Cent. Eur. J. Chem. • 8(4) • 2010 • 913–918
DOI: 10.2478/s11532-010-0068-1

Central European Journal of **Chemistry**

A computational NPA and NMR study of Li-capped armchair GaN Nanotubes

Research Article

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Received 31 December 2009; Accepted 26 March 2010

Abstract: The geometrical structure, the nuclear magnetic resonance (NMR) parameters and natural population analysis (NPA) of the H-capped (raw) and Li-capped armchair single-walled gallium nitride nanotubes (GaNNTs) are computed and reported for the first time. Our results show that the variation of isotropic chemical shielding (ICS) parameters at the sites of ^{15}N and ^{71}Ga along the length of both models- raw and Li-capped- are reversed. The calculations were carried out with B3LYP-DFT method and 6-31G (d) standard basis sets using the Gaussian 03 suite of programs.

Keywords: *Density functional theory • Gallium nitride nanotube • Nuclear magnetic resonance • Li-capped*

1. Introduction

Carbon and non-carbon nanotubes are considered to possess exclusive properties in comparison with the corresponding bulk materials due to the quantum confinement effect, and consequently they have vast potential applications in both nanotechnology and nanoscale engineering. An important difference between the two types of nanotubes is that the conductivity of non-carbon nanotubes is independent of their chirality while carbon nanotubes are either metallic or semiconducting depending upon their tubular diameter and chirality [1,2].

The stability and electronic properties of single-walled GaN nanotubes have been studied by first–principle calculations which ensured their synthesis in 1999 [3]. Recently, GaN nanotubes (GaNNTs) were synthesized by an epitaxial casting approach by Yang and co-workers in 2003 [4]. Theoretical investigations have indicated that larger-diameter GaNNTs have a band gap of about 2 eV [3]. Experimental and theoretical investigations indicate that Li-doped carbon nanotubes can be used for hydrogen storage and indeed the dopant actually enhances storage capacities at ambient pressure and temperature [5-6]. Also, Li-doped carbon nanotubes have been successfully applied as ion batteries with high energy storage density [7].

The calculation of nuclear magnetic resonance (NMR) parameters using ab initio techniques has become a major and powerful tool to investigations of the physical properties of matter in the solid phase [8-11]. Chemical shielding (CS) tensors located at the sites of fractional spin like ^{71}Ga and ^{15}N nuclei are very responsive to electronic density and are easily perturbed; hence, they can show important insights about the electrostatic properties of GaNNTs. In this theoretical task, we follow two objectives: First, we determine doping possibilities and capping models of Li atom(s) in the GaNNTs. Second, the influence of maximum Li-doping or capping on electronic structure properties of the (4, 4) GaNNT is investigated by the DFT-B3LYP calculation of the ^{71}Ga and ^{15}N CS tensors.

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2. Computational approach and geometrical models

Five models of approximately 1.3 nm long (4, 4) single-walled GaNNTs were considered. The length of tubes and the atomic numbers were selected for time saving calculation and their validity has been examined earlier by others [12]. Model No.1 consisted of 32 Ga and 32 N atoms (Fig. 1). Model No.2 is a Li-capped (4, 4) GaNNT model in which the N and Ga atoms are placed in both portals of (4, 4) GaNNT and were capped by Li and H atoms, respectively (Fig. 2). Model No.3 is another Li-capped GaNNT model in which N and Ga atoms of both mouths of the tube were capped by H and Li atoms, respectively (see Fig. 3a). Model No.4 is a Li-doped (4, 4) GaNNT model in which one Li atom has replaced an N atom in the ring of GaNNT (see Fig.3b). The last model, No.5, is a Li-doped GaNNT in which one Li atom is substituted for one Ga atom in the ring of (4, 4) GaNNT (Fig. 3c). Both portals of the nanotubes were capped by H atoms in models No.1, 4, and 5 to avoid dangling bonds.

