THEORETICAL MODELLING OF THE GLYCINE RADICAL ADDITION TO CARBON NANOTUBES*

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Abstract. The addition reactions of the C-centred and the N-centred Glycine radicals to the side walls of an armchair (4,4) Single Walled Carbon Nanotube are investigated by density functional theory. It is found that the N-centred Glycine radical binds strongly to the tube, having an interaction energy of 22 kcal/mol. In contrast the C-centred radical which is 22.7 kcal/mol lower in energy than the N-centred radical, has no binding energy upon addition to the tube walls.

1. INTRODUCTION

Since their discovery in 1991 [1], carbon nanotubes (CNT) have attracted considerable interest in nanotechnology due to their unique shape. Their outstanding mechanical and electronic properties have made them promising materials for new applications such as nanoelectronic devices, fuel storage materials, and energy capacitors [2,3]. However, few applications have so far been reported in biology. The selective opening and closing [4] at the ends of nanotubes provide many opportunities of conducting experiments with biological macromolecules in nanoscale test tubes. The immobilization of oligonucleotides and proteins can be done either inside [5] or outside [6] the nanotubes, without losing their activity and immunological [8,9] properties. This is an example of the potential applications of carbon nanotubes in biomedicine as drug or vaccine [10] carriers and biomolecular recognition.

One basic way to understand the interaction of nanotubes with biomolecules is by means of theoretical modeling. Furthermore, we can predict new properties or model the interactions with new molecules such as peptides and proteins, which have not been studied experimentally yet.

In this study, we examine the '*direct*' interaction of Glycine radical with the walls of a (4,4) armchair carbon nanotube. The Glycine radicals have been successfully produced [11] in the gas-phase reaction of positively charged phenyl radicals with the neutral Glycine molecule. Several other studies [12] have reported the interaction of peptides or aminoacids with functionalized CNTs, but to the best of our knowledge, this is the first study regarding the decoration of pure CNTs with amino acids.

2. COMPUTATIONAL DETAILS

In this letter we investigate structural and energetic properties of CNTs decorated with the Glycine radi-

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cal. We use the Density Functional Theory (DFT) in the cluster approximation. A large enough part of an armchair (4,4) Single Walled Carbon Nanotube (SWNT) containing 56 carbon atoms (or 3 hexagon layers) was separated and treated as an individual system. The dangling bonds at the ends of the tubes were saturated by hydrogen atoms. The resolution of identity DFT (RI-DFT [13]) as implemented in the TURBOMOLE [14] program package in combination the BP86 exchange-correlation functional (Becke 88 exchange and Perdew 86 correlation functionals) along with the SVP auxiliary basis set was employed for the geometry optimizations. All the structures discussed are fully optimized without any symmetry constraints.

3. RESULTS AND DISCUSSION

We are first investigating for the most stable isomers of Glycine radical. Among the possible isomers are the ones from which one hydrogen atom is abstracted either from a) the aC-atom, or b) the N-atom. The most stable conformation found for the C-centred and the N-centred radicals are presented in Fig. 1, with the C-centred favoured over the N-centred isomer by 22.7 kcal/mol. This is in reasonable agreement with the values of 18.5 and 19.9 kcal/mol reported in other ab initio studies [11,15].

The most stable geometries for the complexes of the C- and N-radicals with the (4,4) CNT are shown in Fig. 2. The $C_{tube} - \alpha C_{glycine}$ single bond is 1.61 Å, while the $C_{tube} - N_{glycine}$ is 1.50 Å. The N-centred cluster shows analogous structural characteristics to those reported by Zhao *et al.* [16]. These authors have studied the chemical reactivity of CNTs to Amidogen (·NH$_2$), a species similar to the Glycine radical (·NHCH$_2$COOH). The binding energy for each radical is calculated by the equation:

$B.E_{(radical-CNT)} = E$(CNT-radical)-E(CNT)-E(radical). In fact, the C-radical is endothermic by 1.5 kcal/mol, whereas the N-radical shows a large negative binding energy of 22.0 kcal/mol. We have found similar binding energies for the reaction among NH$_2$ and CNTs using other DFT functionals and computational codes. We were unable to reproduce the value of Zhao *et al.* [16] of 48 kcal/mol.

