The Structures and Bonding of Bismuth-Doped Boron Clusters: BiB₄⁻ and BiB₅⁻

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Abstract: We present an investigation on the structures and chemical bonding of two Bi-doped boron clusters BiB₄⁻ and BiB₅⁻ using photoelectron spectroscopy and theoretical calculations. The electron affinities of BiB₄⁻ and BiB₅⁻ are measured to be 2.22(2) eV and 2.61(2) eV, respectively. Well-resolved photoelectron spectra are obtained and used to compare with theoretical calculations to verify the structures of BiB₄⁻ and BiB₅⁻. Both clusters adopt planar structures with the Bi atom bonded to the periphery of the planar Bₙ moiety. Chemical bonding analyses reveal that the Bₙ moiety maintains σ and π double-aromaticity. The Bi atom is found to induce relatively small structural changes to the Bₙ moiety, very different from transition metal-doped boron clusters.

Keywords: photoelectron spectroscopy; metal boron clusters; bismuth; chemical bonding; planar clusters

1. Introduction

Due to its electron deficiency, boron exhibits a wide range of bulk allotropes and compounds that consist of distinct three-dimensional (3D) building blocks [1–3]. Extensive research has been conducted over the past two decades, employing a combination of experimental and theoretical studies to investigate size-selected boron clusters [4–7]. Unlike their bulk counterparts, small boron clusters predominantly exhibit two-dimensional (2D) structures composed mainly of B₃ triangles. Among the fascinating 2D boron clusters, the C₆v B₃₆ cluster stands out as it provides the first experimental evidence for the existence of atom-thin 2D boron (borophene) [8]. Borophenes have been successfully synthesized on metal substrates [9,10], becoming a novel type of synthetic 2D material [11,12]. Another important boron cluster is B₄₀, which was found to have a cage structure, the first all-boron fullerene (borospherene) [13]. Numerous boron clusters doped with metals have also been generated and investigated [6,14–16], significantly extending the range of nanostructures that can be formed by boron.

After the discovery of ultrahigh thermal conductivity and important electronic properties in the cubic boron arsenide [17–19], the group III–V semiconductor families have gained increasing attention. However, arsenic compounds come with a significant drawback of toxicity [20,21]. On the other hand, bismuth, the heaviest group V element, is considered to be a “green metal” due to its low toxicity [22] and has attracted interest in chemistry and material sciences [23–25]. There is also growing interest in bismuth boride [26–28], but it has not yet been fabricated thus far. Small Bi boride clusters are ideal models to investigate the bonding between bismuth and boron, which lays the foundation to understand the bulk material and may help discover new Bi-B nanostructures.

Toward this goal, we have studied several Bi-B binary clusters using photoelectron spectroscopy (PES) and theoretical calculations, including BiB₄⁻ (n = 6–8) [29] and several di-bismuth boride clusters Bi₂Bₙ⁻ (n = 1–4) [30,31]. Most recently, we have reported an investigation of cold diatomic BiB⁻ using high-resolution photoelectron imaging [32]. In the current article, we present a study on the structures and chemical bonding of two Bi-doped boron clusters, BiB₅⁻ (n = 4, 5), using PES and theoretical calculations. Well-resolved
photoelectron spectra are measured and interpreted using the theoretical results. Both the BiB$_4^-$ and BiB$_5^-$ clusters are found to exhibit 2D structures. The Bi atom is found to be bonded to the edge of B$_4$ and B$_5$, respectively. The Bi atom is observed to induce relatively small structural changes to the B$_n$ motif in comparison to the bare B$_n$ clusters, in contrast to transition metal-doped boron clusters.

