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Substituent Effects in Cluster Species. Photoelectron Spectra of 1-, 2-, and μ-Substituted Pentaborane(9)

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Abstract: The He(I) photoelectron spectra of 1- and 2-XB$_5$H$_8$ where X = Cl, Br, I, and CH$_3$ and 1-, 2-, and μ-SiH$_3$B$_5$H$_8$ are reported. The effect of substitution on one of the skeletal molecular orbitals of the borane fragment is examined and analyzed using a LCBO model. It is shown that the relative isomer stabilities may be understood in terms of two effects: the relative potential at the substituent atom due to the position of substitution on the borane framework (an example of Bent's rule) and the relative strength of conjugative interactions at the different positions of substitution. The analysis is also consistent with the measured relative acidities of the compounds.

Many elements possess an affinity for multicenter bonding which exhibits itself in the formation of cluster species.[1] The boranes and carboranes constitute one system in which there is great variety in cluster formation.[2] It is also a system which has been extensively studied both theoretically and experimentally and, as a result, the principle of the separation of a skeletal bonding system from the exo-skeletal bonding system has been established.[3-5] This has led to a correlation between the geometrical structure of the cluster and the number of skeletal electrons.[6-8] As the number of electron pairs increases in an n atom cluster from $n + 1$ to $n + 2$ to $n + 3$, the cluster structure changes from a closo (triangular faced polyhedron with n vertices) to nido (polyhedron with $n + 1$ vertices, one of which is vacant) to arachno (polyhedron with $n + 2$ vertices, two of which are vacant). It has been pointed out that similar considerations apply to metal carbonyl clusters and transition metal π-complexes and, thus, may be important in understanding cluster formation in general.[7,9]

Clearly, any exo-endo separation is not rigorous and exo atoms or groups must affect the skeletal bonding by the usual electron donating and withdrawing mechanisms. Although these effects may not be evident in the gross structure, they would certainly affect chemical reactivity, for example. The investigation of substituent effects should result in a deeper understanding of cluster species. As boranes serve as structural prototypes of cluster species[7,9,10] they should also serve as models for investigating cluster substituent effects. This aspect of borane chemistry has not been neglected, having been examined from both the theoretical[11] and experimental points of view.[12-14] However, important questions, such as explaining observed relative isomer stabilities, are only beginning to be answered.

A relatively recent technique, photoelectron spectroscopy, yields direct information on the electronic structure of ions and yields a representation of the molecular orbital structure of molecules.[15] As such it is ideally suited to investigate the effects of substituents on electronic structure and it has been fruitfully used for this purpose on a number of previous occasions.[16] In the following we report the pho-

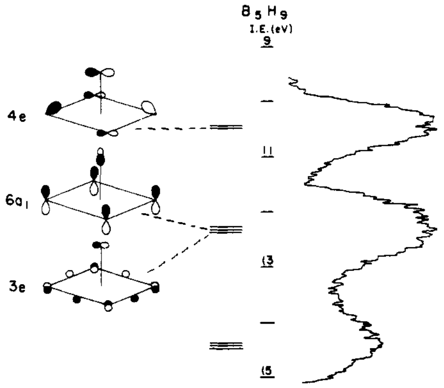

Figure 1. The photoelectron spectrum of B_5H_9 and molecular orbital assignment of bands.

toelectron spectra of 1-, 2-, and μ-substituted pentaborane(9) and show how these spectra reflect the effect of the substituents on the electronic structure of the boron cluster.

Results and Discussion

A Model for Substituent Effects in B_5H_9. The photoelectron spectrum of B_5H_9 is shown in Figure 1 and is the same as that reported elsewhere.[5,17] Although three-center valence bond formalism with resonance structures[3,18] is a convenient description of the bonding in B_5H_9, it is not useful in discussing photoelectron spectra in the Koopmans' approximation.[19] Here a description reflecting the molecular symmetry is required, i.e., a molecular orbital approach. Existing treatments range from simple qualitative discussions[20] to good quality SCF calculations.[11] The latter allow the assignment of the spectrum of B_5H_9.[5,17] The nature of some of the molecular orbitals in terms of their atomic orbital constitution is indicated in Figure 1. Of special interest here is the first band, which has been assigned to ionization from the highest filled 4e molecular orbital. This doubly degenerate orbital results from an antisymmetric combination of sp^n hybrids on opposing basal borons with 2p atomic orbitals of the apical boron.[20] The 4e orbital is a framework orbital and it will be noted that this orbital has π symmetry with respect to exoskeletal bonds. In addition, the associated band in the photoelectron spectrum is well separated from other bands, thereby allowing shifts upon substitution to be unambiguously observed. Such shifts will reflect the effects of substitution on the framework bonding.

