

Aromaticity of Carbon Nanotubes[†]Wolfgang Linert^{*,‡} and István Lukovits[§]

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Carbon nanotubes are composed of cylindrical graphite sheets. Both nanotubes and graphite sheets are benzenoid derivatives composed of sp^2 carbon atoms arranged in a hexagonal pattern. Therefore both systems are aromatic. The extent of the aromatic character of a molecule G (here benzenoids) can be explained in terms of the number of possible Kekulé structures in G . In this work the Kekulé structures in carbon nanotubes and the corresponding, rectangular, graphite-sheets the tubes might originate from, were enumerated. It was shown that (2,2), (3,3), and (4,4) carbon nanotubes are *more* aromatic than the corresponding, rectangular, planar structures. This explains why it might be more difficult to saturate nanotubes by addition reactions than the respective, “narrow”, graphite sheets.

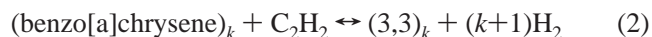
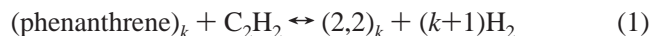
INTRODUCTION

Carbon nanotubes (CNTs) can be derived from graphite by rolling up the sheets along different directions. The tubes are composed of sp^2 carbon atoms, which in turn are arranged in a hexagonal pattern. Both graphite sheets and CNTs are benzenoids, and therefore they are aromatic. In this work “aromaticity” indicates that it is more difficult to saturate the carbon–carbon bonds by using addition reactions than in nonaromatic systems. CNTs were first prepared by Iijima¹ in 1991. For a more detailed discussion of aromatic properties of benzenoids, the reader might consult the detailed review by Randić.²

Aromaticity seems to be closely related to the number of Kekulé (K) structures in the polycyclic conjugated hydrocarbons. In a pair of isomers (like anthracene and phenanthrene, $C_{14}H_{10}$) the molecule with a greater Kekulé count (phenanthrene) is considered to be *more* stable with respect to addition reactions than the derivative with a lower value of K (anthracene). The determination of K is a mathematical problem. Cyvin and Gutman³ reviewed the methods used to calculate K in many finite and a few infinite systems. Sachs, Hansen, and Zheng derived a formula for all types of CNTs.⁴ Similar investigations focus on bucky-tori, though they briefly indicate results for CNTs.⁵ The Kekulé count of buckminsterfullerene has been determined by Trinajstić et al.⁶ and relates to a somewhat earlier article by Klein et al.⁷ Further similar computational results for numerous other fullerenes are found in ref 8. Lukovits et al.⁹ have enumerated the Kekulé structures by using the transfer matrix technique in (1,1) and (2,2) armchair CNTs⁹ and determined the number of conjugated circuits in (1,1) CNTs.⁷ The energetic stability of tori was investigated by Diudea and Kirby, who found that untwisted thin tori are more stable than analogues which

are twisted and thick.¹¹ The conductivity of single walled CNTs was estimated by using the transfer matrix technique.¹² Zhu et al.¹³ determined the resonance energy (≈ 0.17 eV) in an infinite graphite sheet. A related graphite resonance energy is already found in ref 14 by Hite et al. who also derived a Pauling–Wheland VB-model resonance energy model for graphite.¹⁵ Another Kekule-structure-based treatment of selected CNTs is also found by Morikawa et al.¹⁶ Hosoya investigated the relationships between the aromaticity index and stability of polycyclic conjugated hydrocarbons.¹¹

Formally it may be assumed that armchair CNTs are formed by the following reaction scheme



where $(\text{phenanthrene})_k$ denotes a planar, rectangular graphite layer, containing k rows and three columns. Figure 1 depicts $(\text{phenanthrene})_2$ a.k.a. benzo[ghi]perylene. Analogously the symbol $(\text{benzo[a]chrysene})_4$ denotes a rectangular graphite layer, composed of four “rows” and five “columns” (Figure 2), and $(\text{polyphenanthrene})_4$ will denote a similar structure composed of four rows and seven columns. The symbol $(\text{polyacene})_k$ denotes a polyacene composed of k benzene units. Symbols $(2,2)_k$ and $(3,3)_k$ denote (2,2) and (3,3) armchair CNTs composed of k hexagon layers. Figure 3 depicts a $(2,2)_2$ CNT. Similar schemes might be used to relate any $(n,n)_k$ armchair CNT with a rectangular planar structure composed of k rows and $2n-1$ columns. Note that although the reactions 2 and 3 may be hypothetical, they represent the most simple relationship between $(n,n)_k$ CNTs and rectangular, graphite, sheets composed of k “rows” and $(2n-1)$ “columns”.

