Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 252 (2006) 197–203

www.elsevier.com/locate/ijms

Structures and stability of B-doped Al anions: Al_nB^- and $Al_nB_2^-$ ($n = 1$–7)

Zhen-Yi Jiang [a,b,c], Xiao-Min Luo [b], Sheng-Tao Li [c,*], San-Yan Chu [d]

[a] Multidisciplinary Materials Research Center, Xi'an Jiaotong University, Xi'an 710049, China
[b] College of Resource and Environment, Shaanxi University of Science and Technology, Xianyang 712081, China
[c] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China
[d] Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan

Received 8 January 2006; received in revised form 1 March 2006; accepted 2 March 2006
Available online 17 April 2006

Abstract

Various structural possibilities for $Al_nB_m^-$ ($m + n = 3$–8, $m = 1$–2) anionic isomers were investigated using B3LYP/6-31+G(d) and CCSD(T)/6-31+G(d) methods. Our calculations predicted the existence of a number of previously unknown isomers. All structures of the Al_nB^- ($n = 2$–6) may be derived from a substitution of an Al atom by a B atom in the Al_{n+1}^- anions while the geometrical structure of Al_7B^- may be understood as putting centrally a B atom inside the Al_7^- cage-like structure. The strong B—B bond is dominant factor in building-up principle of mixed $Al_nB_2^-$ ($n = 1$–6) anions. All $Al_nB_m^-$ with odd $n + m$ ($2 < n + m < 9$) are relatively more stable. Our present results satisfactorily explain the photoelectron spectroscopy and finally improve our understanding of these experimental observations.

Keywords: Al_nB_m anions; Geometric configuration; Stability; Photoelectron spectra

1. Introduction

Elements belonging to the same group of the periodic table have the similar properties as a whole, and boron and aluminum are an exception. Their differences are very pronounced. The immense variety of physical chemistry, reflecting the preference for forming sp^2 bonds [1] in boron clusters, is not shared by aluminum. It is perhaps not surprising that the structures of the elemental clusters show outstanding differences.

For Al_n clusters, ab initio calculations predicted a transition from planar ($n \leq 5$) to three-dimensional (3D) topologies ($n > 5$) [2–10]. However, for B_n clusters with $n \leq 6$, theoretical studies indicated that they form planar configurations while larger clusters ($n > 6$) prefer quasi-planar cage-like arrangements [10–22]. Important structural information on elemental clusters has been provided in recent years by photoelectron (PE) spectroscopy [5,14,18,23,24]. All available experimental measurements on aluminum and boron clusters are consistent with theoretical predictions [5,14,18].

While the combination of theoretical and experimental studies has led to a rather detailed picture of the elemental clusters, this is not so for mixed Al_nB_m clusters. Though PE spectra [25] of $Al_nB_m^-$ anions have been measured, these observations have not yet been well understood due to lacking reliable structural information.

At present only several investigations on neutral Al_nB_m ($n + m < 9$, $m = 1$–2) and negatively charged $Al_{11}B_2^-$ clusters [26–28] have been reported. The geometrical and electronic structures of smaller anions ($n < 10$) have remained unclear. It is well known that the acceptance of an electron would introduce significant structural distortions to corresponding neutral clusters. The structures of neutral clusters are therefore expected to be less reliable in interpreting the anionic geometries. Hence, it is of interest to carry on an investigation on the aluminum–boron anions and finally to improve our understanding of the PE spectra [23,25,29].

The rest of the paper is organized as follows. In Section 2, we give a brief description of the computational method used in this work. Results, discussion and stability will be presented

---

* Corresponding author.
E-mail address: jiang_chemphy@yahoo.com (S.-T. Li).

1387-3806/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2006.03.004

in Section 3 for mixed aluminum–boron species. Finally, our conclusions will be summarized in Section 4.

2. Computational methods

Initial geometrical optimizations were performed at the B3LYP/6-31G(d) level without any symmetry constraints, except for those needed to maintain a particular geometry. These isomers were further optimized using B3LYP/6-31+G(d) method. And then harmonic frequencies were evaluated to characterize the stationary points as minima or transition state structures on the potential energy surfaces of corresponding clusters. A single calculation was then carried out at the coupled cluster method (CCSD(T)/6-31+G(d)) level of theory with frozen-core approximation to determine the most stable isomers and that was reported throughout the present paper. All of the obtained most stable negatively charged aluminum–boron clusters were characterized as energy minima without imaginary frequencies. All calculations were carried out using the GAUSSIAN03 program [30].

3. Theoretical results

3.1. Geometry

Geometric parameters and CCSD(T) energies of lowest-energy anionic species are listed in Tables 1 and 2, respectively. The energetically low-lying geometric sketches of $Al_nB_m^-$ clusters containing up to seven Al atoms are shown in Figs. 1–6, respectively. The “bonds” are shown for internuclear separations less than 3.1 Å (Al–Al), 2.2 Å (Al–B) and 1.6 Å (B–B), respectively.

