

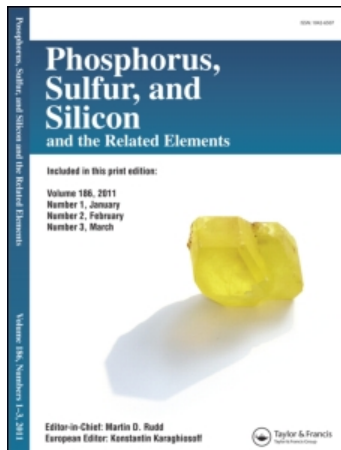
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THE FIRST P^v-P^v COMPOUND: BIS(CYCLENPHOSPHORANE), (C₈H₁₆N₄P)₂

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THE FIRST P^V-P^V COMPOUND:¹ BIS(CYCLENPHOSPHORANE), $(C_8H_{16}N_4P)_2$

JACK E. RICHMAN,* ROBERTA O. DAY, and ROBERT R. HOLMES*

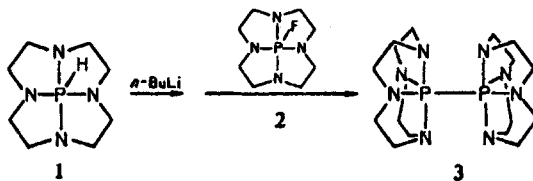
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(Received December 15, 1980)

Synthetic routes leading to the formation of the first P^V-P^V compound, bis(cyclenphosphorane) $(C_8H_{16}N_4P)_2$ (**3**), are described. The coupling reaction between the lithiated derivative of cyclenphosphorane (**1**) and cyclenfluorophosphorane (**2**) yields **3**. Bis(cyclenphosphorane) has also been detected as one of the products formed in the reaction of **1** and benzyl bromide. Single-crystal X-ray diffraction analysis shows that the macrocyclic nitrogen-containing ligands, $N_4(CH_2)_8$, are arranged around the phosphorus atoms, giving a pentacoordinate geometry displaced 33% from the idealized trigonal bipyramid toward the square pyramid. **3** crystallizes in the orthorhombic space group *Ccca*, with $a = 14.777$ (6) Å, $b = 14.549$ (6) Å, $c = 8.664$ (3) Å, and $Z = 4$. Data were collected with an automated Enraf-Nonius CAD 4 diffractometer, out to a maximum $2\theta_{MoK\alpha}$ of 55° . Full-matrix least-squares refinement techniques led to the final agreement factors of $R = 0.038$ and $R_w = 0.055$ based on the 850 reflections having $I \geq 2\sigma_I$. A P–P bond length of 2.264 (2) Å was obtained, indicating normal stability of the P^V-P^V bond. The two symmetry related halves of the molecule are rotated 70° relative to each other, presumably to minimize steric interactions. The P–P midpoint is on a crystallographic 222 site.

INTRODUCTION

The recent insertion of a phosphorus atom into macrocyclic polyamines² leading to tetraaminophosphoranes has provided a novel synthetic route to new classes of phosphorus compounds.³ In a preliminary report,⁴ we described a coupling reaction between the lithiated derivative of cyclenphosphorane (**1**) and cyclenfluorophosphorane (**2**) that resulted in the formation of the first P^V-P^V compound, bis(cyclenphosphorane) (**3**), $(C_8H_{16}N_4P)_2$. The proposed polycyclic structure of **3** was confirmed by X-ray analysis.⁴



In this paper we report details of this synthesis and an alternate route as well as the complete structural analysis of **3** resulting from a single-crystal X-ray diffraction study.

