Electronic Structures of the *closo*-Thiaboranes 1-SB_9H_9 and 1-$SB_{11}H_{11}$. Electrophilic Substitution in 1-SB_9H_9†

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Comparison of the results of MNDO calculations for 1-SB_9H_9 and the previously reported gas-phase photoelectron spectrum enables the cluster-bonding molecular orbitals to be assigned. The electronic structure of 1-SB_9H_9 is compared with those of $[B_{10}H_{10}]^{2-}$, 1,10-$B_{10}H_8(N_2)_2$, and 1,10-$C_2B_8H_{10}$. The cluster bonding in these compounds is found to be very similar. The bonding in 1-$SB_{11}H_{11}$ is also analysed. Possible sites for the substitution of 1-SB_9H_9 by electrophiles X^+ (*e.g.* H^+) are examined. The observed substitution patterns are rationalised on the basis of the calculated atomic charges and the composition of the highest filled molecular orbitals.

Wade's proposal of rules governing the subrogation of BH units in boranes by isoelectronic heteroatom-based groups has rationalised many aspects of Main Group cluster chemistry.[1] To extend our understanding of the bonding in clusters we have used molecular-orbital (m.o.) calculations and gas-phase photoelectron (p.e.) spectroscopy to analyse electronic structures, *e.g.* *closo*-1,10-$B_{10}H_8(N_2)_2$.[2] The cluster bonding in the B_{10} skeletons of 1,10-$B_{10}H_8(N_2)_2$ and $[B_{10}H_{10}]^{2-}$ were shown to correspond extremely closely.[2] The present work analyses the structure of 1-SB_9H_9 and compares the results with those for the B_{10} systems above and 1,10-$C_2B_8H_{10}$. The p.e. spectra of the carborane and thiaborane have been previously reported by Fehlner *et al.*,[3] who offered an analysis of the spectra based on a qualitative apical–equatorial model. In the present analysis we used the MNDO calculation of Dewar and McKee.[4] Similarly we have analysed the structure of 1-$SB_{11}H_{11}$, for which Fehlner *et al.* have reported the p.e. spectrum.[3]

Another aspect of the present study concerns the electrophilic substitution reactions of 1-SB_9H_9. Whereas in general a reasonably good correlation has been found between the calculated atomic charges on BH or CH units in boranes and carboranes and the sites of electrophilic substitution, the results of the only m.o. calculation reported for 1-SB_9H_9 did not correlate with the experimentally determined substitution sites.[5] This calculation was of the extended-Hückel type and less sophisticated than the MNDO calculation presented here.

Experimental

The MNDO program was used as supplied by Quantum Chemistry Program Exchange without alteration.[4] All MNDO calculations were run with complete free variation of all geometry parameters.[2]

Results and Discussion

(*a*) *Molecular and Electronic Structure of* 1-SB_9H_9.—The MNDO calculation for 1-SB_9H_9 converged on a structure of almost exact C_{4v} symmetry, Figure 1. While there is no reported molecular structure of 1-SB_9H_9, the structure of the dimeric compound 2,2′-(1-$SB_9H_8)_2$, Figure 1, has been determined from *X*-ray diffraction data.[6] Table 1 shows the comparable B–S, B–H, and B–B bond lengths. It is clear that the calculated and experimental values are in good agreement with the exception of the bonds between the boron atoms B(6), B(7), B(8), and B(9). The calculated B–B distance was 193 pm compared to the mean value of 184 pm from the solid-state study. Similarly, in the study of 1,10-$B_{10}H_8(N_2)_2$, the equivalent B–B distance between boron atoms in the B_4 rings was calculated to be about 10 pm greater than the experimental value. However, in that case the MNDO calculation gave a description of the electronic structure of the molecule which was in excellent agreement with that provided by the p.e. spectrum.[2]

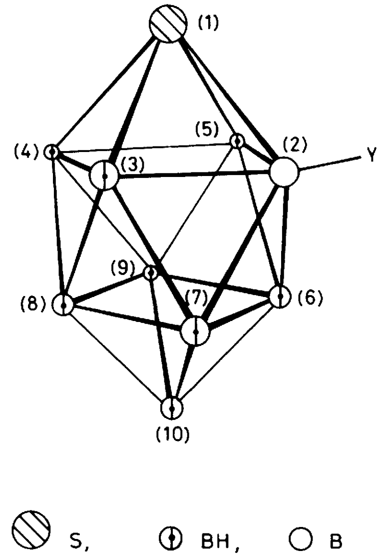

Figure 1. Structure of 1-SB_9H_9 (Y = H) and 2,2′-(1-$SB_9H_8)_2$ (Y = SB_9H_8)

