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Comparative Study of $B_xN_yC_z$ Nanojunctions Fragments

***Fabiana Aparecida de Souza Batista*[a], *Raquel Dastre Manzanares*[a], *Magno dos Reis Júnior*[a],**
Rogério Custódio*[b], *Ana Claudia Monteiro Carvalho*[a]

[a]*Grupo de Desenvolvimento de Estruturas Nanométricas e Materiais Biocompatíveis – GDENB,*
Departamento de Física e Química – DFQ, Instituto de Ciências Exatas – ICE,
Universidade Federal de Itajubá – UNIFEI, CEP 37500-930, Itajubá, MG, Brazil
[b]*Instituto de Química – IQ, Universidade Estadual de Campinas – UNICAMP,*
CP 6154,CEP 13084-862, Campinas, SP, Brazil

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Theoretical analysis of formation energy and geometry was done to compare the relative stabilities of modified carbon nanostructures representative fragments. Structure and energies of formation were calculated at semiempirical level of theory. Depending of B-N pair localization on the molecular structures the formation enthalpy decreases. B-N substitution in tubular structures at low concentration decreases the energy when the tubes have small diameters. Our results are in according to experimental works which have shown that boron and nitrogen are met at region of defects in $B_XC_YN_Z$ nanostructures.

Keywords: *nanostructures, semiempirical methods, doping, boron, nitrogen*

1. Introduction

Carbon nanotubes are considered ideal candidates to the development of nanoelectromechanical (NEMS) devices due the outstanding electronic properties which depend only on their diameter and chirality[1]. Researchers have been done to improve growth techniques of carbon nanotubes pure and structurally perfects. On the other hand, the scientific literature has shown a special interest in the development of experimental techniques which could control the growing of branching and/or doping structures. Boron and nitrogen atoms are considered as natural candidates to the doping process[2-10].

New growth techniques of Y, L, T, H or multi-branching[11-20] junctions constituted by nanotubes with the same chirality (or not) made researches about intermolecular junctions which increase the possibilities to built nanodevices based on carbon nanotubes (Figure 1).

Theoretically, nanojunctions can be produced through introduction of topological defects in the tubular structure. Pentagonal, heptagonal, and octagonal rings are examples of this type of defect. According to Euler rule, it is necessary 12 pentagons to close one hexagonal network. However, if we introduce one heptagon, the number of pentagons increases to 13. Moreover, if pentagonal and heptagonal rings are separated by one or more hexagons, we can create nanojunctions with different shapes[1].

Some studies have shown that heteroatoms (as boron and nitrogen) are met in defective regions of tubes[21]. In the case of nitrogen doping nanotubes, there are two results due the inclusion of this heteroatom: (i) the lone pair repulsion decreases the bond angle between nitrogen and carbon atoms which brings on structural stabilization; (ii) one pentagon with nitrogen simulates a carbon hexagon due the extra electron in the nitrogen atom which stabilizes the electronic structure of joint region[22-23].

Emission mechanisms, conduction, and rectification processes are not understood if they are measure from carbon nanostructures. Relationship between morphology and electronic properties show controversial experimental results which difficult the development of new nanodevices based on nanostructures[24-30].

In this sense, we made a comparative study of the energy involved in the carbon atom substitution in $B_XN_YC_Z$ nanojunctions fragments to propose some rules about the localization of nitrogen and boron atoms in nanojunctions regions of defects.

In the following section we describe the model systems and the theory employed in this study. Next we present a discussion of the results. A final section contains the conclusions.

2. Computational Details

Different semiempirical or hybrid calculations (e.g. ONION)[31] have been used to nanotube geometry description. Ab initio calculations in Hartree-Fock (HF) [32] or Density Functional (DFT) [33] level have been used for low dimension structrures.

In this work, the geometry of pure or doped nanotube fragments were fully optimized through semi-empirical quantum chemical methods Austin Method 1 (AM1)[34] and Parametric Method 3 (PM3)[35]. These semi-empirical methods are derived from the Hartree-Fock theory. The advantages of semiempirical calculations are that they are much faster than ab initio calculations, and can be used for large organic molecules. The disadvantage of semiempirical calculations is that some properties cannot be predicted reliably. In the case of the properties analyzed in this study, both semiempirical methods (AM1 and PM3) are very reliable to predict molecular geometries and heats of formation of carbon materials. AM1 and PM3 error in heats of formation is about 8.0 $\mathrm{Kcal.mol^{-1}}$[36], with respect to the experimental values. Average error in bond length varies from 0.04 Å to 0.05 Å[36].

Carbon nanojunctions fragments analyzed in this work are shown in Figure 2. The dangling bonds at the ends of the model molecules were saturated with hydrogen (H) atoms. Initially, we calculate the geometries and heats of formation of carbon nanojunction fragments.

