

# Carbon doped boron phosphide nanotubes: A computational study

Mahmoud Mirzaei

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**Abstract** A computational study based on density functional theory (DFT) calculations has been performed to investigate the properties of the electronic structure of carbon doped boron phosphide nanotube (C-doped BPNT). Pristine and the C-doped structures of two representative (6,0) zigzag and (4,4) armchair BPNTs have been investigated. At first, the geometries of the structures have been allowed to relax by optimization. Subsequently, NMR parameters have been calculated in the optimized structures. The results indicated that the influence of C-doping was more significant on the geometries of the zigzag model than the armchair one. The difference of band gap energies between the pristine and C-doped armchair BPNT was larger than the zigzag model. Significant differences of NMR parameters of those nuclei directly contributed to the C-doping atoms have been observed.

**Keywords** Boron phosphide nanotube · Carbon doping · Density functional theory · NMR

## Introduction

Since the carbon nanotube (CNT) was discovered [1], numerous studies have been devoted to characterize the properties of this fascinating novel material [2–4]. The CNTs are metal or semiconductor depending on tubular diameter and chirality which bring difficulties to their

synthesis for specific purposes. Therefore, considerable efforts have been stimulated to synthesize non-carbon nanotubes with properties independent of the restricting structural factors [5–7]. The binary compounds of elements of groups three (III) and five (V) of the periodic table could be always semiconductor and could be used as proper alternative materials for the CNTs [8–11]. The properties of the tubular structure of the group III-nitrides, *e.g.*, boron nitride (BN), aluminum nitride (AlN), gallium nitride (GaN), and indium nitride (InN) have more been studied [12–16] than the group III-phosphides, *e.g.*, boron phosphide (BP), aluminum phosphide (AlP), gallium phosphide (GaP), and indium phosphide (InP). Among the group III-phosphides, much more attention has recently been focused on the determination and characterization of BP material [17, 18] because of the known similarity between the properties of the electronic structures of BP and silicon carbide (SiC).

In this computational work, the properties of the electronic structures of pristine and carbon doped (C-doped) boron phosphide nanotubes, p-BPNT and c-BPNT, respectively, have been investigated. To this aim, density functional theory (DFT) calculations have been performed to optimize the structures of representative (6,0) zigzag and (4,4) armchair models of BPNTs in both pristine and C-doped forms. Since nuclear magnetic resonance (NMR) spectroscopy is an insightful technique to study the properties of the electronic structure of matters [19, 20], chemical shielding (CS) tensors have also been calculated for the optimized structures of the investigated BPNTs. The results of the pristine and the C-doped models have been compared to indicate the influences of C-doping on the properties of the electronic structures of the BPNTs. To this point, there have not been available any experimental data for the BPNTs.

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

## Computational details

Within this work, two representative (6,0) zigzag and (4,4) armchair models of the single-walled BPNTs in to pristine and C-doped forms have been investigated. The pristine zigzag model was a 12-Å length (6,0) BPNT consisting of 24 B and 24 P atoms; 12 H atoms saturated the two ends of the nanotube. The pristine armchair model was a 12-Å length (4,4) BPNT consisting of 28 B and 28 P atoms; 16 H atoms saturated the two ends of the tube. In both of the pristine zigzag and armchair BPNTs, three B and three P atoms in the center of nanotube have been replaced by six carbons to create the C-doped BPNTs (c-BPNTs) (Figs. 1, 2 and 3). At first, the investigated structures have individually been optimized employing BLYP exchange-functional and 6-31G\* standard basis set. Earlier studies indicated that the computations based on the BLYP functional could yield reliable results for the properties of the electronic structure of nanotubes [9]. Subsequently, the  $^{11}\text{B}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  CS tensors have been calculated for the optimized structures at the same level of theory based on the gauge included atomic orbital (GIAO) approach [21]. Earlier studies revealed that the employed theoretical level of calculations could yield reliable results for the computational study of nanotubes [22]. Moreover, by earlier studies on BNNTs, we found that the obtained calculated results of the BLYP are very similar to those of the B3LYP [20, 23]. The validities of the considered sizes of nanotubes have been examined earlier [24]. Since quantum chemical calculations yield the CS tensors in principal axes system (PAS) ( $\sigma_{33} > \sigma_{22} > \sigma_{11}$ ), they have been converted to isotropic chemical shielding ( $\text{CS}^{\text{I}}$ ) and anisotropic chemical shielding ( $\text{CS}^{\text{A}}$ ) using Eqs. 1 and 2, respectively. The calculated results of the absolute values of  $\text{CS}^{\text{I}}$  and  $\text{CS}^{\text{A}}$  parameters have been listed through Tables 1, 2, 3 and 4. The CS parameters could also be reported as a chemical shift which is the difference between the calculated CS parameters of the sample and reference [19]. For instance, for carbon atoms, the chemical shift is reported as a difference between the absolute calculated value of carbon atom of sample and that of the

