ARTICLES

Kekulé Count in Capped Zigzag Boron-Nitride Nanotubes

Cheng-de Lin* and Peng Tang

Department of Automation, Xiamen University, Xiamen, P. R. of China, 361005

Received October 28, 2003

Hemi-$B_{16}N_{16}$ capped zigzag boron-nitride nanotube is introduced, and its Kekulé count is studied. With a bond-allocating and coding scheme, recurrence formulas are established as well as for the case of a hemi-$B_{36}N_{36}$ capped zigzag nanotube. Numerical results reveal that the Kekulé counts increase exponentially with respect to the number of layers in the nanotubes concerned.

I. INTRODUCTION

Kekulé structures in benzenoid hydrocarbons (BHs) are systematically studied in the work of Cyvin and Gutman.[1] The number K of Kekulé structures in a BH (the *Kekulé count*) is an interesting parameter both theoretically and practically. Various techniques and methods have been developed to calculate this index.[2]

Following the discoveries of fullerenes and carbon nanotubes, the attention has also turned to the carbon clusters and tubules. Sachs et al.[3] have investigated the Kekulé count in tubular hydrocarbons. For any type of tubulenes with "open ends", i.e., hydrocarbons whose carbon skeleton is a purely hexagonal system embedded in a cylinder, elementary algorithms of low complexity are developed to calculate K. And for two achiral cases, (n,n) armchair and (n,0) zigzag, respectively, recurrence relations and explicit formulas for K are all presented in details.

Kekulé counts for certain C_{60} fullerenes can be seen in ref 4. With the powerful transfer-matrix scheme, Klein and Zhu[5] have established the analytical formulas of K for the finite-sized elemental benzenoid graphs corresponding to hexagonal coverings on the torus and the Klein bottle. In their work, the scheme is also extended, in principle, to zigzag nanotubes with caps in both ends. Since the number and the shape of hemifullerene caps (composed of pentagons and hexagons) compatible with a carbon nanotube of given diameter and helicity (or simply the parameter(n, m)) vary from one case to another,[6] it is difficult to discuss the "Kekulé count" problem as a whole, according to their complicated geometry.

In this paper, we focus our attention at the boron-nitride nanotubes (BN−NTs) with known geometry, more precisely, only at some zigzag nanotubes with predefined caps composed of squares and hexagons. The choice of the predefined caps will be described in Section II. Section III gives a detailed deduction on calculating K for B_8N_8-capped nanotube. The brief formula for $B_{18}N_{18}$-capped nanotube will be presented in Section IV, and finally, some notes will be made in Section V.

* Corresponding author phone: 86-592-5921436; e-mail: cdlin@xmu.edu.cn.

II. BORON-NITRIDE CLUSTERS AND NANOTUBES

The study of fullerenes began in 1985, when Kroto et al.[7] discovered the C_{60} molecule. In 1991, Iijima[8] reported the discovery of carbon nanotubes. Since then, one of the intriguing questions posed was the possible existence of fullerenes and nanotubes based on other elements rather than carbon. The similarities between B−N and C−C bonds made boron and nitrogen natural candidates to form fullerene and nanotube structures. The existence of these B−N analogues was predicted,[9,10] and then, a method to synthesize pure boron-nitride nanotubes was first reported in 1995.[11]

The problem with exact $(BN)_x$ analogues of finite fullerenes (and respectively, nanotubes with both ends closed), e.g. $B_{30}N_{30}$ with the C_{60} framework, is that the twelve pentagonal rings make it impossible to achieve consistent alternation of B and N atoms: somewhere in such a cage two neighbors belong to the same chemical species. One way to avoid this difficulty is to construct $(BN)_x$ cages based on a different class of trivalent polyhedra, in which six faces are square and all others are hexagonal;[12] each square then replaces two fullerene pentagons and the structure is automatically alternant. Indeed, a trivalent polyhedron $(BN)_x$ made of $x - 4$ hexagons and 6 squares is mathematically possible for any value of $x \geq 4$ with the exception of $x = 5$.

Fowler et al.[13] have made a systematic study of all possible square+hexagon trivalent $(BN)_x$ cages in the range $4 \leq x \leq 30$, constructing the full set by graph theoretical methods and evaluating the stability of each by DFTB (Density Functional based Tight-Binding method). It was found that in this range of x the most stable isomer at each nuclearity was one with isolated squares, whenever such a cage was mathematically possible. This result is a clear counterpart of the well-known isolated-pentagon rule for fullerenes.

The further work of Seifert et al.[14] has revealed the structures of the best isomers of the especially stable clusters $(BN)_x$ in the range $4 \leq x \leq 30$. There are four such clusters with $x = 12$, 16, 22, and 28, respectively (cf. Figure 1). By observation, the hemicluster of $B_{16}N_{16}$ (or $B_{22}N_{22}$) can exactly play the role of caps for (6, 0) zigzag nanotube. (Similarly, $B_{12}N_{12}$ for (3, 3) the armchair nanotube, and $B_{28}N_{28}$ for (6, 3) the chiral one, which will be discussed in our successive

10.1021/ci034239l CCC: \$27.50
Published on Web 12/25/2003

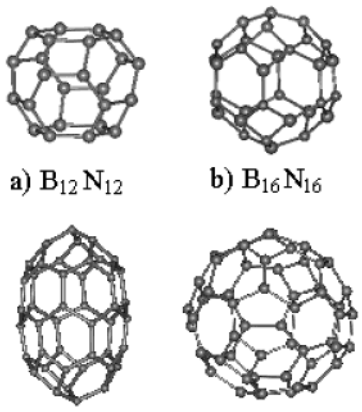

Figure 1. Four stable clusters $(BN)_x$.

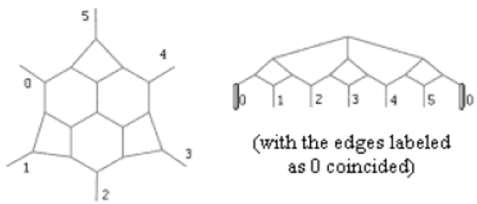

Figure 2. Hemi-$B_{16}N_{16}$ cap and its adjacent sides.

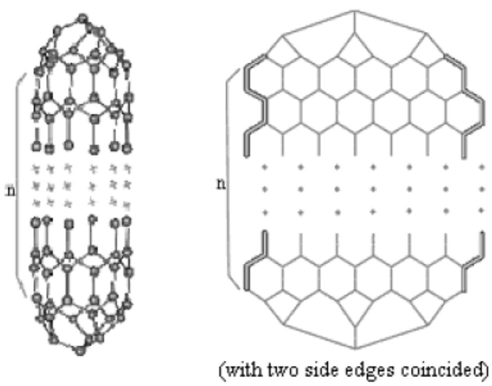

Figure 3. n-layer zigzag BN−NT with hemi-$B_{16}N_{16}$ caps (Geo_1).

works.) Figure 2 presents the “cap” concerned and its adjacent edges with a (6, 0) tubule.

