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Article

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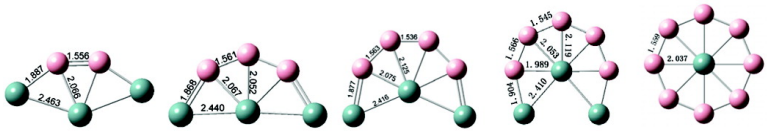

C_{2v} $B_2Si_2Si^-(^2A_2)$ C_{2v} $B_3Si_2Si^-(^1A_1)$ C_{2v} $B_4Si_2Si^-(^2B_1)$ C_{2v} $B_5Si_2Si^-(^1A_1)$ D_{8h} $B_8Si(^1A_{1g})$

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Planar Tetra-, Penta-, Hexa-, Hepta-, and Octacoordinate Silicons: A Universal Structural Pattern

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Abstract: A universal structural pattern has been presented at density function theory level to incorporate planar tetra-, penta-, hexa-, hepta-, and octacoordinate silicons in C_{2v} B_nE_2Si series (E = CH, BH, or Si; n = 2−5) and D_{8h} B_8Si. The equivalence in valence electron counts and one-to-one correspondence of the delocalized π and σ valence orbitals with small boron clusters strongly support the optimized structures containing planar coordinate silicons. Planar B_nE_2Si series are predicted to be aromatic in nature, and the vertical detachment energies of their anions are presented to facilitate future photoelectron experiments. This structural pattern can be applied to form other planar coordinate nonmetals including Ge, P, As, Al, and Ga and needs to be confirmed in experiments to open a new branch of chemistry on planar coordinate main group elements.

Introduction

Considerable progress has been achieved in the past 30 years on planar coordinate carbon and boron, including tetra-,[1−8] penta-,[9,10] hexa-, and heptacoordinate C [11,12] and the newly discovered hepta- and octacoordinate B,[13] while much less attention has been paid to their silicon analogues. The first planar tetracoordinate Si was proposed with controversy about 2 decades ago[14] and observed recently in C_{2v} MAl_4^- and MAl_4 (M = Si and Ge).[15] Recent density functional theory (DFT) investigations have presented the possibility of hosting a planar octacoordinate Si in a B_8Si molecular wheel.[9,16] With a huge gap left between planar tetra- and octacoordinate silicons at the present stage, it is natural to ask if planar penta-, hexa-, and heptacoordinate silicons are viably possible and if the answer is yes, then whether any geometrical or electronic structural patterns exist to host various planar hypercoordinate silicons in a universal format. With the inspiration of the pioneering work of Schleyer and co-workers on planar penta- and hexa-coordinate C [9,11] and previous reports on binary semiconductor clusters,[17,18] in this work, we present a unified structural pattern at the DFT level to incorporate planar tetra-, penta-, hexa-, hepta-, and octacoordinate silicons in C_{2v} B_nE_2Si series (E = CH, BH, or Si; n = 2−5) and D_{8h} B_8Si. These C_{2v} B_nE_2Si clusters featured with the fan-shaped structures (or partial molecular wheels) "grow" gradually along the fan peripheries when the number of B atoms increases and finally achieve a perfect closed octagon at B_8Si (D_{8h}), which contains a planar octacoordinate Si centered in a beautiful molecular wheel. The planar hypercoordinate silicons with the coordination numbers greater than 4 follow the octet rule by forming partial bonds with surrounding B, C, or Si atoms. This structural pattern is applicable to planar coordinate Ge, P, As, Al, and Ga and needs to be confirmed in experiments to open a new branch of chemistry on planar hypercoordinate nonmetals.

Computational Methods

B_nE_2Si (E = CH, BH, or Si; n = 2−5) neutrals and charged ions obtained at DFT B3LYP/Lanl2dz were further optimized at DFT B3LYP/6-311++G(3df,p)[19] and imaginary frequencies checked at the same theoretical levels. The DFT wave functions obtained at the

