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Interaction of (10, 0) single-walled carbon nanotubes with nuclei acid bases: a *first-principles* study

M. R. Gholami [a] and M. D. Ganji [b,*]
[a]*Department of Chemistry, Sharif University of Technology, Tehran, Iran*
[b]*Department of Chemistry, Islamic Azad University of Ghaemshahr, Mazandaran, Iran*

Abstract: The interaction between nucleic acid bases and a (10, 0) single-walled carbon nanotube (CNT) were investigated through calculations within density functional theory based treatments. It has been found that the guanine base adsorption is bound stronger to the outer surface of nanotubes in comparison to the other bases, consistent with the recent theoretical studies. In this work the insertion of nucleic acid bases inside the nanotubes has been also investigated for the first time. Our calculations reveal that the cytosine base exhibits a stronger binding to the inner surface of nanotubes side-wall. Furthermore, when nucleic acid bases were inserted inside the tube, the nanotube shape was deviated from cylinder.

Keywords: Nucleic acid bases; SWCNTs; Adsorption; Insertion; Density functional theory

Introduction

Recently much attention has been attracted to single wall carbon nanotubes (SWCNTs) for their potential applications in the life sciences. Among them, the interactions of nucleic acids and proteins with SWCNTs have been widely investigated [1-7]. In particular, several studies have been devoted on the immobilization of proteins and nucleic acids on nanotubes [1-3] and the attachment of DNA and RNA onto CNTs for improving the solubility and bioavailability of nanomaterials in aqueous solution [8, 9]. It has been also shown that CNTs can reduce and even inhibit polymerase chain reaction [10] and furthermore, hybridization between complementary strands of DNA could be detected on the surface of CNT [11, 12]. Furthermore, Hwang *et al.* showed that CNTs can be employed to utilize as generic nanobiomarkers for the precise detection of a particular gene with very high sensitivity and specificity [13]. Direct DNA binding on CNTs [7] suggests roles of specific nucleic acids bases in direct nucleic acids interaction with nanotubes, though it is acknowledged that we are still in need of a full understanding on the interfaces of these systems. Whether for sensing or for any other intended application, a more detailed picture on bridging carbon nanotubes with biological systems should be essential in designing life sciences-related tools employing these nanomaterials. In spite of numerous experimental investigations however, the theoretical study of the interaction of nucleic acids with the carbon nanotubes has been less considered. This is perhaps due to the quite large unit cell and thus large computation resources needed, especially for finding geometric optimized structures. Indeed, few theoretical works have been reported on the interactions of nucleic acid bases with carbon nanotubes. More recently Gowtham *et al.* used density functional theory method to investigate the adsorption of nucleic acid bases on small-diameters carbon nanotubes [7]. However, they limited their calculations to the adsorption of nucleic acid bases on the outer surface of the nanotubes. Furthermore, the considered nanotubes in their work are very small-diameter, so are not particularly realistic.

In this work, as a starting point in understanding interactions with much more complex biological systems, we carried out geometric optimization calculations within density functional based tight binding (DFTB) method on the interaction of the nucleic acid base molecules adenine (A), cytosine (C), guanine (G), thymine (T), and uracil (U), with a large-diameter single-walled carbon nanotube (SWCNT). We have investigated, for the first time, the insertion of the nucleic acid bases inside the considered carbon nanotube. Details on the model and computational methods employed are explained more thoroughly in the

*Corresponding author. Fax: +(98) 123 2240091 Tel: +(98) 911 113 7150, E-mail: *ganji_md@yahoo.com*

proceeding section, followed by a discussion of our results in Section 3 and a conclusion in the last section.

