

## Nanotubes: Number of Kekulé Structures and Aromaticity

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Carbon nanotubes (CNTs) are composed of cylindrical graphite sheets consisting of  $sp^2$  carbons. Due to their structure CNTs are considered to be aromatic systems. In this work the number of Kekulé structures ( $K$ ) in “armchair” CNTs was estimated by using the transfer matrix technique. All Kekulé structures of the cyclic variants of naphthalene and benzo[*c*]phenanthrene have been generated and the basic patterns have been obtained. From this information the elements of the transfer matrix were derived. The results obtained indicate that  $K$  (and the resonance energy) is greater if tubulenes are extended in the vertical than in the horizontal direction. Tubulenes are therefore more stable than cyclic strips. An illustration, obtained by using scanning probe microscope, has been attached to affirm the existence of thin CNTs.

### INTRODUCTION

In 1991 Iijima discovered a complex, elongated type of fullerene: the carbon nanotube (CNT).<sup>1</sup> It can be imagined as a  $C_{70}$  fullerene with many thousands of carbon rings inserted across its equator, giving a tiny tube with about 1.5 nm of diameter and a length of several microns. The unique structure of CNTs explains their unusual electrical and mechanical properties: CNTs are conductors or semiconductors depending on the tube structure, they have the highest known Young-modulus and yield strength, and they have other remarkable properties, too.<sup>2</sup> In what follows, we shall consider CNTs *without* caps, which are also called tubulenes.<sup>3</sup>

Like graphite, CNTs are also composed of  $sp^2$  carbons, meaning that each carbon is engaged in a single double (C=C) bond and two single (C–C) bonds. Therefore CNTs, like graphite, pyrene, coronene, and many other hexagonal systems immersed in the “sea” of  $\pi$ -electrons, are also “benzenoid” systems. The stability of benzenoids may be approximated by determining the Kekulé structure count ( $K$ ),<sup>4</sup> that is the number of ways the double bonds can be placed in the network consisting of hexagons.

Enumeration of Kekulé structures in aromatic hydrocarbons was first accomplished empirically by Pauling and Wheland<sup>5</sup> already in 1933, by systematic drawing of all Kekulé structures of a molecule and counting them at the end. This approach is always possible to apply, but it is obviously impractical for large systems. Besides it is prone to error. A variant of the empirical method is the fragmentation method discussed by Wheland<sup>6</sup> and elaborated much later by Randić<sup>7</sup> who used graph theoretical tools in casting the Wheland method into the easily applicable graph

theoretical approach to determine  $K$ . The topological properties of all-conjugated carbon species were reviewed by Klein and Zhu,<sup>8</sup> whereas theorems concerning carbon cages were established by Klein and Liu.<sup>9,10</sup> Methods to compute  $K$  in large benzenoid systems were devised by Randić et al.,<sup>11</sup> Gutman and Randić,<sup>12</sup> and Živković et al.<sup>13</sup> Kirby derived several theorems for polyhexes.<sup>14</sup> Aromaticity of benzenoids was also addressed by several studies devoted to elaboration of the conjugated circuit (CC) concept.<sup>15–17</sup> Determination of  $K$  in nanotubes (tubulenes), is a complex problem, and it was addressed first by Sachs, Hansen, and Zheng,<sup>3</sup> Klein and Zhu,<sup>18</sup> and John.<sup>19</sup> The reader may wish to consult reviews of several enumeration methods.<sup>20,21</sup> Kirby<sup>22</sup> determined the  $\pi$ -electron energy of nanotubes, while Klein et al.<sup>23</sup> derived general solution within the  $\pi$ -electron model for all possible buckytubes.

The aim of the present investigation was to determine  $K$  in “armchair”-type nanotubes. The number of Kekulé structures in CNTs has already been determined by Sachs, Hansen, and Zheng,<sup>3</sup> and the authors found that  $K$  is much less in “zigzag” than in “armchair” tubulenes. The main result of the present investigations (in addition to being somewhat simpler than the approach by Sachs et al.<sup>3</sup>) is that aromaticity in terms of the number of Kekulé structures is greater if the tubulene is extended in vertical than in horizontal direction. This result has also been supported by producing an experimental picture (obtained by using scanning-probe microscope) of a relatively “thin” CNT.

