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Topological Properties of Benzenoid Systems

An Identity for the Sextet Polynomial

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The sextet polynomial of non-branched cata-condensed benzenoid molecules is proved to be related (Eq. (3)) to the characteristic polynomial of a tree.

Key words: Benzenoid systems, topological properties of ~

1. Introduction

Several recent investigations [1, 2] have shown that resonance theory gives satisfactory quantitative results when applied to benzenoid hydrocarbons. The combinatorial background of this theory was also studied [3, 4]. Hosoya and Yamaguchi demonstrated [4] that various resonance-theoretical approaches can be unified by means of the sextet polynomial. For a benzenoid hydrocarbon G, the sextet polynomial $B_G(X)$ is defined as

$$B_G(X) = \sum_{k=0}^{m} r(G, k)\, X^k$$

where $r(G, k)$ is the so called "resonant sextet number", namely the number of ways in which k mutually resonant sextets can be selected from G. m is the maximal number of mutually resonant sextets. By definition, $r(G, 0) = 1$. Further details on these resonance-theoretical notions can be found in Refs. [4, 5].

Let the benzenoid molecule possess R rings. Then instead of the sextet polynomial we can consider another polynomial $BB_G(X)$,

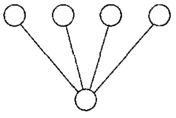
$$BB_G(X) = X^{R+1} B_G(-1/X^2) = \sum_{k=0}^{[(R+1)/2]} (-1)^k\, r(G, k)\, X^{R+1-2k} \tag{1}$$

The form of $BB_G(X)$ resembles much to the characteristic polynomial of a tree (i.e. of an acyclic graph) with $R+1$ vertices (see Eq. (2)).

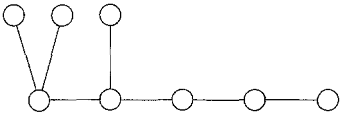
No simple and generally valid algorithm for the calculation of the sextet polynomials is known at present. The usual way of determining $B_G(X)$ by considering all possible selections of resonant sextets in G is not only rather tedious, but is also unreliable for complicated polycyclic systems. In the present paper it will be shown that the calculation of $B_G(X)$ for non-branched cata-condensed benzenoid (NBCCB)[1] molecules is reduced to the finding of the characteristic polynomial of a tree T. This tree can be easily deduced from the structure of the NBCCB network.

Before starting with the consideration of the properties of the sextet polynomial, we shall describe a class of trees.

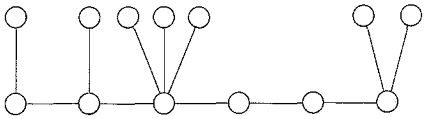
Let P_n denote the path[2] with n vertices. The tree $T(t_1, t_2, \ldots, t_n)$ is obtained by joining t_j new vertices to the j'th vertex of P_n ($j=1, 2, \ldots, n$). Thus t_j is an integer or zero. If $t_1 = t_2 = \cdots = t_n = 0$, then $T(t_1, t_2, \ldots, t_n) \equiv P_n$. The number of vertices of $T(t_1, t_2 \ldots, t_n)$ is $N = t_1 + t_2 + \cdots + t_n + n$. For example we present $T(4)$, $T(2, 1, 0, 0, 0)$ and $T(1, 1, 3, 0, 0, 2)$.



$T(4)$



$T(2, 1, 0, 0, 0)$



$T(1, 1, 3, 0, 0, 2)$

The characteristic polynomial of a tree T has the form [7]:

$$P_T(X) = \sum_{k=0}^{[N/2]} (-1)^k p(T, k) X^{N-2k} \tag{2}$$

where $p(T, k)$ is the number of ways in which k non-incident edges can be selected from T.

The analogy between expressions (2) and (1) is evident. In the following we will demonstrate that there exists indeed a tree T such that for a particular class of benzenoid molecules,

$$BB_G(X) = P_T(X) \tag{3}$$

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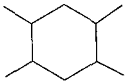
[1] A molecular network which is composed entirely of regular hexagons is called benzenoid. If no three hexagons have a common atom, the system is called cata-condensed (in the opposite case, the system is peri-condensed). If every hexagon of a cata-condensed system has at most two neighbouring hexagons, it is said to be non-branched. [6]

[2] The "path" (or "chain") with n vertices is the graph with the properties that the j'th vertex is adjacent to the $(j-1)$'th and $(j+1)$'th, and only to them ($j=2, 3, \ldots, n-1$).

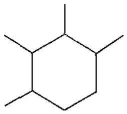
2. Some Topological and Resonance-Theoretical Properties of NBCCB Molecules

Let us consider an R-cyclic NBCCB system G and denote by $\mathrm{R}(j)$ ($j=1, \ldots, R$) its rings. These rings will be numbered successively, so that the ring $\mathrm{R}(j)$ is neighbouring to the rings $\mathrm{R}(j-1)$ and $\mathrm{R}(j+1)$. Hence, $\mathrm{R}(1)$ and $\mathrm{R}(R)$ are terminal rings. Of course [4, 5], $\mathrm{R}(j)$ presents also a resonant sextet.

