Monatsh Chem (2010) 141:491–494
DOI 10.1007/s00706-010-0287-3

ORIGINAL PAPER

A computational study of oxygen-termination of a (6,0) boron nitride nanotube

Maryam Mirzaei · Mahmoud Mirzaei

Received: 1 February 2010 / Accepted: 24 February 2010 / Published online: 18 March 2010

Abstract The effects of oxygen (O) termination on the electronic and structural properties of a (6,0) boron nitride nanotube (BNNT) were investigated by density functional theory (DFT) calculations. All-atomic optimization and calculations of chemical shielding (CS) properties were performed for four models of the investigated BNNT based on different termination of the nanotube by the O atoms: perfect, O_B-end, O_N-end, and O_{BN}-end models. The results indicate that the B–N bond lengths are not changed by O-termination but the tubular diameters, dipole moments, and band gaps are substantially changed, especially for the O_{BN}-end model in which both tips are terminated by the O atoms. The CS properties also indicate that the atoms of the models are divided into layers on the basis of similar electronic environment in each atomic layer. In the O_B-end model where the atoms of the B-tip are substituted by the O atoms, the results are indicative of attraction between the N and O-terminating atoms but in the O_N-end model where the atoms of the N-tip are substituted by the O atoms, strong bonds between the B and O-terminating atoms are detected.

Keywords Nanostructures · Electronic structure · Nuclear magnetic resonance · Density functional theory

Maryam Mirzaei
Department of Electrical Engineering, Islamic Azad University, South Tehran Branch, Tehran, Iran

Mahmoud Mirzaei (✉)
Department of Chemistry, Islamic Azad University, Shahr-e-Rey Branch, Shahr-e-Rey, Iran
e-mail: mdmirzaei@yahoo.com

Introduction

Ever since the carbon nanotube (CNT) was discovered by Iijima [1], a rapidly growing number of researchers have focused on determining the properties of this fascinating novel material [2–5]. The investigations have also demonstrated that there are stable tubular structures other than the CNTs, among which boron nitride nanotubes (BNNT) are among the most important [6–8]. The electronic and structural properties of BNNTs have been investigated by either computational [9, 10] or experimental [11, 12] studies. Initially, the tubular structure of BNNT was established computationally [13]; BNNT were then successfully synthesized [14]. In contrast with CNTs, which exhibit metallic or semiconducting behavior depending on the tubular diameter and chirality, the BNNTs are viewed as always semiconductors without any dependence on structural factors [15]. Moreover, the BNNTs are polar materials because of the slight positive charges of boron (B) atoms and the slight negative charges of nitrogen (N) atoms whereas the CNTs are non-polar. Therefore, the BNNTs are expected to be more appropriate materials than CNTs for specific applications in electronic devices.

Previous studies have demonstrated that the electronic and structural properties of *zigzag* BNNTs are mainly characterized by their two hetero atomic tips, the B-tip and the N-tip [16]. In our current research, termination of the tips of a representative *zigzag* BNNT by oxygen (O) atoms has been investigated. For this purpose, we considered four models of the (6,0) *zigzag* BNNT in our calculations; perfect (Fig. 1), O_B-end (Fig. 2a), O_N-end (Fig. 2b), and O_{BN}-end (Fig. 2c). In the first step, the all-atomic geometries of the investigated models were optimized, and in the second step the nuclear magnetic resonance (NMR) properties were calculated. The NMR properties include

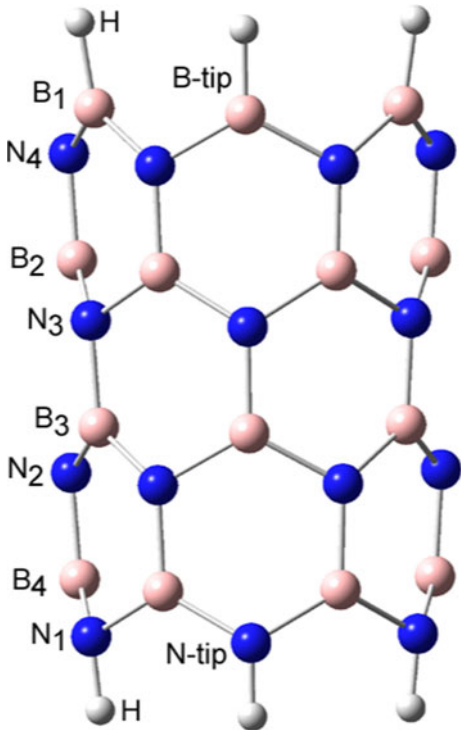

Fig. 1 Two-dimensional views of the perfect model of the (6,0) BNNT

isotropic (σ_{iso}) and anisotropic ($\Delta\sigma$) chemical shielding for the B-11, N-15, and O-17 atoms in the optimized structures. By use of the calculated NMR properties, we investigated the effect of O-termination on the electronic and structural properties of the (6,0) BNNT. It is important to note that NMR spectroscopy is among the versatile techniques for study of the electronic structure of matter. However, because of the complexity of the electronic environment of nanotubes, performing experimental NMR on these materials is a formidable task. Therefore, reproducing the NMR properties by high-level quantum chemical calculations is an advantage of computational studies on the electronic structures of nanotubes. All density functional theory (DFT) calculations were performed by use of the Gaussian 98 package [17].

