Aluminum Avoids the Central Position in AlB_{9}^{-} and AlB_{10}^{-} : Photoelectron Spectroscopy and ab Initio Study

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ABSTRACT: The structures and the electronic properties of two Al-doped boron clusters, AlB₉⁻ and AlB₁₀⁻, were investigated via joint photoelectron spectroscopy and high-level ab initio study. The photoelectron spectra of both anions are relatively broad and have no vibrational structure. The geometrical structures were established by unbiased global minimum searches using the Coalescence Kick method and comparison between the experimental and calculated vertical electron detachment energies. The results show that both clusters have quasi-planar structures and



that the Al atom is located at the periphery. Chemical bonding analysis revealed that the global minimum structures of both anions can be described as doubly (σ - and π -) aromatic systems. The nona-coordinated wheel-type structure of AlB₉⁻ was found to be a relatively high-lying isomer, while a similar structure for the neutral AlB₉ cluster was previously shown to be either a global minimum or a low-lying isomer.

INTRODUCTION

Boron possesses peculiar chemical bonding.^{1,2} Due to its small covalent radius and electron deficiency compared to carbon (boron has four valence atomic orbitals and only three valence electrons), boron forms planar or quasi-planar anionic structures, at least up to 20 atoms. Over the past decade, we have performed combined photoelectron spectroscopy (PES) and theoretical calculations on small boron clusters to investigate their structures and bonding properties.³⁻¹⁶ All of these small boron clusters show strong peripheral two-center-two-electron (2c-2e) B-B σ -bonds and two-dimensional delocalized σ - and/or π -bonds between inner and peripheral boron atoms, giving rise to σ - and π aromaticity, σ - and π -antiaromaticity or conflicting aromaticityantiaromaticity.3-18 It was concluded that the perfectly planar clusters feature multiple aromaticity (σ, π) and the optimum circumference and inner group sizes. One question arises: how do the electronic structure and the bonding change upon doping of the boron clusters with an isoelectronic aluminum atom?

In a previous work, we have shown that Al-doping enhances the planarity of B_7^- and B_{12}^- in AlB_6^- and AlB_{11}^- , by slightly expanding the size of the outer rings.¹⁹ For the perfectly planar AlB_{11}^{-} cluster, we found that two nearly degenerate isomers compete for the global minimum structure and that the second lowest-lying isomer is a coordination complex between the Al atom and B_{11}^{-} anion. Subsequent studies of AlB_7^{-} and AlB_8^{-} have shown that the global minima are umbrella-type structures featuring positively charged Al atoms bonded ionically to the negatively charged B_n (n = 7, 8) counterions.²⁰ Although the multiply charged B_7^{3-} and B_8^{2-} anions are not electronically stable in the isolated state, the overall stability is achieved in AlB₇⁻ and AlB_8^- due to the external field of Al^{2+} and Al^+ cations, respectively. As a comparison, the isoelectronic boron clusters are planar

 $(B_8^{-}, C_{2\nu} - \text{slightly distorted from } D_{7h})$ and perfect octagon (B_9^-, D_{8h}) structures.

Previous experimental studies of mixed Al-B clusters include a mass spectrometry investigation²¹ and a photoelectron spectroscopy study²² of aluminum clusters doped with one or two boron atoms. A number of theoretical calculations on Al-doped boron clusters have also been reported, mostly on neutral clusters.^{23–27} We would like to point out two recent compre-hensive reviews^{28,29} on negative molecular ions where various theoretical techniques and applications were discussed.

In the present work, we set out to investigate the chemical bonding in the two intermediate sized Al-doped boron clusters: AlB_9^- and AlB_{10}^- . One should not expect that geometries of the aluminum-doped clusters are the same as the global minimum structures of unsubstituted ones. Although in this work we found that AlB_9^- has a similar geometry as that of B_{10}^- with one peripheral boron atom substituted by an aluminum atom, whereas AlB_{10}^{-} has a different geometry compared to B_{11}^{-} . The geometrical structures of anionic clusters were established by unbiased global minimum searches and comparison of the experimental (photoelectron spectroscopy) and theoretical photodetachment energies

EXPERIMENTAL SECTION

The experiment was performed using a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source, details of which have been published elsewhere.^{30,31} Briefly, AlB_x^{-1} (x = 9, 10) were produced by means of laser ablation

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Figure 1. Photoelectron spectra of $AlB_9at(a)$ 266 nm and (b) 193 nm photodetachment wavelengths.

