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Structural Characterization of Spirophosphoranes Existing as Nearly Perfect Trigonal Bipyramids[1]

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The single-crystal X-ray characterization of 2,3:7,8-dibenzo-1,4,6-trioxa-9-aza-5λ^5-phosphaspiro[4.4]nona-2,7-diene, IV, and 2,3:7,8-dibenzo-9-methyl-1,4,6-trioxa-9-aza-5λ^5-phosphaspiro[4.4]nona-2,7-diene, V, revealed relatively undistorted trigonal bipyramids with the unique proton ligand occupying an equatorial site. The structures lie along the coordinate connecting idealized trigonal-bipyramidal and rectangular-pyramidal geometries. They are displaced from the trigonal bipyramid by 5.5 (IV) and 11.2% (V) as measured by dihedral-angle differences from polytopal faces. Data for both compounds were collected by using Mo K$\bar{\alpha}$ radiation on an Enraf-Nonius CAD4 automated diffractometer. IV crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 5.729$ (2) Å, $b = 11.218$ (5) Å, $c = 17.234$ (7) Å, and $Z = 4$. Full-matrix least-squares refinement gave $R = 0.032$ and $R_w = 0.042$ for the 1393 reflections having $I \geq 3\sigma_I$ and $2° \leq 2\theta_{Mo\,K\bar{\alpha}} \leq 59°$. V crystallizes in the monoclinic space group $P2_1/c$, with $a = 9.142$ (2) Å, $b = 16.491$ (6) Å, $c = 8.133$ (2) Å, $\beta = 95.90$ (2)°, and $Z = 4$. Full-matrix least-squares refinement gave $R = 0.038$ and $R_w = 0.048$ for the 2062 reflections having $I \geq 3\sigma_I$ and $2° \leq 2\theta_{Mo\,K\bar{\alpha}} \leq 55°$. Examination of the structural data on these and related spirophosphoranes suggests that the small size of the phosphorus-bound proton acts as a principal factor in producing conformations of IV and V little distorted from a trigonal bipyramid. The presence of only one equatorial ring nitrogen atom in IV and V also appears to allow the ideal trigonal bipyramid to be closely approached.

In previous X-ray studies of the structures of spirophosphoranes containing P–H bonds, the basic geometrical arrangement is that of a trigonal bipyramid, I–III.[3-5]


I[3]

II[3,4]

III[5]
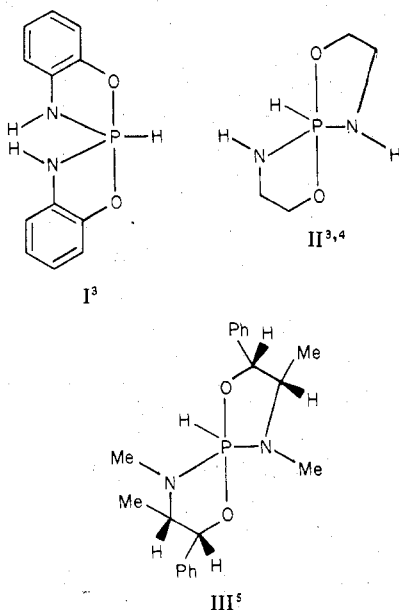
For II, the position of the hydrogen atom was sufficiently resolved to allow the determination of the mode of the distortion. As with previous phosphoranes whose structural parameters have been fully established,[6,7] distortion is found to closely adhere to the Berry coordinate[8] governing ligand exchange.[9] In the case of II, the degree of distortion from the idealized trigonal bipyramid to an ideal rectangular pyramid is 22%,[3] measured by the dihedral-angle method based on unit bond lengths.[6] For derivative I, it is estimated[3] that the degree of distortion from the idealized trigonal bipyramid is approximately the same. However, for II, the point at which the structure rests along this low-energy distortion coordinate

is strongly influenced by intermolecular hydrogen bonding. In the absence of the latter effect, the structure of II is expected to lie closer to a perfect trigonal bipyramid. The presence of two neighboring equatorial nitrogen atoms is also felt to move the structure away from the idealized trigonal bipyramid by way of P–N π bonding serving to widen the N–P–N equatorial angle. The latter is considered a secondary effect.[3]
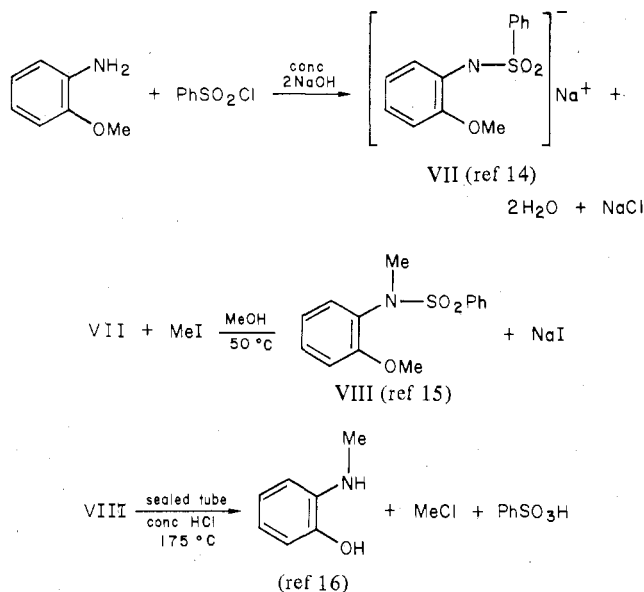
Derivative I contains unsaturated rings in the spiro system in contrast to that in II. From observations on trends in related derivatives,[6,7] ring unsaturation, by way of a more constrained ring system,[10] generally causes large structural distortions toward the rectangular-pyramidal geometry,[10,11] again along the Berry coordinate. However, these latter derivatives have rings containing like heteroatoms directly bonded to phosphorus. Thus, the presence of an equatorially positioned nitrogen atom in the dioxadiazaspirophosphorane I appears to act as a structural determinant in maintaining a much more modest perturbation of the ideal trigonal bipyramid. However, the presence of a proton as a ligand in these derivatives has not been adequately explored.