Results and discussion

The geometrical data obtained by the optimization of the perfect (Fig. 1), the O_B-end (Fig. 2a), the O_N-end (Fig. 2b), and the O_{BN}-end (Fig. 2c) models of the investigated (6,0) BNNT are listed in Table 1. The B–N, B–O, and N–O bond lengths, the tip diameters, the dipole moments, and the band gaps were calculated at the BLYP/6-31G* computational level. The optimized values of the B–N bond lengths of the four models of the (6,0) BNNT do not show any significant changes as a result of O-termination of the tips of the nanotubes. However, the tubular diameters are affected by O-termination and the change is more significant for the O-termination of the N-tip. It is noted that O-termination of one tip of the nanotube does not affect the diameter of the other tip which is in its initial state. The tubular diameter is increased by O-termination of the B-tip whereas it is reduced by O-termination of the N-tip of the BNNT. Comparing the values of the dipole moments for the four models indicates that the value for the O_B-end model is significantly increased whereas those for the O_N-end and O_{BN}-end models are significantly reduced compared with the perfect model, which means that the strengths of the charge points are balanced in the two latter models. For the O_B-end model where the B atoms of the B-tip are substituted by O atoms, it seems that the N_4 and O_1 atoms only attract each other, which yields a larger value of dipole moment compared with the perfect model.

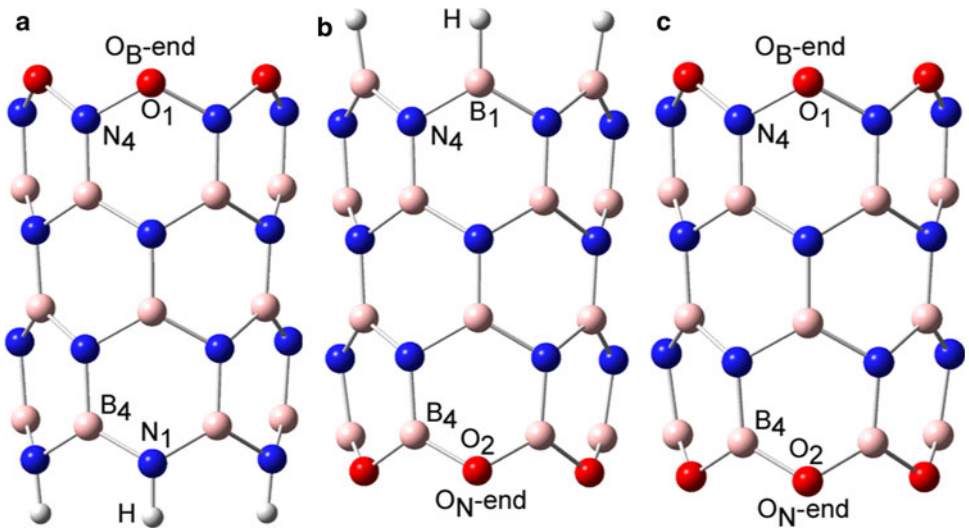

Fig. 2 Two-dimensional views of the O-terminated models of the (6,0) BNNT; **a** the O_B-end model, **b** the O_N-end model, **c** the O_{BN}-end model

Table 1 The geometrical data

Data	Perfect	O_B-end	O_N-end	O_{BN}-end
B–N length (Å)	1.46	1.46	1.46	1.46
B–O length (Å)	–	–	1.39	1.39
N–O length (Å)	–	1.45	–	1.45
B-tip diameter (Å)	4.87	4.94	4.87	4.93
N-tip diameter (Å)	5.13	5.14	4.78	4.79
Dipole moment (Debye)	8.15	12.95	2.85	1.86
Band gap (eV)	3.14	2.5	3.41	2.51

See Fig. 1 for details

Table 2 The NMR properties (ppm)

