BUTYRIC ACID INTERACTION WITH CARBON NANOTUBES: MODELING BY A SEMI-EMPIRICAL APPROACH

APROXIMACIÓN SEMI-EMPÍRICA A LA MODELACIÓN DE LA INTERACCIÓN ENTRE ÁCIDO BUTÍRICO Y NANOTUBOS DE CARBONO

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(Recibido 16/5/2013; Aceptado 7/10/2013)

The quantum interaction properties of the butyric acid radical on the side walls of the single walled carbon nanotubes (CNT) are modeled by PM3 calculations. It is found that the interaction potential of the butyric acid with the tubes forms stable complexes when it reacts with the carbon atom (C^3-centered) and metastable conformations with the C^1 and C^2 atoms. We have studied the effect of the diameter-length characteristics of the CNT on the binding with a fatty acid. Our results suggest that the binding energy decreases as the diameter increases, and it initially increases as the length increases.

Se investigan, mediante cálculos PM3, las propiedades de interacción cuántica del radical de ácido butírico y las paredes laterales de nanotubos mono-pared. Se encuentra que el potencial de interacción del ácido butírico con los tubos forma complejos estables cuando reacciona con el átomo de carbono (C^3-centrado), y configuraciones metaestables con los átomos C^1 y C^2. Hemos estudiado el efecto de las características diámetro-longitud del nanotubo de carbono en su enlace con un ácido graso. Nuestros resultados sugieren que la energía de enlace decrece al aumentar el diámetro, pero se incrementa al aumentar la longitud del nanotubo.

PACS: Carbon nanotubes structure of, 61.48.De. Binding energy solids, 71.15.Nc. Computational techniques electronic structure atoms and molecules, 31.15.-p.

INTRODUCTION

The characteristics and behavior of nano-materials are a new field of science, being limited to nano-scale dimensions (1–100 nm). Nano-structures have a quantum nature due to their atomic and molecular size. A question is how the experiments can approach to the atomic level to do nano-measurements? Carbon nanotubes (CNTs), which were discovered by Iijima [1], can be considered as sheets of graphite wrapped to a cylindrical form. CNT can be synthesized by the techniques of electric arc discharge, laser ablation, and catalytic decomposition of hydrocarbons [2–8]. Because the CNTs have special thermal, mechanical, and electrical properties and the ability to be applied at atomic levels, it makes them promising structures for working in wide fields of applications. Many of these applications are in biology and medicine. The ability of CNT to penetrate into cells offers the potential of using CNT for delivery of drug and antibiotic molecules without toxicity effects [9–20]. In spite of the wide applications of CNT, theoretical studies of the interaction mechanism between the CNTs and biomolecules are few [20,21]. Mavrandonakis *et al.* have studied the interaction of an amino acid with CNT [22], and then few studies followed [23,24]. Butyric acid is a fatty acid occurring in the form of esters in animal fats. It is an important member of the fatty acid subgroup called short-chain fatty acids. Butyric acid is a medium-strong acid that reacts with bases and strong oxidants, and attacks many metals [25]. It enhances apoptosis of T-cells in the colonic tissue thereby eliminating the source of inflammation (IFN-γ production) [26]. This is known as the "butyrate paradox". Butyrate inhibits colonic tumor cells, and promotes healthy colonic epithelial cells [27].

In this work, we examine the interaction of butyric acid radical on the sidewalls of single-walled CNT, which has a bond-alternation pattern defined as an armchair type [28]. Then we examine this interaction as a function of CNT diameter and length. Then, we investigate the effect of changing the position of the butyric acid-CNT bond on the interaction energy. Finally, to study the effect of rotating the butyric acid around of the butyric acid–CNT bond on the interaction energy and then the rotating of carboxyl group in butyric acid.

