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Theoretical Studies of Borylphosphine, Its Conjugate Base, and the Lithium Salt of Its Conjugate Base. The Use of Orbital Kinetic Energies To Determine the Origin of the Driving Force for Changes in Molecular Geometry

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We have studied the ground states of BH_2PH_2, BH_2PH^-, and BH_2PHLi by the methods of ab initio molecular electronic structure theory using a basis set of high quality. While almost nothing is known experimentally about these molecules, they provide useful models for extensive recent experimental work on a series of organic derivatives. For each molecule, we have predicted its molecular geometry, energy, dipole moment, net atomic charges, bond orders, normal vibrational modes, and harmonic vibrational frequencies. The BH_2PH_2 molecule is nonplanar with a 70° out-of-plane angle at phosphorus and an energy 5.9 kcal/mol below the planar form. On going from the planar to the nonplanar form, the B-P bond order of BH_2PH_2 drops from 1.46 to 1.15 (Mayer method) or from 1.64 to 1.35 (Natiello and Medrano method). A study of orbital kinetic energies shows that a shift of one pair of electrons from a weak B-P π bond to a much more stable lone pair on phosphorus provides the main driving force for distortion from planarity. The BH_2PH^- anion is planar with a small BPH angle (100°) and a proton affinity of 15.2 eV. Nonplanar BH_2PHLi lies in a very shallow potential well, 2.1 kcal/mol below the planar form. It may be described as an approximately planar BH_2PH^- anion with an Li^+ cation at an out-of-plane angle of 56°. Our results for these molecules are compared with experimental data for their derivatives with alkyl and aryl substituents and for the BH_2NH_2 molecule.

Introduction

Inorganic analogues of the ethylene molecule are important in chemistry both for their intrinsic interest and for the insights they provide into the nature of the double bond. While boranamine (also called aminoborane), BH_2NH_2, has been extensively studied, except for several theoretical investigations[1] nothing seems to be known of the phosphorus analogue borylphosphine (also called phosphinoborane), BH_2PH_2.

There have been several studies of its organic derivatives. Evidence for formation of the compound Me_2BPH_2 was obtained by Burg and Wagner.[2] Coates and Livingstone[3] have synthesized several compounds with aryl substituents, such as Ph_2BPPh_2, and characterized them as to dipole moment, B-P stretching frequency, solubility, and degree of association in aromatic solvents. Recently the crystal structure of an organic derivative, Mes_2BPPh_2, was determined by Feng, Olmstead, and Power.[4] Bartlett, Feng, Dias, and Power[5] also determined the crystal structures of ion pairs containing the Mes_2BPR^- anion (which may be viewed as a derivative of borylphosphine's conjugate base, BH_2PH^-) as well as complexes of this anion and related anions with the cation $Li(Et_2O)_2^+$. These compounds exhibit several interesting stereochemical features.

To understand the chemical bonding and molecular geometries of compounds of these types, we have undertaken a detailed and comprehensive theoretical inquiry into the "parent" molecule with hydrogen atoms in place of the organic groups, using a basis set of high quality. In spite of the enormous differences in size, we find a remarkably close similarity in many aspects of the stereochemistry of BH_2PH_2 and its organic derivatives. Of course, it would be of interest to compare our results with experimental measurements on the hydrogen compounds, but as far as we can determine, these compounds have yet to be synthesized.

Method

With use of the restricted self-consistent-field (SCF) method, the molecular geometry was optimized by an analytic gradient method[6] until the magnitude of each force (Cartesian and internal coordinate) was less than 1×10^{-7} hartree/bohr. The following basis sets were used: (a) The DZ set is the contracted double-ζ Gaussian basis set of Huzinaga, Dunning, and Hay[7-9] with the hydrogen functions scaled by a factor of 1.2. (b) The DZ + P set was formed by adding to the DZ set six d functions (α = 0.7) for B, six d functions (α = 0.5) for P, and three p functions (α = 0.75) for each H, and for Li, the 10s/4s basis set of Dunning[10] combined with 4p/2p functions consisting of one contracted set of Gaussian functions (exponents 1.488, 0.2667, and 0.07201 with corresponding coefficients of 0.03877, 0.236257, and 0.830448) and one set of Gaussians with exponent 0.0237 was used. This basis set is designated B(9s5p1d/4s2p1d), P(11s7p1d/6s4p1d), H(4s1p/2s1p), Li(10s4p/4s2p). (c) The DZ + 2P + diff set was formed by adding to the DZ basis set one s function (α = 0.019), one set of p functions (α = 0.019), and two sets of d functions (α = 0.45 and 0.95) for B and one s function (α = 0.035), one set of p functions (α = 0.035), and two sets of d functions (α = 0.25 and 0.75) for P and using the DZ + P basis set for H. Analytic second derivatives[11-13] were used to determine the harmonic vibrational frequencies and the corresponding normal modes. In determining configuration interaction (CI) wave functions, we froze the filled inner-shell molecular orbitals. Except for this feature, all singly and doubly excited configurations were included (CISD). The Davidson correction[14] was used to estimate the effect of unlinked quadruple excitations on the molecular energy. (In the following text all energies are Davidson-corrected energies.) The total number of configurations varied from 3284 for planar BH_2PH_2 with the DZ basis set to 42 531 for nonplanar BH_2PH_2 with the DZ + 2P + diff basis set.

The BH_2PH_2 Molecule

On optimizing the structure of planar BH_2PH_2 (**1**) (restricted to C_{2v} symmetry), we obtained the bond lengths, bond angles, and other properties shown in Table I. Perhaps the most interesting feature of this structure is its imaginary PH_2 wagging frequency, indicating a preference for a nonplanar geometry. (Justification for the double bond in **1** and the lone pair in **2** will be given later.)

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[∥] Contribution CCQC No. 18.

(1) (a) Gropen, O. *J. Mol. Struct.* **1977**, *36*, 111. (b) Magnusson, E. *Tetrahedron* **1985**, *41*, 5235. (c) Magnusson, E. *Aust. J. Chem.* **1986**, *39*, 735. (d) Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1987**, 497.

(2) Burg, A. B.; Wagner, R. I. *J. Am. Chem. Soc.* **1953**, *75*, 3872.

(3) Coates, G. E.; Livingstone, J. G. *J. Chem. Soc.* **1961**, 1000.

(4) Feng, X.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 4615.

(5) (a) Bartlett, R. A.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6817. (b) Bartlett, R. A.; Dias, H. V. R.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 1306. See also (c) Arif, A. M.; Boggs, J. E.; Cowley, A. H.; Lee, J.-G.; Pakulski, M.; Power, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 6083. (d) Couret, C.; Escudie, J.; Garrigues, B.; Lazraq, M.; Satge, J. *Can. J. Chem.* **1987**, *65*, 1230.

