Regular article

PHYSICAL CHEMISTRY RESEARCH
Published by the
Iranian Chemical Society
www.physchemres.org
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***Phys. Chem. Res.**, Vol. 1, No. 1, 90-98, June 2013.*

Gallium and Arsenic Doped on (4, 4) Armchair and (8, 0) Zigzag Models of Boron Phosphide Nanotubes: NMR Study

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(Received 25 January 2013, Accepted 16 April 2013)

The structural and electrostatic properties of the single-walled two representative (8, 0) zigzag and (4, 4) armchair models of pristine and GaAs-doped on boron phosphide nanotubes (BPNTs) were investigated by calculating the nuclear magnetic resonance tensors and with performing the density function theory. The geometrical structures of all representative pristine and GaAs-doped models of BPNTs have been allowed to relax by optimization and then the isotropic and anisotropic chemical shielding (CS) parameters (CSI and CSA) of ^{11}B and ^{31}P have been calculated. The results reveal that with doping gallium and arsenic atoms in spite of boron and phosphorus atoms, the geometrical structure, the band gape energy between HOMO and LUMO orbitals and NMR parameters of the boron and phosphorus sites change. Comparisons of results reveal that the variation NMR parameters and band gape energy of zigzag model are more than those of armchair model. The NMR properties of boron atoms show only slight changes but those of phosphorous atoms are more notable.

Keywords: BPNTs, NMR parameters, DFT method, GaAs-doped

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INTRODUCTION

During the last ten years ago, there has been a surge of scientific activities on the nano materials, or even on commercial products in the marketplaces, which are called nano products, due to their unique and fascinating properties, as well as their wide potential applications [1-5]. After the discovery of carbon nanotubes in 1991 the nanotubes composed of other chemical compositions have also been investigated [6-11]. Among them, the nanotubes composed of groupsthree and five of periodic tables are significant, due to their application in device slike semiconductors, electronics, mechanics and optoelectronics and light emittance [12-18]. The complexities of electronic structures of nanotubes make that the measurements of experimental NMR parameters for their nanotubes are almost a formidable task. For this reason, the computational methods play a dominant role in further investigating the NMR properties of nanotubes [19-23]. The NMR properties reveal insightful trends about the electronic properties of matters because any effects on the electronic densities at the atomic sites could properly be detected by these parameters [23-33]. In recent research the NMR parameters of zigzag and armchair models of boron phosphide nanotubes (BPNTs) with doping C-ring, Ga and (Al and N) atoms were investigated [29-31]. In this work, we study the effects of Ga and As doped on the electronic structures and chemical shielding (CS) parameters of zigzag and armchair BPNTs. The structures of the pristine and GaAs-doped of (4, 4) armchair and (8, 0) zigzag single-walled BPNTs (Figs. 1-2) are optimized by performing density functional theory (DFT) (Table 1) and then the isotropic and anisotropic chemical shielding of B and P are calculated (Tables 2-3). To this point, there have not been available any experimental data for the BPNTs.

COMPUTATIONAL DETAILS

In this research we consider the pristine and GaAs-doped models of (8, 0) zigzag and (4,4) armchair BPNTs with 1 nm length and consisting of 32 B and 32 P atoms (Figs. 1-2). In both models, the mouths of nanotube are saturated by H atoms and all models are individually optimized by using DFT with standard 6-31G (d) basis set at B3LYP [34] level of theory and using the Gaussian 03 set of programs [35]. The chemical shielding (CS) tensors at the sites of ^{11}B and ^{31}P nuclei are calculated based on the gauge included atomic orbital (GIAO)