III. KEKULÉ COUNT IN ZIGZAG BN−NTS WITH HEMI-$B_{16}N_{16}$ CAPS

1. Zigzag BN−NTs with Hemi-$B_{16}N_{16}$ Caps. The structure of the element $B_{16}N_{16}$ molecule is shown as Figure 1, and its middle layer is composed of six horizontal side-by-side hexagons, namely “zigzag” in nanotube terminology. Adding another such layer to this structure, we would find that of $B_{22}N_{22}$ (cf. Figure 1). By continuously increasing the number of middle layers, we can easily get a (6, 0)-nanotube structure with both ends closed, shown as Figure 3. We will name it as “zigzag BN−NT with hemi-$B_{16}N_{16}$ caps” or simply “capped zigzag BN−NT”.

According to the relevant position of the two caps at opposite ends of the tubule, there may be two kinds of available structures. We will work mainly with the one shown in Figure 3, which is denoted as “Geo_1”, and give out the relevant result for another geometry (“Geo_2”) at the end of this section.

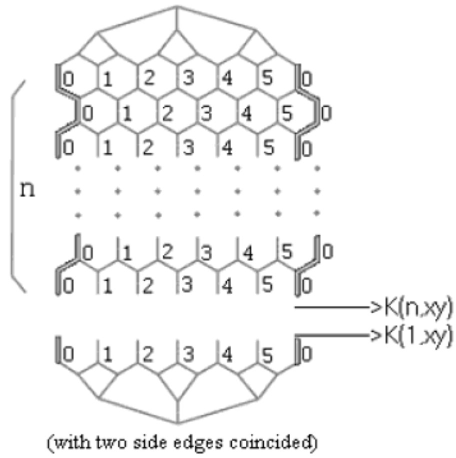

Figure 4. Coding and cut off in Geo_1.

2. Bond Allocating and Coding Scheme. As shown at Figure 2, the cap of our nanotube is composed of 3 hexagons and 3 squares, and it is connected with the tubule by the adjacent edges labeled as 0−5. By assigning these edges as double or single bonds, respectively, we can observe and calculate the Kekulé count of the cap under the relevant boundary condition. We call this scheme “bond allocating”, and its implement is realized by a utility program.

After the bond allocating procedure, we find that the cap will be Kekuléan only when two of its boundary edges are double bonds and the other four are all single ones. There are exactly 15(= C_6^2) such cases.

Let K(xy) be the number of Kekulé structures in the cap when only the two boundary edges, labeled as x and y, respectively, are double bonds. By symmetry, we have

$$K(01)=K(23)=K(45)=4K(12)=K(34)=K(05)=4K(02)=K(24)=K(04)=8$$

$$K(03)=K(25)=K(14)=8K(13)=K(35)=K(15)=6 \qquad (1)$$

Figure 4 shows the coding of all the vertical edges in each middle layer of a zigzag BN−NT with hemi-$B_{16}N_{16}$ caps. Let n be the number of middle layers and K(n) be the Kekulé count of the total nanotube. With cutting off the tubule horizontally as described in Figure 4, we get two separated parts (upper and lower). Let K(n, xy) be the number of Kekulé structures in the upper part when the nth layer has exactly two double bonds, numbered x and y, respectively. The lower part can be treated as a cap with its adjacent edges and may be simply denoted as K′(1, xy) = K(1, xy). By symmetry, we have

$$K(n,01)=K(n,23)=K(n,45)K(n,12)=K(n,34)=K(n,05)K(n,02)=K(n,24)=K(n,04)$$

$$K(n,03)=K(n,25)=K(n,14)K(n,13)=K(n,35)=K(n,15) \qquad (2)$$

3. Recurrence Relations. By enumeration, we have verified that, in the case where two vertical edges in the kth layer are double bonds and the remaining four are singles, the (k-1)th layer must have the same number of double and single bonds. To transfer the double bonds from the kth layer to the (k-1)th layer correctly, by assumption, we should distinguish the two coding modes, i.e., k odd or even, as shown in Figure 5.

Consider the distribution of the double bonds in the neighboring layers. The translation of double bonds from the even layer to the odd layer could be coded in details as following:

$$01 \rightarrow 01, 12, 13, 14, 15$$

$$12 \rightarrow 02, 12, 23, 24, 25$$

$$02 \rightarrow 01, 13, 14, 15, 02, 23, 24, 25$$

$$03 \rightarrow 01, 14, 15, 02, 24, 25, 03, 34, 35$$

$$13 \rightarrow 02, 12, 24, 25, 03, 13, 34, 35$$

By symmetry, they can also be simplified as

$$01 \rightarrow 01, 12, 2\times(13), 03$$

$$12 \rightarrow 2\times(02), 12, 01, 03$$

$$02 \rightarrow 2\times(01), 2\times(13), 2\times(03), 2\times(02)$$

$$03 \rightarrow 01, 3\times(03), 2\times(13), 2\times(02), 12$$

$$13 \rightarrow 2\times(02), 2\times(12), 2\times(03), 2\times(13) \qquad (3)$$

where p×(xy) denotes xy for p times.

Similarly, for the translation of double bonds from the odd layer to the even layer, we have

$$01 \rightarrow 2\times(02), 12, 01, 03$$

$$12 \rightarrow 01, 12, 2\times(13), 03$$

$$02 \rightarrow 2\times(02), 2\times(12), 2\times(03), 2\times(13)$$

$$03 \rightarrow 01, 3\times(03), 2\times(13), 2\times(02), 12$$

$$13 \rightarrow 2\times(01), 2\times(13), 2\times(03), 2\times(02) \qquad (4)$$

Let K1(n) = K(n,01), K2(n) = K(n,12), K3(n) = K(n,-02), K4(n) = K(n,03), K5(n) = K(n,13), by (1)−(4), we can get the following recurrences:

$$K1(1) = 4K2(1) = 4,\ K3(1) = 8,\ K4(1) = 8,\ K5(1) = 6 \qquad (5)$$

for odd n (n>1)

$$K1(n) = K1(n\text{-}1) + K2(n\text{-}1) + 2\times K3(n\text{-}1) + K4(n\text{-}1)$$

$$K2(n) = K1(n\text{-}1) + K2(n\text{-}1) + K4(n\text{-}1) + 2\times K5(n\text{-}1)$$

$$K3(n) = 2\times K2(n\text{-}1) + 2\times K3(n\text{-}1) + 2\times K4(n\text{-}1) + 2\times K5(n\text{-}1)$$

$$K4(n) = K1(n\text{-}1) + K2(n\text{-}1) + 2\times K3(n\text{-}1) + 3\times K4(n\text{-}1) + 2\times K5(n\text{-}1)$$

$$K5(n) = 2\times K1(n\text{-}1) + 2\times K3(n\text{-}1) + 2\times K4(n\text{-}1) + 2\times K5(n\text{-}1) \qquad (6)$$

