BSi$_n$Ge$_{4-n}^+$ ($n = 0–2$): prospective systems containing planar tetracoordinate boron (ptB)

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Dedicated to Professor S. P. Bhattacharyya on the occasion of his 75th birthday

Abstract. The potential energy surface (PES) has been explored for BSi$_n$Ge$_{4-n}^+$ ($n = 0–2$) systems using density functional theory (DFT). The global minima (1a, 1b, and 1c) of the considered systems contain a planar tetracoordinate boron (ptB) center. The neutral states of the systems do not have a ptB in the global minimum structures. The designed BGe$_4^+$, BSiGe$_3^+$, and BSi$_2$Ge$_2^+$ systems have 18 valence electrons. The CCSD(T)/aug-cc-pVTZ level of theory has been applied to compute the relative energies of the low-lying isomers with respect to the global minima. The dynamical stability of BSi$_n$Ge$_{4-n}^+$ ($n = 0–2$) systems is confirmed from the atom-centered density matrix propagation (ADMP) simulation over 20 ps of time at temperatures of 300 K and 500 K. The natural charge computations show that the charges on the ptB are highly negative, indicating strong $\sigma$-acceptance from the peripheral atoms. The 1a, 1b, and 1c structures of BGe$_4^+$, BSiGe$_3^+$, and BSi$_2$Ge$_2^+$ systems, respectively, have $\sigma$/$\pi$-dual aromaticity as predicted from the nucleus-independent chemical shift (NICS) values.

Keywords. planar tetracoordinate boron (ptB); global minima; $\sigma$/$\pi$ aromaticity; Ab initio molecular dynamics simulations; Wiberg bond index (WBI).

1. Introduction

The exploration of structural prerequisites to stabilize the non-classical planar tetracoordinate carbon (ptC) opens a new dimension for the studies on the structure and bonding of planar hypercoordinate species. The traditional idea of tetrahedral tetracoordinate carbon was given by van’t Hoff and Le Bel independently in 1874.1,2 In 1968, Monkhorst first proposed the possibility of a ptC in the hypothetical $D_{4h}$ structure of methane.3 But the actual development of these concepts was done by Hoffmann, Alder, and Wilcox in 1970 with the analysis of the electronic structure of the planar methane.4 They proposed that with the inclusion of appropriate ligands having simultaneous $\sigma$-donating and $\pi$-accepting capacity, ptC structures can be achieved. In 1976, the first structure having a ptC was reported by Collins and co-workers for 1,1-dilithiocyclopropane and 3,3-dilithiocyclopropene systems.5 Since then, different research groups have studied the new ptC molecules and/or ions.6–13 Although many such ptC molecules and/or ions were described computationally, the experimental achievement is restricted.14–20 After that, the ptC concept was extended to planar pentacoordinate carbon (ppC),21–23 planar hexacoordinate carbon (phC),24–27 and planar heptacoordinate carbon (p7C).28,29 Inspired by the achievement of the novel planar hypercoordinate carbon chemistry, people have shown great interest in the possibilities of the other main group elements for planar hypercoordination.30–33 In 2020, Feng et al., designed BPt$_4$S$_4$ cluster and found that the global
minimum structure has a ptB atom in neutral, monoanionic, and dianionic states.\textsuperscript{34} In 2004, Li et al., explored the PES of the BCu$_3$H$_5^−$ system and found planar pentacordinate boron (ppB) in the global minimum structure having $D_{5h}$ point group of symmetry.\textsuperscript{35} In 2009, Wu and co-workers reported that the global minimum structure of B$_4$H$_5^+$ has $D_{5h}$ symmetry with a ppB atom and the system is aromatic in nature.\textsuperscript{36} Recently, Khatun et al., studied the PES of BAl$_4$Mg$_{10}$ systems and found that the anionic and cationic states of the system have a ptB atom, and the neutral state has a ppB atom in the global minima.\textsuperscript{37} The ptB and the ppB structures were reported as kinetically stable and exhibit π/σ double aromaticity. In 2001, Minkin and co-workers designed BB$_6$(CH)$_3$ and BB$_6$X$_2^−$ (X = NH, O) systems having a planar hexacoordinate boron (phB) atom at both \textit{ab initio} and DFT level computations.\textsuperscript{38} Recently, we have also reported a phB atom in the global minimum structures of CB$_6$Al$_{10}^0$+ clusters.\textsuperscript{39} The clusters are kinetically stable enough against isomerization and dissociations.\textsuperscript{40} Wang and co-workers, in 2003, reported combined experimental and computational studies on B$_8^-$ and B$_9^-$ clusters showing planar hepta- and octa-coordinate central boron atoms. The special characteristics of these anionic clusters are planar molecular wheels. The experimental realization of the \textit{in silico} studied planar hypercoordinate carbon species is not easy. If the complexes are thermodynamically stable enough, the experimental characterization could only be possible in the gas phase. Most experimentally characterized ptC systems are organometallic compounds or small clusters produced in the gas phase under thermodynamically controlled conditions. These unusual structures may have interesting, unique physical and electronic properties, but due to a lack of good synthetic methods, the applications of these beautiful compounds are not well established. Some authors predict the possibility of materials featuring one or more ptCs being anodes in Li-ion batteries or, on account of their favorable electronic bandgaps, donors in solar cells.\textsuperscript{41,42}