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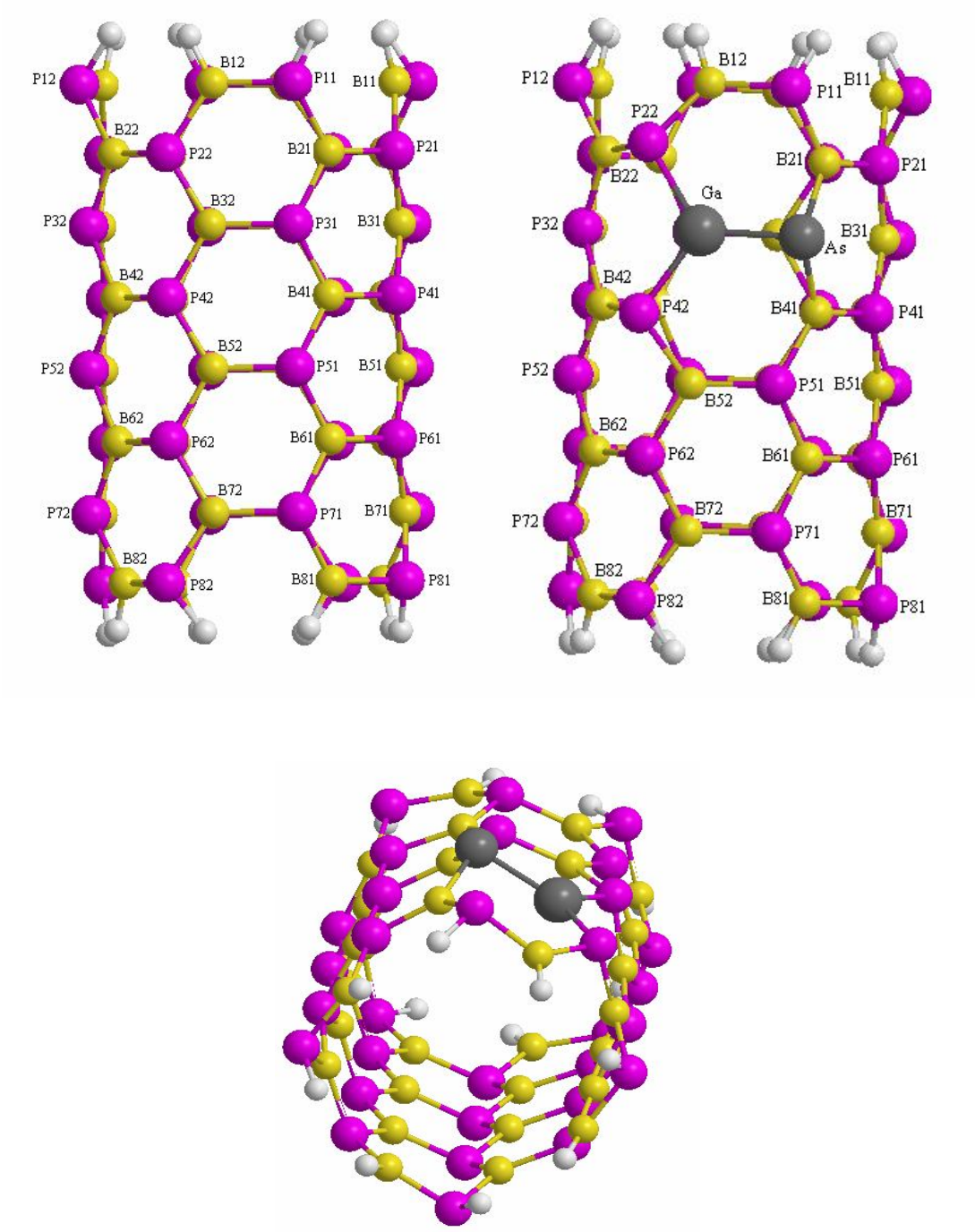

Fig. 1. 3D views of the pristine and GaAs doped of (4, 4) armchair model of BPNTs.

