C_{2h} $(B_nE_mSi)_2H_2$ Molecules (E = B, C, Si; n = 3−6; m = 1, 2) Containing Double Planar Tetra-, Penta-, and Hexacoordinate Silicons

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A density functional theory investigation on a series of S-shaped or cyclic $(B_nE_mSi)_2H_2$ molecules (E = B, C, Si; n = 3−6; m = 1, 2) containing double planar tetra-, penta-, and hexacoordinate silicons has been presented in this work. Further theoretical evidence is provided to support the previously proposed structural pattern to host planar hypercoordinate silicons in small aromatic molecules.

Exploring the bonding capacity of carbon beyond the traditional tetrahedral concept has aroused great interest in the past 30 years. Theoretical and experimental evidence accumulated includes planar tetra-,[1−9] penta-,[10,11] hexa-, and heptacoordinate carbons.[12,13] However, much less attention has been paid to their silicon analogues. Planar tetracoordinate Si was first proposed about two decades ago[14] and was observed recently in C_{2v} MAl_4^- and MAl_4 (M = Si and Ge).[15] The possibility of planar octacoordinate Si in a B_8Si molecular wheel was presented recently.[10,16] In a very recent communication,[17] our group presented a universal structural pattern to host tetra-, penta-, hexa-, and heptacoordinate planar silicons in simple fan-shaped molecules. Following the same construction principle, in this work, we extend the systems to include a series of S-shaped or cyclic C_{2h} $(B_nE_mSi)_2H_2$ molecules (E = B, C, Si; n = 3−6; m = 1, 2) containing double planar tetra-, penta-, and hexacoordinate silicons. Density functional theory (DFT) and Møller−Plesset second-order perturbation theory (MP2) produce essentially the same structures. Both effective σ and π bonds are found to contribute to the aromatic stabilization of these systems.

C_{2h} $(B_nE_mSi)_2H_2$ molecules initially obtained at DFT-B3LYP/Lanl2dz were optimized at DFT-B3LYP/6-311+G(3df)[18] and imaginary frequencies were checked at the same theoretical levels. The DFT structures were further refined at MP2/6-311+G(d) with the frozen-core approximation for defining inner shells to be excluded from the correlation calculation. MP2 method produced essentially the same structures as DFT, with bond lengths slightly shorter (≤5%) in most cases. To assess the aromatic character of these systems, we calculated the nucleus independent chemical shifts (NICS) for the ghost atoms located at the geometric centers of the heavy atom rings[19] employing the gauge-independent atomic orbital (GIAO) approach[20] at the B3LYP/6-311+G(3df) level. Figure 1 shows the optimized structures of C_{2h} $(B_nE_mSi)_2H_2$ series which are true minima without imaginary frequencies, with the corresponding numbers of π electrons, lowest vibrational frequencies, calculated NICS values at the geometric centers of the B_nE_mSi frames, and the total Wiberg bond indices of the planar hypercoordinate Si centers (WBI_{Si}) indicated. Figure 2 shows the occupied π molecular orbitals (MOs) of C_{2h} $(B_nE_mSi)_2H_2$ systems with 6 or 10 π electrons. All the calculations in this work were performed employing the Gaussian 03 program.[21]

Bridging two C_s B_2CBH_2Si, C_{2v} $B_3C_2H_2Si$, and C_s B_4BCH_2-Si monomers (see Figure 3 in ref 17) with a C═C double bond results in C_{2h} $(B_3CSi)_2H_2$ (**1**), C_{2h} $(B_3C_2Si)_2H_2$ (**2**), and C_{2h} $(B_5$-$CSi)_2H_2$ (**6**) shown in Figure 1 with double planar tetra-, penta-, and hexacoordinate silicons, respectively. These S-shaped molecules possess bond parameters similar to those of the corresponding monomers in geometries and follow the $(4n + 2)$ π electron counting rule. They are confirmed to have negative NICS values (as indicated in Figure 1) and therefore be aromatic in nature. As comparisons to structure **2**, two other S-shaped structures **4** (C_s $(B_4CSi)_2H_2$) and **5** (C_{2h} $(B_4CSi)_2H_2$) with double planar pentacoordinate silicons are also depicted in Figure 1. These two structures have 8π electrons. However, as indicated by the negative NICS values shown in Figure 1, they exhibit overall aromaticities in characteristics. This means that, similar to Al_4^{2-}[22] and B_n^- clusters,[23] $(B_nE_mSi)_2H_2$ systems studied in this work are both σ and π aromatic and σ bonds dominate the aromaticity of the molecules violating the $(4n + 2)$ π electron counting rule. It is the delocalized aromatic bonds that keep the planarity of these systems. Figure 2 only depicts the delocalized π orbitals of structures **1**, **2**, and **6**−**8**. In fact, all these planar molecules also have delocalized σ orbitals contributing to the aromaticity of the systems, similar to the situation observed for Al_4^{2-},[22] B_n^-,[23] and B_nE_2Si monomers.[17] Two monomers with penta- and hexacoordinate silicons can also be linked with two ═SiH bridges to form cyclic structures **7** (C_{2h} $(B_4CSiSi)_2H_2$) and **8** (C_{2h} $(B_6SiSi)_2H_2$), which contain double planar penta- and hexacoordinate silicons and have structures similar to the "hyparenes" proposed by Wang et al.[10] to contain double planar pentacoordinate carbons. There is an eight-membered ring with two planar hypercoordinate silicons at the center of these cyclic structures. Replacing one Si center in structure **2** with a C atom produces the distorted planar structure **3** (C_s $(B_3C_2Si)(B_3C_2C)H_2$), which contains one planar penta-