NMR values were computed using density functional theory and they are known to be only somewhat sensitive to the choice of basis set [13], and 6-31G (d) standard basis set for GaN nanotubes have been recommended [14-15]. Accordingly, all calculations were carried out by the B3LYP-DFT methodology and the 6-31G (d) standard basis set using the Gaussian 03 suite of programs [16]. All of the five models were individually optimized (Figs. 1-3 and Tables 1-2) and then for models No.1 and 2, the CS tensors at the sites of ^{71}Ga and ^{15}N nuclei are calculated based on the gauge included atomic orbital (GIAO) approach [17]. London initially recommended local gauge origins to describe the vector potential of the external magnetic field in the study of molecular diamagnetism [18]. The idea was then adapted by Ditchfield [19] in the GIAO method for magnetic shielding calculations. Following Ditchfield's work in which each atomic orbital has its own local gauge origin placed on its center, Giessner-Prettre *et al.* and Fukui *et al.* implemented the GIAO method [20,21]. The calculated CS tensors in principal axes system

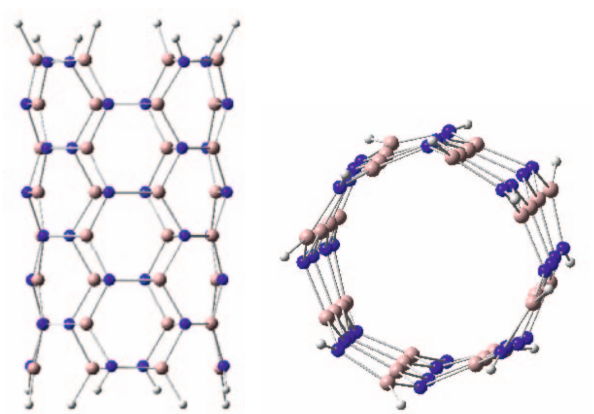

Figure 1. Two 3D views of the raw (4, 4) GaNNT model.

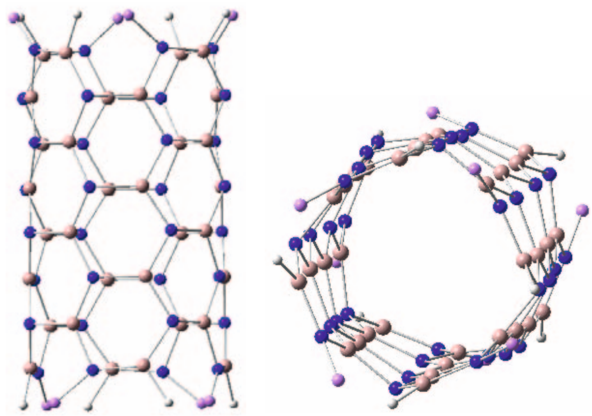

Figure 2. Two 3D views of the Li-capped (4, 4) GaNNT model.

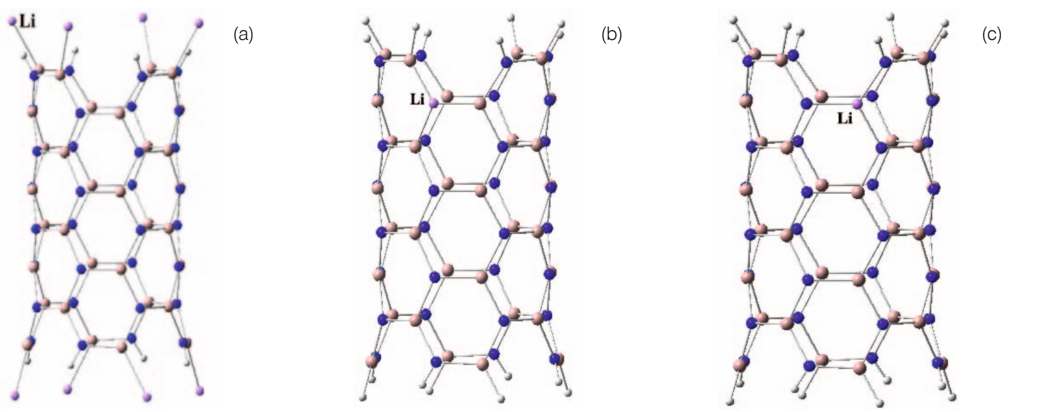

Figure 3. (a) the 3D views of Li-capped (model 3), (b) the 3D views of Li-capped (model 4) and (c) the 3D views of Li-capped GaNNTs (model 5) before optimization.

