Temporary Anion States of *closo*-Carboranes and Diethyl Carborane

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The energies required to attach electrons into the low-lying normally unoccupied molecular orbitals of the carborane ($C_2B_{10}H_{12}$) cage compounds *closo*-1,2-, *closo*-1,7-, and *closo*-1,12-dicarbadodecacarborane, and those of diethyl carborane (*nido*-dicarbahexacarborane) are determined by electron transmission spectroscopy in the gas phase. The lowest lying anion state in each of these compounds in the equilibrium geometry of the neutral molecule is found to be *unstable* with respect to electron ejection, and is formed at a vertical attachment energy of approximately 1 eV. The total yield of negative ions produced by electron impact on *ortho*-carborane was measured and observed to peak near 0 eV and at 0.7 eV. The latter feature has a cross section of 5.1×10^{-17} cm^2. Our data are consistent in energy dependence with relative yield measurements made elsewhere in which the charged product was identified as a metastable anion state of the parent molecule. The results from our calculations seeking to identify the geometry of this anion are reported.

Introduction

Carborane cage compounds are a source material for boron/carbon thin film semiconductor devices as well as for boron−carbide wires and nanotubes, as described elsewhere.[1,2] Because plasma enhanced chemical vapor deposition is widely used to make such devices, electron scattering processes in these compounds are of interest. To provide a clearer picture of the interaction of these compounds with slow electrons, it is useful to locate the temporary anion states arising from the injection of a free electron into the lowest few normally unoccupied molecular orbitals. These transient species produce resonances that typically dominate the total scattering cross section at low electron impact energies and may contribute as well to fragmentation of the parent molecule through the dissociative electron attachment process. Studies of inner shell excitation by photons and electrons[1] have explored these empty orbitals both experimentally and theoretically, however, the complexity of such spectra tends to obscure some details of the underlying empty orbital structure.

In this work, we report a study of three isomers of the carborane cage compounds shown in Figure 1, namely *closo*-1,2-, *closo*-1,7-, and *closo*-1,12-dicarbadodecacarborane, which we will refer to as *ortho*-, *meta*-, and *para*-carborane for simplicity, as well as 1,2-diethyl-*nido*-carborane, $(C_2H_5)_2C_2B_4H_6$, using electron transmission spectroscopy (ETS).[3] With this technique we determine the electron energy required to attach an electron into an empty molecular orbital at the equilibrium geometry of the neutral molecule, namely, the vertical attachment energy (VAE).

The difficulties of determining the energies of temporary anion states theoretically are well-known and, strictly speaking, scattering calculations are required. However, within a number of chemical families, simpler means have been found to be useful. Calculation of the virtual orbital energies of the neutral molecules, for example, and use of the Koopmans' theorem approximation have been found to produce good *relative* values within a given chemical family.[4−6] Shifting and scaling these energies to match a few known experimental VAEs allows the prediction of values for other compounds in the family. A secondary goal of this work is to examine the extent to which the carborane anion energies can be determined from a scaling used previously for unsaturated hydrocarbons.[5]

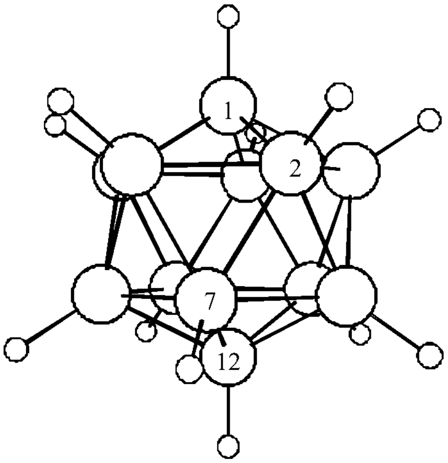

Figure 1. Structure of the *ortho*-, *meta*- and *para*-carboranes. The molecules are all nearly regular dodecahedra with hydrogen atoms sticking out. The ortho compound has carbons at the 1,2 positions, meta at 1,7, and para at 1,12. All of the other atoms in the inner dodecahedron are borons.