2. Experimental and Theoretical Methods

2.1. Photoelectron Spectroscopy

The experiments were conducted with a magnetic-bottle PES apparatus. Details of the experimental apparatus and procedures can be found elsewhere [5] and only essential features pertaining to this work are given here. The Bi-doped boron clusters were generated by laser ablation of a disk target made of Bi and $^{10}$B-enriched boron powders (1/1 Bi/B molar ratio). The plasma induced by the vaporization laser was quenched by a high-pressure He carrier gas containing 5% Ar. Clusters from the nozzle were carried by the carrier gas and cooled via supersonic expansion. Anionic clusters in the beam were extracted into a time-of-flight mass analyzer for mass analyses and cluster size selection. The BiB$_n^-$ ($n = 4, 5$) clusters were each selected by a mass gate and decelerated before crossing a photodetachment laser beam. Three laser wavelengths were used for photodetachment, including 355 nm (3.496 eV) and 266 nm (4.661 eV) from a Nd:YAG laser and 193 nm (6.424 eV) from an ArF excimer laser. Photoelectrons were analyzed in a 3.5 m long electron time-of-flight tube of the magnetic-bottle PES spectrometer. Photoelectron spectra were calibrated with the known transitions of the Bi$^-$ atomic anion. The electron kinetic energy ($E_k$) resolution ($\Delta E_k/E_k$) of the magnetic-bottle analyzer was approximately 2.5%, i.e., about 25 meV for 1 eV electrons.

2.2. Theoretical Methods

Theoretical calculations were carried out to understand the structures and bonding of BiB$_n^-$ ($n = 4, 5$) and help interpret the photoelectron spectra using the Gaussian 09 program packages [33]. Based on our prior experience [29,31], the Bi atoms tend to bond to the periphery of planar boron cluster motifs. Thus, the Bi atom was put around the planar B$_4$ and B$_5$ motifs [5,6], respectively, for the initial structural searches of BiB$_4^-$ and BiB$_5^-$ at the PBE/aug-cc-pVDZ-pp level. The low-lying isomers were reoptimized at the PBE level using the aug-cc-pVTZ basis set for B and the aug-cc-pVTZ-pp basis set with the relativistic pseudopotentials (ECP60MDF) for Bi [34–36]. We computed the adiabatic detachment energy (ADE) as the energy difference between the anion and the corresponding neutral at their optimized structures. The first vertical detachment energy (VDE$_1$) was calculated as the energy difference between the anion and neutral at the optimized geometry of the anion. Higher VDEs were calculated using time-dependent DFT (TD-DFT) calculations at the PBE/aug-cc-pVTZ level of theory at the anion geometry [37,38]. Although spin–orbit coupling effects were not treated explicitly, we have found that the computed ADEs and VDEs in general agree well with the experimental data. We have also tried the calculations using other functionals, including TPSSH, B3LYP, and PBE0. The results are similar, though the PBE results give a better fit to the experiment.

The chemical bonding of BiB$_n^{-}/0$ ($n = 4, 5$) was analyzed with the adaptive natural density partitioning (AdNDP) method [39,40]. The AdNDP method has been proven to be an effective tool for understanding the bonding in boron and metal-doped boron clusters. All the AdNDP calculations were carried out with the multiwfn program [41].

3. Results

3.1. Experimental Results

The photoelectron spectra of BiB$_4^-$ and BiB$_5^-$ are shown in Figures 1 and 2, respectively, at three photon energies. Detachment transitions are labeled with letters, where X refers to detachment transition from the ground electronic state of the anion to that of the corresponding neutral. The detachment bands labeled from A to D for BiB$_4^-$ and A to G
for BiB$_5^-$ represent transitions from the ground state of the anion to excited states of the neutral final states.

**Figure 1.** Photoelectron spectra of BiB$_4^-$ at (a) 355 nm (3.496 eV), (b) 266 nm (4.661 eV), and (c) 193 nm (6.424 eV).

**Figure 2.** Photoelectron spectra of BiB$_5^-$ at (a) 355 nm (3.496 eV), (b) 266 nm (4.661 eV), and (c) 193 nm (6.424 eV).
The photoelectron spectra of BiB⁻ display a relatively simple spectral pattern with well-resolved detachment transitions (Figure 1). The first VDE of BiB⁻ is obtained from band X as 2.27 eV in Figure 1a. The ADE obtained from the onset of band X is 2.22 eV, which also represents the electron affinity (EA) of neutral BiB. The ADE is estimated by drawing a straight line along the leading edge of band X and then adding the spectral resolution to the intersection with the binding energy axis. There is a large energy gap between band X and the broad band A at a VDE of 3.88 eV. Band B is slightly cut off at 266 nm (Figure 1b) but fully observed in the 193 nm spectrum (Figure 1c) at a VDE of 4.31 eV. Two closely spaced bands, C and D, are observed at VDEs of 4.71 eV and 4.96 eV, respectively. No other detachment transitions are observed at higher binding energies. The ADE and all the VDEs are given in Table 1, where they are compared with the theoretical results.