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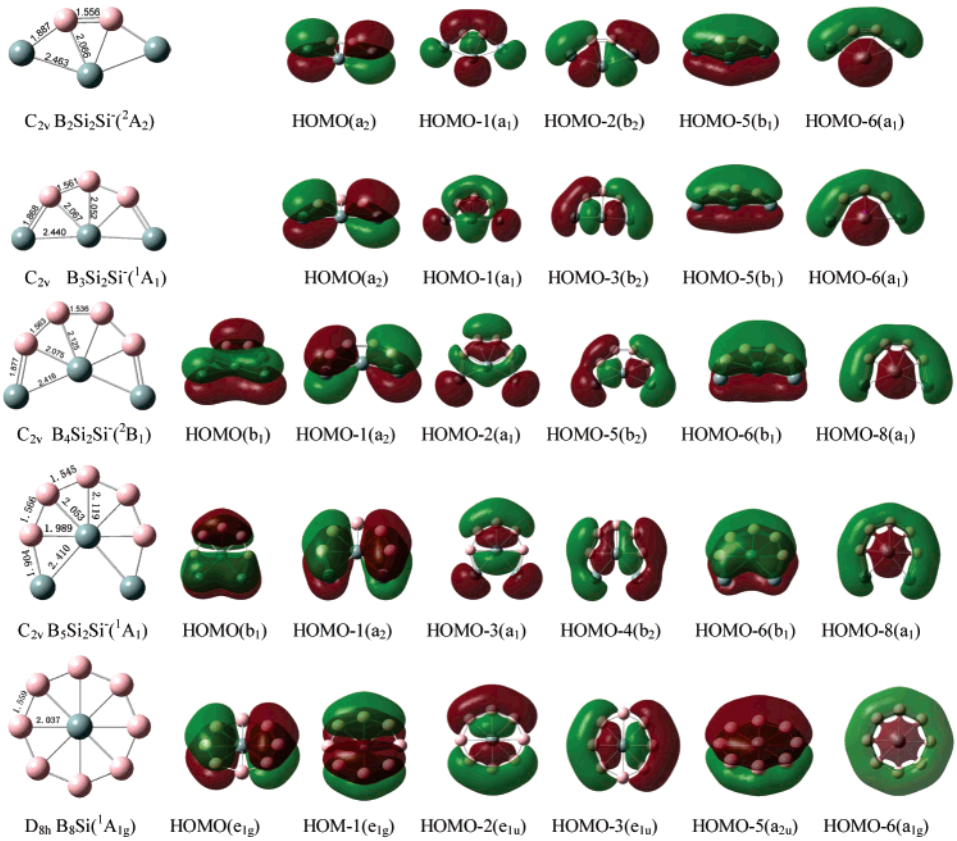

Figure 1. Optimized structures and the corresponding delocalized π and σ valence orbital pictures of $B_nSi_2Si^-$ anions ($n = 2-5$) and B_8Si neutral.

optimized structures were confirmed to be stable. The second-order Møller–Plesset (MP2) procedure[20] produced essentially the same structures as DFT, with bond length differences generally smaller than 0.02 Å. The one-electron vertical detachment energies (VDEs) of the neutrals and anions were calculated with the outer valence Green's function (OVGF) procedure[21] at the basis of 6-311++G(d,p) with the frozen core approximation. To assess the aromatic character of these systems, we calculated the nucleus-independent chemical shifts for the ghost atoms located 1.0 Å above the geometrical center of the heavy atom rings (NICS(1))[22] employing the gauge-independent atomic orbital (GIAO) approach[23] at B3LYP/6-311++G(3df,p) level. Figure 1 depicts the optimized structures of C_{2v} $B_nSi_2Si^-$ ($n = 2-5$) anions and D_{8h} B_8Si neutral and their delocalized π and σ valence orbital pictures involving the planar coordinate silicon centers. The results obtained for C_{2v} B_nSi_2Si neutrals ($n = 2-5$) and B_nSi_2C neutrals and anions ($n = 2, 3$) are shown in Figure 2. Figure 3 shows the optimum structures of $B_nB_2H_2Si$, B_nCBH_2Si, and $B_nC_2H_2Si$ series with necessary bond lengths, NICS(1) values, and the lowest vibrational frequencies indicated. The lowest vibrational frequencies, calculated NICS(1) values, total Wiberg bond indices of the Si centers (WBI_{Si}), and the low-lying one-electron VDEs of $B_nSi_2Si^-$ ($n = 2-5$) and $B_nB_2H_2Si^-$ ($n = 3, 4$) anions are summarized in Table 1. Extensive search performed for $B_nSi_2Si^-$ ($n = 2, 3$) produced no other two- or three-dimensional structures with lower energies than that depicted in Figure 1 (see Supporting Information for details), and detailed electronic structure analyses described below strongly support our optimized results. Concerning the stability of these planar structures, we calculated the binding energy of a singlet D_{8h} B_8Si relative to a triplet D_{7h} B_8 and a triplet free Si atom which turned out to be 3.64 eV. All the calculations in this work were performed using the Gaussian 03 package.[24]

