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Substituent Effects in Cluster Species. 6. Photoelectron Spectra of 5- and 5,6-Substituted 2,4-Dicarba-*closo*-heptaborane(7)

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The He and I photoelectron spectra of 2-X-2,4-$C_2B_5H_6$ and 5,6-X_2-2,4-$C_2B_5H_5$, where X = Cl, Br, and I, are reported. After inductive effects are taken into account, π-type interactions between cluster surface (π-endo) orbitals and filled halogen p orbitals successfully account for the effects of halogen substitution on the photoelectron spectra of the substituted carborane. The results permit comparison of the nature of the 5- and 6-positions relative to sites for substitution in other borane and carborane cages and also of the extent of interaction of X with a seven-membered cluster relative to that with clusters having three to ten members. This work reinforces the idea that the surface orbitals of a cluster play an important role in determining the effect of substitution on cluster properties.

Introduction

Clusters of first-row atoms containing boron and carbon, despite their relative simplicity, exhibit increasingly complex electronic behavior with increasing cage size.[1,2] Our investigation of these systems has proceeded systematically[3] from smaller to larger clusters and, hence, from more easily described systems to more complex systems. Substitution of hydrogen with halogens perturbs the bonding of a cluster in an understandable manner. That is, halogens are substituents containing lone pairs in orbitals with π symmetry with respect to an exo-cluster radial bond. Hence, π-interaction with cluster surface orbitals is possible,[3] and these interactions can serve as a probe of electronic structure.

In our previous work,[3] the experimental method chosen to investigate these substituent effects has been photoelectron spectroscopy (PES) simply because this technique permits direct observation of the binding energies of valence electrons. In earlier studies, a simple three-parameter model has been found adequate to describe the observable substituent interactions in these derivatives.[3b] The PES spectrum of the parent compound 2,4-$C_2B_5H_7$[3e] shows increased complexity compared to that of the six-membered 1,6-$C_2H_4H_6$ cluster.[3d] However, here we present the results of the PES and accompanying theoretical investigations of 5-X-2,4-$C_2B_5H_6$ and 5,6-X_2-2,4-$C_2B_6H_5$ (X = Cl, Br, I). The B(5)-substituted monochloro and monobromo and B(5,6)-substituted dichloro derivatives have been previously prepared and characterized spectroscopically.[3f,4a,5] Slight modification of the reaction conditions led to the formation of B(5)-substituted monoiodo derivative and disubstitution on boron by Br and I.[3f] Since this work was completed, similar preparative routes have been published.[4b-f] The investigation of this seven-membered cluster extends previous studies of substituent effects on five- and six-membered boranes and carboranes.[3]

Results

Photoelectron Spectra. The He I PES of 5-X-2,4-$C_2B_5H_6$ and 5,6-X_2-2,4-$C_2B_5H_5$ (X = Cl, Br, I) are shown in Figures 1 and 2 and the data are collected in Table I. In general appearance, the spectra are similar: at low ionization potential (IP) a number of sharp bands are observed, followed by broad bands at higher IP's. The narrow Franck–Condon envelopes exhibited by the early bands are indicative of significant halogen character. The decrease in IP in going from Cl to I causes the leading peak to be observed at progressively lower IP (Figure 1). The spectra are analyzed empirically by using a simple parametrized model in which the substituent perturbs the cage and is itself perturbed by charge redistribution (inductive effect) and by conjugative substituent interactions that are of a selective nature.[3]

Estimate of Inductive Effect–Monosubstitution. The magnitude of the inductive shift $\Delta\alpha_{cage}$ (Figure 3) may be estimated from the behavior of the third major band in the spectrum of 2,4-$C_2B_5H_7$ upon monosubstitution. This band contains two distinguishable

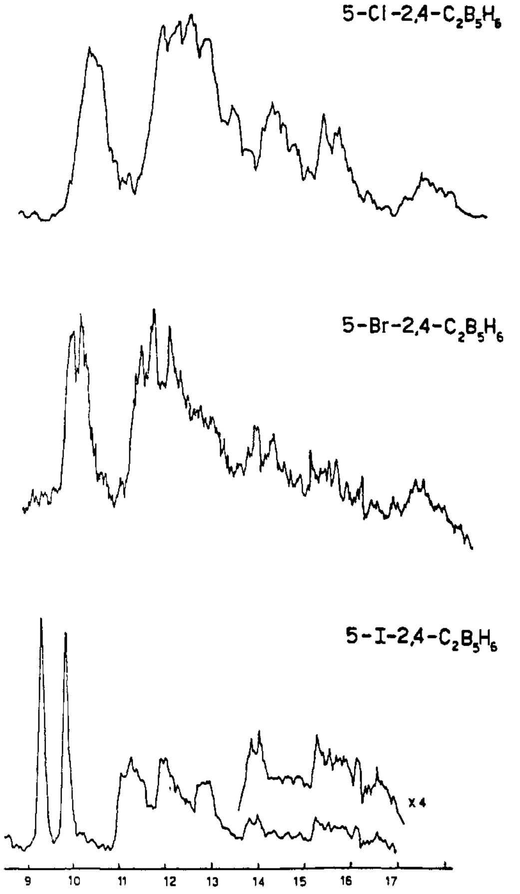

Figure 1. Photoelectron spectra of (a) 5-Cl-2,4-$C_2B_5H_6$, (b) 5-Br-2,4-$C_2B_5H_6$, and (c) 5-I-2,4-$C_2B_5H_6$.

