The stable orientations analysis of linearly arrayed C_{10}H_{16} molecules in single-walled carbon nanotube by using the multiple-molecule model

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Abstract

A multiple-molecule model has firstly been constructed to study the stable orientations of encapsulated C_{10}H_{16} molecules in single wall carbon nanotubes. The average molecular distance of adjacent C_{10}H_{16} molecules is evaluated as 7.26 Å. The orientational analysis show that tube’s confinement effect plays a leading role for the diameter distribution from 9.5 Å to 11.75 Å, in which C_{10}H_{16}s exhibit optimal three- and two-fold axis orientations with the diameter smaller and larger than 11.3 Å, respectively. Then H…H repulsive interaction of adjacent C_{10}H_{16} molecules plays an important role with diameter increased to 12.13 Å, which induces a slant two-fold orientation.

I. Introduction

The remarkable substance, adamantane (C_{10}H_{16}), is the smallest diamondoids molecule that consists of 10 carbon atoms arranged as a single cage surrounded by 16 hydrogen atoms with point group symmetry T_d [1,2]. The unique structures and outstanding chemical and physical stability make C_{10}H_{16} useable for a large variety of applications [2-5]. In investigations in C-H structure systems starting with C_{10}H_{16} molecules is of utility in understanding various molecular interactions and their structural properties. As it’s nearly spherical in shape and nonpolar properties, the rotational dynamical behavior of C_{10}H_{16} molecule is an
important element in determining the relationship between structures and properties of the system. The spectroscopic study by Wu et al shows that the bulk C_{10}H_{16} crystallizes in an orientationally disordered cubic phase with the space group Fm3m at ambient conditions [6]. And it transformed to an ordered tetragonal phase by cooling below 208 K [6,7] or by pressurizing above 0.5 GPa [8,9]. Beyond the temperature and pressure condition, the molecular arrangement and its individual behavior can be manipulated by being confined in the small space of single wall carbon (SWCNT) [10]. Various atoms/molecules, such as Si, C, I, Ag, KI / C_{60}, C_{70} and metallocene etc., have been filled into carbon nanotubes by different physicochemical methods [11-18]. The yielded hybrid structure (so called peapod) exhibits many interesting and useful properties that are lacked in bulk structure. Such as the formed linear, zigzag and helical configurations of encapsulated fullerene molecules is unreachable without the packing of SWCNTs [15,19-20]. The C_{10}H_{16}@SWCNT peapod structure has been successfully prepared in experiment [21] and been proved to possess many interesting and useful properties including electron emission and low-kappa dielectric response et al [22-24], making them of great interest for nanotechnological and other applications. By using the classical molecular dynamics and energy minimizations method, S. B. Legoas et al found that the encapsulated C_{10}H_{16} molecules inside SWCNT also exhibit the complex ordered phases [25]. And growing the
nanowire from the linearly arrayed $C_{10}H_{16}$ molecules has been achieved with the help of CNTs [26,27], which can provide an extraordinary environment for this chemical reaction than the conventional chemistry [19,20,28]. In order to clarify the template growth mechanism of encapsulated $C_{10}H_{16}$ molecules in CNTs, the spectroscopic characterize and numerical simulation methods have been performed in experiment and theory, respectively [2,26]. A key structural property to understand this reaction mechanism is the stabled molecular orientation [29,30]. The confined $C_{10}H_{16}$ molecules should exhibit different orientational behavior in the bulk structure, due to the weakened intermolecular potential with the reduced coordination number and the enhanced confinement effect of the circumambient tube wall [25]. The orientational behavior analysis has been performed by the $^{13}$C nuclear magnetic resonance in experiment, which shows that free rotated $C_{10}H_{16}$ molecules in cubic phase will stop rotating when confined in SWCNTs [21]. While it is extremely difficult to characterize the orientational behavior of encapsulated $C_{10}H_{16}$ molecules in SWCNT by using the experimental techniques due to the small molecule size that display only sp$^3$ hybridization of carbon and hydrogen atoms [21]. Therefore, it is remarkably reasonable to use the numerical simulation method to analyze the orientational behavior of $C_{10}H_{16}$ molecule in SWCNTs, and the simulation method can obtain more detailed information for the application and associated properties.
To study the preferred orientation of encapsulated guest molecule in SWCNT, several useful models have been constructed in theory by using the $O_2$-rotor model in which only one guest molecule is filled into an infinite nanotube. Michel and Verberck et al found that the encapsulated C$_{60}$, C$_{70}$ and C$_{78}$ molecules inside SWCNT exhibit different preferred orientations [31-34]. And this model has been successfully used to analyze the preferred orientation of C$_{60}$H$_{18}$ molecule inside SWCNT in our previous study [35]. Undoubtedly, this model only considered the interaction of guest-SWCNT and neglected the guest-guest intermolecular interaction. It is obvious that the guest-guest intermolecular interaction should be considered for the real peapod system. In our previous study on the preferred orientation of encapsulated C$_{60}$ molecule in SWCNT, two more reasonable models have been constructed, which included not only the C$_{60}$-tube interaction, but also the interaction between adjacent C$_{60}$ molecules [36]. One of them is one-dimension (1-D) periodic model, which contains the periodic arrangement of C$_{60}$ molecules [37]. The simulated results show that the filled C$_{60}$ molecules exhibit different preferred orientations compared with the $O_2$-rotor model. But the disadvantage of this model is that only one axis rotation has been performed to search for the preferred molecular orientation with all the molecules in the same rotating orientation. In order to calculate the interaction energy of adjacent C$_{60}$
molecules adopting different orientations, we constructed a two-molecule model with two $C_{60}$ molecules ($C_{60}$-1 and $C_{60}$-2) filled in an infinity tube [36]. In this model, the rotary path of the studied $C_{60}$-1 molecule covering all the molecular orientations with the $C_{60}$-2 molecule’s orientation is fixed on three special axial orientations. This model is effective for searching for the preferred orientation of encapsulated guest molecule. The simulated results by our constructed two-molecule model clearly show that the $C_{60}$-$C_{60}$ intermolecular interaction can affect its preferred orientation, especially for the large tubes. According to the above brief review, we know that the simulated model is crucial important for searching for the preferred orientation of the encapsulated guest molecules in SWCNT. Strictly speaking, using the two-molecule model to characterize the real peapod system is also insufficient, because there are more than two encapsulated molecules in SWCNT and all the molecular orientations among filled molecules should be taken into account. Thus, constructing a more reasonable model on the preferred molecular orientation analysis of filled guest molecules is an interesting and meaningful work.

