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Electronic structure and NMR study of selected doped and functionalized graphene

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ABSTRACT

In this work, density functional theory (DFT) calculations at the BLYP/6-31G* level was performed to investigate doping and functionalizing effect on the graphene in according geometric, NMR parameters and electronic properties. In the considered models, the energy gap is decreased in doped and functionalized models in respect to the pristine model but there are not significant changes between energy gap of the pristine model and functionalized models. Furthermore, results show the high and low sensitivity of the electronic properties of doped and functionalized models towards pristine model respectively. The results indicate that the formation energies of functionalized models are smaller than doped models ones. The NMR parameters follow the results of structural properties. It was found that for production of electronic devices doped models is better than functionalized models and nitrogen atom is a better choice for this purpose respect to the boron atom. All DFT calculations are performed by the Gaussian 98 package. Copyright © 2014 VBRI press.

Keywords: Graphene; doping effect; functionalization effect; density functional theory; chemical shielding parameters; quantum molecular descriptors.

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Introduction

Graphene is a single planer sheet of graphite made of carbon atoms are disposed in a honeycomb structure which was discovered in 2004 **[1]**. Graphene is a basic building block for many carbon materials such as fullerens, nanotube and graphite related to the hybridization of the carbon atomic orbitals which is usually SP^2 or SP^3. Pristine model of graphene has attracted extensive investigation because of impressive electronic properties **[2-7].**

Modification of the electronic properties of the graphene for specific application such as building of specific electronic devices is important. Any changes in the graphene structure such as doping of them or change in the edge structure including functionalization, distortion would reform the electronic properties of graphene with respect to their pristine model. It has been showed that calculation of nuclear magnetic resonance (NMR) and nuclear quadruple resonance (NQR) **[8-9]** parameters based on the density functional theory (DFT) method are useful for investigation of molecular structure. The chemical shielding (CS) tensors can be calculated experimentally and theoretically **[10-13].**

These parameters are very sensitive to electronic density. So it can be used for study the properties of matter **[14].**

The effect of nitrogen (N) and boron (B) impurities on the properties of graphene and carbon nanotubes has been indicated by previous studies **[15–19].**

In the present work we have investigated doping and functionalizing effect on the electronic and structural properties of pristine model of graphene($C_{28}H_{14}$) using density functional theory (DFT) calculations. The values of chemical shielding (CS) parameters were evaluated for carbon (^{13}C) atoms in the optimized structures of the considered models. The optimized properties were also calculated. In this work doping and functionalizing of graphane were investigated and compared for using of an electronic device which has not been investigated before. Furthermore, boron and nitrogen atom were compared as an impurity for above applications.

Computational method

In this work five models were considered: pristine ($C_{28}H_{14}$), N-doped ($C_{27}H_{14}N$) model, B-doped ($C_{27}H_{14}B$) model, NH_2-functionalized ($C_{28}H_{15}N$) model and BH_2-functionalized ($C_{18}H_{15}B$) model in gas phase. The doped and pristine models had the same number of atoms; the functional groups were located at the top of the graphene instead of one of H atoms (**Fig. 1.**). In the first step, the structures were allowed to relax by all atomic geometrical optimization using the DFT level of BLYP exchange-functional and 6-31G* standard basis set in gas phase.

