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Theoretical Studies of Borylphosphine and Its Conjugate Base. 2. Internal Rotation and Inversion Transition States

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The rotational transition states of BH_2PH_2 and BH_2PH^- have been investigated by the methods of ab initio molecular electronic structure theory using basis sets of high quality, and we have characterized them with respect to their molecular geometries, energies, dipole moments, normal vibrational modes, and harmonic vibrational frequencies. The BH_2PH_2 molecule has two rotational transition states, one of C_s symmetry at 10.0 kcal/mol and one of C_{2v} symmetry at 46.4 kcal/mol above the nonplanar ground state. The BH_2PH^- anion has a rotational transition state of C_s symmetry that is 33.5 kcal/mol higher in energy than the planar ground state and an inversion transition state of C_{2v} symmetry at 53.5 kcal/mol. Results for these molecules are compared with experimental data for derivatives of BH_2PH_2 and BH_2PH^- and with the BH_2NH_2 molecule.

Introduction

In a previous paper[1] we have presented the results of our theoretical studies of the ground states and certain excited states of BH_2PH_2, BH_2PH^-, and BH_2PHLi. In this paper we extend our analysis to the transition states of BH_2PH_2 and BH_2PH^-. An extensive discussion of the rationale for this work is given in ref 1, but it should be mentioned here that these results are of use in connection with experimental studies[2] of internal rotation energy barriers of several organic derivatives of BH_2PH_2 and BH_2PH^-.

There have been several previous reports[3–6] of energy barriers and B–P bond lengths in rotational transition states of BH_2PH_2, but we believe that these states are sufficiently important to warrant an extensive investigation using basis sets of high quality and including a study of the BH_2PH^- anion. Our results will be compared with the results of these other studies at the appropriate point.

Finally we will compare the BH_2PH_2 system with the BH_2NH_2 system, with particular regard for the relative strengths of the boron–phosphorus and boron–nitrogen π bonds.

Method

All calculations were performed with the Gaussian series of programs[7] by using standard keyword choices for methods and options but augmenting the basis set as described below. Molecular geometry specification used the *Z*-matrix approach. The following basis sets were used: (a) The contracted double-ζ Gaussian basis set of Huzinaga, Dunning, and Hay[8–10] was employed with the hydrogen atoms scaled by a factor of 1.2. This set is labeled DZ. (b) To the DZ basis set we added six d functions ($\alpha = 0.7$) for boron, six d functions ($\alpha = 0.5$) for phosphorus, and three p functions ($\alpha = 0.75$) for each hydrogen atom. The resulting basis set, designated DZ + P, may be described as B (9s5p1d/4s2p1d), P(11s7p1d/6s4p1d), H(4s1p/2s1p). (c) A basis set with diffuse functions was formed by adding to the DZ basis set one s function ($\alpha = 0.019$), one set of p functions ($\alpha = 0.019$), and two sets of d functions ($\alpha = 0.45$ and 0.95) for boron; by adding one s function ($\alpha = 0.035$), one set of p functions ($\alpha = 0.035$), and two sets of d functions ($\alpha = 0.25$ and 0.75) for phosphorus; and by using the DZ + P basis set for hydrogen. This basis set is designated DZ + 2P + diff.

The molecular geometry was determined for the restricted self-consistent-field (SCF) method, using an analytic gradient method. Harmonic vibrational frequencies and the corresponding normal modes were determined by analytic second derivatives of the SCF wave function. At the optimized SCF geometries CISD calculations were performed. The configuration interaction wave functions (CISD) included all singly and doubly excited configurations, except that all filled inner-shell molecular orbitals were frozen. The effect of unlinked quadruple excitations on the molecular energy was estimated by the Davidson correction.[11] (In the following text all energies are Davidson-corrected energies.) A preliminary geometry was obtained for each state using the DZ basis set. This was then refined with the DZ + P basis set and, for the BH_2PH^- anion, the DZ + 2P + diff basis set.

