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Theoretical Semiempirical Study of the Biomolecules Interaction with Carbon Nanotubes

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Modeling of the quantum interaction properties of glycine radicals on the sidewalls of the single-walled carbon nanotubes (CNTs) is investigated by MINDO/3 (Modified Intermediate Neglect of Differential Overlap version 3) calculations. It is found that the interaction potential of the N-centered glycine radical with the tubes results in stable complexes when it reacts with the nitrogen atom (N^2 centered) and metastable conformations with C^2 atoms. We have studied the effect of the diameter–length characteristics of the CNT on binding the amino acid. Our results suggest that the binding energy is lower as the CNT diameter increases, while as the CNT length increases, the binding energy initially increases and then slightly fluctuates.

Keywords amino acid, binding energy, CNT, semiempirical calculation

Introduction

The characteristics and behavior of nanomaterials is a new field for science, being limited to nanoscale dimensions (1–100 nm). The nanostructures have a quantum nature due to their atomic and molecular size. Thus, the prediction and understanding of these nanomaterials must be based on experimental and theoretical research. A question is how the experiments can approach to the atomic level to do nanomeasurements? Carbon nanotubes (CNTs), which were discovered by Iigima,[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 make 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 toxic effects.[9–20] In spite of the wide applications for CNT, theoretical studies of the interaction mechanism between the CNTs and biomolecules are few.[20–22] Only Mavrandonakis et al. have studied the interaction of an amino acid with CNT.[22]

In this work, we examine the interaction of four isomers of glycine radicals on the sidewalls of single-walled CNT, which have a bond-alternation pattern defined as armchair type.[23] Then we examine this interaction as a function of CNT length and diameter. Finally,

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we try to investigate the effect of changing the position of the amino acid–CNT bond on the interaction energy.

Theoretical Approach and Computational Details

Theoretical calculations can be used to bridge gaps in understanding experimental results. In many cases, the results of the experimental methods are unable to accurately describe small systems of complex biochemicals. The methods of molecular quantum mechanics can be used to investigate properties beyond the scope of current crystallographic methods. The molecular quantum techniques allow us to study optical, magnetic, and electronic properties that are not easily measured experimentally. Molecular quantum mechanics provides the interaction energies that are not provided by X-ray and NMR (nuclear magnetic resonance) experiments. The theoretical methods can be used to further investigate and to predict the physical and chemical nature of hydrogen bonding interactions. To investigate the structural and electronic properties of CNTs decorated with the glycine radicals, we used MINDO/3 (Modified Intermediate Neglect of Differential Overlap version 3). The problem that arises is how to perform an accurate calculation for a nano-sized system without ending in a prohibitively large computation. The dangling bonds at the ends of the tubes were saturated by hydrogen atoms. The resolution of MINDO/3, as implemented in the HyperChem Release 7.52 for Windows Molecular Modeling System program package (http://www.hyper.com/), was employed for the geometry optimizations.

Results and Discussion

For our investigation, it was important to determine the most stable isomers of the glycine radical. Among the four possible isomers are the ones from which one hydrogen atom

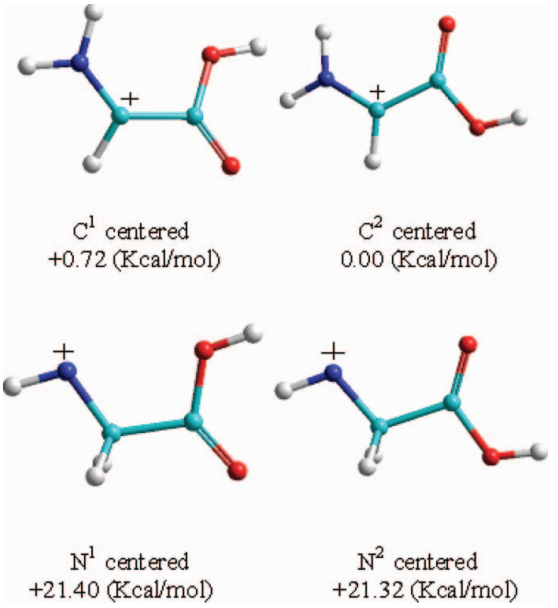

Figure 1. The most stable isomers of the glycine radical and their relative stability (Color figure available online).