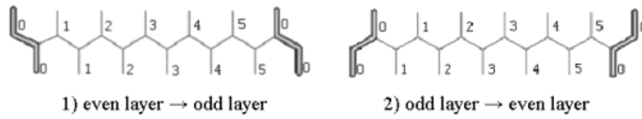

Figure 5. Two coding modes for the translation of double bonds.

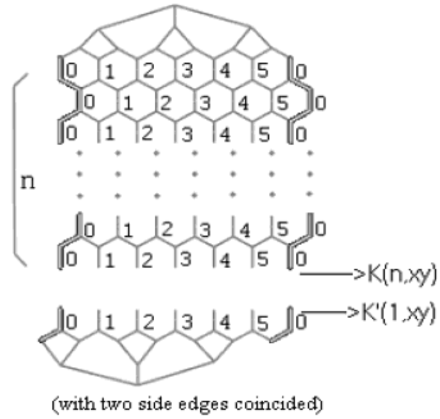

Figure 6. Another geometry of zigzag BN−NT with hemi-$B_{16}N_{16}$ caps (Geo_2).

for even n

$$K1(n) = K1(n\text{-}1) + K2(n\text{-}1) + K4(n\text{-}1) + 2\times K5(n\text{-}1)$$

$$K2(n) = K1(n\text{-}1) + K2(n\text{-}1) + 2\times K3(n\text{-}1) + K4(n\text{-}1)$$

$$K3(n) = 2\times K1(n\text{-}1) + 2\times K3(n\text{-}1) + 2\times K4(n\text{-}1) + 2\times K5(n\text{-}1)$$

$$K4(n) = K1(n\text{-}1) + K2(n\text{-}1) + 2\times K3(n\text{-}1) + 3\times K4(n\text{-}1) + 2\times K5(n\text{-}1)$$

$$K5(n) = 2\times K3(n\text{-}1) + 2\times K2(n\text{-}1) + 2\times K4(n\text{-}1) + 2\times K5(n\text{-}1) \qquad (7)$$

By joining the upper and lower parts together, and with the symmetry, we conclude that

$$K(n) = 3\times K(1,01)\times K(n,01) + 3\times K(1,12)\times K(n,12) + 3\times K(1,02)\times K(n,02) + 3\times K(1,03)\times K(n,03) + 3\times K(1,13)\times K(n,13)$$

or **K(n) = 12**·K1(n) + 12·K2(n) + 24·K3(n) + 24·K4(n) + 18·K5(n), where **K1(n), K2(n), K3(n), K4(n), K5(n)** satisfying (5), (6), and (7).

4. Result of Another Geometry. The zigzag BN−NT with hemi-$B_{16}N_{16}$ caps can also take another geometry, noted as Geo_2 and shown as Figure 6. This structure has the same Kekulé count with Geo_1 as n is even, but when n is odd, their Kekulé counts are not equal. In fact, for this structure

$$K(n) = 3\times K'(1,01)\times K(n,01) + 3\times K'(1,12)\times K(n,12) + 3\times K\cdot(1,02)\times K(n,02) + 3\times K\cdot(1,03)\times K(n,03) + 3\times K\cdot(1,13)\times K(n,13)$$

where K·(1,01) = 4, K·(1,12) = 4, K·(1,02) = 6, K·(1,03) = 8, K·(1,13) = 8 (cf. Figure 6) thus, with the same K1(n), K2(n), K3(n), K4(n) and K5(n) as above, we have

$$\mathbf{K(n) = 12\cdot K1(n) + 12\cdot K2(n) + 18\cdot K3(n) + 24\cdot K4(n) + 24\cdot K5(n)}$$

Table 1. Some Numeric Results of K

no. of layers	Geo_1(**K**(**n**))	Geo_2(**K**(**n**))
1	588	576
2	**4 344**	**4 344**
3	32 448	32 400
4	**242 016**	**242 016**
5	1 806 528	1 806 336
6	**13 483 392**	**13 483 392**
7	100 641 792	100 641 024
8	**751 197 696**	**751 197 696**

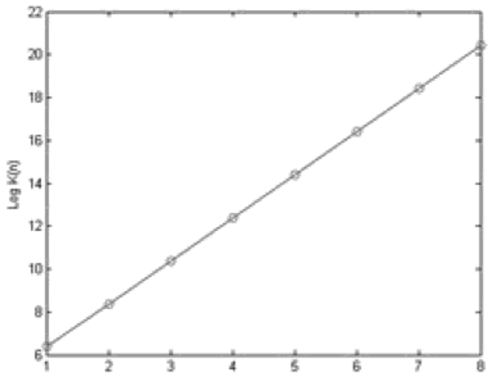

Figure 7. Exponential tendency of K for hemi-B16N16 capped zigzag BN−NT.

For the hemi-$B_{16}N_{16}$ capped zigzag BN−NT with **n** layers (**n** varying from 1 to 8), numeric results of Kekulé count K are presented in Table 1, and the exponentially increasing tendency of K with respect to **n** is shown evidently in Figure 7.

IV. KEKULÉ COUNT IN ZIGZAG BN−NTS WITH HEMI-$B_{36}N_{36}$ CAPS

For the $(BN)_x$ clusters where $x > 30$, it is interesting to investigate the molecule $B_{36}N_{36}$ and its related nanotubes[15] (cf. Figure 8). With the same terminology as in the above section, a middle layer concerned here is composed of nine horizontal side-by-side hexagons, and thus, it corresponds to some (9, 0)-zigzag NT. The cap of this nanotube is composed of 7 hexagons and 3 squares, shown as Figure 9. According to the relevant position of the two caps at opposite ends of the tubule, there may be three kinds of available structures, named as Geo_1, Geo_2, and Geo_3, respectively (cf. Figure 10).