(6) Pulay, P. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 4, pp 53-183.

(7) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(8) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823.

(9) Dunning, T. H., Jr.; Hay, P. J. In ref 6, Vol. 3, pp 1-27.

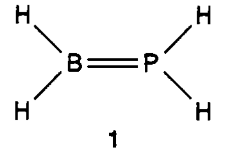
(10) Dunning, T. H., Jr. *J. Chem. Phys.* **1971**, *55*, 716.

(11) Saxe, P.; Yamaguchi, Y.; Schaefer, H. F., III. *J. Chem. Phys.* **1982**, *77*, 5647.

(12) Osamura, Y.; Yamaguchi, Y.; Saxe, P.; Vincent, M. A.; Gaw, J. F.; Schaefer, H. F., III. *Chem. Phys.* **1982**, *72*, 131.

(13) Osamura, Y.; Yamaguchi, Y.; Saxe, P.; Fox, D. J.; Vincent, M. A.; Schaefer, H. F., III. *J. Mol. Struct.* **1983**, *103*, 183.

(14) Davidson, E. R. In *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; Reidel: Dordrecht, 1974; p 17.



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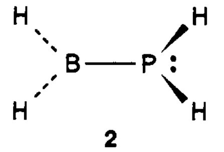

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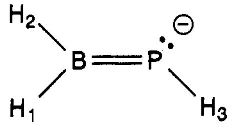
Relaxation of the symmetry to C_s leads to a structure of lower energy, **2**, with a highly pyramidal phosphorus atom in opposition to a slightly pyramidal boron atom. Its properties are also listed in Table I. With the DZ + 2P + diff basis set, the out-of-plane angles are 70.0° at phosphorus and 6.0° at boron.

In spite of the rather striking difference between the two structures, the energy difference is only 5.9 kcal/mol. The orbital occupation of the planar molecule is $1a_1^2 2a_1^2 3a_1^2 1b_2^2 4a_1^2 1b_1^2 5a_1^2 6a_1^2 2b_2^2 3b_2^2 7a_1^2 2b_1^2$ while that of the nonplanar molecule is $1a'^2 2a'^2 3a'^2 1a''^2 4a'^2 5a'^2 6a'^2 7a'^2 2a''^2 3a''^2 8a'^2 9a'^2$. The lowest unoccupied molecular orbitals (LUMOs) are $3b_1$ and $10a'$, respectively. For the planar molecule the HOMO and LUMO are assigned to π and π^* orbitals, respectively. For the nonplanar molecule they are assigned, respectively, to a lone pair orbital and to an unsymmetrical π^* orbital that is mainly localized on boron. The reason why this molecule is nonplanar is discussed in a later section.

The BH_2PH^- Anion

Removal of one of the protons bonded to phosphorus leads to the planar anion **3**. Its properties are summarized in Table II.



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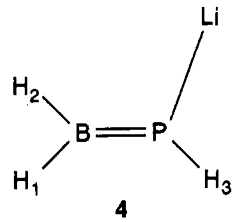
Compared to planar BH_2PH_2, the most striking difference is the anion's strong preference for planarity. Not surprisingly, the anion has a high proton affinity (15.2 eV with the DZ + 2P + diff basis set).

Addition of diffuse functions to the basis set has relatively little effect on the structural parameters or the vibrational frequencies. The most sensitive property studied here is the dipole moment, decreasing from 0.84 to 0.64 D. The reason why this molecule is planar, in contrast to the nonplanar neutral species, is discussed in a later section.

The BH_2PHLi Molecule

Substitution of one of the phosphorus hydrogens of BH_2PH_2 by lithium produces the salt BH_2PHLi, whose geometry was first optimized by assuming planarity, as in structure **4**. With the



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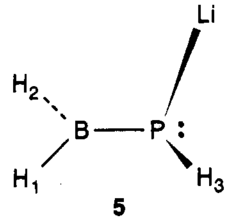

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DZ + P basis set, the Li wag frequency is imaginary (94i cm^{-1}), and thus it was necessary to study the nonplanar structure **5**. An energy minimum was found having the lithium ion at an angle of 56.1° relative to the H_1BP plane. The H_2 and H_3 atoms are slightly depressed and raised, respectively, relative to the H_1BP plane (H_2 down 2.6°, H_3 up 9.7°), so that the Li^+ cation is sharply inclined to an approximately planar BH_2PH^- anion. This structure lies only 2.1 kcal mol^{-1} below the planar structure, and thus the P–Li bond is an example of a "polytopic bond", a structural type first identified by Clementi, Kistenmacher, and Popkie in the LiCN–LiNC system.[15] The properties of the planar and nonplanar structures are listed in Table III.

Table I. Properties of Nonplanar and Planar BH_2PH_2[a]

	nonplanar, $^1A'$	planar, $^1A_1$
r_e(BP)	1.901 (1.899)	1.807
r_e(BH)	1.190 (1.190)	1.187
r_e(PH)	1.403 (1.402)	1.384
θ_e(PBH)	119.8 (119.7)	118.2
θ_e(HBH)	120.0 (120.3)	123.6
θ_e(BPH)	102.7 (102.7)	124.8
θ_e(HPH)	99.4 (99.5)	110.3
θ_e(out of plane at B)[b]	6.1 (6.0)	0.0
θ_e(out of plane at P)[b]	70.1 (70.0)	0.0
energy, SCF[c]	0.0	8.6
energy, CISD[c]	0.0	6.3
energy, Davidson cor[c]	0.0	5.9
dipole moment	0.82 (0.85)	1.21
vibrational freq, ν_e		
asym BH str	2794 (2780), A″	2824, B_2
sym BH str	2698 (2687), A′	2715, A_1
asym PH str	2584 (2573), A″	2724, B_2
sym PH str	2576 (2567), A′	2696, A_1
sym BH_2 bend	1268 (1275), A′	1254, A_1
sym PH_2 bend	1222 (1215), A′	1162, A_1
BH_2 wag	1024 (1021), A′	990, B_1
PH_2 rock − BH_2 rock[d]	964 (957), A″	889, B_2[e]
BP str	746 (736), A′	827, A_1
BH_2 rock + PH_2 rock[d]	588 (581), A″	491, B_2[e]
PH_2 wag	554 (546), A′	497i, B_1
torsion	429 (424), A″	723, A_2

[a] Results with the DZ + 2P + diff basis set are listed in parentheses; other results are obtained with the DZ + P basis set. Bond lengths are in Å, angles are in deg, vibrational frequencies are in cm^{-1} for ^{11}B, ^{31}P, and ^1H isotopes, and dipole moments are in D. For C_{2v} symmetry, the molecular plane is taken as the yz plane (σ_v'). [b] The out-of-plane angle at B is defined as the angle between the BP axis and the H_2B plane. That at P is the angle between the BP axis and the PH_2 plane. [c] Energies are in kcal mol^{-1} relative to the nonplanar structure. [d] Where motion of more than one internal coordinate makes a significant contribution to the normal mode, they are listed in order of decreasing importance. Plus and minus signs indicate relative phases. The rocking (asymmetric bending) motions are considered in phase if two H atoms move toward each other. [e] For the planar molecule, the order of importance is reversed.