Herein, we report 18 valence electronic BSi$_n$Ge$_{4−n}^+$ (n = 0−2) systems with a ptB atom in the global minimum energy structures. The electronic interaction between the central boron atom and the four peripheral atoms makes the 1a, 1b, and 1c structures stable in planar forms. We have used DFT-based computations for the rest of the analysis in support of the stability of the BGe$_4^+$ (1a), BSiGe$_3^+$ (1b), and BSi$_2$Ge$_2^+$ (1c). We have also checked the dynamical stability of the 1a, 1b, and 1c structures by the ADMP simulation approach.

2. Computational Details

The PES was explored for the systems considered in this study with the help of the ABCCluster code based on the artificial bee colony algorithm (ABC).\textsuperscript{43,44} This algorithm was proposed by Karaboga \textit{et al.}, in 2005 and is a swarm-based intelligence algorithm.\textsuperscript{45,46} It is influenced by the foraging behaviour of a bee colony, and only three parameters are required to deal with it. These three parameters are (i) employed honeybees, (ii) onlooker bees, and (iii) food sources. In this algorithm, a colony of artificial forager bees (agents) finds rich artificial food sources (good solutions for a given problem). The studied optimization problem is first transformed into the problem of searching for the best parameter vector that minimizes an objective function. Then, the artificial bees arbitrarily find a population of initial solution vectors and iteratively move towards better solutions while discarding the bad ones. The PBE0-D3/def2-SVP method\textsuperscript{47,48} has been used for this purpose, and 200 stationary points were taken for exploring the PES. After that, the full optimization of the low-lying isomers of the systems was carried out at the PBE0-D3/def2-TZVPP method.\textsuperscript{49} Using the same computational method, we have executed the frequency calculations to ensure that the generated geometries are of minimum energies. The energies without zero point (ZPE) correction of the low-lying isomers were then refined by single-point energy calculations at the CCSD(T)/aug-cc-pVTZ method\textsuperscript{50,51} on PBE0-D3/def2-TZVPP optimized geometries. We have also checked the results using B3LYP, BLYP, BP86, M06, M06-2X, M05-2X, and PBE density functionals in conjunction with the def2-SVP basis set. The global minimum energy structures contain a ptB atom in all the methods. Hence, from these studies, we can say that the true global minima of the studied clusters contain a ptB center. The Gaussian16 program was used for all these calculations.\textsuperscript{52} The kinetic stability of the global minimum structures is studied at 300 K and 500 K temperatures and 1 atm pressure over 20 ps with a time step of 2 fs using the ADMP approach.\textsuperscript{53–56} This simulation uses the velocity Verlet algorithm and the Berendsen thermostat. The thermostat in the ADMP simulation is quite simple, it rescales the velocity of all atoms at every specified step so that the temperature is exactly identical to the given one. This particular simulation has been accomplished at the PBE0-D3/def2-SVP level of theory. For the charge exploration on the atoms, we have performed natural bond orbital (NBO) calculations\textsuperscript{57} at the MP2/aug-cc-pVTZ//PBE0-D3/def2-TZVPP method.\textsuperscript{58–62} The NBO 3.1...
version has been used for the charge calculations which is implemented in Gaussian 16 software. The atoms-in-molecules (AIM)\(^{65}\) analysis has been performed by Multiwfn\(^{64}\) software at the MP2/aug-cc-pVTZ method on PBE0-D3/def2-TZVPP optimized geometries. The NICS calculations were carried out at the PBE0/def2-TZVPP level to ensure the aromatic behaviour of the systems.

