

## Investigation of computational structural and electronic properties of carbon nanotubes doped with boron and nitrogen

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Since the discovery of carbon nanotubes has been studied the properties and applications of these interesting materials. Applications of carbon nanotubes are included a wide range of nano electronics to nano biotechnology and so on. Carbon nanotubes doped with boron and nitrogen have been increased the importance of study of carbon materials. This is due to the physical and chemical properties that when boron and nitrogen atoms are doping is created in the structure of carbon nanotubes. These properties include improved chemical reactivity, the change of conductivity and mechanical properties. In this study, density functional theory calculations on the structural properties of four different types of carbon nanotubes doped with boron and nitrogen have been implemented. Dipole moment, chat bar, the parameters of nuclear magnetic resonance (NMR) have been investigated for five models of carbon nanotubes. The obtained results show that carbon nanotubes doped with boron and nitrogen creates in significant changes in the electronic structure and their properties. The dipole moment increases in nanotubes doped with boron and nitrogen. The band gap amount of the full model of models doped with boron and nitrogen is more. Due to creating changes in the electronic and structural properties, NMR parameters are different for the models are doped with boron and nitrogen from the full model.

**Keywords:** carbon Nanotubes, doping, density functional theory, dipole moment, chat bar, nuclear magnetic resonance.

### INTRODUCTION

Nanotechnology, production capabilities and producing the materials are the new tools and systems in seize control at the nanometer scale or atomic and molecular levels and using the properties that appear in these surfaces, it means the use of materials whose dimensions are about 1-100 nm. By entering to this small space, human can interfere in the arrangement and construction of atoms and molecules involved and to make new materials with different structures. Nanometer equals 1 billionth of a meter or 9-10 meters. This size is 18,000 a millionth times is smaller than the diameter of a human hair and an average of 3 to 6 atoms together make a length of 1 nm which in its turn depends on the type of atom. The first string on the nano-scale in 1970 by Marynobo Endo was prepared from the University of Orleans at France. The strings were of seven nanometers in diameter, and were prepared with Steam growth. Today, however, the name of Sumio Iijima of NEC Laboratories in Tsukuba (Japan) in 1991 was the first person who was able to nanotube, carbon atoms are arranged in a cylindrical structure. That is a hollow tube that its wall made of

see the nano-tubes were located at the top researchers in the field [1]. At the same time, and independently in Moscow scientists were able to detect tiny tubes that the proportion of length to diameter ratio was less than the Iijima. The Russians named this matter bar lens [2]. What Iijima was able to see it, was a multi-layer carbon nanotube that includes 2 and 15 graphite page that is why were told them multi-walled nanotubes, two years later Iijima and Donald Botton and others at the same time in IBM America without the knowledge of each other made the single-walled carbon nanotubes [3,4].

Today, one of the most important nano materials in nanotechnology is carbon nanotubes whose diameter is about 1,000 times smaller than a human hair. The nature of the carbon Nanotubes is because of this, that carbon is a material with lightweight, very stable and easy to carry out the process that is cheaper to produce than metals, they have turned to unique compounds. Nanotubes are made on the basis of constructing of graphite. When the graphite flakes fall into each other, make up tubular structures that we know them as carbon nanotubes [5]. In carbon carbon atoms. Carbon nanotubes like graphite is composed of sp<sup>2</sup> bonds, sp<sup>2</sup> of sp<sup>3</sup> bonds that are in diamonds are tighter. The most important physical property of nanotubes is electrical conductivity of them that depending on the type and the angle of bonds is quite different from another category. For example, nanotube of seat is 1,000 times more

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conductive than copper, while the zigzag type and asymmetric type are semiconductor (semiconductor property varies depending on their types). The electrical nanotubes from the point of view properties are divided into two categories: conductive and semi-conductive, so that type of Chirality and diameter of the nanotube determines their properties. Wide studies to evaluate the diameter and twisting of pipes are done on electrical properties of the nanotube [6]

The most important feature in the characterization of nanotube is expressed as chirality [7, 8, 9, and 10]. Because nanotubes have good strength and ductility are used in the mixed materials with metal, polymer and ceramic field. But the most important factor that has been caused to select as Nanotubes as a string in composite materials (composites), is its low weight means a high strength to weight ratio. On the other hand thermal properties of carbon nanotubes are higher than diamond. So nanotube with such characteristics has the using capacity to cool the interior of your computer. Studies on the thermal conductivity of CNTs show that thermal energy transfers at 10 kilometers per second during the tube. Today, carbons nanotubes are used as fuel cells, very thin conductive wire, catalyst to attract and natural gas and hydrogen-storage [11]. Also are used in the preparation of nanotube diode, nano-tube fibers, bulletproof vests, safety helmets and gloves and nano-composites. Of preparing ways of carbon nanotubes can be noted to the electrical arc discharge, laser ablation and chemical vapor deposition (hot gas) noted. In arc discharge method the rate of extracting the nanotubes includes up to 30% weight of left coal left. This method is produced the nanotubes with a length of 50 microns or less and their size and they formed in random size and directions that cannot be changed the nanotube by controlling the diameter [12]. While the laser ablation technique the rate of extracting the nanotubes to 70 % is weight and the rest are catalysts and soot.

The production rate of nanotubes was low and nanotubes that formed in evaporative form intertwine in each other. Produced nanotubes in a limited range of diameter can be controlled by changing temperature of the reaction, but this method is very costly, because laser equipment is very expensive. In the chemical vapor deposition method (hot gas), is provided a perfect platform for growth in a heating device that can be heated it to 600 ° C and little by little, a gas containing carbon are added such as methane , when gas decomposed the atoms of carbon are released and can be rearranged to form of carbon nanotubes. The

nanotubes extracted in this way are 20 to nearly 100 percent by weight. Chemical vapor deposition method is the easiest way among other methods to produce CNT on an industrial scale.

This method can produce long Nanotubes that can be used as fibers in fiber and composites. But generally produced nanotubes are multi-walled and are usually associated with a fault. As a result, the amount of one tenth of nanotubes are produced by electric arc has strength [13]. One of the new methods of production of carbon Nanotubes, are one-stop production method of CNT with high-quality that takes help of water and directly makes nanotubes from carbon. The strength point of this method is its simplicity, low cost and high efficiency. Properties of nanostructured materials in laboratory conditions alone cannot pass to the technical products. So, large-scale production of nano-materials such as carbon nanotubes is area previous necessity. In many cases of determining the type of nanotubes in predicting the type on interaction has crucial importance. For example, absorption of gases such as oxygen or nitrogen dioxide on the electrical properties of semiconducting nanotubes has high and important effect, but does not have any effect on the electrical properties of the conductive nanotubes. Open nanotubes act like a hollow reed. By capillary action and under certain conditions these molecule reeds can straw some elements within it. Small diameter of single-walled carbon nanotubes and their empty spaces and long length of nanotubes than its diameter and being hydrophobic make its nanotube similar to something like tube or capsule that can be used to store and deliver medications and fluids or gases [14]. Different structural models for hybrid configuration doping nitrogen doped in carbon nanotubes have been proposed which they can be cited pyridine-like, piroli-like and graphite (succession). Doping the carbon nanotubes initially was discussed by Stefan and colleagues [15] in 1994. They synthesized multi-walled carbon nanotubes doped with boron and nitrogen by using arc discharge method. It was proposed single-wall carbon nanotubes doped with nitrogen by evaporation of a catalyst containing graphite rods in a helium/ nitrogen atmosphere produced in an arc discharge test [16]

Based on theoretical studies ion deposition is suggested as a way to enhance selective carbon nanotubes by nitrogen [17, 18]. Carbon doping directly on the walls of nanotubes by nitrogen for the first time was studied by Bern Hulk and Lie by using the density functional theory [19]. Chemical substitution is used through partial substitution

reactions of not doped nanotubes, by using B<sub>2</sub>O<sub>3</sub> vapor and nitrogen gas at 1500-1700 Kelvin for replacing nitrogen in single-walled carbon nanotubes. To build Boron-nitride nanotubes [20] this leads to irregular damage the walls of the nanotubes succession with less than one percent of replacing nitrogen in compare with the electrical arc discharge techniques. The outer doping of the nanotube surfaces can lead to focus electron sites. The disappearance of flatness and ineffective latest on nanotubes cause to chemical activate in pipes.