The aim of this work was to compare the aromatic character of single walled $(n,n)_k$ CNTs and the corresponding $[k \times (2n-1)]$ rectangular graphite planes. The computations indicated that $(n,n)_k$ CNTs are *more* aromatic than the

[†] Dedicated to Professor Nenad Trinajstić on the occasion of his 70th birthday.

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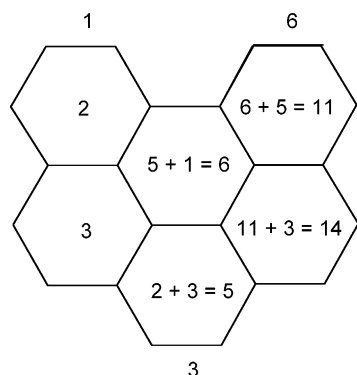


Figure 1. A scheme for the enumeration of Kekulé structures in benzo[ghi]perylene denoted in this work by (phenanthrene)₂.

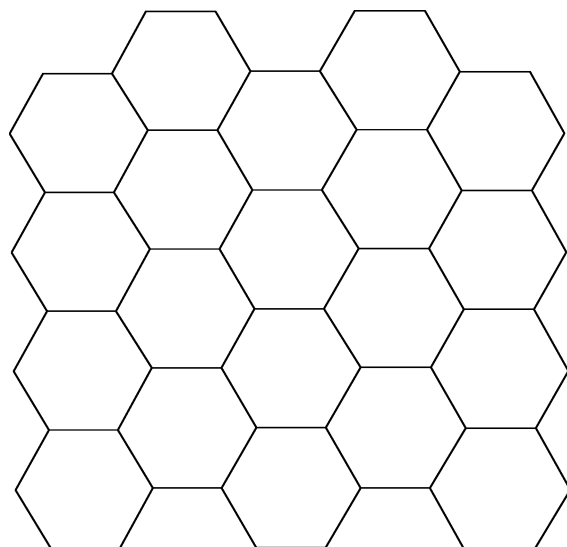


Figure 2. The structure of (benzo[a]chrysene)₄.

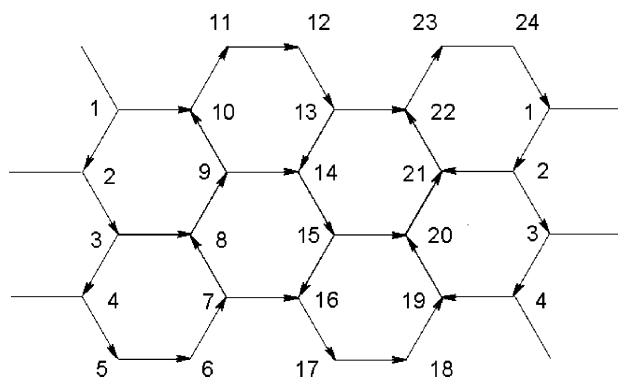


Figure 3. A scheme for systematic numbering of carbons in a (2,2)₂ carbon nanotube. This scheme will ensure that the number of arrows pointing (see text) in a clockwise (and counterclockwise) direction is always odd. An arrow emerging from vertex i and pointing to vertex j denotes an entry of the signed adjacency matrix A_{ij} , being equal to -1 . In this paper $= -1$, if $i < j$, and $A_{ij} = 1$, if $i > j$. The bonds appearing on the left- and right-hand sides indicate hexagons, which have already been depicted in the figure.

corresponding $[k \times (2n-1)]$ planar structures, meaning that during the progress of coiling the entropy increases.

METHODS

The number of Kekulé structures of rectangular planar sheets has been determined by an algorithm proposed recently.¹⁸ Figure 1 is an example of the enumeration in

Table 1. Number of Kekulé Structures, K , in Rectangular Graphite Sheets^a

k	(polyacene) _k	(phenanthrene) _k	(benzo[a]chrysene) _k	(polyphenanthrene) _k
1	2 C ₆ H ₆	5 C ₁₄ H ₁₀	13 C ₂₂ H ₁₄	34 C ₃₀ H ₁₈
2	3 C ₁₀ H ₈	14 C ₂₂ H ₁₂	70 C ₃₄ H ₁₆	353 C ₄₆ H ₂₀
3	4 C ₁₄ H ₁₀	30 C ₃₀ H ₁₄	246 C ₄₆ H ₁₈	2253 C ₆₂ H ₂₂
4	5 C ₁₈ H ₁₂	55 C ₃₈ H ₁₆	671 C ₅₈ H ₂₀	8272 C ₇₈ H ₂₄
5	6 C ₂₂ H ₁₄	91 C ₄₆ H ₁₈	1547 C ₇₀ H ₂₂	26585 C ₉₄ H ₂₆

^a The lower index, k , indicates the number of hexagon strips. The respective chemical formula is given below the actual value of K .

