ORIGINAL RESEARCH ARTICLE

The comparable study of isoelectronic-bodies of single-walled B/N nanotubes

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ABSTRACT

The structure, thermodynamic stability, ionization potential (IP) and electron affinity (EA) energy level difference (E_g) and tension of lowest unoccupied orbit (LUMO) and highest occupied orbit (HOMO) of armchair single wall carbon nanotubes (C-NTs), BN hybrid carbon nanotubes (BC_2N-NTs) and all BN nanotubes (BN-NTs) were systematically studied with AM1 method in this paper. Calculation results show that when n value is constant, (n, n) C-NTs ($n = 3, 4, 5, 6$) has the largest diameter and BN-NTs has the smallest diameter; (n, n) the values of E_g (HOMO-LUMO) and n of C-NTs and BC_2N-NTs are related; POAV analysis shows that different hybrid atoms have different contributions to the hybrid mode of nanotube atoms and the tension of nanotubes.

Keywords: Carbon Nanotubes; BN Nanotubes; Energy Gaps (EHOMO-ELOMO); Hybrid Tension

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1. Introduction

Since the discovery of carbon nanotubes[1], especially single-walled carbon nanotubes[2,3] were found, carbon nanotubes have had potential applications in many aspects due to their unique mechanical, optical and electronic properties[4-6]. Scientists have not stopped their research. In addition to the body, many substitution products of carbon nanotubes have been synthesized, and BN hybrid carbon nanotubes are one of them. Up to now, BN hybrid carbon nanotubes ($B_xC_yN_z$)[7,8] with various components have been synthesized, including isoelectronic isomers of carbon nanotubes, namely nanotubes composed of BC_2N and all boron nitrogen BN nanotubes[9,10]. All BN nanotube is a semiconductor material with an energy gap close to 5.8 eV, which is similar to the electronic properties of a large number of hexagonal BN network structures, and the size of the energy gap is independent of the diameter, helicity and the interaction between tubes and tubes of BN nanotube[11]. This electronic property of $B_xC_yN_z$ nanotube is obviously different from that of carbon nanotube, because the size, diameter, length and helicity of the electron energy level band gap (E_{gap}) of carbon nanotubes are related[11].

Taking three kinds of isoelectronic nanotubes (n, n) C-NTs, BC_2N-NTs and BN-NTs ($n = 3, 4, 5, 6$) as research objects, we systematically studied the relationship between their geometric structure, thermodynamic stability, ionization potential, electron affinity and

tension with diameter by using semi empirical AM1 calculation method, having revealed the diameter effect and hybrid effect of boron nitrogen heteroatomized carbon nanotubes, which provides a theoretical method for relevant research law and theoretical basis[12,13].

2. The way of calculation

In this paper, the full optimization of the molecular geometry of nanotube (n, n) C-NTs, BC_2N-NTs and BN-NTs ($n = 3, 4, 5, 6$) is based on the AM1 method in the Gaussian 98 package[14]. In order to ensure that all the optimized geometries are the minimum points of the geometric potential energy surface, based on the same method, all the optimization results are frequency analyzed, and no virtual frequency is found. In addition, the tension calculation (strains,) of these optimized configurations are done in the program POAV[15] provided by Professor Haddon.

It is reported that all BN nanotubes BN-NTs can have many structures, and the most thermodynamically stable structure is shown in **Figure 1c** [this paper takes (3, 3) BN-NT as an example]. In **Figure 1c**, all B atoms are separated by an equal number of N atoms. Similarly, All N atoms are also separated by an equal number of B atoms. For BC_2N-NTs, although there are many different composition structures, both experiments[16,17] and theory[18,19] have confirmed that **Figure 1b** is the most stable structure; in **Figure 1b**, the number of carbon strips and BN strips reaches the maximum. For the convenience of research, the pure C nanotube (3, 3) C-NT is also listed in **Figure 1a**. It should be noted that in Figure 1a, b and c, for each sawtooth nanotube, there are only two kinds of bonds, namely vertical bond (V, the abbreviation of vertical) and oblique bond (S, the abbreviation of sloppy). The vertical bond (V) is the bond between atoms at positions 1 and 2, and the oblique bond (S) is the bond between atoms at positions 2 and 3.

