

## Structure and properties of unknown haloboranes

I. Novak

Department of Chemistry, National University of Singapore, Singapore 0511 (Singapore)

(Received July 24, 1990; revised November 5, 1990)

### Abstract

Molecular and electronic structures of several little known haloboranes:  $\text{BH}_2\text{F}$ ,  $\text{BH}_2\text{Cl}$ ,  $\text{BH}_2\text{Br}$ ,  $\text{BH}_2\text{I}$ ,  $\text{BHFCI}$ ,  $\text{BHBr}_2$  and  $\text{BHI}_2$  have been studied using non-relativistic *ab initio* calculations employing extended basis sets (6-31G\*\*, MIDI-4\*\*). The results are discussed in relation to the theoretical and experimental data obtained for other members of the haloborane family.

### Introduction

Chemical bonding in boron compounds continues to be a subject of interest to the present time [1]. Small boron compounds and boron halides (haloboranes) in particular represent interesting systems for the application of various MO and VB methods. Experimental methods and in particular photoelectron spectroscopy allowed direct probing of molecular energy levels and ionic states. While various theoretical methods are useful for their description of bonding and electronic structure they also provide measurable constants of the molecules, e.g. molecular equilibrium geometry, electric moments etc. Calculation of the latter quantities for unknown haloboranes is the subject of this paper with the aim of stimulating interest in their synthesis on the one hand and providing a test of predictive ability of theoretical methods on the other.

Electronic structure and bonding in haloboranes has been discussed in several papers [2–6] and they provide help in the analysis of as yet unknown molecules.

### Details of calculation

The *ab initio* MO method implemented in the Gaussian 86 and MICROMOL VI programme packages [7] has been used in this work. The extended basis sets used in the calculation were selected on the basis of cost effectiveness and reliability of calculated molecular structures. The 6-31G\*\* set was used for chloro- and fluoro-substituted boranes while boranes containing heavier halogens were calculated with MIDI-4\*\* basis sets [8]. Both sets are expected

to provide semi-quantitative values for molecular properties.

Full geometry optimization was performed for each molecule. Since no post HF treatment of correlation energy was included in the calculation we estimated the correlation contribution to orbital energies by

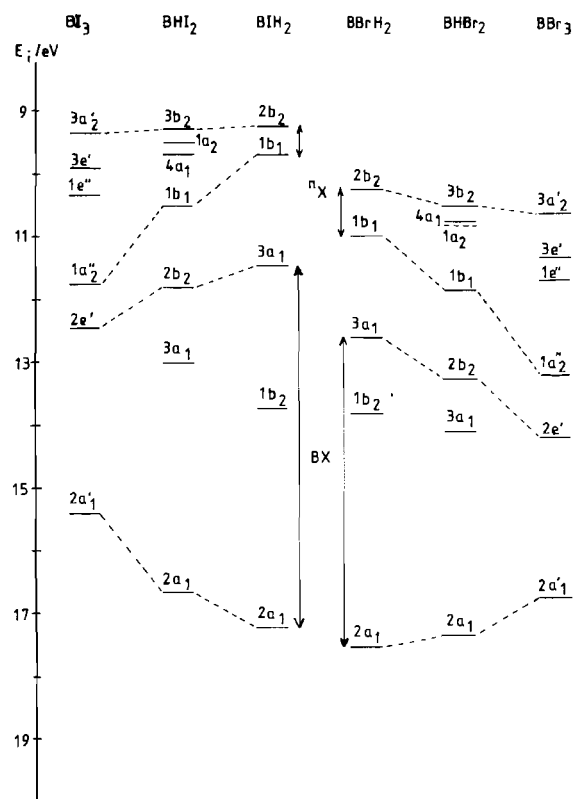


Fig. 1. Energy level diagram for bromo- and iodoboranes.