(532 nm) of a disk target made of isotopically enriched ¹⁰B (10%), Al (2.5%), balanced by Bi which acted as a target binder and, also, provided calibration for the photoelectron spectra. The clusters were entrained by a 5% Ar in He carrier gas and underwent a supersonic expansion to form a collimated molecular beam. The composition and the cooling of the clusters were controlled by the time delay between the carrier gas pulse and the ablation laser.^{32,33} The negatively charged clusters were extracted and analyzed with a Time-of-Flight Mass Spectrometer. The species of interest were mass-selected and decelerated before being photodetached by a pulsed laser beams at 193 nm (6.424 eV) or 266 nm (4.661 eV). Photoelectrons were collected at nearly 100% efficiency by a magnetic bottle and analyzed in a 3.5 m long electron flight tube. The resolution of the apparatus, $\Delta E/E$, was better than 2.5%, i.e., 25 meV for 1 eV electron.

THEORETICAL METHODS

The search for the global minima structures of the AlB₉⁻ and AlB_{10}^{-} clusters was performed using the Coalescence Kick (CK) program, written by Averkiev.³⁴ The program randomly generates a large number of structures which undergo a coalescence procedure during which all atoms are gradually pushed to the molecular center of mass to avoid generation of fragmented structures and then optimized to the nearest local minima. All CK calculations were performed using the B3LYP³⁵⁻³⁷ hybrid method with the $3-21\hat{G}^{38}$ basis set. The low-lying isomers were reoptimized with follow up frequency calculations at the B3LYP/ 6-311+G* level of theory.³⁹⁻⁴² In order to avoid high spin contamination at the UCCSD(T) method, single point energy calculations for the lowest isomers of AlB₉⁻ were performed using the restricted coupled cluster [RCCSD(T)] method⁴³⁻⁴⁵ with the 6-311+G(2df) basis set at the B3LYP/6-311+G^{*} optimized geometries. These calculations were performed with the Molpro program.⁴⁶ Single point calculations for the lowest energy structures for AlB_{10}^{-} were done with the Gaussian 03 software⁴⁷ using coupled cluster [RCCSD(T)] method and the 6-311+G(2df) basis set at the B3LYP/6-311+G* optimized geometries.

The VDEs were calculated using the RCCSD(T)/6-311+G-(2df) method, the restricted outer valence Green Function method [ROVGF/6-311+ G(2df)]⁴⁸⁻⁵¹ (for AlB₁₀⁻ only) and the time-dependent DFT method^{52,53} TD-B3LYP/6-311+G(2df) and TD-PBE1PBE/6-311+G(2df),^{54,55} all at B3LYP/6-311+G^{*}



Figure 2. Photoelectron spectra of AlB_{10}^{-} at (a) 266 nm and (b) 193 nm photodetachment wavelengths.

optimized geometries. The first two VDEs for the AlB₉⁻ were calculated at the B3LYP and PBE1PBE levels of theory as the transitions from the doublet ground state of the anion into the final lowest singlet and triplet states of the neutral species at the anion geometry. Then the vertical excitation energies of the neutral species (at the TD-B3LYP and TD-PBE1PBE levels) calculated for the singlet and triplet states were added to the two lowest VDEs with the singlet and triplet final states, respectively, to obtain the second and higher VDEs. Similarly, the first VDE for the AlB_{10}^{-} cluster was calculated at the B3LYP and PBE1PBE levels of theory as the lowest transition from the singlet state of the anion into the final lowest doublet state of the neutral AlB₁₀ species at the AlB_{10}^{-} optimized geometry. Then the vertical excitation energies of the neutral species (at the TD-B3LYP and PBE1PBE levels) were added to the first VDE to obtain the second and higher VDEs. Core electrons were frozen in treating the electron correlation at the CCSD(T) and ROVGF levels of theory.