Table I. Properties of BH_2PH_2 Rotational Transition States[a]

	C_s transition state, $^1A'$	C_{2v} transition state, $^1A_1$
r_e(BP)	1.972	1.959
r_e(BH)	BH_1, 1.191 BH_2, 1.192	1.190
r_e(PH)	1.414	1.379
θ_e(PBH)	PBH_1, 120.3 PBH_2, 120.8	120.3
θ_e(HBH)	118.9	119.4
θ_e(BPH)	94.8	122.3
θ_e(HPH)	93.7	115.4
θ_e(out of plane at P)[b]	82.9	0.0
energy, SCF[c]	8.9	44.4
energy, CISD[c]	9.8	46.0
energy, Davidson cor[c]	10.0	46.4
dipole moment	1.11	0.60
vibrational freq, ν_e		
asym BH str	2784, A′	2795, B_2
sym BH str	2690, A′	2698, A_1
sym PH str	2510, A′	2714, A_1
asym PH str	2508, A″	2751, B_1
sym BH_2 bend	1280, A′	1295, A_1
sym PH_2 bend	1186, A′[d]	1122, A_1
BH_2 wag	1078, A″[e]	1068, B_1
BH_2 rock	931, A′[f]	852, B_2
BP str	699, A′[g]	717, A_1
PH_2 rock	695, A″[h]	517, B_1
PH_2 wag	637, A′[i]	985*i*, B_2
torsion	372*i*, A″	1011*i*, A_2

[a] All results were obtained with the DZ + P basis set. Bond lengths are in Å, angles are in deg, harmonic vibrational frequencies are in cm^{-1} for ^{11}B, ^{31}P, and ^{1}H isotopes, and dipole moments are in D. For the C_{2v} transition state, the BH_2 group is in the *yz* plane. [b] The out-of-plane angle at P is the angle between the BP axis and the PH_2 plane. [c] Energies are in kcal/mol relative to the nonplanar ground state. [d] sym PH_2 bend–PH_2 wag. [e] BH_2 wag – PH_2 rock. [f] PH_2 wag – BH_2 rock. [g] BP str – BH_2 rock – PH_2 wag. [h] PH_2 rock + BH_2 wag. [i] BH_2 rock + PH_2 wag + BP str.

BH_2PH_2 Transition States

The BH_2PH_2 molecule has a nonplanar ground state, **1**, and a planar form, **2**, that is 5.9 kcal/mol higher in energy.[1] The

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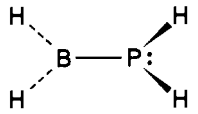
planar form is a transition state for inversion between two equivalent nonplanar forms. Properties of these two states are listed in ref 1.



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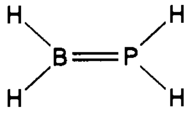

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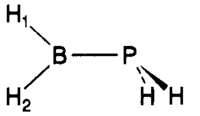
From its nonplanar ground state, the molecule may undergo internal rotation through either a low-energy transition state of C_s symmetry, **3**, at 10.0 kcal/mol above the ground state, or a high-energy (double saddle) transition state of C_{2v} symmetry, **4**, at 46.4 kcal/mol. Thus internal rotation (at 10.0 kcal/mol) is not much more costly than inversion (at 5.9 kcal/mol). Properties of the two rotational transition states are summarized in Table I. (Note that the C_{2v} conformation is also a transition state for inversion of one C_s transition state to its equivalent form.) For comparison, results obtained by other workers for the energies relative to the ground state of these various geometries are as follows: planar, 8.1,[3] 4.2,[5] and 4.5[6] kcal/mol; C_s transition state, 6.6,[3] 22.7,[4] 10.6,[5] and 10.4[6] kcal/mol; C_{2v} transition state, 48.5,[3] 44.2,[5], and 44.6[6] kcal/mol.