The reported He(I) and Ne(I) p.e. spectra of 1-SB_9H_9 showed five distinct bands between 9.5 and 18 eV.[3] These are listed in Table 2 together with the corresponding results from the MNDO calculation. The MNDO calculated energy levels are shifted by +1.5 eV. This is of the order generally accepted as satisfactory in calculations involving third-row atoms. Comparison of the results shows that in general there is reasonably good agreement with the experimental data in terms of the energy differences between m.o. levels. The MNDO calculated assignments agree with the assignments of Fehlner *et al.*[3] for the first band (9.5—11.5 eV) and the second band (11.5—13.5 eV) except for one point. A sulphur 'lone pair' ionisation was located at 11.4 eV based on the intensity differences in the Ne(I) and He(I) spectra. Although the a_1 (11.17 eV) and *e* (12.28 eV) m.o.s (Table 2) have substantial contributions from S, it is not of a 'lone pair' character. Thus the calculation provides no support for the previous assignment, instead it locates the 'lone pair' in

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† *Non-S.I. units employed:* eV ≈ 1.60×10^{-19} J, cal = 4.184 J.

Table 1. Experimental and calculated bond lengths (pm) in the SB_9H_9 cluster

Bond	Experimental[6] from 2,2′-(1-SB_9H_8)$_2$	MNDO Calculated
S–B(2)	192	193
B(2)–B(3)	193	197
B(2)–B(6)	179	180
B(6)–B(7)	184	193
B(6)–B(10)	169	173
B–H	109	117

Table 2. Calculated MNDO energy levels for 1-SB_9H_9 and corresponding ionisations observed in the gas-phase p.e. spectrum[3]

MNDO			p.e. Spectrum	
Symmetry	Energy (eV)[a]	Band	i.p. (eV)[b]	No. of ionisations assigned
e	10.33	1	10.3	5
b_1	10.57		10.8	
b_2	11.05			
a_1	11.17			
e	12.28	2	12.1 (sh)	6[c]
e	12.63		12.6	
a_1	13.17		13.2 (sh)	
a_1	15.38	3	13.8	
a_1	16.50	4	14.5	1
b_1	17.04	5	15.5	1
b_2	17.39			
e	18.42			
a_1	21.14			
e	24.87			
a_1	27.94			
a_1	36.92			

[a] All MNDO values shifted by +1.5 eV. [b] Energies refer to band centres, sh indicates a shoulder on a band. [c] Bands 2 and 3 combined are assigned six ionisations.

an almost pure (>90%) sulphur 3*s* orbital at much lower energy, a_1 (21.14 eV). This appears surprising since one may intuitively expect sulphur lone pairs to be in 3*p* orbitals, however it is explicable in terms of the influence of the lowest-energy S^σ, P^σ cluster orbitals. We have previously shown that all *closo*-boranes have as their most stable orbitals four cluster m.o.s (S^σ, P^σ) composed essentially of B 2*s* atomic orbitals. Replacing one B atom by S in a ten-apex system leaves these four orbitals localised on the nine boron atoms. The S 3*s* orbital is too high in energy to contribute significantly to the S^σ orbital and is calculated as interacting with the P_z^σ orbital of the B_9H_9 fragment. This interaction produces two m.o.s of P_z^σ–S,3*s* character which account for virtually all the S 3*s* involvement in occupied orbitals. This causes no loss of P_z^σ character as far as the B_9 system is concerned but isolates the S 3*s* as a lone-pair non-cluster bonding orbital.

The description of the S 3*s* orbital is supported by a localised-orbital calculation. This provides a set of m.o.s equivalent to those discussed above but corresponding to a valence-bond description. It reveals a sulphur 'lone pair' of *ca.* 90% 3*s* composition, nine B–H two-centre bonding orbitals, eight three-centre boron localised cluster orbitals, and three sulphur–boron localised orbitals which are essentially two-centre bonds, Figure 2. This is one of a resonance-related set which give equivalent bonding in all equivalent faces and bonds.

