

**Electronic Structure Analysis of Hydrogenated Nano Scale Boron Clusters:  
DFT Study of Anionic and Cationic Complexes of  $B_mH_n$  ( $m=5-10$  and  $n \leq m$ )**Mustafa Bykata<sup>1,a</sup>, Cem zdođan<sup>2,b</sup> and Ziya B. Gvenc<sup>3,\*</sup><sup>1</sup>Department of Physics, Bozok University, 66200 Yozgat, Turkey<sup>2</sup>Department of Computer Engineering, ankaya University, Balgat, 06530 Ankara, Turkey<sup>3</sup>Department of Electronic and Communication Engineering, ankaya University, Balgat, 06530 Ankara, Turkey\* guvenc@cankaya.edu.tr, <sup>a</sup> boyukata@erciyes.edu.tr, <sup>b</sup> ozdogan@cankaya.edu.tr**ABSTRACT**

Energetic and structural stability of hydrogen bonded boron micro clusters have been studied via DFT-B3LYP/6-311++G(d,p). The possible stable geometries of anionic and cationic complexes of  $B_mH_n$  ( $m=5-10$  and  $n \leq m$ ) boron hydrides, their binding energies, and HOMO-LUMO energy gaps have been determined. Effects of the number of hydrogen atoms on the cage structures and distortion of the cage configurations of the boranes are assessed. Relatively more structural changes are observed for the odd  $m$  values, e.g.,  $B_5H_n$ ,  $B_7H_n$ , and  $B_9H_n$  series of complexes. On the other hand, the complexes with the even  $m$  values are more stable compared to the others.

**Keywords:** Boron, hydrogen, boron hydrides, DFT, ab initio, cluster.

**1. INTRODUCTION**

Hydrogen storage is one of the most important issues for the utilization of hydrogen as an alternative clean energy source. The boron and its compounds may play a key role for hydrogen storage. Therefore, the ground-state structures of the boron hydride series have been actively studied [1-11]. The reason for this is that the boron can form diverse nano scale structures with electron-donor atoms, and can link three or more atoms due to different level of hybridization of the valence  $s^2p^1$  electrons. This behavior of boron yields short distance covalent and strong directed chemical bonds with itself and with the other electron-donor atoms.

Computational methods are efficient alternative means and also they are complementary parts for the experimental studies to obtain the desired physical and chemical quantities. One of them is the density functional theory (DFT) method, which has a potential for describing the intermolecular interactions of various systems with high accuracy [11-13], and valuable results have been reported in the literature. Related examples are; boron hydrides,  $B_nH_n$  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 our previous studies, we investigated the hydrogen bonded neutral  $B_4H_n$  ( $n=1-11$ ) and anionic  $[B_4H_{11}]^{-1}$  clusters by using B3LYP/6-311++G(d,p) level of computations [6] and reported the neutral complexes of the hydrogen bonded cage borane ( $B_mH_n$ ,  $m=5-10$  and  $n \leq m$ ) [7]. In Ref. [6], it was observed that the most stable configurations correspond to the singlet and doublet states. Therefore, in Ref. [7], and the present work, the analysis has been carried out for the lower-lying singlet and doublet electronic states. In this work which is the continuation of the previous works [6,7], we have investigated anionic  $[B_mH_n]^{-1}$  and cationic  $[B_mH_n]^{+1}$  forms of the hydrogen bonded boron complexes for  $m=5-10$  and  $n \leq m$  by DFT/B3LYP calculations with the 6-311++G(d,p) basis set.

Effects of the hydrogen atoms on the cage forms of the isomers of the boron clusters have been analyzed (this time for the non-neutral cases). In addition to the stabilities, their binding energies and HOMO-LUMO energy gaps are determined. This systematic study fills the lack in the literature and provides qualitative and quantitative information for these particular borane micro complexes. This enables us to follow up the effect of (-1) and (+1) charge states on the distortion and major structural changes of the cage configurations of the boranes as the hydrogen number increases. Following this introduction, the methodology employed in this survey is presented in Section 2. The results and discussions are carried out in Section 3 while conclusions are briefly presented in Section 4.

## 2. METHODOLOGY

For these calculations, the same procedure is followed as in Refs. [6,7,13] and Gaussian-03 [14] is used. In this work; the initial geometries for optimization are mainly taken from Ref. [7]. For the sake of the completeness of this paper and the readers the procedure in Ref. [7] is briefly summarized in the following. We have started with an optimized bare cage form of a boron cluster, e.g.,  $m=5$  case, and then one hydrogen atom is added. 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. 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. In this work, the anionic  $[B_m H_n]^{-1}$  and cationic  $[B_m H_n]^{+1}$  complexes are formed and optimized, and the physical quantities mentioned above are calculated. By using the energetics, the total binding energies of the anionic and cationic clusters are calculated from,

$$E_b[B_m H_n]^q = -E[B_m H_n]^q + mE[B] + nE[H] \quad (1)$$

in which the  $-E[B]$  (671.105 eV) and  $-E[H]$  (13.667 eV) are the energies of a single boron and single hydrogen atoms with the zero-point-energy (ZPE) corrections, respectively. The  $q$  is  $-1$  or  $+1$  indicating the charge state. The average binding energies per atom can be obtained from  $E_b[B_m H_n]^q / (m+n)$ . The  $m$  and  $n$  are the numbers of the boron and hydrogen atoms, respectively. The second finite difference of the optimized clusters is calculated;

$$\Delta_2 E = E[B_m H_{n+1}]^q + E[B_m H_{n-1}]^q - 2E[B_m H_n]^q \quad (2)$$

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 calculated from

$$\langle r_B \rangle = \frac{1}{m} \sum_{i=1}^m r_B^i, \quad \langle r_H \rangle = \frac{1}{n} \sum_{j=1}^n r_H^j, \quad r_B^i = |R_B^i - R_{c.m.}|, \quad r_H^j = |R_H^j - R_{c.m.}|, \quad R_{c.m.} = \frac{1}{m} \sum_{i=1}^m R_B^i \quad (3)$$

in which the  $R_B^i$  and  $R_H^j$  being the position of the  $i^{\text{th}}$  and the  $j^{\text{th}}$  B and H atoms, respectively, and the  $R_{c.m.}$  being the position vector of the c.m. of the  $B_m$ .

## 3. RESULTS AND DISCUSSIONS

In the present study, the lower-lying singlet and doublet electronic states of the anionic  $[B_m H_n]^{-1}$  and cationic  $[B_m H_n]^{+1}$  complexes are investigated. Those optimized geometries given in Ref. [7] are used as the initial configurations of the corresponding complexes. Afterwards the charge states are modified and then the entire systems are fully optimized.

