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Molecular Modeling Study for Graphene modified with CH_3, COOH, NH_2 and O_2

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Abstract
A model molecule was built of graphene consists of 50 carbon atoms, after that was modified with CH_3, COOH, NH_2 and O_2 forming 20 model molecules. These functional groups are connected to graphene sheet throughout its corners (position 1, position 2 position 3 and position 4) and its center (position 5). Each model was then calculated at density functional theory DFT: B3LYP/6-31G(d,p). Results indicated that, the studied physical properties suffer strong changes in total dipole moment (TDM) and HOMO/LUMO band gap energy (ΔE) for the different position of the interaction. The interaction of graphene with CH_3 and NH_2 becomes more reactive for the connection at the center position where it shows highest TDM and lowest ΔE. COOH shows the highest TDM when interact with graphene at position 1 and the lowest ΔE when interact with graphene at position 2. While the reactivity of the interaction of graphene with O_2 increased at position 2. Form the molecular electrostatic potential (MESP) calculation, it is clear that, the negativity increased by interaction of graphene with O_2 at the corner in position 1 and position 4.

Keywords: Graphene, Two-dimensional materials, TDM, HOMO/LUMO band gap energy, DFT

1. Introduction

Graphene, that is a two-dimensional (2D) and atomically thin crystal, consists of a single layer of carbon packed in a hexagonal lattice, which considered as the mother material of carbon materials like graphite, fullerene and carbon nanotubes. In 2004, the discovery of that 2D crystal of graphene was attributed to Geim's group [1]. And so far, the scientific compete is at its highest to study this material in all its possible ways. It has unique electrical, optical, thermal and mechanical properties [2]–[8]. So, its contribution in applications in different fields is appreciated from scientists [9]–[12]. However, graphene has a zero band-gap energy that does not allow using it as a semiconductor and it's not suitable in nanoelectronic devices [13]. This problem of pristine graphene can be solved by functionalization that helps in changing the electronic structure of graphene as well as tuning its gap energy that improves its role in several applications [14]. In 2009, Al-Aqtash and Vasiliev [15] observed significant structural changes in graphene after the attachment of the COOH group to its surface. In 2011, Denis and Iribarne [16] considered that very high levels of functionalization are needed to open a band gap in nitrene-modified graphene. In 2012, Wei and Qu [17] reported that functionalization cannot only stabilize graphene's unique properties, but also can introduce some new properties. In 2018, Hazem et al. [18] reported that carboxyl group significantly enhances the studied properties of GQDs by increasing their reactivity. Molecular modeling calculations were used to elucidate the electronic properties of many systems and molecules [19-21]. Special care of molecular modeling was directed into carbon nano materials [22-23] such as carbon nanotubes, fullerene, graphene etc. Special interest of scientists was directed toward computational analyses of graphene [24-27] as well as modified graphene [28-29]. Recently many computational efforts with different models were paid into functionalize graphene to illustrate its possible applications [30-34].

In this work, chemical functionalization of graphene strip shown in figure 1 was considered. The strip consists of 50 carbon atoms and has five sites of interaction (4 in the corners and 1 in the center). The

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functional groups were CH_3, COOH, NH_2 in addition to oxygen O_2. The effect of each group on some of the physical properties such as total dipole moment (TDM) and HOMO-LUMO band gap energy (ΔE), was studied.

2. Calculations Details

All the studied structures were calculated with Gaussian 09 [35] software at Spectroscopy Department, National Research Centre. Each structure is calculated at density functional theory DFT:B3LYP/6-31G(d,p) [36-38]. Total dipole moment (TDM), HOMO/LUMO band gap energy (ΔE), molecular electrostatic potential (MESP) was calculated at the same level of theory.

3. Results and Discussion

3.1. Building model molecules.

A model molecule of graphene structure is indicated in figure1. The structure of graphene consists of a strip of graphene containing 50 carbon atoms. Some modifications were conducted upon graphene; some functional groups were modified with graphene corners (4 corners) also at the center of graphene. The functional groups were CH_3, COOH, NH_2 and O_2 forming 20 model molecules for modified graphene as indicated in figure 2, figure 3, figure 4 and figure 5 respectively. The functional groups are connected in the four corners and the center of the graphene as indicating in figure1. CH_3 is connected to the four corners and the center as shown in figures (2-a) to figure (2-d) and figure (2-e) respectively. With the same manner connecting COOH in the four corners (figures (3-a) to (3-d)) and to the center (figure (3-3)). Also, NH_2 was connected to graphene in the four corners in figures (4-a) to (4-d) and connected to the center as shown in figures (4-e). Finally, the oxygen was connected to graphene at the four corners and the center as indicated in figures (5-a) to (5-d) and figure (5-e) respectively.

