N(1) equatorial bond is in the plane of the figure. Refer to Figures 1 and 2 for the full molecular structure of III and IV, respectively.

(2)-H---O(2) = 3.090 (4) Å, but has an N_{eq}-P-N_{eq} angle of 121.8 (1)°, close to that observed[12] for II, 123°, which lacks hydrogen-bonding capability.

The difference in intermolecular hydrogen bonding between III and IV is portrayed in Figure 5. The two views for III in the top portion of the figure, an equatorial and an axial orientation, show the N-H---O arrangements to be essentially linear at the observed N_{eq}-P-N_{eq} angle of 130.8 (1)°. Similar views for IV in the lower portion of the figure show dissimilar N-H---O hydrogen bonds, one approximately linear and one nonlinear. The positioning of the oxygen atoms for IV is such as to make the resultant hydrogen bonding contract rather than expand the N_{eq}-P-N_{eq} angle.

In agreement with the N-H---O positioning for IV in Figure 5, infrared data[2a] indicate that the two hydrogen bonds differ in strength. A Nujol mull spectrum shows two N-H stretching frequencies, 3338 and 3388 cm^{-1}. In CCl$_4$ solution, where presumably intermolecular hydrogen bonding is absent, a single N-H stretch is observed at 3460 cm^{-1}. Most likely the stronger hydrogen bond is the near-linear N(1)-H---O(1) bond. As a result of the nonlinear orientation of the N(2)-H---O(2) hydrogen-bonding interaction, intermolecular hydrogen bonding is less effective in influencing the N_{eq}-P-N_{eq} angle in IV compared with the hydrogen bond system in III.

Equatorial in-plane p–d π bonding has been mentioned as a secondary factor tending to widen the N_{eq}-P-N_{eq} angle for III. Because of delocalization of the nitrogen π electrons into the planar ring system in IV, this effect should be reduced in this derivative. The resultant effect of the weak intermolecular hydrogen bonding tending to reduce the N_{eq}-P-N_{eq} angle, countered by the repulsion of residual P-N π-electron density concentrated in the equatorial plane, is to produce a N-P-N angle (121.8°) only slightly greater than 120°.

The small degree of tilting of the oxygen atoms toward the equatorial P-H bond in IV, opposite from that in III, probably also is associated with the planarity of the unsaturated ring system; i.e., because of a slight resultant tendency toward opening of the N_{eq}-P-N_{eq} angle, puckering at the phosphorus atom away from the equatorial hydrogen atom (cf. planes V

and VI of Table VIII) accommodates this movement. This effect then outweighs the P-H bond electron-pair repulsion effect, discussed[13] for III, which would tend to tilt the apical P-O bonds away from the equatorial P-H linkage.

On the basis of structural principles[3] correlating[3,10a] observed geometries for cyclic phosphoranes, we would expect structure IV to be more distorted toward the RP, relative to III, owing to the presence of ring unsaturation. The very similar degrees of distortion calculated here for these two derivatives (~25%) appear to be a result of differences in unit cell packing as discussed above. Equatorial ring opening via intermolecular hydrogen bonding assists III along the Berry distortion coordinate toward the RP, whereas this lattice effect leaves structure IV relatively unaltered.

It is apparent from this study that introduction of five-membered rings containing nitrogen–oxygen heteroatoms in a hydridospirophosphorane is capable of exerting structural changes amounting to a displacement along the Berry coordinate of about 25% toward the RP. This is in contrast to the catechol derivatives[4-7] mentioned in the Introduction which have geometries closer to the RP. Apparently, the presence of ring nitrogen atoms is a significant structural determinant by maintaining their strong preference for equatorial sites of a TP conformation. This preference is partially attributable to the presence of P-N π bonding which is particularly effective when localized in the equatorial plane of a TP.[26,27] It remains, however, to establish the importance of the special effects of the equatorial proton as a structural determinant. As with other cyclic phosphoranes containing equatorial nitrogen atoms,[28-32] the nitrogen and attached atoms in III are coplanar. It is presumed that this situation also prevails for IV.

As with other phosphoranes containing unsaturated ring systems, the apical P-O bonds in IV are longer than those in related saturated cyclic derivatives.[10a] The average apical P-O bond distance in IV is 1.731 Å (Table VI) compared with 1.710 Å (Table III) for III. The average value of an apical P-O bond length for a number of other unsaturated cyclic phosphoranes that have near-TP geometries is 1.75 Å.[10a] This compares with an average value of 1.63 Å for corresponding equatorial P-O bonds in these unsaturated derivatives. As the structure of cyclic phosphoranes becomes more RP, the two different P-O bond distances converge toward the value of 1.66 Å.[10a]

The pattern of ring bond distance and angle alternation observed for the dibenzo derivative IV (Table VI) is entirely analogous to that discussed[6] in some detail for the near-rectangular-pyramidal spirophosphorane (C$_6$H$_4$O$_2$)PC$_6$H$_5$, I (R = Ph).

