Aminoborane: He I Photoelectron Spectrum and Semiempirical/ab Initio Investigation of the Ground and First Excited Cationic States

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Abstract: The He I photoelectron spectrum of the unstable aminoborane molecule, H_2NBH_2, is reported. This species, produced by controlled thermal decomposition of the ammonia–borane adduct, has five ionization potentials up to 21.2 eV, which can be correlated with those of the isoelectronic ethylene molecule. Koopmans' theorem calculations for the ground-state molecule using semiempirical (MNDO) and ab initio (3-21G, 6-31G*) SCF methods give a good correspondence with the observed IP's. At this level the first occupied orbital is π. The ground and first excited cationic states were geometry optimized at the 6-31G* level and the relative ordering of these states was confirmed with the inclusion of correlation energy to third order. The ground cationic state ($^2B_1$) arising from ionization of a π electron is predicted to be twisted (90°) with an increased BN bond length. The first excited cationic state ($^2B_2$) is planar within C_{2v} limitations with a distorted BH_2 group.

Aminoborane, H_2NBH_2, an inorganic analogue of ethylene, has occupied a fundamental position in boron–nitrogen chemistry, following the proposal of its intermediacy in the formation of borazine, $(HNBH)_3$, from diborane and ammonia.[1] As one of the simplest species with a BN bond, it has also been the subject of considerable theoretical attention, ranging from extended Hückel to ab initio CI methods[2–10] with particular emphasis on the questions of planarity, the torsional barrier, the BN π character, and the valence bond description which places a positive charge on N. Spectroscopic observations of a discrete monomer have, however, been hampered by the instability of H_2NBH_2 in the gas phase due to formation of ring compounds and a variety of polymeric species.[11,12] Mass spectrometric and thermogravimetric methods have suggested that H_2NBH_2 is a component of the vapors above ammonia borane (NH_3BH_3),[13,14] can result from the pyrolysis of $(H_2NBH_2)_2$,[15] and is also produced as one of the products in the radio frequency discharge of borazine, identified by low-temperature solid-phase IR spectra.[16] Vibrational frequencies have been calculated by using the semiempirical MNDO method[17] and compared with the solid-phase IR spectrum.

Unambiguous evidence for gas-phase aminoborane has only recently been provided by observation of the microwave spectrum following flow pyrolysis (500 °C) of an ammonia/diborane mixture.[18,19] Analysis of five isotopic species confirmed the planar nature of this molecule and the BN double bond character (r(BN) = 1.391 Å). More recently a simple and effective preparative procedure has been devised which generates H_2NBH_2 in good yield,[20] thereby permitting FTIR observation of all 9 infrared active fundamentals above 700 cm^{-1}.

We now report the He I photoelectron (PE) spectrum of this semistable molecule, an assignment of the molecular orbitals, an assessment of the BN π bond, and a comparison with semiempirical and ab inito electronic structure calculations at, and beyond, the Hartree-Fock (HF) level. Of some relevance is the structure of the ground ionic state of $H_2NBH_2^+$ which like that in $C_2H_4^+$ is predicted to be twisted.

Experimental Section

Aminoborane was prepared by controlled thermal decomposition of ammonia borane.[20] A commercial sample (Alfa Products) was heated to 80–90 °C, and the resulting vapors were pumped slowly through the ionization chamber of a photoelectron spectrometer specifically designed to study unstable species.[21] The initial vapor-phase products of a fresh sample showed evidence for an (as yet) unknown species, which after a short time was replaced by a spectrum assigned to H_2NBH_2. At 80–90 °C, copious evolution of H_2NBH_2 was obtained, and for optimum results the temperature was then lowered to 62–65 °C. A second furnace maintained at ca 250 °C ensured complete decomposition of the starting material. Spectra were calibrated by using the known ionization potentials (IP's) of H_2 and NH_3. Resolution was typically 30–40 meV but was difficult to maintain due to pressure shifts.

Computational Methods

The semiempirical MNDO method[22] with the Davidon–Fletcher–Powell geometry optimization procedure was used to determine molecular and cationic geometries with complete relaxation of all symmetry constraints. Orbital energies were compared (within the limitations of Koopmans' theorem) to the observed IP's.

