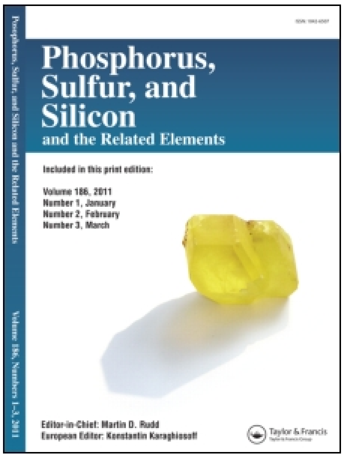


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STRUCTURAL EVALUATION OF A DIBENZOBICYCLIC PHOSPHORANE. ANOTHER EXAMPLE OF A BERRY EXCHANGE COORDINATE

Rosalinda Contreras[a]; Apolonia Murillo[a]; Pedro Joseph-nathan[a]
[a] Departmento de Química., Centro de Investigación y de Estudios Avanzados del I. P. N., México D.F., México

To cite this Article Contreras, Rosalinda , Murillo, Apolonia and Joseph-nathan, Pedro(1990) 'STRUCTURAL EVALUATION OF A DIBENZOBICYCLIC PHOSPHORANE. ANOTHER EXAMPLE OF A BERRY EXCHANGE COORDINATE', Phosphorus, Sulfur, and Silicon and the Related Elements, 47: 1, 215 — 224

To link to this Article: DOI: 10.1080/10426509008046863

URL: http://dx.doi.org/10.1080/10426509008046863

Phosphorus, Sulfur, and Silicon, 1990, Vol. 47, pp. 215–224
Reprints available directly from the publisher
Photocopying permitted by license only

STRUCTURAL EVALUATION OF A DIBENZOBICYCLIC PHOSPHORANE. ANOTHER EXAMPLE OF A BERRY EXCHANGE COORDINATE

ROSALINDA CONTRERAS,† APOLONIA MURILLO and PEDRO JOSEPH-NATHAN

Departmento de Química. Centro de Investigación y de Estudios Avanzados del I.P.N., Apartado Postal 14–740, 07000-México, D.F. México

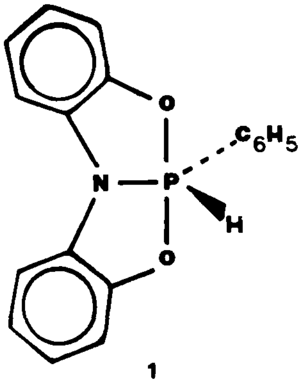
(Received February 24, 1989; in final form April 20, 1989)

The single crystal X-ray diffraction study and the structural evaluation of 1-phenyl-5-aza-2,8-dioxa-1-phospha(V)-dibenzo[c,f]bicyclo[3,3,0]octane, **1** show that the compound lies on the Berry coordinate approximately 50% between a trigonal bipyramid with the oxygen atoms in axial positions and a rectangular pyramid.

Key words: X-ray-diffraction; dibenzobicyclic-phosphorane; Berry exchange-coordinate.

INTRODUCTION

We recently reported the synthesis and reactivity of the dibenzobicyclic phosphorane **1** of unusual high chemical stability.[1] Its stability is attributable to a very rigid and planar structure, and therefore it was of interest to perform a single crystal X-ray diffraction study. Some studied heterocyclic phosphoranes show a geometry that bears some degrees of distortion between structures close in energy like the trigonal bipyramid (TBP), and the square (SP) or rectangular pyramid (RP).[2,3] It has been shown that the distorsion in each case can be understood in terms of low angle bending force constants associated with the Berry coordinate[4] governing intramolecular ligand exchange,[5,6] Figure 1.



1

---

† Author to whom correspondence should be addressed.