As a zigzag nanotube, the deduction of the recurrence formulas for the Kekulé count in hemi-$B_{36}N_{36}$ capped BN−NT is similar with that in the above section. By coding the

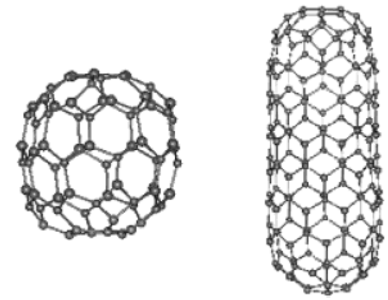

Figure 8. $B_{36}N_{36}$ and related BN−NT.

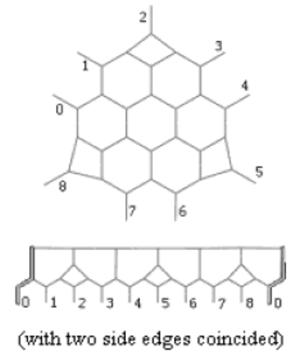

Figure 9. Hemi-$B_{36}N_{36}$ cap and its adjacent edges.

Table 2. Some Numeric Results of K (Hemi-$B_{36}N_{36}$ Capped)

no. of layers	Geo_1	Geo_2	Geo_3
1	24 300	**23 175**	**23 175**
2	**451 575**	**451 575**	455 625
3	8 772 300	**8 681 175**	**8 681 175**
4	**167 360 175**	**167 360 175**	167 961 600
5	3 228 504 075	**3 220 138 800**	**3 220 138 800**
6	**61 967 496 825**	**61 967 496 825**	62 038 355 625
7	11 929 112 326 675	**1 192 088 593 125**	**1 192 088 593 125**
8	**22 931 825 296 275**	**22 931 825 296 275**	22 939 597 620 900

9 vertical edges in each layer as number 0−8, and using bond allocating, we find that the cap will be Kekuléan only in the cases where three of its boundary edges are double bonds and the remaining six are all single ones. Furthermore, when three vertical edges in the kth layer are double bonds and the other six are singles, the (k-1)th layer must have the same number of double and single bonds. These can be easily coded and deduced as in the case of section III. The detailed calculation is omitted, and all the recurrence formulas for three isomers can be found in the Appendix.

By programming, it is not difficult to perform the procedure, and we have some numeric results for this

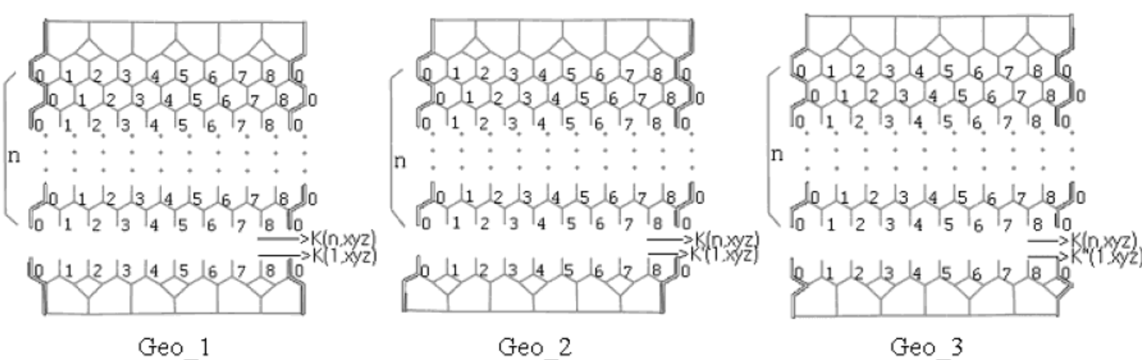

Figure 10. Three structures of zigzag BN−NT with hemi-$B_{36}N_{36}$ caps.

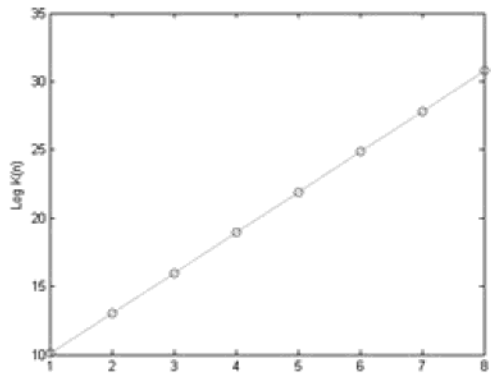

Figure 11. Exponential tendency of K for hemi-$B_{36}N_{36}$ capped zigzag BN−NT.

problem, as shown in Table 2. By symmetry, it is well predicted that the values for Geo_2 are coincided either with that of Geo_1 or that of Geo_3. As in the case of hemi-$B_{16}N_{16}$ capped zigzag BN−NT, the exponentially increasing tendency of K with respect to **n** is also demonstrated in Figure 11.

V. NOTES

For the Kekulé count in zigzag nanotubes with predefined caps (composed of squares and hexagons), a scheme called bond allocating is proposed in this paper, to decide the bond-distribution on the cap and its boundary. By the transfer-relation of the double bonds along the tubule layers and a proper coding, two such capped zigzag nanotubes (with hemi-$B_{16}N_{16}$ caps and hemi-$B_{36}N_{36}$ caps, respectively) have been treated. Detailed deduction for the recurrence formulas is given in section III. Some numerical results of K for both cases are also presented, which demonstrate the slight difference between the isomers for each case. The exponentially increasing tendency of the Kekulé count K with respect to the layer-number **n** is also revealed. With the help of the PC utility program, one can implement the calculation of K for similar nanotubes with suitable diameter.

The method used in this paper is, in principle, valid for armchair nanotubes, such as (3, 3) BN−NTs with hemi-$B_{12}N_{12}$ caps already mentioned in section II. The detailed work will be published in our next paper.

For the four especially stable clusters[14] $(BN)_x$ in the range $4 \le x \le 30$, only the case of $B_{28}N_{28}$ remains unsolved. By observation, it corresponds to some nanotubes of (6, 3)-chiral type. Because of the more complicated symmetry induced by chirality, further research is needed to simplify the solution.

All the work mentioned in this paper can be extended to the case of closed pure carbon nanotubes (with caps composed of pentagons and hexagons) without much difficulty, on the condition that the geometry of the caps is predefined and the diameter of the tubule is reasonable when working on PC.

ACKNOWLEDGMENT

We are grateful to Qian-er Zhang and Fuji Zhang for profitable discussions to this subject. This work is supported by the Natural Science Foundation of Fujian Province, China (Grant No. A0010001). The first author Lin is also supported by NSFC (Grant No. 10371102).

