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# Hydrogen hosting of nano scale boron clusters

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**Abstract.** In this paper the Density Functional Results of hydrogen bonded boron micro clusters with B3LYP/6-311++G(d,p) level of computations will be presented. Energetics and structural stability with their possible stable geometries of various selected micro complexes of $\mathrm{B}_m\mathrm{H}_n$ (for $m$ and $n \leq 11$) boron hydrides have been analysed, and their binding energies with HOMO-LUMO energy gaps have been determined. Mainly, effects of the number of hydrogen atoms on the structures of the boranes are assessed. Moreover, for the cage configurations their distortions have been investigated for the neutral, anionic and cationic cases. It has been observed that there have been two opposing factors for the cage configurations. One of which is the "peeling" of the cage structures by the hydrogen atoms, and the other one is reforming a smaller cage form simultaneously with the remaining boron atoms inside. This is observed mostly for the odd values of m. From our studies it has been also observed that with the bare boron clusters alone, it is difficult to increase the capacity of the hydrogen storage. Therefore, further studies are necessary with the boron complexes.

## 1. Introduction

Due to the utilization of hydrogen as an alternative clean energy source, studies on the hydrogen storage have become an active research area for the scientists. It may be said that, at nano scale, the boron and its compounds are vital and inescapable materials to tackle the hydrogen storage problems [1–12]. The boron can make short distance covalent and strong directed chemical bonds with itself and with the other electron-donor atoms because it can form diverse nano-scale structures with the electron-donor atoms, and can link three or more atoms due to different level of hybridizations of the valence $s^2p^1$ electrons.

Quantum chemical calculations are accepted as an efficient routine tool for obtaining the energies and the structures of molecular species [13], which are also complementary parts for the experimental studies to obtain the desired physical and chemical quantities. In addition, the density functional theory (DFT) has also a potential to describe the inter- and intra-molecular interactions of various systems for the computational studies [14, 15].

In the literature various theoretical studies have sought to analyze the properties of boron hydrides complexes. Some of the selected examples are; $B_nH_n$ for $n = 4$, 12, 32 and 60 by using electronic-structure method, based upon the local-density-approximation (LDA) [2], and several neutral and cationic nano scale boron hydrides by the ab initio and electron propagator theory [3] were investigated. Hypercloso boron hydrides, $B_nH_n$, for $n = 5$–13, 16, 19 and 22, were studied by the DFT-B3LYP/6-31G(d) [4]. The structure and stability of closo-hexaborane were worked by applying ab initio (MP2(full)/6-311+G**) and density functional (B3LYP/6-311+G**) methods [5]. In spite of the intense research efforts to determine energetics and structural parameters of the boron hydrides, our understanding of their physical and chemical properties is still rudimentary.

In our previous studies, by using B3LYP/6-311++G(d,p) level of computations, we investigated the hydrogen bonded neutral $B_4H_n$ ($n = 1$–11) and anionic $[B_4H_{11}]^{-1}$ clusters [6], the neutral complexes of the hydrogen bonded cage borane ($B_mH_n$, $m = 5$–10 and $n \leq m$) [7] and their anionic $[B_mH_n]^{-1}$ and cationic $[B_mH_n]^{+1}$ forms [8] for the lower-lying singlet and doublet electronic states. In these works, mainly, our ultimate goals were to analyze the effects of the hydrogen atoms on the cage forms of the isomers of the boron clusters for the neutral and non-neutral cases. In addition to the stabilities, their binding energies and HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) energy gaps were determined to fill the lack in the literature, and provide qualitative and quantitative information for these particular small borane complexes. This enables us to follow up the effect of the charge states on the distortion and major structural changes of the cage configurations of the boranes as the hydrogen number increases in the system.

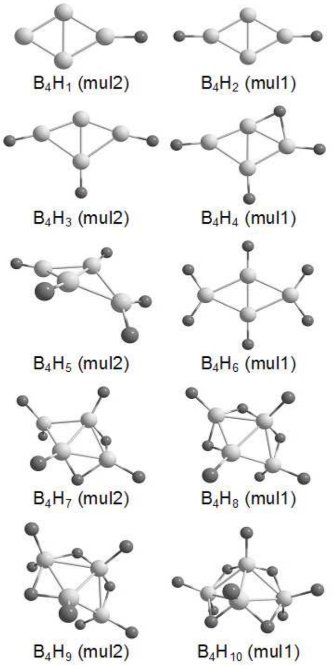
In this article you will find some of our recent results obtained about the hydrogen hosting on nano scale boron clusters. This work is organized as follows. In section 2 the computational method is shortly described. This is followed by a presentation of our results in Section 3. Finally, our conclusions are given in Section 4.