In this work, we firstly evaluate the average molecular distances of encapsulated $C_{10}H_{16}$ molecules inside SWCNT by calculating the interaction energy of two molecules adopting different relative orientations. Then, we systematically study the orientational behaviors of
C_{10}H_{16} molecules in SWCNTs with the diameter ranging from 9.5 Å to 13.32 Å. Considering the disadvantage of O_{2}-rotor, 1-D and two-molecule models, we constructed a multiple-molecule model, in which five C_{10}H_{16} molecules are filled into an infinite SWCNT with the rotary path of each one covering all the molecular orientations. For this model, we use the lowest-energy orientation transmission method (LEOT) to search for the optimal orientation of each C_{10}H_{16} molecule. We focus on the competing mechanism of C_{10}H_{16}-tube and C_{10}H_{16}-C_{10}H_{16} interaction on the preferred orientation of encapsulated guest molecules. In Sec.II, the details of our model and calculated method are presented. Then, we give the calculated results and make a further discussion in Sec.III. The major conclusion is enumerated in Sec.IV.

II. Model and simulation method

As shown in Fig.1, the C_{10}H_{16} molecule with the carbon skeleton in it composes of four interlocking six membered C rings with all the C-C-C bond angle of 109 45° and C-C bond length of 1.54 Å [2,8-10]. The molecule is assumed to be rigid. We define the single- and three-hydrogen position along the C_{3V} axis direction as the molecular Head and Tail, respectively. Thus, we can obtain three relative molecular orientations (Head-Head, Head-Tail and Tail-Tail) in the three-fold axis direction and one molecular orientation in the two-fold axis direction (see Fig.2). In the model of studying the preferred molecular orientation as
shown in Fig. 3, we fix the nanotube in the Cartesian coordinate system \((X, Y, Z)\) with the center of mass in the origin \(O\), and the \(Z\) axis coincides with the tube’s long axis. The edge effect of tube can be ignored due to the fact that the length (~98 Å) of nanotube is long enough compared to the size of the linear array of \(C_{10}H_{16}\) molecules. Five \(C_{10}H_{16}\) molecules (\(C_{10}H_{16\_1}, C_{10}H_{16\_2}, C_{10}H_{16\_3}, C_{10}H_{16\_4}\) and \(C_{10}H_{16\_5}\)) are put on the tube axis position with the center of mass on the origins \(o_1(x_1, y_1, z_1), o_2(x_2, y_2, z_2), o_3(x_3, y_3, z_3), o_4(x_4, y_4, z_4)\) and \(o_5(x_5, y_5, z_5)\) in the coordinate system separately. Origins \(o_1, o_2, o_3, o_4\) and \(o_5\) locate at \((0, 0, -14.52\ \text{Å}), (0, 0, -7.26\ \text{Å}), (0, 0, 0\ \text{Å}), (0, 0, 7.26\ \text{Å})\) and \((0, 0, 14.52\ \text{Å})\) in the \((X, Y, Z)\) coordinate system. Thus, the center-center distance of adjacent \(C_{10}H_{16}\) molecules is 7.26 Å, which is also determined in our simulation. We specify the molecular orientation by using two Euler angles \(\beta\) and \(\gamma\), which correspond to the \(z_i\) and \(x_i\) axis rotation angles, respectively. The starting orientation, so called the standard orientation