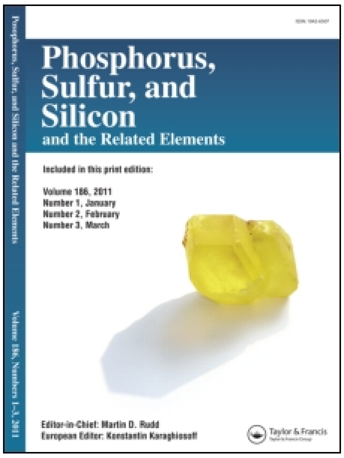


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Theoretical Study of the P-B Bond Nature in Cis-Borylphosphinoethenes and its Cyclization with Double Bonds

L. V. Ermolabva[a]; S. G. Vul'fson[a]; B. A. Arbuzov[a]
[a] Arbuzov Institute of Organic & Physical Chemistry, Kazan, USSR

To cite this Article Ermolabva, L. V. , Vul'fson, S. G. and Arbuzov, B. A.(1992) 'Theoretical Study of the P-B Bond Nature in Cis-Borylphosphinoethenes and its Cyclization with Double Bonds', Phosphorus, Sulfur, and Silicon and the Related Elements, 65: 1, 57 — 60

To link to this Article: DOI: 10.1080/10426509208055317

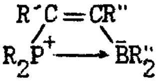
URL: http://dx.doi.org/10.1080/10426509208055317

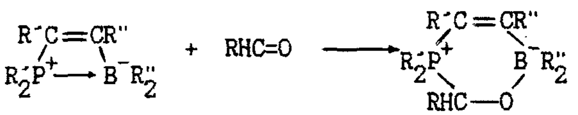
Phosphorus, Sulfur, and Silicon, 1992, Vol. 65, pp. 57–60
Reprints available directly from the publisher
Photocopying permitted by license only

THEORETICAL STUDY OF THE P—B BOND NATURE IN CIS-BORYLPHOSPHINOETHENES AND ITS CYCLIZATION WITH DOUBLE BONDS

L.V.ERMOLAEVA*, S.G.VUL'FSON, B.A.ARBUZOV
Arbuzov Institute of Organic & Physical Chemistry ,Arbuzov
str.8, Kazan 420083 , USSR

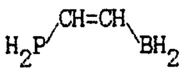
Abstract Structures, energies, and electronic properties of $H_2PCH{=}CHBH_2$ (1) have been studied with ab initio molecular orbital theory by using STO-3G and 3-21G (d(P)) basis sets. The Z-1 isomer with the perpendicular arrangement of BH_2 group is less stable than Z-1 and E-1 ones with the planar orientation of BH_2 group. The short P-B contact of the former is obtained only at STO-3G level. It's bond critical point data, binding energy, localized molecular orbital suggest the presence of weak covalent bonding between the phosphorus and boron atom.

The short P-B contact in cis-borilphosphinoethenes ($R_2P{-}CR'{=}CR''{-}BR''_2$) has been determined by various physical methods.[1-3] The dipolar structure  was suggested by Köster.[1] However, oxygen, sulfur, selenium and CS_2 can easily insert into the P-B bond.[4,5] The latter undergoes a cleavage under pyridine.[2] A cyclic phopsphinoborane and aldehydes react with exothermic effect.[6] The addition proceeds on the contrary to the charge density on the $P^+{-}B^-$ bond:

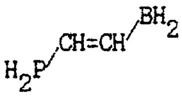


The weak P-B bonding is in accordance to it's chemical properties, and the strong P-B interaction is pointed out by physical data.

To analyse these features in more detail we have performed calculations of the model structures Z and E-1:



(Z)-1



(E)-1

Two conformations have been considered in each case: the conformation A with the orthogonal BH_2 orientation, and the conformation B with planar C=C-BH_2 fragment, the lone electron pair of the P atom (LP(P)) eclipsing the C=C bond. Geometry optimization was performed with the STO-3G and 3-21 G (d(P)) basis set.