## 2. Methods

The same methodologies described in our previous works ([6–8, 15]) have been followed up. Therefore, here, some important points are briefly explained. The Gaussian-03 [16] program is used for the computations. For the hydrogen addition to a bare or hydrogenated boron clusters, previously optimized boron clusters have been used. After that, the entire system is fully optimized. In the next step, the second hydrogen atom is added and the system is again fully optimized, and so on. Sometimes, an initial configuration of a smaller one was prepared by removing one hydrogen atom from a larger complex, and then, it is optimized. Our principle strategy is whether we can preserve the cage form of the boron part of the cluster or not as the number of hydrogen atoms increases. For the optimized geometries, by using the computed total energy values, the total binding energies of the clusters and the average binding energies per atom are calculated with the zero-point-energy (ZPE) corrections. The second finite difference of the optimized clusters is calculated as a function of the number of hydrogen atoms for a given number of boron atoms. In order to investigate the structural properties of the clusters, the mean values of the distances of B and H atoms to the center of mass (c.m.) of the $B_m$ part of the optimized complexes are also calculated.

## 3. Results

The most stable structures (lower-lying electronic states) of the obtained molecular geometries in [6] with DFT-B3LYP/6-311++G(d,p) level calculations are presented in Fig. 1 for the $B_4H_n$ ($n$ = 1–10) series. Their multiplicities are given in the parentheses.



$B_4H_1$ (mul2)
$B_4H_2$ (mul1)
$B_4H_3$ (mul2)
$B_4H_4$ (mul1)
$B_4H_5$ (mul2)
$B_4H_6$ (mul1)
$B_4H_7$ (mul2)
$B_4H_8$ (mul1)
$B_4H_9$ (mul2)
$B_4H_{10}$ (mul1)

**Fig. 1.** Determined stable structures of $B_4H_n$ (for $n$ = 1–10) clusters [6].

In [6] the lower-lying electronic states (singlet, doublet, triplet, quartet, quintet and hexed states) of a number of differently sized and shaped isomers of these binary hydrides series have been analyzed in detail. The most stable configurations dominantly are from the singlet and the doublet states [6].

As shown in Fig. 1 the most stable structures of the $B_4H_1$, $B_4H_2$, $B_4H_3$, $B_4H_4$ and $B_4H_6$ boranes have planar configurations. With the increasing number of hydrogen atoms the complexes and their core boron atoms lose their planer configurations. Mainly, the most stable structures grow from previous smaller complexes. The $B_4H_{10}$ cluster, for instance, is produced from the most stable isomer of the $B_4H_9$.

The Point Groups (PG), electronic states (ES), average B-H bond lengths ($<r_{B-H}>$, calculated by considering the distances lower than 1.5 Å), minimum ($f_{min}$) and maximum ($f_{max}$) values of vibrational frequencies of the determined structures of the $B_4H_n$ ($n$ = 1–10) boron hydrides are tabulated in Table 1. The smallest value of the mean distances between the hydrogen and its neighboring boron atoms is observed in $B_4H_3$ as 1.17 Å. The largest one is 1.27 Å in $B_4H_{10}$.

**Table 1.** Point Groups (PG), electronic states (ES), average B-H bond lengths ($<r_{B-H}>$, Å), minimum ($f_{min}$) and maximum ($f_{max}$) values in $cm^{-1}$ of vibrational frequencies of the determined structures of the $B_4H_n$ ($n$ = 1–10) [6]

| $n$ | PG | ES | $<r_{B-H}>$ | $f_{min}$ | $f_{max}$ |
|---|---|---|---|---|---|
| 1 | $C_{2v}$ | $^2$A' | 1.18 | 235 | 2733 |
| 2 | $D_{2h}$ | $^1$A' | 1.18 | 161 | 2747 |
| 3 | $C_{2v}$ | $^2$A | 1.17 | 186 | 2796 |
| 4 | $C_s$ | $^1$A | 1.23 | 252 | 2784 |
| 5 | $C_s$ | $^2$A | 1.23 | 107 | 2782 |
| 6 | $C_s$ | $^1$A | 1.22 | 50 | 2803 |
| 7 | $C_s$ | $^2$A | 1.25 | 187 | 2734 |
| 8 | $C_s$ | $^1$A | 1.21 | 345 | 2729 |
| 9 | $C_s$ | $^2$A | 1.26 | 206 | 2696 |
| 10 | $C_{2v}$ | $^1$A | 1.27 | 216 | 2687 |

