Theoretical Studies of Boranamine and Its Conjugate Base. Comparison of the B–N and B–P π Bond Energies

Thomas L. Allen* **and William H. Fink**

Department of Chemistry, University of California, Davis, California 95616

Received November 24, 1992[⊗]

To answer questions that have arisen about the relative strengths of the B–N and B–P π bonds, we have investigated BH_2NH_2 and BH_2NH^- 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. With the aid of the latter we have been able to resolve several disagreements in the literature on the interpretation of the BH_2NH_2 infrared absorption spectrum. Aminoborane has two rotational transition states, one of C_s symmetry at 32.4 kcal/mol above the planar ground state and one of C_{2v} symmetry at 37.9 kcal/mol. The former has a BNH angle of 110.5° and an out-of-plane angle at nitrogen of 55.4°. Surprisingly, it is the d orbitals of the nitrogen atom that give the C_s transition state its lower energy and its approximately tetrahedral geometry at nitrogen. The BH_2NH^- anion has planar geometry and a BN bond length of 1.366 Å. It has an inversion transition state at 20.8 kcal/mol above the ground state, but it has no rotational transition state. Finally, comparison of BH_2NH_2 and BH_2PH_2 shows that the B–P π bond is stronger than the B–N π bond (40.5 versus 37.9 kcal/mol). Furthermore, it is shown that these bonds are overwhelmingly of pπ–pπ type.

Introduction

In our studies[1,2] of borylphosphine, BH_2PH_2, we made a series of comparisons with its nitrogen analogue, boroanamine, BH_2NH_2. Quite a bit is known about the latter molecule; for example, the structure[3] and vibrational frequencies[4–8] of the ground state have been determined experimentally. But for some properties, especially those relating to transition states and to the strength of the boron–nitrogen π bond, one must rely on theoretical investigations with small basis sets that gave inconsistent results. Even less is known about the anion BH_2NH^-. To rectify this situation we have undertaken a thorough study of BH_2NH_2 and BH_2NH^-. The results shed new light on the surprisingly strong boron–phosphorus π bond. They are also useful in the assignment of experimental vibrational frequencies to the various normal modes of BH_2NH_2.

Method

The Gaussian series of programs[9] was used throughout. Methods and options were selected by standard keyword choices. The Z-matrix approach was used to specify molecular geometry.

The following three basis sets were employed: (a) The DZ set used the contracted double-ζ Gaussian basis set of Huzinaga, Dunning, and Hay[10–12] with the hydrogen atoms scaled by a factor of 1.2. (b) The DZ + P basis set was formed from the preceding set by adding six d functions ($a = 0.7$) for boron, six d functions ($\alpha = 0.8$) for nitrogen, and three p functions ($\alpha = 0.75$) for each hydrogen atom. It may be described as B(9s5p1d/4s2p1d), N(9s5p1d/4s2p1d), H(4s1p/2s1p). (c) The DZ + 2P + diff basis set, with two sets of polarization functions as well as diffuse functions on the heavy atoms, was formed from the DZ basis set by adding 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 ($\alpha = 0.048$), one set of p functions ($\alpha = 0.048$), and two sets of d functions ($\alpha = 0.55$ and 1.05) for nitrogen; and by using the DZ + P basis set for hydrogen.

The restricted self-consistent-field (SCF) method with an analytic gradient method was used to determine the molecular geometry. Analytic second derivatives of the SCF wave function were used to determine the harmonic vibrational frequencies and corresponding normal modes. Configuration interaction wave functions (CISD) including all singly and doubly excited configurations (except that inner-shell molecular orbitals were frozen) were obtained at the optimized SCF geometries. The Davidson correction[13] was used to estimate the effect on the molecular energy of unlinked quadruple excitations. (In the following text all energies are Davidson-corrected energies.) After a preliminary geometry with the DZ basis set was obtained, the structure was refined with the DZ + P basis set and, for the BH_2NH_2 ground state and the BH_2NH^- anion, the DZ + 2P + diff basis set.

To obtain more accurate vibrational frequencies for the ground state of BH_2NH_2, a second-order Møller–Plesset (MP2) correlation energy correction was used, with no frozen orbitals.

Ground State of the BH_2NH_2 Molecule

Aminoborane has an ethylene-like planar ground state, **1**. Our results for the properties of this state are listed in Table I. For comparison, the r_s structural parameters determined experimentally[3] are as follows: r(BN), 1.391(2) Å; r(BH), 1.195(4) Å; r(NH), 1.004(2) Å; θ(HBH), 122.2(2)°; θ(HNH), 114.2(2)°. We regard the agreement between experiment and theory as satisfactory.

