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

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ABSTRACT

Using *ab initio* calculations it is found that endohedral complexes $C@Si_{18}H_{12}$, $Si@Si_{18}H_{12}$ and $Ge@Si_{18}H_{12}$ are less kinetically stable than pure [3,6]silaprismane $Si_{18}H_{12}$. Moreover, kinetic stability of $Si_{18}H_{12}$ is higher than the stability of its carbon molecular analogue $C_{18}H_{12}$. The height of the minimum energy barrier preventing the $Si_{18}H_{12}$ 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 $Si_{18}H_{12}$ cage that is directly affect the optical characteristics of the systems considered. Thus, the doped $Si_{18}H_{12}$s can be experimentally divided from each other due to the changes in their optical spectra.

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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 structures are already synthesized [7,8]. One of the reason of their synthesis is the obtaining of endohedral complexes that consist of [*n,m*]silaprismane as a host, and some atom or nanosystem as a guest. Such compounds can be potentially suitable in the biomedical sector as light-emitting devices to photothermal cancer treatment or in the field of photovoltaics [9]. It is quite difficult to place atom inside the carbon cage (the embedded atom leads to its decay), while even the rather small silicic framework is able to store quite heavy atoms owing to its structural characteristics,

such as silicon or germanium atoms [10]. Thus, the question of stability of these nanostructures arises. If the thermodynamic stability of such compounds is intensively discussed in literature [11–14], there are no published data on the kinetic stability of even small silaprismanes and, a fortiori, more complex systems. The problem of electronic and optical properties of doped silaprismanes is also still open. The dependence of electronic characteristics (namely, HOMO-LUMO gaps) on the effective size of pure [*n,m*] silaprismane is already confirmed [15], but there is no data obtained about the influence of embedded atoms on the electronic and optical properties of silicic cage.

In order to predict the kinetic stability of silicic cage compounds and to obtain their electronic and optical properties, we performed the high-level quantum-chemical calculations on small [3,6]silaprismane $Si_{18}H_{12}$ and its endohedral complexes $C@Si_{18}H_{12}$, $Si@Si_{18}H_{12}$ and $Ge@Si_{18}H_{12}$. The main purpose of this work is to obtain the minimum energy barriers preventing the isomerization of silicic cages, to estimate their lifetimes at characteristic temperatures, to analyze their electronic and optical properties, and to compare these results with the data for corresponding carbon prismane $C_{18}H_{12}$.

2. Computational details

Our calculations of thermodynamic and kinetic stability are based on density functional theory (DFT) and are performed using

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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 $C_{18}H_{12}$, $Si_{18}H_{12}$, $C@Si_{18}H_{12}$, and $Si@Si_{18}H_{12}$ molecular systems) and the 6-31++G(d,p) (for the $Ge@Si_{18}H_{12}$) 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^{-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 $C_{18}H_{12}$, $Si_{18}H_{12}$, $C@Si_{18}H_{12}$, $Si@Si_{18}H_{12}$ and $Ge@Si_{18}H_{12}$ 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 $C@Si_{18}H_{12}$ 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
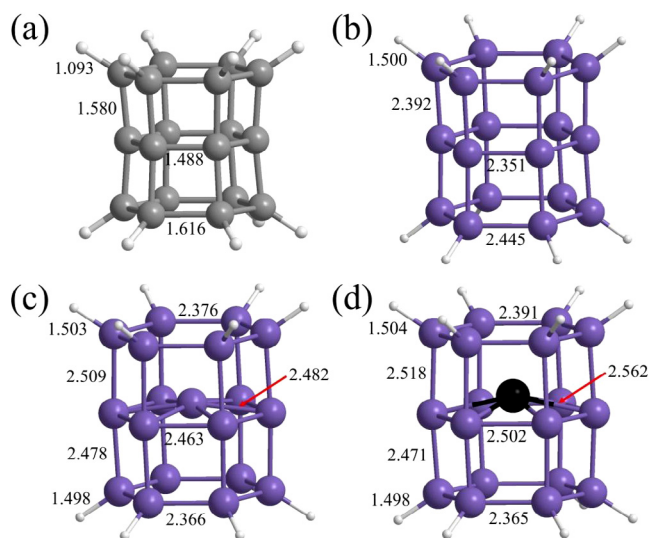

Fig. 1. Optimized structures of prismanes at B3LYP/6-311++G(d,p) and B3LYP/6-31++G(d,p) levels of theory: $C_{18}H_{12}$ (a), $Si_{18}H_{12}$ (b), $Si@Si_{18}H_{12}$ (c), and $Ge@Si_{18}H_{12}$ (d). The bond lengths are in Angstroms.
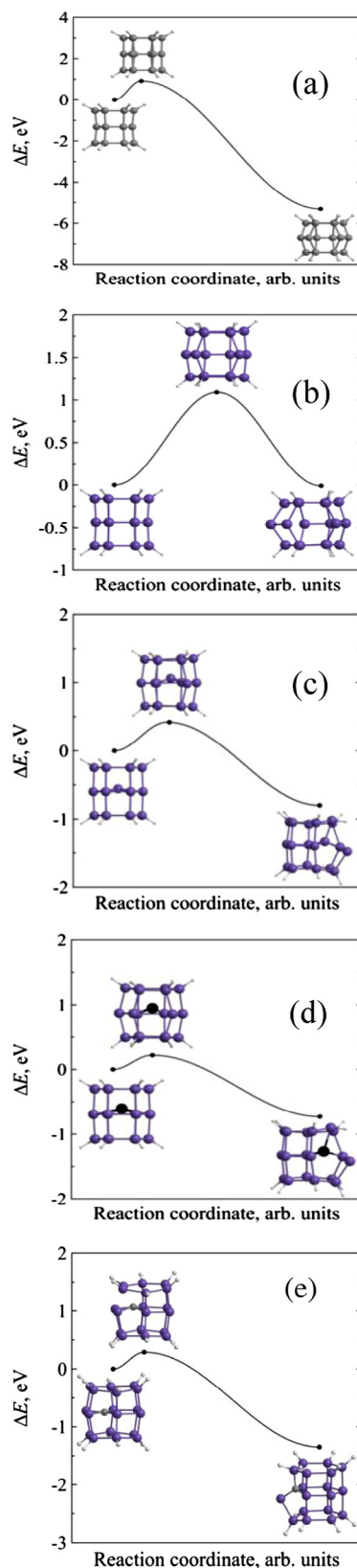

Fig. 2. Potential energies ΔE of $C_{18}H_{12}$ (a), $Si_{18}H_{12}$ (b), $Si@Si_{18}H_{12}$ (c), $Ge@Si_{18}H_{12}$ (d), and $C@Si_{18}H_{12}$ (e) molecular systems along the reaction coordinate during the framework decay. The insets show the transition state and molecular configurations corresponding to the local minima.