3.2. Total dipole moment and HOMO/LUMO energy gap calculation:

The reactivity of graphene as well as the modified graphene will be discussed through the calculated physical parameters. It is stated earlier that, both TDM and ΔE are reflecting the reactivity of the studied chemical structure [**39-41**]. Increasing the TDM with decreasing ΔE indicated that the corresponding structure is able to interact with its surrounding molecules. Total dipole moment (TDM) and HOMO-LUMO band gap energy (ΔE) were calculated for graphene and modified graphene for all interaction possibilities at the same level of DFT using the same bases set. Table1 presented TDM and HOMO/LUMO energy for the proposed structures of for graphene and modified graphene. Table1 indicates that graphene has no TDM has zero valued while its band gap energy ΔE is equal 0.5137 eV. After modification of graphene with the functional groups the values of TDM and ΔE are changed. For CH_3 group, the values of TDM in position1, position2, position3, position 4 and the center position are 3.8017, 3.4609, 1.9967, 2.8604 and 5.3812 Debye respectively while the values of ΔE at the same sites are 0.3181, 0.7978, 0.7314, 0.2988 and 0.5056 eV. For the connection of CH_3 group with graphene at the center position, the structure becomes more reactive. For COOH group, the values of TDM are 3.7856, 2.0049, 3.4277, 2.3253, 2.8144 Debye while the values of ΔE in are 0.8245, 0.3358, 0.4735, 0.7350 and 0.6191 eV at position1, position2, position3, position 4 and the center position respectively. COOH shows the highest TDM when interact with graphene at position1 and the lowest ΔE when interact with graphene at position2. The values of TDM for NH_2 group at the five sites are 1.8464, 5.0059, 2.5031, 7.7428, 17.4893 Debye respectively. The calculated ΔE at 4 corners and the center are 0.9671, 0.4531, 0.6036, 0.6174 and 0.3154 eV. As a result, the interaction of graphene with NH_2 group becomes more reactive when they connected from the center position. Finally, for oxygen group, the values of TDM are 2.0129, 2.4038, 2.1493, 1.7593 and 1.0308 Debye at position1, position2, position3, position 4 and the center position respectively. And the values of ΔE in the same sites are 0.5901, 0.4914, 0.5067, 0.6068 and 0.8025 eV. For the interaction of graphene with O_2, position 2 is more reactive.

3.3. Molecular electrostatic potential calculations.

Molecular electrostatic potential (MESP) is a good property that helps us to indicate the reactivity of the studied molecule with its surrounding[42-43], through mapping the contours that show the distribution of charges in the molecules. The distribution can be indicated by colors that represent certain charges. Colors change from red to blue indicating the negativity through a certain scheme order: red > orange > yellow > green > blue

Figures 6 present the calculated MESP at B3LYP/6-31G(d,p) level of DFT for graphene. The figure shows the mapping of ESP of graphene in a yellow color contour. Figure 7 presented the mapped ESP of the modified molecules of graphene with CH_3 at the five possible sites (4 corners and the center). All the modified molecules of graphene with CH_3 show the appearance of two sites with red color while the yellow color is distributed through the rest of the graphene sheet. Figures 8 show the distribution of charges through the mapped ESP contours for graphene with COOH functional group at different

position of interaction. The connection of COOH functional group at different position shows two sites with red color and the yellow color at the rest of the graphene sheet. The ESP charge distribution of graphene with NH_2 as contour is shown in figures 9. Figures 9-a to figures 9-e (at different interaction position) show the same distribution of colors like CH_3 and COOH with two sites in red color and the yellow color at the rest of the graphene sheet.

Finally, ESP charge distribution for the interaction of graphene with oxygen at the five different positions is shown in figure10. Figures 10-b, figure 10-c and 10-e show the same distribution of colors like the interaction of graphene with CH_3, COOH and NH_2 which show two sites in red color and the yellow color at the rest of graphene sheet. Figures 10-a and figures 10-d present the ESP charge distribution for the interaction of graphene with oxygen in the first and fourth position. The figure shows appearance of three sites in red color while the yellow color is distributed in the rest of the graphene sheet.