3. Results and Discussion

3.1 Geometries

The PES of the designed systems were extensively searched and found 1a, 1b, and 1c for BGe\(_4^+\), BSiGe\(_3^+\), and BSi\(_2\)Ge\(_2^+\), respectively, as the global minimum having planar tetracoordinate boron (ptB) atom. We have presented the optimized structures of the global minimum structures of BGe\(_4^+\) (1a), BSiGe\(_3^+\) (1b), and BSi\(_2\)Ge\(_2^+\) (1c) in Figure 1 with all the important bond distances. The 1a, 1b, and 1c structures correspond to the \(D_{4h}\), \(C_{2v}\), and \(C_{2v}\) symmetries in the singlet spin states. In the 1c structure, two Ge and/or two Si atoms are in the \(cis\) position. Figures 2, 3, and 4 contain the low-lying structures, respectively. The B–Ge and B–Si bond lengths, the electronic energies of the global minimum of considered clusters at different levels of theories, are given in Table S1 (SI). We have also searched for the PES of BSi\(_n\)Ge\(_{4–n}^+\) clusters and are shown in Figure S2 (SI). Moreover, we have also explored the PES of BSi\(_n\), BSi\(_3\)Ge\(_3^+\), and BSi\(_2\)Ge\(_2^+\) systems to find out the possibility of having a ptB atom. But unfortunately, we did not find a planar global minimum. For BGe\(_4^+\), BSiGe\(_3^+\), and BSi\(_2\)Ge\(_2^+\) systems, the closest competitive isomers (2a, 2b, and 2c, respectively) are located at higher energy than the global minimum 1a, 1b, and 1c structures, respectively. Hence, experimentally in the gas phase, only the ptB structures will be generated exclusively for BGe\(_4^+\), BSiGe\(_3^+\), and BSi\(_2\)Ge\(_2^+\) systems.

3.2 Kinetic stability

The kinetic stability of the 1a, 1b, and 1c structures is tested with the help of the ADMP simulation at 300 K and 500 K temperatures over 20 ps of time. The changes in the total energies with simulation time are plotted and given in Figure 5. Throughout the simulation, the structural deformation of the global minimum structures occurs, but the geometries are not entirely broken. We have also calculated the changes in the B–Ge and B–Si bond lengths with respect to the equilibrium values during the simulation. The changes in the \(r_{B-Ge}\) with respect to that in the optimized 1a, 1b, and 1c ptB geometries for BGe\(_4^+\), BSiGe\(_3^+\), and BSi\(_2\)Ge\(_2^+\) systems, respectively, are presented in Figure 6. Similarly, the changes in the \(r_{B-Si}\) with respect to that in the optimized 1b, and 1c ptB geometries for BSiGe\(_3^+\), and BSi\(_2\)Ge\(_2^+\) systems, respectively, are given in Figure 7. The changes in the \(r_{B-Si}\) are within 0.3 Å for BSiGe\(_3^+\) and BSi\(_2\)Ge\(_2^+\) systems. Whereas, for the BSiGe\(_3^+\) system, the changes in the \(r_{B-Ge}\) are within 0.3 Å and for BGe\(_4^+\), and BSi\(_2\)Ge\(_2^+\) systems, it is within 0.4 Å. From these plots, we can say that the structural integrity is well-maintained during the simulation. Hence, this

