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The effects of F_2 adsorption on NMR parameters of undoped and 3C-doped (8, 0) zigzag BPNTs

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Abstract

In this research, we studied the structure, properties and NMR parameters of interaction F_2 gas with pristine and 3C-doped (8, 0) zigzag models of boron phosphide nanotubes (BPNTs). In order to reach these aims, we considered four different configurations for adsorption of F_2gas on the outer and inner surfaces of BPNTs. The structures of all models were optimized by using density functional theory (DFT).The chemical shielding (CS) tensors at the sites of ^{11}B and ^{31}P nuclei were computed from the optimized structures and then the computed chemical shielding tensors were converted to isotropic chemical shielding (CSI) and anisotropic chemical shielding (CSA). Due to the donor electron effects of 3C doped atoms, the chemical shielding isotropic (CSI) of F_2 gas on surface of BPNTs was significantly more than pristine models. The results showed that F_2 adsorption on surface of nanotube was exothermic and 3C-doped decreased the adsorption energy values. The calculated results proved that the chemical activity of complex BPNTs/F_2 has increased and hence the chemical stability of the nanotube has decreased.

Keywords: BPNTs; NMR; F_2adsorption; 3C-doped.

Introduction

After discovery and synthesis of the novel nano material, numerous researches has been done to investigate the properties, structural, mechanical, chemical, physical, electronic properties and applications as novel

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materials [1-6]. In the recent years, the experimental and theoretical study of nanotubes groups three and five elements in the periodic table, such as BNNTs and BPNTs have been an interesting subject for many investigations [7-11] due to good physical properties and applications. One of the most important applications of these nanotubes is in adsorption process of many chemical species and production of new sensitive industrial sensors and control process due to their unique properties, such as greater adsorptive capacity, extensive pore surface area, developed internal pore structure, unique surface chemistry and adsorption of gases at low temperatures [12-21]. Fluorine is a univalent poisonous gaseous halogen, it is pale yellow-green and it is the most chemically reactive and electronegative of all the elements. Fluorine is very often used in various industrial processes, for example, in the production of polymers and preparation of nuclear fuels. Moreover, this gas is toxic even at low concentrations. Therefore, there is a great demand for sensors for this gas and alarm systems controlling the environment [22-25]. After our previous research on the study of electronic properties of BPNTs and other nanotubes [26-31], in this research, we attempted to study the properties of the electronic structure of the F_2-adsorption on BPNTs by performing density functional theory (DFT) and calculations of the NMR parameters of representative four models (8, 0) zigzag BPNTs (Figure 1). However, to the best of our knowledge, quantum-mechanical study of the interaction of F_2 with undoped and 3C-doped BPNTs has not been reported, and the results of this study provide a better understanding of chemical properties and F_2 adsorption capacity of BPNTs and the effect of 3C doped. The electronic structure, properties including bond lengths, bond angles, adsorption energy, band gaps, NMR parameters of the F_2 adsorption on undoped and 3C-doped models of (8,0) zigzag BPNTs are investigated by calculations of the CS tensors at the sites of ^{11}B and ^{31}P atoms.

Computational methods

In this work, for calculating the structural and electrical properties of F_2 adsorption on the outer and inner surface of undoped and 3C-doped (8, 0) zigzag single-walled BPNTs (Figure 1), we used density function theory at B3LYP level of theory using the Gaussian 03 set of programs [32]. The standard 6-31G* basis set was used for all calculations. Regarding all models, the mouths of all nanotube models are capped by hydrogen atoms in order to saturate the dangling bonds

of the boundaries and also to simulate a longer tube. Moreover, they are used to prevent the closure of the mouth ring and also to decrease calculation time. During the first step, All structures of F_2 adsorption on the undoped and 3C-doped BPNTs at (A−D) models are optimized and then, the adsorption energy, gap energy (E_{gap}=E_{LUMO}-E_{HOMO})and chemical shielding (CS) tensors at the sites of ^{11}B, ^{31}P nuclei are calculated based on the gauge including atomic orbital (GIAO) approach and same level of theory[33-34]. The calculated CS tensors in the principal axes system (PAS) ($\sigma_{33} > \sigma_{22} > \sigma_{11}$) are converted to measurable NMR parameters, chemical shielding isotropic (CSI) and chemical shielding anisotropy (CSA) by using equations (1) and (2), respectively [26-31]. The evaluated NMR parameters of the sites of ^{11}B, ^{31}P nuclei are presented in Tables 2 and 3.