Table II. Properties of the Planar BH_2PH^- Anion[a]

	$^1A'$
r_e(BH_1)	1.212 (1.210)
r_e(BH_2)	1.214 (1.212)
r_e(PH_3)	1.428 (1.424)
θ_e(PBH_1)	125.2 (124.5)
θ_e(PBH_2)	119.3 (119.1)
θ_e(BPH_3)	100.0 (100.3)
proton affinity, SCF[b]	15.63 (15.37)
proton affinity, CISD[b]	15.60 (15.25)
proton affinity, Davidson cor[b]	15.56 (15.18)
dipole moment[c]	0.84 (0.64)
vibrational freq, ν_e	
asym BH str	2564 (2563), A′
sym BH str	2527 (2525), A′
PH str	2396 (2391), A′
sym BH_2 bend	1269 (1269), A′
BPH bend − BH_2 rock	977 (965), A′
BH_2 wag	956 (958), A″
BP str	836 (815), A′
torsion	747 (718), A″
BPH bend + BH_2 rock	646 (647), A′

[a] Results with the DZ + 2P + diff basis set are listed in parentheses; other results were obtained with the DZ + P basis set. See footnote in Table I for units, etc. [b] The proton affinity is the energy in eV relative to nonplanar BH_2PH_2 with the same basis set. [c] The dipole moment is taken with respect to the center of mass.

Justification for describing this molecule in terms of a Li^+ cation and a BH_2PH^- anion rests on several criteria. These include the low frequencies of those normal coordinates that involve angular

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[15] Clementi, E.; Kistenmacher, H.; Popkie, H. *J. Chem. Phys.* **1973**, *58*, 2460.

Table III. Properties of the BH_2PHLi Molecule[a]

	planar, $^1A'$	nonplanar, ^1A
$r_e(BP)$	1.838	1.855
$r_e(BH_1)$	1.194	1.196
$r_e(BH_2)$	1.198	1.202
$r_e(PH_3)$	1.402	1.410
$r_e(PLi)$	2.306	2.355
$\theta_e(PBH_1)$	122.4	123.3
$\theta_e(PBH_2)$	118.2	118.4
$\theta_e(BPH_3)$	108.5	103.3
$\theta_e(BPLi)$	125.5	98.0
$\theta_e(H_1BH_2)$	119.4	118.3
$\theta_e(H_3PLi)$	126.0	111.3
θ_e(out of plane of H_2 at B)[b]	0.0	2.6 down
θ_e(out of plane of H_3 at P)[b]	0.0	9.7 up
θ_e(out of plane of Li at P)[b]	0.0	56.1 up
energy, SCF[c]	1.0	0.0
energy, CISD[c]	1.8	0.0
energy, Davidson cor[c]	2.1	0.0
dipole moment	7.93	7.60
vibrational freq, ν_e		
asym BH str	2729, A′	2709, A
sym BH str	2641, A′	2621, A
PH str	2577, A′	2521, A
sym BH_2 bend	1262, A′	1268, A
BH_2 wag	988, A″	998, A
BPH bend − BH_2 rock	962, A′	960, A[d]
BP stretch	805, A′	787, A
BH_2 rock + BPH bend	664, A′	632, A[e]
torsion	646, A″	700, A
PLi str	524, A′	494, A
BPLi bend	121, A′	85, A
Li wag	94i, A″	207, A

[a] All results were obtained with the DZ + P basis set. See footnote *a* in Table I for units, etc. [b] The out-of-plane angle of H_2 at B is defined as the angle between the BH_2 axis and the H_1BP plane, with corresponding definitions for the other out-of-plane angles. [c] Energies are in kcal mol^{-1} relative to the nonplanar structure. [d] BPH bend − BH_2 rock − BH_2 wag. [e] BH_2 rock + BPH bend − torsion.

Table IV. Energies of Boron–Phosphorus Molecules[a]

	energy		
molecule	SCF	CISD	Davidson cor
nonplanar BH_2PH_2	−367.711 03	−367.938 80	−367.961 03
	(−367.717 93)	(−367.959 69)	(−367.985 13)
planar BH_2PH_2	−367.697 27	−367.928 72	−367.951 64
planar BH_2PH^-	−367.136 64	−367.365 45	−367.389 34
	(−367.153 10)	(−367.399 45)	(−367.427 38)
nonplanar BH_2PHLi	−374.599 18	−374.825 53	−374.848 81
planar BH_2PHLi	−374.597 60	−374.822 73	−374.845 55

[a] Results with the DZ + 2P + diff basis set are listed in parentheses; other results were obtained with the DZ + P basis set. Energies are in hartrees.

motion of lithium, and the shallow potential energy surface. Both of these results indicate that we have a spherical Li^+ ion that is rather indifferent to its angular position relative to an approximately spherical BH_2PH^- ion. Other criteria include the traditional view of lithium, with its low electronegativity, as forming ionic compounds with atoms of higher electronegativity, the very similar structures of the free BH_2PH^- anion (Table II) and the BH_2PH part of this molecule, and the very large dipole moments of this molecule in its two forms.

Energy data for all of the molecules reported in this paper are summarized in Table IV.

Bond Order of the Boron–Phosphorus Bond

An interesting question regarding BH_2PH_2 and its derivatives is, Do any of these molecules have a boron–phosphorus double bond? The classical approach to this question is through a study of bond lengths. Data on covalent bond radii lead to estimates of 1.94–1.98 Å for the B–P single-bond length and 1.79–1.84 Å for the double bond.[4] Comparing the results in Tables I–III with these estimates, we see that the planar molecules all have B–P bond lengths that fall within the estimated range of values for a double bond. Nonplanar BH_2PHLi (with its almost planar BH_2PH moiety) has a B–P bond length that is only slightly longer. On the other hand, nonplanar BH_2PH_2 has a B–P bond length about halfway between the single-bond and double-bond estimates.