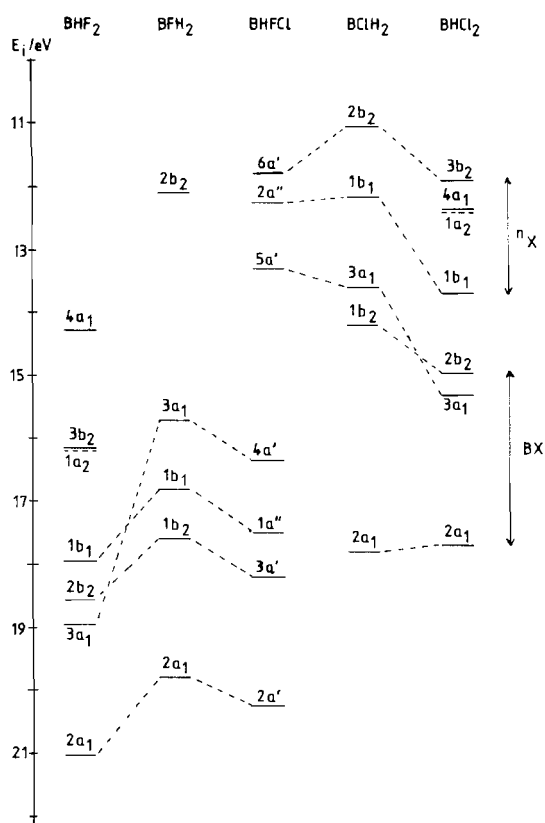


Fig. 2 Energy level diagram for fluoro- and chloroboranes.

using the 0.92 scaling factor to correct HF eigenvalues ('92% rule') [9]. The comparison of corrected values for, for example,  $\text{BHBr}_2$  and vertical ionization energies obtained from the photoelectron spectrum [5] showed that experimental and theoretical values agreed to within  $<0.7$  eV. Such an approach does not provide quantitative accuracy but helps one to discern more readily trends in the electronic structure of related compounds. For the same reason the orbital energies are not presented in numerical form but are given instead as energy level diagrams with corrected HF energies.

In the calculations the  $yz$  plane was defined as the molecular plane. All the calculations converged to bound states.

## Results and discussion

The electronic structures for the molecules studied are given in Figs. 1 and 2 as derived from photoelectron spectra (where available) and *ab initio* calculations. The calculated molecular structures and dipole moments are presented in Table 1 with population analysis in Table 2.

TABLE 1. Molecular geometries, dipole moments and enthalpies of formation for haloboranes<sup>a</sup>

Molecule (symmetry)	Geometry (nm, °)	$\mu$ (D)	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )
$\text{BFH}_2$ ( $C_{2v}$ )	$r(\text{BF}) = 0.13134$ $r(\text{BH}) = 0.11916$ $\angle \text{HBH} = 123.52$ $\angle \text{FBH} = 118.24$	0.84	-319.8
$\text{BClH}_2$ ( $C_{2v}$ )	$r(\text{BCl}) = 0.17534$ $r(\text{BH}) = 0.11836$ $\angle \text{HBCl} = 118.24$ $\angle \text{HBH} = 123.52$	1.20	-78.1
$\text{BBrH}_2$ ( $C_{2v}$ )	$r(\text{BBr}) = 0.19209$ $r(\text{BH}) = 0.11910$ $\angle \text{HBBr} = 118.12$ $\angle \text{HBH} = 123.76$	1.21	-1.4
$\text{BIH}_2$ ( $C_{2v}$ )	$r(\text{BI}) = 0.21505$ $r(\text{BH}) = 0.11880$ $\angle \text{HBI} = 117.67$ $\angle \text{HBH} = 124.66$	1.25	+94.8 <sup>a</sup>
$\text{BHFC1}$ ( $C_s$ )	$r(\text{BF}) = 0.13023$ $r(\text{BCl}) = 0.17548$ $r(\text{BH}) = 0.11778$ $\angle \text{FBCl} = 118.78$ $\angle \text{HBF} = 120.68$ $\angle \text{HBCl} = 120.54$	1.12	-477.3 <sup>a</sup>
$\text{BHBr}_2$ ( $C_{2v}$ )	$r(\text{BBr}) = 0.19105$ $r(\text{BH}) = 0.11852$ $\angle \text{BrBBr} = 121.56$ $\angle \text{HBBr} = 119.22$	0.81	-105
$\text{BHI}_2$ ( $C_{2v}$ )	$r(\text{BI}) = 0.21406$ $r(\text{BH}) = 0.11852$ $\angle \text{IBI} = 122.78$ $\angle \text{HBI} = 118.61$	0.65	+82.9 <sup>a</sup>

<sup>a</sup>Values obtained using bond additivities only.