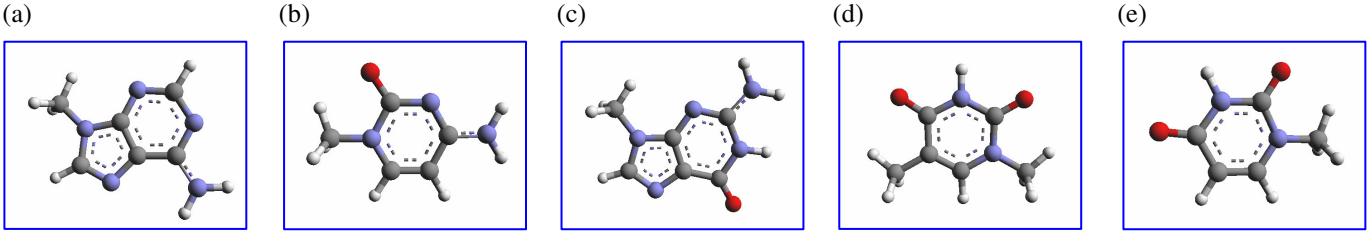
Computational methods

The structural optimizations of carbon nanotubes and nucleic acid bases are carried out using the recently developed DFTB+ code [14]. The DFTB+ uses the density functional based tight binding method based on a second-order expansion of the Kohn-Sham total energy in density functional theory with respect to charge density fluctuations. The DFTB approach, unlike the typical approximate Hartree-Fock/DFT methods, uses a tabulated set of integrals derived from *ab initio* DFT calculations [15], leading to a substantial speed-up of the method since explicit integration is not required in the method. Furthermore, unlike conventional tight-binding method it is possible to produce parameterizations capable of accuracy close to LDA/GGA with minimal adjustable parameters and also transferable between different systems. The basis functions of the DFTB method are also available, allowing the reconstruction of actual wave functions from the calculations. Further details of the method have been fully reviewed for instance in [14-17]. In this work the Slater-Koster (S-K) type parameter set [18] was implemented. Furthermore, the dispersion corrections for the nonbonding van der Waals interaction were implemented via the Slater-Kirkwood type model [19]. To simulate the realistic situation in DNA and RNA, the base molecules were terminated with a methyl group where the bond to the sugar ring had been cut in order to generate an electronic environment in the nucleic acid bases rather than that of just individual isolated bases by themselves. Geometries of CNTs and nucleic acid bases are optimized separately prior to the optimization of whole system. Periodic boundary conditions and supercell approximations with a lateral separation of 18 Å between tubes centers are used to make sure that the nanotubes plus nucleic acid bases do not interact with their periodic images. The unit is periodic in the direction of the tube and the length is 11.524 Å for the CNTs structures being studied. Along the tubes *k*-points were used for axes, 1×1×4 Monkhorst–Pack the Brillouin zone integration. Structural optimizations were performed using the conjugate gradient algorithm. The total energy calculations for the interaction between CNTs and nucleic acid bases are carried out using the *ab initio* DFT code SIESTA [20, 21]. We use the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation for the exchange-correlation potential. [22] The core electrons are represented by improved Troullier-Martins pseudopotentials, and a numerical atomic orbital basis with polarization is used for the valance electrons. All total energy calculations were done with a double-ζ plus polarization (DZP) basis set.

Results and discussion

The fact that nucleic acid bases have several component atoms implies that a full simulation of the adsorption process should involve a number of degrees of freedom (as depicted in Fig. 1). Hence, in our calculations the variation of the substrate separation, adsorbate internal coordinates and rotational orientation have not been considered. It should be further noted that separately optimized geometries for the carbon substrates and nucleic acid bases were used in the combined system. The initially configuration of all five nucleic acid bases were assigned so that their aromatic rings are oriented almost exactly parallel to the CNT surface. For instance, the cytosine acid approaching to the outer surface of the nanotube has been represented in Fig. 2(a).

Figure 1. Equilibrium geometry of nucleic acid bases were terminated with a methyl group where the bond to the sugar ring has been cut. (a) adenine, (b) cytosine, (c) guanine, (d) thymine, and (e) uracil.