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EXPERIMENTAL

Synthesis. Bis(cyclenphosphorane) (3) from 2 and the Lithiated Derivative of 1. The lithiation of cyclenphosphorane (**1**) was accomplished by adding an equivalent (0.9 mL) of 1.6 M *n*-butyllithium in hexane to a slurry of 275 mg (1.37 mmol) of cyclenphosphorane^{3a} in 3 mL of anhydrous tetrahydrofuran stirred at -78°C . The mixture was warmed to 20°C , and 300 mg of crystalline cyclen fluorophosphorane² (**2**) was added followed by refluxing for 1 h. The mixture was concentrated under nitrogen and the residue sublimed in a bulb-to-bulb distillation apparatus, giving 150 mg (27% yield) of crystals of **3** collected at an oven temperature of 180 – 190°C (0.1 mm): mp (sealed capillary) 320 – 330° ; mass spectra M^{+} 398 (5.2), 39 (1.1), 219 (3.6), 218 (5.3), 217 (1.5), 201 (1.8), 200 (23.6), 199 (100), 198 (6.1), 197 (5.0); ^1H NMR (CDCl_3), 2.5–3.3 ppm (br symmetrical m); ^{31}P NMR (C_6D_6) -36.8 ppm (upfield from 85% H_3PO_4); IR (KBr) 2830 (br, s), 1459 (w), 1360 (w), 1342, 1334, 1244, 1232, 1201 (s), 1192 (s), 1130 (s), 1070 (s), 880, 865, 751, 676, 593, and 473 cm^{-1} (w); UV (cyclohexane) sh 225 (ϵ 2370), end absorbance. Anal. Calcd for $\text{C}_{16}\text{H}_{32}\text{N}_8\text{P}_2$: C, 48.23; H, 8.10; N, 28.13 Found: C, 48.48; H, 8.55, N, 28.65.

Bis(cyclenphosphorane) (3) from the Reaction of Benzyl Bromide with the Lithiated Derivative of 1. A solution of 2.0 g of **1**^{3a} in 30 mL of anhydrous tetrahydrofuran was lithiated as above (6.5 mL 1.6 M *n*-BuLi/ $-78 \rightarrow 0^{\circ}\text{C}$) and then was cooled to -78°C and treated dropwise with 1.2 mL of benzyl bromide. This mixture was stirred overnight at 25°C and then was refluxed for 2 h and concentrated. The residue was dissolved in hexane and filtered, and the solids were washed several times with hexane. The combined washes and filtrates were concentrated and distilled bulb-to-bulb. The first fraction collected at 80°C (0.1 mm) (3 h) (0.79 g) was shown by NMR to be 1,2-diphenylethane contaminated with 10–15% of recovered **1**. A second fraction collected at 100 – 105°C (0.1 mm) (1.0 g) was identified as the expected phosphorus benzylated product, cyclenbenzylphosphorane: mass spectrum m/e 290 (0.3%); ^1H NMR, 5.28 (d, 16, $J_{\text{PH}} = 11$ Hz), 3.1 (d, 2, $J_{\text{PH}} = 18$ Hz), and 7.2 (s, 5); and ^{13}C NMR 44.2 (NCH_2 , $J_{\text{PC}} = 8.8$ Hz), 42.3 (PCH_2 , $J_{\text{PC}} = 138.3$ Hz), and aryl ring carbons (J_{PC}) at 124.9 (4.4 Hz), 127.3 (3.0 Hz), 130.3 (5.9 Hz) and (weak?) 138 ppm. A third fraction in the bulb-to-bulb distillation at 120 – 180°C (0.1 mm) gave 10 mg of crystals shown by melting point and mass spectroscopy to be bis(cyclenphosphorane) (vide *supra*).

