

## Study of Encapsulation of Alkylamines Inside Single-Walled Carbon Nanotubes

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The density functional theory has been used to investigate the interaction between the tertiary butylamine molecule and single-walled carbon nanotubes. It has been found that tertiary butylamine molecules prefer to be adsorbed on the top of C atom of the tube side-wall. Compared to the case for carbon nanotubes with large diameters, the adsorption energy is found to be reduced in the low-curvature case. The encapsulation of the tertiary butylamine molecule inside the carbon nanotubes has also been investigated and the results show that tertiary butylamine molecules were incorporated inside the nanotubes can form more stable complex in comparison to the adsorbed molecule on the outer surface of the nanotubes. The present study provides an improved understanding in alkylamines interactions with inner/outer surface of carbon nanotubes of varying diameters.

**Key Words:** Organic compounds, Nanostructures, *ab initio* Calculations, Surface properties.

### INTRODUCTION

There has been a steady increase in interest over the past years in the interaction of carbon nanotubes (CNTs) with organic compounds<sup>1-7</sup>. The focus rested on a new way to separate the CNTs bundles into individual single-walled carbon nanotubes (SWNTs) for various practical applications. Usually this is achieved by means of ultrasonic agitation, together with the chemical functionalization of defect sites at the tube ends and side walls. However, such functionalization may damage SWNT or significantly change its properties<sup>1</sup>.

It has been shown that alkylamines can help to debundle the nanotubes without destroying them or introducing any defects into the tube structure<sup>2</sup>. Kong and Dai<sup>3</sup> by using the electrical transport measurements of SWNTs with adsorbed organic amines showed that there is a charge transfer between the amine and the nanotube. Two possible mechanisms of amine-nanotube interaction were also represented by Chattopadhyay *et al.*<sup>4</sup>. More recently, Pupysheva *et al.*<sup>5</sup> used density functional theory (DFT) method to investigate the nature of the amine adsorption on the nanotube side-wall and its role in nanotube debundling. They showed that the tertiary

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butylamine affinity for the semiconducting nanotube [CNT (10, 0)] is slightly stronger than for similar diameters metallic one [CNT (6, 6)]. They limited, however, their calculations to the adsorption of alkylamine on the outer surface of the nanotube.

In the present study we carried out geometric optimization calculations within DFT based treatment on the adsorption/encapsulation of tertiary butylamine, which will henceforth denote as tertiary butylamine (TBA), on/inside the single-walled carbon nanotubes. Furthermore, the influence of the nanotube curvature on the alkylamines adsorption on the CNTs has also been investigated. It is well-known that the main factors which influence the stability of such systems are weak but numerous non-bonding van der Waals (vdW) interactions thus, in the present study, the dispersion corrects for the van der Waals interaction have also been considered. Details on the model and computational methods employed are explained more thoroughly in the proceeding section, followed by a discussion of present results.

### COMPUTATIONAL METHODS

We employed a supercell approach in all present calculations. The unit cell of a (10, 0) single-walled carbon nanotube consisting of a ring of 40 carbon atoms with a diameter of about 8 Å was repeated three times along the tube axis. In the direction perpendicular to the tube axis, a distance of at least 18 Å was kept between repeated units to avoid interactions between adjacent CNTs. We used a  $1 \times 1 \times 3$  Monkhorst-Pack grid for k-point sampling of the Brillouin zone.

The structural optimizations of carbon nanotubes and alkylamine are carried out using the recently developed DFTB+ code<sup>8</sup>. 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 uses a tabulated set of integrals derived from *ab initio* DFT calculations<sup>9</sup>, leading to a substantial speed-up of the method since explicit integration is not required in the method. 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. Further details of the method have been fully reviewed by reported method<sup>8-11</sup>. In this work the Slater-Koster (S-K) type parameter set<sup>12</sup> was implemented. The dispersion corrects for the van der Waals interaction have been considered *via* the Slater-Kirkwood type model<sup>13</sup>.