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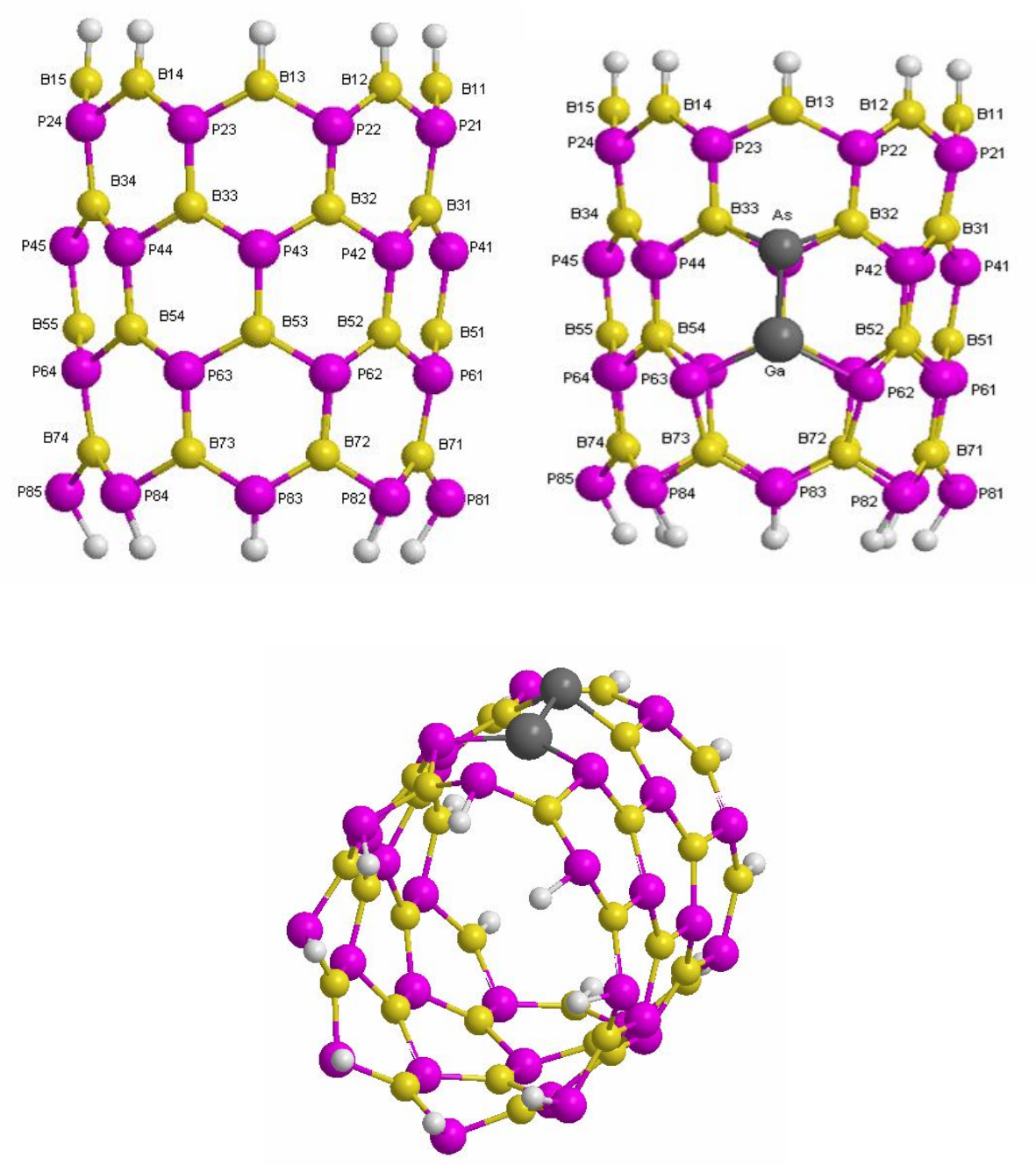

Fig. 2. 3D views of the pristine and GaAs doped of (8, 0) Zigzag model of BPNTs.

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Table 1. The Structural Optimized Parameters of (4,4) Armchair and (8, 0) Zigzag Form of BPNTs, and GaAs-doped