Results and Discussion

As can be seen from Figure 1, planar tetra-, penta-, hexa-, and heptacoordinate silicons can be systematically obtained by consecutively adding B atoms in the C_{2v} $B_nSi_2Si^-$ molecular fan peripheries, and a perfect planar octacoordinate Si is finally achieved at D_{8h} B_8Si,[9,16] completing a structural transition from molecular fans to a perfect molecular wheel. C_{2v} B_6Si_2Si, which is absent in Figure 1, has been confirmed to be unstable with an octacoordinate planar Si center. Replacing the two periphery Si atoms in it with two smaller B atoms produces the perfect octagon B_8Si shown in Figure 1. All the planar C_{2v} $B_nSi_2Si^-$ anions possess the lowest vibrational frequencies greater than

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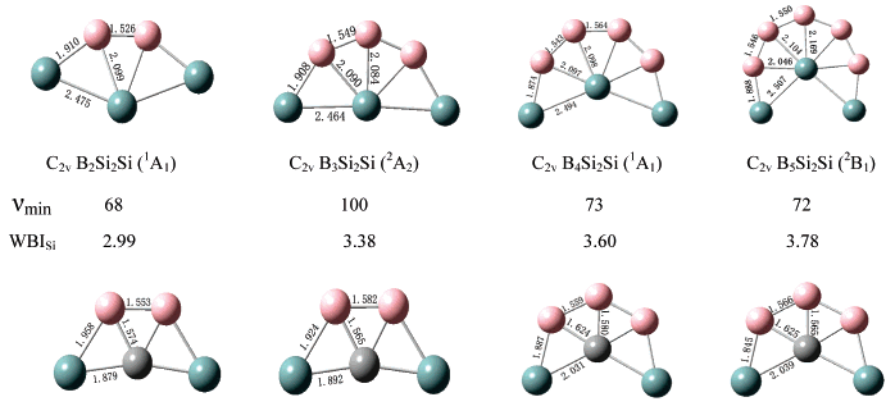

	C_{2v} B_2Si_2Si ($^1A_1$)	C_{2v} B_3Si_2Si ($^2A_2$)	C_{2v} B_4Si_2Si ($^1A_1$)	C_{2v} B_5Si_2Si ($^2B_1$)
ν_{min}	68	100	73	72
WBI_{Si}	2.99	3.38	3.60	3.78

	C_{2v} B_2Si_2C ($^1A_1$)	C_{2v} $B_2Si_2C^-$ ($^2A_2$)	C_{2v} B_3Si_2C ($^2A_2$)	C_{2v} $B_3Si_2C^-$ ($^1A_1$)
ν_{min}	193	269	108	122
WBI_C	3.38	3.49	3.55	3.66

Figure 2. Optimized structures of B_nSi_2Si neutrals ($n = 2-5$) and B_nSi_2C neutrals and anions ($n = 2, 3$) with necessary bond lengths (Å), the lowest vibrational frequencies (ν_{min}/cm^{-1}), and calculated total Wiberg bond indices (WBIs) of the central atoms indicated.

Table 1. Calculated NICS(1) Values (ppm), the Lowest Vibrational Frequencies (ν_{min}/cm^{-1}), the Total Wiberg Bond Indices of the Planar Coordinate Si Centers (WBI_{Si}), and the Low-Lying Vertical Detachment Energies (VDEs/eV) with Pole Strengths Greater than 0.80 Obtained for $B_nSi_2Si^-$ ($n = 2-5$), B_8Si, and $B_nB_2H_2Si^-$ ($n = 3, 4$)

