# Silicon−Bismuth and Germanium−Bismuth Clusters of High Stability

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Mixed metal−semiconductor clusters of the form $Bi_2Si_{n-2}$ and $Bi_2Ge_{n-2}$, $n = 3-8$, 12, are studied theoretically by ab initio methods including density functional theory with the hybrid B3LYP functional, second-order perturbation, and coupled cluster CCSD(T) theory using the doubly polarized TZV2P basis sets. These clusters are characterized by high stability and symmetry and relatively large highest occupied−lowest unoccupied molecular orbital (HOMO−LUMO) energy gaps. It is shown that the lower energy structures of these clusters and their bonding and electronic characteristics are fully compatible with very powerful stability rules and structural laws similar to the ones for the corresponding isovalent boranes, carboranes, and bisboranes. This is particularly true for the $Bi_2Ge_{n-2}$ clusters, the global minima of which are identical to the ones of the corresponding isovalent carboranes and bisboranes, obtained by proper substitutions from the corresponding dianions. The $Bi_2Si_{n-2}$ clusters for $n > 8$, although isolobal to the homologous $Si_n^{2-}$ clusters, are not fully isolobal with the corresponding boranes, carboranes, and bisboranes as the $n = 3-8$ clusters. For the $Bi_2Si_{n-2}$ clusters with $n \leq 8$, a strange odd−even effect is observed. For the even-$n$ $Bi_2Si_{n-2}$ clusters, in contrast to those of odd-$n$, the structures obtained from the $Si_n^{2-}$ dianions through the so-called "boron connection" compete with those obtained from substitutions on the corresponding neutral cluster structures. The even-$n$ $Bi_2Si_{n-2}$ clusters are fluxional or isomerizable. The $Bi_2Si_4$ cluster in particular is fluxional and structurally similar to the corresponding $Si_6$ cluster. The differences between the $Bi_2Si_{n-2}$ and $Bi_2Ge_{n-2}$ clusters are attributed mainly to the inert pair effect in $Bi_2Ge_{n-2}$. For this reason, although the lowest energy structure of the $Bi_2Si_{10}$ cluster has relatively low ($C_s$) symmetry derived from the corresponding $Si_{12}^{2-}$ structure, the homologous $Bi_2Ge_{10}$ cluster is characterized by high $D_{5d}$ symmetry obtained from the $Ge_{12}^{2-}$ dianion of full icosahedral symmetry, similar to the corresponding $(B_{12}H_{12})^{2-}$ borane. The present rationalization of the silicon/germanium−bismuth clusters is very promising for deeper understanding and future functionalization toward useful chemical and technological applications.

## I. Introduction

The physical and chemical properties of silicon clusters, besides their scientific significance, are also very important for nanoscience and nanotechnology in view of the continued miniaturization of the electronic devices, which is pushing toward the nano- and molecular scales. Thus, in the past two decades,[1−7] silicon clusters have been the subject of extensive experimental and theoretical studies, not always unambiguously.[6,7] On the other hand, metal-adsorbed or metal-embedded silicon clusters, in particular with transition metals,[8−16] have attracted special attention not only on their own merit (due to their high stability, high symmetry, and large HOMO−LUMO gaps, as compared to bare silicon clusters) but also for providing a good model of the metal−semiconductor interface, which is very important for technological applications.[8,9] Semimetals such as bismuth (which is the heaviest group V semimetal) could be also very interesting in this respect. Transition metal-embedded silicon clusters are well-known for stabilizing silicon cage-like structures. It will be shown below that bismuth also can stabilize small cage structures with high symmetry and large HOMO−LUMO gaps. In this case, substitution (of two silicon or germanium atoms of the cage by Bi), rather than doping (as in the transition metal atoms), is applied. Furthermore, in this latter case, contrary to the single (transition) metal-embedded or adsorbed clusters, there are some guiding principles and structural rules to determine the structures of such dibismuthic silicon and germanium clusters. These structural and stability rules are based on similar well-known powerful structural rules and stability principles, originally developed and tested over the years for isovalent (isoelectronic) boranes and carboranes and bisboranes.[17−20] These rules, with possible small deviations, are expected to be valid for the binary Bi−Si and Bi−Ge clusters. The underlying concept, which is instrumental and responsible for transferring the structural and stabilization rules from boranes and carboranes into such a type of "dimetallic" silicon and germanium clusters, has come to be known as "the boron connection".[21,22] This concept, which has originated from the fluxionality of the magic $Si_6$ cluster[7] and the analogy between deltahedral boranes and silicon clusters (and/or cluster dianions),[7,23] actually goes back to Mingos and collaborators,[24] and Wales[25] (in a slightly different context). The essence of "the boron connection" in its broadest and most general expression is that for any B−H bond-bearing compound, the replacement of B−H by isovalent Si or Ge[21] would be expected to lead to a low-energy local (or global) minimum of the corresponding Si-containing "homologous" structure. This is particularly true for carborane compounds, as has been shown earlier.[21,22] In reality, the (BH) → Si replacement rule is only a special (expanded, under certain conditions) case of the more general $(BH)^{2-} \rightarrow Si^{2-}$ rule or $(B_nH_n)^{2-} \rightarrow Si_n^{2-}$, and apparently the $(B_nH_n)^{2-} \rightarrow Ge_n^{2-}$ rule, $n = 3-8$. The (small) differences can be attributed to the different behavior of the Si lone pairs as compared to

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B−H radial bonds and the induced strains resulting from the tendency to $sp^3$ bond-angle optimization.[21−23] These effects are expected to be weaker in the germanium species ($Ge_n^{2-}$) due to the relative weakening of $sp^3$ bonding in relation to the "inert pair effect" as we go down the period of the periodic table.[22]

This rule, combined with the well-known and well-tested analogy (which leads to isolobal carboranes), expressed symbolically as $2BH^{1-} \rightarrow 2CH$ or (more generally) $(B_nH_n)^{2-} \rightarrow C_2B_{n-2}H_n$, leads to the analogy of the $C_2B_{n-2}H_n$ carboranes with the isolobal $Si_{n-2}C_2H_2$ and $Ge_{n-2}C_2H_2$ clusters,[21,22] $C_2B_{n-2}H_n \rightarrow Si_{n-2}C_2H_2 \rightarrow Ge_{n-2}C_2H_2$. In fact, the $2BH^{1-} \rightarrow 2CH$ rule can in principle be extended to any system bearing five valence electrons, such as bismuth (instead of CH), leading to $Bi_2Si_{n-2}$ clusters.[26,27] The $2BH^{1-} \rightarrow 2Bi$ analogy is not purely academic, but it has been tested in practice, through the synthesis of the well-known bisboranes[28] of the form $Bi_2B_{n-2}H_{n-2}$. Combining this with the "boron connection" isolobal analogy, we can anticipate the analogy $Bi_2B_{n-2}H_n \rightarrow Bi_2Si_{n-2} \rightarrow Bi_2Ge_{n-2}$, and thus apply the same structural rules for the $Bi_2Si_{n-2}$ and $Bi_2Ge_{n-2}$ clusters. The $Bi_2Ge_{n-2}$ clusters in full analogy to the corresponding $Bi_2Si_{n-2}$ clusters would be expected to be obtained from the corresponding $Ge_n^{2-}$ dianions, which are not always (in particular for large values of $n$, for example, $n = 12$) similar to $Si_n^{2-}$ dianions.[22,29]

The purpose of the present work is to study the small binary $Bi_2Si_{n-2}$ and $Bi_2Ge_{n-2}$ clusters, exploring at the same time the validity of and the possibility to establish similar structural rules for such clusters, rationalizing and predicting their structural, bonding, and electronic characteristics. As will be shown below, the $Bi_2Ge_{n-2}$ clusters fit better to this scheme as compared to the isovalent $Bi_2Si_{n-2}$ clusters.