TMS. All DFT calculations have been performed by GAUSSIAN 98 package [25].

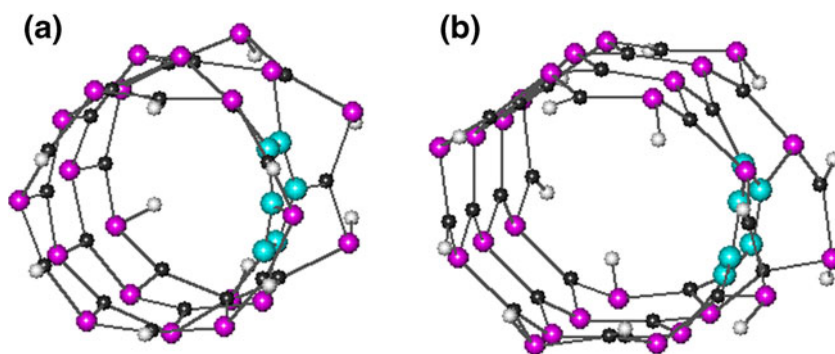
$$\text{CS}^{\text{I}}(\text{ppm}) = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (1)$$

$$\text{CS}^{\text{A}}(\text{ppm}) = \sigma_{33} - \frac{1}{2}(\sigma_{11} + \sigma_{22}) \quad (2)$$

