Photoelectron Spectra of the Aminodifluoroboranes NH_2BF_2, $NHMeBF_2$, and NMe_2BF_2

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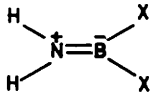
Photoelectron spectra of the aminodifluoroboranes NH_2BF_2, $NHMeBF_2$, and NMe_2BF_2 have been recorded. The results are discussed and compared with theoretical calculations. The first ionization potentials of NH_2BF_2, $NHMeBF_2$, and NMe_2BF_2 are 11.47, 10.45, and 9.49 eV respectively. The study shows that BF_3 reacts with NH_3, NH_2Me, and $NHMe_2$ to form solid products which on vaporisation yield species resulting from the elimination of HF from the classical donor–acceptor complexes NH_3BF_3, NH_2MeBF_3, and $NHMe_2BF_3$ respectively.

Boron trihalides (BX_3) form donor–acceptor complexes with Lewis bases such as amines, amides, and carbonyl compounds.[1–3] The complexes formed between amines and boron trihalides are of particular interest in that they may eliminate HX to give unstable species. It is possible to draw two alternative structures for the resulting molecules, one which has a multiple bond between the boron and nitrogen atoms and one which has a single bond (see below).



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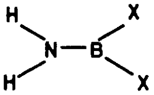

These aminodihalogenoboranes are generally unstable with respect to polymerization, but gas-phase techniques can be successful in studying the monomers. Lovas and Johnson[4] detected NH_2BF_2, in the vapour pumped off from heated NH_3BF_3, by microwave spectroscopy. The rotational spectrum of monomeric $NHMeBF_2$ has been observed in the vapour of heated NH_2MeBF_3[5] and an i.r. study of NMe_2BF_2 has indicated the presence of the monomer in the gas phase[6] whereas investigations of the liquid and solid revealed only polymeric material.[7] The first ionization potential (i.p.) of NMe_2BF_2 has also been obtained by photoelectron spectroscopy.[8] The monomeric analogues NMe_2BX_2 (X = Cl, Br, or I) have been studied in the gas phase by photoelectron spectroscopy.[8,9] Very few of the parent complexes of BX_3 have been studied in the gas phase, probably due to the instability of the donor–acceptor bond with respect to dissociation, and the tendency to eliminate HX. The exceptions to this observation are NMe_3BF_3, studied in the gas phase by Bryant and Kuczkowski,[10] Lake,[11] and Cassoux *et al.*,[12] and $NHMe_2BF_3$.[11] NMe_3BF_3 in fact appears to be stable under low-pressure pyrolysis, its microwave spectrum showing no change at temperatures up to 1 110 °C.[5]

The photoelectron spectra of the monomeric aminodifluoroboranes NH_2BF_2, $NHMeBF_2$, and NMe_2BF_2 have been detected in the vapour released by gentle heating of the solid products of reacting BF_3 with NH_3, NH_2Me, and $NHMe_2$ respectively. *Ab-initio* molecular orbital (m.o.) calculations have been carried out on the above aminodifluoroboranes and the results compared with the experimental ionization potentials.

Experimental

Samples of the amine–boron trifluoride adducts (~1 g) were prepared by distilling equimolar ratios of boron trifluoride and the appropriate amine into a 100-cm^3 bulb cooled in liquid nitrogen. The bulb was then isolated and allowed to warm slowly until a vigorous reaction occurred. The reaction mixture was cooled at intervals in order to stop any build up of pressure in the bulb. On completion of the reaction the resultant fine white solid was pumped at room temperature to remove excess reactants and any volatile reaction products.

Table 1. Geometries of the aminodifluoroboranes; distances (Å) and angles (°)

	NH_2BF_2[a]	$NHMeBF_2$[b]	NMe_2BF_2[c]
r(BF)	1.325	1.325	1.325
r(NH)	1.003	1.003	1.003
r(NC)		1.474	1.474
r(BN)	1.402	1.427	1.440
BNH	121.53	121.53	
BNC		121.53	121.53
NBF	121.05	121.05	
NCH		109.47	109.47

[a] From ref. 3. [b] From ref. 4. [c] Assumed from other geometries.

