

## Theoretical Semi-empirical Study of the Amino Acid Interaction with Surface of Magnesium Oxide Nanotubes

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### Abstract:

*Modelling of the quantum interaction properties of glycine radicals on the surface of the single walled magnesium oxide nanotubes (MgONTs) is investigated by MINDO/d 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<sup>2</sup>-centered) and metastable conformations with C atoms. The effects of the diameter-length characteristics of the MgONT on binding of the amino acid have been studied. Our results suggested that the binding energy is higher as the MgONT diameter increases, while as the MgONT length increases, the binding energy initially decreases. The N<sup>2</sup>-centered glycine radicals prefer to bond within the region (in and near the middle) of the MgONT. There is ability of interaction of two radicals of glycine on the surface of the MgONT.*

**Key words:** amino acid, binding energy, MgONT, semi-empirical

calculation, nanotubes.

## Introduction

Nanomaterials are of wide interest due to their scale (1-100 nm), unique optical, magnetic and electrical properties. Also nanomaterials have the potential for a great impact in electronics, medicine and other fields. The nanostructures have a quantum nature due to their molecular size, thus, the prediction and understanding of these nanomaterials should be based on experimental and theoretical research. The question is how can the experiments reach the atomic level to achieve nano-measurements? Carbon nanotubes (CNTs) the first nanotubes (discovered by Iijima) can be considered as sheets of graphite wrapped to a cylindrical form [1]. Also, there are other nanotubes, such as magnesium oxide nanotubes, where some studies tried to investigate the adsorption of CO and NO molecules on their surfaces ( as illustrated in scheme 1) [2, 3]. Others noted that doping the magnesium oxide nanotubes by impurity TM atom, allows a noticeable enhancement of nucleophilic reactivity ability of MgO nanotube, as shown in scheme 2. The high adsorption energy is found when CO adsorbs on 3-fold Pt in Pt-doped magnesia nanotubes, implying that this kind of the doping TM atom has a significant influence on the chemical reactivity [4]. The studies of the IR, Raman spectra and properties of nonlinear optical (NLO) of MgO nanotubes depend on the density functional theory. This theory (DFT) shows that the IR spectra are matched closely to those in the corresponding MgO cluster and bulk materials [5]. Structural information for neutral magnesium oxide clusters has been obtained by a comparison of their experimental vibrational spectra with predictions from theory. The comparison shows that clusters of the composition (MgO) form

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hexagonal tubes like structures containing hexagonal MgO rings [6]. The first principle calculation with a topological method combined is used to examine isomer structures and to search for the potential energy surface of  $(\text{MgO})_n$  clusters with  $n = 2-7$ . Many new metastable isomer structures have been established. The growth pattern of MgO clusters can be classified into three motifs: the expansion of two-dimensional ring-like structures, the combination of basic units like quadrangle and hexagon, and the addition of atoms to smaller-sized clusters. The size-dependent stability and electronic properties of MgO clusters are analyzed. A hexagonal ring-like unit is found highly stable for  $(\text{MgO})_n$  clusters, while the  $(\text{MgO})_5$  cluster is not as stable as the clusters of other sizes [7,8]. The ability of nanotube to penetrate into cells offers the possibility of using nanotubes for delivery of drug and antibiotic molecules without toxic effects [9–20]. Despite the wide employments of MgO nanotubes (MgONT), the theoretical studies of the interaction mechanism between the nanotubes and biomolecules are few [21, 22]. A few articles have studied the interaction of an amino acid with carbon nanotubes only [22-26].

In this work, we examined the interaction of four isomers of glycine radicals on the single-walled magnesium oxide nanotube (SWMgONT). Then, we tried to investigate this interaction as a function of MgONT length and diameter. Later, we tried to investigate the effect of changing the position of the amino acid on the surface of the MgONT on the interaction energy. Finally, we studied the ability of interaction of two radicals of glycine on the surface of MgONT.