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1993.

(1) Allen, T. L.; Scheiner, A. C.; Schaefer, H. F., III. *Inorg. Chem.* **1990**, *29*, 1930.

(2) Allen, T. L.; Fink, W. H. *Inorg. Chem.* **1992**, *31*, 1703.

(3) Sugie, M.; Takeo, H.; Matsumura, C. *J. Mol. Spectrosc.* **1987**, *123*, 286.

(4) Gerry, M. C. L.; Lewis-Bevan, W.; Merer, A. J.; Westwood, N. P. C. *J. Mol. Spectrosc.* **1985**, *110*, 153.

(5) Anderson, W. D.; Gerry, M. C. L.; Lewis-Bevan, W.; Merer, A. J.; Steunenberg, D. M. *41st Symposium on Molecular Spectroscopy*, Columbus, OH, June 1986, cited by: Jacox, M. *J. Phys. Chem. Ref. Data* **1990**, *19*, 1387.

(6) Barry, J. A. Ph.D. Dissertation, University of British Columbia, 1988.

(7) Gerry, M. C. L. Private communication.

(8) Carpenter, J. D.; Ault, B. S. *J. Phys. Chem.* **1991**, *95*, 3502.

(9) Binkley, J. S.; Frisch, M. J.; Defrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fleuder, E. M.; Pople, J. A. *Gaussian 82*; Carnegie-Mellon University: Pittsburgh, PA, 1983. Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. *Gaussian 86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984. *Gaussian 88*; Gaussian, Inc.: Pittsburgh, PA, 1988.

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

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

(12) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3, pp 1–27.

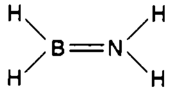
(13) Davidson, E. R. In *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; Reidel: Dordrecht, The Netherlands, 1974; p 17.

0020-1669/93/1332-4230$04.00/0

Table I. Properties of the BH_2NH_2 $^1A_1$ Ground State[a]

	SCF		MP2
	DZ + P	DZ + 2P + diff	DZ + P
r_e(BN)	1.395	1.393	1.399
r_e(BH)	1.194	1.194	1.191
r_e(NH)	0.996	0.995	1.011
θ_e(NBH)	119.4	119.2	118.6
θ_e(HBH)	121.2	121.5	122.7
θ_e(BNH)	123.1	123.0	123.2
θ_e(HNH)	113.9	114.0	113.6
dipole moment	1.74	1.68	1.72

[a] Bond lengths are in Å, angles are in deg, and dipole moments are in D.



1

In Table II we list the vibrational frequencies of aminoborane, both theoretical and experimental. Assignments of the two experimental B_1 frequencies require explanation. In their original paper[4] Gerry and co-workers state that "... the intense central spike of the C-type fundamental ν_7 at 1005 cm^{-1} (the BH_2 out-of-plane wagging motion) is obvious." However, in their Table I the 1005-cm^{-1} frequency was assigned to the NH_2 wag, and this assignment was carried forward in later work.[5] In ref 6, which represents the current view of the University of British Columbia group,[7] the B_1 assignments are reversed, and the 1005-cm^{-1} frequency is assigned to the BH_2 wag. Our theoretical results are in agreement with these latest assignments. (Assignment of the gas-phase 1005-cm^{-1} frequency to the BH_2 out-of-plane wag has been previously suggested by Carpenter and Ault,[8] who have also noticed the difference in ref 4 between text and table.)

With this reassignment there is satisfactory agreement between theory and experiment, the mean deviations being 7.5%, 7.2%, and 4.6% for the comparisons of columns 4, 5, and 6, respectively, with column 7. Previous workers[14,15] have found that for smaller molecules one can expect differences of ~4% between MP2 (DZP) harmonic frequencies and "experimental" harmonic frequencies if available. Also, in each case the result for the theoretical harmonic frequency lies above the experimental frequency, as is typical in studies of this kind.

In a study of the BH_2NH_2 planar ground state using a 3-21G basis set, Ha[16] reports that the higher B_1 frequency (1102 cm^{-1}) is the NH_2 wag and the lower one (828 cm^{-1}) is the BH_2 wag, a conclusion opposite to that reached above. We have repeated this work, and although we obtain the same SCF energy as reported by Ha, we again find that the higher B_1 frequency is the BH_2 wag (albeit mixed with a relatively small contribution from the NH_2 wag) and the lower frequency is the NH_2 wag, consistent with our results using larger basis sets. Furthermore, the 3-21G frequencies we obtain are somewhat different from those reported by Ha. The two B_1 frequencies are 1103 and 821 cm^{-1}. The others are as follows (cm^{-1}): A_1, 3736, 2700, 1831, 1438, and 1227; A_2, 874; B_2, 3827, 2768, 1241, 805.