In order to relate shifts in the 4e band to effects of substitution it is necessary to develop a model. Although good quality complete molecular orbital calculations could be used, once the spectrum of an unsubstituted molecule has been assigned, changes in a related series can be understood using less rigorous approaches.[16] From the point of view of the practical chemist such approaches, though less exact, tend to be more useful.

An appealing approach is to break molecules into fragments and to consider any observed species to result from fragments combined using simple perturbation theory.[21] This type of approach has been used fruitfully in the past to interpret photoelectron spectra in terms of physically meaningful ideas of the role of the substituent in modifying the electronic structure of the substituted molecule.[22,23]

The "fragment method" of interest here is the linear combination of bond orbitals (LCBO) method in which fragment orbitals of proper symmetry are combined in a bonding and antibonding sense.[16,24,25] The parameters used are the energy of each fragment orbital (α) and the conjugative interaction parameter (β). The fragment orbital energy may change between substituted and unsubstituted compounds due to a symmetry independent inductive effect. This is caused by an effective change in the core potential of the substituted atom by the substituent. On the other hand, the conjugative effect is symmetry dependent, resulting from the mixing of orbitals on the substituent with those on the substituted species. In the LCBO model this interaction is exclusively between filled orbitals. However, in certain cases the interaction between filled orbitals on the substrate and empty orbitals on the substituent as well as that between empty antibonding orbitals on the substrate and filled orbitals on the substituent must be considered, i.e., back-bonding. In most cases it is not possible to separate inductive from conjugative effects much less demonstrate back-bonding. That is, more parameters than available data are required. However, there are special situations in which the inductive and conjugative effects may be separately considered.[26] These models have been used to discuss π-π, π-σ, etc. interactions.[16] Here we apply this model to f-π and f-σ interactions where f refers to a framework or skeletal molecular orbital.

Both of these models involve equating ionization potentials to negatives of orbital energies. This assumption, known as Koopmans' theorem,[19] is particularly bad when the molecular orbital in question is localized in part of the molecule such that reorganization and correlation effects no longer cancel.[27] In the boranes, however, delocalization is extensive and comparison of SCF calculations of boranes and carboranes with photoelectron spectra via Koopmans' theorem is good.[5,28] As we propose to show below, delocalization is also significant in the substituted pentaboranes, and we do not expect this approximation to cause any qualitative errors. Reorganization and correlation effects are undoubtedly included in the empirical parameters α and β; thus, one must be careful not to attach chemical significance to the absolute magnitudes of these parameters.

Application of the Model to Substituted Pentaboranes. In Figure 2, the fragment model is applied to XB_5H_8 with X in the 1-, 2-, and μ-positions using the 4e orbital of B_5H_9 and orbitals of X having π symmetry. The inductive effect, $\delta\alpha$, causes a shift to either lower or higher energy depending on whether the effective core charge of the substituted atom is increased or decreased. However, it does not remove the degeneracy of the 4e orbital. In the 1-substituted case the conjugative effect also will not remove the degeneracy and, if the interaction of X with other molecular orbitals is small, will cause a symmetrical splitting as indicated. For 2-substitution, the conjugative effect will remove the degeneracy of the 4e orbital because only one of the X π type orbitals has the proper symmetry for interaction. The unaffected orbital will exhibit inductive effects only; thus, the splitting δE reflects the conjugative effect alone. The interaction parameter, β, is calculated as indicated. Note that β is proportional to orbital overlap and for a fixed β, δE decreases for increasing ($\alpha_X - \alpha_{4e}$). For μ-substitution, there can be little conjugative effect as the atomic orbitals involved in the major interaction are no longer coplanar. In this case there will only be an inductive effect.

The Halopentaboranes. We begin by considering the photoelectron spectra of the iodopentaboranes shown in Figure 3. The first band in 1-IB_5H_8 exhibits a splitting of 0.52 eV and is clearly due to ionization from a molecular orbital having mainly halogen character. The second band then is attributed to ionization of an orbital correlating with the 4e orbital of B_5H_9. In the 2-IB_5H_8 the splitting of the first halogen band has increased to 0.62 eV and the second band is now clearly split with the component at higher ionization potential having the greater intensity as expected from the greater halogen character.[29] If one assumes that the inductive effect for 1- and 2-substitution is the same[30] then α_{4e}