The photoelectron spectra [25] of Al_nB^- ($n = 4$ and 6) clusters are similar to those of pure Al_{n+1}^- clusters in the peak positions and their envelopes. This similarity indicates that the substitution of an Al atom by a B atom in Al_{n+1}^- clusters does not change either the geometrical and electronic structures substantially. This is attributed to the fact that both B and Al atoms take a similar valence structure due to the same family in the periodic table. The structures of Al_5^- and Al_7^- are known to be a trapezoidal planar and capped trigonal antiprism, respectively [7,8]. Thus, the calculated geometrical and electronic structures of Al_nB^- ($n = 4$ and 6) clusters should be analogous to those of pure Al_{n+1}^- clusters.

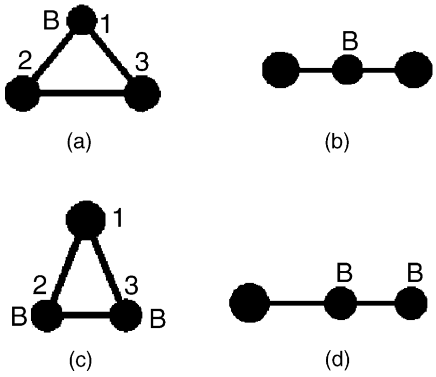

Fig. 1. low-lying isomers of (a and b) Al_2B^- and (c and d) AlB_2^- clusters.

Table 1
Distances between two atoms (L, Å) in Al_nB^- and $Al_nB_2^-$ anions

	Symmetry	Type	L		Symmetry	Type	L
Al_2B^-	C_{2v}	1-2	2.016			2-3	1.539
		2-3	2.598	$Al_2B_2^-$	C_{2v}	1-2	2.193
Al_3B^-	C_{2v}	1-2	2.069			2-3	1.515
		1-3	1.975	$Al_3B_2^-$	C_{2v}	1-2	2.188
		2-3	3.226			2-3	1.554
Al_4B^-	C_{2v}	1-2	2.039			2-4	2.057
		1-3	2.235			4-5	2.768
		2-3	2.646	$Al_4B_2^-$	C_{2v}	1-2	1.598
		3-4	2.606			2-3	2.128
Al_5B^-	C_s	2-3	2.536			1-5	2.152
		4-5	3.936			1-4	2.093
		2-5	2.630			4-5	2.954
		1-2	2.187	$Al_5B_2^-$	C_s	1-2	1.586
		1-4	2.195			4-5	3.624
		1-6	2.138			2-4	2.096
		4-6	2.788			1-3	2.240
Al_6B^-	C_s	2-3	2.499			2-3	2.716
		4-5	3.054			1-6	2.250
		2-5	2.652			4-6	3.994
		3-7	3.039			4-7	2.688
		4-7	2.617			6-7	2.785
		1-2	2.184	$Al_6B_2^-$	C_s	2-3	2.887
		1-4	2.232			4-5	3.858
		1-6	2.126			2-5	2.631
		4-6	2.779			1-2	2.159
Al_7B^-	C_{2v}	2-3	3.084			1-5	2.277
		3-5	2.746			2-7	2.751
		2-4	2.743			4-7	3.693
		1-2	2.168			4-8	3.396
		2-7	2.764			7-8	2.877
		7-8	2.805			6-7	2.170
AlB_2^-	C_{2v}	1-2	2.045			6-8	2.104

3.1.1. Al_2B^-

The energetically most favorable structure is a triangle (C_{2v}, $^1A_1$) (Fig. 1(a)), whose bond angle of Al–B–Al atoms is 80.22°. This may be viewed as replacing an Al atom with a B atom in a triangle Al_3^- cluster [5,7,10]. Another low-lying isomer (Fig. 1(b)) is a linear ($D_{\infty h}$, $^3\Sigma_g^+$), whose Al–B bond length is 2.032 Å, lying 0.70 eV higher in energy.

The triangle (C_{2v}, $^2A_1$) (Fig. 1(a)) is also predicted to be the most stable in neutral cluster, whose bond angle of Al–B–Al

Table 2
CCSD(T) energies and B3LYP ZPEs at 6-31+G(d) level for $Al_nB_m^-$

n/m	Symmetry	CCSD(T) (a.u.)	ZPE (a.u.)
2/1	C_{2v}	508.6199	0.0031
3/1	C_{2v}	750.6191	0.0042
4/1	C_{2v}	992.6305	0.0061
5/1	C_s	1234.6213	0.0070
6/1	C_s	1476.6370	0.0091
7/1	C_s	1718.6477	0.0099
1/2	C_{2v}	291.3728	0.0049
2/2	C_{2v}	533.3755	0.0053
3/2	C_{2v}	775.3850	0.0079
4/2	C_{2v}	1017.3881	0.0094
5/2	C_s	1259.3943	0.0111
6/2	C_s	1501.3967	0.0124

