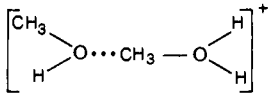
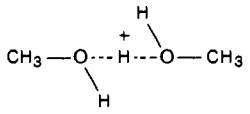
s^{-1} is in very good agreement with the range of values deduced by Bowers for the gas-phase analogue discussed above. Of equal significance is the observation that the reaction proceeds only for a specific cluster size and hence displays significant variation with the degree of ion solvation in the cluster as well as in the isolated ion–molecule reactions. These results establish further connection between changes in reaction processes proceeding in the gas compared to the condensed phase due to the effects of solvation.

It is interesting to speculate on reasons for the variation in reactivity. A number of structures have been proposed for the parent ion species of mass 65 amu that decays unimolecularly via loss of H_2O. Isotope-labeling work of Kleingeld and Nibbering[17] suggests an intermediate of structure I while Bowers' and co-



I

workers'[10] interpretation of kinetic results suggests a structure II.



II

The studies of Morton and co-workers[15] indicate that, at least for the case of 2-butanol, reaction to form the meso isomer of the ether occurs by backside displacement. It is suggested that a vibrationally excited proton-bound dimer undergoes rearrangment to expel water. The work of Bowers and colleagues provides some evidence for structure II, although they admit to the possibility that internally excited ions may react via structure I as suggested by the findings of Kleingeld and Nibbering.

The fact that we observe metastable loss of H_2O and CH_3OH subsequent to the formation of the protonated dimer suggests the possibility of two distinct intermediates (structures I and II). Structure II might be the species initially formed following ionization with the possibility of isomerization to structure I occurring in the microsecond time frame observable by our reflectron technique. The energy acquired upon the rearrangement of the alcohol molecules about the newly formed charged center would undoubtedly provide considerable excess energy for structural interconversion. We estimate this excess energy to be 0.6, 1.1, and 1.3 eV for the unprotonated trimer, tetramer, and pentamer ions, respectively. This estimate is based on energetics of the proton transfer reaction, rearrangement energy, and hydrogen bond energy.[18,19] Structure I would seem to be appropriate for the facile loss of H_2O. Following the ionization of larger neutral clusters, structures involving protonated alcohol molecules corresponding to higher analogues of structure II may be an appropriate description. Perhaps at larger degrees of solvation (more analogous to the liquid phase) there is a hinderance to the necessary rearrangement to structure I, thus preventing the loss of H_2O as an important product channel in the reaction. It is also possible that another core ion exists in the case of the trimer[20] and higher clusters. However, our estimates suggest that reaction channels corresponding to the loss of H_2O should be energetically competitive with those leading to loss of CH_3OH, but we only observe the latter process.

Acknowledgment. We thank Dr. Robert G. Keesee for helpful discussions during the course of this work. Support by the U. S. Department of Energy, Grant No. DE-AC02-82ER60055, is gratefully acknowledged.

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He I Photoelectron Spectra of the Unstable Substituted Aminoboranes, Aminodifluoro-, Aminodichloro-, and Aminodibromoborane. An Experimental and Theoretical Study

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Abstract: He I photoelectron spectra are reported for the unstable aminodifluoro-, aminodichloro-, and aminodibromoborane molecules, H_2NBF_2, H_2NBCl_2, and H_2NBBr_2. High yield routes to these molecules have been demonstrated, and the identities and orbital assignments have been established by a comparison with other similar molecules, notably the more stable methyl-substituted analogues and the isoelectronic ethylenes. The HOMO in all cases is π. Electronic and geometric structures have been investigated theoretically at the semiempirical (MNDO) and ab initio (3-21G*) levels; these provide an investigation of the structures of the H_2NBCl_2 and H_2NBBr_2 molecules, the H_2NBF_2 cation, and the barriers to internal rotation for the molecules. In conjunction with results for the unsubstituted H_2NBH_2 molecule these experimental and theoretical studies provide an assessment of B-halogenation and hence π donating ability on the nature of the BN π bond.

Small alkyl-substituted aminohaloboranes are unstable as monomeric species, having a tendency to form dimers and trimers, with the result that they have not been well-characterized.[1-4] The dimethylamino derivatives are perhaps the most widely studied, but these also undergo self-association,[2,5] and the simplest aminoboranes, unsubstituted on nitrogen, exist only as transient in-

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termediates. These fundamental aminoboranes are, however, of interest for several reasons, notably because they are precursors to ring trimers analogous to substituted cyclohexanes and potential sources of heteroaromatic borazines $(XBNH)_3$ and various polymeric $(X_2BNH_2)_n$, $(XBNH)_n$, and $(BN)_n$ species.[2] In addition, the monomeric species provide a direct comparison with the isoelectronic ethylenes but with acidic and basic sites within the same molecule. They also provide the starting point for further synthetic work, e.g., reaction with excess ammonia can lead to the formation of the hitherto unknown halogen-substituted bis(aminoboranes) $XB(NH_2)_2$. Without bulky alkyl substituents they are also amenable to reasonably large ab initio calculations which can provide geometries, energies, and insight into the π electron distributions. Thus these features of the parent aminoborane molecule, H_2NBH_2, and the aminodifluoro derivative, H_2NBF_2, have prompted several theoretical investigations with a view to determining their geometries, the nature of the BN π bond, the direction of the dipole moment, and the barrier to internal rotation. For aminoborane these studies are summarized in ref 6 and 7 and for aminodifluoroborane see ref 7, 8, and 9. No calculations are available for the other molecules of interest in this work: aminodichloroborane H_2NBCl_2, where its existence has not been unambiguously established, and aminodibromoborane H_2NBBr_2, a previously unknown molecule.

