



## The Influence of Tyrosine on Energetic Property in Graphene Oxide: A DFT Study

ROYA AHMADI and REZA SOLEYMANI\*

Department of Chemistry, Shahre-Rey Branch, Islamic Azad University, Tehran, Iran.

\*Corresponding author: reza.soleymani@hotmail.com

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### ABSTRACT

Using the Computational methods, the interaction effect of Tyrosine Amino acid on Graphene was investigated. For this purpose, the Density Functional Theory (DFT) (in the ground state of 6-31G) was used, and the interaction effects of Tyrosine on Graphene was investigated through attachment to three different base positions. Different parameters such as energy levels, the amount of Chemical Shift in different atoms, the amount of HOMO/LUMO values and related parameters like Electrophilicity scale, chemical hardness, Chemical potential, and the maximum amount of electronic charge transferred. The Graphene oxide has the capability to act as a drug nano carrier and also as a mixture with *special electrical* properties. The results of this investigation also show that the attachment of Tyrosine Amino acid, as an organic compound, to the chemical structure of Graphene can change these capabilities to a great extent and also increase the role that this mixture already plays in medical, Pharmaceutical, and electronic industries.

**Key words:** DFT, Tyrosine, HOMO/LUMO, Electrophilicity.

### INTRODUCTION

Nanostructures can be categorized into following forms according to their structures: diamonds with  $SP^3$  hybridization, Graphites with  $SP^2$  hybridization, Hexagonal diamonds with  $SP^3$  hybridization, fullerenes with  $SP^2$  hybridization, Nanoparticles, Graphenes, single-layer and multi-layer nanotubes, *Crystal Nanostructures*. All these forms of nanostructures produce unique Pharmaceutical and electronic properties. Graphenes have a two-dimensional structure of a single layer of

carbon chicken wire<sup>1-5</sup>. The production of Graphene from Graphene acid began in the 19<sup>th</sup> century and the most common methods for this production were Brodie, *Staudenmaier*, and Hummers. But Graphene oxide is one of the derivatives of Graphene which is produced mainly by Brodie, *Staudenmaier*, and Hummers methods. All these methods oxidize the Graphene, using strong acids and oxidizers. The oxidation level of this process is dependent upon the kind of method, the type of the Graphene, and also the circumstances of the chemical interaction. The Graphene oxide can be used for a number

of purposes such as saving energy, acting as a chemical sensor, and also acting as a drug nano carrier<sup>5-9</sup>. Tyrosine is a group of amino acids which are synthesized in the body from phenylalanine. It is found in the structure of the most of the body's proteins. Tyrosine is also found in the structure of most of the neurotransmitters such as Dopamine, L- Dopamine, Epinephrine, and Norepinephrine. Because of the role that tyrosine plays in the structure of neurotransmitters, it can probably have an effect in the emergence and improvement of diseases like Parkinson's disease, depression, and many other kinds of mental disorders. The findings show that L-Tyrosine can be beneficial for those who suffer from depression and can be used for the treatment of diseases of this kind. The early researches show that L-Tyrosine can also be beneficial to those who suffer from brain diseases such as Alzheimer's disease. It has been found that Because of the role that this amino acid plays in the structure of Epinephrine and Norepinephrine, it can help reduce the environmental, physical, and mental stress. In the skin cells, Tyrosine converts into a substance called Melanin. This substance can protect the skin from ultraviolet rays. Tyrosine is also used in the structure of thyroid hormones which play an important role in body's metabolism. The persons who excrete a lot of proteins due to Kidney diseases, are open to deficit of amino acids, including Tyrosine amino acid [10]. Moreover, some persons genetically suffer from a disorder called Phenylketonuria. The Electrophilicity parameter was first defined and investigated by Parr *et al.* the Electrophilicity parameter can be used in the investigation of the most of the systems and also in the description of the chemical reactions in different organic ways. Besides, in some of the chemical reactions, this factor has been regarded as an effective factor in the amount of outcome in Diels–Alder reactions. The Electrophilicity parameter is caused by the electronic structure of the substance and is independent from the effects of molecular nucleus. In a series of studies, Domingo *et al* investigated the relation among the electronic effects of substitutions, electrophilicity parameter, and Hammett equation in a *mixture of ethylene*. The Electrophilicity values, the maximum amount of electronic charge transferred, chemical hardness, and also Chemical potential can be calculated using the relations 1 to 4. In these relations, the (I) represents "ionization potential" and (A) stands for

"electron affinity"<sup>13-21</sup>.

