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The Curiously Stable B_{13}^{+} Cluster and its Neutral and Anionic Counterparts: The Advantages of Planarity[†]

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The cationic, neutral, and anionic charge states of the B_{13} cluster are examined through the use of density functional theory. Several different isomers are studied and compared with a special emphasis given to the electronic structure of the lowest lying isomers. Included among the isomers are three which have been proposed earlier and a pair of new ones. While no minima that corresponded to a filled icosahedron could be found for the cluster, an intriguing atom-in-a-cage structure was found that is a local minimum on the cationic, neutral, and anionic surfaces. The structure found for the B_{13}^{-} anionic cluster has D_{3h} symmetry, and the 12 external boron atoms are arranged as three six-membered rings back-to-back. The planar and quasi-planar structures are seen to be more stable than three-dimensional isomers, but the ordering by stability of the planar and quasi-planar structures changes depending on the charge. Relative energies, selected geometric features, ionization potentials, and electron affinities are reported for these structures and some justification for the differences seen among the isomers is given. The planar structures benefit from π delocalization. In the case of the global minimum of the $B_{13}{}^{+}$ cationic cluster this delocalization is reminiscent of aromaticity.

1. Introduction

The $B_{13}{}^{+}$ bare cluster first proved to be an interesting species through works from Anderson's group in Stony Brook. Hanley, Whitten, and Anderson in 1988[1] found that the mass distribution of $B_n{}^{+}$ from laser ablation showed numerous "magic numbers" in the range $n = 1-20$. Their collision-induced dissociation (CID) results, however, indicated the presence of the noted "magic" clusters; only $B_5{}^{+}$ and $B_{13}{}^{+}$ were especially stable, both showing significant differences in the appearance potentials for B^{+} and $B_{n-1}{}^{+}$ when compared to $B_n{}^{+}$ clusters of similar size. Additionally, in the case of $B_{13}{}^{+}$ the appearance of B^{+} occurs at a potential slightly lower than the potential at which $B_{12}{}^{+}$ appears. This is in sharp contrast to the other large cationic clusters in which the appearance potential for $B_{n-1}{}^{+}$ is lower than that of B^{+}.

In the following years, Anderson's group performed a series of reactivity studies.[2−5] The $B_{13}{}^{+}$ cationic cluster was seen to demonstrate anomalous reactivity in all reactions studied (with O_2, D_2O, CO_2, and N_2O). For example, in the case of reaction with O_2, the threshold for oxidation is approximately two electron volts higher than for any other cluster ion studied.[2] Also, in reacting with D_2O, although no barrier to reaction exists, the reactivity of $B_{13}{}^{+}$ was 2 orders of magnitude lower than that of similarly sized clusters.[3]

Anomalous experimental results providing a favorite playground for theoreticians, the results of Anderson's group inspired several theoretical studies of small boron clusters and especially the $B_{13}{}^{+}$ cation.[6−13] Ihsan Boustani investigated the B_n ($n = 2-14$) neutral clusters using small basis sets and a variety of methods (HF-SCF, direct CI, LSD, and NSD).[9] He predicted a quasi-planar ground state equilibrium geometry for the B_{13} neutral cluster, as opposed to the filled icosahedron originally postulated by Anderson's group.[1] Boustani has since then expanded significantly the study of bare boron clusters. Especially interesting have been the discussion of π delocalization in quasi-planar, tubular, layered, and the hypothetical boron quasicrystal.[11,14−17]

Ricca and Bauschlicher in 1996 reported a rounder, planar structure as the ground state of the $B_{13}{}^{+}$ cationic cluster in which a central triangle of atoms is surrounded by a ring of 10 atoms.[10] They used the B3LYP/6-31G* level of theory to optimize the structures of the cationic clusters $B_n{}^{+}$ ($n = 2-14$) and applied some calibration to their energetics through the use of the CCSD(T)/cc-pVTZ level of theory.

Most recently, Gu *et al.*[13] characterized a series of 19 various structures of the $B_{13}{}^{+}$ cation cluster (also using the B3LYP/6-31G* level of theory) and found that the planar and near-planar structures were consistently more stable than any 3-dimensional structure. They also found no atom-in-a-cage minima. In their concluding remarks, they note, "The reason for the high abundance of $B_{13}{}^{+}$ among the $B_n{}^{+}$ clusters is still an unsolved problem that challenges further experimental and theoretical investigation."

Here we provide further theoretical investigation of this very peculiar cluster. We utilize levels of theory similar to those which have been used earlier, but extend the application to include the cationic, neutral, and anionic B_{13} clusters as we did for the Al_{13} cluster in an earlier study.[18] This allows a more complete investigation of the electronic structure of these clusters and therein lies the explanation of the curious stability and planarity of the $B_{13}{}^{+}$ cationic cluster.

2. Methods

All geometries were fully optimized using the B3LYP gradient-corrected density functional method[19−22] analytic gradients. Harmonic vibrational frequencies were determined by numerical differentiation of gradients.