**Table 1.** The experimental adiabatic (ADE) and vertical (VDE) detachment energy for BiB⁻ in comparison with the calculated values at the PBE/aug-cc-pVTZ level for the GM C₁ (A) structure (Figure 3a). All energies are in eV.

<table>
<thead>
<tr>
<th>Final State and Electron Configuration</th>
<th>VDE/ADE (exp) *</th>
<th>VDE/ADE (theo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X (2.27/2.22)</td>
<td>2A ··(18a)²(19a)²(20a)²(21a)²(22)²(22a)²</td>
<td>2.16/2.11</td>
</tr>
<tr>
<td>A (3.88)</td>
<td>2A ··(18a)²(19a)²(20a)²(21a)²(22)²</td>
<td>3.68</td>
</tr>
<tr>
<td>B (4.31)</td>
<td>2A ··(18a)²(19a)²(20a)²(21a)²(22)²</td>
<td>4.10</td>
</tr>
<tr>
<td>C (4.77)</td>
<td>2A ··(18a)²(19a)²(20a)²(21a)²(22)²</td>
<td>4.71</td>
</tr>
<tr>
<td>D (4.97)</td>
<td>2A ··(18a)²(19a)²(20a)²(21a)²(22)²</td>
<td>4.96</td>
</tr>
</tbody>
</table>

* The experimental uncertainties are ±0.02 eV.

The photoelectron spectra of BiB⁻ (Figure 2) exhibit more complicated and congested spectral features due to its open-shell electronic structure. At 355 nm (Figure 2a), three closely spaced detachment transitions (X, A, B) are observed. The broader band X at a VDE of 2.74 eV should represent the transition from the ground electronic state of BiB⁻ to that of neutral BiB. The ADE is estimated from band X to be 2.61 eV, i.e., the EA of BiB. The A and B bands at VDEs of 2.99 and 3.15 eV, respectively, are sharp with partially resolved vibrational structures. The vibrational spacings for bands A and B are estimated to be 640 and 400 cm⁻¹, respectively. Following an energy gap, a series of congested detachment transitions (C to G) are observed above 4 eV. Bands C and D at 3.95 and 4.05 eV, respectively, are very closely spaced and are shown to be quite sharp at 266 nm (Figure 2b). The 193 nm spectrum reveals three more bands, E, F, and G, at 4.33, 4.86, and 5.02 eV, respectively (Figure 2c). The signal-to-noise ratios are too poor above 5 eV in the 193 nm for definitive identification of more detachment features. The ADE and all VDEs for BiB⁻ are given in Table 2, where they are compared with the theoretical results.

**Table 2.** The experimental adiabatic (ADE) and vertical detachment energy (VDE) for BiB⁻ in comparison with the calculated values at the PBE/aug-cc-pVTZ level for the GM C₁ (A) structure (Figure 4a). All energies are in eV.