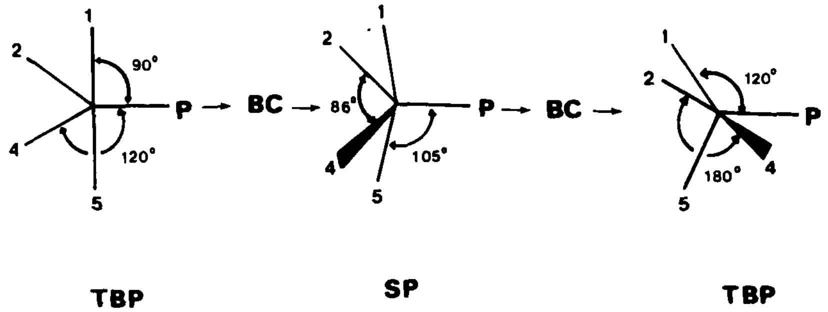


FIGURE 1 Intramolecular ligand exchange between two trigonal bipyramids TBP passing through a square pyramid SP and the Berry coordinate BC.

The structural shape at specific points along the coordinate is determined by the ligand construction which influences the energy difference between the idealized TBP, SP, or RP framework,[2] Figure 2.

It seems that on going along the Berry coordiante from a TBP arrangement to the SP shape, there appears to be a correlation between the electronegativity of substituents and the ring structure of phosphoranes, and also with the decreasing electronegativity of the atom regarded as the pivotal ligand (p in Figure 1) which connects the idealized TBP and SP for each structure.[2] Therefore, it is of interest to evaluate and to correlate the distribution of bonds around the phosphorus atom in a dibenzobicyclic phosphorane like **1** bearing a cyclic and planar framework possessing atoms of different electronegativity attached to phosphorus.

Furthermore, the dibenzobicyclic ring could be considered as an analogue of the very interesting planar unsaturated bicyclic phosphine **2**[7] that differs from aliphatic systems of pyramidal geometry,[8] compound **3**, Figure 3. Also, compound **1** is a pseudo-tautomer of a phenyl boronate **4** recently reported by us,[9] Figure 4. Both compounds have a similar framework, but differ in the nature of the central atom and the position of the hydrogen. Therefore comparison of the structures of all mentioned compounds with **1** is of interest.

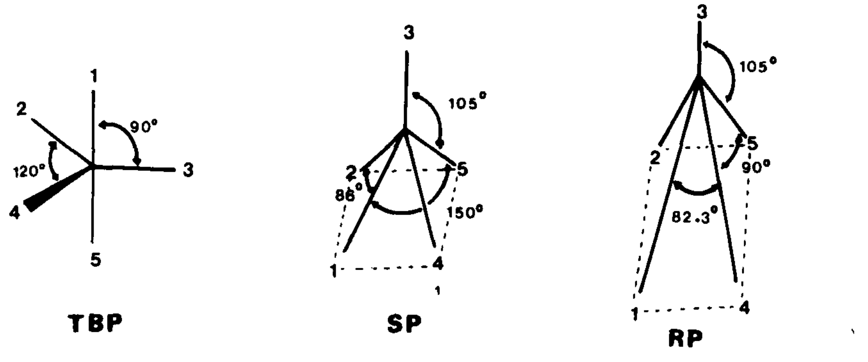
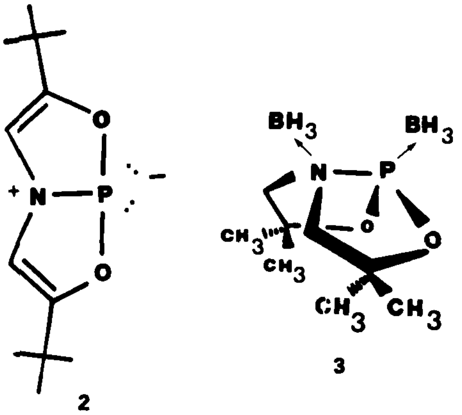


FIGURE 2 Idealized geometries and angles of trigonal bipyramid TBP, square pyramid SP and rectangular pyramid RP of pentacoordinated phosphorus atom.



