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Heteroborane analogs of silicon clusters: Experimental and theoretical studies on Bi_2Si_5 and $Bi_2Si_5^-$

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We have investigated the electronic structure of anionic and neutral Bi_2Si_5 by means of anion photoelectron spectroscopy and density functional calculations. Both the experiments and calculations reveal that the $Bi_2Si_5^-$ anion prefers to adopt a distorted trigonal-bipyramidal structure with Bi_2 bridges. Following the isolobal analogy between divalent Si and B–H group, we show that both neutral Bi_2Si_5 and neutral $Bi_2B_5H_5$ adopt similar pentagonal-bipyrmidal geometries and have analogous orbital energy patterns. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2988727]

I. INTRODUCTION

Despite numerous studies,[1–8] silicon clusters continue to fascinate. Part of the intrigue comes from the fact that unlike metallic clusters, which have strongly delocalized electrons and prefer to follow simple electron counting rules such as those originating from Jellium models,[9,10] there are no simple rules of thumb that can be used to understand the diverse structures of silicon clusters.[11] Driven by strong covalent interactions and aided to some degree by π-delocalization, silicon clusters prefer to adopt a variety of structural motifs, which differ sharply from the clusters of silicon's neighbors in the Periodic Table. However, over the last couple of decades, there have been attempts[12–15] to connect the structure and bonding of silicon clusters to a large class of well-studied three-dimensional boron hydride compounds namely, *closo*-boranes, $B_nH_n^{2-}$. In 1990, Jemmis *et al.*[16] proposed an isolobal analogy between divalent silicon (e.g., $:SiH_2$) and trivalent boron (e.g., $H:BH_2$). By equating the σ-lone pair of divalent silicon to a B–H bond, it was shown that the frontier orbitals of both units are similar. In several examples,[14,17] it was found that an interchange between Si atom and a B–H unit alter neither the ground state nor the valence electronic structure. Meanwhile, Zdetsis[15] systematically studied the one-to-one correspondence between Si_n^{2-} and the corresponding *closo*-boranes, $B_nH_n^{2-}$, by comparing their structural and electronic features. His study concluded that the silicon clusters adopt similar structural patterns to those of boranes, when $n=5$, 6, 7, 8, 10, and 13. For example, Si_7^{2-} adopts a pentagonal-bipyramidal (PBP) structure that is similar to that of $B_7H_7^{2-}$. Furthermore, heavier congeners of Si, such as Sn, have also been demonstrated to be isolobal to BH unit.[18,19]

Based on the same concept, neutral analogs for *closo*-boranes, $B_nH_n^{2-}$, can also be constructed by replacing two BH^- (five valence electrons each) units with other isovalent units. For instance, two BH^- units can be replaced with two CH units resulting in $C_2B_nH_{n+2}$ (carboranes),[20,21] or replaced with two atoms from group 15 (such as N, P, Bi, etc.),[22] which also possess five valence electrons. The question then arises, whether similar neutral analogs of Si_7^{2-} can be envisioned. We propose that Bi_2Si_5 can be viewed as a neutral analog of Si_7^{2-}, thereby resembling its borane counterpart, $Bi_2B_5H_5$, which in turn is a neutral analog of the *closo*-borane dianion, $B_7H_7^{2-}$. In this communication, our combined photoelectron spectroscopic studies and theoretical calculations show that Bi_2Si_5 indeed adopts the PBP structure, just as $Bi_2B_5H_5$ and $B_7H_7^{2-}$ (Ref. 15) do. However, unlike the borane derivatives, there exist several possible low-lying ground state structures of Bi_2Si_5 that exhibit a variety of different structural patterns. We also report that anionic $Bi_2Si_5^-$ prefers a structure in which the bismuth dimer is attached to a trigonal-bipyramidal (TBP) silicon cluster, while the *closo*-structures (PBP) are higher in energy.