A ring in a NBCCB hydrocarbon can be annelated exactly in two distinct ways, namely in a linear (L) or in an angular (A) mode.

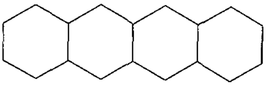


L-mode



A-mode

Therefore, the ring $\mathrm{R}(j)$ can be labelled by a symbol S_j, where either $S_j=L$ or $S_j=A$. The two terminal rings can have arbitrary labels, but it is convenient to denote them by L. Thus an ordered sequence $S=S(G)=S_1S_2\ldots S_R$ of L and A symbols (an "L, A-sequence") can be associated with every NBCCB system G. For example, molecules **1** and **2** have $S(1)=LLLL$ and $S(2)=LAALAALAL$.



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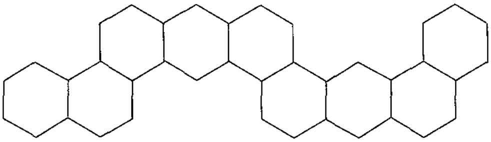

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For brevity we will denote LL by L^2, LLL by L^3 etc.

In a general case the L, A-sequence S is of the form

$$S=(L)^{s_1}A(L)^{s_2}A\ldots(L)^{s_{n-1}}A(L)^{s_n} \tag{4}$$

where s_j are non-negative integers. In other words, the rings $\mathrm{R}(s_1+1)$, $\mathrm{R}(s_1+s_2+2), \ldots, \mathrm{R}(s_1+s_2+\cdots+s_{n-1}+n-1)$ are assumed to be of A-mode, while all others of the L-mode. Since G has R rings, $R=s_1+s_2+\cdots+s_n+n-1$.

Theorem 1. Eq. (3) holds for every G which is a NBCCB hydrocarbon. If the L, A-sequence of G is given by Eq. (4), then $T=T(s_1, s_2\ldots, s_n)$.

Proof. If T is a tree with R edges (and therefore with $R+1$ vertices), such that for all i, j the edges e_i, e_j are mutually non-incident if $\mathrm{R}(i)$ and $\mathrm{R}(j)$ are mutually resonant, then

$$p(T, k)=r(\mathrm{G}, k)$$

from which Theorem 1 is deduced straightforwardly. Therefore, in order to demonstrate the validity of Theorem 1, it is sufficient to prove the following

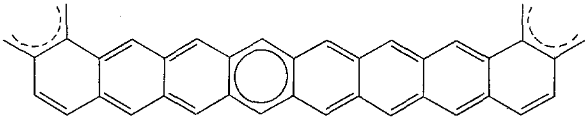
Theorem 2. The edges of the graph $T(s_1, s_2, \ldots, s_n)$ can be labelled in such a way that any pair of edges e_i, e_j is non-incident, whenever R(i) and R(j) are mutually resonant in G, with S(G) being given by Eq. (4).

Proof. Let us consider the ring R(p) of G. Then the sequence $\boldsymbol{S}$ is of the form

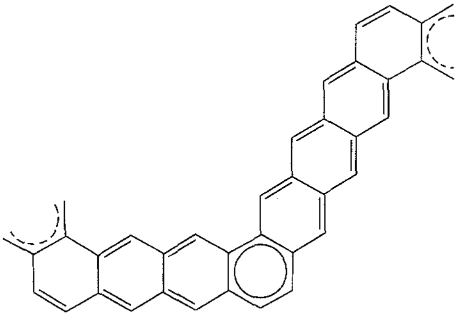
$$\boldsymbol{S} = \ldots A(L)^{a-1} S_p(L)^{b-1} A \ldots \tag{5}$$

where a and b are integers. In other words, we assume that R($p-a$) and R($p+b$) are the nearest (relative to R(p)) angularly annelated rings.

Now, it can be verified straightforwardly that the sextets R($p-a$), ..., R($p-1$), R($p+1$), ..., R($p+b$) can never be resonant if the sextet R(p) is resonant. This occurs simply because the double bonds in R($p-a$), ..., R($p-1$), R($p+1$), ..., R($p+b$) become localized after R(p) is deleted from G. Let us illustrate this on two examples. The resonant sextet R(p) is indicated by a circle.



$S_p = L$, $a = 2$, $b = 3$



$S_p = A$, $a = 2$, $b = 3$

Furthermore, since the double bonds in the rings R(1), ..., R($p-a-1$), R($p+b+1$), ..., R(R) are not localized when R(p) is deleted from G, the sextets R(p), R(i) and R(j) are mutually resonant, where $i = 1, \ldots, p-a-1$ and $j = p+b+1, \ldots, R$.

This discussion leads to the following conclusion.

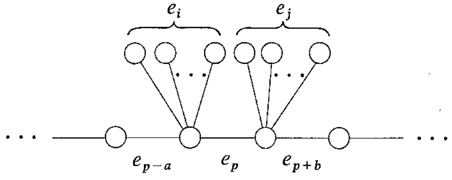
a) If $S_p = A$, any two sextets R(i), R(j) are mutually resonant for $i = p-a+1, \ldots, p-1$ and $j = p+1, \ldots, p+b-1$.

b) If $S_p = L$, no two such sextets R(i), R(j) are mutually resonant.

