

CRYSTAL STRUCTURE DETERMINATION OF THE 2,6-DIPHENYL-1,3,6,2-DIOXAZAPHOSPHOCANE-P-MONOBORANE ADDUCT. EVIDENCE FOR THE LACK OF TRANSANNULAR INTERACTION AND OBSERVATION OF A PHOSPHORUS<sup>IV</sup> ATOM DEFORMATION TOWARDS PSEUDOPENTACOORDINATION

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**Abstract** - The X-ray crystal structure of the title compound shows a crown conformation of the ring and a strong 1,3 diaxial interaction between the P-BH<sub>3</sub> group and the two corresponding hydrogens. This interaction leads an approach between the phosphorus and nitrogen. As a result the structure of phosphorus<sup>IV</sup> changes towards a pseudopentacoordinated geometry. The intracyclic Lewis interaction between N and P atoms is discarded due to the observed planarity of intracyclic anilic nitrogen.

Our interest in the relative reactivity of intracyclic phosphorus (III) and nitrogen atoms with borane lead us to synthetize a series of heterocyclic compounds owing to 1,3,6,2-dioxazaphosphocane derivatives.<sup>1-2</sup>

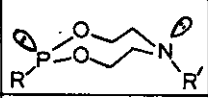
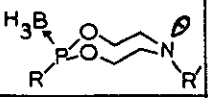
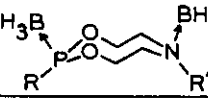
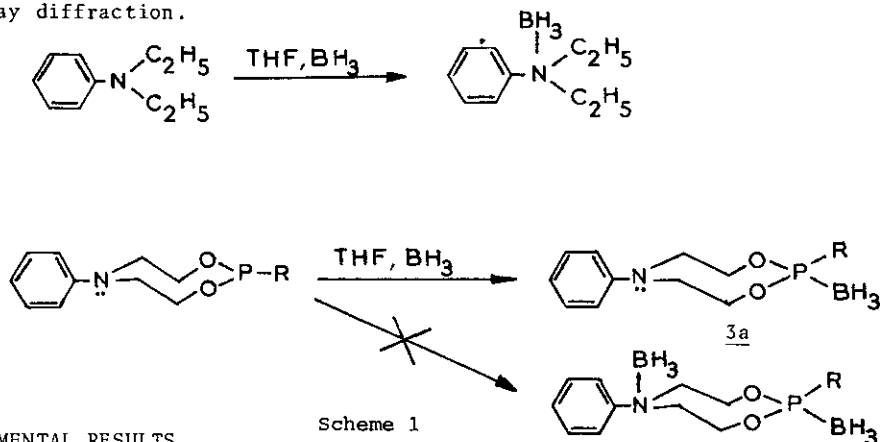
R	R'			
C <sub>6</sub> H <sub>5</sub>	H	<b>1</b>	—	<b>1b</b>
N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	<b>2</b>	<b>2a</b>	—
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	<b>3</b>	<b>3a</b>	—

Figure 1

We have shown that compound **1** reacts with two equivalents of BH<sub>3</sub> given (even with default of BH<sub>3</sub>) the double Lewis salt **1b**.<sup>1</sup> Dreiding models of **1** show a chair-chair conformation of the eight member ring, allowing the fixation of two BH<sub>3</sub> groups on the two basic sites of the molecule without strong steric hinderances.

Concerning compounds 2 and 3, the boration reaction takes place exclusively on the phosphorus atom giving the mono P-BH<sub>3</sub> adducts 2a and 3a.<sup>2</sup> The anilinic cyclic nitrogen does not present any affinity towards BH<sub>3</sub>.

Independently we have checked that the diethyl aniline reacts with BH<sub>3</sub> to give a very stable Lewis salt<sup>3</sup> (scheme 1). The last reaction shows that the low basicity of the intracyclic nitrogen is not responsible for its lack of reactivity in compounds 2 and 3. Two hypothesis were proposed<sup>2</sup> to explain this fact: a steric hinderance or a transannular interaction between nitrogen and phosphorus assisted by BH<sub>3</sub> coordination. In this aim we have determined the crystal structure of 3a by X-ray diffraction.