### 3.1 Anionic $[B_mH_n]^{-1}$

The optimized anionic molecular structures of  $[B_mH_n]^{-1}$  ( $m=5$  to  $10$  and  $n=1$  to  $m$ ) hydrides are illustrated in Fig. 1, respectively. Since, 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; we haven't searched for the lowest energy forms for all the sizes. If the boron part of the cluster cannot take a cage form for a given  $m$  and  $n$  values, then we have optimized the configuration that may not be the lowest energy form for those  $m$  and  $n$  values. We did not fully search the potential energy surface to obtain the lowest energy forms. This is not a critical point for our goal. Point groups (PG), electronic states (ES), the average bond lengths of the B-B ( $\langle r_{B-B} \rangle$ ) and B-H ( $\langle r_{B-H} \rangle$ ) distances, total energies (E) including ZPE, HOMO-LUMO energy gaps for alpha electrons ( $gap_{HL}$ ), minimum ( $f_{min}$ ), and maximum ( $f_{max}$ ) values of the vibrational frequencies of all the fully optimized structures for the anionic  $[B_mH_n]^{-1}$  boron hydrides are given in Table 1, respectively.

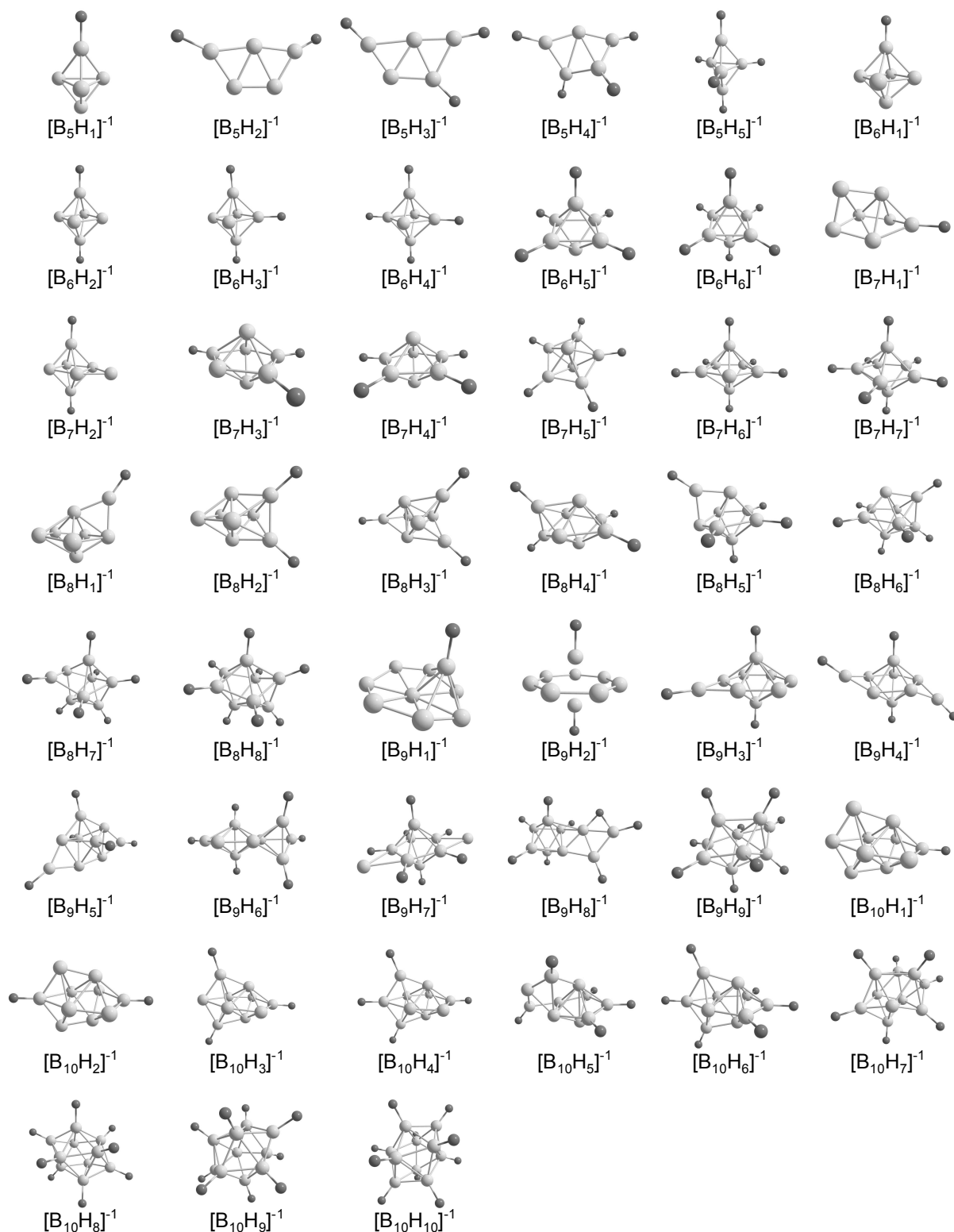
As shown in Fig. 1 the cage structure of the  $B_5$  in the  $[B_5H_1]^{-1}$  converts its form to a planar configuration in the  $[B_5H_2]^{-1}$  and the  $[B_5H_3]^{-1}$  geometries. These structures have the same forms as their corresponding neutral cases [7]. The cage form (trigonal bipyramid) of five-atom bare boron cluster is not stable for the  $[B_5H_2]^{-1}$ ,  $[B_5H_3]^{-1}$  and  $[B_5H_4]^{-1}$  complexes. The  $B_5$  cluster with four hydrogen atoms,  $[B_5H_4]^{-1}$ , has a quasi planar geometry. It is slightly different from its neutral counter part. It has only one imaginary frequency. On the other hand, the  $B_5$  again prefers a cage form of trigonal bipyramidal structure in the  $[B_5H_5]^{-1}$ . However, it was a square pyramid for the neutral case [7]. The structure of the  $[B_5H_5]^{-1}$  is in good agreement with that reported in Ref. [4]. They have the same symmetry,  $C_{2v}$ . It is observed that the square bipyramid form of  $B_6$  is a highly stable cage because the cage  $B_6$  structures preserve its cage-like forms for all the  $n$  values. McKee et al. [4] has also obtained an anionic  $[B_6H_6]^{-1}$  boron hydride with square bipyramid form with  $D_{2h}$  symmetry. In this work we have obtained a cage form of  $[B_6H_6]^{-1}$  resembling a square bipyramid with  $S_2$  symmetry. In the  $[B_6H_n]^{-1}$ , all the boron atoms have 5-coordination including one hydrogen atom. Moreover, in the  $[B_6H_n]^{-1}$  series only the  $[B_6H_1]^{-1}$  has two imaginary frequencies.