Finally, we augment our study by measuring the total cross section for production of negative ions in *ortho*-carborane as a function of electron energy. Such anions most generally are formed by the dissociative electron attachment (DEA) process, $e + AB \rightarrow AB^{-*} \rightarrow A + B^-$. Less commonly observed is attachment in molecules in which a metastable parent anion is produced.

Experimental Section

The ETS technique has been discussed previously in the literature along with its applications to complex molecules.[7−9]

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Briefly, an energy-selected beam is directed through a gas cell containing a sufficient density of the target compound to partially attenuate the beam. The scattered electrons are rejected at a retarding electrode following the collision region, and the transmitted current, comprising the unscattered electrons, is collected. A sharp dip in this current as a function of electron energy signals the presence of a peak in the scattering cross section arising from the formation of a temporary anion state. To accentuate this structure, the energy of the electrons is modulated in the cell with a small ac voltage and the derivative of the transmitted current with respect to energy is acquired using a synchronous detector.[3] Each "resonance" is therefore characterized by a minimum and a maximum in the derivative signal. The energy of the midpoint between these features is assigned to the VAE. The VAEs are energy calibrated to within ± 0.05 eV by admitting N_2 to the cell and referring to well-known features arising from the N_2^- temporary anion state. The full-width at half-maximum of the electron beam distribution is approximately 50 meV. *Ortho*-Carborane (98% pure) from Strem Chemicals was employed as a source for synthesis of the meta and para isomers which were purified by trap-to-trap distillation and chromatography. The *para*-carborane sample contained approximately 1.5 to 2% of the other isomers but at this level the ETS results are not affected.

The production of negative ions under electron impact was explored in two separate instruments. The first of these[10] used a crossed electron and molecular beam configuration and accelerated the anions to a multichannel plate electron multiplier where they were counted. Mass analysis is not available on this apparatus and there is no guarantee that charged fragments with different masses will be detected with equal efficiency. However, this apparatus can be operated at electron energies down to the beam cutoff with high energy resolution.

Total cross sections for production of negative ions were measured in an apparatus described in more detail elsewhere.[11] This instrument incorporates a trochoidal monochromator,[12] as in the ETS apparatus, to inject a magnetically collimated beam of electrons into a collision cell, within which is a cylindrical electrode 10 cm in length for collection of negative ions produced along the path of the electron beam. The gas pressure in the cell is determined by a temperature-regulated capacitance manometer and corrected for thermal transpiration effects. The temperature of the collision cell was ≈65 °C.

Theory

Calculations were carried out using GAMESS programs.[13] Ground-state geometries of the neutral molecules were optimized and virtual orbital energies (VOEs) obtained using the 6-31G* basis set. Predicted VAEs are estimated by scaling the energies of the virtual orbitals using the relationship, $\mathrm{VAE(eV)} = (\mathrm{VOE} - 2.33)/1.31$, given by Chen and Gallup.[5] This relationship was determined from ETS data and calculations tabulated by Heinrich et al.[4] for 21 alkenes, alkynes, and ketones. Only the lowest temporary $^2\Pi$ anion state of each compound was used for this correlation. In general we expect the shifting and scaling procedure to be most accurate for the ground anionic states and to become increasingly less reliable for the higher lying anion states of a given molecule.