Despite their instability the simplest of the aminoborane species, H_2NBH_2, has been identified recently in the gas phase as a discrete molecule by using photoelectron,[6] infrared,[10] microwave,[11,12] and mass spectroscopy.[13] The fluoro-substituted species, aminodifluoroborane, H_2NBF_2, has been observed by microwave spectroscopy[14] and mass spectroscopy.[15] During the course of this work a photoelectron spectroscopic study was reported for this species and some N-methyl derivatives,[16] but only five or six ionization potentials (IP's) were observed for H_2NBF_2.

For the chloro-substituted species H_2NBCl_2 there is a paucity of data due not only to its own instability but also of its precursor the $H_3N{\cdot}BCl_3$ adduct.[17] A mass spectrometric and solid state infrared study[18] of the BCl_3/NH_3 reaction does give evidence for the H_2NBCl_2 molecule, although appearance potentials (AP's) could not be determined. The bromo-substituted species H_2NBBr_2 has not been previously investigated.

We now wish to report a considerably improved He I photoelectron (PE) spectrum of the semistable H_2NBF_2 molecule in which all nine of the ionization potentials up to 21.2 eV can be identified and assigned. The existence of the transitory H_2NBCl_2 and H_2NBBr_2 molecules is also established by a study of their PE spectra. These studies are complemented by semiempirical and ab initio electronic structure calculations, with a view to assessing the electronic and geometric structures and the nature of the BN bond.

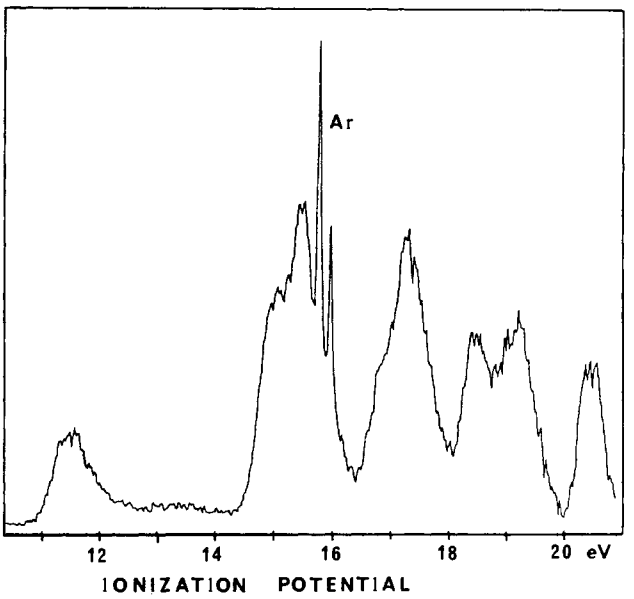

Figure 1. He I photoelectron spectrum of H_2NBF_2 produced by thermolysis (ca. 150 °C) of solid $H_3N{\cdot}BF_3$; Ar is labeled.

Table I. Ionization Potentials, Calculated Values, and Orbital Assignments for Aminodifluoroborane

orbital symmetry	experimental[a] (eV)	calculated		
			ab initio	
		MNDO	3-21G*[b]	6-31G**[c]
$2b_1$ π	(11.1), 11.65	11.69	11.28	11.14
$8a_1$	15.12	14.93	15.02	15.32
$5b_2$	15.52	15.31	15.09	15.52
$1a_2$ π	15.52	15.29	15.42	15.97
$4b_2$	17.1	17.04	16.56	16.85
$1b_1$ π	17.26	17.69	16.97	17.37
$7a_1$	18.35	18.72	18.07	18.27
$3b_2$	19.02	19.13	18.39	18.85
$6a_1$	20.3	20.67	19.43	19.95
$5a_1$		34.69	29.54	29.44

[a] Adiabatic IP in parentheses; IP's 1–4 and 6–8, ±0.03 eV; IP's 5 and 9, ±0.1 eV. [b] $E_T = -277.86244$ au. Quoted values are $0.92 \times KT$ value. [c] Reference 7. The values are $0.92 \times KT$ value.

Experimental Section

Aminodifluoroborane. Aminodifluoroborane was prepared on-line into an ultraviolet photoelectron spectrometer located at McMaster University,[19] specifically designed for the study of unstable gas-phase molecules. Sampling was achieved by heating the solid $H_3N{\cdot}BF_3$ adduct to approximately 150 °C directly into the ionization chamber. The adduct was synthesized by addition of ammonia gas to the boron trifluoride etherate complex;[20] the white adduct was subsequently filtered and dried.