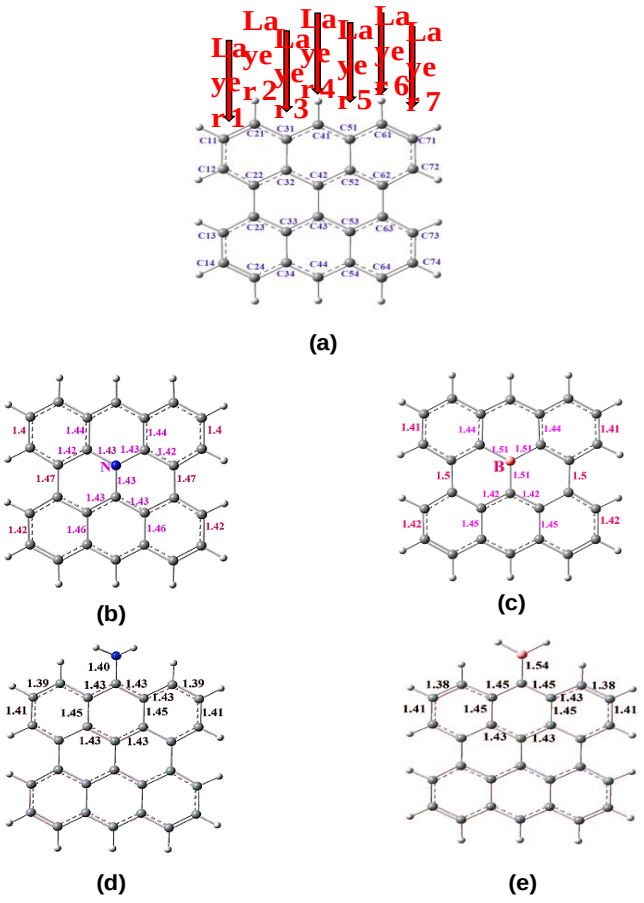

Fig. 1. The planar forms of the investigated 442rapheme models. (a)pristine,(b) N-doped,(c) B-doped,(d) N-functionalized model and (e) B-functionalized model. The values of lengths are written on the selected bonds.

The structural properties including bond lengths, dipole moment (DM), formation energy and quantum molecular descriptors **[20]** were calculated for all structures (**Tables 1, 2**).

Table 1. Optimized bond lengths/Å for selected models (a: pristine, b: N-doped, c: B-doped, d:-NH_2 functionalized and e: -BH_2 functionalized models) *

	a	b	c	d	e		a	b	c	d	e
C11-C21	1.38	1.38	1.40	1.39	1.38	C14-C24	1.38	1.38	1.38	1.38	1.38
C21-C31	1.43	1.43	1.43	1.43	1.43	C24-C34	1.43	1.43	1.43	1.43	1.43
C31-C41	1.41	1.40	1.44	1.43	1.45	C34-C44	1.41	1.40	1.42	1.41	1.41
C41-C51	1.42	1.40	1.44	1.43	1.45	C44-C54	1.41	1.40	1.42	1.41	1.41
C51-C61	1.43	1.43	1.43	1.43	1.43	C54-C64	1.43	1.43	1.43	1.43	1.43
C61-C71	1.38	1.38	1.40	1.39	1.38	C64-C74	1.38	1.38	1.38	1.38	1.38
C12-C22	1.40	1.42	1.42	1.40	1.40	C11-C12	1.42	1.40	1.41	1.41	1.41
C22-C32	1.44	1,43	1.42	1.45	1.45	C31-C32	1.45	1.44	1.44	1.45	1.46
C32-C42	1.43	1.43	1.51	1.43	1.43	C51-C52	1.45	1.44	1.41	1.45	1.46
C42-C52	1.43	1.43	1.51	1.43	1.43	C71-C72	1.42	1.40	1.44	1.41	1.41
C52-C62	1.44	1.43	1.42	1.45	1.45	C13-C14	1.42	1.42	1.42	1.42	1.42
C62-C72	1.40	1.42	1.42	1.40	1.40	C33-C34	1.45	1.46	1.45	1.45	1.45
C13-C23	1.40	1.40	1.40	1.40	1.41	C53-C54	1.45	1.46	1.45	1.45	1.45
C23-C33	1.44	1.44	1.46	1.44	1.44	C73-C74	1.42	1.42	1.42	1.42	1.42
C33-C43	1.43	1.43	1.42	1.43	1.43	C22-C23	1.48	1.47	1.50	1.48	1.48
C43-C53	1.43	1.43	1.42	1.43	1.43	C42-C43	1.46	1.43	1.51	1.45	1.46
C53-C63	1.44	1.44	1.46	1.44	1.44	C62-C63	1.48	1.47	1.50	1.48	1.48
C63-C73	1.44	1.40	1.40	1.40	1.41						

*see fig. 1 for details.