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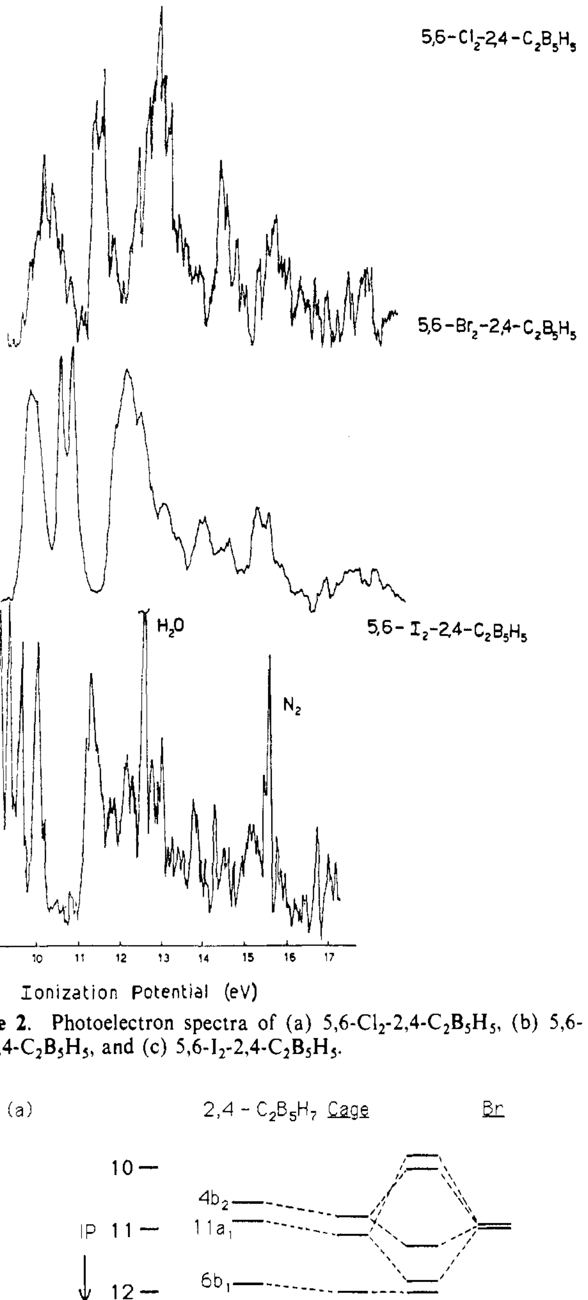

Figure 2. Photoelectron spectra of (a) 5,6-Cl_2-2,4-$C_2B_5H_5$, (b) 5,6-Br_2-2,4-$C_2B_5H_5$, and (c) 5,6-I_2-2,4-$C_2B_5H_5$.

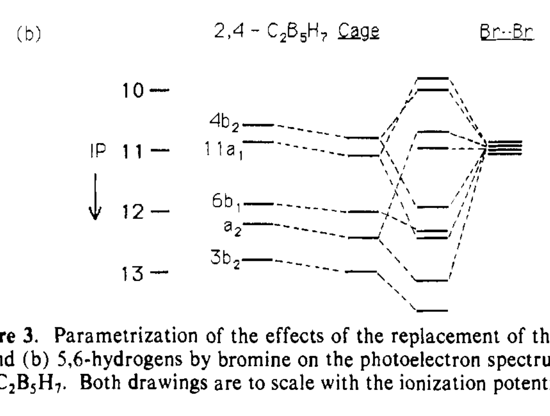

Figure 3. Parametrization of the effects of the replacement of the (a) 5- and (b) 5,6-hydrogens by bromine on the photoelectron spectrum of 2,4-$C_2B_5H_7$. Both drawings are to scale with the ionization potential in eV.

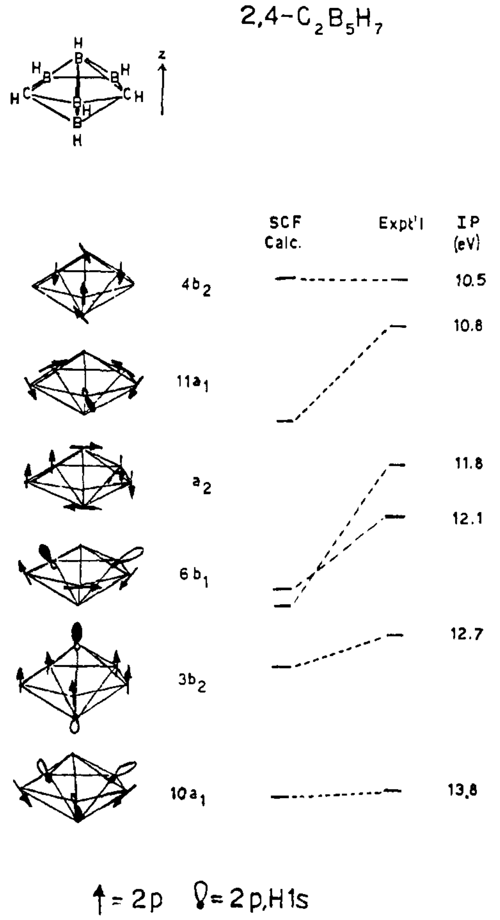

Figure 4. Schematic description of the filled molecular orbitals for 2,4-$C_2B_5H_7$.[9] The ionization potentials are taken from ref 3e. The SCF MO energies are from this work.

peaks, previously assigned to the $10a_1$ and $9a_1$ orbitals (Figure 4)[6] with IP's of 13.8 and 14.1 eV, respectively. The orbitals are well suited for σ-exo interaction with substituents at the 5- and 6-positions, and the associated IP's may be unambiguously assigned from experimental results. Thus, they are suitable monitors of the inductive effect. The IP's observed at 14.2 and 14.6 eV for Cl, 13.9 and 14.5 eV for Br, and 13.8 and 14.4 eV for I substitution are assigned to the $10a_1$ and $9a_1$ orbitals in the 5-X-2,4-$C_2B_5H_6$ series. Averaging the energy changes of each peak upon substitution allows the inductive effects to be estimated: Cl, 0.45 eV; Br, 0.25 eV; I, 0.15 eV. Although this set of values is not unique, the inductive shifts used have little effect on the calculated values for the interaction parameters $-\beta$ (see below) and the trends in $-\alpha_{\text{cage}}$ values are also independent of the method of assignment.

