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Aromaticity of Carbon Nanotubes*

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Carbon nanotubes (CNTs) are aromatic, peri-condensed benzenoids, composed of sp^2 carbon atoms; the carbons are arranged in a graphite-like, hexagonal pattern. The aromatic character of armchair and zigzag nanotubes was compared with the corresponding rectangular graphite sheets, from which CNTs may be derived. The number of Kekulé structures in $(2,2)_m$ and $(4,0)_m$ CNTs and in planar rectangular graphite sheets of equivalent size, where m denotes the number of strips making up the CNTs ($1 \le m \le 5$), was determined. The aromatic character of the structures was estimated by using the Swinborne-Sheldrake equation. It was found that (2,2) CNTs are more aromatic than their planar counterparts and (4,0) CNTs. (4,0) CNTs are less aromatic compared to the corresponding planar structures. Hence it is more difficult to saturate (and functionalize) armchair CNTs than the corresponding planar graphite structures and zigzag CNTs.

Keywords
conjugated systems
benzenoids
functionalization
Kekulé count

INTRODUCTION

Carbon nanotubes (CNTs) are peri-condensed benzenoids, composed of sp^2 carbon atoms, which in turn are ordered in a graphite-like, hexagonal pattern. CNTs may be derived from graphite by rolling up the rectangular sheets along certain vectors. All benzenoids (including graphite and CNTs) are aromatic structures, meaning that in contrast to other unsaturated systems, it is relatively difficult to saturate these compounds by using addition reactions. Aromaticity is closely related to the number of Kekulé structures, K. The greater K is, the more aromatic is the underlying structure. A review on aromaticity and ring currents was written by Gomes and Mallion.[1] Randić[2] wrote an extensive review on aromaticity of polycyclic conjugated hydrocarbons.

Enumeration of Kekulé structures[3,4] and conjugated circuits[5,6] became an important topic in chemical graph theory. There are currently three approaches that can be used to obtain K:

1. constructive enumeration;[7]
2. Kasteleyn's formula;[8]
3. various algorithms and formulas for special classes of structures.

Details concerning enumeration by the use of algorithms and formulas were reviewed by Trinajstić.[9] Methods of enumerating Kekulé structures of rectangle-shaped benzenoids were discussed by Rongsi *et al.*[10] General explicit formulas were obtained by Klein *et al.*[11] for benzenoid polymers with armchair edges. An efficient algorithm for determining K in cata-condensed benzenoids

* Dedicated to Professor Haruo Hosoya on the occasion of his 70th birthday.

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† Deceased on March 12, 2007.

TABLE I. Number of carbon atoms, Kekulé structures and the resonance energy/electron (eV) in rectangular [*m*,3] graphite sheets and $(2,2)_m$ armchair carbon nanotubes

m	$\#_C = 8m + 6$	$\#_C = 8(m + 1)$	K_{sheet}	$K_{(2,2)}$	$REPE_{sheet}$	$REPE_{(2,2)}$
1	14	16	5	9	0.136	0.163
2	22	24	14	41	0.142	0.183
3	30	32	30	178	0.134	0.192
4	55	40	55	769	0.125	0.197
5	91	48	91	3329	0.116	0.200

was devised by Gordon and Davison.[12] Another algorithm for rectangular graphite sheets and incomplete, rectangular patterns was devised by Lukovits.[13] Graph theoretical methods have been used to estimate the resonance energy in graphite.[11,14] Enumeration of Kekulé structures in armchair CNTs was first accomplished by Lukovits *et al.*[15] Besides accounting for the aromatic character of benzenoids, enumeration of *K* may also be used to determine the weight of a given bond in a conjugated system by calculating the Pauling index.[16]

It is noteworthy that the semi-empirical graph theoretical approaches used to estimate the aromatic character of conjugated molecules, like the enumeration of Kekulé structures and conjugated circuits, in most cases cannot be replaced by quantum chemical calculations because of the computer time needed for structures of this size.

