Effect of the embedded atom on the electronic, optical properties and kinetic stability of [3,6]silaprismane

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1. Introduction

Carbon [n,m]prismanes can be regarded as stacked layers of dehydrogenated cycloalkane molecules, where m is the number of vertices of a closed carbon ring, and n is the number of layers. For large n they represent single-walled carbon nanotube analogs with an extremely small cross-section as a regular polygon [1]. Carbon prismanes are of considerable fundamental and practical interest: their physical and chemical properties attract significant scientific attention [2–6]. However, it is a special interest to replace the carbon framework with silicic one to obtain the quasione-dimensional nanostructures possessing novel structural, energy, electronic and optical properties, in addition, some of such small dimensional nanostructures possessing novel structural, energy, electronic and optical properties of silicic cage.

Using ab initio calculations it is found that endohedral complexes C@Si18H12, Si@Si18H12 and Ge@Si18H12 are less kinetically stable than pure [3,6]silaprismane Si18H12. Moreover, kinetic stability of Si18H12 is higher than the stability of its carbon molecular analogue C18H12. The height of the minimum energy barrier preventing the Si18H12 isomerization is found to be 1.09 eV and its lifetime at room temperature will reach several hours that is acceptable not only for its immediate experimental observation but for the laboratory synthesis without using the extreme temperature conditions as well. It is also found that embedded atoms can significantly change the electronic properties of Si18H12 cage that is directly affect the optical characteristics of the systems considered. Thus, the doped Si18H12 can be experimentally divided from each other due to the changes in their optical spectra.

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Becke’s three-parameter hybrid method and the Lee-Yang-Parr exchange-correlation energy functional (B3LYP) [16,17] with the 6-311++G(d,p) (for the C\textsubscript{18}H\textsubscript{12}, Si\textsubscript{18}H\textsubscript{12}, C@Si\textsubscript{18}H\textsubscript{12}, and Si@Si\textsubscript{18}H\textsubscript{12} molecular systems) and the 6-31++G(d,p) (for the Ge@Si\textsubscript{18}H\textsubscript{12}) basis sets [18]. The geometries of all prismanes and the corresponding transition states (saddle points) are obtained using the TeraChem program package [19,20]. All molecular structures are relaxed until residual forces on atoms are less than 10\textsuperscript{–4} hartree/bohr. The vibrational properties of these systems, calculated from the Hessian matrix determined using the GAMESS program [21] at the same level of theory, is applied for validating that the obtained structures are true minima or transition states on the potential energy surface. The presence of local minima of energy is confirmed by the reality of all frequencies, and for the transition state the only one imaginary frequency takes place. In addition, intrinsic reaction coordinate analysis is carried out to confirm the connection between local minima and corresponding transition states. To obtain the electronic properties of all considered structures, we employed PBE [22] functional and 6-311++G(d,p) basis set [18] by using GAMESS program [21]. Optical absorption spectra are obtained using CAM-B3LYP method and the same 6-311++G(d,p) standard basis set.

3. Results and discussion

3.1. Kinetic stability

We obtained the structures of C\textsubscript{18}H\textsubscript{12}, Si\textsubscript{18}H\textsubscript{12}, C@Si\textsubscript{18}H\textsubscript{12}, Si@Si\textsubscript{18}H\textsubscript{12} and Ge@Si\textsubscript{18}H\textsubscript{12} as shown in Fig. 1. At the level of theory considered, they have all real vibrational frequencies and represent minima on the potential energy surface. Certainly, interatomic bond lengths in silaprismanes are quite longer than in carbon one. Despite the fact that in endohedral complexes the Si–Si bonds increase owing to interstitial atoms the Si–H distances almost stay constant in all silaprismanes. Note that during structural optimization of C@Si\textsubscript{18}H\textsubscript{12} complex, silicon cage loses its prismane identity and carbon atom is moving from the center to the periphery forming the so-called tetracoordinate carbon atom with a planar configuration of bonds (Fig. 2e). The problem of design and synthesis of

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**Fig. 1.** Optimized structures of prismanes at B3LYP/6-311++G(d,p) and B3LYP/6-31+G(d,p) levels of theory: C\textsubscript{18}H\textsubscript{12} (a), Si\textsubscript{18}H\textsubscript{12} (b), Si@Si\textsubscript{18}H\textsubscript{12} (c), and Ge@Si\textsubscript{18}H\textsubscript{12} (d). The bond lengths are in Angstroms.