Atoms	Perfect	O_B-end	O_N-end	O_{BN}-end
$^{11}B_1$	74; 53	–	73; 52	–
$^{11}B_2$	77; 38	85; 33	76; 38	86; 33
$^{11}B_3$	77; 36	76; 34	75; 38	75; 37
$^{11}B_4$	79; 39	79; 39	81; 16	81; 16
$^{15}N_1$	159; 94	152; 94	–	–
$^{15}N_2$	129; 178	124; 176	122; 165	123; 161
$^{15}N_3$	124; 187	135; 171	120; 186	135; 170
$^{15}N_4$	93; 228	−67; 18	89; 228	−67; 16
$^{17}O_1(B_1)$	–	−29; 28	–	−26; 29
$^{17}O_2(N_1)$	–	–	148; 213	148; 215

See Figs. 1 and 2 for details. In each column, the first number is the isotropic (σ_{iso}) chemical shielding and the second number is the anisotropic ($\Delta\sigma$) chemical shielding

For the O_N-end model where the N atoms of the N-tip are substituted by O atoms, it seems that the B_4–O_2 bond is stronger than the B–N bond, in which the dipole moment is significantly reduced in this model. For the O_{BN}-end model in which the atoms of both tips are substituted by the O atoms, the smallest value of dipole moment is because of the equality of the atoms of two tips and the strong B–O bond. The value of band gap of the perfect model is reduced in the O_B-end and O_{BN}-end models whereas it is increased in the O_N-end model. It seems that the electronic densities of the O_B-end and O_{BN}-end models are larger than in the O_N-model in which the strong B–O bond could cause this result.

Table 2 presents the NMR isotropic (σ_{iso}) and anisotropic ($\Delta\sigma$) CS properties for the ^{11}B, ^{15}N, and ^{17}O atoms calculated at the BLYP/6-31G* computational level for the four optimized models of the investigated (6,0) BNNT (Figs. 1, 2). The values of NMR properties are divided into four layers for the models according to the similarities of the electronic environments in each layer. For the perfect model (Fig. 1), the largest value of σ_{iso} for ^{11}B atoms is that for atoms of B_4-layer which are chemically bonded to the atoms of N-tip whereas the largest value of $\Delta\sigma$ is that for atoms of B_1-layer which make the B-tip of the nanotube. The nature of the valence shells of the N atoms, which have lone pair of electrons, and the B atoms, which have a lack of electrons, are different; therefore, different behavior of the CS properties are expected and are also observed for these atoms. The values of NMR properties for the ^{15}N atoms of the perfect model indicate that the largest value of σ_{iso} is that for the atoms of N_1-layer which make the N-tip of the nanotube but the largest value of $\Delta\sigma$ is that for the atoms of N_4-layer which are chemically bonded to the atoms of B-tip of the nanotube. The larger values of σ_{iso} for the B_4 and N_1 layers indicate that the chemical bonding of B_4–N_1 could be weaker than that of B_1–N_4 in the perfect model. For the O_B-end model (Fig. 2a) where the atoms of B_1-layer are substituted by the O atoms, the similarities of the values of the CS properties for the atoms of each layer are observed. The values of the CS properties of the B_3, B_4, N_1, and N_3 layers are not substantially affected by O-termination of the B-tip but those of other layers are affected. The most significant change of the CS properties is observed for the atoms of the N_4-layer which are chemically bonded to the O-terminating atoms.

For the O_N-end model (Fig. 2b) in which the atoms of the N-tip are substituted by O atoms, the results indicate that the CS values of the B_1, B_2, B_3, N_3, and N_4 layers are not affected by O_N-termination. This trend and the parallel one for the O_B-end model indicate that the size of our study model is valid for our purpose because the values of the atoms of the tips of the nanotubes are not affected by O-termination of the opposite tips. For the O_N-end model, the atoms of B_4-layer are directly chemically bonded with the O-terminating atoms and only their NMR properties are affected by O_N-termination of the other B atoms. For the O_{BN}-end model (Fig. 2c) in which both tips of the investigated BNNT are terminated by the O atoms, the results indicate that there are similarities in the electronic environments of this model and the other models in similar atomic positions. Indeed, comparison of the results of this model with the O_B-end and O_N-end models demonstrates that the similarities in the calculated values of the CS properties could be observed in equal positions of the models. It is noted that double termination of the nanotube by the O atoms has the most significant effect on the electronic properties of the investigated *zigzag* BNNT.