cluster	N_π	NICS	ν_{min}	WBI_{Si}	VDEs
$B_2Si_2Si^-$	3	−15.3	110	3.02	α: 2.72 (a_2), 3.25 (a_1), 4.18 (b_2), 4.31 (a_1), 4.90 (b_1) β: 3.21 (a_1), 3.99 (b_2), 4.17 (a_1), 4.60 (b_1), 4.90 (b_2)
$B_3Si_2Si^-$	4	−8.9	126	3.43	2.93 (a_2), 3.72 (a_1), 4.40 (b_2), 4.45 (b_2), 5.28 (b_1), 5.11 (a_1)
$B_4Si_2Si^-$	5	−11.9	138	3.65	α: 2.38 (b_1), 3.42 (a_2), 4.19 (a_1), 4.45 (b_2), 4.94 (a_1), 5.13 (b_2), 5.80 (b_1) β: 3.20 (a_2), 4.01 (a_1), 4.36 (b_1), 4.77 (a_1), 4.98 (b_2), 5.40 (b_1)
$B_5Si_2Si^-$	6	−21.7	101	3.89	2.91 (b_1), 3.74 (a_2), 3.81 (b_2), 4.71 (a_1), 5.11 (b_2), 5.49 (a_1)
B_8Si	6	−24.5	140	3.77	8.64 (e_{1g}), 9.87 (e_{1u}), 11.15 (b_{2g}), 11.36 (a_{2u}), 12.28 (a_{1g}) 12.59 (e_{3u})
$B_3B_2H_2Si^-$	4	−7.5	175	3.41	2.49 (a_2), 3.70 (a_1), 4.18 (b_2), 5.12 (b_1), 6.30 (a_1), 6.95 (b_2), 8.49 (a_1)
$B_4B_2H_2Si^-$	5	−12.0	181	3.60	α: 2.20 (b_1), 3.35 (a_2), 4.37 (a_1), 4.59 (b_2), 5.76 (b_1), 6.28 (a_1) β: 3.05 (a_2), 4.23 (a_1), 4.59 (b_2), 5.18 (b_1), 6.09 (a_1)

100 cm^{-1}. These structures have normal bond lengths with $r_{Si'-B} = 2.03-2.13$ Å, $r_{Si'-Si} = 2.41-2.46$ Å, $r_{Si-B} = 1.86-1.91$ Å, and $r_{B-B} = 1.53-1.57$ Å, and the corresponding Wiberg bond indices of $WBI_{Si'-B} = 0.40-0.84$, $WBI_{Si'-Si} = 0.47-0.67$, $WBI_{Si-B} = 1.16-1.56$, and $WBI_{B-B} = 1.33-1.56$ (Si′ denotes the planar coordinate Si center). The bond parameters shown in Figure 1 (also Figure 2 and Figure 3) indicate that the constituent atoms in these systems match in geometries to form the planar coordinate silicons. Si′−B and Si′−Si interactions are either single or partial bonds, while Si−B and B−B interactions have obviously double bond characteristics. Planar coordinate silicon centers in B_nE_2Si series follow the octet rule by forming partial bonds with surrounding B, Si, or C, as indicated by the total WBIs of Si centers which range from 3.02 to 3.89 in the anionic series. Natural charge analyses indicate that the planar coordinate Si centers carry positive charges, while B atoms are negative in $B_nSi_2Si^-$ anions. For instance, $B_3Si_2Si^-$ has the calculated natural atomic charges of Si′ +0.45, Si +0.13, B −0.76, and B′ −0.20 |e|, respectively. As indicated in Figure 1 and Figure 2, C_{2v} B_nSi_2Si neutrals, which possess the same geometries as the corresponding $B_nSi_2Si^-$ anions, have slightly longer bond lengths and obviously lower lowest vibrational frequencies than the anions. A systematic investigation indicates that this structural pattern is applicable to Al, Ga, Ge, P, and As, except $B_2Si_2Ga^-$ which has an imaginary vibrational frequency at 203*i* cm^{-1}. Figure 2 indicates that planar tetra- and pentacoordinate C atoms can also be stabilized in B_nSi_2C neutrals and anions. Both C_{2v} B_2Si_2C and B_3Si_2C neutrals and anions obtained here have practically the same B−B bond lengths as that of hyparene $B_3(CH)_2C$ (1.578Å),[9] while the C−B bonds are about 0.1 Å shorter than the corresponding values in $B_3(CH)_2C$. The C_{2v} B_nSi_2C series ($n = 2, 3$) possess slightly longer C−Si distances (within 0.2 Å) than the C−Si bonds observed in the monocyclic C_{2v} CAl_3Si^-, which contains a planar tetracoordinate carbon center.[3]