In order to more clearly establish the competing effects of these equatorial ligands as well as the role of ring unsaturation in a spirophosphorane like I, the derivatives IV and V were chosen for X-ray studies. Use of one rather than two ring

IV, R = H
V, R = CH$_3$
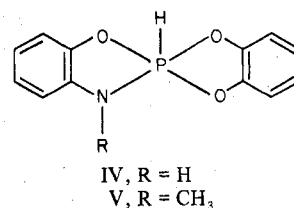
nitrogen atoms, as in I–III, removes the possible structural complication associated with π p–d effects in the equatorial bonding arrangement, N–P–N. Further, the influence of possible intermolecular hydrogen bonding in IV relative to its
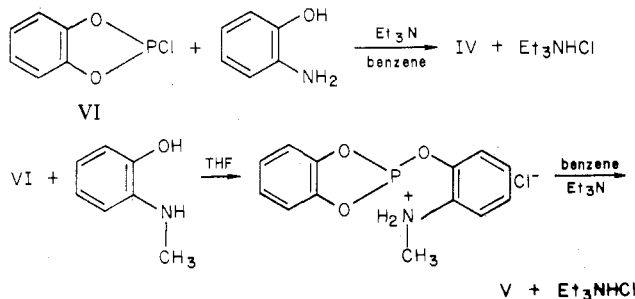
Scheme I

VII (ref 14)

$2H_2O + NaCl$

$VII + MeI \xrightarrow[50\ °C]{MeOH}$ VIII + NaI

VIII (ref 15)

$VIII \xrightarrow[175\ °C]{\text{sealed tube} \atop \text{conc HCl}}$ + MeCl + $PhSO_3H$

(ref 16)

absence in V may be revealed.

Experimental Section

Preparation. 2,3:7,8-Dibenzo-1,4,6-trioxa-9-aza-5λ^5-phosphaspiro[4.4]nona-2,7-diene, IV, and 2,3:7,8-dibenzo-9-methyl-1,4,6-trioxa-9-aza-5λ^5-phosphaspiro[4.4]nona-2,7-diene, V, were prepared as described by Burgada.[12] The procedure involved reaction of the *o*-aminophenol and *N*-methyl-*o*-aminophenol, respectively, with *o*-phenylene phosphorochloridite, VI. Recrystallization of derivative

VI

$VI + \xrightarrow[\text{benzene}]{Et_3N}$ IV + Et_3NHCl

$VI + \xrightarrow[]{THF}$ $\xrightarrow[Et_3N]{\text{benzene}}$

V + Et_3NHCl

IV from ether yielded colorless crystals suitable for a detailed X-ray study; mp (uncor) 130–131 °C (lit.[12] 120 °C). For V, recrystallization from benzene gave suitable crystals for an X-ray analysis; mp (uncor) 103–105 °C (lit.[12] 99 °C).

The phosphorochloridite VI was obtained by the addition of PCl_3 to catechol in the presence of a catalytic amount of water, essentially as described by Crofts et al.[13]

In order to obtain *N*-methyl-*o*-aminophenol for use in preparing V, the sequence of reactions in Scheme I was followed based on previous literature methods[14-16] (parenthesized references). The resulting air-sensitive *N*-methyl-2-aminophenol was purified by sublimation at 42–45 °C in vacuo; mp (uncor) 89 °C (lit.[16] 88–90 °C).

Space Group Determination and Data Collection for IV. A well-formed crystal having dimensions 0.39 × 0.29 × 0.40 mm was mounted in a thin-walled glass capillary which was sealed as a precautionary measure against hydrolysis. Preliminary investigations using an Enraf-Nonius CAD4 automated diffractometer and graphite-monochromated Mo Kα radiation (fine-focus tube, 45 kV, 20 mA, takeoff angle 3.1°, $\lambda_{K\alpha_1}$ 0.709 26 Å, $\lambda_{K\alpha_2}$ 0.713 54 Å) indicated orthorhombic (*mmm*) symmetry. From the observed extinctions $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), $00l$ ($l = 2n + 1$), the space group was uniquely determined as $P2_12_12_1$-D_2^4.[17] The lattice constants as determined by the least-squares refinement of the diffraction geometry for 23 reflections having $29° \leq 2\theta_{Mo\ K\alpha} \leq 34°$ as measured at an ambient laboratory temperature of 22 ± 2 °C are $a = 5.729\ (2)$ Å, $b = 11.218\ (5)$ Å, and $c = 17.234\ (7)$ Å. A unit cell content of four molecules gives a calculated density of 1.482 g/cm³ in agreement with

the value of 1.48 (2) g/cm³ as measured by flotation in a CCl_4–C_6H_6 mixture.

Data were collected by using the θ–2θ scan mode with a θ scan range of $(0.85 + 0.35 \tan \theta)°$ centered about the calculated Mo Kα peak position. The scan range was actually extended an extra 25% on either side of the aforementioned limits for the measurement of background radiation. The scan rates varied from 0.50 to 4.0°/min, the rate to be used for each reflection having been determined by a prescan. The intensity, I, for each reflection is then given by $I = (FF/S)(P - 2(B1 + B2))$, where P is the number of counts accumulated during the peak scan, $B1$ and $B2$ are left and right background counts, S is an integer for which the scan rate is inversely proportional, and FF is either unity or a multiplier to account for the occasional attenuation of the diffracted beam. The standard deviations in the intensities, σ_I, were computed as $\sigma_I^2 = (FF^2/S^2)(P + 4(B1 + B_2)) + 0.002I^2$. A total of 1779 independent reflections having $2° \leq 2\theta_{Mo\ K\alpha} \leq 59°$ were measured in the region $+h,+k,+l$. Eight standard reflections monitored after every 8000 s of X-ray exposure time gave no indication of crystal deterioration or loss of alignment. No correction was made for absorption ($\mu_{Mo\ K\alpha} = 0.248$ mm⁻¹), and the intensities were reduced to relative amplitudes, F_o, by means of standard Lorentz and polarization corrections.

