X-ray) and strongly support the notion that the iodobismuthates have analogous structures. It is quite apparent that bridged structures do exist for BiX_5^{2-}, $Bi_2X_9^{3-}$, and BiX_4^- complexes and that no lone pairs are present.

The analysis of the force constants determined from the stretching frequencies demonstrated an interesting competition between the different halogen atoms for the electron density on bismuth required for bonding. Bridged halogens, which form weaker Bi–X bonds than external halogens, utilize less electron density and allow the other bonds in their complexes, especially those trans to them, to be proportionally stronger. Previous studies[20] on systems such as $[PtCl_3X]^-$, $Pt(PEt_3)_2(H)X$, and $Ru(NH_3)_4(NO)X$ have shown decreases in $\nu(PtCl)$, $\nu(PtH)$, and $\nu(RuNO)$ frequencies with increasing trans effect of the X group. Since the trans influence for halogens is in the order $Cl < Br < I$, it is not surprising to see a similar effect for the bromo- and iodobismuthates. These ions are unique, however, in that the relative magnitude of the observed trans influence is determined not only by which atoms are trans to a particular group but also by whether these atoms are bridged or external. The observed trans influence from this study shows Br(bridged) < Br(external) and I(bridged) < I(external). We have also carried out similar studies on haloantimonates,[21] but the trans effect in these ions is less pronounced. This probably reflects the fact that the smaller antimony atom is less polarizable and thus less susceptible to trans influences.

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Registry No. $BiBr_6^{3-}$, 15978-03-7; $(CH_3NH_3)_3BiBr_6$, 29532-34-1; $(C_6H_5CH_2NH_3)_3BiBr_6$, 29532-27-2; $(n\text{-}C_3H_7NH_3)_3BiBr_6$, 29532-31-8; $(C_3H_5NH_3)_3BiBr_6$, 29532-28-3; (4-picolinium)$_2$BiBr$_5$, 71733-94-3; (pyridinium)$_2$BiBr$_5$, 71733-95-4; $(Et_3NH)_3Bi_2Br_9$, 30815-45-3; $(i\text{-}Bu_2NH_2)_3Bi_2Br_9$, 29532-24-9; (quinolinium)BiBr$_4$, 28961-38-8; (3-picolinium)BiBr$_4$, 28961-39-9; BiI_6^{3-}, 14636-73-8; $(n\text{-}C_3H_7NH_3)_3BiI_6$, 19478-43-4; $(Cr(en)_3)BiI_6$, 71733-85-2; $(Me_2NH_2)_3Bi_2I_9$, 12327-10-5; (piperidinium)$_3$Bi$_2$I$_9$, 69853-26-5; (4-picolinium)$_3$Bi$_2$I$_9$, 12327-81-0; $(n\text{-}C_3H_7NH_3)BiI_4$, 71733-86-3; $((CH_3)_2CHNH_3)BiI_4$, 71733-87-4.

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and University of Michigan, Ann Arbor, Michigan 48109

Ultraviolet Photoelectron Spectroscopy of Thiaboranes

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The He I and Ne I photoelectron spectra of $1\text{-}SB_9H_9$, $1\text{-}SB_{11}H_{11}$, $6\text{-}SB_9H_{11}$, $10\text{-}CH_3\text{-}1\text{-}SB_9H_8$, $10\text{-}Br\text{-}1\text{-}SB_9H_8$, and $6\text{-}Br\text{-}1\text{-}SB_9H_8$ as well as the He I spectra of $1,10\text{-}C_2B_8H_{10}$, $1,12\text{-}C_2B_{10}H_{10}$, and $B_{10}H_{14}$ are reported. Observed band characteristics allow a qualitative description of the highest occupied molecular orbitals of $1\text{-}SB_9H_9$ to be developed. Parameterization of the observed substitution effects defines the availability of electron density at the 6- and 10-positions of $1\text{-}SB_9H_9$ relative to other borane frameworks.

In past work we have demonstrated that UV photoelectron spectroscopy can be used effectively to empirically characterize the electronic structure of small boranes and heteroboranes.[2] This technique yields an exact, but not very detailed, description of the lowest lying radical cation states which can be translated into a description of the occupied molecular orbitals of the molecule.[3] Further, the examination of substituted boranes has revealed the nature of the perturbation of framework orbitals by cage substituents.[4,5] Here we extend this work to some large frameworks, particularly those containing sulfur as the heteroatom.

Recent investigations have shown that thiaborane structures[6] are reminiscent of borane and carbaborane frameworks and appear to be predictable by electron-counting systematics.[7] The directive effects of the sulfur in the electrophilic substitution reactions of $1\text{-}SB_9H_9$ and $SB_{11}H_{11}$ have also been defined.[8,9] Initial substitution does not appear to correlate with the ground-state charge distribution as apparently is the case with the carbaboranes. Also, the first facile hydroboration reaction by a polyhedral borane was recently demonstrated for $6\text{-}SB_9H_{11}$.[10] Thus, it seems that the sulfur heteroatom imparts a unique chemistry to thiaboranes.

