Research paper

Geometry and bonding of small binary boron-aluminum clusters B_nAl_n ($n = 1-7$): Electron donation and interlocking aromaticity

Dang Thi Tuyet Mai^d, Hung Tan Pham^c, Nguyen Minh Tam^{a,b}, Minh Tho Nguyen^{a,b,d,*}

^a Computational Chemistry Research Group, Ton Duc Thang University, Ho Chi Minh City, Viet Nam

^b Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Viet Nam

^c Institute for Computational Science and Technology, Ho Chi Minh City, Viet Nam

^d Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

HIGHLIGHTS

- B and Al atoms do not mix together but prefer to be assembled in two separated B_n and Al_n components.
- The B_n moiety in a binary B_nAl_n system prefers a quasi-planar geometry as in pure B_n clusters.
- Electron transfer induces strong electrostatic interaction $B_n^{\delta-} \cdot Al_n^{\delta+}$ for B_nAl_n clusters.
- The Al_7B_7 cluster exhibits a double B_7 and Al_7 layer structure.
- Two electron flows in B_4Al_4 are interlocking with each other and independent on each other.

ABSTRACT

Binary B_nAl_n clusters ($n = 1-7$) were investigated using both DFT/TPSSH and G4 calculations. B and Al atoms do not mix together but prefer to be assembled in two separated but interacting B_n and Al_n components. Large electron donation from Al to B atoms induces a donor-acceptor stabilization. Planar B_3Al_3 is a σ aromatic compound. B_4Al_4 exhibits two aromatic electron flows that are interlocking in two perpendicular planes and circulate independently. The B_7Al_7 cluster appears as a double layer structure and this suggests formation of B_n and Al_n layers in larger clusters connected by electrostatic interactions.

1. Introduction

During the past decades, the field of cluster science has gained much attention of experimental and theoretical scientists alike. Not only particular geometries but also non-conventional chemical bonding characters have continuously been, and still are, revealed. Knowledge on geometry and chemical bonding of atomic clusters is necessary for the design of novel building blocks, as well as on how these units interact with each other [1–5] in such a way that significantly novel kinds of 2D and 3D materials can be proposed for synthesis [6–9].

There has been considerable interest in the clusters of both boron (B) and aluminum (Al) atoms, the first two elements of Group IIIA of the Periodic Table. Although both B and Al atoms share a similar valence shell of $(ns^2 np^1)$, their clusters are quite different from each other in terms of shape and bonding. With a size n starting from 6 atoms, Al_n clusters have tendency to form icosahedral shape, whereas geometry of boron B_n clusters follows a fluctuation between planar, tubular, bowl, cage and fullerene... [10–12].

Of the Al-based clusters, the anion Al_{13}^- is regarded as a typical

example for special feature of bonding pattern where formation of closed electron shell gives rise to a high thermodynamic stability. In an I_h (or O_h) geometry, each Al atom provides three valence electrons, in combination with one extra electron, to form a closed electron shell of $[1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^6 \dots]$ containing 40 electrons [10,11]. Such a stabilizing mechanism has a profound impact on the design of novel materials, particularly magnetic superatom based materials [1,2,12–15]. Generated upon removal of one electron from the anion Al_{13}^- , the neutral Al_{13} was shown to be a superhalogen having a large electron affinity exceeding those of halogen atoms. Such a behaviour does not emerge for the boron counterpart. $B_{13}^{-/0/+}$ are unusually stable in a planar form, whereas an icosahedral B_{13} structure having the Al_{13}^+ shape is highly unstable. Some careful investigations using various approaches including topology resonance energy (TRE) [16], atom in molecule theory (AIM) [17], electron localization function (ELF) [18] and ring current calculation [19] on bonding of B_{13}^+ pointed out that a double aromaticity in which both π and σ aromaticity have significant contributions, is regarded as a driving force to establish a B_{13}^+ planar structure.

* Corresponding author at: Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium.

E-mail addresses: nguyenminhtho@tdtu.edu.vn, minh.nguyen@kuleuven.be (M.T. Nguyen).

