

Computation of the NMR Parameters of H-Capped (10, 0) and (5, 5) Single-Walled SiC Nanotubes

Goudarz M. Rouzbehani¹, Temer S. Ahmadi² and Ahmad Seif^{1*}

¹Nanoscience Computation Lab, Boroujerd Branch, Islamic Azad University, Boroujerd, Iran

²Department of Chemistry, Villanova University, Villanova, PA, USA

ABSTRACT

Geometrical structure, nuclear magnetic resonance (NMR) chemical shielding tensors, and chemical shifts of silicon and carbon nuclei are investigated for two finite size zigzag and armchair single-walled silicon carbide nanotubes (SiCNTs). Geometrical structures of SiCNTs, Si-C bonds and bond angles of Si and C vertices in both zigzag and armchair nanotubes, indicate that bond lengths are approximately constant in the armchair model but vary in the zigzag model. The NMR parameters of C nuclei change more in the zigzag model as compared to the armchair model in agreement with geometrical structure changes. The calculations were performed with B3LYP DFT method and 6-31G (d) standard basis sets using the Gaussian 03 package.

Keywords: Silicon carbide nanotubes; Nuclear magnetic resonance (NMR); Chemical shielding; Chemical shift

INTRODUCTION

Since the discovery of carbon [1] and non-carbon [2-3] nanotubes, an extensive research field in the nano scale opened up because of the exceptional electronic, mechanical, thermal and transport properties of these systems. An important class of such materials is the silicon carbides (SiC) which form a solid through primarily covalent bonding. These compounds have various outstanding properties including: (1) large band gap from 2.2 to 3.3 eV[4], (2) very high decomposition temperature of about 2545 °C[5], (3) high thermal conductivity up to about 500 W/(m K) at room temperature [6], and (4) thermal expansion coefficient smaller than 6 μ /K [7]. It is therefore not surprising that SiC is finding application in high temperature electronics, high temperature atom environment [8], and high strength composites [9].

Carbon nanotubes (CNTs), depending on their chirality, have been found to be either metallic or

semiconducting. CNTs are highly aromatic systems. Replacing one-half of the C atoms in CNTs by Si atoms decreases the aromaticity of each six-membered ring and leads to the formation of silicon carbide nanotubes (SiCNTs). The decrease in aromaticity leads to a decrease in stability. Therefore, the exterior surface of SiCNTs is more reactive than that of single-walled CNTs. For example, the electronic structures of SiCNTs can be altered by selective hydrogenation [19].

Recently silicon carbide nanotubes (SiCNTs) [10, 11], SiC nanobelts [12], SiC nanowires [13-14] and SiC nanowebs [15] have been synthesized. The structure and stability of SiC nanotubes have been investigated in detail using ab initio density functional theory [16]. Such studies show

*Corresponding Author: Ahmaseif@yahoo.com

that the SiC nanotubes with alternating Si-C bonds are more stable than the forms which contain C-C or Si-Si bonds [16]. SiCNTs are always semiconductors with direct band gaps for the zigzag tubes and indirect band gaps for the armchair and chiral tubes, as calculations indicate [17]. The nature of the chemical bonds in CNTs and SiCNTs are different. As a consequence, SiCNTs are polar materials due to the higher electronegativity of carbon atom with respect to the silicon atom in the SiCNTs. Hence, physical properties of SiCNTs are different from those of the covalently bonded homo polar CNTs. For example, zigzag SiCNTs may become piezoelectric, and also show second-order nonlinear optical response [18].

Nuclear magnetic resonance (NMR) spectroscopy is among the most versatile techniques to study the electronic structure properties of matter [20]. Nuclei with nuclear spin angular momentum greater than zero (magnetic nuclei) e.g. ^{29}Si and ^{13}C , are detected by NMR. The chemical shielding (CS) tensors are very sensitive to the electronic density at the sites of magnetic nuclei, and feel changes by any perturbations. Both experimental and theoretical NMR studies, carried out on CNTs, successfully reveal that NMR parameters are powerful tools to determine and characterize structures of nanotubes [21-22]. In recent years, aluminum and boron nanotubes (AlNNTs and BNNTs) have been theoretically and experimentally studied using NMR spectroscopy [23-24].

In this work, calculations of NMR parameters are applied for the first time to study the electronic structure and properties of two SiCNTs including (10, 0) and (5, 5) types.