For these boron hydrides, discussed here, Table 2 shows the total energies ($E_{tot}$) including ZPE, HOMO-LUMO energy gap ($gap_{HL}$), binding energies per atom and binding energies per hydrogen of the $B_4H_n$ ($n$ = 1–10) boron hydrides [6]. The binding energies have been obtained over the single point energy values of the arrangements of the particles in the complexes. Energetically, the complexes with the 2, 4, 6, 8 and 10 hydrogen atoms are relatively more stable than their neighbors. The $B_4H_{10}$ is observed as the most stable one in this boron-hydride series (for details see the related figures in [6]). There is not a considerable fluctuation in the mean binding energies per atom. It is observed that the HOMO-LUMO energy gap also increases with the increasing number of hydrogen atoms. Moreover, in [6], the $B_4H_{11}$ was also studied. Fragmentation of the $B_4H_{11}$ and its anionic configuration $[B_4H_{11}]^{-1}$ were analyzed. For the neutral complex $B_4H_{11} \rightarrow B_3H_8 + BH_3$ channel has been obtained as one of the fragmentation paths. The higher stability of the anionic $[B_4H_{11}]^{-1}$ form was pointed out.

**Table 2.** Total energies ($E_{tot}$) including ZPE, HOMO-LUMO energy gap ($gap_{HL}$), binding energies per atom and binding energies per hydrogen of the $B_4H_n$ ($n$ = 1–10) [6]

| $n$ | [eV] | | $E_b$ [eV / atom] | |
|---|---|---|---|---|
| | $E_{tot}$ | $gap_{HL}$ | Particle | Hydrogen |
| 1 | –2715.210 | 3.198 | –3.424 | –4.153 |
| 2 | –2733.221 | 3.574 | –3.578 | –5.772 |
| 3 | –2750.336 | 4.648 | –3.559 | –4.570 |
| 4 | –2767.534 | 4.560 | –3.556 | –4.803 |
| 5 | –2783.009 | 4.065 | –3.361 | –4.277 |
| 6 | –2800.264 | 5.184 | –3.384 | –4.179 |
| 7 | –2815.958 | 4.450 | –3.261 | –3.541 |
| 8 | –2833.198 | 5.901 | –3.287 | –3.839 |
| 9 | –2848.380 | 6.601 | –3.150 | –3.474 |
| 10 | –2865.606 | 8.852 | –3.180 | –3.728 |

Later, we have investigated the lower-lying singlet and doublet electronic states of the neutral [7], the anionic $[B_mH_n]^{-1}$ and cationic $[B_mH_n]^{+1}$ [8] complexes for the $m$ = 5–10 and $n$ = 1–m, respectively. Figures 2–4 show the selected results of structurally optimized geometries of the cage boron hydrides, $B_mH_1$ and $B_mH_m$. For the initial configurations of the particular complexes the cage isomers of the bare clusters were selected from $B_5$ to $B_{10}$ [7]. In these cases [7, 8], we haven't searched for the lowest energy forms for all the sizes. Preserving the cage form of the boron part of the cluster was the principle strategy. However, if the cage form cannot be preserved, then, we have optimized the configuration that may not be the lowest energy form. It means that the potential energy surface is not fully searched to obtain the lowest energy forms, which is not a critical point for our goal. There may be various isomers lower in energy than these obtained non-cage structures.

The optimized neutral molecular structures in [7] are illustrated in Fig. 2. The $B_5$ keeps its trigonal bipyramid structure in the $B_5H_1$geometry. However, the cage form of five-atom boron cluster is not stable in the $B_5H_n$ complexes with $n$ = 2–4 [7].

In the $B_5H_5$ cluster there is a cage form of square pyramidal symmetry due to the pairing principle of the incompletely filled degenerate orbitals [7]. That is, a stable structure results when all of the cage bonding orbitals are filled in which a single boron atom is located on the 4-fold axis leading to five cage-bonding orbitals [4, 7].