The aim of this work was to compare the aromatic character of armchair and zigzag CNTs with the aromaticity of the corresponding, rectangular graphite sheets. Rectangular sheets may be rolled up along a vertical axis, yielding zigzag CNTs, or along the horizontal axis, yielding armchair CNTs. Figure 1 shows an (2,2) armchair CNT composed of four strips (structure III), and Figure 2 displays a (4,0) zigzag CNT composed of thee strips (structure VI). The number of strips (*m*) determines the length of the tube. The aromatic character of the CNTs and graphite sheets was estimated using the Swinborne-Sheldrake equation.[17] It was found that relatively short armchair CNTs are already more aromatic than the corresponding graphite sheets and zigzag CNTs.

METHODS

Resonance energy per electron (REPE) is often used to account for the aromatic character of the structure under investigation. In this study, REPE was obtained by the Swinborne-Sheldrake equation:[17]

$$REPE\ (eV) = 1.185 \ln K/\#_C \qquad (1)$$

where $\#_C$ denotes the number of carbon atoms. This approach yields 0.137 (eV) for benzene and 0.130 (eV) for naphthalene while by using the more elaborate conjugated circuit method,[5,6] we obtain 0.137, and 0.132 (eV), respectively.[18] Because of rather similar results, it seemed reasonable to use the less elaborate approach – enumeration of Kekulé structures.

The number of Kekulé structures in $(n,0)_m$ zigzag CNTs is equal to:[19]

$$K = 2^{m+1} \qquad (2)$$

Note that *K* does not depend on *n*. For rectangular graphite structures, *K* was obtained by a simple recursion equation.[13] The number of Kekulé structures in (2,2) armchair CNTs was determined by a variant of the transfer matrix technique.[15]

RESULTS AND DISCUSSION

Figure 1 shows two rectangular sheets containing four »rows« (*i.e.*, strips composed of hexagons) and three (I) and four »columns« (II), respectively. Structure III rep-

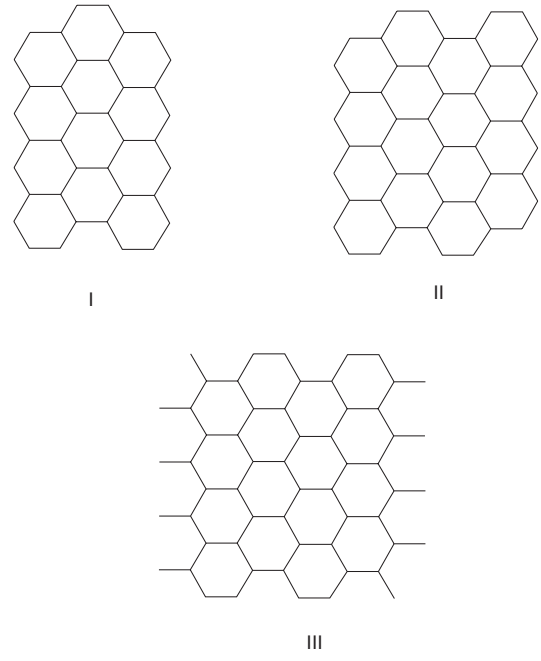

Figure 1. Rectangular graphite sheets composed of four »rows« and three »columns« (I), four »rows« and four »columns« (II) and a $(2,2)_4$ armchair carbon nanotube composed of four strips (III).

TABLE II. Number of carbon atoms, Kekulé structures and the resonance energy/electron (eV) in rectangular [3,*m*] graphite sheets and $(4,0)_m$ zigzag carbon nanotubes

m	$\#_C = 8m + 6$	$\#_C = 8(m + 1)$	K_{sheet}	$K_{(4,0)} = 2^{m+1}$	$REPE_{sheet}$	$REPE_{(4,0)}$
1	14	16	4	4	0.117	0.103
2	22	24	10	8	0.124	0.103
3	30	32	30	16	0.134	0.103
4	55	40	85	32	0.139	0.103
5	91	48	246	64	0.142	0.103

resents an (2,2) armchair CNT composed of four strips, which will be denoted by $(2,2)_4$. Let us assume that the formation of a $(2,2)_m$ armchair nanotube (Figure 1, structure III) can be explained by the following chemical reaction:

$$C_{8m+6}H_{2m+8} + C_2H_2 \rightarrow C_{8m+8}H_8 + (m + 1)H_2 \quad (3)$$

where the first entry is the chemical formula of the rectangular sheet composed of *m* rows and three columns, denoted by symbol [*m*,3], and the first entry on the right hand side is the chemical formula of the $(2,2)_m$. CNT. An analogous formula applies for the formation of $(4,0)_m$ zigzag CNTs (Figure 2, structures IV and VI)) where the rectangular sheets have been rotated by 90°. Although the reaction equation (3) – being quite credible – may never be realized, it is still reasonable to compare the aromatic character of the reactant and the product (whereby noting that acetylene and hydrogen are not aromatic molecules at all in this series of compounds). Table I lists the number of Kekulé structures, the number of carbon atoms ($\#_C$), and the values of REPE of the planar [*m*,3] structures and the corresponding $(2,2)_m$ tubes.

Note that because of Eq. (3) the number of hexagons increases in the course of the »reaction«. In order to take into account this effect, [4,*m*] planar structures have also been considered ($1 \le m \le 5$). Figure 3 shows the values of REPE in terms of *m*.

It can be seen that the additional column of hexagons alone (in [4,*m*] structures) barely affects the values of REPE, while the aromatic character increases substantially in tubes. This means that $(2,2)_m$ CNTs are more aromatic, and therefore less reactive, than their planar counterparts.

The formation of zigzag CNTs was found to be less favorable. Table II lists the number of Kekulé structures, the number of carbon atoms ($\#_C$), in [3,*m*] planar structures and the values of REPE of the corresponding $(4,0)_m$ tubes. The effect of an additional row of hexagons in planar structures (the [4,*m*] planar structures, see Structure V, Figure 2) was also taken into account. Figure 4 depicts the values of the REPE of these structures in terms of *m*. The REPE is constant in all $(n,0)_m$ zigzag CNTs and does not depend on the actual value of *n*. It can be seen that [4,*m*] structures were found to be less aromatic than the [3,*m*] planar structures, but aromaticity in both series seems to increase in terms of *m*. $(4,0)_m$ tubes are clearly less aromatic than the corresponding [3,*m*] and [4,*m*] planar structures.

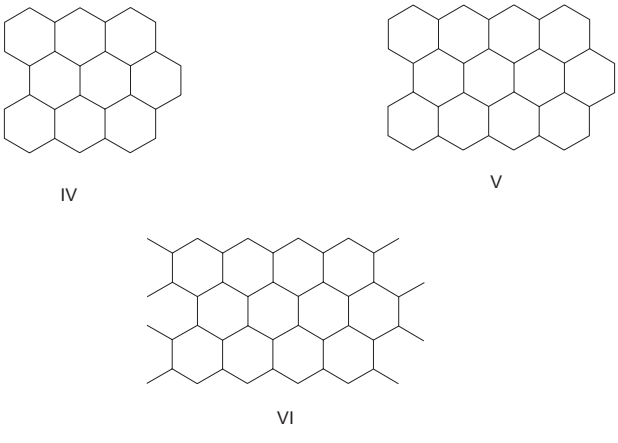

Figure 2. Rectangular graphite sheets composed of three »rows« and three »columns« (IV), four »rows« and three »columns« (V, see also structure I in Figure 1) and a $(4,0)_3$ zigzag carbon nanotube composed of three strips (VI). Definitions of rows and columns are the same as in Figure 1.

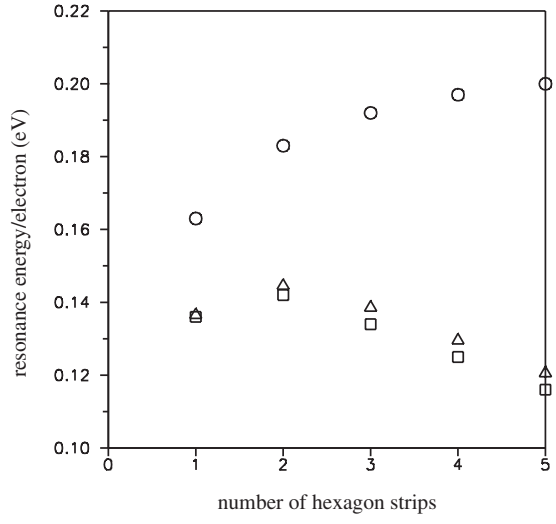

Figure 3. Resonance energy of $(2,2)_m$ carbon nanotubes (○) and rectangular graphite sheets composed of *m* »rows« and three (□) or four »columns« (△), in terms of *m* ($1 \le m \le 5$).