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Such differences in geometry and bonding between B and Al clusters give us a motivation to look further at binary boron-aluminum systems. On the basis of mass spectra of Al_nB_m^- anions ($n = 5\text{--}30$, $m = 0\text{--}3$) [20] and photoelectron spectra of $\text{Al}_{n-m}\text{B}_m^-$ anions ($n \geq 5$ for $m = 1$ and $n \geq 10$ for $m = 2$) along with quantum chemical computations [21], the anion Al_{12}B^- was suggested to exhibit a structure and an enhanced stability similar to those of Al_{13}^- . It was characterized by a closure of the 2P electron shell and a close-packing icosahedral motif [20,21]. Additionally, a theoretical study on doubly B-doped $\text{Al}_n\text{B}_2^{0/-}$ clusters with $n = 1\text{--}7$ showed that two B atoms consistently connect with each other to form a B-B bond and thereby becomes a dominant contributor to the geometry of $\text{Al}_n\text{B}_2^{0/-}$ series [22,23]. Regarding boron clusters, introduction of Al dopant does not induce significant modification in geometry as indicated by previous investigations. With sizes up to 14 boron atoms, $\text{Al}_x\text{B}_n^{0/-}$ with $x = 1, 2$, stable structures tend to be formed by addition of Al into various positions of B_n , or by substitution of one B atom by one Al counterpart [24–29].

Previous studies [24–29] also showed that on the one hand, Al-dopants give a charge transfer to boron counterparts, and on the other hand, Al atoms tend to connect with B_n through electrostatic interaction. Motivated by geometrical differences of B_{13} and Al_{13} , the series of $\text{Al}_{13-x}\text{B}_x$ clusters was explored [30]. Accordingly, the B_x counterpart dominates the geometry of $\text{Al}_{13-x}\text{B}_x$ clusters. Another examination of the dianions $\text{B}_n\text{Al}_{6-n}^{2-}$ in going from B_6^{2-} to Al_6^{2-} suggested that the covalency tends to govern the cluster shape. In fact, covalent bonds can only be achieved through $s\text{--}p$ hybridization in direct B-B interaction which induces delocalization and then favours a planar form [31]. Most previous studies on Al-B clusters were thus mainly focused on the doping effects of either B or Al atom on clusters of the other element while the structural transition as well as the growth mechanism of such binary B_nAl_n systems, which is of fundamental interest, have not been considered in detail yet. In this context, a legitimate question emerges about the behaviour of binary B-Al clusters having the same number of B and Al atoms. Motivated by these issues and insights into the structural pattern of B-Al mixture, we set out to carry out an investigation on a series of small B_nAl_n clusters in the neutral state using quantum chemical methods. In this paper, we report on peculiar aspects of a few small mixed clusters B_nAl_n with n going from 1 to 7, with regard to their structural characteristics as well as the bonding in some remarkable systems. This series of small mixed clusters could be served for an understanding of the growth pattern of larger binary B-Al systems.

2. Computational methods

In order to explore the potential energy surfaces of B_nAl_n clusters, all possible initial B_nAl_n isomers are generated using a stochastic genetic algorithm [32], and then rapidly optimized using density functional theory (DFT) with the TPSSH functional [33], in conjunction with the 6–31G(d) basis set. In another way, a series of possible B_nAl_n structures are manually constructed by either combining pure B_n and Al_n clusters or replacing n B atoms of the B_{2n} skeleton by n Al atoms at different positions, and vice versa, or attaching one BAl unit into a known $\text{B}_{n-1}\text{Al}_{n-1}$ cluster. Geometries and harmonic vibrational frequencies of the lower-lying B_nAl_n isomers are further determined using the same TPSSH functional but with the larger 6–311 + G(d) basis set [34]. The TPSSH functional was abundantly calibrated and shown to provide reasonable relative energies for boron isomers when compared to results obtained using the coupled-cluster theory CCSD(T) method [35,36]. However, in order to confirm the global minima of clusters considered, energies of some lowest-lying geometries obtained from TPSSH/6–311 + G(d) computations are refined using the composite G4 method [37]. Bonding characteristics are subsequently examined using the electron localization function (ELF) technique [38]. Aromatic character is explored by using the magnetic ring current technique [39,40]. Geometry optimizations and NBO calculations are performed using the Gaussian 09 package [41].