Space Group Determination and Data Collection for 3. A well-formed multifaceted crystal of **3**, which can be described as approximately spherical, with a diameter of 0.35 mm was mounted inside a thin-walled glass capillary tube which was sealed. Preliminary investigations using an Enraf-Nonius CAD4 automated diffractometer and graphite-monochromated Mo $K\alpha$ radiation (line focus tube, 40 kV, 26 mA, takeoff angle = 3.1° , $\lambda(K\alpha_1) = 0.70930\text{ \AA}$, $\lambda(K\alpha_2) = 0.71359\text{ \AA}$) indicated orthorhombic (*mmm*) symmetry. From the observed extinctions hkl ($h + k = 2n + 1$), $h0l$ ($l = 2n + 1$), $hk0$ ($h = 2n + 1$), and $0kl$ ($l = 2n + 1$), the space group was uniquely determined as *Ccca* (D_{2h}^{22} —No. 68).⁵ The lattice constants as determined by the least-squares refinement of the diffraction geometry for 25 reflections having $10.82^{\circ} \leq \theta_{\text{MoK}\alpha} \leq 14.50^{\circ}$ as measured at an ambient laboratory temperature of $22 \pm 2^{\circ}\text{C}$ are $a = 14.777$ (6) $\text{\AA}$, $b = 14.549$ (6) $\text{\AA}$, and $c = 8.664$ (3) $\text{\AA}$. A unit cell content of four molecules gives a calculated volume of $17.9\text{ \AA}^3$ per nonhydrogen atom, which is in the range to be expected for such compounds. Since the general equipoint for *Ccca* is 16, the assignment of $Z = 4$ implies one-fourth of a molecule per asymmetric unit, with the molecule conforming to 222 symmetry. The assignment of $Z = 4$ was confirmed by all subsequent stages of solution and refinement of the structure.

Data were collected on an Enraf-Nonius CAD4 diffractometer using the θ - 2θ scan mode with a θ scan range of $(0.65 + 0.35 \tan \theta)^{\circ}$ centered about the calculated Mo $K\alpha$ 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 0.74 to $4.00^{\circ}/\text{min}$, the rate to be used for each reflection having been determined by a prescan. The intensity, I , for each reflection is then given by $I = ((\text{FF})/S)(P - 2(B1 + B2))$ where P are the counts accumulated during the peak scan, $B1$ and $B2$ are the left and right background counts, S is an integer which is inversely proportional to the scan rate, 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 $\sigma_i^2 = ((\text{FF})^2/S^2)(P + 4(B1 + B2) + 0.002I^2)$. A total of 1074 independent reflections ($+h$, $+k$, $+l$) having $2^{\circ} \leq \theta_{\text{MoK}\alpha} \leq 55^{\circ}$ was measured. Five standard reflections monitored after every 12 000 s of X-ray exposure time gave no indication of crystal deterioration or loss of alignment. No corrections were made for absorption ($\mu_{\text{MoK}\alpha} = 0.258\text{ mm}^{-1}$), and the intensities were reduced to relative amplitudes by means of standard Lorentz and polarization corrections, including corrections for the monochromator.

Solution and Refinement of 3. Initial coordinates for the seven independent nonhydrogen atoms were determined by direct methods (MULTAN). Isotropic unit-weighted full-matrix least-squares refinement⁶

of the structural parameters for these atoms and a scale factor gave a conventional residual $R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$ of 0.114 and a weighted residual $R = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$ of 0.135 for the 483 independent reflections having $I \geq 3\sigma_I$ and $(\sin \theta)/\lambda \leq 0.52$. Anisotropic refinement then gave $R = 0.101$ and $R_w = 0.125$. A comparison of F_o 's with F_c 's at this point indicated that three very strong low-angle reflections were suffering from extinction, and these were excluded from subsequent refinement. Initial coordinates for the eight independent hydrogen atoms were then inferred from the required geometry of the molecule. Inclusion of the hydrogen atoms as isotropic scatterers in the unit-weighted refinement then gave $R = 0.039$ and $R_w = 0.042$ for the 494 reflections having $I \geq 2\sigma_I$ and $(\sin \theta)/\lambda \leq 0.52$. Subsequent refinement including the high-angle data and using variable weights ($w^{1/2} = 2F_o \sin \theta / \sigma_I$) led to the final values of $R = 0.038$, $R_w = 0.055$, and $\text{GOF}^7 = 1.656$ for the 850 reflections having $I \geq 2\sigma_I$. During the final cycle of refinement, the largest shift in any parameter was less than 0.01 times its estimated standard deviation. A final difference Fourier synthesis showed a maximum density of $0.262 \text{ e}/\text{\AA}^3$.