II. METHODS

A. Experimental

The $Bi_2Si_5^-$ anion was generated in a laser vaporization disk source. A mixed Bi–Si (50%-50%) disk target was vaporized by a pulsed laser beam of 532 nm photons from a Nd:YAG (yttrium aluminum garnet) laser. The plasma was cooled by supersonically expanding plume of helium carrier gas issuing from a general-purpose pulsed valve with a backing pressure of ~4 atm. Negatively charged clusters produced in this way were then extracted into a time-of-flight mass spectrometer. The $Bi_2Si_5^-$ anions were next mass selected and decelerated just before being photodetached by a third harmonic (355 nm, 3.49 eV) photons from a Nd:YAG laser. The ejected electrons were energy analyzed by a magnetic bottle, electron energy analyzer with a resolution of ~35 meV at 1 eV electron kinetic energy. Since negative ion photoelectron spectroscopy is governed by the energy-conserving relationship $h\nu=\text{EKE}+\text{EBE}$, where $h\nu$ is the photon energy, EKE is the measured electron kinetic energy,

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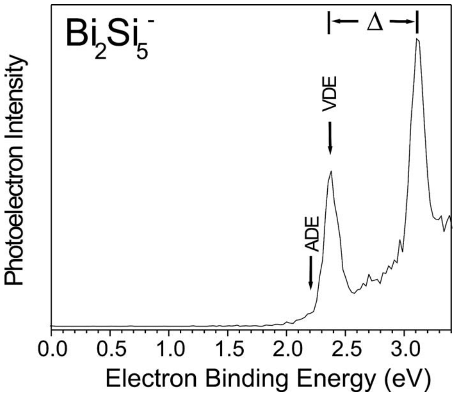

FIG. 1. Photoelectron spectrum of $Bi_2Si_5^-$ recorded with 355 nm photons. The measured values for the ADE, VDE, and HOMO-LUMO gap (Δ) are indicated.

and EBE is the electron binding energy. EBE can be obtained by measuring the EKE. The details of our apparatus have been previously described elsewhere.[23]

B. Computational

Initial search for the most stable structures were done at B3-LYP/LANL2DZ level of theory. Lowest energy structures were reoptimized with Stuttgart quasirelativistic pseudopotentials for Bi and 6−311+G* basis set for Si, B, and H. All the calculations were done without any symmetry constraints, and harmonic vibrational frequencies at the same level of theory were performed to examine the nature of the stationary points. All the calculations were carried out with GAUSSIAN 03.[24]

III. RESULTS AND DISCUSSIONS

In Fig. 1, we present the photoelectron spectrum of $Bi_2Si_5^-$. Peaks in the spectrum are due to transitions from the ground electronic state of the anion to the ground and excited vibronic states of the resulting neutral species. In the spectrum of $Bi_2Si_5^-$, two transitions are observed. The EBE of the onset region of the spectrum gives a good estimate for the adiabatic detachment energy (ADE) of $Bi_2Si_5^-$. The ADE is the energy difference between an anion and its corresponding neutral with that neutral relaxed into its nearest local minimum. The ADE is also the adiabatic electron affinity when both the anion and its corresponding neutral are in their ground states. The EBE of the maximum of the lowest EBE transition in the spectrum is the vertical detachment energy (VDE), which is defined as the energy difference between the anion and the neutral at the geometry of the anion. In addition, the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gaps Δ of the neutral clusters can be estimated from the spacing between the first two transitions in the spectrum. Therefore, from the spectrum of $Bi_2Si_5^-$, we extract the VDE=2.38 eV, ADE =2.25 eV, and Δ=0.73 eV.