### EXPERIMENTAL SECTION

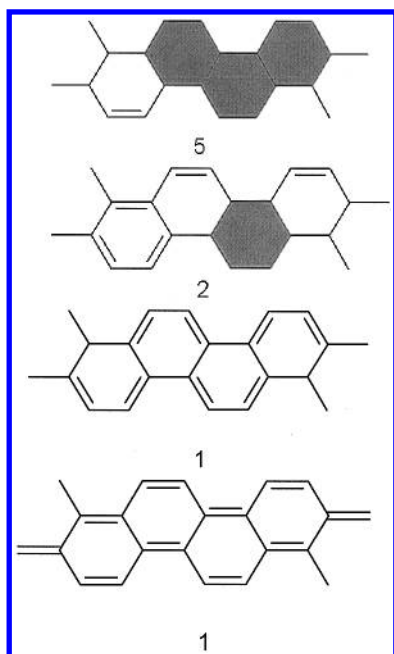
We synthesized CNTs by using the electrochemical method.<sup>24</sup> A mixture of chloride salts was melted in a vacuum oven in carbon crucible<sup>2</sup> and electrolyzed with carbon electrodes for some minutes.<sup>25–27</sup> After switching off the current, the cathode was separated from the melt, and the

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**Figure 1.** Determination of  $K$  in cyclic benzo[*c*]phenanthrene. The two edges on the left-hand side (right-hand side) indicate the fourth (first) hexagon, depicted already. Grey areas denote phenanthrene and benzene substructures (with five and two Kekulé valence structures), respectively. In addition there are two more structures, which do not have counterparts in benzo[*c*]phenanthrene.

shot—containing CNTs—was found both on the surface of cathode and in the frozen salt. The samples were investigated in a Hitachi 570 type scanning electron microscope (Hitachi Ltd., Tokyo) equipped with a Rontec M5 energy dispersion analyzer (Rontec GmbH, Berlin) and Nanoscope III atomic force microscope (Digital Instruments, Santa-Barbara, U.S.A.) using the 10  $\mu\text{m}$  scanner in tapping mode.

#### THE NUMBER OF KEKULE STRUCTURES IN NANOTUBES

Figure 1 illustrates an “elementary” CNT consisting of a single cyclic benzo[*c*]phenanthrene strip. Benzo[*c*]phenanthrene has eight Kekulé structures, whereas its cyclic counterpart has nine. The last two structures (Figure 1) do not appear in benzo[*c*]phenanthrene. Figure 1 also shows that the Gutman–Randić theorem,<sup>12</sup> stating that within each Kekulé valence structure there are  $K - 1$  conjugated circuits (including all combinations of simple circuits), also holds in tubulenes. But the conjugated circuits obtained are not the lowest ones of the length of six and ten.

We derived recursive formula for the number of Kekulé structures in cyclic polyphenanthrene strips in the following way. First a double bond in the leftmost hexagon has been fixed (Figure 1, first structure) and the opposite (upper) bond is single, by definition. Then all five Kekulé valence structures of phenanthrene contribute to  $K^C$  where  $K^C$  denotes the number of Kekulé structures in a cyclic strip containing  $h$  hexagons. The procedure can be generalized: in case of  $h$  hexagons ( $h$  is even) the contribution to  $K_h^C$  is  $K_{h-1}$ . Next let us assume that the upper edge in the leftmost hexagon is double bond and the opposite, lower edge is a single bond by definition (Figure 1, second structure). Then we have two more contributions to  $K^C$  and in general, the contribution to