Computations were done on a CDC Cyber-175 computer using LINEX, a modification of the Busing and Levy full-matrix least-squares program (ORFLS), Johnson's thermal ellipsoid plot program (ORTEP), the Oak Ridge Fortran function and error program (ORFFE), Zalkin's Fourier program (FORDAP), and several locally written programs.

RESULTS AND DISCUSSION

Synthesis

The ready synthesis of bis(cyclenphosphorane) (**3**), the first example of the elusive class of compounds containing a bond between two pentacoordinate phosphorus atoms, demonstrates again^{3a} the stabilization of unusual valence states for phosphorus in cyclenphosphorane derivatives. The coupling of the lithiated derivative of cyclenphosphorane with the fluorophosphorane **2** might proceed by a straightforward nucleophilic substitution (i.e., addition of the tetracoordinate phosphorus anion to **2** to form a hexacoordinate phosphorus anion followed by loss of fluoride anion); however, see below.

In the closely related reaction of benzyl bromide with the lithiated derivative of cyclen, we have observed that traces of **3** and a moderate yield of 1,2-diphenylethane are formed in addition to the expected benzylphosphorane. The formation of **3** and 1,2-diphenylethane can be accounted for by a halogen-metal interchange mechanism, but we believe that an electron-transfer mechanism involving the cyclenphosphoranyl radical and benzyl radical intermediates is more likely. It is also likely an analogous electron-transfer mechanism operates in the coupling of lithiated cyclenphosphorane and the fluorophosphorane **2**. We are presently attempting to characterize the cyclenphosphoranyl radical, the expected intermediate in the electron-transfer reaction.

The thermal stability of **3** (mp 320–330°C under nitrogen) indicates normal stability for the P^V–P^V bond and suggests no special stability for the cyclenphosphoranyl radical. On the other hand, the P^V–P^V bond in **3** is quite easily oxidized as evidenced by the decomposition at ~180°C of crystals of **3** exposed to air. An oxide, C₁₆H₃₂N₈P₂O, has been identified in the decomposition products by mass spectroscopy. This oxide apparently is identical with the oxide obtained when the coupling of **1** and **2** is done without careful exclusion of water.⁸ The structure of this oxide (presumably the P–O–P compound) is presently under investigation.

The structure (vide infra) and thermal stability of **3** show that, contrary to previous expectations, the P^V–P^V bond shows quite normal stability, at least in the case of bis(cyclenphosphorane).

Structure

Atomic coordinates, thermal parameters, and refined hydrogen parameters for the bis(cyclenphosphorane) (**3**) are given in Tables I–III, respectively. Unique bond lengths and angles for nonhydrogen atoms are listed in Table IV. An ORTEP drawing in Figure 1 indicates the general geometrical configuration. The molecule has crystallographic 222 symmetry. Since the phosphorus atoms lie on a twofold axis, each half of each macrocycle will generate the other half. The highly symmetric nature of **3** is expressed in Figure 2 where a view down the aforementioned twofold axis is given. Each half of the dimer has approximate mm symmetry with the pseudo-mirror planes passing through the nitrogen atoms.

As expected,⁹ the P–N axial bond lengths (required by symmetry to be equal) of 1.782 (2) Å are longer than the P–N equatorial bond lengths of 1.694 (2) Å. The P–P bond length of 2.264 (2) Å is approximately twice the single-bond covalent radius of P (1.10 Å¹⁰).

Using the dihedral angle method¹¹ and unit bond lengths, we calculate, with respect to the geometry about phosphorus, that the structure is displaced 32.9% along the Berry coordinate¹² from the trigonal bipyramid to the square pyramid. If actual bond lengths are used, the displacement is 25.3%. The structural distortion from the idealized trigonal bipyramid is partially reflected in the values of the N–P–N axial and equatorial angles of 169.6 (1) and 131.1 (1)°, respectively.