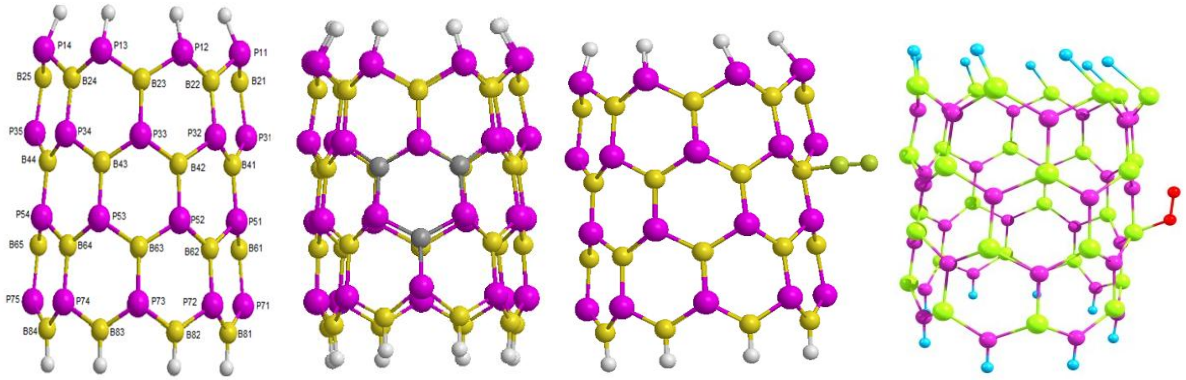
$$CSI(ppm) = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (1)$$

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

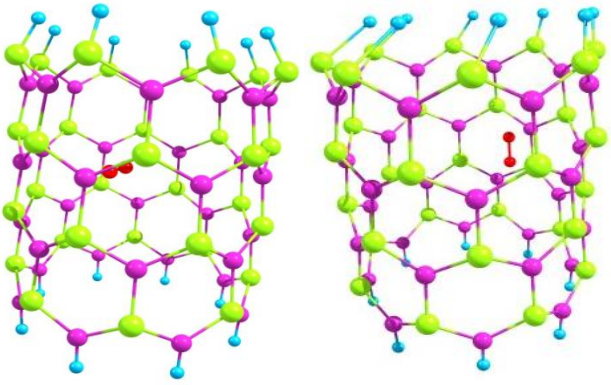
The adsorption energy of F_2 on the all models of BPNTs is calculated as follows:

$$E_{ads} = E_{BPNTs-F2} - (E_{BPNTs} + E_{F2}) \quad (3)$$

Where $E_{BPNTs-F2}$was obtained from the scan of the potential energy of the BPNTs–F_2, E_{BPNTs} and E_{F2} are the energy of the optimized BPNTs and F_2structure respectively.



(a) (b) (c) (d)



(e) (f)

Figure 1. 2D views of (a) pristine and (b) 3C doped of (4, 4) armchair model of BPNTs,
(c) A–model shows the vertical adsorption F_2 gas on the outer surface of BPNTs.
(d) B–Model shows the horizontal adsorption F_2 gas on the outer surface of BPNTs.
(e) C–Model shows the vertical adsorption F_2 gas on the inner surface of BPNTs.
(f) D–Model shows the horizontal adsorption F_2 gas on the inner surface of BPNTs.

Results and discussion

The structural parameters

During the first study which revealed the effects of 3C doped on the adsorption of F_2gas on the outer and inner surface of (8, 0) zigzag BPNTs, we considered four adsorption models. (A−D models, Figure 1). The electronic structural properties consisting of the B–P bond lengths, bond angles, and adsorption energy of investigated models of the (8, 0) zigzag BPNTs are summarized in Table 1. The calculated results indicated that the values of the average of the B–P bond lengths are 1.88 Å and with doping 3C the bond lengths decrease significantly from original values. The bond lengths of P32–B42/C, P33–B43/C and P53–B63/C at the (A, B, and D) models of pristine BPNTs are1.88, 1.87 and 1.89 Å respectively. However, those bond lengths at the D model are 1.88, 2.02 and 1.83 Å. With doping 3C atoms in spite of three B atoms the bond lengths of P32–B42/C, P33–B43/C and P53–B63/C at all models decrease from the original values, because the radius of carbon is lower than boron atoms. On the other hand, the bond angles yield some structural deformations. It must be noted that the significant changes of geometries are just for those atoms placed in the near neighbourhood of 3C atoms and those of other atoms were almost remained unchanged.