## **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 complexity. The methods of molecular quantum mechanics can be used to investigate properties beyond the scope of current crystallographic methods. The molecular quantum techniques allowed the study of optical, magnetic and electronic properties that are not easily measured experimentally and provide 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 predict the physical and chemical nature of the hydrogen bonding interactions [27]. We used MNDO/d (Modified Neglect of Differential Overlap with d-orbital) to investigate the structural and electronic properties of CNTs decorated with the glycine radicals. MNDO/d is a version of MNDO with d-orbital capability. In addition to the previous MNDO parameter sets, parameters for several new elements are included in the implementation of the MNDO/d method, such as Na, Mg, Cd and Sn [28, 29]. The problem that arises is how to perform an accurate calculation for a nanosized system without ending in a prohibitively large computation. The resolution of MNDO/d, as implemented in the HyperChem Release 7.52 for Windows Molecular Modelling System program package (<http://www.hyper.com/>), was employed for the geometrical 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 is abstracted from either the C atom or the N atom (see Fig. 1). According to their relative stabilities ( $\Delta E$ ), it was found that the N<sup>2</sup>-centered radical is preferred rather than the N<sup>1</sup>, C<sup>1</sup> and C<sup>2</sup>-centered ones by 0.002, 18.863 and 19.404 Kcal/mol respectively, these results were obtained by using the MINDO/d method. The N<sup>2</sup>-centered radical, being preferred rather than

the C<sup>2</sup>-centered radical isomer by 19.404 Kcal/mol, which was not showing reasonable agreement with that reported in other ab initio calculations [24, 25] and semi-empirical (MNDO/3) calculations [26]. We then tested the interaction binding energy (BE), of the four isomers of the glycine radicals on the magnesium oxide nanotubes (MgONT),  $BE = E_{\text{Glycine+MgONT}} - (E_{\text{Glycine}} + E_{\text{MgONT}})$ , where  $E_{\text{Glycine+MgONT}}$  is the energy of the complex (glycine with MgONT). The C<sup>1</sup> and C<sup>2</sup>-centered glycine connects with MgONTs at the oxygen atoms of MgONT, while in issues of N<sup>1</sup> and N<sup>2</sup>-centered glycine connects with MgONTs at the magnesium atoms of MgONT. For this purpose the MgONT's diameter is 3.829 Å and its length 7.845 Å. We found that upon reaction with the single tube wall, where the glycine radical forms stable complexes when the MgONT reacts with the nitrogen atom (N<sup>2</sup>-centered) and metastable conformations with the carbon atom (C<sup>2</sup>-centered), as shown in Fig. 2 along with their relative stabilities ( $\Delta E$ ) and relative binding energies ( $\Delta BE$ ). There is an increase in the density ( $\Delta \rho$ ) relative to the C<sup>1</sup>-centered radical density, so that the viscosity of the complex will increase and the ability of penetration decreases. According to the bonds between the glycine radicals and MgONTs, the N<sup>1</sup> and N<sup>2</sup> centered offer long a bond as compared with the issues of C<sup>1</sup> and C<sup>2</sup> centered. Conformity to the binding energy (Dissociation Energy) of the N<sup>1</sup> and N<sup>2</sup> centered with MgONT may be classified within the hydrogen bonds. Moreover, during this present study we will adopt the the N<sup>2</sup>-centered only to study the interaction of the glycine radical with MgONT. The first interesting factor is the interaction of glycine with MgONT as a function of the MgONT diameter, so that the MgONT which adopted with a length equal to 7.774Å. In the N<sup>2</sup>-centered glycine binding the single covalent  $N_{\text{Glycine}}-Mg_{\text{MgONT}}$  bond is formed on the middle of the MgONT surface. The effect of increasing the MgONT diameter on the BE of the N<sup>2</sup>-centered glycine radicals on the MgONT is shown in Fig. 3. Where an increase in the diameter of the MgONT leads to a