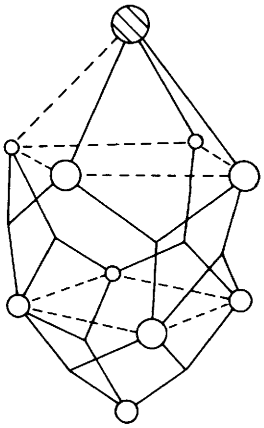

Figure 2. Localised bonding scheme in 1-SB_9H_9

For ten-apex *closo* systems we expect seven 'π-*endo*' cluster-bonding orbitals at high energy, *i.e.* in Stone's terminology, $5D^\pi$, $2F^\pi$.[2] The *exo* bonding orbitals are at lower energy, and four cluster-bonding orbitals (S^σ, $3P^\sigma$) occur at very low energy. This ordering is not completely rigid, for example in 1,10-$B_{10}H_8(N_2)_2$ the presence of apical BN_2 groups stabilises one of the D^π orbitals into the *exo* region. The calculation for 1-SB_9H_9 shows the seven highest orbitals to be cluster bonding, although the reduction in symmetry from D_{4d} to C_{4v} introduces some complications. The two F^π orbitals transform as e in C_{4v} symmetry as do two of the D^π orbitals, hence D^π–F^π mixing is possible. This directly involves the sulphur atom with its $3p_x$,$3p_y$ orbitals, which contribute to these π m.o.s and also transform as e. Two e pairs are calculated, the highest occupied molecular orbitals (h.o.m.o.s) (10.33 eV, Table 2) which are only *ca.* 10% on the sulphur atom and *ca.* 5% on the adjacent B_4H_4 belt, and a pair at lower energy (12.28 eV, Table 2) which are 35% on sulphur and 25% on the adjacent B_4H_4 belt. This distribution of the e orbitals to either end of the molecule is possible as the centre of symmetry of the cluster has been lost and thus prohibits identification of either pair as uniquely D^π or F^π. The three non-degenerate orbitals between the two e pairs are remarkably unaffected by the lowering of symmetry. The b_1, b_2 orbitals cannot have apical contribution and are both evenly distributed over the eight boron atoms. They are very similar to their D_{4d}, D^π e, precursors. The a_1 orbital is again evenly distributed on these eight atoms, but involves apical z (σ)-direction contributions, namely 16% S $3p_z$ and 35% B(10)–H σ bonding. This is very similar to the situation with $B_{10}H_8(N_2)_2$ where the orbital was stabilised by similar *exo* mixing. Overall the seven orbitals are remarkably similar to those of the other ten-apex systems, except for the localisation of the two e pairs on either end of the molecule.

The role of the S atom in SB_9H_9 is noteworthy since it formally replaced a BH^{2-} unit according to Wade's rules.[1] Sulphur has a non-cluster bonding 'lone pair' filled 3*s* orbital which is equivalent in effect, if not in distribution, to the B–H bonding pair in a BH unit. In the B–H bond the B component of the *sp* hybrid is derived predominantly from the $2p_z$ orbital. The 2*s* orbital contributes to the S^σ and P^σ orbitals, and $2p_x$,$2p_y$ contribute to the 'π-*endo*' orbitals. In the SB_9H_9 system the four 'cluster bonding' electrons from S are distributed approximately as three in the $3p_x$,$3p_y$ orbital pair which interact with the B_9H_9 unit to form cluster bonds, and one in $3p_z$ which is essentially non-bonding. The overall orbital occupancy for S is $s^{1.90}$,$p_x^{1.36}$,$p_y^{1.36}$,$p_z^{1.16}$. This may be compared with that for the