THEORETICAL APPROACH AND COMPUTATIONAL DETAILS

Theoretical calculations are used to bridge gaps in understanding the experimental results, so in many issues the results of the

experimental methods are unable to accurately describe small components of biochemical. While the molecular quantum mechanics methods can be used to investigate properties beyond the scope of current crystallographic methods, the theoretical methods can be used to further investigation and to predict the physical and chemical nature of hydrogen bonding interactions [29, 30]. To investigate the structural and electronic properties of CNTs decorated with the butyric acid radicals, we used semi-empirical method PM3. PM3 or Parameterized Model number 3, developed by James Stewart [31,32], is a re-parameterization of AM1 method, which is based on the neglect of differential diatomic overlap (NDDO) integral approximation. The PM3 method uses the same formalism and equations as the AM1 method. The differences are: (1) PM3 uses two Gaussian functions for the core repulsion function, instead of the variable number used by AM1 (which uses between one and four Gaussians per element); (2) the numerical values of the parameters are different. The other differences lie in the philosophy and methodology used during the parameterization: whereas AM1 takes some of the parameter values from spectroscopical measurements, PM3 treats them as optimizable values. The parameters for PM3 were derived by comparing a much larger number and wider variety of experimental versus computed molecular properties. Typically, non-bonded interactions are less repulsive in PM3 than in AM1. PM3 method is primarily used for organic molecules, but is also parameterized for many main group elements. Several modifications that have been made to the NDDO core-core interaction term and to the method of parameter optimization are described. These changes have resulted in a more complete parameter optimization, called PM6, which has, in turn, allowed 70 elements to be parameterized [33].In an attempt to expand the range of applicability, a new method called PM7 has been developed. PM7 was parameterized using experimental and high-level *ab initio* reference data, augmented by a new type of reference data intended to better define the structure of parameter space [34].The problem that arises is how we can perform the accurate calculations to a nano-sized system without ending in aprohibitive large computation. The dangling bonds at the ends of the tubes were saturated by hydrogen atoms. The resolution of PM3 and QSAR model (Quantitative structure–activity relationship models) as implemented in the HyperChem™ Release 7.52 for Windows Molecular Modelling System program package (http://www.hyper.com/) was employed for the geometry optimizations.

RESULTS AND DISCUSSION

To connect the butyric acid with CNT surface, so that one hydrogen atom must be omitted from the butyric acid. The butyric acid contain three carbon atoms, so there three probable positions (isomers). For our investigation it was important to find the most stable isomers of the butyric acid (fatty acid) radicals. These three isomers appear according to omitted hydrogen atom from the three carbon atoms in butyric acid respectively. Among the three possible isomers are the ones from which one hydrogen atom is abstracted from the C-atom, see figure 1. The geometry optimized for these three isomers were calculated by PM3. Also the neutral butyric acid optimized before omit hydrogen atom. The relative energy $\Delta E = \Delta\varepsilon^{*} - \Delta\varepsilon$; $\Delta\varepsilon = \varepsilon^{neutral} - \varepsilon^{radical}$; $\varepsilon^{neutral}$ is the optimized energy forthe butyric acid and $\varepsilon^{radical}$ is the optimized energy for the radical of butyric acid after one hydrogen atom is abstracted from the C-atom and $\Delta\varepsilon^{*}$ is the lowest $\Delta\varepsilon$. According to the relative energy ΔE, it is found that the C^2-centered radical is favored over the C^1 and C^3-centered one by 6.81 and 1.27 kcal/mol, respectively, employing the PM3 method. These energy differences among the isomers of the butyric acid are not much comparable with the isomers of amino acid (glycine) [22,23].

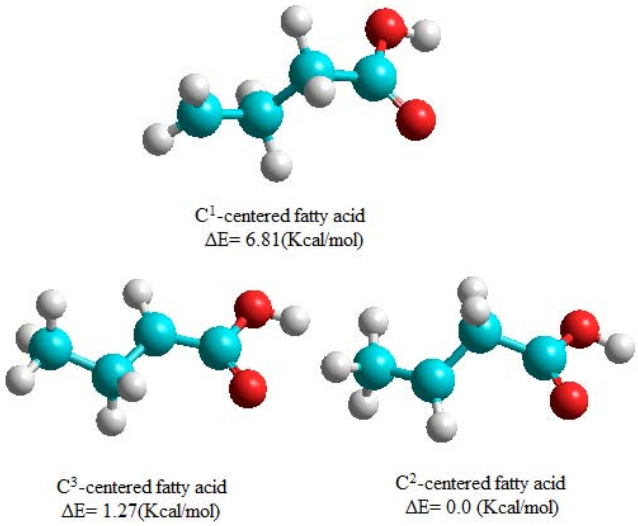

Figure 1. The geometry optimized of the three isomers of the butyric acid radicals and their relative stability ΔE.