Figure 1. The global minimum structures of BGe\(_4^+\) (1a), BSiGe\(_3^+\) (1b), and BSi\(_2\)Ge\(_2^+\) (1c) systems contain a ptB. Bond lengths are given in Å units.
simulation indicates the dynamical stability of 1a, 1b, and 1c ptB geometries at both considered temperatures.

### 3.3 Molecular orbitals

This particular analysis has importance in the bonding context in the 1a, 1b, and 1c structures of the considered systems. We have provided the canonical molecular orbitals (CMOs) in the global minima 1a, 1b, and 1c in Figure 8, along with the corresponding orbital energies. The electronic delocalization within the whole system is well understood from the HOMO–3 (π-delocalization) and HOMO–8 (σ-delocalization) orbitals in all the global minimum structures. For BGe$_4^+$ and BSiGe$_3^+$ systems, the global minimum structures (1a and 1b, respectively) lie on the XY-plane, and hence the π-delocalized molecular orbitals are formed by the perpendicular $2p_z$ orbitals of the central boron and the peripheral atoms. But in the case of the BSi$_2$Ge$_2^+$ system, the π-delocalized molecular orbital is formed by the perpendicular $2p_z$ orbital of the boron and the peripheral atoms.

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**Figure 2.** Low-lying isomers of BGe$_4^+$ system on the PES. The values without and within parentheses are the relative energies in kcal/mol without ZPE correction at PBE0-D3/def2-TZVPP and CCSD(T)/aug-cc-pVTZ methods, respectively. The number of imaginary frequencies (NImag) obtained for each stationary point is indicated underneath the geometries.

**Figure 3.** Low-lying isomers of BSiGe$_3^+$ system on the PES. The values without and within parentheses are the relative energies in kcal/mol without ZPE correction at PBE0-D3/def2-TZVPP and CCSD(T)/aug-cc-pVTZ methods, respectively. The number of imaginary frequencies (NImag) obtained for each stationary point is indicated underneath the geometries.
Figure 4. Low-lying isomers of BSi$_2$Ge$_2$ system on the PES. The values without and within parentheses are the relative energies in kcal/mol without ZPE correction at PBE0-D3/def2-TZVPP and CCSD(T)/aug-cc-pVTZ methods, respectively. The number of imaginary frequencies (NImag) obtained for each stationary point is indicated underneath the geometries.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Symmetry</th>
<th>Energy (without ZPE)</th>
<th>Energy (with ZPE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>$C_{2v}$</td>
<td>0.00 (0.00)</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>$C_{2v}$</td>
<td>10.44 (12.88)</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>$C_{2v}$</td>
<td>15.50 (15.89)</td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>$C_{2v}$</td>
<td>16.74 (16.35)</td>
<td></td>
</tr>
<tr>
<td>5a</td>
<td>$C_{2v}$</td>
<td>18.94 (17.94)</td>
<td></td>
</tr>
<tr>
<td>6a</td>
<td>$C_{2v}$</td>
<td>19.42 (18.06)</td>
<td></td>
</tr>
<tr>
<td>7a</td>
<td>$C_{2v}$</td>
<td>25.39 (21.36)</td>
<td></td>
</tr>
<tr>
<td>8a</td>
<td>$C_s$</td>
<td>29.33 (28.09)</td>
<td></td>
</tr>
<tr>
<td>9a</td>
<td>$C_s$</td>
<td>71.05 (67.02)</td>
<td></td>
</tr>
<tr>
<td>10a</td>
<td>$C_s$</td>
<td>71.51 (67.95)</td>
<td></td>
</tr>
<tr>
<td>11a</td>
<td>$C_s$</td>
<td>75.40 (69.45)</td>
<td></td>
</tr>
<tr>
<td>12a</td>
<td>$C_s$</td>
<td>80.60 (72.37)</td>
<td></td>
</tr>
<tr>
<td>13a</td>
<td>$C_s$</td>
<td>82.12 (73.24)</td>
<td></td>
</tr>
</tbody>
</table>