The total energy calculations for the interaction between CNTs and alkylamine are carried out using the *ab initio* DFT code SIESTA<sup>14,15</sup>. We use the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange-correlation potential<sup>16</sup>. The core electrons are represented by improved Troullier-Martins pseudopotentials and a numerical atomic orbital basis with polarization is used for the valence electrons. All total energy calculations were done with a double- $\zeta$  plus polarization (DZP) basis set. From the well known expression for calculating the molecular adsorption binding energies,  $E_{\text{ads}}$  are obtained for various cases of our study.

$$E_{\text{ads}} = E_{\text{CNT-TBA}} - E_{\text{CNT}} - E_{\text{TBA}} \quad (1)$$

where  $E_{\text{CNT-TBA}}$  is the total energy of the CNT with an encapsulated/adsorbed tertiary butylamine molecule,  $E_{\text{CNT}}$  is the pure CNT and  $E_{\text{TBA}}$  is the total energy of the isolated tertiary butylamine molecule.

## RESULTS AND DISCUSSION

In this section we discuss the adsorption binding energy values of adsorbed TBA molecule on the outer side-wall of (10, 0) SWCNT. Four different sites were tested, including the top site of the carbon atom (C), the hollow site of the hexagon ring, the bridge site over an axial C-C bond and the bridge site over a zigzag C-C bond, as shown in Fig. 1(a)-(d), respectively. In all the configurations<sup>5</sup>, the amine molecule is initially oriented so that the nitrogen atom is the closest to the nanotube surface. After full structural optimization, the TBA molecule always locates on the top site of the carbon atom [Fig. 1(a)], regardless of the initial location. Fig. 2 represents the optimized geometric structure of the considered systems. The binding energy for the energetically favourable complex and the equilibrium distance between the closest atom (N) of the TBA to the C atom of the nanotube are about -0.57 eV (-13.17 kcal/mol) and 2.78 Å, respectively, in agreement with the *ab initio* DFT-GGA result of Pupysheva *et al.*<sup>5</sup> in that the adsorption binding energy is -0.59 eV. The present result differs however from the work of Pupysheva *et al.*<sup>5</sup> in the most favourable states. This difference may be due to the consideration of nonbonding van der Waals interactions in the present DFTB calculations, which influence the stability of such systems.

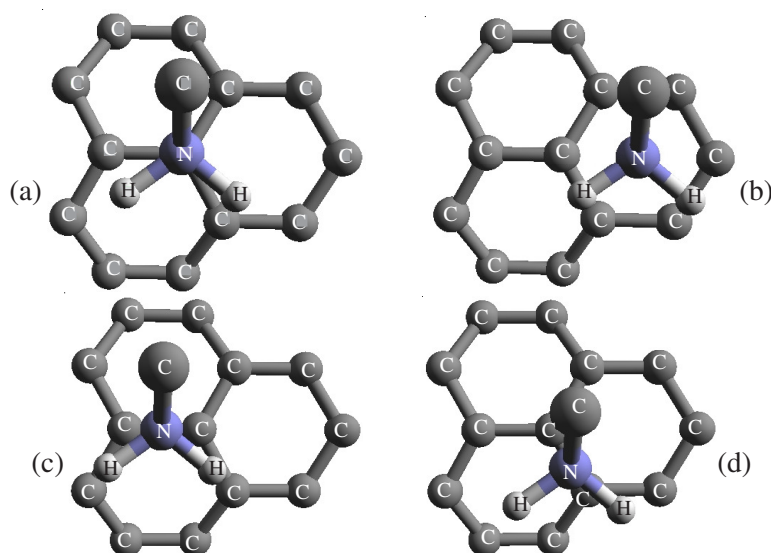


Fig. 1. Four different configurations of tertiary butylamine molecule (a) over a carbon atom, (b) above the center of a hexagon of carbon atoms and upon the centers of two non-equivalent C-C bonds (c) parallel and (d) non-parallel to the nanotube axis. (The nanotube axes are horizontal. Only amine group with adjacent carbon atom is shown for tertiary butylamine)