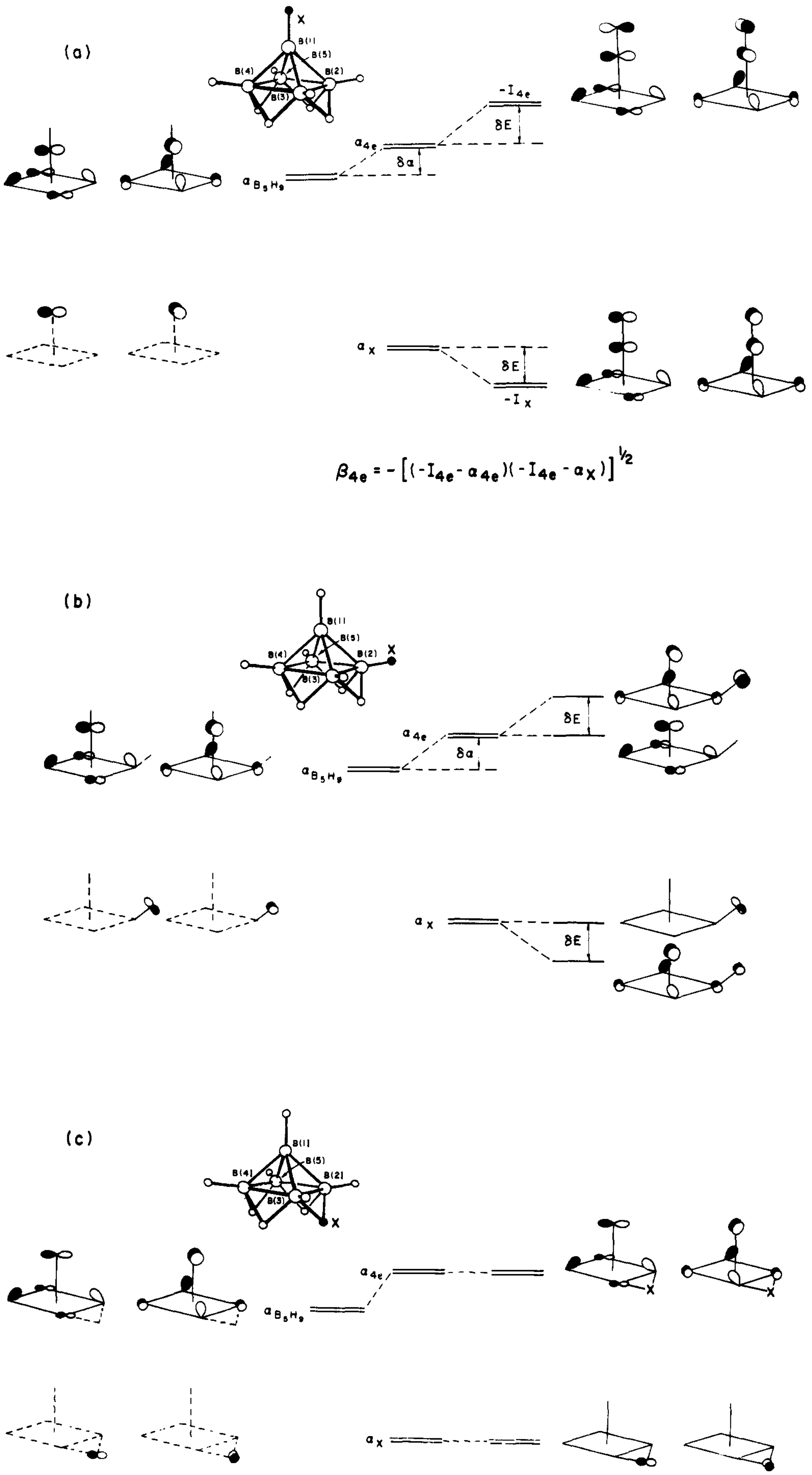

Figure 2. General scheme for interaction of substituent molecular orbitals with the 4e molecular orbital of B_5H_9: (a) 1-XB_5H_8, (b) 2-XB_5H_8, (c) μ-XB_5H_8.

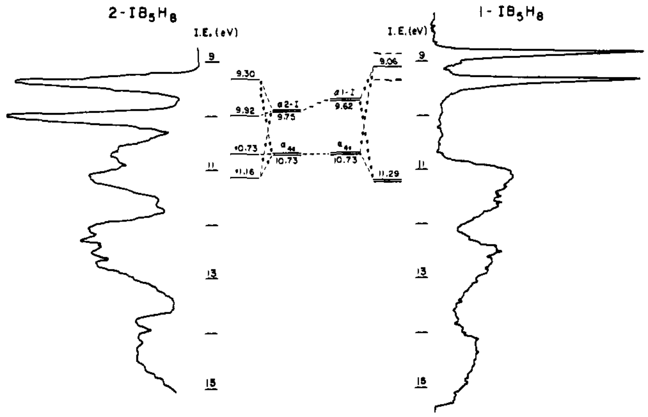

Figure 3. The photoelectron spectra of 2- and 1-IB$_5$H$_8$ and assignment of bands.