The samples were then transferred into a single-ended quartz pyrolysis tube and connected directly to a Perkin-Elmer P.S.16 photoelectron spectrometer. The tube was wrapped in electric heating tape, heated to *ca.* 140 °C over its whole length, and the resultant vapour pumped continuously through the cylindrical probe of the P.S. 16 spectrometer. To stop the sample from condensing in the probe inlet and the probe itself, it was necessary to heat the whole inlet system to *ca.* 100 °C. Initially only the spectra of the starting amines were observed, but after a short period of time, usually only a few minutes, the spectra of the aminodifluoroboranes appeared. Experiments using the solid probe of the P.S. 16 instrument, whereby solid samples were introduced directly into the ionization region of the spectrometer and heated *in situ* to *ca.* 140—200 °C, proved unsuccessful, the only products observed, even after pumping for 1 h, being the starting amines and boron trifluoride.

Molecular-orbital calculations were carried out using the GAUSSIAN 76 set of programs. The geometries used are shown in Table 1. The computed eigenvalues were obtained using a 4-31G extended basis and the m.o. coefficients are those from STO-3G calculations.

Results

Analysis of Spectra.—In the Figure the photoelectron spectra of NH_2BF_2, $NHMeBF_2$, and NMe_2BF_2 are depicted to scale so that the spectroscopic changes observed with the successive introduction of methyl groups are clearly evident. The values of the ionization potentials for the various bands are listed together with the results of the 4-31G theoretical calculations in Table 2. The first i.p. is clearly identified for all the species as a *pπ* orbital on nitrogen. The calculations suggest that there is little delocalization into the vacant B orbital. However, the microwave spectra of both NH_2BF_2 and $NHMeBF_2$ show clearly that the molecules are planar. NH_2BF_2 has a small positive inertial defect, and $NHMeBF_2$ an inertial defect value consistent with the moment of inertia of a methyl group only. These values show conclusively that NH_2BF_2 is planar and that in $NHMeBF_2$ all the heavy nuclei are coplanar.

The clear effect of destabilization of the highest occupied molecular orbital upon the introduction of methyl groups is seen in the variation of the first i.p. (Table 2). This can be explained, in the standard way, by hyperconjugative effects in which the methyl group pseudo π orbitals interact with the nitrogen *pπ* orbital in a slightly antibonding configuration. The theoretical calculation suggests that the feature at 14.8—16.0 eV in the spectrum of NH_2BF_2 is a composite band due to the second, third, and fourth i.p.s which are bunched together, according to the calculation, between 16.7 and 17.5 eV. These belong to the molecular orbitals composed mainly of fluorine π orbitals. The second i.p. is expected to contain some contribution from the *pσ* orbital on nitrogen whereas the third and fourth i.p.s are associated with ionization involving the in-plane b_2 and out-of-plane b_1 *p* orbitals of fluorine respectively. The calculations suggest that the next feature in NH_2BF_2 is around 17 eV, where a strong band due to BF_3 slightly obscures the spectrum. From the calculations the fifth i.p. is assigned to an orbital localized mainly in the B–F σ framework with some in-plane π character, and the sixth is a bonding orbital in the overall *pπ* system. The spectra of $NHMeBF_2$ and NMe_2BF_2 are complicated by the appearance of bands due to the methyl groups at *ca.* 16 eV. Apart from the usual overall over-estimation of the 4-31G calculations the agreement between calculation and experiment is excellent.