In order to save computer time and accuracy, the nanotube (n, n) C-NTs, BC_2N-NTs and BN-NTs ($n = 3, 4, 5, 6$) models in this paper contain 8 layers of atoms, and the suspended bonds at both ends are saturated with H atoms (as shown in **Figure 1**). The molecular formulas of BC_2N-NTs and C-NTs are

expressed as $B_{8n}N_{8n}H_{4n}$, $B_{4n}C_{8n}N_{4n}H_{4n}$ and $C_{16n}H_{4n}$, respectively.

3. The result and discussion
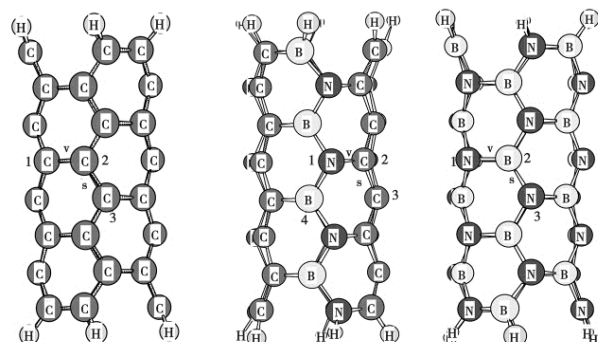
(a) Carbon nanotube of (3,3); **(b)** BC_2N nanotube of (3,3); **(c)** BN Nanotube of (3,3)
"V" and "S" represent vertical keys and diagonal keys respectively

Figure 1. Schematic diagram of three isoelectronic nanotubes.

3.1 Geometry

Based on the AM1 method, the geometric structures and Millikan charges of nanotubes (n, n) C-NTs, BC_2N-NTs and BN-NTs ($n = 3, 4, 5, 6$) are calculated. The calculated nanotube diameter and corresponding key bond length are listed in **Table 1**, and the Millikan charges carried by each key atom are listed in **Table 2**.

It can be seen from **Table 1** that for nanotubes C-NTs, BC_2N-NTs and BN-NTs ($n = 3$ or 4 or 5 or 6) with the same n value, the diameter increases slightly from the former to the latter. Taking nanotubes (3, 3) C-NT, BC_2N-NT and BN-NT as examples, the diameter calculated by AM1 is 4.110 respectively, 4.241 and 4.321 Å, gradually increase, and the diameters of other (n, n) nanotubes C-NT, BC_2N-NT and BN-NT also show a similar trend. This shows that BN substitution reaction can increase the diameter of carbon nanotubes, and the more the number of BN bonds, the more obvious the diameter increase. It can be seen from **Table 1**, The oblique bond lengths of nanotubes (3, 3) C-NT and BC_2N-NT are 1.453 (C2-C3) and 1.427 (average bond lengths of C2-C3 and N1-B4), respectively. The latter is 0.022 Å longer than the former. The bond lengths of the two vertical bonds are 1.428 (C1-C2) and 1.427 Å (N1-C2) respectively, which is almost the same, indicating that the oblique bond contributes more to the increase of nanotube diameter than

Table 1. Diameters and key bond lengths of (*n n*) (*n* = 3, 4, 5, 6) C-NTs, BC₂N-NTs and BN-NTs nanotubes calculated by AM1 method/Å

(n, n)	C-NTs			BC₂N-NTs				BN-NTs		
	Diameters	Bond length		Diameters	Bond length			Diameters	Bond length	
		C1-C2	C2-C3		N1-C2	C2-C3	N1-B4		N1-B2	B2-N3
(3, 3)	4.110	1.428	1.453	4.214	1.427	1.479	1.479	4.321	1.508	1.504
(4, 4)	5.487	1.413	1.446	5.645	1.412	1.473	1.461	5.754	1.493	1.494
(5, 5)	6.776	1.407	1.443	6.986	1.407	1.471	1.453	7.099	1.487	1.490
(6, 6)	8.147	1.404	1.441	8.389	1.405	1.470	1.450	8.530	1.483	1.487