Chemical bonding analysis was performed using the Adaptive Natural Density Partitioning (AdNDP) method recently developed by Zubarev and Boldyrev. 56-59 AdNDP is based on the concept of an electron pair as the main element of chemical bonding models. Thus, it represents the electronic structure in terms of *n*c-2e bonds. With *n* spanning the interval from one to the total amount of atoms in the particular atomic assembly, AdNDP recovers both Lewis bonding elements (1c-2e and 2c-2e objects, corresponding to the core electrons and lone pairs, and two-center two-electron bonds) and delocalized bonding elements, which are associated with the concepts of aromaticity and antiaromaticity. From this point of view, AdNDP achieves seamless description of systems featuring both localized and delocalized bonding without invoking the concept of resonance. Molecular structure visualization was done with the MOLDEN 3.4⁶⁰ and Molekel 5.4.0.8⁶¹ programs.

EXPERIMENTAL RESULTS

The photoelectron spectra of AlB_9^- and AlB_{10}^- are shown in Figures 1 and 2, respectively, each at 266 and 193 nm. Since better spectral resolution is obtained for low kinetic energy photoelectrons, i.e., near the excitation threshold of an electronic transition, we employ multiple photodetachment conditions to achieve spectra with enhanced electronic and vibrational resolution. The spectral bands were labeled with letters (X, A, B, C, ...)

			VDE (theoretical)		
feature	VDE $(exp.)^b$	final state and electronic configuration	TD-B3LYP ^c	TD-PBE1PBE ^d	$RCCSD(T)^e$
Х	3.15(5)	${}^{1}\!A_{\!,\!.\!.\!}9a^{(2)}10a^{(2)}11a^{(2)}12a^{(2)}13a^{(2)}14a^{(2)}15a^{(2)}16a^{(0)}$	3.08	3.21	3.01
А	3.36(4)	${}^{3}\!A_{\!,\!.\!.\!}9a^{(2)}10a^{(2)}11a^{(2)}12a^{(2)}13a^{(2)}14a^{(2)}15a^{(1)}16a^{(1)}$	3.28	3.33	3.43
		${}^{1}\mathbf{A},9a^{(2)}10a^{(2)}11a^{(2)}12a^{(2)}13a^{(2)}14a^{(2)}15a^{(1)}16a^{(1)}$	3.88	4.01	f
В	4.40(4)	${}^{3}\textbf{A},9a^{(2)}10a^{(2)}11a^{(2)}12a^{(2)}13a^{(2)}14a^{(1)}15a^{(2)}16a^{(1)}$	4.21	4.35	f
		${}^{1}A,9a^{(2)}10a^{(2)}11a^{(2)}12a^{(2)}13a^{(2)}14a^{(1)}15a^{(2)}16a^{(1)}$	4.59	4.79	f
С	4.79(5)	${}^{3}A$,9 $a^{(2)}10a^{(2)}11a^{(2)}12a^{(2)}13a^{(1)}14a^{(2)}15a^{(2)}16a^{(1)}$	4.70	4.78	f
D	4.91(5)	${}^{3}\textbf{A},9a^{(2)}10a^{(2)}11a^{(2)}12a^{(1)}13a^{(2)}14a^{(2)}15a^{(2)}16a^{(1)}$	4.82	4.93	f
		${}^{1}\mathbf{A},9a^{(2)}10a^{(2)}11a^{(2)}12a^{(2)}13a^{(1)}14a^{(2)}15a^{(2)}16a^{(1)}$	5.02	5.20	f
		${}^{1}\!A_{\!,\!.\!.\!}9a^{(2)}10a^{(2)}11a^{(2)}12a^{(1)}13a^{(2)}14a^{(2)}15a^{(2)}16a^{(1)}$	5.32	5.47	f
Е	5.36(5)	${}^{3}\textbf{A},9a^{(2)}10a^{(2)}11a^{(1)}12a^{(2)}13a^{(2)}14a^{(2)}15a^{(2)}16a^{(1)}$	5.36	f	f
		${}^{3}A_{\mu}$ 9 $a^{(2)}10a^{(1)}11a^{(2)}12a^{(2)}13a^{(2)}14a^{(2)}15a^{(2)}16a^{(1)}$	5.42	f	f
		${}^{1}\mathbf{A},9a^{(2)}10a^{(2)}11a^{(1)}12a^{(2)}13a^{(2)}14a^{(2)}15a^{(2)}16a^{(1)}$	5.78	5.96	f
		${}^{1}A_{\mu}9a^{(2)}10a^{(1)}11a^{(2)}12a^{(2)}13a^{(2)}14a^{(2)}15a^{(2)}16a^{(1)}$	5.95	f	f