RESULTS AND DISSCUSSION The total energies and geometrical parameters of P-C=C-B fragment are given in Table I. We also report here available experimental determinations .[8-9] The STO-3G bond lengths agree with experiment within 0.03 Å. Bond angles were reproduced within 3.4°. It is quite reasonable agreement with experimental structural data, if take into account substituent effects. The 3-21G (d(P)) geometry of Z-1A is in a poor agreement with experiment. This method does not reproduce the short P-B distance in this form, and thus we chose the HF/STO-3G level to optimize the geometries of model structures.

TABLE I Energies(a.u.) and selected bond lengths (Å) and bond angles in the Z and E isomers of PH_2-CH=CH-BH_2(I) for two forms:A - the BH_2 group is perpendicular to the double bond plane; B - the BH_2 group lies in the doble bond plane. Values are at the STO-3G and 3-21G (d(P)) levels (in parentheses).

Form		Total Energy	P-B	C=C	P-C	B-C	PCC	BCC
Z-1	A	-439.52607	2.074	1.320	1.793	1.612	99.5	106.0
	A	(-442.37226)	2.875	(1.328)	(1.818)	(1.581)	(114.4)	(119.6)
exptl[a]	A		2.104	1.353	1.802	1.608	96.1	109.3
	B	-439.52702		1.326	1.836	1.542	126.4	125.1
E-1	A	-439.52022		1.313	1.826	1.564	124.7	123.9
	B	-439.52966		1.325	1.833	1.540	124.4	122.3
exptl[a]	B			1.345	1.810	1.561	128.9	121.8

[a] Experimental data for $Ph\overline{P-CPh=CBu-B}Bu_2$,[8] and E-Ph-CH=CH-B(Mes)$_2$.[9]

The most stable is E-isomer in B conformation. It is favorable than the A by 5.0 kcal mol^{-1}. A cyclic form of Z-1A has been predicted theoretically to lie over 2.3 and 0.6 kcal·mol^{-1} above a global minimum and a conjugated conformation of Z-1,respectively. The calculated data clearly idicate the preference of B conformation with $p(BH_2)$-π(C=C) conjugation. An energy difference between A and B conformation of the Z-1 is small. One can expect that sterically hindered substituents at boron atom result in a destabilization of Z-1B with respect to Z-1A. In the latter LP(P) and $p(BH_2)$ lies in the same plane. Their overlap is enough to reduce the P-B distance and P-C=C, B-C=C angles up to 2.074 Å, 99°,106°, respectively (Table I). Both theoretical and experimental P-B distances are greater than sum of its covalent radii (1.9 Å).

To investigate in more detail the P-B bonding we have calculated the electron distribution in Z-1A.

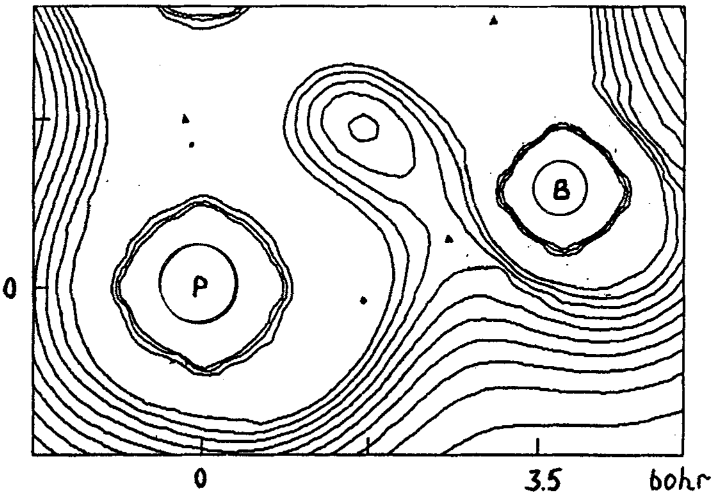


Figure 1 Display of the counter charge density in the P-C=C-B plane (e·bohr^{-3}). (•) - the localized MO centroids, (•) - the bond critical point