Our results shed some light on two other reassignments of the gas-phase experimental frequencies[4] proposed by Carpenter and Ault:[8]

(1) They suggest reassignment of the 1131-cm^{-1} band[4,5] (most recent gas-phase observation[6] at 1122.2 cm^{-1}) from ν_{11} to ν_5, the BH_2 symmetric bend. Our MP2 (DZ + P) result for ν_{11} (1161 cm^{-1}) is closer to either 1131 or 1122.2 cm^{-1} than is our result for ν_5 (1181 cm^{-1}), and therefore we tend to side with the original assignment. (The differences are rather small, and the agreement is excellent in either case.) Furthermore, in support of their proposed reassignment Carpenter and Ault cite the observation by Gerry and co-workers[4] of "overlapping and additional structure belonging to the ^{10}B species." We can explain this observation on the basis of our results. We find that there is a strong component of BH_2 rock in ν_{11}; in fact, with the MP2 (DZ + P) method, the NH_2 rock and BH_2 rock contribute about equally to ν_{11} and ν_{12}.

Table II. Vibrational Frequencies and Intensities of the BH_2NH_2 $^1A_1$ Ground State[a]

sym	normal mode[b]	SCF DZ + P	SCF DZ + 2P + diff	MP2 DZ + P	expt[c] (gas phase)
ν_1 A_1	NH sym str	3840	3822	3674 (39)	3451
ν_2	BH sym str	2676	2659	2667 (94)	2495
ν_3	NH_2 sym bend + BN str	1765	1770	1660 (80)	1617
ν_4	BN str + BH_2 sym bend – NH_2 sym bend	1416	1420	1374 (58)	1337.47
ν_5	BH_2 sym bend – BN str	1214	1211	1181 (<1)	1145
ν_6 A_2	torsion	867	864	887 (0)	837[e]
ν_7 B_1	BH_2 wag	1114	1110	1062 (21)	1004.68[f]
ν_8	NH_2 wag	625	624	619 (211)	612.20s[f]
ν_9 B_2	NH asym str	3946	3927	3789 (37)	3533.8
ν_{10}	BH asym str	2748	2730	2765 (153)	2564
ν_{11}	NH_2 rock – BH_2 rock	1216	1216	1161[d] (36)	1122.2
ν_{12}	BH_2 rock + NH_2 rock	792	789	754[d] (<1)	742 vw

[a] Harmonic vibrational frequencies are in cm^{-1} for ^{11}B, ^{14}N, and ^1H isotopes. The molecular plane is taken as the *yz* plane. Infrared intensities in km mol^{-1} are shown in parentheses. [b] 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. The NH_2 symmetric bend and BN stretch are considered in phase if the N atom moves toward the H atoms as the HNH angle increases. [c] Frequencies from ref 6; intensities from ref 5. [d] The two motions have about equal weight. [e] Reference 5: "Value estimated from appearance of perturbation." [f] The two B_1 assignments in ref 4 and 5 have been reversed—see text.

(2) They suggest reassignment of the gas-phase 1225-cm^{-1} band[4,5] (most recent gas-phase observation[6] at 1145 cm^{-1}) from ν_5, the BH_2 symmetric bend, to an overtone of one of the fundamental frequencies, on the basis of a ^{15}N shift observed for an argon matrix band at 1216 cm^{-1}. However, we find that the BN stretch contributes significantly to ν_5 and that might explain the ^{15}N shift. Our MP2 (DZ + P) result of 1181 cm^{-1} for ν_5 is consistent with the newer experimental result[6] of 1145 cm^{-1}, and we are therefore inclined to support that assignment. A definitive resolution of the ν_5 assignment will probably be difficult because our predicted intensity indicates that it is very weak and it could be masked by an overtone or combination band.

A proposal by Brint and co-workers[17] to interchange the assignments of ν_8 and ν_{12} was based on the earlier experimental data[4] which had $\nu_8 > \nu_{12}$. The newer data[5,6] have $\nu_8 < \nu_{12}$ in agreement with the theoretical results, and thus no interchange is necessary.

The vibrational intensities in Table II may be of use in sorting out any remaining ambiguities in assigning the various vibrational bands. At this point we have only the designations "strong" for ν_8 and "very weak" for ν_{12} in ref 5, and these are consistent with the theoretical intensities. (In addition, ν_6 is of course infrared-inactive.)