The pentagonal bipyramid geometry of the bare  $B_7$  cluster is also significantly affected by the addition of the hydrogen atoms. The  $B_7$  with one hydrogen atom has a form of connected a trigonal and a tetragonal pyramids. With two hydrogen atoms, binding to the polar boron atoms, it cannot keep its original pentagonal cage form either. It is converted to a capped square bipyramid form. The capping atom is in the equatorial plane. The neutral forms of these anionic  $[B_7H_1]^{-1}$  and  $[B_7H_2]^{-1}$  clusters have different structures as reported in Ref. [7]. However, the  $B_7$ , in the  $[B_7H_3]^{-1}$ ,  $[B_7H_4]^{-1}$ ,  $[B_7H_5]^{-1}$ ,  $[B_7H_6]^{-1}$  and  $[B_7H_7]^{-1}$  forms, keeps its initial cage form. This obtained form of the  $[B_7H_7]^{-1}$  complex is in good agreement with the results of B3LYP/6-311+G(d)//B3LYP/6-31G(d) levels [4]. The  $[B_8H_n]^{-1}$  series have cage forms of  $B_8$  and they are approximately the same as their neutral counter parts [7] except the  $n=1$  case. The  $[B_8H_1]^{-1}$  has a capped pentagonal bipyramidal form. From  $n=2$  to  $8$  the cages have nearly double capped square bipyramidal forms. One may also say that the  $[B_8H_8]^{-1}$  is more like a closed cage structure. The same isomer in Ref. [4] was obtained for the  $[B_8H_8]^{-1}$  with  $D_{2d}$  symmetry. Each one of the  $[B_8H_1]^{-1}$ ,  $[B_8H_3]^{-1}$  and  $[B_8H_6]^{-1}$  clusters have one imaginary frequency.

In the  $[B_9H_n]^{-1}$  series different forms of the  $B_9$  are obtained for almost all  $n$  values. The cage isomer of  $B_9$  cluster cannot preserve its initial symmetric geometry as seen in Fig. 1 Increasing the number of hydrogen atoms leads to a three-member BBB bridge in the  $[B_9H_3]^{-1}$ . The particles keep two of the bridges around the equatorial site of the pentagonal bipyramidal core of the  $[B_9H_4]^{-1}$ ,  $[B_9H_5]^{-1}$  and  $[B_9H_7]^{-1}$  complexes. The neutral case [7] of the  $[B_9H_8]^{-1}$  complex has the same structures as that of the corresponding anionic one. The  $[B_9H_9]^{-1}$  follows a growing pattern from the  $[B_8H_8]^{-1}$  structure as in the neutral case. The  $[B_9H_5]^{-1}$  has two imaginary frequencies and the  $[B_9H_7]^{-1}$  and  $[B_9H_8]^{-1}$  have one imaginary frequency. The  $B_{10}$  keeps its cage-like structure in almost all  $n$  values for the  $[B_{10}H_n]^{-1}$  complexes. From  $[B_{10}H_1]^{-1}$  to  $[B_{10}H_4]^{-1}$  complex the boron atoms are in closed cage arrangements. The  $[B_{10}H_5]^{-1}$  and  $[B_{10}H_7]^{-1}$  complexes have open sites on

their cage geometries. The obtained  $[B_{10}H_{10}]^{-1}$  structure with  $C_{2v}$  symmetry has the same cage configuration as in Ref. [4]. In this series only the  $[B_{10}H_3]^{-1}$  has an imaginary frequency.

As a result, the anionic cases of the  $B_6$ ,  $B_8$  and  $B_{10}$  series, the clusters can keep their original cage-like forms of the bare boron clusters. The cage structures of the  $[B_mH_m]^{-1}$  are in good agreement with the results of Ref. [4]. The hydrogen atoms are more effective on the  $B_5$ ,  $B_7$  and  $B_9$  structures



**Figure 1: Anionic structures of the  $[B_mH_n]^{-1}$  complexes ( $m=5-10$ ,  $n=1-m$ ).**

**Table 1: Point group (PG), electronic states (ES), the average bond lengths of the B-B ( $\langle r_{B-B} \rangle$ ) and B-H ( $\langle r_{B-H} \rangle$ ) distances, total energies (E), HOMO-LUMO energy gap ( $\text{gap}_{HL}$ ), minimum ( $f_{\min}$ ) and maximum ( $f_{\max}$ ) values of frequencies of the determined anionic  $[\text{B}_m\text{H}_n]^-$  ( $m=5-10$ ,  $n=1-m$ ) boron hydrides.**

m	n	PG	ES	$\langle r_{B-B} \rangle$ (Å)	$\langle r_{B-H} \rangle$ (Å)	E (eV)	$\text{gap}_{HL}$ (eV)	$f_{\min}^*$ ( $\text{cm}^{-1}$ )	$f_{\max}$ ( $\text{cm}^{-1}$ )
5	1	$C_s$	$^2A$	1.706	1.188	-3391.191	2.393	23	2626
	2	$C_2$	$^1A$	1.636	1.191	-3411.613	2.560	188	2609
	3	$C_s$	$^2A$	1.648	1.184	-3428.318	2.763	271	2697
	4	$C_2$	$^1A$	1.708	1.196	-3445.175	4.408	245 <sup>(1)</sup>	2627
	5	$C_{2v}$	$^2A$	1.732	1.194	-3461.790	4.328	80	2632
6	1	$C_s$	$^1A$	1.716	1.186	-4067.123	1.344	251 <sup>(2)</sup>	2632
	2	$D_{4h}$	$^2A$	1.704	1.187	-4085.877	2.492	281	2639
	3	$C_{2v}$	$^1A$	1.698	1.189	-4103.451	2.699	345	2625
	4	$D_{2h}$	$^2A$	1.719	1.187	-4121.341	4.240	318	2638
	5	$C_s$	$^1A$	1.725	1.188	-4138.815	3.615	288	2646
	6	$S_2$	$^2A$	1.754	1.193	-4155.601	5.150	362	2617
7	1	$C_s$	$^2A$	1.724	1.190	-4744.870	2.876	214	2603
	2	$C_s$	$^1A$	1.704	1.183	-4762.222	1.933	217	2670
	3	$C_s$	$^2A$	1.702	1.194	-4779.222	2.052	40	2579
	4	$C_{2v}$	$^1A$	1.719	1.190	-4797.249	2.410	290	2617
	5	$C_s$	$^2A$	1.744	1.189	-4814.793	4.863	428	2618
	6	$C_s$	$^1A$	1.776	1.192	-4832.167	4.269	238	2626
	7	$C_s$	$^2A$	1.779	1.194	-4848.422	5.357	216	2618
8	1	$C_s$	$^1A$	1.719	1.187	-5420.059	2.432	239 <sup>(1)</sup>	2649
	2	$C_s$	$^2A$	1.741	1.191	-5437.279	2.318	315	2595
	3	$C_s$	$^1A$	1.733	1.186	-5455.917	3.343	226 <sup>(1)</sup>	2688
	4	$C_2$	$^2A$	1.748	1.189	-5472.525	2.151	229	2617
	5	$C_s$	$^1A$	1.743	1.194	-5490.141	3.225	276	2615
	6	$C_2$	$^2A$	1.770	1.194	-5507.454	2.514	382 <sup>(1)</sup>	2596
	7	$C_s$	$^1A$	1.771	1.192	-5524.619	3.736	187	2709
	8	$D_{2d}$	$^2A$	1.784	1.193	-5541.811	4.607	383	2619
9	1	$C_s$	$^2A$	1.731	1.185	-6097.946	2.699	117	2649
	2	$C_s$	$^1A$	1.518	1.194	-6115.234	5.135	305	2555
	3	$C_s$	$^2A$	1.786	1.192	-6131.891	3.451	126	2643
	4	$C_2$	$^1A$	1.756	1.189	-6149.192	3.047	169	2638
	5	$C_s$	$^2A$	1.761	1.191	-6166.150	2.854	363 <sup>(2)</sup>	2619
	6	$C_s$	$^1A$	1.760	1.187	-6182.493	3.787	96	2683
	7	$C_s$	$^2A$	1.780	1.193	-6194.801	1.761	55 <sup>(1)</sup>	2658
	8	$C_s$	$^1A$	1.746	1.215	-6216.744	4.212	72 <sup>(1)</sup>	2728
	9	$C_s$	$^2A$	1.794	1.193	-6233.450	3.903	233	2710
10	1	$C_{2v}$	$^1A$	1.755	1.193	-6771.979	2.797	351	2570
	2	$D_{2d}$	$^2A$	1.768	1.190	-6788.631	2.299	156	2593
	3	$C_{2v}$	$^1A$	1.773	1.192	-6805.994	1.741	253 <sup>(1)</sup>	2591
	4	$C_2$	$^2A$	1.779	1.188	-6824.051	1.776	184	2624
	5	$C_s$	$^1A$	1.750	1.188	-6842.838	4.293	208	2656
	6	$C_2$	$^2A$	1.779	1.187	-6859.070	2.990	199	2640
	7	$C_s$	$^1A$	1.760	1.190	-6876.749	3.137	164	2628
	8	$C_2$	$^2A$	1.775	1.190	-6893.957	2.594	303	2629
	9	$C_s$	$^1A$	1.782	1.190	-6911.736	3.788	335	2653
	10	$C_{2v}$	$^2A$	1.796	1.190	-6928.112	5.775	122	2654