Then, we calculated the interaction of the butyric acid radicals with the CNTs. For this purpose the armchair type of CNT which adopted with diameter and length equal to 5.78 Å and 9.925 Å respectively. Then we connected the three isomers on the surface of CNT. The geometry optimized for these three issues were calculated by PM3. The binding energy $BE = \varepsilon^{Butyric\text{-}CNT} - (\varepsilon^{CNT} + \varepsilon^{Butyric})$; $\varepsilon^{Butyric\text{-}CNT}$ is the optimized energy for the butyric acid with the CNT, ε^{CNT} is the optimized energy for the CNT alone and $\varepsilon^{Butyric}$ is the optimized energy for the radical of butyric acid (C^1, C^2 and C^3 respectively).The relative binding energy $\Delta BE = BE - BE^{*}$; BE^{*} is the binding energy for the highest one. The relative energy $\Delta E = \varepsilon^{*} - \varepsilon$; $\varepsilon = \varepsilon^{Butyric\text{-}CNT}$ and ε^{*} is the optimized energy for the lowest one. We find that upon reaction with the single tube wall, the butyric acid radical forms stable complexes when it reacts with the carbon atom (C^3-centered) and metastable conformations with C^1 and C^2-centered butyric acid, see figure 2, along with their relative binding energies BE and relative stabilities ΔE. Thus, we have had the interest to study the interaction of the C^3-centered with CNTs only. If we compared the relative densities $\Delta\rho$, $\Delta\rho = \rho - \rho^{*}$; ρ^{*} is the density of the lowest butyric acid radical, among these three isomers, the C^3-centered with CNT owned the highest one. So, it has ability to enter inside the cells lower than the two other isomers, because of the viscosity η increases, which is proportional to the density $\eta \sim \rho$.

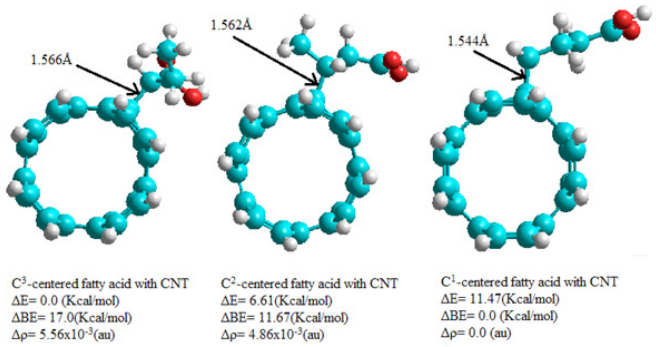

Figure 2. Geometry optimized structures of butyric acid with CNT.

The first important factor is examining the nature of the interaction of butyric acid (C^3-centered) with CNT as a function of the diameter of the CNT, so the armchair type of CNT which adopted with length equal to 5.149 Å. Note that in each case, we put the $C_{\text{butyric acid}}$ - C_{CNT} bond on the middle of CNT surface. The geometry optimized for each change in the diameter of CNTs was calculated by PM3. The increasing effect in the CNT diameter on the binding energy between the C^3-centered butyric acid radicals with CNT were shown in figure 3. Where any increase in the diameter of CNT will lead to rapid decrease in the binding energy between the C^3-centered butyric acid radicals with CNT. The behavior of rapid decreasing was not expected comparable to the behavior of glycine with CNT [23]. The binding energy becomes semi-constant as the CNT diameter wide than 5 Å. This case may reflect the mechanism of lower binding between the butyric acid with CNT in future. Generally, the CNT that has diameter more than 3.5 Å was more sensitive to the amino acid, if we compare it to the fatty acid.

