

# Topological Properties of Benzenoid Systems. XXXVII. Characterization of Certain Chemical Graphs

Ivan Gutman [1]

Max-Planck-Institut für Strahlenchemie, Mülheim

Sherif El-Basil

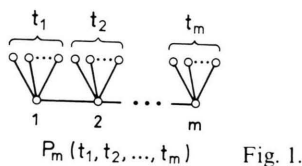
Faculty of Pharmacy, Kasr El-Aini Street, Cairo, Egypt

Z. Naturforsch. **40a**, 923–926 (1985); received May 7, 1985

Caterpillar trees, playing a significant role in the aromatic sextet theory of benzenoid hydrocarbons, have been characterized.

## Introduction

A caterpillar tree (or simply a caterpillar) is defined [2] to be the tree obtained by attaching vertices of degree one to the vertices of a path  $P_m$ . If  $t_j$  vertices of degree one ( $t_j \geq 0$ ) are added to the  $j$ -th vertex of  $P_m$ ,  $j = 1, 2, \dots, m$ , then the symbol  $P_m(t_1, t_2, \dots, t_m)$  will be used for the resulting caterpillar:



The importance of caterpillar trees in the topological theory of benzenoid systems lies in the following. Let  $B$  be a non-branched cata-condensed benzenoid hydrocarbon (that is a hydrocarbon containing linearly and angularly condensed rings). If we associate a symbol  $L$  to each linearly condensed ring (and also to the two terminal ones) and a symbol  $A$  to each angularly condensed ring, then the so-called  $L, A$ -sequence [3, 4] is obtained, which is of the form  $L^{t_1} A L^{t_2} A \dots L^{t_{m-1}} A L^{t_m}$ . Let  $C(B)$  be the Clar graph [4, 5] corresponding to  $B$ . Let, in addition, the sextet polynomial [6] of  $B$  be written in the form

$$1 + s(B, 1)x + s(B, 2)x^2 + \dots + s(B, m)x^m,$$

where  $s(B, k)$  denotes the number of ways in which  $k$  mutually resonant aromatic sextets can be placed in  $B$ .

It has been shown that [3]

$$s(B, k) = p(P_m(t_1, t_2, \dots, t_m), k), \quad (1)$$

where  $p(G, k)$  denotes the number of  $k$ -matchings (i.e. the number of selections of  $k$  independent edges) in the graph  $G$ . Furthermore [5]

$$s(B, k) = o(C(B), k),$$

where  $o(G, k)$  denotes the number of selections of  $k$  independent vertices in the graph  $G$ . The Clar graph of  $B$  is the line graph of  $P_m(t_1, t_2, \dots, t_m)$ .

The matching polynomial of a graph  $G$  with  $n$  vertices is defined as [7]

$$\chi(G, x) = \sum_{k=0}^{\lfloor n/2 \rfloor} (-1)^k p(G, k) x^{n-2k}. \quad (2)$$

In the case of trees, the matching polynomial coincides with the characteristic polynomial [7]. In particular

$$\chi(P_m(t_1, t_2, \dots, t_m), x) = \Phi(P_m(t_1, t_2, \dots, t_m), x), \quad (3)$$

where  $\Phi(G, x)$  denotes the characteristic polynomial of the graph  $G$ .

Because of (1), (2) and (3), is  $B$  is a non-branched cata-condensed benzenoid system, then the zeros of the polynomial

$$x^{2m} - s(B, 1)x^{2m-2} + s(B, 2)x^{2m-4} - \dots + (-1)^m s(B, m) \quad (4)$$

are real numbers and are just the non-zero eigenvalues of the tree  $P_m(t_1, t_2, \dots, t_m)$ . Aihara [8] considered the sum of the positive zeros of (4) and used it as a resonance energy. According to (1), (2) and (3), Aihara's resonance energy of  $B$  is (formally)

Reprint requests to Prof. Dr. Ivan Gutman, Faculty of Science, P.O. Box 60, 34000 Kragujevac, Yugoslavia.

0340-4811 / 85 / 0900-0923 \$ 01.30/0. – Please order a reprint rather than making your own copy.



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

equal to the Hückel total  $\pi$ -electron energy of  $P_m(t_1, t_2, \dots, t_m)$ .