$$\mu = (\epsilon_H + \epsilon_L)/2 \quad \dots(1)$$

$$\eta = \epsilon_L - \epsilon_H \quad \dots(2)$$

$$\omega = \mu^2/2\eta = \chi^2/2\eta \quad \dots(3)$$

$$\chi = -\mu = -(\zeta_E/\zeta_N)_{V(r)} \approx (1+A)/2 \approx -1/2 (\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}}) \quad \dots(4)$$

$$\eta = (\zeta_{2E}/\zeta_{N2})_{V(r)} = (I-A) \approx (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}) \quad \dots(5)$$

$$\Delta N_{\text{max}} = -\mu/\eta \quad \dots(6)$$

### Computational details

All these calculations are done under the assumption of standard state of gas phase, pressure of 1 atmosphere, and temperature of 25 degrees centigrade. The calculations are performed, using a Pentium 4 PC with a Windows 7 OS and a Core i7 processor. After the initial optimization of the mixtures, the *Gaussian 09* software is used for final optimization. For the calculation of HOMO/LUMO values, the Gauss sum software is used<sup>18,21</sup>.

## RESULTS AND DISCUSSION

The related structures are named in the following way: GO: Graphene oxide without any attachment to structure of Tyrosine Amino acid GO-B1: Graphene oxide when attached to the first base position in the structure of Tyrosine Amino acid GO-B2: Graphene oxide when attached to the second base position in the structure of Tyrosine Amino acid GO- B3: Graphene oxide when attached to the third base position in the structure of Tyrosine Amino acid. In GO-B1, the attachment of Tyrosine structure to Graphene oxide is done through the attachment of O45 in Graphene oxide structure to N70 in Tyrosine structure.

- In GO-B2, the attachment of Tyrosine structure to Graphene oxide is done through the attachment of C43 in Graphene oxide structure to N69 in Tyrosine structure.
- In GO-B3, the attachment of Tyrosine structure to Graphene oxide is done through the attachment of O67 in Graphene oxide structure to N70 in Tyrosine structure.

One of the parameters that can be calculated by *Computational chemistry is the value of HOMO and LUMO and their related parameters such as chemical hardness, Chemical potential, Electrophilicity, the most amount of surrounded electric charge, and the energy gap*. The results of the study are tabulated in the table NO 1.

As the figure No 1 shows, the attachment of Tyrosine changes the trend of values related to HOMO and LUMO. For comparing the energetic level of structures, after the optimization of the structures by Density Functional Theory at a theory level of

B3LYP, different structural forms are compare with one another. The results of this comparison which are tabulated in table No 2 show that the attachment of Tyrosine structure to the structure of Graphene oxide changes the values of energy.

The results show that the attachment of Tyrosine structure to the structure of Graphene oxide reduces the total energy level. As the results of *Zero-Point Energy also show, the reduction in total energy level is also present in zero-point energy level*. The values of Entropy also show that the attachment of Tyrosine structure to the structure

**Table 1: Values of energies of the frontier molecular orbitals ( $\epsilon_{\text{HOMO}}$  and  $\epsilon_{\text{LUMO}}$ , eV), electronic chemical potential,  $\mu$  (eV), chemical hardness,  $\eta$  (eV), electrophilicity,  $\omega$  (eV) and maximum amount of electronic charge transfer for all of Geraphene Oxide structures calculated at the B3LYP/6-31G level of theory**

Method Structure	B3LYP/6-31G				
	GO-B1	GO-B2	GO-B3	GO	TR
HOMO	-0.19611	-0.19327	-0.19007	-0.19811	-0.21308
LUMO	-0.17867	-0.17562	-0.17349	-0.18077	-0.01807
Chemical Potential	-0.18739	-0.18444	-0.18178	-0.18944	-0.11557
Chemical Hardness	0.01744	0.01765	0.01658	0.01734	0.19501
Electrophilicity	1.00673	0.96373	0.99650	1.03481	0.03424
$\Delta N_{\text{Max}}$	10.7448	10.4501	10.9638	10.9250	0.59266

**Table 2: The values of different position energies for Geraphene Oxide calculated at the B3LYP/6-31G level of theory**

Method Structure	B3LYP/6-31G				
	GO-B1	GO-B2	GO-B3	GO	TR
Total energy(Hartree)	-3325.4514	-3250.3262	-3325.4580	-2697.0456	-629.6277
ZPVE(Kcal/mol)	405.55973	403.52363	405.23424	296.28579	121.51554
Rotational constant(GHz)	0.04677	0.05419	0.04521	0.06565	2.34377
	0.02055	0.01976	0.03207	0.04739	0.33704
	0.01634	0.01589	0.02276	0.03083	0.31371
Entropy(Cal/Mol-Kelvin)					
Total	308.700	307.304	305.375	246.615	111.970
Translational	46.304	46.251	46.304	45.652	41.488
Rotational	41.145	41.065	40.406	39.346	31.540
Vibrational	221.251	219.988	218.664	161.617	38.943
Heat capacity(Cal/Mol-Kelvin)	212.111	208.502	212.460	165.635	47.226
Dipole moment(D)	4.6276	6.7374	4.6509	4.5859	1.8667