Transition States of BH_2NH_2

The BH_2NH_2 molecule has two rotational transition states, one of lower energy and C_s symmetry, **2**, and one of higher energy

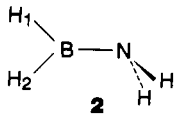
---

(14) Simandiras, E. D.; Handy, N. C.; Amos, R. D. *Chem. Phys. Lett.* **1987**, *133*, 324.

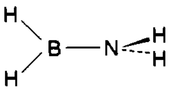
(15) Simandiras, E. D.; Amos, R. D.; Handy, N. C.; Lee, T. J.; Rice, J. E.; Remington, R. B.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1988**, *110*, 1388.

(16) Ha, T.-K. *J. Mol. Struct.* **1986**, *136*, 165.

(17) Brint, P.; Sangchakr, B.; Fowler, P. W. J. Chem. Soc., *Faraday Trans. 2* **1989**, *85*, 29.



2



3

and C_{2v} symmetry, **3**. The former has an out-of-plane angle at nitrogen of 55.4° and a BNH angle of 110.5°, and it lies 32.4 kcal/mol above the planar ground state. The latter is at 37.9 kcal/mol, and thus relaxation of the nitrogen atom from trigonal planar to approximately tetrahedral geometry lowers the energy by 5.5 kcal/mol. Surprisingly, almost all of this energy difference must be ascribed to the effect of polarization functions, for with a DZ basis set the corresponding energy change is only 0.2 kcal/mol (from 39.7 to 39.5 kcal/mol) and there is very little change in geometry. (The BNH angle decreases slightly in going from **3** to **2**, (122.8° to 121.8°), and the out-of-plane angle at nitrogen of **2** is only 15.8°.) The properties of these two transition states are summarized in Table III. It should be noted that **3** is also a transition state for inversion of **2** to its equivalent form. Previous results for the two rotational energy barriers are as follows (kcal/mol): C_s, 33.3,[18] 29.4,[19] 33.0;[20] C_{2v}, 40.5,[18] 43.1,[19] 38.3,[20], 33.8.[21]

There is a striking contrast between the C_s rotational transition states of BH_2NH_2 and its phosphorus analogue, BH_2PH_2. With the DZ + P basis set, the latter is only 10.0 kcal/mol above the nonplanar ground state and only 4.1 kcal/mol above the planar form.[2] Its BPH angles are 94.8°, and its out-of-plane angle at phosphorus has the extremely high value of 82.9°, in keeping with the well-known tendency of tervalent phosphorus to approach an orthogonal geometry. On the other hand the C_{2v} transition states of BH_2NH_2 and BH_2PH_2 are remarkably similar, with energies of 37.9 and 40.5 kcal/mol,[2] respectively, above the planar forms. As measures of π-bond energies, these C_{2v} barriers are of particular importance; we shall return to this point in a later section.

Addition of polarization functions has relatively little effect on the BH_2PH_2 rotational barriers. With a DZ basis set, they are 9.6 (C_s) and 40.8 (C_{2v}) kcal/mol above the planar form,[22] compared to the 4.1 and 40.5 kcal/mol noted above with the DZ + P basis set. For the C_s rotational transition state, the out-of-plane angles at phosphorus are 80.2° (DZ) and 82.9° (DZ + P). It thus appears that d orbitals on the nitrogen atom, but not on the phosphorus atom, are important for nonplanarity.

To better understand the role being played by the polarization functions in establishing the pyramidal geometry about N and P, we first examined the molecular orbitals. In BH_2NH_2 the coefficients of the nitrogen d orbitals in the occupied molecular orbitals are really quite small. In this respect a little bit goes a long way. (The coefficient of largest magnitude was –0.0346 for d_{xz} in the 1a″ MO.) We surmise that the main effect of the d orbitals on N is to concentrate the lone pair and bonding orbitals in space, thus reducing interpair repulsions and allowing the out-of-plane angle at nitrogen to increase.