The number of Kekulé structures of  $B$  satisfies the identity [6, 9, 10]

$$K(B) = 1 + s(B, 1) + s(B, 2) + \dots + s(B, m).$$

Having in mind (1), we see that

$$\begin{aligned} K(B) &= 1 + p(P_m(t_1, t_2, \dots, t_m), 1) \\ &\quad + p(P_m(t_1, t_2, \dots, t_m), 2) \\ &\quad + \dots + p(P_m(t_1, t_2, \dots, t_m), m). \end{aligned}$$

Thus the number of Kekulé structures of  $B$  is equal to Hosoya's topological index [11] of  $P_m(t_1, t_2, \dots, t_m)$ .

For previous work on the caterpillar trees see [3, 4, 12]. For review of topological properties of benzenoid systems see [13].

### Some General Properties of Caterpillar Trees

It is easy to see that a caterpillar  $P_m(t_1, t_2, \dots, t_m)$  has  $m + T$  vertices and  $m + T - 1$  edges, where  $T$  stands for  $t_1 + t_2 + \dots + t_m$ . Hence

$$p(P_m(t_1, t_2, \dots, t_m), 1) = m + T - 1. \quad (5)$$

In order to show that

$$\begin{aligned} p(P_m(t_1, t_2, \dots, t_m), 2) &= [T^2 - T_2 + 2mT - 6T \\ &\quad + m^2 - 5m + 6 + 2t_1 + 2t_m]/2, \end{aligned} \quad (6)$$

where  $T_2 = t_1^2 + t_2^2 + \dots + t_m^2$ , we need the formula [14]

$$p(G, 2) = \left[ p(G, 1)^2 + p(G, 1) - \sum_{i=1}^n d_i^2 \right] / 2, \quad (7)$$

which holds for a graph  $G$  whose vertex degrees are  $d_1, d_2, \dots, d_n$ . Taking into account that  $P_m(t_1, t_2, \dots, t_m)$  has  $T$  vertices of degree one and additional  $m$  vertices of degree  $t_1 + 1, t_2 + 2, t_3 + 2, \dots, t_{m-1} + 2$  and  $t_m + 1$ , (6) follows from (5) and (7).

In order to avoid ambiguities we shall always assume that  $t_1$  and  $t_m$  are greater than zero.

$P_m(t_1, t_2, \dots, t_m)$  cannot have  $(m + 1)$ -matchings. Hence

$$p(P_m(t_1, t_2, \dots, t_m), k) = 0 \quad \text{for } k > m.$$

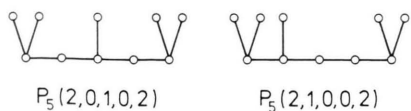


Fig. 2.

It is also immediate that

$$p(P_m(t_1, t_2, \dots, t_m), m) = t_1 \cdot t_2 \cdots t_m.$$

Consequently,  $P_m(t_1, t_2, \dots, t_m)$  has  $m$ -matchings if and only if all  $t_j$ 's are positive. If some of the  $t_j$ 's are zero, then it is not easy to determine the maximal number of matchings in  $P_m(t_1, t_2, \dots, t_m)$ . For example,  $P_5(2, 0, 1, 0, 2)$  has 3-matchings, but no 4-matchings. On the other hand, its isomer  $P_5(2, 1, 0, 0, 2)$  has 4-matchings.

The matching polynomial of  $P_m(t_1, t_2, \dots, t_m)$  conforms to the following recursion relations:

$$\begin{aligned} \alpha(P_m(t_1, t_2, \dots, t_m), x) &= x \alpha(P_m(t_1, t_2, \dots, t_m - 1), x) \\ &\quad - x^{t_m - 1} \alpha(P_{m-1}(t_1, t_2, \dots, t_{m-1}), x) \end{aligned}$$

and

$$\begin{aligned} \alpha(P_m(t_1, t_2, \dots, t_m), x) &= (x^{t_m + 1} - t_m x^{t_m - 1}) \alpha(P_{m-1}(t_1, t_2, \dots, t_{m-1}), x) - \\ &\quad - x^{t_m - 1 + t_m} \alpha(P_{m-2}(t_1, t_2, \dots, t_{m-2}), x). \end{aligned} \quad (8)$$

These are obtained by standard methods of the theory of matching polynomials [7].