APPENDIX

Recurrence formulas for the Kekulé count in zigzag BN−NTs with hemi-$B_{36}N_{36}$ caps:

(1) Geo_1

$$K(n) = 15\cdot K1(n)+15\cdot K2(n)+30\cdot K4(n)+30\cdot K5(n)+15\cdot K6(n)+15\cdot K7(n)+30\cdot K8(n)+30\cdot K9(n)+5\cdot K10(n)+45\cdot K11(n)+30\cdot K12(n)+30\cdot K13(n)+45\cdot K14(n)+45\cdot K15(n)+45\cdot K16(n)+45\cdot K17(n)+45\cdot K18(n)+45\cdot K19(n)+60\cdot K20(n)+60\cdot K21(n)+60\cdot K22(n)+60\cdot K23(n)+75\cdot K24(n)+75\cdot K25(n)+90\cdot K26(n)+90\cdot K27(n)+35\cdot K28(n)+35\cdot K29(n)+20\cdot K30(n)$$

Geo_2

$$K(n) = 15\cdot K2(n)+15\cdot K3(n)+15\cdot K4(n)+30\cdot K5(n)+30\cdot K6(n)+30\cdot K7(n)+30\cdot K8(n)+15\cdot K9(n)+30\cdot K10(n)+45\cdot K11(n)+45\cdot K12(n)+45\cdot K13(n)+45\cdot K14(n)+30\cdot K15(n)+45\cdot K16(n)+45\cdot K17(n)+45\cdot K18(n)+60\cdot K19(n)+60\cdot K20(n)+45\cdot K21(n)+90\cdot K22(n)+75\cdot K23(n)+60\cdot K24(n)+90\cdot K25(n)+75\cdot K26(n)+60\cdot K27(n)+20\cdot K28(n)+35\cdot K29(n)+35\cdot K30(n)$$

Geo_3

$$K(n) = 15\cdot K1(n)+15\cdot K3(n)+30\cdot K4(n)+15\cdot K5(n)+30\cdot K6(n)+30\cdot K7(n)+15\cdot K8(n)+30\cdot K9(n)+45\cdot K10(n)+30\cdot K11(n)+45\cdot K12(n)+45\cdot K13(n)+30\cdot K14(n)+45\cdot K15(n)+45\cdot K16(n)+45\cdot K17(n)+45\cdot K18(n)+60\cdot K19(n)+45\cdot K20(n)+60\cdot K21(n)+75\cdot K22(n)+90\cdot K23(n)+90\cdot K24(n)+60\cdot K25(n)+60\cdot K26(n)+75\cdot K27(n)+35\cdot K28(n)+20\cdot K29(n)+35\cdot K30(n)$$

where **K1(n)−K30(n)** satisfying **(8)**, **(9)**, and **(10)**

$$K1(1)=5;\ K2(1)=5;\ K3(1)=0;\ K4(1)=10;\ K5(1)=10;\ K6(1)=5$$

$$K7(1)=5;\ K8(1)=10;\ K9(1)=10;\ K10(1)=15;\ K11(1)=15;\ K12(1)=10$$

$$K13(1)=10;\ K14(1)=15;\ K15(1)=15;\ K16(1)=15;\ K17(1)=15;\ K18(1)=15$$

$$K19(1)=15;\ K20(1)=20;\ K21(1)=20;\ K22(1)=20;\ K23(1)=20;\ K24(1)=25$$

$$K25(1)=25;\ K26(1)=30;\ K27(1)=30;\ K28(1)=35;\ K29(1)=35;\ K30(1,)=20 \quad (8)$$

when n is odd (n > 1)

$$K1(n)= K1(n-1)+ K2(n-1)+K4(n-1)+ K5(n-1)+ K10(n-1)+ K11(n-1)+ K16(n-1)$$

$$K2(n)= K2(n-1)+ K3(n-1)+ K7(n-1)+ K8(n-1)+ K13(n-1)+ K14(n-1)+ K18(n-1)$$

$$K3(n)= K1(n-1)+ K3(n-1)+ K6(n-1)+ K9(n-1)+ K12(n-1)+ K15(n-1)+ K17(n-1)$$

$$K4(n)= K2(n-1)+K4(n-1)+K5(n-1)+K7(n-1)+ K8(n-1)+K10(n-1)+ K11(n-1)+ K16(n-1)+K19(n-1) + K20(n-1)+K22(n-1)+K25(n-1)$$

$$K5(n)=K2(n-1)+K4(n-1)+K5(n-1)+K7(n-1)+ K8(n-1)+K13(n-1)+K14(n-1)+K18(n-1)+K20(n-1)+ K21(n-1)+K26(n-1)+K27(n-1)$$

$$K6(n)=K1(n-1)+K4(n-1)+K5(n-1)+K6(n-1)+ K9(n-1)+K12(n-1)+K15(n-1)+K17(n-1)+K20(n-1)+ K21(n-1)+K26(n-1)+K27(n-1)$$

$$K7(n)= K3(n-1)+K6(n-1)+K7(n-1)+K8(n-1)+ K9(n-1)+K12(n-1)+K15(n-1)+K17(n-1)+K19(n-1)+ K20(n-1)+K22(n-1)+ K25(n-1)$$

$$K8(n)=K3(n-1)+K6(n-1)+K7(n-1)+K8(n-1)+ K9(n-1)+K13(n-1)+K14(n-1)+K18(n-1)+K19(n-1) + K21(n-1)+K23(n-1)+K24(n-1)$$

$$K9(n)= K1(n-1)+K4(n-1)+K5(n-1)+K6(n-1)+ K9(n-1)+K10(n-1)+K11(n-1)+K16(n-1)+K19(n-1) + K21(n-1) +K23(n-1)+K24(n-1)$$

$$K10(n)= K2(n-1)+K5(n-1)+K8(n-1)+K10(n-1)+ 2\times K11(n-1)+K14(n-1)+K16(n-1)+K19(n-1) + K20(n-1)+K22(n-1)+2\times K25(n-1)+K26(n-1)+ K29(n-1)$$

$$K11(n)=K2(n-1)+K5(n-1)+K8(n-1)+K11(n-1)+ K13(n-1)+2\times K14(n-1)+K18(n-1)+K20(n-1) + K21(n-1)+K25(n-1)+2\times K26(n-1)+K27(n-1)+ K29(n-1)$$

$$K12(n)= K1(n-1)+K4(n-1)+K9(n-1)+K10(n-1)+ K12(n-1)+2\times K15(n-1)+K17(n-1) + K20(n-1)+ K21(n-1)+K24(n-1)+K26(n-1)+2\times K27(n-1)+ K28(n-1)$$

