

A computational investigation on NMR Characterization and electronic properties of some zigzag nanotubes

M. Anafcheh¹, F. Naderi^{2*}, M. Ezatvar² and H. Masoomi²

¹ Department of Chemistry, Shahr-e-Ray Branch, Islamic Azad University, Tehran, Iran

² Department of Chemistry, Shahr-e-Qods Branch, Islamic Azad University, Shahr-e-Qods, Tehran, Iran

Received June 2014; Accepted August 2014

ABSTRACT

DFT calculations were applied to evaluate the electronic and magnetic properties of zigzag BC₂N nanotubes based on the ¹³C, ¹⁵N, and ¹¹B NMR parameters and natural charge analysis. We considered three types of zigzag nanotubes, ZZ-1, ZZ-2, and ZZ-3 (n, 0) with n = 8, 12, and 14. The obtained results indicated the divisions of the electrostatic environments around C nuclei into a few layers, consistent with the calculated natural charges on C atoms. There was a good correlation between the layers of chemical shielding isotropy as well as anisotropy, σ_{iso} , and $\Delta\sigma$, and the five local structures around carbon atoms. Successive BN units lead to larger ¹⁵N σ_{iso} values in comparison with the individual BN units in the ZZ-2(n, 0) and ZZ-3(n, 0). Slight differences in the values of ¹¹B σ_{iso} clarified diminutive diversity in the electron densities of boron nuclei, while $\Delta\sigma$ values indicated the more apparent range of changes.

Keywords: BC₂N nanotube; Density Functional Theory; NMR; Natural Charge

INTRODUCTION

The physical and chemical properties of carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs) attracted research wide interest ever since their discovery [1, 2]. There were a lot of differences between BNNTs and CNTs in spite of their structural similarities. BNNTs showed a higher thermal conductivity [3]. They were more chemically and thermally stable compared with CNTs [4, 5].

An interesting possibility arises from the inclusion of substitutional carbon atoms in the BN structure, leading to the formation of ternary B–C–N compounds, with distinct stoichiometries.

B–C–N nanotubes synthesized by electrical arc discharge [6, 7 and 8], laser ablation [9] and more recently by laser vaporization [10], motivating a large number of theoretical investigations [11–15]. These compounds were expected to have intermediate qualities, between CNTs and BNNTs. Therefore, it opened the possibility to produce materials with tunable electronic properties with potential applications in nano device engineering. Among BCN nanostructures, the BC₂N was believed to be one of the most stable stoichiometries [16], which was first reported in 1995 by Weng-Sieh et al. [17].

*Corresponding author: fnaderi2@yahoo.com

Cohen and collaborators [18,19] were the first to calculate the electronic structure of BC₂N compounds in the framework of the local density functional formalism. The structural stability of BC₂N have also been studied by Itoh and co-workers [20-23] using an empirical molecular mechanics simulation.

In this work, we attempted to explore the electronic properties of BC₂N nanotubes, which have different diameter and chairality, by calculating CS tensors and natural charges at the sites of various ¹³C, ¹¹B and ¹⁵N nuclei [24] which was useful to fully understand the local environment of atoms within those nanotubes. Compared with carbon nanotubes, there can be more than one type of zigzag or armchair BC₂N nanotubes, depending on how a BC₂N sheet was rolled up [24]. Adopting the same notations as those in Ref. 24, we considered three types of zigzag nanotubes: ZZ-1, ZZ-2 and ZZ-3 (n, 0) with n=8, 12, and 14, see Fig.1. We have also performed natural bonding orbital (NBO) analysis as a very popular and proper tool to exhibit the contributions of the natural charges on atoms [25]. It should be noticed that the “natural population analysis” method has been developed to calculate atomic charges and orbital populations of the molecular wave functions in general atomic orbital basis sets [26].