The difference between these two isomers can be explained by the nature of the newly formed bond between the tube and Glycine. In the first case (C-centred radical), a single covalent $C_{glycine} - C_{tube}$ bond of 1.6 Å is formed, which has no significant electron transfer. In contrast, the N-centred isomer has a $N_{glycine} - C_{tube}$ bond, which is shorter (1.5 Å) and shows a substantial electron transfer. The nitrogen atom is negatively charged by about 0.3|e|.

Furthermore, the stability of these isomers can be explained if we consider the stereochemical repulsions between the tube and the radical. In the first case, strong repulsions exist, because of the fact that the whole backbone of the Glycine can interact with the tube walls. In the second case, only the NH group is close enough to the tube walls, so that strong repulsions are avoided.

We have also investigated the potential energy curves of the Glycine (N-radical) addition/dissociation to/from the tube walls. We consider two cases. In the first case, we keep fixed the $N_{glycine} - C_{tube}$ distance and optimize all other degrees of freedom, repeatedly for several distances, from 1.5 Å to 10 Å. In this way, we examine the chemisorption of the Glycine to the tube. In the second case, the Glycine radical approaches the tube walls from very large distances. At every step, all degrees of freedom are kept frozen. Consequently, we can construct the physisorption plot of the Glycine to the tube walls. These two adsorption phenomena are presented in Fig. 3 by a continuous line (Chemisorption) and a dashed line for the Physisorption. We clearly see two minima in the Fig. 3. The first minimum at 1.5 Å corresponds to the chemical adsorption of the radical to the tube walls, whereas the second minimum at 3.25 Å to the physical adsorption. The physisorption minimum is also verified by the dashed line. The value for the physisorption energy is estimated to be about 1 kcal/mole. A similar value has been reported [17] for the physisorption energy and equilibrium distance of the ammonia molecule to CNT walls.

The cluster that we study, is a system with one unpaired electron. When the two fragment molecules are far apart, the spin density is mainly located on
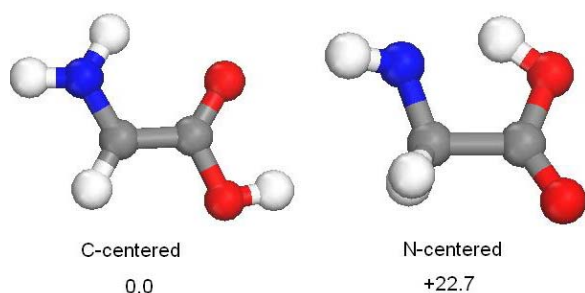

C-centered
0.0

N-centered
+22.7

Fig. 1. The most stable isomers of the Glycine radical.

C-centered
+ 1.0 kcal/mol
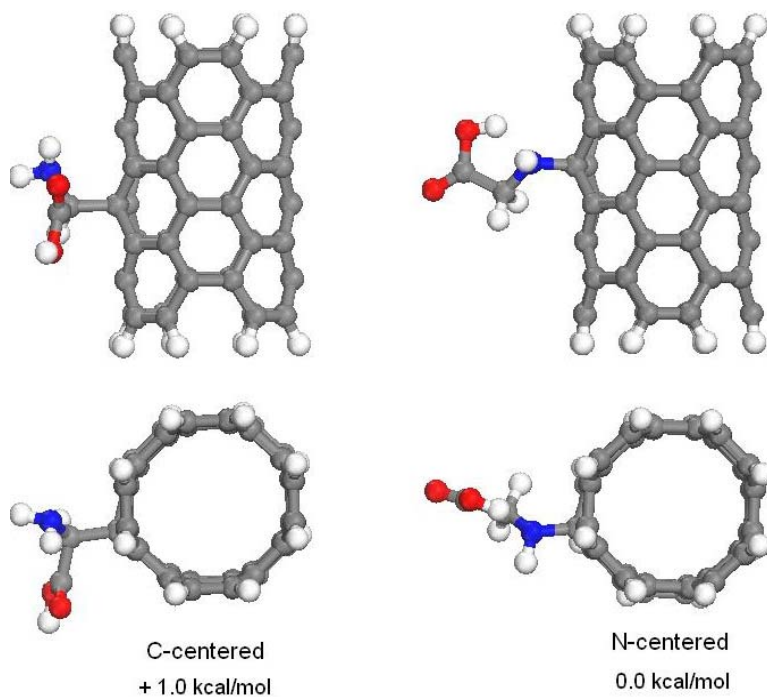
N-centered
0.0 kcal/mol