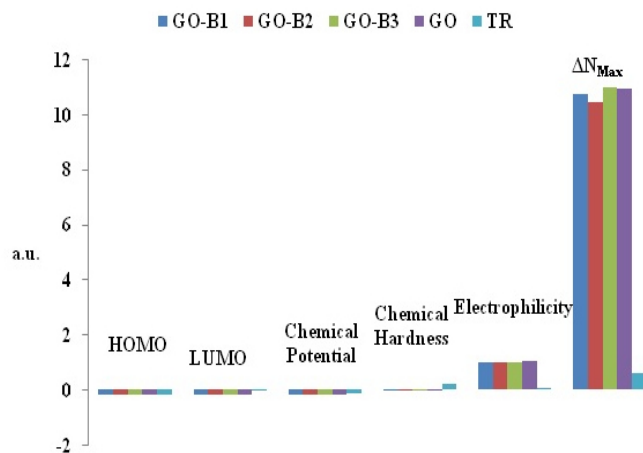


Fig. 1: Displays the trend of the HOMO/LUMO changes in the various charts

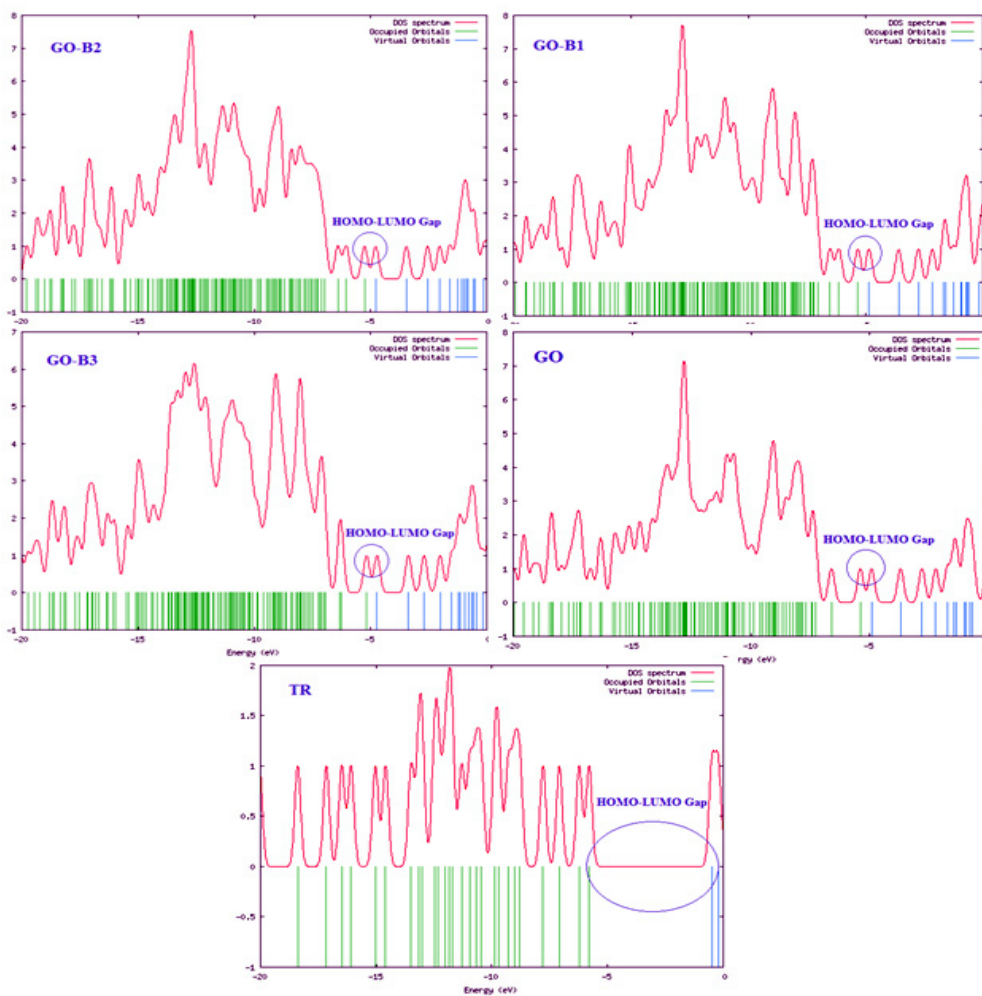
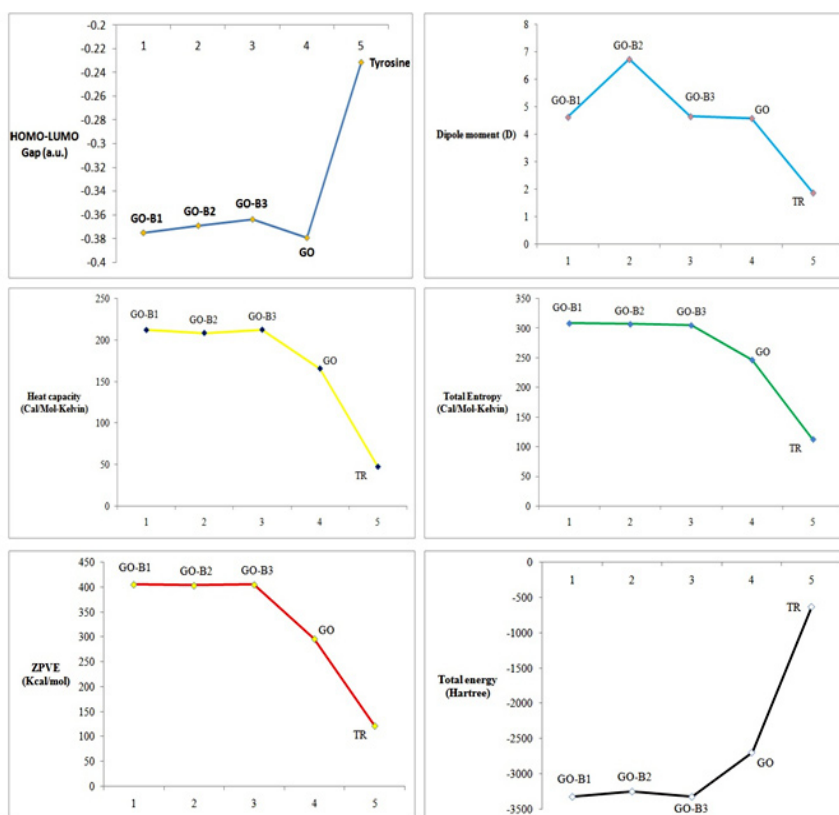