	Armchair form			Zigzag form	
Properties	Undoped[b,c]	As/Ga-doped	Properties	Undoped[b,c]	As/Ga-doped
	Bond length (Å)			Bond length (Å)	
B21-P31/As	**1.89 Å**	**2.02 Å**	B32-P43/As	**1.89 Å**	**2.26 Å**
P22-B32/Ga	**1.89 Å**	**2.26 Å**	B33-P43/As	**1.89 Å**	**2.26 Å**
P42-B32/Ga	**1.89 Å**	**2.26 Å**	P63-B53/Ga	**1.89 Å**	**2.02 Å**
B41-P31/As	**1.89 Å**	**2.02 Å**	P62-B53/Ga	**1.89 Å**	**2.02 Å**
P31-B32/As-Ga	**1.89 Å**	**2.33 Å**	P43-B53/As-Ga	**1.89 Å**	**2.04 Å**
B41-P51	1.89 Å	1.90 Å	P42-B32	1.89 Å	1.91 Å
P42-B52	1.89 Å	1.90 Å	P44-B33	1.89 Å	1.92 Å
P51-B52	1.89 Å	1.90 Å	P44-B54	1.89 Å	1.90 Å
P21-B21	1.89 Å	1.90 Å	P63-B54	1.89 Å	1.91 Å
B31-P41	1.89 Å	1.90 Å	B32-P42	1.89 Å	1.91 Å
B41-P41	1.89 Å	1.90 Å	P42-B52	1.89 Å	1.92 Å
B12-P12	1.89 Å	1.90 Å	B52-P62	1.89 Å	1.90 Å
B12-P22	1.89 Å	1.90 Å	P62-B72	1.89 Å	1.91 Å
B22-P32	1.89 Å	1.90 Å	P63-B73	1.89 Å	1.90 Å
	Bond angle			Bond angle	
<P12-B21-P31,As	**111^0**	**115^0**	<B33-P43,As-B32	**111^0**	**123^0**
<B12-P22-B32, Ga	114^0	104^0	< P43-As,B32- P22	119^0	105^0
< P22-B32,Ga,-P31,As	**121^0**	**123^0**	< P22-B13-P23	123^0	107^0
<B32,Ga-P31 As-B21	111^0	100^0	<P44-B33-P43,As	121^0	99^0
< Ga,B42- P32-B32	111^0	93^0	<B33,P43, As-B53,Ga	116^0	106^0
< P21-B21- P31, As	121^0	115^0	<P43,As-B53,Ga-P63	119^0	101^0
<B21-P31, As-B41	121^0	121^0	<P43-B32, As-P42	121^0	99^0
< P41- B31- P21	117^0	120^0	<B52-P62-B53,Ga	**110^0**	**128^0**
<B32, Ga-P42-B52	117^0	108^0	<B53,Ga-P62-B72	115^0	111^0
<B32-Ga-P22-B22	111^0	102^0	<P63-B53,Ga-P62	121^0	99^0
<B42-P42-B32, Ga	111^0	102^0	<P62-B72-P83	119^0	114^0

[b]See Figs. 1,2 for details, [c] undoped form (Ref. [8,10,29-31]).

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Table 2. The NMR Parameters of the ^{9}Band ^{31}P nuclei in (4, 4) Armchair BPNTs

B-15 nuclei	CSI (ppm)	CSA (ppm)	P-31 nuclei	CSI (ppm)	CSA (ppm)
B11	36[b]36	86 [b]84	P11	414[b] 415	**115[b]113**
B12	36 36	86 73	P12	414414	115119
B21	**35 33**	**85 116**	P21	360362	124175
B22	35 36	**85 122**	P22	**360354**	124185
B31	4040	7358	P31	358-	233-
B32	40 -	73 -	P32	358358	**233195**
B41	**4239**	**91105**	P41	359359	139175
B42	42 47	**91 109**	P42	**359348**	139205
B51	**4236**	8299	P51	359363	**238171**
B52	42 46	**82 103**	P52	**359345**	**238206**
B61	4042	8944	P61	**358352**	124219
B62	4039	89 73	P62	358416	124204
B71	3541	**99116**	P71	**360356**	**235202**
B72	**3527**	9958	P72	360412	**235157**
B81	3660	11263	P81	**414397**	103 122
B82	**3624**	11229	P82	414420	**10347**
Ga	- 1446	27	As	- 1662	- 225

See Fig. 1 for details, in each row, the first number is undoped form (Ref. [8,10,29-31]); the second one is for Ga and As-doped BPNTs model.

approach [36]. The calculated CS tensors in principal axes system (PAS) ($\sigma_{33} > \sigma_{22} > \sigma_{11}$) are converted to measurable NMR parameters, chemical shielding isotropic (CSI) and chemical shielding anisotropic (CSA) by using Eqs. (1) and (2), respectively [28-31].

$$CSI(ppm) = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (1)$$

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

The evaluated NMR parameters at the sites of ^{11}B and ^{31}P nuclei are given in Tables (2-3).

RESULTS AND DISCUSSION

The Structural Parameters of BNNTs

The B-P bond lengths, and bond angles (B-P-B) of the (4, 4) armchair and (8, 0) zigzag forms of BPNTs and Ga, Asdoped on B and P sites of presented BPNTs are gathered in Table 1 (see Figs. 1-2). The average B-P bond length for armchair and zigzag models of BPNTs is 1.89 Å which is in agreement with other studies [8,16,29-31]. The results reveal equivalent positions in the two models of the pristine BPNTs which have similar bond lengths; however, in GaAs-doped region, this similarity is interrupted. In both of the armchair