Results

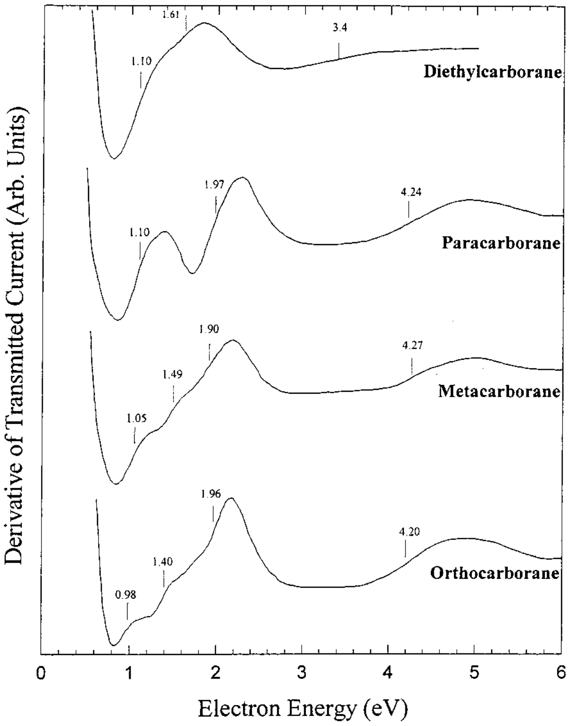

Figure 2. Derivative of transmitted current as a function of electron energy in *para*-, *ortho*-, *meta*-carborane and diethyl carborane. The vertical lines indicate the locations of the VAEs.

(a) ETS. Figure 2 displays the ET spectra of the three carborane cage molecules and diethylcarborane. The derivative with respect to energy of the transmitted current is plotted as a function of the electron impact energy. Vertical lines indicate the midpoints of the various temporary anion features and the associated VAEs. In Table 1, we list these energies along with the virtual orbital energies and the scaled values determined as described above. For convenience, Figure 3 shows the scaled VOEs (SVOEs) and the measured VAEs in an energy level diagram. The 10 lowest scaled VOEs in each compound are shown.

Considering the *closo* compounds first, the ET spectra in the energy range from 0 to 2 eV display three rather narrow but overlapping features in *ortho*- and *meta*-carborane, and two rather well-separated resonances in *para*-carborane. Between 2 and 6 eV, only a single feature near 4.2 eV is observed in each compound. The scaled VOEs associated with occupation of the lowest unoccupied molecular orbitals (LUMOs) of the three *closo*-carboranes are in excellent agreement with the experimental VAEs, differing by less than 0.07 eV. In *para*-carborane, our calculations predict the anion ground state to arise from a doubly degenerate e_{1g} orbital, and above this lies a degenerate e_{2g} orbital. The leading term[14] in a partial wave expansion of the wave functions of each of these orbitals is $l = 2$, indicating a high angular momentum barrier and relatively long resonance lifetime. For example, at a radius halfway between the H atoms and the C or B atoms to which they are bonded, the $l = 2$ centrifugal potential is calculated to be ~5.4 eV. In contrast, the a_{1g} orbital whose scaled VOE lies just below 2 eV has a leading term of $l = 0$. This suggests that the anion formed by occupation of the latter orbital may have a much shorter lifetime and consequently be too broad to be distinguished in the presence of the other resonances. Thus we assign the lowest two features in the *para*-carborane spectrum to electron occupation of the e_{1g} and e_{2g} orbitals.

In a similar fashion we associate the low-lying resonances in *ortho*- and *meta*-carborane with those orbitals whose angular momentum components possess the largest leading terms. (We should note that the presence of static electric dipole moments in *ortho*- and *meta*-carborane may alter the effective values of

TABLE 1: Orbital Symmetries, Calculated Virtual Orbital Energies, Shifted and Scaled Virtual Orbital Energies (see text), and Experimental Vertical Attachment Energies[a]

compound	orbital	VOE	scaled VOE	VAE
para-carborane	e_{1g}	3.670	1.0298	1.10
	e_{2g}	4.6151	1.7443	1.97
	a_{1g}	4.8818	1.9479	- -
	a_{1g}	6.3947	3.1028	- -
	a_{2u}	6.7811	3.3978	
	a_{2u}	7.2138	3.7281	
	e_{1u}	7.3580	3.8382	4.24
ortho-carborane	a_2	3.5157	0.9051	0.98
	a_1	4.0491	1.3123	- -
	b_2	4.0709	1.3289	1.40
	a_1	4.5471	1.6924	- -
	b_1	4.5797	1.7173	1.96
	b_2	6.0301	2.8245	
	a_1	6.8573	3.4560	
	b_1	7.2220	3.7343	
	a_1	7.2655	3.7676	
	b_2	7.2845	3.7821	4.20
meta-carborane	b_1	3.6491	1.0069	1.05
	b_2	4.1280	1.3725	1.49
	a_1	4.1879	1.4182	- -
	a_2	4.5498	1.6945	1.90
	a_1	4.8845	1.9500	- -
	b_2	6.1063	2.8827	
	a_1	6.6641	3.3085	
	b_2	7.2764	3.7759	
	b_1	7.3226	3.8112	4.27
	a_1	7.4451	3.9047	
diethylcarborane	a''	4.0545	1.3164	1.10
	a'	4.4137	1.5906	1.61
	a'	5.9512	2.7643	
	a'	6.3675	3.0821	
	a''	6.6043	3.2628	3.4
	a'	7.0587	3.6097	
	a''	7.1322	3.6658	
	a'	7.4097	3.8776	
	a''	7.8587	4.2204	
	a'	8.0084	4.3346	