COMPUTATIONAL METHOD

Schematic diagrams for all the considered structures were depicted in Fig. 1. We considered nine models of (n, 0) zigzag BC₂N single-wall nanotubes with a length of 1.2-1.3 nm, see Fig. 1. These systems all have approximately 120-170 atoms, and the dangling bonds at the ends were tied off with hydrogen atoms. All density functional theory (DFT) calculations were

performed using Gaussian 98 program package [27]. Geometries of all the systems were allowed to be fully relaxed during the B3LYP/6-31G* optimization process. The standard 6-31G* basis set was employed due to being affordable and accurate enough for geometry optimization of even large molecules [28,29]. Frequency calculations were carried out for all of the systems at the same level of theory, and real frequencies were obtained, confirming that all of them were structures with the minimum energy. ¹³C, ¹¹B and ¹⁵N CS tensors were calculated at the B3LYP/6-31G* level based on the gauge independent atomic orbital (GIAO) approach [30].

The evaluated NMR parameters at the sites of ¹¹B and ¹⁵N nuclei were presented in Tables 1 and 2, respectively. NBO analyses [31] were performed on the wave functions calculated at the B3LYP/6-31G* level of theory, as a standard option in the Gaussian 98 program. The NBO method corresponds closely to the picture of the localized bonds and lone pairs as basic units of the molecular structure, i.e., it transforms the delocalized many-electron wave function into the optimized electron-pair bonding units, corresponding to the Lewis structure picture. Starting from a given input atomic orbital basis set {φ_i}, the program performs a series of transformations to form “natural” atomic orbitals (NAOs), natural hybrid orbitals (NHOs), and natural bond orbitals (NBOs).

RESULTS AND DISCUSSION

We optimize the three types of zigzag nanotubes, ZZ-1 (n, 0), ZZ-2(n, 0), and ZZ-3(n, 0) with n = 8, 12 and 14 employing the B3LYP/6-31G* computational level. In ZZ-1(n, 0) nanotubes containing diagonal BN belt around the circumference of nanotube, BN

units were consecutive, but in the structural arrangements of ZZ-2 (n, 0) and ZZ-3 (n, 0), they were not; see Fig. 1.

There were two kinds of C-C bonds (r1-CC and r2-CC) and B-N bonds (r1-BN and r2-BN) in the ZZ-1(n, 0), as shown in Fig. 1; r1-CC and r1-BN represent the covalent bonds along the tube axis, while r2-CC and r2-BN represent those around the circumference, see Table 1.

All bonds along the tube axis become smaller than those around the circumference of nanotube, except for the B-N bonds in ZZ-1(14, 0), and become larger with increasing tube diameter. The

optimized structures of ZZ-2 (n, 0) and ZZ-3 (n, 0) nanotubes have the uniform C-C and BN bond lengths, see Fig. 1. As you can see in Fig.1 there were one kind of CC and BN bond lengths in optimized structures of ZZ-2 (n, 0) and ZZ-3 (n, 0). The calculated values of CC and BN bond lengths were listed in table 1. CC bond lengths were slightly shorter than normal C-C bond lengths in CNTs (1.42 Å) [33], meanwhile BN bond lengths in ZZ-2 (n, 0) and ZZ-3 (n, 0) nanotubes were in good agreements with experimental values of BN bond lengths in the middle of the BNNTs as reported in ref 34.

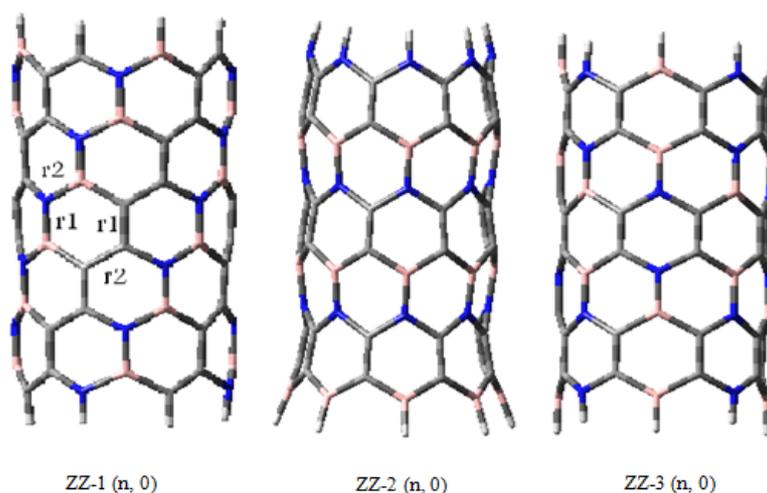


Fig. 1. Schematic structures of zigzag and armchair BC₂N nanotubes.