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Table 3. The NMR Parameters of the ^{9}B and ^{31}P nuclei in (8, 0) Zigzag BPNTs

B-15 nuclei	CSI (ppm)		CSA (ppm)		P-31 nuclei	CSI (ppm)		CSA (ppm)	
B11	29	31	**29102**		P21	404	404	**10583**	
B12	**2944**		12034		P22	404	401	105113	
B13	29	26	**29104**		P23	404	404	**10583**	
B14	**2941**		120	107	P24	404	408	105108	
B31	45	33	**84**	**91**	P41	371	373	77	196
B32	45	20	84	49	P42	**371**	**350**	**237**	**86**
B33	45	20	84	49	P43	371	-	77	-
B34	45	46	84	62	P44	**371**	**344**	237	263
B51	41	38	**22**	**80**	P61	345	352	195	254
B52	**41**	**46**	111	91	P62	**345**	**334**	195	122
B53	41	-	22	-	P63	345	421	**195**	**74**
B54	41	38	111	80	P64	345	421	**195**	**74**
B71	**47**	**50**	94	51	P81	239	339	90	194
B72	47	46	**94**	**113**	P82	239	339	277	194
B73	47	24	94	52	P83	239	340	90	234
B74	47	50	94	51	P84	239	494	**277**	**241**
Ga	-	1405		123	As		1838		428

See Fig. 2 for details, in each row, the first number is undoped form (Ref. [29-31]); the second one is for Ga and As-doped BPNTs model.

and the zigzag models, doping of Ga and As atoms, on the B and P atoms respectively increase the B-P bond length of about 1.89 Å up to 1.92 Å. This trend would mean that the influence of Ga and As-doping instead of the B and P atoms on the properties of the electronic structure of the BPNTs is significant. The calculated bond lengths also show that the lengths of B-As in the armchair model is 2.02 Å and in zigzag model is 2.26 Å, on the other hand the bond lengths of Ga-P is 2.26 Å in armchair model and is 2.02 Å in zigzag model. The As-Ga bond length in armchair model is 2.33 Å and in zigzag model is 2.04 Å. It is noteworthy that Ga and As atoms, which have larger number of valence electrons than those of B and P atoms, repel each other at the neighbour of doping so the covalent radius is increased it could yield such significant difference between the diameters of two bond length in the zigzag and armchair BPNTs. By doping Ga and As on the sites of B32 and P31, respectively in the armchair model of BPNTs the bond angles <P21-B2-As, <P22-Ga-As and <P41-B31-P21 are increased from original values and other sites are decreased. In the zigzag model of BPNTs by doping of Ga and Ason the sites of B53 and P43 respectively the bond angles <B33-As-B32, <B52-P52-Ga are increased and on other sites are decreased.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are calculated from geometrical results. The value of differences between HOMO and LUMO energies, band gap energies, in the optimized structures yielded 2.95 eV for the armchair model

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and 2.57 eV for zigzag models of BPNTs. By doping GaAs the band gap in armchair model does not change. While in zigzag model it increases to 2.64 eV. Comparison of the results show that the band gap energy in the pristine and GaAs-doped of armchair model is larger than that of the zigzag model, therefore the change of band gap energy in zigzag model is larger than that of the armchair. The same results have been observed in previous work by doping Ga in BPNTs [31].

The NMR Parameters of Boron

The chemical shielding tensors at the sites of ^{11}B nuclei are calculated from optimized structures of armchair and zigzag models of BPNTs. In order to directly relate the calculated tensors to the experimentally measurable parameters, the chemical shielding (CS) tensors are converted to the CSI and CSA parameters using Eqs. (1) and (2), the results are given in Tables (2-3). A quick look at the results in the pristine model of the (4, 4) armchair model and (8, 0) zigzag models of BPNTs reveal that the values of the CS parameters are divided into four layers (Tables 2-3 and Figs. 1-2). This means that the CS tensors at the sites of the nuclei of each layer feel equivalent chemical environment and electrostatic properties around similar nuclei [29-32]. In the (4, 4) armchair model of BPNTs the CSI values of the layers (1, 8), (2, 7), (3, 6) and (4, 5) are 36, 35, 40 and 42 ppm, respectively. And in the (8, 0) zigzag model of BPNTs the CSI values of the layers 1, 3, 5 and 7 are 29, 45, 41 and 47 ppm, respectively. The results show that the firstlayer, at the end of the tube, forms the B-end of zigzag model and the (2, 7) layers of armchair model have the smallest CSI values, among all layers. Since the electrostatic properties are mainly dependent on the electronic densities at the sites of nuclei, this layer plays a significantly different role among the other layers in the raw model. By doping Ga on B32 site and As on P31 site of armchair model the CSI values of B21, B41, B51, B72 and B81 sites are significantly reduced compared to that of the pristine model. Comparison between pristine and Ga doped on B53 site and As on P43 site of zigzag model reveal that the CSI values for ^{11}B nuclei in all layers decrease expect on B12, B14, B52, B71 sites.