Ab initio calculations were performed on the ground-state molecule at the restricted HF SCF level by using GAUSSIAN 82[23] with the internal 3-21G, 4-31G, and 6-31G* split valence basis

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Table I. Experimental IP's and Calculated Orbital Energies for H_2NBH_2

		calculated (this work)				calculated				
orbital	IP (eV)[a]	3-21G	4-31G	6-31G*	MNDO	EH[c]	ab initio[d]	ab initio[d]	ab initio[d]	ab initio[e]
	(10.8)									
$1b_1(\pi)$	11.36[b]	11.77	11.81	11.78	11.86	13.77	12.11	12.49	12.24	11.94
$2b_2$	12.08	12.44	12.49	12.49	12.38	13.11	12.46	12.35	12.00	12.49
$5a_1$	14.12	14.89	14.99	14.97	15.44	14.46	14.86	15.26	14.88	15.08
$1b_2$	17.18	18.53	18.65	18.63	18.59	16.40	19.35	19.24	18.86	18.57
$4a_1$	18.12	19.36	19.47	19.45	21.05	18.82	19.56	19.48	19.29	19.59

[a] Adiabatic IP in parentheses, ±0.1 eV (all other values ±0.05 eV). [b] Vibrational structure, 1100 ± 80 cm^{-1}. [c] Reference 2. [d] Reference 4 with three different basis sets. [e] Reference 8.

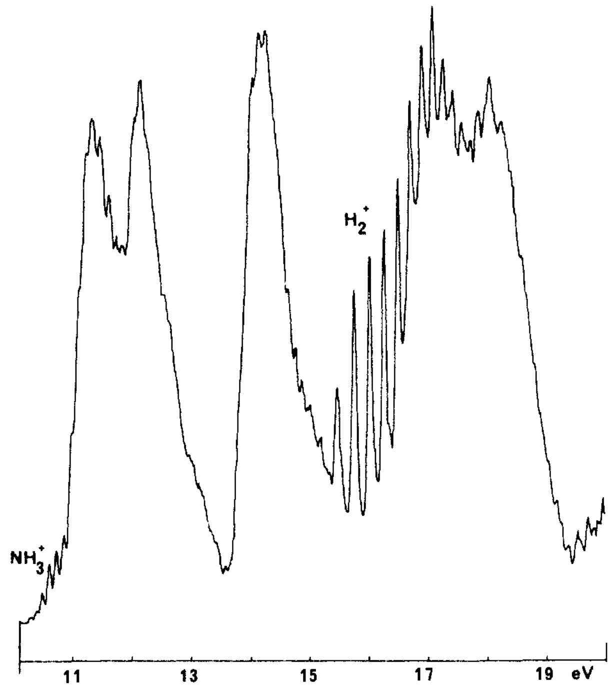

Figure 1. He I photoelectron spectrum of H_2NBH_2 produced by H_2 elimination from NH_3BH_3. The H_2^+ vibrational progression is labeled, as is a trace of NH_3^+ at the onset to the first IP.

sets. Geometry optimization using analytic gradient procedures was performed within the established[18-20] C_{2v} structure. Calculation of the harmonic vibrational frequencies (all real values) confirmed the minimum on the 6-31G* potential surface. These results provided an assessment of the Koopmans' orbital energies with basis set size. Optimized geometric structures for the ground and first excited state cations were pursued at the unrestricted HF SCF level (3-21G, 6-31G*) to establish the relative energies of the first two ionic states and their respective geometries. The cations were permitted to twist with planar symmetric configurations retained around the individual B and N atoms. Inclusion of electron correlation was handled to third order with Møller–Plesset perturbation theory by performing single-point calculations on the optimized 6-31G* structures (UMP3/6-31G*//HF/6-31G*).

All calculations were performed on a VAX 11/750.

Results

The He I PE spectrum of NH_3BH_3 has been reported previously[24,25] and will not be discussed here. The PE spectrum of the NH_3BH_3 decomposition product (Figure 1) shows five distinct bands which can be ascribed to one molecular species; the IP values are given in Table I. Some vibrational structure is observed on the first IP. The strong vibrational progression of H_2^+ is seen commencing at 15.45 eV. Also evident at the onset of the first IP is a trace of NH_3 (adiabatic IP, 10.07 eV) produced by further decomposition; surprisingly, no evidence for B_2H_6 is observed in the PE or FTIR[20] experiments, although we do note that additional broadening of the Franck–Condon envelopes of some bands, particularly around 13 and 15 eV, indicates the presence of minor amounts of other material. The five main bands can, however, be assigned to the H_2NBH_2 molecule on the basis of the FTIR experiments, on their correlation with the known IP's of the isoelectronic C_2H_4 molecule, and by comparison with the semiempirical and ab initio calculations. The adiabatic IP is 10.8 ± 0.1 eV, in excellent agreement with an appearance potential measurement of 11.0 ± 0.1 eV.[16] Also shown in Table I are the present and previous semiempirical and ab initio results.