Table 1. Experimentally Observed and Theoretically Calculated VDEs for the I.1 Isomer $(C_{11}^{2}A)$ of AlB₉^{-a}

^{*a*} All energies are in eV. ^{*b*} Numbers in parentheses represent the uncertainty in the last digit. ^{*c*} VDEs were calculated at TD-B3LYP/6-311+G(2df)// B3LYP/6-311+G*. ^{*d*} VDEs were calculated at TD-PBE1PBE/6-311+G(2df)//B3LYP/6-311+G*. ^{*c*} VDEs were calculated at RCCSD(T)/6-311+G(2df)//B3LYP/6-311+G*. ^{*f*} We were not able to calculate these VDEs at the TD-PBE1PBE/6-311+G(2df)//B3LYP/6-311+G*. ^{*f*} VDE value cannot be calculated at this level of theory.

Table 2. Experimentally Observed and Theoretically Calculated VDEs for II.1 Isomer $(C_{s}, {}^{1}A')$ of AlB₁₀^{-a}

			VDE (theoretical)			
feature	VDE $(exp.)^b$	final state and electronic configuration	TD-B3LYP ^c	TD-PBE1PBE ^d	ROVGF ^e	RCCSD(T) ^f
Х	3.61(5)	${}^{2}A''$, $5a''^{(2)}8a'^{(2)}6a''^{(2)}9a'^{(2)}10a'^{(2)}7a''^{(1)}$	3.51	3.61	3.52 (0.88)	3.67
А	3.78(5)	${}^{2}A'$, $5a''^{(2)}8a'^{(2)}6a''^{(2)}9a'^{(2)}10a'^{(1)}7a''^{(2)}$	3.55	3.55	3.79 (0.88)	3.80
В	4.26(5)	${}^{2}A'$, $5a''^{(2)}8a'^{(2)}6a''^{(2)}9a'^{(1)}10a'^{(2)}7a''^{(2)}$	4.09	4.19	4.24 (0.88)	g
С	4.91(5)	${}^{2}A''$, $5a''^{(2)}8a'^{(2)}6a''^{(1)}9a'^{(2)}10a'^{(2)}7a''^{(2)}$	4.74	5.00	5.11 (0.88)	g
D	5.31(5)	${}^{2}A'$, $5a''^{(2)}8a'^{(1)}6a''^{(2)}9a'^{(2)}10a'^{(2)}7a''^{(2)}$	5.23	5.44	5.51 (0.86)	g
		${}^{2}A''$, $5a''^{(1)}8a'^{(2)}6a''^{(2)}9a'^{(2)}10a'^{(2)}7a''^{(2)}$	5.89	5.96	6.29 (0.83)	g

^{*a*} All energies are in eV. ^{*b*} Numbers in parentheses represent the uncertainty in the last digit. ^{*c*} VDEs were calculated at TD-B3LYP/6-311+G(2df)// B3LYP/6-311+G*. ^{*d*} VDEs were calculated at TD-PBE1PBE/6-311+G(2df)//B3LYP/6-311+G*. ^{*c*} VDEs were calculated at ROVGF/6-311+G(2df)// B3LYP/6-311+G*. Values in parentheses represent the pole strength of the OVGF calculation. ^{*f*} VDEs were calculated at RCCSD(T)/6-311+G(2df)// B3LYP/6-311+G*. ^{*s*} VDEs were calculated at this level of theory.

and VDEs were given in Table 1 and 2. The X band represents the transition between the ground states of the anion and the neutral species, while the higher binding energy bands (A, B, ...) denote transitions to electronically excited states of the neutral.