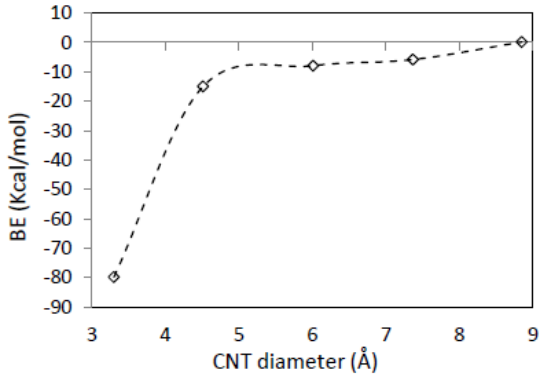

Figure 3. The binding energy between the C^3-centered butyric acid with the C_{CNT} as a function of the CNT diameter.

In the C^3-centered binding, a single covalent $C_{\text{butyric acid}}$ - C_{CNT} bond is formed with CNT. The $C_{\text{butyric acid}}$ - C_{CNT} bond becomes long as the diameter of CNT increase, see figure 4. Whereas the increases the CNT diameter will increase the covalent bond length and this may decrease the binding energy, see figure 3. Table 1 displays the results of QSAR model, where, as the CNT diameter increases, also there is an increase in the density ρ. The viscosity η will increase, so the ability of butyric acid with CNT to enter inside the cell may decrease. By this away, we can lower or higher the ability of entering the fatty acid-CNT into the cells.

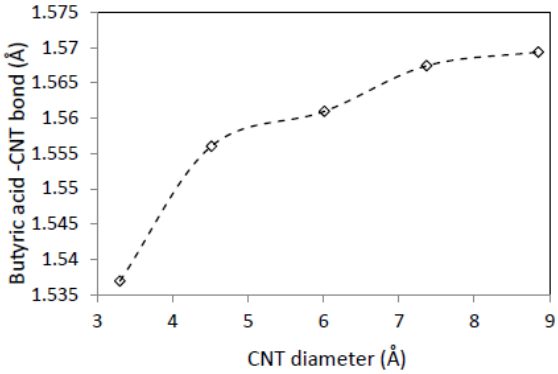

Figure 4. The length of the $C_{\text{butyric acid}}$-C_{CNT} bond as a function of CNT diameter.

Table 1
Relative density $\Delta\rho$ for the butyric acid with the CNT diameters.

CNT diameter (Å)	$\Delta\rho$
3.302	0.000
4.516	0.049
6.0135	0.063
7.371	0.067
8.852	0.069

The second important factor is the interaction of butyric acid with different lengths from CNT, so the armchair type of CNT which adopted with diameter equal to 5.78 Å. Note that in each case, we put the $C_{\text{butyric acid}}$ - C_{CNT} bond on the middle of CNT surface. The geometry optimized for each change in the length of CNTs was calculated by PM3. The operation of increase the CNTs length during their synthesis is very important property. The binding energy of the C^3-centered butyric acid radicals with CNT may dependon the length of CNT, see figure 5. As the length of CNTs increases, the binding energy between the C^3-centered butyric acid radicals with CNTs also increases. Generally, butyric acid behavior with the CNTs length was same as to the behavior of glycine [23]. With few orders of length the change of binding energy lowers. If we compare between the effect of CNTs diameter and length on the binding energy, we may note that the binding between the butyric acid and CNT depending on the diameters of CNTs more than depend on their lengths. The $C_{\text{butyric acid}}$ - C_{CNT} bond length as a function of CNT length is shown in figure 6, where its length is lowering and then increases in its values as the CNT lengths increase. Table 2 displays how the increasing of CNT lengths will increase the relative density. The viscosity will increase with CNT lengths more than the CNT diameter increasing.

Where does the butyric acid prefer to link on the surface of CNT? There are many positions may be the butyric acid prefer to connect on the CNTs surface, see figure 7. The geometry optimized for each position on the surface of CNTs was calculated by PM3. The relative stability of the C^3-centered butyric acid radicals with CNT will decreases as a function of the position of the $C_{\text{butyric acid}}$ - C_{CNT} bond on the cylindrical surface of the CNT, where this position change from the middle of the CNT surface forward one of their two ends. Figure 7 shows the positions 1,2 …6 of butyric acid on

the CNT surface. The butyric acid radical with the single tube wall, become more stable, when the butyric reacts with the CNT at position 3, which at the half distance between the middle position and the end of the CNT. Generally, the butyric acid prefers to link at position 3 on the CNT surface.