COMPUTATIONAL METHOD and GEOMETRICAL STRUCTURES

In this work, all computations are carried out via Gaussian 03 package [25] at the level of density functional theory (DFT) using the hybrid exchange-functional B3LYP method. NMR values calculated using density functional theory are only somewhat

sensitive to the basis set [26], and 6-31G (d) basis set have been recommended [27]. Our considered models of SiCNTs are (10, 0) zigzag and (5, 5) armchair types (designated as model 1 and model 2, respectively). Model 1 is the (10, 0) SiCNT consisting of 40 Si and 40 C atoms where the two ends of the tube are capped by 20 H atoms (Figure 1.). Model 2 is the (5,5) armchair SiCNT consisting of 40 Si, 40 C atoms where the two ends of the tube are capped by 20 H atoms (Figure 2.). Firstly, the considered models were allowed to fully relax during the geometrical optimization by the B3LYP exchange-functional method and the 6-31G (d) basis set. Secondly, the natural population analysis (NPA), natural bond orbital (NBO) analysis and the quantum chemical calculations were performed on the two geometrically optimized models by B3LYP method and the above-mentioned standard basis sets were used to evaluate natural charges, bond order and the Si-29 and C-13 NMR parameters. The quantum chemical calculations yield the chemical shift (δ) tensors in the principal axes system (PAS) ($\delta_{11} < \delta_{22} < \delta_{33}$); therefore, equations (1), (2) and 3 are used to evaluate the isotropic chemical shielding (ICS), anisotropic chemical shielding (ACS) and chemical shifts (δ) parameters [28].

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

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

$$\delta \text{ (ppm)} = \text{ICS}_{\text{reference}} - \text{ICS} \quad (3)$$

RESULTS AND DISCUSSION

As a first step, each of the considered zigzag and armchair representative models of SiCNTs were allowed to fully relax during the geometrical optimization at the level of the B3LYP DFT method and 6-31G (d) standard basis set. The results of Table 1. indicate that Si-C bond lengths in the zigzag nanotube are not equivalent. Specifically, the 1, 6 bond (designated as 'a') is 1.79 Å which is shorter than the 5, 6 bond (designated as 'b' with a length of 1.84 Å).

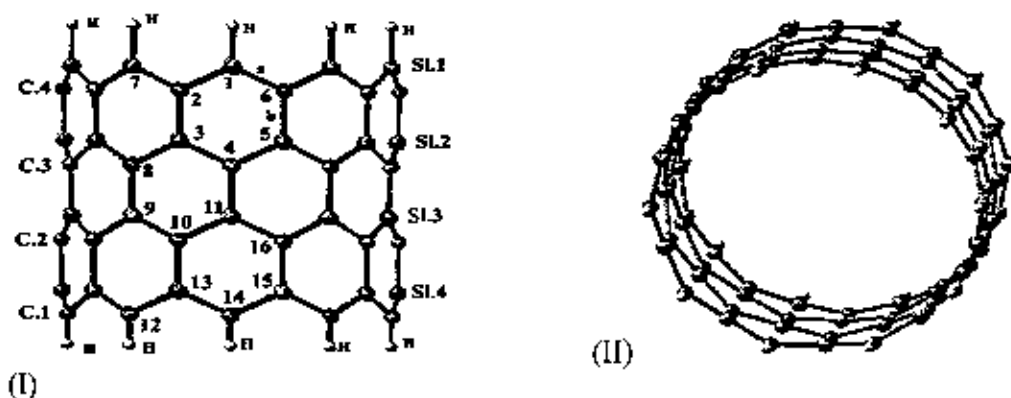
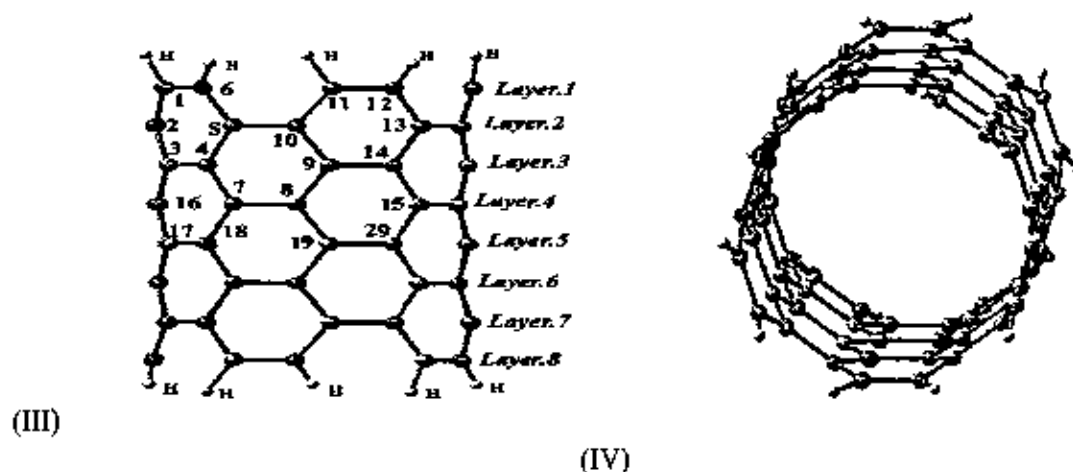


Fig. 1. (I) 2D view of zigzag (10,0) SiCNT and (II) 3D view of zigzag (10,0) SiCNT.