Table 2. Mulliken charge/e calculated by AM1 of carbon nanotube (*n n*) (*n* = 3, 4, 5, 6) C-NTs, BC₂N-NTs and BN-NTs

	C-NTs			BC₂N-NTs				BN-NTs		
	C1	C2	C3	N1	C2	C3	B4	N1	B2	N3
(3, 3)	−0.007	−0.007	-0.007	−0.335 5	0.226 9	−0.295 5	0.367 8	−0.362 2	0.349 8	−0.362 2
(4, 4)	−0.005	−0.005	−0.005	−0.336 8	0.227 0	−0.273 4	0.357 7	−0.372 9	0.363 8	−0.372 9
(5, 5)	−0.005	−0.005	−0.005	−0.333 3	0223 5	−0.263 0	0.351 6	−0.379 3	0.371 8	−0.379 3
(6, 6)	−0.004	−0.004	−0.004	−0.331 1	0.220 9	−0.257 5	0.348 0	−0.383 5	0.376 7	−0.383 5
Average	−0.005	−0.005	−0.005	−0.334 2	0.224 6	−0.272 4	0.356 3	−0.374 5	0.365 5	−0.374 5
Δ(Q⁺−Q⁻)		−0.000			0.69				0.74	

the vertical bond. In the process of C-C bond being further replaced by B-N bond and finally becoming fully substituted BN nanotube, both vertical and oblique bonds contribute to the increase of diameter. Taking (3, 3) tube as an example, it can be seen from Table 1 that the bond lengths of vertical and oblique bonds of (3, 3) BN-NT are 1.508 and 1.504 Å respectively. The bond lengths of (*n*, *n*) BC₂N-NT are longer than those of (*n*, *n*) BN-NT. Therefore, from the fact that the bond lengths of C-NT, BC₂N-NT and BN-NTs increase gradually, it can be seen that the stability of nanotubes decreases gradually due to the progress of BN substitution.

It can also be seen from **Table 1** that on the basis of AM1 calculation, the diameters of (3, 3), (4, 4), (5, 5) and (6, 6) C-NTs are 4.110, 5.487 '6.776 and 8.147 Å respectively, gradually increasing; The corresponding vertical bond (C1-C2) bond lengths are 1.428, 1.413, 1.407 and 1.404 Å, respectively, and the corresponding oblique bond (C2-C3) bond lengths are 1.453, 1.446, 1.443 and 1.441 Å, respectively. The vertical and oblique bonds of BC₂N-NT and BN-NT tubes also gradually decrease with the increase of diameter. This shows that for C-NTs, BC₂N-NT and BN-NT tubes, the vertical and

oblique bonds become more and more stable with the increase of diameter. Accordingly, the thermodynamic stability of the corresponding nanotubes becomes stronger and stronger.

Table 2 lists the values of Mulliken charges carried by the key atoms of (*n*, *n*) (*n* = 3, 4, 5, 6) C-NTs, BC₂N-NTs and BN-NTs based on AM1. It is obvious that for any n value, whether C-NTs, BC₂N-NTS or BN-NTs, there is no obvious relationship between the charge on its atom and its diameter, which is almost constant. For example, the charges on N1, C2, C3 and B4 atoms on (3, 3) BC₂N-NT tubes are −0.3342, 0.2246, −0.2724 and 0.3563 e respectively, which are almost equal to the charges on the corresponding atoms on the (4, 4), (5, 5) and (6, 6) BC₂N-NT tube.

It can also be seen from **Table 2** that for the same kind of nanotube, even for the same atom, the charges on it are very different, which is particularly obvious for BC₂N-NTs tubes, although C2 and C3 atoms in BC₂N-NTs tubes are carbon atoms. However, the average charges are 0.2246 and −0.2724 e respectively, which is very different because the two C atoms are in different chemical environments. Specifically, C2 atom is connected

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with one N atom and two C atoms, while C3 atom is connected with one B atom and two other C protons (as shown in **Figure 1b**). As we all know, the electronegativity of N atom is much greater than that of B atom, so the electrons on C2 atom connected to N atom will be attracted by N atom, so C2 will be positively charged, while C3 atom connected to B atom with less electronegativity will attract the charges on B atom, so it will be negatively charged.