Table V. Bond Orders[a]

	bond order			
molecule	B–P	B–H	P–H	P–Li
	DZ + P Basis Set			
planar BH_2PH_2	1.46 (1.64)	0.99 (0.97)	0.96 (0.96)	
nonplanar BH_2PH_2	1.15 (1.35)	0.99 (0.98)	0.97 (0.97)	
planar BH_2PH^-	1.83 (2.01)	0.98 (0.98)[b]	0.94 (0.99)	
planar BH_2PHLi	1.42 (1.62)	0.99 (0.96)[b]	0.97 (0.96)	0.77 (0.90)
nonplanar BH_2PHLi	1.35 (1.59)	0.99 (0.96)[b]	0.96 (0.96)	0.75 (0.83)
	DZ + 2P + diff Basis Set			
nonplanar BH_2PH_2	1.14 (1.41)	0.99 (0.92)	0.99 (0.94)	
planar BH_2PH^-	1.61 (2.02)	0.99 (0.92)[b]	0.99 (0.98)	

[a] All bond orders are based on SCF wave functions. The first number is calculated by Mayer's method; the number in parentheses, by the method of Natiello and Medrano. [b] Differences between B–H_1 and B–H_2 are slight.

Methods of evaluating bond orders from wave functions have a long and troubled history. Recently two new methods, one proposed by Mayer[16] and one proposed by Natiello and Medrano,[17] have gained attention. A recent paper by Baker compares results obtained by using these two methods.[18] (He refers to the two methods as the "Mulliken" analysis and the "Löwdin" analysis, respectively.)

We have applied these methods to our wave functions, and the results are presented in Table V. They indicate substantial B–P double-bond character in all of the planar molecules, with the highest bond order being 2.02 for planar BH_2PH^- with the Natiello–Medrano method and the DZ + 2P + diff basis set. Nonplanar BH_2PH_2 has B–P bond orders that indicate much less double-bond character (1.15 and 1.35 by the Mayer and Natiello–Medrano methods, respectively, with the DZ + P basis set). These bond order data are consistent with the decreases in B–P stretching frequency (827 to 746 cm^{-1}) and torsion frequency (723 to 429 cm^{-1}) on going from planar to nonplanar BH_2PH_2. In all cases the B–H and P–H bond orders are pleasingly close to 1. The lower bond order of the P–Li bond is to be expected for partially ionic bonding.

For two molecules, the data in Table V show the effect on calculated bond orders of expanding the basis set to include diffuse functions on boron and phosphorus. The largest change is a drop in the B–P bond order of planar BH_2PH^- from 1.83 to 1.61 with the Mayer method. But these changes are not nearly so drastic as those found by Baker for bond orders by the Mayer ("Mulliken") method on going from the 3-21G basis to the 3-21 + G basis.[18]

For the BH_2PH^- anion, other criteria that support the assignment of a double bond between boron and phosphorus are (a) its planarity and (b) the relatively high frequency of its out-of-plane bending modes (BH_2 wag and torsion), as shown in Table II. If one accepts this argument, then the fact that the BP stretching frequencies in planar BH_2PH_2 and planar BH_2PHLi are comparable to that of the BH_2PH^- anion indicates that we have a double bond in these other molecules as well. And of course this conclusion is consistent with the arguments based on bond lengths and calculated bond orders discussed earlier.

We are then faced with the question: Why do BH_2PH_2 and BH_2PHLi favor nonplanar structures? In the case of BH_2PH_2, we suggest that it is energetically favorable for the π-bonding pair of electrons to move, at least partially, to a lone-pair position on the phosphorus atom. This point will be explored in more detail in a later section. In the case of BH_2PHLi, the BH_2PH part of the molecule retains its planarity to a high degree. It appears

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(16) Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270; **1984**, *110*, 440; *Int. J. Quantum Chem.* **1986**, *29*, 73.

(17) Natiello, M. A.; Medrano, J. A. *Chem. Phys. Lett.* **1984**, *105*, 180; **1984**, *110*, 445.

(18) Baker, J. *Theor. Chim. Acta* **1985**, *68*, 221.

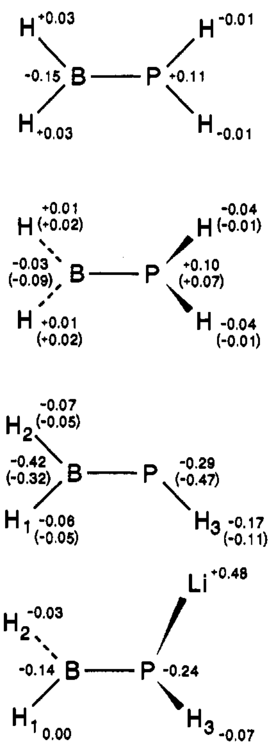
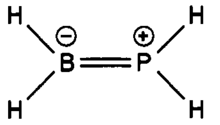


Figure 1. Net atomic charges from Mulliken population analysis of the wave functions for planar and nonplanar BH_2PH_2, planar BH_2PH^- anion, and nonplanar BH_2PHLi. Results with the DZ + 2P + diff basis set are shown in parentheses; other results were obtained with the DZ + P basis set.

that the Li^+ ion is moving well out of plane to a point of higher electron density. At this point, the out-of-plane angle is so large that this structure may be regarded as a distorted π complex.

Net Atomic Charges and Dipole Moments

Net atomic charges were computed by a Mulliken population analysis,[19] and the results are shown in Figure 1. It is rather striking that, in both planar and nonplanar BH_2PH_2, boron is more negative than phosphorus, even though phosphorus is considered to be slightly more electronegative than boron.[20] We suggest that this charge distribution reflects the influence of the B–P double bond, which imparts a negative formal charge to boron and a positive formal charge to phosphorus, as in structure 6. When the planar structure relaxes to a single-bonded nonplanar structure, 7, or, as seems more likely, to a resonance hybrid of structures with single and double bonds, there is a reduction in the magnitude of the formal charges. Correspondingly there is a reduction in the difference between the net atomic charges of boron and phosphorus: B is more negative than P by 0.26 e in the planar structure, and by only 0.13 e in the nonplanar structure (DZ + P basis set). At the same time the dipole moment drops, in spite of the lengthening of the B–P bond.



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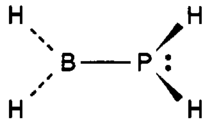

7

Use of the more extensive DZ + 2P + diff basis set gives results for nonplanar BH_2PH_2 that are very similar to the DZ + P results. However, for the BH_2PH^- anion the differences are rather large, so much so that the polarity of the molecule changes from a more negative BH_2 end of the molecule with a DZ + P basis to a more negative PH end of the molecule with the extended basis. As a result, the component of the total dipole moment along the B–P axis changes sign, going from +0.76 to −0.09 D. This is yet another example of the importance of using diffuse functions for anions.

