Probing the structural and electronic properties of boron cluster anions doped with one or two aluminum atoms

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ABSTRACT

The structures and electronic properties of a series small mixed aluminum boron clusters AlB_n^- and $Al_2B_n^-$ ($n = 1-9$) have been investigated systematically with the density functional approach. Results show that the ground state prefers the lowest spin state except Al_2B^- and the Al atom tends to be adsorbed at the surface in both boron–aluminum systems. Moreover, results about the stability indicate clusters AlB_8^- and $Al_2B_7^-$ have the considerable enhanced stability among the clusters of AlB_n^- and $Al_2B_n^-$ ($n = 1-9$). Besides, the electronic and magnetic properties for two systems are also investigated, and the total magnetic moments as a function of cluster size show a dramatic odd–even alternative behavior for clusters AlB_n^-, while the addition of one more Al atom makes the total magnetic moments of the clusters $Al_2B_n^-$ contrary except $n = 1$.

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1. Introduction

Boron clusters have been proved to be a subject of considerable interest in both experimental and theoretical fields as their interesting physical and chemical properties, as well as their potential application in the aspect of hydrogen storage [1,2]. Over the past decade, photoelectron spectroscopy studies in conjunction with *ab* initio calculations have been carried out on small anionic boron (B_n^-) clusters to investigate their structures and bonding properties [3–15]. These studies have confirmed the planar or quasi-planar structures are more stable than any three-dimensional structures for an extended size range at least up to $n = 23$. While for the aluminum atom belonging to the same group with that of the boron atom in the periodic table, the structure transition of the Al_n clusters from planar to three-dimensional (3D) occurs at $n = 5$ [16–24]. The substitution of boron clusters by aluminum atoms provides unique chemical environment, which may induce a significant change of the electronic properties and the possibility of new types of materials. Hence, it is very interesting to investigate the Al substituted effects on the planar boron cluster B_n^- anions.

Although many investigations [25–45] estimating the metal substituted effects on pure boron clusters have been conducted, studies about the di-metal doped boron clusters especially for the $Al_2B_n^-$ clusters are rare. To the best of our knowledge, only one work about this system was performed by Jiang et al [44] and only the properties of Al_2B^- and $Al_2B_2^-$ clusters were discussed in their work. Up to now, there is no systematically theoretical investigation on the growth pattern behaviors and electronic properties of the $Al_2B_n^-$ ($n \geqslant 3$) clusters is performed. Therefore, we carried out the related studies on the properties of the $Al_2B_n^-$ ($n = 1-9$) clusters in the present paper and performed a comparison with those of the AlB_n^- clusters within the density functional theory (DFT).

The paper is organized as follows. Details of the computational method are given in Section 2. Then results and discussions are presented in Section 3. Finally, the concluding remarks are offered in Section 4.

2. Theoretical methods and computational details

To obtain the most stable structures of the AlB_n^- ($n = 1-9$) clusters, we considered lots of possible initial geometries obtained by directly adding or substituting one aluminum atom on the pure B_n^- and B_{n+1}^- clusters, which were presented in the previous studies [11–15]. On the basis of the obtained AlB_n^- geometries, we constructed the initial structures of the $Al_2B_n^-$ by the following three ways. The first way is to cap two aluminum atoms on possible equilibrium geometries of the pure B_n^- clusters [11–15]. The second way is to substitute two boron atoms on the various sites of B_{n+2}

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clusters with Al atoms. The third way is to add or substitute one Al atom on the top, bridge and face sites of the AlB_n^- and AlB_{n+1}^- clusters. All the initial geometries of AlB_n^- and $Al_2B_n^-$ ($n = 1-9$) clusters were optimized by means of the generalized gradient approximation (GGA) to DFT using the *GAUSSIAN* 03 programs [46]. The Becke's three-parameter hybrid functional incorporating the Lee–Yang–Parr correlation functional known as B3LYP [47–49] along with the 6-311 + G(d) basis set was employed in the process of the optimization. Different possible spin multiplicities were also considered for each isomer to determine the preferred spin states of these clusters. Spin-restricted hybrid DFT calculations were employed for the singlet state, while spin-unrestricted hybrid DFT calculations were employed for all other electronic states. Meanwhile, vibrational frequency calculations were performed to ascertain the stability of the isomers. In order to obtain more accurate energetic value, single-point energy calculations for the revealed low-lying isomers of both AlB_n^- and $Al_2B_n^-$ ($n = 1-9$) clusters were performed using the restricted (unrestricted) coupled cluster method CCSD(T) with the 6-311 + G(2df) basis set. The total energies of these clusters were then applied to study the evolution of their first vertical detachment energies VDEs (VDE = $E_{neutral \ at \ optimized \ anion \ geometry}$ − $E_{optimized \ anion}$), average binding energy and relative stability as a function of cluster size. Finally, all charge populations were obtained with the method of natural population analysis (NPA) [50,51]. Here, it should point out that since the zero-point energies (ZPEs) of the isomers of a specific cluster size are so small that they are not included in the total energies of the AlB_n^- and $Al_2B_n^-$ ($n = 1-9$) clusters.

3. Results and discussion

3.1. Geometries and growth pattern behaviors

We display the optimized geometries, symmetries, electronic states and relative energies of the isomers of AlB_n^- and $Al_2B_n^-$ ($n = 1-9$) clusters in Figs. 1 and 2. According to the total energies from low to high, these isomers are designated by na, nb, nc, and nd, n is the number of B atoms.