Figure 3 indicates that planar tetra-, penta-, and hexacoordinate silicons are stable in the molecular fans of $B_nC_2H_2Si$, $B_nB_2H_2Si$, and B_nCBH_2Si series ($n = 2-4$) with the lowest vibrational frequencies greater than 140 cm^{-1} and the total Wiberg bond orders of the silicon centers ranging from 2.2 to 3.6. It should be pointed out that, as indicated in Figure 2, the Si−C bonds exhibit obvious double bond characteristics in $B_nC_2H_2Si$ series which have the highest lowest vibrational frequencies obtained in this work. The natural charge distribution of these clusters follows the electronegativity order of C > B > Si. The typical situation happens in $B_4C_2H_2Si$ which has the natural atomic charges of Si +1.53, B′ −0.32, B +0.37, C −1.08, and H +0.27 |e| (B′ represents the top two B atoms in the structure). A planar heptacoordinate Si center does not match in size in either $B_5C_2H_2Si^+$ or $B_5B_2H_2Si^-$ for the reason that the distances between Si and the top periphery B are too big (2.24 Å) to form the seventh bond required.

The driving force to form these unusual planar structures originates from their unique valence electron counts and the

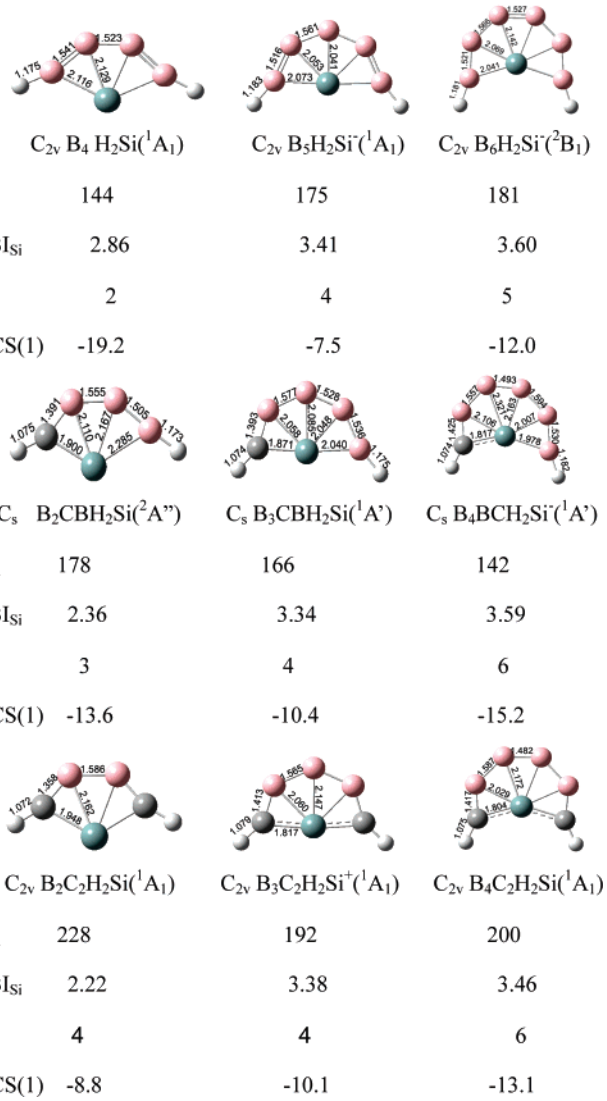

Figure 3. Optimized structures of $B_nB_2H_2Si$, B_nCBH_2Si, and $B_nC_2H_2Si$ ($n = 2-4$) series, with necessary bond lengths (Å), the lowest vibrational frequencies (ν_{min}/cm^{-1}), the number of π electrons (N_π), the calculated total Wiberg bond indices of the central Si (WBI_{si}), and the calculated NICS(1) values (ppm) indicated.