slight decrease in the binding energy of the N<sup>2</sup>-centered glycine radicals on MgONT, the BE increases gradually until the MgONT diameter is 6.092Å, while a rapid decrease took place later. There is no continuous decrease or increase in BE as a function of the MgONT diameter, such as investigated in the case of the carbon nanotubes diameters [26]. This case is not an indication for a good mechanism to lower the binding energy between the amino acid and MgONT as the MgONT diameter increases. The N<sub>Glycine</sub>-Mg<sub>MgONT</sub> bond does not impact due to the increase in the diameter of the MgONT (see Fig. 4). The N<sub>Glycine</sub>-Mg<sub>MgONT</sub> bonds showed rapid increase. The approximate increasing of the MgONT diameter showed an increase in the covalent bond length and decrease in the binding energy (see Fig. 3). If we do comparable studies between the behavior of BE and N<sub>Glycine</sub>-Mg<sub>MgONT</sub> bond with MgONT diameter, we can note three cases; the first where diameter increases from 2.68 to 3.83Å, there is no interesting change. The second, where the diameter increases from 3.83 to 6.09Å so that their behaviour differs, and the BE increases while the N<sub>Glycine</sub>-Mg<sub>MgONT</sub> bond decreases. In this case the molecular axis of glycine is parallel to the MgONT's axis. This indicates some attraction between the glycine's oxygen atom with MgONT's magnesium atoms. It is noted that, in the first case their axis are not parallel. The third where the diameter is equal to 7.11Å the glycine's axis is approximately the same as with the first case. This suggests that there is a relationship between the increase in the covalent bond length and the decrease in the binding energy which depends on the glycine's geometrical effect. The second important factor is the interaction of the N<sup>2</sup>-centered glycine radical with different lengths of MgONT. It was noticed that, as the MgONT lengths increase, there is very little increase in diameters of these MgONTs, which is approximately equal to 3.993± 0.205 Å. In each case we put the N<sub>Glycine</sub> -Mg<sub>MgONT</sub> bond on the middle of the MgONT surface. The binding energy of the N<sup>2</sup>-centered glycine radicals with MgONT depends on the

length of MgONT, as shown in Fig. 5. as the length of the MgONTs increases, the binding energy between the N<sup>2</sup>-centered glycine radicals and MgONT does not show sensible change except at MgONT length equal to 3.952Å the molecule frame of glycine were far from the MgONT surface. With few Angstroms of length, the binding energy was not changed. Thus we may adopt that the binding between the glycine and MgONT depends on the diameters of the MgONTs more than their lengths. The N<sub>Glycine</sub>-Mg<sub>MgONT</sub> bond length as a function of MgONT length is shown in Fig. 6. There is a fluctuation in its values as the MgONT length increases. Generally, the N<sub>Glycine</sub>-Mg<sub>MgONT</sub> bond decreases as the length of MgONT increases and the bond length of N<sub>Glycine</sub>-Mg<sub>MgONT</sub> is equal to 2.209±0.031 Å which shows slight change. In order to study the probe position to link the N<sup>2</sup>-centered glycine on the MgONT tube surface, we use MgONT with diameter 3.83Å and length 23.579Å. The relative stability (ΔE) of the N<sup>2</sup>-centered glycine radicals with MgONT decreases as a function of the N<sub>Glycine</sub>-Mg<sub>MgONT</sub> bond position on the cylindrical surface of MgONT, where this position changes from the middle of the MgONT surface towards one of their two ends, as shown in Fig. 7. The complexes formed by the N<sup>2</sup>-centered glycine radical on the MgONT surface are more stable when the reaction occurs within the region in and near the middle of the MgONT surface, while near one of their two ends the stability is lowed. In the same time the N<sub>Glycine</sub>-Mg<sub>MgONT</sub> bond has constant length until the position 4 approximately, see Fig. 8. The N<sub>Glycine</sub>-Mg<sub>MgONT</sub> bond length decreases suddenly when N<sub>Glycine</sub>-Mg<sub>MgONT</sub> bond is linked at position approaches toward their two ends. Approximately, the N<sub>Glycine</sub>-Mg<sub>MgONT</sub> bond length has a value equal to 2.166±0.039Å. Investigating the ability of linking the two N<sup>2</sup>-centered glycine radicals on the surface of MgONT thus for this purpose the MgONT is adopted with a diameter and length 3.83Å and 23.579Å respectively, see Fig. 9. There are two issues, first: when the two N<sup>2</sup>-centered radicals of glycine