Aminodichloroborane. Aminodichloroborane was prepared by gently heating (30–60 °C) the elusive[17,18] $H_3N{\cdot}BCl_3$ adduct directly into a PE spectrometer located at the University of Guelph. The adduct was prepared as a white solid by on-line reaction of BCl_3 and NH_3 gases just external to the ionization chamber.

Aminodibromoborane. Comparable techniques to those employed for the aminodichloroborane generation failed; heating of a deposited white species presumed to be $H_3N{\cdot}BBr_3$ does not give H_2NBBr_2. However, heating to 240 °C during the mixing of equimolar amounts of gaseous NH_3 and BBr_3 produces a good yield of H_2NBBr_2 plus HBr. This result is indicative of the tenuous nature of $H_3N{\cdot}BBr_3$[17] compared to the lighter halogen adducts.

The ultraviolet photoelectron spectrometer located at the University of Guelph used for the study of the aminodichloro and the aminodibromo molecules is also designed for the study of gas-phase unstable molecules and will be described elsewhere.

It should be noted that although dehydrohalogenation occurs to give the desired products, in all three cases there is competition with other

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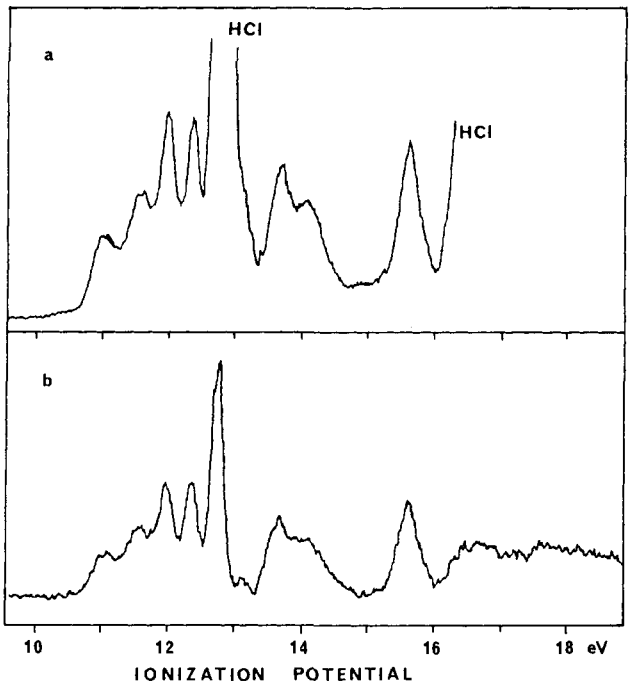

Figure 2. He I photoelectron spectrum of H_2NBCl_2 produced by thermolysis (30–60 °C) of solid H_3NBCl_3: (a) initial spectrum with intense HCl peak at 12.8 eV and (b) spectrum with HCl reduced by digital subtraction.

reactions involving either ring or polymer formation and the concomitant production of involatile materials. In the H_2NBCl_2 case, HCl is liberated into the gas phase from the solid; for H_2NBBr_2, HBr elimination occurs from the gas-phase mixture, and for H_2NBF_2, the HF is apparently incorporated into the solid.

Spectra were recorded at a resolution of 30–60 meV, depending upon the spectrometer conditions. Calibration was accomplished with the known IP's of HCl, Ar, and N_2.[21]

Computational Methods. Semiempirical MNDO calculations using the Davidon–Fletcher–Powell geometry optimization procedure were performed on H_2NBF_2, H_2NBCl_2, and H_2NBBr_2 by using the MOPAC program[22] to determine molecular and cationic geometries as well as barriers to internal rotation. Orbital energies were compared, assuming Koopmans' theorem, to experimental IP's.

Ab initio calculations were performed on the ground-state molecules H_2NBF_2 and H_2NBCl_2 at the restricted HF SCF level by using GAUSSIAN 82, with an internal split-valence basis set (3-21G*).[23] Given the known planarity of such molecules,[11,12,14,16] geometry optimization was initiated with planar C_{2v} symmetry by using the standard optimization procedures available in GAUSSIAN 82. The molecular orbital energies were compared to experimental IP's by using the accepted[24] 92% of the Koopmans' calculated values.

All calculations were done by using a VAX 11/750.

Results

The He I PE spectrum of H_2NBF_2 (Figure 1), obtained by heating the adduct, is relatively clean (Ar is labeled) and consists of a set of nine IP's ranging from 11–21 eV. These are listed in Table I together with the calculated values from the semiempirical and ab initio calculations. The first IP has a broad Franck–Condon envelope, with no resolvable vibrational structure (compare H_2NBH_2, $\nu' = 1100\ cm^{-1}$).[6] The spectrum can be assigned to the H_2NBF_2 molecule by comparison to the molecular orbital calculations by using Koopmans' theorem, by the correlation with the isoelectronic difluoroethylene molecule, and by agreement with the previous PE spectrum.[16] The measured AP of 12.4 ± 0.4 eV[15] is somewhat removed from the adiabatic IP of 11.1 eV measured in this work.