The electronic structure of haloboranes can be analyzed in terms of halogen lone pairs ( $n_x$ ) and boron-halogen/hydrogen (BX) bonding orbitals. This distinction is however less meaningful than in halomethanes because of X-B ( $p-p$ )  $\pi$ -bonding which mixes heavily the two types of orbitals. With that qualification in mind one can observe the orbital energy levels (Figs. 1 and 2) and make the usual observations about the energy level positions, MO characters and degree and type of halogenation. We include the diagrams mainly to suggest the possible symmetries of ionic states for the unknown haloboranes. It is worth noting that our orbital assignments for  $\text{BHBr}_2$  agree very well with those suggested by Frost *et al.* [5] on the basis of photoelectron spectra. Mulliken population analysis (Table 2) reveals that formal charges on the boron atom increase with the degree of halogenation and electronegativity of the halogen.

TABLE 2. Mulliken population analysis\*

	B			H		X(F, Cl, Br, I)			
	s	p	d*	s	p*	s	p	d*	d
<b>BFH<sub>2</sub></b>									
g.o.p.	2.92	1.47	0.090	1.102	0.011	3.762	5.396	0.137	
n.a.c.		+0.520			-0.113		-0.295		
<b>BClH<sub>2</sub></b>									
g.o.p.	2.96	1.73	0.101	1.003	0.003	5.932	11.24	0.031	
n.a.c.		+0.213			-0.006		-0.201		
<b>BBrH<sub>2</sub></b>									
g.o.p.	2.99	1.67	0.073	1.022	0.018	7.98	17.22	0.104	9.89
n.a.c.		+0.272			-0.040		-0.191		
<b>BIH<sub>2</sub></b>									
g.o.p.	3.01	1.71	0.065	1.016	0.019	9.95	23.17	0.072	19.96
n.a.c.		+0.217			-0.034		-0.149		
<b>BHBr<sub>2</sub></b>									
g.o.p.	2.93	1.63	0.136	0.990	0.020	7.98	17.18	0.11	9.89
n.a.c.		+0.305			-0.008		-0.148		
<b>BHI<sub>2</sub></b>									
g.o.p.	2.98	1.71	0.123	0.984	0.020	9.95	23.11	0.08	19.96
n.a.c.		+0.188			-0.005		-0.092		
<b>BHFCl</b>									
g.o.p.	2.80	1.46	0.178	1.064	0.007	3.77	5.38	0.134(F)	
n.a.c.		+0.570			-0.071	5.94	11.25	0.0322(Cl)	
						-0.282(F)		-0.216(Cl)	

\*p\*, d\* represent polarization functions; g.o.p.=gross orbital population; n.a.c.=net atomic charge.

Iodoboranes BH<sub>2</sub>I and BHI<sub>2</sub> present an interesting exception to this rule. A possible explanation may be formulated in terms of dπ-pπ backbonding between I 4d and B 2pπ orbitals which prevents depletion of electron density from boron.

All optimized molecular geometries were planar. Trends in bond lengths can be summarized by saying that boron-halogen bond length decreases upon increasing halogenation in all molecules studied. Bond angles change only marginally throughout the series remaining close to trigonal geometry with approximately 120° angles.

The relative stabilities of haloboranes can be judged on the basis of thermodynamic data. Semi-empirical methods like AM1 were used recently [10] for extensive calculations on boron compounds but we prefer to rely on experimentally derivable values. In order to estimate ΔH<sub>f</sub><sup>°</sup> for fluoro-, chloro- and bromoboranes we have used the bond additivity scheme with neighbouring bond interactions. The latest thermochemical values [11] were used in the calculation. Such data are rather scarce and allowed the estimates for only BH<sub>2</sub>F, BH<sub>2</sub>Cl and BH<sub>2</sub>Br to be made. Applicability of the model was tested on the examples of BF<sub>2</sub>Cl, BFCl<sub>2</sub>, BF<sub>3</sub> and BCl<sub>3</sub> where the estimated

ΔH<sub>f</sub><sup>°</sup> values were within 3 kJ mol<sup>-1</sup> of experimental ones. The expression used in our work was:

$$\text{BH}_2\text{X} = (\text{BH}_3 - \text{BX}_3 + 3\text{BHX}_2)/3$$

(X = F, Cl, Br)

where empirical formulae refer to ΔH<sub>f</sub><sup>°</sup> for each compound. For the rest of the molecules the bond additivity scheme only was used due to lack of reliable data for related compounds. Thermochemical data indicate that BH<sub>2</sub>F, BH<sub>2</sub>Cl and BHFCl should be reasonably stable molecules.

#### Acknowledgement

The author wishes to thank Dr S. M. Colwell, University of Cambridge for making available a copy of the MICROMOL VI programme.

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