 AlB_9^- . The 266 nm spectrum of AlB_9^- displays three wellresolved electronic bands (X, A, B), with no apparent vibrational structure. The measured VDEs of the first two bands are closely spaced in values, 3.15 ± 0.05 eV (X band) and 3.36 ± 0.04 eV (A band), which indicate possible electronic transitions from a ground doublet anionic state to singlet and triplet neutral ground state. For the third band, B, we measured a VDE of 4.40 \pm 0.04 eV. In addition to the features revealed by the 266 nm spectrum, three more features are identified in the 193 nm PES (C-E). The VDEs values are summarized in Table 1. All spectral features identified in the PES (X, A-E) are slightly broad, indicating some degree of geometry change between the ground state of AlB₉⁻ and respective states of the AlB₉. The absence of any resolved vibrational structure, especially for the near-threshold bands, B at 266 nm and E at 193 nm, suggests that low energy vibrational modes might be active in the photodetachment transitions. No spectral features were observed beyond 5.5 eV.

AlB₁₀⁻. At 266 nm, the PES shows also three peaks without resolved vibrational structures. The first two peaks, with VDEs of $3.61 \pm 0.05 \text{ eV}$ (X) and $3.78 \pm 0.05 \text{ eV}$ (A) are not well resolved. The third peak, B, is broader and has a measured VDE value of $4.26 \pm 0.05 \text{ eV}$. In addition to these features, we note the presence of a small feature at the low binding energy side of the X peak. The presence of this feature prevents us from measuring the ADE value for the X transition, for which we estimate a threshold value of $3.4 \pm 0.1 \text{ eV}$. Since the expansion conditions were identical to those used to create the AlB₆⁻ and AlB₁₁⁻ clusters, which were shown to be vibrationally cold, ¹⁹ we believe that this feature should be attributed to higher energy metastable isomers of AlB₁₀⁻ rather than vibrational hot bands. Another two electronic transitions, C and D, are identified in the 193 nm spectrum. The VDEs values are summarized in Table 2. Similarly to the AlB₉⁻ spectrum, no spectral features were observed beyond 5.5 eV.

THEORETICAL RESULTS

AlB₉⁻. The lowest-lying isomers of AlB₉⁻ ($\Delta E < 20$ kcal/mol) revealed by the CK global minimum search at the B3LYP/3-21G



Figure 3. Isomers of the AlB_9^- cluster, their point group symmetries, spectroscopic states, and relative energies. Relative energies are given at the RCCSD(T)/6-311+G(2df)//B3LYP/6-311+G^{*} and the B3LYP/6-311+G^{*} (in brackets) levels of theory. All of the relative energies are ZPE corrected.

level of theory were then reoptimized at B3LYP/6-311+G^{*} and single point energy calculations were performed for the isomers at RCCSD(T)/6-311+G(2df) on the B3LYP/6-311+G^{*} geometries. The global minimum structure and four lowest isomers are presented in Figure 3.

According to the computational results at our highest level of theory (RCCSD(T)/6-311+G(2df)//B3LYP/6-311+G*) structure I.1 is the global minimum and the other low-lying isomers I.2, I.3, I.4, and I.5 are 8.3, 10.6, 11.7, and 16.7 kcal/mol higher in energy, respectively. It is interesting to compare these results with those obtained at the same level of theory for the neutral AlB₉ cluster.²⁴ The structures of the five low-lying isomers of AlB₉ are similar to those found for the AlB₉⁻ anion, however, the order of the isomers is different. Two almost degenerate isomers were found for the neutral AlB₉ cluster: one similar to the global minimum I.1 of AlB₉⁻ and another similar to the wheeltype isomer I.5 of AlB₉⁻, whereas, the global minimum isomer I.1 of AlB_9^- is significantly lower in energy than the wheeltype structure I.5. Thus, addition of an extra electron substantially altered the relative stability of one of the two practically degenerate lowest isomers.