\* numbers in the parentheses show imaginary frequencies.

as observed in the case of the neutral ones [7]. As seen in Table 1, there is not a clear relation between the sizes of the clusters and their frequencies. The most of the complexes obey the  $C_s$  symmetry in their configurations.

### 3.2 Cationic $[B_mH_n]^{+1}$

The optimized cationic molecular structures of  $[B_mH_n]^{+1}$  ( $m=5$  to  $10$  and  $n=1$  to  $m$ ) hydrides are shown in Fig. 2. The determined PGs and ESs for these complexes and the  $\langle r_{B-B} \rangle$ ,  $\langle r_{B-H} \rangle$ , total energy,  $gap_{HL}$ ,  $f_{min}$  and  $f_{max}$  values of the optimized isomers for these boron hydrides are given in Table 2, respectively. As shown in Fig. 2 the cationic cases of  $[B_5H_n]^{+1}$  complexes from 1- to 4-hydrogen atoms are in planar configurations. The  $[B_5H_5]^{+1}$  has a cage form of square pyramidal symmetry as that of the neutral case [7]. This  $[B_5H_n]^{+1}$  ( $n=1-5$ ) is the only group without any imaginary frequency. The  $[B_6H_1]^{+1}$ ,  $[B_6H_2]^{+1}$  and  $[B_6H_4]^{+1}$  can preserve their cage-like geometries. However,  $[B_6H_5]^{+1}$  and  $[B_6H_6]^{+1}$  have an open site on the  $B_6$  structure. On the other hand, the  $[B_6H_3]^{+1}$  has a planar form. This may show that the square bipyramid cage structure is not stable against to the detachment of an electron. The  $[B_6H_2]^{+1}$  and  $[B_6H_4]^{+1}$  have two and  $[B_6H_5]^{+1}$  has one imaginary frequencies.

Removing an electron from  $B_7H_1$  cluster has no effect on the pentagonal bipyramid structure of the bare  $B_7$ . The  $B_7$  keeps its pentagonal bipyramid form in the  $[B_7H_1]^{+1}$ ,  $[B_7H_2]^{+1}$ ,  $[B_7H_3]^{+1}$ ,  $[B_7H_4]^{+1}$  and  $[B_7H_5]^{+1}$  clusters. The pentagonal bipyramid form of the  $B_7$  is destroyed in the  $[B_7H_6]^{+1}$ . The  $[B_7H_7]^{+1}$  complex is in the same geometry as its neutral counter part [7]. The  $[B_7H_4]^{+1}$  has one and  $[B_7H_5]^{+1}$  have three imaginary frequencies. In the  $[B_8H_n]^{+1}$  series the  $B_8$  has cage forms for the  $n=1-4$ , 6 and 8, similar to their neutral forms [7]. The  $[B_8H_5]^{+1}$  has a double capped square bipyramid structure, with an open site of the cage  $B_8$ . In the  $[B_8H_7]^{+1}$  the  $B_8$  has an open cage form. We observed one imaginary frequency in the  $[B_8H_2]^{+1}$  and two in the  $[B_8H_8]^{+1}$  clusters.

As in the same manner of the neutral and anionic  $B_9H_n$  structures, the cationic structures do not keep the symmetric geometry of the  $B_9$  cluster either. There are different forms of the  $B_9$  in almost all parts of the  $[B_9H_n]^{+1}$  series, the  $[B_9H_2]^{+1}$  and  $[B_9H_4]^{+1}$  have closer configurations to that of the bare  $B_9$ . In this case, as previously observed in Ref. [7], increasing the number of hydrogen atoms leads to a three-member BBB bridges in the cationic  $[B_9H_n]^{+1}$  clusters for the  $n=2, 3, 4, 5, 7, 8$  and  $9$ . Mainly, the bridges are around the equatorial sites of the pentagonal bipyramidal or cage core of the complexes. Moreover, the  $[B_9H_9]^{+1}$  grows from the  $[B_8H_8]^{+1}$  structure. The  $[B_9H_5]^{+1}$ ,  $[B_9H_6]^{+1}$  and  $[B_9H_7]^{+1}$  have one imaginary frequency. Although there are some distortions, for the  $[B_{10}H_n]^{+1}$  complexes, the  $B_{10}$  keeps its cage-like structures in all the steps. The  $[B_{10}H_2]^{+1}$  and  $[B_{10}H_6]^{+1}$  complexes are different than their neutral and anionic forms. In this series only the  $[B_{10}H_3]^{+1}$  and  $[B_{10}H_4]^{+1}$  have one imaginary frequency. The cage structures of the  $[B_mH_n]^{+1}$  (for  $m=n$  case) are correlated with the anionic geometries and those of the neutral complexes [7] despite the fact that there are some structural differences. It may be said that addition of the hydrogen atoms (in the studied cationic complexes) is relatively more effective on the structures of  $B_5$ ,  $B_7$  and  $B_9$ . There is also not a clear relation between the sizes of the clusters and their frequencies for the cationic cases as seen in Table 2. Here too mostly  $C_s$  symmetry has been observed.