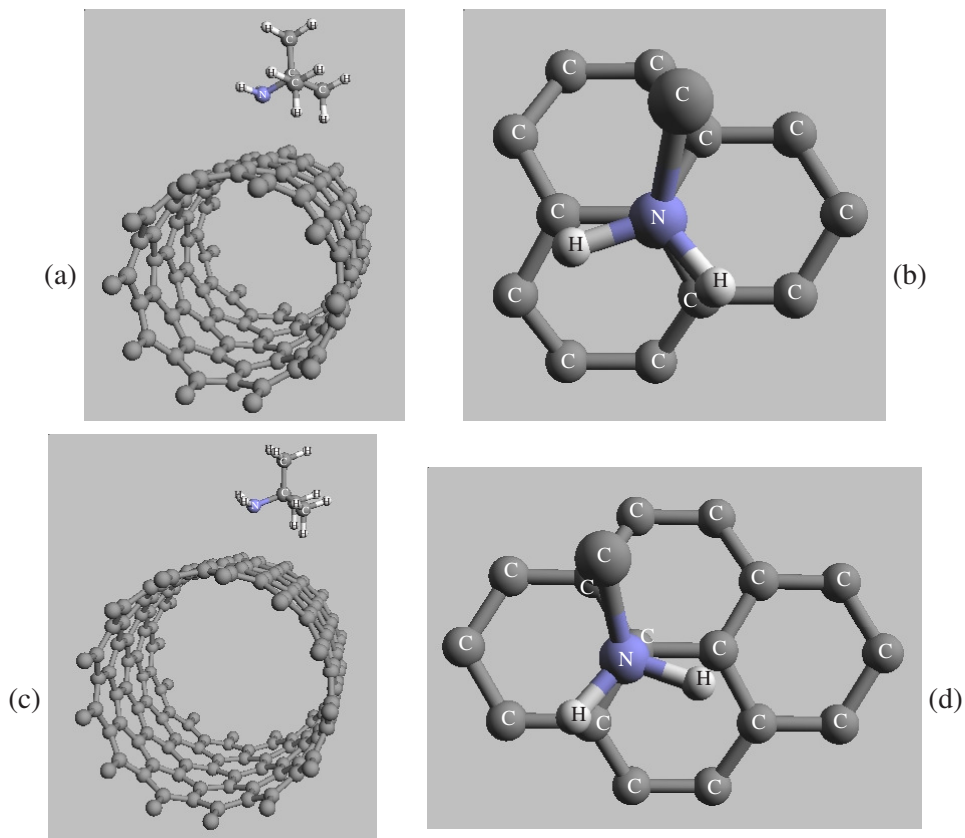


Fig. 2. Energetically favourable orientations of tertiary butylamine molecule regarding CNT (10, 0) [(a), (b)] and CNT (13, 0) [(c), (d)], obtained by the optimization of the starting configurations of the Fig. 1

We furthermore calculated the charge transfer between the TBA molecule and the CNT. It is found from Mulliken analysis that  $0.03 e$  charge transferred from the  $\text{NH}_2$ -group to the nanotube, consistency with the both experimental<sup>3</sup> and theoretical results<sup>5</sup>. The relatively far equilibrium TBA-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. The present results reveal also that alkylamines are weakly bound to the outer surface of the nanotube, having adsorption energies comparable to that for amino acids, nucleic acid bases and gas molecules on carbon nanotubes<sup>7,17-25</sup>, which reported adsorption energies in the range of about  $-0.1$  to  $-0.8$  eV).

We now investigated the adsorption of TBA molecule on the outer surface of a larger diameter (lower curvature) (13, 0) SWCNT. Following a similar procedure employed in the previous system with CNT (10, 0), we started by carrying out the optimization process for the TBA molecule approaching to the side-wall of the (13, 0)

SWCNT. Our results of calculation show that the top site of the carbon atom of the tube is the most stable adsorption site for the TBA molecule, with a binding energy of  $-0.55$  eV ( $-12.69$  kcal/mol) and a C-N binding distance of  $2.85$  Å. Comparing these results with those obtained for the TBA/CNT (10, 0) system, we clearly see that the binding energy of the TBA molecule is substantially increased for physisorption on small-diameter CNTs with high curvature. As we know the curvature allows the TBA molecule to approach the surface more closely and hence leads to a stronger binding to the nanotube side-wall.

To further investigate the interaction between alkylamines and CNTs, it is also evaluated the encapsulation of the TBA molecule inside the (10, 0) and (13, 0) SWCNTs. We first incorporated the TBA molecule inside the CNTs at the center of the tubes and then performed the optimization procedure for the considered complexes. The optimized geometric structure of the considered systems is represented in Fig. 3. As one can see from the figure the TBA molecule prefers to reside closely to the inner side-wall of the (13, 0) CNTs while, for the TBA/CNT (10, 0) complex the TBA molecule resides at the center of the tube. The calculated binding energies for incorporated TBA inside the (10, 0) CNT and (13, 0) CNT are  $0.11$  and  $-0.98$  eV, respectively. It can be seen from the obtained binding energies that the encapsulated TBA molecule inside the (10, 0) CNTs has positive binding energy (endo-thermic process) which is thermodynamically unfavourable (metastable) while the encapsulated TBA molecule inside the (13, 0) CNTs can form the stable complex (negative binding energy). Interestingly, for encapsulated TBA molecule inside (13, 0) nanotubes present results show 43 % increase in adsorption binding energy compared to adsorbed molecule on the (13, 0) tube and also 41 % increase compared to adsorbed molecule on the (10, 0) tube. From the discussions of these present results, it is evident that alkylamines might readily form more stable bindings with the inner surface of carbon nanotubes in comparison to the outer sidewall of the tubes.