**Fig. 2.** Potential energies $\Delta E$ of C\textsubscript{18}H\textsubscript{12} (a), Si\textsubscript{18}H\textsubscript{12} (b), Si@Si\textsubscript{18}H\textsubscript{12} (c), Ge@Si\textsubscript{18}H\textsubscript{12} (d), and C@Si\textsubscript{18}H\textsubscript{12} (e) molecular systems along the reaction coordinate during the framework decay. The insets show the transition state and molecular configurations corresponding to the local minima.
configurations with a planar arrangement of bonds at tetracoordinate carbon was originally raised by Hoffmann and co-workers [23] and further developed by groups of Radom [24,25] and Minkin [26]. In our case planar tetracoordinate carbon atom is located inside the small three-membered ring. Such type of stabilization was explained by Schleyer and co-workers [27]. This was explained by the fact that the angular strain in three- or four-membered cycles would be lower than in the case of the tetrahedral configuration. Note that the hyperconjugation of carbon atom, i.e., appearing of hexacoordinate carbon in C@Si18H12, is hardly possible due to the factor of mismatching the carbon atom size and the size of atoms of surrounding cyclic Si-framework (comparing with Si or Ge atom) that leads to the elongation and weakening of interatomic bonds with the framework. In general, the results obtained are in good agreement with previous data calculated in terms of ab initio approaches [10,15].

The binding energies per atom are calculated by
\[
E_b = \frac{1}{N_{at}} \left( N_{Si} E(Si) + N_{C} E(C) + N_{Ge} E(Ge) + N_{H} E(H) \right) - E_{tot}(prismane),
\]
where \(E(Si), E(C), E(Ge), E(H)\) and \(E_{tot}(prismane)\) are the energies of isolated silicon, carbon, germanium, hydrogen atoms and total energy of a given prismane, respectively; \(N_{Si}, N_{C}, N_{Ge}, N_{H}\) are the numbers of silicon, carbon, germanium, hydrogen atoms in the prismane, respectively, and \(N_{at} = N_{Si} + N_{C} + N_{Ge} + N_{H}\) is the total number of atoms in the prismane. The binding energies calculated for the different prismanes are presented in Table 1. Thus, one can see that the carbon prismane has the highest binding energy among all the systems considered. Nevertheless, as we shall see below, pure carbon prismane is less kinetically stable than the pure silicic one. For endohedral complexes C@Si18H12, Si@Si18H12 and Ge@Si18H12 we also calculate the encapsulation energy \(E_{encap}\) that is defined as follows
\[
E_{encap} = E(\text{host} – \text{guest complex}) – E(\text{host}) – E(\text{guest}),
\]
where \(E(\text{host} – \text{guest complex})\) is the energy of endohedral complex C@Si18H12, Si@Si18H12 or Ge@Si18H12, \(E(\text{host})\) is the energy of Si18H12 pure prismane, and \(E(\text{guest})\) is the energy of embedded atom C, Si or Ge. All encapsulation energies are summarized in Table 1. From these data one can see that encapsulation of Si-atom inside the silicon cage is the most energetically favorable. This result is qualitatively agrees with the previous calculations [28]. Note that according to Löwdin population analysis (see Table 1) all embedded atoms have the negative partial charge. In order to know the kinetic stability of the prismanes we should find the barrier heights along reaction pathways surrounding the equilibrium geometries. The kinetic stability of a given prismane is determined by the activation energy or energy barrier – the minimal energy, which is required to initiate the isomerization. Energy barriers preventing the isomerization are defined as the energy differences between the corresponding transition state and minimum on the potential energy surface. So, we find the transition states for all molecular structures introduced above. Fig. 2 displays the potential energies of prismanes along the reaction coordinate during the carbon/silicic framework decay. Note that for the isomerization path for all prismanes (except C@Si18H12) we select the breaking of middle Si–Si or C–C bond perpendicular to the main axis (see Fig. 2), since it was earlier shown that for the carbon [3,6]prismane this decay path possessed the lowest energy barrier [5]. For the C@Si18H12 the breaking of Si–Si bond parallel to the main axis (see Fig. 2e) was chosen.