The electron distribution has a bond critical point ($\rho_c(r)$=0.523 e·Å^{-3}, $\nabla^2\rho(r)$=-16.3 e·Å^{-5}) between P and B atoms and a minimum inside the four-membered ring. The critical bond is outside of the ring and is shifted from the middlepoint of the P-B straight line by 0.1 (perpendicular to it) and 0.33 Å (along the line towards to B atom). It reflects a charge transfer from P to B atom. A negative value of $\nabla^2\rho_c(r)$ indicates the covalent bonding.[10]

We also carried out a calculation of the localized molecular orbitals (LMO).[11] All LMO are bonding in Z-1A. LMO(P-B) is localized (80%) at phosphorus atom mainly and 10% at boron. The centroid of this LMO lies at 1.01 Å from the P atom and at 0.26 Å from the point, which is the LP(P) centroid in E-1B. Both approach show a charge transfer, resulting from the LP(P)-p(BH_2) interaction. The interaction energy was evaluated by the quantitative PMO procedure.[11] The molecule was subdivided into three fragments: the double bond, PH_2 and BH_2 group. The energy effect of the LP(P)-p(BH_2) interaction (ΔE) is 16 kcal mol^{-1}. On the other hand, an energy difference between the E-1A and the Z-1A (2.7 kcal mol^{-1}) may be considered as the total energy effect due to the P-B bonding accompanied by the distortion of the bond angles. The weakness of the P-B bond is illustrated by the lower $\rho_c(r)$ in the comparison with a corresponding data for the P-C (1.046) and B-C (1.012 e · Å^{-3}) bonds.

The charge redistribution due to the P-B coordination takes place in the Z-1A: the B atom accepts 0.2 e and the P atom loses 0.1 e. This charge shift leads to the increasing of a total dipole moment (by 2.9 D).A theoretical value (3.6 D) of the latter is the same order as experimental one (R=R'=Ph; R''=Bu, DM=4.6 D).[2]

Thus, the P-B bond is a weak dative one in spite of the rather short distance and noticable charge transfer. Chemical behavior of borylphosphinoethenes proves this conclusion. Recently borylphosphinoethenes were shown to undergo [4+2]-cycloaddition reactions with heterocumulenes, which result in the formation of heterosubstituted 1-aza-5-phosphonia-2-boratacyclohexa-3-enes .[5,12]

REFERENCES

1. P.Binger, R.Köster, J.Organometal.Chem., 73, 205 (1974).
2. S.G.Vul'fson, N.N.Sarvarova, A.S. Balueva, O.A.Erastov, B.A. Arbuzov, Izv.AN SSSR.Ser.khim., 1445 (1988).
3. L.A.Hagelee,R.Köster. Synth. React. Inorg. Org. Chem.,
4. L.V.Ermolaeva, A.S.Balueva, O.A.Erastov, N.N.Sarvarova, S.G.Vul'fson, B.A.Arbuzov, Zh.obshch.khim., 60, 755 (1990).
5. B.A.Arbuzov,G.N.Nikonov, Reviews on Heteroatom Chemistry,3, 1 (1990)
6. A.S.Balueva, O.A.Erastov, Izv.AN SSSR.Ser.khim., 1199 (1987).
7. C.Schade, P.v.R.Schleyer, J.Chem.Soc.,Chem.Commun.,1399 (1987).
9. O.A.Erastov,I.A.Litvinov,L.V.Ermolaeva et al.,XI Inter.Conf. Phosphorus Chemistry ,Abstracts.Tallinn.USSR,1,71 (1989).
8. Z.Yuan, N.J.Taylor, T.B.Marder, I.D.Williams, S.K.Kurtz, L.-T.Cheng,J.Chem.Soc.,Chem.Commun., 1489 (1990).
10. R.F.W.Bader, T.S.Slee, D.Cremer, E.Kraka, J.Am.Chem.Soc., 105, 5061 (1983).
11. M.Peterson, R.Poirier, MONSTERGAUSS, Chem.Dept.Univ.Toronto (1981).
12 B.A.Arbuzov , R.M.Kamalov , G.N.Nikonov et al..,Tetrahedron Letters. 1990 in press.