2

3

FIGURE 3 Examples of a planar and a bent phosphane.

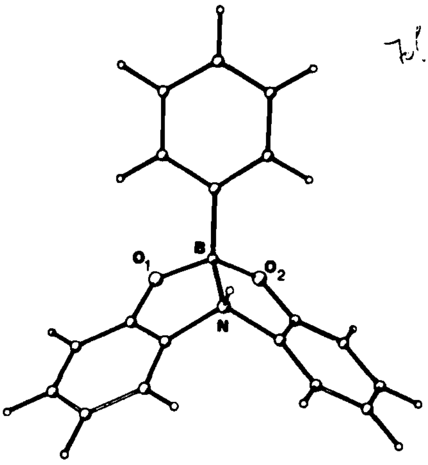


FIGURE 4 X-ray diffraction structure of compound 4, bent tautomer of phosphorane 1.

RESULTS AND DISCUSSION

The structure determination of 1 by single crystal X-ray diffraction was done using a Nicolet R3m four-circle automatic system using CuKα radiation and the programs provided by the manufacturer. The data (Tables I–III, Figures 5–6) show that two molecules of 1 crystallize with one molecule of benzene. Using the dihedral angle method shows that the geometry in terms of dihedral angles is closer to the RP than the SP: C–RP = 132.9 versus C–SP = 133.1. Or using unit vectors: C–RP = 122.0 versus C–SP 122.2. And that the percent displacement from the TBP towards the RP is 38.9% using dihedral angles or 43.9% using unit vectors.[2] Pertinent structural features which allow this conclusion are seen from the data in Table IV which compare the experimental angles at the phosphorus

TABLE I

Crystal data, collection and refinement parameters for 1-phenyl-5-aza-2,8-dioxa-1-phospha(V)-dibenzo[c,f]bicyclo[3,3,0]octane with one half a molecule of benzene of crystallization

A. Crystal parameters	
chemical formula	$C_{18}H_{14}O_2N_1P_1 \cdot C_3H_3$
molecular weight	346.338
crystal system	monoclinic
space group	$P2_1/a$
crystal size, mm	0.5 × 0.4 × 0.1
crystal color	rose
cell constants	
a, Å	13.8323(58)
b, Å	9.7127(46)
c, Å	14.2297(44)
α, deg	90.000(00)
β, deg	112.882(29)
γ, deg	90.000(00)
cell volume, Å3	1761.30(127)
ρ(calc), g/cm^3	1.16
Z	4
F(000), e^-	640
B. Data collection parameters	
μ, cm^{-1}	14.2
scan width, below $K_{\alpha 1}$, above $K_{\alpha 2}$, deg	1.0, 1.2
2θ limits, deg	3.0°–110.0°
scan speed (variable), deg min^{-1}	(4.0, 29.3)
exposure time, h	54.53
total no. reflections collected	2500
no. unique reflections	1887
C. Structure refinement	
reflections for final refinement	1869
parameters refined	236
R(F), %	5.65
R(W), %	6.31
goodness of fit for the last cycle	1.055

atom with those of idealized TP, SP and RP geometries. Turnstile (TR) geometry is discarded because it is not compatible with the data.

An evaluation of the data shows that the oxygen atoms occupy the axial positions because the O^1–P–O^2 angle has the largest value. In addition the O–P–O angle is close some 14° in relation to the idealized TBP arrangement while the N–P–H angle is open the same 14°. There are four small angles O^2–P–N; O^2–P–H; O^1–P–N and O^1P–H that are the smallest angles in RP. As a consequence the phenyl group can be considered as the pivot. Also, it is interesting to note that the nitrogen atom is completely planar as is shown by the sum of their angles C–N–C; C–N–P and C–N–P = 359.6°. The sp^2 structure of the nitrogen provides evidence about the electron delocalization in the ligand. The planar nature of the nitrogen explains the very low reactivity of compound **1**[1] compared with its aliphatic analogue **5**[10,12] since protonation of the nitrogen is a requirement for tautomerization (Figure 7). It is noteworthy to compare the data with the X-ray parameters of the two reported compounds **6**[13] and **7**,[14] which present the same framework, Table V. Both compounds have a Berry coordinate structure.