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[†] This paper is dedicated to Professor J. Elguero on the occasion of his 65th birthday.

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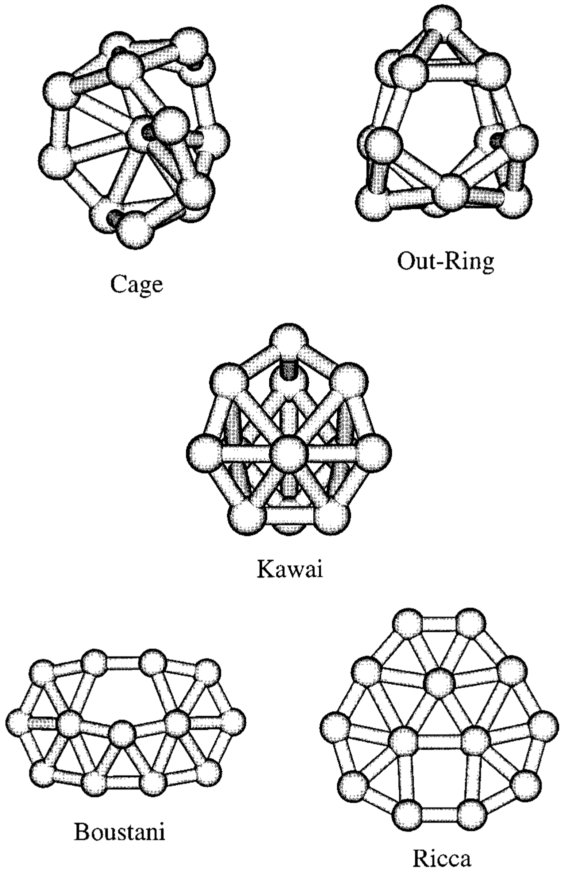

Figure 1. The various local minima characterized on the B_{13}^+ potential energy surface.

The D95 basis set[23] composed of a double-ζ set of functions was used for initial calculations. As this set does not include d functions, it was necessary to add a set of five pure-angular-momentum d functions to this basis in order to properly describe the high-valency of the boron atoms. The exponent of the added set of d functions was 0.7.

In order to improve the determination of the relative energies of the various isomers, several larger basis sets were applied at the B3LYP/D95(d) optimized geometries. The first expansion made to the basis set was the addition of one set of seven pure-angular-momentum f functions with an exponent of 0.5 to construct the D95(df) basis set. Additionally, two large standard basis sets were used: 6-311G(2d) and 6-311G(2df)[24] for each of the stationary points.

All calculations were carried out with the GAUSSIAN94 package.[25] The figures were generated using the MOLDEN program.[26]

3. The $B_{13}^{+/0/-}$ Stationary Points

3.1. The Cationic B_{13}^+ Clusters. As mentioned previously, the cationic B_{13}^+ cluster has been the object of several former studies and is, of course, the ion of experimental interest. We selected the two lowest lying (near-)planar isomers and one of the two lowest lying three-dimensional structures presented in the work of Gu et al.[13] for comparison with the new isomers characterized in this study. We have followed the same naming scheme used by those authors. That is, we have named the isomer for the first author who proposed that structure. The five isomers studied in detail in this work are depicted in Figure 1 and in Table 1 can be found a summary of the geometrical parameters of the various local minima found for the B_{13}^+ cationic cluster. Included are the number of bonds (as defined below), the range of bond lengths, and the average bond length.

TABLE 1: Geometric Parameters of the Various Minima Found on the B_{13}^+ Potential Energy Surface

isomer	symmetry	no. of bonds	range	average
Ricca[a]	C_{2v}	25	1.553−1.988[d]	1.710
Boustani[b]	C_s	24	1.577−1.880	1.689
Kawai[c]	C_{3v}	30	1.566−2.015	1.753
Out-Ring	C_s	27	1.580−2.058	1.720
Cage	C_1			
center-shell		12	1.840−2.131	1.982
shell-shell		18	1.573−1.821	1.673

[a] Structure first proposed in ref 10. [b] Structure first proposed in ref 9. [c] Structure first proposed in ref 6. [d] Bond lengths are reported in angstroms.

Our structures labeled "Ricca" with C_{2v} symmetry, "Boustani" with C_s symmetry (the plane of symmetry cuts through the cluster, relating the left and right halves of the figure), and "Kawai" with C_{3v}, symmetry are fairly similar in geometrical parameters to those presented by Gu et al.[13] and thus we will avoid commentary on those specifics. The two new isomers reported here are those labeled "Cage" and "Out-Ring". Both are local minima on the cation potential energy surface and have C_1 and C_s, symmetry, respectively.

The Cage isomer is the first minimum reported in the literature with an atom-in-a-cage type structure. Gu et al.[13] do, however, characterize an atom-in-a-tube type minimum. In the Cage structure, the center-to-exterior distances range from 1.840 to 2.131 Å and have an average length of 1.982 Å. In describing the exterior bond lengths, it is necessary to apply some cut-off length for determining what is a bond and we have chosen the longest center-to-exterior distance (though at 2.131 Å, this is quite long for B−B interactions). The natural cutoff for bond lengths displays itself, however, as the 18 exterior bond lengths range from 1.573 to only 1.821 Å (despite our rather generously defined cutoff distance), with an average of 1.673 Å.