### 3.3 Energetics

The average binding energies per atom are presented for all the anionic boron hydrides in Fig. 3a. Figures 3b and 3c show the second finite difference of the total energies and the HOMO-LUMO energy gaps of the optimized anionic complexes, respectively. There are a few considerable fluctuations in the energies for the  $[B_5H_n]^{-1}$  and  $[B_9H_n]^{-1}$  series, but in general, they are slightly decreasing in magnitude with the increasing number of hydrogen atoms. This degree of sharp increase in the energy value, from  $B_5H_1$  to  $B_5H_2$ , is being reduced with the increasing number of boron atoms as observed for the neutrals [7]. The decrease in the average binding energies with the increasing number of hydrogen atoms can be assumed to be a common trend for these particular anionic complexes. As seen in Fig. 3b the complexes of  $B_5$ ,  $B_6$ ,  $B_7$  and  $B_9$  with two hydrogen

atoms are relatively more stable. It is obviously seen that  $[\text{B}_7\text{H}_6]^{-1}$ ,  $[\text{B}_8\text{H}_3]^{-1}$ ,  $[\text{B}_9\text{H}_6]^{-1}$ ,  $[\text{B}_9\text{H}_8]^{-1}$ ,  $[\text{B}_{10}\text{H}_5]^{-1}$ ,  $[\text{B}_{10}\text{H}_7]^{-1}$  and  $[\text{B}_{10}\text{H}_9]^{-1}$  clusters are more stable than their neighbors in their series. These all have even number of electrons. It is not an easy task to reach a general conclusion for these particular anionic clusters. The  $[\text{B}_9\text{H}_7]^{-1}$  complex has an exceptional behavior staying outside of the trends. It may be due to the isomeric difference, i.e., there may be another isomer having

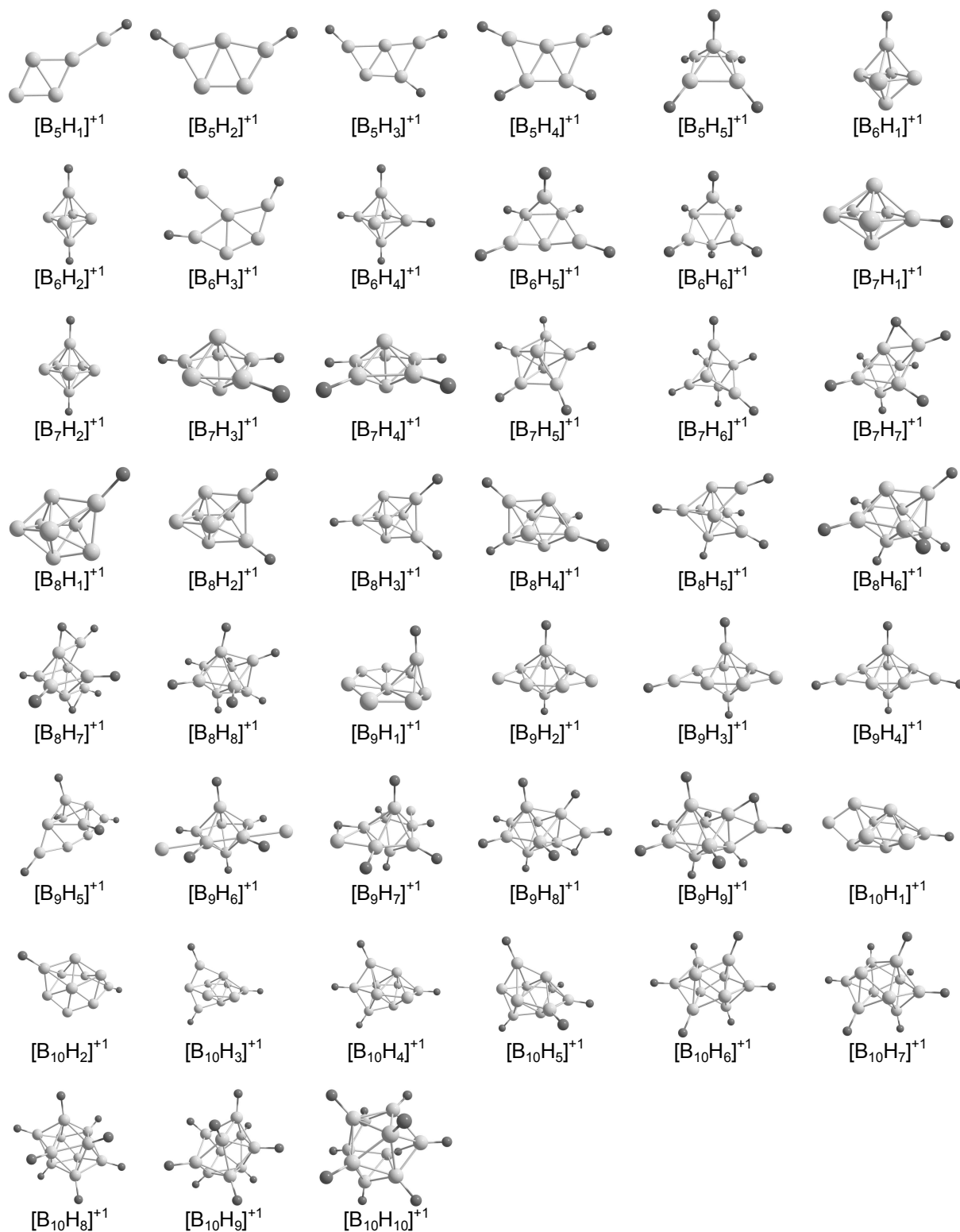


Figure 2: Cationic structures of the  $[\text{B}_m\text{H}_n]^+$  complexes ( $m=5-10$ ,  $n=1-m$ ).