TABLE II

Atom coordinates ($\times 10^4$) and temperature factors (Å$^2 \times 10^3$) for 1-phenyl-5-aza-2,8-dioxa-1-phospha(V)-dibenzo[c,f]bicyclo-[3,3,0]octane with one half a molecule of benzene of crystallization

Atom	x	y	z	U_{eq}
P	6515(1)	4524(1)	1672(1)	49(1)[a]
N	5302(2)	3943(3)	1555(2)	46(1)[a]
O(1)	6955(2)	2855(2)	1941(2)	53(1)[a]
O(2)	5919(2)	6026(2)	1108(2)	58(1)[a]
C(3)	6246(2)	1969(3)	2072(2)	47(1)[a]
C(4)	5270(2)	2563(3)	1851(2)	45(1)[a]
C(5)	4469(3)	1789(4)	1935(3)	58(1)[a]
C(6)	4687(3)	422(4)	2273(3)	65(2)[a]
C(7)	5657(3)	−151(4)	2491(3)	62(2)[a]
C(8)	6474(3)	622(3)	2407(3)	53(1)[a]
C(9)	4908(3)	6158(3)	1025(2)	52(1)[a]
C(10)	4509(2)	4953(3)	1280(2)	47(1)[a]
C(11)	3481(3)	4916(4)	1210(3)	57(1)[a]
C(12)	2866(3)	6100(4)	897(3)	70(2)[a]
C(13)	3270(3)	7290(4)	656(3)	71(2)[a]
C(14)	4298(3)	7346(4)	709(3)	67(2)[a]
C(15)	7300(2)	5229(3)	2914(2)	50(1)[a]
C(16)	7726(3)	4386(4)	3767(3)	70(2)[a]
C(17)	8339(4)	4933(5)	4708(3)	89(2)[a]
C(18)	8538(3)	6315(4)	4828(3)	82(2)[a]
C(19)	8130(3)	7164(4)	3996(3)	82(2)[a]
C(20)	7502(3)	6639(3)	3039(3)	64(2)[a]
C(21)	4458(3)	4098(5)	4239(4)	95(2)[a]
C(22)	5172(4)	4979(6)	4130(3)	100(2)[a]
C(23)	5721(4)	5867(5)	4881(4)	95(2)[a]
H(1)	7066(21)	4549(26)	1014(19)	42(7)
H(5)	3691	2227	1746	71(5)
H(6)	4071	−197	2362	71(5)
H(7)	5794	−1223	2734	71(5)
H(8)	7253	185	2596	71(5)
H(11)	3159	3980	1396	73(5)
H(12)	2057	6088	840	73(5)
H(13)	2775	8202	420	73(5)
H(14)	4613	8281	512	73(5)
H(16)	7572	3283	3681	114(6)
H(17)	8668	4254	5366	114(6)
H(18)	9021	6739	5573	114(6)
H(19)	8285	8268	4082	114(6)
H(20)	7172	7317	2381	114(6)
H(21)	4033	3375	3633	167(12)
H(22)	5306	4968	3424	167(12)
H(23)	6302	6549	4786	167(12)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Compound **6** has a wide O-P-O angle and the oxygen atoms are in axial positions. The pivot is the P—C bond. In compound **7** an interesting situation arises because of the impossibility to have a five membered ring by using two equatorial bonds. This situation constrains the nitrogen atom which is less electronegative than an oxygen, to occupy an axial position. Therefore, the molecule adopts a

TABLE III

Bond lengths (Å) and angles (deg.) for 1-phenyl-5-aza-2,8-dioxa-1-phospha(V)-dibenzo[c,f]bicyclo[3,3,0]octane with one half a molecule of benzene of crystallization