Addition of the hydrogen atoms is more effective on the structures of $B_5$, $B_7$ and $B_9$. One hydrogen atom is on one of the equatorial sites of a pentagonal bipyramid form of the $B_7$ cluster. The cage isomer of $B_9$ cluster with one hydrogen atom looses its initial symmetric geometry. However, "down sizing" transformation of the cage form from a pentagonal bipyramid to a capped octahedron occurs first time at the $B_7H_7$ size. This transformation was also observed for the $B_9$ series, *i.e.*, the cages from bipyramidal form of a seven-atom ring to a pentagonal bipyramidal cage, and finally a capped square bipyramidal cage form was obtained for the $B_9H_n$ through the increase of the number of hydrogen atoms. In the $B_9H_9$ structure a hydrogen atom is in the bridging position.

The cage $B_6$, $B_8$ and $B_{10}$ structures preserve their cage-like geometries in their series. Almost all complexes of $B_6$ have closed cage forms except in $B_6H_5$ [7]. This shows that the square bipyramid form of $B_6$ is a highly stable cage structure. In the $B_6H_6$, all the boron atoms have 5 coordinations [7]. Mostly, the double capped square bipyramid forms have been observed in $B_8H_n$ series complexes. From $n = 1$ to 6 the cages have nearly double capped square bipyramid forms, but for the $n = 7$ and 8 closo cage structures have been determined [7]. The $B_{10}$ keeps its cage-like structures in all the steps and the obtained $B_{10}H_{10}$ structure has $C_{3v}$ symmetry.

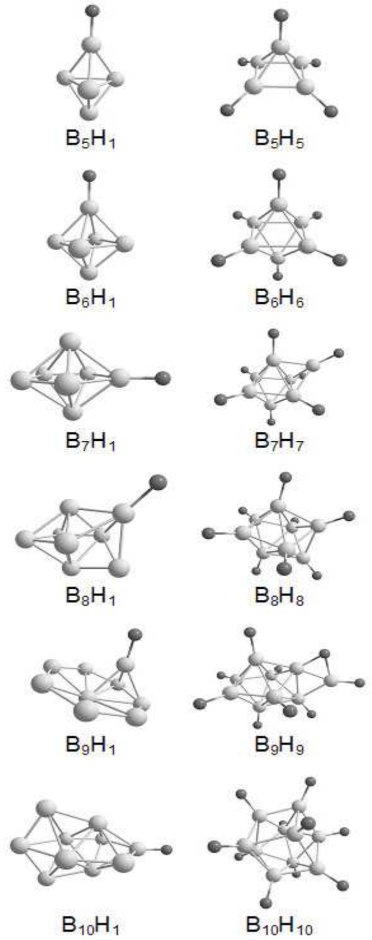


**Fig. 2.** Determined stable structures of neutral cage $B_mH_1$ and $B_mH_m$ (for $m = 5$–10) clusters [7].

Within a similar manner anionic form of $[B_mH_n]^{-1}$ ($m = 5$ to 10 and $n = 1$ to $m$) hydrides have been studied [8]. The selected geometries of their molecular structures are depicted in Fig. 3. Structural morphologies of $B_5$, $B_6$, $B_9$ and $B_{10}$ with one hydrogen atom are similar to their neutral geometries (see Fig. 2). On the other hand, one electron addition leads to structural changes in $B_7H_1$ and $B_8H_1$, different from their neutral configurations. The $[B_7H_1]^{-1}$ is in the form of connected a trigonal and a tetragonal pyramids. The $[B_8H_1]^{-1}$ has a caped pentagonal bipyramidal form.