Table 1. Optimized bond lengths(Å) for zigzag BC₂N nanotubes

BC ₂ N-NT	R1-CC	R2-CC	R1-BN	R2-BN	CN	CB	BC ₂ N-NT	CC	BN	CN	CB
ZZ1-(8,0)	1.445	1.404	1.452	1.459	1.396	1.528	ZZ2-(8,0)	1.363	1.448	1.434	1.518
ZZ1-(12,0)	1.448	1.401	1.456	1.458	1.390	1.524	ZZ3-(8,0)	1.379	1.434	1.414	1.551
ZZ1-(14,0)	1.449	1.400	1.460	1.442	1.389	1.523	ZZ2-(12,0)	1.365	1.449	1.441	1.498
							ZZ3-(12,0)	1.396	1.447	1.400	1.533
							ZZ2-(14,0)	1.366	1.452	1.444	1.493

¹³C NMR characterization

Based on optimized structures, we have calculated the isotropic ¹³C NMR shielding (σ_{iso}) of the carbon atoms of the BNNTs. The calculated CS tensors in the principal axes system (PAS) ($\sigma_{33} > \sigma_{22} > \sigma_{11}$) were converted to measurable NMR parameters, chemical shielding isotropy (σ_{iso}) and chemical shielding anisotropy ($\Delta\sigma$), using the following equations [35]:

$$\sigma_{\text{iso}}(\text{ppm}) = 1/3(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (1)$$

$$\Delta\sigma(\text{ppm}) = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2 \quad (2)$$

According to these equations, CSI parameter means the averaged electronic density at the atomic site but the CSA parameter means the difference between the orientation of the electronic density perpendicular to the molecular plane (z axis) and the orientation of the electronic density in the molecular plane (x–y axes).

All the BC₂N nanotubes contain five local structures, C.1, C.2, C.3, C.4 and C.5 around carbon nuclei. So, we made an attempt to find correlations between these local structures and ¹³C chemical shifts in BC₂N nanotubes. The way that we named these local structures were shown in Fig. 2. The ¹³C chemical shielding (CS) parameters (ppm) and natural atomic charges in BC₂N nanotubes versus considered local structures were listed in table 2. The ZZ-1(n, 0) nanotubes were composed of C.1 and C.2 sites. The table 2 elucidates that increasing diameter and decreasing curvature of ZZ-1(n, 0) nanotubes results in widening the range of σ_{iso} from 67.2 and 16.7 in ZZ-1(8, 0) to 88.3 and 37.7 ppm in ZZ-1(14, 0) for the C.1 and C.2 sites respectively. There was the same trend in the ZZ-2(n, 0) nanotubes for the C.3 and C.4 sites. On the other words, the σ_{iso} values of C.3 and C.4 sites increase from 68.9 ppm and -4.6 ppm in ZZ-2 (8, 0) to 87.4 and 30.3 ppm in

ZZ-2(14, 0) nanotube.