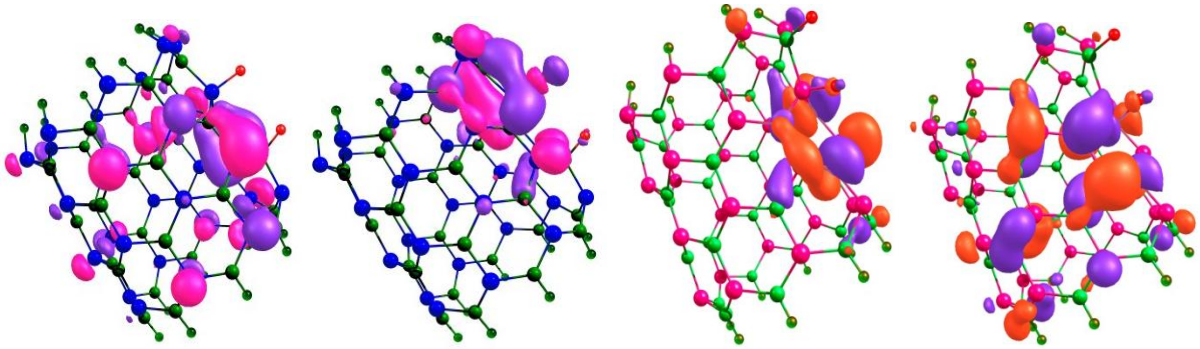
The adsorption energy of F_2 gas on the surface of undoped and 3C doped BPNTs is calculated by Eqs. 3 and calculated results are given in Table 1. The results show that the adsorption energy in the all models is exothermic and have negative values. It is notable that the adsorption energy for (A, B, C and D)undoped models are–31.86, –32.24, –30.88 and–31.10 Kcal/mol and with doping of 3C in spite of 3B atoms those values are –6.96, –5.49, –6.04 and –6.25 Kcal/mol. Comparison of results prove that doping of impurity atoms increase the adsorption energy and this phenomena is not favorable from the thermodynamic point of view, any of the 3C doped models are not suggested for using the sensor for F_2 gas.

Table 1. Structures and energy parameters of F_2 adsorption on (A-D) undoped and 3C-doped models of (8.0) zigzag models of BPNTs. (Figure 1)

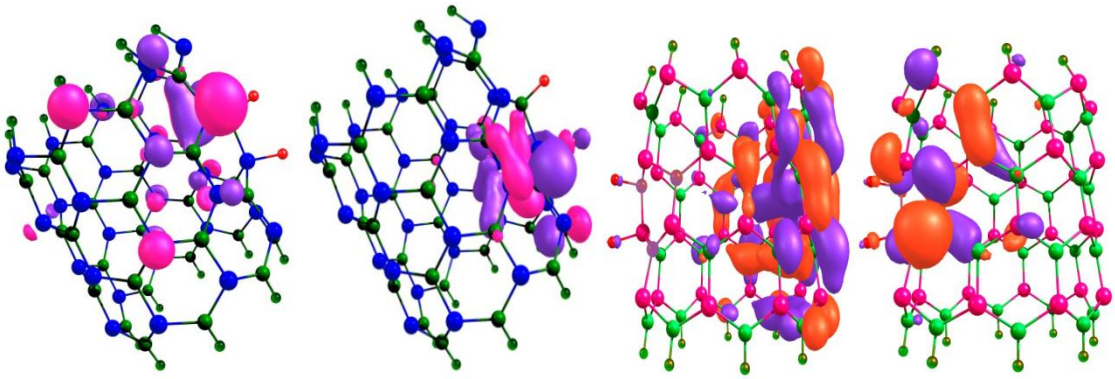
Bond lenght	**A-model**		**B-model**		**C-model**		**D-model**	
	undoped	**3C-doped**	**undoped**	**3C-doped**	**undoped**	**3C-doped**	**undoped**	**3C-doped**
P32-B42/C	1.88	1.78	1.88	1.77	1.88	1.79	1.88	1.77
P33-B43/C	1.87	1.79	1.87	1.93	2.02	1.91	1.87	1.83
P53-B63/C	1.89	1.73	1.89	1.72	1.83	1.83	1.89	1.79
P73-B63/C	1.88	1.81	1.89	1.82	1.87	1.81	1.89	1.83
P52-B42/C	1.82	1.81	1.88	1.88	1.95	1.74	1.89	1.73
P73-B82	1.88	1.88	1.87	1.84	1.86	1.88	1.87	1.87
P51-B41	1.82	1.86	1.89	1.86	1.90	1.91	1.88	1.86
Bond angle								
B64-P53-B43/C	116	119	116	118	112	104	114	110
P53-B43/C-P34	120	122	119	115	106	107	116	124
B62-P52-B63/C	122	100	111	107	117	114	109	111
B42/C-P33-B43/C	115	103	110	107	103	96	111	100
P53-B63/C-P52	121	123	120	128	113	124	120	123
B63/C-P52-B42/C	116	107	117	108	118	117	116	116
B43/C-P53-B63/C	118	116	116	115	112	103	118	108
Energy								
E_{HOMO}/ev	–5.98	–4.90	–5.92	– 4.77	–5.98	–5.51	–6.05	–4.97
E_{LUMO}/ev	–3.95	–3.56	–3.88	–3.39	–3.99	–3.38	–3.84	–3.27
Egap)/ev (	2.03	1.34	2.04	1.38	1.99	2.13	2.21	1.7
E_{ads}/kcal mol^{-1}	–31.86	–6.96	–32.24	–5.49	–30.88	–6.04	–31.10	–6.25