Table 2. Quantum molecular descriptors including η = Global hardness, μ = Chemical potential, and ω= electrophilicity and dipole moment (D_M) in selected models (a: pristine, b: N-doped, c: B-doped, d:-NH2 functionalized and e: -BH2 functionalized models)*

	a	b	c	d	e
E_{HOMO}/eV	-3.729	-3.229	-3.709	-3.445	-4.003
E_{LUMO}/eV	-2.792	-2.867	-3.284	-2.610	-3.157
$[E_{LUMO}–E_{HOMO}]$ /eV	0.936	0.362	0.425	0.835	0.847
$[\eta = -(E_{LUMO}–E_{HOMO})/2]$ /eV	0.468	0.181	0.213	0.418	0.432
$\mu = (E_{HOMO} + E_{LUMO})/2]$ /eV	-3.261	-3.048	-3.496	-3.027	-3.580
$[S = 1/2\eta]$ /eV^{-1}	1.068	2.765	2.351	1.197	1.181
DM/Debye	0.0046	0.937	0.904	2.70	3.76

*see Fig.1 for details

The quantum molecular descriptors including, electronic chemical potential (μ),global hardness (η),**[21],** energy gap (*Eg=ELUMO - EHOMO*), global softness (*S*) were calculated as follows:

$\mu = (E_{LUMO} + E_{HOMO})/2$,

$\eta = (E_{LUMO} - E_{HOMO})/2$

$S = 1/2\eta$

For study doping and functionalizing effects on the electronic and structural properties of pristine model, the nuclear magnetic resonance (NMR) spectroscopy including isotropic and anisotropic chemical shielding (CSI and CSA) parameters were also computed **[17]**.

Therefore the CS tensors of ^{13}C atoms were calculated for the optimized structures. The calculated CS tensors in the principal axis system (PAS) with order$\sigma 33 > \sigma 22 > \sigma 11$ were converted to measurable NMR parameters, the isotropic chemical shielding (CSI) and anisotropic chemical shielding (CSA) parameters. Bellow equations are used to convert the calculated CS tensors to the isotropic (CSI) and anisotropic (CSA) parameters.

CSI (ppm) =1/3 ($\sigma 11 + \sigma 22 + \sigma 33$),

CSA (ppm) = $\sigma 33 - 1/2(\sigma 11 + \sigma 22)$

All DFT calculations were performed by the Gaussian 98 package **[22].**

Results and discussion

Structural properties

The structural properties of selected models **(Fig. 1)** including the bond lengths, band gaps, dipole moments and binding energies are calculated. Bond lengths and band gap are presented in **Table 1**. The structure of base model (pristine model) is divided into seven layers (**Fig. 1.a**) for easier analysis. The results show that for equivalent positions, C-C bond lengths are similar and average of them is 1.386A^0.

The value of C-C bond lengths indicate the effects of doping and functionalizing are important for C-C bond distances close to N-doped, B-doped, -NH_2 and –BH_2 functionalized regions. But these results indicate slightly difference in comparison to the pristine model. The average of C-C bond length is changed from 1.426. A^0 in pristine model to 1.420, 1.400, 1.426 and 1.428 A^0 in N-doped, B-doped, -NH2 and –BH2 functionalized models respectively.

The values of dipole moments indicate effect of functionalization on DM of graphene is more than doping. Comparing the values of DM of –BH_2 and –NH_2 functionalized models indicate that this parameter for–BH_2 functionalized models more than –NH_2 functionalized model. This order of value is also seen for doped models which could mean that the Boron atom could play more significant role in increasing the magnitude of this parameter.