In the process of this search, a strange odd−even effect was found for the $Bi_2Si_{n-2}$ in contrast to the $Bi_2Ge_{n-2}$ clusters. Although the lowest energy structures of the odd-$n$ ($n = 3$, 5, 7) $Bi_2Si_{n-2}$ and all (even and odd) $Bi_2Ge_{n-2}$ clusters are indeed fully obtained from the common $Si_n^{2-}$ and $(B_nH_n)^{2-}$ dianions, the lowest energy structures of the even-$n$ $Bi_2Si_{n-2}$ clusters (but not of $Bi_2Ge_{n-2}$) include (and sometimes prefer) lowest energy structures obtained by direct substitution on the corresponding $Si_n$ neutral clusters (see section IV). This is particularly true for $Bi_2Si_4$, the lowest energy structure(s) of which are fluxional and very much resembling the corresponding fluxional multistructures[6,7] of $Si_6$.

For the odd clusters and especially for $n = 7$, it has been shown both experimentally and theoretically[26] that the boron connection indeed works. Such clusters would be expected to have relatively high stability and large HOMO−LUMO gaps. It is shown below that this is indeed true.

The technical details of the present calculations are given in section II. The main results of this work for $Bi_2Si_{n-2}$ and $Bi_2Ge_{n-2}$, $n = 1−8$, clusters, which are "isolobal" to each other and the corresponding bisboranes and boranes $Bi_2Si_{n-2}$, are presented, discussed, and compared to each other in section III. The results presented in this section are fully compatible with the "boron connection". These include all $Bi_2Ge_{n-2}$ clusters and the majority of $Bi_2Si_{n-2}$ clusters, and in particular the odd-$n$ clusters. The even-$n$ $Bi_2Si_{n-2}$ clusters ($n = 4$, 6, 8) show a peculiar behavior (especially the $n = 6$ cluster), which seems to deviate from the expected behavior on the basis of the "boron connection", because their structure is not related to the isostructural $Si_n^{2-}$, $Ge_n^{2-}$, and $(BH)_n^{2-}$ dianions. These clusters are re-examined and augmented with additional results in section IV. In this section, all results for the even-$n$ $Bi_2Si_{n-2}$ clusters are integrated and re-examined in comparison to or within the "boron connection" analogy. In both cases, the boron connection is fully operative, but for the even-$n$ $Bi_2Si_{n-2}$ clusters there are additional low-lying structures related to the neutral clusters, beyond the "boron connection". A similar and yet different situation exists for the $n = 12$ clusters where the lowest lying structures are different for the silicon and germanium species. However, here the $Si_n^{2-}$, $Ge_n^{2-}$, and $(BH)_n^{2-}$ dianions are not isostructural.[22] The $Ge_{12}^{2-}$ and $(BH)_{12}^{2-}$ are icosahedral, while $Si_{12}^{2-}$ is of low $C_s$ symmetry. The $n = 12$ results are discussed in section V. Finally, the conclusions and plans for future studies are summarized in section VI.

## II. Technical and Computational Details

The geometry optimizations (symmetry constrained and unconstrained) and single point calculations for all structures were performed within the density functional theory (DFT), using the hybrid exchange and correlation functional of Becke-Lee, Parr, and Yang (B3LYP)[30] and the triple-$\zeta$ valence doubly polarized (TZV2P) basis set.[31] This basis set, implemented in the TURBOMOLE program package[32] under the label def-TZVPP, is comparable to 6-311G(2df)[33,34] quality. For Bi, compatible effective core potentials (ECPs) were used, which include scalar relativistic effects.[32,35] In all cases, several initial geometries were used (including the ones that are similar to those of $Si_n^{2-}$ and $Si_{n-2}C_2H_2$), and a plethora of structures was studied. Initial geometries for $Bi_2Si_{n-2}$ (and correspondingly for $Bi_2Ge_{n-2}$) were generated in four different ways: (1) by 2 Bi substitutions on geometries of $Si_n$ in all conceivable ways, using not only the lowest but also several lower energy structures, (2) by $Bi_2$/$Si_2$ attachments on $Si_{n-2}$ geometries, (3) by 2 Bi substitutions on $Si_n^{2-}$ and $Ge_n^{2-}$ dianions, similar to $Si_{n-2}C_2H_2$ and deltahedral carboranes/bisboranes, and (4) by using best-case and worse-case geometries generated by chemical intuition (based on valency and coordination) and symmetry. All of these runs were performed without symmetry constraints using initially the TZVP basis set and the BP86[36] or B3LYP functional. The structures were afterward reoptimized using the TZV2P basis set and the B3LYP functional, and symmetrized (using loose symmetry constraints initially) wherever possible. Frequency calculations were run in all cases. For structures in which very small energy differences occurred, second-order Møller−Plesset (MP2) perturbation theory[33,37] was also used employing the same (def-TZVPP or simply TZV2P) basis set. Both DFT-B3LYP/TZV2P and MP2/TZV2P (single point and geometry optimizations) calculations were performed with the TURBOMOLE program package.[32] In addition to MP2, in several critical cases single-point high level coupled clusters, CCSD(T),[33,38] calculations were performed at the B3LYP/TZV2P and MP2/TZV2P geometry, using the same (def-TZVPP or TZV2P) basis sets and effective core potentials. These calculations were performed with the Gaussian program package.[33] The nucleus-independent chemical shifts (NICS)[39] were calculated with the gauge-independent atomic orbital method (GIAO) using the Gaussian program package.[33]

## III. Results and Discussion for $Bi_2Si_{n-2}$ and $Bi_2Ge_{n-2}$ Clusters, $n = 3−8$, in the Framework of the "Boron Connection"

**A. Structural and Energetic Characteristics.** In Figure 1, we have selected from the plethora of the structures examined the lowest and second lowest energy structures of $Bi_2Si_{n-2}$ and $Bi_2Ge_{n-2}$, $n = 3−8$, which were found completely compatible with the boron connection. These are truly the lowest energy isomers for all $Bi_2Ge_{n-2}$ and the majority of the $Bi_2Si_{n-2}$ clusters

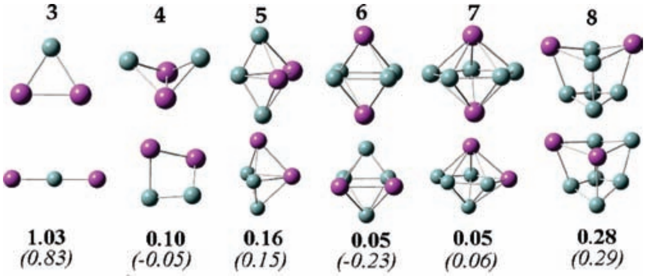

**Figure 1.** The structure of the lowest (top) and second lowest (bottom) energy structures of $Bi_2Si_{n-2}$, $Bi_2Ge_{n-2}$, $n = 3-8$ clusters, in full analogy to the corresponding bisboranes. The numbers below the structures indicate the energy differences between the top and bottom structures of $Bi_2Ge_{n-2}$ clusters (which are fully compatible with the "boron connection") in eV. The corresponding energy differences for the homologous $Bi_2Si_{n-2}$ clusters are shown in italics inside parentheses.

including all odd-$n$, but not all even-$n$ $Bi_2Si_{n-2}$ clusters, which will be reexamined in section V. This is why in this figure the energetic ordering of $Bi_2Ge_{n-2}$ clusters is given first, while the corresponding energy differences for the homologous structures of the $Bi_2Si_{n-2}$ clusters are given (in parentheses). For the even-$n$ $Bi_2Si_{n-2}$ clusters, the (isolobal) structures shown in Figure 1, although very low-lying energetically, are not always the lowest (see discussion in section IV). As could be anticipated on the basis of the isolobal analogy, these $Bi_2Ge_{n-2}$ clusters are fully analogous to the corresponding isovalent $Si_{n-2}C_2H_2$ and $Ge_{n-2}C_2H_2$ clusters. The same is true for the odd-$n$ $Bi_2Si_{n-2}$ clusters but not for the even-$n$ ones, for which the isolobal structures, although very low, are not the lowest. The different behavior of the $Bi_2Ge_{n-2}$ and $Bi_2Si_{n-2}$ clusters is similar but not identical to the differences between $Si_{n-2}C_2H_2$ and $Ge_{n-2}C_2H_2$ clusters[22] for $n = 12$.

