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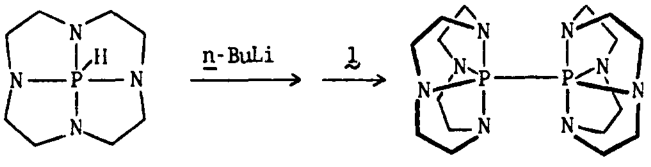
Synthesis and Structural Study of the First P(V)-P(V) Compound

Sir:

We report herein the synthesis and X-ray study of the first compound known to contain a P(V)-P(V) bond. Reaction of cyclen fluorophosphorane (**1**)[1,2] with the lithiated derivative of the related cyclen phosphorane (**2**)[3] resulted in the formation of the dicyclenphosphorane (**3**, $C_{16}H_{32}N_8P_2$) in 20-30% yield.[4]



2 3

The mass spectrum of **3** shows a molecular ion at *m/e* 398. The physical and spectroscopic properties of **3** are consistent with the polycyclic structure: mp >300 °C (sealed under N_2), sublimes at 150 °C (0.1 mm), soluble in warm hexane, ^{31}P chemical shift −36.8ppm (C_6D_6),[5] and a symmetrical AA′BB′ ^1H NMR spectrum. The structure was confirmed by single-crystal X-ray diffraction analysis of colorless crystals of **3** grown from warm hexane by cooling and slow evaporation at room temperature.

Crystal Data. $C_{16}H_{32}N_8P_2$, orthorhombic, space group *Ccca* ($D2h^{22}$-No. 68),[6] with a = 14.777 (6), b = 14.549 (6), c = 8.664 (3) Å; z = 4; 1074 independent reflections measured on an Enraf-Nonius CAD4 automated diffractometer, using graphite-monochromated Mo K$\bar{\alpha}$ radiation and the θ-2θ scan mode, out to a maximum $2\theta_{\mathrm{Mo}\ K\bar{\alpha}}$ of 55°. The structure was solved using direct methods (MULTAN). Full-matrix least-squares refinement[7] (anisotropic for nonhydrogen atoms, isotropic for hydrogen atoms) has led to a conventional unweighted residual $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.038 for the 850 reflections having $I \geq 2\sigma_I$.

The molecule has crystallographic 222 symmetry, with the two phosphorus atoms lying on a 2-fold axis parallel to $\bar{a}$. Each half of the dimer has approximate *mm* symmetry, with the psuedo-mirror planes passing through a pair of nitrogen atoms and intersecting at the phosphorus atom. The P-P bond length of 2.264 (2) Å is 0.06 Å longer than twice the single bond covalent radius of phosphorus.[8a] Crowding between halves of the dimer is mitigated by a rotation about the P-P bond of 70.6° away from an eclipsed configuration. The distance between eclipsed axial N atoms would be 2.546 (4) Å (0.5 Å less than the van der Waals sum)[8b] in the absence of such a rotation. In the actual structure this distance is 3.301 (4) Å, and the only close contacts between halves of the dimer involve H atoms. With respect to the geometry about phosphorus, the structure is displaced 32.9% along the Berry coordinate (unit vectors) from the trigonal bipyramid toward the rectangular pyramidal configuration.[9,10] In keeping with trigonal-bipyramidal geometry, the P-N_{ax} bond is 0.088 (4) Å longer than the P-N_{eq} bond. (See Figure 1 caption.)

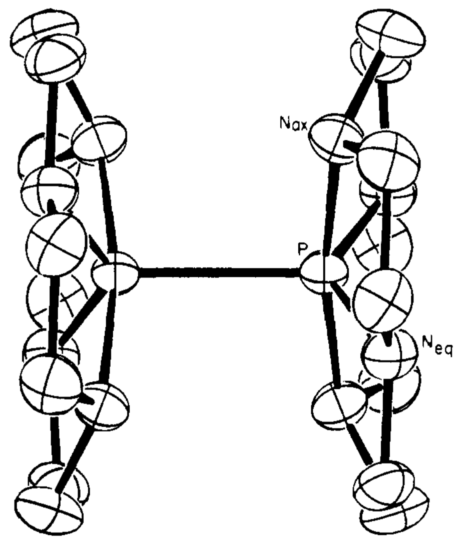


Figure 1. ORTEP plot of the cyclen phosphorane dimer viewed along the 2-fold axis parallel to $\bar{c}$, with thermal ellipsoids shown at the 50% probability level. Bond lengths: P-P = 2.264 (2), P-N_{ax} = 1.782 (2), P-N_{eq} = 1.694 (2) Å. Bond angles: N_{ax}-P-N_{ax} = 169.6 (1), N_{eq}-P-N_{eq} = 131.1 (1), N_{eq}-P-P = 114.4 (1), N_{ax}-P-P = 95.2 (1), N_{ax}-P-N_{eq} = 87.8 (1) and 87.9 (1)°.

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References and Notes

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(5) Positive shifts are downfield from the standard, 85% H_2PO_4.
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