<table>
<thead>
<tr>
<th>Final State and Electron Configuration</th>
<th>VDE/ADE (exp) *</th>
<th>VDE/ADE (theo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X (2.74/2.61)</td>
<td>1A' ··(17a)²(18a)²(19a)²(20a)²(21a)²(22a)²</td>
<td>2.92/2.70</td>
</tr>
<tr>
<td>A (2.99)</td>
<td>3A' ··(17a)²(18a)²(19a)²(20a)²(21a)²(22a)²</td>
<td>2.93</td>
</tr>
<tr>
<td>B (3.15)</td>
<td>1A'' ··(17a)²(18a)²(19a)²(20a)²(21a)²(22a)²</td>
<td>3.25</td>
</tr>
<tr>
<td>C (3.95)</td>
<td>3A'' ··(17a)²(18a)²(19a)²(20a)²(21a)²(22a)²</td>
<td>3.85</td>
</tr>
<tr>
<td>D (4.05)</td>
<td>3A'' ··(17a)²(18a)²(19a)²(20a)²(21a)²(22a)²</td>
<td>3.99</td>
</tr>
<tr>
<td>E (4.33)</td>
<td>1A' ··(17a)²(18a)²(19a)²(20a)²(21a)²(22a)²</td>
<td>4.43</td>
</tr>
<tr>
<td>F (4.86)</td>
<td>1A' ··(17a)²(18a)²(19a)²(20a)²(21a)²(22a)²</td>
<td>4.63</td>
</tr>
<tr>
<td>G (5.02)</td>
<td>1A' ··(17a)²(18a)²(19a)²(20a)²(21a)²(22a)²</td>
<td>5.03</td>
</tr>
</tbody>
</table>

* The experimental uncertainties are ±0.02 eV.
3.2. Theoretical Results

The global minima and low-lying isomers for BiB\(_4^-\) and BiB\(_5^-\) are displayed in Figures 3 and 4, respectively, as well as the corresponding neutral structures. The global minimum of BiB\(_4^-\) (GM, Figure 3a) was found to be closed-shell (\(^1\)A) with a quasi-planar structure (\(C_1\) symmetry) at the PBE level of theory. The \(B_4\) motif of BiB\(_4^-\) is similar to the global minimum of the bare \(B_4\) cluster. In fact, the Bi atom can be viewed as replacing a B atom in B\(_5^-\), which has a planar \(C_{2v}\) structure. A 3D isomer is located for BiB\(_4^-\), which is 1.30 eV above the GM structure (Iso1, Figure 3a).

\[
\begin{align*}
\text{GM (C\(_1\), } ^1\text{A)} & \quad 0 \text{ eV} \\
\text{Iso1 (C\(_1\), } ^1\text{A)} & \quad 1.30 \text{ eV} \\
0 \text{ kcal/mol} & \quad 29.98 \text{ kcal/mol}
\end{align*}
\]

![Figure 3](image-url)

**Figure 3.** The global minima and a low-lying isomer of (a) BiB\(_4^-\) and (b) BiB\(_4\). Relative energies are given in eV and kcal/mol at the PBE/aug-cc-pVTZ level.

\[
\begin{align*}
\text{GM (C\(_{2v}\), } ^2\text{A}) & \quad 0 \text{ eV} \\
\text{Iso1 (C\(_{2v}\), } ^2\text{A)} & \quad 1.29 \text{ eV} \\
0 \text{ kcal/mol} & \quad 29.75 \text{ kcal/mol}
\end{align*}
\]

![Figure 4](image-url)

**Figure 4.** The global minima and low-lying isomers of (a) BiB\(_5^-\) and (b) BiB\(_5\). Relative energies are given in eV and kcal/mol at the PBE/aug-cc-pVTZ level.

The neutral ground state (Figure 3b) is similar to that of the anion, except that it is planar with a doublet spin state (\(C_s\), \(^2\)A\(^\prime\)). The low-lying isomer of neutral BiB\(_4\) (Iso1, Figure 3b) is also similar to that of the anion, but it is more symmetric with \(C_{2v}\) symmetry. The large energy difference between Iso1 and the GM structure of the anion is maintained in the neutral system. The computed ADE and VDEs for the global minimum of BiB\(_4^-\) are compared with the experimental results in Table 1.