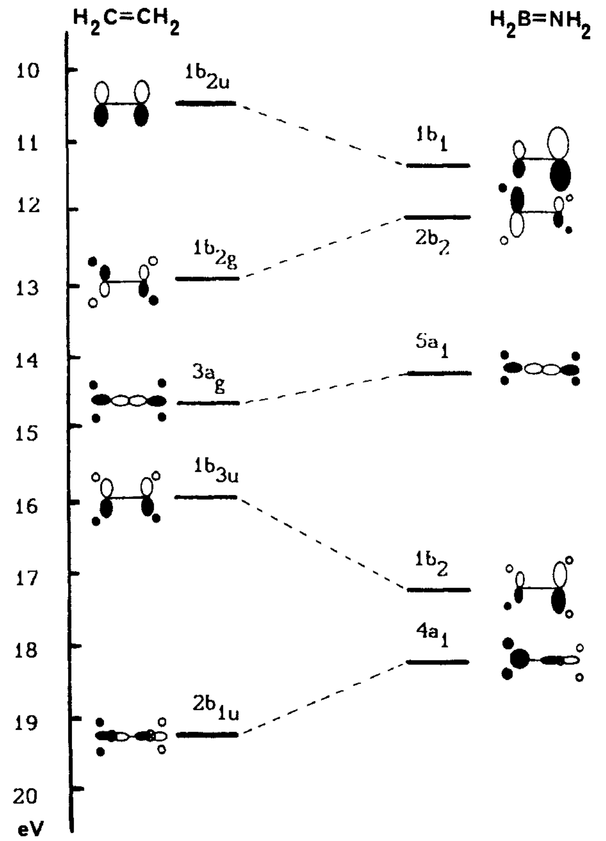

Figure 2. Orbital sketches for the five uppermost filled levels of H_2NBH_2 and the isoelectronic H_2CCH_2 molecule; correlation of their ionization potentials.

Discussion

Assignment of the PE Spectrum. As evidenced by the He I photoelectron spectrum (Figure 1), the thermal decomposition of the NH_3BH_3 adduct is an excellent source of H_2NBH_2 giving, apart from H_2, a relatively clean PE spectrum. The five vertical IP's at 11.36, 12.08, 14.12, 17.18, and 18.12 eV are assigned respectively to the $1b_1(\pi)$, $2b_2$, $5a_1$, $1b_2$, and $4a_1$ orbitals, which are shown schematically in Figure 2, together with the corresponding ethylene energy levels and orbitals.

Assuming Koopmans' theorem this orbital ordering is in agreement with the present geometry optimized ab initio calculations at the HF level using 3-21G, 4-31G, and 6-31G* basis sets

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Table II. Total Energies of Optimized H_2NBH_2 and $H_2NBH_2^+$ Structures (au)

$H_2NBH_2(^1A_1)^a$		$H_2NBH_2^+(^2B_1)^b$ (ground state)		$H_2NBH_2^+(^2B_2)^c$ (excited state)	
basis set	E	basis set	E	basis set	E
STO-3G	−80.46590	3-21G		3-21G	
3-21G	−81.04344	planar (C_{2v})	−80.70976	planar (C_{2v})	−80.66008
4-31G	−81.37858	45° (C_2)	−80.71205		
6-31G*	−81.48910	90° (C_{2v})	−80.71338	6-31G*	
MP2/6-31G*[d]	−81.73077	6-31G*		planar (C_{2v})	−81.10772
MP3/6-31G*[d]	−81.74926	planar (C_{2v})	−81.15498		
		45° (C_2)	−81.15687	MP2/6-31G* (C_{2v})[d]	−81.33740
		90° (C_{2v})	−81.15769	MP3/6-31G* (C_{2v})[d]	−81.35427
		MP2/6-31G* (C_{2v})[d]	−81.35356		
		MP3/6-31G* (C_{2v})[d]	−81.37835		

[a] Planar C_{2v} symmetry constraint. [b] Formed by removal of a π electron. [c] Formed by removal of a σ electron. [d] Møller–Plesset to second (or third) order at the optimized 6-31G* stationary point.

and the semiempirical MNDO calculations (Table I). Features to note include the reasonable correspondence of the MNDO calculations, particularly for the closely spaced first two IP's, and the present ab initio results where the assignment is qualitatively (ordering) and quantitatively (absolute magnitude) retained with increasing size of basis set (see later). Taking 92% of the Koopmans' calculated values (6-31G*) provides an average deviation of 0.34 eV. We thus assign the HOMO to the π bonding orbital ($1b_1$) on the basis of the observed vibrational structure (1100 cm^{-1}, a reduced BN stretching frequency; for the ground-state molecule[20] ν_4 = 1337 cm^{-1}) and the absence of a shift upon fluorination (BF_2NH_2, first IP = 11.47 eV[26]). The first IP is thus stabilized by 0.85 eV relative to the first IP of the isoelectronic C_2H_4 molecule, not unexpectedly since the π orbital is displaced toward the more electronegative N atom. This feature weakens the π bond, reduces the barrier to rotation, and contributes to the geometry of the resulting ion.