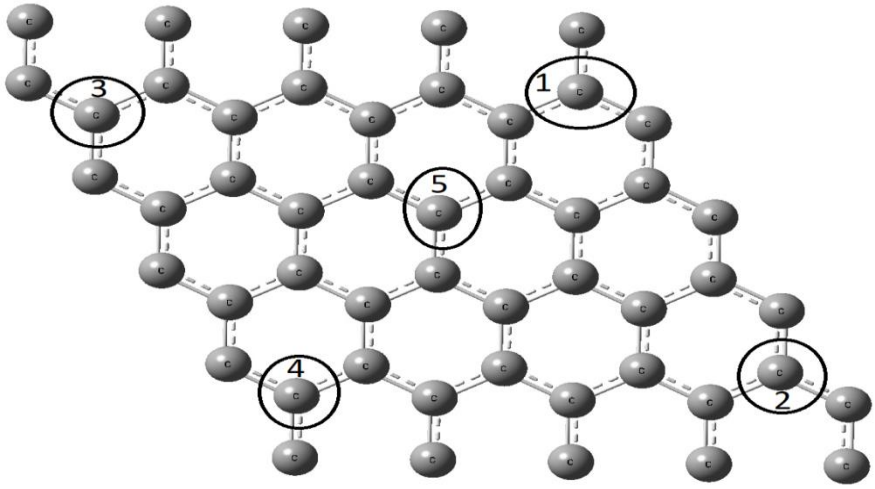


Figure 1. Model molecule for graphene consists of 50 carbon atoms, the model shows four corners each one could carry functional group beside the central atom of graphene marked from 1 to 5.

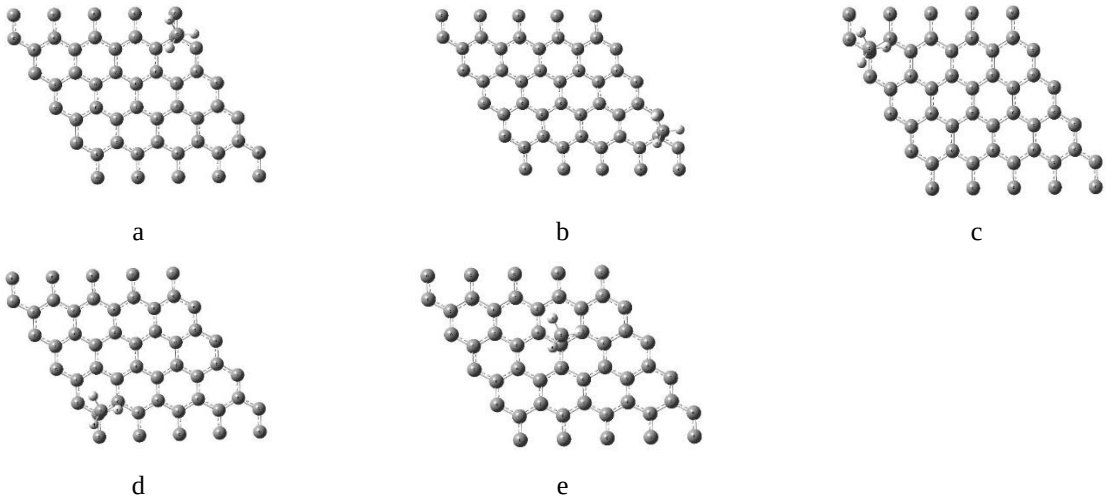
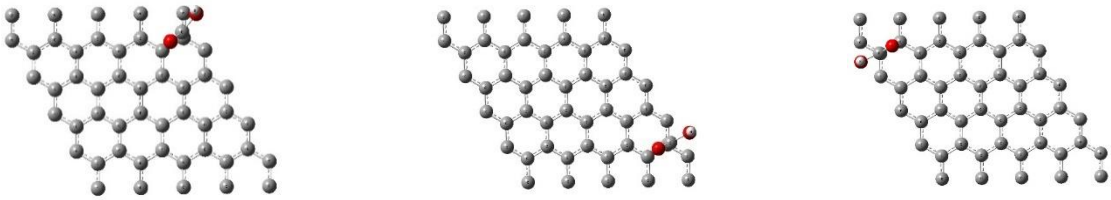


Figure 2. B3LYP/6-31G(d,p) model structures for graphene modified with CH_3 in a) position 1, b) position 2, c) position 3, d) position 4 and e) position 5 which indicated in figure 1.



