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Structures and aromaticities of carbon-rich semiconductor microclusters $\text{Ge}_l\text{Si}_m\text{C}_n$: An *ab initio* study

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Density functional theory and second-order Moller–Plesset perturbation theory investigations show that carbon-rich semiconductor microclusters $\text{Ge}_l\text{Si}_m\text{C}_n$ ($7 \leq l+m+n \leq 10$ with $n=5-8$) possess linear or planar structures and the aromaticity of the singly- or doubly charged H-saturated planar derivatives with $(4n+2)$ delocalized π electrons decreases with the increasing of noncarbon atoms. © 2003 American Institute of Physics. [DOI: 10.1063/1.1604373]

There have been, in the past two decades, extensive theoretical and experimental studies focused on group IV elemental clusters, especially on C_n and Si_n , which represent quite different bonding characteristics and cluster growth patterns. In contrast, much less attention has been paid to binary A_mB_n and ternary $\text{A}_l\text{B}_m\text{C}_n$ clusters (A,B,C=C,Si,Ge), though corresponding bulk systems are important ceramics and semiconductor materials in application.¹⁻¹⁰ *Ab initio* calculations started to appear on small Si_mC_n like Si_2C , Si_4C , Si_2C_4 , Si_2C_2 , Si_3C_3 , Si_3C_2 , GeSi , Si_2Ge_2 , and Si_2Ge_4 in the past 10 years.^{1,4-10} Our group performed a systematic investigation on Ge_mSi_n ($m+n \leq 10$)² and $\text{Ge}_l\text{Si}_m\text{C}_n$ ($l+m+n \leq 6$)¹¹ using the density functional theory (DFT) and configuration interaction with all singles and doubles substitutions [CISD(full)] over the past 2 years. These C-containing semiconductor microclusters are found to take optimum structures with C atoms connected in chains or at transannular positions, for which C=C double bonds dominate the relative stability of different isomers and Si=C interactions play important roles, while other bonds are found much less important in defining the cluster geometries. In a very recent study, we also presented a MP2 investigation¹² on the aromaticities of binary and ternary semiconductor systems with three- or four-membered planar rings. These strained ring systems are confirmed to be featured with delocalized π orbitals perpendicular to the molecular planes and have high negative nucleus-independent chemical shifts (NICS) at the geometrical centers of heavy atoms. The concept of NICS has been used widely as a criterion of aromaticity for both planar and spherical

systems,¹³⁻¹⁵ and recent publications¹⁵⁻¹⁷ confirmed the existence of aromaticities in pure metallic Ga_3^{2-} and Al_4^{2-} with two π electrons and isoelectronic heterocyclic XAl_3^- containing one group IV atom (X=Si,Ge,Sn,Pb).

In this work, we expand the study to carbon-rich binary and ternary clusters $\text{Ge}_l\text{Si}_m\text{C}_n$ containing up to 10 atoms ($7 \leq l+m+n \leq 10$ with $n=5-8$) by utilizing both density functional theory and MP2 methods. Various initial structures are optimized at the B3LYP/6-311+G(3df) level and frequency analyses are made to check for imaginary frequencies at the same theoretical level. The geometries obtained for small $\text{Ge}_l\text{Si}_m\text{C}_n$ ($l+m+n \leq 6$) at the B3LYP level agree quite well with corresponding results at CISD reported in Ref. 11, though the bond lengths at B3LYP are systematically a bit longer. To study the aromaticities of these carbon-rich systems and compare results with our earlier publications, we further optimized the structures of singly- or doubly charged H-saturated clusters $\text{Ge}_l\text{Si}_m\text{C}_6\text{H}_x$ ($x=3-5$) at MP2(full)/6-311+G(d) with the inclusion of all electrons and calculated their absolute NICS values using the gauge-independent atomic orbital (GIAO) approach at the B3LYP/6-311+G(3df) level. To investigate the shielding effect of molecular ring current in more details, NICS values are calculated at three kinds of sites A, B, and C at the geometrical centers of C_6 ring, CSiC triangle, and CGeC triangle, as shown for structure VIII in Fig. 2. The bonding nature shown as double or triple bonds in Figs. 1 and 2 is the direct output of the GAUSSVIEW program. All the calculations are performed utilizing the GAUSSIAN 98 package.¹⁸

At the B3LYP level, the lowest-energy structures of ter-

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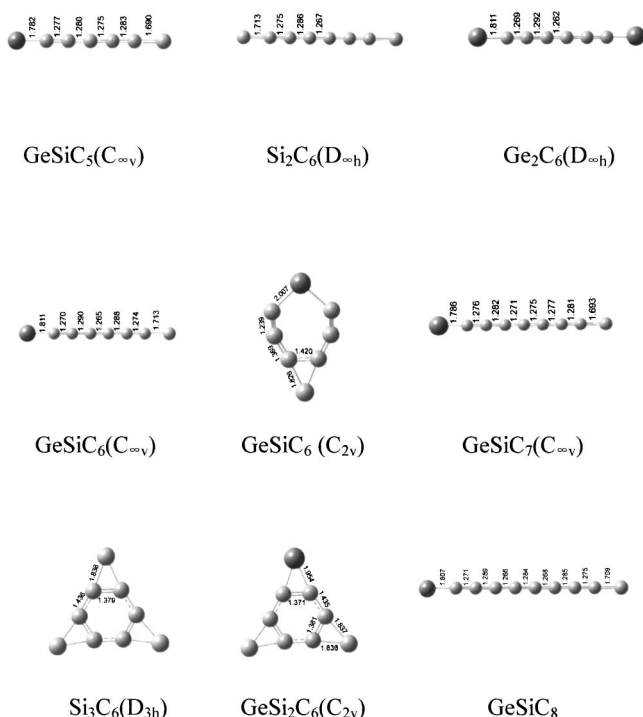