The next occupied orbital ($2b_2$) is close in energy ($IP_2 - IP_1$ = 0.72 eV) and represents a significant difference from the ethylene molecule where the separation of the π and σ orbitals is 2.34 eV.[27] As noted in Table I, the π, σ ordering in aminoborane is in partial disagreement with previous EH[2], and ab initio[4] calculations, which predict a σ level *above* the π. In the ab initio case,[4] this appears to be basis set dependent, the level ordering $\pi\sigma\sigma$—switching to $\sigma\pi\sigma$—with an improving basis set. We do not observe this basis set effect (vide supra). Since the ground and first excited cationic states, $^2B_1$ and $^2B_2$ (assuming planar C_{2v} symmetry), are indeed so close in energy, we have performed separate calculations on these cations at the UHF/6-31G* and UMP3/6-31G* levels to investigate this further. These results will be discussed in the next section.

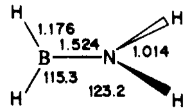
In contrast to the stabilization of the HOMO, the second occupied molecular orbital ($2b_2$) is destabilized by ~0.8 eV relative to the first IP of C_2H_4; this is a reflection of the predominant B–H bonding character (Figure 2) vs. the C–H bonding in C_2H_4. The third ($5a_1$) and fourth ($1b_2$) orbitals of H_2NBH_2 are, respectively, destabilized and stabilized by comparison with the corresponding C_2H_4 levels, and again this is a function of the difference between CH_2/CC and BH_2/NH_2/BN bonding character. The fifth orbital ($4a_1$) is destabilized by some 1 eV in H_2NBH_2 and is due to dominant B 2s character in this BN/BH bonding orbital.

Molecular and Cationic States. Table II shows the SCF energies for the optimized planar aminoborane molecule at the STO-3G, 3-21G, 4-31G, and 6-31G* levels. These are in agreement with those available from the Carnegie–Mellon Quantum Chemistry Archive.[28] The geometry obtained at the biggest basis set provides bond lengths within 0.008 Å and bond angles within 0.5° of those determined from a microwave evaluation of five isotopic species[19] and lends some credence to the following results for the cations. Also shown are the energies obtained by inclusion of electron correlation to second (MP2) and third (MP3) order. In accord with previous observations,[29] the calculated harmonic frequencies are typically some 390–90 cm^{-1} higher than the observed values,[20] except for the BN stretching frequency which is calculated some 110 cm^{-1} too low. The usual factor of 0.89 brings the average of all frequencies (except BN stretch) within 50 cm^{-1} of the experimental values.

A preliminary optimization of the ground state cation using UHF/MNDO indicated a twisted configuration (89.9°) with an increased BN bond length (from 1.37 Å in the molecule to 1.47 Å in the cation). The improvement in energy between a planar (C_{2v}) and an orthogonal (C_{2v}) cation was 25.6 kcal mol^{-1} although the potential is almost flat between 60 and 120°. To lend some support to this result we performed similar MNDO calculations for $C_2H_4^+$ which reproduced the 25° twist for the ethylene cation.[30]

At the UHF SCF level the ab initio calculations employing the 3-21G and 6-31G* basis sets again gave an orthogonal cation although the potential surface was much flatter than in the semiempirical case (ΔE(twisted-planar) = 1.7 kcal mol^{-1}). The total energies at the planar, 45° (C_2) and orthogonal geometries are shown in Table II for both the 3-21G and 6-31G* basis sets. Charge analysis indicates removal of 0.3 e from the N atom, 0.1 e from the B, and the remainder fairly evenly distributed over the four H atoms.