#### EXPERIMENTAL RESULTS

The synthesis of 3a has been previously described.<sup>2</sup> This compound crystallizes in the monocyclic system (P2<sub>1</sub>, a = 11.534(3), b = 6.492(1), c = 11.744(3) Å, β = 113.21(2)°) R = 0.039. The main atomic coordinates, bond lengths and angles are given in Tables 1, 2 and 3 respectively. Figure 2 shows PLUTO drawing of the molecule. A further detailed structure determination of 3a has been reported.<sup>4</sup>

Table 1. Atom Positional Parameters.  
(Fractional Coordinates x 10<sup>4</sup>) of the Main Atoms

	X/A	Y/B	Z/C		X/A	Y/B	Z/C
P(1)	1095(2)	0(0)	3370(2)	H(B4)	1228(79)	3597(168)	3303(80)
O(2)	842(6)	-1909(12)	2479(7)	H'(B4)	50(88)	2858(152)	1872(85)
O(3)	260(6)	-257(16)	4152(5)	H''(B4)	1829(83)	2273(147)	2306(77)
B(4)	1002(17)	2615(22)	2622(16)	H(C6)	-1272(8)	626(21)	4558(9)
N(5)	-1903(7)	-673(14)	1573(8)	H'(C6)	-1077(8)	1991(21)	3347(9)
C(6)	-1018(8)	495(21)	3769(9)	H(C7)	-2883(9)	-595(22)	2721(9)
C(7)	-1937(9)	-900(22)	2793(9)	H'(C7)	-1676(9)	-2459(22)	3112(9)
C(8)	-50(8)	-1901(22)	1207(9)	H(C8)	-44(8)	-407(22)	805(9)
C(9)	-1360(9)	-2322(18)	1115(11)	H'C(8)	222(8)	-3063(22)	701(9)
C(10)	2589(8)	-670(16)	4563(9)	H(C9)	-1322(9)	-3689(18)	1654(11)
C(16)	-2548(8)	935(17)	818(9)	H'(C9)	-1967(9)	-2598(18)	158(11)

Table 2. Main Bond Length and Interatomic Distances. (Å)

Bond Lengths			Atomic Distances		
O(2)-P(1)	1.573(0.005)	C(9)-N(5)	1.447(0.008)	P(1)-N(5)	3.293
O(3)-P(1)	1.579(0.004)	C(16)-N(5)	1.382(0.007)	B(4)-N(5)	3.748
B(4)-P(1)	1.895(0.008)	C(7)-C(6)	1.516(0.009)	H(B4)-N(5)	4.367
C(10)-P(1)	1.794(0.006)	C(9)-C(8)	1.497(0.009)	H'(B4)-N(5)	3.135
C(8)-O(2)	1.442(0.007)	H(B4)-B(4)	0.974(0.062)	H''(B4)-N(5)	4.473
C(6)-O(3)	1.446(0.007)	H'(B4)-B(4)	1.116(0.057)	C(6)-C(8)	3.919
C(7)-N(5)	1.455(0.007)	H''(B4)-B(4)	1.173(0.054)	C(7)-C(9)	2.492

Table 3. Main Bond and Dihedral Angles. (°)

Bond Angles		Dihedral Angles			
O(3)-P(1)-O(2)	107.9(0.3)	C(16)-N(5)-C(7)	119.4(0.5)	O(3)-C(6)-C(7)-N(5)	-74.9
B(4)-P(1)-O(2)	115.8(0.4)	C(16)-N(5)-C(9)	121.5(0.5)	O(2)-C(8)-C(9)-N(5)	69.8
B(4)-P(1)-O(3)	115.3(0.5)	C(7)-C(6)-O(3)	110.9(0.6)		
C(10)-P(1)-O(2)	101.4(0.3)	C(6)-C(7)-N(5)	113.5(0.5)		
C(10)-P(1)-O(3)	98.0(0.2)	C(9)-C(8)-O(2)	111.2(0.6)		
C(10)-P(1)-B(4)	116.1(0.4)	C(8)-C(9)-N(5)	114.2(0.5)		
C(8)-O(2)-P(1)	123.8(0.4)	H(B4)-B(4)-P(1)	104.9(3.6)		
C(6)-O(3)-P(1)	124.3(0.4)	H'(B4)-B(4)-P(1)	110.5(3.2)		
C(9)-N(5)-C(7)	118.3(0.6)	H''(B4)-B(4)-P(1)	94.2(3.0)		