Let us now represent every ring R(j) of G by an edge e_j and try to construct a tree T with the properties required in Theorem 2. Then statements a) and b) read,

a*) If $S_p = A$, any two edges e_i, e_j are mutually non-incident if $i = p - a + 1, \ldots, p - 1$ and $j = p + 1, \ldots, p + b - 1$.
b*) If $S_p = L$, any two of such edges e_i, e_j are incident.

This situation can be uniquely realized by the graph fragments **3** (for $S_p = A$) and **4** (for $S_p = L$):
a**) If $S_p = A$



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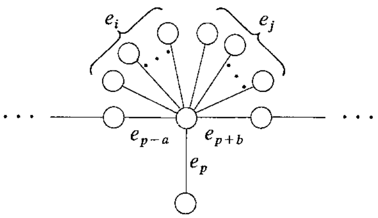
b**) If $S_p = L$



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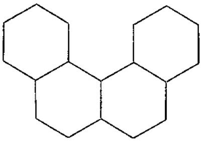
But the graph fragments **3** and **4** are exactly Theorem 2 applied to Eq. (5). The extension of a**) and b**) to the whole sequence $\boldsymbol{S}$ given by Eq. (4), completes finally the proof of Theorem 2.

Corrolary 1. Every tree $T(t_1, t_2, \ldots, t_n)$ can be associated with an L, A-sequence (Eq. (4)) and thus with a class of NBCCB molecules.

For example, the trees $T(4)$, $T(2, 1, 0, 0, 0)$ and $T(1, 1, 3, 0, 0, 2)$ correspond to sequences $LLLL$, $LLALAAA = LLALAAL$ and $LALALLLAAALL$, respectively.

Corrolary 2. If two NBCCB systems have the same L, A-sequence, and therefore the same associated tree, they are indistinguishable from the viewpoint of resonance theory. The smallest such molecules are **5** and **6**; both have an $LAAL$ sequence, with P_5 being their associated tree.

Using Theorem 1, it is rather simple to construct the tree T associated with any NBCCB hydrocarbon. For example, the trees corresponding to molecules **1** and **2** are $T(4)$ and $T(1, 0, 1, 0, 1, 1)$, respectively.



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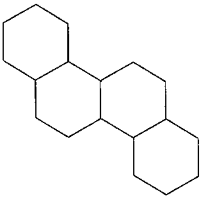

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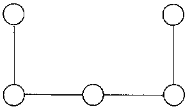
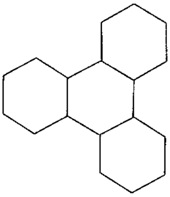


$T(1,0,1) \equiv P_5$

Finally, it is important to note that the validity of Theorem 1 cannot be simply extended, neither to branched cata-condensed, nor to peri-condensed molecules. Namely, for the smallest branched cata-condensed (**7**) and peri-condensed (**8**) benzenoid systems, the corresponding $r(\mathrm{G}, k)$ values cannot be related to the coefficients of the characteristic polynomial of any graph.



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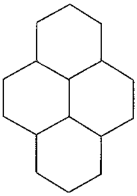
$B_7(X) = 1 + 4X + 3X^2 + X^3$



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$B_8(X) = 1 + 4X + X^2$

3. Discussion

Theorem 1 is, as to the author's knowledge, the first case that graph spectral theory plays some role in the theory of conjugated compounds *independently of the Hückel molecular orbital model.* The main applicability of our result is in determining $B_{\mathrm{G}}(X)$'s. There are well known simple graph-theoretical techniques [8] for the calculation of the characteristic polynomial of a tree. Hence, for example, the characteristic polynomials of $T(4)$, $T(1,0,1,0,1,1)$ and $T(1,0,1)$ are $X^5 - 4X^3$, $X^{10} - 9X^8 + 26X^6 - 27X^4 + 8X^2$ and $X^5 - 4X^3 + 3X$, respectively. Therefore, $B_1(X) = 1 + 4X$, $B_2(X) = 1 + 9X + 26X^2 + 27X^3 + 8X^4$ and $B_5(X) = B_6(X) = 1 + 4X + 3X^2$. The evaluation of $B_2(X)$ without the use of our theorem would be rather tedious.

Since $B_{\mathrm{G}}(1)$ is equal to the number of Kekulé structures $K = K(\mathrm{G})$ of the molecule G [4], from Eq. (3) it follows,

$$K(\mathrm{G}) = \sum_{k=0}^{[(R+1)/2]} p(T, k) = Z_T$$

where Z_T is the topological index of Hosoya [7, 9]. The K value of the molecule **2** ($=71$) could hardly be obtained by "brute force" enumeration.

As a final application we mention that recently Aihara [2] found that the roots of

$B_G(X)$ can be used for the calculation of the resonance energy (and thus aromaticity) of G. Because of Eq. (3), these roots are closely related to the spectrum of *T*, and therefore the resonance energy of a NBCCB hydrocarbon is obtained from the spectrum of its associated tree *T*.

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