Solution and Refinement for IV. Initial coordinates for the 17 nonhydrogen atoms of the asymmetric unit were determined by direct methods (MULTAN). The distinction between the nitrogen atom and the three oxygen atoms bonded to the phosphorus atom was based initially on analysis of the thermal parameters treating all four atoms as oxygen and was confirmed by the appearance of the N–H hydrogen atom on a subsequent difference Fourier synthesis. Isotropic unit-weighted full-matrix least-squares refinement[18] of the parameters for these 17 atoms and a scale factor gave a conventional residual $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ of 0.081 and a weighted residual $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2\}^{1/2}$ of 0.080 for the 668 reflections having $I \geq 3\sigma_I$ and $(\sin \theta)/\lambda \leq 0.5$. Anisotropic refinement led to $R = 0.067$ and $R_w = 0.063$. Initial coordinates for the eight hydrogen atoms bonded to ring carbon atoms were then inferred from the required geometry of the molecule. Subsequent refinement including these eight hydrogen atoms as isotropic contributions and using variable weights ($w^{1/2} = 2LpF_o/\sigma_I$) gave $R = 0.041$ and $R_w = 0.058$ for the 1393 reflections with $I \geq 3\sigma_I$. A difference Fourier synthesis then gave initial coordinates for the hydrogen atoms bonded to phosphorus and nitrogen. Inclusion of these two atoms (isotropic) in the refinement led to the final values of $R = 0.032$, $R_w = 0.042$,[19a] and GOF = 1.326[19b] for the 1393 reflections having $I \geq 3\sigma_I$ and $2° \leq 2\theta_{Mo\ K\alpha} \leq 59°$. During the final cycle of refinement, the largest shift in any parameter was 0.01 times its estimated standard deviation. A final difference Fourier synthesis showed a maximum density of 0.19 e/Å³.

Space Group Determination and Data Collection for V. The conditions for data collection and reduction were the same as described for IV, unless otherwise noted. A well-formed crystal having dimensions of 0.20 × 0.20 × 0.30 mm was mounted in a sealed thin-walled glass capillary. Preliminary diffractometric investigations indicated monoclinic (2/m) symmetry. From the observed extinctions $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$), the space group was uniquely determined as $P2_1/c$-C_{2h}^5.[20] The lattice constants as determined by the least-squares refinement of the diffraction geometry for 23 reflections having $26° < 2\theta_{Mo\ K\alpha} < 36°$ are $a = 9.142\ (2)$ Å, $b = 16.491$ (6) Å, $c = 8.133\ (2)$ Å, and $\beta = 95.90\ (2)°$. A unit cell content of four molecules gives a calculated density of 1.422 g/cm³, in agreement with the observed density of 1.41 (2) g/cm³.

A total of 2859 independent reflections having $2° \leq 2\theta_{Mo\ K\alpha} \leq 55°$ were measured in the region $\pm h,+k,+l$. Eleven standard reflections monitored after every 8000 s of X-ray exposure time showed a slight ($\sim$10% overall) decline in intensities indicating crystal degradation. A step-function correction was applied for this change as follows. For each measurement of the standard reflections, a correction factor f for all reflections measured between this group and the preceding group was computed as $f = {}^1/_{11}\sum_{i=1}^{11} I_i/I_i^0$, where I_i is the current intensity and I_i^0 the initial intensity for control reflection i. The corrected intensities for reflections in the interval were then calculated as $I_{cor} = I_{obsd}/f$. The maximum value for f was 0.907. No correction was made for absorption ($\mu_{Mo\ K\alpha} = 0.230$ mm⁻¹).

Solution and Refinement for V. Initial coordinates for the 18 independent nonhydrogen atoms were determined by direct methods (MULTAN). The conditions for refinement were the same as stated for IV. Isotropic unit-weighted refinement of the parameters for these

Table I. Atomic Coordinates for $(C_6H_4O_2)(C_6H_5NO)PH$, IV[a]

atom[b]	10^4x	10^4y	10^4z
P	9502 (1)	5485 (1)	6775 (1)
N	7155 (3)	6240 (2)	7043 (1)
O1	8184 (3)	5194 (1)	5896 (1)
O2	11788 (3)	6070 (1)	6337 (1)
O3	10784 (3)	5809 (1)	7646 (1)
1C1	9594 (4)	5499 (2)	5284 (1)
1C2	9123 (4)	5338 (2)	4498 (1)
1C3	10837 (5)	5722 (2)	3980 (1)
1C4	12883 (5)	6238 (2)	4222 (1)
1C5	13346 (4)	6396 (2)	5017 (1)
1C6	11672 (4)	6006 (2)	5525 (1)
2C1	9455 (4)	6545 (2)	8101 (1)
2C2	10053 (4)	6976 (2)	8832 (1)
2C3	8450 (4)	7712 (2)	9201 (1)
2C4	6342 (5)	8019 (2)	8854 (1)
2C5	5748 (4)	7566 (2)	8124 (1)
2C6	7321 (4)	6819 (2)	7766 (1)

a Numbers in parentheses are the estimated standard deviations in the last significant figure. *b* Atoms labeled to agree with Figure 1.

18 atoms and a scale factor gave $R = 0.093$ and $R_w = 0.094$ for the 1090 reflections having $I \geq 3\sigma_I$ and $(\sin \theta)/\lambda \leq 0.5$. Anisotropic refinement, including the high-angle data and using variable weights, gave $R = 0.071$ and $R_w = 0.107$ for the 2062 reflections with $I \geq 3\sigma_I$. Initial coordinates for the eight H atoms bonded to ring carbon atoms were inferred from the required geometry of the molecule.

Subsequent refinement including these eight atoms as isotropic contributions gave $R = 0.052$ and $R_w = 0.077$. A difference Fourier synthesis then gave initial coordinates for the phosphorus-bonded and methyl hydrogen atoms. Inclusion of these four atoms (isotropic) in the refinement led to the final values of $R = 0.038$, $R_w = 0.048$, and GOF = 1.510[21] for the 2062 reflections having $I > 3\sigma_I$ and $2° \leq 2\theta_{MoK\alpha} \leq 55°$. During the last cycle of refinement, the largest shift in any parameter was 0.01 times its estimated standard deviation. A final difference Fourier synthesis showed a maximum density of 0.40 e/Å^3.

Computations were done on a CDC 6600 computer (Model Cyber 74–18) by using the direct methods program MULTAN by Main, Germain, and Woolfson, Zalkin's Fourier program FORDAP, Prewitt's full-matrix least-squares program SFLS, Johnson's thermal ellipsoid plot program ORTEP, and several locally written programs.