Confirmation that the Berry coordinate is followed is obtained by noting that the value of the dihedral angle between the plane containing the two axial nitrogen

TABLE I
Atomic Coordinates in Crystalline (C₈H₁₆N₄P)₂ (**3**)^a

atom type ^b	coordinates		
	10 ⁴ x	10 ⁴ y	10 ⁴ z
P	766.0 (4)	2500 ^c	2500 ^c
N1	1240 (1)	3112 (1)	1047 (2)
N2	875 (1)	1505 (1)	1316 (2)
C1	1195 (2)	2713 (2)	−480 (3)
C2	1242 (2)	1672 (2)	−209 (3)
C3	1192 (2)	4100 (2)	1180 (3)
C4	1269 (2)	719 (2)	2097 (3)

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

TABLE II
Thermal Parameters in Crystalline (C₈H₁₆N₄P)₂ (**3**)^a

atom type ^b	anisotropic parameters					
	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
P	0.0288 (4)	0.0243 (4)	0.0249 (4)	0.000 ^d	0.000 ^d	−0.0004 (3)
N1	0.040 (1)	0.033 (1)	0.031 (1)	−0.002 (1)	0.008 (1)	0.001 (1)
N2	0.039 (1)	0.030 (1)	0.031 (1)	0.004 (1)	0.002 (1)	−0.005 (1)
C1	0.045 (1)	0.052 (2)	0.028 (1)	−0.005 (1)	0.007 (1)	0.002 (1)
C2	0.048 (1)	0.047 (1)	0.034 (1)	0.003 (1)	0.006 (1)	−0.010 (1)
C3	0.046 (1)	0.030 (1)	0.046 (1)	−0.007 (1)	0.006 (1)	0.006 (1)
C4	0.059 (1)	0.028 (1)	0.051 (2)	0.011 (1)	−0.003 (1)	−0.004 (1)

^a See footnote a to Table I. ^b See footnote b, Table I. ^c Anisotropic thermal parameters are of the form $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$. ^d Fixed.

TABLE III
Refined Parameters for Hydrogen Atoms in Crystalline
($C_8H_{16}N_4P_2$) (3)^a

atom type ^b	coordinates			B_{iso} , ^c Å ²
	10^3x	10^3y	10^3z	
H11	168 (2)	294 (2)	-107 (3)	2 (1)
H12	60 (2)	291 (2)	-106 (3)	2 (1)
H21	191 (2)	148 (2)	-30 (3)	3 (1)
H22	85 (2)	137 (2)	-100 (3)	1 (1)
H31	168 (2)	440 (2)	62 (3)	1 (1)
H32	64 (2)	432 (2)	80 (3)	1 (1)
H41	193 (2)	65 (2)	176 (3)	2 (1)
H42	95 (2)	18 (2)	174 (3)	2 (1)

^a See footnote *a*, Table I. ^b Hydrogen atoms are labeled according to the carbon atoms to which they are bonded, where H11 and H12 are bonded to C1, etc. ^c The isotropic thermal parameter. Refinement with isotropic thermal parameters for all hydrogen atoms fixed at 3.5 Å² resulted in no significant differences in any of the refined parameters.

TABLE IV
Unique Bond Lengths (Å) and Bond Angles (Deg) for
Nonhydrogen Atoms in ($C_8H_{16}N_4P_2$) (3)^a

Lengths			
P-P'	2.264 (2)	N2-C2	1.449 (3)
P-N1	1.694 (2)	N2-C4	1.451 (3)
P-N2	1.782 (2)	C1-C2	1.535 (4)
N1-C1	1.446 (3)	C3-C4'	1.520 (4)
N1-C3	1.443 (3)		
Angles			
P'-P-N1	114.4 (1)	N2-C2-C1	106.8 (2)
P'-P-N2	95.2 (1)	N2-C4-C3'	107.0 (2)
N1-P-N1'	131.1 (1)	P-N1-C1	116.7 (2)
N2-P-N2'	169.6 (1)	P-N1-C3	116.3 (1)
N1-P-N2	87.8 (1)	C1-N1-C3	118.1 (2)
N1-P-N2'	87.9 (1)	P-N2-C2	115.0 (2)
N1-C1-C2	104.7 (2)	P-N2-C4	114.1 (2)
N1-C3-C4'	104.3 (2)	C2-N2-C4	114.1 (2)