3.1.1. Single Al-doped boron cluster anions AlB_n^-

As displayed in Fig. 1, all possible AlB_2^- geometries such as C_{2v} and $C_{\infty v}$ isomers are optimized as the stable structures. The calculated results illustrate that the isosceles triangle 2a isomer with the symmetry of C_{2v} and electronic state of $^1A_1$ is the lowest-energy structure, which can be regarded as two substitutions of Al atoms by B atoms in a triangle Al_3^- anion [17,20,21] and can also be viewed as a substitution of a B atom by an Al atom in the equilateral triangle B_3^- cluster [12]. The energetically closest isomer 2b is a triplet state with $C_{\infty v}$ symmetry, which is consistent with that offered in Ref. [44]. Isomer 2c with a bond length (Al–B) of 2.152 Å and an apex angle of 127.243° is an obtuse triangle. For AlB_3^- clusters, the ground-state structure 3a and low-lying isomers 3c and 3d can be obtained by adding the boron atom directly to the different positions of the most stable structure of 2a. The structure of the most-stable 3a isomer (C_{2v}, $^2A_1$) is similar to that of the ground-state B_4^- cluster [12]. And the Y-shaped structure 3b (C_{2v}, $^2B_2$), which is also a low-lying isomer of the B_4^- cluster presented in Ref. [12], can be obtained by capping one Al atom on the apex of the pure B_3^- cluster. The most stable isomer of AlB_4^- cluster was found to be a planar C_s structure with the electronic state of $^1A'$, which is similar to the ground-state structures of B_5^- [15], B_4Li [52] and B_4Al [38,43] clusters. This phenomenon indicates that the impurity Al atom has no influence on the ground-state structure of the pure B_4^- [12]. The three-dimensional (3D) X-like structure 4c and planner X-like structure 4d has a relatively higher

symmetry of D_{2d} and C_{2v} respectively, compared with 4a and 4b. With regard to the AlB_5^- clusters, the lowest-energy structure 5a and three other low-lying isomers 5b, 5c, and 5d can be obtained by adding one Al atom on the peripheral site of the state B_5^- with a little distortion. Obviously, the first 3D ground-state structure for AlB_n^- occurs at $n = 5$. And it is worth pointing out that the present calculated results (symmetry, electronic state, and shape) about the AlB_5^- cluster are in excellently agreement with that reported in Ref. [33]. In addition, the exciting thing is that all the ground-state structures of AlB_6^-, AlB_7^-, AlB_8^- and AlB_9^- clusters are in good agreement with the results reported in literatures [35–37]. Besides, it should be noted that the structure of the low-lying isomer 9b obtained in this work is the ground-state geometry of the RuB_9^-, CoB_9^-, RhB_9^-, and IrB_9^- clusters reported in Refs. [27,30,32,34]. This may be caused by the differences of the properties between the Al and the atoms of Ru, Co, Rh, and Ir.

3.1.2. Multiple Al-doped boron cluster anions $Al_2B_n^-$

The most stable structures and low-lying isomers for each size of the clusters $Al_2B_n^-$ ($n = 1-9$) are presented in Fig. 2. From Fig. 2, we can clearly find that the number of the planar ground-state structures of the $Al_2B_n^-$ ($n = 1-9$) clusters are more than that of the AlB_n^- clusters. This may be originated from the fact that the impurity atom (Al) can expand the outer boron-ring due to its larger size. With regard to the Al_2B^- cluster, only the ground-state structure of Al_2B^- cluster has a relatively higher spin multiple of triplet state while others are single or double states, among the ground-state structures of $Al_2B_n^-$ ($n = 1-9$) clusters. Surprisingly, the first 3D ground-state structure for $Al_2B_n^-$ ($n = 1-9$) clusters occurs at $n = 2$, which is earlier than that of the AlB_n^- clusters. For $Al_2B_2^-$ clusters, the lowest-energy structure 2a can be described as a deviation from two substitutions of Al atoms by B atoms in a tetragonal Al_4^- anion [20], and the results about 2a isomer accord with that obtained by Jiang et al [44]. The planar structure of the low-lying isomer 2b with a high symmetry of D_{2h} is similar to that of the isomer 2d, which can be obtained by substituting two B atoms in the most-stable B_4^- cluster [12] with two Al atoms. And it is noteworthy that the structure of 2b and 2d is the most-stable structure of $Ta_2B_2^-$ cluster [29]. When $n = 3$, the four isomers 3a, 3b, 3c, and 3d can be obtained by adding one Al atom on the peripheral site of the ground-state structure of the AlB_3^- cluster with a little distortion. The most stable geometry of $Al_2B_4^-$ is a planar C_{2v} structure, it can be obtained by replacing the boron atom which in the third isomer of the AlB_5^- cluster with aluminum atom. For $Al_2B_5^-$ clusters, only the 3D structures are found to be more stable though the two- and three-dimensional initial structures have been considered during optimization. The most stable isomer of the $Al_2B_6^-$ anion is a planar structure with C_s symmetry, which can be obtained by capping one aluminum atom on one of the edge of the third stable isomer of AlB_7^-. When one boron atom on the peripheral site of the ground-state structure of AlB_7^- was substituted by aluminum atom, the third isomer of the $Al_2B_6^-$ cluster is generated. Similarly, both the second stable isomer of the $Al_2B_7^-$ cluster and the ground-state $Al_2B_8^-$ anion can also be yielded using the same information as a guide. The ground-state isomer 9a of the $Al_2B_9^-$ cluster is a planar ichthyoid structure and the two aluminum atoms at the tail fin. And the other three low-lying isomers 9b, 9c, and 9d can be obtained by adding one Al atom on the periphery of the most stable state of the AlB_9^- cluster with little distortion. Besides, it is worth noting that the structure of 9b, 9c, and 9d isomers is the same as that of the lowest-energy state of the AlB_{10}^- cluster found in Ref. [37].

3.1.3. Structural properties

The optimized structures show that the ground-states of AlB_n^- and $Al_2B_n^-$ ($n = 1-9$) clusters prefer the lowest spin states (single