P-H(1)	1.419(33)	P-N	1.715(3)
P-O(1)	1.722(2)	P-O(2)	1.714(2)
P-C(15)	1.811(3)	N-C(4)	1.411(4)
N-C(10)	1.409(4)	O(1)-C(3)	1.371(4)
O(2)-C(9)	1.364(4)	C(3)-C(4)	1.388(4)
C(3)-C(8)	1.386(4)	C(4)-C(5)	1.381(5)
C(5)-C(6)	1.404(5)	C(6)-C(7)	1.372(5)
C(7)-C(8)	1.400(5)	C(9)-C(10)	1.401(5)
C(9)-C(14)	1.396(5)	C(10)-C(11)	1.385(5)
C(11)-C(12)	1.397(5)	C(12)-C(13)	1.384(6)
C(13)-C(14)	1.396(6)	C(15)-C(16)	1.391(5)
C(15)-C(20)	1.395(5)	C(16)-C(17)	1.382(5)
C(17)-C(18)	1.368(6)	C(18)-C(19)	1.372(6)
C(19)-C(20)	1.396(5)	C(21)-C(22)	1.361(8)
C(21)-C(23†)	1.367(8)	C(22)-C(23)	1.353(7)
C(23)-C(21†)	1.367(8)		
N-P-H(1)	134.2(9)	O(1)-P-H(1)	85.9(10)
O(2)-P-H(1)	87.7(10)	C(15)-P-H(1)	111.4(9)
N-P-O(1)	87.7(1)	N-P-O(2)	87.8(1)
O(1)-P-O(2)	165.9(1)	N-P-C(15)	114.3(2)
O(1)-P-C(15)	96.5(1)	O(2)-P-C(15)	97.5(1)
P-N-C(4)	115.3(2)	P-N-C(10)	115.1(2)
C(4)-N-C(10)	129.2(3)	P-O(1)-C(3)	114.3(2)
P-O(2)-C(9)	114.2(2)	O(1)-C(3)-C(4)	113.2(3)
O(1)-C(3)-C(8)	124.0(3)	C(4)-C(3)-C(8)	122.8(3)
N-C(4)-C(3)	108.7(3)	N-C(4)-C(5)	131.5(3)
C(3)-C(4)-C(5)	119.7(3)	C(4)-C(5)-C(6)	118.2(3)
C(5)-C(6)-C(7)	121.4(4)	C(6)-C(7)-C(8)	120.9(3)
C(3)-C(8)-C(7)	116.9(3)	O(2)-C(9)-C(10)	113.2(3)
O(2)-C(9)-C(14)	125.2(3)	C(10)-C(9)-C(14)	121.6(3)
N-C(10)-C(9)	108.1(3)	N-C(10)-C(11)	131.9(3)
C(9)-C(10)-C(11)	120.0(3)	C(10)-C(11)-C(12)	118.9(4)
C(11)-C(12)-C(13)	120.8(4)	C(12)-C(13)-C(14)	121.4(4)
C(9)-C(14)-C(13)	117.4(3)	P-C(15)-C(16)	121.2(2)
P-C(15)-C(20)	120.7(2)	C(16)-C(15)-C(20)	118.1(3)
C(15)-C(16)-C(17)	120.7(3)	C(16)-C(17)-C(18)	121.1(4)
C(17)-C(18)-C(19)	119.2(4)	C(18)-C(19)-C(20)	120.8(4)
C(15)-C(20)-C(19)	120.1(3)	C(22)-C(21)-C(23†)	119.1(4)
C(21)-C(22)-C(23)	121.3(5)	C(22)-C(23)-C(21†)	119.6(5)

† Symmetry related atom.

transversal position of the bicyclic framework, compared with those of compounds **1** and **6**, in this case the pivot being the oxygen atom O^4. Comparison between molecules, **1**, **6** and **7** shows that distorsion is independent of the electronegativity of the atoms bonded to the phosphorus atom, also from the position of the bicyclic ring system, and from the presence of another ring. Moreover, the unsaturated planar structure of the bicycle is not enough to prevent a deformation of the molecule, this showing that the Berry coordinate must be a stable structure for bicyclic pentacoordinated phosphorus molecules.