Fig. 2. Geometry optimized structures of the clusters Glycine$_{radicals}$ – CNT.

the nitrogen atom of the Glycine (with a value of 0.86). When the two fragments are bonded, the spin density is delocalized on the tube walls, whereas no spin density remains on the nitrogen atom. Upon separation of Glycine from the tube walls the process is reversed with the spin density on the nitrogen atom starting to increase, and finally at long distances it receives its initial value. From the inset plot in Fig. 3, we clearly see that at 3.7 Å the spin density on the nitrogen atom has received its final value and practically no interaction between CNT and Glycine radical exists after this distance.
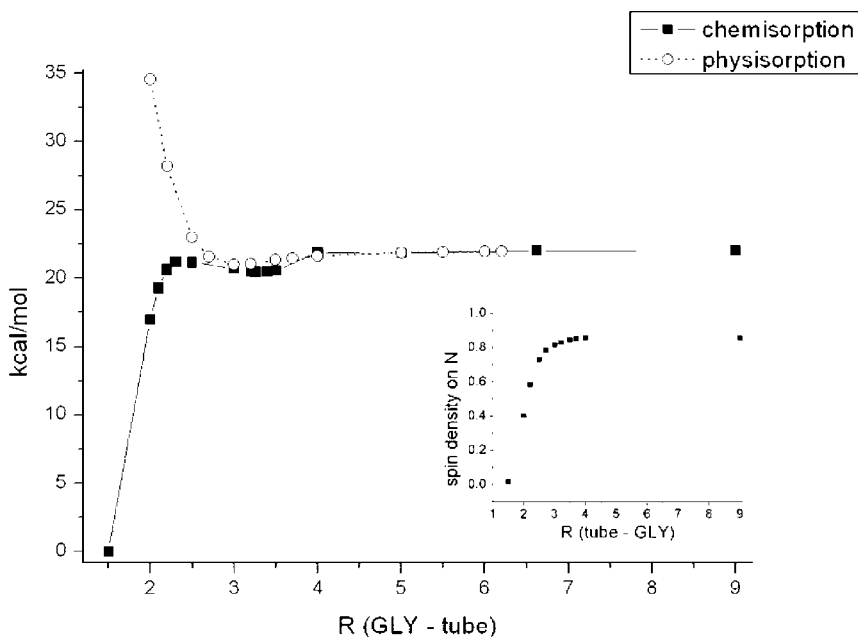

Fig. 3. Chemisorption and Physisorption energy curves of the Glycine radical to the tube walls. *Inset picture:* Plot of the spin density on the N-atom with respect to Glycine-tube distance.

4. CONCLUSIONS

We have performed density functional calculations on the energetic and structural properties of a (4,4) CNT upon adsorption of various gaseous Glycine radicals. Among these clusters, more stable and with large binding energy is the cluster between CNT and N-centred Glycine. The adsorption potential curve shows two minima: a) a 22 kcal/mole at 1.5 Å, and b) a shallow minimum of approximately 1 kcal/mole at 3.25 Å.

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