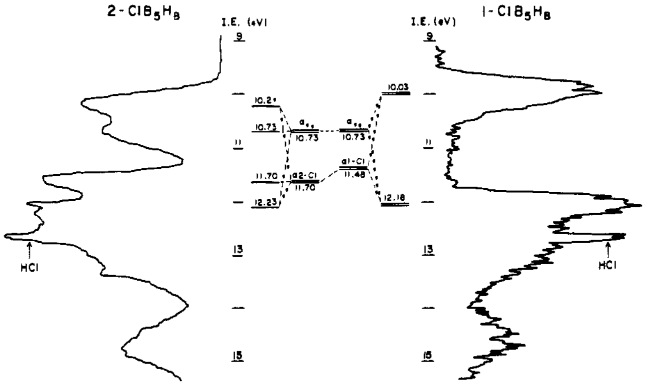

Figure 4. The photoelectron spectra of 2- and 1-ClB$_5$H$_8$ and assignment of bands.

Table I. Parameters (eV) Characterizing the Effect of Substituents on the 4e Molecular Orbital of Pentaborane(9)

X	1-XB$_5$H$_8$		2-XB$_5$H$_8$		μ-XB$_5$H$_8$	
	$-\alpha_{4e}$[a]	$-\beta_{4e}$[a]	$-\alpha_{4e}$[a]	$-\beta_{4e}$[a]	$-\alpha_{4e}$[a]	$-\beta_{4e}$[a]
Cl	(10.73)[b]	1.01	10.73	0.85		
Br	(10.73)[b]	0.98	(10.73)[b]	0.84		
I	(10.73)[b]	0.97	10.73	0.80		
CH$_3$	(10.38)[b]	0.79	10.38	0.55		
SiH$_3$	(10.42)[c]	—[d]	(10.42)[c]	—[d]	10.17	

[a] Defined in the text. [b] Assumed values. [c] Estimated as indicated in the text. [d] Cannot be calculated.

Table II. Parameters (eV) Characterizing the Effect of B$_5$H$_8$ on the "Lone Pair" Orbitals

X	$-\alpha X$[a] est	$-\alpha_{1\text{-}X}$[a]	$-\beta_{1\text{-}X}$[a]	$-\alpha_{2\text{-}X}$[a]	$-\beta_{2\text{-}X}$[a]
Cl	11.9	11.48	(1.01)[b]	11.70	(0.85)[b]
Br	10.9	10.65	(0.98)[b]	11.07	(0.84)[b]
I	10.0	9.62	(0.97)[b]	9.75	0.82

[a] Defined in the text. [b] Assumed values.

for the pentaborane framework is −10.73 eV, i.e., $\delta\alpha_{4e} \approx -10.53 + 10.73 = 0.2$ eV. This leads to a net conjugative interaction of 0.56 and 0.43 eV in the 1- and 2-compounds, respectively. With the α_I's obtained below, these splittings lead to β_{4e} values of 0.97 and 0.80 eV, respectively.[31]

The complication caused by the splitting of the lowest bands by a combination of spin-orbit and substituent interactions does not allow a simple determination of the conjugative effect on the "lone pair" orbitals. However, this complication has been treated previously.[32] The observed splitting in the symmetrical 1-IB$_5$H$_8$ (0.52 eV) is a sensitive probe of the relative participation of the 4e framework orbital and the iodine p orbitals in the "lone pair" orbital. To the extent that boron atomic orbitals are mixed with those of iodine, the observed splitting of the band resulting from ionization of the "lone pair" orbital will be reduced. Taking the spin-orbit splitting in the absence of any mixing as 0.63 eV[33] leads to an estimate of 9% for the relative participation of the 4e orbital in the "lone pair" orbital. In 2-IB$_5$H$_8$ the splitting of the first band is 0.63 eV and the breadth of the peaks indicates significant mixing with the boron framework. This case, in which there is unsymmetrical interaction with the "lone pairs", has also been discussed previously, and we use the model given.[32] With $\alpha_{4e} = -10.73$ eV, $\alpha_{2\text{-}I} = -9.75$ eV, $\beta_I = -0.82$, and a spin-orbit interaction of 0.62 eV, the positions of the first four peaks in the photoelectron spectrum of 2-IB$_5$H$_8$ are reproduced. The value of the new parameter generated by this procedure, $\alpha_{2\text{-}I}$, is quite reasonable as one estimates from BI$_3$ an $\alpha_I \approx -10.0$.[34] Finally, using the conjugative interaction parameter, β_{4e}, and the center of gravity of the spin-orbit split first band of 1-IB$_5$H$_8$, an $\alpha_{1\text{-}I} = -9.62$ eV is calculated. It will be noted that $\beta_{4e} \approx \beta_I$ which indicates that the main conjugative interaction is with the 4e orbital as might be expected on the basis of the fact that all the other orbitals of B$_5$H$_9$ are at considerably lower energy. The parameters for the framework interaction are gathered in Table I and those for the "lone pair" interaction in Table II.