Table VI. Orbital Kinetic Energies of the BH_2PH_2 Molecule[a]

	planar[b]		nonplanar[b]		change
core	$1a_1$	106.219 76	1a′	106.219 81	0.000 05
core	$2a_1$	10.910 39	2a′	10.911 32	0.000 93
core	$3a_1$	15.843 48	3a′	15.851 08	0.007 60
core	$4a_1$	14.763 98	4a′	14.764 70	0.000 72
core	$1b_1$	14.782 73	5a′	14.781 64	−0.001 09
$\sigma(PH)_+$	$5a_1$	1.503 24	6a′	1.444 49	−0.058 75
$\sigma(BH)_+$	$6a_1$	1.016 73	7a′	0.971 06	−0.045 67
$\sigma(BP)$	$7a_1$	1.178 16	8a′	1.152 77	−0.025 39
π	$2b_1$	1.102 69	9a′	1.257 35[c]	0.154 66
core	$1b_2$	14.755 72	1a″	14.757 88	0.002 16
$\sigma(PH)_-$	$2b_2$	1.004 81	2a″	0.896 02	−0.108 79
$\sigma(BH)_-$	$3b_2$	0.766 95	3a″	0.847 42	0.080 47
2 × total		367.697 28[d]		367.711 08[d]	0.013 80[d]

[a] DZ + P basis set. Energies in hartrees. [b] Corrected to satisfy virial theorem by multiplication by 1.000 247 23 (planar) and 1.000 230 70 (nonplanar). [c] The 9a′ orbital is assigned to a lone pair on phosphorus. Other assignments for the nonplanar structure are similar to those of the planar structure. [d] Roundoff errors are 1×10^{-5} (planar), 5×10^{-5} (nonplanar), and 5×10^{-5} (change).

As expected, the lithium salt has a rather large positive charge on lithium. (Planar BH_2PHLi has atomic net charges that are almost identical with the nonplanar distribution shown in Figure 1.) Comparing this molecule with planar BH_2PH_2, we see that replacing H by Li releases −0.49 e of negative charge, and that the bulk of this (−0.35 e) goes to phosphorus. The large net atomic charges of the lithium salt are reflected in its high dipole moment (planar, 7.93 D; nonplanar, 7.60 D).

Orbital Kinetic Energies

In trying to understand why one particular molecular structure is more stable than another, an important quantitative approach has been to study the changes in the energies of SCF orbitals, as summarized by Walsh's rules.[21] This method suffers from the fact that the sum of orbital energies differs from the total energy of the molecule, leading to a number of notable exceptions to Walsh's rules. One way of improving the correlation between equilibrium bond angle and the sum of orbital energies is to use internally consistent SCF orbital energies in place of canonical orbital energies.[22]

An alternative method, based on the quantum-mechanical virial theorem, is to partition the total energy into a sum of kinetic energies for the various chemical bonds, lone pairs, and inner shells.[23] While this method was originally formulated for a wave function constructed from geminals, we decided to look at orbital kinetic energies as a method of partitioning the total SCF energy. Attractive features of this approach are the fact that the virial theorem guarantees additivity of orbital kinetic energies for any molecular structure at a stationary point on the potential energy surface and also the relative ease of construction of SCF wave functions. (Note that with the kinetic energy method one avoids making any assumption about partitioning of the potential energy or the orbital energies.) A possible disadvantage is the fact that the SCF wave function is invariant under a unitary transformation; hence, the kinetic energies of the canonical SCF orbitals would be expected to differ from, for example, the kinetic energies of localized orbitals. Nevertheless, the success of Walsh's rules, which are also based on the canonical SCF orbitals, encouraged us to look at this approach.

The specific case we examined was the deformation of planar BH_2PH_2 to a nonplanar geometry. What features of the nonplanar form make it more stable than the planar form? To answer this question, we calculated the orbital kinetic energies for each

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(19) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 1841, 2338, 2343.
(20) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; p 146.
(21) Walsh, A. D. *J. Chem. Soc.* **1953**, 2260.
(22) Stenkamp, L. Z.; Davidson, E. R. *Theor. Chim. Acta* **1973**, *30*, 283.
(23) Allen, T. L.; Shull, H. *J. Chem. Phys.* **1961**, *35*, 1644.

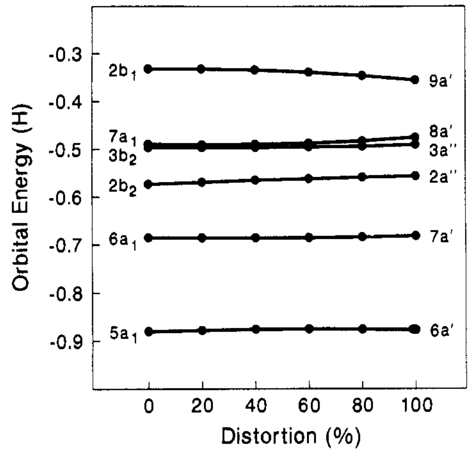

Figure 2. Valence orbital energies of BH_2PH_2 as a function of distortion from planarity. The 0% and 100% distortions refer to the planar and nonplanar structures, respectively, listed in Table I, except that a DZ basis set was used here. Intermediate structures were obtained by interpolation of bond lengths, bond angles, and out-of-plane angles at boron and phosphorus.

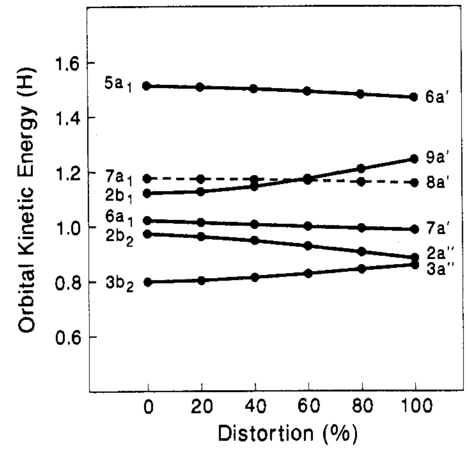

Figure 3. Orbital kinetic energies of BH_2PH_2 as a function of distortion from planarity. For clarity the $7a_1$–8a′ correlation is shown as a dashed curve.

structure, and the results are shown in Table VI. These data were obtained from the DZ + P wave function; similar results were obtained with the DZ wave function. Because of slight imperfections in the wave functions, the total kinetic energies differed slightly from the negative of the total energies. To bring the data into conformity with the virial theorem, we multiplied the orbital kinetic energies by the factors listed in Table VI.

To determine the correlation pattern between orbitals for the two forms, we constructed SCF functions for intermediate structures with deformations of 20, 40, 60, and 80%. The valence orbital energies are shown in Figure 2. The order of valence orbital energies is unaffected by deformation, producing the correlation shown in Table VI.