To evaluate the stability of nucleic acid bases/CNT complexes, we first optimized the structures of a complex between nucleic acid bases and CNT by DFTB method, then calculated the binding energy of the considered systems via the *ab initio* DFT calculations by using the equation:

$$E_b = E_{CNT-NAB} - E_{CNT} - E_{NAB} \qquad (1)$$

where $E_{CNT\text{-}NAB}$ is the total energy of the CNT with an adsorbed nucleic acid base (NAB) molecule, E_{CNT} the pure CNT and E_{NAB} is the total energy of the isolated nucleic acid bases. After full structural optimization of the considered NAB/CNT systems, we found that the guanine/CNT system is the most stable complex, consistent with the result of Gowtham *et al*. [7]. The binding energy for the energetically favorable complex and the equilibrium distance between the closest atom of the guanine to the nanotube (C in the CNT and N in the guanine) are about -0.481 eV (-11.103 kcal/mol) and 3.016 Å, respectively. The obtained binding energy is comparable with the first principles results of Gowtham *et al*. that reported the binding energy of about -0.49 eV for the guanine base approaching the substrate of (5, 0) CNTs. The presented results suggest that guanine is weakly bound to the nanotube sidewall, having adsorption energies comparable to that for amino acid bases and gas molecules (see for instance Ref. [23-27], which reported adsorption energies in the range of about -0.1 to -0.8 eV). The relatively far equilibrium guanine-carbon substrate separation, small adsorption energy, and absence of significant charge localization associated in strong chemical bonds all suggest the involvement of only non-covalent interactions in the adsorption. Furthermore, the results show that the bond lengths of guanine exhibit only small changes during its binding to the CNT (the lengths of the C–O bond, C–C bond (bond between pentagon and hexagon rings) and the C–N bond (out of rings) of guanine change from 1.228 to 1.229 Å, 1.404 to 1.405 Å and from 1.373 to 1.377 Å, respectively). The calculated binding energies E_b for the energetically favorable adenine/CNT, cytosine/CNT, thymine/CNT and uracil/CNT complexes are summarized in Table 1(a). These results indicate that the nucleic acid bases are also weakly bound to the nanotube sidewall, having adsorption energies comparable to that for the guanine base, amino acids and gas molecules. We found also that nucleic acid bases possess different interaction strength and calculated binding energies follow the hierarchy G > U > T > A > C. The present results is however in contrast to the results of Gowtham *et al*. in which the interaction strength of nucleic acid bases was ordered as G > A > T > C > U. This disagreement indicates that interaction strength of bases molecules depend to the tubes curvature.

To further investigate the interaction between nucleic acid bases and carbon nanotubes, similar calculations has been carried out for the insertion of nucleic acid bases inside the nanotube. A schematic representation of a base molecule, for instance cytosine molecule, inserted inside the nanotube has been given in Fig. 2(b). The calculated binding energies for optimized systems are given in Table 1(b). The most stable complex is found to be the cytosine/CNT system, which follow the uracil/CNT complex. Other complexes have positive binding energies, which seems to be unstable. The results reveal that adsorbed nucleic acid bases on the outer surface of CNTs are most stable than that inside the inner surface of nanotube sidewalls. The schematic representation of the optimized geometric structure of the considered systems is shown in Fig. 3. As it can be seen from the figure when base molecules inserted inside the tube, the nanotube shape deviates from a cylinder. It is well known that this deformation is due to the repulsive energy between nucleic acid bases and nanotube side-wall [28].

The adsorption processes modeled here suggest that if for specific applications nucleic acid bases or even entire DNA are to be attached on the nanotubes through the bases discussed in this paper, then doing so through guanine base may give the most favorable results. Though additional modeling may be necessary, the current results provide base information on possible contributions of nucleic acid bases chain-terminating methyl groups.