The Out-Ring structure is so labeled because this local minimum was discovered as a result of extracting the central atom *out* of the Cage structure (as will be discussed for the anion) and reoptimizing. The final result is quite different from the Out isomer of the neutral and anionic cases. In this structure, the B−B bond lengths range from 1.580 to 2.058 Å and the average among the 27 bond lengths is 1.720 Å.

Energetically, the most stable among all the isomers located is the Ricca structure. The total energy of the C_{2v} structure first proposed by Ricca and Bauschlicher[10] and the relative energies of the other isomers can be found in Table 2. The B3LYP/D95(d) optimized geometries were used for these B3LYP single-point energy calculations, and the B3LYP/D95(d) zero-point vibrational energy correction has been applied. Also included in Table 2 are the B3LYP/6-31G* results of Gu et al.,[13] and again our results for the Ricca, Boustani, and Kawai isomers are very similar to theirs. The addition of *f* functions to the D95(d) basis set has a rather large effect on some of the relative energies, but when the more complete 6-311(2d) basis is augmented with one set of *f* functions, the change in relative energies is minimal. This is reasonable because the 6-311(2d) basis set already has the valence space well-described.

3.2. Neutral B_{13} Clusters. The neutral B_{13} clusters are similar in aspect to either the cationic or anionic clusters and thus there we present no figure especially for them. The Kawai and Ricca neutral structures are more similar in geometric arrangement to their cationic counterparts, while the Cage, Out, and Boustani neutral structures are more easily related to the anionic isomers

TABLE 2: Total Energies of the Ricca Structure and Relative Energies of the Various Other Structures Found for the B_{13}^{+} Cationic Cluster: These Energies Computed with the B3LYP Method at the B3LYP/D95(d) Geometries and Corrected for the Zero-Point Vibrational Energy Determined at That Same Level[a]

isomer	D95(d)	D95(df)	6-311G(2d)	6-311G(2df)	B3LYP/6-31G*[13]
Ricca[b]	−322.447619	−322.470492	−322.550518	−322.559303	−322.54419
Boustani[c]	27.8	29.1	27.3	27.6	26.7
Kawai[d]	51.4	58.5	49.1	49.7	44.6
Out-Ring	71.9				
Cage	82.5	89.3	87.3	87.9	

[a] Total Energies of the Ricca structure in Hartree, relative energies in kcal/mol. [b] Structure first proposed in ref 10. [c] Structure first proposed in ref 9. [d] Structure first proposed in ref 6.

TABLE 3: Geometric Parameters of the Various Minima Found on the B_{13} Potential Energy Surface

isomer	symmetry	state	no. of bonds	range	average
Ricca[a]	C_{2v}	$^2B_1$	25	1.540−1.935[d]	1.703
Boustani[b]	C_{2v}	$^2A_1$	26	1.593−1.813	1.692
Kawai[c]	C_{3v}	$^2A_1$	30	1.563−1.992	1.762
Out	C_1	^2A	27	1.577−1.943	1.705
Cage	C_2	^2B			
center-shell			12	1.905−1.912	1.908
shell-shell			21	1.611−1.815	1.707

[a] Structure first proposed in ref 10. [b] Structure first proposed in ref 9. [c] Structure first proposed in ref 6. [d] Bond lengths are reported in angstroms.

TABLE 4: Total Energies of the Ricca Structure and Relative Energies of the Various Other Structures Found for the B_{13} Neutral Cluster: These Energies Were Computed with the B3LYP Method at the B3LYP/D95(d) Geometries and Are Corrected for the Zero-Point Vibrational Energy Determined at That Same Level[a]

isomer	D95(d)	D95(df)	6-311G(2d)	6-311G(2df)
Ricca[b]	−322.709970	−322.733062	−322.811550	−322.820702
Boustani[c]	9.7	10.5	9.0	8.8
Kawai[d]	50.8	58.4	52.1	53.0
Out	74.5	81.2	74.5	74.8
T.S.	91.7			
Cage	80.4	87.4	86.2	86.4

[a] Total Energies of the Ricca structure in Hartree, relative energies in kcal/mol. [b] Structure first proposed in ref 10. [c] Structure first proposed in ref 9. [d] Structure first proposed in ref 6.

(shown below). All these structures are local minima and the transition state for center atom extraction which relates the Cage and Out structures has also been located. In Table 3 can be found geometrical parameters for the neutral clusters.

The neutral Cage structure is a ^2B state with C_2 symmetry. The range of center-to-exterior bond lengths is quite limited in the neutral in comparison with that of the cationic structure. The values range from 1.905 to 1.912 Å, with an average length of 1.908 Å, significantly shorter than the bond length in the cation. The bonds among the exterior twelve boron atoms are also more regular than were those same bonds in the cationic case, ranging from 1.611 to 1.815 Å, and there is a slight increase in the average. It should be noted, though, that the average is taken over 21 exterior bonds, as opposed to the 18 exterior bonds of the cationic Cage isomer.