[a] All energies in eV.

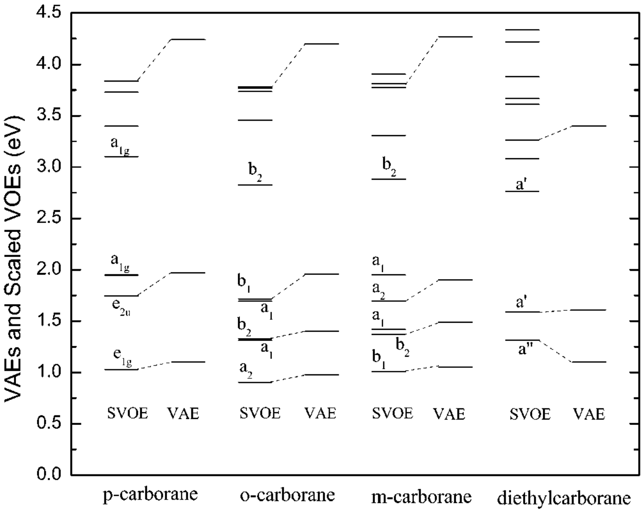

Figure 3. Energy level diagram showing the calculated VOEs, shifted and scaled as determined in the text (SVOEs), and the measured VAEs in the *closo*-carboranes and diethyl carborane.

the momentum components.[15]) With these assignments, the scaled VOEs for the next few higher anion states differ by less than 0.24 eV from the experimental VAEs, still acceptable agreement for this approximate semiempirical treatment. If the a_1 orbitals lying close by give rise to resonances, these are apparently too broad to be discerned in the neighborhood of the narrower features. The fact that three closely spaced resonances can be observed in both *ortho*- and *meta*-carborane must be a tribute not only to the relatively long lifetimes of these states but to fairly narrow Franck−Condon overlaps between the potential surfaces of the ground state of the neutral molecules and those of the lowest anion states observed by ETS. This is evidence in part that the wave functions of the temporarily occupied orbitals are delocalized over the whole molecule (as borne out in the molecular orbital calculations) and that the minima in the two potential surfaces are not substantially displaced from each other. We return to this point below with regard to the ortho compound.

The assignment of the feature or features near 4.2 eV in the *closo*-carboranes is not certain. Given that the scaled VOEs near 2 eV are stable by 0.24 eV relative to the experimental values, it is not unreasonable to believe that the scaled VOEs near 4 eV lie even further below the measured anion energies. According to the calculations, *para*-carborane possesses an empty e_{1u} orbital (doubly degenerate) lying 0.4 below the 4.24 eV feature. Similarly *ortho*- and *meta*-carborane have closely spaced b_1 and b_2 orbitals 0.45 eV below the corresponding features. Each of these orbitals has a leading term of $l = 1$, and we tentatively assign these symmetries to the 4.2 eV resonances, respectively. It should be noted, however, that no structure appears near 3 eV where the scaled VOEs predict anion states with b_2 orbitals in *ortho*- and *meta*-carborane. It is well-known that nonminimal basis sets can generate solutions that are artifacts, and that other procedures (such as the stabilization method) may be required to distinguish those virtual orbitals leading to anion states from the rest.[16] The scaled VOEs below 2 eV are much less likely to be afflicted with this problem.