The differences between $Si_{n-2}C_2H_2$ and $Ge_{n-2}C_2H_2$ clusters have been discussed elsewhere.[22] These differences are related to the inert pair effect in germanium[22] and the relative weakness of Ge−Ge and C−Ge interactions as compared to Si−Si and C−Si interactions. As a result, the $Ge_{n-2}C_2H_2$ clusters always prefer structures with the two C atoms in adjacent positions. For similar reasons (inert pair effect, weakening of the $sp^3$ bonding), the energy differences between high symmetry $Ge_n^{2-}$ dianion structures (in particular for $n = 12$) similar to the $B_nH_n^{2-}$ boranes and low symmetry ($C_s$) structures preferred by $Si_{12}^{2-}$ for the optimization of the $sp^3$ bonding are significantly reduced and practically diminished.[35] As will be shown below in section V, this is also true for the $Bi_2Si_{10}$ and $Bi_2Ge_{10}$ clusters obtained from the $Si_{12}^{2-}$ and $Ge_{12}^{2-}$ dianions. The same trend must be responsible for the stabilization of the highly symmetric ($I_h$) $Sn_{12}^{2-}$ dianion (the stannaspherene).[40,41]

In Figure 1, we can also see the energetic ordering (between first and second lowest structures of $Bi_2Ge_{n-2}$ and odd-$n$ $Bi_2Si_{n-2}$ clusters), which is slightly different as compared to $Si_{n-2}C_2H_2$ and $Ge_{n-2}C_2H_2$ clusters. The ordering differences between $Bi_2Ge_{n-2}$, $Bi_2Si_{n-2}$, $Si_{n-2}C_2H_2$, and $C_2B_{n-2}H_n$ (for $n = 3-8$) can be attributed to the large size of bismuth relative to carbon and/or boron atoms. Such differences in ordering are similar to the differences between the corresponding carboranes and bisboranes.[28]

More specifically, for each $n$ we have the following:

For $n = 3$, the classical isosceles triangle is the "ground-state structure" for both $Bi_2Ge$ and $Bi_2Si$, as well as for $SiC_2H_2$, $GeC_2H_2$, and $C_2BH_2$.

For $n = 4$, the puckered rhombus of $C_{2v}$ symmetry of Figure 1 (4) is the ground-state structure for $Bi_2Ge_2$ and $C_2B_2H_3$. The $C_2$ symmetric nonplanar puckered trapezoidal structure in the second row is the lowest energy structure (by only 0.05 eV) for both $Bi_2Si_2$ and $Si_2C_2H_2$. The energy gain of the puckered trapezoidal structure is related to a better optimization of the $sp^3$ bond angles[21] in $Si_2C_2H_2$ and $Si_2Bi_2$. Both structures are connected through a diamond−square−diamond (DSD) transformation.[21] We can again verify that the $sp^3$ bonding is weaker in $Bi_2Ge_2$ (in germanium versus silicon) as compared to $Bi_2Si_2$.

For $n = 5$, both lowest and second lowest energy structures of $Bi_2Ge_3$ and $Bi_2Si_3$ are obtained from the corresponding $D_{3h}$ symmetric $Si_5^{2-}$ and $Ge_5^{2-}$ dianions[23] by (2,3)- and (1,2)-substitutions, respectively, whereas the corresponding isovalent $Si_3C_2H_2$ and $C_2B_3H_5$ ground states are obtained by (1,5)-substitution of two Si (or B) atoms (lying on $C_3$ axis)[21] on the corresponding $Si_5^{2-}$ and $(B_5H_5)^{2-}$ dianions. For these species, the energetic ordering is: (1,5-) < (1,2-) < (2,3-). This ordering is in full agreement with known empirical valence rules[42] and topological charge stabilization[19,43] concepts, developed originally for the isovalent carboranes. $Ge_3C_2H_2$, on the other hand, like $Ge_3Bi_2$, is obtained by (1, 2)-substitution and, therefore, does not follow these stability rules for reasons already explained.[22]

For $n = 6$, two possible structures of $Bi_2Ge_4$ and $Bi_2Si_4$ can be obtained from the corresponding $O_h$ symmetric $Ge_6^{2-}$ and $Si_6^{2-}$ dianions:[7,23] the $D_{4h}$ structure (6) on the top row of Figure 1, obtained by (1,6)-substitution, and the $C_{2v}$ structure in the second row of Figure 1, obtained by (2,3)- (or equivalently by (1,2)-substitution). These two structures, respectively, are the lowest and second lowest energy structures of $Bi_2Ge_4$. For $Bi_2Si_4$, however, both structures have been pushed to higher energies in the third and fourth lowest energies (in reverse order): the (2,3)-structure of $C_{2v}$ symmetry is the third, and the (1,6)- is the fourth low energy structures (0.33 and 0.55 eV higher than the lowest energy structure of $Bi_2Si_4$, respectively), as will be shown in section IV. The (2,3)-$C_{2v}$ symmetric structure is the "ground state" of the corresponding bisborane, $B_4H_4Bi_2$. On the contrary, the lowest energy structure of the homologous carborane $C_2B_4H_6$ and isovalent $Si_4C_2H_2$ cluster is the $D_{4h}$ symmetric (1,6)-isomer, in full agreement with the known empirical valence rules[42] and topological charge stabilization[19,43] concepts. $Bi_2Ge_4$ and $Ge_4C_2H_2$ behave completely oppositely as compared to $Bi_2Si_4$ and $Si_4C_2H_2$. Thus, $Bi_2Ge_4$ prefers the (1,6)-$D_{4h}$ structure, whereas the lowest energy structure of $Ge_4C_2H_2$ is the (2,3)-$C_{2v}$ isomer.

For $n = 7$, both $Bi_2Ge_5$ and $Bi_2Si_5$ clusters in Figure 1 (7) share the $D_{5h}$ pentagonal bipyramidal structure of $Ge_7^{2-}$, $Si_7^{2-}$, and $(B_7H_7)^{2-}$ dianions,[23] in full agreement with the experimental and theoretical results of Li et al.[26] The pentagonal bipyramid is also the ground-state structure of the corresponding bisborane, $B_5H_5Bi_2$. The second lowest energy structure for $Bi_2Si_5$ is the (1,2)-$C_s$ symmetric isomer, shown in the second row of Figure 1. For $Bi_2Ge_5$, the second lowest energy isomer is not the (1,2)-, but the (2,4)-isomer (not shown in Figure 1) of $C_{2v}$ symmetry. This (2,4)-isomer, which allows the optimization of alternating charges, is the lowest energy structure of the isovalent carborane $C_2B_5H_7$ and the isolobal $Si_5C_2H_2$ cluster.[21,22] The NICS(0) value is positive, similarly to the $D_{5h}$ $Si_7^{2-}$ dianion, and for the same reasons as for the high symmetry $Si_6^{2-}$ dianion.

For $n = 8$, the lowest energy structure of both $Bi_2Ge_6$ and $Bi_2Si_6$ clusters is the $C_{2v}$ symmetric puckered square Archimedean antiprism, shown in the top row of Figure 1 (8), which has been obtained by (1,7)-substitution[22] from the $D_{2d}$ symmetric $Ge_8^{2-}$ and $Si_8^{2-}$ dianion.[23] The same structure is also the lowest energy structure of $Si_6C_2H_2$, whereas the isovalent $C_2B_6H_8$ carborane