The structure labeled Out is the result of extracting the central boron atom of the Cage isomer through one of the three open faces and reoptimizing resulting in a structure very similar to the anionic Out isomer (presented below). The final structure has C_1 symmetry and a doublet ground state. The atom that formerly was in the center of the cage is now located in the center of one of the six-membered-ring faces. Those six bonds range in length from 1.666 to 1.943 Å. Overall, the bond lengths range from 1.577 to 1.943 Å, with an average length of 1.705 Å for the 27 bonds.

The neutral Kawai cluster maintains its C_{3v} symmetry and has a $^2A_1$ ground state. The range of bond lengths for the neutral cluster is only slightly different from that of the cationic cluster, showing a minor change in the direction of shorter bonds. However, the shorter limits may be misleading because the average bond length is slightly longer in the neutral than it was in the cation.

Adding an electron to the Boustani cationic structure leads to the quasi-planar minimum originally proposed by Ihsan Boustani in his study of neutral boron clusters.[9] This isomer has C_{2v} symmetry and a $^2A_1$ ground state. The range of bond lengths is significantly changed from the cationic case, again with a tendency towards homogenization, and like the case of the external Cage bonds, the average length increases a bit, but there are more bonds. The atom located in the center of the cluster now is bonded to six other boron atoms, yet it was only bonded to four in the cationic cluster, making for a total of 26 bonds.

The neutral Ricca cluster, with at $^2B_1$ ground state, maintains both the C_{2v} symmetry and the atomic arrangement of the cation. This is the only isomer for which the longest, shortest, and average bond lengths are shortened upon the addition of an electron to the cationic cluster. However, it should be remembered that no additional bonds have been formed.

In Table 4 can be found the total energy of the Ricca isomer and the relative energies of the other isomers calculated at various levels of theory. Again, the B3LYP/D95(d) geometries and zero-point-vibrational-energy corrections were used. There are several data of interest in this table. First, it should be remarked that T.S. stands for the transition state connecting the Cage and Out structures. The barrier to center-atom extraction, then, is 11.3 kcal/mol at the B3LYP/D95(d) level of theory. As in the case of the cations, there is a relatively large f function effect when said functions are added to the D95(d) basis set, but the effect of augmenting the 6-311G(2d) basis is minimal. Most interesting, though, is the dramatic change in relative energy between the Ricca and Boustani structures. For the cations there is an energy difference of 27.6 kcal/mol at the highest level of theory applied. It takes only the addition of a single electron to drop that relative energy to just 8.8 kcal/mol.

3.3. Anionic B_{13}^{-} Clusters. Figure 2 depicts the structures of the five minima located on the B_{13}^{-} potential energy surface. Selected geometrical features for those isomers can be found in Table 5.

The Cage structure of the ionic cluster has D_{3h} symmetry and can be imagined as a cage built by three six-membered rings back to back with one atom in the center. With such high symmetry, there are only two types of center-to-exterior bonds (measuring 1.873 and 1.926 Å), and three types of exterior bonds (measuring 1.601, 1.709, and 1.753 Å). The high symmetry of the anion, and decreasing symmetry of the neutral and cationic species is reminiscent of the $Al_{13}^{+/0/-}$ clusters, where the anionic cluster is a center-filled icosahedron and the neutral loses all

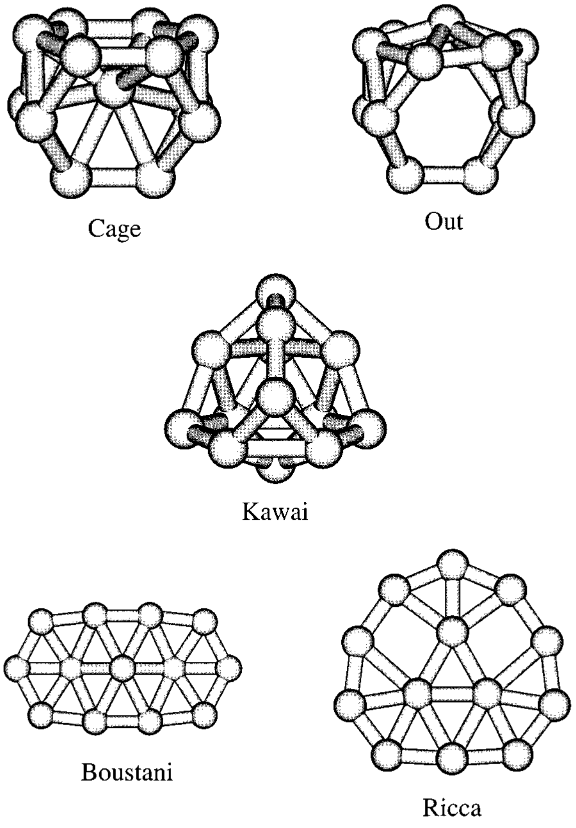
Cage
Out
Kawai
Boustani
Ricca

Figure 2. The various local minima characterized on the B_{13}^- potential energy surface.

