

# Structural Study of Boron - Nitride Nanotube with Magnetic Resonance (NMR) Parameters calculation via Density Functional Theory method (DFT)

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**Abstract**—A model of (4, 4) single-walled boron-nitride nanotube as a representative of armchair boron-nitride nanotubes studied. At first the structure optimization performed and then Nuclear Magnetic Resonance parameters (NMR) by Density Functional Theory (DFT) method at  $^{11}\text{B}$  and  $^{15}\text{N}$  nuclei calculated. Resulted parameters evaluation presents electrostatic environment heterogeneity along the nanotube and especially at the ends but the nuclei in a layer feel the same electrostatic environment. All of calculations carried out using Gaussian 98 Software package.

**Keywords**—Boron-nitride nanotube, Density Functional Theory, Nuclear Magnetic Resonance (NMR).

## I. INTRODUCTION

SINCE the discovery of carbon nanotubes (CNTs)[1], considerable attention has been attracted for synthesizing them due to their unique properties[2] and potential applications[3]-[5]. People have so far synthesized various structural and morphological CNTs such as multi-, single-, and double- walled[6],[7], as well as Y-, bamboo-, and cone-shaped CNTs[8],[9]. Recently boron nitride nanotubes (BNNT) in which BN unit is isoelectronic to C-C unit in CNT, have attracted increasing attention. The stability of BNNT was predicted firstly on the basis of semi-experiential tight binding (TB)[10] and local density approximated (LDA) density functional theory[11] calculations in 1994, and their synthesis was realized in 1995 with arc-charging method using the BN electrode packed into a metal casing[12]. Other preparation methods have been developed subsequently, such as arc-melting[13], high temperature chemical reaction[14], carbon nanotube templates[15], and laser ablating[16]. At same time, further theoretical investigations for the structures and electronic properties of BNNT have been reported [17]–[27]. Nuclear Magnetic Resonance (NMR) is a powerful tool for

studying material structural features since the position of the NMR signal of each nucleus depends on the nature of nucleus electrostatic environment. Magnetic nuclei chemical shielding tensors for nuclei with fractional spin like  $^{11}\text{B}$  and  $^{15}\text{N}$  nuclei, exhibit very valuable information about physical environment and especially electrostatic environment around the nucleus. But because of complex nanotubes electrostatic environment, the practical spectrometry that has a direct relation to around nucleus electrostatic environment has much difficulty. So quantum calculations play very significant role in measurable nanotubes nuclear magnetic resonance parameters.

In this article, a structure of (4, 4)single-walled armchair boron-nitride nanotube, 1 nm length and two mouths H-atom capped consisting of 36 B and 36 N atoms as a representative of armchair boron-nitride nanotubes is picked to structural study (Fig. 1). At first, structure optimization performed and then Nuclear Magnetic Resonance (NMR) parameters by density Functional Theory (DFT) method calculated on the optimized structure. Isotropic chemical shielding parameters ( $\sigma_{\text{iso}}$ ) at  $^{11}\text{B}$  And  $^{15}\text{N}$  nuclei are presented in Table I.

## II. CALCULATION FEATURES

All Density Functional Theory (DFT) quantum calculations are performed using Gaussian 98 program package on structure of (4, 4)single-walled armchair boron-nitride nanotube, 1 nm length and two mouths H-atom capped consisting 36 B and 36 N atoms as a exemplary of armchair nanotubes (Fig. 1). The structure first optimized with Becke3, Lee-Yang-Parr (B3LYP) method and 6-311G\*\* basis set and then Nuclear Magnetic Resonance (NMR) parameters at  $^{11}\text{B}$  and  $^{15}\text{N}$  nuclei optimized structure calculated by B3LYP method and 6-311++G\*\* basis set (Table I). There are five d-type Gaussian polarization functions on each non-hydrogen atom and three p-type polarization functions on each hydrogen atoms in the large Pople's valence triple-zeta 6-311G\*\* and 6-311++ G\*\* [28] basis sets in which pluses are added to indicate the diffuse functions on all atoms in the latter one [29]. Both of 6-311 G\*\* and 6-311++ G\*\* basis sets are added to indicate the diffuse functions on all atoms in the latter one [29]. Both of 6-311 G\*\* and 6-311++ G\*\* basis sets are adapted to reproduce reliable NMR properties [30], [31]. Chemical shielding tensors that obtain from calculation are in

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principal axis system (PAS) ( $\sigma_{11} > \sigma_{22} > \sigma_{33}$ ) that converts it to isotropic chemical shielding ( $\sigma_{\text{iso}}$ ) in ppm unit by relation (1).