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*e-mail: anaclaudia@unifei.edu.br

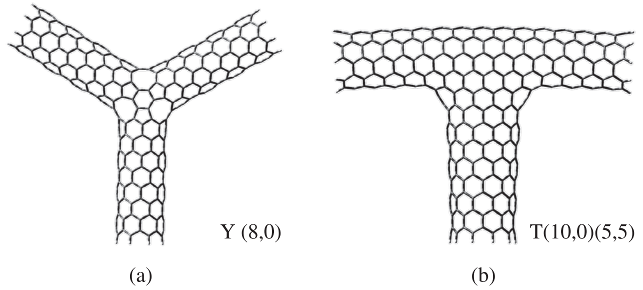

Figure 1. Examples of nanojunctions: a) $Y_{(8,0)}$ formed by three (8,0) semiconducting nanotubes and connected by six pentagons and six octagons; b) $T_{(10,0)(5,5)}$ formed by one metal (5,5) and one semiconducting (10,0) nanotubes. This T-junction has in your defect region four heptagonal rings.

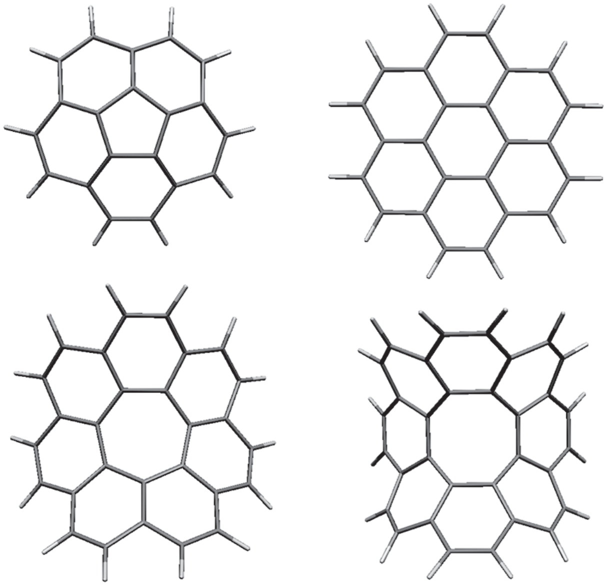

Figure 2. Model molecules geometries calculated through AM1 semiempirical method. In this picture carbon atoms (C) are in gray color and hidrogen atoms (H) are in white color (It was considered structures constituted by one pentagon and five hexagons (PENT), seven hexagonal rings (HEXA), one heptagon and seven hexagons (HEPT), and one octagonal ring rounded by hexagons (OCT)).

These model molecules were then doped with a Boron-Nitrogen pair (BN-pair) and the geometries were re-optimized. Nitrogen (N) and boron (B) atoms were systematically placed substituting carbons in pentagonal, hexagonal, heptagonal, and octagonal rings. For these substitutions, we adopted the following criteria: (i) adjacent B-B or N-N atoms should not be substituted; (ii) the substitution of even number of atoms is preferable because a closed shell system is formed. The results of heat of formation after BN-pair substitution are shown in Table 2. These calculations were performed within the quantum chemical packages GAMESS[37] and Gaussian03[38].

3. Results and Discussions

3.1. Structural properties and enthalpy of formation

Model molecules are depicted in Figure 2. The selected molecules have five, six, seven and eight-membered rings which are rounded by hexagonal rings.

These fragments have been taken because they are met in some nanojunctions described in the literature[38-41]. After geometry and formation energy calculations of pure carbon nanostructures, a systematic substitution of carbon atoms by BN-pair was done.

The objective of this study was to identify some rules about the localization of nitrogen and boron atoms in nanojunctions regions of defects. In this sense, we analyzed the theoretical results of the energy associated to BN-pair incorporation. This energy was calculated as the difference in formation enthalpy of BN-pair doped and pure carbon systems divided by the number of BN-pairs. Comparing theoretical results of the enthalpies of formation before and after the substitution of carbon atoms, we concluded that some BN-pair distributions are more desirable than other. In the case of small fullerenes some works have suggested some low energy configurations[42,43].

Results for the heat of formation calculated through AM1 semiempirical method are shown in Table 1.

In Table 1 fragments constituted by one pentagon rounded by five hexagons are called PENT; HEPT corresponds to a seven-membered ring rounded by seven hexagons; model molecules with one octagonal ring is called OCT; and model molecules with seven hexagonal rings are called HEXA. Numbers from one to six corresponds to different BN-pair positions. Equivalents substitutions, due the model molecules symmetry, were avoided.

