The Interaction between Glycine and Carbon Nanostructure

Fereshteh Naderi*\textsuperscript{a}, Ali Karami\textsuperscript{b}, Behjat Naderi\textsuperscript{b}
\textsuperscript{a}Department of Chemistry, Shahr-e- Qods branch, Islamic Azad University, Shahr-e Qods, Tehran, Iran.
\textsuperscript{b}Shahr-e- Qods branch, Islamic Azad University, Shahr-e Qods, Tehran, Iran

*E-mail: fnaderi2@yahoo.com

Received date: September 3, 2011

Abstract

The Density Functional Theory (DFT) based method B3LYP/6-31G** were carried out to study the interaction of carbon nanostructure with glycine. Formation energy of compounds, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and the HOMO-LUMO band gap were calculated. We present a theoretical study of the binding of amino acids (AA, namely glycine, Gly) to graphene (Gr), using density functional theory calculations. It is found that binding of Gly, to Gr thermodynamically favorable yet depend on the amino acid orientation and always very weak. The results presented in this work provide fundamental insights on the quantum interactions of glycine with carbon-based nanostructures and can be useful for developments in bio and nanotechnology fields.

Keywords: DFT, HOMO- LUMO gap, Graphene, Glycine

1. Introduction

New materials induce new applications, and this is certainly the case for graphene. This one-atom thin 2D material has been subjected to a lot of experimental and theoretical investigation, since its discovery in 2004,\textsuperscript{1} and it seems there is no limit to the number of possible applications.\textsuperscript{2} In comparison with carbon nano tubes (CNTs), graphene as a single layer two-dimensional material composed of a layer of carbon atoms forming six membered rings, presents long and reactive edges which make it not only notably more accessible to doping and chemical modification but also more susceptible to structural defects and impurities, which becomes more exciting materials being
investigated. A noteworthy feature of graphene is that the energy of the electrons is linearly dependent on the wave vector near the crossing points in the Brillouin zone, which open new ways of fabrication of new nano electronics for molecular transport, detection, and separation, and medical diagnostic purposes. Unfortunately, until now, only a few applications have so far been reported in biology, although there are many aspects yet to be investigated. The structure and stability of Gly (NH$_2$CH$_2$COOH), Pro (NH$_2$C$_4$H$_7$COOH) and Hyp (NH$_2$C$_4$H$_6$(OH)COOH) amino acids have been studied intensively in the last decade by means of experiments and theory because of their biological interest.

In this work, we present a theoretical study of the binding of glycine to graphene by means of density functional theory (DFT). DFT is a first-principles approach that has already been demonstrated to describe interactions in graphene-amino acid (Gr–AA), and DFT predictions on Gr–AA systems can be considered as reasonably accurate.

2. Computational Methods

DFT calculations based on the B3LYP exchange-correlation functional and the 6-31G** standard basis set have been performed by the Gaussian 98 package. At the first step, the investigated structures of the original model glycine (Fig. 1-a), graphene (Fig. 1-b) and graphene – glycine system (Fig. 1-c) have been relaxed during the all-atomic optimization processes.

Subsequently, the optimized properties (Table 1) have been evaluated in the optimized structures. In order to estimate the adsorption energy, $E_{\text{ads}}$, of Gly amino acids to graphene, we use the equation:

$$E_{\text{ads}} = E_{\text{system}} - (E_{\text{Gr}} + E_{\text{Gly}})$$

where $E_{\text{system}}$ is the total energy of the fully geometry optimized Gr–Gly system and the other two terms correspond to the energy of the Gr and Gly independently relaxed.

3. Results and Discussion

First, we performed a geometry optimization for the glycine and graphene and Gly–Gr systems separately. For graphene we obtain an interatomic C–C distance of 1.42 Å (see Fig. 1). These figures are in excellent agreement with previous first-principles calculations and experimental data.