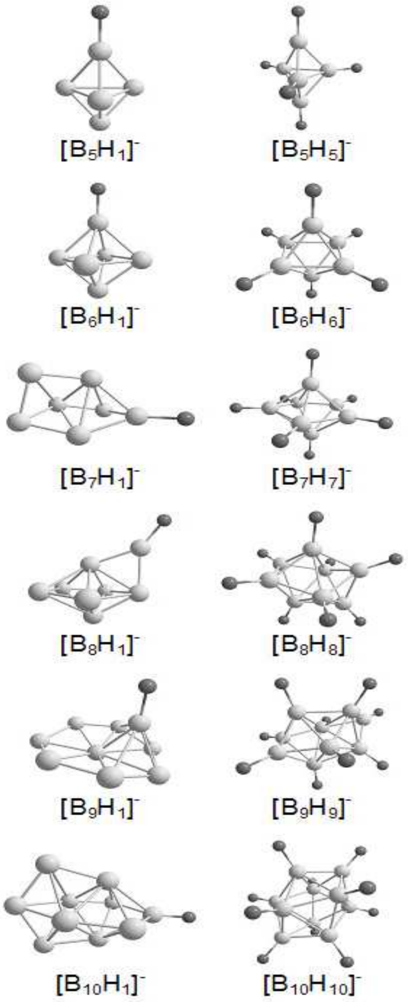


**Fig. 3.** Determined stable structures of anionic cage $B_mH_1$ and $B_mH_m$ (for $m = 5$–10) clusters [8].]

For the anionic complexes, with the equal number of hydrogen and boron atoms, it was possible to obtain cage forms of the boron atoms for all the clusters. The $B_5$ prefers a cage form of trigonal bipyramidal structure in the $[B_5H_5]^{-1}$, in a good agreement with that reported in [4] for B3LYP/6-311+G(d)//B3LYP/6-31G(d) level of calculations. However, it is a square pyramid for the neutral case [7]. The obtained form of the $[B_7H_7]^{-1}$ complex is also in good agreement with the results of the same calculations [4]. The $[B_8H_8]^{-1}$ is also a closed cage structure. The $[B_9H_9]^{-1}$ like in the neutral case follows a growing pattern from the $[B_8H_8]^{-1}$ structure. The obtained $[B_{10}H_{10}]^{-1}$ structure with $C_{2v}$ symmetry has the same cage configuration as in [4].

Removing an electron from these neutral clusters is also effective on their structures. As given in Fig. 4 the cationic case of $[B_5H_1]^{+1}$ complex is in planar configuration.

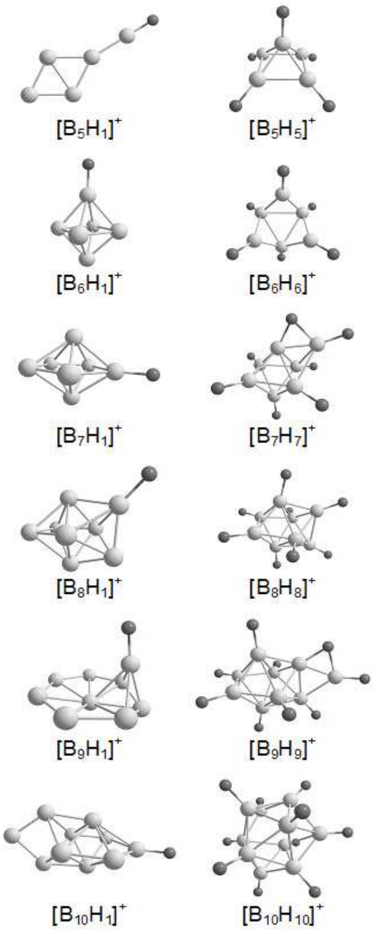

$[B_5H_1]^+$ $[B_5H_5]^+$
$[B_6H_1]^+$ $[B_6H_6]^+$
$[B_7H_1]^+$ $[B_7H_7]^+$
$[B_8H_1]^+$ $[B_8H_8]^+$
$[B_9H_1]^+$ $[B_9H_9]^+$
$[B_{10}H_1]^+$ $[B_{10}H_{10}]^+$

**Fig. 4.** Determined stable structures of cationic cage $B_mH_1$ and $B_mH_m$ (for $m$ = 5–10) clusters [8].

The $[B_5H_5]^{+1}$ has a cage form of square pyramidal symmetry as that of the neutral case [7]. The $[B_6H_1]^{+1}$ preserves its cage-like geometries. However, the $[B_6H_6]^{+1}$ have an open site on the $B_6$ structure. The square bipyramid cage structure of $B_6$ is not stable against to the detachment of an electron. The $B_7$ keeps a pentagonal bipyramid form in the $[B_7H_1]^{+1}$ clusters. The $[B_7H_7]^{+1}$ complex is in the same geometry as its neutral counter part [7]. The $B_8$ has cage forms in both $[B_8H_1]^{+1}$ and $[B_8H_8]^{+1}$ complexes, similar to their neutral cases [7]. There is also a three-member BBB bridges in the cationic $[B_9H_9]^{+1}$ cluster around the equatorial sites of the pentagonal bipyramidal or cage core of the complexes. The $B_{10}$ keeps its cage-like structures in all the complexes. On the studied cationic complexes hydrogen is relatively more effective on the structures of $B_5$, $B_7$ and $B_9$. In Tables 3–5 Point groups (PG), electronic states (ES), total energies ($E_{tot}$) including ZPE corrections and the HOMO-LUMO energy gaps for the alpha electrons ($gap_{HL}$) are collected for these selected geometries for the neutral, ionic and cationic cases, respectively.