Assignment of 5-Br-2,4-$C_2B_5H_6$. Once the magnitude of the inductive effect has been estimated, it is possible to use the approach described previously[3d,3e,6] to assign the experimental PES spectra. A trial assignment is obtained by applying the inductive shift to all IP's obtained in the PES spectrum of the parent compound and by assuming π-type conjugative interaction between surface orbitals of the cage (orbitals containing mainly p functions tangential to a sphere containing the cage atoms) and the appropriate p orbitals on the halogen. A schematic representation of the π-exo–endo interaction is shown in Scheme I, and a presentation of the assignment for the intermediate Br case is given

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Table I. Vertical Ionization Potentials, Relative Band Areas, and Band Areas Expected Based on the Assignments

molecule	band	IP, eV	IP(calc),^{a} eV	A(rel)	A(expected)
2,4-$C_2B_5H_7$	1	10.5		1.95	2
		10.8			
	2	11.8			
		12.1		3.40	3
		12.7 sh			
	3	13.8		2.00	2
		14.1			
	4	15.1			
		15.4 sh			
	5	17.8			
		17.9 sh			
5-Cl	1	10.2	10.15	2.00	2
		10.4 sh	10.40		
	2	11.8	11.78		
		12.0	12.25		
		12.4	12.35	5.02	5
		12.7	12.55		
		13.4 sh	13.15		
	3	14.2		0.82	1
		14.6 sh			
	4	15.3			
		15.6			
	5	17.6			
5-Br	1	9.9	9.90	2.00	2
		10.1	10.10		
	2	11.4	11.40		
		11.9	11.90		
		12.1	12.05	4.30	5
		12.8 sh	12.35		
		13.1 sh	12.95		
	3	13.9			
		14.5			
	4	15.1			
		15.8 sh			
5-I	1	9.2	9.20	1.00	1
	2	9.7	9.68	1.00	1
	3	11.0	10.49	1.60	2
		11.3	11.35		
	4	11.8	11.95	1.60	2
		12.2 sh	12.25		
	5	12.7	12.85	1.00	1
	6	13.8			
		14.4			
	7	15.1			
		15.8 sh			
5,6-Cl_2	1	10.1	10.13		
		10.4	10.37	2.00	2
	2	11.4	11.36		
		11.5	11.52	1.60	2
	3	12.3	12.43		
		12.6	12.60	3.4	3
		12.8	12.68		
		13.0 sh	12.99		
		13.9 sh	13.50		
	4	14.5			
		15.0			
	5	15.8			
		16.1 sh			
	6	17.9			
		18.2 sh			
5,6-Br_2	1	9.9	9.85		
		10.0	10.00	2.00	2
	2	10.6	10.60		
		10.9	10.90	2.20	2
	3	11.8	11.85		
		12.2	12.05		
		12.3	12.29	5.71	5
		13.0 sh	12.45		
		13.6 sh	12.95		
	4	13.9			
		14.5			
	5	15.3			
		15.6			
	6	17.7			
5,6-I_2	1	9.1	9.13	1.18	1
	2	9.4	9.38	1.00	1
	3	9.7	9.70	1.09	1
	4	10.0	10.00	1.30	1
	5	11.3	11.22	2.00	1
	6	11.8 sh	11.74	1.00	1
	7	12.2	11.95	1.40	2
		12.5	11.97		
	8	12.9	12.85		
	9	13.9			
	10	14.4			
	11	15.1			
		15.6 sh			

^{a}See text.

in Figure 3. The empirical assignment was carried out as follows.

The first band of 5-Br-2,4-$C_2B_5H_6$ contains IP's with significant halogen character that must, since they are at lower IP than any bands in the parent carborane, arise from an antibonding interaction of the two highest occupied cage orbitals with bromine "lone-pair" orbitals. Thus, the π-interaction arises from cage orbitals having ionization potentials of 10.8 and 11.0 eV interacting with Br atomic orbitals with IP's ($-\alpha_{Br}$) yet to be determined. A π-bonding interaction is necessarily paired with the π-antibonding interaction just discussed and provides the key to the complete assignment. The π-bonding pair of ip's are implied at ($-\alpha_{Br}$ + 0.65 eV) and ($-\alpha_{Br}$ + 1.15 eV) to match the IP's occurring at ($-\alpha_{Br}$ − 0.65 eV) and ($-\alpha_{Br}$ − 1.15 eV), i.e., 10.1 and 9.9 eV, for the antibonding set. A value of $-\alpha_{Br}$ can be estimated by fitting the values of the IP's of the four orbitals corresponding to π-interaction with the cage as next described.

Relative areas suggest that the second band of 5-Br-2,4-$C_2B_5H_6$ contains five ionizations. Three of these IP's are due to the inductively shifted a_2, $6b_1$, and $3b_2$ (Figure 4) ionizations of 2,4-$C_2B_5H_7$.[6] The other two must correspond to those expected for the π-bonding interaction between the halogen and the cage. If the same inductive effect of Br on the cage (0.25 eV) is used, the IP's at 11.8, 12.1, and 12.7 eV of the parent compound would be anticipated at 12.05, 12.35, and 12.95 eV in the bromo derivative. There are IP's in the monobromo compound at 12.1, 12.8, and 13.1 eV, and thus, the IP's at 11.4 and 11.9 eV are assigned to the cage π-bonding interaction. These last two bands

Scheme I

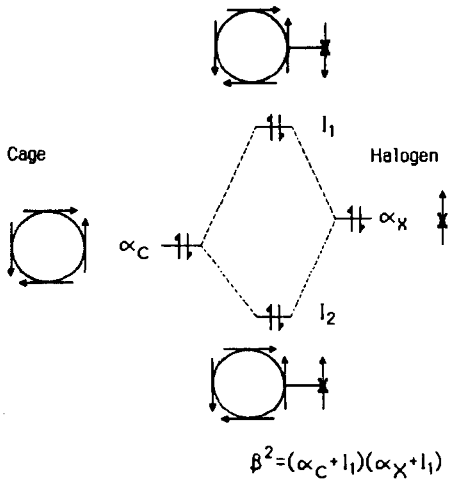

Table II. Empirical Parameters (eV) Characterizing the Effects of Halogen Substituents on the $4b_2$ and $11a_1$ Molecular Orbitals of $2,4\text{-}C_2B_5H_7$

