Effect Different Donors And Acceptors On Quantum Chemical Parameters of Zigzag Graphene Nanoribbon

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Abstract

Exchange-correlation functional B3LYP with standard 6-31G basis sets was carried out for DFT calculations of pure zigzag GNR and two of donor-GNR-acceptor structures. The results showed good relax was obtained for studied structures. Pure zigzag GNR has small energy gap and it was reduced by adding donors and acceptors to the ribbon depending on the type of both donor and acceptor. Donor-GNR_s-Acceptor have low value of global electrochemical hardness and high electronic softness than those for pure GNR, an electron can be easily transfer from valence to conduction band. Also, the electrophilic index for GNR in case of presence of donors and acceptors is greater than that for pure GNR, therefore, donor-GNR_s-acceptor can easily interact with surrounding species in comparison with pure GNR. Generally, 3-D materials was constructed based on 2-D graphene can be used for different electronic applications.

Introduction

In 2004, Novoselov et al. are the first physicians that discovered the graphene material [1]. As known, graphene is a single atomic layer has thickness 0.34 nm of sp² hybridized carbon atoms covalently bonded to three other atoms arranged in a honeycomb lattice [1–4]. Graphene is one of the most significant areas in materials science due to its unique electronic and structural characterization and its high carrier mobility [5–9]. Many carbon-based materials are graphene forms such as fullerene [10–14], carbon nanotubes [15–19], and graphite [20–25]. Graphene has exclusive properties with great potential applications, such as electrochemical sensors [26, 27], nano-electronic devices [28], storage systems [29], nanocomposites [30]. Graphene could be considered as an ideal material to study the properties of other two-dimensional systems. Graphene is a zero-gap semiconductor material, because its conduction and valence bands meet at Dirac points.

Graphene nanoribbons GNRs can have a long arbitrarily long length are considered a quasi-one dimensional material due to the high aspect ratio. GNR is a new class of nanomaterials with either metallic or semiconducting properties. There are two types of ideal GNR, armchair GNRs, which has an armchair cross section at the edges, and zigzag GNRs which has a zigzag cross-section. Also, the GNRs are labeled by the number of armchair or zigzag chains present in the width direction of the armchair GNR and zigzag GNR, respectively [3]. Our study focuses on the effect of different donors and acceptors on quantum chemical parameters of zigzag graphene nanoribbon such as global electrochemical hardness, global electronic softness and electrophilic index.

Computation Details

Exchange-correlation functional was used with standard 6-31G basis sets to carry out the calculations of DFT for two donor-GNR-acceptor based on pure zigzag GNR. Berny analytical gradient optimization method was used for relax the studied structures. Energy gap for GNR_s was calculated as a difference of LUMO and HOMO energies [31].

$$E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$$

Vertical energy method, so called Koopman^s theorem was used to compute Ionization Energy IE and Electron Affinity EA, where [32–34]:

$$\text{IE} = -E_{\text{HOMO}} \text{ and } \text{EA} = -E_{\text{LUMO}}$$

Electrophilic index ω was calculated according to the following formula[32–34]:

$$\omega = \mu^2 / 2H$$

Where μ is the electronic chemical potential and H is the global electrochemical hardness. They are defined as [32–36]:

$$\mu = -(\text{IE} + \text{EA})/2 \text{ and } H = (\text{IE} - \text{EA})$$

All calculations were carried out using Density Functional Theory DFT by employing the Exchange-correlation functional B3LYP with standard 6-31G basis sets at Gaussian 09 package of programs [37]. The structures of GNR_s were designed at Gauss View 5.0.8 program.

Results And Discussion

In Fig. 1(a), the Zigzag Graphene Nano Ribbon GNR was designed at Gauss View 5.0.8 and relax under the SCF-DFT to minimum energy E (B3LYP) = -1994.366 a. u by employing 6-31G basis sets after 5 cycles with convergence 0.2762×10^{-8} for virial ratio -V/T = 2.0053. These SCF calculations refer to good relax was obtained for the structure of GNR in which the minima energy for isolated carbon and hydrogen atoms were computed at the same level of theory are - 37.774 a. u and - 0.5 a. u, respectively. Figure 1(b) represents the relax structure of donor-GNR-acceptor, pyrazine molecule and benzothiadiazole molecule are added to the GNR as donor and acceptor, respectively, and constructs GNR1. GNR2 relax structure was drawn in Fig. 1(c), where carbazole is the donor and TCNE is an acceptor. The optimize structures of GNR1 and GNR2 were relax at the same level of theory to reach the minimum energy E (B3LYP) = -2994.758 a. u after 5 cycles with convergence 0.126×10^{-8} for virial ratio -V/T = 2.0049 for GNR1, and E (B3LYP) = -2957.822 a. u after 10 cycles with convergence 0.504×10^{-8} for virial ratio -V/T = 2.0055 for GNR2. It is important to mention that the stationary points from Berny analytical gradient optimization were considered by frequency controls in which the optimization were done without any imaginary frequency for all studied GNR_s.