**Table 3.** Point Groups (PG), electronic states (ES), total energies ($E_{tot}$) including ZPE and HOMO-LUMO energy gap ($gap_{HL}$) of the determined neutral structures of the $B_mH_1$ and $B_mH_m$ ($m$ = 5–10) boron hydrides [7]

| $m$ | $n$ | PG | ES | E [eV] | $gap_{HL}$ [eV] |
|---|---|---|---|---|---|
| 5 | 1 | $C_s$ | $^1A$ | –3388.941 | 3.078 |
|  | 5 | $C_2$ | $^1A$ | –3459.289 | 4.366 |
| 6 | 1 | $C_s$ | $^2A$ | –4065.220 | 2.147 |
|  | 6 | $C_{3v}$ | $^1A$ | –4152.048 | 3.146 |
| 7 | 1 | $C_s$ | $^1A$ | –4741.983 | 1.941 |
|  | 7 | $C_s$ | $^1A$ | –4846.042 | 5.423 |
| 8 | 1 | $C_s$ | $^2A$ | –5417.449 | 2.788 |
|  | 8 | $D_2$ | $^1A$ | –5538.608 | 3.912 |
| 9 | 1 | $C_s$ | $^1A$ | –6096.431 | 4.909 |
|  | 9 | $C_s$ | $^1A$ | –6230.912 | 4.226 |
| 10 | 1 | $C_{2v}$ | $^2A$ | –6769.199 | 2.923 |
|  | 10 | $C_{3v}$ | $^1A$ | –6924.369 | 4.770 |

In order to compare the energetic characteristics of the discussed cage structures, their average binding energies per particles are plotted as functions of the number of boron atoms (m) for the neutral and ionic complexes of $B_mH_1$ and $B_mH_m$ clusters in Fig. 5, respectively. These binding energies have been calculated from their total energies given in Tables 3–5.

**Table 4.** Same as in Table 3 for anionic boron hydrides [8]

| $m$ | $n$ | PG | ES | E [eV] | $gap_{HL}$ [eV] |
|---|---|---|---|---|---|
| 5 | 1 | $C_s$ | $^2A$ | –3391.191 | 2.393 |
|  | 5 | $C_{2v}$ | $^2A$ | –3461.790 | 4.328 |
| 6 | 1 | $C_s$ | $^1A$ | –4067.123 | 1.344 |
|  | 6 | $S_2$ | $^2A$ | –4155.601 | 5.150 |
| 7 | 1 | $C_s$ | $^2A$ | –4744.870 | 2.876 |
|  | 7 | $C_s$ | $^2A$ | –4848.422 | 5.357 |
| 8 | 1 | $C_s$ | $^1A$ | –5420.059 | 2.432 |
|  | 8 | $D_{2d}$ | $^2A$ | –5541.811 | 4.607 |
| 9 | 1 | $C_s$ | $^2A$ | –6097.946 | 2.699 |
|  | 9 | $C_s$ | $^2A$ | –6233.450 | 3.903 |
| 10 | 1 | $C_{2v}$ | $^1A$ | –6771.979 | 2.797 |
|  | 10 | $C_{2v}$ | $^2A$ | –6928.112 | 5.775 |

**Table 5.** Same as in Table 3 for cationic boron hydrides [8]

| $m$ | $n$ | PG | ES | E [eV] | gap$_{\mathrm{HL}}$ [eV] |
|---|---|---|---|---|---|
| 5 | 1 | $C_s$ | $^2A$ | –3382.167 | 2.828 |
| | 5 | $C_{4v}$ | $^2A$ | –3450.162 | 3.811 |
| 6 | 1 | $C_s$ | $^1A$ | –4057.243 | 3.794 |
| | 6 | $C_{3v}$ | $^2A$ | –4142.430 | 3.176 |
| 7 | 1 | $C_{2v}$ | $^2A$ | –4734.257 | 2.565 |
| | 7 | $C_s$ | $^2A$ | –4836.652 | 4.699 |
| 8 | 1 | $C_s$ | $^1A$ | –5409.785 | 2.189 |
| | 8 | $C_s$ | $^2A$ | –5528.766 | 3.319 |
| 9 | 1 | $C_s$ | $^2A$ | –6087.369 | 4.331 |
| | 9 | $C_s$ | $^2A$ | –6222.180 | 4.642 |
| 10 | 1 | $C_{2v}$ | $^1A$ | –6761.579 | 3.355 |
| | 10 | $C_s$ | $^2A$ | –6914.589 | 3.770 |