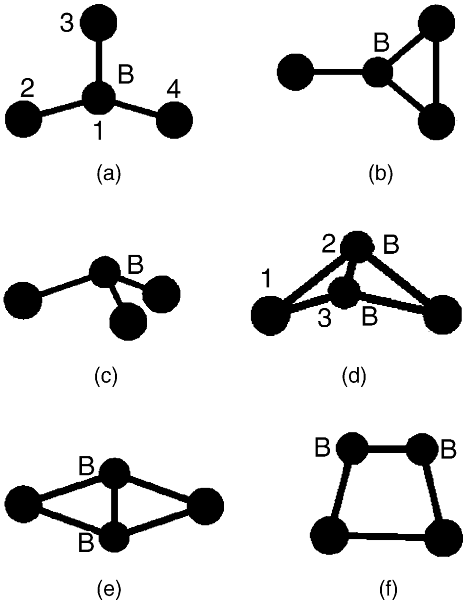

Fig. 2. low-lying isomers of (a–c) Al_3B^- and (d–f) $Al_2B_2^-$ clusters.

atoms is 78.41°. Loss of an electron to the C_{2v} isomer slightly decreases the bond angle α_{AlBAl}.

Our calculations predict the energies required to detach an electron from anion (vertical detachment energy, VDE) for the isomers (Fig. 1(a and b)) are 1.83 eV (C_{2v}) and 1.16 eV ($D_{\infty h}$), respectively. No photoelectron measurement has yet been performed for this cluster, but the pronounced difference between their VDEs should facilitate the analysis of future data.

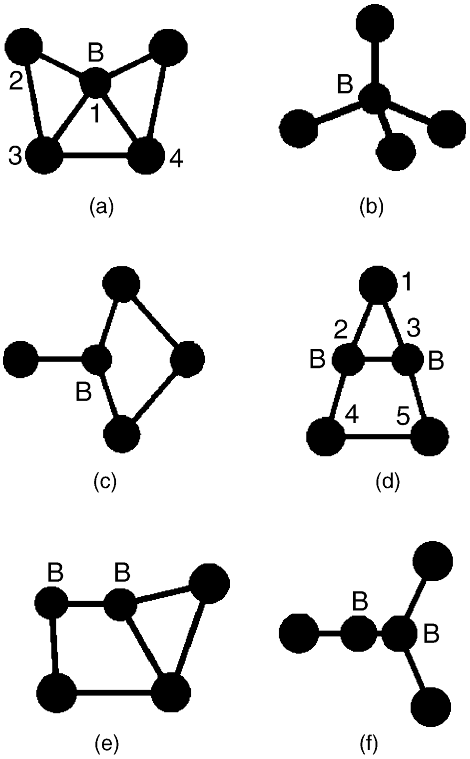

Fig. 3. low-lying isomers of (a–c) Al_4B^- and (d–f) $Al_3B_2^-$ clusters.

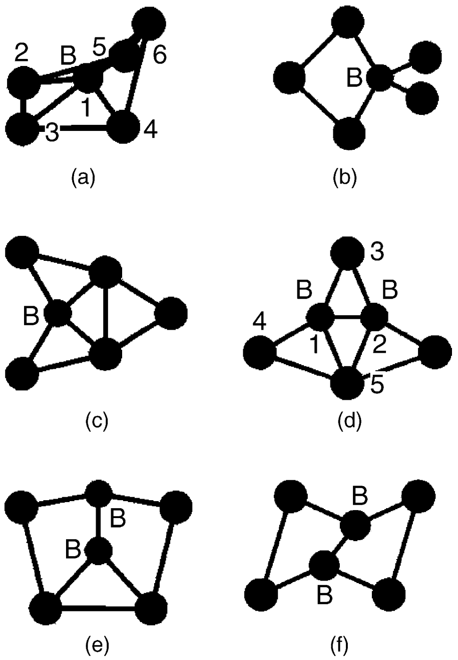

Fig. 4. low-lying isomers of (a–c) Al_5B^- and (d–f) $Al_4B_2^-$ clusters.

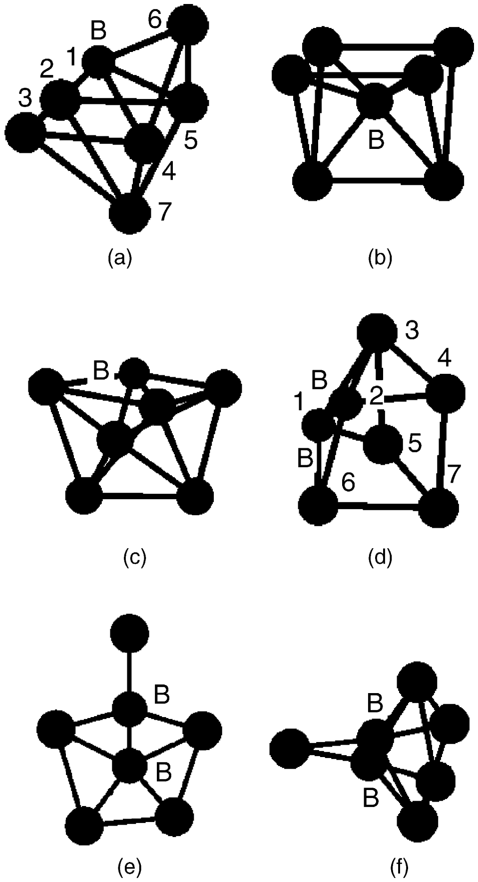

Fig. 5. low-lying isomers of (a–c) Al_6B^- and (d–f) $Al_5B_2^-$ clusters.