The He I PE spectrum of H_2NBCl_2 (Figure 2) shows seven bands ranging between 10–17 eV. The intense band at 12.8 eV is HCl, produced by elimination from the adduct; in Figure 2b a spectrum subtraction procedure has been used to reduce the intensity of this band. The observed IP's are listed in Table II together with the calculated values. From simple molecular orbital arguments the eighth and ninth IP's should be around 18–19 eV and may be hidden under the HCl second band, and the broad feature around 18 eV. The spectrum can be assigned to a single species, and specifically to the H_2NBCl_2 molecule, by comparison with the calculated molecular orbital energies by using Koopmans' theorem (Table II) as well as correlation to the H_2CCCl_2,[25,26] and

Table II. Ionization Potentials, Calculated Values, and Orbital Assignments for Aminodichloroborane

orbital symmetry	experimental[a] (eV)	calculated MNDO	calculated ab initio 3-21G*[b]
$3b_1\ \pi$	(10.8), 11.03	11.79	11.01
$8b_2$	11.60	12.42	11.20
$2a_2\ \pi$	11.99	12.73	11.53
$11a_1$	12.34	12.92	11.93
$2b_1\ \pi$	13.66	14.67	13.43
$7b_2$	14.1	15.00	13.64
$10a_1$	15.61	17.62	15.46
$6b_2$	(17.5–18.5)	19.49	18.04
$9a_1$		21.67	18.51
$5b_2$		25.54	27.31

[a] Adiabatic IP in parentheses; IP's 1–5 and 7, ±0.03 eV; IP 6, ±0.1 eV; IP's 8 and 9 (see text). [b] E_T = −994.79694 au. Quoted values are 0.92 × KT value.

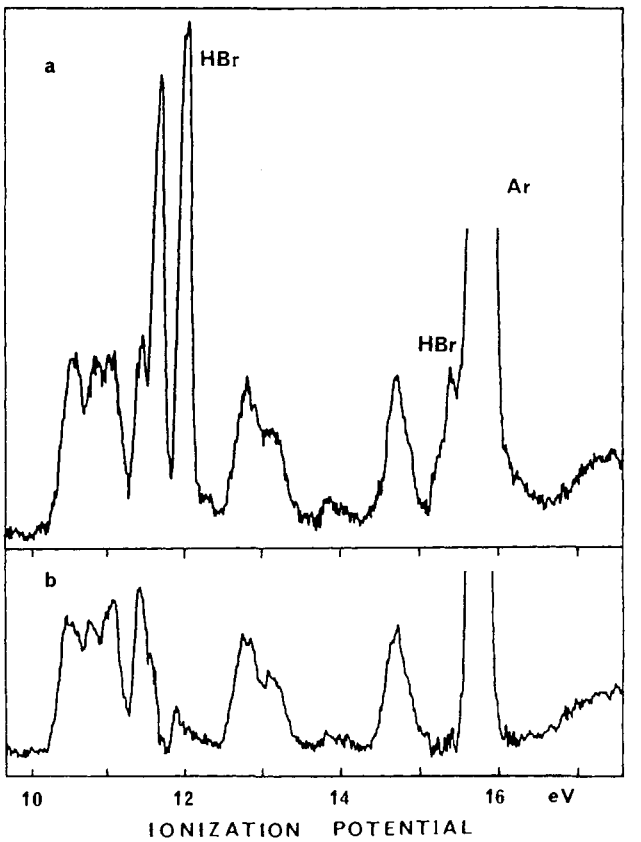

Figure 3. He I photoelectron spectrum of H_2NBBr_2 produced by thermolysis (240 °C) of an equimolar NH_3 and BBr_3 gas mixture: (a) initial spectrum showing HBr at 11.7 and 12.0 eV and (b) spectrum with HBr reduced by digital subtraction.

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Table III. Ionization Potentials, Calculated Values, and Orbital Assignments for Aminodibromoborane

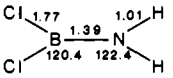
orbital symmetry	experimental[a] (eV)	calcd MNDO
$4b_1\ \pi$	(10.2), 10.57	11.44
$11b_2$	10.86	11.42
$3a_2\ \pi$	11.08	11.74
$14a_1$	11.46	12.00
$3b_1\ \pi$	12.83	13.93
$10b_2$	13.2	13.88
$13a_1$	14.74	16.98
$9b_2$	(17–18)[b]	19.37
$12a_1$		21.52

[a] Adiabatic IP in parentheses; IP's 1–5 and 7, ±0.03 eV; IP 6, ±0.1 eV. [b] IP's 8 and 9 may lie under this feature.

the H_2NBF_2 PE spectra. More convincingly, the dimethylamino derivative previously observed by PE spectroscopy[27,28] shows a direct correspondence of the first four IP's when Me shifts are taken into account.