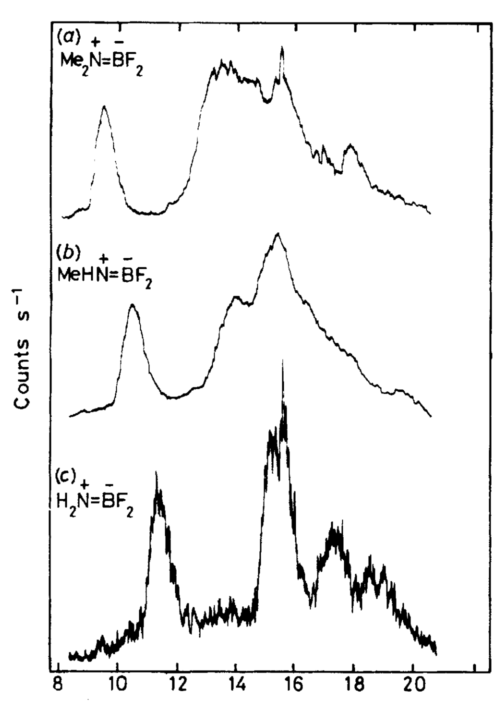

Figure. The photoelectron spectra of (*a*) NMe_2BF_2, (*b*) $NHMeBF_2$, and (*c*) NH_2BF_2 (eV ≈ 1.60 × 10^{-19} J)

Discussion

A most interesting aspect of these molecules relates to the amount of π bond character between nitrogen and boron. From the calculations there would appear to be very little (Table 3). However, microwave studies indicate that the molecules are indeed quite planar. In fact, there is no evidence even for incipient non-planarity as this would also introduce the possibility of inversion at the nitrogen and microwave results indicate that this does not occur. Indeed the torsional oscillation frequency of NH_2BF_2 is *ca.* 440 cm^{-1} (ref. 4) whereas in $CF_2{=}CH_2$ which has a bona-fide double bond it is 438 cm^{-1}.[13] Thus the main contributor to the relatively strong tendency towards planarity is probably repulsion between the F atoms and the *pπ* orbital on the N atom. The photoelectron data show nicely the gradual lowering of the first i.p. on the introduction of successive Me groups which can be explained by a mesomeric interaction between the Me group pseudo π orbital and the *pπ* electron on N.

Although NMe_3BF_3 is very easily observed in the gas phase[5,10] the present results indicate that not only is the classical donor–acceptor complex NH_3BF_3 an elusive species in the free state but the solid product of mixing NH_3 with BF_3 may also be more complicated. In those experiments HF was not

Table 3. Theoretically determined coefficients for *p*(N) and *p*(B) in aminoboranes

	NR_2BF_2			NR_2BH_2	
	p(N)	*p*(B)	*p*(F)	*p*(N)	*p*(B)
NH_2BX_2	0.90	0.12	−0.28	0.90	0.29
$NHMeBX_2$	0.87	0.15	−0.24	0.85	0.30
NMe_2BX_2	0.86	0.16	−0.22	0.83	0.31

Table 2. Ionization potentials (eV) of the aminodifluoroboranes

NH_2BF_2			$NHMeBF_2$			NMe_2BF_2		
	Exp.	Calc.		Exp.	Calc.		Exp.	Calc.
$2b_2$	11.47	12.37	$4a''$	10.45	11.18	$3b_2$	9.49	10.44
$8a_1$	15.1 15.6	16.70	$16a'$	~13.95	14.88	$11a_1$	~13.4	14.45
$5b_1$		17.10	$15a'$		15.99	$8b_1$		14.47
$1a_2$		17.48	$3a''$		16.55	$2a_2$		15.34
$4b_1$	~17.1	18.40	$14a'$	~15.2	17.04	$7b_1$	~15.6	16.27
$1b_2$	~18.4	19.13	$13a'$		17.46	$10a_1$		16.99
			$2a''$		17.67	$1a_2$		17.24
			$1a''$		19.12	$6b_1$		17.36
			$12a'$		19.85	$2b_2$		17.46
						$5b_1$	~18.0	19.14
						$1b_2$		19.71

detected and in general it was possible to observe essentially pure aminodifluoroboranes. This circumstantial evidence suggests that the solid formed from NH_3 and BF_3 may consist of polymers of the form $(NH_2BF_2)_n$ and NH_4BF_4; NH_2Me and $NHMe_2$ forming the respective methylated analogues. Extensive attempts to observe gaseous species such as $\overset{+}{N}H{=}\overset{-}{B}F$ in which two HF fragments have been eliminated were unsuccessful.

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