In addition, it can be seen from Table 2 that the average charge difference between adjacent C atoms in C-NT tube is approximately zero, the average charge difference between adjacent B and N atoms in BC$_2$N-NT tube is 0.69 e, and the average charge difference between adjacent B and N atoms in BN-NT tube is 0.74 e. Among the three nanotubes, the electron delocalization degree of C-NT tube is the largest, followed by BC$_2$N-NT tube, and BN-NT tube is the smallest, that is, the bond strength between adjacent atoms in C-NT tube is the largest, followed by BC$_2$N-NT, BN-NT is the smallest, which further proves the previous conclusion on the stability order of the three nanotubes: C-NT > BC$_2$N-NT > BN-NT.

3.2 Atomic energy (H_{at})

To further explore the relative thermodynamic stability of nanotubes (n, n) C-NTs, BC$_2$N-NTs and BN-NTs (n = 3,4,5,6), these three nanotubes are also evaluated from the perspective of atomization energy. The definition of atomization energy can be expressed as: $H_{at}(b_x c_y n_z) = H_f(B_x C_y N_z) - xH_f(B) - yH_f(C) - zH_f(n)$. Here, $H_f(x)$ represents the heat of formation of atom (molecule) X. it is obvious that the greater the negativity of atomization energy hat, the better the stability of the tube, **Figure 2** shows the atomization energy of the above nanotubes. It can be seen from **Figure 2** that BN heteroatomization reaction increases the number of corresponding nanotubes, indicating that the thermodynamic stability is reduced, which is similar to the previous conclusion and the BN heteroatomization conclusion of fullerenes[20].

It can also be seen from **Figure 2** that whether (n, n) C-NT, BC2N-NT or BN-NT, $H_f(x)$ gradually decreases with the increase of n, indicating that

their thermodynamic stability gradually increases with the increase of diameter. This conclusion is also consistent with the consensus on the thermal stability law of nanotubes generally accepted by the scientific community at present: that is, the larger the diameter of nanotubes, the stronger the thermodynamic stability.
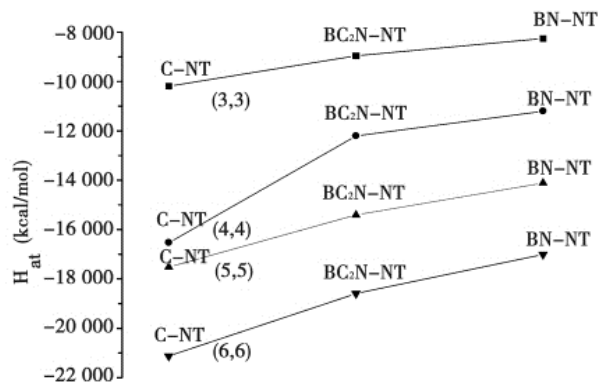
Figure 2. Isoelectronic nanotube (n, n) (n = 3, 4, 5, 6) C-NT, atomization energy based on AM1 method of BC2N-NT and BN-NT.

3.3 Ionization potential (IP), electron affinity potential (EA) and lowest unoccupied orbital (LUMO)

Ionization potential (IP) and electron affinity (EA) are two important concepts related to chemical reaction. According to Koopmans' theoretical viewpoint: IP = $-E_{HOMO}$, EA = $-E_{LUMO}$. In this paper, the ionization potential (IP) and electron affinity (EA) of (n, n) C-NTs, BC$_2$N-NTs and BN-NTs (n = 3, 4, 5, 6) calculated by AM1 method are listed in **Table 3**.