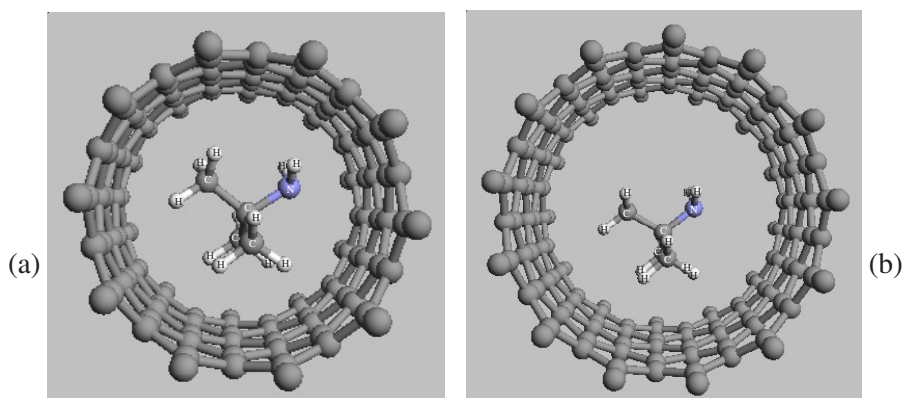
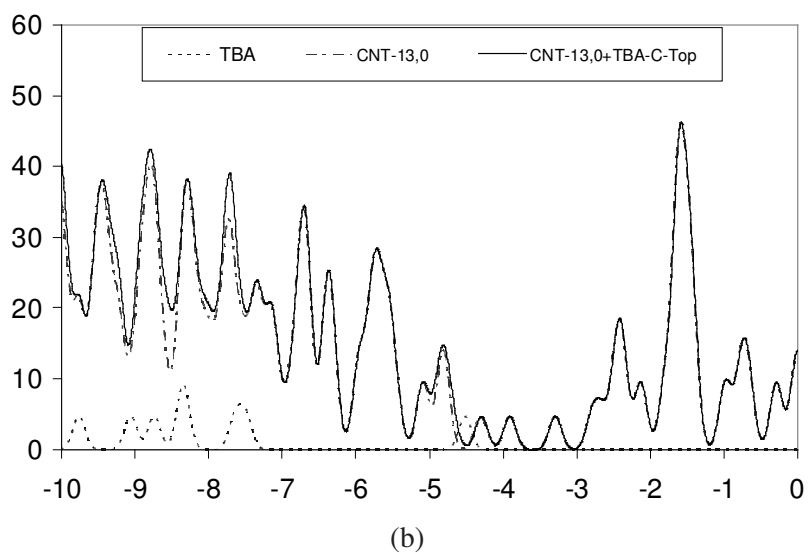
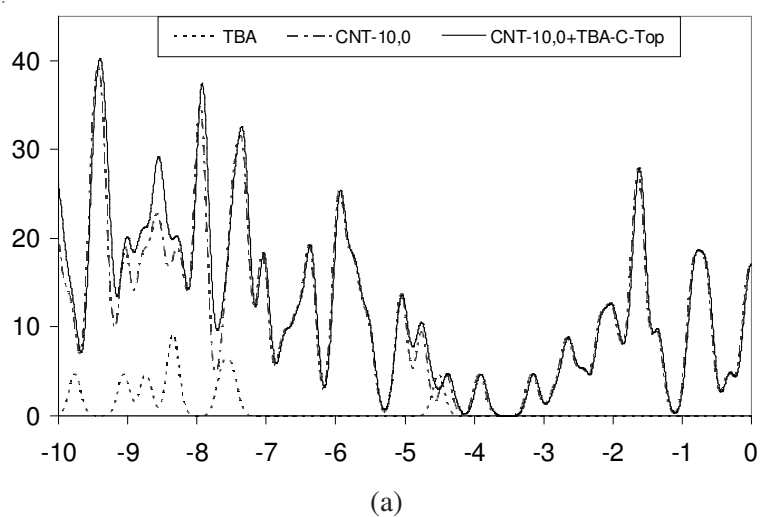