In diethylcarborane, the scaled VOE for the a'' LUMO is less stable than the ETS value for the lowest resonance, in contrast to the *closo* compounds, but only by 0.2 eV. The ET spectrum suggests an overlapping second anion state close to the calculated a' orbital energy. At higher energy, there is evidence for a very broad but weak feature near 3.4 eV. This could be associated with the a'' orbital lying 0.15 eV lower.

Overall, the lower scaled VOEs reveal surprisingly good agreement with the experimental anion energies, and we stress again that the scaling was derived from the π^* orbitals of a group of unsaturated hydrocarbons. They confirm that the *lowest* valence anion states in these compounds, *in the geometries of the neutral molecules*, are unstable with respect to emission of an electron, that is, the VAEs > 0, or alternately, the vertical electron affinities are < 0. Taken together with the first ionization energies of such compounds, approximately 11 eV as determined by photoelectron spectroscopy[17] in *ortho*-carborane, these results indicate a large HOMO−LUMO gap in these compounds.

Our results largely confirm the extended Hückel (EHMO) calculations of Hitchcock et al.[1] for the empty orbitals of the *closo* molecules in their ground states with regard to ordering and symmetry assignment. The only exception is the lowest a_1 orbital of *ortho*-carborane which appears as LUMO+1 in our calculation rather than LUMO+2. This is likely to be an effect arising from differences in basis sets. The most significant difference is that the EHMO energies are overall too stable by about 5.7 eV, thus they imply that the anion states are stable, in contrast to our ETS results showing them to be temporary anion states.

(b) Negative Ion Production. To address questions of the stability of the *closo* compounds under slow electron impact, it

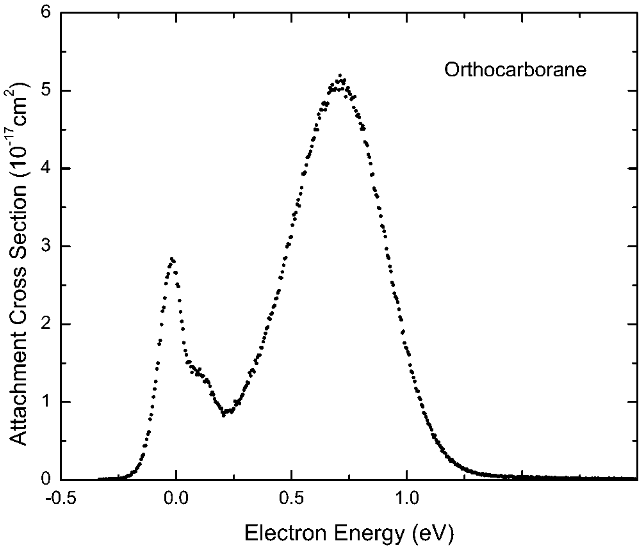

Figure 4. The total cross section for production of negative ions as a function of electron energy in *ortho*-carborane.

is useful to observe anions produced by resonant attachment processes. We report here a measurement of the total cross section for anion production in *ortho*-carborane and its energy dependence. Unfortunately we do not have provisions for mass analysis of these anions.

Figure 4 shows the production of such anions as a function of electron impact energy in *ortho*-carborane. The relative shape of this cross section is that determined in our ion counting apparatus. Below 2 eV, the cross section displays a pronounced peak at 0.7 eV with a full-width at half-maximum of 0.5 eV. This feature is accompanied by a smaller peak near zero energy and a shoulder at approximately 0.1 eV. Because of the small widths of the structure near zero energy, its magnitude corresponds to an effective cross section reflecting the convolution of the actual cross section with our electron energy distribution. The absolute cross section scale was determined by normalizing the relative data to the cross section at the 0.7 eV peak, namely 5.1×10^{-17} cm^2 $\pm$ 20%, as determined in our total collection system.

An examination with the ion counting apparatus of the negative ions produced in *para*-carborane yielded a curve with a very similar dependence on electron energy. The magnitude of the cross section was much smaller, however, and entirely consistent with known amounts of the *ortho*-carborane impurity in the sample.