(phenanthrene)₂. The enumeration starts from the top of the left-hand column by writing a 1 *above* this column and inserting the number 2 into the first hexagon. Number 3 is inserted into the next hexagon, as the first column is a polyacene with $K = h + 1$, where h denotes the number of hexagons. The last entry of the first column (3) is written *below* the second column. Then this number (3) and the entry appearing in the row above the actual hexagon (2) have to be added and inserted into the lowest hexagon of the second column. The identical procedure has to be performed for the next hexagon (second from the bottom of column 2) and in turn for all “empty” hexagons. Finally the entry in the last hexagon denotes the Kekulé count ($K = 14$) of the given structure (phenanthrene)₂. The scheme may be easily generalized for any rectangular graphite sheet composed of m columns and n rows. Table 1 lists the results obtained for all planar systems investigated in this study.

The Kekulé count of (1,1) and (2,2) CNTs has been determined earlier.⁹ Enumeration of the Kekulé structures in (3,3) and (4,4) CNTs was carried out by using Kasteleyn’s theorem¹⁹

$$K = ||S||^{1/2} \quad (3)$$

where $||S||$ is the absolute value of the determinant of the signed adjacency matrix. The signed adjacency matrix may be derived from a directed graph, G , representing the underlying structure. In G arrows replace the edges connecting the vertices. Entry $S_{ij} = -1$ if the arrow emerges from vertex i and points to vertex j . Then entry S_{ji} will be equal to 1. According to Kasteleyn’s method, in each cycle of G the number of arrows arranged counterclockwise must be odd. This condition is automatically fulfilled in cycles composed of an odd number of vertices, but special care must be devoted to cycles composed of an even number of vertices. It might be mentioned here that Kasteleyn’s method has been extended to make conjugated-circuits counts.²⁰

Figure 3 represents a scheme of numbering the vertices in a (2,2)₂ CNT that will ensure that Kasteleyn’s condition is met automatically, provided that $S_{ij} = -1$ if $i < j$. Standard numerical methods used to calculate the determinant of the signed adjacency matrix have been used. The computational time was a small fraction of the time that would be needed by any quantum chemical approach entailing the computation of eigenvalues. Table 2 lists the Kekulé counts of (1,1)_k, (2,2)_k, (3,3)_k, and (4,4)_k CNTs ($1 \leq k \leq 5$).

Table 2. Number of Kekulé Structures, K , in Armchair Carbon Nanotubes^a

k	$(1,1)_k$	$(2,2)_k$	$(3,3)_k$	$(4,4)_k$
1	5	9	20	49
	C_8H_4	$C_{16}H_8$	$C_{24}H_{12}$	$C_{32}H_{16}$
2	13	41	169	769
	$C_{12}H_4$	$C_{24}H_8$	$C_{36}H_{12}$	$C_{48}H_{16}$
3	34	178	1258	9826
	$C_{16}H_4$	$C_{32}H_8$	$C_{48}H_{12}$	$C_{64}H_{16}$
4	89	769	9701	142913
	$C_{20}H_4$	$C_{40}H_8$	$C_{60}H_{12}$	$C_{80}H_{16}$
5	233	3329	75725	1611113
	$C_{24}H_4$	$C_{48}H_8$	$C_{72}H_{12}$	$C_{96}H_{16}$

^a The lower index, k , indicates the number of hexagon strips. The respective chemical formula is given below the actual value of K .

The aromatic character of the structures (expressed as the resonance energy per number of π -electrons—REPE) has been estimated by using the equation proposed by Swinborne-Sheldrake, Herndon, and Gutman²¹ which has recently been reanalyzed by Gutman and Radenovic.²² A similar relation has already been proposed quite some time ago from Carter²³

$$\text{REPE} = 1.185 \ln K/\#_C \quad (4)$$

where $\#_C$ denotes the number of carbon atoms, being equal to the number of available π -electrons.