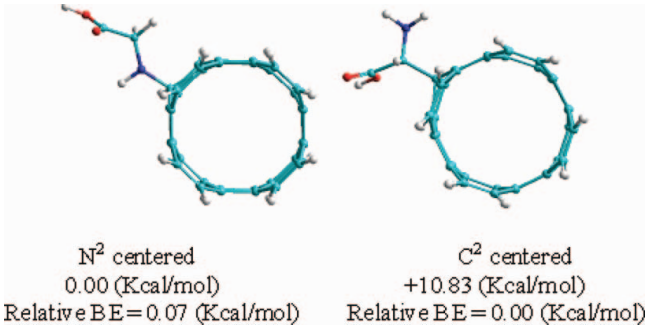

Figure 2. Geometry optimized structures of glycine–CNT (Color figure available online).

is abstracted from either the C atom, or the N atom (see Fig. 1). It was found that the C^2-centered radical is favored over the C^1, N^2, and N^1 centered ones by 0.72, 21.32, and 21.40 kcal/mol, respectively, employing the MINDO/3 method. The C^2-centered radical being favored over the N^2-centered radical isomer by 21.32 Kcal/mol is in reasonable agreement with the values of 18.5 and 19.9 kcal/mol reported in other ab initio calculations.[24,25] Then, we calculated the interaction, binding energy (BE), of the glycine radicals with the CNT, $BE = E_{glycine+CNT} - (E_{glycine} - E_{CNT})$, where $E_{glycine+CNT}$ is the energy of the complex of glycine and CNT. We find that upon reaction with the single tube wall, the glycine radical forms stable complexes when the CNT reacts with the nitrogen atom (N^2 centered) and metastable conformations with the C^2 atom, as shown in Fig. 2 along with their relative binding energies (BE) and relative stabilities. Thus, we further studied only the interaction of the N-centered radical with CNT. The first important factor is the interaction of glycine with CNT as a function of the CNT diameter. The effect of increases in the CNT diameter on the BE of the N^2 centered glycine radicals with CNT are shown in Fig. 3. An increase in the diameter of the CNT leads to a decrease in the binding energy of the N^2-centered glycine radicals with CNT. This case shows the mechanism of lower binding between the amino acid and CNT as the CNT diameter increases. In the N^2-centered binding, a single covalent $N_{glycine}$–C_{CNT} bond is formed with CNT. The $N_{glycine}$–C_{CNT} bond becomes longer as the diameter of the CNT increases (see Fig. 4). The increases of the CNT diameter shown

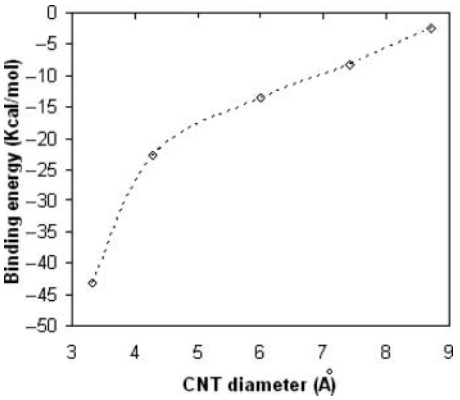

Figure 3. The binding energy between the N^2-centered glycine and the C_{CNT} as a function of the CNT diameter.

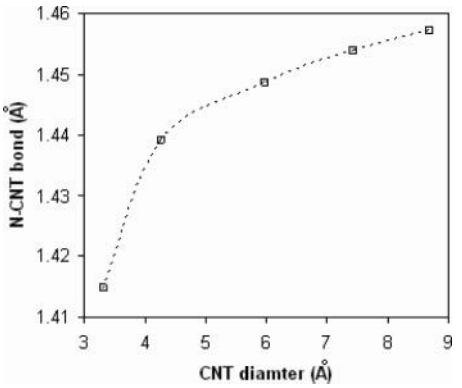

Figure 4. The $N_{glycine}$–C_{CNT} bond as a function of CNT diameter.