Results and Discussion

Figure 1 illustrates the molecular geometry and atom labeling for the trioxaazaspirophosphorane IV. The refined positional and thermal parameters for the nonhydrogen atoms are listed in Tables I and II, respectively. Table III lists the corresponding parameters for the hydrogen atoms. Refined
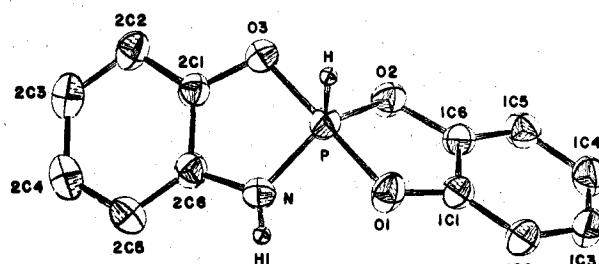

Figure 1. ORTEP plot of the molecular geometry of $(C_6H_4O_2)(C_6H_5NO)PH$, IV. Thermal ellipsoids are shown at the 50% probability level.
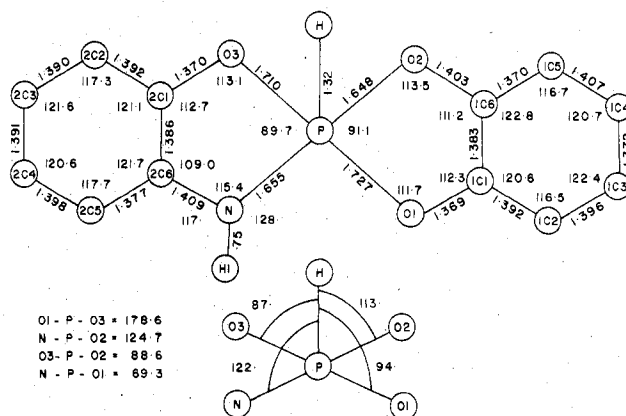

Figure 2. Principal bond parameters illustrated for $(C_6H_4O_2)(C_6H_5NO)PH$, IV.
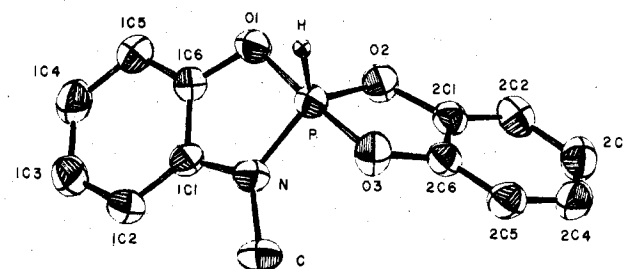

Figure 3. ORTEP plot of the molecular geometry of $(C_6H_4O_2)(C_7H_7NO)PH$, V. Thermal ellipsoids are shown at the 50% probability level.

bond lengths and angles are tabulated in Table IV and are summarized schematically in Figure 2 for all bond parameters

Table II. Thermal Parameters in $(C_6H_4O_2)(C_6H_5NO)PH$, IV[a]

atom[b]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	2.52 (2)	3.29 (2)	2.33 (2)	0.00 (2)	−0.12 (2)	−0.14 (2)
N	2.3 (1)	4.3 (1)	2.7 (1)	0.4 (1)	−0.3 (1)	−0.4 (1)
O1	3.1 (1)	4.7 (1)	2.5 (1)	−1.1 (1)	−0.1 (1)	−0.4 (1)
O2	2.6 (1)	4.0 (1)	2.8 (1)	−0.4 (1)	−0.4 (1)	−0.1 (1)
O3	2.9 (1)	5.0 (1)	2.6 (1)	1.0 (1)	−0.5 (1)	−0.7 (1)
1C1	2.7 (1)	2.7 (1)	2.7 (1)	0.0 (1)	−0.1 (1)	−0.1 (1)
1C2	3.5 (1)	3.5 (1)	2.8 (1)	−0.2 (1)	−0.5 (1)	−0.6 (1)
1C3	4.4 (1)	4.0 (1)	2.5 (1)	0.6 (1)	0.2 (1)	−0.2 (1)
1C4	3.8 (1)	4.1 (1)	3.3 (1)	0.6 (1)	1.0 (1)	0.5 (1)
1C5	2.7 (1)	3.3 (1)	3.6 (1)	0.0 (1)	0.3 (1)	0.4 (1)
1C6	2.6 (1)	2.6 (1)	2.7 (1)	0.2 (1)	−0.2 (1)	−0.1 (1)
2C1	2.6 (1)	3.0 (1)	2.4 (1)	−0.1 (1)	0.1 (1)	0.2 (1)
2C2	3.3 (1)	3.6 (1)	2.5 (1)	−0.8 (1)	0.0 (1)	0.2 (1)
2C3	4.1 (1)	3.5 (1)	2.8 (1)	−1.0 (1)	0.6 (1)	−0.5 (1)
2C4	3.9 (1)	3.7 (1)	3.8 (1)	0.2 (1)	1.2 (1)	−0.5 (1)
2C5	2.7 (1)	4.3 (1)	3.9 (1)	0.3 (1)	0.4 (1)	0.0 (1)
2C6	2.6 (1)	3.4 (1)	2.7 (1)	−0.4 (1)	0.2 (1)	0.1 (1)

a Numbers in parentheses are estimated standard deviations in the last significant figure. Anisotropic temperature factors used during refinement are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; the B_{ij} given above in Å^2 are related to the dimensionless β_{ij} as $B_{ij} = 4\beta_{ij}/a_i*a_j*$. *b* Atoms are labeled in agreement with Figure 1.

Table III. Refined Parameters for Hydrogen Atoms in $(C_6H_4O_2)(C_6H_5NO)PH$, IV^a

atom[b]	10^3x	10^3y	10^3z	B_{iso}, $Å^2$
H	979 (4)	435 (2)	695 (1)	3.3 (5)
H1	604 (6)	632 (3)	682 (2)	6.0 (8)
1H2	779 (5)	499 (2)	432 (1)	3.2 (5)
1H3	1054 (5)	558 (2)	347 (1)	4.9 (6)
1H4	1385 (5)	653 (2)	385 (1)	3.6 (5)
1H5	1463 (5)	672 (2)	522 (1)	4.0 (6)
2H2	1156 (5)	679 (2)	903 (1)	3.4 (5)
2H3	893 (5)	806 (2)	968 (1)	3.7 (5)
2H4	551 (5)	858 (2)	907 (2)	5.4 (7)
2H5	431 (6)	774 (3)	792 (2)	6.7 (8)

^{a} See footnotes to Table I. ^{b} The prefix 1 or 2 identifies the location of the ring hydrogen atoms relative to the labeling scheme given in Figure 1.