Table 1. Binding energy E_b of the DNA/RNA nucleic acid bases (a) on the outer surface of a (10, 0) single-walled CNT and (b) inside the nanotube

Table 1(a)

Complex Base/CNT	Guanine	Cytosine	Adenine	Thymine	Uracil
Binding Energy (eV)	-0.481	-0.320	-0.335	-0.366	-0.380

Table 1(b)

Complex Base/CNT	Guanine	Cytosine	Adenine	Thymine	Uracil
Binding Energy (eV)	2.294	-0.369	0.997	0.027	-0.082

Figure 2. Model for adsorption states for a cytosine base molecule, (a) on the outer surface of a (10, 0) single-walled CNT and (b) inside the nanotube. The similar adsorption states have been considered for the other nucleic acid bases interacting with the carbon nanotube.

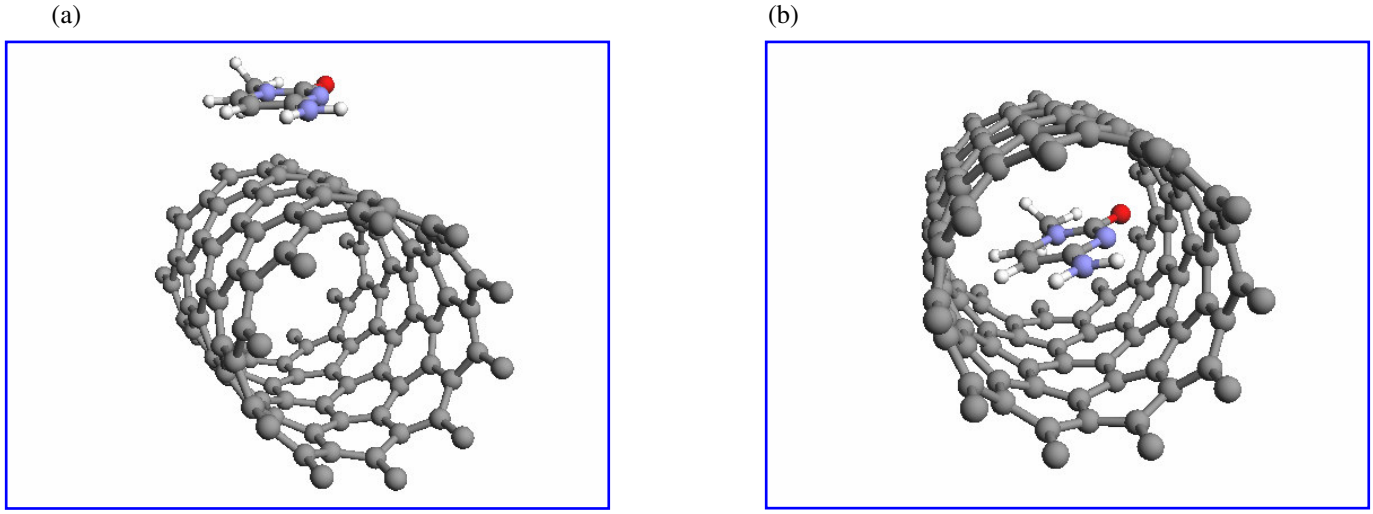
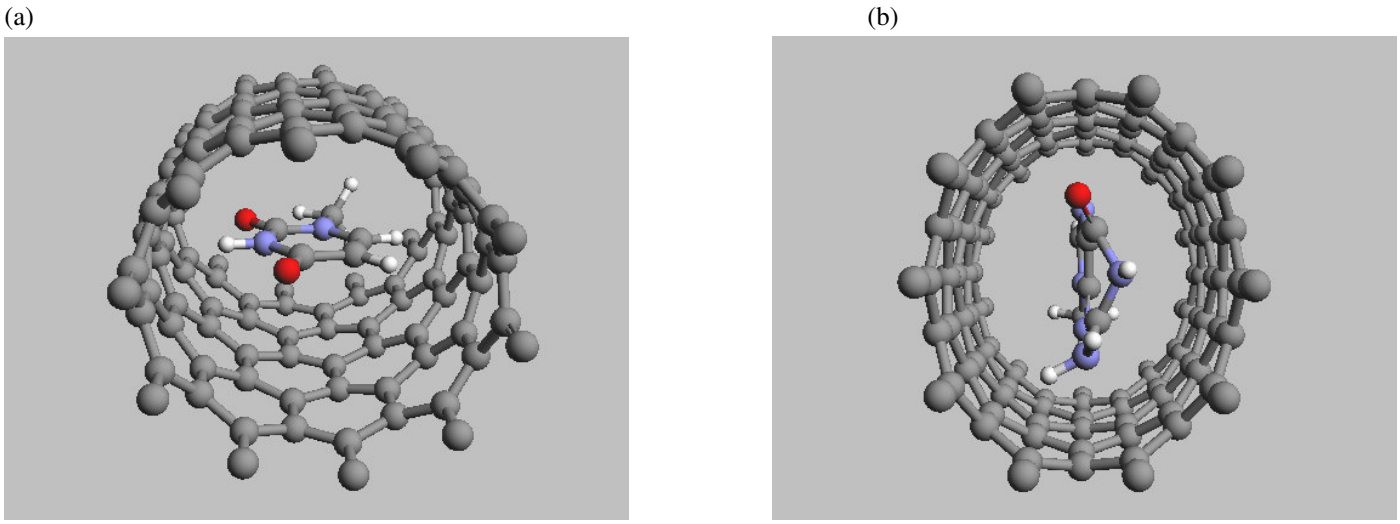