Fig. 1. Shapes and symmetry point groups of the lowest-lying structures of B_nAl_n ($n = 1\text{--}7$) using TPSSH and B3LYP (in G4 method) functionals.

3. Results and discussion

We first describe specific geometric aspects of B-Al clusters, followed by an analysis of some remarkable bonding features of the B_3Al_3 , B_4Al_4 and B_7Al_7 systems.

3.1. Structure of B_nAl_n clusters

The shape and symmetrical point group of both series of neutral B_nAl_n clusters are depicted in Fig. 1. For the purpose of comparison, the shape of pure B_n and Al_n clusters are also given. Each structure considered in the following sections is designated by the letters and numbers $n.Y$ in which $n = 1\text{--}7$ is the number of B or Al atoms and $Y = 1, 2, \dots$ indicates the ordering of isomers in terms of relative stability with respect to the lowest-lying isomer $n.1$. For simplicity in the presentation of results, these structures are displayed in Fig. S1 of the Supplementary Information (SI) file. Table S1 (SI file) lists the Cartesian coordinates of the lowest-lying isomers $n.1$. In what follows, relative

energies, when mentioned, are invariably referred to the **n.1** isomer (reference at 0 kcal/mol) and obtained at the G4 level.

Let us note that in the G4 composite method, geometries are optimized using the B3LYP functional. In general, there is no significant difference between TPSSh and B3LYP geometries for the species considered. The bond distances quoted in following sections are taken from TPSSh computations. Both DFT/TPSSh and G4 energetic results are also internally consistent showing that at all sizes, the ground electronic state of all neutrals considered has a low spin multiplicity, namely a closed-shell singlet state for a neutral.

BAl. For the simplest mixed dimer BAl, the ground state neutral ($C_{\infty v}$) is in high-spin triplet, in agreement with previous reports [42,43]. The singlet-triplet energy gaps amount to 14, 11 and 6 kcal/mol (G4 values) in going from B_2 to BAl and to Al_2 , respectively. Thus, replacement of B by Al tends to decrease the S-T energy separation.

B_2Al_2 . For B_2Al_2 neutrals, the most stable **2.1** (C_{2v}) is a skewed rhombus around the B-B bond, in which two Al atoms, whose Al-Al distance amounts to 2.54 Å, are apparently added into two different sides of the B_2 bond (1.49 Å). This result is consistent with that of Loukhovitski and coworkers [44], but different from a planar rhombus (D_{2h}) advocated by Jiang *et al.* [23]. The planar rhombus is characterized as a second-order saddle point having two imaginary frequencies. The energy difference between both skewed and planar forms amounts however to only ~3 kcal/mol indicating a rather fluxional species.

B_3Al_3 . The high symmetry and planar configuration **3.1** (D_{3h}) is found to be the global minimum. A similar shape was previously found for the dianion $B_3Al_3^{2-}$ [31]. The shape of **3.1** can be regarded arising from insertion of a B_3 unit into an Al_3 unit inducing a breaking of all Al-Al bonds, or from capping of three Al atoms on the edges of a B_3 triangle. In each configuration, B atoms create an equidistant triangle whose B-B distance is ~1.65 Å, which is longer than B-B distance in pure clusters, being 1.62 Å in B_2 and of 1.55 Å in B_3^- . Three Al atoms are symmetrically located around the B_3 triangle with B-Al distances of 2.12 Å, which is somewhat longer than the B-Al distance of 2.03 Å in the dimer BAl. The Al-Al distance is stretched now to 4.26 Å, being thus much longer than that of 2.75 Å in Al_2 .