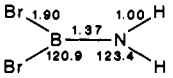
The He I PE spectrum of H_2NBBr_2 (Figure 3) also shows seven distinct bands with the two peaks at 11.7 and 12.0 eV belonging to the first band of HBr (split by spin-orbit effects). Figure 3b shows a spectrum with HBr almost removed by digital subtraction. The observed IP's are listed in Table III together with the calculated values. A direct comparison of the spectra in Figures 2b (H_2NBCl_2) and 3b (H_2NBBr_2) demonstrates the similarity of the spectra and shows the expected shifts upon replacement of Cl by Br.

The geometry optimizations performed by using the 3-21G* basis set were found to correspond well with microwave data[14] for H_2NBF_2, within 0.02 Å for bond lengths and 0.8° for bond angles. Given that no structural data are available for H_2NBCl_2 the present calculated C_{2v} results at the 3-21G* level (below) should provide a good starting point for structural analysis.



In particular, the BN and BCl bond lengths and the ClBN angle compare very favorably with the known structure, from electron diffraction, of dimethylaminodichloroborane, viz. r_{BN} = 1.379 Å, r_{BCl} = 1.77 and ⟨ClBN = 122.1°.[29]

Since we do not have basis sets for Br, the calculated structure for H_2NBBr_2 shown below is that obtained from a semiempirical MNDO calculation.



Given that the MNDO result for H_2NBCl_2 is within 0.014 Å for bond lengths and 0.8° for angles of the ab initio (3-21G*) results the above semiempirical structure for H_2NBBr_2 is anticipated to be reasonable.

Discussion

Assignment of the PE Spectrum of H_2NBF_2. As seen in Figure 1 the PE spectrum consists of eight observable vertical IP's at 11.65, 15.12, 15.52 17.1, 17.26, 18.35, 19.02, and 20.3 eV. The band at 15.52 eV comprises two IP's giving a total of nine valence IP's and the overall ordering of molecular orbitals obtained from the 3-21G* ab initio calculations as $2b_1$ (π), $8a_1$, $5b_2$, $1a_2(\pi)$, $4b_2$, $1b_1(\pi)$, $7a_1$, $3b_2$, and $6a_1$, respectively.

In both the MNDO and 3-21G* calculations the closely placed $8a_1$, $5b_2$, and $1a_2$ orbitals are all within the 0.4-eV range (experimentally, 15.12–15.52 eV) with the $5b_2$ and $1a_2$ orbitals being switched (barely) in the MNDO case (Table I). The average deviation over all nine IP's, of observed minus calculated is 0.4 eV for the 3-21G* calculations, 0.24 eV for the 6-31G** calculations recently reported,[7] and 0.22 eV for the MNDO calculations. The next IP ($5a_1$) is predicted at 29.54 eV (92%, 3-21G*) and 34.69 eV (MNDO), well beyond the range of the HeI light source, and thus all nine IP's are accounted for in contrast to the earlier work[16] where only 5 or 6 IP's were observed.

The first IP (11.65 eV) which correponds to a π orbital with considerable N pπ character unambiguously confirms that the first IP of H_2NBH_2 (11.36 eV)[6] is also π, since there is essentially no shift upon fluorination. The σ orbital in H_2NBH_2 (b_2, 12.08 eV) is stabilized by the perfluoro effect to 17.1 eV ($4b_2$, fifth IP) in the fluoro species. In H_2NBF_2 the next three orbitals ($8a_1$, $5b_2$, and $1a_2$) between 15 and 15.5 eV plus the one ($1b_1$) at 17.26 eV are associated with the F 2p type orbitals. The remaining three orbitals ($7a_1$, $3b_2$, and $6a_1$) are all σ-like and correspond to the last three σ orbitals of H_2NBH_2, stabilized by incorporation of some F 2p character. The assignment of the PE spectrum of the difluoro derivative can thus be satisfactorily accounted for by comparison with the unsubstituted derivative; the calculations provide excellent confirmation of this.

From a comparison with the PE spectrum of the ethylene analogue F_2CCH_2,[25] the first IP of H_2NBF_2 is stabilized by 1.07 eV (cf. H_2CCH_2/H_2NBH_2, 0.85 eV),[6] due to the greater electronegativity of nitrogen. The Mulliken population analysis of the HOMO in both the semiempirical and ab initio calculations indicates an increased electron density around nitrogen, giving an unsymmetrical BN π type bond. The remaining 7 or 8 IP's in F_2CCH_2 are distributed over four peaks from 14.79–19.68 eV;[25] as a full assignment of the F_2CCH_2 spectrum has not been made, and the IP's are obviously superimposed, we shall not take the comparison any further.

Assignment of the PE Spectrum of H_2NBCl_2. The He I PE spectrum of H_2NBCl_2 is shown in Figure 2 and consists of seven observable vertical IP's at 11.03, 11.60, 11.99, 12.34, 13.66, 14.1, and 15.61 eV; a further two IP's may exist under the broad features from 17.5–18.5 eV. From the 3-21G* ab initio calculations these IP's correspond to the molecular orbitals $3b_1$ (π), $8b_2$, $2a_2$ (π), $11a_1$, $2b_1$, $7b_2$, and $10a_1$, respectively. For this second row molecule the ab initio calculations with partial polarization functions fare better than MNDO, average deviations being 0.30 and 0.83 eV, respectively, over the first seven IP's. The $6b_2$, $9a_1$, and $5b_2$ orbitals are predicted at 18.04, 18.51, and 27.31 eV, respectively (0.92 × 3-21G*).