The model rationalizes the interaction of iodine with the 4e framework orbital but, to be of value, it must do so for the other halogenated pentaboranes as well. Consider next the spectra of the chloropentaboranes shown in Figure 4. Here the halogen band will be at higher ionization potential than the 4e band as the estimated α_{Cl} from BCl$_3$ is about −11.9 eV.[34] The relative intensities of the first two bands are consistent with this expectation. The first band is assigned to ionization from an orbital derived from the pentaborane 4e orbital and the second to an orbital derived from the chlorine nonbonding orbitals. In 2-ClB$_5$H$_8$ the first band is split but, in contrast to the 4e band in 2-IB$_5$H$_8$, the component at lower ionization potential has the higher intensity due to greater halogen character. One of the expected two components of the chloro band is somewhat obscured by an impurity band. We then identify $\alpha_{4e} = -10.73$ eV (which is identical with that for iodopentaboranes) which leads to a conjugative interaction of 0.70 and 0.49 eV for the 1- and 2-compounds, respectively. With the assumption of no significant interaction of the "lone pair" orbitals with the other borane orbitals, one calculates $\alpha_{1\text{-}Cl} = -11.48$ eV and $\alpha_{2\text{-}Cl} = -11.70$ eV.[35]

In the iodo compounds the 4e orbital was stabilized by the substituent interaction while in the chloro compounds the 4e was destabilized. The bromo compounds represent the intermediate situation as one estimates from BBr$_3$, $\alpha_{Br} \approx -10.9$ eV,[34] which is nearly equal to α_{4e}. In the spectrum of 1-BrB$_5$H$_8$, illustrated in Figure 5, the relative intensities and the spin-orbit splitting of 0.26 eV clearly identifies the first band as resulting from the ionization of an orbital derived mainly from bromine. As with 1-IB$_5$H$_8$ this splitting leads to an estimate of 10% for the relative participation of the 4e orbital. In 2-BrB$_5$H$_8$, three bands appear in the region of interest having the intensity ratio of about 1:2:1 and the second of the three appears to be split. In this case the assumption of $\alpha_{4e} = -10.73$ suggests that the first band in 2-BrB$_5$H$_8$ has mainly B$_5$H$_8$ 4e character. The result is a conjugative interaction of 0.94 and 0.69 eV for the 1- and 2-compounds, respectively. Again assuming $\beta_{Br} = \beta_{4e}$, $\alpha_{1\text{-}Br} = -10.65$ eV, and $\alpha_{2\text{-}Br} = -11.07$ eV.[36]

Comparing the parameters for the 4e framework orbitals, gathered in Table I, one sees that in all cases the β values

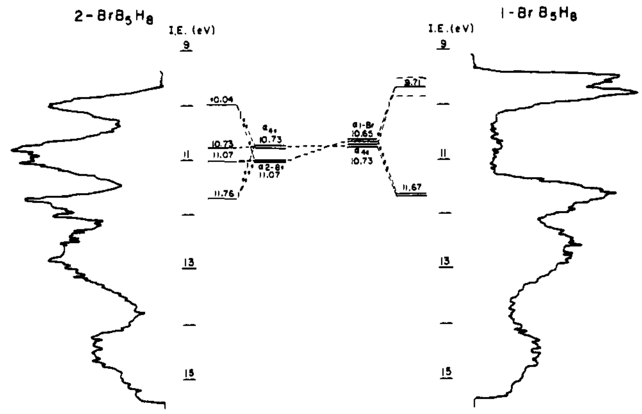

Figure 5. The photoelectron spectra of 2- and 1-BrB_5H_8 and assignment of bands.

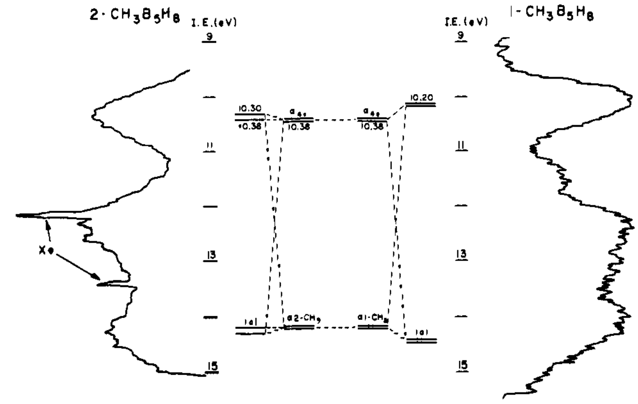

Figure 6. The photoelectron spectra of 2- and 1-$CH_3B_5H_8$ and assignment of bands. (a) The position of the CH_3 band cannot be determined with certainty.