In a previous study, **3.2** (C_s) displayed in Fig. S1, which is an opened B_3 triangle with three surrounding Al atoms, was reported as the lowest-lying isomer of B_3Al_3 [31]. Our G4 calculations predict instead that **3.2** becomes the second most stable isomer but with a small energy gap of ~2 kcal/mol. Within the expected accuracy of the G4 methods, being ± 2 kcal/mol, both structures can in fact be considered as isoenergetic.

B_4Al_4 . Using molecular dynamics simulations within the DFT framework, Chacko *et al.* reported that an Archimedean antiprism constructed by a pair B and Al is the most stable form of the neutral B_4Al_4 [45]. Our G4 results do not support for such assignment, but instead emphasize the high symmetry **4.1** (D_{2h}) which is composed of an Al_4 rhombus perpendicular to a B_4 rectangle. This is in contrast with the shape of two separated tetramers in which B_4 is a planar rhombus whereas Al_4 is a square (cf. Fig. 1). In fact, B-B distances in **4.1** become now short (1.62 Å) and long (2.33 Å), and Al-Al distances are stretched to 3.02 Å, whereas B-Al distances of 2.06 and 2.21 Å remain short.

B_5Al_5 , B_6Al_6 and B_7Al_7 : Formation of double layer structure. As shown in Fig. 1, Al_5 and B_5 clusters share similar geometric characteristics, namely a planar C_{2v} symmetry. Interestingly, our calculations find that the B_5 unit still maintains its shape in Al_5B_5 . The lower-lying isomers of B_5Al_5 are clearly formed upon population of five Al atoms around the most stable B_5 structure, as given in Fig. S1 of ESI file. Among them, **5.1** (C_1) is identified as the ground state of B_5Al_5 . Actually, this structure is totally different from both Al_{10} and B_{10} geometries. On the other hand, Al_5B_5 cluster is neither a substitution of five B atoms of B_{10} nor that of five Al atoms of Al_{10} .

The stable isomers of B_6Al_6 show a particular behaviour of Al_6 and B_6 clusters when they combine together to establish B_6Al_6 cluster. The most stable isomer **6.1** of B_6Al_6 is definitely viewed as a double layer

including B_4 planar shape and Al_6B_2 layer (Fig. 1). A double layer structure is observed for **6.2** which is constructed by B_6 and Al_6 planes. The appearance of **6.1** and **6.2** illustrates that substitution by Al or B atoms in B_{12} or Al_{12} is not a significant pathway to release B_6Al_6 , but by contrast the B_6Al_6 cluster is dominated by a special form, namely a double layer structure.

Concerning the B_7Al_7 cluster, our intensive calculations demonstrate that the double layer form is again favoured. In lower-lying isomers including **7.1**, **7.2** and **7.3** the B_7 moiety is the same as the free B_7 cluster, and the most stable structure has the highest symmetry. Within **7.1**, seven Al atoms establish a planar shape being similar to the B_7 , and then they combine together along the C_6 axis connecting two central B and Al atoms giving rise to the most stable structure **7.1** of B_7Al_7 . The 3D geometry character of free Al_7 (Fig. 1) shows that B_7Al_7 is not formed by combination of two most stable B_7 and Al_7 clusters. Similarly, substitution of the fullerene B_{14} and the cage Al_{14} does not induce the geometry of mixed B_7Al_7 .

The stable structures of B_5Al_5 , B_6Al_6 and particularly the appearance of the double layer B_7Al_7 present novel structural motifs for doped boron clusters. Within each structure, the boron counterpart maintains planar shape as in pure B_n clusters, and it induces a planar shape for Al_n moieties, and finally, combination of two planar forms gives rise to double layer B_nAl_n structures.

The B_7Al_7 is in relation with single layer boron sheet which has recently been synthesized with silver substrate [46]. Concerning the latter boron sheet, it is constructed by B_7 as well as B_6 units, that are exactly similar to the B_7 and B_6 moieties of B_7Al_7 and B_6Al_6 . On the other hand, B_7Al_7 and B_6Al_6 clusters can also be viewed as building units of boron sheet on aluminum substrate.