Theoretical calculations revealed several local minimum structures for anionic $Bi_2Si_5^-$. They are shown in Fig. 2, along with their calculated VDE, ADE, and Δ values. At all levels of theory, the most stable $Bi_2Si_5^-$ anion isomer is the one in which the five silicon atoms form a distorted TBP structure and a Bi_2 unit bridges two silicon atoms (structure 1 in Fig. 1). While almost all of the Si–Si bonds in the TBP structure are within the expected range of 2.30–2.50 Å, the Si–Si bond opposite to the bridging bismuth atoms is much longer (2.88 Å). This is due to the rehybridization of the silicon orbitals due to bridging. In fact, a similar stretching of Si–Si bond length is observed in Si_5H_2,[25] where the two hydrogen atoms bind to the silicon cluster moiety at the same positions that the two bismuth atoms occupy in $Bi_2Si_5^-$ (structure 1). Despite the elongation, there is still a significant bonding interaction between the silicon atoms as indicated by the large Wiberg bond index (calculated to be 0.55), which measures the bond order between atoms in a molecule (typical values are 1 for the single bond, 2 for the double bond, and 3 for the triple bond). The calculated Bi–Bi bond length of 2.96 Å in structure 1 is much longer than the Bi–Bi triple bond (2.65 Å),[26] close to that in HBi=BiH (2.82 Å),[26] and nearly identical to that in $HBi{=}BiH^-$ (2.96 Å),[26] indicating that a double bond likely exists between the two bismuth atoms. The second isomer (structure 2 in Fig. 1), which is only 0.14 eV higher in energy than the ground state, can be viewed as a derivative of a cube with one vertex missing. All the bond distances in this isomer are within the expected range with one notable exception: The Bi–Bi bond is longer (3.25 Å) than normal single Bi–Bi bond (3.03 Å for C_{2h} $H_2Bi{-}BiH_2$).[26] The third isomer (structure 3) is interesting. All of the silicon atoms form a planar triangulated ring with the two bismuth atoms laying on top of the ring but with a long Bi–Bi bond. Energetically, this structure is 0.35 eV higher than the ground state structure. The structures 4 and 5 are even higher in energy com-

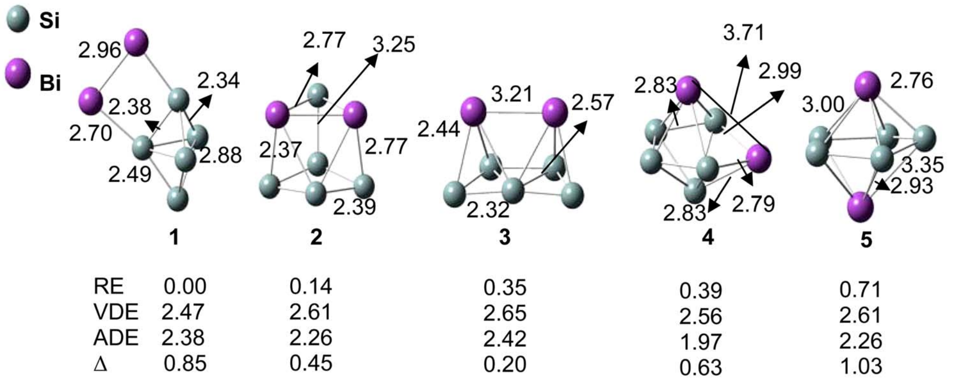

FIG. 2. (Color online) Calculated most stable structures of anionic $Bi_2Si_5^-$. All bond lengths are given in angstrom. For each species, the RE, VDE, ADE and HOMO-LUMO gap (Δ) are given in eV.

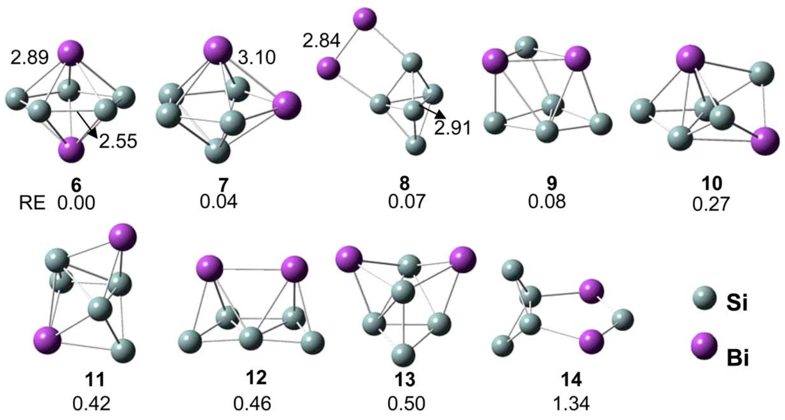

FIG. 3. (Color online) Calculated most stable structures of neutral Bi_2Si_5. The RE for each species is given in eV.

pared to the ground state, i.e., 0.39 and 0.71 eV, respectively. These two isomers can be viewed as derivatives of PBP structure of Si_7^{2-} with the Bi atoms replacing Si atoms at positions 1,2 (structure 4) and positions 1,7 (structure 5), respectively.