As can be seen from **Table 3**, firstly, the effects of BN substitution on IP, EA and E_g between the highest occupied orbit and the lowest occupied orbit of C-NTs are very obvious. For example, when (3, 3) C-NT is replaced by BN to form (3, 3) BC2N-NT, IP becomes smaller, EA increases. When BN substitution continues to occur and pure (3,3) BN-NT is finally generated, IP becomes smaller and EA becomes larger. Therefore, E_g of (3, 3) BN-NT is the largest (13.64 eV), followed by (3,3) BC$_2$N-NT, which is 7.39 eV, and the energy level C-NT is the smallest, which is 5.42 eV. This shows that BN hybridization not only reduces the ability of obtaining electrons, but also the ability of losing electrons, that is, BN heteroatomization of C-NTs

Table 3. IP, EA and E_g of (n n) (n = 3, 4, 5, 6) C-NTs, BC$_2$N-NTs and BN-NTs in AM1 method

	C-NTs			BC$_2$N-NTs			BN-NTs		
	IP	EA	E_g	IP	EA	E_g	IP	EA	E_g
(3,3)	−5.29	0.14	5.42	−6.57	0.82	7.39	−10.12	3.52	13.64
(4,4)	−5.56	0.40	5.96	−6.50	0.93	7.43	−10.04	3.65	13.69
(5,5)	−5.47	0.23	-5.70	−6.32	1.02	7.35	−9.97	3.72	13.69
(6,6)	−5.22	-1.90	3.33	−6.25	10.3	7.28	−9.88	−3.77	13.66

Table 4. POAV analysis results of nanotube (n n) (n = 3, 4, 5, 6) C-NTs, BC$_2$N-NTs and BN-NTs

Nanotubes	S^{a}P			SP^b			$\overline{\theta_p^z}$		
	C	B	N	C	B	N	C	B	N
(3, 3) BN-NT		0.085 3	0.068 3		2.256 1	2.204 9		0.033 9	0.027 5
(4, 4) BN-NT		0.033 2	0.047 0		2.099 5	2.140 7		0.014 8	0.020 7
(5, 5) BN-NT		0.024 8	0.022 9		2.074 2	2.068 8		0.011 5	0.010 6
(6, 6) BN-NT		0.016 2	0.015 3		2.048 7	2.046 1		0.007 7	0.007 3
(3, 3) BC$_2$N-NT	0.046 9	0.055 1	0.108 8	2.139 9	2.165 3	2.326 2	0.020 3	0.023 4	0.044 0
(4, 4) BC$_2$N-NT	0.026 9	0.039 6	0.027 3	2.080 7	2.118 8	2.081 8	0.012 6	0.018 2	0.012 8
(5, 5) BC$_2$N-NT	0.015 4	0.020 8	0.018 4	2.046 1	2.065 5	2.055 1	0.007 4	0.010 5	0.008 8
(6, 6) BC$_2$N-NT	0.010 4	0.011 9	0.013 5	2.031 2	2.035 8	2.040 4	0.005 1	0.005 8	0.006 6
(3, 3) C-NT	0.046 8			2.140 3			0.021 5		
(4, 4) C-NT	0.024 9			2.074 8			0.011 9		
(5,5) C-NT	0.015 1			2.045 5			0.007 4		
(6,6) C-NT	0.010 0			2.029 8			0.004 9		

Note: a and b are the re hybridization of s orbital component and p orbital component in hybrid atom respectively, and $\overline{\theta_p^z}$ is the calculated tension of the corresponding carbon nanotube.

can effectively reduce its oxygen. From **Table 3**, it can also be seen that E_g increases by 2.09 eV from (3, 3) to (6, 6) C-NTs, and from (3, 3) to (6, 6) BC$_2$N-NTs. E_g increased by 0.11 eV, but from (3, 3) to (6, 6) BN-NTs, E_g increased by only 0.02 eV, which is almost negligible. This shows that compared with C-NTs and BC$_2$N-NTs, E_g of BN-NTs has almost nothing to do with the diameter. This characteristic of BN-NTs has also been confirmed by relevant experiments: according to the report in literature[21], regardless of the number, diameter and helicity of BN-NTs tubes, they have a stable electron gap (energy gap, ~ 5 eV). Therefore, Pure BN-NTs is a very suitable insulating or semiconductor material.