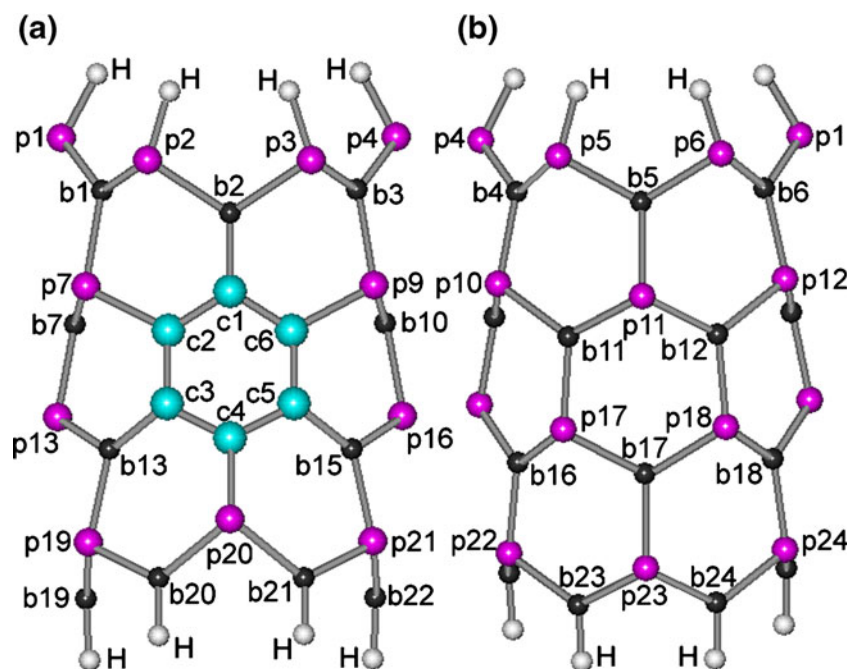
## Results and discussion

The properties of the electronic structures of the pristine and the carbon doped boron phosphide nanotubes, p-BPNT and c-BPNT, respectively, have been investigated in this DFT work. The representative (6,0) zigzag (Fig. 2) and (4,4) armchair (Fig. 3) BPNTs have been allowed to relax during all geometrical optimization where the results have been listed in Tables 1 and 2. The average B-P bond length in the (6,0) p-BPNT was 1.91 Å but this value was changed in the c-BPNT due to the C-doping. In the p-BPNT, instead of binding with H, there was just B-P bonds whereas there were B-C, C-P, and C-C bonds in addition to B-P in the c-BPNT. These changes of the structural bindings yielded different bond lengths and angles in the c-BPNT. In the zigzag model (Table 1 and Fig. 2), P8, P14, and P15 are replaced by C1, C3, and C5, respectively, and B8, B14, and B9 have been replaced by C2, C4, and C6, respectively. The average C-C bond length of 1.45 Å versus the B-P bond length of 1.91 Å caused some structural deformations in the c-BPNT. However, the effects of this deformation were significant just at the geometrical properties of the nearest atoms to the C-doped ring whereas those of other atoms were almost remained unchanged. Furthermore, the changes of the bond angles were more than those of the bond lengths in the zigzag c-BPNT. In the armchair p-BPNT (Table 2 and Fig. 3), the average B-P bond length was 1.90 Å but this value also was changed by the

**Fig. 1** The 3D views of (a) the zigzag and (b) the armchair c-BPNT



**Fig. 2** The 2D views of (a) the front and (b) the back sides of the zigzag c-BPNT. To ease, the C-doped model is only exhibited. The p-BPNT model does not contain the C atoms

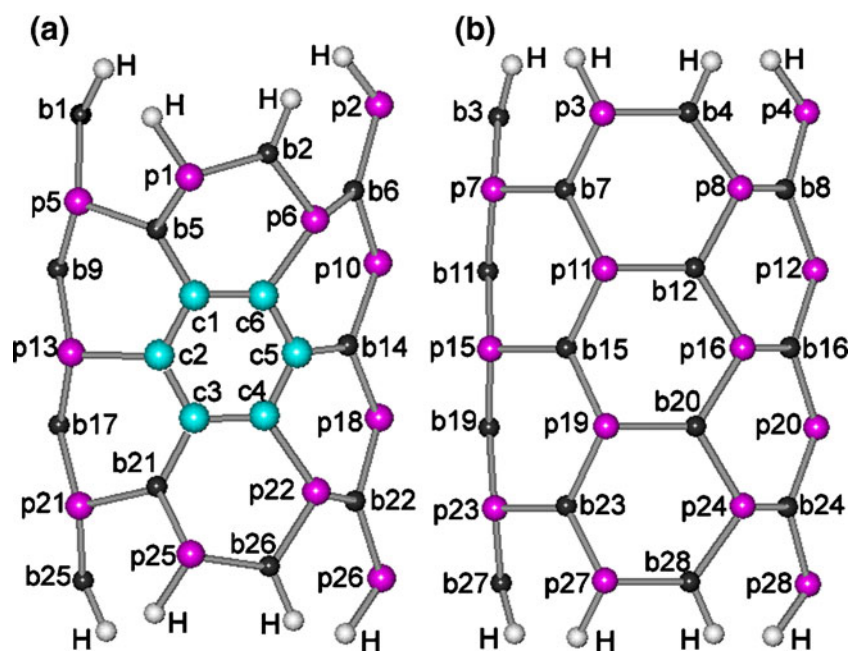


C-doping in the c-BPNT due to existence of B-C, C-P, and C-C bonds in addition to B-P one. The average C-C bond length of 1.45 Å versus the B-P bond length of 1.90 Å caused some structural deformations in the c-BPNT; however, in comparison to the zigzag model, the effects of C-doping on the geometries of armchair model were less significant. The angles in the armchair c-BPNT did not significantly differ from those of the p-BPNT whereas these changes were seen more in the zigzag model. This trend

revealed that in the C-doped BPNTs, the geometries of the armchair BPNT were less influenced by the C-doped ring than the zigzag model.