Figure 3. The optimized geometric structures of the considered configuration for (a) the cytosine and (b) guanine molecule inserted into the nanotube.



Conclusions

In light of understanding interactions with more complex biomolecules, we have looked into the interaction of the nucleic acids bases with a (10, 0) single-walled carbon nanotube by using density functional theory based treatment. It has been found that the guanine base molecule form a most stable complex with the outer surface of the nanotube wall while, the cytosine base exhibit a stronger binding with the inner surface of the side-wall. We showed also that nucleic acid bases adsorb through noncovalent interactions having adsorption energies comparable to previous results involving amino acid bases and gas molecules. Although DNA and RNA are much more complicated than these nucleic acids bases however, they contain adenine, cytosine, guanine, thymine and uracil bases. Therefore, from the calculation results involving in this paper, one can predict that DNA and RNA might readily form stable bindings with outer surface of CNTs via their base molecules.

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References

[1] Balavoine, F.; Schultz, P.; Richard, C.; Mallouh, V.; Ebbesen, T.; Mioskowski, C. *Angew. Chem. Int. Ed.* **1999**, *38*, 1912.

[2] Tsang, S. C.; Davis, J.J.; Malcolm, L.; Green, H.; Allen, H.; Hill, O.; Leung, Y. C.; Sadler, P. J. *J. Chem. Soc. Chem.Commun*. **1995**, *17,* 1803.

[3] Tsang, S. C.; Guo, Z.; Chen, Y. K.; Green, M. L. H.; Allen, H.; Hill, O.; Hambley, T. W.; Sadler, P. J. *Angew. Chem. Int. Ed. Engl.* **1997**, *36,* 2197.

[4] Chen, R. J.; Bangsaruntip, S.; Drouvalakis, K. A.; Kam, N. W. S.; Shim, M.; Li, Y.; Kim, W.; Utz, P.; Dai, H. *Proc. Natl. Acad. Sci*. **2003**, *100,* 4984.

[5] Besteman, K.; Lee, J.; Wiertz, F. G. M.; Heering, H.; Dekker, C. *Nano Lett*. **2003**, *3,* 727.

[6] Star, A.; Gabriel, J. C. P., Bradley, K., Gruner, G. *Nano Lett.* **2003**, *3,* 459.