The HOMO (highest occupied molecular orbital) and the LUMO (Lowest unoccupied molecular orbital) of all adsorption models are calculated from optimized structures. The results are shown in Figure 2. As shown in Figure 2, the HOMO orbitals of (A–D) undoped BPNTs models are localized on the P and B sites of the neighbour of F_2 adsorption. It is remarkable that with doping 3C the density of HOMO orbitals moves around doping sites because the electronagivity of carbon is more than boron atom. However the LUMOs orbitals are located on the B–P bond near the adsorption position. With doping 3C, the density of LUMO orbitals becomes widespread on the

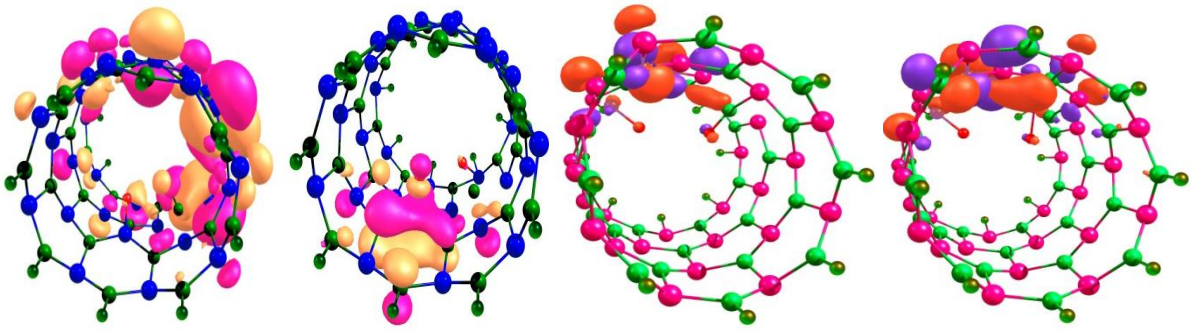
surface of around doping. In order to study the reactivity of chemical adsorption and electronic properties of BPNTs, we evaluated the gap energy between HOMO and LUMO orbitals. The results are given in Table1. The calculated results show that the gap energy of undoped (A, B, C and D) models are 2.03, 2.04, 2.13 and 2.21 eV and with doping 3C, the gap energy of those models decrease to 1.34, 1.38, 1.99 and1.70 eV. The decrease of gap energy can prove that the chemical activity of complex BPNTs/F_2 has increased and hence the chemical stability of the nanotube will decrease.