Table IV. Bond Lengths (Å) and Angles (deg) in $(C_6H_4O_2)(C_6H_5NO)PH$, IV^a

Lengths

P-O1	1.727 (2)	2C1-2C2	1.392 (3)
P-O3	1.710 (2)	2C2-2C3	1.390 (3)
P-O2	1.648 (2)	2C3-2C4	1.391 (4)
P-N	1.655 (2)	2C4-2C5	1.398 (3)
P-H	1.32 (2)	2C5-2C6	1.377 (3)
O1-1C1	1.369 (2)	2C6-2C1	1.386 (3)
O2-1C6	1.403 (2)	N-H1	0.75 (3)
O3-2C1	1.370 (2)	1C2-1H2	0.91 (3)
N-2C6	1.409 (3)	1C3-1H3	0.90 (2)
1C1-1C2	1.392 (3)	1C4-1H4	0.91 (2)
1C2-1C3	1.396 (3)	1C5-1H5	0.89 (3)
1C3-1C4	1.372 (4)	2C2-2H2	0.95 (3)
1C4-1C5	1.407 (3)	2C3-2H3	0.96 (2)
1C5-1C6	1.370 (3)	2C4-2H4	0.87 (3)
1C6-1C1	1.383 (3)	2C5-2H5	0.91 (4)

Angles

O1-P-O3	178.6 (1)^b	1C3-1C4-1C5	120.7 (2)
O2-P-N	124.7 (1)	1H4-1C4-1C5	122 (2)
O1-P-H	94 (1)	1C4-1C5-1H5	126 (2)
O3-P-H	87 (1)	1C4-1C5-1C6	116.7 (2)
O2-P-H	113 (1)	1H5-1C5-1C6	117 (2)
N-P-H	122 (1)	O2-1C6-1C5	126.0 (2)
O1-P-O2	91.1 (1)	O2-1C6-1C1	111.2 (2)
O3-P-N	89.7 (1)	1C5-1C6-1C1	122.8 (2)
O1-P-N	89.3 (1)	O3-2C1-2C6	112.7 (2)
O2-P-O3	88.6 (1)	O3-2C1-2C2	126.2 (2)
P-O1-1C1	111.7 (1)	2C6-2C1-2C2	121.1 (2)
P-O2-1C6	113.5 (1)	2C1-2C2-2H2	118 (1)
P-O3-2C1	113.1 (1)	2C1-2C2-2C3	117.3 (2)
P-N-H1	128 (2)	2H2-2C2-2C3	125 (1)
P-N-2C6	115.4 (1)	2C2-2C3-2H3	117 (1)
H1-N-2C6	117 (2)	2C2-2C3-2C4	121.6 (2)
O1-1C1-1C6	112.3 (2)	2H3-2C3-2C4	121 (1)
O1-1C1-1C2	126.9 (2)	2C3-2C4-2H4	118 (2)
1C6-1C1-1C2	120.8 (2)	2C3-2C4-2C5	120.6 (2)
1C1-1C2-1H2	123 (1)	2H4-2C4-2C5	121 (2)
1C1-1C2-1C3	116.5 (2)	2C4-2C5-2H5	119 (2)
1H2-1C2-1C3	120 (1)	2C4-2C5-2C6	117.7 (2)
1C2-1C3-1H3	116 (2)	2H5-2C5-2C6	123 (2)
1C2-1C3-1C4	122.4 (2)	N-2C6-2C5	129.3 (2)
1H3-1C3-1C4	122 (2)	N-2C6-2C1	109.0 (2)
1C3-1C4-1H4	117 (2)	2C5-2C6-2C1	121.7 (2)

^{a} See footnotes to Table I. ^{b} The direction of bending of the axial oxygen atoms is away from the equatorial proton along a projection in the equatorial plane which is 14.6° displaced from the equatorial P-H bond toward the equatorial P-N bond.

other than the ring C-H bonds.

An entirely analogous set of data are presented in Tables V-VIII for the *N*-methyl-substituted spirophosphorane V. Figures 3 and 4 show the corresponding molecular geometry and pictorial representation of bond parameters for V.

The overall basic structural features of IV and V conform to that of a trigonal bipyramid (TP) with the phosphorus-bonded hydrogen atom occupying an equatorial site and the

Table V. Atomic Coordinates for $(C_6H_4O_2)(C_7H_7NO)PH$, V^a

atom[b]	10^4x	10^4y	10^4z
P	2448 (1)	513 (1)	1719 (1)
N	4218 (3)	326 (1)	2316 (3)
C	5086 (4)	-406 (2)	2031 (5)
O1	2572 (2)	1402 (1)	2783 (3)
O2	1103 (2)	262 (1)	2803 (3)
O3	2239 (2)	-378 (1)	618 (3)
1C1	4913 (3)	933 (2)	3346 (4)
1C2	6348 (4)	982 (2)	4054 (5)
1C3	6747 (4)	1654 (2)	5044 (5)
1C4	5750 (4)	2252 (2)	5316 (5)
1C5	4306 (4)	2208 (2)	4591 (5)
1C6	3923 (3)	1544 (2)	3606 (4)
2C1	525 (3)	-507 (2)	2431 (4)
2C2	-542 (3)	-885 (2)	3224 (4)
2C3	-920 (4)	-1672 (2)	2694 (5)
2C4	-251 (4)	-2039 (2)	1449 (5)
2C5	815 (4)	-1640 (2)	655 (5)
2C6	1200 (3)	-868 (2)	1181 (4)

^{a} Numbers in parentheses are the estimated standard deviations in the last significant figure. ^{b} Atoms labeled to agree with Figure 3.
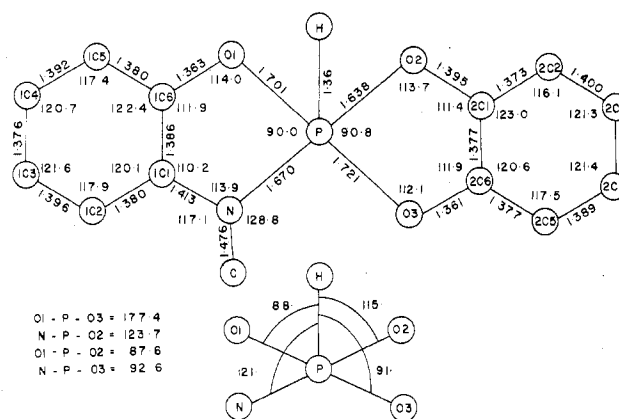
Figure 4. Principal bond parameters illustrated for $(C_6H_4O_2)(C_7H_7NO)PH$, V.

two phosphorus-containing five-membered ring systems each spanning an equatorial and axial site. The equatorial placement of hydrogen and nitrogen atoms is consistent with the electronegativity preference rule[22] as well as the more general substituent effect.[23] Indicative of the trigonal-bipyramidal character for IV, the trans axial angle O1-P-O3 = 178.6 (1)° and the diequatorial angles are within 7° of the 120° required for the ideal TP. Similarly, the axial angle O1-P-O3 for V is 177.4 (1)° and the diequatorial angles are within 5° of that for the ideal TP.