The results show that CSA values of ^{11}B at the sites B21, B22, B41, B42, B52 and B71 in the armchair model and these values at the sites B11, B13, B31 and B72 in the zigzag model are significantly increased from original values and on the other sites of two models decreased. This trend reveals that the CS tensors at the sites of those B nuclei which are directly bonded to the GaAs atoms undergo significant changes but those of the other B nucleiundergo some minor changes.

The NMR Parameters of Phosphor

The evaluated CSI and CSA parameters at the sites of ^{31}P nuclei for the considered models of (4, 4) armchair BPNTs and (8, 0) zigzag BPNTs and GaAs-doped are given in Tables (2-3). Similar results of ^{11}BNMR parameters, the CSI and CSA values for two models of pristine BPNTs (Figs. 1-2) are divided into four layers with equivalent ^{31}P. Since P has a lone pair of electrons in the valence shell, the electronic environment at the P sites is completely different from that of B sites; therefore different behaviors are expected. Comparison between the B and P NMR parameters shows that CSI values of P sites are larger than those for B sites. Because the electro negativity of P atoms is larger than B atoms and it is caused that the electronic charge density transfer from B sites to P sites and yielding asymmetric electronic charge distribution along B-P bond. By doping Ga and As on the B32 and P31 sites of armchair model of BPNTs, respectively, CSI values for ^{31}P nuclei at the sites of P22,P42, P52,P61,P71 and P81 undergo significant decrease in comparison with the undoped model. Other P atoms which are not directly bonded to Ga and As atoms also undergo some changes.

On the other hand by doping Ga and As on the B53 and P43 sites of zigzag model of BPNTs, respectively, CSI values for ^{31}P nuclei at the P42,P44 and P62 sites undergo significant decrease from original values. In contrast with B, and due to the lone pair of electrons, other P nuclei which are not directly bonded to the GaAs-doping atoms also undergo some significant changes. It is worth noting that the changes of the CS tensors at the sites of ^{31}Pnuclei are singularly observed in the front side of nanotube, shown in Figs. (1-2) while those of the back side remain almost unchanged. Due to the GaAs-doping in armchair model, the CSA parameters at the sites P11, P32, P51, P52, P71, P72 and P82 significantly decrease from original values and on the other sites are increased. This trend is observed for zigzag model at the P21, P23, P42, P63, P64 and P84 sites too. Comparisons of NMR parameters

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reveal that with GaAs-doping in BPNTs the structural of nanotube is deformed which in turn, causes changes in electronic structure properties and the NMR parameters of the undoped model. Indeed the significant change in the value of CSI and CSA for this nucleus approves the mentioned trend.

CONCLUSIONS

The effects of GaAs-doping on the electrostatic properties of the (4, 4) armchair and (8, 0) zigzag models of BPNTs are studied by the calculations of the chemical shielding CS tensors at the sites of ^{11}B and ^{31}P nuclei. The results of geometrical structure reveal that the band gap energy for the pristine and GaAs-doped of armchair BPNTs is remains unchanged while in zigzag model of BPNTs this value is increased. The first layer at the end of the tube forms the B-end of zigzag model and the (2, 7) layers of armchair model have the smallest CSI, among all layers. Comparison of NMR parameters reveal that with GaAs-doping in BPNTs the structure of nanotube is deformed which causes changes in the CSI and CSA values at the sites of those nuclei directly bonded to the doping atoms. Other nuclei are almost unchanged; however, The NMR properties of boron atoms only detect slight changes but those of phosphorous atoms are more notable. Indeed the electronic densities at the atomic sites of nanotubes are very important for interactions occurring between nanotube and other molecules or atoms.

ACKNOWLEDGMENTS

The authors would like to thank the Malayer University for providing the necessary facilities to carry out the research.

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