TABLE 5: Geometric Parameters of the Various Minima Found on the B_{13}^- Potential Energy Surface

isomer	symmetry	no. of Bonds	range	average
Ricca[a] ($^3B_2$)	C_{2v}	24	1.548−1.963	1.689
Boustani[b]	C_{2v}	26	1.587−1.807	1.683
Kawai[c]	C_s	29	1.570−2.090	1.753
Out	C_2	27	1.572−1.833	1.707
Cage	D_{3h}			
center-shell		12	1.873, 1.926	1.899
shell-shell		21	1.601−1.753	1.706

[a] Structure first proposed in ref 10. [b] Structure first proposed in ref 9. [c] Structure first proposed in ref 6. [d] Bond lengths are reported in angstroms.

symmetry.[18] The average of the center-to-shell bond lengths decreases with each added electron, yet the number of exterior bonds and average length of those bonds is the same as in the neutral Cage isomer.

The anionic isomer labeled Out has C_2 symmetry. The geometrical parameters do not change much between the neutral and anionic isomers, except for the fact that the anionic structure does have a C_2 axis of symmetry and the longest bond is shorter than the longest bond of the neutral.

The Kawai isomer, which had C_{3v} symmetry in both the neutral and cationic cases, here has only C_s symmetry and has lost one of the 30 bonds found in the structures with fewer electrons. The longest bond length is also greater than any found earlier amongst the Kawai isomers and the average bond length is similar, despite the loss of one bond.

TABLE 6: Total Energies of the Ricca Structure and Relative Energies of the Various Other Structures Found for the B_{13}^- Anionic Cluster. These Energies Computed with the B3LYP Method at the B3LYP/D95(d) Geometries and Corrected for the Zero-Point Vibrational Energy Determined at that Same Level[a]

isomer	D95(d)	D95(df)	6-311G(2d)	6-311G(2df)
Ricca[b] ($^3B_2$)	−322.804716	−322.827874	−322.902383	-322.912082
Boustani[c]	-10.9	-10.5	-12.4	-12.6
Kawai[d]	58.2	66.3	60.9	62.2
Out	59.8	66.7	60.4	61.0
T.S.	81.0	87.9	86.1	86.5
Cage	72.4	79.4	78.9	78.9

[a] Total Energies of the Ricca structure in Hartree, relative energies in kcal/mol. [b] Structure first proposed in ref 10. [c] Structure first proposed in ref 9. [d] Structure first proposed in ref 6.

TABLE 7: Electron Affinity and Ionization Potentials (in eV) of the Various Structures: The Results with larger Basis Sets Computed at the B3LYP/D95(d) Geometries

Electron Affinity

	D95(d)	D95(df)	6-311G(2d)	6-311G(2df)
Ricca[a]	2.58	2.58	2.47	2.49
Boustani[b]	3.51	3.53	3.43	3.45
Kawai[c]	2.24	2.22	2.07	2.07
Out	3.22	3.22	3.10	3.09
Cage	2.94	2.94	2.81	2.83

Ionization Potential

	D95(d)	D95(df)	6-311G(2d)	6-311G(2df)
Ricca	7.13	7.14	7.10	7.11
Boustani	7.95	7.98	7.93	7.95
Kawai	7.11	7.09	6.91	6.91
Cage	7.23	7.23	7.15	7.18

[a] Structure first proposed in ref 10. [b] Structure first proposed in ref 9. [c] Structure first proposed in ref 6.

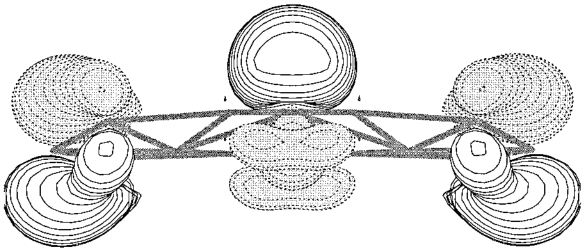

Figure 3. HOMO of the Boustani anion.

The Boustani anion is very similar to the neutral. There is, however, a consistent trend of shortened bond lengths. Both ends of the range are shortened as is the average of all the bond lengths. The anionic structure is also slightly closer to true planarity. While the atoms of the neutral Boustani isomer have and average deviation from the *xy*-plane of 0.126 Å, the atoms of the anionic isomer have an average deviation of 0.105 Å. The average deviation from planarity of the cationic Boustani structure is 0.297 Å.

The anionic Ricca isomer shows an arrangement of atoms different from that of the neutral and cationic structures. The change can be envisioned as a rotation of the center triangle of atoms within the larger ring. A similar structure was identified as a very low-lying transition state for the B_{13}^+ cationic cluster by Gu et al.[13] but for the anion, it is this structure that is the minimum and that depicted in Figure 1 is the low-lying transition state.