Figure 3 illustrates the effect of deformation on the orbital kinetic energies. The only orbital that undergoes a major change is the π orbital of the planar structure. As it changes into a phosphorus lone pair ($2b_1 \rightarrow 9a'$), it is enormously stabilized. For two electrons, the change in orbital kinetic energy of 0.15466 hartree amounts to twice that or 0.30932 hartree (194 kcal mol^{-1}). In addition, the $\sigma(BH)_-$ orbital is stabilized by about half this amount. These changes are largely offset by changes in the opposite direction for the $\sigma(PH)_+$, $\sigma(PH)_-$, $\sigma(BH)_+$, and $\sigma(BP)$ orbitals. As expected the core orbitals are relatively unaffected. The sum of the various changes then amounts to a relatively modest total of only 0.01380 hartree (8.7 kcal mol^{-1}).

In describing these energy changes, we take the point of view (justified by the virial theorem) that any increase in kinetic energy implies a corresponding decrease of exactly the same magnitude in total energy. Conversely, any increase in molecular stability, as evidenced by a decrease in total energy, must be accompanied by an increase in kinetic energy of exactly the same magnitude.

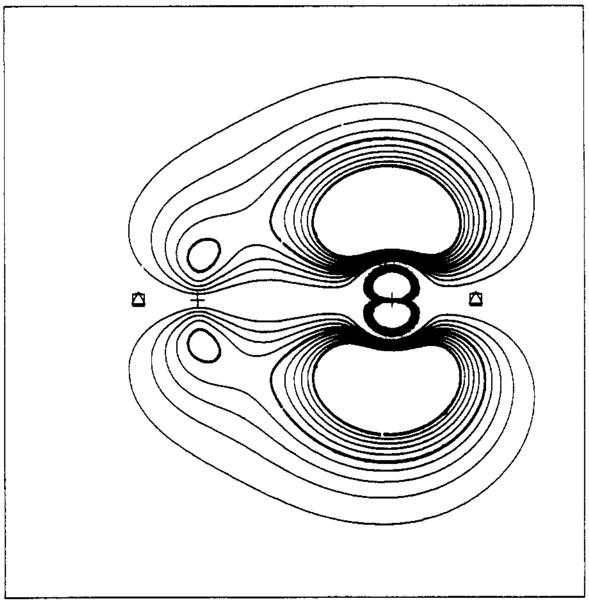

Figure 4. Planar BH_2PH_2: contour diagram in a plane passing through the B and P nuclei and perpendicular to the molecular plane for the $2b_1$ ("π") molecular orbital probability density. B and P are left and right +, respectively. Projections of protons are left and right □ and △. Contours are from 0.01 to 0.10 e Å^{-3} at 0.01 e Å^{-3} intervals. DZ basis set was used.

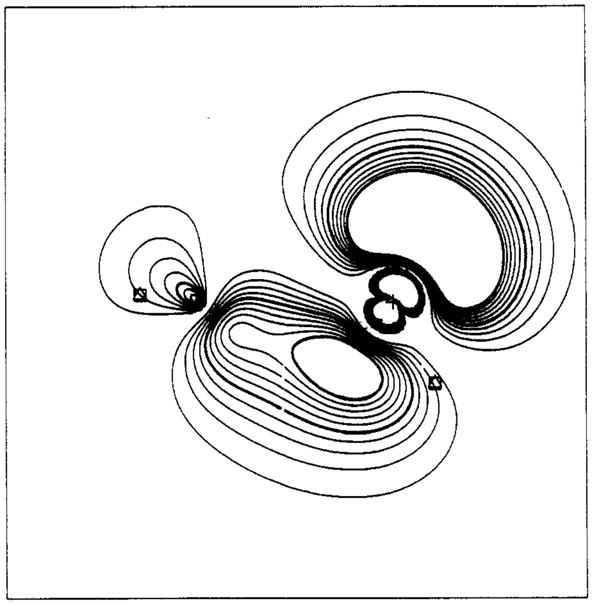

Figure 5. Nonplanar BH_2PH_2: contour diagram in the symmetry plane of the molecule for the 9a′ ("lone pair") molecular orbital probability density. B and P are left and right +, respectively. Projections of protons are upper left and lower right □ and △. Contours are from 0.01 to 0.10 e Å^{-3} at 0.01 e Å^{-3} interval. DZ basis set was used.

Contour diagrams for the π molecular orbital of the planar molecule and the lone-pair molecular orbital of the nonplanar molecule are shown in Figures 4 and 5. It is clear from Figure 4 that the π bond is concentrated on the phosphorus atom, which interacts rather weakly with the boron atom, explaining the relatively low bond order of the B–P bond (Table V).

Figure 5 shows that the lone pair on phosphorus is indeed the dominant feature of the 9a′ orbital, but its formation is actually accompanied by a strengthening of the π bond on the underside of the molecule. In effect, the phosphorus p orbital tilts in such a way that its upper lobe moves away from boron to accommodate the bulk of a lone pair's probability density, while the lower lobe moves toward boron to strengthen that part of the π bond. The fact that there is still some residual π bonding is reflected in the calculated B–P bond order (Table V).

To put the argument in its simplest form, we are led by the orbital kinetic energy data to the conclusion that the shift of one pair of electrons from a weak B–P π bond to a much more stable lone pair on phosphorus provides the main driving force for distortion from planarity and that this effect is largely offset by changes in other orbitals, such that the net energy change is relatively small.

The large changes in orbital kinetic energy observed here are consistent with the results of Murdoch and Magnoli.[24,25] They find that, when a substituent is introduced into a molecule, there are compensating large changes in electron density and in the spatial distribution of kinetic energy, even in cases where energy additivity is obeyed to a high degree.

Finally, we note that the reason for the planarity of the BH_2PH^- anion, in spite of the large out-of-plane angle at P in the neutral BH_2PH_2 molecule, is evident from a simple VSEPR argument. With nonplanar BH_2PH_2, there is a single lone pair. But planar BH_2PH^- already has one lone pair, which occupies an extensive region centered approximately about a line from P to the position previously occupied by the missing proton. Formation of a second lone pair from the B–P π bond would compete for space with this first lone pair, and the repulsion between adjacent lone pairs is sufficiently great to tip the precarious energy balance in favor of planarity.

Other factors to be considered are the different σ and π interactions in the neutral molecule and the anion. For the valence isoelectronic species BH_2NH_2 and BH_2NH^-, it has been shown by Hinde, Pross, and Radom[26] that the NH^- group interacts more favorably with BH_2 than does the NH_2 group, owing to an enhanced π interaction as well as to a diminished unfavorable σ interaction. That PH^- and PH_2 behave similarly in their interaction with BH_2 is indicated by the results of Magnusson,[1b] by the planarity of the anion compared to the nonplanarity of the neutral molecule, and by the bond orders listed in Table IV for BH_2PH^- and planar BH_2PH_2.