After our measurements were carried out, work by Mazunov et al.[18] was brought to our attention in which the relative yield of anions in *ortho*-carborane was determined mass spectrometrically. These authors observed that metastable anion states of the *parent* molecule were produced by electron attachment. Furthermore, the yield as a function of electron energy, aside from effects of their energy resolution (0.3 eV), is very similar to that of Figure 3. This result has also been confirmed independently by Vasil′ev et al.[19]

Metastable parent anions are known to be produced in a few cases well above zero energy through formation of a core-excited state of the anion. However, given the high HOMO−LUMO gap in *ortho*-carborane, it seems unlikely that such states could lie low enough to account for the 0.7 eV peak in Figure 3 and in refs 18 and 19.

Our calculations indicate that *ortho*-carborane possesses an electric dipole moment of approximately 4.5 D. This value is larger than that required to bind an electron in the dipole field. If we model the nearly spherical *ortho*-carborane by a hard sphere of radius 1.7 Å, the lowest dipole anion state, for example, would be bound by ~50 meV. Thus a parent anion state would be expected under circumstances where it could be formed by removal of the excess energy by a third body, but such a state would not be metastable. We are not aware of any compounds in which such a dipole mechanism alone, that is, in the absence of a resonance process, causes the formation of metastable parent anions near zero electron energy in a 2-body collision. We note in passing that these carboranes, the *nido* as well as the *closo* compounds, are examples of molecules for which the dipole moment has an anomalous direction. In all three that have moments, calculations predict that the less electronegative boron atoms are more negatively charged than the carbons.

TABLE 2: SCF and MP2 Energies (Hartree) for Anion I and Predicted AAEs (eV)

level	neutral	ion	AAE[a] (eV)	ZPE[b] corr. AAE (eV)
6-31G* Basis				
SCF	−329.62084	−329.56268	1.583	1.393
MP2	−330.83000	−330.80154	0.774	0.584
6-31+G** Basis				
SCF	−329.63647	−329.58287	1.459	1.269
MP2	−330.92545	−330.90854	0.460	0.270

[a] Adiabatic attachment energy. [b] The zero-point energy correction is −0.190 eV.

(c) Search for the Adiabatic Electron Affinity. In view of the puzzling energy dependence of the production of the parent anions, we initiated ab initio calculations to see if the *adiabatic* electron affinity of *ortho*-carborane could be determined. Geometry optimizations of the (spin) restricted open-shell Hartree−Fock (ROHF) wave function of *o*-$C_2H_{12}B_{10}^-$ were first carried out starting at the C_{2v} geometry of the neutral molecule. The closest minimum was found to have C_2 symmetry. Two different random displacements of the coordinates were used as new starting points and each returned to the same C_2 geometry when minimized. SCF and MP2 energies for this anion structure, which we will refer to as "anion I", are shown in Table 2 for both 6-31G* and 6-31+G** basis sets. The adiabatic attachment energies (AAEs), that is, the *negatives* of the adiabatic electron affinities, are seen to be positive. In other words, anion I is *unstable* with respect to auto-ejection of the electron. (It is important to note however that it is bound with respect to the neutral molecule *in the geometry of anion I*, and thus the calculation of the anion energy is not affected by artifacts due to the diffuseness of the basis set.) Table 2 also shows the AAEs as corrected for the substantial zero point energies of the neutral and anion. The calculation with the largest basis set yields an AAE of only 0.27 eV. Because this value is so small, it appears likely to us that still higher level calculations could support the existence of a stable valence anion state.

Figure 5a shows a stereoscopic view of the neutral structure. The directions that the atoms move in arriving at anion I are indicated, with the lengths multiplied by a factor of 2. The a_2 LUMO of *o*-carborane in the region of the C−C bond is a d-like antibonding orbital. When distorted in C_2 symmetry, this orbital is mixed with a_1-type orbitals yielding a twisting force on the carbon atoms. The start of the distortion could be in either direction, so the ion could appear in either of two chiral forms. The C_{2v} geometry for the ion is thus a saddle point.