Table 1. Structural parameters of the raw (4, 4) GaNNT.

Bonding nuclei	Bond lengths (Å)	Bonding nuclei	Bond lengths (Å)	Bonding nuclei	Bond angles (deg)
Ga-N		**Ga-N**		**Ga-N-Ga**	
2-1	1.87	19-26	1.89	2-1-6	121
2-3	1.88	19-20	1.88	2-3-4	115
6-1	1.87	21-7	1.88	4-5-6	121
6-5	1.89	21-20	1.88	4-7-8=21-7-8	111
4-5	1.89	21-22	1.89	8-9-10	120
4-3	1.88	16-3	1.88	8-9-14	115
4-7	1.89	16-22	1.88	N-Ga-N	
10-11	1.87	24-22	1.89	1-6-5	115
10-5	1.89	24-28	1.89	1-2-3	116
10-9	1.88	27-20	1.88	3-4-5	120
12-11	1.87	27-31	1.87	3-4-7	119
12-13	1.89	27-28	1.89	7-8-9=7-8-18	119
14-13	1.89	32-28	1.89	9-14-15	119
14-15	1.89	30-26	1.89		
14-9	1.88	30-31	1.87		
8-9	1.88	25-23	1.88		
8-18	1.88	25-29	1.87		
8-7	1.89	25-26	1.89		
17-15	1.88	Ga-H	1.56		
17-23	1.88	N-H	1.02		
17-18	1.89				
19-18	1.89				

Table 2. Structural parameters of the Li-capped (4, 4) GaNNT.

Bonding nuclei	Bond lengths (Å)	Bonding nuclei	Bond lengths (Å)	Bonding nuclei	Bond angles (deg)
Ga-N		**Ga-N**		**Ga-N-Ga**	
2-1	1.88	19-26	1.89	2-1-6	109
2-3	1.89	19-20	1.89	2-3-4	115
6-1	1.84	21-7	1.89	4-5-6	115
6-5	1.90	21-20	1.88	4-7-8=21-7-8	111
4-5	1.89	21-22	1.89	8-9-10	121
4-3	1.89	16-3	1.88	8-9-14	115
4-7	1.89	16-22	1.89	N-Ga-N	
10-11	1.88	24-22	1.89	1-6-5	128
10-5	1.91	24-28	1.89	1-2-3	124
10-9	1.89	27-20	1.89	3-4-5	120
12-11	1.84	27-31	1.88	3-4-7	120
12-13	1.90	27-28	1.91	7-8-9=7-8-18	120
14-13	1.89	32-28	1.90	9-14-15	120
14-15	1.89	30-26	1.89		
14-9	1.89	30-31	1.83		
8-9	1.88	25-23	1.89		
8-18	1.89	25-29	1.88		
8-7	1.89	25-26	1.91		
17-15	1.89	Ga-H	1.64		
17-23	1.88	N-Li	1.82		
17-18	1.89				
19-18	1.89				

(PAS) ($\sigma_{11}<\sigma_{22}<\sigma_{33}$) are converted to measurable NMR parameters, isotropic chemical shielding (CSI) and anisotropic chemical shielding (CSA) using Eqs. 1 and 2, respectively which are given below [22]. The evaluated NMR parameters at the sites of ^{71}Ga and ^{15}N nuclei in the two possible models are presented in Tables 3 and 4, respectively.

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

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

The natural population analysis (NPA) was carried out at the sites of Ga and N atoms in both raw and Li-capped models considered here (Tables 5 and 6).

3. Results and Discussion

In order to determine the possible doping and capping models, we performed optimization at the level of the B3LYP-DFT method and 6-31G(d) standard basis set on each of the five armchair GaNNT models- namely raw, Li-capped, and Li-doped. The optimization processes indicated that only models No. 1 and No.2 are possible and other models are not. When the Li atoms replaced H atoms (Ga bonded) the Ga-Li bonds didn't form (model No.3). Substitution of Li atoms for both of Ga (model No.4) and N (model No.5) atoms in a ring are not possible doping models because the ring will open and the nanotube structure will disarrange. Finally only two models of GaNNTs, raw (No.1) and Li-capped (No.2), gave complete optimized structures. Their geometrical structures are investigated via their Ga–N bonds and bond angles (Tables 1 and 2).