$$K13(n)=K3(n-1)+K6(n-1)+K7(n-1)+2\times K12(n-1)+ K13(n-1)+K15(n-1)+K17(n-1)+K19(n-1) + K20(n-1) +2\times K22(n-1)+K23(n-1)+K25(n-1)+ K30(n-1)$$

$$K14(n)= K3(n-1)+K6(n-1)+K7(n-1)+K12(n-1)+ 2\times K13(n-1)+K14(n-1)+K18(n-1)+K19(n-1) + K21(n-1)+K22(n-1)+2\times K23(n-1)+K24(n-1)+ K30(n-1)$$

$$K15(n)=K1(n-1)+K4(n-1)+K9(n-1)+2\times K10(n-1)+ K11(n-1)+K15(n-1)+K16(n-1)+K19(n-1) +K21(n-1)+ K23(n-1)+2\times K24(n-1)+K27(n-1)+K28(n-1)$$

$$K16(n)=K2(n-1)+K5(n-1)+K8(n-1)+K11(n-1)+ K14(n-1)+K16(n-1)+K17(n-1)+K18(n-1)+K20(n-1)+ K22(n-1)+2\times K25(n-1)+2\times K26(n-1)+K27(n-1)+ K29(n-1)$$

$$K17(n)=K1(n-1)+K4(n-1)+K9(n-1)+K10(n-1)+ K15(n-1)+K16(n-1)+K17(n-1)+K18(n-1)+K21(n-1) + K23(n-1)+2\times K24(n-1)+K26(n-1)+2\times K27(n-1)+ K28(n-1)$$

$$K18(n)=K3(n-1)+K6(n-1)+K7(n-1)+K12(n-1)+ K13(n-1)+K16(n-1)+K17(n-1)+K18(n-1)+K19(n-1)+ 2\times K22(n-1)+2\times K23(n-1)+K24(n-1)+K25(n-1)+ K30(n-1)$$

$$K19(n)=K5(n-1)+K6(n-1)+K8(n-1)+K9(n-1)+ K11(n-1)+K12(n-1)+K14(n-1)+K15(n-1)+K17(n-1)+ K19(n-1)+2\times K20(n-1)+K21(n-1)+K22(n-1)+ 2\times K25(n-1)+2\times K26(n-1)+K27(n-1)+K29(n-1)$$

$$K20(n)=K4(n-1)+K7(n-1)+K8(n-1)+K9(n-1)+ K10(n-1)+K13(n-1)+K14(n-1)+K15(n-1)+K18(n-1) + K19(n-1)+K20(n-1)+2\times K21(n-1)+K23(n-1)+ 2\times K24(n-1)+K26(n-1)+2\times K27(n-1)+K28(n-1)$$

$$K21(n)=K4(n-1)+K5(n-1)+K6(n-1)+K7(n-1)+ K10(n-1)+K11(n-1)+K12(n-1)+K13(n-1)+K16(n-1) + 2\times K19(n-1)+K20(n-1)+K21(n-1)+2\times K22(n-1)+ 2\times K23(n-1)+K24(n-1)+K25(n-1)+ K30(n-1)$$

$$K22(n)=K8(n-1)+K9(n-1)+K12(n-1)+K14(n-1)+ 2\times K15(n-1)+2\times K17(n-1)+K18(n-1) +2\times K20(n-1) + K21(n-1)+K22(n-1)+K24(n-1)+2\times K25(n-1)+ 3\times K26(n-1)+3\times K27(n-1)+K28(n-1)+K29(n-1)$$

$$K23(n)=K5(n-1)+K6(n-1)+K11(n-1)+2\times K12(n-1)+ K15(n-1)+K16(n-1)+2\times K17(n-1)+K19(n-1) + 2\times K20(n-1)+3\times K22(n-1)+K23(n-1)+3\times K25(n-1)+ 2\times K26(n-1)+K27(n-1)+ K29(n-1)+K30(n-1)$$

$$K24(n)=K5(n-1)+K6(n-1)+K10(n-1)+2\times K11(n-1)+ K12(n-1)+2\times K16(n-1)+K17(n-1)+2\times K19(n-1)+ K20(n-1)+3\times K22(n-1)+2\times K23(n-1)+K24(n-1)+ 3\times K25(n-1)+K26(n-1)+K29(n-1)+K30(n-1)$$

$$K25(n)=K8(n-1)+K9(n-1)+K13(n-1)+2\times K14(n-1)+ K15(n-1)+K17(n-1)+2\times K18(n-1)+K20(n-1)+ 2\times K21(n-1)+K23(n-1)+2\times K24(n-1)+K25(n-1)+ 3\times K26(n-1)+3\times K27(n-1)+K28(n-1) +K29(n-1)$$

$$K26(n)=K4(n-1)+K7(n-1)+K10(n-1)+2\times K13(n-1)+ K14(n-1)+K16(n-1)+2\times K18(n-1)+K19(n-1)+ 2\times K21(n-1)+K22(n-1)+3\times K23(n-1)+3\times K24(n-1)+ K26(n-1)+2\times K27(n-1)+K28(n-1) +K30(n-1)$$

$$K27(n)=K4(n-1)+K7(n-1)+2\times K10(n-1)+K11(n-1)+ K13(n-1)+2\times K16(n-1)+K18(n-1)+2\times K19(n-1)+ K21(n-1)+2\times K22(n-1)+3\times K23(n-1)+3\times K24(n-1)+ K25(n-1)+K27(n-1)+K28(n-1)+K30(n-1)$$

$$K28(n)=3\times K10(n-1)+3\times K11(n-1)+3\times K16(n-1)+ 3\times K19(n-1)+3\times K22(n-1)+3\times K23(n-1)+ 3\times K24(n-1)+3\times K25(n-1)+K28(n-1)+K29(n-1)+ K30(n-1)$$

$$K29(n)=3\times K13(n-1)+3\times K14(n-1)+3\times K18(n-1)+3\times K21(n-1)+3\times K23(n-1)+3\times K24(n-1)+3\times K26(n-1)+3\times K27(n-1)+K28(n-1)+K29(n-1)+K30(n-1)$$

$$K30(n)=3\times K12(n-1)+3\times K15(n-1)+3\times K17(n-1)+3\times K20(n-1)+3\times K22(n-1)+3\times K25(n-1)+3\times K26(n-1)+3\times K27(n-1)+K28(n-1)+K29(n-1)+K30(n-1) \quad (9)$$