$K_h^C$  is  $K_{h-3}$ . Third let us assume that the two opposite edges in the leftmost hexagon are both single bonds (Figure 1, 3rd structure). Then there is only single possibility to distribute the double bonds in the structure. Similarly (Figure 1, fourth structure), if the opposite edges are both double bonds, there is only a single possibility to attach the double bonds. In general: if there are  $h$  hexagons ( $h$  is even) in such cyclic “armchair” strip, the number of Kekulé structures is equal to

$$K_h^C = K_{h-1} + K_{h-3} + 2 \quad (1)$$

The following recursion formula holds for polyphenanthrenes:<sup>28</sup>

$$K_h = K_{h-1} + K_{h-2} \quad (2)$$

With  $K_{-1} = 1$  and  $K_0 = 1$  we obtain (eq 2)  $K_1 = 2$ ,  $K_2 = 3$ ,  $K_3 = 5$ ,  $K_4 = 8$ , etc. (Note that these are Fibonacci numbers, eq 2 is a Fibonacci recurrence formula.) Expressing  $K_{h-1}$  and  $K_{h-3}$  in eq 1 in terms of  $K_{h-2}$ ,  $K_{h-3}$ ,  $K_{h-4}$ , and  $K_{h-5}$  we obtain

$$K_h^C = K_{h-2} + K_{h-3} + K_{h-4} + K_{h-5} + 2 \quad (3)$$

Therefore the values of  $K_h^C$  of cyclic polyphenanthrenes can be computed in terms of contributions of (noncyclic) polyphenanthrenes. Equation 3 is also a recursion formula. When a cyclic polyphenanthrene is enlarged vertically a naphthalene unit must be inserted, and therefore the value of  $h$  in eq 3 must be even. Replacing  $h$  by  $N$ , the number of naphthalene units, the values of the first few  $K_N^C$ s are  $K_1^C = 5$ ,  $K_2^C = 9$ ,  $K_3^C = 20$ , and  $K_4^C = 49$ .

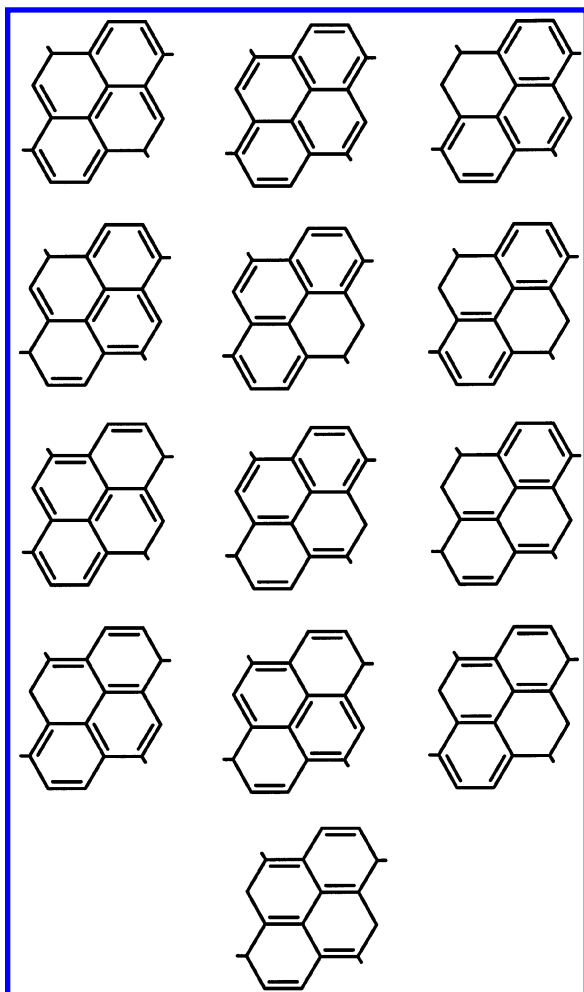
Figure 2 displays a cyclic strip consisting of naphthalene units. Again the number of Kekulé valence structures has been obtained by varying systematically the number and position of the double bonds in the left naphthalene unit: first there is no double bond, then there is a single double bond in three possible positions, then we have two double bonds (again there are three possible positions), and finally, there are three double bonds. In all cases the remaining portion of the tubulene corresponds to a (noncyclic) benzenoid for which  $K$  can be determined by using any of the methods listed earlier. The same sort of strips but of arbitrary width was treated by Klein et al.<sup>29</sup> for quite general boundary condition, including the possibilities of noncyclic, cyclic, Möbius, and even more bizarre boundary conditions.