According to Table 1, there is no significant change in the Ga-N bond lengths in the raw GaNNT model and for those bonds, the average value is 1.88 Å along the length of the armchair tube. Unlike the bond lengths which stay constant, the Ga-N-Ga bond angle reduces from 121° at the end of the tube to 111° at the center. However, the N–Ga–N angles increase from 115° at the armchair H-capped GaNNT's end to 119° at its center. Both mouths of the armchair GaNNT are similar, each consisting of both N and Ga atoms. Hence, the diameter of the tube at both ends is the same but in the armchair model the ends of the tube are elliptically oriented with the N–N distance of 7.22 Å and that of Ga-Ga being 7.36 Å. However, the Ga-N bond lengths for mouths (1.84 Å), in layers 1 and 8, and also of the neighboring bonds (1.90Å) are changed in the Li-capped GaNNT but remain almost unchanged (1.89 Å) for other bonds when compared to the H-capped GaNNT (Table 2). Bond angles change

Table 3. The NMR parameters in the raw (4, 4) GaNNT.

Layers	^{71}Ga		^{15}N	
	ICS(ppm)	ACS(ppm)	ICS(ppm)	ACS(ppm)
Layer 1	1655	83	151	78
Layer 2	1716	179	126	75
Layer 3	1700	178	120	47
Layer 4	1714	214	120	45
Layer 5	1715	219	120	46
Layer 6	1700	170	121	47
Layer 7	1715	180	126	74
Layer 8	1656	82	151	77

Table 4. The NMR parameters in the Li-capped (4, 4) GaNNT.

Layers	^{71}Ga		^{15}N	
	ICS(ppm)	ACS(ppm)	ICS(ppm)	ACS(ppm)
Layer 1	1783	287	67	79
Layer 2	1734	269	95	49
Layer 3	1700	168	106	30
Layer 4	1719	227	114	44
Layer 5	1724	227	113	44
Layer 6	1700	169	104	29
Layer 7	1735	271	94	48
Layer 8	1783	287	67	80

Table 5. The ^{71}Ga and ^{15}N Natural Charges in the (4, 4) GaNNT.

Layers	^{71}Ga	^{15}N
	Natural Charge	Natural Charge
Layer 1	1.360	-1.470
Layer 2	1.620	-1.630
Layer 3	1.630	-1.660
Layer 4	1.620	-1.620
Layer 5	1.620	-1.620
Layer 6	1.630	-1.660
Layer 7	1.620	-1.630
Layer 8	1.360	-1.470

H bonded to Ga= -0.2813
H bonded to N= 0.4229

Table 6. The ^{71}Ga and ^{15}N natural charges in the Li-capped (4, 4) GaNNT.

Layers	^{71}Ga	^{15}N
	Natural Charge	Natural Charge
Layer 1	1.295	-1.660
Layer 2	1.524	-1.600
Layer 3	1.620	-1.650
Layer 4	1.615	-1.620
Layer 5	1.614	-1.612
Layer 6	1.620	-1.650
Layer 7	1.524	-1.600
Layer 8	1.295	-1.660

Li bonded to N=1.300
H bonded to Ga= -0.420

between the raw and Li-capped models. Specifically, the Ga-N-Ga bond angles increase from 109° at the mouth of GaNNT to 111° at the middle, and the N-Ga-N bond angles decrease from 128° at the portal of tube to 120° at the center of Li-capped GaNNT. In other words, the variation trend of Ga-N-Ga and N-Ga-N bond angles from the mouths to the center of the tubes are inversed in the Li-capped GaNNT in comparison to H-capped GaNNT. At each mouth of the Li-capped GaNNT model the diameter of N-N is 6.92 Å and Ga-Ga is 7.05 Å which are shorter than the corresponding values in H-capped model.