A second search was generated by starting from anion I, locating the nearest saddle point, and investigating the topology on its far side. A second minimum in the anion potential surface was located this way, labeled anion II, but its energy was above

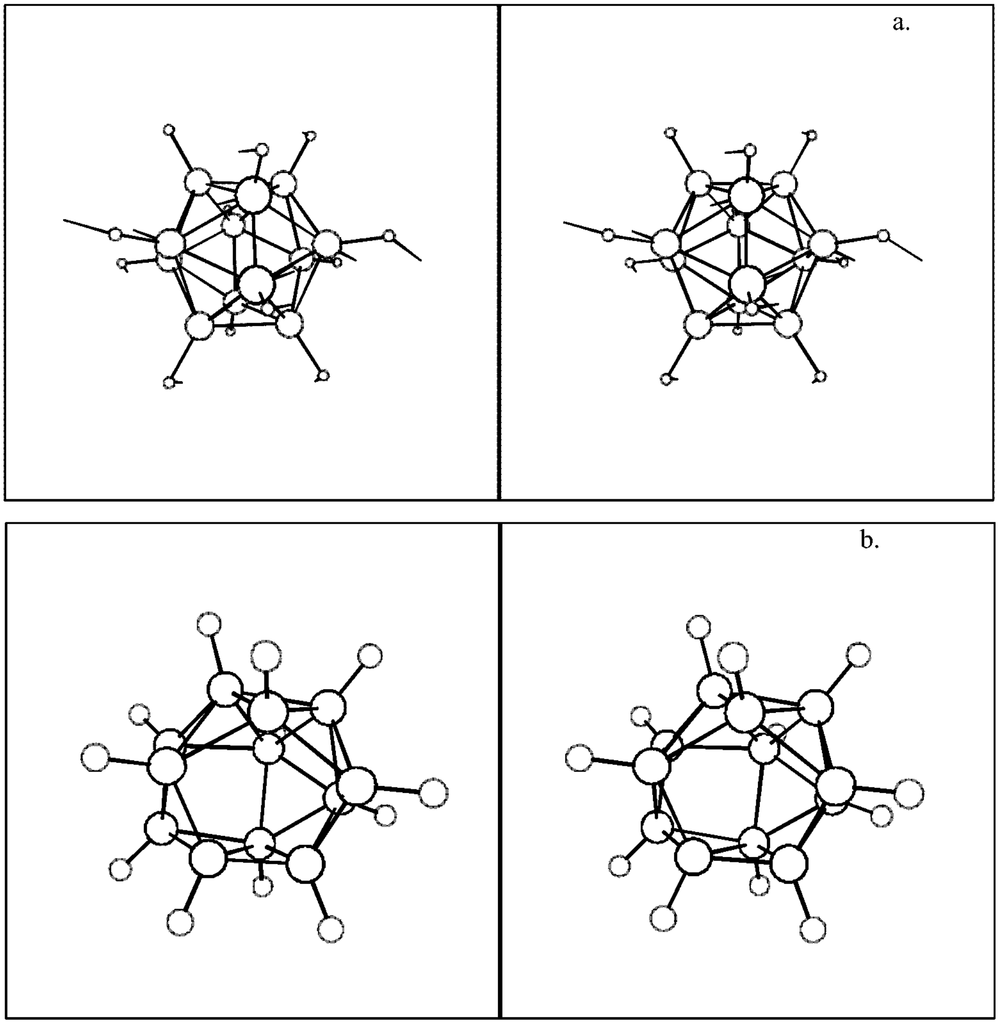

Figure 5. (a) A stereoscopic drawing of the neutral *ortho*-carborane structure with arrows (×2 in length) showing the motion of the atoms in going from the neutral to anion I. (b) The equilibrium geometry of anion II shown in stereoscopic projection. A five-membered ring is visible "in front" and a four-membered ring can be seen "at the back".

TABLE 3: The Maximum, Minimum, and RMS Distances between Corresponding Atoms for the Neutral (N) and Anions I and II of *ortho*-Carborane

pair	max. Å	RMS Å	min. Å
N−I	0.5214	0.1295	0.0308
I−II	1.4060	0.3948	0.0556
N−II	1.5872	0.4551	0.0987

that of anion I by about 1.1 eV with the 6-31G* basis set, and it has not been explored at a higher level. Figure 5b shows a stereoview of the anion II structure. It contains a relatively open five-membered ring on one side and resembles, in this way, the *nido* carborane compounds. Table 3 shows averages for "distances" between the corresponding atoms in the geometries of the neutral molecule and the two anions. The values are for correctly adjusted positions and orientations so that relative translations and rotations are not present. On this basis we see that anion II is "farther" from the neutral than is anion I. The energies of various points on the anion surface are given in Table 4. It is, of course, impossible to show realistic pictures of 3N-6 = 66 dimensional potential energy surfaces (PES), but we have constructed a very schematic version for Figure 6.