RESULTS AND DISCUSSION

The aromatic character of polyacenes decreases in the following order: benzene > naphthalene > anthracene > tetracene > pentacene, etc. In the next series phenanthrene is less aromatic than benzo[ghi]perylene (Table 1), but aromaticity decreases in all derivatives (phenanthrene) $_k$ with $k > 2$. A similar trend can be observed for other rectangular graphite sheets. Figure 4 shows the decrease in aromaticity of polyacenes and (polyphenanthrene) $_k$. It seems that CNTs are more aromatic than the corresponding “narrow” graphite sheets. Comparison of the Kekulé count of polyacenes (Table 1) and corresponding $(1,1)_k$ CNTs (Table 2) clearly indicated that $K_{(1,1)}$ increases, while $K_{\text{polyacene}}$ decreases in terms of k . A similar trend might be observed for (phenanthrene) $_k$, (benzo[a]perylene) $_k$, and (polyphenanthrene) $_k$ and the corresponding CNTs $(2,2)_2$, $(3,3)_k$, and $(4,4)_k$, respectively. Figure 4 depicts the values of the REPE in terms of the number of hexagon strips. The nonexistent $(1,1)_k$ and $(2,2)$ CNTs seem to be the most aromatic structures, while for tubes with greater diameters the aromatic character decreases. As it can be seen from Figure 4, the difference in the values of REPE of the planar structures and the corresponding CNTs decreases in terms of the number of hexagon strips. As the diameter of CNTs increases, the value of the REPE seems to converge to the value of the resonance energy/electron in graphite¹³ (0.17 eV).

The values of the REPE in $[k \times (2n-1)]$ graphite sheets seem to decrease in terms of k (number of hexagon strips). This phenomenon is well-known, as already in polyacenes, with an increasing number of hexagons the value of REPE converges to zero.²⁵ On the other hand, resonance energy increases if the number of columns in rectangular sheets increases.¹⁷

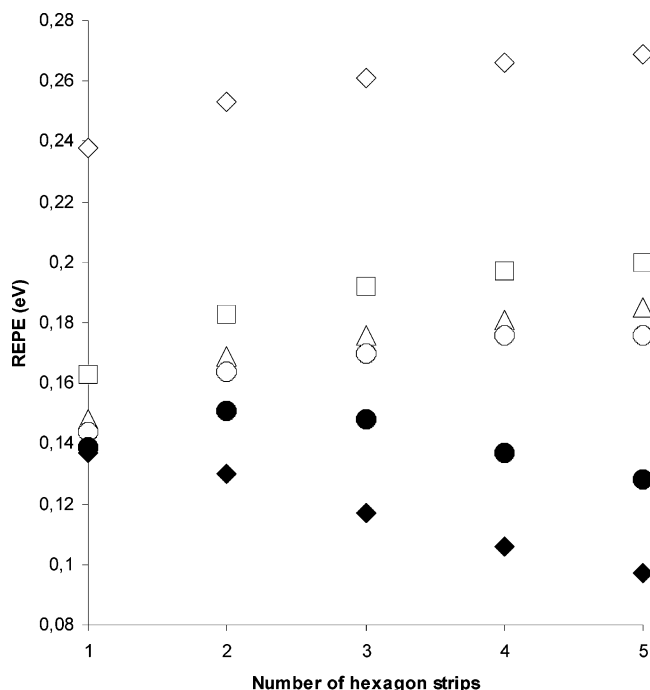


Figure 4. Resonance energy per electron (eV) in terms of the number of hexagon strips in $(1,1)_k$ (\diamond), $(2,2)_k$ (\square), $(3,3)_k$ (\triangle), and $(4,4)_k$ (\circ) carbon nanotubes as well as in (polyacene) $_k$ (\blacklozenge) and (polyphenanthrene) $_k$ -type (\bullet) planar benzenoids.

The net gain in aromaticity in CNTs does not mean that planar structures are less stable than CNTs in terms of free energy. Increase in aromaticity means that planar structures are more vulnerable to addition reactants than CNTs. Besides the planar structures investigated in this work, much greater graphite sheets (composed of 222 carbon atoms) have been synthesized, and it seems that they are sufficiently stable.²³ In fact the enthalpy of planar structures is greater than the enthalpy of the respective tubes ($\Delta H_{\text{sheet}} > \Delta H_{\text{CNT}}$) because the folding of the sheets is energetically unfavorable. It seems that an increase in aromaticity will affect the entropy.

The difference in aromaticity explains why relatively “tight” CNTs have been prepared in most cases. The $(1,1)$ and $(2,2)$ CNTs, although in principle being highly aromatic, cannot exist because of the high curvature of the conjugated system. Obviously, there is an optimum between energy loss because of curvature and stability loss because of aromatic character. At the end of this study the authors would like to encourage experimental research in the chemical stability of CNTs and tight planar graphite sheets.

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