$5\text{-X-}2,4\text{-}C_2B_5H_6$

X	$-\alpha_{11a_1}$	$-\alpha_X$	$-\beta_{11a_1}$	$-\alpha_{4b_2}$	$-\beta_{4b_2}$	$\Delta\alpha_{cage}$
Cl	11.25	11.25	1.10	10.95	0.68	0.45
	11.25	11.52[a]	1.23	10.95	0.78	0.45
Br	11.05	10.75	0.99	10.75	0.65	0.25
	11.05	10.90[a]	1.07	10.75	0.72	0.25
I	10.95	9.76	0.99	10.65	0.28	0.15
	10.95	10.00[a]	1.18	10.65	0.56	0.15

$5,6\text{-}X_2\text{-}2,4\text{-}C_2B_5H_5$

X	$-\alpha_{11a_1}$	$-\alpha_X$	$-\beta_{11a_1}$	$-\alpha_{4b_2}$	$-\beta_{4b_2}$	$-\alpha_{a_2}$	$-\beta_{a_2}$	$\Delta\alpha_{cage}$
Cl	11.60	11.52	1.43	11.30	1.02	12.85	0.49	0.80
Br	11.25	10.90	1.21	10.95	0.92	12.50	0.75	0.25
I	10.95	10.00	1.26	10.65	0.89	12.20	0.87	0.15

[a] Derived from spectra of dihalogenated compounds.

exhibit the narrow line width expected for significant halogen character and permit two independent calculations of $-\alpha_{Br}$ yielding 10.70 and 10.75 eV in the assignment. We have used 10.75 eV as the value of $-\alpha_{Br}$ to calculate the $-\beta$ values listed in Table II.

Assignment of the Disubstituted Cages. Shifts in the IP's from the third main band of $2,4\text{-}C_2B_5H_7$ that were used to gauge the effect of monosubstitutions (see above) can also be used to estimate the effect of substitution by two halogens in the $5,6\text{-}X_2\text{-}2,4\text{-}C_2B_5H_5$ series. The values of $-\Delta\alpha_{cage}$ thus obtained are as follows (eV): Cl, 0.80; Br, 0.25; I, 0.15. In the dibromo case, an approximate value of $-\alpha_{Br}$ can be easily obtained since one Br lone-pair combination is symmetry forbidden from interaction with the cage orbitals. The sharp bands in the spectrum (Figure 2) are easily assigned to halogen IP's. If one ignores the complication of spin–orbit splitting, the band at 10.9 eV can be assigned to the noninteractive lone-pair IP. Along with $-\alpha_{cage}$, this allows the interaction parameter $-\beta$ to be calculated from the spectrum (Table II). The $-\beta$ values are similar to those derived for the monosubstituted derivatives. The $-\alpha_{cage}$ and $-\beta$ values for the monosubstituted molecule can be recalculated by using the $-\alpha_{Br}$ value determined from the dibromo compound and essentially the same fit obtained. The same procedure can be used to assign the spectra obtained for the chloro and iodo derivatives. The results of the calculations are displayed in Table II.

Calculations for the monohalogenated compounds yield values of $-\alpha_X$ that can be compared with those obtained directly from the disubstituted compounds. Indeed, use of the $-\alpha_X$ values obtained from the spectra of the disubstituted compounds yields values of $-\alpha_{cage}$ and $-\beta$ for both the mono- and disubstituted compounds, and the internal consistency of these numbers serves as a test of spectral assignments, parameters, and the applicability of the model.

The assignment shown in Figure 3 fits the IP's of the chloro- and iodo-substituted compounds only modestly well. In the monochloro derivative, the ionization potential assigned to the bonding $11a_1$-halogen interaction is higher than that of the inductively shifted $6b_1$ energy level. In the dihalo series, the bonding $11a_1$ interaction is at higher IP than the a_2 energy level for the dichloro compound and at lower IP than the inductively shifted $6b_1$ level for the diiodo compound. Note that, in assigning the halogenated compounds, the ordering of the $11a_1$ and $4b_2$ levels is reversed from that previously published for the parent compound (ref 3e vs Figure 4). When this ordering is not assumed, the fit of the spectra is very poor. The reversed assignment is also supported by the results of theoretical calculations described below, which predict higher $-\beta$ values for the $11a_1$ molecular orbital than for the $4b_2$ orbital.

Table III

Results of SCF Calculations on Derivatives of $2,4\text{-}C_2B_5H_7$

compd	tot. energy, au	ΔE, kcal	charge on Cl or tot. charge on 2 Cl's
$2,4\text{-}C_2B_5H_7$	−200.782		
5-Cl	−654.827	0	−0.2369
3-Cl	−654.826	0.627	−0.2151
1-Cl	−654.824	1.882	−0.2173
$3,5\text{-}Cl_2$	−1108.869	0	−0.4341
$5,6\text{-}Cl_2$	−1108.869	0	−0.4458
$1,5\text{-}Cl_2$	−1108.866	1.882	−0.4318
$1,3\text{-}Cl_2$	−1108.865	2.510	−0.4108
$1,7\text{-}Cl_2$	−1108.863	3.765	−0.4135

Molecular Orbital Coefficients of π-Endo Orbitals of $2,4\text{-}C_2B_5H_7$

atomic orbital		orbital coeff					
		$6b_1$	a_2	$11a_1$	$4b_2$	LUMO-($3b_2$)	UMO-(a_1)
B(3)	2s	0	0	0	0	0	−0.142
	$2p_x$	−0.328	0	0	0	0	0
	$2p_y$	0	0	0.122	0	0	0
	$2p_z$	0	0	0	−0.305	−0.804	0
B(5)	2s	0.070	0	0.063	0	0	0.113
	$2p_x$	−0.072	0	0.414	0	0	0.265
	$2p_y$	0.253	0	0.114	0	0	0.172
	$2p_z$	0	0.155	0	0.331	−0.253	0
B(1)	2s	0	0	0	0.065	0	0
	$2p_x$	0	0.344	0	0	0	0
	$2p_y$	0	0	0.092	0.395	0	−0.682
	$2p_z$	0	0	0	−0.095	0	0

Finally, a complicating factor in making photoelectron spectral assignments of halogen-containing species is spin–orbit coupling.[7] This factor increases in going from Cl to I. The band splitting that results mixes with that caused by the substituents. However, considering the number of experimental data and the low precision of the IP measurements, a more detailed parametrization was not judged useful. Despite this caveat, the trends in substituent effects and assignments are correctly represented.