Results and Disscussion

Model. The equatorial–apex model used below to discuss the spectra is described by Hoffmann and Lipscomb.[11] In it the orbital structure of the cage is generated from the orbitals of one equatorial and two apical fragments. The advantage of a fragment model such as this is that many oribtals are essentially transferable between different molecules containing the fragment.[12] The model is not exact, however, and is used here simply as a language to facilitate the discussion of the

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(1) (a) University of Notre Dame. (b) University of Michigan.

(2) (a) J. A. Ulman and T. P. Fehlner, *J. Am. Chem., Soc.*, **100**, 449 (1978); (b) J. A. Ulman, E. L. Andersen, and T. P. Fehlner, *ibid.*, **100**, 456 (1978).

(3) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, New York, 1970.

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(9) B. J. Meneghelli and R. W. Rudolph, *J. Organomet. Chem.*, **133**, 139 (1977).

(10) B. J. Meneghelli and R. W. Rudolph, *J. Am. Chem. Soc.*, **100**, 4626 (1978).

(11) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962).

(12) This approach has been found useful in more exact treatments as well. See for example C. Tully, *J. Chem. Phys.*, 64, 3182 (1976).

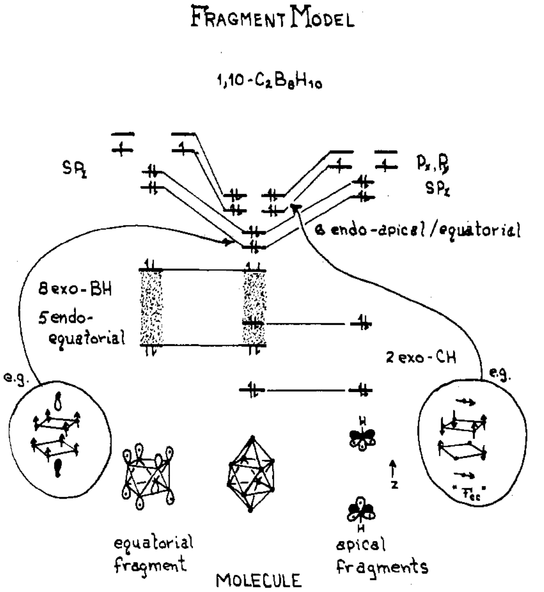

Figure 1. The equatorial–apex model as applied to 1,10-$C_2B_8H_{10}$.

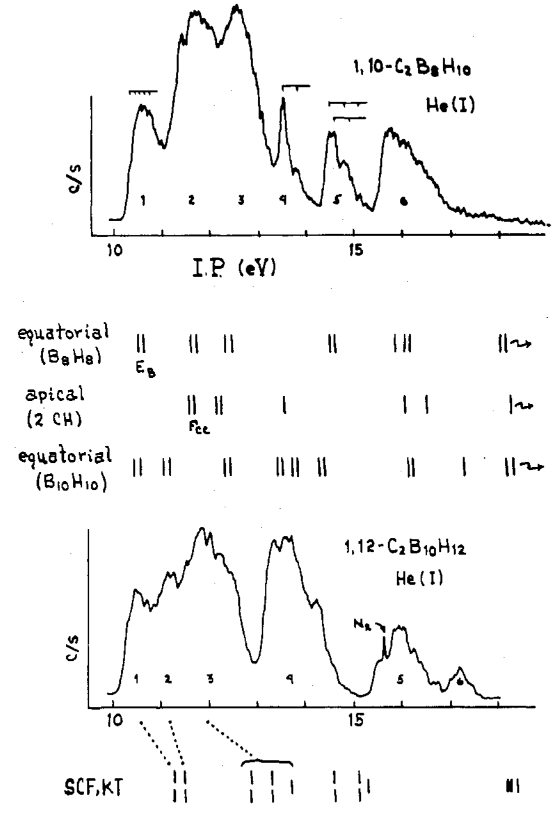

Figure 2. He I spectra of 1,10-$C_2B_8H_{10}$ and 1,12-$C_2B_{10}H_{12}$ with equatorial–apical assignments.

Table I. Vertical Ionization Potentials, Relative Band Areas, and Vibrational Fine Structure

molecule	band[a]	IP,[b] eV	A/E[c]	no. of ionizns assigned	vib struct, cm^{-1}
1,10-$C_2B_8H_{10}$	1	10.5	1.0	2	810
	2	11.4 sh			
		11.7	2.8	8	
	3	12.6	3.3		
	4	13.6	0.6	1	2580
	5	14.5	0.8	2	2440
	6	16.0	1.9	5	
1,12-$C_2B_{10}H_{12}$	1	10.6	1.3	10	
	2	11.2			
	3	12.2			
	4	13.6	1.0	7	
	5	15.9		4	
	6	17.1		1	
1-SB_9H_9	1	10.3	1.0	5	
		10.8			
	2	12.1 sh			
		12.6	1.3	6	
		13.2 sh			
	3	13.8			
	4	14.5		1	
	5	15.5		1	
1-$SB_{11}H_{11}$	1	11.1		5	
	2	12.5	2.8	9	
	3	13.6	1.0	2	
	4	16.0	2.8	6	
6-SB_9H_{11}	1	9.8			
	2	10.5	1.0	1	
	3	11.3	1.4	1	
		12.0	9.8		
		12.7			
	4	13.7			
	5	14.7			
	6	15.3			
10-CH_3-1-SB_9H_9	1	10.0	1.1	2	
	2	10.6	1.0	2	
	3	11.6	4.9	7	
		12.8			
	4	14.1	1.4		
	5	15.3	1.6		
10-Br-1-SB_9H_8	1	9.52	0.6	2	
		9.75			
	2	10.8 sh	1.0	5	
		11.4			
	3	12.5	1.4	6	
	4	15.5			
6-Br-1-SB_9H_8	1	9.51	1.2	2	
		9.84			
	2	10.5	1.0	2	
		10.8			
		11.3	1.5	3	
		11.5			
		11.7			