The calculated heights of energy barriers preventing isomerization are listed in Table 1. Therefore, [3,6]silaprismane possesses the highest energy barrier preventing the isomerization among the molecular systems considered.

Knowing the frequency spectra we also calculate the frequency factor \(A\) of prismane decays according to the Vineyard formula [28], which for the \(N\)-atom cluster has the form
\[
A = \frac{\prod_{i=1}^{3N-6} \nu_i}{\prod_{i=1}^{6} \nu_i}
\]
where \(\nu_i\) are the eigenfrequencies of vibrations of the cluster in the state corresponding to the minimum potential energy for all \(3N – 6\) normal coordinates, and \(\nu_i\) are the frequencies of vibrations at the transition state corresponding to the maximum of potential energy for one normal coordinate and to the minimum for all the other coordinates (since one of the \(3N – 6\) frequencies \(\nu_i\) is imaginary, it is not included in the denominator of expression for \(A\)). Note that this formula determines the frequency factor of a thermally activated process for only one of the possible channels. Even if we restrict our consideration to the case of the most probable transition paths (characterized by the lowest energy barrier), we still need to take into account that there can be several such paths due to the symmetry of the molecular system. Since for all prismanes (except C@Si18H12 configuration) decay occurs upon breaking any of the six middle Si–Si or C–C bonds perpendicular to the main axis of the prismane, the frequency factor in the total rate of isomerization should be 6 times higher than that calculated from Vineyard formula for one channel. Therefore, the result of the calculation from Vineyard formula must be multiplied by the “degeneration factor” \(g = 6\) (for C@Si18H12 \(g\) is equal to 2). The data obtained are summarized in the Table 1. Knowing the energy barrier and frequency factor one can estimate the lifetime \(\tau\) of prismanes considered at any temperature \(T\) according to the Arrhenius equation
\[
\tau \sim A^{-1} \exp(U/kT)
\]
For example, the lifetime of Si18H12 prismane estimated according to formula (4) at room temperature reaches several hours, and at the boiling point of liquid nitrogen (77 K) Si18H12 is stable for any macroscopic period of time once it is obtained.

### 3.2. Electronic and optical properties

For further investigation, we study the electronic and optical properties of the systems considered. We first designed and reported the optimized structure of C18H12 with two different kinds of the symmetries including D6h and D3h point groups that correspond to the initial carbon [3,6]prismane and its isomerization product (see Fig. 2a), respectively. These molecular structures

<table>
<thead>
<tr>
<th>System</th>
<th>(E_{int}), eV/atom</th>
<th>(E_{encap}), eV</th>
<th>Löwdin charge on the embedded atom</th>
<th>(U), eV</th>
<th>(A), s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C18H12</td>
<td>4.70</td>
<td>–</td>
<td>–</td>
<td>0.92</td>
<td>7.24 (10^{14})</td>
</tr>
<tr>
<td>Si18H12</td>
<td>3.06</td>
<td>–</td>
<td>–</td>
<td>1.09</td>
<td>6.60 (10^{14})</td>
</tr>
<tr>
<td>C@Si18H12</td>
<td>3.84</td>
<td>4.38</td>
<td>–0.68</td>
<td>0.29</td>
<td>1.37 (10^{14})</td>
</tr>
<tr>
<td>Si@Si18H12</td>
<td>3.02</td>
<td>–2.98</td>
<td>–0.40</td>
<td>0.42</td>
<td>1.36 (10^{14})</td>
</tr>
<tr>
<td>Ge@Si18H12</td>
<td>3.00</td>
<td>–2.20</td>
<td>–0.40</td>
<td>0.22</td>
<td>1.44 (10^{14})</td>
</tr>
</tbody>
</table>
denoted as (a) and (c) at Fig. 3. The bond lengths and angles of both structures with density of states analyses are recalculated, as shown in Fig. 3.