The first IP is again π type ($3b_1$) with localization on the nitrogen; however, appreciable admixture of antibonding Cl 3p character occurs with a subsequent destabilization to 11.03 eV (compare H_2NBH_2, 11.36 eV).[6] The next four IP's are relatively sharp and comprise the chlorine based orbitals, $8b_2$, $2a_2$, $11a_1$, and $2b_1$, in that order following both the semiempirical and ab initio calculations. As expected the $2b_1$ orbital incorporating some BN bonding character is somewhat stabilized (to 13.66 eV), whereas the sharp, unique $2a_2$ orbital (11.99 eV) is close to its position in $HBCl_2$ (12.35 eV).[30] The IP at 14.1 eV is assigned to the $7b_2$ orbital, the broad Franck–Condon envelope reflecting the B–Cl, B–N, in-plane bonding character. The remaining discernible band at 15.61 eV is then identified with the $10a_1$ orbital, essentially B–Cl, B–N, and B–H bonding.

Since the PE spectrum of Cl_2CCH_2 shows at least eight distinct IP's that have been carefully analyzed,[26] we can draw a direct comparison with our results for H_2NBCl_2. This is shown in Figure 4, where again the HOMO is stabilized by 1.04 eV, but all the other levels, particularly the first three chlorine based orbitals, remain essentially in the same position. Our assignment for the closely spaced $2b_1$ and $7b_2$ orbitals is reversed from that for dichloroethylene, but we justify it on the basis of the peak intensities and Franck–Condon envelopes. The $10a_1$ orbital is also relatively unchanged in position.

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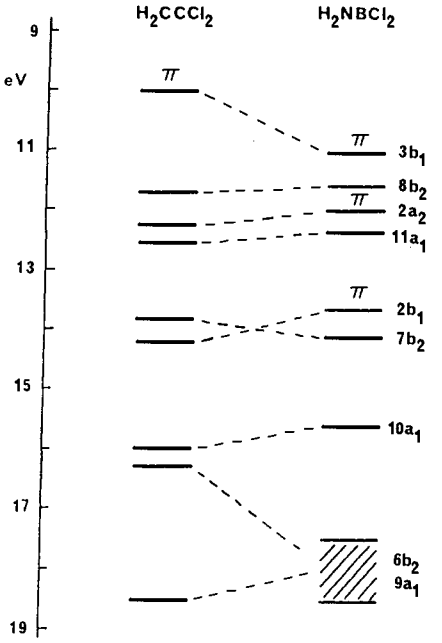

Figure 4. Correlation of the ionization potentials of H_2CCCl_2 and H_2NBCl_2.

To further support the assignment of the spectrum to that of the H_2NBCl_2 molecule, we note that the first four IP's can be directly correlated to those of the Me_2NBCl_2 molecule.[28,29] Here the first IP (nitrogen based) is destabilized by 1.5 eV as expected due to the methyl substituents, whereas the second, third, and fourth chlorine based IP's move in parallel by about 0.5 eV. Above 13 eV ionization arising primarily from the CH_3 groups precludes any further comparison.

Assignment of the PE Spectrum of H_2NBBr_2. The PE spectrum of H_2NBBr_2 (Figure 3) parallels that of H_2NBCl_2, although with replacement of Cl by Br the first IP which is dominantly N$p\pi$ in the F and Cl case now has appreciable Br 4p character. This is reflected in the narrower Franck–Condon envelope and the greater intensity. The MNDO calculations show the highest lying b_2 and b_1 orbitals to be almost degenerate, and a decision on this basis cannot be made. The calculations also prefer to switch the b_2 and b_1 orbitals around 13.0 eV (experimental), although reference to the spectra (Figures 2 and 3) indicates that there is no switch between these two orbitals (ca. 14 eV in H_2NBCl_2 and ca. 13 eV in H_2NBBr_2).

The BN Bond. The present analysis indicates that although a π bond does exist in these molecules (and hence they are planar) it is weak and involves considerable localization onto the N atom. The strength of the bond is then determined primarily by σ donation from B and π back donation from the nitrogen into the empty boron 2p orbital.

Any substituent which influences the availability of N $2p\pi$ electrons should therefore affect the π character of the BN bond. Unfortunately, it is difficult to alter substantially the nitrogen substitution since only alkyl and aryl substituents are known,[3,4] and these all show planar C_{2v} structures for the heavy atoms. It has been noted, however,[31] that aryl substitution tends to weaken the bond due to delocalization into the ring. Substitution on the boron atom is expected to be more subtle, and the work we have done on H_2NBH_2,[6] H_2NBF_2, H_2NBCl_2, and H_2NBBr_2 indicates some interesting trends.