At first, we analyzed the geometry of optimized structures. Model molecules have high curvatures, with exception of ones in the HEXA group. These results are in according to the defective regions met in nanojunctions. Non-hexagonal rings join nanotubes with different chiralities creating different branched structures.

Our analysis of enthalpy of formation for molecules doped with one BN-pair showed that most probable site of these atoms is in the join region of nanojunctions. As closer as boron and nitrogen are one another, lower is that energy (see PentBN_6, PentBN_5, HeptBN_6 in Figure 1 and Table 1). In the case of bonded boron and nitrogen atoms, the better position is nitrogen in the central region and boron in the peripheral region of model molecule. In the case of two BN-pairs, non-carbon atoms need to be located in the central region of defect. Our theoretical results for some model molecules show that the heat of formation decreases with the inclusion of more BN-pairs (compare PentBN_5 with Pent2BN_5, and OctBN_3 with with Oct2BN_3).

Since the discovery of $B_XC_YN_Z$ nanotubes in 1994[44], several experimental[45-57] and theoretical[58-66] works have been done to understand of the properties of this new material. Theoretical studies have revealed that the electronic properties of $B_XC_YN_Z$ nanotubes are unrestricted by geometrical structure and can be controlled by simply varying the chemical composition[61,67,68].

Golbert et al. reported that multiwalled BN nanotubes have preferentially zigzag type chirality along their circumference based on their diffraction patterns[4]. Other theoretical calculations were performed for the zigzagged form of $B_XC_YN_Z$ nanostructures[69,70]. Therefore, we adoptade only zigzag nanotubes (6,0), (7,0), (8,0), and (9,0) to analyze substitution of BN-pair in tubular structures (Figure 3). In these calculations, BN concentrations are lower than 1%.

Our previous works showed that incorporation of nitrogen zigzag nanotubes stabilizes some geometries[22,23]. In the case of carbon atoms substitution by boron and nitrogen atoms, our theoretical results showed that BN-pair substitution depends on the tube diameter. Stressed small diameter tubes are more easily doped by BN-pair than the larger ones. Differently of other works[71], our theoretical results show that the relative positions of boron and nitrogen in the tubular wall are not important to the formation energy. Results about

Table 1. Results to Heat of Formation and dipole moment to fragments studied in this work (Figure 1). In this Table molecules constituted by one pentagon rounded by five hexagons are called PENT; HEPT corresponds to a seven-membered ring rounded by seven hexagons; model molecules with one octagonal ring is called OCT; and model molecules with seven hexagonal rings are called HEXA.

Molecule	Heat of formation (Kcal.mol^{-1})	Dipole (Debye)	Molecule	Heat of formation (Kcal.mol^{-1})	Dipole (Debye)
	HEPT			PENT	
Hept C	160.136	0.000	Pent C	156.557	2.796
Hept BN1	202.453	5.251	Pent BN1	180.063	4.689
Hept BN2	157.108	1.014	Pent BN2	199.436	5.426
Hept BN3	159.145	1.951	Pent BN3	161.618	3.122
Hept BN4	208.971	4.461	Pent BN4	377.646	7.642
Hept BN5	146.694	1.444	Pent BN5	149.483	4.456
Hept BN6	145.486	2.513	Pent BN6	141.036	2.377
Hept 2BN1	188.383	3.168	Pent 2BN1	124.440	2.836
Hept 2BN2	155.618	2.229	Pent 2BN2	–	–
Hept 2BN3	270.580	9.639	Pent 2BN3	–	–
Hept 2BN4	220.832	1.492	Pent 2BN4	210.028	3.072
Hept 2BN5	210.685	7.781	Pent 2BN5	129.411	1.960
Hept 2BN6	–	–	Pent 2BN6	142.334	3.718
			Pent 2BN7	216.457	8.044
			Pent 2BN8	231.519	7.103
	HEXA			OCT	
Hexa C	96.227	0.000	Oct C	219.678	0.000
Hexa BN1	142.897	5.706	Oct BN1	274.777	8.281
Hexa BN2	151.738	5.658	Oct BN2	274.398	3.920
Hexa BN3	102.802	1.894	Oct BN3	213.489	0.923
Hexa BN4	94.520	1.698	Oct BN4	204.497	1.333
Hexa BN5	92.434	0.990	Oct BN5	262.622	4.047
Hexa 2BN1	74.201	1.660	Oct BN6	274.614	5.286
Hexa 2BN2	69.479	2.368	Oct 2BN1	276.609	1.058
Hexa 2BN3	89.861	0.000	Oct 2BN2	207.666	1.010
Hexa 2BN4	89.028	0.000	Oct 2BN3	186.432	0.000
Hexa 2BN5	118.708	3.454	Oct 2BN4	300.946	4.457
Hexa 2BN6	79.305	0.000	Oct 2BN5	192.072	2.604
			Oct 2BN6	180.021	1.418
			Oct 2BN7	213.435	3.883

Numbers from one to six corresponds to different BN-pair positions.