NImag = 0

Figure 5. Time evolution of the total energy of BGe$_4$ (1a), BSiGe$_3$ (1b), and BSi$_2$Ge$_2$ (1c) ptB geometries.
as the 1c structure lies on the YZ-plane. The electronic delocalization (both $\sigma$- and $\pi$-) in the designed systems make the structures stable in planar form. We have discussed more details about the delocalization of electron density in the systems using multi-center-2e bonding in the AdNDP section.

3.4 NBO analysis

This analysis gives important data for the distribution of charges among the atoms in a system and the WBI among two connected atoms. Table 1 contains the results of this analysis for the global minima of the considered systems. The table shows that the natural charges on the ptB atom are highly negative, suggesting a strong $\sigma$-acceptance from the surrounding atoms. The charges on the peripheral atoms are close to one in all the global minima. From the valence electronic configuration of the ptB atom, it is shown that the occupations of $2p_z$ orbitals of the central boron in BGe$_4^+$ (1a), BSiGe$_3^+$ (1b) and 2$p_x$ orbital in BSi$_2$Ge$_2^+$ (1c) are lower than the other two $p$ orbitals. These lower occupations indicate the $\pi$-back donation from the ptB atom to the surrounding atoms. The computed WBI values of the B–Si and B–Ge bonds are presented in Table 1, which indicates that the central boron atom is in a tetracoordinate environment bonded with the peripheral atoms covalently. The WBI$_{B–Si}$ values are higher than the WBI$_{B–Ge}$ values for all the global minimum structures.

Figure 6. Time evolution of changes in the $r_{B–Ge}$ with respect to that in the optimized 1a, 1b, and 1c ptB geometries for BGe$_4^+$, BSiGe$_3^+$, and BSi$_2$Ge$_2^+$ systems, respectively.
Figure 7. Time evolution of changes in the $r_{B-Si}$ with respect to that in the optimized $1b$, and $1c$ ptB geometries for BSiGe$_3^+$, and BSi$_2$Ge$_2^+$ systems, respectively.

Table 1. The natural charges ($q$, $|e|$) on the atoms and the WBI for $B-Si$ and $B-Ge$ bonds in the global minima and the valence electronic configuration of the ptB.

<table>
<thead>
<tr>
<th>Systems</th>
<th>$q_B$</th>
<th>$q_{Si}$</th>
<th>$q_{Ge}$</th>
<th>WBI (B—Si)</th>
<th>WBI (B—Ge)</th>
<th>Valence electronic configuration of B</th>
</tr>
</thead>
<tbody>
<tr>
<td>BGe$_4^+$ (1a)</td>
<td>−2.35</td>
<td>-</td>
<td>0.84</td>
<td>-</td>
<td>0.83</td>
<td>$2s^{1.280}$ $2p_x^{1.322}$ $2p_y^{1.322}$ $2p_z^{1.135}$</td>
</tr>
<tr>
<td>BSiGe$_3^+$ (1b)</td>
<td>−2.35</td>
<td>0.68</td>
<td>0.86, 0.96</td>
<td>0.90</td>
<td>0.80, 0.83</td>
<td>$2s^{1.271}$ $2p_x^{1.316}$ $2p_y^{1.337}$ $2p_z^{1.128}$</td>
</tr>
<tr>
<td>BSi$_2$Ge$_2^+$ (1c)</td>
<td>−2.33</td>
<td>0.69</td>
<td>0.97</td>
<td>0.88</td>
<td>0.79</td>
<td>$2s^{1.262}$ $2p_x^{1.113}$ $2p_y^{1.329}$ $2p_z^{1.327}$</td>
</tr>
</tbody>
</table>