AlB₁₀⁻. We applied a similar global minimum search approach for AlB₁₀⁻, which revealed the presented (Figure 4) order of isomers with the structure II.1 being significantly lower in energy than other isomers. The second lowest-lying isomer II.2 was found to be 7.7 kcal/mol higher in energy than the global minimum II.1.

INTERPRETATION OF THE PHOTOELECTRONIC SPECTRA

AlB₉⁻. The global minimum isomer I.1 is significantly lower in energy than the other isomers, therefore, only isomer I.1 contributes to the experimental PES of AlB_9^- . The calculated VDEs for I.1 at three levels of theory compared with the experimental results are presented in Table 1. We do not report here VDEs calculated at UOVGF/6-311+G(2df)//B3LYP/6-311+G^{*} due to high spin contamination.



Figure 4. Isomers of the AlB_{10}^{-} cluster, their point group symmetries, spectroscopic states, and relative energies. Relative energies are given at the RCCSD(T)/6-311+G(2df)//B3LYP/6-311+G^{*} and the B3LYP/6-311+G^{*} (in brackets) levels of theory. All of the relative energies are ZPE corrected.

The first calculated VDE corresponds to the electron detachment channel from HOMO leading to the final singlet state. The calculated VDEs of 3.01 eV (RCCSD(T)), 3.08 eV (B3LYP), and 3.21 eV (PBE1PBE) correspond to the experimental feature X at 3.15 eV. The second VDE can be assigned to the detachment channel from HOMO-1 leading to the final triplet state. Again, all three theoretically calculated values: 3.43 eV (RCCSD(T)), 3.28 eV (B3LYP), and 3.33 eV (PBE1PBE) are in agreement with the experimental VDE of 3.36 eV (feature A). Higher intensity of the feature A compared to the feature X is consistent with the triplet nature of the second final state since transitions into triplet states are usually more prominent in the experimental photoelectron spectra than those for singlet final state. Therefore, we will further discuss only transitions leading to the final triplet states. The next transition into the second triplet state can be calculated only with TD-DFT methods and the theoretical values of 4.21 eV (B3LYP) and 4.35 eV (PBE1PBE) are consistent with the experimental feature B at 4.40 eV. The third and fourth transitions into the triplet states at 4.70 and 4.82 eV (B3LYP) and 4.78 and 4.93 eV (PBE1PBE) correspond to the features C and D in the experimental spectrum. Finally, two other transitions into the triplet states at 5.36 and 5.42 eV (B3LYP) are responsible for the experimental feature E.

Overall, the experimental data are in excellent agreement with the detachment transitions theoretically calculated for the isomer I.1, clearly confirming that this isomer is the global minimum for the AlB_9^- cluster.

 AlB_{10}^{-} . The global minimum isomer II.1 was found to be significantly more stable than any other isomer of AlB_{10}^{-} and thus, only II.1 is responsible for the experimental PES. The theoretical and experimental data are summarized in Table 2.

Since the AlB_{10}^{-} anion is a closed-shell system single electron detachments lead only to doublet final states. The first calculated VDE corresponds to electron detachment from HOMO (7a"). The theoretical values 3.67 eV (RCCSD(T)), 3.52 eV (ROVGF), 3.51 eV (B3LYP), and 3.61 eV (PBE1PBE) are all congruent to the experimental feature X at 3.61 eV. The second VDE can be assigned to an electron detachment from HOMO-1 (10a'). Although the calculated values at B3LYP (3.55 eV) and PBE1PBE



Figure 5. Chemical bonding elements revealed by AdNDP (B3LYP/6-311+G*) for the AlB₉²⁻ (C_1 , ¹A) at the geometry optimized for the global minimum structure I.1 of the AlB₉⁻ (C_1 , ²A) cluster.