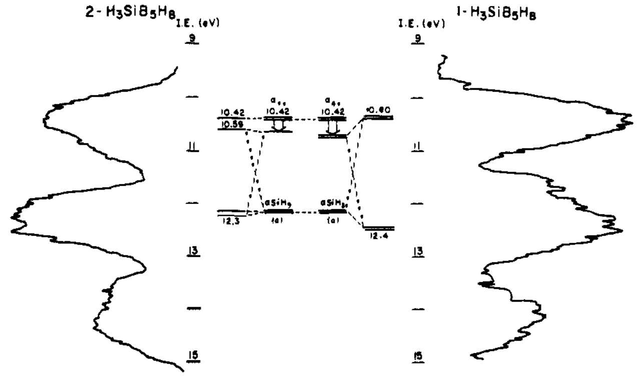

Figure 7. The photoelectron spectra of 2- and 1-$H_3SiB_5H_8$ and assignment of bands. (a) The unknown amount of stabilization due to Si←f back-donation, indicated by the broad arrows, does not allow a determination of α_{SiH_3}.

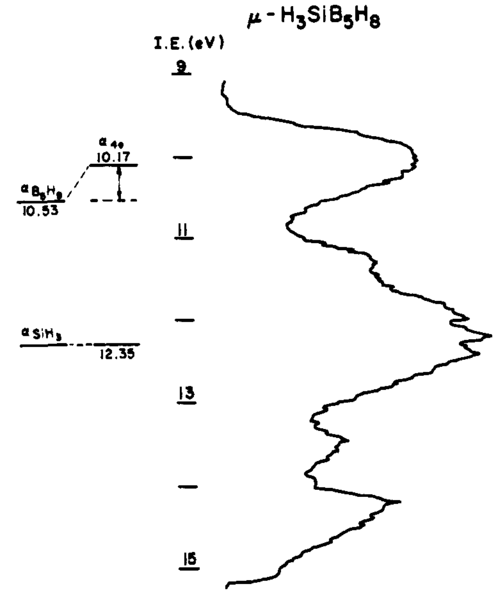

Figure 8. The photoelectron spectrum of μ-$H_3SiB_5H_8$ and assignment of bands.

are larger for the 1-compound and that there is a slight trend of increasing β as one goes from I to Cl. This suggests that, as far as the 4e orbital is concerned, there is a significantly larger conjugative effect for the 1-pentaboranes than the 2-pentaboranes. In addition this effect is relatively constant over the halogens. The inductive effect on the cage boron where substitution takes place is relatively small (0.2 eV) and independent of substitution in the 1- or 2-positions.

The parameters for the substituent orbitals are collected in Table II. The most striking observation is the difference in the halogen α values with position; $\alpha_{2\text{-X}}$ being lower in energy than $\alpha_{1\text{-X}}$ for all three halogens.[37] It appears that the halogen core potential is sensitive to the difference in the 1- and 2-positions, the 2-position producing the higher effective core potential at the substituent atom. This is reasonable as all calculations indicate that in B_5H_9 the apical boron has a greater negative charge than the basal borons.[11]

The Methyl- and Silylpentaboranes. In the methylpentaboranes the methyl group acts both inductively by affecting the effective core charge of the substituted atom and conjugatively by interaction of the 4e framework orbital with the C-H group orbitals of CH_3 having π symmetry. The latter interaction will tend to destabilize the 4e orbital as α_{CH_3} is about -14.2 eV.[16] The spectra of 1- and 2-$CH_3B_5H_8$ are presented in Figure 6 and the first band in both compounds is certainly due to ionization from an orbital derived mainly from the 4e orbital of pentaborane. In contrast to the halopentaboranes there is no clear evidence of splitting of the first band in 2-$CH_3B_5H_8$. However, this band is significantly broader than the corresponding band in 1-$CH_3B_5H_8$. If it is assumed, on the basis of the results for the halopentaboranes, that this increased breadth is due to a conjugative effect, one estimates $\alpha_{4e} = -10.38$ eV and a conjugative effect of 0.2 and 0.1 eV for the 1- and 2-compounds, respectively. As pointed out in the appendix, the conjugative effect in the 2-compound is probably obscured by Jahn-Teller effects. Finally, it is noted that in contrast to the halo compounds the inductive effect tends to destabilize the 4e orbital. Although the changes are not so striking as with the halogen compounds the same interpretation yields a satisfactory explanation.