### Symmetric Caterpillar Trees

In the present section we will be concerned with a special class of caterpillars, namely those for which  $t_1 = t_2 = \dots = t_m = t$ . The graph  $P_m(t, t, \dots, t)$  will be denoted simply by  $P_m(t)$  and called symmetric caterpillar tree.

We wish here to point at the following properties of symmetric caterpillar trees:

$$\alpha(P_m(t), x) = x^{mt} \alpha(P_m, x - t/x), \quad (9)$$

$$p(P_m(t), k) = \sum_{j=0}^k \binom{m-j}{k} \binom{k}{j} t^{k-j}, \quad (10)$$

$$\begin{aligned} \alpha(P_m(t), x) &= x^{(t-1)m} \prod_{j=1}^m \left[ x - \cos \frac{j\pi}{m+1} - \sqrt{\left( \cos \frac{j\pi}{m+1} \right)^2 + t} \right] \\ &\quad \cdot \left[ x - \cos \frac{j\pi}{n+1} + \sqrt{\left( \cos \frac{j\pi}{m+1} \right)^2 + t} \right]. \end{aligned} \quad (11)$$

From (11) the eigenvalues of  $P_m(t)$  can be deduced straightforwardly.

Formula (9) was previously known [15]. It follows, for instance, from the recursion formula (8), which

now reads

$$\alpha(P_m(t), x) = (x^{t+1} - t x^{t-1}) \alpha(P_{m-1}(t), x) - x^{2t} \alpha(P_{m-2}(t), x). \quad (12)$$

For  $m=1$  it is elementary to verify that (9) is true. Supposing that (9) holds for  $m=m_0-1$  and  $m=m_0-2$  we can use (12) to show that then (9) is true also for  $m=m_0$ . This suffices as an inductive proof of (9).

Formula (11) is obtained from (9) having in mind that

$$\alpha(P_m, x) = \prod_{j=1}^m \left[ x - 2 \cos \frac{j\pi}{n+1} \right].$$

In order to deduce (10) one has to remember the well known result

$$p(P_m, k) = \binom{m-k}{k},$$

which substituted back into (9) gives after an appropriate calculation

$$\alpha(P_m(t), x) = x^{(t-1)m} \left[ \sum_{j=0}^{\lfloor m/2 \rfloor} \sum_{i=0}^{m-2j} (-1)^{i+j} \binom{m-j}{j} \binom{m-2j}{i} t^i \right] \cdot x^{2m-2i-2j}.$$

Setting  $i+j=k$  and using the identity

$$\binom{m-j}{j} \binom{m-2j}{k-j} = \binom{m-j}{k} \binom{k}{j}$$

we arrive at (10).

Concluding this section we wish to note that in a recent paper [16] Balaban and Tomescu studied benzenoid systems closely related to, but not identical with those corresponding to symmetric caterpillars. Their  $(j, k)$ -hexes have the  $L, A$ -sequence  $L^{t_1} A L^{t_2} A \dots L^{t_{k-1}} A L^{t_k}$  with  $t_1 = t_k = j$  and  $t_2 = t_3 = \dots = t_{k-1} = j-1$  if  $j > 1$  and the  $L, A$ -sequence  $L A^{k-1} L$  if  $j = 1$ .

#### Recognition of the Matching Polynomial of Symmetric Caterpillars

In various applications of the sextet polynomial a problem can arise, namely to decide whether a given sequence of numbers  $s_1, s_2, \dots, s_h$  can be interpreted as the coefficients of the sextet polynomial of some benzenoid system. Having in mind (1), we may ask whether a caterpillar tree can be characterized by its matching numbers.

In the general case the answer is negative since there exist pairs of caterpillar trees with equal

matching polynomials. The classical example for this is the first discovered pair of non-isomorphic cospectral trees —  $P_2(3, 3)$  and  $P_3(4, 0, 1)$  [17].

We proceed now to examine whether for a given  $h$ -tuple of positive integers  $(s_1, s_2, \dots, s_h)$  there is a symmetric caterpillar, such that  $s_k = p(P_m(t), k)$  for all  $k = 1, 2, \dots, h$  and, in addition,  $p(P_m(t), k) = 0$  for  $k > h$ . We show that this question can be answered and, if such a caterpillar exists, it is unique.