The comparison of the optimized energies revealed that the magnitudes of differences between the energies of the pristine and the C-doped BPNTs in both of the zigzag and the armchair models were equal by 24 keV. By the C-doping, the energy of structure was increased by 24 keV in both models. It is important to note that the

**Fig. 3** The 2D views of (a) the front and (b) the back sides of the armchair c-BPNT. To ease, the C-doped model is only exhibited. The p-BPNT model does not contain the C atoms



**Table 1** The geometries of the zigzag model

Bonds	Length (Å)	Bonds	Angle (°)
B2-P3	1.92 [1.93]	P2-B2-P3	122 [112]
B3-P3	1.92 [1.89]	P3-B3-P4	122 [129]
B3-P4	1.92 [1.91]	P4-B4-P5	122 [124]
B4-P4	1.92 [1.92]	P5-B5-P6	122 [120]
B4-P5	1.92 [1.91]	P3-B2-C1	119 [124]
B5-P5	1.92 [1.92]	P3-B3-P9	119 [110]
B2-C1	1.90 [1.58]	P4-B3-P9	119 [120]
B3-P9	1.90 [1.90]	P4-B4-P10	119 [118]
B4-P10	1.90 [1.91]	P5-B4-P10	119 [117]
B5-P11	1.90 [1.92]	P5-B5-P11	119 [120]
C1-C6	1.91 [1.45]	C2-C1-C6	104 [114]
C6-P9	1.91 [1.89]	C1-C6-P9	122 [121]
B10-P9	1.91 [1.92]	P9-B10-P10	122 [127]
B10-P10	1.91 [1.89]	P10-B11-P11	122 [121]
B11-P10	1.91 [1.92]	B11-P11-B12	104 [105]
B11-P11	1.91 [1.91]	C6-C5-C4	114 [117]
C5-C6	1.90 [1.44]	C6-C5-B15	114 [124]
B10-P16	1.90 [1.87]	B10-P16-B15	114 [106]
B11-P17	1.90 [1.92]	B10-P16-B16	114 [112]
C4-C5	1.91 [1.45]	B11-P17-B16	114 [114]
B15-C5	1.91 [1.57]	B11-P17-B17	114 [115]
B15-P16	1.91 [1.95]	C4-C5-B15	105 [116]
B16-P16	1.91 [1.92]	B15-P16-B16	105 [103]
B16-P17	1.91 [1.91]	B16-P17-B17	105 [104]
B17-P17	1.91 [1.91]	P17-B17-P18	121 [121]
C4-P20	1.91 [1.85]	C5-C4-P20	119 [121]
B15-P21	1.91 [1.90]	C5-B15-P21	119 [127]
B16-P22	1.91 [1.90]	P16-B15-P21	119 [111]
B17-P23	1.91 [1.93]	P16-B16-P22	119 [116]
B21-P20	1.89 [1.88]	P17-B16-P22	119 [123]
B21-P21	1.89 [1.88]	P17-B17-P23	119 [119]
B22-P21	1.89 [1.90]	B20-P20-B21	102 [99]
B22-P22	1.89 [1.90]	B21-P21-B22	102 [106]
B23-P22	1.89 [1.89]	B22-P22-B23	102 [104]
B23-P23	1.89 [1.90]	B23-P23-B24	102 [97]

See Fig. 2 for details of the atomic numbers. The values of c-BPNT are in the brackets while those of the p-BPNT are out of brackets. In the p-BPNT; C1, C2, C3, C4, C5, and C6 are replaced by P8, B8, P14, B14, P15, and B9, respectively

investigation of the process of the C-doping was not the aim of this study; hence, the p-BPNT and c-BPNT were considered as two independent structures. But the calculated energies revealed that the C-doping process requires energy to be occurred. The values of differences between HOMO and LUMO energies, band gap energies, in the optimized structures yielded 1.09 eV for the zigzag and 1.77 eV for the armchair p-BPNT. In the c-BPNTs, the values were increased to 1.11 eV and 1.82 eV for the zigzag and the