References and Notes

(1) (a) Part 30 of the series "Pentacoordinated Molecules". (b) Previous paper in this series: W. Althoff, R. O. Day, R. K. Brown, and R. R. Holmes, *Inorg. Chem.*, preceding paper in this issue.
(2) (a) This work represents in part a portion of the Ph.D Thesis by P. F. Meunier, University of Massachusetts, Amherst. Presented in part at the XVII ICCC, Hamburg, West Germany, Sept 6, 1976; (b) Mai-

tre-Assistant affecté au CNRS (E.R.A. No. 82) Laboratoire des Hétérocycles du phosphore et de l'azote, Université Paul Sabatier, Toulouse, France. Visiting Professor at the University of Massachusetts, 1975–1976.

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Sterically Oriented Structures of Perfluoromethyl-Substituted Spirophosphoranes Centered between the Trigonal Bipyramid and the Rectangular Pyramid[1]

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The crystal and molecular structures of 2,2,3,3-tetrakis(trifluoromethyl)-5-*tert*-butyl-7,8-benzo-1,4,6,9-tetraoxa-5λ^5-phosphaspiro[4.4]nonene, $(C_6H_4O_2)(O_2C_2(CF_3)_4)PC(CH_3)_3$, and 2,2,3,3-tetrakis(trifluoromethyl)-5-phenyl-7,8-benzo-1,4,6,9-tetraoxa-5λ^5-phosphaspiro[4.4]nonene, $(C_6H_4O_2)(O_2C_2(CF_3)_4)PC_6H_5$, have been determined by single-crystal X-ray diffraction analysis. The tertiary butyl derivative crystallizes in the monoclinic system (space group $P2_1/n$) with cell constants $a = 12.285$ (4) Å, $b = 11.766$ (5) Å, $c = 14.116$ (3) Å, $\beta = 90.93$ (3)°, and $Z = 4$. The structure was refined by full-matrix least squares to a final R value of 0.088 and a weighted R value of 0.086 for 3220 independent reflections with $F \geq \sigma(F)$. The molecular geometry is displaced 37% along the Berry intramolecular exchange coordinate. Pertinent features of the molecule relative to a rectangular pyramid are the diagonal O–P–O angles of 131.4 (2) and 164.3 (2)° and the four bond angles between the apical P–C bond of the *tert*-butyl group and the P–O bonds, 118.9 (3), 98.0 (2), 109.7 (7), and 97.5 (3)°. The differences in the P–O bond lengths, 1.709 (4) vs. 1.648 (4) Å for the perfluoropinacol residue and 1.684 (4) vs. 1.618 (4) Å for the benzo residue, are indicative of the trigonal-bipyramidal character. The phenyl derivative crystallizes in the monoclinic space group $C2/c$ with cell constants $a = 18.108$ (8) Å, $b = 16.826$ (7) Å, $c = 14.593$ (3) Å, and $\beta = 112.71$ (2)°. The structure was refined by full-matrix least squares to a final R value of 0.076 and a weighted R value of 0.062 for 2499 independent reflections with $F \geq 3\sigma(F)$. The molecular geometry is displaced 52% along the Berry intramolecular exchange coordinate. For this derivative, the diagonal O–P–O angles are 136.8 (2) and 161.3 (2)° and the four bond angles between the apical P–C bond of the phenyl group and the P–O bonds are 114.9 (2), 98.2 (2), 108.2 (2), and 100.5 (2)°. The differences in the P–O bond lengths, 1.685 (3) vs. 1.665 (3) Å for the perfluoropinacol groups and 1.668 (3) vs. 1.614 (3) Å for the benzo residue, again are indicative of trigonal-bipyramidal character. Conformational minimization shows that intermolecular effects are important in accounting for the smaller displacement along the Berry coordinate for the more sterically hindered *tert*-butyl derivative.

Introduction

Members of the spirocyclic phosphorane series I–VI[1b,3–7] exhibit solid-state structural distortions showing progressive displacement along the C_{2v} constraint of the Berry coordinate,[8] as measured by percent displacement[9] from the trigonal bipyramid toward the rectangular pyramid (given in parentheses). Similar measurements of structural distortions from

X-ray studies[9–13] on related derivatives reveal the following factors favoring the formation of the rectangular pyramid: (1) increasing unsaturation in five-membered cyclic systems, (2) the presence of two such rings compared to the presence of one, (3) the presence of like atoms bonded to phosphorus in any one ring, (4) introduction of a more strained four-membered ring and, (5) the presence of an acyclic ligand in a spirocyclic derivative which is bulky and has low electro-