(3.55 eV) are appreciably lower than the experimental value of 3.78 eV (feature A), the VDEs at RCCSD(T) (3.80 eV) and ROVGF (3.79 eV) are in excellent agreement with it. The next feature B at 4.26 eV can be explained by the detachment of an electron from HOMO-2 (9a'). Indeed, the theoretical results at all three levels B3LYP (4.09 eV), PBE1PBE (4.19 eV), ROVGF (4.24 eV) are very close to the experimental value. The feature C at 4.91 eV can be assigned to the electron transition from HOMO-3 (6a''). Theoretically calculated values 5.11 eV (ROVGF) and 5.0 eV (PBE1PBE) are in a good agreement with the experimental value while the VDE B3LYP (4.74 eV) is somewhat lower in energy. The calculated VDE values for transition from HOMO-4 (8a') of 5.51 eV (ROVGF) and 5.44 eV (PBE1PBE) are congruent with the experimental VDE feature D at 5.31 eV. The calculated VDE at B3LYP (5.23 eV) is again lower than the experimental value. One can see that application of several theoretical methods is required in order to make a solid assignment of the experimental peaks in the AlB_{10}^{-} PES. One method would not be reliable enough to get a clear picture. The global minimum II.1 for the AlB_{10}^{-} cluster was confirmed by the overall agreement between the experimental data and the calculated VDEs.

CHEMICAL BONDING ANALYSIS

AlB₉⁻. Let us first analyze chemical bonding in the global minimum structure I.1. In order to avoid complications due to spin polarization we performed the AdNDP analysis (at B3LYP/ 6-311+G^{*}) for the doubly charged anion AlB₉²⁻ (C_{11} , ¹A) at the geometry optimized (B3LYP/6-311+G^{*}) for AlB₉⁻. Results of the AdNDP analysis are presented in Figure 5. Six B–B and one Al–B 2c-2e σ -bonds with ONs ranging from 1.70 |e| (Al–B) to 1.96 |e| were revealed by AdNDP. There are also five delocalized

Figure 6. AdNDP analysis (B3LYP/6-311+G^{*}) of the AlB₉²⁻ ($C_{2\nu\nu}$ ¹A₁) at the geometry optimized for the isomer I.5 of the AlB₉- ($C_{2\nu\nu}$ ²A₁) cluster.

" σ -bonds", which are responsible for its " σ -aromaticity" and three delocalized " π -bonds", which are responsible for its ' π -aromaticity". We would like to stress here that the cluster is not planar, therefore, our assignment of delocalized bonds to σ and π -types is approximate, yet, we believe that recognizing its σ and π -aromaticity is a useful tool for the explanation of chemical bonding and stability of this cluster. Finally, the AdNDP analysis revealed a lone pair on the aluminum atom with ON of 1.77 |e|. Although we consider this global minimum structure as doubly aromatic, it is not a planar structure. We believe that the reason for the nonplanarity of I.1 is of a mechanical nature: the cavity inside of the eight member external ring is two small to comfortably accommodate two boron atoms. Our analysis was performed for the doubly charged anion AlB₉²⁻, but the assessment of aromaticity is valid for AlB₉⁻ too because the electron is removed from the aluminum lone pair.

It was mentioned above that the isomers found before^{24,26} for the neutral AlB₉ cluster similar to I.1 and I.5 of the AlB₉⁻ anion are nearly degenerate and yet for the anion we observe that the wheel-type structure I.5 is significantly less stable than the global minimum structure I.1. In order to explain the higher energy difference between the anions compared to the neutral clusters we performed the AdNDP analysis of the wheel-type isomer I.5. Again, in order to avoid spin-polarization we analyzed the doubly charged anion AlB₉⁻ ($C_{2\nu}$, ¹A₁) at the geometry optimized for the wheel-type isomer I.5 of AlB₉⁻. The bonding pattern revealed is shown in Figure 6.