We have calculated VDE and ADE values along with HOMO-LUMO gaps Δ for the five lowest energy isomers of the anion (Fig. 2, structure 1–5). The calculated VDE, ADE, and Δ for structure 1 are predicted to be 2.47, 2.38, and 0.85 eV, respectively. These values match well with the experimental observations (2.38 eV for VDE, 2.25 eV for ADE, and 0.73 eV for HOMO-LUMO gap). The excess electron in this anion occupies the π^*-orbital of the Bi–Bi unit. Removing that electron relaxes structure 1 to neutral structure 8 (see Fig. 3), and the Bi–Bi bond is slightly shortened from 2.96 to 2.84 Å. Relatively minor structural changes in the geometry of isomer 1 upon photodetachment are reflected by the sharpness of the first band (see Fig. 1) and the corresponding small energy difference between the measured VDE (2.38 eV) and ADE (2.25 eV). The calculated VDE, ADE, and HOMO-LUMO gap for the next most stable isomers, structures 2 and 3, do not match our experimental results. Therefore, we conclude that the structures 2 and 3 were not observed in our experiments and that structure 1 is likely to be the only isomer that is responsible for the observed transitions in the photoelectron spectrum. Furthermore, the good agreement between theoretical predictions and the experimental results allows us to view the calculations on neutral clusters with greater confidence.

The most stable calculated structures of neutral Bi_2Si_5 are shown in Fig. 3. Eight isomers (structures 6–13) were found within 0.5 eV energy difference. The four most stable isomers (structures 6–9) have essentially the same energies within our capacity to calculate them. The lowest energy structures 6 and 7 prefer PBP structure with the Bi atoms at positions 1,7 and positions 1,2, respectively. Structures 8 and 9, on the other hand, adopt TBP structures that are similar to the two most stable anion structures 1 and 2. To provide a comparison with silicon clusters, we have also computed the corresponding neutral borane analogs, $Bi_2B_5H_5$. Our calculations indicate that ground state neutral $Bi_2B_5H_5$ is also a PBP skeleton with bismuth atoms in positions 1,2, which is 0.83 eV lower in energy than the corresponding 1,7 isomer (see Fig. 4). Therefore, both structures 6 and 7 resemble the PBP cage structures that $Bi_2B_5H_5$ prefers to adopt. While the boron cages are rigid, as judged by the large relative energies difference between 1,2 and 1,7 isomers, the low energy Bi_2Si_5 isomers are flexible and adopt several cagelike motifs with nearly equal energies. Nevertheless, in spite of multiple degenerate lowest energy structures,[27] most of them prefer to adopt *closo*-structures as predicted by the Wade–Mingos rule. Furthermore, the neutral isomers of Bi_2Si_5 generally have shorter Si–Bi and Bi–Bi bond lengths than the corresponding anion (e.g., compare the related structures 5 and 6, 4 and 7, etc.). It should be noted that the relative energy (RE) ordering of various isomers for Bi_2Si_5 and $Bi_2B_5H_5$ is different from that found for the corresponding isovalent $(CH)_2Si_5$ and $(CH)_2B_5H_5$ clusters. These differences may be attributed to the larger size of Bi atom compared to the CH group. Similarly contrasting stabilities have been noted in the case of $X_2B_5H_5$ (X=CH and SiH) and other heteroboranes.[21,28–31]

We have shown that structurally the lowest energy isomers of Bi_2Si_5 resemble those of $Bi_2B_5H_5$. Do they have similar electronic structures as well? In order to explore the isolobal analogy between divalent silicon and the BH group, we have selected the lowest energy structure of Bi_2Si_5 (structure 6) and its analog $1,7\text{-}Bi_2B_5H_5$ for comparison. Note that both species have the same number of valence electrons $(Bi(5)\times 2+Si(4)/BH(4)\times 5=30)$, and the same number of cage bonding electrons. For example, $1,7\text{-}Bi_2Si_5$ has seven lone pairs, one from each Si and Bi atom with the remaining $(30-14=16)$ electrons available for cage bonding. A similar situation is encountered for $1,7\text{-}Bi_2B_5H_5$ as well. There, five