However, the ZZ-3(n, 0) nanotubes contain carbon atoms with similar local structures, C.5, having the same values of chemical shielding parameters. Changes in isotropic chemical shieldings could be due to the different electrostatic environment around the carbon sites, originating from changes in curvature at the corresponding sites of nanotubes. Based on the obtained results, the calculated isotropic chemical shieldings of carbon sites with the C.1 and C.3 local structures were shifted to upfield in compared to those of C.2 and C.4 sites. Since σ_{iso} implies the averaged electronic density at the atomic site, this outcome can be expected due to the smaller electronegativity of the boron atom than that of the nitrogen one. Moreover, the C.4 sites with two nitrogen neighbors were much more deshielded than the C.2 sites connected to a nitrogen and two carbon atoms while C.1 and C.3 sites (with one and two boron neighbors, respectively) have small difference in σ_{iso} values. Therefore, it seems that N nuclei have larger effect than B nuclei on the electronic properties of the carbon nuclei in the case of the considered BC₂N nanotubes, and significantly perturb the density of electronic distribution at the C sites.

As mentioned above the σ_{iso} parameter means the averaged values of electron densities at the atomic center but the $\Delta\sigma$ parameters means the difference between the orientation of the electronic densities perpendicular to the molecular plane (z axis) and the orientation of the electronic densities in the molecular plane (x-y axes). In this basis, the larger magnitudes of the ¹³C $\Delta\sigma$ parameter and the smaller values of the ¹³C σ_{iso} parameter, see table 2, indicates that the density of electronic distribution at the C sites was more directed perpendicular to the molecular plane.

¹¹B and ¹⁵N NMR parameters

The NMR parameters at the sites of ¹¹B and ¹⁵N nuclei were evaluated and presented in Table 3. There were two types of BN in all of the considered BC₂N nanotubes, successive BN units in ZZ-1(n, 0) nanotubes, and individual BN units in the ZZ-2(n, 0) and ZZ-3(n, 0) nanotubes. Depending on the calculated isotropic and anisotropic ¹⁵N chemical shieldings (Table 3), BN units in ZZ-1(n, 0) nanotubes lead to larger σ_{iso} values (86.2 – 109.0 ppm) of N sites in comparison to those of N sites in the BN units in the ZZ-2(n, 0) and ZZ-3(n, 0) nanotubes (70.6 -97.9 ppm in the ZZ-2(n, 0) and 41.5 – 70.8 ppm in the ZZ-3(n, 0)).

In fact, successive BN substitution leads to a raise in the B/C ratio in the first neighborhood of nitrogen sites and hence due to the smaller electronegativity of B than that of C, ¹⁵N σ_{iso} values were expected to increase along with an increase in electronic densities at the nitrogen sites of the nanotubes with successive BN units.

CONCLUSION

Natural charge analysis

We performed a population NBO analysis, providing interesting insights into the charge distribution of the considered models. The result was shown in table 2 and 3.

The results presented in Table 2 indicate

that BC₂N nanotubes were composed of positively charged (C.2 and C.4) and negatively charged (C.1, C.3, and C.5) carbon atoms; the negative charges range from -0.16 to -0.72, and the positive charges range from +0.33 to +0.54, indicating electron transfer from the chemically bonded boron atoms to C.1 and C.3 on the surfaces of the nanotube and electron transfer from the chemically bonded C.2 and C.4 carbon atoms to nitrogen atoms.

Positively charged boron and negatively charged nitrogen atoms were composed in BC₂N nanotubes, see Table 3. The positive charges on B atoms were in the range of +0.708 to +1.000. In concordance with CS parameters, different structural arrangements of BN units in the BC₂N nanotubes were also observed in the calculated natural charges of boron sites. Moreover, it is interesting to note that the absolute values of charges on the boron sites show the tendency of $q(\text{ZZ-1}(n, 0)) > q(\text{ZZ-2}(n, 0)) > q(\text{ZZ-3}(n, 0))$, while this tendency in our previous study on BC₂N nanotubes was $q(\text{ZZ-1}(n, 0)) > q(\text{ZZ-3}(n, 0)) > q(\text{ZZ-2}(n, 0))$, where n was 3, 4 and 5 respectively. Natural charges on the nitrogen atoms do not show significant changes in the different kinds of nanotubes; the negative charges on N atoms range from -0.51 to -0.93.