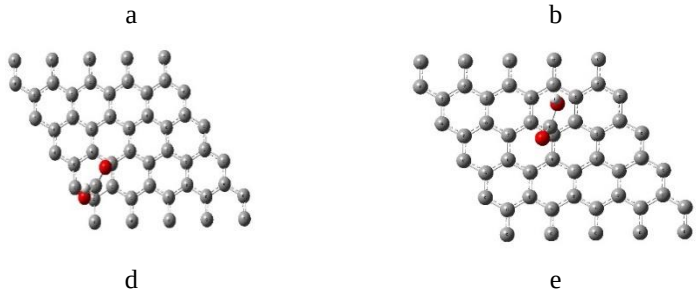


Figure 3. B3LYP/6-31G(d,p) model structures for graphene modified with COOH in a) positions 1, b) position 2, c) position 3, d) position 4 and e) position 5 which indicated in figure 1.

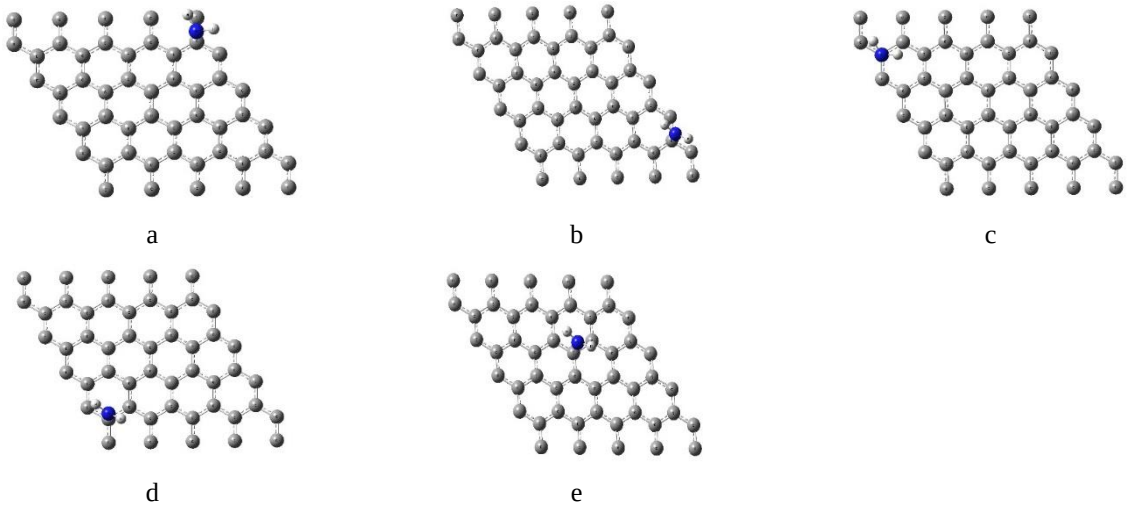


Figure 4. B3LYP/6-31G(d,p) model structures for graphene modified with NH_2 in a) positions 1, b) position 2, c) position 3, d) position 4 and e) position 5 which indicated in figure 1.

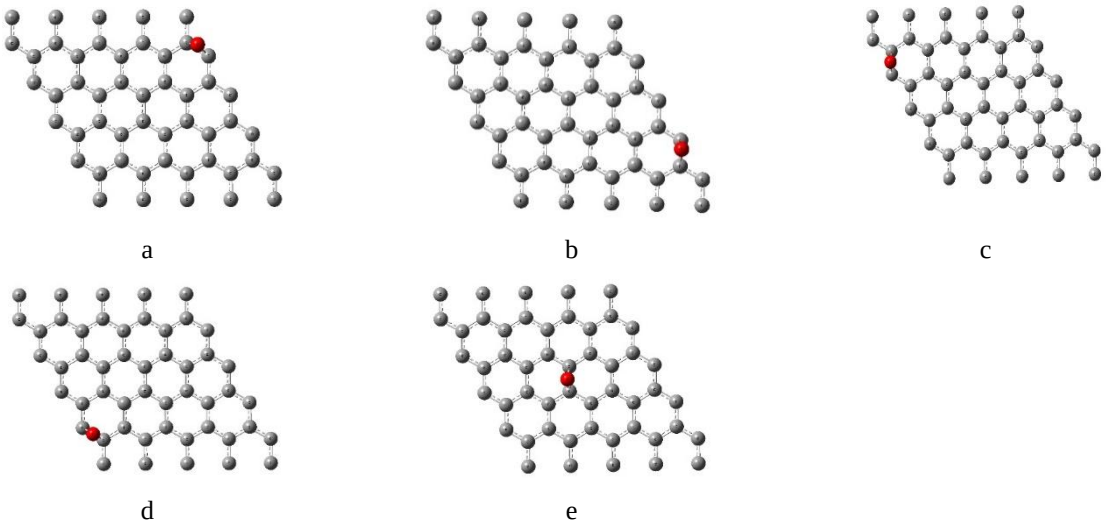


Figure 5. B3LYP/6-31G(d,p) model structures for graphene modified with O_2 in in a) positions 1, b) position 2, c) position 3, d) position 4 and e) position 5 which indicated in figure 1.