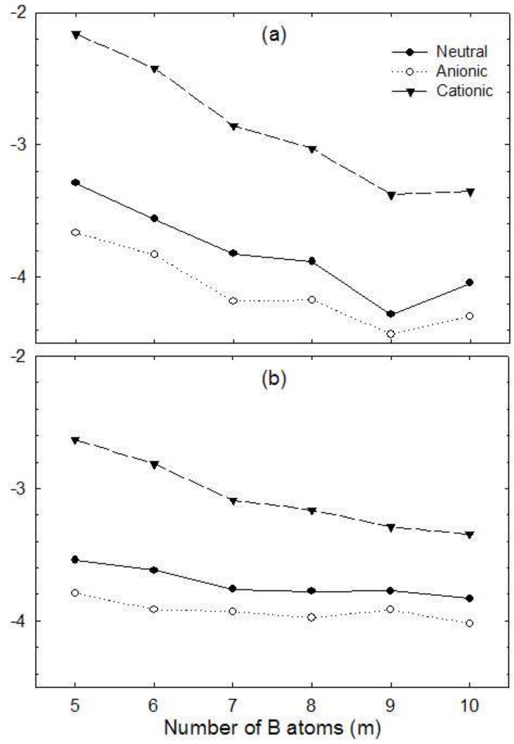


**Fig. 5.** Average binding energies per atom for determined stable structures of neutral [7] and ionic [8] cage clusters; a) for $B_mH_1$ and b) $B_mH_m$.

As shown in Fig. 5a, the binding energies in magnitude have increasing trends for these particular boron hydrides containing one hydrogen atom. This is an expected trend for the binding energy analysis because of the increasing sizes of the clusters.

Electron rich boron hydrides have larger binding energies compared to the neutral and cationic complexes. Namely, increasing the number of electrons leads to more energetic complexes. The energy gap between the anionic and neutral clusters is smaller than the gap between the neutral and cationic clusters. There are minima for $B_9H_1$ complex, especially for the anionic and neutral cases. This may be the result of the big structural changes of this particular size.

Similarly the lines of the binding energies for the $B_mH_m$ complexes (Fig. 5b) clearly show the same trends. However, in this case the minima for the cluster with 9-boron atoms are reduced because the $B_9$ can preserve its cage form as the other sizes. (The detailed analysis has been reported in [7, 8]). The binding energy differences between different ionic and neutral cases are larger for the smaller clusters.

As already indicated in our previous works, the structural behaviors of these particular boron hydride series at nano scale for the neutral [7], anionic and cationic [8] cases showed that, in general, the mean separations of the B atoms from their center of mass have similar trends.

Moreover, the increase in the number of hydrogen atoms results in gradual increase in the size of the clusters. On the other hand, the mean distances of the H atoms from the center of mass of the boron atoms in the complexes become smaller in the most of the series (for detail see [7, 8]).

## 4. Conclusions

In this paper, recent studies of our group on hydrogen hosting of nano scale boron clusters have been briefly reviewed. The geometries, energetics and structural properties of the hydrogen bonded neutral $B_4H_n$ ($n$ = 1–11) clusters [6] and the neutral [7], anionic and cationic [8] complexes of the hydrogen bonded $B_mH_n$, ($m$ = 5–10 and $n \leq m$) boranes have been computationally investigated as mentioned above. Their stabilities, electronic properties, and especially the effect of the hydrogenation were reported. The $B_6$, $B_8$ and $B_{10}$ clusters may be assumed as relatively more stable sizes while the initial cage structures of the $B_5$,$B_7$ and $B_9$ in their complexes are not stable against to the hydrogenations.

Finally, we would like to stress that there is still a lot of work to be done on hydrogen hosting of boron clusters. As a continuation of this work, highly symmetric cage configuration of boron clusters, *e.g.*, the $B_{12}$ should be taken into account in the future studies. Furthermore, it is interesting to focus on the hydrogen hosting of any primitive nano tube of boron clusters or metallic boron complexes as well.

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