**TABLE 1: Comparison of the $Bi_2Si_{n-2}$ and $Bi_2Ge_{n-2}$, $n$ = 3−8, Clusters at the B3LYP/TZV2P Level of Theory: Atomization Energies $E_a$ (and $E_a/n$ Below in Parentheses), Energy Differences $\Delta E_{21}$ between Lowest and Second Lowest Energy Isomers, HOMO−LUMO Gaps, and NICS(0) Values**[a]

| | *n* | | | | | |
|---|---|---|---|---|---|---|
| | 3 | 4 | 5 | 6 | 7 | 8 |
| $Bi_2Si_{n-2}$ $E_a$ | 5.64<br>(1.88) | 8.89<br>(2.22) | 13.12<br>(2.62) | *15.58*<br>*(2.59)* | 18.95<br>(2.71) | 22.98<br>(2.87) |
| $Bi_2Ge_{n-2}$ | 5.36<br>(1.79) | 8.44<br>(2.11) | 12.14<br>(2.43) | 14.56<br>(2.43) | 18.18<br>(2.60) | 21.09<br>(2.64) |
| $Bi_2Si_{n-2}$ $\Delta E_{21}$ | 0.83 | 0.05 | 0.15 | *0.23* | 0.06 | 0.29 |
| $Bi_2Ge_{n-2}$ | 1.03 | −0.10 | 0.16 | −0.05 | 0.05 | 0.28 |
| $Bi_2Si_{n-2}$ H−L | 2.38 | 2.55 | 3.35 | *2.60* | 3.26 | 3.01 |
| $Bi_2Ge_{n-2}$ | 2.50 | 2.56 | 3.32 | 2.95 | 3.60 | 2.76 |
| $Bi_2Si_{n-2}$ NICS(0) | −4.8<br>(−9.6)[b] | −16.2 | −38.8 | *+5.6* | +7.5 | −13.6 |
| $Bi_2Ge_{n-2}$ | −4.4<br>(−9.2)[b] | −14.2 | −34.0 | +17.6 | +2.3 | −14.7 |

[a] Energies are in eV; NICS values in ppm (parts per million). [b] NICS(1) values.

has a fluxional ground state based on a $C_2$ symmetric structure, known as bisdisphenoid,[22] which is nearly isoenergetic with a $C_{2v}$ symmetric square open-face structure. On the other hand, $Ge_6C_2H_2$ adopts a ground-state structure of $C_s$ symmetry similar to the second lowest energy structure of $Bi_2Ge_6$ and $Bi_2Si_6$, shown in the last row of the last column of Figure 1, in which the two carbon units are in adjacent positions.

**B. Cohesive Electronic and Aromatic Characteristics.** The results for the cohesive, electronic, and aromatic properties of $Bi_2Ge_{n-2}$ and the homologous $Bi_2Si_{n-2}$ clusters of Figure 1 have been summarized in a concise form in Table 1. With the exception of $n = 6$ (which will be discussed separately in section IV), the $Bi_2Si_{n-2}$ clusters discussed in this table are the lowest energy structures found after an extensive search and a plethora of structures examined. The $Bi_2Si_4$ results in Table 1 are shown in italics.

First, the atomization energies in the first pair of rows of Table 1 show an increasing trend with increasing number of Ge or Si atoms. This trend has been also observed in the isovalent $Si_{n-2}C_2H_2$ and $Ge_{n-2}C_2H_2$ clusters.[21] However, in the present case, in contrast to $Si_{n-2}C_2H_2$ and $Ge_{n-2}C_2H_2$ clusters, not only the total atomization energy $E_a$, but also the binding energy per atom ($E_a/n$) increases with increasing $n$. Only in the case of $Bi_2Si_4$ (which in Table 1 is not represented by the "ground state") can we observe a small decrease in $E_a/n$ as compared to $Bi_2Si_3$, although $E_a$ increases. A similar effect but much less pronounced is observed for $Bi_2Ge_4$ (the $n = 5$ and $n = 6$ $E_a/n$ values rounded off to the second decimal point are the same). This could be related to the high symmetry ($O_h$) of the parent $Si_6^{2-}$ and $Ge_6^{2-}$ dianions. The trend is the same for both $Bi_2Si_{n-2}$ and $Bi_2Ge_{n-2}$ clusters, with the latter characterized by smaller $E_a$ (and $E_a/n$) values due to the weakening of the $sp^3$ bonding in $Bi_2Ge_{n-2}$. The second pair of rows of Table 1 describes the energy differences between the first and second lowest energy states, which are also given in the lower part of Figure 1. The HOMO−LUMO gaps, which are a zeroth-order measure of chemical hardness, are very large ranging from 2.38 to 3.35 eV for $Bi_2Si_{n-2}$, and 2.50 to 3.60 eV for $Bi_2Ge_{n-2}$.

For both types of clusters, there is no systematic correlation of the HOMO−LUMO gap variation with the changes in the atomization energy as a function of $n$.

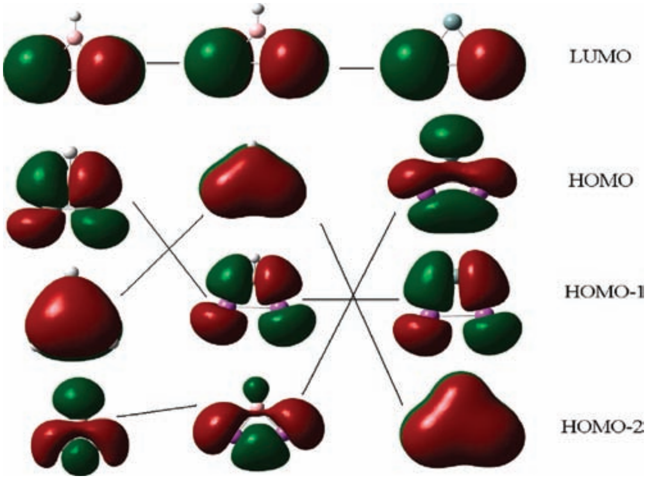

Figure 2. Comparison of the frontier orbitals of $(B_3H_3)^{2-}$, $Bi_2BH$, and $Bi_2Si$ clusters. The interrelation is illustrated by connecting straight lines.

Finally, the aromatic characteristics listed in the last row(s) of Table 1 deserve special attention.

The NICS(0) value, which is one of the best known aromaticity indices,[39,44] characterizes both three-dimensional (3D) or spherical aromaticity (for $n$ = 4−8) as well as normal two-dimensional $\pi$-aromaticity in planar species such as $Bi_2Si$ and $Bi_2Ge$ ($n = 3$). The $\pi$-aromaticity of these species is verified by the value of NICS(1), in parentheses below the NICS(0) value in Table 1. As we can see in this table, for both $Bi_2Si$ and $Bi_2Ge$ there is more aromatic behavior (more diatropic, negative NICS value) at the NICS(1) level, 1 Å above the plane of the molecule, as compared to NICS(0) at the center of the molecule. This is a manifestation of the $\pi$ electron toroid densities. For larger $n$, the 3D aromaticity is characterized by comparable values of NICS(0) values, mostly diatropic except the notable paratropic behavior (positive NICS(0) values) for $n = 6$ and $n = 7$. As has been illustrated earlier,[22,23,39−41,44] this is related to the high symmetry ($O_h$ and $D_{5h}$, respectively) of the parent dianions $Ge_6^{2-}$ and $Ge_7^{2-}$ ($Si_6^{2-}$ and $Si_7^{2-}$), which are also characterized by paratropic NICS(0) values[23] (+10.8 and +5.7 ppm, respectively). The high symmetry results in the mixing of highly paratropic degenerate orbitals (such as the 3-fold degenerate $t_{1u}$ orbital in the case of $Si_6^{2-}$) with normal diatropic orbitals.[23,32] These paratropic values illustrate at the same time the deeper relationship of the two species (pure cluster dianions, $Si_n^{2-}$ and $Ge_n^{2-}$, and $Bi_2Si_{n-2}$ mixed clusters). We can also observe that in the case of $Bi_2Si_4$, where the symmetry ($C_{2v}$) is relatively lower as compared to $Bi_2Ge_4$ ($D_{4h}$), the NICS(0) value is less paratropic (as compared to $Bi_2Ge_4$).

**C. "Isolobal" Characteristics.** All structural, energetic, electronic, and aromatic characteristics examined thus far demonstrate the deeper relationship, analogy, similarity, and homology between $Bi_2Si_{n-2}$ and $Bi_2Ge_{n-2}$ and the corresponding $Si_n^{2-}$ and $Ge_n^{2-}$ dianions, which in turn are homologous and isolobal to the corresponding isovalent boranes, carboranes (and bisboranes). To fully illustrate the isolobal property, we first examine in Figure 2 the structure of the frontier orbitals of $(B_3H_3)^{2-}$, $Bi_2BH$, and $Bi_2Si$ clusters with analogous results for the homologous Ge-containing clusters.