Table 1. B3LYP/6-31G(d,p) calculated total dipole moment (TDM) as Debye, HOMO/LUMO band gap energy (ΔE) as eV for graphene as well as modified graphene at the different five position of interaction.

Structure	**TDM**	**ΔE**
Graphene	0.0000	0.5138
Graphene – CH_3 - 1	3.8017	0.3181
Graphene – CH_3 - 2	3.6409	0.7978
Graphene – CH_3 - 3	1.9967	0.7314
Graphene – CH_3 - 4	2.8604	0.2988
Graphene – CH_3 - Center	5.3812	0.5056
Graphene - COOH - 1	3.7856	0.8245
Graphene - COOH - 2	2.0049	0.3358
Graphene - COOH - 3	3.4277	0.4735
Graphene - COOH - 4	2.3253	0.7350
Graphene - COOH - Center	2.8144	0.6191
Graphene – NH_2 - 1	1.8464	0.9671
Graphene - NH_2 - 2	5.0059	0.4531
Graphene - NH_2 - 3	2.5031	0.6036
Graphene - NH_2 - 4	7.7428	0.6174
Graphene - NH_2 - Center	17.4893	0.3154
Graphene - Oxygen - 1	2.0129	0.5901
Graphene - Oxygen - 2	2.4038	0.4914
Graphene – Oxygen - 3	2.1493	0.5067
Graphene - Oxygen - 4	1.7593	0.6068
Graphene - Oxygen - Center	1.0308	0.8025

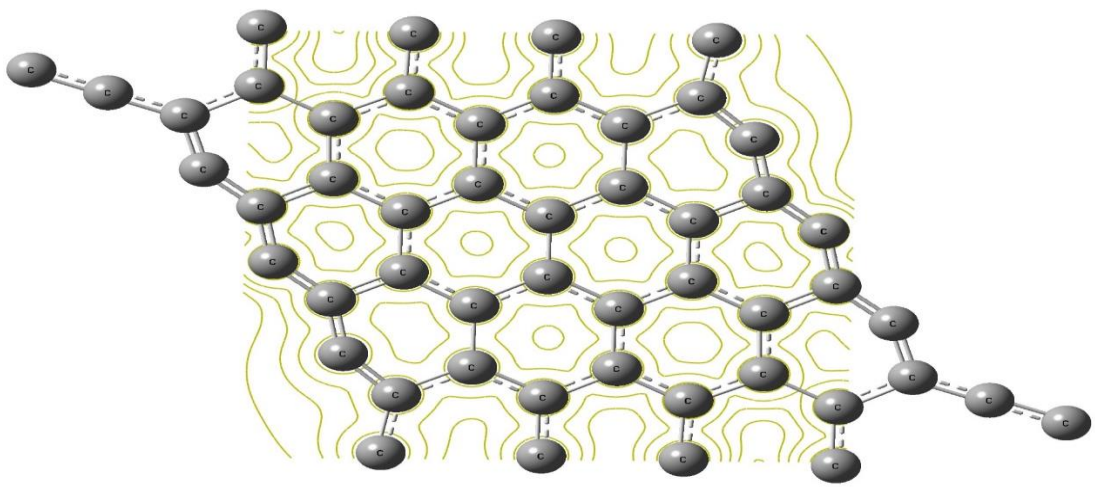


Figure 6. B3LYP/6-31G(d,p) calculated molecular electrostatic potential as contour of graphene.