[a] See Figures for numbering. [b] Energies refer to band centers. Shoulders on bands are indicated by sh following the energy.
[c] Band area, He I, over mean electron energy measured with compensating polar planimeter.

nature of the radical cation states experimentally observed for a related series of molecules.

The basic features of the model are illustrated in Figure 1 for the 10-atom cage 1,10-$C_2B_8H_{10}$. The equatorial fragment shown at the left is constructed from eight BH units and associated with it are eight BH orbitals and five framework BB orbitals. In addition there are six orbitals available for interaction with the two apical fragments. In turn, associated with the apical fragments at the right are two CH oribtals and six orbitals available for interaction with the equatorial fragment. In the complete molecule we expect to find 10 filled cage-exo-hydrogen and 11 filled framework orbitals. The first purpose of this work is to characterize in terms of this model the nature of the lowest lying cation states and, hence, the nature of the highest energy-filled molecular orbitals for 10- and 12-atom cages.

1,10-$C_2B_8H_{10}$ and 1,12-$C_2B_{10}H_{12}$. The He I spectra of these molecules are presented in Figure 2 and the band positions and relative areas are given in Table I. For $C_2B_8H_{10}$ the observed vibrational fine structure (Figure 3) allows bands 1, 4, and 5 to be assigned to ionization of a framework orbital (band 1) and cage-exo-hydrogen orbitals (bands 4 and 5). As band 5 is doubled, it is assigned to two such ionizations. The location of the bands associated with the apical CH units follows from the analysis of smaller carbaboranes.[2a] This leaves nine orbitals associated with the equatorial fragment

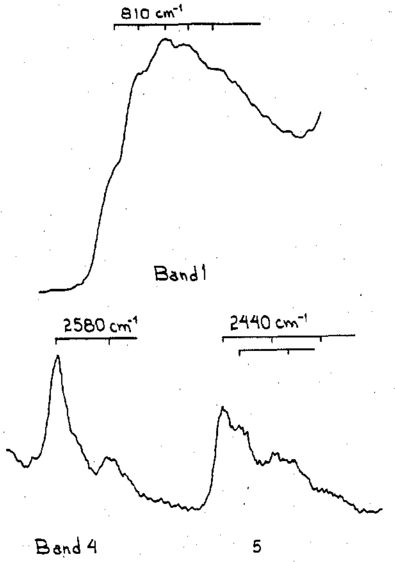

Figure 3. Details of the spectrum of 1,10-$C_2B_8H_{10}$ showing vibrational fine structure.

to be assigned. Two are expected above 18 eV and the other seven are arbitrarily placed as indicated in Figure 2.

A similar partial assignment of the spectrum of $C_2B_{10}H_{12}$ shown at the bottom of Figure 2 can be carried out. The equatorial fragment now consists of a pentagonal antiprism which has ten cage-exo-hydrogen orbitals, seven framework orbitals, and six orbitals for interaction with the apical fragments, i.e., an increase in four filled orbitals compared to $C_2B_8H_{10}$. By comparison of the spectra of the 10- and 12-atom cages it is evident that the major difference is added band intensity in the 13–14-eV region. Keeping the apical assignment the same as for $C_2B_8H_{10}$ results in the equatorial assignment indicated in Figure 2. Calculations of the SCF type have been carried out on 1,12-$C_2B_{10}H_{12}$[13] and application of Koopmans' theorem[14] yields the ionizations at the bottom of Figure 2.[15] The large spread in energies confuses the issue but for band 4 the calculations would seem to favor five rather than the seven ionizations suggested by the relative areas.

1-SB_9H_9. This 10-atom thiaborane is formally generated from $C_2B_8H_{10}$ by replacement of the two apical CH fragments with an S atom and a BH fragment. The major changes in the electronic structure will be associated with the eight apical orbitals as orbitals associated with the equatorial fragment are relatively unaffected. Of these eight the four of π symmetry with respect to the equatorial fragment (see Figure 1) are of interest as they lie at high energy in the complete molecule (bands 2 and 3 in the carbaboranes). In addition, the sulfur "lone pair" ionization that formally replaces one of the CH ionization is of interest as it should lie in the same region.