According to this analysis, AlB_9^{2-} has nine peripheral 2c-2e B-B σ -bonds and four delocalized σ -bonds, making this cluster σ -antiaromatic and three delocalized π -bonds responsible for π -aromaticity in this cluster. Thus, the doubly charged anion exhibits conflicting aromaticity. The neutral AlB_9 (D_{9hn} ¹A₁') cluster is a doubly aromatic system with six delocalized σ - and six



Figure 7. AdNDP analysis (B3LYP/6-311+G^{*}) of the global minimum isomer II.1 ($C_{sr}^{-1}A'$) of AlB₁₀⁻.

delocalized π -electrons,^{24,26} therefore, the AlB₉⁻ cluster with five delocalized σ -electrons and six delocalized π -electrons is 1/2- σ -antiaromatic⁶² and π -aromatic. However, the AdNDP analysis of the neutral AlB₉ C_1 isomer revealed a bonding pattern similar to that of the doubly charged anion, but without the sp-LP on aluminum. Thus, the addition of two extra electrons does not disturb the σ - and π -aromaticity, but leads to the formation of a lone pair on aluminum atom. We believe that the increase in energy difference between the I.1 and I.5 anionic structures is due to the fact that the addition of an extra electron to the neutral double aromatic C_1 structure does not disturb its doubly aromatic nature (the electron is localized on the aluminum atom), whereas, the electron added to neutral wheel-type structure leads to the formation of π -aromatic but 1/2- σ -antiaromatic AlB₉⁻ anion.

AlB₁₀⁻. AdNDP for the AlB₁₀⁻ global minimum structure II.1 (Figure 7) revealed a lone pair on aluminum atom with ON=1.87 [e], eight peripheral 2c-2e B–B σ -bonds with ON = 1.80–1.94 [e], five delocalized ' σ -bonds' responsible for ' σ -aromaticity' and three delocalized " π -bonds" responsible for " π -aromaticity". Again, since the cluster is not planar, the assignment of delocalized bonds to σ - and π - can be done only approximately, though, we believe that recognizing its σ - and π -aromaticity is a useful tool for explanation of chemical bonding and stability of this cluster. Thus, the global minimum structure of the AlB₁₀⁻ cluster is approximately a doubly (σ - and π -) aromatic system. Again, we believe that the reason for nonplanarity is mechanical, since the external ring of eight boron atoms is not large enough to accommodate two internal boron atoms.

CONCLUSIONS

In this joint photoelectron and ab initio work, we probed the structures and the chemical bonding of the AlB_9^- and AlB_{10}^-

clusters. Well-resolved photoelectron spectra were recorded and compared with the theoretically calculated VDEs. Global minimum structures of both anions were established through CK search at B3LYP/3-21G with follow up geometry optimization of the lowest isomers at B3LYP/6-311+G*. The final conclusion on the global minimum structures was based on CCSD(T)/6-311+G(2df)//B3LYP/6-311+G* calculations. VDEs were calculated at the RCCSD(T)/6-311+G(2df), ROVGF/6-311+G(2df), TD-B3LYP/6-311+G(2df), and TD-PBE1PBE/6-311+G(2df), all at the B3LYP/6-311+G* optimized geometries. Good agreement between theoretical and experimental VDEs confirmed the computationally predicted global minimum structures. We found that the nona-coordinated wheel-type structure for AlB₉⁻ is not a global minimum and it is not even a low-lying isomer as was previously found for the neutral AlB9 cluster. We have shown that this is due to the 1/2- σ -antiaromatic nature of the anionic wheeltype structure. However, addition of an extra electron to the C_1 global minimum structure of the neutral AlB₉ cluster does not disturb its double (σ - and π -) aromaticity since the electron is localized on aluminum atom. Thus, the similar C_1 isomer I.1 is the global minimum of the anionic AlB₉⁻ cluster. The global minimum of the AlB₁₀⁻ cluster was also shown to represent a doubly (σ - and π -) "aromatic" system.

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