



## Research paper

# Ab initio study of structural and electronic properties of $\text{Si}_n\text{C}_{5-n}\text{H}_8$ ( $n = 0-5$ ) series: Probing the 2D to 3D structural transition

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## ABSTRACT

In this study, we studied the structural and electronic properties in the  $\text{Si}_n\text{C}_{5-n}\text{H}_8$  ( $n = 0-5$ ) series using ab initio calculations. We performed global minimum and low-lying isomers search for the  $\text{C}_5\text{H}_8$ ,  $\text{SiC}_4\text{H}_8$ ,  $\text{Si}_2\text{C}_3\text{H}_8$ ,  $\text{Si}_3\text{C}_2\text{H}_8$ ,  $\text{Si}_4\text{CH}_8$  and  $\text{Si}_5\text{H}_8$  stoichiometries at the B3LYP/3-21G level of theory. The lowest isomers were recalculated at the CCSD(T)/CBS//B3LYP/6-311++G\*\* level of theory. It was shown that  $\text{Si}_2\text{C}_3\text{H}_8$  structure is more stable than the other structures with high ionization potential and HOMO-LUMO energy gap. We also showed the 2D-3D transition, which occurs only at  $n = 3$ , is due to stronger C–C  $\sigma$  bonds compared to weaker C–Si and Si–Si  $\sigma$  bonds. The results were found in good agreement with available experimental findings.

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## 1. Introduction

Systems containing hydrocarbons having strong covalent bonds are interesting because of their central role in organic chemistry. The simplest form of hydrocarbons are composed of carbon and hydrogen atoms bonded to a chain of carbon atoms [1]. Many hydrocarbons are actually combinations of chains and rings, or multiple rings linked together. An additional feature that adds diversity to hydrocarbon structures is the possibility of ring formation. For example, the cyclopentene structure of  $\text{C}_5\text{H}_8$  has the lowest-energy among the many isomers of hydrocarbons [2–4]. In this regard, the ring arrangement of  $\pi$ -electrons in saturated conjugated compounds may cause a significant effect on the stability of the system [5–22].

Hydrogenated Si–C clusters would be very important for the understanding and modeling of the hydrogenated silicon-carbon alloys [23]. According to this viewpoint, the incorporation of Si atom into a hydrocarbon could induce a significant change in structural and electronic properties of the system. In the literature, a few types of silicon-containing CH compounds were studied. For example, the electronic structure of  $\text{Si}_{1-x}\text{C}_x\text{H}$  was calculated and found the behavior of the alloys changes significantly at around  $x = 0.6$  [24]. In the study, the results show that the bandgap decreases almost linearly with decreasing  $x$ . In addition, SiCH alloy based on the composition of Si atom is found to be a suitable mate-

rial for optoelectronic applications [25]. A recent study shows that hydrogenated Si–C honeycomb structure forms five stable isomers, and the chair conformer which remains stable even at room temperature is most stable [26]. Silicon and carbon substitution also gives rise to 2D-3D transition in series of  $\text{SiC}_5\text{H}_6$  where benzene-like structures become considerably more stable than the other structures [27].

All the mentioned above examples indicate the role of silicon and carbon substitution in Si–C–H system and invite further investigation about the stability, electronic and structure properties of the system to obtain desirable properties. To our knowledge, the ring structure of hexasilabenzene which is similar to benzene has been recently studied in detail [27–30]. Moreover, a structural transition of hydrogenated and pure carbon clusters upon substitution of carbon by other elements have already examined [31,32]. However, the planar aromatic structures like benzene or its derivatives have not been synthesized in the compounds based on silicon. In this regard, a transition from two-dimensional (2D) to three-dimensional (3D) structures is searched in the  $\text{Si}_n\text{C}_{5-n}\text{H}_8$  ( $n = 0-5$ ) series upon sequential substitution of the C atoms by Si atoms in this study. In addition, the structural stability, chemical bonding, the adiabatic ionization potential (AIP), vertical ionization potential (VIP), HOMO-LUMO energy gap ( $E_g$ ), adaptive natural density partitioning (AdNDP) and radial distribution function (RDF) of binary interactions of  $\text{Si}_n\text{C}_{5-n}\text{H}_8$  ( $n = 0-5$ ) series are investigated using density functional theory (DFT) based on optimized structure with the lowest energy among the studied isomers.