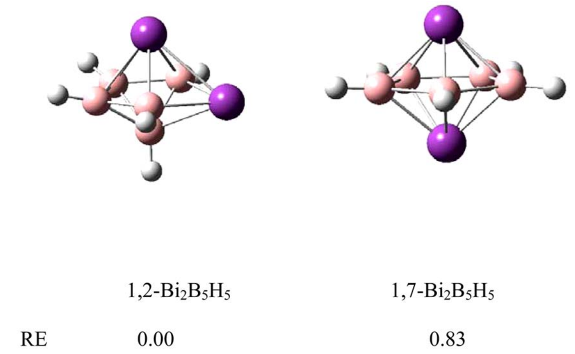

FIG. 4. (Color online) Calculated structures of $1,2\text{-}Bi_2B_5H_5$ and $1,7\text{-}Bi_2B_5H_5$. The RE for each species is given in eV.

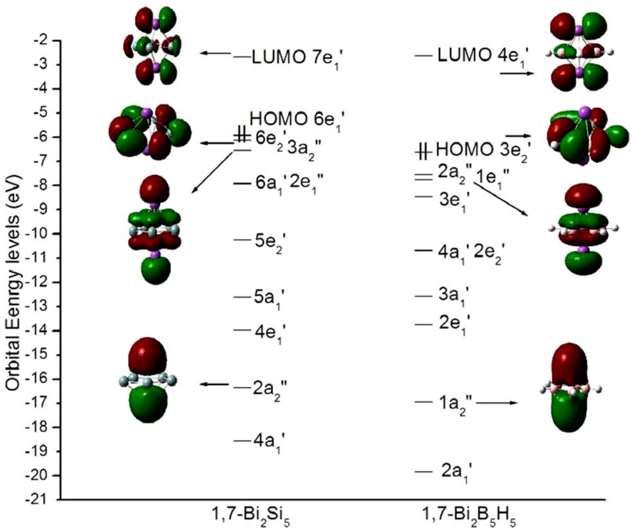

FIG. 5. (Color online) A comparative valence orbital energy diagram for 1,7-Bi_2Si_5 (D_{5h}) and 1,7-$Bi_2B_5H_5$ (D_{5h}).

B–H bonds and two lone pairs from Bi atoms take 14 valence electrons, thereby also leaving 16 of them for cage bonding. Figure 5 shows how these 16 valence electrons are distributed within the valence orbital patterns of the two aforementioned systems. Although there is some reshuffling of the orbital energy levels at the frontier level between the two systems, the overall arrangement of the molecular orbitals (MOs) is quite similar. Here, we discuss a few MOs for comparison. A complete correlation diagram with the full set of MOs is given in the supplementary material.[32] For example, the HOMO of 1,7-$Bi_2B_5H_5$, $3e_2'$, is a B–H bonding orbital and the corresponding orbital, $6e_2'$, for 1,7-Bi_2Si_5 is a silicon lone-pair orbital. Similarly, $2a_2''$ and $3a_2''$ are cage bonding orbitals while $1a_2''$ and $2a_2''$ are Bi lone pair orbitals in 1,7-$Bi_2B_5H_5$ and 1,7-Bi_2Si_5, respectively. Finally, the LUMO, which is a cage antibonding orbital, is also identical for both systems. Thus, 1,7-Bi_2Si_5 and 1,7-$Bi_2B_5H_5$ are isovalent, adopt comparable geometrical structures and have similar orbital patterns. They are therefore isolobal. Furthermore, to investigate relativistic effects on the stabilization of Bi_2Si_5, we conducted calculations comparing Bi_2Si_5 and P_2Si_5 and found that their most stable structures are the same.

In conclusion, the potential energy surfaces of $Bi_2Si_5^-$ and Bi_2Si_5 are rich and varied. The comparison between the experimental results and the theoretical calculations reveals that the most stable, calculated $Bi_2Si_5^-$ isomer (structure 1) is indeed observed in the experiments. This work provides experimental support for the isolobal analogy.

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[32] See EPAPS Document No E-JCPSA6-129-001838 for a correlation diagram of the MOs of 1,7-Bi_2Si_5 and 1,2-$Bi_2B_5H_5$. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.