For this reason doing the pipes are caused good conditions for chemical controlled actions of nanotubes and is provided a way to enable regions along the tube wall. For single-walled nanotubes and for the outer layer of multi-walled nanotubes, this leads to increase the activated levels. By putting the metals inside the nanotube can be improved electrical properties of these materials. According to many researchers the internal single-walled of carbon nanotubes chemically is not active, but recently researchers find that these walls can be enabled. They found that if they put metal rhenium on these walls, then the nanotubes will be chemically active. Yoda Saka and his colleagues observed that the edges of nano-tubules doped with nitrogen [21]. These resulted bulges are used often an indicator that measures the nitrogen involved in the network pentagon. It is proved that oh preferably is attached to carbon atoms adjacent the nitrogen this suggests that nitrogen chemically activates the carbon atoms around inside the pipe. Hence we should expect for changes in reacting nitrogen coating of carbon nanotubes especially in single-walled carbon nanotubes. With regards to the importance of carbon nanotubes and improvement of their properties this study was carried out in order to investigate the substitutions of boron and nitrogen atoms and the changing the carbon nuclear magnetic resonance parameters and the effects of doping on the angles and bond length and energy of HOMO and LUMO orbitals.

#### MATERIALS AND METHODS

In this study, using density functional method (DFT) and utilizing nuclear magnetic resonance (NMR) was investigated doping effect of boron and nitrogen atoms in different sites on single-walled carbon nanotubes (0,6) and structural and electronic properties of single-walled carbon nanotubes (0,6) were discussed for the proposed models. The proposed model consists of four different models were named as models (A), (B), (C) and (D), The

difference of these models was in the positions of doped atoms.

The full model was a zigzag carbon nanotubes (0,6), which was composed only of carbon atoms. In total, the full model contains 48 carbon atoms and 12 hydrogen atoms. CNT length in full model of Angstrom was 9.258 and diameter was 4.837 of each of the openings of CNT in Angstrom model (Fig 1). Carbon nanotubes (0,6) consisting of 8 layers and since carbon nanotubes (0,6) was symmetrical, as a result, layers 1 and 8, 2 and layers 2,7, layers 3 ,6 and layers 4 and 5 were identical with each other mutually. It should be noted that layers 1 and 8 were formed the openings in carbon nanotubes that had been saturated with hydrogen atoms.

In model (A) carbon atoms located on the first layer (openings CNT) and the second layer of full carbon Nanotubes, were replaced with boron and nitrogen atoms, respectively. How doping atoms in the model (A)) is shown in Fig 2. The length of this model was 9.327 Angstrom and a diameter of boron and carbon openings was 4.779 and 4.738 Angstrom respectively. Doped in this model (B) was the Fig of model (A). So that the carbon atoms located on the first layer (openings CNT) full CNT (Fig 2) with atoms of nitrogen and carbon atoms located on the second layer were replaced with boron atoms. How doping atoms in the model (B) is shown in Fig 2 Length of this model was 9.308 Å and a diameter of nitrogen and carbon openings were 5.072 and 4.788 Angstrom respectively.

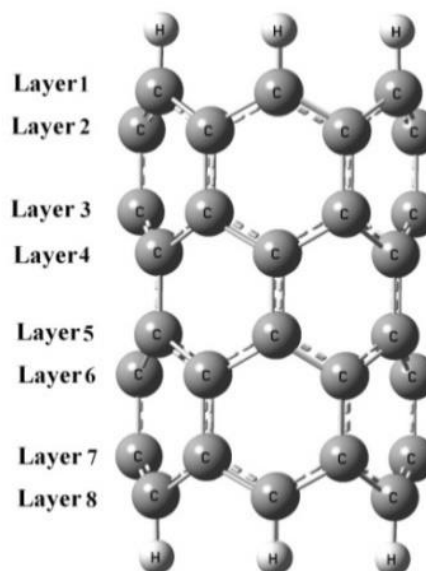
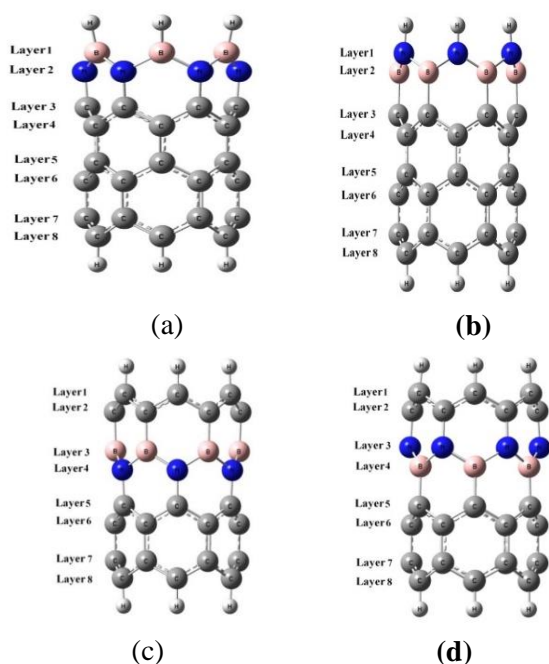


Fig. 1. Figure of full carbon nanotube.



**Fig. 2.** Figure of doped nanotubes studied in different models: a) model A, b) model B, c) model C, d) model D

According to Fig 2 doped way in the proposed model (C) was in this way that the carbon atoms are located on the third layer of full carbon nanotubes with atoms of boron and carbon atoms also located on the fourth layer of full carbon nanotubes were replaced with nitrogen atoms. Length of this model was 9.322 Å and diameter of carbon opening that was near to the place of doped CNTs (the first layer of carbon atoms) and other openings of carbon nanotube were 4.721 and 4.885 Angstrom respectively. Doping ways of atoms in the model (D) was the Fig of model (C). So that the nitrogen atoms were replaced in place of carbon atoms located on the third layer and boron atoms were replaced instead of carbon atoms located on the fourth layer. Length of this model was 9.319 Å and diameter of carbon opening that was near to the doped CNTs location (the first layer of carbon atoms) and other openings of carbon Nanotube were 4.914 and 4.786 Angstrom respectively. In most computing tasks, choosing the right model offers good and comparable results and with experimental results so to select at least length of the studied nanotubes And for being the obtained results closer to reality, as well as for shortening the time in calculation, hydrogen atoms were used to saturate the carbon opening nanotubes. The proposed carbon nanotube has 48 carbon atoms that were added 12 hydrogen atoms to their openings. After the initial design of desired nanotube in optimized length and diameter by using graphics software, computational method