The basic patterns appearing in the first layer of each structure depicted in Figure 2 are displayed in Figure 3. From these patterns the entries of the  $5 \times 5$  transfer matrix **T** were determined:

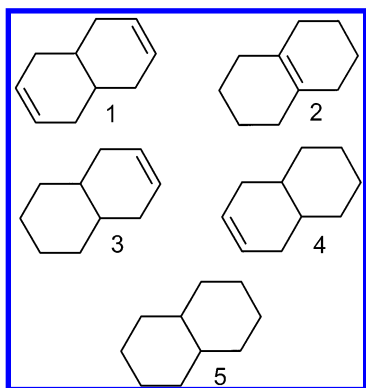
$$\mathbf{T} = \begin{bmatrix} 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 1 \\ 0 & 1 & 0 & 1 & 1 \\ 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 1 \end{bmatrix}$$

$K_N^T$  was obtained by using the following formula:

$$K_N^T = I' \mathbf{T}^{N-1} I \quad (4)$$



**Figure 2.** All 13 Kekulé valence structures of tubular polynaphthalene. The reduced bonds at both sides indicate adjacent naphthalene.

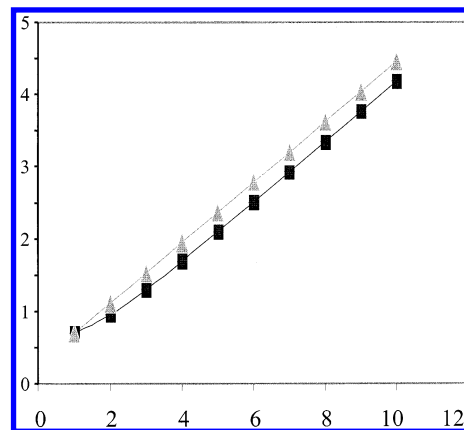


**Figure 3.** Basic patterns of tubular naphthalene.

where the superscript T indicates that the structure count refers to a tubulene,  $I$  denotes a column vector, all elements of which are equal to one, and  $I'$  is the transpose of  $I$ .  $N$  denotes the number of vertical naphthalene layers (Figure 2). Note that eq 4 is slightly different from the recursion formula published in ref 16.

Starting with  $N = 1$ , repeated application of eq 4 yielded the following values: 5, 13, 34, 89, 233, etc. For these values we derived a recursion formula:

$$K_N^T = 3K_{N-1}^T - K_{N-2}^T \quad \text{with } K_{-1}^T = 1, \text{ and } K_0^T = 2 \quad (5)$$



**Figure 4.** Values of  $\log K$  vs number of naphthalene units ( $N$ ) in naphthalene tubes ( $\Delta$ ) and in cyclic-polyphenanthrene strips ( $\square$ ).

**Table 1.** Resonance Energies (eV) of Polyphenanthrenes, Cyclic-Polyphenanthrenes, and Nanotubes Composed of Cyclic Naphthalene Units Divided by the Total Number of  $\pi$ -Electrons (Eqs 7–10)

| no. of<br>naphthalene<br>units $N$ | polyphenanthrenes | cyclic<br>polyphenanthrenes | nanotubes |
|------------------------------------|-------------------|-----------------------------|-----------|
| 1                                  | 0.13019           | 0.23840                     | 0.23840   |
| 2                                  | 0.13690           | 0.16273                     | 0.25329   |
| 3                                  | 0.13876           | 0.14790                     | 0.26117   |
| 4                                  | 0.13967           | 0.14412                     | 0.26595   |
| 5                                  | 0.14022           | 0.14304                     | 0.26915   |
| 6                                  | 0.14059           | 0.14271                     | 0.27143   |
| 7                                  | 0.14087           | 0.14261                     | 0.27314   |
| 8                                  | 0.14107           | 0.14258                     | 0.27447   |
| 9                                  | 0.14123           | 0.14256                     | 0.27553   |
| 10                                 | 0.14136           | 0.14256                     | 0.27641   |