Applying (5)–(7) we conclude that the following two equations must be obeyed:

$$\begin{aligned} s_1 &= m + m t - 1, \\ s_1^2 + s_1 - 2 s_2 &= m t + 2(t+1)^2 + (m-2)(t+2)^2. \end{aligned}$$

In spite of its complicated form, the above system has a unique solution in  $m$  and  $t$ . Expressing  $m$  from the first equation and substituting it in the second one we obtain

$$\begin{aligned} (s_1 - 3) t^2 + (2 s_2 + 4 s_1 - s_1^2 - 5) t \\ + 2 s_2 + 3 s_1 - s_1^2 - 2 = 0. \end{aligned}$$

the solutions of which are  $t = -1$  and

$$t = (s_1^2 - 3 s_1 - 2 s_2 + 2) / (s_1 - 3). \quad (13)$$

Therefrom,

$$m = (s_1 + 1)(s_1 - 3) / (s_1^2 - 2 s_1 - 2 s_2 - 1). \quad (14)$$

Hence  $m$  and  $t$  are uniquely determined by  $s_1$  and  $s_2$ . Knowing  $m$  and  $t$  and using (10), we obtain the number of  $k$ -matchings of  $P_m(t)$  for  $k \geq 3$  and thus immediately check whether  $p(P_m(t), k) = s_k$  holds for all  $k$ . If any of these relations are violated, or if  $m$  and  $t$  (as calculated by (13) and (14)) are not positive integers, then a symmetric caterpillar with the required properties does not exist.

The caterpillar tree determined by the parameters  $m$  and  $t$  is obviously unique.

The expressions for  $t$  and  $m$  given by (13) and (14) do not hold if  $s_1 - 3 = 0$  or if  $s_1^2 - 2 s_1 - 2 s_2 - 1 = 0$ . It can be shown that this will occur only in the case of  $P_2(1, 1) = P_4$  and  $P_1(3)$ . Hence these two graphs are to be considered separately. This is easy since their matching sequences are  $(3, 1)$  and  $(3)$ , respectively.

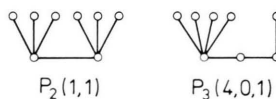


Fig. 3.

*Acknowledgement*

One of the authors (I. G.) thanks the Alexander von Humboldt Foundation for financial support and the staff of the Max-Planck-Institute für Strahlenchemie in Mülheim for assistance and hospitality.

- [1] Alexander von Humboldt fellow 1985. Permanent address: Faculty of Science, University of Kragujevac, Yugoslavia.
- [2] F. Harary and A. J. Schwenk, *Discrete Math.* **6**, 359 (1973).
- [3] I. Gutman, *Theor. Chim. Acta* **45**, 309 (1977).
- [4] I. Gutman and S. El-Basil, *Z. Naturforsch.* **39a**, 276 (1984).
- [5] I. Gutman, *Z. Naturforsch.* **37a**, 69 (1982).
- [6] H. Hosoya and T. Yamaguchi, *Tetrahedron Letters* **1975**, 4659.
- [7] For review on matchings, matching polynomials and their applications in chemistry see: I. Gutman, *Match (Mülheim)* **6**, 75 (1979).
- [8] J. Aihara, *Bull. Chem. Soc. Japan* **50**, 2010 (1977).
- [9] I. Gutman, H. Hosoya, T. Yamaguchi, A. Motoyama, and N. Kuboi, *Bull. Soc. Chim. Beograd* **42**, 503 (1977).
- [10] I. Gutman, *Match (Mülheim)* **11**, 127 (1981).
- [11] H. Hosoya, *Bull. Chem. Soc. Japan* **44**, 2332 (1971).
- [12] S. El-Basil, *Theoret. Chim. Acta* **65**, 207 (1984).
- [13] I. Gutman, *Bull. Soc. Chim. Beograd* **47**, 453 (1982).
- [14] I. Gutman, *Croat. Chem. Acta* **46**, 209 (1974).
- [15] A. J. Schwenk, in: R. Bari and F. Harary (Eds.), *Graphs and Combinatorics*, Springer-Verlag, Berlin 1974, pp. 153–172; C. D. Godsil and B. McKay, *Bull. Austral. Math. Soc.* **18**, 21 (1978); I. Gutman, *Match (Mülheim)* **8**, 291 (1980).
- [16] A. T. Balaban and I. Tomescu, *Match (Mülheim)* **17**, 91 (1985).
- [17] L. Collatz and U. Sinogowitz, *Abh. Math. Semin. Univ. Hamburg* **21**, 63 (1957).