^a See footnote *a*, Table I. ^b Atoms are labeled to agree with Figure 1. Primed atoms are related to unprimed ones by symmetry.

atoms bonded to a given phosphorus atom and the remaining phosphorus atom and the plane similarly constructed from two equatorial nitrogen atoms and both phosphorus atoms is 90.0°. The atoms described in these planes are required by symmetry to be coplanar.

Presumably, so that steric effects could be minimized, the two halves of the dimer are not eclipsed but are staggered, the rotation between the two halves being 70.6°. This results in an $N_{ax}-N_{ax}$ separation of 3.301 (4) Å. If the configuration were eclipsed the $N_{ax}-N_{ax}$ distance would be 2.546 Å, which is considerably less than the van der Waals sum of 3.0 Å.¹³

Two structural features are worth noting, the nonplanar geometry about the

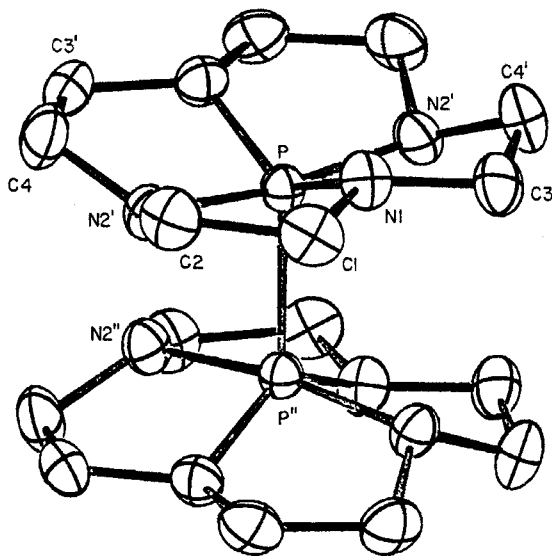


FIGURE 1 ORTEP plot of the $(C_8H_{16}N_4P)_2$ molecule (3) with thermal ellipsoids at the 50% probability level. Primed and double-primed labels represent atoms that are symmetry related to those comprising the asymmetric unit.

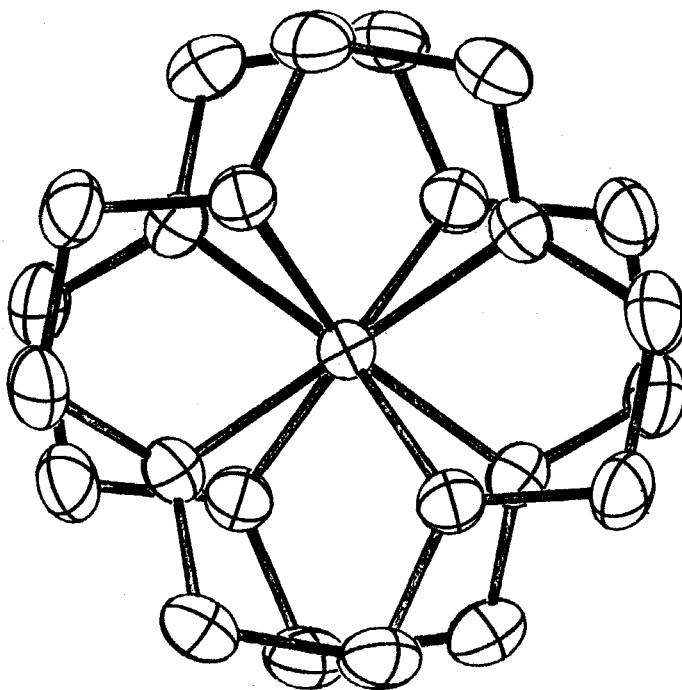


FIGURE 2 View of $(C_8H_{16}N_4P)_2$ (3) along the P-P bond axis showing the staggered configuration of the two macrocyclic ligands, $N_4(CH_2)_8$.