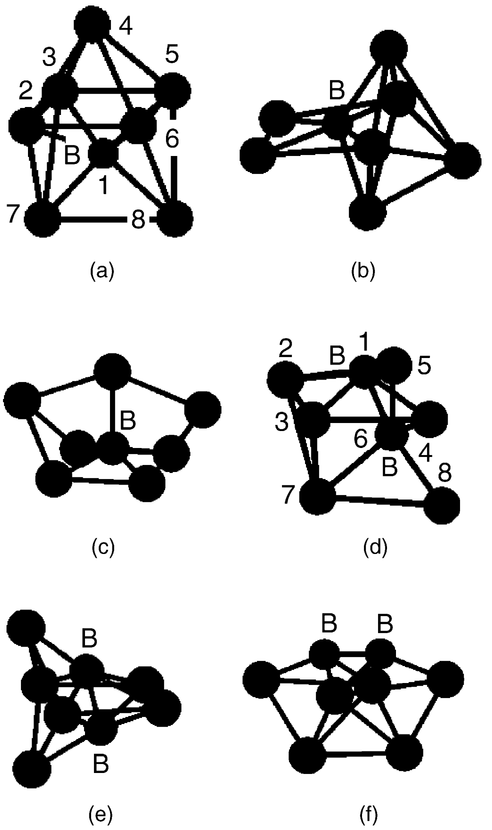

Fig. 6. low-lying isomers of (a–c) Al_7B^- and (d–f) $Al_6B_2^-$ clusters.

3.1.2. AlB_2^-

The anionic AlB_2 may adopt C_{2v} and $C_{\infty v}$ species with comparable energy, the (C_{2v}, $^1A_1$) (Fig. 1(c)) being 1.36 eV more stable than the ($C_{\infty v}$, $^1\Sigma$) (Fig. 1(d)). This triangle topology can be understood as two substitutions of Al atoms by B atoms in a triangle Al_3^- anion [5,7,10]. The optimized bond angle of B–Al–B atoms for the triangle is 44.21°.

The triangle (C_{2v}, $^2A_1$) (Fig. 1(c)) is also found to be most favorable in neutral state, whose bond angle of B–Al–B atoms is 45.17°. Loss of an electron to the C_{2v} isomer cannot largely change the bond angle α_{BAlB}.

Our calculations predict the VDEs for the isomers (Fig. 1(c and d)) are 2.11 eV (C_{2v}) and 2.52 eV ($C_{\infty v}$), respectively. Although no PE spectrum is provided for this cluster at present, the marked difference between their VDEs should be useful for future experimental investigations.

3.1.3. Al_3B^-

The ground state was found to be a (C_{2v}, $^2A_1$) planar (Fig. 2(a)), which can be figured as a deviation from a substitution of an Al atom by a B atom in a tetragonal Al_4^- anion [7]. This is followed by a planar (C_{2v}, $^2B_2$) (Fig. 2(b)), lying only 0.01 eV higher in energy. Their energy difference between the isomers (Fig. 2(a and b) was much smaller than the zero-point energies (ZPEs) (0.11 eV). However, the bond angle between Al–B–Al atoms (105.8°, 105.8° and 148.3°, respectively) in (a) differs significantly from the bond angle (131.8°, 131.8° and 96.5°, respectively) between Al–B–Al atoms in (b). Since atomic vibration belongs to slight movement, it is better to treat them as different isomers. The third is the pyramid (C_{3v}, $^2A_1$) (Fig. 2(c)), which is located at only 0.04 eV higher in energy above the planar (Fig. 2(a)). In fact, all of them (Fig. 2(a–c)) may coexist experimentally.

The neutral lowest-energy state was found to be a (C_{3v}, $^3A_1$) pyramid (Fig. 2(c)). Our calculations predict the VDEs for the isomers (Fig. 2(a–c)) are 1.90 eV ($^2A_1$ state), 1.79 eV ($^2B_2$ state) and 1.73 eV (C_{3v}), respectively. Until now, no photoelectron observation has been available for this cluster.

3.1.4. $Al_2B_2^-$

The global minimum of $Al_2B_2^-$ is a quasi-planar structure (C_{2v}, $^2A_1$) (Fig. 2(d)). Its dihedral angle between two shared-side triangle is 120.37°. This geometrical structure can be described as a deviation from two substitutions of Al atoms by B atoms in a tetragonal Al_4^- anion [7]. The next local minimum is a planar (D_{2h}, $^2B_{3g}$) (Fig. 2(e)), lying 0.38 eV higher in energy. This is followed by a quasi-planar trapezoid (C_2, ^2B) (Fig. 2(f)), 0.62 eV higher in energy above the isomer (Fig. 2(d)).