Table 2. The ¹³C CS parameters (ppm) and Natural atomic charges of BC₂N nanotubes versus considered local structures

BC ₂ N-NT	L.S	σ_{iso}	$\Delta\sigma$	q	BC ₂ N-NT	L.S	σ_{iso}	$\Delta\sigma$	Q
ZZ1-(8,0)	C.1	67.7	149.3	-0.495	ZZ1-(12,0)	C.1	80.3	135.6	-0.472
	C.2	16.7	176.5	0.336		C.2	29.2	171.7	0.326
ZZ2-(8,0)	C.3	68.9	203.4	-0.701	ZZ2-(12,0)	C.3	87.1	197.7	-0.720
	C.4	-4.6	158.4	0.537		C.4	27.8	123.1	0.511
ZZ3-(8,0)	C.5	36.8	181.1	-0.164	ZZ3-(12,0)	C.5	62.7	171.3	-0.092
						ZZ1-(14,0)	C.1	88.3	132.6
						C.2	37.7	167.4	0.326
					ZZ2-(14,0)	C.3	87.4	200.2	-0.720
						C.4	30.3	117.9	0.509

Table 3. The ^{15}N and ^{11}B CS parameters (ppm) and Natural atomic charges of BC_2N nanotubes

$\text{BC}_2\text{N-NT}$	B			N		
	σ_{iso}	$\Delta\sigma$	q	σ_{iso}	$\Delta\sigma$	q
ZZ1-(8,0)	72.2	54.5	1.000	86.2	261.0	0.933
ZZ2-(8,0)	66.8	74.0	0.840	70.6	199.4	-0.682
ZZ3-(8,0)	79.2	82.2	0.730	41.5	323.9	-0.565
ZZ1-(12,0)	74.9	48.9	0.993	79.9	256.7	-0.850
ZZ2-(12,0)	78.1	68.7	0.839	97.9	189.8	-0.634
ZZ3-(12,0)	96.8	74.2	0.708	70.8	314.7	-0.511
ZZ1-(14,0)	82.0	45.6	0.991	109.0	253.3	-0.847
ZZ2-(14,0)	78.1	68.5	0.837	98.1	188.9	-0.631

We considered three types of zigzag nanotubes: ZZ-1, ZZ-2, and ZZ-3 (n, 0) with n = 8, 12, and 14 and the dangling bonds at the ends were tied off with hydrogen atoms. The obtained results indicate that all the BC_2N nanotubes contain five local structures, around carbon nuclei. A good correlation was seen between the layers of ^{13}C σ_{iso} as well as those of $\Delta\sigma$ values, and five local structures around carbon atoms. For example, the C sites with two nitrogen neighbors were much more deshielded than the C sites connected to a nitrogen and two carbon atoms, while C sites with one or two boron neighbors have small differences in σ_{iso} values. Furthermore, successive BN units lead to larger ^{15}N σ_{iso} values (86.2 – 109.0 ppm) of N sites in comparison to those of N sites in the BN units in the ZZ-2(n, 0) and ZZ-3(n, 0) nanotubes (70.6 - 97.9 ppm in the ZZ-2(n, 0) and 41.5 – 70.8 ppm in the ZZ-3(n, 0)). Different electrostatic environments around nuclei in the BC_2N nanotubes were also observed in the calculated natural charges.