The He I and Ne I spectra of this thiaborane are shown in Figure 4 and the data are gathered in Table I. By comparison with the spectrum of $C_2B_8H_{10}$, a major shift of intensity from bands 2 and 3 of the carbaborane to lower ionization potential is obvious. The relative intensity data suggest that at least two ionizations have shifted to lower ionization potential in going from the carbaborane to the thiaborane. These are associated with framework orbitals involving the apical fragments (denoted F_{SB}) and, thus, band 1 is assigned to the ionization of these orbitals as well as two unshifted equatorial orbitals (E_B). The band clearly evident at 11.4 eV in the Ne I spectrum (11.5 eV in the spectrum of 10-1-SB_9H_8) that is not present in $C_2B_8H_{10}$ is tentatively assigned to the sulfur "lone pair" ionization. In Figure 4 it is denoted as replacing one of the cage-exo-hydrogen ionizations.

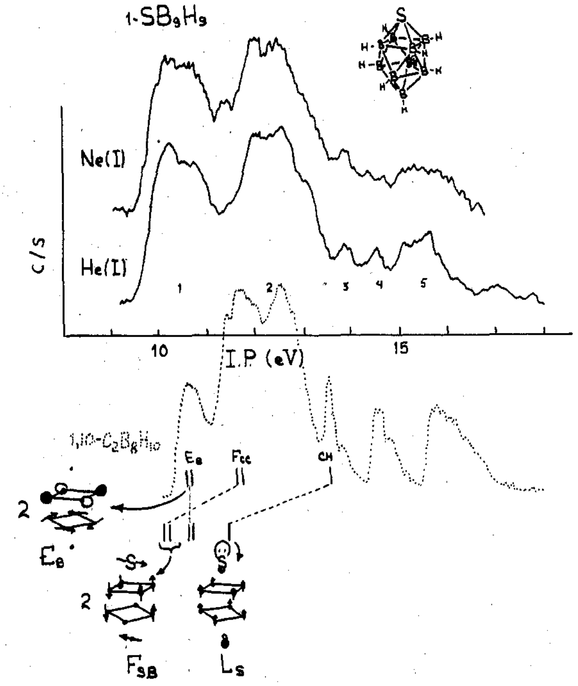

Figure 4. He I and Ne I spectra of 1-SB_9H_9 and assignment of the three bands at lowest ionization potential. The dotted spectrum is that of 1,10-$C_2B_8H_{10}$.

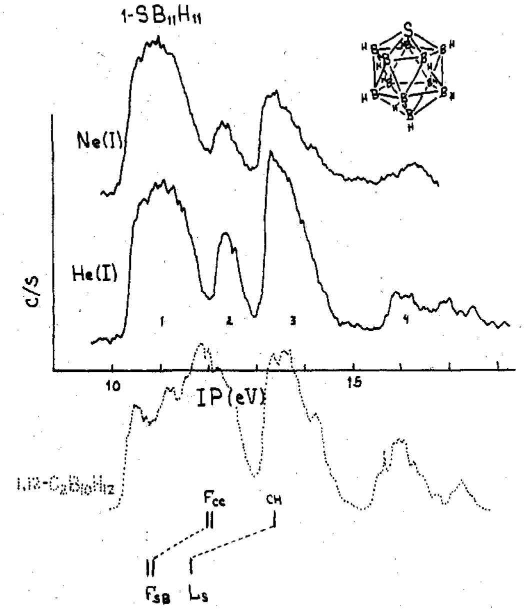

Figure 5. He I and Ne I spectra of 1-$SB_{11}H_{11}$. The dotted spectrum is that of 1,12-$C_2B_{10}H_{12}$.

1-$SB_{11}H_{11}$. Confirmation of the partial assignment of SB_9H_9 results from a comparison of the spectrum of $SB_{11}H_{11}$ with respect to that for $C_2B_{10}H_{12}$ as shown in Figure 5. Although the spectrum cannot be analyzed in detail, there is clearly a shift in intensity from band 3 of the carbaborane to lower ionization potential in going to the thiaborane. The relative intensities suggest at least two ionizations are involved but with a smaller shift than in the case of the 10-member cage (1.0

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(13) W. N. Lipscomb, "Boron Hydride Chemistry", E. L. Muetterties, Ed., Academic Press, New York, 1975, p 71. Note that only 24 orbital energies are listed.

(14) T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1934).

(15) Other calculations have appeared in which the lowest ionization potential of 1,12-$C_2B_{10}H_{12}$ is given as 12.30 eV: D. A. Dixon, D. A. Kleier, T. A. Halgren, J. H. Hall, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **99**, 6226 (1977). For additional discussion of the electronic structure see M. F. Guest and I. H. Hillier, *Mol. Phys.*, **26**, 435 (1973).