The quasi-planar (C_{2v}, $^1A_1$) (Fig. 2(d)) is also predicted to be most stable in neutral cluster. Our calculations predict the VDEs for the isomers (Fig. 2(d–f)) are 1.80 eV (C_{2v}), 1.49 eV (D_{2h}) and 2.23 eV (C_2), respectively. The PE spectrum for this cluster has not yet been reported.

3.1.5. Al_4B^-

A planar (C_{2v}, $^1A_1$) (Fig. 3(a)) was found to be the energetically most favorable, which may be treated as a replacement of an Al atom with a B atom in the planar Al_5^- (C_{2v}) configuration [7,8].

The tetrahedral (D_{2d}, $^1A_1$) (Fig. 3(b)) lies only 0.08 eV higher in energy above the isomer (Fig. 3(a)), and only 0.01 eV below a planar (C_{2v}, $^1A_1$) (Fig. 3(c)). When the ZPEs (0.17 eV) of the isomer (Fig. 3(a)) are taken into account, the isomer (Fig. 3(a–c)) may coexist experimentally.

For neutral state, a planar (C_{2v}, $^2A_1$) (Fig. 3(c)) was found to be the energetically most favorable. Our calculations predict the VDEs for the isomers (Fig. 3(a–c)) are 2.29, 2.20 and 2.04 eV, respectively. The PE spectrum gives a VDE of 2.32 ± 0.03 eV [25], in satisfactory agreement with the calculated value for the isomer (Fig. 3(a)).

3.1.6. $Al_3B_2^-$

The most stable arrangement is a planar C_{2v} ($^1A_1$) configuration (Fig. 3(d)). This may be viewed as a deviation from two substitutions of Al atoms by B atoms in the planar Al_5^- (C_{2v}) trapezoid [7,8]. The strong B–B bond significantly lowers the total energy and then leads to deformation of the planar trapezoid. Two C_s species with $^1A'$ state (Fig. 3(e and f)), are located at 0.04 and 0.45 eV higher in energy above the isomer (Fig. 3(d)), respectively.

The planar C_{2v} ($^2A_1$) (Fig. 3(d)) is also the most stable configuration in the neutral state. Our calculations predict the VDEs for the isomers (Fig. 3(d–f)) are 2.26, 2.47 and 2.27 eV, respectively. Experimental data on the VDE of this cluster is not available at present.

3.1.7. Al_5B^-

A distorted pentagon (C_s, $^2A'$) with a central B to five Al atoms was found to be the ground state (Fig. 4(a)). This may be understood as a deviation from a substitution of Al by B atom in the prism Al_6^- (D_{3h}) [3]. This is the first negative ion that a 3D structure is clearly more stable than planar structures in pure Al_n^- ($n = 6$) series [7].

Another two species (C_2, ^2A) (Fig. 4(b)) and (C_{2v}, $^2A_1$) (Fig. 4(c)) lie 0.32 and 0.37 eV higher in energy than the global minimum, respectively.

A planar pentagon (D_{5h}, $^1A_1'$) [28] with a central B to five Al atoms was found to be the neutral ground state. The calculated values of the VDEs are 2.08 eV (Fig. 4(a)), 1.67 eV (Fig. 4(b)) and 1.97 eV (Fig. 4(c)), respectively. The PE spectrum shows a VDE of 2.22 ± 0.08 eV [25], which provides further support for the isomer (Fig. 4(a)).

3.1.8. $Al_4B_2^-$

The computational search for the global minimum of $Al_4B_2^-$ revealed the planar (C_{2v}, $^2A_1$) (Fig. 4(d)). The preference for sp^2 bonds of boron clusters [1] and special stability of strong B—B bonding lead to the emergence of the planar geometry at this cluster size.

This is followed by two planar isomer (C_{2v}, $^2B_2$) (Fig. 4(e)) and (C_{2h}, ^2A_g) (Fig. 4(f)) lies 0.14 and 0.24 eV higher in energy than the isomer (Fig. 4(d)), respectively.

A quasi-planar C_s ($^1A'$) similar to Fig. 4(e) is predicted to be the most stable configuration in the neutral state. Our calculations predict the VDEs for the isomers (Fig. 4(d–f)) are 2.19, 1.76 and 2.03 eV, respectively. The PE spectrum indicates a VDE of 2.32 ± 0.08 eV [25], which reasonably agree with the calculated value for the isomer (Fig. 4(d)).

3.1.9. Al_6B^-

The energetically most stable structure is a C_s ($^1A'$) configuration (Fig. 5(a)), which may be figured as a substitution of an Al atom by a B atom in the capped trigonal antiprism form [3,7].

The second low-energy isomer has a 3D (C_{2v}, $^1A_1$) structure (Fig. 5(b)). It was found to be only 0.07 eV less stable than isomer (a). The third is a C_{2v} ($^1A_1$) isomer (Fig. 5(c)), located at 0.15 eV higher in energy above the anionic ground state.