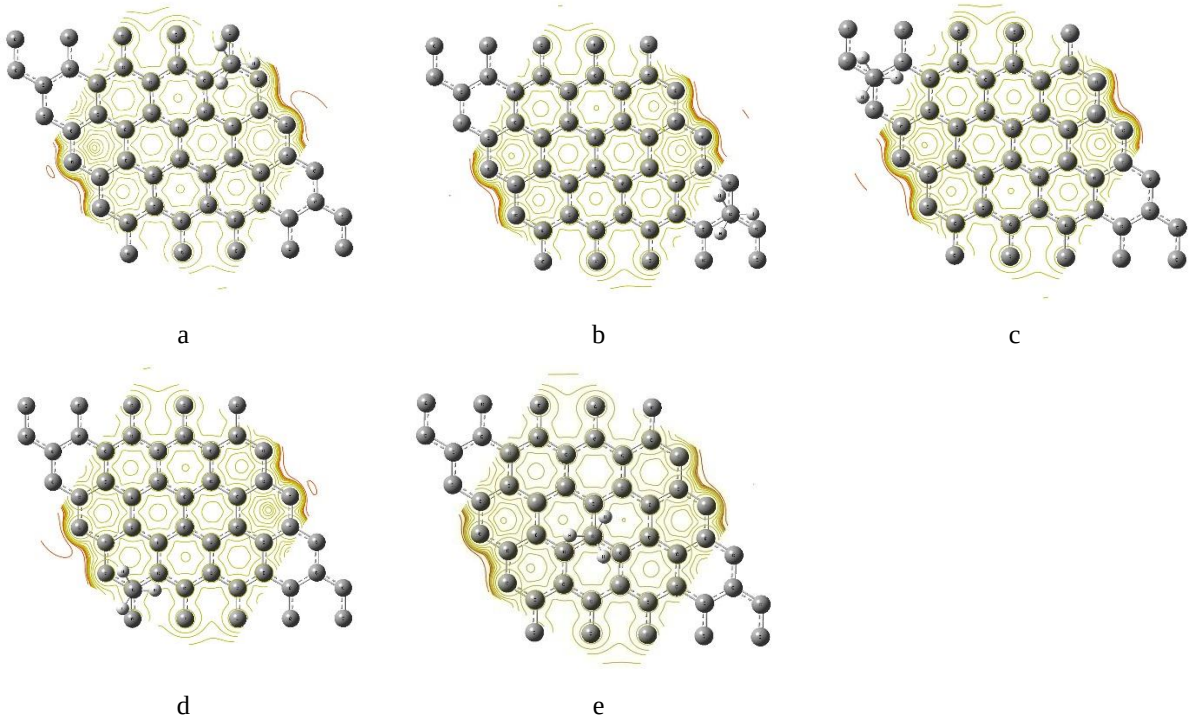


Figure7. B3LYP/6-311G (d,p) calculated molecular electrostatic potential as contour for modified graphene with CH3 in in a) positions 1, b) position 2, c) position 3, d) position 4 and e) position 5 which indicated in figure 1.