Figure 8. Plots of the molecular orbitals of BGe$_4^+$ (1a), BSiGe$_3^+$ (1b), and BSi$_2$Ge$_2^+$ (1c) ptB geometries. The values in the parentheses are the energies of the corresponding molecular orbitals in the eV unit.
3.5 Adaptive natural density partitioning (AdNDP) analysis

The AdNDP\textsuperscript{55,66} analysis has been carried out with the help of the Multiwfn software to know the presence of the multi-center-two-electron bonding in the 1a, 1b, and 1c structures. The generated orbitals with occupation numbers (ONs) for BGe\textsubscript{4}\textsuperscript{+} (1a), BSiGe\textsubscript{3}\textsuperscript{+} (1b), and BSi\textsubscript{2}Ge\textsubscript{2}\textsuperscript{+} (1c) systems are presented in Figure 9. The figure shows that for all the global minima, there are four 1c-2e lone pairs with the ONs 1.96 \textit{e} on Ge atoms and 1.92 \textit{e} on Si atoms. There are three 3c-2e \textsigma\-bonds and one 5c-2e \textpi\-bond in 1a, 1b, and 1c structures with ONs 2.00 \textit{e} of each. So, this analysis supports both the \textsigma\- and \textpi\-electronic delocalization in the 1a, 1b, and 1c structures to make them stable.

3.6 AIM analysis

Various electron density descriptors for the B–Si and B–Ge bonds are computed for BGe\textsubscript{4}\textsuperscript{+} (1a), BSiGe\textsubscript{3}\textsuperscript{+} (1b), and BSi\textsubscript{2}Ge\textsubscript{2}\textsuperscript{+} (1c) ptB geometries, and the results are provided in Table 2. The bond paths ((3,−1) bond critical points (BCPs)) between the central boron atom and the four peripheral atoms are confirmed from this analysis. The values of Laplacian of the electron density [\nabla^2 \rho(r_c)] are positive, and the total energy density (H(r\textsubscript{c})) is negative at the BCPs, suggesting the covalent character of the respective bonds. We have also generated the contour diagram of \nabla^2 \rho(r_c) and the corresponding electron localization function (ELF) plots in the molecular plane for BGe\textsubscript{4}\textsuperscript{+} (1a), BSiGe\textsubscript{3}\textsuperscript{+} (1b), and BSi\textsubscript{2}Ge\textsubscript{2}\textsuperscript{+} (1c) ptB structures which are shown in Figures 10a and 10b, respectively. The generated plots show the delocalization of electron density among the central boron atom and the surrounding atoms. Hence, this analysis supports the stability of the planar 1a, 1b, and 1c structures through an electronic approach.

3.7 Aromaticity analysis

The simple rules to understand the aromaticity of a molecular moiety are cyclic, planar, and conjugated systems which must comprise (4n + 2) numbers of \textpi electrons (n = 0, 1, 2, 3, etc.). The compulsory criterion of aromaticity, the (4n + 2) number of \textpi electrons, was first suggested by Hückel. Although there are many methods to ascertain the aromaticity of a molecular motif, NICS, harmonic oscillator model of aromaticity (HOMA), multi-center bond index (MCI), and ELF, etc. are used mostly.\textsuperscript{67–71} This work discusses the NICS values of the designed systems. The concept of NICS was first given by Schleyer \textit{et al.} The NICS(0) and NICS(1) correspond to the NICS values at the center of a ring and 1 Å above the ring,
respectively. For aromatic and anti-aromatic molecules/ions, the NICS values are negative and positive, respectively. The NICS values correspond to zero for non-aromatic systems.

We have calculated the NICS values of each triangle in BGe$_4^+$ (1a), BSiGe$_3^+$ (1b), and BSi$_2$Ge$_2^+$ (1c) ptB geometries, and the results are presented in Figure 11. The $\sigma$- and $\pi$-aromaticity of the systems are confirmed by the negative values of NICS(0) and NICS(1), respectively. So, this dual aromaticity of the considered systems strongly supports the planar global minimum having a tetracoordinate boron atom.