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## 2. Computational details

The geometries of low-lying isomers of  $\text{Si}_n\text{C}_{5-n}\text{H}_8$  ( $n = 0-5$ ) series was performed using DFT with Becke's three-parameter exchange and Lee-Yang-Parr nonlocal correlation functional (B3LYP) [33]. For the geometry optimizations, about thirty isomers [34] of  $\text{C}_5\text{H}_8$  stoichiometry are first carried out. To generate the structural isomers of other stoichiometries, the following procedures are used. The initial geometries are typically constructed by replacing one C atom by one Si atom in  $\text{C}_5\text{H}_8$  stoichiometry. The obtained new isomers and their permutational isomers are optimized. This procedure continues until each carbon atom takes up the silicon atom, and then the entire series are optimized.

All possible structural patterns of considered series with singlet and triplet states are optimized at the B3LYP/3-21G level without any symmetry constraints. Then, the low-lying isomers for each series are reoptimized at the B3LYP/6-311++G\*\* level. The frequency analysis is also performed at the same level to ensure the stability of all isomers. In order to get more accurate energies, the single-point calculations are performed using coupled cluster with single, double and perturbative triple excitations (CCSD(T)) functional in the CBS and aug-cc-pVXZ ( $X = \text{D}, \text{T}, \text{Q}$ ) basis sets. All ab initio calculations were performed using the Gaussian 09 program package [35]. AdNDP calculation [36,37] has been used to explore electronic structure of closed-shell systems. Molecular structure and orbital visualizations are also performed with the GaussView 5.0.9 [38] and Molekel 5.4.0.8 [39] programs.

## 3. Results and discussion

In the present study, all the possible isomers of  $\text{Si}_n\text{C}_{5-n}\text{H}_8$  ( $n = 0-5$ ) series were examined by ab initio calculations. The cyclopentene, 1,3-pentadiene, 1,4-pentadiene, 1-methylcyclobutene, methylenecyclobutane, ethylenecyclopropane, housane and bicyclopentane structures were found to be the lowest energy isomers of each series. Therefore, we have also separately considered the permutational isomers of each structure. All isomers were ordered according to their energies at the CCSD(T)/CBS//B3LYP/6-311++G\*\* level of theory (see Fig. 1). Additionally, the relative energies (see Figs. S1–S6) and the total energies at B3LYP and CCSD(T) functionals (as Table S1), and the cartesian coordinates optimized at B3LYP/6-311++G\*\* level of theory (see Table S2) for selected isomers are reported in Supporting Information. Note that all the optimized geometry of  $\text{Si}_n\text{C}_{5-n}\text{H}_8$  ( $n = 0-5$ ) series are found to be real minima because there are no imaginary frequencies.

**$\text{C}_5\text{H}_8$  isomers.** Despite the fact that four isomers for  $\text{C}_5\text{H}_8$  stoichiometry: the cyclopentene, 1,3-pentadiene, 1,4-pentadiene, housane and bicyclopentane structures have been isolated and well-known [3,4,14,15]. The cyclopentene structure is found as the most stable among these isomers. In this study, the most stable isomer for  $\text{C}_5\text{H}_8$  stoichiometry is found to be a cyclopentene (I.1) structure ( $C_s$  and 1-A configuration) being 1,3-pentadiene (I.2) structure (9.45 kcal/mol above the global minimum). The energies of the 1,4-pentadiene (I.3) and housane (I.7) structures are found to be as 16.15 and 29.23 kcal/mol, respectively, which are higher than that of the first isomer. The energy of the bicyclopentane (I.8) structure with  $D_{3h}$  point group symmetry is also found to be 39.07 kcal/mol which is higher than the global minimum (see Fig. 1).

**$\text{SiC}_4\text{H}_8$  isomers.** The cyclopentene-like (II.1) structure is very similar to the global minimum structure of  $\text{C}_5\text{H}_8$  and only difference is that one C is substituted by the Si atom. Moreover, the energies of 1,3-pentadiene-like (II.4) and 1,4-pentadiene-like (II.5) structures are found to be 18.10 kcal/mol and 18.41 kcal/mol higher than the global minimum structure, respectively

(see Fig. 1). The energy of the bicyclopentane (II.6) structure ( $C_{3v}$  and 1-A1 configuration) is still significantly higher than cyclopentene-like structure (24.85 kcal/mol), but is now lower than that of housane-like (II.8) structure.