B3LYP / STO-3G on the software Gaussian optimization was used for the optimized initial calculation. After achieving the structures with minimum energy and to ensure the reality of it, the results of B3LYP / STO-3G calculation were used as an input to computing at B3LYP / 6-311G \*\* theory level . The reason of selection this theatrical level was due to low error rate of based set. To optimize the studied structure ,we have used of OPT order and thus have achieved the structures with minimum energy .In the next phase of this study, using software HYPERCHEM7 boron and nitrogen atoms were doped with four different modes in nanotubes; and to determine the minimum amount of energy by using B3LYP / 6-311G \*\* method structures were optimized. With optimization calculation of the energy structure, energy of orbitals of HOMO and LUMO, energy difference of orbitals HOMO and LUMO and the dipole moment rate of the entire system were obtained for the studied models. In the last stage, this main study of this research that includes the studying of magnetic resonance parameters of cores 13C, 11B and 15N was done. Calculation of displacement tensors Chemical was done (CS) also by using B3LYP method and basic series 6-311G.\*\*

## RESULTS AND DISCUSSION

The results of optimization calculations are presented in Table 1. According to the results obviously doped models have different energies compared to the full version because the constituent atoms for the full and doped version are different. Also with investigations on energy of doped models with boron and nitrogen atoms has been determined that in each of the doped models (A), (B), (C) and (D) also is observed a few different energy. However, due to the observed structural models for the nanotubes is obtained the conclusion that these models are structural isomers of each other, because in all doped models with boron and nitrogen atoms , six boron atoms have been replaced with six carbon atoms in one layer and six nitrogen atoms in another layer have been replaced with six carbon atoms. To better understand the structural stability of isomer, amounts of energy are obtained for doped models with boron and nitrogen atoms (A), (B), (C) and ((D)).The results are shown in Table 1. According to the results of the sustainability doped model (A), (B), (C) and ((D) are as  $B > A > D > C$ , which proves that stable isomer is Model B.

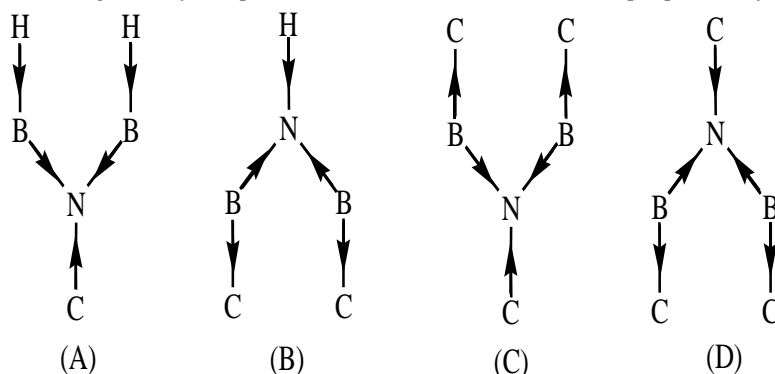
**Table 1.** The structural energy amount, energy orbital (LUMO) HOMO, energy orbitals (EHOMO) LUMO, energy difference orbitals HOMO and LUMO (Eg) and dipole moment (DM) of full nanotubes, doped with boron and nitrogen (A), (B), (C) and (D)

Model	Energy(keV)	Relative energy(eV)	E <sub>HOMO</sub>	E <sub>LUMO</sub>	E <sub>g</sub> (eV)	DM(Debye)
Perfect	-49.969	-	-3.646	2.623	1.023	0.000
A	-50.536	2.731	-3.818	3.184	0.634	5.011
B	-50.539	0.000	-4.016	3.507	0.509	6.245
C	-50.536	3.486	-3.767	3.266	0.501	3.648
D	-50.536	3.025	-4.068	3.478	0.589	3.552

In this research by extracting the energy amounts of orbitals HOMO and LUMO for full-doped nanotubes, the results showed that the amount of energy for the full doped model is different (Table 1). So that, energy level of orbitals HOMO and LUMO are reduced by replacement of carbon atoms with boron and nitrogen atoms. The energy difference between orbitals HOMO and LUMO (Eg), show that the rate Eg is the highest among for full nanotubes. But with the doping of boron and nitrogen atoms in the structure of carbon nanotubes (6, 0) splitting of energy is reduced. This effect can be attributed to replace atoms with different electronegativity that causes changes in the energy levels of HOMO and LUMO orbitals. With regard to it that carbon nanotubes have been formed only of carbon atoms and are symmetrical so they have two similar endings, as result it is not observed the separation load in them, and hence have zero dipole moment. With replacing boron and nitrogen atoms with different the electronegativity than the carbon atoms in the carbon nanotube structure and the loss of symmetry in CNT a significant amount of separation occurs that causes a change in dipole moment. It is noteworthy with regard to that in the doped models, boron and nitrogen atoms in different layers of full carbon nanotubes have been doped, thus is expected that the dipole moment amount of these models are different with each other. The

resulting dipole moment values are shown in Table 1.

According to the results of model B compared to other models has the highest amount of dipole moment. As shown in Fig 3, in the model (B) the nitrogen atom is located at the mouth of carbon nanotubes openings and is connected to atoms of boron and hydrogen. Thus in the model (A) nitrogen atom that is located in the second layer is connected to the boron and carbon atoms with SP2 hybrid. With regard to this that hydrogen atoms have less electronegative than carbon atoms with hybrid SP2 so electron density of nitrogen atoms gets higher in the model (B) than the model (A) and more load separation is observed. As a result, model (B) has greater dipole moment than the model (A). But compared to the models (A) and (B) that the boron atoms or nitrogen atoms are linked to hydrogen atoms, in doped models (C) and (D) (Fig (e4) boron and nitrogen atoms have been doped in the inner layers of carbon nanotubes and are attached to carbon atoms. With regard to the Fig (e4) vectors N-B and BC make each other weak and due to that electron density of nitrogen is reduced and the rate of dipole moment models (C) and (D) than the models (A) and (B) are decreases.