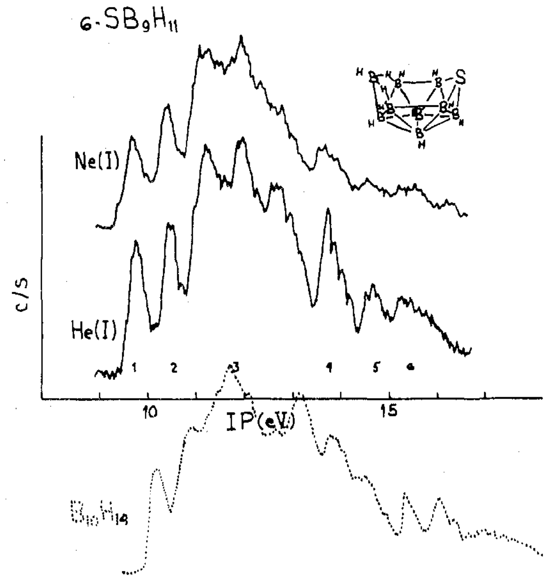

Figure 6. He I and Ne I spectra of 6-SB$_{11}$H$_{11}$ compared to the He I spectrum of B$_{10}$H$_{14}$ (dotted).

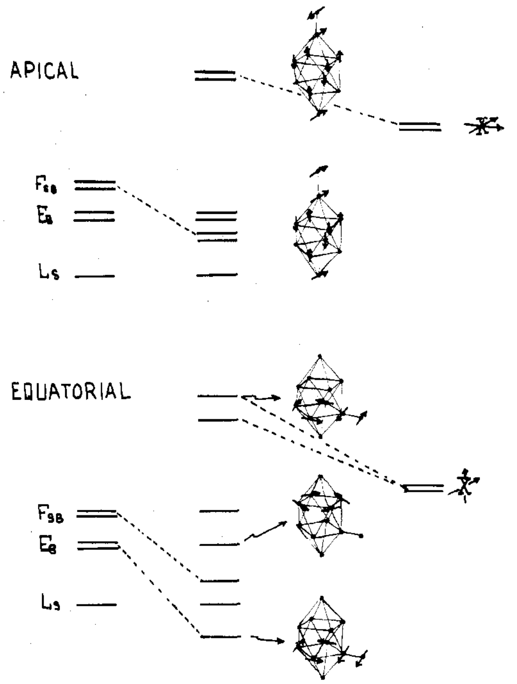

Figure 7. A filled orbital model describing the effects of π substituents in apical and equatorial positions.

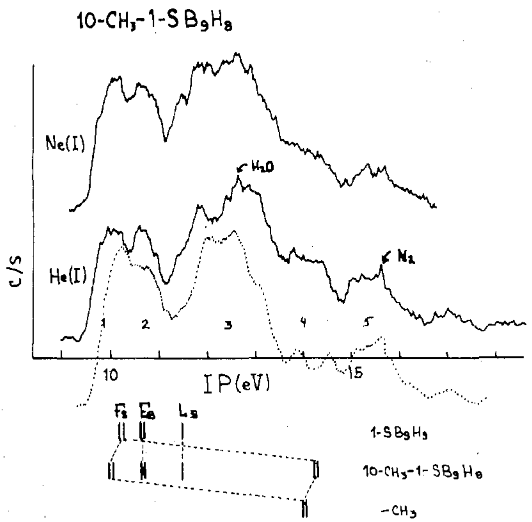

Figure 8. He I and Ne I spectra of 10-CH$_3$-1-SB$_9$H$_9$. The dotted spectrum is that of 1-SB$_9$H$_9$.

vs. 1.4 eV). We suggest that band 1 of the thiaborane contains two F$_{SB}$, the S "lone pair", and four to six equatorial ionizations.

6-SB$_9$H$_{11}$. The structure of this nido thiaborane is given at the top of Figure 6 along with the He I and Ne I spectra. For purposes of comparison, the He I spectrum of B$_{10}$H$_{14}$ is shown at the bottom of the figure. The latter borane has been the subject of numerous theoretical studies[16] and its photoelectron spectrum has been reported as well.[17] The spectrum is complex and has not been completely assigned. According to the calculations, however, the first two bands arise from orbitals with 90% B 2p character, both of which have significant contributions from the atoms in the 6- and 9-positions. Consequently, on the basis of the behavior of the closo systems the substitution of S for BH$_3$ in the 6-position should lead to a loss of intensity in the BHB region (13–14 eV) and a shift of the first two bands of B$_{10}$H$_{14}$ to lower ionization potential. The spectra bear out these predictions. It seems clear that the ostensible behavior of S as a heteroatom is to destabilize two framework orbitals constructed mainly of cage-atom p functions.

Substituent Effects on 1-SB$_9$H$_9$. Exo substitution on the SB$_9$H$_9$ cage allows a more detailed assignment of the spectrum of this molecule and generates parameters that reflect cage charge distributions. The model used to describe the effects of exo substitution has been given elsewhere[4,18] and is summarized in Figure 7. Here a qualitative description of the expected behavior of five of the high-lying orbitals of SB$_9$H$_9$ upon substitution at the 10-position (apical) vs. substitution at the 6-position (equatorial, lower belt) is given. In both cases the major interaction is between filled orbitals on the substituent which have π symmetry with respect to the cage. For apical substitution there is only interaction between the substituent and the F$_{SB}$ pair of orbitals. On the other hand, equatorial substitution will split both the F$_{SB}$ and E$_B$ pairs, leading to a more complex spectrum. Quantitatively, the shifts on substitution are described by using three parameters: namely, α_X, the energy of an electron in the interacting substituent orbital in the field of the cage; α_{cage}, the energy of an electron in a cage orbital in the field of the substituent X; and β, the parameter that describes the extent of substituent–cage interaction.