**Table 2** The geometries of the armchair model

Bonds	Length (Å)	Bonds	Angle (°)
B1-P4	1.89 [1.89]	B1-P5-B5	111 [116]
B2-P1	1.89 [1.89]	B5-P1-B2	106 [94]
B3-P2	1.89 [1.89]	B2-P6-B6	111 [114]
B4-P3	1.89 [1.90]	B6-P2-B3	106 [106]
B1-P5	1.89 [1.88]	B3-P7-B7	111 [110]
B5-P1	1.91 [1.92]	B7-P3-B4	106 [104]
B2-P6	1.89 [1.87]	B4-P8-B8	111 [110]
B6-P2	1.91 [1.90]	B8-P4-B1	106 [109]
B3-P7	1.89 [1.89]	P5-B5-C1	121 [121]
B7-P3	1.91 [1.91]	C1-C6-P6	121 [121]
B4-P8	1.89 [1.90]	P6-B6-P10	121 [112]
B8-P4	1.91 [1.92]	P10-B11-P7	121 [120]
B5-P5	1.90 [1.92]	P7-B7-P11	121 [122]
B6-P6	1.90 [1.89]	P11-B12-P8	121 [121]
B7-P7	1.90 [1.90]	P8-B8-P12	121 [120]
B8-P8	1.90 [1.91]	P12-B9-P5	121 [125]
B9-P5	1.91 [1.88]	P13-C2-C1	122 [119]
B5-C1	1.91 [1.58]	C1-C6-C5	121 [121]
C6-P6	1.91 [1.87]	C5-B14-P10	122 [124]
B6-P10	1.91 [1.88]	P10-B11-P15	121 [121]
B11-P7	1.91 [1.91]	P15-B15-P11	122 [122]
B7-P11	1.91 [1.92]	P11-B12-P16	121 [121]
B12-P8	1.91 [1.92]	P16-B16-P12	122 [122]
B8-P12	1.91 [1.91]	P12-B9-P13	121 [124]
B9-P12	1.89 [1.89]		
C1-C6	1.89 [1.43]		
B11-P10	1.89 [1.89]		
B12-P11	1.89 [1.90]		
B9-P13	1.90 [1.90]		
C1-C2	1.90 [1.45]		
C5-C6	1.90 [1.45]		
B14-P10	1.90 [1.91]		
B11-P15	1.90 [1.91]		
B15-P11	1.90 [1.90]		
B12-P16	1.90 [1.91]		
B16-P12	1.90 [1.91]		
C2-P13	1.90 [1.86]		
B14-C5	1.90 [1.56]		
B15-P15	1.90 [1.90]		
B16-P16	1.90 [1.89]		

See Fig. 3 for details of the atomic numbers. The values of c-BPNT are in the brackets while those of the p-BPNT are out of brackets. In the p-BPNT; C1, C2, C3, C4, C5, and C6 are replaced by P9, B13, P17, B18, P14, and B10, respectively

armchair models, respectively. This trend revealed that by the C-doping, the values of band gap energies were increased; the band gap energy of the armchair model was larger than the zigzag one.

**Table 3** The NMR parameters of the zigzag model

Atom	CS <sup>I</sup> (ppm)	CS <sup>A</sup> (ppm)	Atom	CS <sup>I</sup> (ppm)	CS <sup>A</sup> (ppm)
B1	16 [20]	135 [135]	P1	355 [372]	116 [121]
B2	16 [21]	135 [122]	P2	355 [345]	116 [208]
B3	16 [20]	135 [135]	P3	355 [345]	116 [207]
B4	16 [16]	135 [135]	P4	355 [372]	116 [121]
B5	16 [15]	135 [134]	P5	355 [346]	116 [143]
B6	16 [16]	135 [135]	P6	355 [346]	116 [144]
B7	30 [22]	105 [122]	P7	345 [382]	260 [152]
B8 [C2]	30 [28]	105 [153]	P8 [C1]	345 [43]	260 [196]
B9 [C6]	30 [28]	105 [153]	P9	345 [382]	260 [152]
B10	30 [22]	105 [122]	P10	345 [348]	260 [259]
B11	30 [32]	105 [97]	P11	345 [340]	260 [267]
B12	30 [32]	105 [98]	P12	345 [348]	260 [259]
B13	24 [31]	108 [104]	P13	309 [360]	259 [290]
B14 [C4]	24 [20]	108 [187]	P14 [C3]	309 [39]	259 [174]
B15	24 [31]	108 [104]	P15 [C5]	309 [39]	259 [174]
B16	24 [20]	108 [103]	P16	309 [360]	259 [290]
B17	24 [29]	108 [104]	P17	309 [291]	259 [273]
B18	24 [20]	108 [103]	P18	309 [291]	259 [273]
B19	40 [40]	120 [116]	P19	301 [317]	286 [272]
B20	40 [39]	120 [127]	P20	301 [235]	286 [216]
B21	40 [39]	120 [127]	P21	301 [317]	286 [272]
B22	40 [40]	120 [116]	P22	301 [315]	286 [270]
B23	40 [38]	120 [123]	P23	301 [278]	286 [307]
B24	40 [38]	120 [123]	P24	301 [316]	286 [270]