when n is even

$$K1(n)=K1(n-1)+K3(n-1)+K6(n-1)+K9(n-1)+K12(n-1)+K15(n-1)+K17(n-1)$$

$$K2(n)=K1(n-1)+K2(n-1)+K4(n-1)+K5(n-1)+K10(n-1)+K11(n-1)+K16(n-1)$$

$$K3(n)=K2(n-1)+K3(n-1)+K7(n-1)+K8(n-1)+K13(n-1)+K14(n-1)+K18(n-1)$$

$$K4(n)=K1(n-1)+K4(n-1)+K5(n-1)+K6(n-1)+K9(n-1)+K12(n-1)+K15(n-1)+K17(n-1)+K20(n-1)+K21(n-1)+K26(n-1)+K27(n-1)$$

$$K5(n)=K1(n-1)+K4(n-1)+K5(n-1)+K6(n-1)+K9(n-1)+K10(n-1)+K11(n-1)+K16(n-1)+K19(n-1)+K21(n-1)+K23(n-1)+K24(n-1)$$

$$K6(n)=K3(n-1)+K6(n-1)+K7(n-1)+K8(n-1)+K9(n-1)+K13(n-1)+K14(n-1)+K18(n-1)+K19(n-1)+K21(n-1)+K23(n-1)+K24(n-1)$$

$$K7(n)=K2(n-1)+K4(n-1)+K5(n-1)+K7(n-1)+K8(n-1)+K13(n-1)+K14(n-1)+K18(n-1)+K20(n-1)+K21(n-1)+K26(n-1)+K27(n-1)$$

$$K8(n)=K2(n-1)+K4(n-1)+K5(n-1)+K7(n-1)+K8(n-1)+K10(n-1)+K11(n-1)+K16(n-1)+K19(n-1)+K20(n-1)+K22(n-1)+K25(n-1)$$

$$K9(n)=K3(n-1)+K6(n-1)+K7(n-1)+K8(n-1)+K9(n-1)+K12(n-1)+K15(n-1)+K17(n-1)+K19(n-1)+K20(n-1)+K22(n-1)+K25(n-1)$$

$$K10(n)=K1(n-1)+K4(n-1)+K9(n-1)+K10(n-1)+K12(n-1)+2\times K15(n-1)+K17(n-1)+K20(n-1)+K21(n-1)+K24(n-1)+K26(n-1)+2\times K27(n-1)+K28(n-1)$$

$$K11(n)=K1(n-1)+K4(n-1)+K9(n-1)+2\times K10(n-1)+K11(n-1)+K15(n-1)+K16(n-1)+K19(n-1)+K21(n-1)+K23(n-1)+2\times K24(n-1)+K27(n-1)+K28(n-1)$$

$$K12(n)=K3(n-1)+K6(n-1)+K7(n-1)+K12(n-1)+2\times K13(n-1)+K14(n-1)+K18(n-1)+K19(n-1)+K21(n-1)+K22(n-1)+2\times K23(n-1)+K24(n-1)+K30(n-1)$$

$$K13(n)=K2(n-1)+K5(n-1)+K8(n-1)+K11(n-1)+K13(n-1)+2\times K14(n-1)+K18(n-1)+K20(n-1)+K21(n-1)+K25(n-1)+2\times K26(n-1)+K27(n-1)+K29(n-1)$$

$$K14(n)=K2(n-1)+K5(n-1)+K8(n-1)+K10(n-1)+2\times K11(n-1)+K14(n-1)+K16(n-1)+K19(n-1)+K20(n-1)+K22(n-1)+2\times K25(n-1)+K26(n-1)+K29(n-1)$$

$$K15(n)=K3(n-1)+K6(n-1)+K7(n-1)+2\times K12(n-1)+K13(n-1)+K15(n-1)+K17(n-1)+K19(n-1)+K20(n-1)+2\times K22(n-1)+K23(n-1)+K25(n-1)+K30(n-1)$$

$$K16(n)=K1(n-1)+K4(n-1)+K9(n-1)+K10(n-1)+K15(n-1)+K16(n-1)+K17(n-1)+K18(n-1)+K21(n-1)+K23(n-1)+2\times K24(n-1)+K26(n-1)+2\times K27(n-1)+K28(n-1)$$

$$K17(n)=K3(n-1)+K6(n-1)+K7(n-1)+K12(n-1)+K13(n-1)+K16(n-1)+K17(n-1)+K18(n-1)+K19(n-1)+2\times K22(n-1)+2\times K23(n-1)+K24(n-1)+K25(n-1)+K30(n-1)$$

$$K18(n)=K2(n-1)+K5(n-1)+K8(n-1)+K11(n-1)+K14(n-1)+K16(n-1)+K17(n-1)+K18(n-1)+K20(n-1)+K22(n-1)+2\times K25(n-1)+2\times K26(n-1)+K27(n-1)+K29(n-1)$$

$$K19(n)=K4(n-1)+K7(n-1)+K8(n-1)+K9(n-1)+K10(n-1)+K13(n-1)+K14(n-1)+K15(n-1)+K18(n-1)+K19(n-1)+K20(n-1)+2\times K21(n-1)+K23(n-1)+2\times K24(n-1)+K26(n-1)+2\times K27(n-1)+K28(n-1)$$

$$K20(n)=K4(n-1)+K5(n-1)+K6(n-1)+K7(n-1)+K10(n-1)+K11(n-1)+K12(n-1)+K13(n-1)+K16(n-1)+2\times K19(n-1)+K20(n-1)+K21(n-1)+2\times K22(n-1)+2\times K23(n-1)+K24(n-1)+K25(n-1)+K30(n-1)$$

$$K21(n)=K5(n-1)+K6(n-1)+K8(n-1)+K9(n-1)+K11(n-1)+K12(n-1)+K14(n-1)+K15(n-1)+K17(n-1)+K19(n-1)+2\times K20(n-1)+K21(n-1)+K22(n-1)+2\times K25(n-1)+2\times K26(n-1)+K27(n-1)+K29(n-1)$$

$$K22(n)=K4(n-1)+K7(n-1)+K10(n-1)+2\times K13(n-1)+K14(n-1)+K16(n-1)+2\times K18(n-1)+K19(n-1)+2\times K21(n-1)+K22(n-1)+3\times K23(n-1)+3\times K24(n-1)+K26(n-1)+2\times K27(n-1)+K28(n-1)+K30(n-1)$$

$$K23(n)=K8(n-1)+K9(n-1)+K13(n-1)+2\times K14(n-1)+K15(n-1)+K17(n-1)+2\times K18(n-1)+K20(n-1)+2\times K21(n-1)+K23(n-1)+2\times K24(n-1)+K25(n-1)+3\times K26(n-1)+3\times K27(n-1)+K28(n-1)+K29(n-1)$$