Overall, a particular feature of the mixed clusters is that B and Al atoms do not mix together but prefer to be assembled in two separate B_n and Al_n components. This is due to the inherently weak overlap between $2p(B)$ and $3p(Al)$ orbitals to make B = Al double bond. Such a situation is similar to the low stability of C = Si and C = P compounds because of the reluctance of third-row elements to form double bond with second-row counterparts.

3.2. Relative stability of clusters

To probe the relative stability of $B_nAl_n^{0/-}$ clusters, the average binding energy (E_b) and the cluster mixing energy (E_{mix}) [47] are determined. These energetic parameters can be defined in Eqs. (1) and (2):

$$E_b(B_nAl_n) = [nE(B) + nE(Al) - E(B_nAl_n)]/(n + n) \quad (1)$$

$$E_{mix} = E(B_nAl_n) - [E(B_n/B_nB_n) + E(Al_n/Al_nAl_n)] \quad (2)$$

where $E(B)$ and $E(Al)$ are total energies of the B-atom and Al-atom. $E(B_nAl_n)$, $E(B_n/B_nB_n)$, and $E(Al_n/Al_nAl_n)$ are total energies of B_nAl_n cluster, B_n subcluster in the B_nB_n cluster and Al_n subcluster in the Al_nAl_n cluster, respectively. All of these energetic values are obtained using G4 energies.

The values of the average binding energy (E_b) of B_nAl_n systems are summarized in Table 1. At the first glance, the E_b curves tend to be increased consistently with increasing cluster sizes. The average binding energy increases rapidly from BAl to B_4Al_4 and slightly from B_5Al_5 to B_7Al_7 to attain a certain limit, and gets the highest value at $n = 7$ indicating its high thermodynamic stability.

The relative stability of B_nAl_n clusters as expressed by cluster mixing energy (E_{mix}) is also examined and displayed in Table 1. The E_{mix} values of B_nAl_n systems reveal that B_6Al_6 is characterized by the lowest E_{mix} value and thus expected to exhibit the high degree of mixing of the two types of atoms (B and Al).

Consideration of the kinetic stability of B_nAl_n clusters is relied on the HUMO-LUMO gaps (HLG) of the closed-shell systems, which are obtained using TPSSh/6-311 + G(d) level and given in Table 1. In the

Table 1

Average Binding Energies (E_b , eV), Cluster Mixing Energies (E_{mix} , eV) (G4 approach), HOMO-LUMO Gaps (HLG, eV), Vertical Ionization Energies (VIE, eV), and Vertical Electron Affinities (VEA, eV) (TPSSH/6–311 + G(d)) of B_nAl_n Clusters ($n = 1–7$) Calculations.

n	E_b	E_{mix}	HLG	VIE	VEA
1	0.92	−1.85	–	7.83	1.64
2	2.48	−6.56	0.96	6.99	2.35
3	2.99	−6.63	1.36	6.73	2.41
4	3.57	−7.07	1.66	7.11	2.25
5	3.43	−7.65	1.28	6.98	2.55
6	3.62	−11.04	1.92	7.00	2.17
7	3.64	−8.55	1.00	6.12	2.20

series of clusters selected, B_6Al_6 has the largest gap of 1.9 eV.

Vertical ionization energy (VIE) and electron affinity (VEA) can also be considered as a measure of stability of a neutral and anionic species, respectively. Accordingly, a stable neutral with respect to electron rejection is identified with a high VIE value, whereas with a low VEA, the neutral dislikes to capture an electron. The values for both quantities are defined as:

$VIE = E(\text{cation at the geometry of a neutral ground state}) - E(\text{ground state of a neutral})$

$VEA = E(\text{ground state of a neutral}) - E(\text{anion at the geometry of a neutral ground state})$ are obtained from TPSSH/6–311 + G(d) level and summarized in Table 1. Within the series considered, BAl , B_4Al_4 and B_6Al_6 clusters are more stable with respect to electron detachment and attachment, due to having high VIE and low VEA. This observation is consistent with the above discussion.