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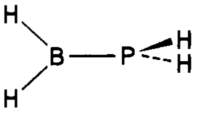

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Clearly the energetics of this molecule in its various conformations is dominated by the tendency of the phosphorus atom to assume a pyramidal form with small bond angles, and it has been shown[1] that this tendency is caused by the strong tendency of phosphorus to form a lone pair of electrons. This leads to BPH bond angles of only 102.7° in the nonplanar ground state and 94.8° in the C_s transition state, compared to 124.8° in the planar form and 122.3° in the C_{2v} transition state. The out-of-plane angles at phosphorus are also very different: 70.1° in the nonplanar ground state and 82.9° in the C_s transition state and of course 0.0° in the planar form and the C_{2v} transition state.

The fact that the energy of the C_{2v} transition state is so much higher than that of the C_s transition state suggests that the former is somewhat irrelevant. However, when the hydrogen atoms of BH_2PH_2 are substituted by large, bulky groups, the out-of-plane angles are typically much smaller.[2] Thus we may conceive that two sets of structures of BH_2PH_2 might serve as models for substituted BR_2PR_2 compounds. At one extreme, with large out-of-plane angles, we have the ground state and the C_s transition state, with an energy barrier of 10.0 kcal/mol. At the other extreme, with zero out-of-plane angles, we have the planar state and the C_{2v} transition state, with an energy barrier of 46.4 − 5.9 = 40.5 kcal/mol.

To see if intermediate nonplanarity might lead to a barrier of intermediate energy, we studied a structure similar to the nonplanar ground state, but with the torsion angle at phosphorus constrained to a value halfway between the planar form and the nonplanar ground state, and we also studied a structure similar to the C_s rotational transition state, but again having its torsion angle at phosphorus constrained to a value halfway between the two rotational transition states. The other structural parameters were fully optimized in both cases. The former had an energy 4.0 kcal/mol above the nonplanar ground state while the latter was at 32.9 kcal/mol, and thus the energy barrier halfway between the two extremes is 32.9 − 4.0 = 28.9 kcal/mol. This is roughly intermediate between the extremes of 10.0 and 40.5 kcal/mol; specifically, it is 62% of the way from the low-energy to the high-energy extreme. (These are Davidson-corrected energies; the corresponding figures for other energies are 57% for SCF energies and 61% for CISD energies.) Thus it seems reasonable to interpolate between the two extremes when trying to understand the rotational energy barriers of substituted compounds having intermediate structures.

Table II. Properties of BH_2PH^- Transition States[a]

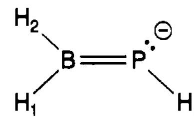
	rotation $^1A'$	inversion $^1A_1$
r_e(BP)	1.933 (1.935)	1.808 (1.813)
r_e(BH)	1.223 (1.216)	1.208 (1.202)
r_e(PH)	1.436 (1.430)	1.374 (1.374)
θ_e(PBH)	124.9 (123.9)	121.1 (120.5)
θ_e(HBH)	110.1 (112.3)	117.7 (119.1)
θ_e(BPH)	88.5 (89.7)	180.0 (180.0)
energy, SCF[b]	33.6 (29.6)	64.5 (60.6)
energy, CISD[b]	38.1 (32.8)	60.9 (55.3)
energy, Davidson cor[b]	39.3 (33.5)	59.7 (53.5)
dipole moment	1.57 (2.76)	1.56 (0.18)
vibrational freq, ν_e		
asym BH str	2460 (2500), A''	2591 (2619), B_2
sym BH str	2469 (2496), A'	2542 (2564), A_1
PH str	2347 (2369), A'	2762 (2754), A_1
sym BH_2 bend	1319 (1294), A'	1247 (1246), A_1
BH_2 wag	1085 (1075), A'[c]	960 (966), B_1
BH_2 rock	811 (787), A''	869 (855), B_2
BP str	712 (701), A'[d]	865 (837), A_1
BPH bend	474 (495), A'[e]	688*i* (710*i*), B_1[f]
torsion	1096*i* (987*i*), A''	1382*i* (1348*i*), B_2[g]

[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] Energies are in kcal/mol relative to the planar ground state. [c] BH_2 wag − BPH bend. [d] BP str − BH_2 wag − BPH bend. [e] BPH bend + BH_2 wag. [f] BPH out-of-plane bend. [g] BPH in-plane bend.