As we can see in the figure, there is a complete one-to-one correspondence between the LUMO and HOMO orbitals of the three species.

A less trivial more complicated case is shown in Figures 3 and 4, which illustrate the "isolobality" and similarity of a larger

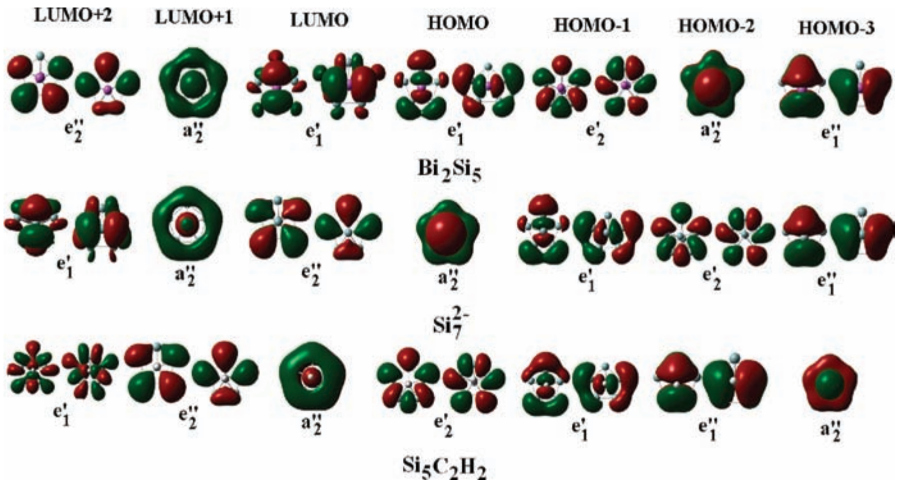

**Figure 3.** The (seven) frontier orbitals of $Bi_2Si_5$ (top), $Si_7^{2-}$, (middle), and $Si_5C_2H_2$ (bottom) clusters (isovalue = 0.02).

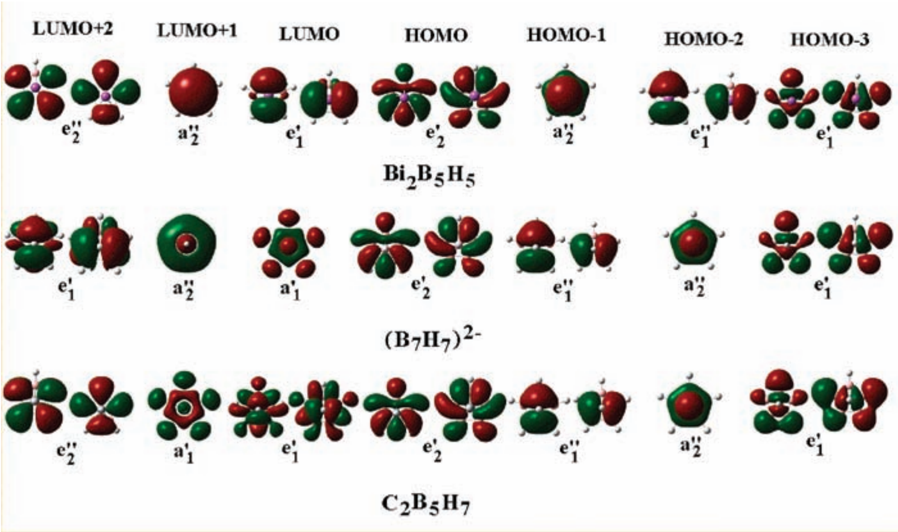

**Figure 4.** Seven frontier orbitals of $(B_7H_7)^{2-}$ (middle), $C_2B_5H_7$ (bottom), and $Bi_2B_5H_5$ (top), for the 0.02 isovalue.

range of frontier orbitals (four occupied and three unoccupied) for the particular case of $n = 7$ and the $Bi_2Si_5$ cluster, for which there are experimental data and theoretical verification.[26] In Figure 3 are examined the isovalent and isolobal $Si_7^{2-}$, $Si_5C_2H_2$, and $Bi_2Si_5$ orbitals, illustrating the "isolobality" between silicon species (which is extended to Ge species).

In Figure 4 is illustrated the similarity (and "isolobality") of the homologous isovalent boranes, carboranes, and bisboranes $(B_7H_7)^{2-}$, $C_2B_5H_5$, and $Bi_2B_5H_5$. Comparison of the two figures (Figures 3 and 4) clearly illustrates the full isolobality of all ($Si_7^{2-}$, $Si_5C_2H_2$, $Bi_2Si_5$ and $(B_7H_7)^{2-}$, $C_2B_5H_5$, $Bi_2B_5H_5$) species involved.

As we can see in Figure 3, there is a (very small) shift in the energetic ordering of the orbitals (decreasing from left to right in Figure 3) depending on the orbital symmetry, which is indicated in the figure. This is not uncommon for isolobal species.[45,46] These small shifts, which are analogous to the shifts for $n = 3$ shown in Figure 2, are apparently due to the different overall chemical environment of the three diverse (and yet similar) species. As a result, there is no unique common symmetry for the HOMO and LUMO (and the other) orbitals. For example, the nondegenerate $a_2''$ orbital is the HOMO for $Si_7^{2-}$, whereas for $Bi_2Si_5$ the doubly degenerate $e_1'$ orbital is the HOMO. The HOMO for $Si_5C_2H_2$ is also doubly degenerate but of different $e_2'$ symmetry. The $a_2''$ orbital, on the other hand, is the HOMO−2 orbital of $Bi_2Si_5$ and the HOMO−3 orbital of $Si_5C_2H_2$. Thus, one of the $Si_7^{2-}$ orbitals has its partner diagonally within the set of the seven orbitals of Figure 3. This is not necessarily true for the orbitals of the $(B_7H_7)^{2-}$, $C_2B_5H_7$, and $Bi_2B_5H_5$ isolobal species in Figure 4.

For instance, the $a_1'$ and $a_2''$ unoccupied orbitals (LUMO and LUMO+1 for $(B_7H_7)^{2-}$) do not have their partners (within the unoccupied orbitals of Figure 4) in the range of Figure 4. On the other hand, the occupied orbitals of $(B_7H_7)^{2-}$, $C_2B_5H_7$, $Bi_2B_5H_5$ are either completely the same (HOMO, HOMO−3) or short-shifted (HOMO−1 and HOMO−2) with very small relative energy differences.[46] What is most important is that the majority of orbitals in Figures 3 and 4 are practically the same. Therefore, the full range of $Bi_2Si_5$, $Si_7^{2-}$, $Si_5C_2H_2$, $(B_7H_7)^{2-}$, $C_2B_5H_7$, $Bi_2B_5H_5$ species can be characterized as isolobal, sharing several structural, electronic, and cohesive characteristics and properties. These common properties can be suitably used to explore the chemical characteristics of the less known species from the corresponding characteristics of the well-known and well-studied molecules.

This is one of the main themes of the present Article. For the $Bi_2Si_{n-2}$ and $Bi_2Ge_{n-2}$ clusters, at least for $n \leq 8$, it has been already illustrated that this is indeed true. Furthermore, for the $Bi_2Ge_{n-2}$ clusters, $3 < n \leq 8$, all isolobal structures obtained from the $Ge_n^{2-}$ dianions (which are similar and isolobal to both $(B_nH_n)^{2-}$ and $Si_n^{2-}$)) are global minima according to the present calculations. This is also true for the odd-$n$ $Bi_2Si_{n-2}$

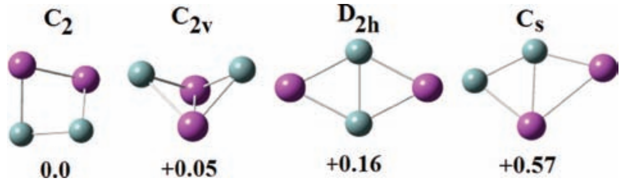

**Figure 5.** The lowest four structures of $Bi_2Si_2$ with their energy separations in eV at the B3LYP/TZV2P level of theory.