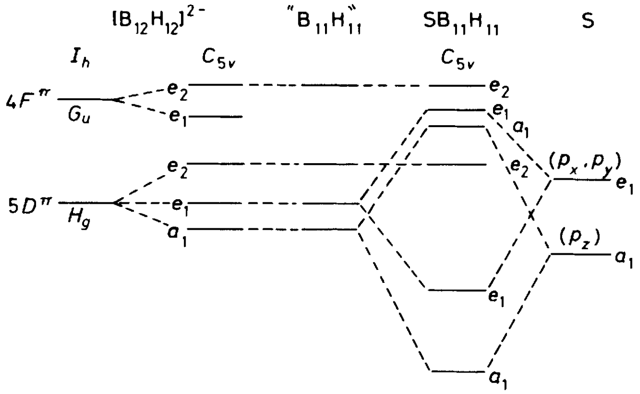

Figure 3. Correlation diagram for $[B_{12}H_{12}]^{2-}$ and 1-$SB_{11}H_{11}$ for the nine h.o.m.o.s

B(10) atom, $s^{1.13}, p_x^{0.60}, p_y^{0.60}, p_z^{0.76}$, which is typical of BH units in clusters including $[B_{10}H_{10}]^{2-}$ and 1,10-$B_{10}H_8(N_2)_2$.

(*b*) *Electronic Structure of* $SB_{11}H_{11}$.—The electronic structure of $SB_{11}H_{11}$ is analogous to that of SB_9H_9. The nine 'π-*endo*' orbitals of $[B_{12}H_{12}]^{2-}$, Figure 3, have C_{5v} symmetry corresponding to the nine highest-energy orbitals of $SB_{11}H_{11}$ calculated by MNDO. Based on $[B_{12}H_{12}]^{2-}$ the orbitals of $SB_{11}H_{11}$ can be constructed as follows. Deletion of a BH^{2-} apex removes an F^{π} orbital pair from the occupied set giving the orbitals of $B_{11}H_{11}$ as shown in Figure 3. Although these are of course not exactly equal to the orbitals of $[B_{12}H_{12}]^{2-}$ they are related. The F^{π} orbitals removed correspond to the symmetry of the π atomic orbitals of the deleted apex that is, e_1. The orbitals of the replacement sulphur atom interact with the D^{π}, e_1 orbitals of the $B_{11}H_{11}$ unit as shown, giving a high-energy e_1 pair localised (80%) on the B(6) to B(11) atoms, and a low-energy e_1 pair localised on sulphur (40%) and its adjacent B(2) to B(5) atoms (20%). This is equivalent to the description given for the corresponding SB_9H_9 orbitals. The only significant difference between the two molecules is that in $SB_{11}H_{11}$ the $3p_z$ atomic orbital is more involved in (non-bonding) mixing with a_1, a_2 symmetry orbitals, particularly those in the *exo* bonding region immediately to lower energy of the nine highest-occupied cluster orbitals. This involvement is reflected in the orbital occupations of sulphur in $SB_{11}H_{11}$: $s^{1.90}, p_x^{1.30}, p_y^{1.30}, p_z^{1.26}$.

The localised-orbital calculation again reveals a pure S 3*s* lone pair and the sulphur atom bonded by two-centre bonds to three of its adjacent boron atoms, the B_{11} cage being bonded by ten three-centre bonds.

The p.e. spectrum of $SB_{11}H_{11}$ shows three featureless bands, one at 10.5—12.0 eV is very broad, one much weaker at 12.0—12.8 eV, and one in the *exo* bonding region, 13.0—15.0 eV. The second band and the lower-energy edge of the third band show wavelength-dependent intensity indicating a contribution from sulphur to the corresponding molecular orbitals. This agrees with our calculated assignments. The second band corresponds to the sulphur-localised e_1 pair of orbitals and the leading edge of the third band to *exo* orbitals with S $3p_z$ mixing.

(*c*) *Electrophilic Substitution of* 1-SB_9H_9.—Rudolph and co-workers[5,6] studied the electrophilic halogenation of 1-SB_9H_9. Generally both 6- and 10-X-1-SB_9H_8 products were isolated when X = Cl, Br, or I with their relative proportions dependent on the reaction conditions. In all cases the 10-X isomer was thermodynamically more stable and it was favoured under forcing conditions. However, the reaction of 1-SB_9H_9 with chlorine under mild conditions gave only the 6-X isomer. This was thermally isomerised to the 10-X derivative. Rudolph and co-workers concluded that the 6 position was the site of initial electrophilic substitution and there followed a rearrangement to the 10-X isomer if the conditions were forcing enough. They attempted to correlate the initial site of substitution with the ground-state atomic charge distribution in 1-SB_9H_9 calculated using extended-Hückel theory. Their results did not correlate with the experimental findings. Other workers, most notably Lipscomb,[7] had previously been generally successful in correlating reactivity with ground-state charges in boranes and carboranes. In some cases where a simple correlation was not found, other unique features were often responsible, *e.g.* the reactivity of B_6H_{10} to electrophilic attack was largely dominated by the unusual unbridged B–B basal bond.