If eq 2 (obtained for polyphenanthrenes) is rewritten in terms of naphthalene units  $N$ , then an equation completely identical to eq 5 can be obtained:

$$K_N = 3K_{N-1} - K_{N-2} \quad \text{with } K_{-1} = 0, \text{ and } K_0 = 1 \quad (6)$$

As it can be seen, recursion eqs 5 and 6 differ only in the starting parameters. Since  $K_N(\text{polyphenanthrene}) \geq K_N(\text{cyclopolyphenanthrene})$ ,  $K_N^T > K_N \geq K_N^C$  indicating that the number of Kekulé structures is greater if the tubulene is extended in the vertical than in the horizontal direction. In Figure 4 the logarithms of  $K_N^C$  and  $K_N^T$  are depicted in terms of  $N$ . Note that the number of carbon atoms is less in the tubule than in the cyclic-polyphenanthrene strip.

Resonance energies (RE) of polyphenanthrenes, cyclopolyphenanthrenes, and tubulenes composed of cyclic-naphthalene units were computed by using the approximation proposed by Swinborne-Sheldrake, Herndon, and Gutman:<sup>30</sup>

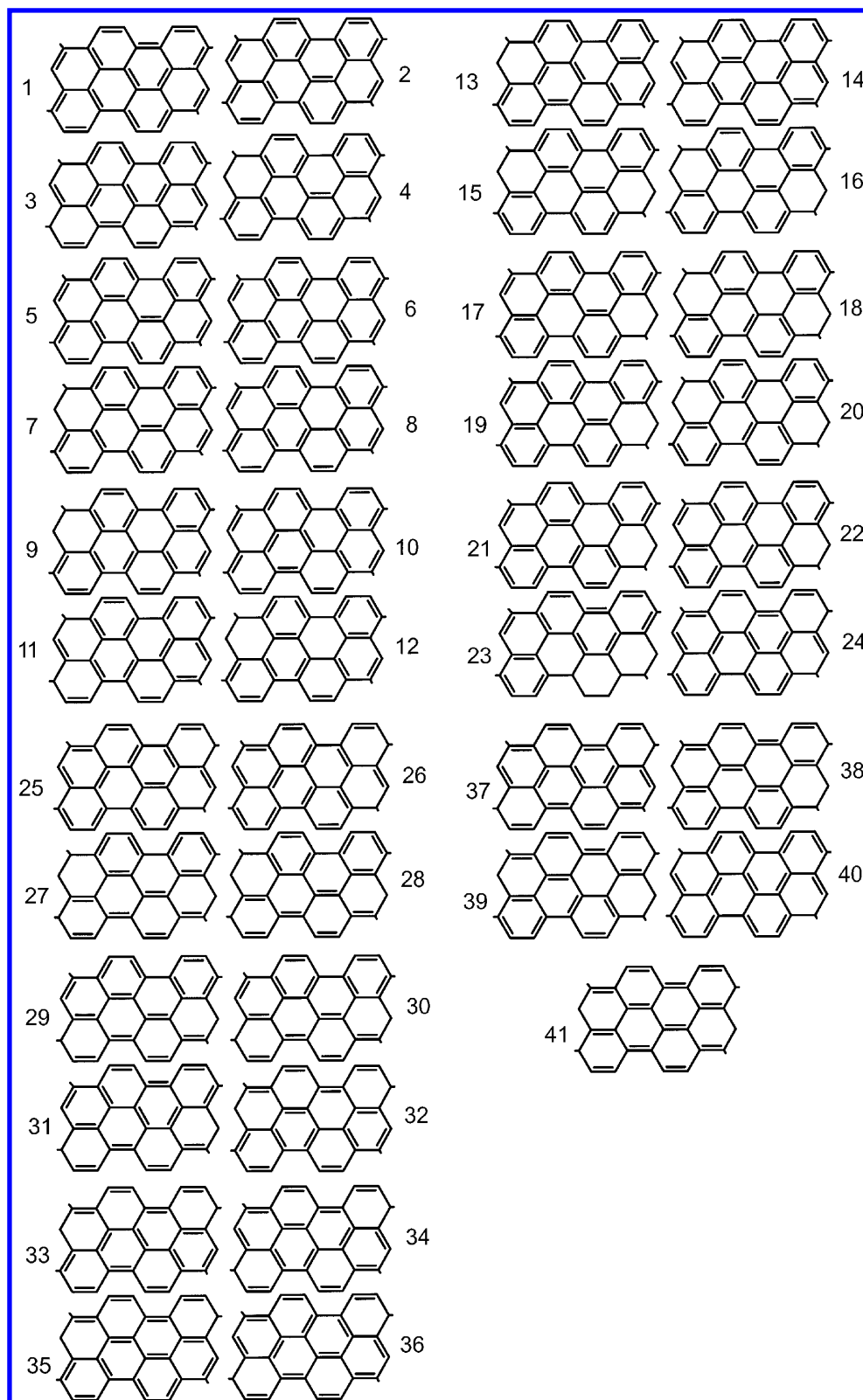
$$\text{RE (eV)} = 1.185 \ln K \quad (7)$$