### Table 2.

Electron Density ($\rho(r_c)$), Laplacian of Electron Density ($\nabla^2 \rho(r_c)$), Kinetic Energy Density ($G(r_c)$), Potential Energy Density ($V(r_c)$), Total Energy Density ($H(r_c)$) for BGe$_4^+$ (1a), BSiGe$_3^+$ (1b), and BSi$_2$Ge$_2^+$ (1c) ptB structures.

<table>
<thead>
<tr>
<th>Systems</th>
<th>BCP</th>
<th>$\rho(r_c)$</th>
<th>$\nabla^2 \rho(r_c)$</th>
<th>$G(r_c)$</th>
<th>$V(r_c)$</th>
<th>$H(r_c)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BGe$_4^+$ (1a)</td>
<td>B-Ge</td>
<td>0.099</td>
<td>0.021</td>
<td>0.057</td>
<td>-0.109</td>
<td>-0.052</td>
</tr>
<tr>
<td>BSiGe$_3^+$ (1b)</td>
<td>B-Si</td>
<td>0.094</td>
<td>0.164</td>
<td>0.097</td>
<td>-0.153</td>
<td>-0.056</td>
</tr>
<tr>
<td></td>
<td>B-Ge</td>
<td>0.106</td>
<td>-0.009</td>
<td>0.057</td>
<td>-0.117</td>
<td>-0.059</td>
</tr>
<tr>
<td>BSi$_2$Ge$_2^+$ (1c)</td>
<td>B-Si</td>
<td>0.097</td>
<td>0.024</td>
<td>0.056</td>
<td>-0.107</td>
<td>-0.050</td>
</tr>
<tr>
<td></td>
<td>B-Ge</td>
<td>0.104</td>
<td>0.024</td>
<td>0.056</td>
<td>-0.107</td>
<td>-0.050</td>
</tr>
</tbody>
</table>

**Figure 10.** Plots of (a) the Laplacian of electron density [$\nabla^2 \rho(r)$], blue dashed and red solid lines indicate $\nabla^2 \rho(r) < 0$ and $\nabla^2 \rho(r) > 0$ regions, respectively, and (b) the ELF basin of BGe$_4^+$ (1a), BSiGe$_3^+$ (1b), and BSi$_2$Ge$_2^+$ (1c) ptB geometries.

4. Conclusions

We have generated several isomers of BSi$_n$Ge$_{4-n}^+$ ($n = 0 - 2$) systems by exploring the PES using the ABCluster code. The 1a, 1b, and 1c structures are the global minima among the low-lying isomers with a ptB atom in BGe$_4^+$, BSiGe$_3^+$, and BSi$_2$Ge$_2^+$ systems, respectively. The nature of bonding in 1a, 1b, and 1c structures is studied in detail. The kinetic stability of the 1a, 1b, and 1c structures is confirmed by the ADMP simulation at 300 K and 500 K temperatures over 20 ps of time. The contour diagram of $\nabla^2 \rho(r)$ and the ELF plots showed the
delocalization of electron density in the molecule, which supports the stability of the global minimum energy structures. The molecular orbital analysis clearly showed the $\sigma$- and $\pi$- electronic delocalization in the systems. Moreover, the $\sigma/\pi$-dual aromaticity of the 1a, 1b, and 1c structures assist the stability of these geometries in planar form. From all the supported analyses, we expect the systems under study to be fascinating to experimentalists and theoreticians to design new ptB molecules/ions. As planar hypercoordinate carbon species were characterized in the gas phase, we hope that the feasibility of the designed systems might be possible in the near future.

**Supplementary Information (SI)**

Table S1, Figures S1-S2, and related information are available at www.ias.ac.in/chemsci.

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**Conflicts of interest** The authors declare no conflicts of interest.

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