Conclusions

We have performed DFT calculations to investigate the electronic and structural properties of the O-end models of a representative (6,0) *zigzag* BNNT. From the results of optimization and NMR calculations, some trends could be

observed. First, the B–N bond lengths are not affected by the O-termination but the tubular diameters are changed substantially. Second, the dipole moments and band gaps are affected by O-termination in the O-end models. Third, the calculated CS properties indicate that the atoms of the models are divided into layers on the basis of the similarities of their electronic environments. Fourth, in the O_B-end model, the results could indicate only attraction between the N and O-terminating atoms whereas there is strong chemical bonding between the B and O-terminating atoms in the O_N-end model. Fifth, the changes of the O_{BN}-end model are the most significant among the models and the O-termination results in similar changes to the O_B-end and O_N-end models in similar atomic positions. Finally, in the one-tip O-end models, the atoms of the tips are not affected by O-termination of the opposite tip.

Computational details

In this research, four models of a 1-nm length of a representative (6,0) *zigzag* single-walled BNNT were investigated by DFT calculations using the Gaussian 98 package [17]. The perfect model (Fig. 1) consists of 24 boron (B) and 24 nitrogen (N) atoms in which the tips of the nanotube are saturated by 12 hydrogen (H) atoms. The O_B-end model (Fig. 2a) consists of 18 B atoms, 24 N atoms, and six oxygen (O) atoms in which six B atoms are substituted by six O atoms and the N-tip is only saturated by six H atoms. The O_N-end model (Fig. 2b) consists of 24 B atoms, 18 N atoms, and six O atoms in which six N atoms are substituted by six O atoms and the B-tip is only saturated by six H atoms. The O_{BN}-end model (Fig. 2c) consists of 18 B and 18 N atoms in which both tips are substituted by 12 O atoms and are not saturated by H atoms. In the initial step, the all-atomic geometries of the structures have been allowed to relax by performing optimization at the level of the BLYP exchange-functional and 6-31G* standard basis set.

In the last step, the chemical shielding (CS) properties were been calculated at the same computational level based on the gauge included atomic orbital approach (GIAO) [18] in the optimized structures. It is worth noting that the size of model considered and the level of theory employed for the study of the electronic and structural properties of the nanotubes have been validated either by results from previous work [19, 20] or the results from this research. Moreover, this is a comparative study in which the properties of the considered models are compared at the same computational level. The quantum chemical calculations yield the CS tensors in the principal axis system (PAS) with the order of $\sigma_{33} > \sigma_{22} > \sigma_{11}$; therefore, Eqs. 1 and 2 are used to convert the calculated CS tensors to the isotropic (σ_{iso}) and anisotropic ($\Delta\sigma$) CS properties [15]. The NMR properties evaluated for the investigated models of the (6,0) BNNT are listed in Tables 1 and 2.

$$\sigma_{iso}\,(\text{ppm}) = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}), \tag{1}$$

$$\Delta\sigma\,(\text{ppm}) = \sigma_{33} - \frac{1}{2}(\sigma_{11} + \sigma_{22}). \tag{2}$$

References

1. Iijima S (1991) Nature 354:56
2. Coleman JN, O'Brien DF, McCarthy B, Barklie RC, Blau WJ (2001) Monatsh Chem 132:53
3. Treboux G, Nakamura S (2009) 140:839
4. de Menezes VM, Fagan SB, Zanella I, Mota R (2009) Microelectron J 40:877
5. Ni MY, Zeng Z, Ju X (2009) Microelectron J 40:863
6. Chen X, Ma J, Hu Z, Wu Q, Chen Y (2005) J Am Chem Soc 127:17144
7. Zhang D, Zhang RQ (2003) Chem Phys Lett 371:426
8. Loiseau A, Willaime F, Demoncy N, Schramcheko N, Hug G, Colliex C, Pascard H (1998) Carbon 36:743
9. Mirzaei M (2009) Z Phys Chem 223:815
10. Mirzaei M (2009) Monatsh Chem 140:1275
11. Song J, Huang Y, Jiang H, Hwang KC, Yu MF (2006) Int J Mech Sci 48:1197
12. Arenal R, Ferrari AC, Reich S, Wirtz L, Mevellec Y-J, Lefrant S, Rubio A, Loiseau A (2006) Nano Lett 6:1812
13. Blasé X, Rubio A, Louie SG, Cohen ML (1994) Europhys Lett 28:335
14. Chopra NG, Luyken RJ, Cherrey K, Crespi VH, Cohen ML, Louie SG, Zettl A (1995) Science 269:966
15. Zhang SL (2001) Phys Lett A 285:207
16. Hou S, Shen Z, Zhang J, Zhao X, Xue Z (2004) Chem Phys Lett 393:179
17. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, 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
18. Wolinski K, Hinton JF, Pulay P (1990) J Am Chem Soc 112:8251
19. Nouri A, Mirzaei M (2009) J Molec Struct (THEOCHEM) 913:207
20. Mirzaei M, Nouri A (2010) J Molec Struct (THEOCHEM) 942:83