**Fig 3.** Orientation of load distribution on the surface of carbon nanotubes and their impact on dipole moment

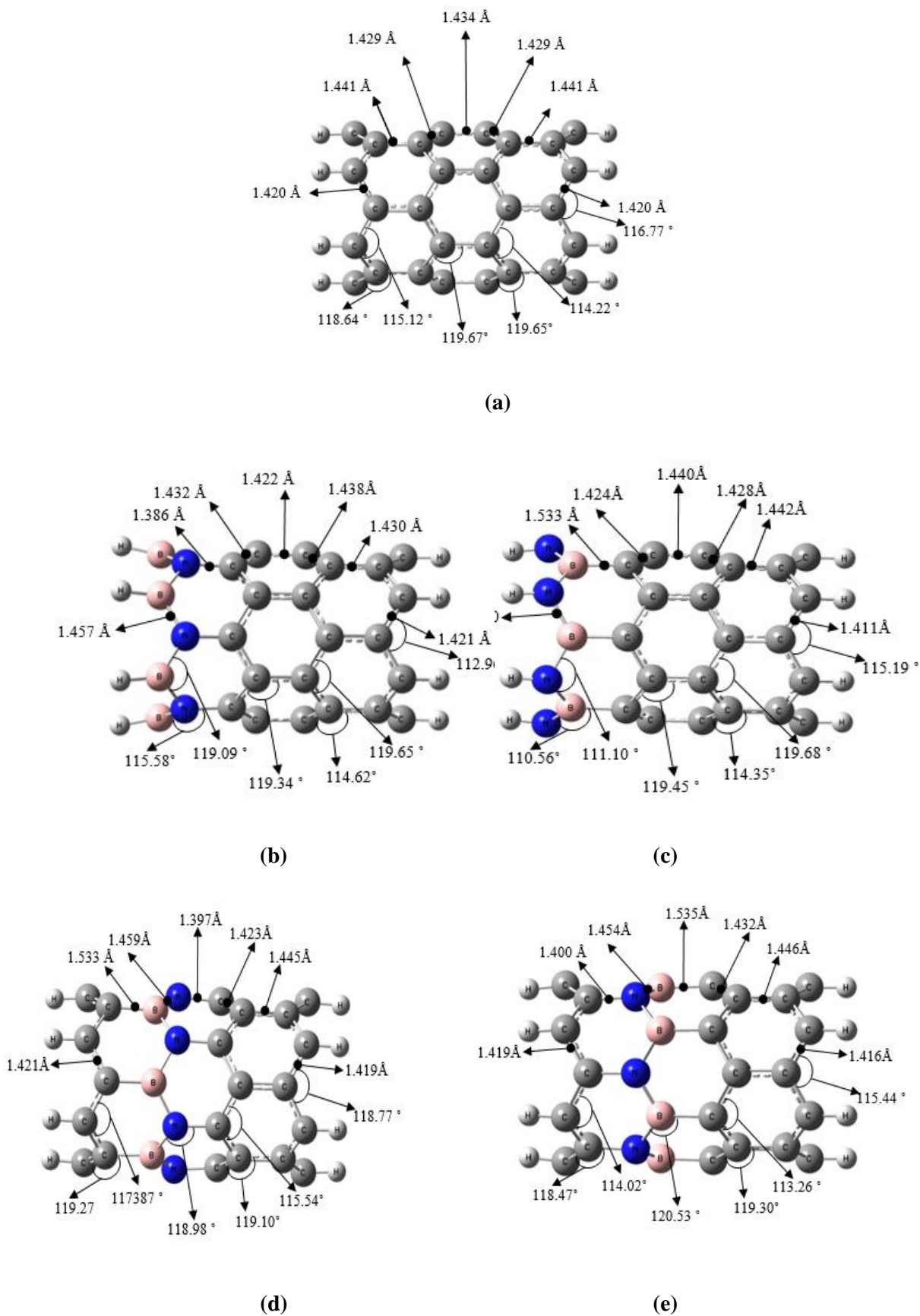
Upon completion of optimization calculations using the software of Gauss View the length of bonds and angles of bonds are obtained for the studied models.

As shown in Fig (a4), a series of CC bonds are in parallel with the main axis of carbon nanotube (CC bonds parallel) while some of these other bonds than the main axis are angular (CC diagonal bonds). The results of the calculations show that C-C parallel bonds length are longer than C-C diagonal bonds to (Fig a4). In the full model regardless of hydrogen, there are only C-C bonds. While in the model doped with boron and nitrogen in addition to C-C bonds, B-N, B-C or N-C bonds or all three types of bonds are also available. These changes in structural bonds make some changes in bond length and bond angles in the model doped with boron and nitrogen.

In model (A) (Fig b 4) in comparison with the full model of diagonal C-C bonds length increases while the C-C parallel bonds length substantially decreases. But in model (B) unlike the (A) compared with diagonal C-C bonds full model decreases while the C-C parallel bonds length increases. Also in the model (A) B-N bond length is equal to 1.457 Å. While the in model (B) (Fig (c4) BN bond length is 1.457 Angstroms. Shorter length of the BN bond in the model (B) than the model (A) can be justified by saying that in the model (B) the nitrogen atom puts its pair non bonded electron to the only boron atom. While in the model (a) in addition to being the electron pair to boron can put also the electron pair to the carbon atoms SP2 and participates in resonant ring. Moreover, as in the Figs (d4) and (e4) is shown,

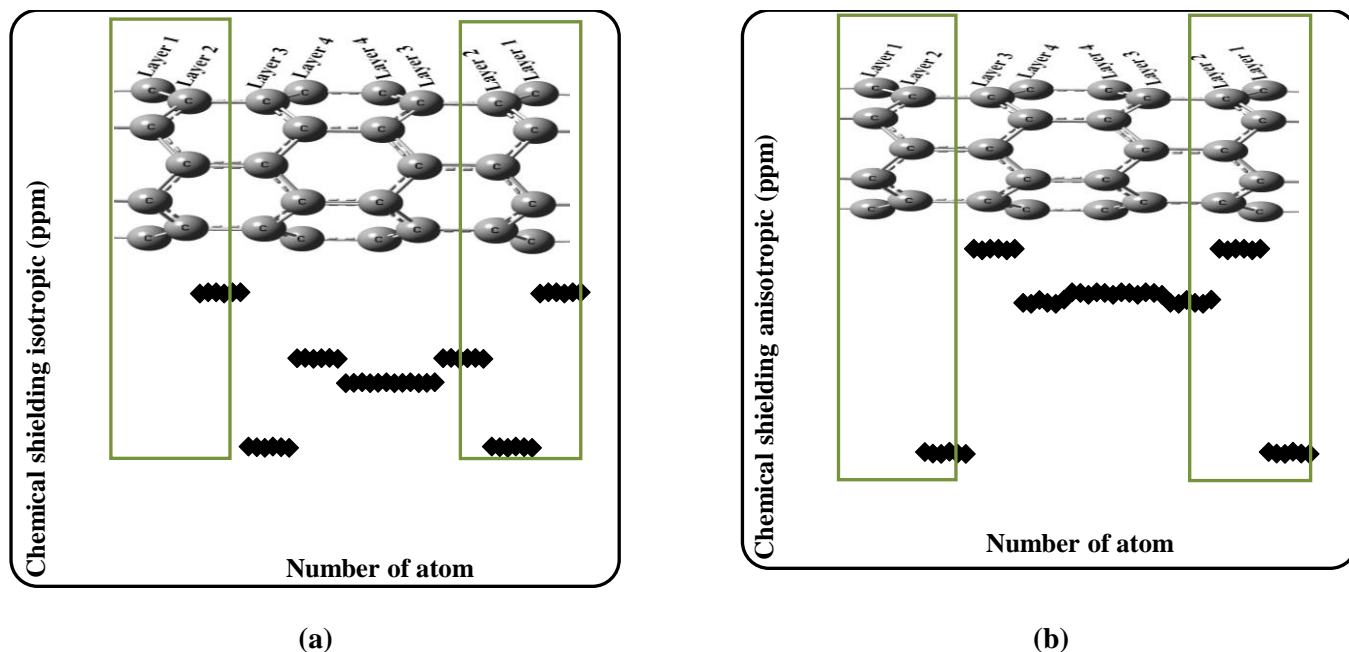
changes in C-C bond lengths for models (C) and (D) also are seen as compared to the full model. The B-N bond length in the model (C) than the model (D) is taller. Also it is noteworthy that, C-C bond length in the models (A), (C) and (D) that are connected directly to the nitrogen is decreased. That it is correspond with the findings of Hols -lie [22] and can be concluded that the doping nitrogen atoms cause a short length of C-C bond that is attached to it. In addition, changes in bond angles (Figs (d4) to (e4)) are greater than the change in bond length. The results of NMR parameters for the full model showed that the atoms in full carbon nanotubes can be divided into different layers that atoms located in each layer feels similar the electronic environment (Fig 5)