A more quantitative approach to the assessment of structural distortions, using dihedral-angle differences from polytopal faces,[6] shows that the structure of IV is displaced only 5.5% from the trigonal bipyramid toward an idealized rectangular pyramid (RP).[7] For V, this structural displacement is 11.2% from the trigonal bipyramid.[7] As commented in the Introduction, IV and V are expected to be less distorted than related derivative I because of the presence of only one equatorial nitrogen atom. Although the appearance of these structures so close to the ideal trigonal-bipyramidal geometry is somewhat surprising, it is not without precedent. Recently, Wunderlich[24] reported that the derivative IX (R = H), containing like ring
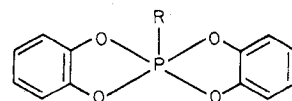

R = H, F, Cl, Ph, adamantyl, CH_3, OPh, *t*-Bu

IX

Table VI. Thermal Parameters in $(C_6H_4O_2)(C_7H_7NO)PH$, V^a

atom[b]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	2.75 (3)	2.92 (4)	3.51 (4)	0.07 (2)	0.25 (2)	−0.21 (3)
N	3.0 (1)	3.0 (1)	3.6 (1)	0.5 (1)	0.4 (1)	0.0 (1)
C	4.0 (1)	3.7 (2)	4.5 (2)	1.3 (1)	0.8 (1)	−0.1 (1)
O1	2.8 (1)	3.2 (1)	6.7 (1)	0.4 (1)	−0.5 (1)	−1.3 (1)
O2	3.3 (1)	3.6 (1)	4.1 (1)	−0.1 (1)	0.7 (1)	−1.0 (1)
O3	3.9 (1)	4.1 (1)	3.9 (1)	−0.7 (1)	1.2 (1)	−1.1 (1)
1C1	3.0 (1)	2.8 (1)	3.3 (1)	0.1 (1)	0.3 (1)	0.6 (1)
1C2	3.2 (1)	3.7 (1)	5.0 (2)	0.4 (1)	−0.2 (1)	0.8 (1)
1C3	3.7 (1)	4.4 (2)	5.7 (2)	−0.6 (1)	−1.3 (1)	0.7 (1)
1C4	4.5 (1)	3.7 (2)	5.3 (2)	−1.0 (1)	−0.5 (1)	−0.3 (1)
1C5	3.9 (1)	3.1 (1)	5.2 (2)	−0.2 (1)	0.3 (1)	−0.4 (1)
1C6	2.8 (1)	2.9 (1)	3.9 (1)	−0.1 (1)	0.3 (1)	0.2 (1)
2C1	2.8 (1)	3.3 (1)	3.2 (1)	0.1 (1)	−0.1 (1)	−0.3 (1)
2C2	3.1 (1)	4.8 (2)	3.3 (1)	−0.1 (1)	0.4 (1)	−0.1 (1)
2C3	3.9 (1)	4.7 (2)	4.2 (2)	−1.0 (1)	−0.1 (1)	1.0 (1)
2C4	4.2 (2)	3.4 (1)	5.2 (1)	−0.4 (1)	−0.6 (1)	0.0 (1)
2C5	3.8 (1)	3.6 (1)	4.1 (2)	0.3 (1)	0.0 (1)	−0.7 (1)
2C6	2.7 (1)	3.4 (1)	3.1 (1)	0.1 (1)	0.0 (1)	−0.1 (1)

a See footnote a to Table II. b Atoms labeled in agreement with Figure 3.

Table VII. Refined Parameters for Hydrogen Atoms in $(C_6H_4O_2)(C_7H_7NO)PH$, V^a

atom	10^3x	10^3y	10^3z	B_{iso}, $Å^2$
1H2	703 (4)	54 (2)	381 (5)	4 (1)
1H3	777 (4)	172 (2)	551 (5)	4 (1)
1H4	606 (4)	272 (2)	600 (5)	5 (1)
1H5	361 (3)	263 (2)	477 (5)	4 (1)
2H2	−96 (4)	−64 (2)	408 (4)	3 (1)
2H3	−167 (4)	−195 (2)	316 (5)	4 (1)
2H4	−60 (4)	−255 (2)	111 (5)	5 (1)
2H5	127 (4)	−188 (2)	−26 (5)	4 (1)
H1C	602 (5)	−26 (2)	156 (5)	5 (1)
H2C	458 (5)	−76 (3)	120 (6)	7 (1)
H3C	539 (4)	−67 (2)	310 (6)	5 (1)
H	203 (3)	95 (2)	33 (4)	3 (1)

a See footnotes to Table V.

Table VIII. Bond Lengths (Å) and Angles (deg) in $(C_6H_4O_2)(C_7H_7NO)PH$, V^a

Lengths

P–O3	1.721 (2)	2C3–2C4	1.376 (6)
P–O1	1.701 (3)	2C4–2C5	1.389 (5)
P–O2	1.638 (2)	2C5–2C6	1.377 (4)
P–N	1.670 (3)	2C6–2C1	1.377 (4)
P–H	1.36 (3)	N–C	1.476 (4)
O1–1C6	1.363 (4)	1C2–1H2	0.99 (3)
N–1C1	1.413 (4)	1C3–1H3	0.98 (3)
O3–2C6	1.361 (4)	1C4–1H4	0.98 (4)
O2–2C1	1.395 (4)	1C5–1H5	0.96 (3)
1C1–1C2	1.380 (4)	2C2–2H2	0.93 (3)
1C2–1C3	1.396 (4)	2C3–2H3	0.94 (3)
1C3–1C4	1.376 (5)	2C4–2H4	0.93 (4)
1C4–1C5	1.392 (5)	2C5–2H5	0.97 (4)
1C5–1C6	1.380 (5)	C–H1C	1.00 (4)
1C6–1C1	1.386 (4)	C–H2C	0.97 (5)
2C1–2C2	1.373 (4)	C–H3C	0.99 (4)
2C2–2C3	1.400 (5)		