**Table 2: Same as in Table 1 for cationic  $[\text{B}_m\text{H}_n]^+$  boron hydrides.**

m	n	PG	ES	$\langle r_{\text{B-B}} \rangle$ (Å)	$\langle r_{\text{B-H}} \rangle$ (Å)	E (eV)	gap <sub>HL</sub> (eV)	$f_{\text{min}}^*$ (cm <sup>-1</sup> )	$f_{\text{max}}$ (cm <sup>-1</sup> )
5	1	C <sub>s</sub>	<sup>2</sup> A	1.598	1.172	-3382.167	2.828	104	2831
	2	C <sub>2</sub>	<sup>1</sup> A	1.686	1.178	-3400.329	3.114	250	2734
	3	C <sub>s</sub>	<sup>2</sup> A	1.657	1.173	-3417.464	4.420	183	2837
	4	C <sub>2</sub>	<sup>1</sup> A	1.658	1.175	-3435.260	4.277	183	2850
	5	C <sub>4v</sub>	<sup>2</sup> A	1.724	1.180	-3450.162	3.811	276	2796
6	1	C <sub>s</sub>	<sup>1</sup> A	1.653	1.171	-4057.243	3.794	389	2789
	2	D <sub>4h</sub>	<sup>2</sup> A	1.685	1.174	-4074.077	3.118	235 <sup>(2)</sup>	2749
	3	C <sub>s</sub>	<sup>1</sup> A	1.654	1.172	-4093.949	3.611	160	2842
	4	C <sub>2h</sub>	<sup>2</sup> A	1.750	1.171	-4108.974	2.913	312 <sup>(2)</sup>	2788
	5	C <sub>s</sub>	<sup>1</sup> A	1.682	1.177	-4126.804	3.683	174 <sup>(1)</sup>	2828
	6	C <sub>3v</sub>	<sup>2</sup> A	1.768	1.180	-4142.430	3.176	177	2745
7	1	C <sub>2v</sub>	<sup>2</sup> A	1.715	1.175	-4734.257	2.565	292	2756
	2	C <sub>2v</sub>	<sup>1</sup> A	1.746	1.171	-4752.536	4.720	270	2799
	3	C <sub>2v</sub>	<sup>2</sup> A	1.729	1.178	-4768.663	3.418	202	2746
	4	C <sub>2v</sub>	<sup>1</sup> A	1.744	1.176	-4785.715	3.052	366 <sup>(1)</sup>	2788
	5	C <sub>s</sub>	<sup>2</sup> A	1.749	1.179	-4802.041	2.073	290 <sup>(3)</sup>	2785
	6	C <sub>s</sub>	<sup>1</sup> A	1.742	1.179	-4820.206	5.074	154	2807
	7	C <sub>s</sub>	<sup>2</sup> A	1.770	1.217	-4836.652	4.699	142	2834
8	1	C <sub>s</sub>	<sup>1</sup> A	1.718	1.175	-5409.785	2.189	103	2757
	2	C <sub>s</sub>	<sup>2</sup> A	1.720	1.173	-5427.781	2.068	339 <sup>(1)</sup>	2767
	3	C <sub>s</sub>	<sup>1</sup> A	1.725	1.173	-5445.956	4.358	328	2776
	4	D <sub>2d</sub>	<sup>2</sup> A	1.738	1.178	-5462.725	4.055	334	2726
	5	C <sub>s</sub>	<sup>1</sup> A	1.758	1.175	-5479.857	4.407	220	2810
	6	C <sub>2</sub>	<sup>2</sup> A	1.775	1.177	-5496.284	3.597	219	2766
	7	C <sub>s</sub>	<sup>1</sup> A	1.717	1.259	-5513.579	5.197	177	2807
	8	C <sub>s</sub>	<sup>2</sup> A	1.796	1.187	-5528.766	3.319	325 <sup>(2)</sup>	2745
9	1	C <sub>s</sub>	<sup>2</sup> A	1.724	1.172	-6087.369	4.331	99	2790
	2	C <sub>s</sub>	<sup>1</sup> A	1.782	1.172	-6103.447	2.719	214	2781
	3	C <sub>s</sub>	<sup>2</sup> A	1.745	1.172	-6121.167	3.870	102	2794
	4	C <sub>2v</sub>	<sup>1</sup> A	1.720	1.172	-6139.199	4.363	122	2798
	5	C <sub>s</sub>	<sup>2</sup> A	1.737	1.180	-6154.841	3.570	165 <sup>(1)</sup>	2784
	6	C <sub>2</sub>	<sup>1</sup> A	1.807	1.193	-6167.118	3.160	48 <sup>(1)</sup>	2774
	7	C <sub>s</sub>	<sup>2</sup> A	1.785	1.223	-6185.262	3.360	96 <sup>(1)</sup>	2758
	8	C <sub>s</sub>	<sup>1</sup> A	1.789	1.214	-6205.883	4.277	123	2830
	9	C <sub>s</sub>	<sup>2</sup> A	1.790	1.209	-6222.180	4.642	65	2830
10	1	C <sub>2v</sub>	<sup>1</sup> A	1.745	1.186	-6761.579	3.355	97	2656
	2	C <sub>s</sub>	<sup>2</sup> A	1.713	1.176	-6779.655	3.487	170	2771
	3	C <sub>2v</sub>	<sup>1</sup> A	1.730	1.180	-6796.335	2.601	231 <sup>(1)</sup>	2721
	4	C <sub>2</sub>	<sup>2</sup> A	1.777	1.176	-6813.937	2.937	301 <sup>(1)</sup>	2759
	5	C <sub>2</sub>	<sup>1</sup> A	1.790	1.177	-6831.387	3.500	11	2754
	6	D <sub>2</sub>	<sup>2</sup> A	1.743	1.176	-6848.863	3.361	125	2752
	7	C <sub>s</sub>	<sup>1</sup> A	1.768	1.176	-6865.944	3.221	158	2766
	8	C <sub>2</sub>	<sup>2</sup> A	1.798	1.176	-6881.983	3.689	290	2791
	9	C <sub>s</sub>	<sup>1</sup> A	1.789	1.179	-6898.347	4.036	205	2761
	10	C <sub>s</sub>	<sup>2</sup> A	1.786	1.182	-6914.589	3.770	165	2795

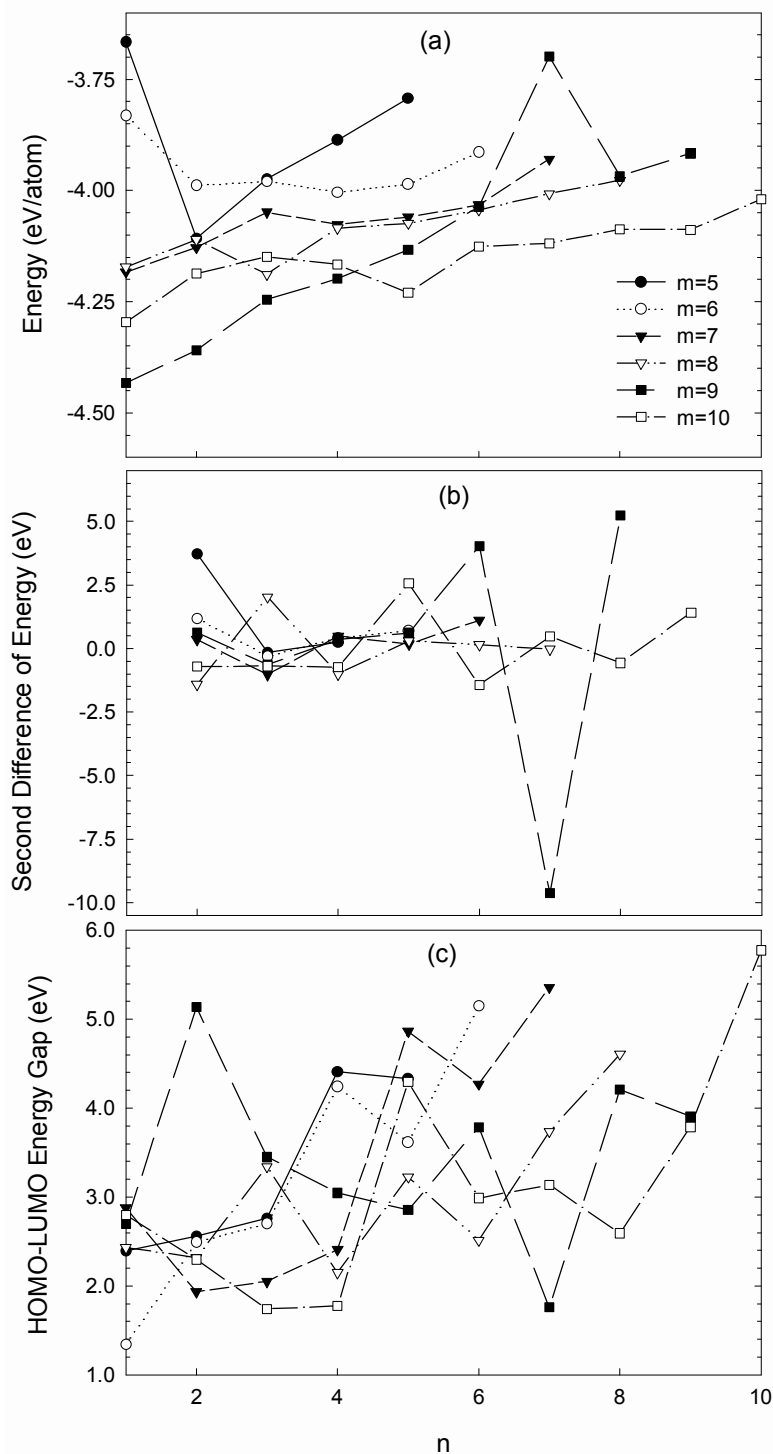
\* numbers in the parentheses show imaginary frequencies.