3.3. Bonding phenomenon and aromaticity in B_3Al_3 and B_4Al_4

With high symmetry geometry and thermodynamic stability, both neutrals B_3Al_3 **3.1** and B_4Al_4 **4.1** deserve a further analysis of their electronic structure and bonding. To probe the stability of boron clusters, aromaticity is often used as a typical indicator. This aspect is analyzed using the magnetic ring current maps (Figs. 2 and 5) and a topological analysis of their electron localization function (ELF, Fig. 4).

As given in Fig. 2a, a diatropic current density map is clearly found for σ electrons of B_3Al_3 **3.1** whereas the ring current of π electrons is not significant. Contributions of different MOs to the ring current flows of **3.1** are displayed in Fig. S2 (SI file). Previous calculations showed that the $B_3^{-/+}$ clusters are doubly aromatic [19]. Formation of B_3Al_3 thus reduces the π aromatic feature of B_3 unit. A similar trend was observed for $[B_3(CO)_3]^+$ and $[B_3(NN)_3]^+$ where two delocalized π electrons do not produce a significant ring current flow [48,49].

A geometry similar to **3.1** was previously found for the dianion $B_3Al_3^{2-}$ in which the three Al atoms give a significant charge transfer to the B_3 moiety. However, the ring current flow performed for the $Al_3B_3^{2-}$ dianion cluster (Fig. S3 of SI file) illustrates that the dianion $B_3Al_3^{2-}$ could better be classified as non-aromatic, according to the responses of its total current density with respect to a magnetic field. Consideration of orbital contributions to the current density shows that the HOMO of $B_3Al_3^{2-}$ produces a strong paratropic current density whereas the delocalized HOMO-2 induces a diatropic ring current flow (Fig. S3 of SI file). In comparison to the neutral B_3Al_3 , the σ aromaticity of the dianion $B_3Al_3^{2-}$ is reduced rather than enhanced.

The geometry of **4.1** is of particular interest. The neutral Al_4 is stable in a D_{4h} ($^3B_{1u}$) shape with Al–Al bond length of 2.56 Å and a Wiberg bond order of 1.1, while the neutral B_4 has a singlet D_{2h} form with bond length of 1.53 Å and bond order of 1.5. Within **4.1** structure, B–B connections become longer than that of the B_4 ground state with bond length of 1.62 Å and bond order of 1.3. For new Al–B connections, their bond lengths and orders are identified as 2.10 Å and 0.7, and 2.21 Å and 0.4. The Al–B bonds of **4.1** are actually not strong and they

Fig. 2. (a) Total, σ and π ring current maps of B_3Al_3 **3.1**, and (b) Ring current maps of B_4Al_4 **4.1**, B_4Li_4 and B_4^{4-} clusters projected into the B_4 planes.

Fig. 3. The molecular orbital diagram of B_4Al_4 cluster.

are even much weaker than a single bond. It is illustrative that an Al–Al connectivity does not correspond to a bond, as its bond order is only 0.1. Four Al atoms in **4.1** do not provide Al–Al covalent bonds as in free Al_4 cluster. NBO charges calculated for **4.1** show that each B atom has a negative charge of about −0.9 electron, whereas the atomic charge of Al

Fig. 4. Electron localization function (ELF) isosurfaces: (a) at bifurcation value of 0.8 and 0.85 of B_3Al_3 **3.1** (D_{3h}); (b) B_4Al_4 **4.1** (D_{2h}) and (c) B_5Al_5 , B_6Al_6 and B_7Al_7 (ELF = 0.75). Electron densities are obtained from TPSSH/6–311 + G(d) computations.

atom is about +0.90 electron. Each Al atom thus makes a charge transfer of about one electron to the B_4 moiety. As a result, **4.1** is in part formed by electrostatic interaction between four Al cations with the negatively charged B_4 moiety giving rise to a type of donor-acceptor interaction.