The global minimum of BiB\(_5^-\) (GM, Figure 4a) has a planar structure with a doublet spin state (\(C_s\), \(^2\)A\(^\prime\)). The Bi atom is bonded to the edge of a planar \(B_5\) motif, which is similar to the bare \(B_5\). In fact, the GM of BiB\(_5^-\) is similar to that of neutral \(B_6\) and the Bi atom can be viewed as substituting an apex B atom of the planar \(B_6\). The next low-lying isomer of
BiB$_5^-$ is 0.35 eV higher in energy than the GM structure at the PBE level, Iso1 ($C_s$, $^2A'$) in Figure 4a. The B$_5$ motif in Iso1 of BiB$_5^-$ is similar to that in the GM structure, but the position of the Bi atom is different. The second low-lying isomer (Iso2, Figure 4a) is a 3D structure, being 0.98 eV higher in energy than the GM structure. In Iso2, the Bi atom is located above a pentagonal B$_5$ motif with $C_1$ symmetry ($^2T_A$). The triangular isomer with the Bi atom at one of the apexes is also found, but it is much higher in energy (1.78 eV above the GM). The neutral BiB$_5$ GM and its low-lying isomers (Figure 4b) are similar to the anion with the same energy ordering. The computed ADE and VDEs for the GM of BiB$_5^-$ are given in Table 2, where they are compared with the experimental results.

4. Discussion

4.1. Comparison between Experiment and Theory

The experimental PES data are essential for verifying the global minima of BiB$_4^-$ and BiB$_5^-$, respectively, according to the computed VDEs for the global minimum of each cluster. The theoretical VDEs are also given as vertical bars under the 193 nm spectra in Figures 5 and 6 for BiB$_4^-$ and BiB$_5^-$, respectively. The valence molecular orbitals are presented in Figures S1 and S2 for BiB$_4^-$ and BiB$_5^-$, respectively.

![Figure 5](image1.png)

**Figure 5.** Comparison of the computed VDEs with the photoelectron spectrum of BiB$_4^-$ at 193 nm. The vertical bars correspond to computed VDEs at the PBE/aug-cc-pVTZ level of theory.

![Figure 6](image2.png)

**Figure 6.** Comparison of the computed VDEs with the photoelectron spectrum of BiB$_5^-$ at 193 nm. The vertical bars correspond to computed VDEs at the PBE/aug-cc-pVTZ level of theory. The longer and shorter bars correspond to transitions to triplet and singlet final states, respectively.
4.1.1. BiB$_4^-$

The computed VDE$_1$/ADE of 2.16/2.11 eV for the GM structure of BiB$_4^-$ at the PBE level agree well with the measured values of 2.27/2.22 eV (Table 1). Even though the isomer Iso1 also gives similar computed VDE$_1$/ADE values (2.34/2.10 eV), its energy is higher than the GM structure by 1.30 eV. Thus, it can be ruled out from any contributions to the experimental spectra. In addition, the large difference between the computed VDE$_1$ and ADE of Iso1, due to the significant geometry change between its neutral and anion (Figure 3), would suggest a broad detachment transition, which is inconsistent with the relatively sharp band X in the spectra of BiB$_4^-$ (Figure 1). The calculated VDE for higher binding energy detachment channels of the C$_1$ global minimum are compared with the experimental data in Table 1 and in Figure 5 as the vertical bars.

The first detachment channel is from the HOMO (22a), a $\pi$-type MO primarily of Bi 6$p_z$ character with a small contribution from the B$_4$ moiety (Figure S1). The electron detachment from the HOMO leads to a geometry change from the quasi-planar structure (C$_1$) to the planar neutral BiB$_4$ (C$_s$) (Figure 3). The narrow width of band X agrees with the small structural change between the ground state of the anion and that of the neutral (Figure S3a). Electron detachment from the HOMO-1 (21a) gives a computed VDE of 3.68 eV, which agrees well with the measured VDE of band A at 3.88 eV. The HOMO-1 is an in-plane $\sigma$-type MO, involved in B–B bonding and Bi–B bonding (Figure S1). The bonding nature of the HOMO-1 is consistent with the relatively broad band A. Electron detachment from the HOMO-2 (20a) results in a theoretical VDE of 4.10 eV, in good agreement with the measured VDE of band B at 4.31 eV. The 20a orbital is also an in-plane $\sigma$-type MO, involved in B–B bonding and Bi–B bonding (Figure S1). Although both the GM structures of BiB$_4^-$ are planar with C$_s$ symmetry, there are significant bond length changes (Figure S3b), in accordance with the broad band X. The first detachment channel is from the 20a′ SOMO of BiB$_4^-$, which is an in-plane $\sigma$-type orbital (Figure S2). The next detachment channel is from the HOMO (5a′), resulting in a high-spin (3A′$^0$) and a low-spin (3A′′$^0$) final state. The computed VDEs for the triplet and singlet final states, 2.93 eV and 3.25 eV (Table 2), agree well with the experimental observation for band A (2.99 eV) and band B (3.15 eV), respectively. Detachment from the HOMO-1 (19a′) similarly gives rise to a triplet (3A′) and a singlet (3A′) neutral state.