It can be seen from Fig. 3 that both these molecular structures are semiconducting materials with the difference in the energies between the HOMO and LUMO that denoted as an energy gap ($E_g$) on density of states (DOS) curve with the amounts of 3.31 and 2.93 eV in $D_{6h}$-C$_{18}$H$_{12}$ and $D_{3h}$-C$_{18}$H$_{12}$, respectively. Their HOMO and LUMO orbitals are shown in Fig. 4. The HOMO and LUMO wave functions concentration are significantly localized on the C–C and C–H bonds of C$_{18}$H$_{12}$ in $D_{6h}$-C$_{18}$H$_{12}$ and $D_{3h}$-C$_{18}$H$_{12}$, respectively.

In Fig. 4b and d, the molecular electrostatic potential (MEP) maps for the $D_{6h}$-C$_{18}$H$_{12}$ and $D_{3h}$-C$_{18}$H$_{12}$ structures are also shown. All isosurfaces are depicted with isovalue of 0.0004 e$/\text{au}^3$ with GaussView software [29]. According to the Fig. 4, MEP map demonstrates the hydrogen atoms in both structures with blue color (denoted as electropositive) in the two heads of C$_{18}$H$_{12}$ functions.

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**Fig. 3.** Optimized structures and densities of states analyses for $D_{6h}$-C$_{18}$H$_{12}$ (a) and (b) and $D_{3h}$-C$_{18}$H$_{12}$ (c) and (d) clusters, respectively.

**Fig. 4.** The HOMO and LUMO wave functions and MEP maps of $D_{6h}$-C$_{18}$H$_{12}$ (a) and (b) and $D_{3h}$-C$_{18}$H$_{12}$ (c) and (d) molecular structures.
as an electron donor and the carbon atoms in center of the structure with red color (denoted as electronegative) functions as an electron acceptor.

In Fig. 5, the structural and electronic properties of Si$_{18}$H$_{12}$, C@Si$_{18}$H$_{12}$, Si@Si$_{18}$H$_{12}$ and Ge@Si$_{18}$H$_{12}$ are presented. Due to the presence of the stabilizing center carbon, silicon, and germanium
atoms, the structural and electronic properties of Si_{18}H_{12} (see Fig. 5a and b) in comparison with C@Si_{18}H_{12}, Si@Si_{18}H_{12} and Ge@Si_{18}H_{12} (Fig. 5c–h) are drastically different. It is to be noted from Fig. 5 that C@Si_{18}H_{12} (Fig. 5c and d) makes more changes on the structural and electronic properties of the host Si_{18}H_{12} cage than Si@Si_{18}H_{12} (Fig. 5e and f) and Ge@Si_{18}H_{12} (Fig. 5g and h) structures. Moreover, it can be said that the carbon atom violates the integrity of the silicic cage making it kinetically unstable. The...
Si_{18}H_{12} structure has D_{6h} symmetry, and contains the HOMO and LUMO energies of −5.18 and −4.01 eV, respectively. After inserting carbon, silicon, and germanium atoms in the center of Si_{18}H_{12} framework, $E_g$ value reduces from 1.17 eV to 0.78, 0.98, and 0.81 eV, respectively. The obtained results demonstrate that the C@Si_{18}H_{12} (Fig. 5c and d) structure has the greatest change on the electronic property of Si_{18}H_{12}. However, the structural symmetry of C@Si_{18}H_{12} (Fig. 5c and d), Si@Si_{18}H_{12} (Fig. 5e and f) and Ge@Si_{18}H_{12} (Fig. 5g and h) are found to be C_{2v}, D_{6h}, and C_{6v} point groups, respectively.

The HOMO and LUMO wave function distribution of the C@Si_{18}H_{12}, Si@Si_{18}H_{12} and Ge@Si_{18}H_{12} are shown in Fig. 6.