with \(\beta=\gamma=0\), of five \(C_{10}H_{16}\) molecules has been defined as the three-fold axis coinciding with the tube’s axis. Thus, the viewing angles on \(Z\)- and \(X\)-axial directions of \(C_{10}H_{16}\) molecule are respectively corresponding to the rotational angles \(\gamma\) and \(\beta\) from the standard orientation. As listed in Table II, the rotational angles \((\beta=n60, \gamma=70)\) with \(n= 0, 2, 4\); \((\beta=n60, \gamma=110)\) with \(n= 1, 3, 5\) and \((\beta, \gamma=0\ or\ 180)\) stands for the standard three-fold axis orientations, and \((\beta=n60, \gamma=125)\) with \(n= 0, 2, 4\) and \((\beta=n60, \gamma= 55)\) with \(n = 1, 3, 5\) stands
for the standard two-fold axis orientations. Similar to the fullerene@SWCNT peapod system, the interaction between $C_{10}H_{16}$ and SWCNT can be described as the van der Waals potential. In order to find the optimal molecular orientation of all the encapsulated molecules, we use the lowest energy orientation transmission (LEOT) method. Namely, we firstly rotate the $C_{10}H_{16}_1$ molecule around the $z_1$ and $x_1$ axes with the angles of $\beta_1=1^\circ-360^\circ$ and $\gamma_1=1^\circ-180^\circ$, respectively. For each rotation of $C_{10}H_{16}_1$ molecule, we calculate the systematic van der Waals interaction potential $V(C_{10}H_{16}_1-C_{10}H_{16}_2)_{1-2}$ and $V(C_{10}H_{16}_2-SWCNT)_{2-T}$ with the rotary path of $C_{10}H_{16}_2$ covering all the molecular orientations (see Fig.4).

The interaction energy can be described as $V(\beta_1, \gamma_1; \beta_2, \gamma_2)_{1-2} = V(\beta_1, \gamma_1; \beta_2, \gamma_2)_{1-2} + V(\beta_2, \gamma_2)_{2-T}$ and the lowest-energy (so called the optimal) orientation $(\beta_2$ and $\gamma_2)$ of $C_{10}H_{16}$-2 molecule corresponds to the minimum value of $V(\beta_1, \gamma_1; \beta_2, \gamma_2)_{1-2}$. Once the optimal orientation of $C_{10}H_{16}$-2 molecule is obtained, we fix its orientation and calculate the interaction energy $V(C_{10}H_{16}_2-C_{10}H_{16}_3)_{2-3}$ and $V(C_{10}H_{16}_3-SWCNT)_{3-T}$ with the rotary path of $C_{10}H_{16}$-3 molecule covering all the molecular orientations. Thus, the optimal orientation $(\beta_3$ and $\gamma_3)$ of $C_{10}H_{16}$-3 molecule could also be obtained from the minimum value of interaction energy $V(\beta_2, \gamma_2; \beta_3, \gamma_3)_{2-3} = V(\beta_2, \gamma_2; \beta_3, \gamma_3)_{2-3} + V(\beta_3, \gamma_3)_{3-T}$. In the same way, we can also obtain the optimal orientations of $C_{10}H_{16}$-4 and $C_{10}H_{16}$-5 molecules by fixing the optimal orientations of $C_{10}H_{16}$-3 and $C_{10}H_{16}$-4 molecule, respectively.
Thus, for each rotation of C10H16_1 molecule, we can obtain the optimal orientations of C10H16_2, C10H16_3, C10H16_4 and C10H16_5 molecules by fixing the optimal orientations of their precursor molecules. At the same time, the optimal orientations of C10H16_2, C10H16_3, C10H16_4 and C10H16_5 molecules have been recorded for each rotation of C10H16_1 molecule. And the total interaction energy of the peapod system can be obtained by the expression:

\[
V(\beta_1, \gamma_1)_{12345} = V(\beta_1, \gamma_1; \beta_2, \gamma_2)_{12} + V(\beta_2, \gamma_2; \beta_3, \gamma_3)_{23} + V(\beta_3, \gamma_3; \beta_4, \gamma_4)_{34} + V(\beta_4, \gamma_4; \beta_5, \gamma_5)_{45}
\]

Finally, we use the average interaction energy \(V(\beta_1, \gamma_1)_{12345} = \frac{V(\beta_1, \gamma_1)_{12345}}{5}\) as the representative of the systematical interaction energy, and the minimum interaction energy of \(V(\beta_1, \gamma_1)_{12345}\) (Kcal/mol\(^{-1}\)) corresponds to the linear arrangement of encapsulated C10H16 molecules adopting the optimal orientations. The van der Waals interaction potential energy can be obtained by summing over all pair interactions:

\[
V_{\tau\lambda} = \sum_{N_\tau} \sum_{N_\lambda} V \left( |r_\tau - r_\lambda| \right) + \sum_{N_\tau} \sum_{N_\lambda^*} V \left( |r_\tau - r_{\lambda^*}| \right)
\]

Where \(\tau, \lambda, \text{and} \lambda^*\) index the atoms of the C\(_{\text{tube}}\), C\(_{10}\text{H}_{16}\) and H\(_{10}\text{H}_{16}\); \(r_i\) and \(N_i\) \((i=\tau, \lambda \text{ and} \lambda^*)\) stand for the coordinates and the resulting number of corresponding atoms, respectively. The Lennard-Jones 6-12 potential has been applied to describe the van der Waals interaction between atoms separated by a distance \(r\).
\[ v(r) = D_0 \left( -2 \left( \frac{R_0}{r} \right)^6 + \left( \frac{R_0}{r} \right)^{12} \right) \]  \tag{2}

This potential with the corresponding potential parameters listed in Table I has been successfully applied to graphite, the generic hydrocarbon system and the filling of carbon nanotubes [38-44].

Table I. The corresponding L-J 12-6 potential parameters used in this work

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<th>Type</th>
<th>C-C</th>
<th>C-H</th>
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<tr>
<td>D_0(kcal mol⁻¹)</td>
<td>3.851</td>
<td>3.3685</td>
</tr>
<tr>
<td>R_0(Å)</td>
<td>0.105</td>
<td>0.0679</td>
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Fig. 1. The sketch map of the head and tail position of $\text{C}_{10}\text{H}_{16}$ molecule.

Fig. 2. The sketch map of adjacent $\text{C}_{10}\text{H}_{16}$ molecules adopted different molecular orientations.
Fig. 3. The constructed model with five C_{10}H_{16} molecules encapsulated in SWCNT with a center-center distance of 7.26 Å. The left and right images are the projections in the (X, Y) and (X, Z) planes, respectively.