Fig. 4 displays the ELF iso-surfaces plotted at the bifurcation value of ELF = 0.80 and 0.85 for B_4Al_4 **4.1**. A localization domain is clearly identified corresponding to a lone pair for each Al atom. Accordingly, each Al atom transfers one electron to the B_4 moiety, and the two remaining electrons are localized around the Al center as a lone pair.

The above results demonstrate that in **4.1** Al_4 donates 4 electrons to fulfill two empty MOs ($2b_{3u}$ and $4a_g$) of the B_4 ring, turning it into a donor-acceptor type of $B_4^{\delta-}.Al_4^{\delta+}$ complex. With reference to the B_4 plane, the corresponding MOs, as given in Fig. 3, are actually delocalized σ and π MOs of B_4 which are determining the aromatic character of B_4Al_4 . As a result, exploration on aromatic feature of **4.1** with reference to the B_4 plane is highly important to understand its intrinsic stability. For this purpose, the magnetic ring current maps of **4.1** are calculated and displayed in Fig. 2b. Due to the fact that each Al atom donates one electron, for purpose of comparison, the ring current maps of the neutral B_4Li_4 and the anion B_4^{4-} are also plotted.

The current density of **4.1** in the B_4 plane is of diatropic nature in

magnetic response, indicating clearly that B_4Al_4 is an aromatic species in that plane (Fig. 2b). A similar aromatic character is also observed for B_4Li_4 in which the four Al atoms of **4.1** are simply replaced by Li atoms without any geometry optimization, as illustrated by a strong diatropic current flow. The pure B_4^{4-} anion, which is isovalent with both B_4Li_4 and B_4Al_4 , also shares a similar ring current flow (Fig. 2b). Because both Al and Li atoms donate electrons to B_4 to form B_4^{4-} , the similarity between their ring current illustrates that electron donation actually gives rise to an aromatic feature. Therefore, the inherent aromaticity of the B_4^{4-} moiety of the $B_4^{\delta-}.Al_4^{\delta+}$ (or $B_4^{\delta-}.4Al^{\delta+}$) complex constitutes an essential contributor to its thermodynamic stability.

Another important aspect concerns electron distribution within the Al_4 plane of **4.1**. Fig. 5 displays the total and orbital magnetic ring current maps in the Al_4 plane. It is clear that both orbitals HOMO-1 and HOMO-2 have significant contributions to the diatropic magnetic current within the Al_4 plane. The ring current flows of B_4Al_4 in both B_4 (Fig. 2) and Al_4 (Fig. 5) planes illustrate a view that the two electron flows circulated in two perpendicular planes are interlocking with each other, and define an apparently independent aromatic character in each plane.

Overall, the electronic structure and stability of B_4Al_4 can be understood by the facts that each Al atom provides one valent electron to

Fig. 5. Ring current maps of B_4Al_4 4.1: (a) in the Al_4 plane, (b) Contribution of HOMO-1 and (c) Contribution of HOMO-2 to the magnetic ring current.

generate donor-acceptor bonds with the B_4 counterpart, as well as to give rise to an aromatic feature for the resulting $B_4^{\delta-} \cdot Al_4^{\delta+}$ complex.

3.4. Interaction between boron and aluminum layers

It is important to explore the interaction between boron and aluminum layers of the double layer structures in B_nAl_n , with $n = 5-7$. For

Table 2
NBO atomic charges of B_nAl_n clusters with $n = 3-7$.

n	Dipole moment (Debye)	NBO atomic charge (au)							
3	0	B atoms	-0.90	-0.90	-0.90				
		Al atoms	0.90	0.90	0.90				
4	0	B atoms	-0.90	-0.90	-0.90	-0.90			
		Al atoms	0.90	0.90	0.90	0.90			
5	1.7	B atoms	-0.56	-0.68	-1.0	-0.45	-0.04		
		Al atoms	0.50	0.76	0.64	0.27	0.54		
6	0.7	B atoms	-0.60	-0.86	-0.60	-0.60	-0.86	-0.39	
		Al atoms	1.1	0.66	0.51	0.51	0.66	0.49	
7	2.2	B atoms	-0.55	-0.55	-0.21	-0.55	-0.55	-0.85	-0.85
		Al atoms	0.58	0.58	0.53	0.61	0.61	0.61	0.61

this purpose, dipole moment as well as NBO atomic charges are calculated and listed in Table 2. B atoms consistently bear negative charges whereas positive charges are located on Al atoms. However, values of dipole moments are not large due to some mutual cancellations. This shows that an Al_n layer transfers a charge to the corresponding B_n layer, and thereby electrostatic interaction turns out to play an important role in connecting both layers.