Table III. Properties of BH_2NH_2 Rotational Transition States[a]

	C_s transition state, $^1A'$	C_{2v} transition state, $^1A_1$
r_e(BN)	1.471	1.458
r_e(BH)	BH_1, 1.196 BH_2, 1.204	1.203
r_e(NH)	1.008	0.996
θ_e(NBH)	NBH_1, 120.0 NBH_2, 122.1	121.6
θ_e(HBH)	117.8	116.8
θ_e(BNH)	110.5	123.0
θ_e(HNH)	103.9	113.9
θ_e(out of plane at N)[b]	55.4	0.0
energy, SCF[c]	29.1	33.2
energy, CISD[c]	31.7	37.0
energy, Davidson cor[c]	32.4	37.9
dipole moment	1.59	0.96
vibrational freq, ν_e		
asym NH str	3762, A″	3950, B_1
sym NH str	3700, A′	3846, A_1
asym BH str	2709, A′	2663, B_2
sym BH str	2623, A′	2615, A_1
sym NH_2 bend	1700, A′	1687, A_1
sym BH_2 bend	1364, A′	1371, A_1
BH_2 wag – NH_2 rock	1236, A″	1216, B_1
BN str – BH_2 sym bend – NH_2 sym bend	1127, A′	1152, A_1
BH_2 rock	1060, A′[d]	1025, B_2
NH_2 rock + BH_2 wag	797, A″	711, B_1
NH_2 wag	758, A′[e]	652*i*, B_2
torsion	752*i*, A″	1084*i*, A_2

[a] All results were obtained with the DZ + P basis set. See footnotes of Tables I and II for units, etc. For C_{2v} symmetry, the BH_2 group is in the *yz* plane. [b] The out-of-plane angle at N is the angle between the BN axis and the NH_2 plane. [c] Energies are in kcal/mol relative to the planar ground state. [d] BH_2 rock – NH_2 wag. [e] NH_2 wag + BH_2 rock.

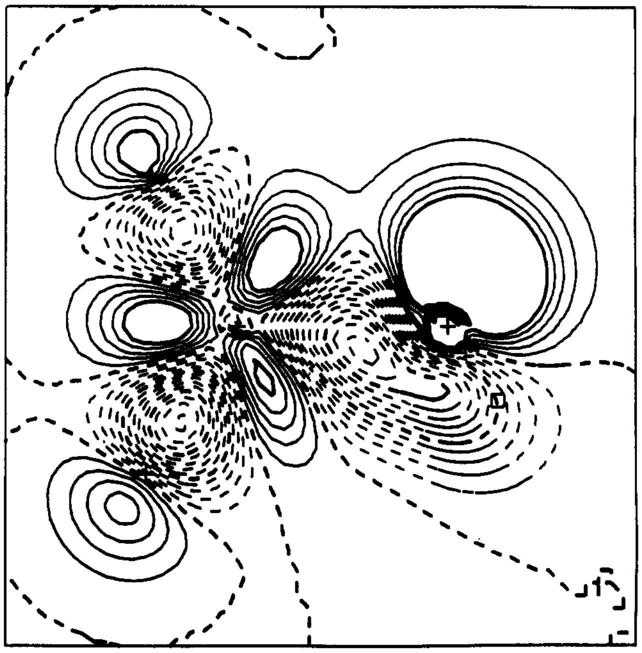


Figure 1. Difference electronic density for the BH_2NH_2 C_s rotational transition state, in a plane passing through the BH_2 nuclei. Contours are shown for the difference in electronic density between calculations with and without polarization functions (DZ + P – DZ). BH_2 (left) and N (right) nuclei in the plane are indicated by +. Projections onto the plane of NH_2 hydrogen nuclei are indicated by □. Contour maximum is 0.05 e/Å^3, and contours decrease at 0.01 e/Å^3 intervals. Solid curves indicate an increase in electronic density on adding polarization functions; dashed curves indicate a decrease.

Figures 1 and 2 present contour diagrams of the difference in electronic density between calculations with and without polarization functions for BH_2NH_2 and BH_2PH_2, respectively. The molecular geometry in each case was that optimized for the C_s transition state structure with the DZ + P basis set. The contours are displayed for a slice through the molecule containing the BH_2 plane. The BH_2 plane bisects the NH_2 (PH_2) angle for the C_s structure, and the prominent feature in solid contours on the right may be identified with the respective lone pairs. We also examined contours in the plane perpendicular to this one, and in the NH_2 plane, but in the interest of economy present only these which provide the greatest insight. The positive contours

---

(18) Gropen, O.; Seip, H. M. *Chem. Phys. Lett.* **1974**, *25*, 206.

(19) Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3402.

(20) Ortiz, J. V. *Chem. Phys. Lett.* **1989**, *156*, 489.

(21) Budzelaar, P. H. M.; Kos, A. J.; Clark, T.; Schleyer, P. v. R. *Organometallics* **1985**, *4*, 429.

(22) Allen, T. L.; Fink, W. H. Unpublished work.

