

Research Article

Theoretical Studies of the Stone-Wales Defect in C_{36} Fullerene Embedded inside Zigzag Carbon Nanotube

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We apply density functional theory at PBE/6-311G(d) level as well as nonorthogonal tight-binding model to study the Stone-Wales transformation in C_{36} fullerene embedded inside the (14,0) zigzag carbon nanotube. We optimize geometries of two different isomers with the D_{2d} and the D_{6h} symmetries and the transition state dividing them. The mechanism of Stone-Wales transformation from D_{2d} to D_{6h} symmetry for the encapsulated C_{36} is calculated to be the same as for the isolated one. It is found that the outer carbon wall significantly stabilizes the D_{6h} isomer. However, carbon nanotube reduces the activation barrier of Stone-Wales rearrangement by 0.4 eV compared with the corresponding value for the isolated C_{36} .

1. Introduction

Carbon peapods are the host-guest compounds (endohedral complexes) that consist of fullerenes encapsulated inside the single-walled carbon nanotubes. Original peapods containing only C_{60} fullerenes were synthesized in 1998 through the catalytic pulsed laser vaporization of graphite [1]. At present peapods are of special interest as they are forming the basis for future nanoelectronic devices, since the fullerenes encapsulated have strong effect on the electronic properties of the outer nanotube [2]. Raman spectroscopy and electronic transport measurements on individual peapod confirm this significant doping impact produced by the encapsulated C_{60} s [3]. In addition, *ab initio* calculations clearly predict the dependence of charge transfer in the carbon peapod on the mutual orientation of the fullerenes [4] and their distribution [5].

The Stone-Wales (SW) defects [6] in the cages of encapsulated fullerenes are the subject of special interest, because they can lead to the significant changes in the electronic structure of peapod [3]. The SW defects occur during the peapods synthesis or as a result of their thermal and ultraviolet treatment

[7]. This type of defects can be regarded as a rotation of single C–C bond around its center through an angle of 90° [6]. It should be noted that SW defects are characterized by the lowest activation energy barrier compared with the other possible atomic rearrangements, but they considerably influence on the physicochemical characteristics of fullerenes and other sp^2 -hybridized carbon systems [8–12]. Furthermore, they play a crucial role in the processes of fullerenes isomerization [13] and coalescence [7]. For example, it is possible to transform peapod to the double-walled carbon nanotube by means of the partial or complete coalescence of the encapsulated fullerenes into the nanotube with smaller diameter under the high temperatures ($\sim 3600^\circ\text{C}$) through the SW mechanism [14, 15]. Recent experiments confirmed that such transformation resulted in the drastic reduction of the conductivity of the whole system [3]. Thus, the introduction of isolated SW defect as well as the initiation of series of SW mechanisms can be regarded as an effective method for the tuning of peapod electronic characteristics.

Here we present a theoretical study of the SW defect formation in the C_{36} fullerene cage embedded inside the

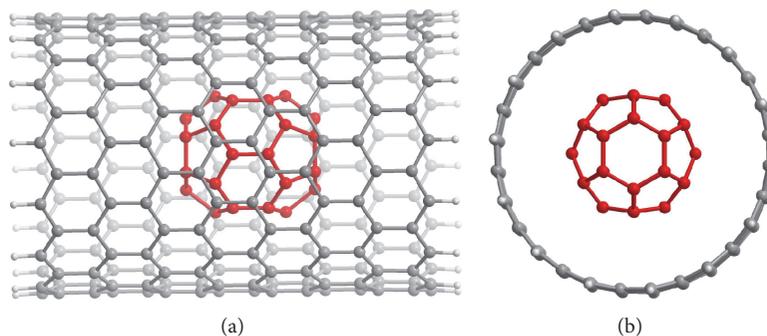


FIGURE 1: Atomistic model of carbon peapod $C_{36}@C_{224}H_{28}$: side view (a) and front view (b).

zigzag carbon nanotube. It should be noted that C_{36} possesses a number of distinctive features compared with C_{60} . It has more strained cage and higher reactivity [16]. In addition, its smaller effective diameter allows one to introduce it inside the thinner carbon nanotubes for peapod formation. The SW activation energy barrier in the isolated C_{36} is equal to 6.23 eV [17], which is lower than the corresponding value 7.16 eV for C_{60} [18]. Therefore, the C_{36} isomerization process can be initiated more easily. Various C_{36} isomers possess different physicochemical properties; for example, they may vary in electronic characteristics (their HOMO-LUMO gaps lie in the range of 0.20–0.83 eV [19]) and in thermodynamic stability. One of the most stable isomers of C_{36} has D_{6h} symmetry; thus, this fullerene is stretched along its symmetry axis. Therefore, it can be expected that the encapsulated D_{6h} - C_{36} s are arranged inside the carbon nanotube so that their symmetry axes are parallel to the main axis of the nanotube. Thus, the inner side of the carbon nanotube wall is able to stabilize the D_{6h} - C_{36} fullerene and to prevent its isomerization. Charge transfer between the tube and the fullerene can also effect on the SW defect formation in C_{36} . Note that for the neutral and positively charged C_{36} the most energetically favorable isomer has D_{2d} symmetry, whereas for the negatively charged C_{36} the D_{6h} isomer is more thermodynamically stable [17]. On the other hand, it was demonstrated that both positive and negative charges changed weakly the SW activation barrier of isolated C_{36} [17]. So, the main purpose of this work is to study the influence of the host zigzag carbon nanotube on the formation of SW defect in the encapsulated C_{36} guest fullerene.