Fig. 2: Partial DOS diagram containing HOMO (left) and LUMO (right) plot of Graphene Oxide derivatives at B3LYP method



**Fig. 3: Displays the trend of the energetic property changes in the various charts**

of Graphene oxide increases the amount of disorder and chaos and consequently the value of Entropy. The trend of these changes are depicted in figure No 2. The value of Heat capacity while the Tyrosine is attached to Graphene oxide is different from that while the Graphene oxide is not attached to Tyrosine. The base position at which the Tyrosine is attached to Graphene oxide also influences the value of heat capacity. The values of dipole moment also show interesting results. GO-B2 shows greater dipole moment value in comparison to other similar forms. In other forms, in comparison to form in which Tyrosine is not attached to Graphene oxide, the attachment of Tyrosine to Graphene oxide from other base positions does not change the value of dipole moment so much.

### CONCLUSION

*Computational Quantum Mechanics* at the theory level of B3LYP/6-31G on the structure

of Graphene oxide was done separately and only when the structure of Tyrosine was attached to it and the results of this computation can be classified as follows:

- 1) The investigation of all the parameters show that the attachment of Tyrosine structure to Graphene oxide structure will influence the energy levels and dipole moment changes and these changes are able to be investigated in the electrical and chemical parameters of Graphene oxide structure.
- 2) The attachment of Tyrosine structure is a reason for the changes in the energy levels and also HOMO and LUMO values.
- 3) The investigation of energy levels and HOMO/LUMO values show that the attachment of Tyrosine structure to Graphene oxide structure form different positions of base will yield different results for chemical hardness, chemical potential, Electrophelicity, and  $\Delta N_{\max}$ , in accordance to the attachment

position; and the most appropriate position is the most symmetrical one.

- 4) We expect that the changes in chemical parameters change the physical, electronic, and even pharmaceutical properties of Graphene oxide and Tyrosine, and these changes are able to be investigated by the specialists of these fields.

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