It is obvious that the HOMO is mainly distributed on Si atoms in the center of D_{6h}-Si_{18}H_{12} and the H atoms in the edge of the structure while those near the LUMO is mainly distributed on the Si–Si bonds. For the C@Si_{18}H_{12} structure the distribution of HOMO wave function is mostly located on the carbon atom inside the cage and the silicon atoms near the carbon, while the LUMO wave function presents the same distribution on the Si atoms of the structure. In the case of Ge@Si_{18}H_{12} systems, the HOMO indicates the different distribution in comparison with other the structures as it is associated with the Ge atom within the structure and so the electron density is strongly dominated on the Si and H atoms in the center and at the edge of the structure.

According to the MEP maps of the various doped Si_{18}H_{12} cages the significant changes in electrostatic potential of the system occur. As for Si@Si_{18}H_{12} and Ge@Si_{18}H_{12} complexes, we can see a significant positive charge (hole) accumulation at the center and one side of the structures which increase the charge polarizability of the corresponding structures due to the internal induced molecular electric field. In fact, this molecular electric field significantly affect electronic structure and HOMO-LUMO gap according to the stark shift of the molecular energy level that can be seen in Fig. 5.

To determine a visible quantity in terms of the sample synthesis we study the optical properties of the considered structures by term of UV–Vis spectrum. In Fig. 7, we indicate the optical absorption spectrum for all structures. The significant changes in optical adsorption are clearly seen due to the changes in structural parameters.

The main excited states for the D_{6h}-C_{18}H_{12} and D_{3h}-C_{18}H_{12} structures are obvious at the wavelengths of 230.6 and 263.2 nm with the oscillator strengths of 0.0033 and 0.0405, respectively (Fig. 7a and b). The transition energies for these structures are
5.375 and 4.710 eV. The main excited state of Si18H12 is 521.3 nm with the oscillator strength of 0.0001 (Fig. 7c). For C@Si18H12 structure, two main transitions were observed at the wavelengths of 816.2 and 533.4 nm with the oscillator strengths of 0.0052 and 0.0019 (Fig. 7d), indicating that these bands can be observed in the region of red-shift and also these results agree well with the mutation of $E_g$ of these structures.

For the Si@Si18H12 and Ge@Si18H12 systems a single peak at different wavelengths of 963.9 and 1018.3 nm can be seen which are properly separated from each other for possible experimental measurements (Fig. 7e and f).

4. Conclusions

In the present work, we perform the quantum chemical calculations to study the kinetic stability of silaprismane Si18H12, its carbon molecular analogue C18H12 and endohedral complexes based on it C@Si18H12, Si@Si18H12 and Ge@Si18H12. The results show that the kinetic stability of Si18H12 is higher than the stability of its carbon molecular analogue C18H12. Its lifetime at room temperature reaches several hours and it can live for indefinite period of time at the boiling point of liquid nitrogen (77 K) once it is obtained. Such times are acceptable not only for its immediate experimental observation but for the laboratory synthesis without using the extreme temperature conditions as well. Despite this, the [3,6]silaprismane cannot be regarded as ultrastable molecule. Moreover, our results obtained impugn the predicted hypothetical synthesis of these molecular systems at high (or even at room) temperatures through the self-assembly in a plasma reactor [14].

Nevertheless, [3,6]silaprismane can form the endohedral complexes unlike the carbon one. However, the trapped atoms decrease its kinetic stability: the heavier atoms, the lower the stability. For example, Si@Si18H12 and Ge@Si18H12 lifetimes at room temperature reach ~1 ns and ~1 ps, respectively, whereas at 77 K they are ~10^13 s and several seconds, respectively. So, the synthesis and investigation of [3,6]silaprismane endohedral complexes is possible only at cryogenic temperatures.

For further investigation, we studied the electronic and optical properties of the molecular systems considered. We found that the doping of Si18H12 with C, Si and Ge atoms can significantly change the molecular electrostatic potential inside the cage which is origin of the strong charge polarizability and molecular electric field. The electronic properties of the doped Si18H12 have significant change as the HOMO-LUMO gap has remarkable variations, which directly affect optical properties of these systems. The optical absorption shows that the endohedral complexes based on the Si18H12 cage can be divided experimentally from each other due to their significant changes in their optical spectra.

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