Fig. 4. The sketch map of molecular rotation around the z- and x-axis.
III. Results and Discussion

Before the orientational analysis, we firstly performed a calculation for determining the average molecular distance of encapsulated $C_{10}H_{16}$ molecules. The van der Waals distance of Head-Tail arrayed $C_{10}H_{16}$ molecules in SWCNT is reported about 6.2 Å in Ref.26. As is well known, the intermolecular distances $d$ directly depend on the relative molecular orientations. Here, we consider the linearly arrayed $C_{10}H_{16}$ molecules adopting different relative orientations. As shown in Fig.2, three and one relative molecular orientations have been obtained with the molecule adopting three-fold and two-fold axis directions, respectively. The interaction energies of adjacent $C_{10}H_{16}$ molecules with the variable molecular distances have been calculated in Fig.5. We can see that the optimal molecular distances of Three-fold axis (Head-Head, Head-Tail and Tail-Tail) and Two-fold axis orientations are 7.88 Å, 6.89 Å, 6.89 Å and 7.38 Å, respectively. The little bigger Head-Tail molecular distance (6.89 Å) obtained here compared to the value (6.2 Å) of previous report may be given rise to the applied different potential function or interaction parameter [26]. As the real molecular orientations should be the inhomogenous distribution in the SWCNT, the molecular distance of the encapsulated $C_{10}H_{16}$ molecules can be evaluated by the average value ~7.26 Å. The intermolecular hydrogen separations (H…H) of four molecular configurations and average values are 2.513 Å, 2.507 Å, 2.549
Å, 2.522 Å and 2.523 Å, respectively. These obtained values are slightly larger than the non-bonded H…H separations of 2.48 Å in Ref.9, this deviation can be interpreted by the fact that the mutual dislocated molecular arrangement in bulk structure of the adjacent molecules is forbidden in the one dimension pea pod system. And this small deviation also proved the reliability of our molecular distances analysis in this work.

Fig.5. The interaction potential of two C$_{10}$H$_{16}$ molecules with the variable molecular distances.

For the orientational analysis, the SWCNTs with different chirality and diameters have been used to study the stable orientations of C$_{10}$H$_{16}$ molecules. As the study of the encapsulation properties by McIntosh et al
indicate that the spontaneous encapsulation of $C_{10}H_{16}$ molecule into SWCNTs can occur for the diameter larger than 9.5 Å [2]. And the linearly arrayed structure of assembling $C_{10}H_{16}$ molecules in quasi one dimension inter space can be formed with the diameter smaller than 13.57 Å [25]. In this work, we mainly carry out the orientational analysis for the encapsulated molecules in the linear array. Thus, the diameter distribution of selected SWCNTs ranges from 9.5 to 13.32 Å, including seven achiral (two armchair and five zigzag) tubes and three chiral tubes. We focus on the competing mechanism of tube’s confinement effect and $C_{10}H_{16}$-$C_{10}H_{16}$ interaction on the orientational behavior of encapsulated guest molecules. As shown in Table III, the first and second columns show the tube’s chirality and corresponding diameter. The Euler angles $\beta$ and $\gamma$ in the third column show the orientational angles of the optimal molecular orientations. As is well known, the $C_{10}H_{16}_1$ is an assistant molecule to search for the optimal orientations of others’ and the $C_{10}H_{16}_1$-SWCNT interaction has not been calculated. Thus, we only present the optimal orientations of $C_{10}H_{16}$ (2, 3, 4 and 5) molecules in the fourth-seventh columns for the discussion. The systematical interaction energy $V(\beta_1, \gamma_1)_{12345}$ is listed in the eighth column.