Comparison with Experimental Data for Substituted Compounds

Our results for the BH_2PH_2 molecule may be compared with crystal structure data for the organic derivative Mes_2BPPh_2.[4] Both exhibit a large out-of-plane angle at phosphorus, 70.0° for BH_2PH_2 and 39.8° for the organic derivative (dihedral angle 140.2°). The B–P bond length is somewhat longer in BH_2PH_2, 1.899 versus 1.859 Å. However, if one supposes that this distance depends on the out-of-plane angle at P in a linear fashion, then a linear interpolation of our planar and nonplanar results gives 1.859 Å for a 39.8° out-of-plane angle, identical with experiment for the organic derivative.

To compare other bond lengths, we examine the differences between bond lengths to phosphorus and boron, which would of course be the same if covalent radii were additive. These differences are indeed very similar: $r_e(PH) - r_e(BH) = 0.212$ Å; $r_e(PC) - r_e(BC) = 0.231$ Å. (Averages were used in the latter case.)

The organic derivative has a small twist angle of 1.6°. This is no doubt caused by the influence of neighboring molecules. For an isolated BH_2PH_2 molecule we find no twist.

For BH_2PH_2 the bond angles at boron are all very close to 120° (HBH = 120.3°; PBH = 119.7°), whereas in the organic derivative the CBC angle is 125.2° and the other angles are 116.2 and 117.9°. The sum of bond angles at B is 359.7° in the parent compound and 359.3° in the organic derivative, and thus in each case the boron atom is nearly planar.

For the anion BH_2PH^-, we may compare our data with crystal structure data for ion pairs containing the Mes_2BPMes^- anion.[5] Of greatest importance is the fact that the former is planar and in the latter the atoms C_2BPC are "virtually coplanar". The B–P bond lengths are closely similar, 1.829 Å in the parent anion and 1.835 Å in the organic derivative. The bond length differences are $r_e(PH) - r_e(BH) = 0.215$ Å and $r_e(PC) - r_e(BC) = 0.262$ Å.

The bond angle at phosphorus is in each case significantly less than 120°: it is 100.3° in BH_2PH^- and 108.2° in the organic derivative. In each case the PBX bond angle trans to the BPX angle is less than 120° (119.1° in the parent anion, 116.7° in the organic anion), while the other PBX angle is greater than 120° (124.5 and 126.0°).

For the lithium salt BH_2PHLi, we may compare our results with crystal structure data for three compounds of the type $R_2BPR'Li(Et_2O)_2$, where R is Mes, Mes, or Trip, and R′ is Mes, Cy, or *t*-Bu.[5] Here the differences are much greater than in the preceding examples. Instead of an approximately planar BH_2PH^- fragment with the Li^+ cation very far out of plane, the organic derivatives have planar C_2BP and planar BPCLi fragments, twisted at angles with respect to one another of 11.7, 3.8, or 33.3°. The B–P bond lengths are 1.823, 1.832, or 1.836 Å, not far from our planar value of 1.838 Å. But the P–Li bond lengths are significantly longer than ours: 2.451, 2.454, or 2.460 Å, compared to our 2.306 Å (planar) and 2.355 Å (nonplanar).

Likely factors responsible for these differences include complexing of the Li^+ cation by two ethyl ether molecules in the organic derivatives and the fact that nonplanar BH_2PHLi has an extremely shallow potential energy well, which apparently disappears when organic groups replace the hydrogen atoms.

Our B–P stretching frequency of 736 cm^{-1} for nonplanar BH_2PH_2 is much lower than the range of values 1412–1487 cm^{-1} observed in the infrared spectra of a series of phosphinodiarylboranes $R_2BPR'_2$ (R = aryl, R′ = alkyl or aryl).[3] In view of the excellent agreement previously observed for the P–P stretching frequencies of *trans*-HPPH and two substituted diphosphenes,[27] it seems unlikely that substitution of organic groups for hydrogen atoms would have such a large effect. Also, it is very likely that in the crystalline state, as well as in concentrated solution, these organic derivatives exist in oligomeric form.[28] Thus we are forced to question the assignment of the observed absorption band in the 1400–1500-cm^{-1} region to the B–P stretching frequency of a monomeric phosphinoborane.

Comparison with Boron–Nitrogen Compounds

The boranamine molecule, BH_2NH_2, has been the subject of several investigations, both theoretical and experimental.[26,29–33] Experimental study is difficult because this substance is an unstable gas that slowly polymerizes, but there is general agreement that it has an ethylene-like planar structure with a boron–nitrogen double bond. From its microwave spectrum, the B–N bond length has been found to be 1.39 Å and the bond angles are near 120° (NBH angle = 118.9°; BNH angle = 122.9°).[33] We find a qualitatively similar picture for the unstable planar form of BH_2PH_2: a PBH angle less than 120° (118.2°) and a BPH angle greater than 120° (124.8°). The B–H bond lengths are about the same (1.195 Å in BH_2NH_2 and 1.187 Å in BH_2PH_2).

Using a 4-31 G basis set, Hinde, Pross, and Radom found that the BH_2NH^- anion is also planar with a somewhat shorter B–N bond (1.360 Å) and a much smaller BNH angle, 115.1°.[26] The NBH angles are 121.2° (trans) and 126.4° (cis). Although the BH_2PH^- anion bond angles show a rough similarity [BPH angle = 100.3°; PBH angles = 119.1° (trans) and 124.5° (cis)], the

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(24) Murdoch, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 588.
(25) Murdoch, J. R.; Magnoli, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 2782.
(26) Hinde, A. L.; Pross, A.; Radom, L. *J. Comput. Chem.* **1980**, *1*, 118.
(27) Allen, T. L.; Scheiner, A. C.; Yamaguchi, Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1986**, *108*, 7579.
(28) Power, P. P. Private communication.
(29) Gerry, M. C. L.; Lewis-Bevan, W.; Merer, A. J.; Westwood, N. P. C. *J. Mol. Spectrosc.* **1985**, *110*, 153.
(30) Ha, T.-K. *J. Mol. Struct.: THEOCHEM* **1986**, *136*, 165.
(31) Westwood, N. P. C.; Werstiuk, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 891.
(32) Kingsmill, C. A.; Werstiuk, N. H.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1987**, *109*, 2870.
(33) Sugie, M.; Takeo, H.; Matsumura, C. *J. Mol. Spectrosc.* **1987**, *123*, 286.

decrease in BPH angle as compared to that in the planar form of the neutral molecule is much more extreme than the change in BNH angle. Furthermore, the B–P bond length is longer in the anion than in the planar form of the neutral molecule (1.829 and 1.807 Å, respectively), while in the nitrogen compounds the B–N bond length is shorter in the anion. The B–H bond lengths are slightly shorter in BH_2PH^- than in BH_2NH^-, while the proton affinity of BH_2PH^- is substantially lower than that of BH_2NH^- (15.2 and 18.0 eV, respectively).