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

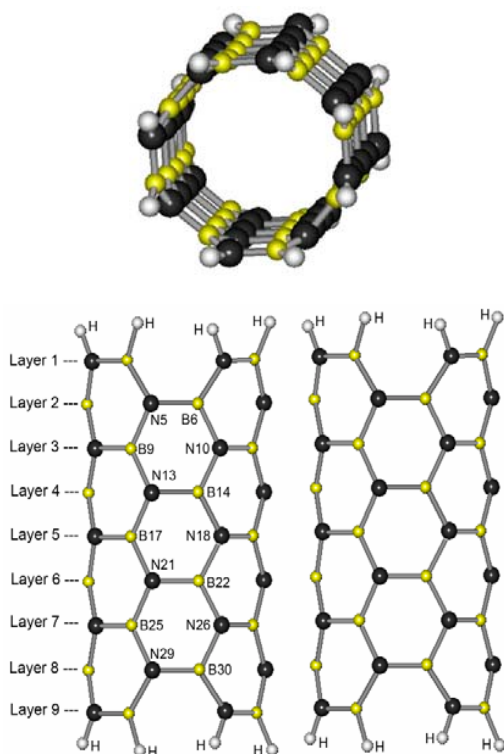


Fig. 1 (4, 4) Boron-nitride nanotube three and two dimensional representation

TABLE I  
(4, 4) BORON-NITRIDE NANOTUBE ISOTROPIC CHEMICAL SHIELDING

Layers	$\sigma_{\text{iso}}(\text{ppm})$	
	$^{11}\text{B}$	$^{15}\text{N}$
Layer 1	68	130
Layer 2	73	115
Layer 3	71	116
Layer 4	74	118
Layer 5	75	114
Layer 6	74	118
Layer 7	71	116
Layer 8	73	115
Layer 9	68	130

See Fig. 1

### III. RESULTS AND DISCUSSION

Structural study of H-capped (4, 4) boron-nitride nanotube to obtain nuclei Magnetic Resonance Parameters via Density Functional Theory method performed. Isotropic chemical shielding parameters ( $\sigma_{\text{iso}}$ ) of nanotube at  $^{11}\text{B}$  and  $^{15}\text{N}$  nuclei is evaluated (Fig. 1 and Table I). Calculated isotropic chemical

shielding parameters ( $\sigma_{\text{iso}}$ ) of the nanotube, divide nuclei electrostatic environment to nine layers and in each layer isotropic chemical shielding parameter is the same to all the layer nuclei. In the following, calculated data at  $^{11}\text{B}$  and  $^{15}\text{N}$  nuclei are discussed respectively.

#### A. Isotropic Chemical Shielding Parameter at $^{11}\text{B}$ Nuclei

As mentioned above, 36 Boron nuclei evaluates as nine layers in the boron-nitride nanotube. As derives from Fig. 1, Layers 1 and 9 are right at nanotube ends and then boron nuclei have similar electrostatic environment and their calculated parameters at Table I show this issue ( $\sigma_{\text{iso}} = 68$  ppm). The boron-nitride nanotube symmetrical locations show the same isotropic chemical shielding at boron nuclei as noted for end layers (layers 1 and 9). Layers 2 and 8, 3 and 7, 4 and 6, also have symmetrical locations in the nanotube and so we expect equal boron nuclei isotropic chemical shielding at any of the layer paired and this expectation proves by Table I calculated parameters. Indeed isotropic chemical shielding of layer 5 in the center of boron-nitride nanotube has maximum value. And it means boron nuclei in the layer have maximum electron shielding from external field but the quantity is minimum at the the ends.

#### B. Isotropic Chemical Shielding Parameter at $^{15}\text{N}$ Nuclei

Considering isotropic chemical shielding values in Table I, like boron nuclei, 36 nitrogen nuclei evaluate as nine layers in the boron-nitride nanotube. As we mentioned in introduction, close resemblance between boron-nitride nanotubes and carbon nanotubes is that the sum of atomic number of one boron atom and one nitrogen atom is equal to two carbon atomic number sum and hence frequently, the number of boron and nitrogen atom nuclei in boron-nitride nanotube are the same as we presented an example of it in this research. But main difference between boron and nitrogen atoms is presence of nonbonding electron pair in nitrogen valence shell but boron atom has valence shell electron lack. This important factor gives boron atom rather acidic property and nitrogen rather basic property and consequently causes the nuclei different behaviors in the boron-nitride nanotube. Based upon the reason, nitrogen nuclei have maximum isotropic chemical shielding in the end layers (Layers 1 and 9) but the quantity in nanotube center, layer 5 at nitrogen nuclei is minimum and this observation is against what we remarked about boron nuclei and somehow refers to basic and acidic property of nitrogen and boron respectively. Equal isotropic chemical shielding at nitrogen nuclei in other layers symmetrical locations (layers 2 and 8, 3 and 7, 4 and 6) observed and in comparing, the layer whose isotropic chemical shielding at boron nucleus is bigger beside previous layer, at nitrogen nuclei, isotropic chemical shielding in that layer is smaller than previous layer. This phenomenon remarks boron and nitrogen different roles in boron-nitride nanotube.

### IV. CONCLUSION

This research probed in to (4, 4) single-walled boron-nitride nanotube as a representative of armchair boron-nitride nanotubes through Nuclear Magnetic Resonance parameters

(NMR). Calculated isotropic chemical shielding for different boron and nitrogen nuclei shows that nanotube various positions do not represent similar structures and there is not a totally homogenous electrostatic environment in nanotube albeit there is thoroughly similar properties in totally symmetrical positions.

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