We select the (8, 8) and (9, 9) tubes as the example and present the contour maps of the systematic van der Waals interaction potential $V(\beta_1, \gamma_1; \beta_2, \gamma_2)_{12}$ of filled $C_{10}H_{16}_2$ molecule in Fig.6. It can be seen that the
deep, light and transition areas show the molecular high, low energy and metastable states, respectively. And the eight and six low potential energy regions show the preferred three- and two-fold axis orientations, respectively. This is consistent with the C$_{60}$@SWCNTs peapod system, in which the systematical repulsive, attractive and corporate interaction will induce the different preferred (three-, two-, five-fold axis or vertex) orientations of filled C$_{60}$ molecule when the tubes adopt the different diameters [31-34]. Subsequently, we extract the optimal molecular orientation from the preferred orientations by using the LEOT method. As shown in Table III, we can see that the C$_{10}$H$_{16}$ (4, 3, 4 and 5) molecules exhibit the optimal three-fold axis orientations for the diameter less than or equal to 11.3 Å. Then the optimal two-fold axis orientations have been obtained for the larger diameter. For a detailed comparative analysis with Table II and III, we find that the optimal molecular orientations for some tubes have a small deviation ($\Delta\gamma \leq 4^\circ$) from the standard orientations with the diameter $d_T \leq 11.75$ Å. Such as the encapsulated C$_{10}$H$_{16}$-2 molecule in (11, 2) and (8, 8) nanotubes as shown in Fig. 7, the optimal orientations are not the standard orientations with the orientational angles of (300, 0) and (120, 70), but are (300, 4) and (121, 69), respectively. Moreover, it is noteworthy that the larger tilted orientations from the standard two-fold axis orientation are observed for the larger diameter. In Fig. 8, we present the optimal molecular
orientations of $\text{C}_{10}\text{H}_{16}$ (2, 3, 4 and 5) molecules in (9, 9) SWCNT. It can be seen that the optimal orientations with the rotated angles $\gamma$ of four encapsulated molecules are deviated from the standard orientations 3°, 13°, 19° and 22°, respectively. The different orientaitonal behavior observed above can be interpreted as follows. Firstly, the strong confinement effect obtained in the small tube depends on the tube’s diameter sensitively and decreases with the increasing diameter rapidly. Secondly, the properties of the unsmooth surface of $\text{C}_{10}\text{H}_{16}$ molecule and tube wall can be magnified for the small tubes due to the small space of guest molecule and inner wall. Thus, a small influence on the preferred molecular orientation can be produced from the tube’s chirality, which can be ignored for the large tubes. Thirdly, the molecules arrayed in standard orientation can make a smaller intermolecular hydrogen (H…H) separation of adjacent $\text{C}_{10}\text{H}_{16}$ molecules than that in the case in slant orientation. Thus, a slightly higher energy can be produced from the H…H repulsive interaction, and the molecule rotates a smaller angle to reduce this interaction energy and make a more stable system. Based on the above analysis, we know that the optimal three- and two-fold orientations obtained for the diameter smaller than 11.75 Å are results from the tube’s confinement effect, which plays the primary role in the case. And the slightly slant three-fold orientations are induced by the minor effect of the tube’s chirality. This is consistent with the
orientational analysis of C$_{60}$@SWCNTs peapod system, in which C$_{60}$ exhibit the standard or slant pentagon orientations for the small tubes due to the strong confinement effect and the small influence of tube’s chirality [31-34]. For the diameter increasing to 12.13 Å, the observed slant two-fold orientation indicates that the C$_{10}$H$_{16}$-C$_{10}$H$_{16}$ (H…H repulsive) interaction also plays an important role in its orientational behavior with the greatly reduced confinement effect. In order to verify our conjecture, we perform two calculations which only consider the C$_{10}$H$_{16}$-C$_{10}$H$_{16}$ interaction with molecular distance set as 7.8 Å and 7.26 Å, respectively. In the first calculation, we find that the C$_{10}$H$_{16}$-2 molecule exhibits the two-fold axis optimal orientations with the orientational angle as (240°, 125°), which shows that the C$_{10}$H$_{16}$-C$_{10}$H$_{16}$ interaction induces a preferred two-fold axis orientation. In the case of intermolecular distance 7.26 Å, we present the van der Waals interaction potential in Fig.9. It can be seen that the obtained three preferred orientations are the slant two-fold axis orientations with the orientational angles being ($\beta$=n60°, $\gamma$=145°) n=0 or 6, 2, 4, respectively. By using the LEOT method, the Euler angles of optimal orientation is ($\beta$=0°, $\gamma$=145°). This optimal orientation has a deviation about 20° from the standard orientation ($\beta$=240°, $\gamma$=125°), which confirms our analysis that the H…H repulsive interaction of adjacent C$_{10}$H$_{16}$ molecules induces the slant two-fold axis orientation. This case is consistent with the first-order phase transformation in bulk
C_{10}H_{16} structure in which the molecular rotation (~9°) is induced by the H...H repulsive interaction of adjacent molecules [6]. While only 3° deviation of C_{10}H_{16}_2 in (9, 9) tube is obtained here, showing that this optimal slant orientation results from the corporate interaction of C_{10}H_{16}-tube and C_{10}H_{16}-C_{10}H_{16}. Another interesting case is that the slant molecule will produce a more slant orientation with a larger deviation angle, such as the obtained optimal orientations of C_{10}H_{16} (, 3, 4 and 5) molecules in the (9, 9), (16, 0) and (17, 0) nanotubes. According to the above discussion, we know that the tube’s confinement effect plays a primary role in the preferred orientations of encapsulated linearly arrayed C_{10}H_{16} molecules with the diameter d_{t} \leq 11.75 \, \text{Å}. The C_{10}H_{16} molecules exhibit the optimal three- and two-fold axis orientations with diameters small and lager than 11.32 \, \text{Å}, respectively. And the tube’s chirality induces a slightly slant three-fold axis orientation for some small tubes. For the diameter increasing to 12.13 \, \text{Å}, the C_{10}H_{16}-C_{10}H_{16} interaction plays an important role in the orientation behaviors of encapsulated C_{10}H_{16} molecules, and the H...H repulsive interaction of adjacent molecules induces a slant two-fold orientation.
Fig. 6. Contour maps of the systematic van der Waals interaction potential $V(\beta_1, \gamma_1; \beta_2, \gamma_2)_{12}$ of C$_{10}$H$_{16}$-2 molecule filled in (8, 8) and (9, 9) nanotubes.