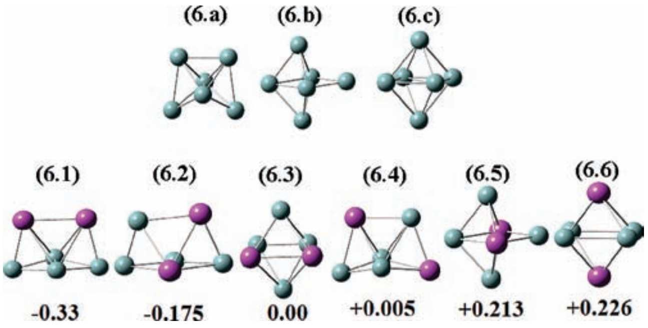

**Figure 6.** The lowest energy structures of $Si_6$ (upper part) and $Bi_2Si_4$ clusters (lower part).

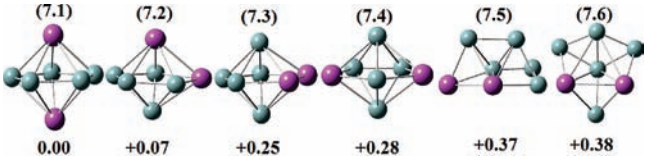

**Figure 7.** The lowest six structures of $Bi_2Si_5$ with their energy separations in eV at the B3LYP/TZV2P level of theory.

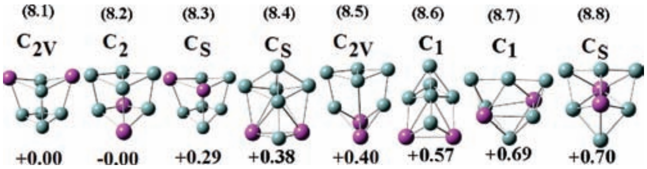

**Figure 8.** The eight lowest structures of $Bi_2Si_6$, with symmetries and energies (in eV).

clusters and the even-*n* clusters except $Bi_2Si_4$, for which the calculated global minimum is obtained from the neutral $Si_6$ cluster rather than from the corresponding dianion. This is further discussed in section IV. For larger values of *n*, for instance, for $n = 12$ for which the full isolobal analogy $Si_n^{2-} \leftrightarrow Si_{n-2}C_2H_2 \Leftrightarrow (B_nH_n)^{2-} \leftrightarrow C_2B_{n-2}H_n$ is not fully valid,[22,23] but still the partial analogy $Si_n^{2-} \leftrightarrow Si_{n-2}C_2H_2$ holds true, we could anticipate that neither $Bi_2Si_{n-2} \leftrightarrow Si_n^{2-} \leftrightarrow Si_{n-2}C_2H_2 \Leftrightarrow (B_nH_n)^{2-} \leftrightarrow C_2B_{n-2}H_n \leftrightarrow Bi_2B_{n-2}H_{n-2}$ would be valid, although the partial analogy $Bi_2Si_{n-2} \leftrightarrow Si_n^{2-} \leftrightarrow Si_{n-2}C_2H_2$ is expected to hold true. This is a partial form of the "boron connection". This question is examined in section V.

## IV. Additional Results for Even-*n* $Bi_2Si_{n-2}$ Clusters Beyond the "Boron Connection"

For $n = 4$ we can see in Figure 5 that we have, within roughly 0.5 eV from the lowest, two more low-lying states, which are not similar to the lowest $Si_2C_2H_2$ isolobal species.

The $D_{2h}$ symmetric rhombus at 0.16 eV is clearly directly related to the $Si_4$ global minimum ($D_{2h}$ rhombus), whereas the $C_s$ structure at 0.57 eV above the global minimum is reminiscent of the third lower energy structure of $Si_2C_2$ (see ref 21b, Figure 1). It is interesting to note that the $D_{2h}$ rhombus is unstable (imaginary frequency) for $Si_2C_2H_2$, reverting to the second lowest $C_{2v}$ structure (at 0.05 eV) after distortion according to the eigenvectors of the imaginary frequency mode and reoptimization.

This trend of obtaining lower or lowest energy structures of $Bi_2Si_{n-2}$ ($n = 4$) by direct substitution on the $Si_n$ global minimum is more pronounced for $n = 6$.

For $n = 6$, it has been illustrated that the bare $Si_6$ cluster is fluxional[6,7] with three well-known nearly isoenergetic structures competing for the ground state. These three structures, in the order of (slightly) increasing energy, are shown in the upper part of Figure 6 (structures a−c) with symmetries $C_s$ (near $C_{2v}$), $C_{2v}$, and $D_{4h}$, respectively.

The $D_{4h}$ structure has been illustrated[6,7] to be a transition state (with imaginary frequencies) at almost all levels of theory [B3LYP, MP3, MP4, CCSD(T)], except MP2. As we can see in Figure 6, the two lowest (6.1) and (6.2) structures together with the fourth lowest (6.4), almost isoenergetic to the third lowest (6.3), all of them of $C_s$ (near $C_{2v}$ symmetry) symmetry, are obtained from the absolutely lowest (6.a) structure of the neutral $Si_6$ cluster. It is easy to see that the fifth lowest (6.5) structure of $C_{2v}$ symmetry is directly obtained from the $C_{2v}$ (6.b) structure of $Si_6$.

Only structures 6.3 and 6.6, which is the lowest energy structure for the $Bi_2Ge_4$ cluster, are directly related to the $O_h$ symmetric $Si_6^{2-}$ dianion. One could argue that even these structures are obtained from the $D_{4h}$ symmetric neutral $Si_6$ cluster of Figure 6c, which, however, is dynamically unstable[6,7] (imaginary frequencies). One possible way to distinguish between the two is the Si−Si bond lengths, which are significantly different (longer) in $Si_6^{2-}$ as compared to the neutral $D_{4h}$ cluster. Consider, for instance, the diagonal bond in the equatorial plane of the $D_{4h}$ neutral $Si_6$ cluster, shown in Figure 6c. This bond is missing (is broken) in the $Si_6^{2-}$ dianion, similarly to the $Bi_2Si_4$ structure in structure 6.6, illustrating that structures 6.6 and 6.3 are directly obtained from the $Si_6^{2-}$ dianion rather than the unstable $D_{4h}$ neutral $Si_6$ cluster of Figure 6c. Thus, in analogy to $Bi_2Si_2$, some of the lowest energy structures of $Bi_2Si_4$ structures are obtained from the $Si_6^{2-}$ dianion [which is isostructural and isolobal to $(B_6H_6)^{2-}$], but there are also several lowest energy structures obtained directly from the neutral $Si_6$ cluster.

This is not restricted to the even-*n* structures, as we can see in Figure 7, which shows the $n = 7$ $Bi_2Si_{n-2}$ structures. Here, however, contrary to $n = 6$, the lowest four structures (from 0 to 0.40 eV) are obtained, as would be expected from the isolobal analogy, directly from the $D_{5h}$ $Si_7^{2-}$ dianion, which is isostructural and isolobal to the corresponding $(B_7H_7)^{2-}$ borane. Structures 7.5 and 7.6 are directly related to the corresponding $Si_7$ neutral cluster.

Structure 7.6 in particular is directly related to the $C_{3v}$ symmetric second lowest energy structure[4,23] of $Si_7$. Because the lowest energy structures of $Si_7^{2-}$ and $Si_7$ share the same $D_{5h}$ symmetry, it could be argued that also structures 7.1−7.4 are obtained from the neutral $Si_7$ cluster. As in the case of $n = 6$, the Si−Si bond lengths constitute the basic criterion. The dianion pentagonal bipyramid has different axial and equatorial bond lengths as compared to the neutral cluster.[23] Also, for $n = 5$ the two lowest energy structures are obtained through the isolobal analogy.

Finally, several (eight) lowest energy structures of $Bi_2Si_6$ are shown in Figure 8.