Pestana and Power have measured experimentally the rotational energy barriers for several substituted BH_2PH_2 compounds, and have analyzed the various factors which influence the barrier height.[2] For the five compounds where both barrier height and out-of-plane angle are known,[12] there is a rough correlation, with barrier height increasing as out-of-plane angle decreases. The low-energy extreme is similar to our BH_2PH_2 results, but the high-energy extreme has a barrier height only about half of what we would have expected. Clearly there are many other factors involved, such as steric and inductive effects, and the presence of more than one boron or phosphorus atom in the molecule.

BH_2PH^- Transition States

Unlike its parent molecule, the BH_2PH^- anion has a planar ground state,[1] **5**. Internal rotation produces the transition state of C_s symmetry, **6**, 33.5 kcal/mol higher in energy than the ground state. (Topology precludes having the two rotational transition states of the parent molecule.) Its properties are summarized in Table II. The anion's large rotational energy barrier of course has the same origin as the neutral molecule's large C_{2v} rotational energy barrier, namely, breaking of the boron–phosphorus π bond.



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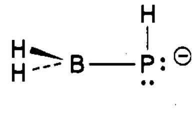

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A noteworthy feature of this transition state is the very small BPH bond angle. With the DZ + P basis set it is actually hyperextended to less than 90°, at 88.5°; with the larger DZ + 2P + diff basis set, it increases slightly to 89.7°. Presumably the small bond angle is a consequence of repulsion of the P–H bond by the electron densities of two lone pairs on phosphorus.

A reviewer has pointed out that one might have expected the BPH angle to increase in going from planar structure **5** to twisted structure **6** so as to put more p character into the phosphorus lone pair orbital, thereby enhancing overlap between the phosphorus lone pair and the empty p orbital of boron, whereas the calculated minimum-energy structures are contrary to this expectation. The

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(12) See Tables I and III of ref 2: $Mes_2BP(1\text{-}Ad)H$, 61.6°, 12.4 kcal/mol; $Mes_2BP(Ad)SiMe_3$, 31.8°, 14.9 kcal/mol; $Mes_2BP(1\text{-}Ad)PPh_2$, 27.5°, 21.1 kcal/mol; $Mes_2BP(Ph)SiPH_3$, 12.0°, 17.0 kcal/mol; $(Mes_2B)_2PPh$, 0°, 21.2 kcal/mol. The *p*-Me barriers are listed above as they constitute the most complete set.

Table III. Energies of Transition States[a]

molecule	energy		
	SCF	CISD	Davidson cor
BH_2PH_2, C_s (rotation)	−367.69683	−367.92314	−367.94503
BH_2PH_2, C_{2v} (rotation)	−367.64032	−367.86553	−367.88712
BH_2PH^-, C_s (rotation)	−367.08315 (−367.10587)	−367.30467 (−367.34710)	−367.32664 (−367.37399)
BH_2PH^-, C_{2v} (inversion)	−367.03390 (−367.05652)	−367.26838 (−367.31137)	−367.29413 (−367.34210)

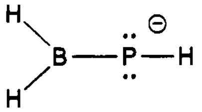
[a] Results with the DZ + 2P + diff basis set are listed in parentheses; other results were obtained with the DZ + P basis set. Energies are in hartrees.

BPH angle actually decreases (100.3° planar, 89.7° twisted).

Examination of the canonical molecular orbitals shows that for both structures it is the second-highest MO that primarily describes the phosphorus lone pair concentrated in and about the plane of the paper, and the two MOs are fairly similar. The coefficients of the relevant p functions of boron change sign in a favorable direction for this argument but their magnitudes remain very small, and the coefficients of the relevant phosphorus p functions actually decrease. Mulliken population analysis of the DZ basis set wave function also shows a decrease in phosphorus pπ orbital occupation (3.44 planar, 2.85 twisted) which is attributable to the loss of the π bond in the twisted structure.