Fig. 7. The image of optimal molecular orientations of C$_{10}$H$_{16}$-2 molecule filled in (8, 8) and (9, 9) SWCNTs.
Fig. 8. The sketch map of optimal molecular orientations of encapsulated $C_{10}H_{16}$ ($2, 3, 4, 5$) molecules in (9, 9) nanotubes.

Fig. 9. Contour maps of the systematic van der Waals interaction potential $V(\beta_1, \gamma_1; \beta_2, \gamma_2)_{1-2}$ of $C_{10}H_{16-1}$-$C_{10}H_{16-2}$ molecule.

Table II. The rotational angles of standard eight three- and six two-fold axis orientations as presented in Fig. 6.

| B; $\gamma(^\circ)$ |   |   |   |   |   |   |
Table III. Column I and II show the tube’s chirality and diameter. Column III shows the optimal rotational angles. The columns IV-VII show the rotational angles of optimal orientations of considered five C\textsubscript{10}H\textsubscript{16} molecules. And column VIII show the systematical total interaction energy (Kcal/mol).

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<th>Å</th>
<th>β: γ(°)</th>
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IV. Conclusions

In summary, a detailed orientational behavior study of encapsulated C$_{10}$H$_{16}$ molecules inside armchair-, zigzag-, and chiral-type nanotubes has been performed by using the systematical van der Waals interaction calculation. We evaluate the average molecular distances (~7.26 Å) of linearly arrayed C$_{10}$H$_{16}$ molecules inside SWCNTs by calculating the C$_{10}$H$_{16}$-C$_{10}$H$_{16}$ interaction potential with the variable molecular distances. Within the constructed multiple molecule model, we study the optimal orientations of linearly arrayed C$_{10}$H$_{16}$ (2, 3, 4 and 5) molecules by using the LEOT method. The results outlined here show that the tube’s confinement effect plays a primary role in the orientational behaviors of encapsulated C$_{10}$H$_{16}$ molecules for the diameters d_T ≤ 11.75 Å, in which C$_{10}$H$_{16}$ molecules exhibit the optimal three- and two-fold axis orientations with the transformation-diameter of 11.3 Å. And this transformation-diameter value depends on the tube’s diameter. The tube’s chirality induces a slightly slant three-fold axis orientation for some small tubes. For the diameters d_T ≥ 12.13 Å, the C$_{10}$H$_{16}$-C$_{10}$H$_{16}$ interaction can not be ignored due to the weakened confinement effect, and the H...H repulsive interaction of adjacent molecules induces a slant two-fold orientation. Our results provide a more comprehensive understanding of the competing mechanisms of the tube’s confinement effect and
$\text{C}_{10}\text{H}_{16}$-$\text{C}_{10}\text{H}_{16}$ interaction on the preferred orientation of filled $\text{C}_{10}\text{H}_{16}$ molecules. And our results also promote the possible application of $\text{C}_{10}\text{H}_{16}$ nanopeapods.

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