Molecular Orbital Calculations. A direct connection between orbital energies and ionization potentials was established by Koopmans.[8] Quantitatively, equating observed ionization potentials to the negative of calculated orbital energies often fails, and Koopman's theorem is only used here in a qualitative sense as a language to identify the states of the radical cations observed in the spectra and to justify the relationship between the trends observed for the radical cations and those of the molecules themselves.

In Table III a summary of calculational results is compiled. The total energy and molecular orbital coefficients for the π-endo orbitals are listed for $2,4\text{-}C_2B_5H_7$. Also tabulated are total energies and halogen charges for the mono- and disubstituted chloro derivatives. Our molecular orbital calculations on the parent compound do not differ in any significant way from those reported by Marynick and Lipscomb.[9] The energies and a representation of the six highest filled orbitals of $2,4\text{-}C_2B_5H_7$ as calculated by Gaussian-80[10] are shown on the left side of Figure 4.

The assignment of orbitals to IP's for the parent compound has been briefly discussed in previous publications.[3e,6] In the Ne I PES spectrum, the higher component of both band 1 and band 2 was found to increase in relative cross section, indicative of an association with orbitals having higher boron content. However, inspection of the calculational results indicates that the assignment of the first two orbitals may be inverted from that reported

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Table IV. Comparison of $-\alpha_X$ Values (eV) with Mulliken Charge for Boron at Substitution site for a Series of Related Boranes and Carboranes

compd	$-\alpha_X$ Cl	Br	I	SCF charge[a]	ref
1-X-B_5H_9	11.5	10.6	9.6	0.00	3e
5-X-2,4-$C_2B_5H_7$	11.5	10.9	10.0	0.06	this work
2-X-B_5H_9	11.7	11.1	9.8	0.06	3e
2-X-1,6-$C_2B_4H_6$	11.9	11.2	10.1	0.10	3d
C_6H_6 (benzene)	11.3	10.6	9.4		3d

[a] For the unsubstituted compound at the position of substitution.

Table V. Comparison of $-\beta$ Interaction Parameters (eV) for Halogen Substituents with B-Containing Clusters

compd	substituent	$-\beta$(mono)	$-\beta$(di)	ref
1-X-B_5H_9	Cl	1.01		3e
2-X-B_5H_9	Cl	0.85		3e
		(4e)		
2-X-/2,4-X_2-1,6-$C_2B_4H_6$	Cl	1.06/0.82	1.41/1.20	3d
	Br	0.99/0.88	1.38/1.20	3d
	I	0.90/0.65	1.40/0.85	3d
		(b_{2g}/e_g)		
5-X-/5,6-X_2-2,4-$C_2B_5H_7$	Cl	1.10/0.68	1.43/1.02	this work
	Br	0.99/0.65	1.21/0.92	this work
	I	0.99/0.28	1.26/0.89	this work
		($11a_1/4b_2$)		
1-X-/1,4-$X_2C_6H_6$	Cl	1.16	1.47	3d
	Br	0.98	1.33	3d
	I	0.83		3d
		(e_g)		

Table VI. Comparison of MO[a] $-\beta$ Interaction Parameters for a Chloro Substituent at Possible Sites with the π-Endo Orbitals of 2,4-$C_2B_5H_7$

compd	$-\beta$, eV	orbital	$-\alpha_c$, eV
5-Cl-2,4-$C_2B_5H_6$	1.48	$11a_1$	10.73
	1.16	$4b_2$	9.69
	0.25	a_2	12.00
3-Cl-2,4-$C_2B_5H_6$	1.06	$6b_1$	12.05
	0.95	$4b_2$	9.69
1-Cl-2,4-$C_2B_5H_6$	1.23	a_2	12.00
	1.27	$4b_2$	9.69

[a] Based on Gaussian-80 results. Inductive effect was estimated at 0.4 eV in all cases, and $-\alpha_X$(Cl) was 11.42 eV.

previously.[3e] The calculations show the $4b_2$ and $11a_1$ orbitals assigned to the first band as 89% B and 75% B, respectively; orbitals $6b_1$ and a_2 assigned to the second band are approximately 55% B and 42% B. Therefore, the order of the filled orbitals, from high energy to low, is $4b_2$, $11a_1$, $6b_1$, and a_2. It should be noted that the experimental energy difference of the first two peaks is much less than the calculated value in any case. Assignment of the third ionization to $6b_1$ is also supported by the unreasonable values of the inductive shift that result when it assigned to the fourth ionization.

Independent of order in energy, the first four orbitals can be classified as π-endo by virtue of their symmetry with respect to radial directions referred to a sphere that contains the atoms of the cage. The fourth orbital does, however, share some σ-exo character with the two lower energy orbitals pictured in Figure 4. According to the model developed to interpret the PES spectra of substituted 1,6-$C_2B_4H_6$ compounds[3d] and applied above to 2,4-$C_2B_5H_7$ compounds, it is the cage surface orbitals that would be expected to have substantial conjugative interaction with the orbitals of appropriate π-symmetry on the substituent (see Figure 4). This is consistent with what is found from the empirical analysis above.

Discussion

Halogen Inductive Parameters. The experimentally measured halogen inductive parameters ($-\alpha_X$) for members of the series derived from 2,4-$C_2B_5H_7$ are in good agreement with those previously determined for other boranes and carboranes (Table IV). Values of $-\alpha_X$ are directly related to electronegativity and, as expected, decrease regularly in the order Cl > Br > I. The change of about 2 eV down the series increases the energy mismatch between the p electrons of the halogen and the π-endo orbitals of the cluster. Thus, the halogen character of the highest occupied molecular orbitals increases, and by iodine, the first bands in the PES spectrum are quite narrow. The halogen character of the two highest occupied energy levels for 5-$FC_2F_5H_6$ is calculated at approximately 50%, but increases to 75% for the chloro analogue, due to this effect.