We believe that the geometry adjustments attendant upon breaking the π bond in the twisted structure are best rationalized with the well-known tendency of phosphorus to pyramidalize and the resulting need to decrease the BPH angle so as to reduce bond-pair–lone-pair repulsions when phosphorus has two lone pairs in the twisted structure. The alternative of increasing the BPH angle tends toward the highly strained (for phosphorus single bonds) value of 180°, leading to the so-called inversion transition state, to which we now turn.

The BH_2PH^- anion also has an inversion transition state, **7**.



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Its properties are summarized in Table II, and the energies of the various transition states studied in this investigation are listed in Table III. The inversion transition state lies considerably higher in energy than the rotational transition state: 53.5 versus 33.5 kcal/mol above the planar ground state. Similar behavior by the phosphorus atom is exhibited in the diphosphene molecule,[13] where the inversion transition state is 66.2 kcal/mol above the *trans*-HPPH ground state, compared to 33.8 kcal/mol for the rotational transition state. An important difference between the HPPH and BH_2PH^- inversion transition states is that the former has only one imaginary vibrational frequency, the torsion frequency being real though quite small (64 cm^{-1}), whereas the latter has two imaginary frequencies.

Rotational energy barriers of two substituted BH_2PH^- anions (in ion pairs) have been measured experimentally by Pestana and Power.[2] Both are about 22 kcal/mol,[14] considerably smaller than our result for the parent anion. The presence of the Li^+ cation is expected to have only a slight effect on the barrier; steric effects are the likely cause of the difference.[2]

Comparison with BH_2NH_2

Unlike BH_2PH_2, the boranamine molecule, BH_2NH_2, has an ethylene-like planar ground state.[15] But like BH_2PH_2, it has a rotational transition state of C_s symmetry with a pyramidal group V atom. The C_s rotational barrier is about 30 kcal/mol: the results of various theoretical investigations are 33.3,[16] 29.4,[17] and 33.0[18] kcal/mol. This is much higher than the BH_2PH_2 C_s barrier of 10.0 kcal/mol. In fact, the more apt comparison between the two molecules is obtained by subtracting the inversion barrier. There is then only 10.0 − 5.9 = 4.1 kcal/mol between the C_s transition state and the planar form of BH_2PH_2. The marked difference between the two molecules is a manifestation of the phosphorus atom's much stronger tendency to have pyramidal geometry.

One might also be tempted to invoke, as another reason for this difference, the traditional view that phosphorus forms much weaker π bonds than nitrogen. We think that this would be a mistake, for to compare the strengths of the π bonds in the two molecules one should consider the energy of the C_{2v} rotational transition state relative to the planar structure in each case. By so doing one eliminates the different tendencies of N and P to form lone pairs.

The C_{2v} rotational barrier of BH_2NH_2 is about 40 kcal/mol, various investigations having given 40.5,[16] 43.1,[17] 38.3,[18] and 33.8[19] kcal/mol. For BH_2PH_2, we have seen that the C_{2v} transition state is 40.5 kcal/mol above the planar structure. Thus the phosphorus atom forms a π bond with boron that is of about the same strength as the boron–nitrogen π bond. It is the much stronger tendency of phosphorus to form pyramidal structures with lone pairs that has masked the strength of its π bonds. This conclusion is a unifying theme of this and previous ab initio electronic structure calculations of phosphorus involved in π bonds.[1,5,6] As yet another example of the substantial strength of the boron–phosphorus π bond, we mention its role in reducing the inversion barrier from a very high value [31.8 kcal/mol experimental, including an estimated correction for anharmonicity;[20] 34.2 kcal/mol calculated[21]] in phosphine, PH_3, to 5.9 kcal/mol[1] in BH_2PH_2.

Acknowledgment. We wish to express our thanks to Philip P. Power for helpful discussions.

Registry No. BH_2PH_2, 14809-29-1; BH_2PH^-, 100462-97-3.

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