Table 3. Contributions of cluster units to the five h.o.m.o.s in 1-SB_9H_9

		Molecular orbitals				
Position	Unit	e		b_1	b_2	a_1
1-S	S	0.09	0.09	—	—	0.19
B(2) to B(5)	B	0.02	0.02	0.13	0.07	0.04
	H	—	—	—	0.04	—
B(6) and B(8)	B	0.20	0.04	0.07	0.13	0.04
	H	0.04	—	0.05	—	0.01
B(7) and B(9)	B	0.04	0.20	0.07	0.13	0.04
	H	—	0.04	0.05	—	0.01
B(10)	B	0.22	0.22	—	—	0.19
	H	—	—	—	—	0.21
Energy gap (eV)		$e \xleftrightarrow[0.25]{} b_1 \xleftrightarrow[0.48]{} b_2 \xleftrightarrow[0.12]{} a_1$				

The MNDO calculated atomic charges were 0.22 (sulphur), −0.10 [B(2) to B(5)], −0.09 [B(10)], −0.08 [B(6) to B(9)], and 0.07 for all H atoms. It is clear that in terms of ground-state charges the BH units in 1-SB_9H_9 are not really distinguishable and hence the site of initial electrophilic attack cannot be correlated directly with these charges. Of course, the BH site adjacent to S would be less likely than either of the other two sites on the basis of the relatively high positive charge on the S atom which would repel an incoming electrophile, but even so no clear choice can be made between the 6 or 10 positions on the basis of atom charges.

It is pertinent at this stage to consider the composition of the highest-lying filled m.o.s. These m.o.s are grouped within 0.8 eV and have *e* (h.o.m.o.s), b_1, b_2, and a_1 symmetry in C_{4v}. The next two (*e*) filled orbitals are a further 1.1 eV to lower energy and are essentially composed of contributions from S bonding to the B(2) to B(5) ring and BH units in the B(6) to B(9) ring. At almost 2 eV from the h.o.m.o.s these (*e*) orbitals can be considered as too stable to interact significantly with an incoming electrophile.

The approach of an electrophile H^+ will be determined by the repulsive interactions with the S atom and the H atoms of the BH units. Hence it will approach the open triangular (B–B–B) faces of which there are three types, *i.e.* B(10)B(6)B(9), B(5)B(6)B(9), or B(2)B(5)B(6), Figure 4. Each of these situations will be considered in turn although it is clear from the composition of the h.o.m.o.s and the next three highest-lying orbitals that the face B(10)B(6)B(9) has overall substantially more involvement in these orbitals, Table 3, than the other faces. The approach of the proton to the B(10)B(6)B(9)