Also, it should be pointed out that while the average bond length does decrease upon the addition of an electron, the number of bonds decreases from 25 to 24 in this new arrangement. Electronically, the Ricca anion, with a $^3B_2$ ground state, is the *only* isomer found in this entire study for which the ground state is not one of the lowest possible spin. All other cations and anions were closed-shell singlet ground states and the neutrals all had doublet ground states.

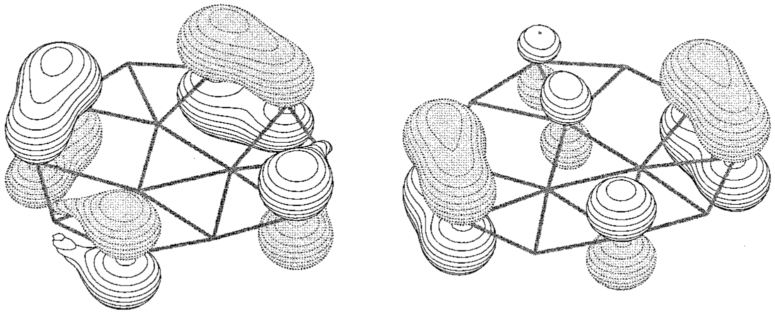

Figure 4. SOMOs of the Ricca anion.

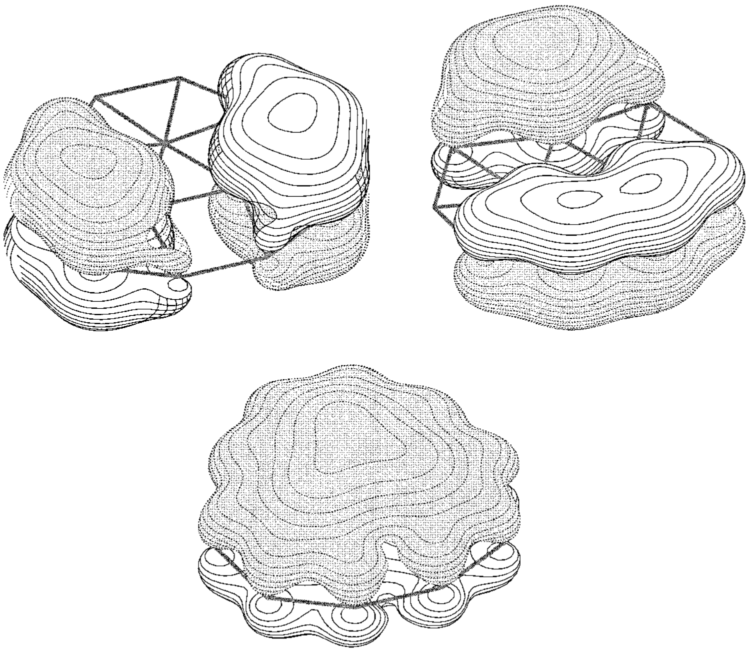

Figure 5. Doubly-occupied π orbitals of the Ricca cation.

In the comparison of energetics (Table 6) we again see data of special interest. The Boustani isomer, which, among the cations, lies 27.6 kcal/mol above the Ricca global minimum and 8.8 kcal/mol in the neutrals, is now the global minimum. The shift in relative energy upon the addition of an electron to the neutral species is slightly more than 20 kcal/mol, whereas it was somewhat less than 20 kcal/mol when adding an electron to the cations. The relative energies of the Out and Cage structures compared to the Ricca isomer are also lower in the anionic case than they are in the neutral and cationic cases. Finally, the transition state for extracting the central atom from the Cage structure presents a barrier of only 7.6 kcal/mol.

In Table 7 can be found adiabatic ionization potentials and electron affinities for the various isomers studied in this work. These numbers can be derived from the other tables given, but are presented here in this format for the convenience of the reader. These results compare reasonably well with the IP and EA of the boron atom.[27] The additional electronic structure flexibility is demonstrated by the fact that all of the cluster IPs are lower than the 8.3 eV of the atom, and all of the EAs are higher than the atomic value of 2.0 eV (though the EA of the Kawai isomer is only slightly so).

4. Electronic Structure

One of the advantages of studying various charge states of a species is that a more complete understanding of the electronic structure is achievable. Experiment tells us that the B_{13}^+ cation is especially stable. Theory indicates that the structure which is especially stable for the cation becomes relatively unstable as electrons are added. An examination of the electronic structure of our two lowest lying isomers will allow us to understand why.

First, to understand why the Boustani isomer becomes relatively more stable as electrons are added, we need to know into which orbitals the electrons are being placed. Figure 3 depicts the highest occupied molecular orbital (HOMO) of the Boustani anion (singly occupied in the neutral). Through examination of this orbital, we can see that the neutral Boustani isomer gains the C_{2v} symmetry and two bonds not found in the cationic structure as a result of π interactions between the central atom and edge atoms. What is more, this orbital is π-bonding along the short axis in three regions, and non-bonding along the long axis. This π delocalization has been remarked upon previously by Boustani[11] in discussion of the neutral B_{13} cluster. Figure 4 depicts the two singly-occupied molecular orbitals (SOMO) of the Ricca $^3B_2$ anion. Each has some π-bonding character among pairs of outer-ring atoms, but the overall character is more nonbonding than was seen for the HOMO of the Boustani anion. The greater stability and bonding character of the Boustani anion's HOMO, then, provides the answer as to why the relative stabilities change so significantly as electrons are added.