The calculated VDE for the A′′ triplet state (3.85 eV) is consistent with band C at 3.95 eV, whereas that for the singlet 1A′′ final state (4.43 eV) is consistent with band E at 4.33 eV. Detachment from the HOMO-2 (18a′) gives a high-spin final state (3A′) with a computed VDE of 3.99 eV and a low-spin (1A′) final state with a computed VDE of 5.03 eV.
in good agreement with band D at 4.05 eV and F at 4.86 eV, respectively. Finally, detachment from the HOMO-3 (17a') leads to a triplet final state (3 A') with a computed VDE of 4.63 eV and a singlet final state (1 A') with a computed VDE of 5.15 eV. Band E has a broad shoulder on the high binding energy side (not labeled), which agrees with the computed VDE of the triplet final state of the 17a' HOMO-3, whereas the singlet final state is assigned to band G at 5.02 eV. The open-shell nature of BiB5− results in the congested spectral features, making their definitive assignment rather challenging. Nevertheless, the overall spectral pattern from the computed VDEs is in reasonable agreement with the experiment, as shown in Figure 6, providing credence for the C4 GM structure of BiB5−.

4.2. Chemical Bonding in the Bismuth–Boron Clusters

To gain insights into the structures and bonding of the BiB4− and BiB5− clusters, we conducted AdNDP analyses, as depicted in Figures 7 and 8, respectively. The 6s2 electrons of the Bi atom are strongly stabilized due to the relativistic effects [42], rendering them less active in chemical bonding. Consequently, chemical bonding in Bi compounds primarily involves the 6p orbitals with little sp hybridization. The 6s2 electrons remain as a lone pair in all bismuth–boron clusters [29–32]. Similarly, we find a 6s2 lone pair in the current bismuth–boron clusters, whereas the 6p, and 6p orbitals participate in σ-bonding with the Bn moiety and the 6p orbital engages in π-bonding with the Bn moiety. Because of the large size of the Bi atom and the strong B–B bonds, it is not favorable for the Bi atom to insert into the Bn moiety. Thus, in both BiB4− and BiB5− we find that the Bi atom is bonded to the edge of the planar Bn moiety, similar to other binary Bi-B clusters [29,31].

**Figure 7.** AdNDP bonding analysis for the global minimum structure of BiB4−. ON stands for occupation number.

**Figure 8.** AdNDP bonding analysis for the global minimum structure of BiB5−. ON stands for occupation number.
In addition to the 6s lone pair, the AdNDP analysis for BiB$_4^-$ (Figure 7) reveals four two-center two-electron (2c-2e) σ-bonds (three B–B bonds and one Bi–B bond) on the edge of the quasi-planar BiB$_4^-$ cluster, one 2c-2e Bi–B π-bond, one delocalized 3c-2e σ-bond (BiB$_2^-$), one delocalized 4c-2e σ-bond, and one delocalized 4c-2e π-bond on the B$_4$ moiety. Each of the delocalized 4c-2e σ- and π-bond satisfies the 4N + 2 Hückel rule for aromaticity, rendering the B$_4$ moiety doubly aromatic, similar to the doubly aromatic bare B$_4$ cluster [43]. Thus, the BiB$_4^-$ cluster can be considered as Bi bridge-bonded to a doubly aromatic B$_4$ cluster. It should be noted that the Bi atom has two different Bi–B bonds (2.20 and 2.41 Å) in BiB$_4^-$ (Figure S3a). The shorter Bi–B bond is similar to a Bi=B double bond according to Pyykkö’s self-consistent atomic covalent radii of B and Bi (2.19 Å) [44].