one-to-one valence orbital correspondence with that of planar boron clusters. For instance, $B_2Si_2Si^-$, $B_3Si_2Si^-$, $B_4Si_2Si^-$, and $B_5Si_2Si^-$ anions are isoelectronic to B_6^-,[25] B_7^-,[26] B_8^-,[13] and B_9^{-13} in their valence electrons, while B_8Si is typically an electronic isomer of B_9^-. B_4H_2Si, $B_5H_2Si^-$, and $B_6H_2Si^-$ have the same numbers of valence electrons as B_6, B_7^-, and B_8^-. As a $-$CH group is equivalent to a B atom in bonding capacity, $B_2C_2H_2Si$, $B_3C_2H_2Si^+$, and $B_4C_2H_2Si$ can be regarded as equivalents of B_5^-,[27] B_6, and B_7^-, respectively. Recent DFT theory and photoelectron investigations have confirmed that C_{2v} B_5^-,[27] C_{2h} B_6, and D_{2h} B_6^-,[25] C_{2v} B_8^-, and D_{8h} B_9^- [13] all possess planar ground-state structures, while B_7^- has two low-lying structures with slight structural deviations from the perfect planar D_{6h} isomer.[26] It is well-known in chemistry that valence electrons determine the bonding properties of the molecules and isoelectronic systems possess similar geometrical structures. As valence electron analogues of the experimentally known planar boron clusters, B_nE_nSi series studied in this work inherently follow boron clusters to form similar planar structures. Our DFT molecular fans have close similarity in geometries with their boron cluster analogues. Here, the n electron-deficient B atoms define the basic structural frames, and the introduction of the quasi-boron groups ($-$CH, $-$BH, or Si) modulates the size of the clusters to host the planar coordinate silicons and totally removes the orbital degeneracy of the systems by lowering their geometrical symmetries to C_{2v}.

A brief look at Figure 1 reveals that $B_4Si_2Si^-$, $B_5Si_2Si^-$, and B_8Si all have three similar delocalized π orbitals and three delocalized σ bonds, while both $B_2Si_2Si^-$ and $B_3Si_2Si^-$ have two delocalized π and three delocalized σ. All the $B_nSi_2Si^-$ anions start with a delocalized π HOMO and the last delocalized horseshoe σ orbital (a_1) expands continuously in size along the molecular periphery and finally forms a beautiful σ orbital wheel at B_8Si. The MO next to the horseshoe σ is a typical π orbital totally delocalized on both sides of the C_{2v} molecular plane. Obviously, these delocalized σ orbitals play an important role in maintaining the stability and rigidity of the planar periphery structures, and the delocalized π interactions contribute most to keeping the Si center and the periphery in one plane. Similar delocalized π and σ orbitals exist in B_nSi_2Si neutrals and both $B_nC_2H_2Si$ and $B_nB_2H_2Si$ series ($n = 2-4$). Detailed MO analyses further help to understand the bonding nature of the systems. For instance, in the closed-shell C_{2v} $B_5Si_2Si^-$ ($^1A_1$) which has the valence electron configuration of $1a_1^21b_2^22a_1^22b_2^23a_1^24a_1^23b_2^21b_1^25a_1^24b_2^26a_1^25b_2^26a_2^22b_1^2$, the doubly occupied molecular orbitals (MOs) $2b_1$, $6a_2$, and $1b_1$ correspond to the three delocalized π orbitals, while $6a_1$, $4b_2$, and $4a_1$ belong to the three σ interactions which are also highly delocalized and look very similar to the π orbitals as shown in Figure 1. These delocalized orbitals have one-to-one correspondence with the six delocalized valence orbitals of D_{8h} B_9^-.[13] The energy level of D_{8h} B_8Si ($1a_{1g}^21e_{1u}^41e_{2g}^41e_{3u}^42a_{1g}^2$-$1a_{2u}^21b_{2g}^22e_{1u}^41e_{1g}^4$) is slightly different from that of D_{8h} B_9^-, but the two electronic isomers have exactly the same delocalized π and σ valence orbitals as shown in Figure 1 and ref 13. The open-shell system C_{2v} $B_6H_2Si^-(^2B_1)$ possesses the electronic configuration of $1a_1^21b_2^22a_1^22b_2^23a_1^23b_2^24a_1^25a_1^21b_1^24b_2^26a_1^2$-$1a_2^22b_1^1$, in which $2b_1$, $1a_2$, and $1b_1$ are delocalized π orbitals, while $6a_1$, $4b_2$, and $3a_1$ are delocalized σ orbitals, similar again to the six delocalized valence orbitals of C_{2v} B_8^-.[13] With one more electron than $B_6H_2Si^-$, $B_6H_2Si^{2-}$ has a doubly occupied HOMO $2b_1$ and six π valence electrons, but the strong Coulomb repulsion makes this dianion 2.74 eV less stable than the monoanion. C_{2v} $B_4C_2H_2Si$, which can be treated as isoelectronic to B_7^- as discussed above, has the electronic configuration of $1a_1^21b_2^22a_1^22b_2^23a_1^24a_1^23b_2^24b_2^21b_1^25a_1^21a_2^26a_1^22b_1^2$. Here, $2b_1$, $1a_2$, and $1b_1$ are delocalized π orbitals, and $6a_1$, $4b_2$, and $4a_1$ belong to the locally delocalized σ orbitals. It is important to notice that the delocalized π and σ valence orbitals of all the C_{2v} B_nE_nSi series studied here possess the same irreducible representations and have the one-to-one correspondence with the delocalized π and σ valence orbitals of the corresponding pure boron clusters. Clearly, the constituent atoms in B_nE_nSi series match in both geometries and valence orbitals to form the required planar coordinate silicon centers.