The energetically most stable structure is a C_2 (^2B) configuration (similar to Fig. 5(b)) in the neutral state [28]. The calculated values of the VDEs are 2.54 eV (Fig. 5(a)), 2.91 eV (Fig. 5(b)) and 2.19 eV (Fig. 5(c)), respectively. The PE spectrum gives a VDE of 2.60 ± 0.08 eV [25], which provides further support for the isomer (Fig. 5(a)).

3.1.10. $Al_5B_2^-$

Our calculations indicated the 3D structure (C_s, $^1A'$) (Fig. 5(d)) to be the most favorable, which may be figured as two substitutions of Al atoms by B atoms in the capped trigonal antiprism form [3,7]. We note that there always exists B—B bond in this series clusters. This is ascribed to the larger bonding energy of B—B over Al—Al bond.

This is followed by two 3D species (C_2, ^1A) (Fig. 5(e)) and (C_{2v}, $^1A_1$) (Fig. 5(f)), lying 0.23 and 0.28 eV higher in energy relative to the lowest-energy state (Fig. 5(d)), respectively. Isomers (Fig. 5(d–f)) may coexist experimentally after considering the ZPEs (0.30 eV) of the isomer (d).

The cage-like isomer (C_s, $^2A'$) (Fig. 5(d)) is found to be the most favorable in neutral state. Our calculations predict the VDEs for the isomers (Fig. 5(d–f)) are 2.24, 2.44 and 2.83 eV, respectively. The PE spectrum gives a VDE of 2.77 ± 0.08 eV [25], in agreement with the calculated value for the isomer (Fig. 5(f)).

3.1.11. Al_7B^-

The C_{2v} ($^2B_1$) (Fig. 6(a)) is the most stable conformation, which may be understood as putting centrally a B atom inside the Al_7^- cage-like structure [7]. The B atom prefers to locate in the center of the larger cage-like structure due to smaller diameter. Similar situation also appears in the Al_nB ($n = 11–14$) clusters [26,31]. These results seem to imply that the B atom tends to locate inside the cage-like structure Al_n^- ($n > 6$) for the sake of their enough interspaces.

Another two 3D C_{2v} ($^2A_1$) isomers (Fig. 6(b and c)) are 0.68 and 0.82 eV less stable than (a).

For neutral state, the isomer C_{2v} ($^1A_1$) (Fig. 6(a)) is the most stable conformation. Our calculations show the VDEs for the isomers (Fig. 6(a–c)) are 2.37, 2.01 and 1.98 eV, respectively. The PE spectrum gives a VDE of 2.89 ± 0.08 eV [25]. This has not yet been observed for this isomer.

3.1.12. $Al_6B_2^-$

The energetically most favorable structure is a C_s ($^2A'$) configuration (Fig. 6(d)). The strong B—B bonds are favored over Al—B bonds, and Al—Al bindings are of smaller importance for the geometrical arrangement even in Al—B mixed clusters.

There exist two nearly degenerate conformers (C_s, $^2A'$) (Fig. 6(e)) and (C_{2v}, $^2A_1$) (Fig. 6(f)), lying at 0.07 and 0.08 eV less stable, respectively. Isomers (Fig. 6(d–f)) coexist experimentally when the ZPEs (0.34 eV) of the isomer Fig. 6(d) are taken into account.

The energetically most favorable neutral structure is a C_2 (^1A) configuration [very similar to the isomer Fig. 6(f)]. Our calculations predict the VDEs for the isomers (Fig. 6(d–f)) are 2.43, 2.29 and 2.02 eV, respectively. The PE spectrum gives a VDE of 2.32 ± 0.08 eV [25], which agrees with the calculated value for the isomer (Fig. 6(e)).

3.2. Relative stability

The anionic VDEs from theoretical calculations and experimental measurements are shown in Figs. 7 and 8. All of theoretical VDEs agree well with available measurements except Al_7B^-, which strongly suggest the correction of our predictions of those geometrical structures. Those VDEs of energetically most favorable Al_4B^-, Al_5B^-, $Al_4B_2^-$, Al_6B^- isomers can satisfactorily interpreted their corresponding photoelectron spectra [25]. It is also reasonable that the VDEs of the iso-

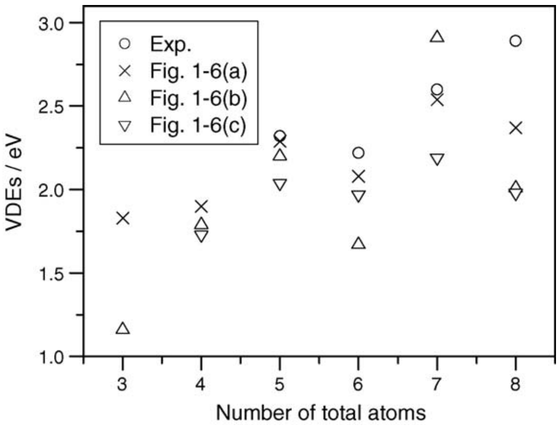

Fig. 7. The VDEs vs. the number of total atoms $n+m$ for Al_nB^- anions.