$$K24(n)=K8(n-1)+K9(n-1)+K12(n-1)+K14(n-1)+2\times K15(n-1)+2\times K17(n-1)+K18(n-1)+2\times K20(n-1)+K21(n-1)+K22(n-1)+K24(n-1)+2\times K25(n-1)+3\times K26(n-1)+3\times K27(n-1)+K28(n-1)+K29(n-1)$$

$$K25(n)=K4(n-1)+K7(n-1)+2\times K10(n-1)+K11(n-1)+K13(n-1)+2\times K16(n-1)+K18(n-1)+2\times K19(n-1)+K21(n-1)+2\times K22(n-1)+3\times K23(n-1)+3\times K24(n-1)+K25(n-1)+K27(n-1)+K28(n-1)+K30(n-1)$$

$$K26(n) = K5(n\text{-}1)+K6(n\text{-}1)+K10(n\text{-}1)+2\times K11(n\text{-}1)+ K12(n\text{-}1)+2\times K16(n\text{-}1)+K17(n\text{-}1)+2\times K19(n\text{-}1)+ K20(n\text{-}1)+3\times K22(n\text{-}1)+2\times K23(n\text{-}1)+K24(n\text{-}1)+ 3\times K25(n\text{-}1)+K26(n\text{-}1)+K29(n\text{-}1)+K30(n\text{-}1)$$

$$K27(n) = K5(n\text{-}1)+K6(n\text{-}1)+K11(n\text{-}1)+2\times K12(n\text{-}1)+ K15(n\text{-}1)+K16(n\text{-}1)+2\times K17(n\text{-}1)+K19(n\text{-}1)+ 2\times K20(n\text{-}1)+3\times K22(n\text{-}1)+K23(n\text{-}1)+3\times K25(n\text{-}1)+ 2\times K26(n\text{-}1)+K27(n\text{-}1)+ K29(n\text{-}1)+K30(n\text{-}1)$$

$$K28(n) = 3\times K12(n\text{-}1)+3\times K15(n\text{-}1)+3\times K17(n\text{-}1)+ 3\times K20(n\text{-}1)+3\times K22(n\text{-}1)+3\times K25(n\text{-}1) + 3\times K26(n\text{-}1)+3\times K27(n\text{-}1)+K28(n\text{-}1)+K29(n\text{-}1)+ K30(n\text{-}1)$$

$$K29(n) = 3\times K10(n\text{-}1)+3\times K11(n\text{-}1)+3\times K16(n\text{-}1)+ 3\times K19(n\text{-}1)+3\times K22(n\text{-}1)+3\times K23(n\text{-}1) + 3\times K24(n\text{-}1)+3\times K25(n\text{-}1)+K28(n\text{-}1)+K29(n\text{-}1)+ K30(n\text{-}1)$$

$$K30(n)=3\times K13(n\text{-}1)+3\times K14(n\text{-}1)+3\times K18(n\text{-}1)+ 3\times K21(n\text{-}1)+3\times K23(n\text{-}1)+3\times K24(n\text{-}1) + 3\times K26(n\text{-}1)+3\times K27(n\text{-}1)+K28(n\text{-}1)+K29(n\text{-}1)+ K30(n\text{-}1) \quad (10)$$

REFERENCES AND NOTES

(1) Cyvin, S. J.; Gutman, I. *Kekulé Structures in Benzenoid Hydrocarbons*; Lecture Notes in Chemistry, 46, Springer-Verlag: Berlin, 1988.

(2) John, P.; Sachs, H. Calculating the Numbers of Perfect Matchings and of Spanning Trees, Pauling's Orders, the Characteristic Polynomial, and the Eigenvectors of a Benzenoid System. In *Advances in the Theory of Benzenoid Hydrocarbons;* Gutman, I., Cyvin, S. J., Ed.; Topics in Current Chemistry, 1990; Vol. 153, pp 145−179.

(3) Sachs, H.; Hansen, P.; Zheng, M. Kekulé Count in Tubular Hydrocarbons. *Match* **1996**, *33*, 169−241.

(4) Austin, S. J.; Fowler, P. W.; Hansen, P.; Manolopoulos, D. E.; Zheng, M. Fullerene Isomers of C_{60}. Kekulé Counts versus Stability. *Chem. Phys. Lett.* **1994**, *228*, 478−484.

(5) Klein, D. J.; Zhu, H. Resonance in Elemental Benzenoids, *Discuss. Appl. Math.* **1996**, *67*, 157−173.

(6) Brinkmann, G.; Fowler, P. W.; Manolopoulos, D. E.; Palser, A. H. R. A Census of Nanotube Caps. *Chem. Phys. Lett.* **1999**, *315*, 335−347.

(7) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. C60: Buckminsterfullerene. *Nature* **1985**, *318*, 162−163.

(8) Iijima, S. Helical Microtubules of Graphitic Carbon. *Nature* **1991**, *354*, 56−58.

(9) Rubio, A.; Corkill, J. L.; Cohen, M. L. Theory of graphitic boron nitride nanotubes. *Phys. Rev. B* **1994**, *49*, 5081.

(10) Blase, X.; Rubio, A.; Louie, S. G.; Cohen, M. L. Stability and band gap constancy of boron nitride nanotubes. *Europhys. Lett.* **1994**, *28*, 335.

(11) Chopra, N. G.; Luyken, R. J.; Cherrey, K.; Crespi, V. H.; Cohen, M. L.; Louie, S. G.; Zettl, A. Boron nitride nanotubes. *Science* **1999**, *269*, 966−967.

(12) Fowler, P. W.; Heine, T.; Monolopoulos, D. E.; Mitchell, D.; Orlandi, G.; Schmidt, R.; Seifert, G.; Zerbetto, F. Energetics of Fullerences with Four-Membered Rings. *J. Phys. Chem.* **1996**, *100*, 6984−6991.

(13) Fowler, P. W.; Heine, T.; Mitchell, D.; Schmidt, R.; Seifert, G. Boron−nitrogen analogues of the fullerences: The isolated-square rule. *J. Chem. Soc., Faraday Trans.* **1996**, *92*(12), 2197−2201.

(14) Seifert, G.; Fowler, P. W.; Mitchell, D.; Porezag, D.; Frauenheim, Th. Boron−nitrogen analogues of the fullerences: electrnic and structureal properties. *Chem. Phys. Lett.* **1997**, *268*, 352−358.

(15) Alexandre, S. S.; Mazzoni, M. S. C.; Chacham, H. Stability, Geometry, and Electronic Structure of the Boron Nitride $B_{36}N_{36}$ Fullerene. *Appl. Phys. Lett.* **1999**, *75*(1), 61−63.

CI034239L