2. Materials and Methods

In our study we consider C_{36} fullerenes with the D_{2d} and the D_{6h} symmetries both isolated and encapsulated inside the center of the (14,0) zigzag carbon nanotube. Previous *ab initio* calculations confirmed that such type of nanotubes with the encapsulated C_{36} s demonstrated the highest binding energy among all zigzag [20] and armchair [21] tubes. In our simulations carbon nanotube is constructed from 224 carbon atoms. To avoid the dangling bonds hydrogen passivation of the tube edges is performed. So, carbon nanotube considered is 11 Å in diameter with the length of 16 Å. Note that the same representation was used in [20]. Finally, our atomistic model

of peapod has the chemical view $C_{36}@C_{224}H_{28}$ as it is shown in Figure 1.

The geometries of minima and transition states of C_{36} and $C_{36}@C_{224}H_{28}$ molecular systems are obtained within the nonorthogonal tight-binding model (NTBM) [22]. Previously, we successfully used this model to simulate the C_{60} s coalescence in peapods [3], to determine the SW mechanism in isolated C_{36} [23, 24] and other fullerenes [23–25], and so forth. Initial molecular structures are relaxed without any symmetry constrains until the residual forces acting on atoms are less than 10^{-3} eV/Å. For each configuration obtained the Hessian matrix and normal frequencies are also calculated in the framework of NTBM model to confirm the energy minima (imaginary frequencies are absent) or transition state (the frequency spectrum has only one imaginary frequency). Next, using the geometries found at NTBM level the total energies of various C_{36} configurations (both minima and transition state) are computed by means of the density functional theory (DFT) approach via the single-point energy calculation procedure. All the quantum-chemical DFT calculations are performed in the frame of GAMESS software package [26]. The hybrid Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [27] is used along with the 6-311G(d) basis set [28]. It was shown that this basis set was good enough to provide an adequate description of SW defect formation in isolated C_{36} [17]. Finally, the peapod total energy is calculated according to the following formula [29]:

$$E(C_{36}@C_{224}H_{28}) = E_{\text{NTBM}}(C_{36}@C_{224}H_{28}) - E_{\text{NTBM}}(C_{36}) + E_{\text{DFT}}(C_{36}), \quad (1)$$

where $E_{\text{NTBM}}(C_{36}@C_{224}H_{28})$, $E_{\text{NTBM}}(C_{36})$, and $E_{\text{DFT}}(C_{36})$ are the total energies of the peapod sample and encapsulated C_{36} obtained at the corresponding level of theory (NTBM or DFT, resp.). Grimme empirical dispersion corrections [30] are taken into account for all energies. GAMESS program package is used for their calculation. Note that formula (1) is applicable both to reactant/product configurations and to transition state.

3. Results and Discussion

First of all, we optimize the geometries of isolated C_{36} isomers with the D_{2d} and the D_{6h} symmetries and the transition state

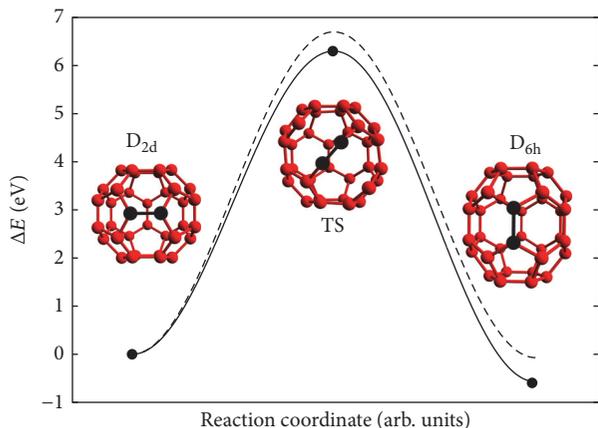


FIGURE 2: Potential energies ΔE of endohedral complex $C_{36}@C_{224}H_{28}$ (solid line) and isolated C_{36} fullerene (dashed line) during the SW transformation $D_{2d}-C_{36} \rightarrow D_{6h}-C_{36}$. The insets show the C_{36} isomers with the D_{2d} and the D_{6h} symmetries and the transition state (TS). Rotation of C–C bond during the SW transformation is indicated in black. The atoms of carbon nanotube are not displayed for clarity.