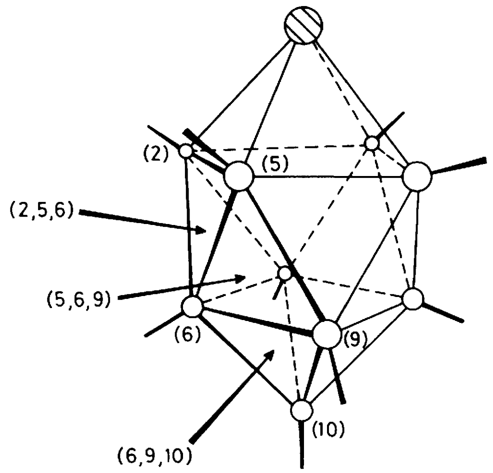

Figure 4. Possible sites for H^+ attack on 1-SB_9H_9

face changes the symmetry of the system to C_s. Accordingly the symmetry of the orbitals changes as $e \longrightarrow a' + a''$, $b_1 \longrightarrow a''$, $b_2 \longrightarrow a'$, and $a_1 \longrightarrow a'$. Only orbitals of a' symmetry will interact with the incoming H^+. The a' orbitals of the weak $H^+ \cdots SB_9H_9$ complex are shown in Figure 5 together with the contribution from atoms B(6) to B(10). It is clear that the major interaction of H^+ is with the a' orbital derived from the h.o.m.o.s. Moreover there is a larger contribution (30%) along the B(6)—B(9) vector than along the B(6)- or B(9)–B(10) vector (26%) and the H^+ would be displaced towards the B(6)–B(9) bond. Consideration of the lower orbitals shows that the b_1 orbital of SB_9H_9 plays no part, but b_2 and a_1 do. The b_2 orbital was located purely on the B(6) to B(9) ring (13% each) and in the B_4H_4 unit adjacent to S. The a_1 orbital is located mainly in the B(10)–H bond (40%) and on S (19%) with only 4% located on each B atom of B(2) to B(9). Hence this orbital cannot strongly interact with the incoming electrophile. In summary it is expected that the H^+ will go predominantly towards the B(6) to B(9) sites of SB_9H_9 in an initial substitution at the B(10)B(6)B(9) face.

Similar analyses may be considered for attack at the other faces. Attack at the B(5)B(6)B(9) face leads to a reduction of the C_{4v} symmetry of SB_9H_9 to C_s and the orbitals derived from SB_9H_9 have the same symmetries as in the case described previously. For bonding in the B(5)B(6)B(9) face, only orbitals $b_1 \longrightarrow a''$ and $b_2 \longrightarrow a'$ provide any significant electron density and the a'' orbital has incompatible symmetry with the H^+ electrophile. It is clear from Table 3 that atoms B(6) and B(9) would contribute more to the $H^+ \cdots SB_9H_9$ interaction and substitution would be expected at these atoms. In the case of attack at the B(2)B(5)B(6) face the electron density in the five highest-lying m.o.s is located predominantly in orbitals b_1 and b_2 of SB_9H_9. Attack by H^+ at the centre of the face lowers the symmetry of these orbitals to a' and a'' respectively. Therefore if attack on this face were occurring, substitution at B(2) or B(5) would be preferred (Table 3). Clearly the proximity of the positively charged S atom effectively deters substitution at these atoms in preference to the B(6) site.

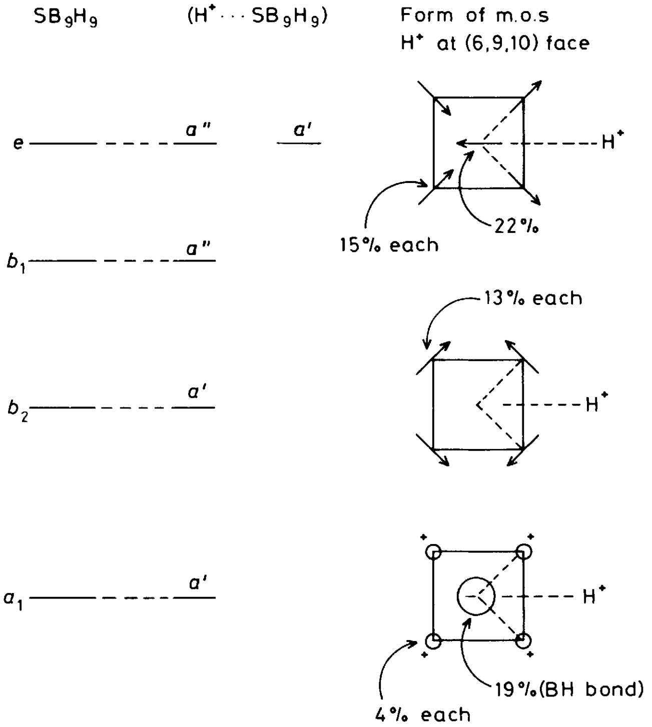

Figure 5. Form of h.o.m.o.s for H^+ attack at the B(6)B(9)B(10) face, viewed along the B(10)–H axis

Rudolph and co-workers[6] reported the heat of isomerisation of 6-Br-1-SB_9H_8 to 10-Br-1-SB_9H_8 to be 6.8 kcal mol^{-1}. The value from MNDO calculations is 1.6 kcal mol^{-1}, in good agreement with the experimental value.

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