Concerning the geometry relaxations, the optimized AA structures are in very good agreement with respect to previous ab initio results obtained with a LCAO implementation of DFT. Reproducibility of previously reported ab initio results and measurements provides confidence about the accuracy of the methodology employed throughout. Only neutral Gly configurations have been analyzed in this study. Zwitterions, which are the preferred configurations of AAs in water, are observed to rearrange to their neutral form upon geometry optimization (as already has been reported.
We report here the lowest-energy Gr–Gly structures resulting from our full geometry optimizations relative to the carbon surface and adsorption sites. According to this definition, and completely ignoring thermal effects, a negative value of $E_{\text{ads}}$ means that adsorption of the Gly on the Gr considered is thermodynamically favorable. For Gly, the adsorption on Gr is thermodynamically favorable (that is, $E_{\text{ads}} < 0$). In particular, the smallest $E$ value is obtained when the plane defined by atoms C–N–C in Gly is oriented parallel to the carbon surface (Table 1). This configuration bears the signature of weak π–π interactions, which are also present in Gr–aromatic amino acid complexes and CNT–DNA nucleobase hybrids.21, 29 As will be shown later, the calculated adsorption energies of Gly on Gr is negative yet quite small in magnitude ($|E_{\text{ads}}| = 20 – 90$ meV). In this most favorable case, $E_{\text{ads}}$ amounts to $-90$ meV which indicates very weak binding of Gly to the graphite sheet.

**Figure 1.** a) Glycine, b) graphene and c) graphene – glycine optimized structures.
Table 1. Obtained some descriptors by B3LYP/6-31G** level

<table>
<thead>
<tr>
<th>Descriptors</th>
<th>Glycine</th>
<th>Graphene</th>
<th>Gr-Gly</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{opt}(\text{eV})$</td>
<td>-284.52</td>
<td>-2068.98</td>
<td>-2353.41</td>
</tr>
<tr>
<td>$\Delta E_f(\text{eV})$</td>
<td>-</td>
<td>-</td>
<td>-0.013</td>
</tr>
<tr>
<td>HOMO (a.u.)</td>
<td>-0.253</td>
<td>-0.182</td>
<td>-0.182</td>
</tr>
<tr>
<td>LUMO (a.u.)</td>
<td>0.006</td>
<td>-0.078</td>
<td>-0.079</td>
</tr>
<tr>
<td>HOMO-LUMO GAP (a.u.)</td>
<td>0.259</td>
<td>0.104</td>
<td>0.103</td>
</tr>
</tbody>
</table>

In Table 2, the interatomic distances on final optimized geometries are reported. In general, it is observed that Gr and amino acids do not distort significantly with respect to their isolated optimized forms when joining to form Gr–AA systems. An interesting application of carbon-based nanostructures is the sensing of molecules.30-32 The principle upon which these applications work is that changes on the electronic/optical properties of the nanostructure in question can be unequivocally identified with the entities that attach to its surface.

Table 2. Optimized geometry of Glycine, Graphene and Gly-Gr in gas phase

<table>
<thead>
<tr>
<th>Descriptors</th>
<th>Glycine</th>
<th>Graphene</th>
<th>Gr-Gly</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-O</td>
<td>1.358</td>
<td>-</td>
<td>1.362</td>
</tr>
<tr>
<td>N-O</td>
<td>1.358</td>
<td>-</td>
<td>1.362</td>
</tr>
<tr>
<td>N-H</td>
<td>1.018</td>
<td>-</td>
<td>1.022</td>
</tr>
<tr>
<td>C-C</td>
<td>1.419</td>
<td>1.422</td>
<td></td>
</tr>
</tbody>
</table>

Understanding of charge transfer in biomolecule–graphene complex materials is very important to design and synthesize better materials and further improve device performances. Since the HOMO and LUMO, respectively, mediate the hole and electron transfers through biomaterials, the spatial distributions of HOMO and LUMO are of crucial importance for the charge transfer. The HOMO and LUMO distributions for the glycine, graphene and graphene – glycine system are shown in Table 1.

The electronic transport properties of graphene are expected not to change significantly upon adsorption of glycine. No significant electron transfers were found for glycine molecule adsorption. The HOMO and LUMO are distributed on the graphene layer in graphene-glycine systems, indicating the electron conduction through the graphene.
The formation energy values, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and the HOMO-LUMO band gap have been found as a measure of the structural stability properties. These descriptors for the complexes and each component listed in Table 2. As can be observed the complexes between glycine and graphene are more stable than the single agents.

4. Conclusion

In this ab initio computer simulation study, we have investigated the adsorption of glycine to graphene. Our study shows that the binding of amino acids to Gr is thermodynamically a little favorable.

References and Notes

N.; Strain, M.C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.;
Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko,
Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Gonzalez, C.; Head-Gordon, M.;
27. Elias, D. C.; Nair, R. R.; Mohiuddin, T. M. G.; Morozov, S. V.; Blake, P.; Halsall, M. P.; Ferrari, A. C.;