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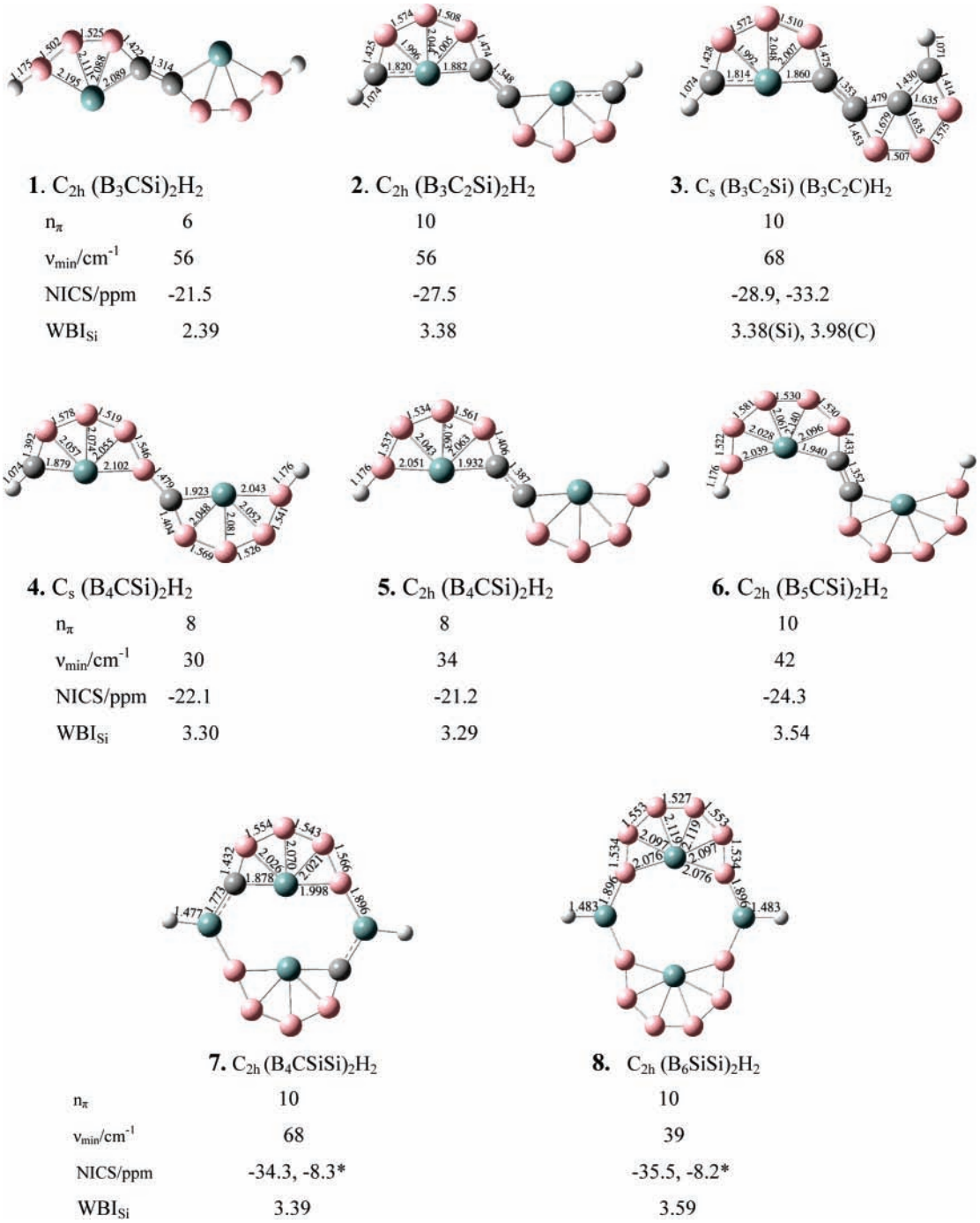