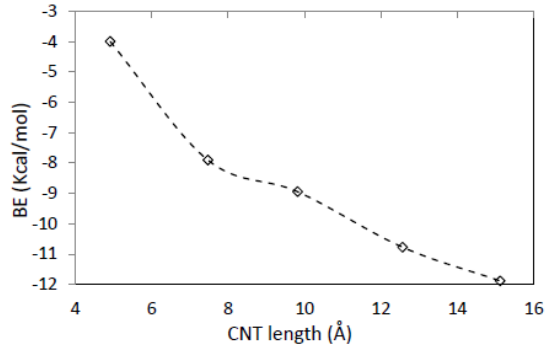

Figure 5. The binding energy of the C^3-centered butyric acid radicals with the CNTs as a function of CNT length.

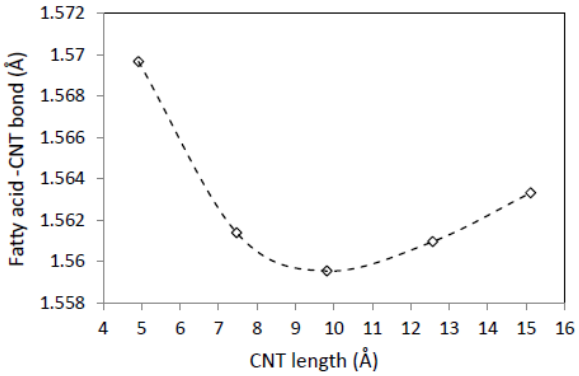

Figure 6. The length of the $C_{butyric\ acid}$-C_{CNT} bond as a function of CNT length.

Table 2
Relative density $\Delta\rho$ with the CNT lengths.

CNT length (Å)	$\Delta\rho$
4.92	0.000
7.47	0.045
9.83	0.080
12.57	0.077
15.12	0.124

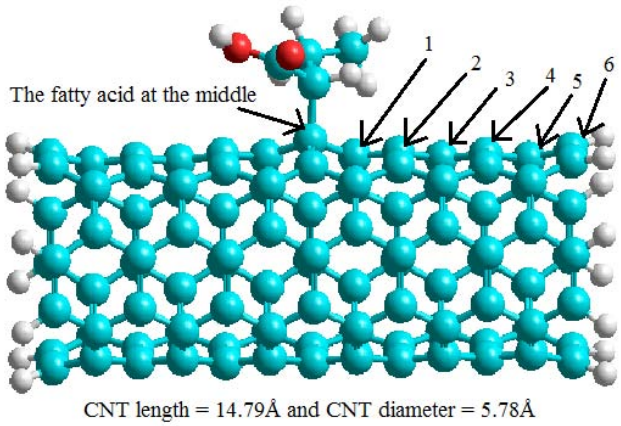

Figure 7. The positions of the $C_{butyric\ acid}$ - C_{CNT} bond on the cylindrical surface of CNT that expecting.

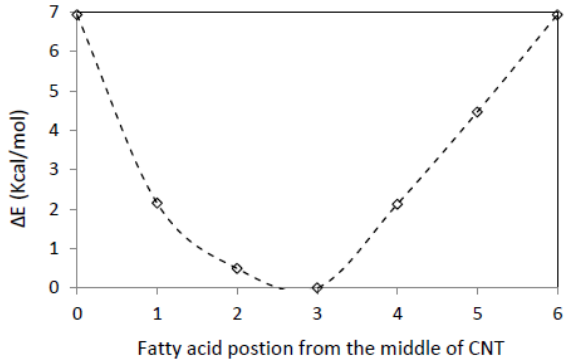

Figure 8. The relative stability of the C^3-centered butyric acid radicals with CNT as a function of the position of the single covalent $C_{butyric\ acid}$-C_{CNT} bond that formed, from the middle of the CNTs forwards their two ends.