Figs. 2 (III) 2D view of armchair (5,5) SiCNT and (IV) 3D view of armchair (5,5) SiCNT

Natural bond orbital (NBO) analysis shows that bond orders for a bonds and b bonds are 0.85 and 1.06, respectively. The C-Si-C bond angles at the Si-end of zigzag tube is 120° ; however, this value increases to 123° at the C-end. It is worth mentioning that the optimized tube diameters at the two ends of zigzag SiCNT considered here are not equal; at the C-end this value is 10.20 Å and at the Si-end this is 10.07 Å. This, of course, means that the C atoms are relaxed outward while Si atoms are relaxed inward in contrast to CNTs where all the atoms are placed on the same surface of the nanotube. However, the geometrical properties of those nuclei in the center of the tube are almost similar and show small differences.

The results of our calculation for the armchair SiCNTs are shown in Table 2. The

Si-C bond lengths have almost negligible fluctuations with average values of 1.81 Å along the length of armchair tube (Table 2.). On the other hand, the C-Si-C bond angles reduces from 122° at the end of the tube to 119° at the center while the change of Si-C-Si bond angles from the end of tube to the center is negligible. However, in contrast to the zigzag SiCNTs which have two different ends, the ends of the armchair SiCNTs are similar to each other having both Si and C nuclei. Hence, the diameters of the tube at both ends are the same as well in the armchair model but the ends of the tube are elliptically oriented. At each end, the C-C diameter is 8.51 Å and that of Si-Si is 8.42 Å. Meanwhile, natural bond orbital (NBO) analysis show that bond order for Si-C bond is almost 0.96 in the armchair model.

Table 1. Structure parameters in the zigzag (10, 0) SiCNT

Bonding nuclei	Bond lengths (Å)	Bonding nuclei	Bond angles (deg)	Bonding nuclei	Bond angles (deg)
Si-C		C-Si-C		Si-C-Si	
a=(1-2)=(1-6)=(3-4)=(5-4)	1.79	2-1-6	120	7-2-1	120
=(9-10)=(11-10)=(11-16)		8-3-4	120	3-4-5	118
=(13-14)=(15-14)=(13-12)		10-11-16	120	9-10-11	117
		12-13-14	123	13-14-15	119
3-2)=(5-6)=(9-8)=(11-14)	1.84				
(b=(13-10)=(15-16)=					

Table 2. Structure parameters in the armchair (5, 5) SiCNT

Bonding nuclei	Bond lengths (Å)	Bonding nuclei	Bond angles (deg)	Bonding nuclei	Bond angles (deg)
Si-C		C-Si-C		Si-C-Si	
All of those	1.81	2-1-6	122	1-2-3	117
		2-3-4	119	1-6-5	118
		4-5-6	117	3-4-5	119
		4-7-8	119	3-4-7	117
		8-9-10	120	7-8-9	117
		8-9-14	119	9-14-15	117

Table 3. The NMR parameters in the (10, 0) SiCNT

Layers	²⁹ Si			¹³ C		
	ICS(ppm)	ACS(ppm)	δ(ppm)	ICS(ppm)	ACS(ppm)	δ(ppm)
Layer 1	297	133	113	125	89	63
Layer 2	300	122	110	119	96	69
Layer 3	300	121	110	118	95	70
Layer 4	290	122	120	86	149	102

Table 4. The NMR parameters in the (5, 5) SiCNT

Layers	²⁹ Si			¹³ C		
	ICS(ppm)	ACS(ppm)	δ(ppm)	ICS(ppm)	ACS(ppm)	δ(ppm)
Layer 1	292	145	118	111	109	77
Layer 2	289	140	121	120	97	68
Layer 3	289	141	121	113	98	75
Layer 4	290	138	120	119	92	69
Layer 5	290	139	120	119	92	69
Layer 6	289	141	121	113	98	75
Layer 7	289	140	121	120	96	68
Layer 8	292	145	118	111	109	77

Table 5. The ²⁹Si and ¹³C Natural Charges in the zigzag (10, 0) SiCNT

Layers	²⁹ Si	¹³ C
	Natural Charge	Natural Charge
Layer 1	1.4241	-1.4731
Layer 2	1.8413	-1.8466
Layer 3	1.8369	-1.8430
Layer 4	1.7175	-1.7780

Table 6. The ^{29}Si and ^{13}C Natural Charges in the armchair (5, 5) SiCNT

Layers	^{29}Si	^{13}C
	Natural Charge	Natural Charge
Layer 1	1.4241	-1.5055
Layer 2	1.8119	-1.8403
Layer 3	1.8477	-1.8363
Layer 4	1.8571	-1.8620
Layer 5	1.8573	-1.8620
Layer 6	1.8477	-1.8363
Layer 7	1.8123	-1.8401
Layer 8	1.4239	-1.5054