10-CH$_3$-1-SB$_9$H$_8$. The He I and Ne I spectra of this axial substituted thiaborane are shown in Figure 8, and the vertical ionization potentials appear in Table I. The main substituent interaction is between the degenerate pair of CH$_3$ orbitals with π symmetry with respect to the cage[19] and the F$_{SB}$ cage orbitals. As the CH$_3$ orbitals are expected and do appear at about 14 eV,[18] the interaction results in a destabilization of the cage orbitals. This destabilization (0.25 eV) is seen in a comparison of the bands of lowest ionization potential in the substituted and unsubstituted compounds. The comparison yields both confirmation of the presence of F$_{SB}$ in band 1 of SB$_9$H$_9$ and its location within the band. The calculated in-

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(16) See for example: E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **94**, 4467 (1972); M. F. Guest and I. H. Hillier, *J. Chem. Soc., Faraday Trans. 2*, 2004 (1974).

(17) D. R. Lloyd, N. Lynaugh, P. J. Roberts, and M. F. Guest, *J. Chem. Soc., Faraday Trans. 2*, 1382 (1975).

(18) See also H. Bock and B. G. Ramsey, *Angew. Chem., Int. Ed. Engl.*, **12**, 734 (1973).

(19) The π orbitals are those molecular orbitals that lie in or near the surface of the sphere defined by the centers of the cluster atoms and that have π symmetry with respect to a radial direction.

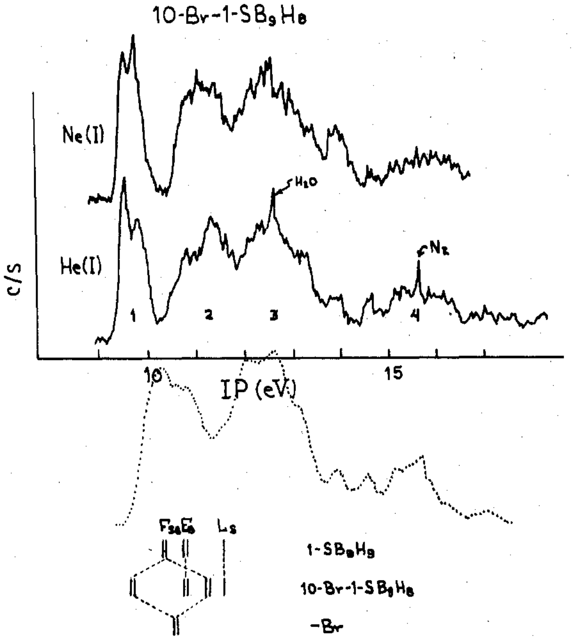

Figure 9. He I and Ne I spectra of 10-Br-1-SB_9H_8 compared to the He I spectrum of 1-SB_9H_9 (dotted).

teraction parameter, β, is -1.0 eV, approximately equal to that observed for a five-atom cage.[4]

10-Br-SB_9H_9. As the energy of the Br p orbitals is closer to that of the π-type cage orbitals, a much larger orbital energy shift is expected. The spectra of this axial substituted molecule are shown in Figure 9. The band at lowest ionization potential is split by 0.23 eV,[20] is relatively sharp, and is in the 10-eV region. It is thus assigned to ionizations of orbitals with large bromine p character. Comparison of the spectra of substituted and unsubstituted compounds indicates a stabilization of the F_{SB} bands of about 0.7 eV. This substituent shift, which is in the opposite direction to that exhibited by the methyl derivative, unambiguously demonstrates that the highest occupied molecular orbital of 1-SB_9H_9 is the F_{SB} degenerate pair.

6-Br-1-SB_9H_8. The region containing the lowest ionization potentials of this example of a lower belt, equatorially substituted thiaborane is shown in Figure 10, where it is compared to the same region for 10-Br-1-SB_9H_8. The spectra are different, substitution in an equatorial position producing the more complex spectrum. By use of the information presented thus far an internally consistent fit of both spectra as shown in Figure 10 is developed, yielding the following parameters: for axial substitution, $\alpha_x = -10.3$, $\alpha_{F_{SB}} = -10.5$, $\beta = -0.7$ eV; for equatorial substitution, $\alpha_x = -10.5$, $\alpha_{F_{SB}} = -10.5$, $\beta_{F_{SB}} = -0.8$, $\alpha_{F_{EB}} = -10.8$, $\beta_{F_{EB}} = -1.1$ eV. The numerical values of these parameters are in line with those found in previous work.[4,5]

The parameters α reflect the perturbation of one fragment by the other. As in the case of B_5H_9[4] and 1,6-$C_2B_4H_6$[5] halogen substitution causes the cage parameter $|\alpha_{F_{SB}}|$ to increase from 10.3 eV in SB_9H_9 to 10.5 eV in $BrSB_9H_8$; i.e., the cage orbital sees a more positive potential on halogen substitution. Of more interest is the change in the halogen parameter α_{Br} as it is a measure of the effective availability of electron density at the position of substitution.[22] In Table II the α_{Br} values measured for the thiaborane are compared to those previously measured for two smaller cages. The results suggest that the 6- and 10-positions of the thiaborane are more negative than the 1- and 2-positions of B_5H_9 and the 2-position of 1,6-$C_2B_4H_6$. The results also suggest that there should be a preference for electrophilic attack at the 10-position compared to the 6-position. It has been shown experimentally that even though initial electrophilic attack is more rapid at the 6-position, the 10-position is thermodynamically favored.[8] It appears that the parameter α_{Br} does not reflect kinetic considerations.