The ELF maps of B_nAl_n clusters are displayed in Fig. 4. At the bifurcation value of $ELF = 0.75$, no localization domain appears in the region between two layers, indicating that both B_n and Al_n layers interact with each other by electrostatic force. This result is consistent with NBO charges mentioned above from which the role of electrostatic interaction is emphasized. Regarding the most relevant structure B_7Al_7 7.1, its localization domain shows a similarity with that of free B_7 cluster with the delocalized character of the B_7 layer. The B_7 cycle maintains its delocalized bond when it forms a double layer shape with the Al_7 . Additionally, three-center $V(Al,Al,B)$ basins are now observed for 7.1 structure. The existence of these $V(Al,Al,B)$ basins suggests that three-center bonds emerge in both Al_7 and B_7 layers, even though they should significantly be polarized due to electron transfer to the B_7 unit.

These results agree with previous report on stabilization of B_7 cycle which becomes the most stable form at triply negative charge [50]. Regarding the trianion B_7^{3-} , it has been pointed out that a full occupation of three π -MOs induces stability, and as for a prediction, this phenomenon possibly causes a planar shape of B_7Al_7 . To further understand on stabilization of B_7Al_7 double layer, their molecular orbitals are examined and displayed in Fig. 6. It is illustrative from Fig. 6 that, quite similar to B_7^{3-} , three π -MOs of B_7Al_7 are fully occupied and thereby give rise to a stability for B_7Al_7 double layer. Additionally, as displayed in Table 2, the B_7 moiety of B_7Al_7 has a negative charge of ~ -3.5 electron indicating that the B_7 planar moiety reaches the most stable form of B_7 cycle.

4. Concluding remarks

In the present work, we performed a systematic investigation on geometries and electronic structures of small binary boron-aluminum B_nAl_n with $n = 1-7$ using both DFT/TPSSH and composite G4 methods. The growth pattern for the neutral B_nAl_n clusters can be established as follows:

- B and Al atoms do not mix together but prefer to be assembled in two separate B_n and Al_n components. This is due to the inherently weak overlap between $2p(B)$ and $3p(Al)$ orbitals.
- The global minima of small sizes B_nAl_n with $n = 1-4$ tend to be formed by combination of the pure B_n and Al_n components in which the B_n plays as a core, while the larger sizes follow a trend in which superposition between separated B_n and Al_n parts is favoured.
- The B_n moiety in a binary system prefers a quasi-planar geometry as in pure B_n clusters. The B_7Al_7 cluster clearly presents a double

Fig. 6. The molecular orbital diagram of B_7Al_7 cluster.

layer structure.

- (iv) The Al_n unit supplies electrons to the B_n counterpart. In fact, the enhanced stability of the neutral B_3Al_3 and B_4Al_4 is likely due to a large electron donation from Al atoms to B_n ring. Such an electron transfer induces strong donor-acceptor ($B_n^{\delta-} Al_n^{\delta+}$) electrostatic interaction. On the other hand, electron transfer helps to fill electron shells and thereby gives rise in the case of B_3Al_3 a σ aromatic character, and in B_4Al_4 an aromatic character in each of the two perpendicular B_4 and Al_4 planes. The two electron flows in B_4Al_4 are interlocking with each other and apparently independent on each other.

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Appendix A. Supplementary material

Table lists Cartesian coordinates of the lowest-lying isomers B_nAl_n considered. Figures display the shapes of low-lying isomers B_nAl_n , and ring current maps of B_3Al_3 and $B_3Al_3^{2-}$. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cplett.2018.10.065>.

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