The first three structures in Figure 8 (8.1, 8.2, and 8.3) are very similar to the corresponding $Si_6C_2H_2$ clusters and $C_2B_6H_8$ carborane, which are obtained from the $D_{2d}$ symmetric corre-

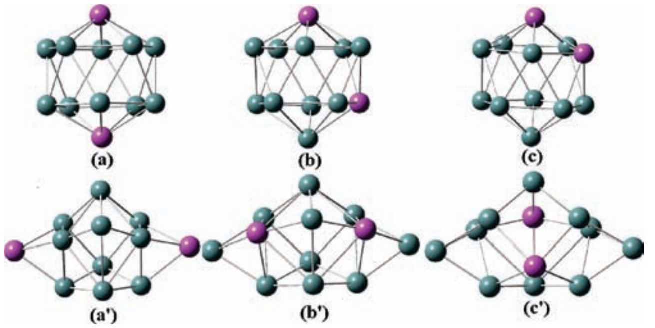

**Figure 9.** The lowest energy structures of $Bi_2Si_{10}$ and $Bi_2Ge_{10}$ clusters. The structures in (a), (b), and (c) are obtained by *para*-, *meta*-, and *ortho*-Bi substitutions on the $I_h$ symmetric $Si_{12}^{2-}$ and $Ge_{12}^{2-}$ isomers, respectively. The (a′), (b′), and (c′) structures originate from the $C_s$ symmetric $Si_{12}^{2-}$ and $Ge_{12}^{2-}$ dianions.

sponding $Si_8^{2-}$ and $(B_8H_8)^{2-}$ dianions, respectively. Both $Si_6C_2H_2$ and $C_2B_6H_8$ are fluxional[22] with two structures of $C_2$ and $C_{2v}$ symmetry nearly isoenergetic (see ref 22 and related references therein), and so is $Bi_2Si_6$. Again, one could argue that the neutral $Si_8$ cluster is also characterized by two low-lying $C_2$ and $C_{2v}$ structures.[4,23] However, based on bond lengths and other characteristics,[23] it can be seen that both of these structures (which are fluxional, contrary to the corresponding neutral $Si_8$ structures) originate from the $Si_8^{2-}$ dianion.

The remaining five structures in Figure 8 seem to be related to the neutral $Si_8$ structures rather than to the $Si_8^{2-}$ cluster dianion. Structure 8.4 is related to the fourth lowest energy $C_{2v}$ symmetric structure of $Si_8$ (see ref 4 and in particular their Figure 1, 8d). Although structure 8.5 is derived from the $Si_8^{2-}$ dianion, it could be also considered as coming from the $C_{2v}$ second lowest energy structure of the neutral $Si_8$ cluster.[4,23] This structure could be also seen as the magic $Si_4$ rhombus joint together with the lowest $C_{2v}$ structure of $Bi_2Si_2$ in structure 1.4 (top row). Finally, structures 8.6−8.8 seem to be related to the $C_{2v}$ second lowest energy structure of the neutral $Si_8$ cluster.[4,23]

Thus, for both even-*n* and odd-*n* $Bi_2Si_{n-2}$ clusters, most (or some) of the structures are obtained from the $Si_n^{2-}$ dianion [which is isostructural and isolobal to $(B_nH_n)^{2-}$ for $n = 3-8$] and some from the neutral $Si_n$ clusters. For the odd-*n* clusters (and several of the even-*n*), the lowest and at least the second lowest energy structures are directly related to the corresponding $Si_n^{2-}$ dianion. For the even-*n*, and in particular for $n = 6$, the two lowest energy structures are directly related to the corresponding, $Si_6$, neutral cluster.

## V. Results for the Characteristic Case of $n = 12$

The three lowest energy isomers generated from the icosahedral [similar to the $(B_{12}H_{12})^{2-}$] and $C_s$ symmetric $Si_{12}^{2-}$ dianions are shown in Figure 9. It has been earlier shown[15,23] that the $Si_{12}^{2-}$ dianion, contrary to the isovalent $(B_{12}H_{12})^{2-}$ borane, has no high $I_h$ symmetry, distorted to $C_s$ (near $C_{2v}$) symmetry to optimize $sp^3$ bonding. The same trend but to a much lesser extent, due to the “inert pair effect”,[22,35] is also shown by the $Ge_{12}^{2-}$ dianion for which the $I_h$ and $C_s$ isomers are nearly isoenergetic.[22,29,35] At the DFT B3LYP/TZV2P level of theory, the $I_h$ $Ge_{12}^{2-}$ isomer is the ground state by 0.36 eV lower than the $C_s$ isomer. At the fourth-order Møller−Plesset perturbation theory including single, double, triplet, and quadruplet excitations (MP4SDTQ), the difference is reduced to only 0.03 eV in favor of the $I_h$ isomer, whereas at the CCSD(T)/TZV2P level the small difference (−0.06 eV) is reversed in favor of the $C_s$ isomer. This is highly suggestive of fluxional behavior.[7,23] As a result of this behavior, the highly symmetric *para*- ($D_{5d}$) and *ortho*- ($C_{2v}$) $Ge_{10}C_2H_2$ isomers (contrary to $Si_{10}C_2H_2$) generated from the $I_h$ symmetric $Ge_{12}^{2-}$ structure are much lower in energy from all but one (the *ortho*-$C_s$) $C_s$ isomers.[22] As we can see in Figure 9 and Table 2, something similar happens for the $Bi_2Ge_{10}$ (in comparison to $Bi_2Si_{10}$) isomers: the $D_{5d}$ symmetric $Bi_2Ge_{10}$ structure in Figure 9a is practically isoenergetic (with a marginal difference of 0.04 eV) to the lowest energy $C_s/C_{2v}$ structure of Figure 9a′. This is in contrast to $Bi_2Si_{10}$, for which the difference between the corresponding two structures is −2.22 eV in favor of the $C_s$ isomer. Also, in full analogy to the $Si_{10}C_2H_2$, $Ge_{10}C_2H_2$ species,[22] all $C_s$ originating $Bi_2Si_{10}$ isomers are lower in energy from all $I_h$ generated $Bi_2Si_{10}$ structures, whereas for $Bi_2Ge_{10}$ only one $C_s$ generated isomer is lower (by a very small amount) from the lowest $I_h$ isomer, exactly as in $Si_{10}C_2H_2$, $Ge_{10}C_2H_2$ species.[22]

**TABLE 2: Cohesive and Electronic Characteristics of the $Bi_2Si_{10}$ and $Bi_2Ge_{10}$ Clusters at the B3LYP/TZV2P Level of Theory: Atomization Energies $E_a$, Energy Differences $\Delta E$ with Respect to the High Symmetry ($D_{5d}$) *meta*-Isomer of Figure 9a, and HOMO−LUMO Gaps in eV**[a]

| structure: | (a) | (b) | (c) | (a′) | (b′) | (c′) |
|---|---|---|---|---|---|---|
| symmetry: | $D_{5d}$ | $C_{2v}$ | $C_{2v}$ | $C_s/C_{2v}$ | $C_s/C_{2v}$ | $C_s$ |
| $Bi_2Si_{10}$ $E_a$ | 34.12 | 34.47 | 33.98 | 36.34 | 34.45 | 35.34 |
| $Bi_2Ge_{10}$ | 32.69 | 32.64 | 32.55 | 32.73 | 31.76 | 31.99 |
| $Bi_2Si_{10}$ $\Delta E$ | 0.00 | −0.35 | +0.14 | **−2.22** | −0.33 | −1.22 |
| $Bi_2Ge_{10}$ | 0.00 | +0.05 | +0.16 | **−0.04** | +0.93 | +0.70 |
| $Bi_2Si_{10}$ H−L | 2.01 | 2.22 | 1.99 | 2.54 | 2.20 | 1.86 |
| $Bi_2Ge_{10}$ | 2.60 | 2.52 | 2.56 | 2.38 | 2.10 | 1.82 |

[a] The various isomers are characterized by the labels of Figure 9 and their symmetry.