lower in energy. Even though there is no clear relationship between the HOMO-LUMO energy gaps and the number of hydrogen atoms, despite to the large fluctuations, it slightly increases with n as seen from Fig. 3c. The HOMO-LUMO energy gaps indicate the chemical hardness of the



complexes. The largest and smallest values of the gaps over all the clusters are 5.775 eV and 1.344 eV obtained for the  $[B_{10}H_{10}]^{-1}$  and  $[B_6H_6]^{-1}$ , respectively.

Similarly, the average binding energies per atom for the cationic complexes are displayed in Fig. 4a. In Figures 4b and 4c the second finite difference of the total energies and the HOMO-LUMO energy gaps of the cationic complexes are presented, respectively. For the energies there are smaller fluctuations, and it is increasing slightly as a function of  $n$  with some exceptions (just opposite to the trends observed for the anionic and neutral [7] complexes). The



**Figure 3:** a) The average binding energies per atom of the optimized configurations of anionic  $[B_mH_n]^{-1}$  boranes, b) The second finite difference of their total energies and c) HOMO-LUMO energy gaps as a function of  $n$ .

$[B_5H_2]^+$ ,  $[B_7H_2]^+$  and  $[B_{10}H_2]^+$  complexes are relatively more stable as shown in Fig. 4b. These also have even number of electrons. The  $[B_5H_4]^+$ ,  $[B_6H_3]^+$ ,  $[B_6H_5]^+$ ,  $[B_7H_4]^+$ ,  $[B_7H_6]^+$ ,  $[B_8H_3]^+$ ,  $[B_8H_5]^+$ ,  $[B_8H_7]^+$ ,  $[B_9H_5]^+$ ,  $[B_9H_8]^+$ , and  $[B_{10}H_7]^+$  clusters in their series are relatively more stable. There are fluctuations in the HOMO-LUMO energy gaps however they are over all in a narrow interval (Fig. 4c). The values of the HOMO-LUMO energy gaps for the cationic boron hydrides are listed in Table 2. The largest and the smallest values of the gaps among all the cationic clusters are 5.197 eV and 2.068 eV observed for the  $[B_8H_7]^+$  and  $[B_8H_2]^+$ , respectively. Their differences will give the fluctuation intervals for all the complexes, which are 4.431, 3.708 [7] and 3.129 eV for the anionic, neutral and cationic states, respectively.