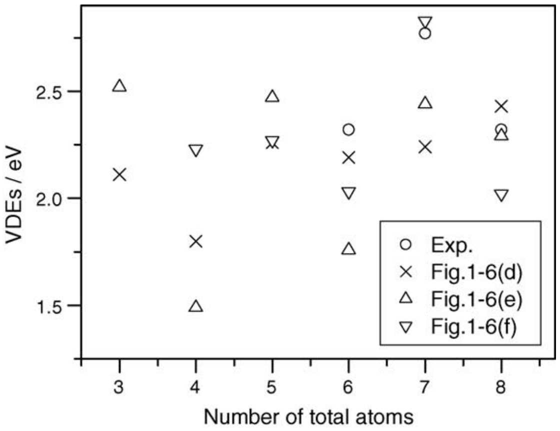

Fig. 8. The VDEs vs. the number of total atoms $n+m$ for $Al_nB_2^-$ anions.

mers Figs. 6(e) and 5(f) consist with photoelectron observations [25] because several isomers Fig. 6(d–f) (or Fig. 5(d–f)) coexist experimentally.

To study the relative stability of anions, it is instructive to analyze the adiabatic electron affinities (EAs). The adiabatic EAs from theoretical calculations and experimental measurements are shown in Fig. 9. Excellent agreement was obtained for all clusters except Al_7B between theoretical and experimental adiabatic EAs [25]. The experimental EA of Al_7B has a larger value relative to the theoretical calculations and it is the largest value in all of the experimental EAs. This discrepancy can be ascribed to experimental error based on two reasons as follows. First, both experimental and theoretical EAs of Al_7B should have the same trend as those of Al_6B_2; second, the larger experimental EA of Al_7B implies its anionic state should have relatively high stability, which cannot be understood by molecular orbital theory as will be stated next. The EAs with odd-numbered $n+m$ have the maximum values, which correspond to relatively stable anionic states.

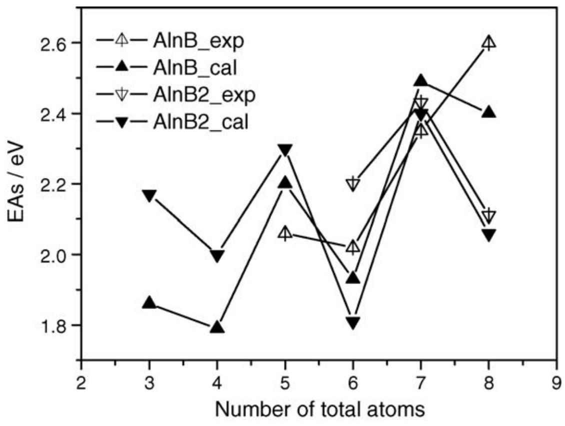

Fig. 9. The adiabatic EAs vs. the number of total atoms $n+m$.

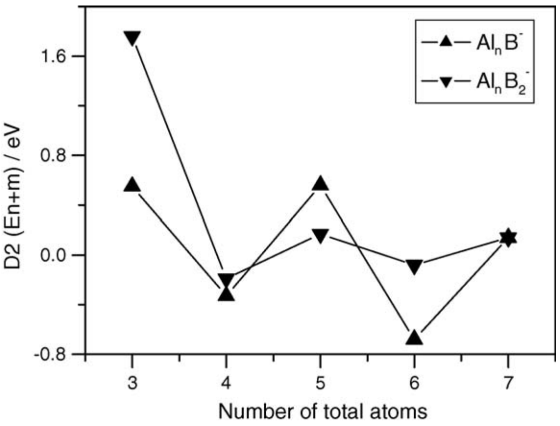

Fig. 10. The second difference in energy vs. the number of total atoms $n+m$.

To further test the relative stabilities of $Al_nB_m^-$ anions, the following energy variation of reactions is considered:

$$2(Al_nB_m^-) \rightarrow (Al_{n+1}B_m^-) + (Al_{n-1}B_m^-)$$

We define the energy variation in the formula as $D2(E_{n+m}) = E_{n+m+1} + E_{n+m-1} - 2E_{n+m}$, which is the second difference in energy for $Al_nB_m^-$. Hence, we obtain the curves shown in Fig. 10 corresponding to the energy variations in the formula as $n+m$. It is evident that the $D2(E_{n+m})$ is larger as odd $n+m$ and lower as even $n+m$ in Fig. 10, which suggests that those $Al_nB_m^-$ species corresponding to odd $m+n$ are more stable. The oscillating behavior of the second difference in energy reflects the change of spin multiplicity of the ground state of this series, whose spin multiplicity of odd-numbered anions is singlet whereas that of the even-numbered $n+m$ ones is a doublet. It is more difficult to remove an electron from the doubly occupied HOMO of a closed-shell system than from a single occupied HOMO of an open-shell system.