FIG. 1. The optimized linear and planar structures of $\text{Ge}_l\text{Si}_m\text{C}_n$ at B3LYP level with necessary bond lengths indicated. The big dark balls stand for Ge atoms while Si and C are represented as gray balls with C in smaller sizes.

ary GeSiC_n ($n=5,6,7,8$) are linear chains with Si and Ge as ending atoms, except GeSiC_6 , which favors a Ge-bridged structure with a severe distortion to the C_6 ring as shown in Fig. 1. The C_{2v} planar GeSiC_6 is found to be 0.135 eV lower

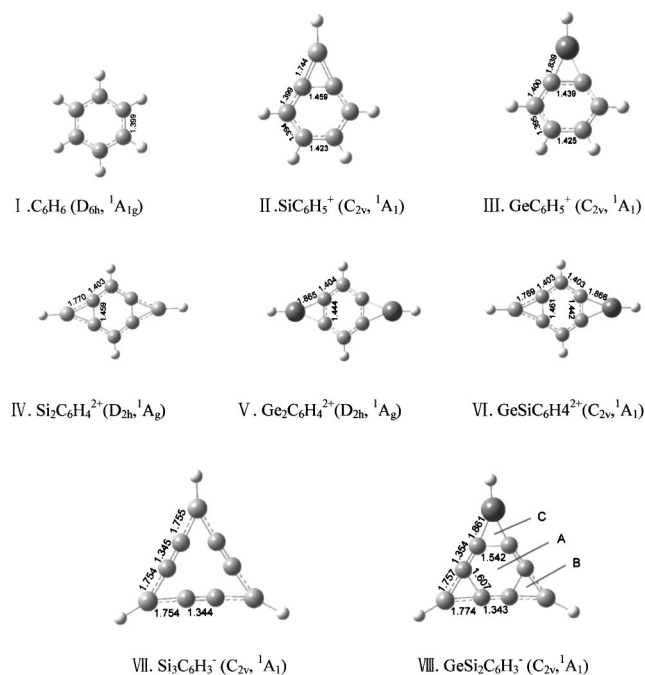


FIG. 2. The optimized structures of planar $\text{Ge}_l\text{Si}_m\text{C}_6\text{H}_x$ ($l,m=1-3$, $x=3-5$) cations and anions at MP2 level with bond lengths indicated. The three sites at the centers of C_6 ring, CSiC triangle, and CGeC triangle are labeled as A, B, C in structure VIII. Ge, Si, and C atoms are depicted with the same symbols as that in Fig. 1, with H represented as the smallest gray balls.

TABLE I. The calculated NICS values of $\text{Ge}_l\text{Si}_m\text{C}_6\text{H}_x$ ($l,m=1-3$, $x=3-5$) at B3LYP/6-311+G(3df) level at sites A, B, and C illustrated in Fig. 2.

| Cluster | Symmetry | N_{π}^a | NICS/ppm | | |
|--|----------|-------------|----------|-------|-------|
| | | | A | B | C |
| C_6H_6 | D_{6h} | 6 | -7.8 | | |
| SiC_6H_5^+ | C_{2v} | 6 | -4.9 | -20.4 | |
| $\text{Si}_2\text{C}_6\text{H}_4^{2+}$ | D_{2h} | 6 | -4.3 | -13.0 | |
| $\text{Si}_2\text{C}_6\text{H}_4$ | D_{2h} | 8 | +11.7 | | |
| $\text{Si}_2\text{C}_6\text{H}_4^{2-}$ | D_{2h} | 10 | +3.6 | | |
| $\text{Si}_3\text{C}_6\text{H}_3^-$ | D_{3h} | 10 | -1.8 | -0.9 | |
| GeC_6H_5^+ | C_{2v} | 6 | -4.4 | | -15.8 |
| $\text{Ge}_2\text{C}_6\text{H}_4^{2+}$ | D_{2h} | 6 | -3.5 | | -8.7 |
| $\text{GeSiC}_6\text{H}_4^{2+}$ | C_{2v} | 6 | -4.0 | -14.0 | -7.4 |
| $\text{GeSi}_2\text{C}_6\text{H}_3^-$ | C_{2v} | 10 | +2.7 | -19.0 | -19.7 |

^a n_{π} =number of π electrons.

in energy than the corresponding linear chain at B3LYP, while both Si_2C_6 and Ge_2C_6 are confirmed to favor linear structures. It is the cumulene-like carbon chains containing 5 to 8 C atoms that stabilize the linear structures, and the ending $\text{C}=\text{Si}$ double bond and $\text{C}-\text{Ge}$ single bond best fit the bonding requirement of the linear geometry. Relative to the triplet states of component atoms, the binding energies of GeSiC_n series increase linearly from 35.83, 41.56, 48.55 to 54.27 eV with the number of C atoms increasing from $n=5, 6, 7$ to 8. This finding is in line with the observation from linear GeSiC_3 and GeSiC_4 obtained at the CISD level in Ref. 11.