Because carbon nanotubes are symmetrical, so both ends of the nanotubes are similar. As a result, the carbon nanotubes can be divided into two parts, each part consists of 4 different layers. The results show that atoms located in different layers have different NMR values that it shows that the zigzag carbon nanotube structure of atoms in different chemical environments (6, 0) in different layers of feeling. According to the results obtained through nuclear magnetic resonance spectroscopy (NMR) for full carbon nanotubes can be concluded that the carbon atoms located at the opening of the CNT has the largest amount of CSI (13C) and the lowest amount is CSA (13C)



**Fig 4.** The bond lengths in term of Å and bond angles in term of degrees. a) the full version, b) model A, c) Model B, d) Model C, e) Model D





**Fig. 5.** The chemical shifts of isotropia (a) and anisotropy (b)  $^{13}\text{C}$  show full carbon nanotubes in front of the numbers of atoms

As previously mentioned in surveyed models (A) and (B) carbon atoms located on the first and second layers of carbon nanotubes have been doped with boron and nitrogen atoms. Doping the boron and nitrogen atoms in the structure of the full carbon nanotubes structural symmetry of that is lost and therefore the parameters of nanotubes NMR, models (A) and (B) are divided into 8 different layers. So that in the model (A) the first layer includes B11-B16 and the second layer includes the atoms N21-N26 (Fig a2). While in the model (B) the first layer and includes the atoms N11-N16 B21-B26 (Fig a2)

However, as has been shown in the Figs (6) and (7) for both models (A) and (B) layers the third, fourth, fifth, sixth, seventh and eighth respectively include C31-C36, C41-C46, C51-C56, C61-C66, C71-C76 and C81-C86. Data obtained by Calculations shows that the cores  $^{13}\text{C}$  NMR in models (A) and (B) consists of 6 different layers (layers three to eight) that carbon atoms are located in each layer has a same isotropic and anisotropic chemical displacement amount as a result they feel the same chemical environment. Table 2 shows NMR calculations for model (A). According to Table 2 can be realized with doping atoms of boron and nitrogen, respectively, in the first and second layers of carbon nanotube model (A) compared to the full model, some changes are observed in the CS tensors in different sites  $^{13}\text{C}$ . So that the doped boron atoms in the first layer and doping the nitrogen atoms in the second layer is put in the amount of CSI

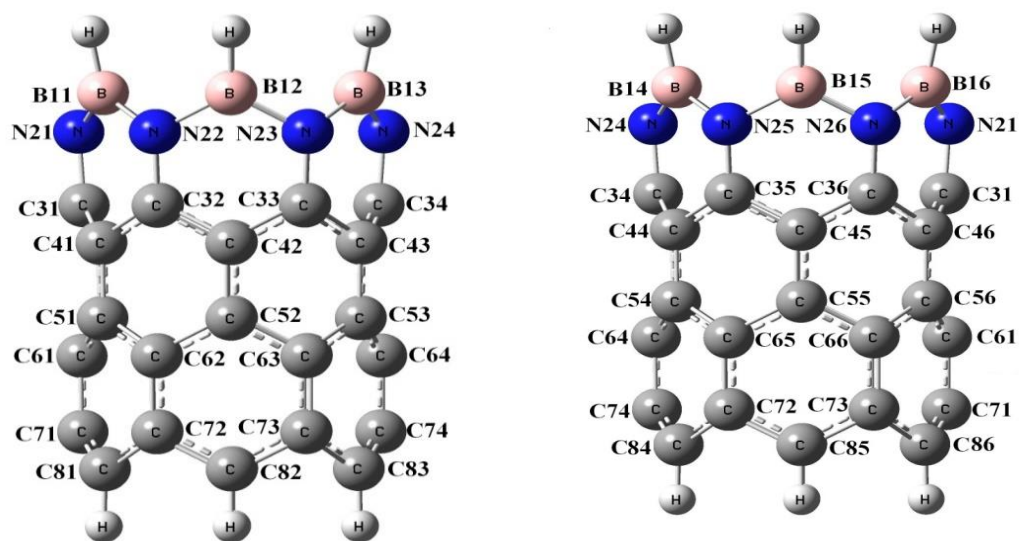
( $^{13}\text{C}$ ) for all cores  $^{13}\text{C}$  are located through three to layers is observed  $^{13}\text{C}$  substantial increasing.

However, the CSA ( $^{13}\text{C}$ ) for all carbon atoms located in the third to the eighth layers are decreased.

It is noteworthy that most of the changes CSI ( $^{13}\text{C}$ ) and CSA ( $^{13}\text{C}$ ) are observed to carbon atoms located on the fourth layer. That isotropia increase also are showed that the magnetic field caused by the electron cloud around the cores of carbon after doping has had more impact on spin moment of core and reduction the anisotropy carbon atoms forming the carbon nanotube in the model (A) shows that symmetry of the electron cloud of nanotubes doped with boron and nitrogen atoms are increased. But the survey NMR parameters for model (B), are viewed that with doping of nitrogen atoms in the first layer and doping the boron atoms on the second layer for carbon atoms located on the third layer, fourth, seventh and eighth, the CSI ( $^{13}\text{C}$ ) rate increases of CSA ( $^{13}\text{C}$ ) decreases. Here reduction of the anisotropy is approved the symmetric electron cloud around carbons. While for carbon atoms have been located on the fifth and sixth layers, CSI ( $^{13}\text{C}$ ) decreases and the CSA ( $^{13}\text{C}$ ) increased. By comparing the results obtained for the models (A) and (B) we can understand this point that since in the model (A) nitrogen atoms in the second layer are in the neighborhood of carbon atoms as a result, its electron pairs puts for carbon atoms that are located near to them as to participate in resonance cycle. As a result causes the greater symmetry of an electron cloud around carbon cores but because nitrogen



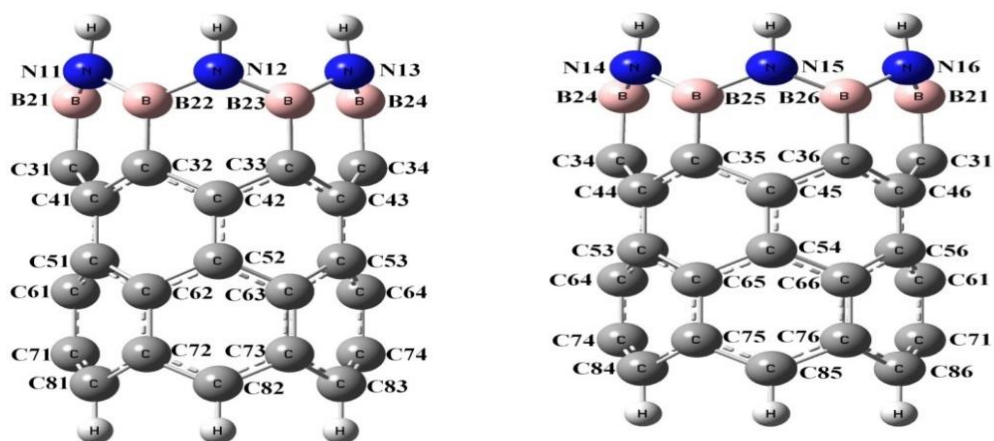
atoms to model (B) are in the first layer, it is not observed such resonance for this model.