Still, the experimentally observed[1−5] special stability of the B_{13}^+ cationic cluster is unexplained, but there is something

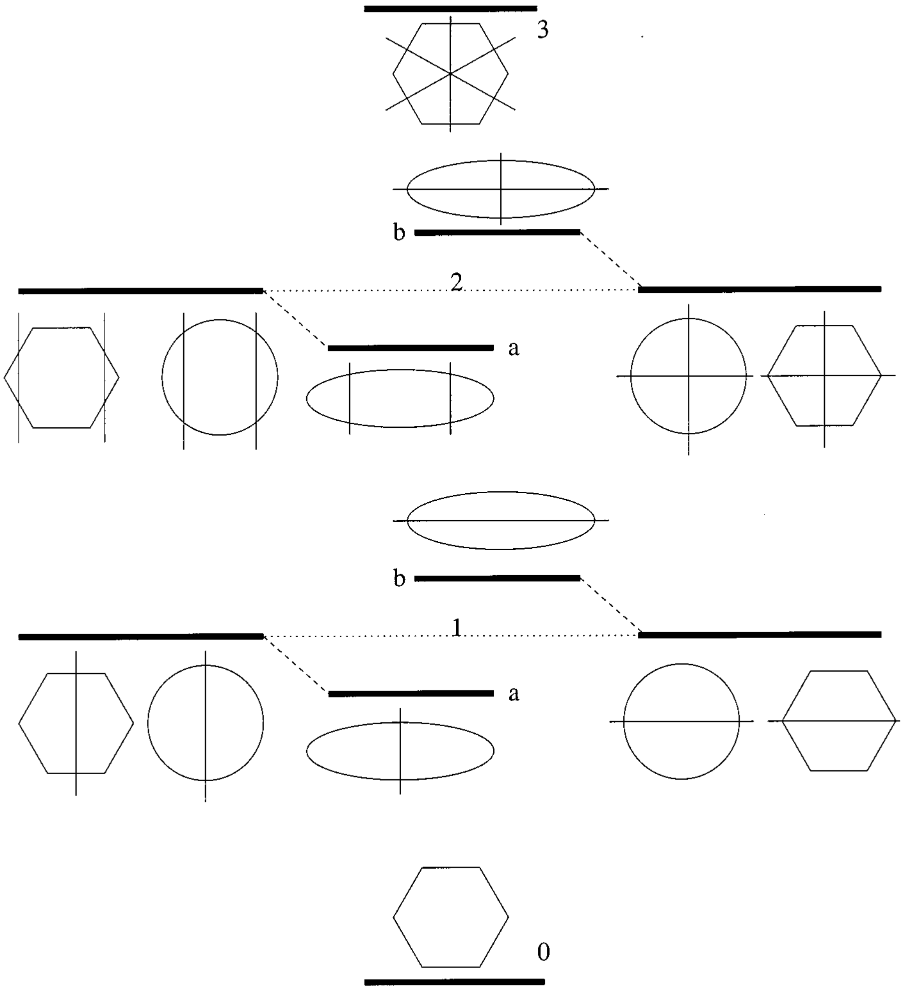

Figure 6. Simple molecular-orbital energy diagram for the π MOs of the benzene molecule related to those of the B_{13} clusters. The Ricca and Boustani isomers are represented by basic models: a circle and an oval, respectively. Numbers have been assigned by the number of nodes in the MO. In the cationic cases, orbitals 0, 1a, and 1b are doubly occupied. The filling of the orbitals with two nodes takes place as electrons are added. Note also that these rudimentary models can be related to the earlier figures. Orbitals 0, 1a, and 1b of the Ricca cation appear in Figure 5, the 2a and 2b orbitals of the Ricca anion are demonstrated in Figure 4, and orbital 2a of the Boustani anion is depicted in Figure 3.

familiar about the SOMOs of the Ricca anion. Basically, they are π orbitals of a round system, each with two nodes. Remembering basic molecular orbital theory, in order to be filling such orbitals there must be other π orbitals already filled in the cationic case: one with no nodes, and two with one node. That is exactly the case as can be seen in Figure 5 which shows the three doubly occupied π orbitals of the Ricca cation. Three doubly filled π electrons gives six π electrons in a round system, a situation reminiscent of benzene and Hückel aromaticity.