4. Summary

Geometries, electronic structures and relative stability of $Al_nB_m^-$ ($n+m=3$–8 and $m=1$–2) have been studied using the density functional theory and the coupled cluster method with the basis set of 6-31+G(d). All structures of the Al_nB^- ($n=2$–6) may be derived from a substitution of an Al atom by a B atom in the Al_{n+1}^- anions while the geometrical structure of Al_7B^- may be understood as putting centrally a B atom inside the Al_7^- cage-like structure. Boron atom can delay emergence of the 3D configuration in the $Al_nB_2^-$ anion. The strong B–B bond is dominant factor in building-up principle of mixed $Al_nB_2^-$ ($n = 1$–6) anions. The ground states of negative clusters correspond to the lowest spin multiplicities. All $Al_nB_m^-$ with odd $n+m$ are relatively more stable, which can be explained by difficultly removing an electron from the doubly occupied HOMO of a closed-shell system.

Acknowledgement

The authors acknowledge the support of Postdoctoral Science Foundation of China under Grant No. 2004036454.

References

[1] A. Ricca, C.W. Bauschlicher Jr., Chem. Phys. 208 (1996) 233.
[2] R.O. Jones, Phys. Rev. Lett. 67 (1991) 224.
[3] R.O. Jones, J. Chem. Phys. 99 (1993) 1194.
[4] A.K. Ray, B.K. Rao, J. Phys. Condens. Matter 9 (1997) 2859.
[5] K.K. Baeck, R.J. Bartlett, J. Chem. Phys. 109 (1998) 1334.
[6] R. Ahlrichs, S.D. Elliott, Phys. Chem. Chem. Phys. 1 (1999) 13.
[7] B.K. Rao, P. Jena, J. Chem. Phys. 111 (1999) 1890.
[8] G.D. Geske, A.I. Boldyrev, X. Li, L.-S. Wang, J. Chem. Phys. 113 (2000) 5130.
[9] M.D. Deshpande, D.G. Kanhere, I. Vasiliev, R.M. Martin, Phys. Rev. B 68 (2003) 035428.
[10] A.E. Kuznetsov, A.I. Boldyrev, Struct. Chem. 13 (2002) 141.
[11] J.M.L. Martin, J.P. Francois, R. Gijbels, J. Chem. Phys. 90 (1989) 6469.
[12] A.K. Ray, I.A. Howard, K.M. Kanal, Phys. Rev. B 45 (1992) 14247.
[13] J. Niu, B.K. Rao, P. Jena, J. Chem. Phys. 107 (1997) 132.
[14] H.-J. Zhai, L.-S. Wang, A.N. Alexandrova, A.I. Boldyrev, J. Chem. Phys. 117 (2002) 7917.
[15] Q.-S. Li, H.-W. Jin, J. Phys. Chem. A 106 (2002) 7042.
[16] A.N. Alexandrova, A.I. Boldyrev, H.-J. Zhai, L.-S. Wang, E. Steiner, P.W. Fowler, J. Phys. Chem. A 107 (2003) 1359.
[17] M. Wyss, E. Riaplov, A. Batalov, J.P. Maier, T. Weber, W. Meyer, P. Rosmus, J. Chem. Phys. 119 (2003) 9703.
[18] H.-J. Zhai, L.-S. Wang, A.N. Alexandrova, A.I. Boldyrev, V.G. Zakrzewski, J. Phys. Chem. A 107 (2003) 9319.
[19] A.N. Alexandrova, A.I. Boldyrev, H.-J. Zhai, L.-S. Wang, J. Phys. Chem. A 108 (2004) 3509.
[20] A.N. Alexandrova, H.-J. Zhai, L.-S. Wang, A.I. Boldyrev, Inorg. Chem. 43 (2004) 3552.
[21] Q.-S. Li, Q. Jin, J. Phys. Chem. A 108 (2004) 855.
[22] R. Linguerri, I. Navizet, P. Rosmus, S. Carter, J.P. Maier, J. Chem. Phys. 122 (2005) 034301.
[23] C.Y. Cha, G. Ganteför, W. Eberhardt, J. Chem. Phys. 100 (1994) 995.
[24] A.N. Alexandrova, A.I. Boldyrev, H.-J. Zhai, L.-S. Wang, J. Chem. Phys. 122 (2005) 054313.
[25] H. Kawamata, Y. Negishi, A. Nakajima, K. Kaya, Chem. Phys. Lett. 337 (2001) 255.
[26] J. Wan, R. Fournier, J. Chem. Phys. 119 (2003) 5949.
[27] Y.-H. Qu, X.-F. Bian, J. Mol. Struct. (THEOCHEM) 677 (2004) 91.
[28] Z.-Y. Jiang, C.-J. Yang, S.-T. Li, J. Chem. Phys. 123 (2005) 204315.
[29] X. Li, H.-B. Wu, X.-B. Wang, L.-S. Wang, Phys. Rev. Lett. 81 (1998) 1909.
[30] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuta, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision A1, Gaussian Inc., Pittsburgh, PA, 2003.
[31] A. Nakajima, T. Kishi, T. Sugioka, K. Kaya, Chem. Phys. Lett. 187 (1991) 239.