Formation energy

For defected systems formation energies of the structures which are an important concept **[23]** were calculated by:

E_f = E(X-doped model) - E(pristine model) + E_C - E_X doped models

E_f = E(R- functionalized model) + E_H - E (pristine model) - E_R functionalized model.

Where E(X-doped model), E(R- functionalized model) and E (pristine model) are the total energy of X(B/N) doped, R- functionalized, (R=BH2/NH2) and pristine models. E_C, E_H and $E_X$are the atomic energies of C,H and X(B/N) atoms respectively and E_R is the total energy of isolated form of –NH_2/-BH_2 groups. The formation energies are listed in **Table 2**.The results indicate that the formation energies of functionalized models are smaller than doped models ones. Furthermore, the formation energies of B-doped and BH_2-functionilized models are smaller than N-doped and NH_2-functionilized models, respectively. Also, the formation of –BH_2 functionalized is exothermic. So, the values indicate that the formation of functionalized models could be much more favorable than doped models and making impurity by B atom is more favorable than N atom from the formation energy view point.

Quantum molecular descriptors

The quantum molecular descriptors such as energy gap (E_{HOMO}-E_{LUMO}), global hardness (η) and softness (S) for all selected models were calculated and listed in **Table 3**. In the considered models, the energy gap decreases from 0.92 eV in the pristine model to 0.42, 0.36, 0.85 and 0.84eV at the B, N-doped and BH_2, NH_2 functional groups respectively so, the energy gaps are in the order N-doped< B-doped< -NH_2 functionalized<- BH_2 functionalized<pristine models. These values indicate that in the doped models the energy gaps are reduced significantly as compared to the pristine model but for functionalized models this reduction are fewer and the nitrogen atom could play more significant role than boron atom in decreasing the value of energy gap. The smaller energy gap at a special temperature leads to the larger electric conductivity **[24]**. The significantly changes in energy gap values of doped models, show the high sensitivity of the electronic properties of doped models towards pristine model.

Table 3. Formation energy (Ef), and HOMO– LUMO energy gap (Eg) for investigated models. (a: pristine, b: N-doped, c:B-doped, d:-NH_2 functionalized and e: -BH_2 functionalized models)*.

Investigated models	Ef	Eg
b	-0.11	0.847
c	0.57	0.835
d	13.33	0.425
e	13.40	0.362

*see Fig.1 for details

Also, it is found that the formation energy (E_f) of investigated models (doped and functionalized models) is decreased with increasing of the calculated energy gap.
The global hardness (η) and softness (S) of doped models and functionalized models are calculated which are decreased and increased respectively with respect to the pristine model with opposite order of energy gap's changes. This reduction is notable for doping models. So, it could be mean that doping process increases the reactivity of pristine model of graphene more than functionalization process and nitrogen atom could play a significant role in the increasing the value of this parameter.

The NMR parameters

The NMR parameters, isotropic chemical shielding (CSI) and anisotropic chemical shielding (CSA), for ^{13}C atoms of optimized structures are calculated and listed in **Table 4** and **5**. The NMR parameters follow the results of structural properties. So, these parameters are similar for symmetrical positions. The CSI parameter relates to the average electronic density at the atomic site **[25]**. For a better understanding, CSI and CSA parameters are shown based on **Fig. 2** to **5**. A quick view at **Fig. 2** shows that CSI parameters for pristine model at the C_{12}, C_{13} (layer1), C_{72}, C_{73} (layer7) have highest values. While, the minimum values could be observed at the C_{22}, C_{23} (layer2) C_{62}, C_{63} (layer6).

Table 4. NMR parameters/ppm of investigated models for sites of various ^{13}C atoms*.