REFERENCES

- [1]. A. Rubio; J. L. Corkill; M. L. Cohen, Phys. Rev. B (1994), 49, 5081.
- [2]. N. G. Chopra; R. J. Luyken; K. Cherrey; V. H. Crespi; M. L. Cohen; S. G. Louie; A. Zettl, Science (1995), 269, 966.
- [3]. CW. Chang, WQ Han, A Zettl, Appl. Phys. Lett. (2005) 86,173102.
- [4]. J. J. Pouch; A. Alterovitz, Synthesis and Properties of Boron Nitride, Trans. Tech. Publ.: Switzerland, (1990), Vols. 54-55.
- [5]. Y. Chen; J. Zhou; S. J. Campell; G. L. Caer, Appl. Phys. Lett. (2004), 84, 2430.
- [6]. O. Staphan, P.M. Ajayan, C. Colliex, Ph. Redlich, J.M. Lambert, P. Bernier, P. Lefin, Science 266 (1994) 1683.
- [7]. P. Redlich, J. Loeffler, P.M. Ajayan, J. Bill, F. Aldinger, M. Ruhle, Chem. 260 (1996) 465.
- [8]. R. Sen, B. C. Satishkumar, A. Govindaraj, K.R. Harikumar, G. Raina, J.P. Zhang, A. K. Cheetham, C.N. Rao, Chem. Phys. Lett. 287 (1998) 671.
- [9]. Y. Zhang, H. Gu, K. Seunaga, S. Iijima, Chem. Phys. Lett. 279 (1997) 264.
- [10]. S. Enouz, O. Stéphan, J. L. Cochon, C. Colliex, A. Loiseau, Nano Lett. 7 (7) (2007) 1856.
- [11]. Y. Miyamoto, A. Rubio, M. L. Cohen, S.G. Louie, Phys. Rev. B 50 (1994) 4976.
- [12]. X. Blase, J.C. Charlier, A.D. Vita, R. Car, Appl. Phys. Lett. 68 (1999) 293.
- [13]. X. Blase, Comput. Mater. Sci. 17 (2000) 107.
- [14]. S. Azevedo, R. de Paiva, J.R. Kaschny, J. Phys.: Condens. Matter. 18 (2006) 10871.

- [15]. E. Hernandez, C. Goze, P. Bernier, A. Rubio, Phys. Rev. Lett. 80 (1998) 4502
- [16]. Rupp CJ, Rossato J, Baierle RJ (2009) J. Chem. Phys. 130: 114710.
- [17]. Z. Weng-Sieh, K. Cherrey, N.G. Chopra, X. Blase, Y. Miyamoto, A. Rubio, M L. Cohen, SG. Louie, A. Zettl, R. Gronsky Phys. Rev. B (1995) 51:11229.
- [18]. A. Y Liu; M. Wentzcovitch; M. L. Cohen, Phys. ReV. Lett. B (1989), 39, 1760.
- [19]. Y. Miyamoto; M. L. Cohen; S. G. Louie, Phys. ReV. B(1995), 52, 14971.
- [20]. H. Nozaki; S. Itoh, Phys. ReV. B (1996), 53, 14161.
- [21]. H. Nozaki; S. J. Itoh, Phys. Chem. Solids (1996), 57, 41.
- [22]. H.Nozaki; S.Itoh, Physica B(1996), 219, 487.
- [23]. Y. Tateyama;T. Ogitsu; K. Kusakabe; S. Tsuneyuki; S. Itoh, Phys. ReV. B(1997), 55, 10161.
- [24]. H.Pan, YP.Feng, JY.Lin Phys. Rev. B (2006) 73: 035420.
- [25]. AE. Reed, LA. Curtiss, F. Weinhold Chem. Rev. (1988) 88: 899-926.
- [26]. LD McPherson, M Drees, SI Khan, T Strassner, MM Abu-Omar Inorg. Chem. (2004) 43: 4036-4050.
- [27]. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (1998) Gaussian 98, Gaussian Inc, Pittsburgh PA.
- [28]. PC.Hariharan, JA.Pople Mol. Phys (1974) 27:209-214.
- [29]. Y Zhang, AWu, X Xu, Y Yan J. Phys. Chem. A(2007) 111: 943-9437.
- [30]. K Wolinski, JF Hilton, P Pulay J. Am. Chem. Soc (1990). 112: 8251-8260.
- [31]. AE Reed, LA Curtiss, F Weinhold, Chem. Rev. (1988) 88: 899-926.
- [32]. M Anafcheh, R Ghafouri, StructChem (2012) 23: 1921–1929
- [33]. H Pan, YP Feng, J Lin Phys Rev B(2006) 74:045409
- [34]. RS Drago Physical Methods for Chemists, 2nd edition, Saunders College Publishing,