Angles

O1–P–O3	177.4 (1)[b]	1C2–1C3–1C4	121.6 (4)
N–P–O2	123.7 (1)	1H3–1C3–1C4	118 (2)
O3–P–H	91 (1)	1C3–1C4–1H4	120 (2)
O1–P–H	88 (1)	1C3–1C4–1C5	120.7 (4)
O2–P–H	115 (1)	1H4–1C4–1C5	119 (2)
N–P–H	121 (1)	1C4–1C5–1H5	121 (2)
O2–P–O3	90.8 (1)	1C4–1C5–1C6	117.4 (3)
N–P–O1	90.0 (1)	1H5–1C5–1C6	122 (2)
N–P–O3	92.6 (1)	O1–1C6–1C5	125.7 (3)
O1–P–O2	87.6 (1)	O1–1C6–1C1	111.9 (3)
P–O1–1C6	114.0 (2)	1C5–1C6–1C1	122.4 (3)
P–O2–2C1	113.7 (2)	O2–2C1–2C2	125.6 (3)
P–O3–2C6	112.1 (2)	O2–2C1–2C6	111.4 (3)
P–N–1C1	113.9 (2)	2C2–2C1–2C6	123.0 (3)
P–N–C	128.8 (2)	2C1–2C2–2H2	122 (2)
1C1–N–C	117.1 (3)	2C1–2C2–2C3	116.1 (3)
N–C–H2C	112 (3)	2H2–2C2–2C3	122 (2)
N–C–H3C	109 (2)	2C2–2C3–2H3	120 (2)
N–C–H1C	110 (2)	2C2–2C3–2C4	121.3 (4)
H2C–C–H3C	115 (4)	2H3–2C3–2C4	119 (2)
H2C–C–H1C	105 (4)	2C3–2C4–2H4	117 (3)
H3C–C–H1C	106 (4)	2C3–2C4–2C5	121.4 (3)
N–1C1–1C2	129.8 (3)	2H4–2C4–2C5	122 (2)
N–1C1–1C6	110.2 (3)	2C4–2C5–2H5	122 (2)
1C2–1C1–1C6	120.1 (3)	2C4–2C5–2C6	117.5 (3)
1C1–1C2–1H2	118 (2)	2H5–2C5–2C6	120 (2)
1C1–1C2–1C3	117.9 (3)	O3–2C6–2C1	111.9 (3)
1H2–1C2–1C3	124 (2)	O3–2C6–2C5	127.5 (3)
1C2–1C3–1H3	120 (2)	2C1–2C6–2C5	120.6 (3)

a See footnotes to Table V. b The direction of bending of the axial oxygen atoms is away from the equatorial nitrogen atom along a projection in the equatorial plane which is 61.4° from the equatorial P–H bond.

atoms bonded to phosphorus, has a nearly ideal trigonal-bipyramidal structure (~1.7% displaced from the TP).[7] In comparison, structures of IX containing the other R ligands are highly displaced toward the rectangular pyramid, in the range 65–90%.[6,7] Thus, the proton poses a special case. The very modest distortions from a TP encountered with its presence as a ligand appear to be related to its unusually small size. Only when the larger R ligands are present does size appear to compete with ligand electronegativity, ring unsaturation, and the presence of dissimilar ring atoms bonded to phosphorus as factors controlling the structural displacement between the ideal TP and RP conformations.[7,10,25]

Taking the sum of these dihedral-angle differences from both the ideal TP and RP[6] and comparing them[7] show that the structures of IV and V are along the coordinate connecting these two idealized configurations. Further, the local C_{2v} constraint of the Berry coordinate is closely adhered to. This is apparent from the values of the dihedral angle between the least-squares planes 1 and 2 of Tables IX and X, 89.3° for IV and 89.9° for V compared to 90.0° required for C_{2v} symmetry.

The most significant angular distortions from an ideal trigonal bipyramid are those associated with the equatorial bonds. For IV, the relative magnitudes of these angles, O2–P–N = 124.7 (1)° > H–P–N = 122 (1)° > H–P–O2 = 113 (1)°, are consistent with expectations based on atom–atom sizes. The corresponding nonbonded distances between equatorial atoms are N---O2 = 2.926 (2) Å > H---N = 2.61 (2) Å > H---O2 = 2.48 (2) Å (Table XI). Entirely analogous values of these parameters are found for V. The values of the angles in this case are O2–P–N = 123.7 (1)° > H–P–N = 121 (1)° > H–P–O2 = 115 (1)°. Since intermolecular hy-

Table IX

Atom Distances from Least-Squares Planes (Å)
for (C₆H₄O₂)(C₆H₅NO)PH, IV[a]

	plane			
	1	2	3[b]	4[b]
P	−0.027	−0.003	0.000	0.000
O1		0.002	0.000	
O2	0.008			0.000
O3		0.002		0.000
N	0.009			0.000
H	0.010	0.000		

plane 5		plane 6		plane 7		plane 8	
1C1	−0.004	2C1	−0.011	1C1	−0.004	2C1	−0.013
1C2	0.003	2C2	0.011	1C2	−0.001	2C2	0.001
1C3	0.005	2C3	0.016	1C3	0.003	2C3	−0.001
1C4	−0.004	2C4	−0.011	1C4	−0.002	2C4	−0.008
1C5	−0.009	2C5	−0.014	1C5	−0.003	2C5	0.003
1C6	0.004	2C6	0.006	1C6	0.008	2C6	0.014
O1	−0.006	N	0.019				
O2	0.011	O3	−0.016				
		H1	0.051[c]				

Some Dihedral Angles between Least-Squares Planes (deg)

planes	angle	planes	angle
1, 2	89.3	3, 5	3.2
3, 4	55.3	4, 6	−3.7[d]

[a] Atoms labeled to agree with Figure 1. [b] These planes are not least-squares fitted since only three nonlinear points are required to define a plane. [c] Indicates atom was *not* included in the definition of a particular least-squares plane. [d] The negative value means that the benzo ring system shown on the left in Figure 1 is displaced away from the P–H bond.