Binary and ternary $\text{Ge}_l\text{Si}_m\text{C}_6$ with three noncarbon atoms take the C_6 -ring-centered planar structures as shown in Fig. 1 at the B3LYP level and the corresponding singly- or doubly charged H-saturated derivatives of $\text{Ge}_l\text{Si}_m\text{C}_6\text{H}_x$ at MP2 are shown in Fig. 2. Various T-shaped and zigzag $\text{Ge}_l\text{Si}_m\text{C}_6$ neutrals are confirmed to be less stable in energy or have imaginary frequencies. Orbital analyses indicate that the charged $\text{Ge}_l\text{Si}_m\text{C}_6\text{H}_x$ ($x=3-5$) with 6 or 10 p_z electrons are characterized with delocalized π orbitals perpendicular to the molecular planes lying lower in energies than their highest occupied molecular orbitals (HOMOs). In fact, the delocalized π orbitals of aromatic systems are not always required to be their HOMOs. For example, the delocalized π orbital of benzene lies at HOMO-4 (an A_{2u} orbital) at the MP2 level, and that of SiAl_3^- and GeAl_3^- are HOMO-1 with the irreducible representation of B_1 .¹⁷ Effective π bonds are found to be formed between Si and its neighboring C atoms in these clusters, while $\text{Ge}-\text{C}$ interactions exist basically as single bonds for the reason that the p_z orbital of Si atom matches better with that of C in energy. Typical situations occur in linear GeSiC_n as shown in Fig. 1 and planar $\text{GeSiC}_6\text{H}_4^{2+}$ and $\text{GeSi}_2\text{C}_6\text{H}_3^-$ in Fig. 2. In $\text{Si}_3\text{C}_6\text{H}_3^-$, the $\text{C}=\text{C}$ bonds in the C_6 ring are broken alternatively by effective π interactions between Si and C, leaving the cluster practically a triangle with very weak aromaticity.

The calculated NICS values are summarized in Table I and compared with corresponding value of -7.8 obtained for benzene at the same theoretical level. Our results show that with one or two noncarbon atoms present, all these planar

structures have negative NICS values between -3.5 and -4.9 at site A, indicating the existence of shielding effect of the ring current covering the molecular plane and the weaker aromaticity in these systems compared to benzene. It is interesting to notice that C_6 centers forming bonds with only Si atom(s) always have higher negative NICS values than that forming bonds with only Ge atom(s). In consequence, the NICS value of ternary $GeSiC_6H_4^{2+}$ lies between that of binary $Si_2C_6H_4^{2+}$ and $Ge_2C_6H_4^{2+}$. For binary $Si_3C_6H_3^-$, which contains three Si atoms, the NICS at the center of the molecular triangle takes a small negative value of -1.8 , indicating that this anion is still weakly aromatic in nature. However, for $GeSi_2C_6H_3^-$, which has only one atom difference from $Si_3C_6H_3^-$, the NICS value at site A turns out to be $+2.7$, a positive value implying the antiaromatic nature of this ternary anion. This is the only case in which the ring current is destroyed by the addition of three noncarbon atoms, of which one is Ge at which the cyclic delocalized π bond is broken. In most cases, the calculated NICS at both sites B and C have big negative values varying in large ranges, indicating the existence of local ring currents and therefore site aromaticities in CSiC and CGeC triangles in corresponding systems. The NICS values calculated at A sites for $SiC_6H_5^-$ anion and $Si_2C_6H_4$ neutral with $8p_z$ electrons have the values of $+9.6$ and $+11.7$, respectively, while the $Si_2C_6H_4^{2-}$ dianion with $10p_z$ electrons has an NICS value of $+3.6$, showing that these systems are antiaromatic. The $Si_2C_6H_4^{2-}$ dianion is unstable due to the high negative charge it carries, though it complies with the $(4n+2)$ π electron counting rule. We conclude that the aromaticity of a specific system depends on both the number of possible delocalized electrons complying with certain electron counting rules and the characteristics of the molecular structures sustaining the ring current.

In summary, by using *ab initio* methods, we have predicted in this work the structures of carbon-rich microclusters $Ge_lSi_mC_n$ containing up to 10 atoms and the aromatic

properties of singly or doubly charged $Ge_lSi_mC_nH_x$ complying with the $(4n+2)$ π electron counting rule. The existence of planar aromaticity depends on the delocalized π bonds sustained by the closed cyclic molecular skeletons. This study brings new insight into the properties of ternary semiconductor systems and provides important reference in future experimental characterizations of these cluster neutrals and charged ions.

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