(a)

(b)

**Fig 6.** Two-dimensional view of model (A) of carbon nanotubes doped with nitrogen boron; (a) front view and (b) is a back view of the model.



(a)

(b)

**Fig 7.** View of the two-dimensional model (B) carbon nanotubes doped with nitrogen boron (a) front view and (b) back view of this model.

**Table 2.** Parameters of CSI and CSA, cores 13C, 11B and 15N (ppm) for model (A). In this table, for full model in each layer is noted the average value

CS <sup>I</sup>		CS <sup>A</sup>		CS <sup>I</sup>		CS <sup>A</sup>	
Perfect	A model	Perfect	A model	Perfect	A model	Perfect	A model
Layer1				Layer5			
C1	45.7	165.9		C5	30.6	191.2	
B11	79.1		46.9	C51		57.3	167.1
B12	78.9		47.1	C52		58.3	165.8
B13	79.0		46.9	C53		57.8	166.3
B14	79.1		46.9	C54		57.3	167.1
B15	78.9		47.1	C55		58.3	165.8
B16	79.0		46.9	C56		57.8	166.3
Layer2				Layer6			
C2	19.7	198.2		C6	34.7	189.9	
N21	78.1		245.4	C61		74.3	140.2
N22	77.8		245.5	C62		74.1	139.4
N23	78.0		245	C63		74	138.6
N24	78.1		245.4	C64		74.2	140.2
N25	77.8		245.5	C65		74.2	139.4
N26	78.0		245.0	C66		74	138.6
Layer3				Layer7			
C3	34.7	189.9		C7	19.7	198.2	
C31	57.6		139.4	C71		43.1	168.6
C32	57.5		138.7	C72		44.0	171.4
C33	57.2		137.8	C73		45.1	175.6
C34	57.6		139.4	C74		43.0	168.6
C35	57.5		138.6	C75		43.9	171.4
C36	57.2		137.8	C76		45.1	175.1
Layer4				Layer8			
C4	30.6	191.2		C8	45.8	165.9	
C41	83.1		129.8	C81		71.1	116.7
C42	83.7		129.2	C82		64.3	126.7
C43	83.5		129.6	C83		67.2	122.8
C44	83.1		129.8	C84		71.1	116.7
C45	83.7		129.2	C85		64.3	126.7
C46	83.5		129.6	C86		67.2	122.8

**Table 3.** Parameters of CSI and CSA and cores 13C, 11B and 15N (ppm) for model (B). In this table, for each layer is noted the average value

CS <sup>I</sup> (ppm)		CS <sup>A</sup> (ppm)		CS <sup>I</sup> (ppm)		CS <sup>A</sup> (ppm)	
Perfect	B model	Perfect	B model	Perfect	B model	Perfect	B model
Layer1				Layer5			
C1	45.7	165.9		C5	30.6	191.2	
N11	117.4		142.6	C51	19.1		212.9
N12	117.3		143.2	C52	19.1		212.7
N13	117.4		143.3	C53	19.0		212.9
N14	117.4		142.6	C54	19.1		212.9
N15	117.3		143.2	C55	19.1		212.7
N16	117.4		143.3	C56	19.0		212.9
Layer2				Layer6			
C2	19.7	198.2		C6	34.7	189.9	
B11	59.6		69.9	C61	24.0		207.6
B12	59.7		69.8	C62	23.9		208.1
B13	59.7		69.8	C63	24.0		207.8
B14	59.6		69.9	C64	24.0		207.6
B15	59.7		69.8	C65	23.9		208.1
B16	59.7		69.8	C66	24.0		207.8
Layer3				Layer7			
C3	34.7	189.9		C7	19.7	198.2	
C31	54.4		172.6	C71	54.6		145.8
C32	54.6		172.6	C72	54.3		146.4
C33	54.5		172.6	C73	54.5		146.2
C34	54.4		172.6	C74	54.6		145.8
C35	54.6		172.6	C75	54.3		146.3
C36	54.5		172.6	C76	54.5		146.2
Layer4				Layer8			
C4	30.6	191.2		C8	45.8	165.9	
C41	39.5		171.8	C81	71.2		123.5
C42	39.8		171.2	C82	71.3		123.4
C43	39.5		172.0	C83	71.2		123.6
C44	39.5		171.8	C84	71.2		123.5
C45	39.8		171.2	C85	71.3		123.4
C46	39.5		172.0	C86	71.2		123.6

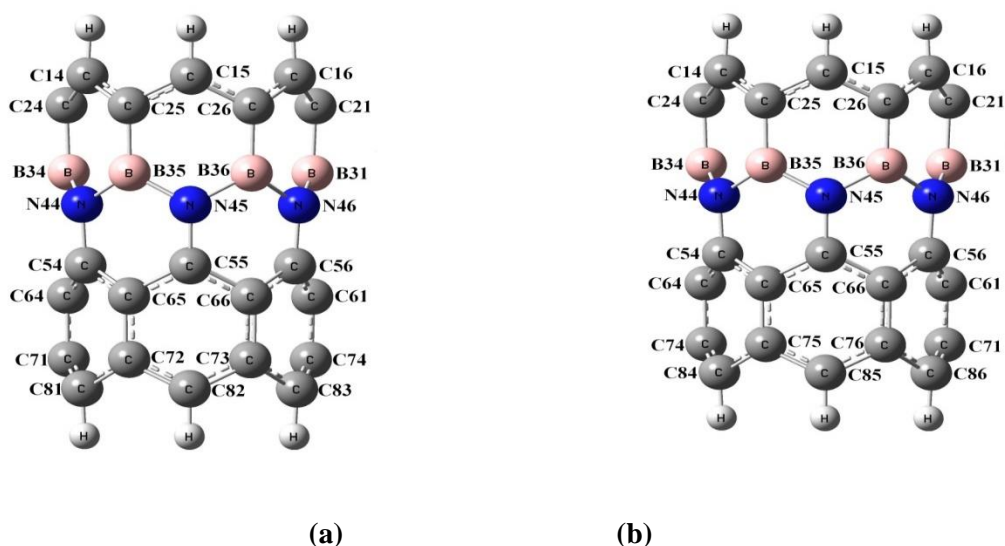
According to Tables (2) and (3) the amount CSI (11 B) in model (A) is nearly about 79 ppm while in the model (B) of CSI (11B) is the equivalent 7.59ppm. In model (A) boron atoms are connected to hydrogen and nitrogen while in the model (B) atoms of boron are connected carbon, nitrogen with hybrid SP<sup>2</sup>. As a result, since the carbon SP<sup>2</sup> electronegativity is greater than hydrogen, the density of electron cloud around the cores Boron in the model (A) compared with the model (B) is higher and the amount of chemical shifts CSI (11B)

for the model ( A) is more than model (B). The amount of CSI (15N) for model (A) is less than the model (B). Because in the model (A) nitrogen atoms are connected to boron and carbon atoms with less electronegativity than the SP<sup>2</sup> linked carbon, which this increases the density of the electron cloud around the nitrogen cores and consequently the amount of CSI (15N) for model (A) is less than the model (B). The amount of CSA (11B) and CSA (15N) for models (A) and (B) are different with each other that it is due to difference in symmetry with