The silylpentaboranes present two additional features along with those already touched upon. First the μ-isomer can be examined for the first time and secondly there is the possibility that the conjugative effect may include interaction between filled pentaborane orbitals and empty silicon d orbitals, i.e., Si←f back-donation.[16] The spectra of 1-, 2-, and μ-$SiH_3B_5H_8$ are presented in Figures 7 and 8. As α_{SiH_3} is about -12.5 eV,[16] the first band in the spectra of all three compounds must be due to ionization of the orbital correlating with the 4e of pentaborane. As pointed out in the preliminary discussion above, the effect of μ-substitution can only be inductive in nature and the spectrum shows a destabilization of the 4e orbital by 0.36 eV upon substitution. As μ-substitution results in strong interaction with two basal borons one might expect the inductive effect to be approximately half as large in 1- and 2-$SiH_3B_5H_8$. This would

Table III. Contribution of Electronic Effects to Relative Isomer Stabilities

X	Relative potential	X←f	f*←X	Observed stabilities
Cl	2– > 1–		1– > 2–	2– ~ 1–
Br	2– > 1–		1– > 2–	1– > 2–
I	2– > 1–		1– > 2–	1– >> 2–
CH_3	2– > 1–	—	—	2– > 1–
SiH_3	1– > 2–	1– > 2	—	1– > 2–

suggest that α_{4e} for these compounds should be -10.35 eV. If there were only a conjugative effect between filled orbitals, such as in the case of CH_3, then the ionization potentials of the 1- and 2-compounds should be *less* than 10.35 eV. Instead they are somewhat higher. This indicates that either there is no conjugative effect or Si←f interaction is significant. The former does not appear to be correct as there is measurable conjugative interaction in the methylpentaboranes and, if past experience is correct,[16] there should also be a measurable effect for the silyl derivative. Therefore, quite independent of the details of the interpretation to follow, the qualitative difference in the μ- and 1-, 2-spectra indicate a significantly different situation for SiH_3 as compared to CH_3. Recently, back-bonding in the silyl derivatives has been suggested to account for the shorter B–Si distance in 1-$SiH_3B_5H_8$.[13] Our data support this interpretation.

It will be noted that the first band of the 2-compound is considerably broader than that of the 1-compound. If it is assumed again that this increased breadth is due to a net conjugative effect, the detailed interpretation schematically illustrated in Figure 7 follows. Here the broad arrows indicate an unknown amount of stabilization by the Si←f interaction. This interaction has the same symmetry requirements as the conjugative effects discussed above. The dotted lines indicate the conjugative effects between the filled orbitals. This leads to an $\alpha_{4e} = -10.42$ and a net conjugative effect of 0.02 and -0.17 eV for the 1- and 2-compounds, respectively. It is not useful to calculate the β parameters in this case.

Isomer Stabilities. The relative stabilities of the various isomers of XB_5H_8 is an intriguing question that has yet to be satisfactorily explained. For X = CH_3 the 2-isomer is more stable than the 1-isomer while for X = SiH_3 the 1-isomer is more stable than the 2-isomer which in turn is more stable than the μ-isomer. For the halopentaboranes, 1-Cl is about as stable as 2-Cl, 1-Br is slightly more stable than 2-Br, while 1-I is more stable than 2-I.[38,39] The results discussed above provide the basis for a rational explanation of these relative stabilities.

The relative stabilities are a resultant of competing effects. Here we consider only electronic effects as steric effects do not appear important for the compounds under consideration. There are two qualitative conclusions resulting from the interpretation of the photoelectron spectra given above that are important here. First, for the halo compounds, the more positive basal borons yield a relative substituent orbital stabilization for 2-substitution, i.e., $\alpha_{2\text{-}X}$ is consistently lower than $\alpha_{1\text{-}X}$ (Table II). This is consistent with the application of Bent's rule[40] which predicts that substituents more electronegative than hydrogen will "prefer" the basal boron because of its lower s character. This effect is expected to be more important the smaller the halogen.[41] Another way to view this is that the center of gravity of the first four bands is lower for the 2- than for the 1-substituted compound. Therefore π interactions should always lead to a preference for the 1-isomer. Two π effects may be considered. Evidence was presented above for Si←f back-bonding in $SiH_3B_5H_8$. In addition, for the halogens, one must consider the possibility of f*←X, i.e., π donation to an empty antibonding orbital. This should also lead to a preference for the 1-isomer. Although it is not necessary to include f*←X donation to explain the photoelectron spectra, we suggest that if Si←f is significant f*←X should be as well.