Values of $-\alpha_X$ are sensitive experimental measures of electronic charge at the site of substitution, higher values correlating with greater concentrations of positive charge at the point of attachment. In Table IV, Mulliken charges calculated for the substitution sites are compared to the measured $-\alpha_X$ values. The B(5) position of the 2,4-$C_2B_5H_7$ cage thus lies between the B(1) and B(2) positions of B_5H_9 and is considerably less electronegative than the B(2) position in 1,6-$C_2B_4H_6$. As the substituted atom is boron in all cases, this reflects a difference in the cage positions due to cluster structure. The charges correlate well with the magnitude of α_X for all three halogens.

Although $-\alpha_X$ was not measured for substitution at B(1) and B(3), the calculated charges provide a comparison of these positions with B(5). Mulliken charges calculated for the 1- and 3-positions in 2,4-$C_2B_5H_7$ are 0.118 and 0.112, respectively, (compared to 0.064 for B(5)), and match those previously reported by Marynick and Lipscomb.[9] As in previous cases, the B with the least association with the carbon is the most negative. Marynick and Lipscomb attributed the observed preference for electrophilic substitution at the 5-position to the high concentration of negative charge on both B(5) and H(5). Our calculations on 5-Cl-, 3-Cl-, and 1-Cl-2,4-$C_2B_5H_6$ show that the charge trends (5 > 1 > 3) for the parent compound are also followed for charge withdrawal by the halogen (Table III). Thus, of the three possible substitution sites, the boron at the 5-position makes the most charge available to the halogen and its formation by electrophilic attack is therefore favored.

Interaction Parameters. The values of $-\beta_X$ are measures of the extent of π-type interaction between the π-endo orbitals of the cluster and the p orbitals of the halogen. Generally speaking, the values obtained are similar in magnitude to those obtained for related compounds (Table V). Comparing the parameters for the $4b_2$ and $11a_1$ orbitals at B(5), one observes that, independent of the halogen, the $-\beta$ value is larger for interaction with the $11a_1$ orbital than for the $4b_2$ orbital. The same trend holds when corrections for the different AO coefficients at the position of substitution are applied. The higher value of $-\beta$ obtained for the $11a_1$ orbital indicates a more effective π-bonding interaction between this orbital and the halogen.

The calculated B(5) MO coefficients corroborate this observation. For the frontier orbital set represented by $11a_1$ and $4b_2$, the pertinent B_{2p} coefficients are 0.43 and 0.33, respectively (Table III). The larger $11a_1$ coefficient is in the *xy* plane while that of the $4b_2$ orbital is in the axial (*z*) direction (Figure 4). In agreement with this result, $-\beta$ values obtained by treating the results of ab initio calculations on the chloro derivatives in the same manner as the PES data are higher for the $11a_1$ than for the $4b_2$ orbital (Table VI). This supports both the present assignments made in the analysis of the PES spectra and the ability of the calculations to model the interaction of the polyhedral surface orbitals with substituents. The trends observed in the monosubstituted carboranes are matched in the disubstituted cases.

PES spectra for the 3-Cl and 1-Cl isomers were not obtained, but interaction parameters ($-\beta$) and cluster orbital energies ($-\alpha_{cage}$) were calculated for all three isomers based on the results of ab initio calculations (Table VI). That is, the calculated MO energies were parametrized in the same manner as the PE spectra. For all three isomers, π interaction with the $4b_2$ orbital is symmetry allowed. For the 1-Cl case, interaction with the a_2 orbital is significant, while for 3-Cl, the $6b_1$ orbital has appropriate symmetry for interaction.

It is interesting to compare the stability order of the halogen isomers as measured by studies of the rearrangement of 5-X-2,4-$C_2B_5H_6$ (3 > 5 > 1)[4b,f] with the trend in the magnitude of the interaction parameters. In order to get a measure of the intrinsic strength of the substituent interaction, these β values must be corrected for the AO coefficients at the position of attachment (Table III). If one does so and then looks at the single common MO in the series ($4b_2$) the order is 5 > 1 > 3, i.e., 3.50, 3.21 and 3.11 eV. Although this does not correspond to the relative stability order, it does correspond to the trend in BH coupling constants in the parent carborane, i.e., 5 < 1 < 3.[4c] On empirical grounds, Onak has suggested that greater electrophilic reactivity correlations are associated with lower $J(^{11}BH)$ values.[4c] Hence, our observations allow greater electrophilic reactivity to be associated with larger halogen π interactions at the site of substitution.

As noted by Marynick and Lipscomb[9] in their discussion of sites of probable nucleophilic attack on 2,4-$C_2H_5H_7$, the LUMO is dominated by π-type character at the 3-position so that halogen to cage back-bonding cannot be excluded as a possible isomer-stabilizing influence. This effect cannot be directly observed by using PES methods in which only the energies of filled orbitals are revealed by ionization. However, even the relative total energies from ab initio methods do not correspond to the experimental values (5 > 3 > 1, Table III). On the other hand, the stability pattern for the CH_3– derivatives differs from that of the halogens.[11a] As inductive effects are sufficient to explain the stability pattern of the methyl derivatives,[11b] back-bonding in the case of the halogens becomes more attractive. Recent work, however, shows that heats of formation from the MNDO method correspond to isomer stabilities.[11c] In addition, ab initio calculations at much higher levels do give energies that correspond to isomer stabilities.[11d]

The π-interaction of an exo substituent with the cage as measured by the interaction parameter $-\beta$ has maintained its presence as size and composition of cage changes. Hence, surface π-interactions can be expected in clusters of different sizes as well as with different cluster atoms.