	Pristine model		Doped models			
			B-doped model		N-doped model	
	σ_{iso}	σ_{aniso}	σ_{iso}	σ_{aniso}	σ_{iso}	σ_{aniso}
C_{11}	66.16	150.04	63.28	149.72	65.82	150.16
C_{12}	72.27	144.61	68.16	151.68	75.97	136.01
C_{13}	72.27	144.61	65.51	155.93	79.81	137.48
C_{14}	66.16	150.04	66.41	149.22	65.87	151.66
C_{21}	64.66	132.39	60.67	142.46	69.99	119.93
C_{22}	58.88	158.94	52.63	170.76	64.92	141.88
C_{23}	58.88	158.95	55.94	166.29	63.15	156.28
C_{24}	64.66	132.39	61.71	138.91	68.21	126.04
C_{31}	59.13	178.58	52.71	180.71	59.88	157.72
C_{32}	64.88	172.14	55.22	210.65	56.51	116.42
C_{33}	64.88	172.14	59.97	183.22	69.1	161.65
C_{34}	59.12	178.58	61.15	186.66	59.18	174.17
C_{41}	65.27	110.42	57.58	108.01	75.09	92.5
C_{42}	63.32	157.86	-	84.68	-	170.61
C_{43}	63.32	157.85	55.45	215.99	59.77	106.41
C_{44}	65.25	110.42	56.93	124	73.48	100.95
C_{51}	59.13	178.58	52.71	180.71	59.98	157.72
C_{52}	64.88	172.13	55.22	210.65	56.51	116.42
C_{53}	64.88	172.14	59.97	183.22	69.1	161.65
C_{54}	59.12	178.58	61.15	186.66	59.18	174.17
C_{61}	64.66	132.39	60.67	142.46	69.99	119.93
C_{62}	58.88	158.94	52.63	170.76	64.92	141.88
C_{63}	58.87	158.93	55.94	166.29	63.15	156.29
C_{64}	64.66	132.38	61.71	138.91	68.21	126.04
C_{71}	66.16	150.04	63.28	149.72	65.81	150.16
C_{72}	72.27	144.61	68.16	151.68	75.97	136.01
C_{73}	72.26	144.61	65.51	155.93	79.81	137.48
C_{74}	66.17	150.02	66.41	149.22	65.87	151.66

*see fig. 1 (a, b and c) for details.

Table 5. NMR parameters/ppm of investigated models for sites of various ^{13}C atoms*.

	Pristine model		Functionalized models			
			-BH2 Functionalized model		-NH2 Functionalized model	
	σ_{iso}	σ_{aniso}	σ_{iso}	σ_{aniso}	σ_{iso}	σ_{aniso}
C_{11}	66.16	150.04	65.27	151.73	67.60	147.80
C_{12}	72.27	144.61	71.88	147.39	72.07	145.98
C_{13}	72.27	144.61	70.44	147.45	73.49	142.25
C_{14}	66.16	150.04	65.63	151.41	66.48	148.86
C_{21}	64.66	132.39	62.8	152.81	73.49	144.70
C_{22}	58.88	158.94	60.10	158.70	57.90	160.23
C_{23}	58.88	158.95	58.70	161.26	59.23	158.44
C_{24}	64.66	132.39	64.14	133.42	64.96	131.27
C_{31}	59.13	178.58	49.96	185.51	70.75	156.43
C_{32}	64.88	172.14	64.66	172.37	64.63	171.43
C_{33}	64.88	172.14	64.47	174.86	65.88	170.38
C_{34}	59.12	178.58	59.63	179.20	58.82	177.56
C_{41}	65.27	110.42	53.49	177.35	54.41	130.58
C_{42}	63.32	157.86	54.64	168.28	71.01	147.33
C_{43}	63.32	157.85	64.33	159.93	62.93	157.49
C_{44}	65.25	110.42	60.39	117.18	68.83	104.66
C_{51}	59.13	178.58	46.96	185.51	70.75	156.43
C_{52}	64.88	172.13	64.66	172.37	64.63	171.43
C_{53}	64.88	172.14	64.47	174.86	65.88	170.38
C_{54}	59.12	178.58	59.63	179.20	58.82	177.56
C_{61}	64.66	132.39	62.79	152.82	73.49	144.70
C_{62}	58.88	158.94	60.10	158.70	57.90	160.23
C_{63}	58.87	158.93	58.70	161.26	59.23	158.44
C_{64}	64.66	132.38	64.14	133.42	64.96	131.27
C_{71}	66.16	150.04	65.27	151.73	67.60	147.80
C_{72}	72.27	144.61	71.88	147.39	72.07	145.98
C_{73}	72.26	144.61	70.44	147.45	73.49	142.25
C_{74}	66.17	150.02	65.63	151.41	66.48	148.86