The actual values of RE were divided by the number of  $\pi$ -electrons  $e$  (Table 1). The number of  $\pi$ -electrons is

$$e = 8N + 2 \quad (8)$$

in polyphenanthrenes,

$$e = 8N \quad (9)$$



**Figure 5.** All 41 Kekulé valence structures of cyclic benzo[c]phenanthrene. The reduced bonds at both sides indicate adjacent naphthalene.

in cyclic polyphenanthrenes, and

$$e = 4N + 4 \quad (10)$$

in tubulenes composed of  $N$  cyclic naphthalene units.

The procedure delineated for tubes composed of cyclic naphthalene was repeated for tubulenes composed of cyclic benzo[c]phenanthrene. If there are two layers of cyclic benzo-

[c]phenanthrene, 41 possible Kekulé structures can be obtained (Figure 5). The basic units of cyclic benzo[c]phenanthrene are depicted in Figure 6. The elements of the transfer matrix (Table 2) can be obtained by observing the first and second layer in Figure 5. From Table 2 the transfer matrix **T** can easily be constructed and is displayed below (zeros were omitted for the sake of clarity):

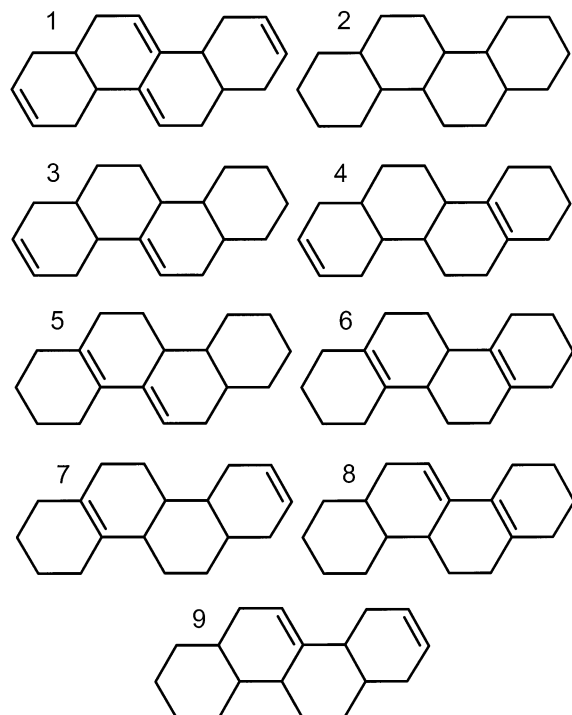


Figure 6. Basic patterns of cyclic benzo[c]phenanthrene.