(TS) dividing them (see Figure 2). The choice of these isomers is caused by their high thermodynamic stability [16] and by their interconversion from one to another through the SW mechanism [17]. We obtain that the length of “rotated” C–C bond (see Figure 2) is equal to 1.455, 1.296, and 1.459 Å for $D_{2d}-C_{36}$, TS- C_{36} , and $D_{6h}-C_{36}$ atomic configurations, respectively. These data coincide well with the corresponding values of 1.443, 1.292, and 1.445 Å, calculated in [17] at DFT/B3LYP/6-311G(d) level of theory. Moreover, NTBM model predicts that the energy difference between the $D_{6h}-C_{36}$ and $D_{2d}-C_{36}$ neutral isomers is equal to 0.14 eV [23]. This result is in good agreement with the value of 0.11 eV also reported in [17]. Note that the simplified single-point energy calculations also give the small absolute value of energy difference of 0.07 eV, which indicates that $D_{6h}-C_{36}$ and $D_{2d}-C_{36}$ states lie very close in energy. Thus, the activation energy barrier obtained for the $D_{2d}-C_{36} \rightarrow D_{6h}-C_{36}$ SW transformation of 6.7 eV agrees with the more accurate value of 6.3 eV [17]. So, NTBM model provides adequate geometries of the C_{36} local minima and transition state.

We also calculate the energy and structure of the analogous $D_{6h}-C_{36}$ and $D_{2d}-C_{36}$ isomers as well as TS- C_{36} embedded inside the $C_{224}H_{28}$ sample nanotube. It is confirmed that there are no intermediate states along the isomerization reaction path as it was earlier established for the isolated neutral and charged $C_{36}s$ [17]. Nevertheless, negligible changes in bond lengths of the encapsulated C_{36} are identified compared with the isolated one. The “rotated” C–C bond length decreases by only 0.003, 0.001, and 0.002 Å for the $D_{2d}-C_{36}$, TS- C_{36} , and $D_{6h}-C_{36}$ atomic configurations, respectively. This slight reduction in bond lengths confirms that the (14,0) carbon nanotube possesses too large diameter for significant compression of the C_{36} cage. On the other hand, we obtain the carbon nanotube effects on the comparative thermodynamic

stability of two C_{36} isomers considered. For the encapsulated C_{36} atomic configuration, axially stretched D_{6h} isomer lies lower in energy than the more spherical D_{2d} one by 0.57 eV. Thus, the embedded $D_{6h}-C_{36}$ is more thermodynamically stable than the $D_{2d}-C_{36}$.

The activation energy barrier for the $D_{2d}-C_{36} \rightarrow D_{6h}-C_{36}$ SW transformation inside the carbon nanotube is found to be 6.3 eV. This value is less than the activation energy barrier for the corresponding isomerization reaction for the isolated C_{36} by $\Delta E = 0.4$ eV. For estimation of the sensitivity of ΔE to the DFT functional used, we recalculate the values of transition barriers for the $D_{2d}-C_{36} \rightarrow D_{6h}-C_{36}$ SW transformation (for isolated C_{36} and embedded one) in the frame of wB97X-D functional, which contains Grimme empirical dispersion corrections by default [31, 32]. The same corrections are applied to NTBM energies as well. As a result, we obtain that the energy barrier for SW transformation in isolated fullerene is equal to 7.8 eV, and the analogous barrier for the encapsulated C_{36} is equal to 7.5 eV. Although these values are higher than the corresponding ones obtained within the PBE functional, one can see that ΔE depends weakly on the functional choice.

The results obtained demonstrate that the activation of SW mechanism in the encapsulated C_{36} becomes $\sim \exp(\Delta E/k_B T)$ times faster compared with the isolated fullerene (here T is the temperature and k_B is the Boltzmann constant). For example, the factor $\exp(\Delta E/k_B T)$ is equal to 3.6 at $T = 3600$ K (this value is typical for the fullerenes coalescence [14]) and achieves $\sim 5 \cdot 10^6$ at room temperature (300 K).

4. Conclusions

In this paper we presented the study of SW defect formation in C_{36} fullerene placed inside the (14,0) zigzag carbon nanotube. We obtain that the isomerization reaction passes through the in-plane C–C bond rotation without any intermediate steps. The presence of carbon nanotube leads to the negligible changes in the geometry of reactants, products, and transition state. It is found that the most thermodynamically stable C_{36} isomer in the case of host-guest compound has D_{6h} symmetry whereas the most thermodynamically stable unrelated C_{36} isomer possesses D_{2d} symmetry. The activation energy barrier for the $D_{2d}-C_{36} \rightarrow D_{6h}-C_{36}$ SW transformation inside the nanotube is less than the corresponding value for the isolated C_{36} isomerization reaction by 0.4 eV. However, the carbon nanotube significantly stabilizes the $D_{6h}-C_{36}$ isomer. We believe that the data reported in this article will be useful for the further theoretical and experimental studies on the $C_{36}s$ isomerization or their coalescence inside the carbon peapods.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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