Thus, the isolobal principle, in this particular respect (similarity of $Bi_2Si_{10}$, $Bi_2Ge_{10}$ and $Si_{10}C_2H_2$, $Ge_{10}C_2H_2$ species with each other and $Si_{12}^{2-}$, $Ge_{12}^{2-}$), works partially for $n = 12$. This means that the lowest energy structures of $C_s$ (near $C_{2v}$) symmetry for the $Bi_2Si_{10}$, $Si_{12}^{2-}$, and $Si_{10}C_2H_2$ are fully homologous and isolobal to each other and to the corresponding $Bi_2Ge_{10}$, $Ge_{12}^{2-}$, and $Ge_{10}C_2H_2$ clusters (but not to the isovalent $Bi_2B_{10}H_{10}$, $(B_{12}H_{12})^{2-}$, and $C_2B_{10}H_{12}$ molecules). This is the main difference from the corresponding smaller species for $3 < n \leq 8$. We can have something analogous to Figure 3, but not to Figure 4, for $n = 12$, or in other words, two separate analogies: $Bi_2Si_{n-2} \leftrightarrow Si_n^{2-} \leftrightarrow Si_{n-2}C_2H_2$, and $(B_nH_n)^{2-} \leftrightarrow C_2B_{n-2}H_n \leftrightarrow Bi_2B_{n-2}H_{n-2}$, not connected to each other.

We can also observe in Table 2 that the atomization energy (of the most stable isomer) for both $Bi_2Si_{10}$ and $Bi_2Ge_{10}$, following the trend for smaller *n* in Table 1, is larger as compared to the $Bi_2Si_8$ and $Bi_2Ge_8$ values. Not only the atomization energy but also the “reduced atomization energy per atom” ($E_a/n$), 3.03 eV for $Bi_2Si_{10}$ and 2.73 eV for $Bi_2Ge_{10}$, are larger as compared to the corresponding values for $n = 3-8$, following the trend of increasing $E_a/n$ with increasing *n*. This is highly suggestive that larger than $n = 12$ clusters could be stabilized and functionalized to form complex larger units suitable for appropriate applications in chemistry, materials science, and even medicine.[47]

## VI. Conclusions

It has been illustrated on the basis of atomization energies that silicon−bismuth clusters of the form $Bi_2Si_{n-2}$ are very stable with increasing atomization energies (per *n*) as the number of Si atoms increases. For small values of *n*, $3 \leq n \leq 8$, the lowest energy structures (global minima) of odd-*n*, and most even-*n*, except $n = 6$, $Bi_2Si_{n-2}$ clusters are obtained from the $Si_n^{2-}$ dianion [which is isostructural and isolobal to $(B_nH_n)^{2-}$ for $n = 3-8$]. The structural, bonding, and electronic characteristics of these clusters are fully analogous and homologous to the $Si_n^{2-}$ and $Si_{n-2}C_2H_2$ clusters and the corresponding isovalent and isolobal boranes, carboranes, and bisboranes: $(B_nH_n)^{2-}$, $C_2B_{n-2}H_n$, and $Bi_2B_{n-2}H_{n-2}$.

The lowest and second lowest energy structures of $Bi_2Si_4$ are directly related to and obtained by ($2Si \rightarrow 2Bi$) from the neutral $Si_6$ cluster. For the third and fourth lowest energy structures, there is a strong competition between structures obtained from (isolobal to) the $Si_6^{2-}$ dianion and the $Si_6$ neutral cluster. Such structures, related to the neutral $Si_n$ clusters rather than the $Si_n^{2-}$ dianions, are found in all even-*n* and most odd-*n* $Bi_2Si_{n-2}$ clusters. However, only for $Bi_2Si_4$ is the global minimum (and second lowest structure) such a neutral cluster related structure. Perhaps the "magicity" and fluxionality of $Si_6$ (see refs 6, 7) are indirectly responsible for such behavior. The preference for structures obtained from the neutral $Si_n$ clusters in $Bi_2Si_{n-2}$, $n = 3-8$, could be related to the almost equal (~1.7) electronegativity of Si and Bi (Alfred-Rochow value[48] 1.74 for Si and 1.67 for Bi), coupled with the tendency for $sp^3$ bond-angle optimization. In this particular case ($n = 6$), the "boron connection" is still valid (fully, not partially as for $n = 12$), but the corresponding $Bi_2Si_4$ structure, although low-lying, is not the global minimum.

For the $Bi_2Ge_{n-2}$, all lowest energy structures (global minima) are obtained structures from the homologous $Ge_n^{2-}$ dianion, which are isovalent and isolobal. For these clusters, the isolobal analogy known as "the boron connection", a term coined recently by the present author,[7,21−23] is fully valid: $Bi_2Ge_{n-2} \leftrightarrow Ge_n^{2-} \leftrightarrow Ge_{n-2}C_2H_2 \Leftrightarrow (B_nH_n)^{2-} \leftrightarrow C_2B_{n-2}H_n \leftrightarrow Bi_2B_{n-2}H_{n-2}$, similarly to the lowest energy structures of all $Bi_2Si_{n-2}$, except $Bi_2Si_4$, clusters.

In many cases, this analogy is also valid for the second and third lowest energy structures.

For values of *n* larger than 8, and in particular for $n = 12$, we are faced with a (drastically) different situation. The $Si_{12}^{2-}$ dianion has much lower symmetry ($C_s$) than $(B_{12}H_{12})^{2-}$, which is characterized by full icosahedral ($I_h$) symmetry. This has been attributed[22,23] to stronger optimization of the $sp^3$ bonding in $Si_{12}^{2-}$ as compared to $(B_{12}H_{12})^{2-}$. Thus, the "boron connection" is not fully and strictly valid in this case, although the isolobal principle is still partially operative in the sense that the $C_s$ (near $C_{2v}$) symmetric $Bi_2Si_{n-2}$, $Si_n^{2-}$, and $Si_{n-2}C_2H_2$ ($n = 12$) structures are isolobal to each other ($Bi_2Si_{n-2}{}^{-} \leftrightarrow Si_n^{2-} \leftrightarrow Si_{n-2}C_2H_2$) but not to the isovalent boranes bisboranes and carborabes: $(B_nH_n)^{2-}$, $Bi_2B_{n-2}H_{n-2}$, $C_2B_{n-2}H_n$ ($n = 12$), which are all based on $I_h$ underlying symmetry.

For $Bi_2Ge_{n-2}$, $Ge_n^{2-}$, and $Ge_{n-2}C_2H_2$ clusters, including $n > 8$ clusters, the "boron analogy" works much better, although the energetic ordering in $Ge_{n-2}C_2H_2$ structures could be worse. For $n = 12$, in particular, the structures of $Bi_2Ge_{10}$, $Ge_{12}^{2-}$, and $Ge_{10}C_2H_2$ are much closer to $Bi_2B_{n-2}H_{n-2}$, $(B_nH_n)^{2-}$, and $C_2B_{n-2}H_n$ ($n = 12$), because the $C_s$ and $D_{5d}$ isomers of $Bi_2Ge_{10}$ are practically isoenergetic with a very small energy margin of about 0.04 eV in favor of the $C_s$ isomer. This is due to the fact that the $C_s$ and $I_h$ isomers of the $Ge_{12}^{2-}$ dianion are practically isoenergetic[22] (at the B3LYP/TZV2P level, the $I_h$ dianion is clearly the lowest energy structure). This is attributed to the "inert pair effect" and the resulting weakening of the $sp^3$ bonding as we move down the period of the periodic table. Thus, as we go deeper in the period, the "boron connection" is getting better and becomes again strong and fully valid.[35] Therefore, it would be expected that in the case of tin the $Sn_{12}^{2-}$ dianion would be of $I_h$ symmetry. This is indeed the case. The synthesis and properties of $Sn_{12}^{2-}$, the "stannaspherene",[40] are in a sense another experimental verification of the boron connection.[35]

It is rather evident that we can rationalize the silicon/germanium−bismuth clusters through the paradigm of the "boron connection" in its extended (full or partial) form, taking advantage of the corresponding concepts and knowledge for boranes, carboranes, and bisboranes. This could facilitate possible future chemical and technological applications of these clusters, on their own merit, or as model systems of the semimetal−semiconductor interface.

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