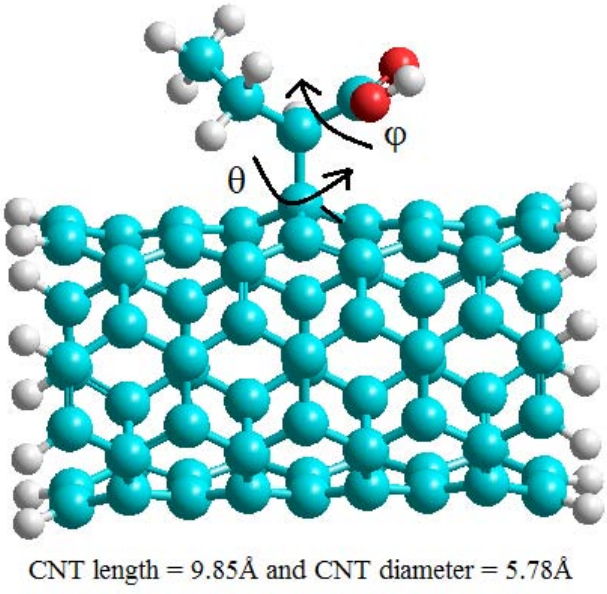

Figure 9. The rotating of the butyric acid bout the $C_{butyric\ acid}$ - C_{CNT} bond θ, and then rotating of the carboxyl group φ.

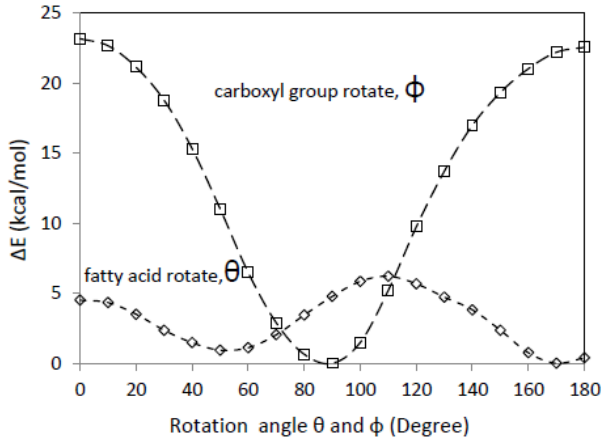

Figure 10. The relative stability of the C^3-centered butyric acid radicals with CNT as a function the rotating of the butyric acid bout the $C_{butyric\ acid}$ - C_{CNT} bond θ, and then rotating of the carboxyl group φ.

The final important factor is the effect of rotating the butyric acid bout the $C_{butyric\ acid}$ - C_{CNT} bond by angle θ, and then rotating of the carboxyl group by angle φ on the relative stability ΔE, see Fig. 9, with rotating step 10°. The geometry optimized for each rotating, the butyric acid or carboxyl group, on the surface of

CNTs was calculated by PM3. Figure 10 shows fluctuated in relative stability as the angle θ increases, so there are two stable points, the firstat $\theta = 50°$ and the second at $\theta = 170°$. The range of relative stability ΔE is not high, so the thermal energy may be able to do this rotation. While the rotating of the carboxyl group shows wide change in ΔE compare with the θ. Where the highest stability at $\varphi = 90°$. The rotating of carboxyl group φ shows higher effected on the relative stability compare with the increasing of the θ angle.

CONCLUSIONS

We have performed PM3 calculations of the structural properties of CNT upon adsorption of various fatty acids (butyric acid radicals). Among these three isomers, the C^3-centered butyric radical forms stable complexes with CNT. The results of the diameter and length of the CNTon the binding energies with C^3-centered butyric show a decrease as the CNT diameter increases, while the binding energies increase with CNT length increase. The C^3-centered butyric radicals are shown to prefer to bond at the half distance between the middle and one of their two ends of the CNT cylindrical surface. The stereo geometry (curvature of CNT surface) between the butyric radicals and CNTmay limit the binding energies behaviour. Also, there was a good agreement between the PM3 calculations and other calculations in terms of energies [23,24,35,36].

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