See Fig. 2 for details of the atomic numbers. The values of c-BPNT are in the brackets while those of the p-BPNT are out of brackets. The CS<sup>I</sup> and CS<sup>A</sup> parameters are the absolute values of isotropic and anisotropic chemical shieldings

### NMR parameters of the zigzag model

The calculated NMR parameters of the zigzag (6,0) p-BPNT and c-BPNT models (Fig. 2) have been listed in Table 3. The zigzag p-BPNT model consisted of 24 B and 24 P atoms; these atoms were divided into four groups by the calculated NMR parameters; 1 to 6, 7 to 12, 13 to 18, and 19 to 24. In each group, there were similar NMR parameters; however, the values of different groups were not similar. The zigzag BPNT has hetero B-terminated and P-terminated ends; therefore, from one end to the other end of the nanotube the NMR parameters detected some changes. The terminating atoms at the ends of the nanotube had the largest average values of the CS<sup>I</sup> among other atoms whereas the values were decreased by going to the opposite ends. In contrast, the values of the CS<sup>A</sup> of the terminating atoms were not the largest ones among the atoms. For B, the values of the atoms of 1 to 6 which were located near the P-terminated end were the largest among the B atoms.

B8, B9, and B14 were respectively doped by C2, C6, and C4 in the c-BPNT (Fig. 2a). Due to this doping, the changes of the NMR parameters of the c-BPNT were expected in comparison with the p-BPNT. Among the B atoms, the values of the CS<sup>I</sup> of B19 to B24, which were the

B-terminated end of nanotube, did not detect significant changes; however, some differences were viewed in the values of their CS<sup>A</sup> parameters. This trend indicated that the average values of the CS tensors did not detect changes; however, the directions of the CS tensors orientations were changed in these atoms. For B1 to B6, which were near the P-terminated end, B2 was contributed to B-C bond instead of B-P one; therefore, the values of the CS<sup>I</sup> and CS<sup>A</sup> parameters detected the most significant changes among the other five B atoms of this group. The NMR parameters of B1 and B3 were influenced by indirect effects of the C-doping whereas those of B4, B5, and B6 remained unchanged. The values of the CS<sup>I</sup> parameters of both B7 and B10, which were located in the rings with two C members, were decreased whereas their CS<sup>A</sup> values were increased. In contrast, the values of the CS<sup>I</sup> of B11 and B12 were increased whereas the values of the CS<sup>A</sup> parameters were decreased. B13 and B15 contributed to B-C bonds instead of B-P ones; therefore, parallel to the results of B2, the values of the CS<sup>I</sup> parameters were increased whereas the values of the CS<sup>A</sup> parameters were decreased. The NMR parameters of B16, B17, and B18 were also influenced by the C-doped ring.