Experimental Section

The photoelectron spectrometer used in these studies was the same as that described previously.[6] Spectra were obtained by using He I radiation, the instrument was operated at a resolution of 25 meV (full width at half-maximum) at 5-eV electron energy, and scanning was accomplished by variation of the analyzer voltage. Calibration was carried out by using an internal standard consisting of a mixture of argon and xenon.

The carborane 2,4-$C_2B_5H_7$ was purchased from Chemical Systems, Inc., Irvine, CA, the chlorine (research purity) from Matheson, and the bromine and iodine (analytical reagent) from Mallinckrodt. Manipulations were carried out in a standard high-vacuum apparatus. Mass spectra were measured on an Associated Electrical Industries MS 902 mass spectrometer. Gas-phase infrared spectra were recorded on a Perkin-Elmer 475 spectrometer. The ^{11}B NMR spectra were recorded on a Varian XL-100 spectrometer at 25.2 MHz with $(C_2H_5)_2O\ BF_3$ as an internal standard.

5-Cl-, and 5-Br-2,4-$C_2B_5H_6$ were prepared according to published procedures[5,12] by using aluminum trihalides as a catalyst for the direct halogenation of the carborane in an evacuated flask. The ^{11}B NMR data on these compounds agree with published data.[4a,b]

5,6-Cl_2-2,4-$C_2B_5H_5$. Although similar preparations of the following compounds have been published since this work[3f] was completed, we summarize our procedure in the following. About 3 mmol of $AlCl_3$ was introduced into a 500-mL bulb provided with a 12-mm Teflon stopcock, and $AlCl_3$ was sublimed onto the walls. Then about 3 mmol each of 2,4-$C_2B_5H_7$ and Cl_2 were condensed into the reactor at −195 °C. The chlorine color disappeared rapidly, and after 4 h of reaction at room temperature, the mixture was fractionated in the vacuum line with traps at −45, −78, and −196 °C. The contents of the −45 °C trap were identified as the desired product; the contents of the −78 °C trap were identified as the monochlorinated compound by comparison with published spectra.[4a,12] The dichlorinated compound is characterized by a mass spectrum with the appropriate high mass cutoff of m/e 158 and infrared bands at (cm^{-1}) 3090 w, 2650 vs, 1250 vs, 1185 m, 1128 vs, 1055 m, 1025 sh, 920 m, 855 m, and 748 w, and the ^{11}B resonances are in good agreement with published data.[4a]

Table VII. Rearrangement Data for Monosubstituted Derivatives of 2,4-$C_2B_5H_7$[a]

compd	% compn at equilib	W	ΔH_{exptl}, J	ref
1-Br	23.1 ± 2.0	2	4600	this work
	18.9 ± 1.0	2	5550	4b
3-Br	30.2 ± 2.0	1	0	this work
	30.6 ± 1.0	1	0	4b
5-Br	46.2 ± 2.0	2	1300	this work
	50.5 ± 1.0	2	910	4b

[a] The equilibrium temperature was 300 °C for the bromo rearrangements. The relationship used to calculate enthalpy was $\Delta H = -RT(\ln K) + T\Delta(-R \ln W)$.

5,6-Br_2-2,4-$C_2B_5H_5$. About 4 mmol of bromine was introduced into a 100-mL bulb provided with a 12-mm Teflon stopcock and containing about 1 mmol of aluminum metal. After degassing, the mixture was allowed to react for 4 h at room temperature to give aluminum tribromide. 2,4-$C_2B_5H_7$ (1.5 mmol) was then condensed into the reactor at −196 °C and warmed to room temperature. The bromine color gradually disappeared, and after 4 h, the mixture was fractionated in the vacuum line with traps at −45, −78, and −196 °C. The −78 °C trap contained 5-Br-2,4-$C_2B_5H_6$ as identified by published spectra.[4b,5] The −45 °C trap contained a product identified as 5,6-$Br_2C_2B_5H_5$. It is characterized by a mass spectrum cutoff at m/e 246, infrared bands at 2650 m, 1230 s, 1190 w, 1105 s, 1052, s, 910 w, 880 m, and 850 vw, and ^{11}B resonances similar to those reported previously.[4b]

5-I-2,4-$C_2B_5H_6$ and 5,6-I_2-$C_2B_5H_5$. About 2 mmol of I_2 and 1 mmol of aluminum metal were placed in a break-seal bulb and heated to 180 °C for 24 h to produce aluminum triiodide. After cooling, about 1 mmol of 2,4-$C_2B_5H_7$ was added, the bulb resealed, and the mixture heated at 85 °C for 24 h during which time the iodine color disappeared. The mixture was then fractionated on the vacuum line. The only volatile iodocarborane was trapped at −78 °C and later identified as 5-$IC_2B_5H_6$. The nonvolatile residue was dissolved in methylene chloride (previously dried over P_2O_5), and the resulting solution was then transferred to a sublimator. After the solvent had been distilled off, bright orange crystals of 5,6-$I_2C_2B_5H_5$ were sublimed onto the cold finger at −40 °C.

The high mass cutoff for 5-I-2,4-$C_2B_5H_6$ was m/e 212, the infrared spectrum showed bands (cm^{-1}) at 3105 w, 2605 s, 1220 s, 1065 s, 985 w, 920 m, 900 m, 800 ms, 750 w, and 650 ms, and ^{11}B resonances were in agreement with those reported previously. For the diiodo compound, the high mass cutoff was m/e 338 and 11B NMR resonances were observed similar to those reported previously.[4b]

Thermal Rearrangement of 5-Br-2,4-$C_2B_5H_6$. Samples were sealed in vacuo in 60-mL heavy-walled glass tubes and heated at 300 ± 10 °C for times ranging between 2 and 7 h. The analysis of the composition of the isomeric mixtures was carried out by using integrated peak areas from gas chromatography analysis. ^{11}B NMR was used to identify the position of substitution for each. The 1-Br and 3-Br isomers were identified by the similarity of their NMR spectra and retention times to those of the chloro analogues. The composition of the product mixture changed little in the period from 3 to 7 h.