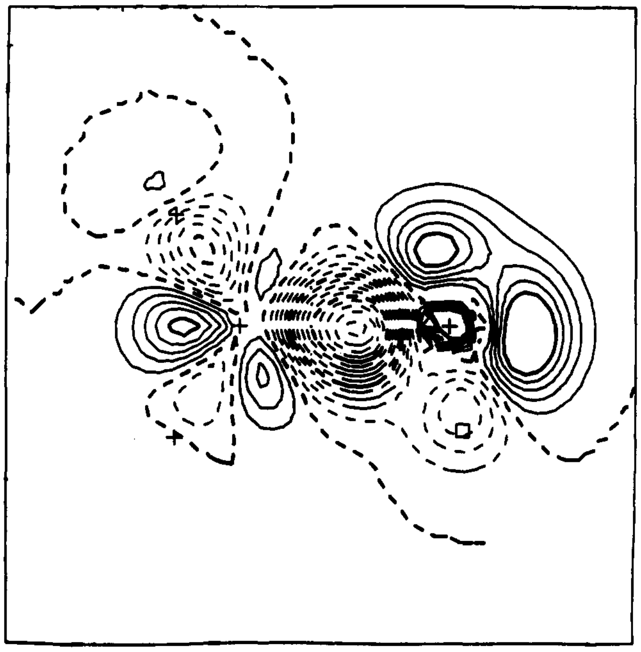
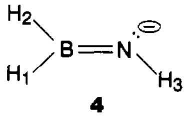


Figure 2. *Difference electronic density for the BH_2PH_2 C_s rotational transition state, in a plane passing through the BH_2 nuclei. The same conventions were followed as in Figure 1, except that P replaces N.*

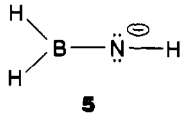
correspond with those regions of space which have augmented electron density upon addition of the polarization functions to the basis set, and the dashed contours correspond with those regions of space which have had electron density removed to accomplish these augmentations. A small square is plotted at the location of the projection of the hydrogens attached to nitrogen (phosphorus) into this plane. It is clear that the effect of the addition of the polarization functions to the basis set has been to move some electron density from the region between the amino (phosphino) hydrogens and the BN (P) bond into the lone pair. In both figures the maximum positive contour plotted is 0.05 electron/Å^3. This value is approximately the maximum change observed in the region of the phosphorus lone pair, but the nitrogen change continues to increase to about 0.2 electron/Å^3 in contours not shown to enhance legibility. These contour diagrams confirm the greater importance of d orbitals on nitrogen over their role on phosphorus for this basis set.

The BH_2NH^- Anion

The conjugate base of aminoborane, BH_2NH^-, has a planar ground state of C_s symmetry, **4**. It also has an inversion transition state of C_{2v} symmetry, **5**. In these respects it resembles its phosphorus analogue, BH_2PH^-.[1,2] But unlike BH_2PH^- it has no rotational transition state. The properties of **4** and **5** are summarized in Table IV. It may be seen that, with the largest basis set, the inversion transition state lies 20.8 kcal/mol above the ground state. This is much lower than the corresponding figure for BH_2PH^-, 53.5 kcal/mol.[2]

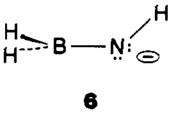


4



5

We studied a constrained rotational transition state, **6**, in which the BNH angle was fixed at the same value as in the planar ground state and the other geometrical parameters were optimized. With the largest basis set it was 30.3 kcal/mol above the ground state, or 9.5 kcal/mol above the inversion transition state. But when the constraint was removed, the anion relaxed to the inversion transition state. In fact, the BNH force decreased monotonically as the BNH angle was changed from 85 to 180°.



6

Table IV. Properties of the BH_2NH^- Ground and Inversion Transition States[a]