are linked at two ends of the MgONT surface and on the same side. We tried to examine the stability of the complex, when the second N<sup>2</sup>-centered radical approaches the first one. The Second issue is the same as the first, but the second radical is linked on the opposite side due to the first one. Figure 10 shows the relative stability of the complex as a function of the second glycine position relative to the first glycine, which is remaining in the same position. According to the relative stability results, the second radical of glycine will prefer to link at the position 2 on the MgONT surface and on the opposite side, see Fig. 10. Now, we adopted the former case, but each one from these two N<sup>2</sup>-centered glycine will move within the same step from the two ends of the MgONT toward the middle of MgONT surface, see Fig. 11. There are two issues; first when the two N<sup>2</sup>-centered radicals of glycine are on the same side on the MgONT surface. Examining the stability of the complex both radicals must approach each other at the same number of steps. The second issue is similar to the first, but the second radical is at the opposite side to the first radical of glycine. According to the relative stability results, the two N<sup>2</sup>-centered glycine radicals will prefer to link at the position 2 with opposite side, see Fig. 11. In another step we studied the ability of two N<sup>2</sup>-centered radicals of glycine to approach one each other around the the MgONT surface. For this purpose the MgONT is adopted with a diameter and length 7.573Å and 3.974Å respectively. Figure 12 shows the three issues of connecting the two N<sup>2</sup>-centered radicals of glycine on the surface of the MgONT. According to the relative stability, the best position was the issue 2. We realised that there was no motivating change in their relative density. If we repeat the former issue, but at the circular end of the MgONT to know the probable positions with the same dimensions of the MgONT. Figure 13 shows the three different styles of connecting the two N<sup>2</sup>-centered radicals of glycine on the circular end of the MgONT. As conformity to the relative stability, the best position for the two radicals of glycine are at

the end of the MgONT occurs at issue 3. These three issues show few differences about the density. The magnesium oxide nanotubes (MgONT) may be able to do many linkages with amino acid, in comparison with the carbon nanotubes CNTs [26].

## Conclusions

We have performed MINDO/d calculations on the structural properties of MgONT upon adsorption of various glycine radicals. Among these four isomers, the N<sup>2</sup>-centered glycine radical forms stable complexes with CNT. The results of the diameter and length of the MgONT on the binding energies with N<sup>2</sup>-centered glycine show an increase as the MgONT diameter increases, while the binding energies decrease while CNT length increases. The N<sup>2</sup>-centered glycine radicals are shown to prefer to bond within the region (in and near) the middle of the MgONT. The stereo geometry (curvature of CNT surface) between the glycine radicals and MgONT may limit the binding energies behavior. There is ability of linking of the two radicals of glycine on the surface of the MgONT.

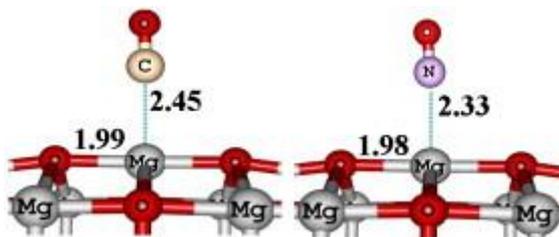
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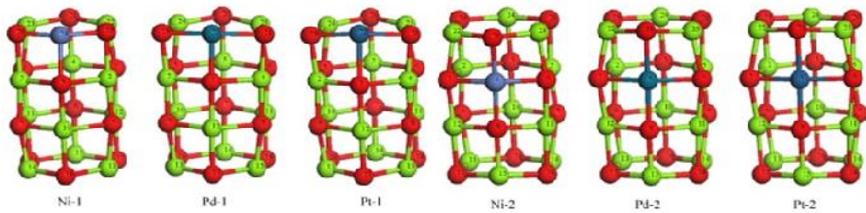
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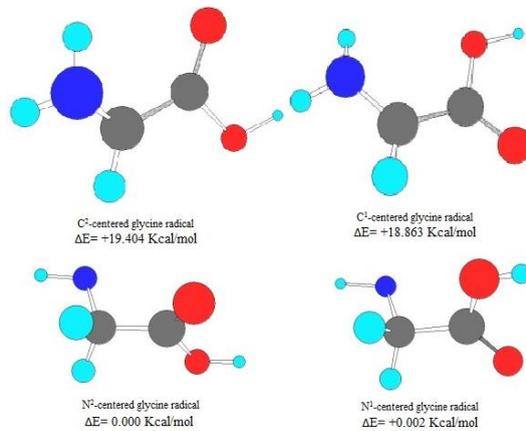
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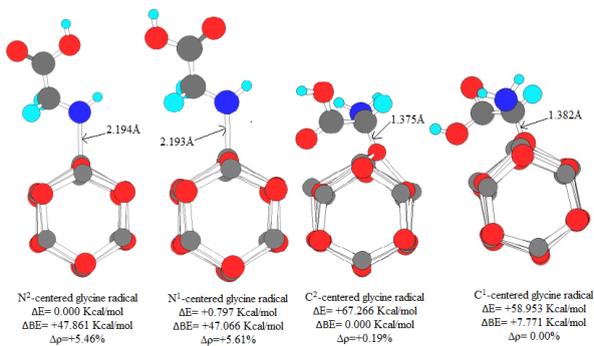
**Scheme 1.** Presentation of CO and NO adsorptions on the surface of the MgO nanotubes [2].