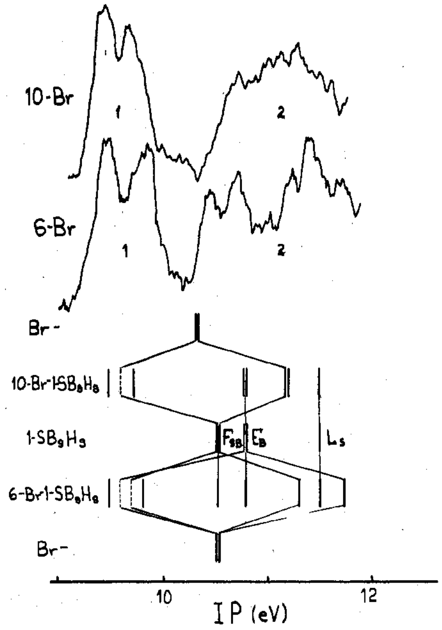

Figure 10. A comparison of the bands at lowest ionization potential in the He I spectra of 10-Br- and 6-Br-1-SB_9H_8 and an assignment of the substituent shifts.

Table II. A Comparison of α_{Br} Values (eV) for Five-, Six-, and Ten-Atom Cages

compd	$-\alpha_{Br}$	compd	$-\alpha_{Br}$
2-Br-1,6-$C_2B_4H_5$	11.2[a]	6-Br-1-SB_9H_8	10.5
2-Br-B_5H_8	11.1[b]	10-Br-1-SB_9H_8	10.3
1-Br-B_5H_8	10.6[b]		

[a] Reference 5. [b] Reference 4.

Conclusions. This work has defined the qualitative nature of the lowest lying cation states of the thiaborane 1-SB_9H_9 and, by inference, the nature of the highest lying molecular orbitals. These consist of a pair of framework orbitals involving B 2p and S 3p functions lying in the surface of the sphere containing the cage atoms followed closely by a pair of framework orbitals involving mainly B 2p functions from atoms in the equatorial belt.

Experimental Section

The two carboranes, 1,10-$C_2B_8H_{10}$ and 1,12-$C_2B_{10}H_{12}$, were gifts from Professor M. F. Hawthorne, the $B_{10}H_{14}$ was purchased (Ventron Corp.), and the thiaboranes, 6-SB_9H_{11},[6] 1-SB_9H_9,[6] $SB_{11}H_{11}$,[6] 10-CH_3-1-SB_9H_8,[9] 10-Br-1-SB_9H_8,[8] and 6-Br-1-SB_9H_8,[8] were prepared and purified as described in the literature.

The photoelectron spectra were recorded in the gaseous state by using He I (21.2 eV) and in some cases Ne I (16.8 eV) radiation. The spectrometer used has a resolution of 20 meV (fwhm) at 5-eV

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(20) The splitting of the first band is due to spin–orbit interactions and may be used as a measure of the mixing of the substituent filled p orbitals with the cage orbitals.[21] The square of the coefficient of the bromine p orbital is calculated to be 0.7 which can be compared to 0.8 for 1-Br-B_5H_8. Clearly there is significant mixing of the formally nonbonding halogen orbitals with the cage π system.

(21) F. Brogli and E. Heilbronner, *Helv. Chim. Acta*, **54**, 1423 (1971).

(22) The binding energy of the Br 4p electrons will depend on the relative shielding of the Br nucleus which in turn depends on the electron density surrounding the nucleus. But this density is sensitive to the relative availability of electrons at the position of substitution. Thus, the greater this availability, the greater the shielding, and the lower the binding energy, i.e., $|\alpha_{Br}|$.

electron energy.[23] An analyzer voltage scan was used, and a mixture of xenon and argon was used for internal calibration of the energy scale.

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Registry No. 1,10-$C_2B_8H_{10}$, 23653-23-8; 1,12-$C_2B_{10}H_{12}$, 20644-12-6; 1-SB_9H_9, 41646-56-4; 1-$SB_{11}H_{11}$, 56464-75-6; 6-SB_9H_{11}, 12447-77-7; 10-CH_3-1-SB_9H_8, 64173-76-8; 10-Br-1-SB_9H_8, 58568-92-6; 6-Br-1-SB_9H_8, 58575-43-2.