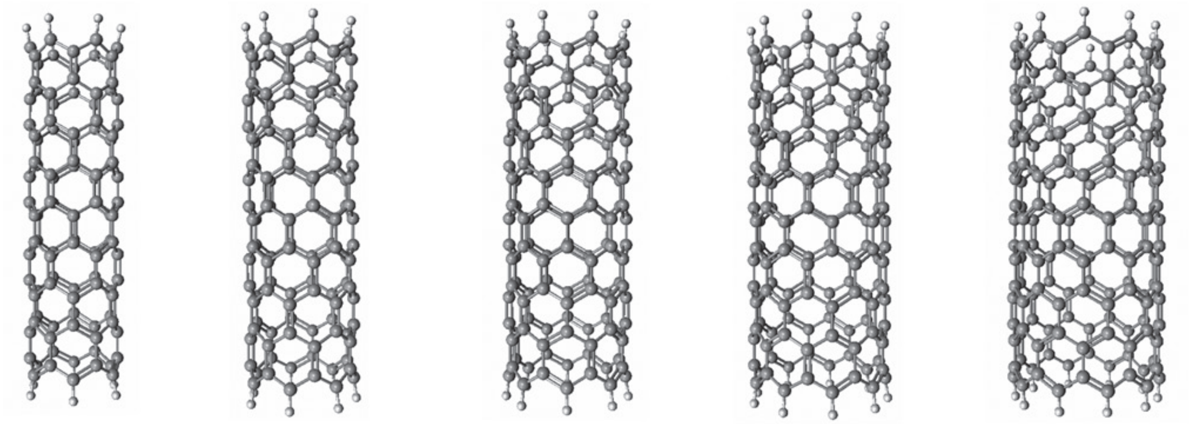

Figure 3. Longitudinal view of zig-zag carbon nanotubes. From left to right: nanotubes (6,0), (7,0), (8,0), (9,0), and (10,0), respectively. All structures were optimized through semiempircal method AM1 (see text).

Table 2. Results for Heat of Formation calculated before and after BN-pair substitution.

Nanotube	Heat of formation (Kcal.mol^{-1})	Heat of formation (Kcal.mol^{-1})
	AM1	PM3
(6,0)	1542.84	1360.98
(6,0) BN1	1516.73	1314.85
(6,0) BN2	1516.70	1314.83
(6,0) BN3	2822.67	–
(6,0) BN4	1516.70	1314.83
(7,0)	1456.89	1273.41
(7,0) BN1	1469.34	1267.22
(7,0) BN2	1469.38	1267.05
(7,0) BN3	1469.39	1266.85
(7,0) BN4	–	–
(8,0)	1459.47	1269.42
(8,0) BN1	1441.04	–
(8,0) BN2	1457.87	–
(8,0) BN3	–	–
(8,0) BN4	1444.19	1233.36
(8,0) BN5	1457.96	–
(9,0)	1447.61	1249.69
(9,0) BN1	1450.23	1229.75
(9,0) BN2	1450.23	1230.34
(9,0) BN3	1450.72	1230.14
(9,0) BN4	1450.88	1229.58
(9,0) BN5	–	1230.37
(10,0)	–	1232.85
(10,0) BN1	–	1233.04
(10,0) BN2	–	1233.05
(10,0) BN3	–	1232.71
(10,0) BN4	–	1232.92
(10,0) BN5	–	1233.38

BN-pair energy substitution to zigzag nanotubes at concentration higher than 1% have been analyzed (Table 2).

4. Conclusions

In this theoretical work, it has been analyzed the geometry and enthalpy of formation of zig-zag nanotubes and representative fragments of the join region in nanojunctions, through quantum chemical methods.

The geometry of carbon nanotubes has not yet experimentally measured. AM1 results to tubular structures are in according to currently accepted bond lengths in the order of 1.43 Å (average error of 0.04 Å). This result show that AM1 semiempirical method is adequate to geometry calculations to nanotube, nanojunctions, and model molecules analyzed in this work.

After our calculations we can conclude that: (i) the BN-pair substitution decrease the heat of formation of small diameter tubes. The relative positions of boron and nitrogen in the tubular wall are not important to the results of formation energy; (ii) the heat of formation to the fragments depends on the BN-pair localization in the non-hexagonal rings. Non-carbon atoms need to be closer, and the energy decreases with the inclusion of more BN-pairs.

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