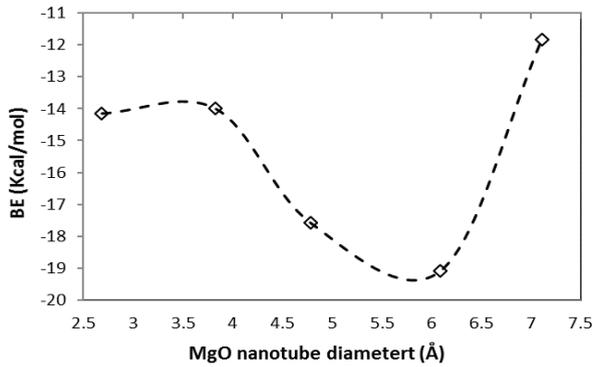
**Scheme 2.** The geometrical structures of TM-doped MgO nanotubes (TM = Ni, Pd and Pt). The green and red balls represent Mg and O atoms. The impurity atom represents TM atom [4].



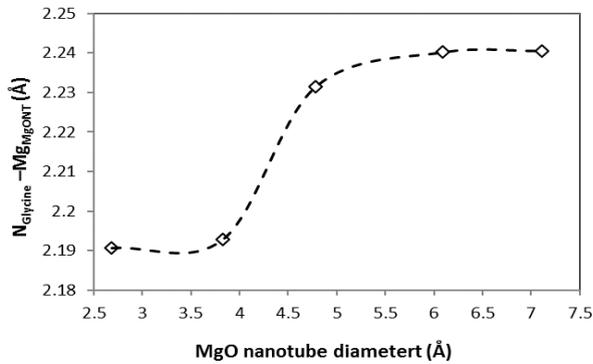
**Figure 1.** The most stable isomers of the glycine radical and their relative stability ( $\Delta E$ ).



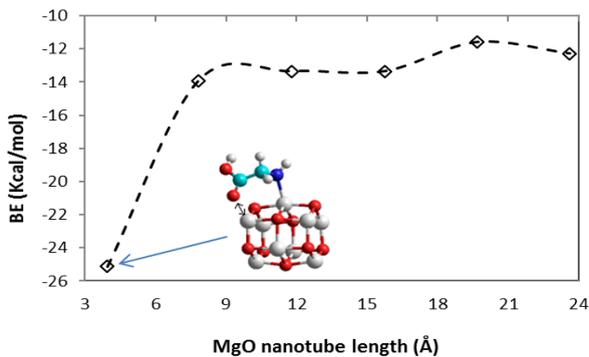
**Figure 2.** Geometrical optimized structures of glycine–MgONT.



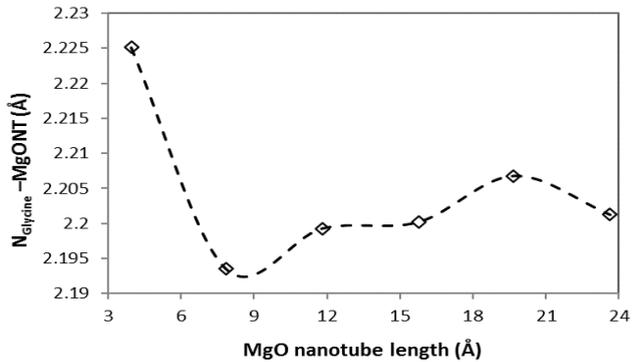
**Figure 3.** The binding energy between the N<sup>2</sup>-centered glycine radical and the Mg<sub>MgO</sub>NT as a function of the MgO<sub>NT</sub> diameter.