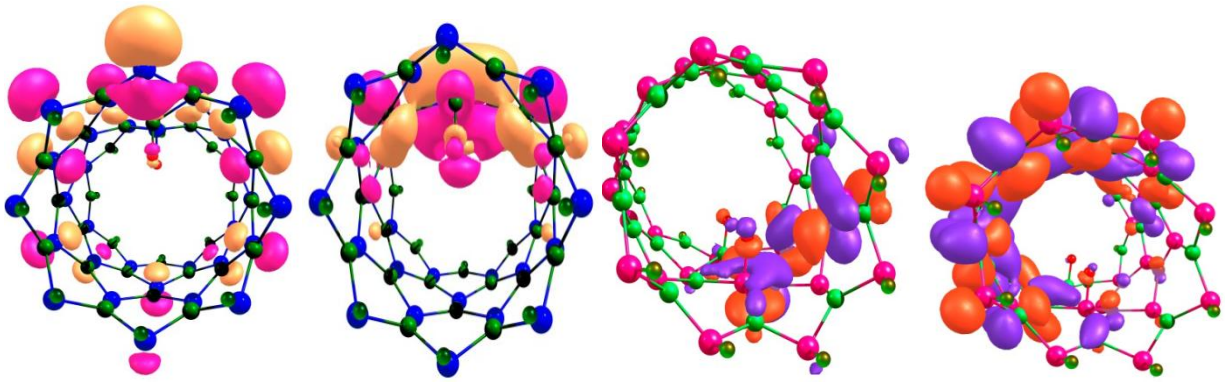
A1 – undoped A1-3C doped A2-undoped A2-3C doped



B_1 – undoped B_1-3C doped B_2-undoped B_2-3C doped



C_1 – undoped C_1-3C doped C_2-undoped C_2-3C doped



D_1 – undoped D_1-3C doped D_2-undoped D_2-3C doped

Figure 2. HOMO/ LUMO structures of F_2 adsorption on the undoped and 3C doped of (4,4) armchair model of BPNTs, index (1) used for HOMO and index (2) for LUMO of (A–D) adsorption models (Figure 1)

The NMR parameters of 3C-doping in the BPNTs

In this work, we investigated the effects of 3C doping and F_2 adsorption on the electronic structure properties and NMR properties of BPNTs. For this purpose, the chemical shielding (CS) tensors at the sites of various ^{11}B and ^{31}P atoms are calculated. In order to directly relate the calculated tensors to the experimentally measurable parameters, the tensors are converted to the isotropic CS (CSI) and the anisotropic CS (CSA) parameters. The CSI is the average value of the eigen values of the CS tensors, Eq. 1, and the orientation of the eigen values of the CS tensors into the z-axis play a dominant role in determining the value of the CSA parameter, Eq. 2. Tables 2 and 3 show the evaluated CSI and CSA values for ^{11}B and ^{31}P in all undoped and 3C doped of (8, 0) zigzag BPNTs (Figure 1). In the previous work, we showed that the 32 B and 32 P atoms in pristine nanotube of BPNTs are divided into eight layers with equivalent ^{31}P and ^{11}B, NMR parameters for each layer [28-29].

The results in Table 2 show that the CSI values of the B atom at layers 2,4,6,8 are 29, 44, 40 and 47 *ppm*, respectively, and at layers 1, 3, 5 and 7 for P sites are (396, 363, 337 and 329 *ppm*) respectively; it reveals the fact that the CSI values of the sites of the nuclei of each layer feel equivalent chemical environment. The results show that with doping 3C on the pristine and all (A–D) models of adsorption F_2 the CSI values for ^{11}B sites in the sites B24, B43, B44, B64 and B83 decrease from the original values, and the other sites these valves increase

significantly from original values because carbon atoms have four electrons in valence shell and caused the donor electron effect on the surface of nanotubes. It is notable that decrease in the CSI valued with doping of 3C on the B model is larger than other models. Therefore, adsorption F_2 on the horizontal direction of nanotube will significantly decrease the CSI values at the B24, B43, B44, B64 and B83 sites and the charge density at this site is lower than other sites. The CSI values of ^{31}P sites at the P31, P37, P58 and P78 nuclei at all models with doping of 3C carbons decrease significantly from original values and, on the other hand, the CSI values of ^{31}P sites at the other sites increase from original values. It is notable that decrease in CSI values of B nuclei on the B models is larger than other models. The adsorption of F_2 and doping 3C on the CSI values of B model is more effective than other models and the charge density of electron at this model change more significantly than other adsorption models.