**$\text{Si}_2\text{C}_3\text{H}_8$  isomers.** In this size, the permutational isomers of each structure were examined in detail. Accordingly, the most stable isomer is still cyclopentene-like (or 1,3-disilacyclopentene) structure which is very similar to the global minimum structure of  $\text{SiC}_4\text{H}_8$ . The second isomer, bicyclopentane (III.2) structure, has  $D_{3h}$  point group symmetry, and it is now a close-lying (8.52 kcal/mol) the first isomer. Additionally, the energy of the 1,3-pentadiene-like (III.6) and 1,4-pentadiene-like (III.7) structures are now much higher than cyclopentene-like structure.

**$\text{Si}_3\text{C}_2\text{H}_8$  isomers.** Here we specially investigated the permutational isomers of cyclopentene-like and bicyclopentane structures. For the  $\text{Si}_3\text{C}_2\text{H}_8$  stoichiometry, we found that bicyclopentane (IV.1) structure is now the global minimum with  $C_{2v}$  point group symmetry. The energy of the cyclopentene-like (IV.1) or 1,2,3-trisilacyclopentene structure is found to be 0.52, 2.79 and 2.98 kcal/mol at CCSD(T)/CBS//B3LYP/6-311++G\*\*, CCSD(T)/aug-cc-pVQZ//B3LYP/6-311++G\*\* and CCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G\*\* levels, respectively, which are higher energy than the global minimum structure. According to our calculations, the 2D–3D transition occurs at  $n = 3$ , where bicyclopentane structure becomes a little more stable than the nearest planar two-dimensional structure. On the other hand, the cyclopentene-like structure is the global minimum (at B3LYP/6-311++G\*\* and CCSD(T)/aug-cc-pVDZ//B3LYP/6-311++G\*\* levels (Supporting Information, Fig. S4); however, the single-point calculations indicate that planar cyclopentene-like (IV.2) structure is the second lowest isomer at CCSD(T)/CBS//B3LYP/6-311++G\*\*, CCSD(T)/cc-pVQZ//B3LYP/6-311++G\*\* and CCSD(T)/cc-pVTZ//B3LYP/6-311++G\*\* levels, which are becoming more accurate and reliable (see Fig. 1). Note that the relative energies obtained by the CCSD(T)/cc-pVTZ//B3LYP/6-311++G\*\*, CCSD(T)/aug-cc-pVQZ//B3LYP/6-311++G\*\* and CCSD(T)/CBS//B3LYP/6-311++G\*\* levels are compatible with each series. In addition, the energies of the housane-like (IV.5), 1,3-pentadiene-like (IV.7) and 1,4-pentadiene (I.8) structures are found to be 24.12, 43.16 and 46.21 kcal/mol, respectively, which are higher than the global minimum (see Fig. 1).

**$\text{Si}_4\text{CH}_8$  isomers.** The most stable isomer for  $\text{Si}_4\text{CH}_8$  has a bicyclopentane (V.1) structure ( $C_{2v}$  and 1-A1 configuration) being cyclopentene-like (V.2) structure (7.83 kcal/mol above the global minimum). The energy of the housane-like (V.3) structure is now 10.64 kcal/mol which is higher than global minimum structure. Moreover, 1,3-pentadiene-like (V.7) and 1,4-pentadiene (V.8) structures are found to be 47.45 and 49.36 kcal/mol, respectively. These energy values are higher than the most stable isomer (Fig. 1).

**$\text{Si}_5\text{H}_8$  isomers.** The bicyclopentane (VI.1) structure ( $D_{3h}$  and 1-A1' configuration) is significantly more stable than the other isomers. The energy of the housane-like (VI.2) structure is found to be 14.87 kcal/mol which is higher than the first isomer. The global minimum of  $\text{Si}_5\text{H}_8$  stoichiometry has been reported by Li et al. [40]. The most stable isomer presented in our work is in excellent agreement with those found in literature [40]. Additionally, the energies of the cyclopentene-like (VI.3), 1,3-pentadiene-like (VI.7) and 1,4-pentadiene-like (VI.8) structures are 17.17, 58.23 and 62.52 kcal/mol, respectively. These values are higher than the global minimum (see Fig. 1). From the results mentioned above, we can conclude that the most stable isomers of the carbon-rich series are cyclopentene-like structure with 2D, whereas the most stable isomers of silicon-rich series are bicyclopentane structure with 3D.

**Bond lengths.** All bond lengths for the most stable isomers are shown in Fig. 2. In  $\text{Si}_n\text{C}_{5-n}\text{H}_8$  series, C = C double bond lengths for

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