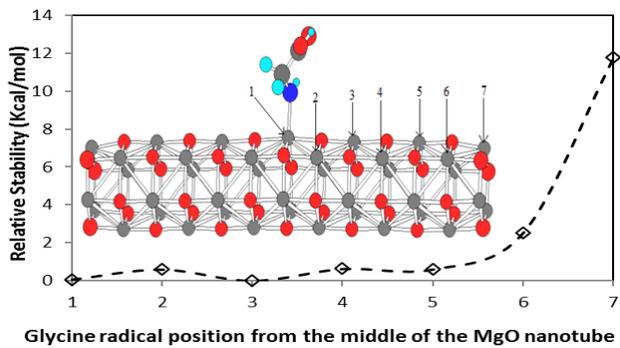
**Figure 4.** The N<sub>Glycine</sub>-Mg<sub>MgO</sub> bond as a function of MgO<sub>NT</sub> diameter.



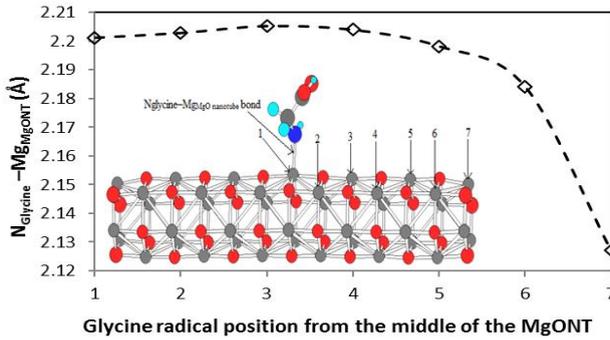
**Figure 5.** The binding energy of the N<sup>2</sup>-centered glycine radicals with the Mg<sub>MgO</sub>NT as a function of MgO<sub>NT</sub> length.



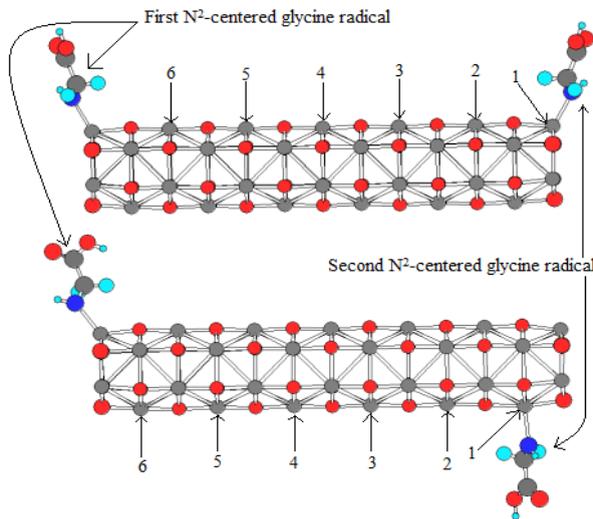
**Figure 6.** The  $N_{\text{Glycine}}-\text{Mg}_{\text{MgONT}}$  bond length as a function of the MgONT length.



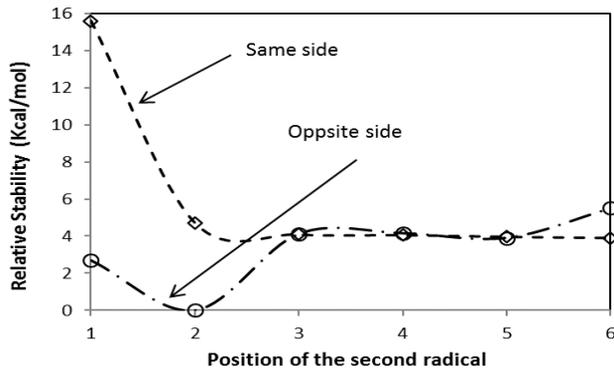
**Figure 7.** The relative stability of the  $N^2$ -centered glycine radicals with MgONT as a function of the position of the single covalent  $N_{\text{Glycine}}-\text{Mg}_{\text{MgONT}}$  bond that formed, from the middle of the MgONT toward their two ends.