	ground state, $^1A'$	inversion, $^1A_1$
r_e(BN)	1.366 (1.366)	1.329 (1.328)
r_e(BH)	BH_1, 1.244 (1.246) BH_2, 1.235 (1.234)	1.259 (1.258)
r_e(NH)	1.010 (1.009)	0.978 (0.978)
θ_e(NBH)	NBH_1, 125.5 (124.6) NBH_2, 121.6 (121.7)	125.1 (124.8)
θ_e(HBH)	112.9 (113.7)	109.9 (110.4)
θ_e(BNH)	110.7 (110.9)	180.0 (180.0)
prot aff/energy, SCF[b]	17.52 (17.29)	21.5 (19.8)
prot aff/energy, CISD[b]	17.41 (17.11)	22.9 (20.5)
prot aff/energy, Davidson cor[b]	17.33 (17.02)	23.4 (20.8)
dipole moment[c]	1.57 (1.72)	1.79 (1.30)
vibrational freq, ν_e		
NH str	3661 (3655), A′	4169 (4131), A_1
sym BH str	2392 (2377), A′	2256 (2239), A_1
asym BH str	2301 (2265), A′	2127 (2091), B_2
BN str + *sym* BH_2 bend	1510 (1491), A′[d]	1582 (1551), A_1
sym BH_2 bend − BN str	1253 (1238), A′[e]	1302 (1287), A_1
BNH bend − BH_2 rock	1201 (1179), A′	1049*i* (995*i*), B_2[f]
BH_2 wag	1048 (1046), A″	1060 (1061), B_1
torsion	977 (950), A″	489 (514), B_1[g]
BH_2 rock + BNH bend	884 (874), A′	1032 (1011), B_2[h]

[a] Results with the DZ + 2P + diff basis set are listed in parentheses; other results were obtained with the DZ + P basis set. See footnotes of Tables I and II for units, etc. [b] The proton affinity of the ground state is the energy in eV relative to the planar BH_2NH_2 ground state with the same basis set. The energy of the inversion transition state is in kcal/mol relative to the BH_2NH^- ground state. [c] The dipole moment is taken with respect to the center of mass. [d] BN str + sym BH_2 bend + BNH bend. [e] sym BH_2 bend − BN str − BNH bend. [f] BNH in-plane bend. [g] BNH out-of-plane bend. [h] BH_2 rock + BNH in-plane bend.

For the related molecules HN=NH and HP=PH it has been noted previously that the inversion barrier lies below the rotation barrier for the nitrogen compound, while the opposite is true of the phosphorus compound.[23] A similar situation holds for BH_2NH^- and BH_2PH^-, except that with BH_2NH^- one can obtain the rotational transition state only by means of a constraint. As a consequence, the BH_2NH^- inversion transition state has only one imaginary vibrational frequency, compared to two for the corresponding BH_2PH^- state.

Unfortunately there seem to be no experimental data for comparison with the results in Table IV. In a theoretical study of the ground state, Hinde, Pross, and Radom[24] obtained the following structural parameters with a 4-31 G basis set: BN, 1.360 Å; BH_1, 1.241 Å; BH_2, 1.228 Å; NH, 1.016 Å; NBH_1, 126.4°; NBH_2, 121.2°; BNH, 115.1°.

Table V summarizes the energies of the various states studied in this investigation.

Comparison of B-N and B-P π Bond Energies

Not too many years ago a popular textbook stated that phosphorus had no known pπ–pπ bonds, but recent studies have shown that the phosphorus atom can form planar structures with remarkably strong π bonds. This characteristic is usually masked by the much stronger tendency of phosphorus to form pyramidal structures having lone pairs. Schade and Schleyer[25] concluded that "Planarized phosphino groups are good to excellent pπ-donors,

---

(23) Allen, T. L.; Scheiner, A. C.; Yamaguchi, Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1986**, *108*, 7579.

(24) Hinde, A. L.; Pross, A.; Radom, L. *J. Comput. Chem.* **1980**, *1*, 118.

(25) Schade, C.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1399.

Table V. Energies of BH_2NH_2 and BH_2NH^- States[a]

state	energy		
	SCF	CISD	Davidson cor
BH_2NH_2, ground	−81.510 55 (−81.515 16)	−81.779 48 (−81.797 74)	−81.802 28 (−81.822 39)
BH_2NH_2, C_s rotational	−81.464 17	−81.728 90	−81.750 72
BH_2NH_2, C_{2v} rotational	−81.457 70	−81.720 56	−81.741 93
BH_2NH^-, ground	−80.866 82 (−80.879 71)	−81.139 83 (−81.168 94)	−81.165 33 (−81.197 07)
BH_2NH^-, inversion	−80.832 51 (−80.848 08)	−81.103 29 (−81.136 24)	−81.128 11 (−81.163 95)

[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.

sometimes comparable to amines." Coolidge and Borden[26] have found that in borylphosphine, BH_2PH_2, the conjugation energy and the pyramidalization energy are similar in magnitude (but opposite in sign) at various pyramidalization angles. In our own study of borylphosphine,[2] we found that the B–P π bond is about as strong as the B–N π bond, but it was difficult to compare the two because of considerable uncertainty about the latter. (Earlier studies had a spread of about 10 kcal/mol, from 33.8[21] to 43.1[19] kcal/mol.)