Table X

Atom Distances from Least-Squares Planes (Å)
for (C₆H₄O₂)(C₇H₇NO)PH, V[a]

	plane			
	1	2	3[b]	4[b]
P	−0.028	−0.022	0.000	0.000
O1		0.013	0.000	
O2	0.009			0.000
O3		0.012		0.000
N	0.009		0.000	
H	0.009	−0.003		

plane 5		plane 6		plane 7		plane 8	
1C1	0.007	1C1	0.003	2C1	0.001	2C1	−0.016
1C2	−0.002	1C2	−0.011	2C2	−0.002	2C2	−0.009
1C3	−0.004	1C3	−0.009	2C3	−0.001	2C3	0.006
1C4	0.005	1C4	0.009	2C4	0.005	2C4	0.015
1C5	0.000	1C5	0.010	2C5	−0.006	2C5	−0.007
1C6	−0.006	1C6	−0.001	2C6	0.003	2C6	−0.012
		O1	0.015			O2	0.017
		N	−0.017			O3	0.007
		C	0.138[c]				

Some Dihedral Angles between Least-Squares Planes (deg)

planes	angle	planes	angle
1, 2	89.9	3, 6	−1.0[d]
3, 4	56.2	4, 8	−4.6[d]

[a] Atoms labeled to agree with Figure 3. [b-d] Footnotes to Table IX apply except d refers to Figure 3.

drogen bonding is not possible in the *N*-methyl compound V, the close similarity in the set of equatorial angles for these two derivatives suggests another cause.

With regard to the possibility of hydrogen bonding for IV, the nonlinear orientation of the N–H---O arrangement in the crystal (the N---O2″ distance is 3.31 Å and the N–H---O2″

**Table XI.** Selected Intramolecular Nonbonded Distances (Å)[a]

(C₆H₄O₂)(C₆H₅NO)PH		(C₆H₄O₂)(C₇H₇NO)PH	
O1–O3	3.437 (2)	O1–O3	3.421 (3)
O2–N	2.926 (2)	O2–N	2.917 (3)
O3–N	2.373 (2)	O1–N	2.383 (3)
O1–O2	2.410 (2)	O2–O3	2.393 (3)
O2–O3	2.346 (2)	O1–O2	2.312 (3)
N–O1	2.377 (2)	N–O3	2.452 (3)
H–O3	2.11 (2)	H–O1	2.14 (4)
H–O2	2.48 (2)	H–O2	2.53 (3)
H–O1	2.24 (2)	H–O3	2.21 (3)
H–N	2.61 (2)	H–N	2.64 (3)
H–2C6	3.42 (2)	H–1C1	3.41 (3)
H–2C1	3.17 (2)	H–1C6	3.18 (3)
H–1C6	3.26 (2)	H–2C1	3.33 (3)
H–1C1	3.15 (2)	H–2C6	3.19 (3)
		C–O3	2.736 (4)
		C–P	2.838 (4)
		C–1C1	2.465 (5)
		C–1C2	2.982 (5)

[a] Footnotes to Tables I and V apply.

angle is 162°) compares with an almost linear arrangement of these same atoms in spirophosphorane II which has a considerably shorter N–H---O distance, 3.05 Å.[3,4] It was argued that the latter hydrogen bonding was effective in widening the N_{eq}–P–N_{eq} angle in II.[3,4] In the present instance, a much weaker intermolecular hydrogen bond, if any, is indicated for IV and, as commented above, is apparently ineffectual in widening the N_{eq}–P–N_{eq} angle.

Superimposed on the steric atom sizes mentioned for the ordering of equatorial angles in IV and V is the operation of the likely effects of some degree of π p–d repulsion originating from back-donation of the lone pair on the nitrogen atom. This allows for the ordering of equatorial angles in opposition to that expected from bond electron-pair repulsions[26] based on purely electronegativity differences.

For V, the axial oxygen atoms are tilted slightly away from the equatorial nitrogen atom (O1–P–O3 = 177.4 (1)°). This direction of tilt reinforces an overriding steric effect due to the *N*-methyl group commented on later. In derivative IV, the axial oxygen atoms are tilted away from the equatorial proton in agreement with an enhanced P–H bond VSEPR attributable to the low electronegativity of the hydrogen atom. The same effect was found to hold for compound II.[3,4] The direction of tilting indicates in some measure that the concentration of π p–d bonding from nitrogen is in the equatorial plane in keeping with theoretical considerations[27] suggesting that this is the most effective orientation. Stronger evidence of the latter π orientation is found in the planar arrangement of the ligands attached to the nitrogen atom in each of the structures IV and V. A similar observation of planarity at nitrogen in compounds like X[28] indicates that the planarity is not a result of ring constraints but rather π p–d bonding.

X
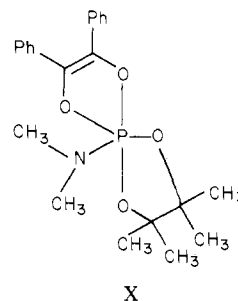
As observed with other spirophosphoranes lying close to an idealized trigonal bipyramid, the axial bonds are longer than

equatorial bonds to like atoms.[6,7] The axial P–O bond lengths in IV average 1.719 (2) Å compared to 1.648 (2) Å for the equatorial P–O bond. As usually found, the P–O bond lengths are longer than those in related saturated cyclic derivatives.[6] For example, in II,[3,4] III,[5] and X,[28] the average P–O axial length is 1.697 (5) Å. The greater value of axial P–O bond lengths in the unsaturated derivatives has been associated with inherent ring strain effects resulting from ring planarity constraints.[10] The high degree of planarity commonly found for the unsaturated rings bound to phosphorus produces an alternation in the ring bond lengths such that the nonphosphorus bond connected to the axial atom is shorter than the corresponding bond attached to the equatorial atom.[10] It is felt that σ and π bond electron density delocalization differences stemming from the differences in axial and equatorial bonding characteristics in the trigonal bipyramid represent the principal cause for the observed bond length variations.[10]

This variation is seen in Figures 2 and 4 for derivatives IV and V, respectively. The high degree of planarity of the "catechol" and "o-aminophenol" moieties in IV is apparent from the small average atom displacements determined for planes 5 and 6 of Table IX, 0.005 and 0.013 Å, respectively. Similarly, for V the atom displacements from these same planes average 0.009 and 0.011 Å, respectively (planes 6 and 8 of Table X).

A secondary effect of ring planarity in these phosphoranes[25,29] results in a compression of angles in the benzo unit at atom positions 1C2, 1C5, 2C2, and 2C5 below 120° relative to an expansion above 120° for atoms at other ring positions (cf. Figures 2 and 4).

A final feature worth noting is the longer P–N bond length in the N-methyl derivative V, 1.670 (3) Å, compared to a value for this same bond in IV of 1.655 (2) Å or an average P–N length of 1.654 (3) Å in I.[3] This may be attributed to a steric interaction involving the methyl group attached to the ring nitrogen atom. The nonbonded distance C–O3 = 2.736 (4) Å (Table XI) compares with a contact distance of about 3.5 Å.[30] Since the ligands attached to nitrogen form a planar arrangement, relaxation of the steric interactions through elongation of the P–N bond is likely.

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