Fig. 3. Optimized geometric structures of the encapsulated TBA molecule inside the (a) CNT (10, 0) and (b) CNT (13, 0)

To further understanding of the interaction between the alkylamines and CNTs, the density of state (DOS) for the combined system of TBA/CNTs was also and compared with the corresponding density of state (DOS) for the individual parts, *i.e.*, CNT and TBA molecule separated. Fig. 4 shows the total electronic density of state for the considered systems. It can be seen from the figures that the density of state of the combined system is almost exactly the superposition of the density of state of the individual parts. This finding highlights that the TBA and CNTs are interacting rather weakly and that no significant hybridization between the respective orbitals of the two entities takes place, the unveiling the small interaction obtained quantitatively in terms of binding energies.



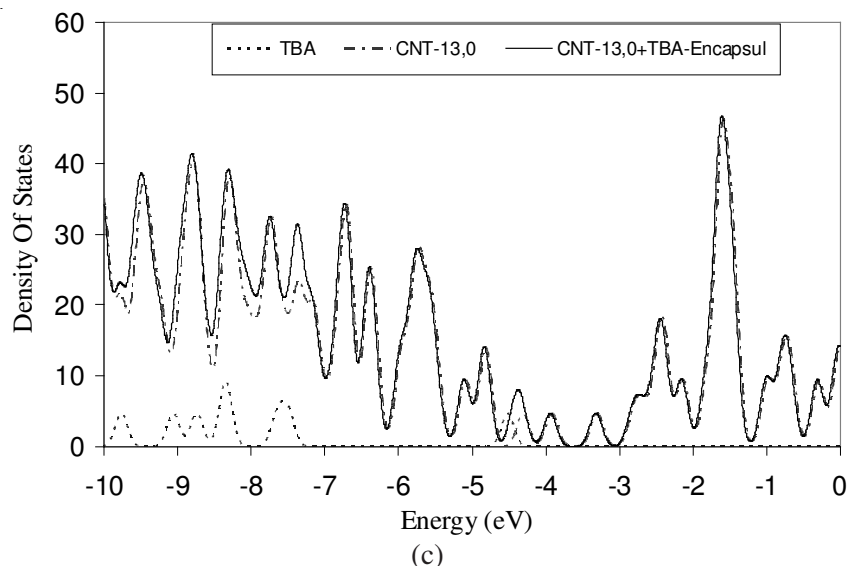


Fig. 4. Comparison between the density of states for (a) an isolated TBA molecule (dotted curves), an isolated (10, 0) carbon nanotube (dashed curves) and the adsorbed TBA on the CNT at equilibrium geometry (CNT+TBA), (solid curves). (b) and (c) represent the obtained results for the TBA molecule adsorbed on the CNT (13, 0) and encapsulated inside the CNT (13, 0), respectively

## Conclusion

In summary, we have investigated the interaction of the TBA molecule with the (10, 0) and (13, 0) CNTs by using the density functional theory (DFT) based treatments. From the calculations, the TBA molecule is found to be adsorbed on the C atom of the tube surface of both (10, 0) and (13, 0) CNTs. When comparing the results for physisorption on the small-diameter CNTs [high curvature (10, 0) CNT] considered with those on large-diameter CNTs ((13, 0) CNT), it is observed that the interaction strength of alkylamines with the outer surface of tubes is smaller for the large-diameter tubes. Thus, it appears that introducing surface curvature increases the binding energy between the alkylamine molecule and the substrate.

We have also investigated the encapsulation of the TBA molecule inside the carbon nanotubes. The results indicated that there is a considerable increase in the adsorption binding energy of the order of 40 % due to the encapsulation of the TBA inside the CNTs, which will definitely affect the alkylamines adsorption by carbon nanotubes. This result may prove to be an interesting one that needs more attention on the aspect of encapsulation inside single walled carbon nanotube and also other nanostructures.

## ACKNOWLEDGEMENT

The authors gratefully acknowledged the support of this work by the Azad University of Ghaemshahr.



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(Received: 8 October 2009;

Accepted: 5 May 2010)

AJC-8666