*see fig. 1(a,d and e) for details.

The CSA parameter indicates the difference between the distribution of the electronic densities perpendicular to the molecular plane (z axis) and within the molecular plane (x – y axes) **[27]**. The highest values of CSA for the pristine model are attributed to the C_{31}, C_{34} (layer3), C_{61}, C_{64} (layer6). While the lowest values of CSA were observed at the C_{41} and C_{44} (layer 4).

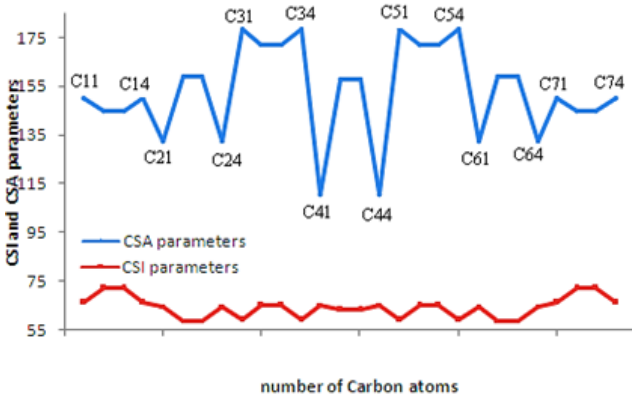

Fig. 2. The NMR parameters of ^{13}C atoms for pristine model.

Doping of N/B atom on the graphene sheet can change geometrical, electronic and magnetic parameters. **Fig. 3** shows the values of CSI parameter for N-doped and B-doped models. Doping effect on the variation of CSI for N-doped model is different to B-doped model. As can be seen, CSI parameters for carbon atoms of N-doped model are increased (with the exception of C_{32} and C_{52}) while decreasing of this parameter is observed for the B-doped model (with the exception of C_{34} and C_{54}). Opposite behavior in the studied models is due to some subjects such as, net charge on the atoms and the shape of polarized charges on the atom. Above factors can effect on the CS tensors.

Doping of B/N atom can be affected the values of CSA parameters. Results show that the highest values of CSA are related to C_{34} and C_{54} for the N-doped model and C_{43} for the B-doped model. It is noticeable that the minimum value of CSA is related to the C_{41} atom in the both B/N doped model (**Fig. 5**.).

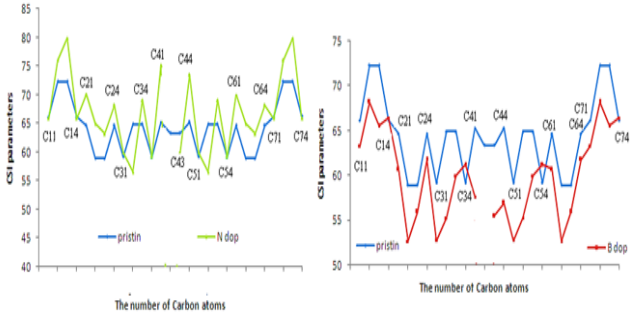

Fig. 3. The CSI parameters of ^{13}C atoms for pristine and N-doped models/ pristine and B-doped models.