	1. C_{2h} $(B_3CSi)_2H_2$	**2.** C_{2h} $(B_3C_2Si)_2H_2$	**3.** C_s (B_3C_2Si) $(B_3C_2C)H_2$
n_π	6	10	10
ν_{min}/cm^{-1}	56	56	68
NICS/ppm	-21.5	-27.5	-28.9, -33.2
WBI_{Si}	2.39	3.38	3.38(Si), 3.98(C)

	4. C_s $(B_4CSi)_2H_2$	**5.** C_{2h} $(B_4CSi)_2H_2$	**6.** C_{2h} $(B_5CSi)_2H_2$
n_π	8	8	10
ν_{min}/cm^{-1}	30	34	42
NICS/ppm	-22.1	-21.2	-24.3
WBI_{Si}	3.30	3.29	3.54

	7. C_{2h} $(B_4CSiSi)_2H_2$	**8.** C_{2h} $(B_6SiSi)_2H_2$
n_π	10	10
ν_{min}/cm^{-1}	68	39
NICS/ppm	-34.3, -8.3*	-35.5, -8.2*
WBI_{Si}	3.39	3.59

Figure 1. Optimized structures of $(B_nE_mSi)_2H_2$ series (E = B, C, Si; $n = 3-6$; $m = 1, 2$) at DFT-B3LYP/6-311+G(3df) level, with necessary bond lengths, numbers of π electrons n_π, lowest vibrational frequencies ν_{min}, calculated NICS values, and total Wiberg bond indices of Si centers (WBI_{Si}) indicated. Pink balls stand for B, gray balls stand for C, and light green ones stand for Si. The asterisk (*) indicates the NICS value at the center of the central eight-membered ring.

coordinate Si and one planar pentacoordinate C and exhibits aromatic characteristics as indicated by the negative NICS values.

Natural bond orbital (NBO) analyses help in understanding the bonding nature of these molecules. In these neutral planar structures, Si centers lose electrons and carry positive natural charges, while C and B centers (especially C) gain partial electrons and turn out to be negative. For instance, C_{2h} $(B_5CSi)_2H_2$ (**6**) possesses the natural atomic charges of Si +1.20, C −0.69, and B −0.21 |e| (B stands for the B atoms bonded to H), respectively, corresponding to the atomic electron configurations of Si[Ne]$3s^{0.91}3p^{1.83}$ ($3s^{0.91}3p_x^{0.72}3p_y^{0.56}3p_z^{0.55}$), C[He]$2s^{1.01}$-$2p^{3.64}$ ($2s^{1.01}2p_x^{1.32}2p_y^{1.17}2p_z^{1.15}$), and B[He]$2s^{0.89}2p^{2.30}$ ($2s^{0.89}$-$2p_x^{0.95}2p_y^{0.75}2p_z^{0.60}$). Obviously, a C atom here hybridizes in sp^2 to form the three in-plane σ bonds and its $2p_z$ orbital contributes the most to form the delocalized π MOs perpendicular to the molecular plane, while Si and B provide their partially occupied np_z orbitals to participate in the π bonding processes to a lesser extent. Similar electron transfer happens in the cyclic structures **7** and **8**. For example, structure **7** has the atomic charges of the central Si +1.23, the bridging Si +1.12, and C −1.36 and its opposite B −0.78 |e|, respectively. This charge distribution is