Thus bond order calculations indicate that halogen substitution weakens the BN bond; the values (MNDO) are H_2NBH_2, 1.46; H_2NBF_2, 1.23; and H_2NBCl_2, 1.40. At the 3-21G* ab initio level the calculated overlap populations are 0.81, 0.63, and 0.79, respectively; this result is confirmed at a higher level (6-31G**)[7] where the values are, H_2NBH_2, 0.924, and H_2NBF_2, 0.880. This conclusion is in contrast to the increased vibrational frequency upon halogenation viz. H_2NBH_2,[10] 1337 cm^{-1}; $(CH_3)_2NBH_2$,[32] 1447 cm^{-1}; $(CH_3)_2NBCl_2$,[5,32] 1528 cm^{-1}; and $(CH_3)_2NBF_2$,[5] 1562 cm^{-1}, but it is well established that there is no direct correlation between vibrational frequency and force constant (and hence bond order).[33] Explicit evaluation of the force constants through a normal coordinate analysis would be required. However, even a simple acid/base picture indicates that a π donor such as a halogen atom substituted on the boron will increase the π electron density on the vacant B $2p\pi$ orbital thereby effectively reducing that available from nitrogen, i.e., the Lewis acidity of the H_2B moiety is reduced upon halogenation, and fluorine substitution has the greatest effect. Such a picture is confirmed not only from the bond orders and overlap populations (above) and the barriers to rotation (below) but is also reflected in the bond lengths: H_2NBH_2, r_{BN} (experimental)[12] = 1.391 Å, and H_2NBF_2, r_{BN} (experimental)[14] = 1.402 Å.

Similarly boron–nitrogen bond dissociation energies have been estimated from thermochemical quantities to be for H_2NBH_2, 8.1 eV, and for H_2NBF_2, 7.6 eV.[15]

Twisting, of course, will switch off the π overlap. We have evaluated the p orbital electron density for the B, N, H, and halogen (F, Cl) atoms in H_2NBH_2, H_2NBF_2, and H_2NBCl_2 by using MNDO, at planar and 15°, 45°, 75°, and 90° (orthogonal) twisted molecular geometries. It is to be noted that most of the excess electron density on nitrogen is derived from the adjacent hydrogen atoms. At each twist angle the geometry was reoptimized, although rigid rotation is assumed for the present. The results, taken with a reduction in the BN bond order from 1.5 to 1.0–1.1, and the increase in r_{BN} confirm the general feature that the π bond is weakened upon twisting.[34] For the H_2NBH_2 molecule, approximately 0.3 e is transfered to the nitrogen atom resulting in an increased electron distribution on nitrogen. If the trigonal geometry around nitrogen is relaxed, i.e., nonrigid 90° structure, then the H_2NBH_2 molecule is pyramidal at nitrogen, a result confirmed by our MNDO results and a variety of ab initio calculations.[7,35-38] The bond order is then indicative of a single bond. The halogen-substituted molecules, however, indicate a much smaller transfer of electrons to nitrogen upon rotation; 0.10 and 0.15 e for H_2NBF_2 and H_2NBCl_2, respectively; nevertheless, pyramidality still exists at nitrogen.

The calculated (MNDO) barrier to internal rotation drops by about one half to one third for the halo-substituted aminoborane species (Table IV) again implying a weaker π bond. This large drop upon halogenation is in contrast to results for the isoelectronic halo-substituted ethylenes (Table IV) where substitution has very little effect due to the more symmetrical disposition of the electrons in the π bond. The calculated (MNDO) results for the aminoboranes are, however, in accord with ΔG^* values obtained by ^{13}C NMR studies[39] on some dialkylaminophenylboranes; typically ΔG^* for such molecules is in the range, 17–24 kcal mol^{-1}, and the more

Table IV. Calculated (MNDO) Barriers to Rotation[a]

ethylenes		aminoboranes		ab initio[b]
H_2CCH_2	62.5	H_2NBH_2	29.3	34.2
H_2CCF_2	57.2	H_2NBF_2	15.6	24.2
H_2CCCl_2	55.3	H_2NBCl_2	19.4	

[a] Energy difference (kcal mol^{-1}) between a planar and a twisted (90°) structure. Rigid rotation is assumed. [b] Reference 7.

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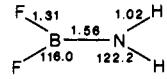
electronegative halogen tends to decrease the barrier. These values are also consistent with those obtained from large basis set ab initio calculations on H_2NBH_2 and H_2NBF_2 which are included in Table IV; we have therefore not repeated the ab initio calculations on these barriers, as we expect the ab initio trend to follow the semiempirical results.

The π bond can also be weakened by ionization, thereby allowing for a possible twisting of the cation; ionization from the HOMO of H_2NBH_2 gives a ground-state cation with an orthogonal structure at both the MNDO and ab initio 3-21G* and 6-31G* levels.[6] The MNDO and ab initio calculations on H_2NBF_2 and $H_2NBF_2^+$ indicate the expected lengthening of the BN bond



upon ionization by 0.14 and 0.17 Å, respectively. However, the potential surface for twisting the cation is extremely flat; 0.5 kcal mol^{-1} are between a planar and a 90° structure with the latter favored by MNDO, whereas the 3-21G* ab initio calculation supports a planar C_{2v} structure by 1.17 kcal mol^{-1}. This result (above) was confirmed as a minimum on the surface by a frequency calculation (no negative eigenvalues).