All 12 vibrational frequencies have been measured experimentally for the BH_2NH_2 molecule.[29] When these results are compared with our data in Table I for planar BH_2PH_2, the most striking difference is of course the imaginary PH_2 wagging frequency versus 1005 cm^{-1} for the NH_2 wag. The BP stretching frequency of 827 cm^{-1} is much smaller than the BN stretch, 1337 cm^{-1}, but the torsion frequencies are about the same (723 cm^{-1} for the phosphorus-containing molecule and 763 cm^{-1} for the nitrogen-containing molecule). Of the remaining nine frequencies, the four that primarily involve P or N are smaller for the phosphorus-containing molecule, averaging about 76% of the nitrogen-containing molecule's frequencies. On the other hand, four of the five frequencies that primarily involve B are larger in planar BH_2PH_2. The largest difference is found with the BH_2 wag: 990 cm^{-1} for the phosphorus-containing molecule and 670 cm^{-1} for the nitrogen-containing molecule. However, the latter value as well as two other frequencies are estimates based on perturbations in another frequency.

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Tetrasolventoberyllium(II): High-Pressure Evidence for a Sterically Controlled Solvent-Exchange-Mechanism Crossover[1,2]

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The kinetics of solvent S exchanges on tetrasolventoberyllium(II) have been studied by variable-temperature and -pressure ^1H NMR spectroscopy with S = dimethyl sulfoxide (DMSO), trimethyl phosphate (TMPA), *N*,*N*-dimethylformamide (DMF), tetramethylurea (TMU), dimethylpropyleneurea (DMPU) or ^{17}O NMR spectroscopy with S = H_2O. The nonaqueous solvent-exchange reactions were studied in the inert diluent nitromethane to allow the determination of the k_1 and k_2 terms contributing to the observed rate k_{obs}, according to $k_{obs} = k_1 + k_2[S]$. For DMSO and TMPA the second-order rate law ($k_1 = 0$) implies an interchange I or associative A mechanism, whereas for TMU and DMPU the first-order rate law ($k_2 = 0$) indicates a dissociative D mechanism. For DMF both k_1 and k_2 terms contribute to k_{obs}. The pseudo-first-order rate constant k_{ex} for water exchange in neat H_2O was obtained from measurements of the bound-water transverse relaxation rate in the presence of Mn^{2+} as a relaxation agent. The results were $k_{ex}^{298} = 733 \pm 56\ s^{-1}$, $\Delta H^* = 59.2 \pm 1.5$ kJ mol^{-1}, $\Delta S^* = +8.4 \pm 4.5$ J K^{-1} mol^{-1}, and $\Delta V^* = -13.6 \pm 0.5$ cm^3 mol^{-1}. In the absence of a rate law, the very negative value of the activation volume ΔV^* is interpreted in terms of an A mechanism. The negative values of ΔV^* for the k_2 path (−2.5, −4.1, and −3.1 cm^3 mol^{-1} for S = DMSO, TMPA, and DMF) support evidence of an I_a or A mechanism, whereas the positive values of ΔV^* for the k_1 path (+10.5 and +10.3 cm^3 mol^{-1} for S = TMU and DMPU) confirm the operation of a D mechanism. These data suggest together that a mechanism crossover is taking place, from associative A for the smallest H_2O to dissociative D for the bulky TMU and DMPU.

Introduction

It is apparent from previous nonaqueous studies,[3-10] mainly from Lincoln's group, that the mode of activation for solvent exchange (eq 1) on the small tetrahedrally coordinated beryllium(II) ion

$$[BeS_4]^{2+} + 4S^* \overset{k_{ex}}{\rightleftharpoons} [BeS^*_4]^{2+} + 4S \qquad (1)$$

can vary from dissociative to associative depending upon the nature of the exchanging solvent. The mechanistic assignments[8] were based on correlations between both the stereochemistry and the electron-donating power of the solvent S and its propensity to exchange through a first- and/or second-order pathway in noncoordinating high-dielectric diluents, like nitromethane. Considering the success of high-pressure NMR spectroscopy in the elucidation of the mechanisms of solvent-exchange reactions on metal ions, in particular in showing a gradual mechanism changeover[11] along both series of divalent and trivalent high-spin first-row hexasolvated transition-metal ions, we have complemented the beryllium(II) nonaqueous solvent-exchange work by a high-pressure proton NMR study in the diluent nitromethane.

Further, the available variable-temperature data[12,13] for water exchange on beryllium(II) are still subject to criticism. The recourse to manganese(II) as relaxation agent for the bulk-water oxygen-17 NMR signal, successfully used in the case of $[Al(H_2O)_6]^{3+}$,[14] $[Ga(H_2O)_6]^{3+}$,[15] and $[Pd(H_2O)_4]^{2+}$,[16] will be very helpful in obtaining accurate exchange rates in dilute solutions. Moreover, in this case where no rate law is available due to the lack of a suitable diluent for water, the determination of the activation volume is essential for the assignment of the water-

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(1) High-Pressure NMR Kinetics. 44. For part 43, see ref 2. Taken, in part, from the Ph.D. thesis of P.-A. P.

(2) Turin-Rossier, M.; Hugi-Cleary, D.; Frey, U.; Merbach, A. E. *Inorg. Chem.* **1990**, *29*, 1374.

(3) Lincoln, S. F.; Tkaczuk, M. N. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85*, 433.

(4) Füldner, H. H.; Devia, D. H.; Strehlow, H. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 499.

(5) Delpuech, J. J.; Péguy, A.; Rubini, P.; Steinmetz, J. *Nouv. J. Chim.* **1977**, *1*, 133.

(6) Crea, J.; Lincoln, S. F. *J. Chem. Soc., Dalton Trans.* **1973**, 2075.

(7) Tkaczuk, M. N.; Lincoln, S. F. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, *86*, 147.

(8) Lincoln, S. F.; Tkaczuk, M. N. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, *86*, 221.

(9) Tkaczuk, M. N.; Lincoln, S. F. *Aust. J. Chem.* **1982**, *35*, 1555.

(10) Matwiyoff, N. A.; Movius, W. G. *J. Am. Chem. Soc.* **1967**, *89*, 6077.

(11) Merbach, A. E. *Pure Appl. Chem.* **1987**, *59*, 161.

(12) Neely, J. W. Ph.D. Thesis, University of California, Berkeley, 1971; Report UCRL-20580.

(13) Frahm, J.; Füldner, H. H. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84*, 173.

(14) Hugi-Cleary, D.; Helm, L.; Merbach, A. E. *Helv. Chim. Acta* **1985**, *68*, 545.

(15) Hugi-Cleary, D.; Helm, L.; Merbach, A. E. *J. Am. Chem. Soc.* **1987**, *109*, 4444.

(16) Helm, L.; Elding, L. I.; Merbach, A. E. *Helv. Chim. Acta* **1984**, *67*, 1453.