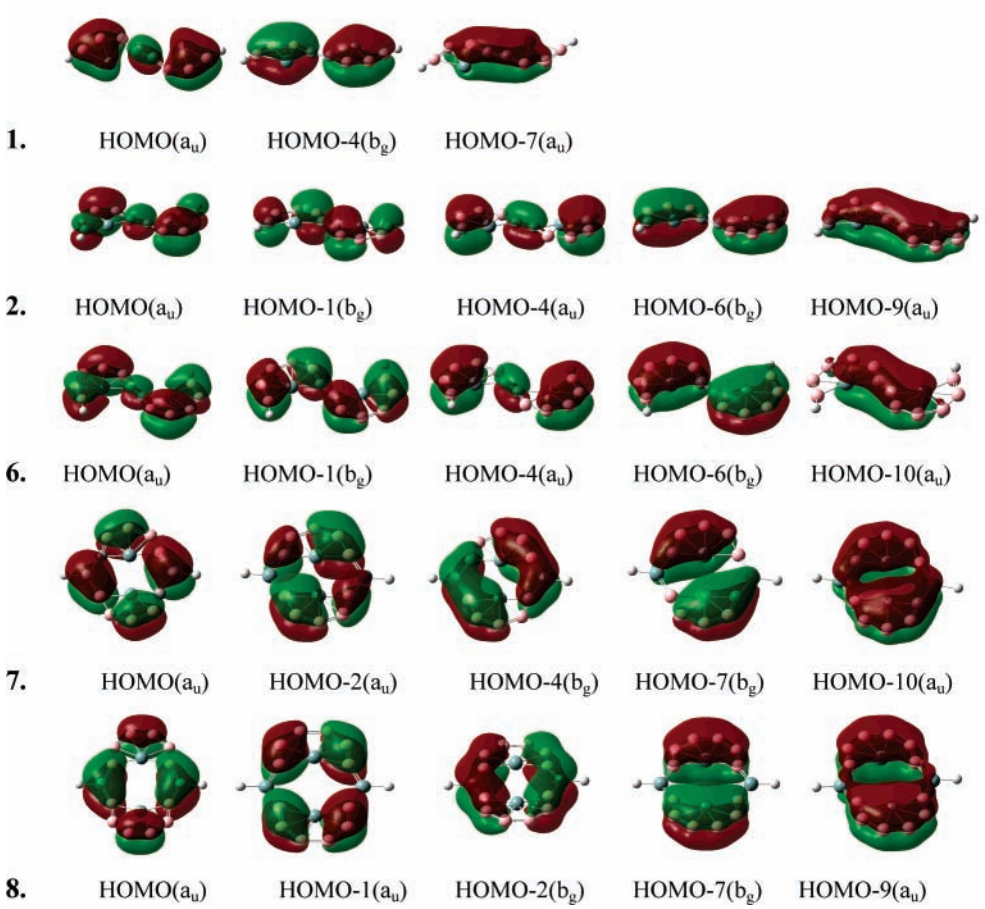

Figure 2. Occupied π MO pictures of $(B_nE_mSi)_2H_2$ (represented with SCF densities) conforming with the $(4n + 2)$ π electron counting rule (n = 1, 2). Structure labels are the same as those defined in Figure 1.

reflected in the lowest occupied π MO pictures shown in Figure 2 and corresponding orbital coefficients, where the HOMO−7(a_u) of structure **1**, HOMO−9(a_u) of **2**, and HOMO−10(a_u) of **6** are mainly composed of the contribution from the two bridging C atoms located at the structural centers, while the HOMO−10(a_u) of **7** and HOMO−9(a_u) of **8** (both π orbitals have very low electron densities at the Si bridges) mainly represent the contribution from the periphery B and C atoms. The total Wiberg bond indices (WBIs) of the central Si atoms quoted in Figure 1 vary in the range of $WBI_{Si} = 2.39-3.59$, indicating that partial bonds are formed between the central Si atom and its surrounding B and C ligands. For instance, the bond orders of the central-Si-involving bonds in structure **8** are Si−B_1 0.556, Si−B_2 0.511, and Si−B_3 0.756 (B atoms are labeled from the top B atom downward), respectively, and the bond order of central-Si−C interaction in structure **7** is 0.756.

In summary, we have presented at DFT and ab initio levels a series of S-shaped or cyclic $(B_nE_mSi)_2H_2$ molecules containing double planar tetra-, penta-, and hexacoordinate silicons, providing further theoretical evidence to support the structural pattern we previously proposed to host planar hypercoordinate silicons. Fan- or S-shaped or cyclic B_n and heterocyclic B_nE_m frames (E = B, C, Si) can serve as effective ligands to coordinate nonmetal centers such as C, B, Si, and Ge. Examples include D_{6h} B_6C^{2-}[12] and D_{8h} B_8Si,[16] C_{2v} $B_n(CH)_2Si$ ($n = 2-4$),[17] and $(B_nE_mSi)_2H_2$ studied in this work. These systems feature both σ and π aromaticities and partial bonds between the nonmetal center and its ligands and may serve as interesting targets in future experiments.

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