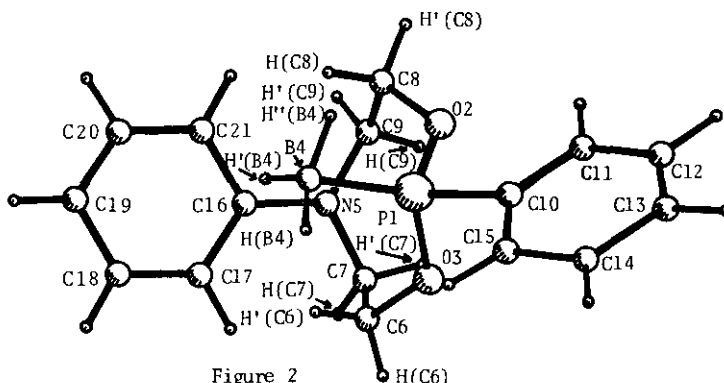


Figure 2

## DISCUSSION

The 1,3,6,2-dioxazaphosphocane **3a** adopts a crown conformation ( $C_2$  symmetry) which is the more stable conformation of cyclooctane.<sup>5</sup> The torsion angles around the two intracyclic carbon-carbon atoms O(3)-C(6)-C(7)-N(5) and O(2)-C(8)-C(9)-N(5) are respectively  $74.9^\circ$  and  $69.8^\circ$ . These two values are quite different from those calculated for crown conformation of cyclooctane.<sup>5</sup> (Minimum conformational energy:  $97^\circ$ ). Dreiding models show that the observed torsion angles can only be obtained to relieve the steric interactions of the hydrogen atoms H(C<sub>8</sub>) and H'(C<sub>6</sub>) (figure 2). These two atoms are in axial and *cis* position related to the BH<sub>3</sub> group which is itself also in axial position. Therefore, these three substituents [H(C<sub>8</sub>), H'(C<sub>6</sub>) and BH<sub>3</sub>] are between them in 1,3 diaxial interaction.

Another remarkable result is that the hydrogen H'(B4) atom bonded to the boron atom is directly oriented to the carbon C(16) atom of the phenyl group bonded

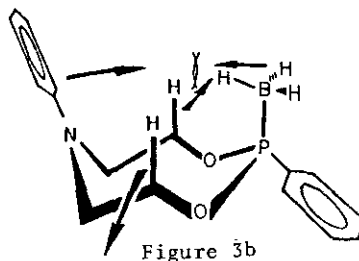
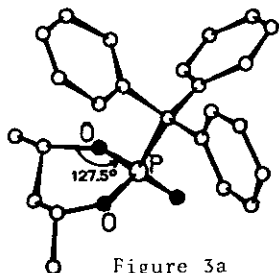
to nitrogen N(5) atom, this fact reflects the least hinderance position with respect to the axial atoms, (vide infra).

Distances between these different atoms are the following:

H'(B4)-C(16)	2.85 Å
H'(B4)-H'(C6)	2.45 Å
H'(B4)-H(C8)	2.17 Å
H'(C6)-H(C8)	~3.5 Å

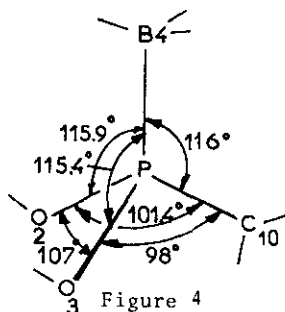
The three first distances are very short, as a result of a strong steric interaction between the two cis hydrogens H'(C<sub>6</sub>) and H(C<sub>8</sub>). The P-O bond lengths (1.573 and 1.579 Å) are found very close to those obtained from several 1,3,2-dioxaphosphorinanes<sup>6</sup> (P-O average value 1,565 Å). On the other hand the intracyclic C-O-P angle average value for the same compounds<sup>6</sup> (eight values) is significantly smaller than those obtained for compound 3a (vide supra). The literature average value<sup>6</sup> for angle C-O-P is 119.2°, while the average value for 3a is 126.55° [P(1)-O(2)-C(8) = 128.8°; P(1)-O(3)-C(6) = 124.3°].

On inspecting the extremely hindered cyclic phosphonate: cis -4,6-dimethyl-2-oxo-2-triphenylmethyl-1,3,2-dioxaphosphorinane a similar angle average value has been found<sup>7</sup> figure 3a. For this compound the strong steric interaction between the triphenylmethyl group (position 2) and the two axial methyl groups (position 4 and 6) flatten the cycle to the half chair conformation, energetically unfavorable. In this case the C-O-P angles showed an average value of 127.5°, similar to that found for 3a. This last point confirms the existence of strong 1,3 diaxial interactions discussed before. Dreiding models show that the main effect of these interactions is to put away the two cis hydrogens held by carbon atoms C(6) and C(8), this motion draws together the phosphorus and borane group towards the nitrogen and N-phenyl group, (see figure 3b). The distances H'(B4)-C(16); H'(B4)-N(5) and P(1)-N(5) are respectively 2.85, 3.13 and 3.29 Å.

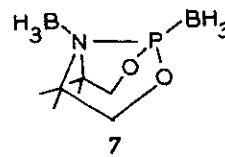
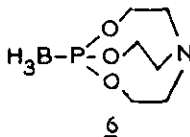
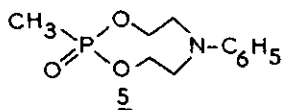


This approach yields a new interaction between the BH<sub>3</sub> and phenyl groups which

induce a strong deformation of the angles around phosphorus atom, (figure 4).