P8, P14, and P15 were respectively doped by C1, C3, and C5 in the c-BPNT (Fig. 2). In comparison with the B

**Table 4** The NMR parameters of the armchair model

Atom	CS <sup>I</sup> (ppm)	CS <sup>A</sup> (ppm)	Atom	CS <sup>I</sup> (ppm)	CS <sup>A</sup> (ppm)
B1	36 [39]	128 [121]	P1	387 [397]	150 [134]
B2	36 [40]	128 [134]	P2	387 [386]	150 [137]
B3	36 [36]	128 [132]	P3	387 [392]	150 [142]
B4	36 [33]	128 [132]	P4	387 [380]	150 [170]
B5	36 [33]	111 [116]	P5	330 [318]	260 [278]
B6	36 [36]	111 [114]	P6	330 [334]	260 [140]
B7	36 [31]	111 [115]	P7	330 [327]	260 [256]
B8	36 [32]	111 [108]	P8	330 [338]	260 [251]
B9	40 [36]	98 [106]	P9 [C1]	324 [50]	256 [169]
B10 [C6]	40 [32]	98 [150]	P10	324 [328]	256 [276]
B11	40 [38]	98 [99]	P11	324 [320]	256 [258]
B12	40 [36]	98 [94]	P12	324 [330]	256 [231]
B13 [C2]	44 [50]	100 [157]	P13	326 [339]	257 [152]
B14	44 [56]	100 [90]	P14 [C5]	326 [43]	257 [177]
B15	44 [40]	100 [104]	P15	326 [334]	257 [254]
B16	44 [39]	100 [99]	P16	326 [322]	257 [256]
B17	40 [36]	98 [106]	P17 [C3]	324 [50]	256 [169]
B18 [C4]	40 [32]	98 [150]	P18	324 [329]	256 [276]
B19	40 [38]	98 [99]	P19	324 [321]	256 [258]
B20	40 [36]	98 [94]	P20	324 [330]	256 [231]
B21	36 [33]	111 [116]	P21	330 [318]	260 [278]
B22	36 [36]	111 [114]	P22	330 [334]	260 [139]
B23	36 [31]	111 [115]	P23	330 [326]	260 [256]
B24	36 [32]	111 [108]	P24	330 [338]	260 [251]
B25	36 [39]	128 [121]	P25	387 [397]	150 [133]
B26	36 [40]	128 [134]	P26	387 [386]	150 [137]
B27	36 [36]	128 [132]	P27	387 [392]	150 [142]
B28	36 [33]	128 [132]	P28	387 [380]	150 [170]

See Fig. 3 for details of the atomic numbers. The values of c-BPNT are in the brackets while those of the p-BPNT are out of brackets. The CS<sup>I</sup> and CS<sup>A</sup> parameters are the absolute values of isotropic and anisotropic chemical shieldings

atoms, P has a lone pair of electrons in the valence shell; therefore, discrepancies were expected between the properties of the electronic structures of B and P atoms. The NMR parameters of P1 to P6, which were the atoms of the P-terminated end, detected the changes due to the C-doping but those of the B-terminated end did not detect any significant changes in a parallel case. The values of the CS<sup>I</sup> of P1 and P4 were increased whereas those of P2, P3, P5, and P6 were decreased in the c-BPNT. On the other hand, the values of the CS<sup>A</sup> of all six P atoms were increased in the c-BPNT. This observation was more significant for P2 and P3 atoms which were located in the rings with the C members. The values of the CS<sup>I</sup> of P7 and P9, which were contributed to the C-P bonds instead of the B-P ones, were increased whereas the values of the CS<sup>A</sup> parameters were decreased. The changes of the NMR parameters of P10, P11, and P12 due to C-doping were almost negligible. The values of the CS<sup>I</sup> of P13 and P16, which were located in the rings with two C members, were increased whereas those of P17 and P18 were decreased in the c-BPNT. On the other hand, the CS<sup>A</sup> values of all four P atoms were increased in

the c-BPNT. The values of the CS<sup>I</sup> and CS<sup>A</sup> of P20, which were contributed to the C-P bond instead of the B-P one, were decreased; however, due to shorter C-P bond length of 1.85 Å against B-P bond length of 1.91 Å, stronger C-P bond rather than B-P bond was suggested in this case. The values of the CS<sup>I</sup> of P19, P21, P22, and P24 were increased whereas the values of the CS<sup>A</sup> parameters were decreased in the c-BPNT. However, the value of CS<sup>I</sup> of P23 was decreased whereas the value of CS<sup>A</sup> parameters was increased in the c-BPNT.