Tables 3 and 4 present the evaluated NMR parameters (CSI and CSA) in the two optimized H-capped (Fig. 1) and Li-capped (Fig. 2) models of (4,4) armchair GaNNTs considered in this work. There are 32 Ga and 32 N atoms in each model of GaNNT (No.1 and No.2) which form eight distinct layers in each model. The N atoms in both mouths of H-capped GaNNT- layers 1 and 8- saturated by H atoms, have the largest ICS and ACS values (151 and 78 ppm) of all the layers, which means that the electronic densities at the sites of these nuclei are higher than other layers. It is important to point out that the natural charge difference between the Ga (1.360) and N (-1.470) within both mouths is 0.1, which is the maximum difference when compared to other layers (Table 5). By going from end layers to middle layers of the tube, the values of ^{15}N parameters are decreased and for these layers; the CSI values are 126,120,120 and 120 ppm and the CSA values are 75, 47, 45 and 46 ppm, respectively. These values indicate that the two mouth-layers of H-capped GaNNT are completely different from those at the middle of the tube. This is because of the abrupt variation of the environment of the N atoms, due to the presence of hydrogen atoms. The Ga atoms in both portals of Model No.1- layers 1 and 8- saturated by H atoms have the smallest ICS and ACS values (1655 and 83 ppm, respectively) among other layers. Moving inwards to the middle layers, the ICS (1716, 1700, 1714 and 1715 ppm) and the ACS (179,178, 214, and 219 ppm) values increased. Table 5 shows the natural charges for Ga and N atoms. As shown, for both mouths of nanotube this parameter has minimum values of 1.360, and -1.470 for Ga and N atoms, respectively. These values are in full agreement with the NMR parameters.

Since eight H atoms (N bonded) are doped by eight Li atoms in the Li-capped model, the NMR parameters at the sites of ^{71}Ga and ^{15}N in the neighborhood of the doping Li atoms are significantly perturbed. This is because the electronegativity of H atom (e_H =2.1) is considerably larger than that of Li atom (e_{Li} =1.0) and that changes inter-atomic distances and bond angles of the nanotube. The Ga atoms in both mouths of Li-capped GaNNT have the largest ICS and ACS values (1783 and 287 ppm) among other layers and for the middle layers, the ICS (1716, 1700, 1714 and 1715 ppm) values decreased. On the contrary, N atoms placed in both ends of Model No.2 have the smallest ICS values (67 ppm) and the largest ACS (79 ppm) values among all other layers. Moving to the middle layers ICS (95,106,114 and 113 ppm) values of N atoms increased. For these parameters too, we observe that the ICS values in the Li-capped model follows a reverse trend to that of the H-capped model. This different trend in ICS parameters in both models of GaNNT is related to geometrical structures (differences in surrounding bonds of each atom, diameters of tubes and bond angels of Ga or N atoms). For Ga and N atoms from both portal layers to middle layers the variations trend of the ICS values is in agreement with bond angles in both models of H-capped and Li-capped GaNNTs. In other words, the trend of ICS values for nuclei in Li-capped model is in disagreement with the trend of natural charges (Table 6), and bond angles seemingly play a major part in here.

4. Conclusion

The B3LYP-DFT method is applied to study geometrical structure, the NMR parameters and NPA values of the N and Ga atoms in both ,H- and Li-capped models of (4,4) GaNNTs. In the first and eighth layers (the two mouth layers at the ends) of the H-capped armchair GaNNT, the Ga and N atoms have the smallest and the largest of the NMR (ICS and ACS) parameters among other layers, respectively. This trend is in agreement with the natural charge of Ga and N atoms, respectively- with the charges of the two atoms being different, of course. Since in these layers the Ga atoms have the lowest electronic density and the N atoms have the highest, they can respectively be electron acceptor and electron donor in the H-capped GaNNT model. In comparison with the H-capped model, the Ga atoms and N atoms in both mouths have the largest and the smallest ICS values among other layers in the Li-capped model, respectively. In the latter model, the nanotube structure will deform after geometry optimization which causes such variations. In other words, more variations are observed in the calculated ICS values of ^{71}Ga and ^{15}N nuclei when they are placed in both mouths of GaNNT in the Li-capped model.

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