|   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|   | 1 |   |   |   |   |   |   |
|   | 1 | 1 | 1 |   |   |   |   |
|   | 1 | 1 |   | 1 |   |   |   |
|   | 1 | 1 | 1 | 1 | 1 |   |   |
|   | 1 | 1 | 1 | 1 | 1 | 1 |   |
|   | 1 | 1 | 1 | 1 | 1 |   | 1 |
|   | 1 | 1 | 1 | 1 | 1 | 1 | 1 |

When the basic patterns of cyclic benzo[c]phenanthrene were derived, two simple rules had to be observed:

Rule 1. The cyclic structures depicted in Figure 5 contain 24 carbons; therefore, each structure must contain at least 12 double bonds. Examples: structures 15, 16, 18, 20, 27, 28, 38, 39, and 41. Since several double bonds appear twice, the structures may contain 13 or 14 double bonds, respectively. (Examples for 13 double bonds: structures 3, 4, 7, 8, 9, 11, 12, 13, 14, 17, 19, 21, 22, 23, 24, 25, 26, 29, 30, 31, 32, 33, 34, 35, 36, 37, and 40. Examples for 14 double bonds: structures 1, 2, 6, 10.)

Rule 2. Each double bond should be considered only once. This means that structure 11 (Figure 5) is composed of two basic patterns no. 7. A similar problem arises with structure 37 (Figure 5), which is composed of patterns no. 2 and no. 9, but the first layer might also be interpreted as pattern no. 3. In this case, however, the left double bond would be considered twice, and this would clearly violate our rule. Moreover the lower benzo[c]phenanthrene unit would contain only one double bond.

The Kekulé count  $K_{BP}^T$  of tubes composed of cyclic benzo[c]phenanthrene units increases rapidly with the number of benzo[c]phenanthrene units (where lower index BP refers to the number of benzo[c]phenanthrene units). Examples:  $K_1^T = 9$ ,  $K_2^T = 41$ ,  $K_3^T = 178$ ,  $K_4^T = 769$ ,  $K_5^T = 3329$ , etc.

Table 2. Rules for Top–Bottom Transition of Basic Benzo[c]phenanthrene Units (Figures 5 and 6)<sup>a</sup>

| starting<br>(top) pattern<br>(Figure 6) | final<br>(bottom) pattern | starting<br>(top) pattern<br>(Figure 6) | final<br>(bottom) pattern |
|---|---------------------------|---|---------------------------|
| 1                                       | 1 (40)                    | 7                                       | 2 (28)                    |
| 2                                       | 2 (41)                    |   | 3 (16)                    |
|   | 3 (38)                    |   | 4 (20)                    |
|   | 4 (39)                    |   | 5 (4)                     |
|   | 5 (35)                    |   | 6 (9)                     |
|   | 6 (32)                    |   | 7 (11)                    |
|   | 7 (34)                    | 8                                       | 2 (29)                    |
|   | 8 (33)                    |   | 3 (17)                    |
|   | 9 (37)                    |   | 4 (21)                    |
| 3                                       | 3 (24)                    |   | 5 (5)                     |
| 4                                       | 2 (36)                    |   | 6 (8)                     |
|   | 3 (25)                    |   | 8 (10)                    |
|   | 4 (26)                    | 9                                       | 2 (27)                    |
| 5                                       | 2 (31)                    |   | 3 (15)                    |
|   | 3 (23)                    |   | 4 (18)                    |
|   | 5 (1)                     |   | 5 (7)                     |
| 6                                       | 2 (30)                    |   | 6 (12)                    |
|   | 3 (19)                    |   | 7 (14)                    |
|   | 4 (22)                    |   | 8 (13)                    |
|   | 5 (2)                     |   | 9 (3)                     |
|   | 6 (6)                     |   |                           |

<sup>a</sup> The numbers in parentheses refer to structures depicted in Figure 5.

So far no recursion formula could be derived for this series of numbers.