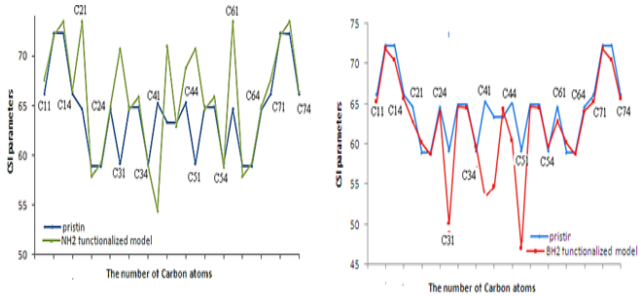

Fig 4. The CSI parameters of ^{13}C atoms for pristine and –NH2 functionalized models/ pristine and $–BH_2$ functionalized models

Fig. 4 shows the values of CSI parameters of $–BH_2$ and $-NH_2$ functionalized models. The variations of CSI for these models are changed at opposite way. The CSI parameter for carbon atoms of $–NH_2$ functionalized model are increased (with the exception of C_{22}, C_{41} and C_{62}) while decreasing of this parameter is observed for the $-BH_2$ functionalized model (with the exception of C_{43}). The result of CSA parameters of functionalized models are shown at **Fig. 6**. Thehighest values of CSA are related to C_{31}, C_{34}, C_{51}, C_{54} for the $-NH_2$ functionalized model and C_{31}, C_{51} for the $-BH_2$ functionalized model. .It is noticeable that the lowestvalue of CSA is related to the same atom, C_{44} atom, in the both $–NH_2$/$-BH_2$functionalized model.

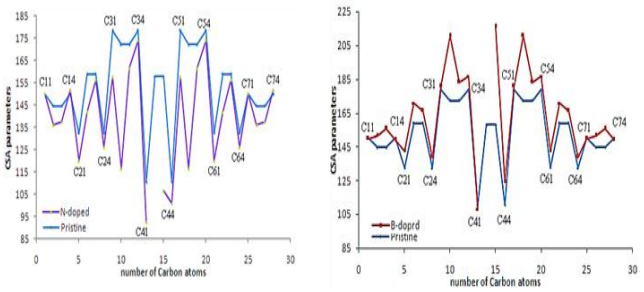

Fig 5. The CSA parameters of ^{13}C atoms for pristine and N-doped models/pristine and B-doped models.

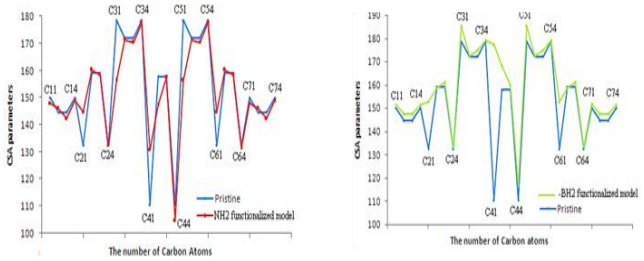

Fig 6. The CSA parameters of ^{13}C atoms for pristine and $–NH_2$ functionalized models/ pristine and $–BH_2$ functionalized models.

Conclusion

Density functional theory (DFT) calculations at the BLYP/6-31G* level was performed to investigate doping and functionalizing effect on graphene. The Structural properties show that for equivalent positions, C-C bond lengths are similar. The NMR parameters follow the results of structural properties. So, these parameters are similar for symmetrical positions. By making impurity, opposite behavior are seen which is due to some subjects such as, net charge on the atoms and the shape of polarized charges on the atom. Above factors can effect on the CS tensors. It was found that doping more than functionalizing and nitrogen atom more than boron atom could decrease value of pristine model's energy gap. Afterwards, the reactivity of functionalized and specially doped models are decrease and increase respectively, with respect to the pristine model and nitrogen atom could play a significant role in increasing the value of this parameter. It could be said that doping model in comparison of functionalized model is a better choice for production of electronic devices such as chemical and biological sensors and other innovations because of their larger electric conductivity and reactivity. Also, the N-doped model in comparison of the B-doped model is a better choice.

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