3.4 Rehybridizations and strains

Similar to spherical fullerenes, carbon nanotubes and their derivatives will produce nonparallel π orbitals due to curved surfaces, so the electron delocalization phenomenon on the surface will be reduced and the conjugation will be destroyed to a certain extent. Because the nanotubes BC$_2$N-NTs and BN-NTs can be regarded that they are formed by the C-C bond in C-NTs through BN substitution reaction. Therefore, these BN heteroatoms will also affect the π bond on carbon nanotubes.

To explore this effect, the rehybridizations and strains of molecular orbitals of nanotubes (n, n) C-NTs, BC2N-NTs and BN-NTs (n = 3, 4, 5, 6) are calculated by POAV program, and the calculation results are listed in **Table 4**, where s^{a}p represents the rehybridization of π orbitals and sp^b represents σ Orbital rehybrid, $\overline{\theta_p^z}$ represents the square of the

pyramid angle between adjacent *p* orbitals, which can qualitatively describe the change of nanotube tension caused by BN hybridization.

It can be seen from **Table 4** that because nanotubes BC₂N-NTs and BN-NTs have different element compositions (C or B or N), each element has its own contribution to the rehybrid and tension of molecular orbitals. This paper takes (3, 3) BN-NT as an example to illustrate this problem. The analysis results of POAV show that the s^ap values of element B and element N of (3, 3) BN-NT are 0.0853 and 0.0683 respectively, the sp^b values are 22,561 and 2.2049 respectively, and the values are 0.0339 and 0.0275 respectively. This shows that compared with element B, the N element in (3, 3) BN-NTs is closer to hybridization, so its contribution to nanotube tension is smaller. However, when the diameters of BC₂N-NTs and BN NTS gradually increase, the contribution of different elements to the rehybridization and tension of molecular orbitals becomes smaller and smaller. For example, the difference of element B and element N's a, b and of nanotube (3, 3) BN-NT are 0.0170, 0.0512 and 0.0064 respectively; however, the difference of element B and element N's a, b and of nanotube (6, 6) BN-NT decrease to 0.0009, 0.0026 and 0.0004 respectively. Although N atom has a pair of lone pair electrons and its electronegativity is greater than that of B atom and C atom, with the increase of tube diameter, the π - π conjugation on the tube wall also gradually increases, and N atom makes these absorbed excess electrons return to the original C atom or B atom through the π - π conjugation system, thus, the electrons of the whole system tend to average among atoms.

We can also see from **Table 4** that with the increase of diameter, the s component (*a*) of π orbital rehybridization (s^ap) of nanotube C-NTs, BC₂N-NTs and BN-NTs, and the P component (*n*) of σ orbital rehybrid (sp^b) decrease gradually with the increase of diameter, which indicates that the increase of diameter will make the C atom or B atom or N atom on the tube gradually close to the classical plane hybrid mode of SP². In addition, with the increase of diameter, the C atom in C-NTs, BC₂N-NTs and BN-NTs, B atom or N atom, the value of also decreases gradually, which indicates that the larger the diameter of the meter tube, the smaller the tension, so that the system is more stable.

4. Conclusion

Based on the AM1 method, the equilibrium geometry, Hat, IP and EA, E_g between the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO), and plane tension, etc. of nanotubes (*n, n*) (*n* = 3, 4, 5, 6) C-NTs, BC₂N-NTs and BN-NTs are systematically studied. The results show that the diameter of nanotubes increases slightly and the stability decreases due to the BN substitution reaction, which is consistent with the calculation results of atomic energy. The results of POAV analysis show that, although B atom, N atom and C atom have different contributions to molecular orbital rehybridization and tube tension in BC₂N-NTs and BN-NTs nanotubes, the difference of rehybridization and tension contribution between these different atoms becomes smaller and smaller with the increase of tube diameter. And the result also show that E_g between the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO) of BN-NTs tubes is not related to the diameter, but E_g of the other two nanotubes, BNC₂-NTs and C-NTs, decreases with the increase of the diameter.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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