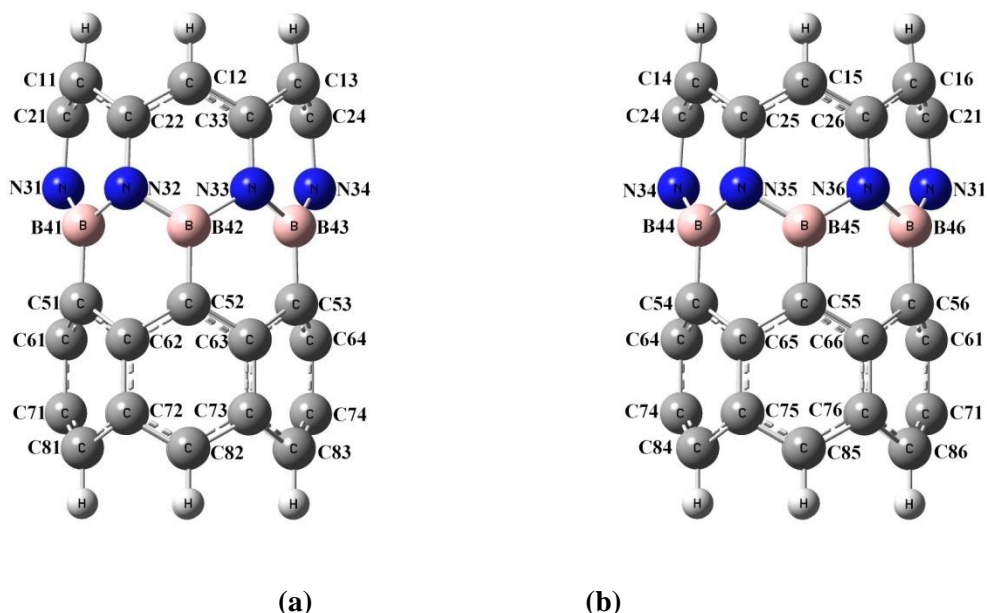
each electron cloud around the cored of boron and nitrogen.

In surveyed models (C) and (D) as previously mentioned, the carbon atoms located on the third and fourth layer of carbon nanotubes have been doped with boron and nitrogen atoms. Doping the boron and nitrogen atoms and becoming asymmetric the carbon nanotubes complete structure and with regard to the parameters of NMR, models (C) and (D) are divided -N36 and B41-B46.

into 8 different layer. So that in the models (C) and (D) layers first, second, fifth, sixth, seventh and eighth respectively include atoms C11-C16, C21-C26, C51-C56, C61-C66, C71-C76 and C81-C86 (Fig 8) and Fig (9) . In model (C) third and fourth layers respectively include B31-B36 and N41-N46. While in the model (D), respectively third and fourth layers include N31



**Fig 8.** Two-dimensional view of model (C) carbon nanotube doped with nitrogen boron (a) front view and (b) back view of this model



**Fig 9.** Two-dimensional view of model (C) carbon nanotube doped with nitrogen boron (a) front view and (b) back view of this model.

By comparing the amount of CSI CSA parameters for carbon cores on the first layer can be concluded that in the model (C) atoms within the first layer near to the boron atoms, due to the direct

impact of boron atoms on this layer is observed direct reduction in the amount of CSI (13C) part. Doped the boron atoms also cause subtle changes in the amount of CSA (13C) for carbon

atoms in the first layer. These changes caused by disturbing the symmetry of the electron cloud around carbon cores. It is noteworthy, with regard to that carbon atoms in first layer of the model (D) unlike the (C) model are located in adjacent to the nitrogen atoms, because they feel different electrostatic environment a significant increase is observed in CSI (13C) amount. However, in the amount CSA (13C) for these cores in the model (D) is observed a significant reduction.

By comparing the parameters of CSI (13C) and CSA (13C) to carbon atoms located on the second tier in models (C) and (D) can be concluded that the parameters amount CSI (13C) increases. However, the amount of CSA (13C) decreases. In fifth layer in doped model (C) carbon cores directly are connected to the nitrogen atoms. As a result, the amount of CSI (13C) and CSA (13C) of these cores were reduced. But in model (D) carbon atoms are connected to the boron atoms in the fifth layer and the amount of CSI (13C) It is not seen much change while the CSA (13C) amount is reduced.

In the sixth and eighth layers due to the indirect effects of nitrogen atoms in the model (C) and the indirect effects of boron atoms in the model (D) significant changes are observed in the values of CSI (13C) and CSA (13C) of carbon cores located in this layer. So that the value CSI (13C) increased and CSA (13C) decrease. It should be noted that the process down to sixth and eighth layer of carbon atoms is observed for the model (D). In the seventh layer in proposed models (C) and (D) the indirect effects of boron and nitrogen atoms and isotropic and anisotropic chemical tensors sensitivity to small changes in the amount of CSI (13C) and CSA (13C) significant changes are observed for this cores in models (C) and (D).

According to the results of tables (4) and (5) the amount of CSI and CSA parameters for boron and nitrogen cores can be understood this point that because of the same chemical environment that each of the cores of boron and nitrogen that feel in both models, changing amount of CSI and CSA to cores of boron and nitrogen in the doped models is almost at the same size. The results show that the value CSI (11B) in the model (C) is almost equal to the amount 63 ppm and this amount is 66 ppm in model (D). The amount of CSI (15N) for models (C) and (D) is 72 ppm. It is noteworthy that it is not observed big differences between the parameters of the CSA (11B) and CSA (15N).

#### CONCLUSION

It was shown in this study that in the doped models by boron and nitrogen atoms in addition to bonds of C = C, there are also bonds of B-N, B-C,

and N-C that is causing some structural changes in doped nanotube with atoms of boron and nitrogen, and these changes effect on the electronic structural properties of carbon nanotube than the full model. Also in doped models (A), (B), (C) and (D) in addition to carbon atoms, there are also boron and nitrogen atoms. As a result have different optimizing energy than full carbon nanotubes. By comparing the relative amount of energy and structure energy that obtained for doped models with boron and nitrogen (A), (B), (C) and (D) has concluded that all doped models are structural isomer for each other and doped model (B) is more stable than other models. On the other hand, with the doping of boron and nitrogen atoms in the structure of carbon nanotubes (6, 0) decreases the amount of energy cleavage. Because of the doped carbon nanotubes with boron and nitrogen atoms, which changes the amount of dipole moment in structures that slightly showed the load turbulent in the doped models. In the full model, according to calculations of NMR, carbon atoms located at the opening of the CNT have the highest amount of CSI (13C) and the lowest amount of CSA (13C). Doping the boron and nitrogen atoms in the structure of carbon nanotubes, full symmetry carbon nanotube completely is lost as a result the two ends of the carbon nanotubes are not equal with each other. As a result of doped carbon nanotubes based on NMR parameters can be divided into eight different layers that in the layer 6 of doped models for carbon atoms, one layer for boron atoms and 1 layer for nitrogen atoms. Because of doping of boron atoms in the first layer and doping of nitrogen atoms in the second layer, the amount of CSI (13C) for all the cores 13C located in layers three to eight would be observed significant increase. While the CSA (13C) decreases for carbon atoms within the layers. By studies of NMR parameters for model (B) is observed that for carbon atoms located in the layers the third, fourth, seventh and eighth the amount of CSI (13C) increases and the amount of CSA (13C) decreases. While the amount of CSI (13C) decreases and the CSA (13C) increases for carbon atoms in the fifth and sixth layers. Significant changes in the parameters of CSI (13C), CSA (13C) and models (C) and (D) were also observed. But these changes did not have a specific order. The amount of CSI (15N) for model (A) was less than the model (B). The reversed process was observed for CSI (11B). Values CSA (11B) and CSA (15N) for models (A) and (B) were different due to difference in the symmetry of the electron cloud around the cores of boron and nitrogen. By comparing the amount of CSI and CSA parameters for cores boron and nitrogen for the models (C) and (D) to realize that

because of the same chemical environment that each boron and nitrogen cores is almost the same size in of the cores of boron and nitrogen feels in both doped models. models, the amount of changes of CSI and CSA for