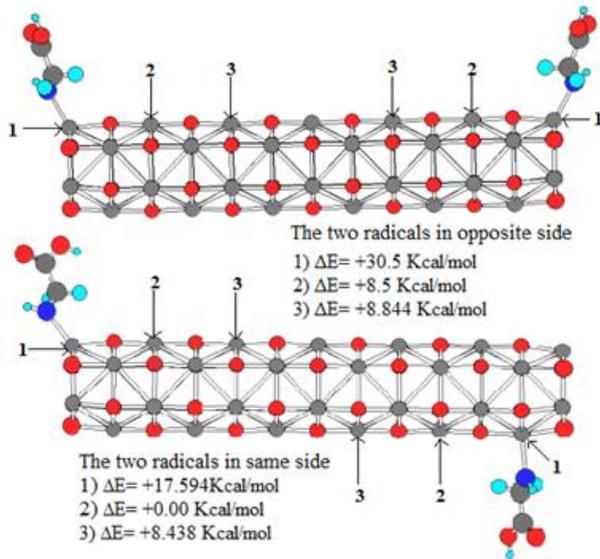
**Figure 8.** The  $N_{\text{Glycine}}\text{-Mg}_{\text{MgONT}}$  bond length as a function of the position of the single covalent  $N_{\text{Glycine}}\text{-Mg}_{\text{MgONT}}$  bond that formed, from the middle of the MgONT towards one of their two ends.



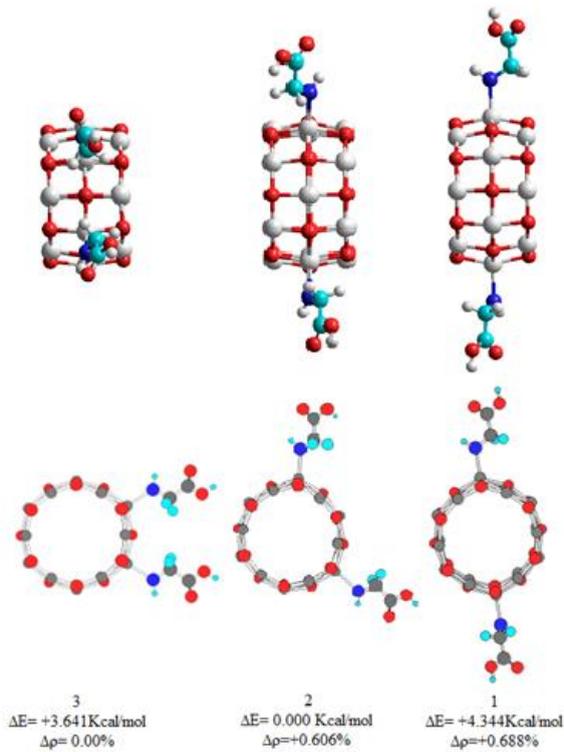
**Figure 9.** The interaction of the two radicals of glycine with the MgONTs, so that the two radicals are in same side (above) or in opposite side (below). The numbers show positions of the second radical of glycine, which must in each step toward the first radical, so that the first radical of glycine remain in the same position.



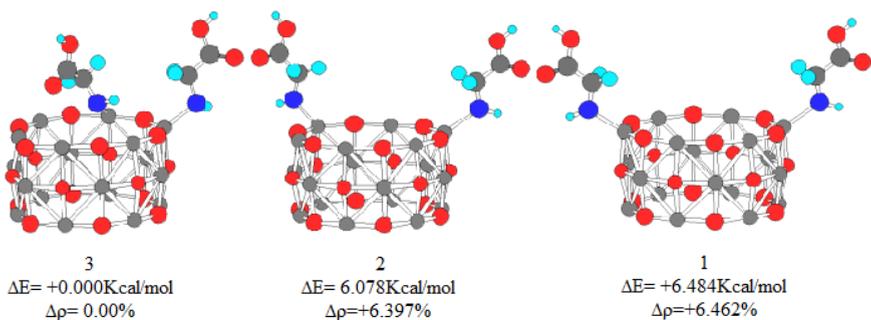
**Figure 10.** The relative stability of the complex due to the positions of the second glycine related to the first glycine.



**Figure 11.** The interaction of the two radicals of glycine with the MgONTs, so that the two radicals are in same side (above) or in opposite side (below). The numbers show positions of the two radicals of glycine, which must have the same number of position.



**Figure 12.** Shows the three issues of connect two radicals of glycine on the MgONT.



**Figure 13.** Shows the three issues of connect two radicals of glycine on the cycle end of the MgONT.