Table 1 explain the calculated values of electronic states energies E-HOMO and E-LUMO, and energy gap E_{gap} in eV for the two graphene ribbons GNR1 and GNR2 and comparing with the pure GNR. We showed the gap between the two frontier molecular orbitals in the studied GNR_s is very small with energy gap below 0.5 eV. Pure GNR has 0.4 eV, adding pyrazine donor and benzothiadiazole acceptor at the zigzag surface of the ribbon reducing the energy gap to 0.38 eV, and the reducing the energy gap to 0.26 eV by adding carbazole donor and TCNE acceptor to the pure GNR. Theoretical Fermi level calculated for two ribbons are 3.74 eV for GNR1 and 3.81 eV for GNR2, these values are approximately close to the Fermi

level for pure GNR 3.67 eV. Above results expect that one can be suggest other types of donor and acceptor molecules to construct new GNR_s structures for different applications.

Table 1
E-HOMO, E-LUMO and E_{gap} for GNR_s.

Ribbon	E-HOMO eV	E-LUMO eV	E _{gap} eV
GNR	-3.874	-3.47	0.404
GNR1	-3.937	-3.551	0.385
GNR2	-3.945	-3.681	0.263

Figure 2 illustrates the distribution of wave functions for the studied GNR_s. For pure GNR, the molecule wave function HOMO was distributed symmetrically as linear combination of atomic wave functions positive charges (green color) and negative charges (red color), while the positive charges are more contribution to construct the LUMO wave function for GNR. For the two donor-GNR-acceptor (GNR1 and GNR2), there is asymmetric distribution for HOMO and LUMO shapes. The presence of donors and acceptors take place in rearranging the combination of atomic orbitals in the new ribbons due to presence various atoms of different atomic numbers.

Figure 3 illustrates the population of degeneracy for both HOMO and LUMO and the density of states DOS spectrum for GNR_s. As seen, very narrow separation between the two bands Conduction and valence in all GNR_s. So, the degeneracy of electronic states in HOMO is more than the degeneracy of those in LUMO for all ribbons. The spectrum of DOS showed the number of degeneracy in the ribbons is in the ranking GNR2 > GNR1 > GNR. Above results refer to the GNR2 and GNR1 are more electrophilic and they have high ability to interact with other species in comparison with the pure GNR.

Figure 4 shows the Electrostatic potential distribution of the studied GNR_s. Pure GNR has high symmetrical charge distribution with zero dipole moment due to its C_s point group. GNR1 has asymmetric distribution of charge, it has 2.358 Debye dipole moment due to its C_{2v} group symmetry, therefore, the charge in GNR1 was dragged towards the location of high electronegativity, benzothiadiazole as an acceptor in case of GNR1. On the other hand, GNR2 lies in the same point group C_{2v}, it has the largest dipole moment 7.791 Debye with high asymmetric charge distribution. Above result refers to construct new 3-D materials based on 2-D graphene can be used for different electronic applications.

Table 2 illustrates the effect of different donors and acceptors on some electronic properties of GNR. The results showed all GNR_s have low values of global electrochemical hardness $H < 1$ eV, in which this refers to small separation between the valence band and conduction band, and therefore, GNR_s have high ability to allow for an electron to transfer from valence to conduction band. On the other hand, GNR_s are all soft structures with global electronic softness $S > 1$ for each eV [38, 39]. This means very small energy

was required for an electron to transfer from valence to conduction band in the studied GNR_s. Large soft molecule can easily interact with large other species in the space of the molecule. If the softness is the ranking of electronic activity of molecules, then: GNR2 > GNR1 > GNR. The results in Table 2 showed strong electrophilic indices were recorded for the studied GNR_s, all studied ribbons have electrophilic index > 3 eV and this give the GNR_s high ability to a strong interaction with other molecules in the surrounding of the ribbons.

Table 2
Global hardness and softness, and electrophilic index for GNR_s.

Ribbon	Hardness eV	Softness 1/eV	Electrophilic index eV
GNR	0.404	1.237	16.687
GNR1	0.386	1.295	18.157
GNR2	0.264	1.893	27.535

Conclusions

Good relax was obtained at stationary points for GNR and its adducts by carry out the calculations of DFT depending on the exchange-correlation functional B3LYP with standard 6-31G basis sets. The small energy gap calculated for pure zigzag graphene nanoribbon was reduced by adding donors and acceptors to the ribbon depending on the type of the donor and acceptor. Donor-GNR_s-Acceptor have low value of global electrochemical hardness and high electronic softness than those for pure GNR. The index of electrophilic for the GNR in case of presence of donors and acceptors is greater than that for pure GNR, therefore, donor-GNR_s-acceptor can easily interact with surrounding species in comparison with pure GNR. In general, 3-D materials was constructed based on 2-D graphene can be used for different electronic applications.

Declarations

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Conflicts of interest/Competing interests: it have not Conflicts of interest

Availability of data and material: data and material are available

Code availability: Software is available (Gaussian09 program and GaussSum)

Authors' contributions: Dr.Nidhal M. Al Shareefi 40% , Rabab Abdulzahrah 30%, Dr.Hamid Ibrahim 30%

Areas of interest and specialization : 1-Computational Chemistry 2-Materials Modeling

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Figures

(a) GNR

(b) GNR1

(c) GNR2

Figure 1

Relax structure of (a) GNR and (b) GNR1 and (c) GNR2.

GNR

GNR1

GNR2

Figure 2

HOMO (left) and LUMO(right) distribution for GNRs.

Figure 3

DOS spectra for GNRs.

GNR

GNR1

GNR2

Figure 4

ESP distribution for GNRs, 3D (left), 2D-contour (right).