The double Bi=B bond is borne out by the AdNDP analysis (Figure 7), where a 2c-2e Bi–B σ-bond and a 2c-2e Bi–B π-bond are clearly seen. The longer Bi–B bond in BiB$_4^-$ is actually weaker than a single Bi–B bond (2.36 Å according to Pyykkö’s covalent atomic radii), because the longer Bi–B bond is involved in the delocalized 3c-2e σ-bond. The Bi atom induces relatively small structural changes to the B$_4$ moiety compared to the bare B$_4$. This bonding situation is very different from transition metal MB$_n$ clusters [16], where the strong M–B bonding can completely change the B$_n$ moiety relative to the bare B$_n$. For example, the ReB$_4^-$ cluster has a pentagonal structure and displays Möbius aromaticity due to the strong participation of the Re 4d orbitals in chemical bonding with boron [45,46].

For BiB$_5^-$, we chose to conduct the AdNDP analysis on the closed-shell BiB$_5$ neutral for convenience, as shown in Figure 8. The AdNDP results reveal the expected 6s lone pair on Bi, three 2c-2e σ-bonds (two B–B bonds and one Bi–B bond) on the periphery of the planar BiB$_5$ cluster, three delocalized 3c-2e σ-bonds (two over two B$_3$ units and one over the BiB$_2$ unit), one delocalized 3c-2e π-bond over the BiB$_2$ unit, one delocalized 5c-2e π-bond, and one delocalized 5c-2e σ-bond over the B$_5$ moiety. The delocalized σ- and π-bonds over the B$_5$ moiety render it doubly aromatic, similar to the bare B$_5$ cluster [43]. Thus, BiB$_5$ can be viewed as a Bi atom bridge-bonded to the periphery of the B$_5$ moiety. The two Bi–B bonds in BiB$_5$ are also asymmetric, similar to those in BiB$_4^-$ . Again, the Bi atom in BiB$_5$ induces relatively small changes in the B$_5$ moiety in comparison to the bare B$_5$ cluster, very different from transition metal MB$_5$ clusters [26]. For example, the TaB$_5$ cluster has a fan-shaped structure, in which the Ta atom is bonded to all five B atoms. We found that the larger BiB$_n^-$ (n = 6–8) clusters behave similarly [29], in that their GM structures can be viewed as Bi bonded to the edge of the planar B$_n^-$ clusters, respectively.

5. Conclusions
In conclusion, we report an investigation of the structures and bonding of two Bi-doped boron clusters, BiB$_4^-$ and BiB$_5^-$, using photoelectron spectroscopy. Well-resolved photoelectron spectra are obtained and interpreted using theoretical calculations. Electron affinities of BiB$_4$ and BiB$_5$ are measured to be 2.22(2) eV and 2.61(2) eV, respectively, and the experimental vertical detachment energies are compared with theoretical calculations to verify the structures of BiB$_4^-$ and BiB$_5^-$ . The BiB$_4^-$ cluster is found to be quasi-planar with $C_1$ symmetry ($^1A'$), whereas BiB$_5^-$ is found to be planar with $C_s$ symmetry ($^2A'$). Chemical bond analyses show that the Bi atom is bridge-bonded on the periphery of the respective B$_n$ clusters with relatively small structural change relative to the bare B$_n$ clusters. The two Bi–B bonds in the two clusters are asymmetric with a Bi=B double bond and a weak Bi–B single bond in both clusters.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics11100405/s1. Figure S1. The valence MOs of the global minimum of BiB$_4^-$ ($C_1$, $^1A'$). Figure S2. The valence MOs of the global minimum of BiB$_5^-$ ($C_s$, $^2A'$). Figure S3. The bond lengths (in Å) for (a) the ground state of BiB$_4^-$ ($C_1$, $^1A'$) and BiB$_4$ ($C_s$, $^2A'$) and (b) the ground state of BiB$_5^-$ ($C_s$, $^2A'$) and BiB$_5^-$ ($C_s$, $^1A'$).


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