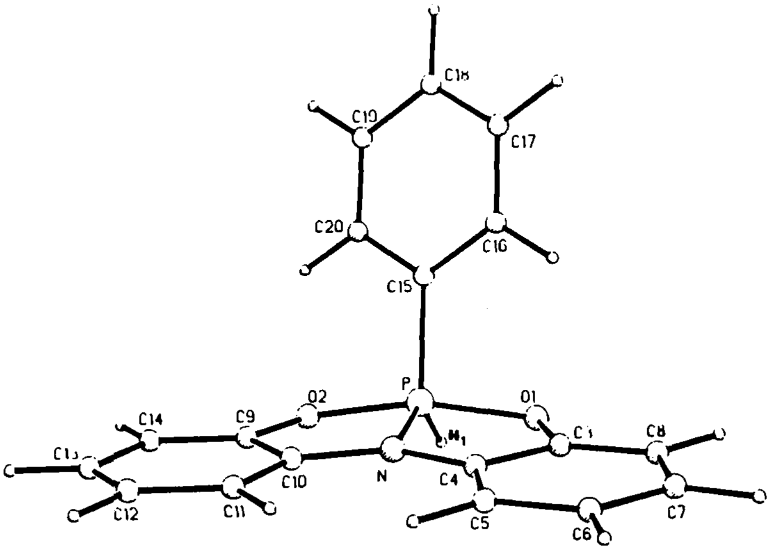


FIGURE 5 Single crystal X-ray diffraction structure of **1**. The non-bonded H_5/H_{11} distance is 1.84 Å.

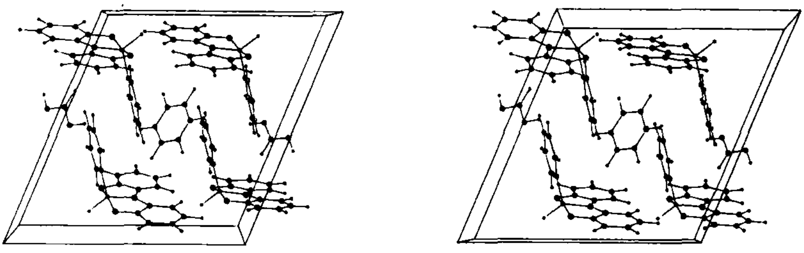


FIGURE 6 Stereoview of the unit cell of compound **1**.

TABLE IV

Comparison phosphorus angles of compound **1** with the angles of idealized TBP, SP and RP geometries

	Compound 1	TBP	SP	RP
O^1-P-O^2	165.9	180	150	150
N-P-H	134.2	120	150	150
N-P-C	114.3	120	105	105
C-P-H	111.4	120	105	105
O^2-P-C	97.5	90	105	105
O^1-P-C	96.5	90	105	105
O^2-P-N	87.8	90	86	90
O^2-P-H	87.7	90	86	90
O^1-P-N	87.7	90	86	82.3
O^1-P-H	85.9	90	86	82.3

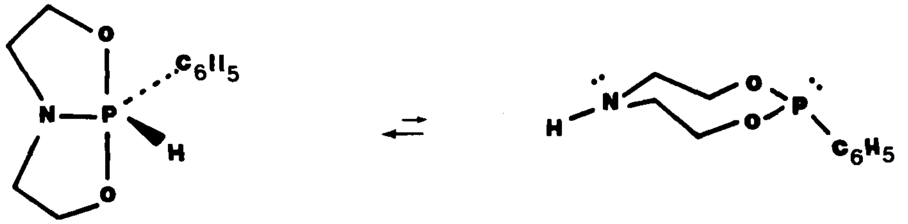


FIGURE 7 Tautomeric equilibrium between a bicyclic phosphorane and a monocyclic phosphane by rupture of the P–N bond.