The results of the rearrangement studies are reported in Table VII in terms of both the equilibrium concentrations of each isomer and the relative stabilization of isomers compared to the 5-X starting material. The stabilization is expressed as an relative enthalpy of formation, considering only symmetry corrections to the entropy, calculated from the expression $\Delta H = -RT(\ln K) + T\Delta(-R \ln W)$. Also included are results previously reported by Onak and co-workers for thermal rearrangement of the 5-Br[4b] derivative.

Calculations. The geometry of 2,4-$C_2B_5H_7$ was taken from the results of a microwave study[13] and was used throughout for the structure of the cluster. The B–X bond distance assumed for Cl was 1.72 Å and that for F was 1.26 Å. The SCF (fixed point) calculations were performed on

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the IBM 370/168 computer using a minimum basis set of Slater orbitals (STO-3G). The program used for these ab initio calculations was Gaussian-80.[10]

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Correlation of Experimentally Obtained Isomer Stability Data with MNDO and ab Initio MO Calculations for *closo*-2,4-Dicarbaheptaborane Derivative Isomer Sets

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Experimentally determined stabilities among certain *closo*-2,4-$C_2B_5H_7$ derivatives in various isomer sets are correlated to results obtained from the application of the MNDO semiempirical MO method and, in one isomer set, by the application of the Gaussian-86 ab initio method. Specifically, the stabilities for the carboranes *B*-X-*closo*-2,4-$C_2B_5H_6$ (X = Cl, Br, I, C_2H_5, $(CH_3)_3N^+$; 3 isomers each), *B,B'*-X_2-*closo*-2,4-$C_2B_5H_5$ (X = Br, I, C_2H_5; 5 isomers each), *B*-Cl-*B',B''*-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ (11 isomers), and *B,B'*-(*closo*-2,4-$C_2B_5H_6$)$_2$ (6 isomers) are considered.

Introduction

Recently we have applied the MNDO[1] semiempirical MO method to various boron-substituted methyl, chloro, and chloromethyl derivatives of *closo*-2,4-$C_2B_5H_7$.[2] Although small energy differences between isomers in each isomer set are found, the MNDO order of stabilities within various isomers sets, in general, parallels experimental observations. Access to a newer version of MNDO that contains the parameters for many of the higher elements has made it possible to extend this work to various bromo and iodo derivatives of $C_2B_5H_7$. Also, experimental stability data for *B*-X and *B,B'*-X_2 (X = Br, I) derivatives of *closo*-2,4-$C_2B_5H_7$ are available[3] for comparison to the calculated stabilities. Additionally, because experimental stability data on chlorodiethyl and mono- and diethyl derivatives of this same carborane,[4] as well as on coupled C_2B_5 compounds (*B,B'*-$(C_2B_5H_6)_2$)[5] and on *B*-$(CH_3)_3N^+$ derivatives,[6] are also published, it is convenient to include MNDO calculations on these in an effort to complete a comparison of MNDO isomer stabilities with all *closo*-dicarbaheptaborane isomer sets in which (relative) experimental stabilities have been assessed.

It is also desirable to see if ab initio calculations, employing the readily available Gaussian-86 program, could predict relative isomer stabilities. Unfortunately, Gaussian-86 calculational time needed for most all compounds mentioned in the present work would be prohibitive. Sufficient CPU time was available, however, to allow ab initio stability comparisons at reasonably high basis set levels to be made for the three *B*-Cl-*closo*-2,4-$C_2B_5H_6$ isomers.

Experimental Section

The MNDO semiempirical calculations were performed by employing MOPAC,[1,7] version 3.11, available for our use on the Cray X-MP/48 at the San Diego Supercomputer Center through the consortium at San Diego State University and on the SCS-40 computer situated at California State University, Sacramento, CA. The general approach that was used in finding a closo-geometry stationary point on the potential surface for each *closo*-$C_2B_5H_7$ derivative (atom labeling and the structure of the parent *closo*-2,4-$C_2B_5H_7$ and derivatives are illustrated in Figure 1) was as follows: (a) the geometry of the parent carborane, *closo*-2,4-$C_2B_5H_7$,[8] was modified by replacing the appropriate boron-bonded hydrogen(s) with substituents(s) directed along the former B–H bond spatial vectors; (b) initial guess bond distances (in pm) were 177 for B–Cl, 187 for B–Br, 202 for B–I, 167 for B–N, 157 for *exo*-B–C, and 162 for *exo*-B–B; (c) the initial geometry input for MNDO energy optimization was subject only to (parent) cage symmetry constraints as well as enforced planar configuration of the equatorial 2,3,4,5,6-CBCBB plane of the pentagonal bipyramidal carborane cage (Figure 1); (d) the MNDO output geometry from operation *c* was then input for further MNDO optimization, this time with no symmetry or other geometry restrictions (i.e., full optimization). In all but two cases, no difficulty was encountered in finding a *closo*-C_2B_5 stationary point geometry for each isomer that was nearly identical with that obtained with symmetry restrictions imposed. In those two instances, the 3-Cl-5,6-$(C_2H_5)_2$ and 3-Cl-1,5-$(C_2H_5)_2$ derivatives, application of the (c) → (d) approach resulted in a classical norbornane type of structure for the cage atoms (note: the MNDO norbornane structure was some 27.5 kcal/mol more stable than the corresponding closo framework). An additional approach was then implemented in an attempt to find a stationary point corresponding to a closo-cage structure. For both of these isomers the MNDO output geometry from a C(2)–B(3)–C(4)–B(5)–B(6) pentagonal planar-enforced (bipyramidal) molecule was utilized as the closo input geometry for further optimization (with all geometry restrictions released). A stationary point closo (pentagonal pyramidal) geometry was then found for both compounds. In all instances, the geometry-optimized output and consequent heat of formation obtained from operation d (labelled "total optimization" in the Figures) was very close to that obtained from operation c. For both the 3-Cl-5,6-$(C_2H_5)_2$ and 3-Cl-1,5-$(C_2H_5)_2$ derivatives, the MNDO-optimized pentagonal planar-enforced geometries and consequent heats of formation

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