We commented earlier upon the narrowness of the $^2A_2$ ETS peak in *ortho*-carborane. As was pointed out, because of the symmetries involved, the anion in C_{2v} geometry is a saddle point on its PES. The gradient there is zero in *all* directions. We have made an attempt to represent this in Figure 6. Calculation of the Hessian matrix for the anion PES at the geometry of the neutral molecule shows that this is actually a *hyper*-saddle point. Excluding the 6 translational and rotational Hessian eigenvalues, there are three that are negative and the remaining 63 are positive. The "directions" associated with the negative eigenvalues have symmetries a_2, b_1, and b_2, in that order of increasing eigenvalues, i.e., the a_2 direction has the most negative curvature. Thus the narrow width of the $^2A_2$ resonance of *ortho*-carborane seen in electron transmission can be attributed, in part, to the saddle-point nature of the ion surface vertically above the neutral minimum geometry. The majority of molecules have vertical transitions in which at least one of the motions of the ion has a nonzero gradient, and this leads to an increased width from Franck−Condon effects that is separate from broadening due to the finite lifetime of the resonance.

TABLE 4: 6-31G* Results for the Anion Surface

geometry	energy (Hartree)	energy[a] (eV)	corrected[b] (eV)
I	−329.56268	1.583	0.4
saddle point	−329.51818	2.794	1.6
II	−329.52033	2.735	1.5

[a] Above the energy of the neutral molecule in its equilibrium geometry. [b] Assuming the same decrease for MP2 and vibrational differences as seen in the neutral molecule.

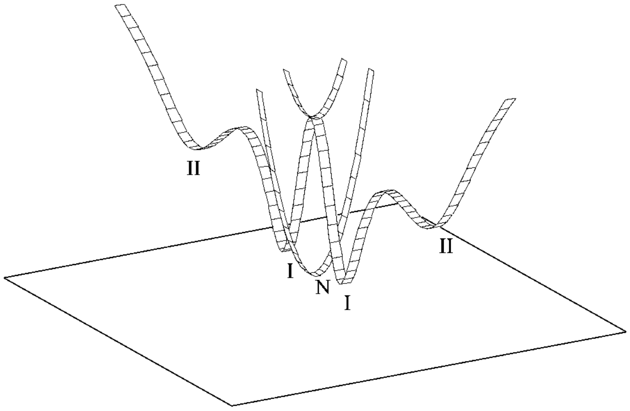

Figure 6. A schematic representation of the *ortho*-carborane neutral and anion surfaces. See text for explanation.

To summarize the search, our calculations suggest the following interpretation. Vertical attachment into the lowest anion state leads to the structure at 0.98 eV in the ETS spectrum of *ortho*-carborane. A minimum in the potential surface of the lowest anion state, at the geometry of anion I, is likely to be adiabatically stable. The existence of a zero energy peak in the production of the metastable parent anion suggests that anion I can be accessed from the wings of the vibrational wave function of the neutral molecule. The shoulder at 0.1 eV in Figure 4 may represent attachment to other vibrationally excited levels. At higher electron energies, the ion potential surface “opens up” to a larger effective phase-space, sampling the region labeled anion II, that is much more anharmonic. With less certainty we suggest that this may be the origin of the 0.7 eV peak in the anion production cross section.

We have not carried out such extensive calculations on the *meta*- and *para*-carboranes, but at the 6-31G* (spin) restricted Hartree−Fock (RHF) and ROHF levels, the meta and para anion energies lie about 0.3 and 1.0 eV, respectively, *above* the corresponding values for *ortho*-carborane. This could be enough to prevent the formation of the metastable anions in these compounds.

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