[7] Gowtham, S.; Scheicher, R. H.; Pandey, R.; Karna S. P.; and Ahuj, R. *Nanotechnology* **2008**, *19,* 125701.

[8] Nakashima, N.; Okuzono, S.; Murakami, H.; Nakai, T.; and Yoshikawa, K. *Chem. Lett.* **2003,** *32***,** 456.

[9] Ke, P. C.; and Qiao, R. *J. Phys.: Condens. Matter* **2007**, *19***,** 373101.

[10] Yi, C.; Fong, C.-C.; Chen, W.; Qi, S.; Tzang C.-H.; Lee S.-T.; and Yang, M. *Nanotechnology* **2007,** *18***,** 025102.

[11] Star, A.; Tu, E.; Niemann, J.; Gabriel, J.-C. P.; Joiner, C. S.; and Valcke, C. *Proc. Natl Acad. Sci. USA* **2006,** *103***,** 921.

[12] Jeng, E. S.; Moll A. E.; Roy, A. C.; Gastala, J. B.; and Strano, M. S. *Nano Lett.* **2006,** *6***,** 371.

[13] Hwang, E.-S.; Cao, C.; Hong, S.; Jung, H.-J.; Cha, C.-Y.; Choi, J.-B.; Kim, Y.-J.; and Baik, S.; *Nanotechnology* **2006,** *17***,** 3442.

[14] Aradi, B.; Hourahine, B.; and Frauenheim, Th.. *J. Phys. Chem. A* **2007**, *111,* 5678.

[15] Seifert, G.; Porezag, D.; and Frauenheim, Th. *Int. J. Quantum Chemistry* **1996**, *58,* 185.

[16] Frauenheim, Th.; Seifert, G.; Elstner, M.; Hajnal, Z.; Jungnickel, G.; Porezag, D.; Suhai, S.; and Scholz, R. *Phys. Stat. Sol.* **2000**, *271,* 41.

[17] Frauenheim, Th.; Seifert, G.; Elstner, M.; Niehaus, T.; Kohler, C.; Amkreutz, M.; Sternberg, M.; Hajnal, Z.; Di Carlo, A.; and Suhai. S. *J. Phys.: Condensed Matter* **2002**, *14,* 3015.

[18] Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, J.; Haugk, M.; Frauenheim, Th.; Suhai, S.; and Seifert, G.; *Phys. Rev. B* **1998**, *58,* 7260.

[19] Elstner, M.; Hobza, P.; Frauenheim, Th.; Suhai, S.; and Kaxiras, E. *J. Chem. Phys.* **2001**, *114,* 5149.

[20] Ordejón, P.; Artecho, E.; and Soler, J. M. *Phys. Rev. B* **1996**, *53,* 10441.

[21] Soler, J. M.; Artecho, E.; Gale, J. D.; Garcýa, A.; Junqera, J.; Ordejón, P.; and Sanchez-Portal, D. J. *Phys.: Condens. Matter* **2002**, *14,* 2745.

[22] Perdew, J. P., Burke, K.; and Ernzerhof, M. *Phys. Rev. Lett*. **1996**, *77,* 3865.

[23] Peng, S.; Cho, K. *Nanotechnology* **2000**, *11,* 57.

[24] Zhao, J.; Buldum, A.; Han, J.; Lu, J. P. *Nanotechnology* **2002**, *13,* 195.

[25] Roman, T.; Dino, W. A.; Nakanishi, H.; and Kasai, H. *Eur. Phys. J. D* **2006**, *38,* 117.

[26] Ganji, M. D. *Diam. Related. Matt.* **2008** (Accepted for publication).

[27] Ganji, M. D. *Nanotechnology* **2008**, *19,* 025709.

[28] Pupysheva, O.V.; Farajian, A.A.; and Yakobson, B.I. *Nano Lett.* **2008***, 8*, 3.