Table 2. CSI parameters of F_2 adsorption on (A-D) models (8, 0) zigzag BPNTs (Figure 1), the first number for undoped and the second number in [ ] for 3C-doped

B-11	**CSI /(*ppm*)**					**P-31**	**CSI /(*ppm*)**				
Nuclei	**pristine**	**A-model**	**B-model**	**C-model**	**D-model**	**Nuclei**	**pristine**	**A-model**	**B-model**	**C-model**	**D-model**
B21	29[46]	32 [50]	25 [38]	22 [26]	23 [42]	P11	396[417]	406 [431]	400 [416]	401 [415]	408 [430]
B22	29[35]	27 [37]	25 [39]	31 [32]	23 [38]	P12	395[408]	399 [410]	402 [414]	403 [407]	400 [410]
B23	29[30]	25 [26]	30 [29]	27 [29]	30 [26]	P13	396[398]	399 [394]	414 [393]	408 [402]	404 [398]
B24	29[24]	27 [23]	36 [21]	47 [26]	29 [24]	P14	395[398]	406 [394]	399 [393]	406 [399]	403 [399]
B25	29[29]	32 [28]	29 [25]	29 [27]	28 [28]	P15	396[408]	413 [412]	414 [408]	401 [410]	403 [410]
B26	29[35]	46 [37]	29 [36]	47 [26]	28 [33]	P16	396[417]	397 [411]	399 [425]	404 [412]	403 [412]
B27	29[46]	30 [46]	36 [60]	29 [33]	29 [45]	P17	396[419]	398 [404]	414 [428]	403 [410]	404 [422]
B28	29[28]	46 [59]	30 [27]	46 [27]	30 [27]	P18	396[419]	413 [404]	402 [403]	408 [405]	400 [400]
B41	44[57]	45 [59]	40 [61]	29 [41]	59 [44]	P31	363[329]	370 [340]	371 [329]	414 [373]	417 [333]
B42	44[46]	41 [45]	43 [50]	43 [46]	35 [39]	P32	363[362]	374 [366]	371 [360]	347 [352]	417 [364]
B43	44[41]	41 [39]	51 [39]	48 [43]	45 [41]	P33	363[372]	374 [372]	370 [369]	353 [370]	345 [373]
B44	44[41]	45 [39]	58 [37]	44 [44]	45 [42]	P34	363[375]	374 [378]	358 [375]	340 [372]	370 [372]
B45	44[46]	56 [47]	58 [42]	25 [35]	45 [45]	P35	363[372]	370 [369]	376 [372]	369 [358]	371 [373]
B46	44[57]	63 [58]	58 [64]	50 [96]	45 [53]	P36	363[362]	342 [367]	376 [370]	347 [400]	371 [363]
B47	44[-]	63 [-]	51 [-]	27 [-]	45 [-]	P37	363[329]	307 [346]	358 [312]	371 [278]	370 [328]
B48	44[-]	56 [-]	43 [-]	97 [-]	35 [-]	P38	363[342]	342 [288]	370 [323]	347 [322]	345 [369]
B61	40[46]	45 [61]	37 [77]	32 [38]	37 [97]	P51	337[350]	343 [338]	345 [370]	367 [338]	286 [330]
B62	40[48]	39 [48]	37 [53]	44 [46]	37 [37]	P52	337[343]	346 [341]	350 [347]	343 [346]	319 [342]
B63	40[39]	36 [38]	42 [42]	38 [39]	36 [38]	P53	337[348]	346 [349]	343 [345]	365 [346]	344 [345]
B64	40[34]	39 [33]	54 [32]	47 [38]	41 [35]	P54	337[348]	343 [347]	317 [348]	340 [344]	347 [346]