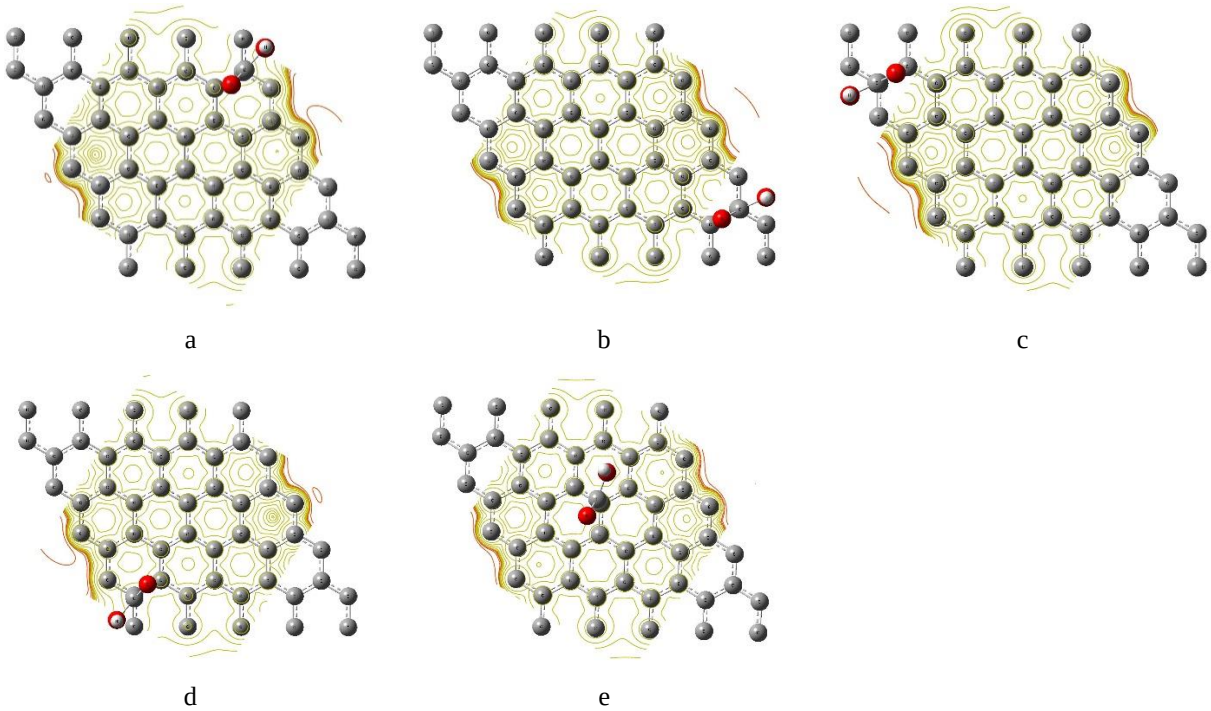


Figure8. B3LYP/6-311G (d,p) calculated molecular electrostatic potential as contour for modified graphene with COOH in in a) positions 1, b) position 2, c) position 3, d) position 4 and e) position 5 which indicated in figure 1.

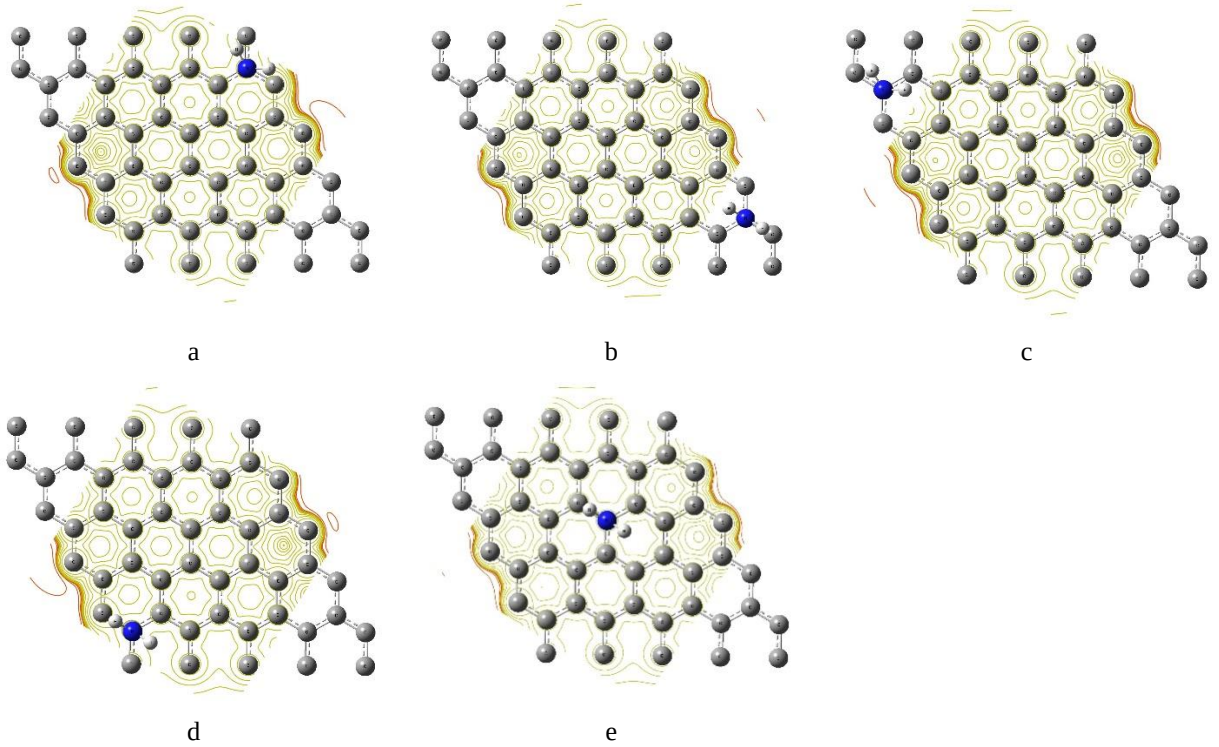


Figure 9. B3LYP/6-311G (d,p) calculated molecular electrostatic potential as contour for modified graphene with NH_2 in a) positions 1, b) position 2, c) position 3, d) position 4 and e) position 5 which indicated in figure 1.