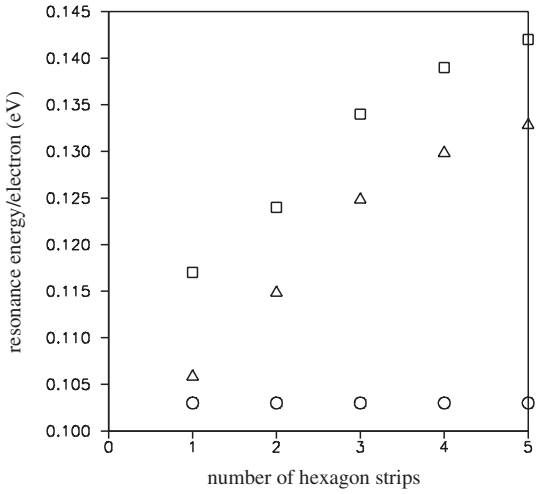

Figure 4. Resonance energy of $(4,0)_m$ carbon nanotubes (○) and rectangular shaped graphite sheets composed of m »columns« and three (□) or four »rows« (△), in terms of m ($1 \le m \le 5$).

In agreement with earlier studies,[13] it was found that extending the planar structure I (Figure 1) by adding columns to it will increase, while adding rows to structure I will decrease its aromatic character.

Both zigzag and armchair CNTs are more aromatic than parallelogram-type graphite sheets, in which, if there are enough rows and columns,[20] the REPE is practically equal to zero.

As stated in the Introduction, aromaticity is a kinetic feature of the chemical reaction rather than an energetic one. The wrapping of the graphite sheets and the formation of the corresponding CNT is an energy consuming process, and therefore the total free energy is positive ($\Delta G > 0$). The stability of armchair CNTs is related to the difficulty of attaching electrophilic reagents to the carbon surface. Zigzag CNTs and carbon sheets are more reactive, accounting for the fact that the existence of planar sheets has not been reported so far, and in samples prepared by using the high pressure CO technique, the zigzag CNTs seem to be much more rare than chiral CNTs.[21] These observations might indicate that it is much more difficult to functionalize armchair CNTs than planar sheets and zigzag CNTs.

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SAŽETAK

Aromatičnost ugljikovih nanocjevčica

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Ugljikove nanocjevčice su aromatični peri-kondenzirani benzenoidi, koji se sastoje od sp^2 hibridiziranih ugljikovih atoma u kojima su ugljikovi atomi složeni u cilindričnu hexagonalnu mrežu. Aromatični karakter armchair i zig-zag nanocjevčica uspoređen je s pravokutnim grafitnim plohama iz kojih su građene ugljikove

nanocjevčice. Također je određen broj Kekuléovih struktura u $(2,2)_m$ i $(4,0)_m$ ugljikovim nanocjevčicama i planarnim pravokutnim grafitnim plohama jednake veličine (indeks m označuje broj traka koje služe za gradnju ugljikovih nanocjevčica, $1 \le m \le 5$). Aromatični karakter istraživanih struktura određen je pomoću relacije koju su predložili Swinborne-Sheldrake, Herndon i Gutman (Ref. 17). Nađeno je da su (2,2) ugljikove nanocjevčice aromatičnije od odgovarajućih planarnih grafitnih ploha i (4,0) ugljikovih nanocjevčica, a da su (4,0) ugljikove nanocjevčice manje aromatične od odgovarajućih planarnih grafitnih ploha. Autori su također zaključili da se znatno teže zasićuju armachair ugljikove nanocjevčice nego odgovarajuće planarne grafitne plohe i zig-zag ugljikove nanocjevčice.