TABLE V
Atom Distances (Å) from Some Least-Squares Mean Planes for
($C_8H_{16}N_4P$)₂ (3)^{a,b}

	I		II		III		IV		V	
P	0.0	P	0.0	P	0.021	-0.013	(0.812)			
N1	0.0	N2	0.0	N1	0.172	0.009	0.0			
N1'	0.0	N2'	0.0	N2	0.003	0.017	(0.636)			
P''	0.0	P''	0.0	C1	-0.254	(-0.431)	0.0			
				C2	0.057	-0.013	0.0			
	VI		VII		VIII		IX		X	
P	-0.041	-0.004	(0.854)	N2	0.0	P	0.0			
N1	0.040	0.003	0.0	P	0.0	P''	0.0			
N2'	0.108	0.005	(0.700)	P''	0.0	N2''	0.0			
C3	-0.302	(-0.458)	0.0							
C4'	0.198	-0.004	0.0							
	XI		XII		XIII		XIV			
P	0.020	0.0	P	0.232	0.0					
N1	0.193	(0.263)	N2	-0.282	(-0.373)					
C1	-0.161	0.0	C2	-0.200	0.0					
C3	-0.052	0.0	C4	0.251	0.0					

^a Entries in parentheses are for atoms not included in the calculation of the plane. ^b Selected dihedral angles between the planes indicated: I and II = 90.0°, IV and V = 28.2°, VII and VIII = 30.3°, and IX and X = 70.6°. Atom designations are given here for planes I, II, IX, and X in order to define the dihedral angles.

nitrogen atoms and the puckering effects in the five-membered rings. The sum of the angles formed by atoms attached to the equatorial nitrogen atom N1 is 351.1°; the sum at the axial atom N2 is 343.2°. The greater planarity found for the equatorial nitrogen atoms is consistent with a larger degree of P–N π bonding expected¹⁴ for equatorial compared to axial nitrogen atoms. Earlier, it was found^{15,16} that cyclic pentacoordinated structures containing equatorial (CH_3)₂N groups adhered to strict planarity for the atoms bonded to nitrogen. However, the presence of ring constraints in **3** apparently restricts the atoms from achieving this configuration.

With regard to puckering in the five-membered rings (only two are unique due to symmetry), C1, attached to the equatorial nitrogen atom N1, is the flap atom projecting 0.431 Å from the plane of the remaining ring atoms P, N1, N2, C2 (plane IV, Table V) toward the other cyclen system containing P'' (Figure 1). The atom C3, also attached to N1, is the flap atom in the PN1C3C4'N2' ring and is similarly displaced (0.458 Å) (plane VII, Table V) toward P''. These puckering effects likely are a consequence of the greater pyramidal character of the axial nitrogen atoms compared to the equatorial nitrogens.

ACKNOWLEDGEMENT

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Registry No. **1**, 64317-97-1; **2**, 61754-87-8; **3**, 74385-57-2; benzyl bromide, 100-39-0; 1,2-diphenylethane, 103-29-7.

Supplementary Material Available: A compilation of observed and calculated structure factor amplitudes and a table of bond parameters involving hydrogen atoms for **3** (5 pages). Ordering information is given on any current masthead page.

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6. The function minimized was $\sum w(|F_o| - |F_c|)^2$. Mean atomic scattering factors were taken from ref 5, Vol. IV, 1974, pp 72–98. Real and imaginary dispersion corrections for P were taken from the same source, pp 149–150.
7. Goodness of fit = GOF = $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$, where N_o = the number of observations = 850, and N_v = the number of variables = 92.
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