Now that we have examined the boranamine molecule with the aid of extensive basis sets and configuration interaction computations, we find that the B–P π bond is actually somewhat *stronger* than the B–N π bond. We here use a common measure of π-bond energy—the energy difference between planar BH_2XH_2 and the 90° twisted (C_{2v}) BH_2XH_2. With Davidson-corrected energies, the B–N π bond energy is 37.9 kcal/mol (Table III), compared to a B–P π bond energy of 40.5 kcal/mol.[2] (Similar differences are found with SCF and CISD energies.)

Of course, the question arises, are these mainly pπ–pπ or pπ–dπ bonds? Our studies indicate that they are overwhelmingly of pπ–pπ type. With the DZ basis set, which has no d orbitals, the comparable energies are 39.7 kcal/mol for B–N (this study) and 40.8 kcal/mol for B–P.[22]

The fact that the SCF π-bond energies are somewhat lower than those with configuration interaction indicates that hyperconjugation may be of some minor importance in these molecules. On the other hand, the absence of any significant variation of the difference between the B–N and B–P results at different levels of theory suggests that the contribution of hyperconjugation is rather similar in the two molecules.

Another common measure of bond strength is bond length. Using the DZ + P results for BH_2NH_2, we find that the B–N bond is 4.3% shorter in the planar form than in the twisted (C_{2v}) form. The corresponding shortening of the B–P bond in BH_2PH_2 is 7.8%, again indicating that the B–P π bond is the stronger of the two.

Table VI. Dipole Moments[a] and Mulliken Atomic Charges

state	dipole moment	component[b]	B	N	each H on B	each H on N
BH_2NH_2, planar	1.74	−1.74	0.06	−0.47	−0.03	0.24
rot tr, C_s	1.59	−0.16	0.20	−0.56	−0.02 (H_1) −0.04 (H_2)	0.21
rot tr, C_{2v}	0.96	−0.96	0.22	−0.64	−0.04	0.24
BH_2NH^-, planar	1.57	0.05	−0.23	−0.62	−0.14 (H_1) −0.12 (H_2)	0.10
inv tr	1.79	−1.79	−0.21	−0.64	−0.15	0.16

[a] Dipole moments are in D. [b] Component of the dipole moment along the BN internuclear axis, taken from N to B.

A contrary trend would seem to be provided by examination of the vibrational frequencies. Using DZ + P SCF data, the BN stretching frequency increases by 23% on going from the twisted (C_{2v}) form to the planar form for BH_2NH_2 but only by 15% for BH_2PH_2. However, these frequencies include the effect of the larger phosphorus mass on the frequency. When the BN stretching constant from the force constant matrix is examined, the corresponding changes are 28% (from 0.370 to 0.473 atomic units) and 33% (from 0.184 to 0.245 atomic units), respectively, indicating a slightly tighter BP bond. Of course these are only measures of the shape of the potential well in the vicinity of the energy minima and not the well depth itself.

As still another measure of π-bond strength, consider what happens to the HOMO energy when we change from the planar to twisted (C_{2v}) structure. For the planar form, the HOMO is the $1b_1$ (BH_2NH_2) or $2b_1$ (BH_2PH_2) MO, occupied by the π bonding electrons. For the twisted form, the HOMO is the $2b_2$ (BH_2NH_2) or $3b_2$ (BH_2PH_2) MO, occupied by electrons in a sort of bifurcated lone pair on the nitrogen or phosphorus atom, with the electron density distributed equally on either side of the XH_2 plane.

For BH_2NH_2 the HOMO energy changes from −11.86 eV in the planar form to −9.66 eV in the twisted form, an increase of 2.20 eV. For BH_2PH_2 the corresponding data are −8.93 and −7.54 eV, or an increase of 1.39 eV. Thus the π-bonding electrons in planar BH_2NH_2 lie at a much more negative energy, relative to the twisted form, that do the π-bonding electrons in planar BH_2PH_2 relative to its twisted form. Taking these data in isolation, one would conclude that the BN π bond is the stronger of the two. The fact that the total energy of the molecule indicates the opposite result, as discussed above, shows that one cannot isolate the electronic structure changes taking place to a single canonical MO energy.

Dipole Moments and Atomic Charges

In each of the structures studied here, the Mulliken populations indicate that the nitrogen atom is more negative than the boron atom. But, because of the influence of the hydrogen atoms, the polarity along the BN internuclear axis has the direction $B^-–N^+$, with one exception. That exception occurs for the planar BH_2NH^- anion. The relevant data are summarized in Table VI.

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

---

(26) Coolidge, M. B.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 1704.