In Table III these ideas are applied to the XB_5H_8 compounds studied here. As may be seen, they adequately explain the relative stabilities observed provided that the relative potential effect increases in the order I < Br < Cl < F. Thus, we predict that for fluorine, the 2-isomer will be much more stable than the 1-isomer. In fact, only 2-FB_5H_8 has been prepared.[14]

In summary, the 2-position is favored by highly electronegative substituents while the 1-position is favored by substituents with low electronegativities that are π acceptors or π donors. This rationalization of relative stabilities, although based on empirical observations, is neither complete nor rigorous. However, it should be of practical value in predicting and discussing substituent effects in other cluster species.

Relative Acidities. The relative Brönsted acidities of some substituted pentaboranes have been measured[12] with the result 1-ClB_5H_8 > B_5H_9 > 1-$CH_3B_5H_8$ ≈ 2-$CH_3B_5H_8$. In terms of Koopmans' approximation, $\delta\alpha = \alpha_{4e}(B_5H_9) - \alpha_{4e}(XB_5H_8)$ is a measure of the relative stabilization or destabilization of the framework by the substituent X. Table I shows that $\delta\alpha_{Cl}$ is 0.20 eV while $\delta\alpha_{CH_3}$ is -0.15 eV, i.e., Cl acts to increase the effective core potential of the framework while CH_3 tends to reduce it. This is an alternative way of saying Cl tends to withdraw electrons while CH_3 tends to donate electrons—the same conclusion suggested by the relative acidities.[12] Again in agreement with the acidity measurements, the photoelectron spectra indicate $\delta\alpha$ is independent of substitution in the 1- or 2-position. Finally, we would predict the acidity order 1-$CH_3B_5H_8$ ≈ 1-$SiH_3B_5H_8$ > μ-$SiH_3B_5H_8$. It has, in fact, been found that the reagents commonly used to abstract a proton from B_5H_9 and its derivatives will not deprotonate μ-$H_3SiB_5H_8$.[42]

Experimental Section

The photoelectron spectrometer used in these studies was the same as that used previously.[5] Spectra were obtained using He(I) radiation only. The resolution of the instrument was 50 meV (full width at half-height) at 10 eV electron energy and scanning was accomplished by variation of the analyzer voltage. Calibration was carried out using an internal standard consisting of a mixture of argon and xenon.

Pentaborane(9) was obtained from the Callery Chemical Co., Callery, Pa., and was used without further purification. The pentaborane derivatives were synthesized in essentially the same manner as reported in the literature. 1-IB_5H_8,[43] 1-BrB_5H_8,[44] and 1-ClB_5H_8[45] were prepared by the aluminum halide-catalyzed halogenation of B_5H_9 at room temperature. 2-Iodo-[43] and 2-bromopentaborane[44] were prepared by isomerization of their apically substituted isomers. 2-Chloropentaborane was produced by heating 1-BrB_5H_8 and $AlCl_3$ in a sealed flask.[46] 1-$CH_3B_5H_8$ was obtained by the reaction of CH_3Cl and B_5H_9 in the presence of $AlCl_3$,[47] and was then isomerized to yield 2-$CH_3B_5H_8$.[48] μ-, 2-, and 1-$H_3SiB_5H_8$ were prepared by the reaction of LiB_5H_8 with H_3SiBr followed by base-catalyzed isomerizations.[49,50]

These compounds were handled in standard high vacuum apparatus.[51] Their purity was established by gas-phase infrared (recorded on the Perkin-Elmer 457 infrared spectrometer) and boron-11 NMR (Varian XL-100) spectra.

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Appendix

Jahn–Teller Effect. In the process of ionization where an electron is removed from a doubly degenerate state it is not uncommon to observe a removal of the degeneracy in the ionic state, i.e., Jahn–Teller effect.[15] Such an effect could account for the excessive breadth (0.9 eV) of the 4e band in pentaborane. Substitution in the 1-position is not expected to remove the Jahn–Teller splitting while for 2-substitution there will be a "competition" between the Jahn–Teller effect and the substituent effects (pseudo-Jahn–Teller effect).[52] It is interesting to note then that the relative width of the 4e bands in the 2-compounds is roughly half that in B_5H_9, e.g., 2-BrB_5H_8, FWHM ≈ 0.5 eV. This suggests a Jahn–Teller splitting of 0.3–0.4 eV in pentaborane itself. If this analysis is correct then the real conjugative effects in the methylpentaboranes would be somewhat larger than those estimated above. However, this would not change the arguments presented above.

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