The optimized (6-31G*) geometry of the ground state cation ($^2B_1$) shown in **1** was found to be a stationary point from a frequency calculation (no negative eigenvalue) and so this aminoborane cation is considerably more twisted than that of $C_2H_4^+$



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where an angle of 25–27° has been established from analysis of vibrational structure on the first PE band.[31,32] As mentioned previously, this is not surprising since aminoborane has a much weaker π bond than ethylene and a correspondingly smaller barrier to rotation (H_2NBH_2, $E_{\text{planar}} \rightarrow E_{\text{perp}}$(MNDO) = 29.3 kcal; C_2H_4, $E_{\text{planar}} \rightarrow E_{\text{perp}}$(MNDO) = 62.5 kcal). The primary result of ionization of the π electron is therefore a lengthening of the BN bond (by 0.135 Å) and a twisting of the molecule; indeed these two effects are linked. Unfortunately we have insufficient resolution on the first PE band to establish excitation of a torsional mode (predicted in the ground-state molecule at 763 cm^{-1}),[20] as

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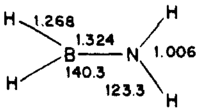
identified in the $C_2H_4^+$ case.[31,32] The observed structure of 1100 ± 80 cm^{-1} is most reasonably assigned to a reduced BN stretching frequency; this can be compared with the calculated ionic BN frequency of 890 cm^{-1} when account is taken of the fact that the calculated ground-state molecular frequency is some 110 cm^{-1} too low.

The first excited cationic state, $^2B_2$, formed by ionization from the B–H bonding σ orbital ($2b_2$) is close in energy to the $^2B_1$ ground state as expected from the PE spectrum, but as shown in Table II, there is a clear distinction between them. The results for the excited cationic state were obtained from a clean convergence to this configuration. The planar optimized geometry for this state at the 6-31G* level **2** indicates increased HBN angles and increased BH bond lengths as expected from ionization out of a B–H σ bonding orbital. Inspection of the charges indicates 0.8 e removed from the BH_2 grouping.



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At the SCF level, the separation between the $^2B_1$ and $^2B_2$ states is 1.35 eV (3-21G) and 1.2 eV (6-31G*). The effect of correlation which can, in principle, switch closely spaced levels was investigated by post HF SCF calculations using second- and third-order Møller–Plesset perturbation theory. The total energies for the two cationic states at the MP2 and MP3 levels are included in Table II and demonstrate that the relative ordering is retained, although the gap is narrowed. Thus $\Delta(^2B_1 - {}^2B_2) = 0.44$ eV (MP2), somewhat overcompensated, and $\Delta(^2B_1 - {}^2B_2) = 0.66$ eV (MP_3), in good agreement with the experimental value of 0.72 eV. The separate calculations with and without the correlation energy corrections for the molecule and the two cationic states enable us to obtain the IP's using the difference in energy between the molecule and the cations. Thus $IP_1 = 9.02$ eV (HF/6-31G*), 10.26 eV (MP2/6-31G*), and 10.09 eV (MP3/6-31G*). $IP_2 =$ 10.38 eV (HF/6-31G*), 10.70 eV (MP2/6-31G*), and 10.75 eV (MP3/6-31G*). It should be noted that these correspond to adiabatic IP's, since they reflect optimized ground-state and cationic geometries.

Although the ground-state cation is unambiguously twisted to 90°, there is some evidence that a shift of a H atom may occur for the first excited state cation, giving a species at a lower energy than the planar C_{2v} structure described here as **2**. The present results[33] indicate a 1,2-hydrogen shift to give a $HBNH_3^+$ species and suggests yet another example of a stabilized cation in an unusual valence state.[34]

Summary and Conclusions

We have demonstrated, using He I photoelectron spectroscopy, that the unstable aminoborane molecule can be generated in good yield in the gas phase. The spectrum can be assigned by comparison with that of the isoelectronic ethylene molecule and semiempirical/ab initio calculations.

In order to improve the quantitative evaluation, and preclude correlation effects, separate calculations were performed for the ground-state molecule and the ground and excited ionic states; these calculations included electron correlation to third order. The HOMO is shown to be π, in disagreement with earlier EH and ab initio calculations but as expected by analogy with ethylene.

The ground ionic state is twisted to 90° (compare $C_2H_4^+$, 25°), as shown by MNDO, 3-21G, and 6-31G* calculations. This should be compared with the $C_2H_4^+$ case where a variety of basis sets and configuration interaction gave conflicting results.[35] The present result is a function of the weaker, asymmetric π bond in aminoborane and relaxation of the planar constraint upon ionization. The excited ionic state is 0.66 eV above the ground ionic state at the MP3/6-31G* level and exhibits a planar geometry with a distorted BH_2 fragment. Preliminary results indicate the possibility of a low-energy $HBNH_3^+$ isomer.

As it is quite likely that the Rydberg states[36] of H_2NBH_2 possess similar geometries, particularly leading to the twisted ground-state cation (compare $C_2H_4^+$ ground state[37]), an experimental resolution to this theoretical prediction could be achieved through detailed analysis of multiphoton ionization via an appropriate Rydberg level.

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