#### NMR parameters of the armchair model

The NMR parameters of the armchair (4,4) p-BPNT and c-BPNT have been listed in Table 4 (Fig. 3). The armchair p-BPNT model had 28 B and 18 P atoms; the atoms have been divided into seven groups by the calculated NMR parameters; 1 to 4, 5 to 8, 9 to 12, 13 to 16, 17 to 20, 21 to 24, and 25 to 28. Similar NMR parameters were observed for the atoms of each group. In contrast with different atomic terminated zigzag BPNTs, armchair BPNTs have

two similar atomic terminated ends yielding two symmetric parts; the atoms 13 to 16 were located at the center of symmetry in the considered nanotube of this study. Therefore, the results of groups 1 to 4; atoms 1 to 16, have been discussed. B1 to B4, which were located at the end of p-BPNT had the smallest values of the  $CS^I$  parameters but the largest values of the  $CS^A$  parameters among the B atoms in the p-BPNT. The values of the  $CS^I$  of B5 to B8 did not differ from those of the first B group; however, the values of the  $CS^A$  parameters differed. The values of the  $CS^I$  of B9 to B12 were larger than two previous B groups; however, the values of the  $CS^A$  parameters were decreased. This trend was also viewed for the values of the  $CS^I$  and the  $CS^A$  of B13 to B16. As mentioned earlier, since P atom has a lone pair of electrons in the valence shell, their results show discrepancies in behavior than those of B atoms. In the armchair p-BPNT, P1 to P4, which were located at the end of nanotube, had the largest values of  $CS^I$  but the smallest values of  $CS^A$  parameters among other P atoms. By going to the second P group; P5, P6, P7, and P8, the values of  $CS^I$  parameters were decreased but the  $CS^A$  ones were increased. The values of  $CS^A$  parameters were significantly changed from the first group to the second group but this change was not viewed from the second group to third or fourth groups. The change of the values of  $CS^I$  parameters was significant just from the first group to the second one.

B10, B13, and B18 were respectively doped by C6, C4, and C2 in the c-BPNT (Fig. 3a). The NMR parameters of B1 to B16 were influenced by indirect and direct effects of the C-doped ring; however, significant changes were not viewed among the B atoms. This trend revealed that although the C-doped ring caused some structural deformations, but the NMR parameters of the B atoms in the armchair c-BPNT did not detect significant changes. P9, P14, and P17 were respectively doped by C1, C5, and C3 in the c-BPNT (Fig. 3a). The values of  $CS^I$  of P atoms in the c-BPNT were not significantly differed from those of p-BPNT; however, the values of  $CS^A$  parameters were more changed. This trend revealed that the average values of CS tensors were not differed by the C-doped ring. In some cases, the values of  $CS^A$  parameters were increased but in the other cases, they were decreased. At the end of the nanotube, the values of  $CS^A$  of P1, P2, and P3 were decreased whereas that of P4 was increased. For the second P group, the values of  $CS^A$  of P5 were increased whereas those of P6, P7, and P8 were decreased. P6 was contributed to the C-P bond instead of the B-P bond; therefore, the values of  $CS^A$  parameters were significantly decreased. In a similar case, the value of  $CS^A$  of P13, which was also contributed to the C-P bond, was significantly decreased. In summary, the NMR parameters of armchair model were less influenced by the C-doped ring than the zigzag BPNT.

## Conclusions

This DFT study at the level of BLYP exchange-functional and 6-31G\* standard basis set revealed that in the zigzag and armchair p-BPNTs, the B and P atoms were divided into some groups with the same NMR parameters in each group. However, different groups had different NMR parameters. In the c-BPNT, this harmony was interrupted by the existence of the C-doped ring. For the zigzag model, both of the  $CS^I$  and  $CS^A$  parameters were significantly changed due the C-doped ring; however, this change was less significant for the armchair model. In the armchair case, the values of  $CS^A$  of those P contributed to the C-P bonds were significantly decreased whereas those of other B and P atoms detected just small changes. The difference between the band gap energies between the p-BPNT and c-BPNT was larger in the armchair model than the zigzag one.

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