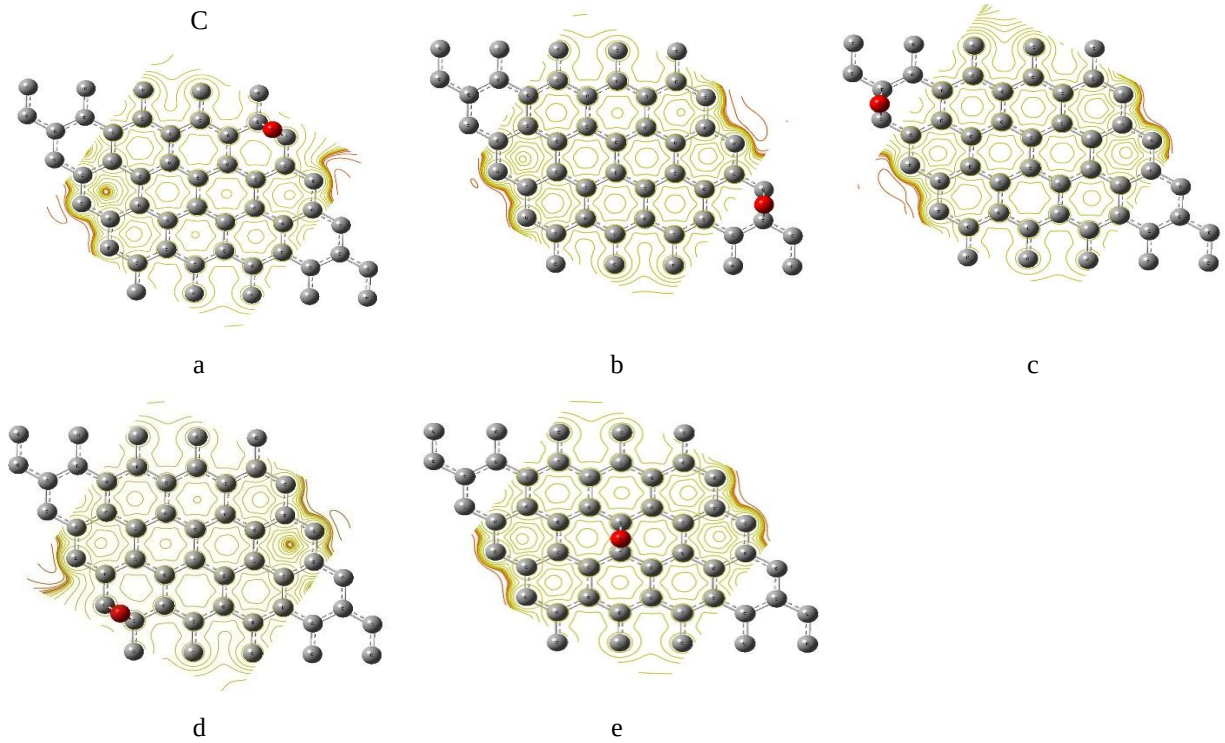


Figure10. B3LYP/6-311G (d,p) calculated molecular electrostatic potential as contour for modified graphene with O_2 in in a) positions 1, b) position 2, c) position 3, d) position 4 and e) position 5 which indicated in figure 1

Conclusion:

Quantum mechanical calculations of DFT are utilized to study the interaction of different functional groups with graphene connected at different poisons at B3LYP/6-311G (d,p) basis set. The four corners and center of graphene sheet are chosen to be the position of the connection with CH_3, COOH, NH_2 and O_2 functional groups**.** Total dipole moment (TDM), HOMO-LUMO band gap energy (ΔE) and MESP are calculated for all the studied structure. Based on the results, the studied physical properties suffer strong changes in TDM and ΔE for the different position of the interaction. The interaction of graphene with CH_3 and NH_2 functional groups becomes more reactive for the connection at the center position where it shows highest TDM and lowest ΔE. COOH shows the highest TDM when interact with graphene at position 1 and the lowest ΔE when interact with graphene at position2. While the reactivity of the interaction of graphene with O_2 increased at position 2. Form the MESP calculation, the graphene shows a yellow color of charge distribution. All the studied structures of graphene with CH_3, COOH and NH_2 show two sites in red color and the yellow color at the rest of graphene sheet. MESP charge distribution for the interaction of graphene with oxygen in the second, third and fifth position shows the same behavior as the interaction with CH_3, COOH and NH_2. MESP charge distribution for the interaction of graphene with oxygen in the first and fourth position shows appearance of three sites in red color while the yellow color is distributed in the rest of the graphene sheet. This means that the negativity increased by interaction of graphene with O_2 at the corner in position one and four.

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