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Small boron clusters are known to be either 2-fold (π and σ) aromatic or single (π or σ) aromatic except B_6^- which is antiaromatic.[13,25−27] It is reasonable to expect that their analogues B_nE_2Si exhibit similar behaviors. For systems with both delocalized π and σ valence orbitals, even when the $(4n + 2)$ π Huckel rule in closed-shell systems or the $4n$ π requirement in triplet states are broken, the delocalized σ valence orbitals at lower energy levels are still maintained and the systems remain aromatic. This statement gets support from the calculated NICS-(1) values listed in Figure 3 and Table 1, which all turned out to be negative (the calculated NICS(1) value of benzene is −10.3 ppm). The NICS data also indicate that systems with 2 or 6 π electrons have the highest negative NICS values, 4 π electron clusters possess the smallest NICSs, while 3 or 5 π electron systems lie somewhere between. These results show that the B_nE_2Si series are aromatic in nature and their aromaticities vary in overall agreement with Huckel rule for planar aromaticity. It should also be pointed out that, different from pure boron clusters in overall molecular spin multiplicities, all the systems with an even number of electrons studied in this work prefer singlet states over triplet ones. For instance, C_{2v} $B_3C_2H_2Si^+$ prefers a singlet state ($^1A_1$) over the triplet ($^3B_1$) by 1.61 eV, and singlet C_{2v} $B_4C_2H_2Si$ ($^1A_1$) lies 0.82 eV lower in energy than the corresponding triplet state ($^3A_2$).

The calculated low-lying one-electron VDEs of $B_nSi_2Si^-$ ($n = 1-5$), B_8Si, and $B_nB_2H_2Si^-$ ($n = 3, 4$) tabulated in Table 1 can be utilized to facilitate future characterization of these novel structures in photoelectron spectroscopy measurements. $B_nSi_2Si^-$ bared anions and the partially hydronated $B_nB_2H_2Si^-$ anions are expected to exist in gas phase in laser vaporization of B and Si mixed powders and be detected in photoionized cluster beams. In open-shell systems the coexistence of α and β transitions may complicate the spectral analyses in PES measurements.

In summary, we have presented a universal structural pattern to incorporate planar coordinate Si, Ge, Al, Ga, P, and As in B_nE_2X neutrals and charged ions with the coordination numbers ranging from 4 to 8. Planar tetra- and pentacoordinate carbons can also be stabilized in this pattern. The equivalence in valence electron counts and one-to-one correspondence of the delocalized π and σ valence orbitals with small boron clusters provide strong support for our DFT structures containing planar coordinate silicons. The optimized structural templates obtained in this work maybe utilized as building blocks to construct large systems with multiple planar coordinate silicon and other nonmetal centers.

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Supporting Information Available: Detailed results obtained for 61 B_nE_2X neutrals and charged ions containing planar coordinate Si, Ge, P, As, Al, Ga C, and B. This material is available free of charge via the Internet at http://pubs.acs.org.

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