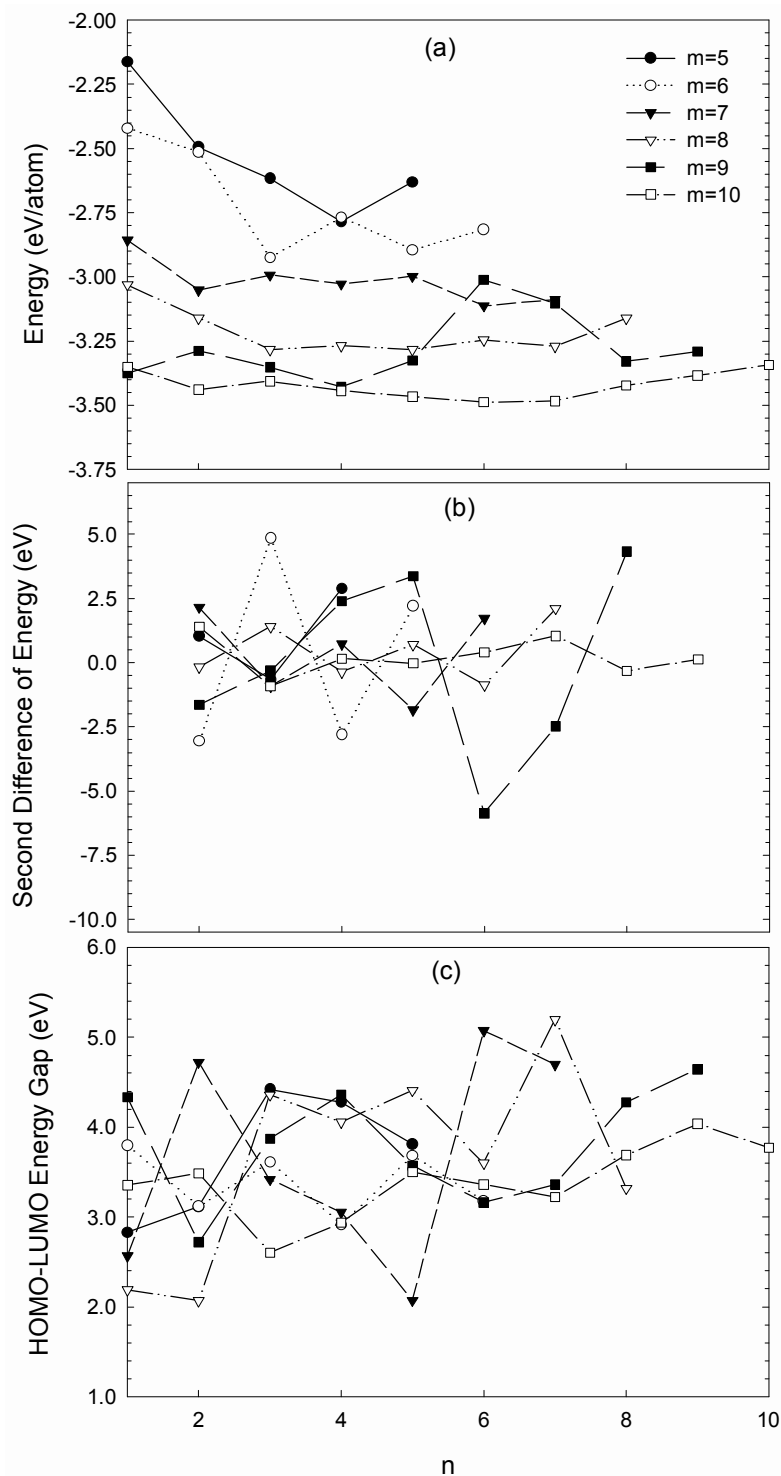
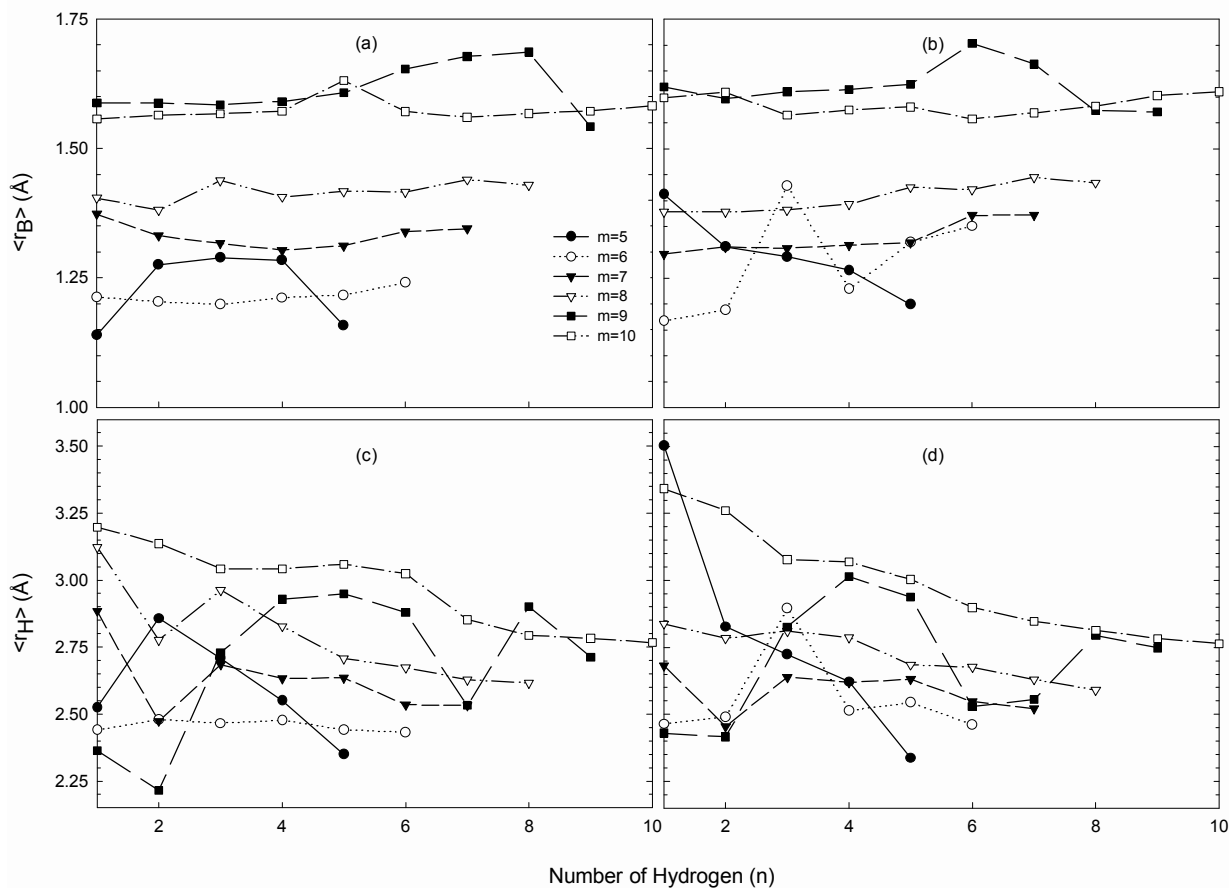


Figure 4: Same as Figure 3 for cationic  $[B_m H_n]^+$  boranes.



**Figure 5: Mean distances of the atoms from the center of mass of the  $B_m$  in the stable isomers; a) for B atoms in the anionic  $[B_mH_n]^-$ , b) in the cationic  $[B_mH_n]^+$  and c) for H atoms in the anionic  $[B_mH_n]^-$ , d) in the cationic  $[B_mH_n]^+$  complexes ( $m=5-10$ ,  $n=1-m$ ).**

### 3.4 Structural Analysis

The structural behaviors of the anionic and cationic clusters of the optimized  $B_mH_n$  ( $m=5$  to  $10$  and  $n=1$  to  $m$ ) boranes are analyzed using the average distances of the B and H atoms from the c.m. of the core  $B_m$  (Figure 5). Figures 5a to 5d show the mean distances for the B atoms in the  $[B_mH_n]^-$  and in the  $[B_mH_n]^+$ , and for the H atoms in them, respectively. In general, the mean values for the B ( $\langle r_B \rangle$ ) have similar trends for both ionic cases, which is also similar to the neutral cases [7] in spite of the very small increase with small oscillations. Mainly, the clusters become gradually larger by increasing the number of hydrogen atoms. Due to the structural changes of the cluster, such as in  $B_5$  series, more fluctuations are observed. On the other hand, there are much smaller fluctuations in the  $B_{10}H_n$  series among all the ionic clusters because they preserve cage configurations in their entire series. Namely, the  $B_{10}$  more or less preserves its shape compared to the others while the number of the hydrogen atoms increases (among all the neutral [7] and ionic cases). The mean values for the Hs ( $\langle r_H \rangle$ ) are getting smaller with some oscillations in the most of the series of these ionic clusters (Figs. 5c-5d), e.g., they are clearly visible for the  $B_8H_n$  and  $B_{10}H_n$  boranes among all the ionic and neutral cases [7]. This means that the  $B_8$  and  $B_{10}$  structures remain more or less stable and can preserve their cage forms. However, for the  $B_5$ ,  $B_7$ ,  $B_9$  clusters, the significant structural changes result in irregular arrangements of the particles in the complexes.

## 4. CONCLUSIONS

The geometries, energetics and structural properties of the anionic and cationic  $B_mH_n$  ( $m=5-10$  and  $n=1-m$ ) boranes have been computationally investigated to understand their stabilities as well as the electronic properties, and especially to observe the effect of hydrogenation. It may be concluded that the cage forms of the complexes with  $B_6$ ,  $B_8$  and  $B_{10}$  clusters are relatively more stable. However, the initial cage structures of the  $B_5$ ,  $B_7$  and  $B_9$  in their complexes are not stable

and the boron coordination numbers of several boron atoms are reduced by the hydrogen atoms. For both ionic cases the “peeling” off the cage forms of the structures by the hydrogen atoms and forming a smaller cage structures inside by the remaining boron atoms are also observed as in the case of the neutral ones [7].

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