Next, the calculated chemical shielding (CS) tensors at the sites of ^{13}C and ^{29}Si nuclei in both models of SiCNTs, zigzag and armchair, are converted to the NMR parameters (ICS, ACS and δ) which are shown in Tables 3-6, along with the computed natural charges for the above mentioned nuclei. Almost no significant difference is observed in the calculated NMR parameters and the natural charges for the atoms of each layer; therefore, just the average calculated values in each layer for ^{13}C and ^{29}Si nuclei are reported in Tables 3-6. In the case of SiCNTs, carbon atoms possess negative and silicon atoms have positive charges because electronegativity of C ($e\text{C} = 2.5$) is larger than that of Si ($e\text{Si} = 1.8$). This difference in the electronegativity values lead to a charge transfer from Si to C such that the electronic charge density distribution along the Si-C bond becomes asymmetric. Therefore, Si atoms act as cations whereas C atoms act as anions in SiC nanotubes.

As Table 3. shows, Si.4 layer is at the C-end of zigzag tube and its ICS, ACS and δ show no important variation from other layers, while their values for the Si.1 layer change about 7, 11 and 7 ppm, respectively. C.1 layer is at the C-end of the tube. The maximum ICS, 125 ppm, minimum ACS 89 ppm and minimum δ , 63 ppm of C. 1 layer remain approximately constant in the middle of the tube; their actual values are found to

be about 119, 96 and 69 ppm for ICS, ACS and δ , respectively.

By going from Si-end to opposite end in the zigzag model of SiCNT, the ICS parameters of Si nuclei, i.e. 297, 300, 300, and 290 ppm, change in agreement with the trend in the natural charges, 1.4241, 1.8413, 1.8369, and 1.7175 (in units of electron charge). In this model, the ICS values for C nuclei reduce from C-end to Si-mouth (125, 119, 118, and 86 ppm) which parallels with C-Si-C bond angles and goes against the trend of the natural charges (see Table 1.). In other words, C-Si-C bond angles' role is more important than the role of natural charge in this model.

The NMR parameters of (5, 5) SiCNT are shown in Table 4. There are 40 Si and 40 C atoms in our (5, 5) model of SiCNT which could be separated into 8 layers (Figure 2(III)). For Si atoms, those atoms located at the edges of the armchair nanotube, namely layers 1 and 8, have the largest ICS (292 ppm) and ACS (145 ppm) values but the smallest δ value (118) among all the other Si layers. The values of ICS and ACS decrease from the edge of the nanotube to the center while that of δ increases going in the same direction. On the other hand, the ICS parameters change in agreement with C-Si-C bond angles' changes (not natural charges).

Also in Table 4., different behaviors are noticed for C atoms; layers 1 and 8, have the smallest ICS (111 ppm) value but the largest ACS (109 ppm) value among other C layers.

Since the electrostatic properties are mainly dependent on the electronic densities at the sites of C nuclei, the C atoms saturated by H atoms, plays a significantly different role among the other layers in the considered armchair model. The NMR parameters of this layer are the smallest which means that the electronic densities at the sites of these nuclei are less than those of other C layers. By going from the mouth of the armchair nanotube to the center, the values of ^{13}C 's ICS parameters (111,120,113,119 ppm) vary in parallel with the change in the natural charges (-1.5055, -1.8403, -1.8363, -1.8620). In our previous work, the variations of the NMR parameters of N nuclei along the zigzag AlNNT was found to be larger than that of C nuclei in the SiCNTs, which we attributed to the lone pair of electrons in the valence shell of N [29].

CONCLUSION

DFT theory and hybrid functional B3LYP are applied to study geometrical structure, NMR parameters of the zigzag and armchair

SiCNTs. After geometrical optimization and calculation of NMR parameters, some trends can be concluded from the results: (1) The optimization process reveals that Si-C bond lengths are approximately constant along the armchair model but those differ in the zigzag model of SiCNT. (2) The tube diameters at the two ends of armchair SiCNT considered are equal. That is not true at the C-end and Si-end for the zigzag model. (3) The calculated ICS and chemical shift tensors reveal that various Si and C nuclei in the length of models, armchair and zigzag SiCNTs, are divided into some layers with equivalent electrostatic properties in each layer. (4) The chemical shift tensor's values of the Si and C nuclei along the zigzag SiCNT change more in the armchair SiCNT model. (5) In the zigzag model the C.1 layer, C-mouth, has the largest ICS but in the armchair model the C atoms saturated by H atoms (layers 1 and 8) have the smallest ICS among other C atoms.

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