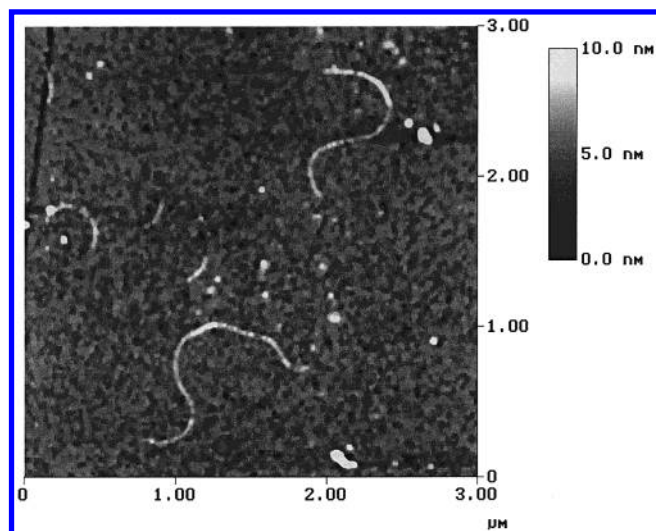
## DISCUSSION

It was possible to extend the transfer matrix technique for tubulenes. Whereas computations are fairly simple once the basic patterns and the corresponding transfer matrix are known, it is relatively complicated to derive the correct transfer matrix itself. In view of the structure of the transfer matrix related to benzo[c]phenanthrene, it seems that the choice of numbering of the basic patterns was a correct decision. What has to be done is to find out the rules of forbidden transitions (i.e. zero entries of **T**). Also a method must be formulated allowing the extension of the concept of basic patterns to longer polyphenanthrene strips.

The number of Kekulé structures is greater in polyphenanthrenes than in their cyclic analogues, but, as can be seen by comparing the relative resonance energies RE/e (Table 1), the latter values converge to the same value. Tubulenes have more Kekulé valence structures than the corresponding cyclic strips. Therefore if the tube increases vertically (i.e. gets longer) it will be more stable than increasing horizontally (Figure 4 and Table 1). Note that with increasing values of *N*, the value of resonance energy increases (Table 1).

By using the same method the value of RE/e is 0.136 for benzene ( $K = 2$ ) and 0.186 for buckminsterfullerene ( $K = 12500$ ).<sup>31</sup> Buckminsterfullerene has 1812 isomers. Among these 20 isomers have more Kekulé structures than buckminsterfullerene.<sup>32</sup> However, these are destabilized by abutted (adjacent) pentagons. Nanotubes we have been investigating are composed of only hexagons, and therefore the number of Kekulé structures is a valid criterion for their aromatic stability. In view of these values (RE/e  $\cong$  0.27), the (hypothetical) tubulenes, composed of cyclic naphthalene units, are fairly aromatic.





**Figure 7.** Atomic force microscopic picture of carbon-tubes, thickness = 1.6.

Therefore relatively thin tubes of about  $1.6 \text{ nm} = 16 \text{ \AA}$  may be stabile. A tube of this diameter contains about 20 hexagons along its perimeter. Iijima<sup>1</sup>—by using a laser technique—produced rather thin CNTs of about 1.5 nm. Our method<sup>24–26</sup> is based on electrochemical procedures and therefore is quite different from that of Iijima. Nevertheless, the tubes we have obtained are nearly of the same thickness as those made by Iijima. The experimentally detected diameter is  $\approx 1.6 \text{ nm}$ , measured as the *height* of the *spaghetti* like (some authors<sup>33</sup> call these structures *bamboo*-shaped) structures in Figure 7. The width of the stripe is greater than the tube diameter, because of the tip artifact. The curved shape of the nanotubes is a characteristic of the electrochemical process and indicates the presence of pentagons and heptagons in the structure. Defects will always cause bending through the appearance of pentagons.<sup>34</sup> Therefore strain is compensated by the greater Kekulé count. According to this result our nanotubes are single-walled.

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