B65	40[39]	45 [41]	48 [36]	43 [40]	42 [39]	P55	337[343]	344 [347]	280 [348]	368 [344]	346 [340]
B66	40[48]	50 [52]	48 [50]	48 [37]	42 [46]	P56	337[350]	343 [343]	317 [351]	315 [310]	347 [348]
B67	40[46]	99 [50]	54 [50]	44 [50]	41 [50]	P57	337[282]	343 [315]	343 [313]	311 [255]	344 [258]
B68	40[-]	50 [-]	42 [-]	48 [-]	36 [-]	P58	337[282]	344 [275]	350 [299]	325 [299]	319 [219]
B81	47[54]	47 [55]	46 [55]	42 [51]	49 [48]	P71	329[346]	334 [341]	337 [323]	263 [350]	340 [344]
B82	47[48]	44 [48]	47 [49]	46 [47]	41 [49]	P72	329[335]	338 [330]	337 [336]	334 [335]	340 [335]
B83	47[43]	44 [43]	48 [44]	46 [45]	46 [45]	P73	329[337]	339 [333]	335 [333]	336 [339]	337 [335]
B84	47[43]	47 [45]	48 [43]	46[46]	47 [44]	P74	329[341]	338 [337]	326 [340]	338 [338]	335 [340]
B85	47[48]	49 [48]	45 [47]	36 [47]	48 [48]	P75	329[337]	334 [336]	342 [338]	335 [334]	337 [334]
B86	47[54]	47 [54]	48 [58]	52 [51]	47 [52]	P76	329[335]	346 [329]	342 [334]	338 [332]	337 [336]
B87	47[53]	47[53]	48 [51]	46 [51]	46 [51]	P77	329[346]	338 [349]	326 [344]	339 [333]	335 [339]
B88	47[53]	49 [53]	47 [55]	44 [48]	41 [49]	P78	329[276]	346 [287]	335 [290]	337 [297]	337 [289]

The CSA values of B and P sites are given in Table 3.The comparison results show that, The CSA values for all models have the different behavior so that with doping of 3Cand the trend of CSA values in the layers are different and at the sites B and P site increase and decrease. The CSA values of B sites at B61 site decrease more significantly than other sites and at the B66 site increase more significantly than other sites. However the CSA values of P nuclei at the P31, P37, P38, and P58 sites decrease more than other sites and at the P52, P54 and P56 sites increase more than other sites. Due to the donor effects of 3C the variation of NMR parameters at sites of near atoms doping has lager change than other sites and the electronic properties of these layers or sites are important for other research.

Table 3. CSA parameters of F_2 adsorption on (A-D) models (8, 0) zigzag BPNTs (Figure 1), the first number for undoped and the second number in [ ] for 3C-doped

B-11	**CSA /(*ppm*)**					**P-31**	**CSA /(*ppm*)**				
Nuclei	**Pristine**	**A-model**	**B-model**	**C-model**	**D-model**	**Nuclei**		**A-model**	**B-model**	**C-model**	**D-model**
B21	91[45]	116 [77]	100 [36]	30 [51]	104 [85]	P11	115[28]	104 [90]	110 [99]	105 [82]	122 [103]
B22	91[117]	38 [115]	100 [109]	116 [117]	104 [133]	P12	72[59]	104 [71]	82 [120]	98 [110]	81 [85]
B23	91[46]	135 [46]	105 [91]	110 [56]	95 [30]	P13	115[101]	104[101]	109 [96]	112 [103]	123 [111]
B24	91[126]	38 [74]	96 [111]	48 [129]	96 [122]	P14	72[101]	104[99]	91 [103]	95 [112]	75 [96]
B25	91[46]	116 [63]	58 [43]	70 [50]	97 [58]	P15	[59]115	111[82]	62 [88]	112 [92]	119 [108]
B26	91[117]	38 [113]	58 [123]	103 [129]	97 [111]	P16	72[28]	91[90]	91 [118]	81 [131]	74 [107]
B27	91[45]	129 [57]	96 [91]	117 [69]	96 [32]	P17	115[88]	91[166]	109 [92]	125 [79]	123 [77]
B28	91 [68]	38 [42]	105 [127]	62 [121]	95 [149]	P18	72[88]	111[186]	82 [86]	71 [112]	81 [112]
B41	106[63]	89 [82]	109 [60]	61 [72]	23 [44]	P31	186[62]	241[68]	198 [79]	154 [89]	152 [81]
B42	23[91]	80 [90]	36 [108]	102 [98]	52 [73]	P32	[241]186	97[234]	198 [225]	232 [251]	153 [249]