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An Experimental Test of Cryptate Assumptions in the Assignment of Single-Ion Enthalpies of Transfer

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Enthalpies of transfer of cryptand 222 between six solvents have been obtained from calorimetric measurements on heats of solution of the cryptand. Combination of these measurements with known enthalpies of complexation and known enthalpies of transfer of cations enables the corresponding enthalpies of transfer of the cryptate cations, $[M^+222]$, to be obtained. It is shown that for transfers between two given solvents values of $\Delta H_t^\circ([M^+222])$ depend on the complexed metal, M^+, and hence that single-ion assumptions such as (a) $\Delta H_t^\circ([M^+222]) = \Delta H_t^\circ(222)$ and (b) $\Delta H_t^\circ([M^+222]) = 0$ are not generally valid.

Introduction

In the first paper that dealt with the thermodynamic parameters for transfer of cryptate electrolytes between solvents, Villermaux and Delpuech[1] showed that the free energy of transfer of ($[Na^+221]X^-$) between water and aqueous methanol was the same as the free energy of transfer of X^- ($X^- = Cl^-, N_3^-$), when the latter was expressed by using the Ph_4As^+/Ph_4B^- assumption. Villermaux and Delpuech[1] tentatively suggested that their results on the water/methanol system could open the way to a new method for the assignment of single-ion free energies of transfer. The implied extra thermodynamic assumption in the above work is that $\Delta G_t^\circ([Na^+221]) = 0$. We use the symbol $[Na^+221]$ to indicate the cryptate[2] formed between Na^+ and the cryptand 221; cryptates formed from metal ions and cryptand 222 are similarly denoted as $[M^+222]$, with the general symbol $[M^+L]$ used for cryptates between any univalent metal ion and any cryptand.

As we have previously shown,[3] thermodynamic parameters for the transfer of cryptates from a reference solvent, A, to another solvent, B, can usefully be discussed in terms of the cycle, shown for the enthalpy function in eq 1. Here, ΔH_A°

$$\begin{tikzcd} M^+ + L \arrow[r, "\Delta H_A^\circ"] \arrow[d, "\Delta H_t^\circ(M^+)"'] \arrow[d, shift left=6, "\Delta H_t^\circ(L)"] & {[M^+L]} \arrow[d, "\Delta H_t^\circ([M^+L])"] \\ M^+ + L \arrow[r, "\Delta H_B^\circ"'] & {[M^+L]} \end{tikzcd} \qquad (1)$$

and ΔH_B° are the enthalpies of complexing of M^+ with L in solvents A and B, respectively, and ΔH_t° represents the enthalpy of transfer of a species from solvent A to solvent B. Thus if ΔH_A° and ΔH_B° are known from studies on the complexation in solvents A and B and if $\Delta H_t^\circ(L)$ is obtained by experiments on heats of solution, then knowing $\Delta H_t^\circ(M^+)$, it is possible to obtain experimentally the value of $\Delta H_t^\circ([M^+L])$ from the cycle:

$$\Delta H_t^\circ([M^+L]) = \Delta H_B^\circ - \Delta H_A^\circ + \Delta H_t^\circ(M^+) + \Delta H_t^\circ(L)$$

A similar cycle, of course, can be constructed for any other thermodynamic parameter. Using the cycle, and also using experimental results that yield directly $\Delta H_t^\circ([M^+L])$ from heats of solution of salts ($[M^+L]X^-$) in solvents A and B, we were able[3] to obtain $\Delta H_t^\circ([M^+222])$ values for transfer from water to methanol. We found that $\Delta H_t^\circ([M^+222]) \neq 0$ when values of $\Delta H_t^\circ(M^+)$ were chosen by using the Ph_4As^+/Ph_4B^- assumption and hence that such an extra thermodynamic assumption as $\Delta H_t^\circ([M^+222]) = 0$ could not generally hold for enthalpies of transfer in the water/methanol system.

In spite of these results, two sets of workers[4,5] have recently advocated "cryptate assumptions" in order to obtain single-ion free energies and single-ion enthalpies of transfer between various solvents. Following Schneider and co-workers,[4] we state these assumptions as (a) and (b). As with all extra

$$\begin{gathered} \Delta G_t^\circ([M^+L]) = \Delta G_t^\circ(L) \\ \Delta H_t^\circ([M^+L]) = \Delta H_t^\circ(L) \end{gathered} \qquad \text{(a)}$$

$$\Delta G_t^\circ([M^+L]) = 0 \quad \Delta H_t^\circ([M^+L]) = 0 \qquad \text{(b)}$$

thermodynamic assumptions involving single-ions, neither (a) nor (b) can directly be proved or disproved; all that can be done is to determine whether or not one or the other assumption is compatible with some other extrathermodynamic assumption such as the Ph_4As^+/Ph_4B^- assumption. However, both (a) and (b) require that for a given cryptand, L, the identity (2) must hold for different metal ions M_1^+ and M_2^+.

$$\begin{gathered} \Delta G_t^\circ([M_1^+L]) = \Delta G_t^\circ([M_2^+L]) \\ \Delta H_t^\circ([M_1^+L]) = \Delta H_t^\circ([M_2^+L]) \end{gathered} \qquad (2)$$

It should be noted that assumptions a or b and the identity (2) could be valid in terms of *G* but not in terms of *H* or vice

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