**Table 4.** Parameters of CSI and CSA, cores 13C, 11B and 15N in terms of ppm for the model (C) in this table, for full model in each layer its average value is noted

CSI		CS <sup>A</sup>		CSI		CS <sup>A</sup>	
perfect	C model	perfect	C model	perfect	C model	perfect	C model
Layer 1				Layer 5			
C1	45.7	165.9		C5	30.6	191.2	
C11	22.6		162.9	C51	18.0		178.2
C12	22.7		162.6	C52	17.9		
C13	22.7		162.8	C53	18.2		177.9
C14	22.6		162.9	C54	18.0		178.2
C15	22.7		162.6	C55	17.9		178.4
C16	22.7		162.8	C56	18.2		177.9
Layer2				Layer6			
C2	19.7	198.2		C6	34.7	189.9	
C21	44.7		183.4	C61	47.3		164.6
C22	44.7		183.2	C62	47.4		164.3
C23	44.8		183.3	C63	47.5		164.3
C24	44.7		183.4	C64	47.3		164.6
C25	44.7		183.2	C65	47.4		164.3
C26	44.8		183.3	C66	47.5		164.3
Layer3				Layer7			
C3	34.7	189.9		C7	19.7	198.2	
B31	62.7		58.2	C71	15.8		210.3
B32	62.6		58.3	C72	15.8		210.0
B33	62.6		58.4	C73	15.9		210.2
B34	62.7		58.2	C74	15.8		210.3
B35	62.6		58.3	C75	15.8		210.0
B36	62.6		58.4	C76	15.9		210.2
Layer4				Layer8			
C4	30.6	191.2		C8	45.8	165.9	
N41	72.6		255.9	C81	52.9		155.0
N42	72.3		255.9	C82	52.9		155.2
N43	72.4		255.6	C83	53.0		154.9
N44	72.6		255.9	C84	52.9		155.0
N45	72.3		255.9	C85	52.9		155.2
N46	72.4		255.6	C86	53.0		154.9



**Table 5.** Parameters of CSI and CSA, cores 13C, 11B and 15N in terms of ppm for the model (D) in this table, for full model in each layer its average value is noted

CS <sup>I</sup>		CS <sup>A</sup>		CS <sup>I</sup>		CS <sup>A</sup>	
perfect	D model	perfect	D model	perfect	D model	perfect	D model
layer 1				layer 5			
C1	45.7	165.9		C5	30.6	191.2	
C11	76.0		109.5	C51	30.1		216.2
C12	76.1		109.2	C52	30.2		216.0
C13	76.1		108.9	C53	30.0		216.4
C14	76.0		109.5	C54	30.1		216.2
C15	76.1		109.2	C55	30.2		216.0
C16	76.1		108.9	C56	30.0		216.4
layer2				layer6			
C2	19.7	198.2		C6	34.7	189.9	
C21	23.1		163.1	C61	11.0		221.2
C22	23.2		163.2	C62	11.0		221.5
C23	23.1		163.2	C63	11.2		221.3
C24	23.1		163.1	C64	11.0		221.2
C25	23.2		163.2	C65	11.0		221.5
C26	23.1		163.2	C66	11.2		221.3
layer3				layer7			
C3	34.7	189.9		C7	19.7	198.2	
N31	72.1		264.3	C71	21.1		210.6
N32	72.4		264.2	C72	21.1		210.8
N33	72.2		264.4	C73	21.1		210.6
N34	72.1		264.3	C74	21.1		210.6
N35	72.4		264.2	C75	21.1		210.8
N36	72.2		264.4	C76	21.1		210.6
layer4				Layer8			
C4	30.6	191.2		C8	45.8	165.9	
B41	66.7		59.4	C81	30.3		178.3
B42	66.7		59.4	C82	30.3		178.2
B43	66.7		59.4	C83	30.2		178.3
B44	66.7		59.4	C84	30.3		178.3
B45	66.7		59.4	C85	30.3		178.2
B46	66.7		59.4	C86	30.2		178.3

REFERENCES

1. C. Bai, J. Sarkis, *J. Clean Prod.* **47**, 318 (2013).
2. D. Blumberg, *J. Bus. Log.*, **20**, 141 (1999).
3. B. Bossone, *Intel. J. Soc. Econ.*, **17**, 15 (1990). <http://ssrn.com/abstract/4423654>.
4. C. Caruso, A. Colorni, M. Paruccini, *Eurp. J. Operl. Res.* **70**, 16 (1993).
5. R. D'Aveni, *Hypercompetition: Managing the Dynamics of Strategic Maneuvering*, Free Press, New York, NY, 1994.
6. S. Dowlatshahi, *Interfaces*, **30**, 155 (2000).
7. A. El korch, D. Millet, *J. Clean Prod.* **19**, 588 (2011)
8. L. Genandrialine P. Psyche, M. Fontanos, *J. Mat. Cyc. Was. Manag.*, **8**, 39 (2006).
9. S. Genchev, R. Richey, C. Gabler, *Intl. J. Log. Mang.*, **22**, 242 (2011).
10. R. Giuntini, T. Andel, *Trans. Distrib.*, **36**, 97 (1995).
11. K. Hai-Y, M. Julie, *Environ. Sci. Technol.*, **40**, 1672 (2006).
12. P. Helo, *Ind. Mang. Data Sys.*, **104**, 567 (2004).
13. L. Hilty, *Environ. Imp. Ass. Rev.*, **25**, 431 (2005).
14. H. Kang, J. Schoenung, *Res., Cons. & Rec.*, **11**, 65 (2005).

15. A. Knemeyer, T. Ponzurick, C. Logar, *Intl. J. Phys. Distrib. Log. Mang.*, **32**, 455 (2002).
16. R. Kopicki, M. Berg, L. Legg, V. Dasappa, C. Maggioni, *Reuse and Recycling: Reverse Logistics Opportunities*, Council of Logistics Management, Oak Brook, Illinois, 1993.
17. K. Lau, Y. Wang, *Sup. Chain Mang. Intl. J.* **14**, 447 (2009).
18. I. Nnorom, O. Osibanjo, *Res. Conv. Rec.*, **52** 843, (2008).
19. T. Pohlen, M. Farrisi, *Intel. J. of Phys.Distrib. Log. Mang.* **22**, 47 (1992).
20. V. Ravi, *J. Cl. Prod.*, **20**, 151 (2012).
21. J. Sarkis, *Intel. J. Env. Cons. Des. Manuf.*, **4**, 52 (1995).