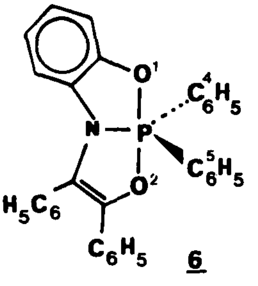
It was also interesting to compare the data of **1** with those of two bicyclic compounds 5-aza-2,8-dioxa-1-phospha-3,7-terbutylbicycle[3.3.0]octa-2,4,6-triene **2**[7] and a bis(borane)aminophosphane **3**[8] Table VI, Figure 3.

In compounds **2** the O–P–O angle is very similar to those of compounds **1**, **6** and **7**, a situation that also holds for O–P–N angles (84.0° and 84.9°) similar to the O^2–P–N and O^1–P–N angles (87.8° and 87.7°, respectively). This, might mean that compound **2** has some distortion toward a Berry coordinate, due to the existence of a pentacoordinated structure when the two lone pairs are considered. Compound **3** does not have a true tetrahedral structure, because one bond angle is quite open (N–P–B, 125.4°) and two are very closed (O^1–P–N 95.0° and O^2–P–N 97.7°). This distortion can be attributable to the bicyclic framework.

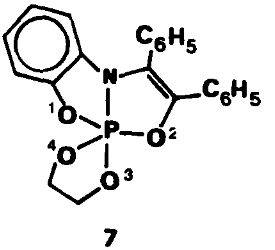
Comparison of compound **1** with the phenyl boronate **4** provides interesting data due to the fact that both atoms (boron and nitrogen) are tetrahedral. Intracyclic boron angles are more open than intracyclic phosphorus angles as can

TABLE V

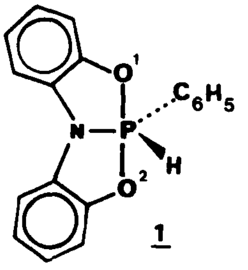
Comparison of angles around phosphorus of compound **1** and the bicyclic phosphoranes **6**[13] and **7**[14]



6



7



1

O^1-P-O^2	171.6	N-P-O^3	172.4	O^1-P-O^2	165.9
N-P-C^4	130.6	O^1-P-O^2	134.0	N-P-H	134.2
N-P-C^5	116.5	O^1-P-O^4	115.6	N-P-C	114.3
C^4-P-C^5	112.8	O^2-P-O^4	110.4	C-P-H	111.4
O^2-P-C^5	94.7	O^3-P-O^4	94.1	O^2-P-C	97.5
O^1-P-C^5	93.3	N-P-O^4	93.5	O^1-P-C	96.5
O^1-P-C^4	89.7	O^2-P-O^3	89.6	O^2-P-N	87.8
O^2-P-C^4	89.4	O^1-P-N	89.3	O^2-P-H	87.7
O^1-P-N	87.6	O^2-P-N	88.4	O^1-P-N	87.7
O^2-P-N	86.6	O^1-P-O^3	86.9	O^1-P-H	85.9

TABLE VI

Angles around phosphorus and boron atoms in compounds **2** and **3**

2		**3**	
O^1-P-O^2	167.7	O^1-P-O^2	113.9
O^1-P-N	83.5	O^{1}P-N	95.0
O^2-P-N	84.5	O^2-P-N	97.7
		B-P-N	125.4
		O^1-P-B	113.9
		O^2-P-B	112.9

TABLE VII

Comparison of central angles of compounds **1** and **4**

1		**4**	
O^1-P-O^2	165.90	O^1-B-O^2	110.3
N-P-C	114.3	N-B-C	114.1
O^1-P-N	87.7	O^1-B-N	101.1
O^2-P-N	87.8	O^2-B-N	101.1
O^1-P-C	96.5	O^1-B-C	114.4
O^2-P-C	97.5	O^1-B-C	114.4

be seen in Table VII. The bicyclic framework introduces a distortion in the boronate molecule opening the carbon–boron–oxygen and carbon–boron–nitrogen angles.