In Figure 6 is the standard depiction of the molecular orbital energy diagram of the π orbitals of benzene (hexagon) augmented with primitive models of our Ricca and Boustani systems, a circle and an oval, respectively. The lines which cut the models are nodes in the π MOs. Because the Ricca isomer is more or less round, the pairs of orbitals with an equal number of nodes remain almost degenerate, but the MOs of the Boustani system are split because of its oval shape. Both the Boustani and Ricca cationic clusters have six π electrons, meaning that the orbitals labeled 0, 1a, and 1b (where the numbers indicate the number of nodes) are filled with two electrons each. Note that the cationic Boustani structure adopts a C_s structure so that the central atom does not lies along the central node seen in 1a of Figure 6. This reduces the favorable interactions between that atom and the two atoms on the other side of the loop. Considering this geometric feature and the highly favorable π delocalization of the rounder Ricca structure helps in understanding why the Ricca structure is the most stable of the cations.

As we move to the neutral and anionic cases, electrons are placed in the π orbitals with two nodes. The 2a orbital of the Boustani cluster will, of course, be filled first, but the Ricca cluster has open a pair of quasi-degenerate orbitals, both of which lie higher in energy than that available to the Boustani isomer. Thus, the addition of one electron to the cationic clusters reduces the energetic difference between the two. This effect is repeated when a second electron is added making the Boustani anion more stable than the Ricca anion.

This very basic diagram is in perfect agreement with the prediction of a singlet ground state for the Boustani anion, a triplet ground state for the Ricca anion, and the difference in relative energies among the various charge states. It is also in support of the argument that the B_{13}^+ cationic cluster is especially stable because it is aromatic.

5. Conclusions

We have studied various isomers of the $B_{13}^{+/0/-}$ clusters and found that throughout the various charge states planar or quasi-planar structures are preferred over three-dimensional isomers.

The global minimum among the cationic clusters is a round structure, first proposed by Ricca and Bauschlicher.[10] According to the highest level of theory applied [B3LYP/6-311G(2df)//B3LYP/D95(d)], this isomer lies 27.6 kcal/mol below the second-lowest-energy isomer of this work, a structure similar to that first proposed by Ihsan Boustani.[9] The global minimum of the neutrals is also the Ricca structure, but the energetic difference between that isomer and the Boustani isomer is reduced to 8.8 kcal/mol. The addition of one additional electron changes the energetic ordering of these two structures and the Boustani anion lies 12.6 kcal/mol *below* the Ricca anion. The reason for this change in ordering is that the orbital being filled is one which is π-bonding along the short axis of the Boustani isomer and nonbonding along the long axis, while the two orbitals which are singly occupied in the Ricca anion are essentially nonbonding.

There does exist a local minimum with an atom-in-a-cage structure on the cationic, neutral, and anionic potential energy surfaces of the B_{13} cluster. In the case of the anionic cluster, it is a highly symmetric (D_{3h}) structure with a barrier to central atom extraction of approximately 8 kcal/mol. The neutral and cationic structures are less symmetric, reflecting the reduced bonding capacity.

As reported by others previously,[9,10,13] (quasi-)planar structures are more stable than three-dimensional ones for the B_{13}^+ cationic cluster. This trend holds true for the neutral and anionic clusters as well. This is due, at least in part, to the fact that the planar and quasi-planar structures are stabilized by π delocalization.

The B_{13}^+ cationic cluster, known experimentally to be especially stable,[1-5] is a round system with six π electrons. The occupied π orbitals shown in Figure 5 are very reminiscent of the molecular orbitals of benzene. Upon addition of two more electrons, the same type of structure becomes unstable relative to other isomers studied and the ground state becomes a triplet. All of these data support the argument that the B_{13}^+ cationic cluster could be especially stable because it is aromatic.

Can it be said with security that the B_{13}^+ cationic cluster is aromatic? If so, then there would be other implications. For example, B_{13}^+ has six π electrons which can be thought of as half an electron per boron atom, dropping the final half for the charge. Applying the $4n+2$ rule for aromaticity to this formula for boron cationic cluster stability implies that the B_5^+ [$(5 - 1)/2 = 2$], and B_{21}^+ [$(21 - 1)/2 = 10$] clusters should show some special stability. The B_5^+ cluster *is* especially stable[1] and there is some evidence that two isomers of B_{21}^+ exist,[4] perhaps suggesting that even such a large cluster could have one stable planar structure. What's more, B_9^+ [$(9 - 1)/2 = 4$] should be antiaromatic. Ricca and Bauschlicher predict a non-planar global minimum for that cluster[10] and the B_9^+ cluster has been seen to be especially reactive.[2,4,5] Then, turning to the neutral boron clusters, could the B_{12} cluster be especially stable? The B_{13}^+ cluster does dissociate more easily to $B_{12} + B^+$,[1] a sharp contrast to the other B_n^+ clusters, which have a lower appearance potential for B_{n-1}^+ in the CID experiments.[1] This could be an indication that B_{12} is especially stable among the neutrals.

Aromaticity is a concept that has proven to be very useful to experimentalists and very much debated by theoreticians even to this day.[28-30] If the concept can be applied to small boron clusters in a sense that it increases our understanding and predictive ability, then the use of the term is justified. Consequently, this topic deserves further investigation and it is our hope that this article will trigger such interest.

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