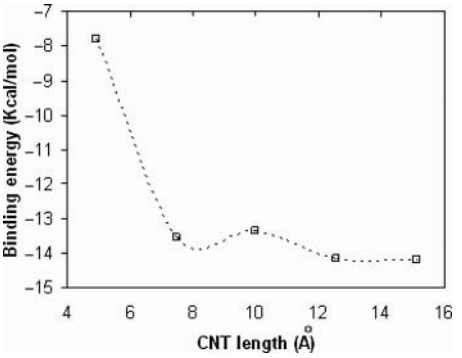

Figure 5. The binding energy of the N^2-centered glycine radicals with the C_{CNT} as a function of CNT length.

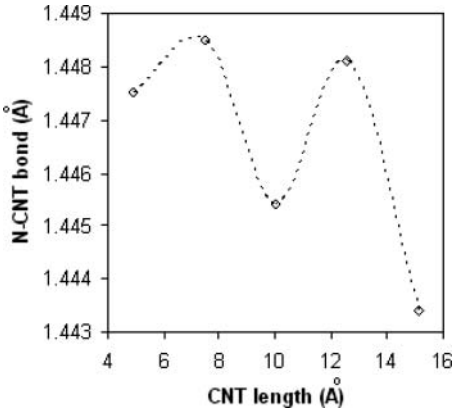

Figure 6. The $N_{glycine}$–C_{CNT} bond length as a function of CNT length.

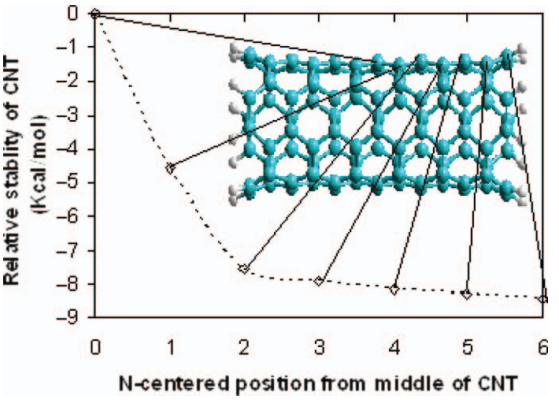

Figure 7. The relative stability of the N^2-centered glycine radicals with CNT as a function of the position of the single covalent $N_{glycine}$–C_{CNT} bond that formed, from the middle of the CNT towards one of their two ends (Color figure available online).

(3∼6 Å) increase the covalent bond length and decrease the binding energy (see Fig. 3). This suggests that there is a relationship between the covalent bond length increase and the decrease in the binding energy.

The second important factor is the interaction of glycine with different lengths of CNT evaluated (for constant diameter equal 5.45 Å). The CNT length during their synthesis is a very important property. The binding energy of the N^2-centered glycine radicals with CNT depends on the length of CNT, as shown in Fig. 5. As the length of the CNTs increases, the binding energy between the N^2-centered glycine radicals and CNT also increases. Note that in each case, we put the $N_{glycine}$–C_{CNT} bond in the middle of the CNT. Above a few Angstroms of length, the binding energy essentially did not change. Thus we conclude that the binding between the glycine and CNT depends on the diameters of CNT more than their lengths. The $N_{glycine}$–C_{CNT} bond length as a function of CNT length is shown in Fig. 6. There is a fluctuation in its values as the CNT length increases. Generally, however, the $N_{glycine}$–C_{CNT} bond decreases as the length of CNT increases. The relative stability of the N^2-centered glycine radicals with CNT decreases as a function of the $N_{glycine}$–C_{CNT} bond position on the cylindrical surface of CNT, as this position changes from the middle of the CNT towards one of their two ends, as shown in Fig. 7. The complexes formed by the glycine radical and the single tube wall are more stable when the reaction occurs in the middle of the CNT.

Conclusions

We have performed MINDO/3 calculations on the structural properties of CNT upon adsorption of various glycine radicals. Among these two isomers, the N^2-centered glycine radical forms stable complexes with CNT. The results of the diameter and length of the CNT on the binding energies with N^2-centered glycine show a decrease as the CNT diameter increases, while the binding energies increase with CNT length increase. The N^2-centered glycine radicals are shown to prefer to bond in the middle of the CNT cylindrical surface. The stereo geometry (curvature of CNT surface) between the glycine radicals and CNT may limit the binding energies behavior. Also, there was a good agreement between the MINDO/3 calculations and other ab initio calculations in terms of energies.[24,25]

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