It is clear that the two angles  $O(2)-P(1)-B(4)$  and  $O(3)-P(1)-B(4)$  are widely open:  $115.4^\circ$  and  $115.9^\circ$  respectively, whereas the  $C(10)-P(1)-O(2)$  and  $C(10)-P(1)-O(3)$  are relatively closed:  $101.4^\circ$  and  $98.0^\circ$  respectively. It is possible to calculate the deformation of the tetrahedral geometry of the phosphorus atom towards a trigonal bipyramid assuming that the steric hinderance, shown in figure 4, plays the role of an entering group perpendicularly to the  $B(4)-O(2)-O(3)$  plane. This deformation can be calculated knowing that i) the sum of the three angles defined by the three equatorial bonds in a trigonal bipyramid are  $360^\circ$ , ii) the sum of the three equivalent angles in tetrahedric geometry is  $327^\circ$ , iii) the sum of the three equivalent angles in structure 3a is  $338.3^\circ$ . According to that, the deformation is 33% from the tetrahedric geometry towards the pseudopentacoordination. This relatively large value could lead to a misleading interpretation like a transannular Lewis interaction. A few models, carrying a tetrahedric phosphorus which X-ray structure are known, have been reported for compound 5<sup>8</sup> and compound 6<sup>9</sup>, for which the transannular P-N distances are 3.22 and 3.098 Å respectively. The distance between  $P(1)-N(5)$  in the case of 3a is 3.24 Å. These three distance values are smaller than the sum of the Van der Waals radii (3.4 Å), which is obviously larger than a P-N axial bond in a pentacoordinated molecule<sup>10</sup> (1.75 Å) or a P-N bond in a bis (borane) amino phosphorane adduct<sup>11</sup> 7 (1.757 Å).



Other interesting features are the planarity of the anilinic nitrogen atom  $N(5)$  and the very short distance (1.38 Å) found between this N atom and the  $C(16)$  aromatic carbon compared to  $C(7)-N(5)$ : 1.455 and  $C(9)-N(5)$ : 1.447 Å respectively.

This fact indicates a  $sp_2$  hybridization of the N(5) atom and a strong conjugation between the p orbital of this atom and  $\pi$  system of the phenyl group bonded to it. This allows us to deduce that the N(5) atom must have a very low basicity and in these conditions the Lewis transannular interaction is unlikely.

A last remarkable feature of structure 3a is the value of C-O-P angles, P(1)-O(3)-C(6) and P(1)-O(2)-C(8):  $124.3^\circ$  and  $128.3^\circ$  respectively, which let us to assume a  $sp_2$  hybridization of the two oxygen bonded to phosphorus and consequently a retro co-ordination  $p\pi-d\pi$  from oxygen to phosphorus. This bonding can be evidenced considering the P-B lengths of Lewis salts between three coordinated phosphorus and  $BH_3$  (table 4).

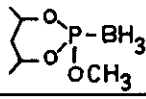
Ref.11	$F_3P-BH_3$	$(H_2N)P-BH_3$		$(CH_3)_3P-BH_3$	$(C_6H_5)_3P-BH_3$	$H_3P-BH_3$
P-B (Å)	1.836	1.887	1.88	1.93		

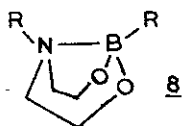
Table 4

The P-B bond length is inversely related to the  $\pi$  donor character of phosphorus, so this length allow us to detect the retro co-ordination  $p\pi-d\pi$  from oxygen to phosphorus.

Two important conclusions are obtained from this work:

A Explanation of the lack of reactivity of intracyclic nitrogen atom with a borane molecule.

The intracyclic Lewis interaction in eight membered ring has been well demonstrated in the case of compound 8.<sup>13</sup> According to that, we had been assumed<sup>2</sup> that this kind of interaction would exist in the case of compound 3a based on the lack of reactivity of nitrogen with borane, (scheme 1).



The X-ray crystal structure allow to discarded the last idea showing that the second entering molecule of borane would be strongly hindered approaching by the internal side of the ring, the only possibility is by the external side. In this case the nitrogen would move to the  $sp_3$  tetrahedral geometry. The observation of this change in the Dreiding models indicates that the phenyl group would approach closer to borane. This motion seems to be unlikely according to steric effects and accounts to the lack of reactivity pointed out before.

B Absence of interaction between intracyclic P and N atoms.

The points which have been discussed:

- a) 1,3 Steric interaction between axial hydrogens and BH<sub>3</sub> group.
- b) Weak basicity of the nitrogen.
- c) Weaker acidity of phosphorus by oxygen conjugation.
- d) Distances between P-N atom.

Allow us to conclude the absence of Lewis transannular interaction between P and N. The approach of this two atoms is only due to a steric interaction between the substituents in the cycle. This is also in agreement with some published results related to the hydrolysis of cyclic phosphates for which the role played by a transannular nucleophilic catalysis remains very poor.<sup>12</sup>

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