B43	106[58]	80 [59]	109 [35]	116 [68]	110 [90]	P33	186[110]	253[113]	206 [192]	228 [127]	225 [83]
B44	23[58]	39 [48]	53 [99]	46 [95]	27 [64]	P34	186[222]	96[135]	216 [212]	124 [243]	184 [236]
B45	106[91]	91[100]	44 [76]	63 [88]	109 [96]	P35	186[110]	241[137]	85 [108]	157 [143]	197 [130]
B46	23[63]	52 [72]	53 [88]	111 [7]	28 [67]	P36	186[241]	116 [234]	86 [236]	240 [243]	197 [229]
B47	106[-]	52 [-]	109 [-]	94 [-]	110 [-]	P37	186[62]	237 [47]	216 [114]	228 [118]	183 [39]
B48	23[-]	91 [-]	36 [-]	10 [-]	52 [-]	P38	186[20]	116 [104]	206 [59]	145 [108]	225 [90]
B61	84[22]	113 [11]	82 [9]	51[25]	125 [3]	P51	246[186]	213 [210]	260 [142]	139 [157]	210 [226]
B62	84[112]	31 [115]	82 [110]	108 [110]	125 [109]	P52	67[209]	198 [217]	93 [255]	230 [232]	200 [194]
B63	84[38]	113 [29]	93 [79]	101 [48]	89 [28]	P53	246[160]	198 [110]	259 [93]	226 [162]	247 [213]
B64	84[89]	31 [86]	86 [100]	62 [111]	81 [110]	P54	67[160]	212 [92]	124 [220]	126 [231]	73 [152]
B65	84[38]	113 [49]	58 [39]	63 [38]	88 [49]	P55	246[209]	199 [229]	241 [174]	155 [184]	254 [229]
B66	84[112]	37 [113]	58 [109]	109 [115]	88 [110]	P56	67[186]	167 [204]	124 [230]	214 [261]	73 [160]
B67	84[22]	38 [51]	86 [79]	107 [26]	81 [20]	P57	246[72]	168 [153]	259 [55]	370 [130]	247 [181]
B68	84[-]	37 [-]	93 [-]	74 [-]	89 [-]	P58	67[72]	198 [183]	93 [84]	358 [107]	200 [175]
B81	115[94]	100 [98]	102 [80]	47 [81]	126 [102]	P71	219[140]	283 [167]	204 [98]	167 [100]	256 [183]
B82	41[104]	74 [102]	52 [112]	108 [109]	51 [92]	P72	219[277]	109 [287]	204 [259]	257 [274]	256 [270]
B83	115[18]	74 [91]	115 [50]	105 [69]	116 [95]	P73	219[130]	263 [125]	242 [217]	180 [154]	220 [101]
B84	41[18]	100 [78]	58 [110]	57 [92]	45 [76]	P74	219[168]	109 [231]	234 [248]	263 [266]	217 [269]
B85	115[104]	95 [106]	122 [91]	112 [86]	112 [109]	P75	219[130]	283 [156]	187 [122]	147 [109]	226 [158]
B86	41[94]	89 [98]	58 [108]	120 [98]	45 [86]	P76	219[277]	116 [284]	188 [281]	260 [282]	226 [274]
B87	115[23]	90 [70]	115 [61]	113 [63]	116 [91]	P77	219[140]	275 [132]	234 [220]	213 [168]	216 [105]
B88	41[23]	95 [57]	52 [104]	82 [90]	51 [61]	P78	219[56]	116 [216]	242 [222]	289 [152]	220 [183]

Conclusion

In this work, We have performed density functional theory (DFT) to study the electronic structures and NMR parameters (CSI and CSA) of the F_2 adsorption on the undoped and 3C doped (8,0) zigzag models boron phosphide nanotube. For this purpose, we considered four models for adsorption F_2 on surface of BPNTs. The results revealed that with doping 3C atoms, in spite of three B atoms, the bond lengths of P32–B42/C, P33–B43/C and P53–B63/C at all models decreased significantly from the original values because the radius of carbon is lower than boron atoms. On the other hand, the bond angles yield some structural deformations. It must be noted that the significant changes of geometries are just for those atoms placed in the neighbourhood of 3C atoms and those of other atoms were almost remained unchanged. The gap energies of the 3Cdoped models are significantly decreased in comparison to the pristine models. The adsorption energy in the all models is exothermic and has negative values. The adsorption energy for (A, B, C and D)undoped models are more than 3C doped. It is notable that decrease in CSI values on the B models is larger than other models; this is the same as results from B

sites. The adsorption of F_2 and doping 3C on the CSI values of B model is more effective than other models and the charge density of electron at this model change more significant than other adsorption models.

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