The P–O bond distances of phosphorane **1** (1.714 Å and 1.722 Å) are similar to those of its analogue **6**[13] (1.763 and 1.700 Å). Unexpectedly, they are shorter than those of the bicyclic phosphine **2**[7] (1.835 and 1.792 Å) where some kind of aromatic character is assumed, and are longer than those of compound **7**[14] (1.637 and 1.635 Å) where P–O bonds are in equatorial positions.

The P–N distance of compound **1** (1.715 Å) is similar to that of compounds **6**[13] (1.703 Å) and **2**[7] (1.703 Å) and shorter than the axial P–N bond of compound **7**[14] (1.755 Å). The C–N bond distances of phosphorane **1** (1.41 Å) have an average value between C_{sp2}–N (1.36 Å) and C_{sp3}–N (1.47 Å),[15] the same is observed for the C–O bond distances of **1** (1.37 Å) compared with C_{sp2}–O (1.34 Å) and C_{sp3}–O (1.41 Å).[15] Finally C–N and C–O bonds in **1** are longer than expected due to the aromatic character of the ligand.

ACKNOWLEDGEMENTS

We are grateful to Proyectos Estratégicos-SEP (México) for partial financial support. And to a referee for recalculating the magnitude of structural deviation.

REFERENCES

1. R. Contreras, A. Murillo, G. Uribe and A. Klaebe, *Heterocycles*, **23**, 2187 (1985).
2. R. R. Holmes and J. A. Deiters, *J. Am. Chem. Soc.*, **99**, 3318 (1977).

3. R. R. Holmes, Progress in Inorganic Chemistry, 32, 119 (1987), edited by S. J. Lippard, Wiley & Sons, N.Y.
4. R. S. Berry, *J. Chem. Phys.*, **32,** 933 (1960).
5. R. Luckenbach, "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements", Georg Thieme Verlag, Stuttgard, (1973).
6. W. E. McEwer and K. D. Berlin, Ed., "Organophosphorus Stereo-chemistry". Parts I and II, Dowden, Hutchinson and Ross, Stroudsburg, Pa. (1975).
7. A. J. Arduengo III, C. A. Stewart, F. Davidson, D. A. Dixon, J. Y. Becker, S. A. Culley and M. B. Mizen, *J. Am. Chem. Soc.*, **109,** 627 (1987).
8. D. Grec, L. G. Hubert-Pfalzgraf, J. G. Riess and A. Grand, *J. Am. Chem. Soc.*, **102,** 7133 (1980).
9. N. Farfán, P. Joseph-Nathan, L. M. Chiquete and R. Contreras, *J. Organomet. Chem.*, **348,** 149 (1987).
10. R. Contreras, D. Houalla, A. Klaebe and R. Wolf, *Tetrahedron Lett.*, 3953 (1981).
11. D. Houalla, H. Ramdane and R. Wolf, Nouv. *J. Chim.*, **9,** 189 (1985).
12. M. Aresta, D. Ballivet-Tkachenko and M. Bonnet. *Nouv. J. Chim.*, **9,** 321 (1985).
13. A. Schmidpeter, D. Schomburg, W. S. Sheldrick and J. M. Weinmaier, Angew. *Chem. Int. Ed. Engl.*, **15,** 781 (1976).
14. W. S. Sheldrick, A. Schmidpeter and J. H., Weinmaier, Angew. *Chem. Int. Ed. Engl.*, **14,** 490 (1975).
15. J. March, "Advanced Organic Chemistry", McGraw-HIll Kogakusha, LTD. Tokyo, (1977).