We have not explored the potential surface for internal rotation of the H_2NBCl_2 cation by ab initio methods, but MNDO again indicates that the surface is extremely flat with the 90° conformation favored over the planar structure by 3.2 kcal mol^{-1}.

The indications are, therefore, that halogenation has reduced the tendency for rotation in the cation; this may be attributed to a decrease in hyperconjugation from the NH bonds back into the boron $2p\pi$ orbital which can occur in the orthogonal structure.

A final feature of these intriguing, simple-substituted aminoboranes is the direction of the dipole moment which is the subject of some debate. On the basis of the charge distributions it was suggested initially[40] that the nitrogen atom has the largest negative charge, and therefore the valence bond description $\rangle B^-{=}N^+\langle$ is incorrect. Mullikan population analyses from ab initio calculations[7,34,37,41] tend to support the negative-charge-on-nitrogen concept, e.g., from our 3-21G* calculations the excess electron density on nitrogen for H_2NBH_2, H_2NBF_2, and H_2NBCl_2 is 0.89, 0.99, and 0.93 e, respectively. Nevertheless, our calculated dipole moments for all three molecules are in the sense $>\overleftarrow{B-N}<$, a result supported by higher level calculations for H_2NBH_2[7,37,42,43] and H_2NBF_2[7,43] and confirmed by a detailed comparative study of dipole moments.[11,12,42]

Conclusion

We have demonstrated the preparation of the unstable H_2NBF_2, H_2NBCl_2, and H_2NBBr_2 monomers via dehydrohalogenation of the $H_3N{\cdot}BF_3$ and $H_3N{\cdot}BCl_3$ solid adducts and a NH_3/BBr_3 gas-phase mixture by use of on-line He(I) photoelectron spectroscopy. The spectra were assigned (assuming Koopmans' theorem) by using MNDO and ab initio calculations which turn out to be quite reasonable for these molecules. The HOMO is shown to be π, as in the isoelectronic substituted ethylenes, although stabilized by about 1 eV thereby narrowing the σ–π gap. A correlation of the IP's of H_2NBH_2, H_2NBCl_2, and H_2NBF_2 is shown in Figure 5 which demonstrates the effect of halogen substitution upon the π and σ levels of the unsubstituted molecule. The five IP's of H_2NBH_2 are supplemented by four additional bands due to the halogen based p orbitals. In the dichloro case these encroach on the N-based HOMO, and in the dibromo molecule the semiempirical calculation indicates a near degeneracy of the π (b_1) and halogen-based (b_2) levels. In the difluoro case all σ orbitals are stabilized by the perfluoro effect leaving a discrete π orbital as the HOMO.

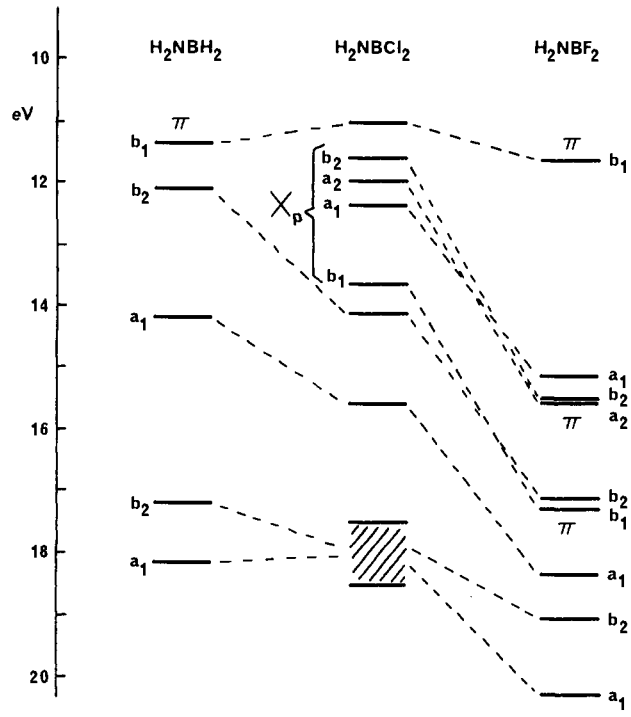


Figure 5. Correlation of the ionization potentials of H_2NBH_2, H_2NBCl_2, and H_2NBF_2.

Our ab initio calculations at the 3-21G* level also provide a calculated geometry for the H_2NBCl_2 species (C_{2v} and structurally similar to the Me_2NBCl_2 molecule) and indicate that the H_2NBF_2 cation is planar, unlike the $H_2NBH_2^+$ species which adopts an orthogonal configuration. Calculated (semiempirical and ab initio) bond orders and overlap populations indicate that B-halogenation weakens the π bond. This is further indicated by the calculated barriers to internal rotation (approximately one half to one quarter of those of the corresponding ethylenes).

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