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ON THE NUMBER OF KEKULÉ STRUCTURES OF UNBRANCHED BENZENOID CHAINS

Ratko Tošić and Olga Bodroža
Institute of Mathematics, University of Novi Sad, 21000 Novi Sad, Yugoslavia

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ABSTRACT. A new polynomial expression is obtained for the number of Kekulé structures (K numbers) of an arbitrary unbranched benzenoid chain composed from n linearly condensed segments containing $x_1, x_2, \ldots, x_n$ hexagons respectively.

1. INTRODUCTION

The enumeration of Kekulé structures (perfect matchings) of benzenoid polycyclic hydrocarbons is important because the stability and many other properties of these hydrocarbons have been found to correlate with the number of their Kekulé structures.

The classical paper of Gordon and Davison [5] contains a general algorithm for the enumeration of Kekulé structures (K numbers) of catacondensed benzenoids, branched and unbranched. Cyvin [2] gave an alternative derivation for the case of unbranched chains. This case was revisited by Cyvin and Gutman [3], who produced a useful modification of the Gordon and Davison algorithm. Tošić [7] gave an improved algorithm of time complexity O(n) for calculating the number of Kekulé structures of an arbitrary unbranched benzenoid chain composed from n linearly condensed segments.

Balaban and Tomescu [1] elaborated a system for producing explicit algebraic formulas for the K numbers of an arbitrary catacondensed benzenoid. This system had to be somewhat complicated

as a consequence of the general nature of the problem. Tošić and Bodroža [8] gave an explicit formula for the K number of an arbitrary unbranched benzenoid chain. In this paper we deduce a much simpler formula for the same number.

2. DEFINITIONS AND NOTATION

In this paper we shall consider only undirected graphs comprised of 6-cycles. Let there be a total of m such cycles which we shall denote as C_1, C_2,..., C_m in each graph of interest. Because the problem we treat arises from chemical studies of certain hydrocarbon molecules, we impose upon C_1, C_2,..., C_m the following conditions to reflect the underlying chemistry:

(i) Every C_i and C_{i+1} shall have a common edge denoted by e_i, for all $1 \leq i \leq m-1$.

(ii) The edges e_i and e_j shall have no common vertex for any $1 \leq i < j \leq m-1$.

By representing the 6-cycles as regular hexagons in the plane such a graph is ilustrated as in Figures 1a and 1b. In organic chemistry such graphs correspond to unbranched benzenoid chains.

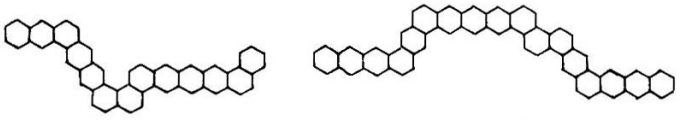

Figure 1

By $[x_1,x_2,\ldots,x_n]$ we denote an unbranched benzenoid chain (i. e. the corresponding graph) composed from n linearly condensed portions (segments) consisting of x_1, x_2,..., x_n hexagons respectively. Figures 1a and 1b show [2,3,1,1,4,2] and [3,2,4,1,1,2,4]

respectively.

An unbranched benzenoid chain may have a number of hexagons of an A mode (kinks) separating linear segments. Each of n-1 kinks of $[x_1,x_2,\ldots,x_n]$ is considered as belonging to exactly one segment. It means that the first segment does not contain any kink while each of n-1 remaining segments has exactly one kink which is the first hexagon of that segment. So the total number of hexagons in $[x_1,x_2,\ldots,x_n]$ is $m = x_1+ x_2+\ldots+ x_n$. The adopted notation enables us to suppose that $x_i \geq 1$, for $i = 1, 2, \ldots, n-1$, and $x_n \geq 2$. Sometimes, however, we consider $[x_1,\ldots,x_{n-1},1]$ to be the same chain as $[x_1,\ldots,x_{n-1}+ 1]$.

We denote by $K_n[x_1,x_2,\ldots,x_n]$ the number of Kekulé structures of $[x_1,x_2,\ldots,x_n]$. In a previous paper [8] by $K_n(x_1,x_2,\ldots,x_n)$ was denoted the number of Kekulé structures of $L(x_1,x_2,\ldots,x_n)$. The notation adopted in this paper implies

$$[x_1,x_2,\ldots,x_n] = L(x_1+ 1,x_2+ 1,\ldots,x_{n-1}+1,x_n)$$

and consequently,

$$K_n[x_1,x_2,\ldots,x_n] = K_n(x_1+ 1,x_2+ 1,\ldots,x_{n-1}+ 1,x_n).$$

3. THE RESULTS

It is easy to deduce the K formula for a single linear chain (polyacene) of x hexagons, say [x] (see [4]):

$$K_1[x] = 1 + x. \tag{1}$$

We define

$$K_0 = 1. \tag{2}$$

It may be interpreted as the number of Kekulé structures for "no hexagons".

Theorem. For each positive integer n and arbitrary positive integers $x_1, x_2, \ldots, x_n$,

$$K_n[x_1,x_2,\ldots,x_n] = 1 + \sum x_{\ell_1} x_{\ell_2} \ldots x_{\ell_k} , \qquad (3)$$

where the sum is taken over all subsets $\{\ell_1,\ell_2,\ldots,\ell_k\}$ of $\{1,2,\ldots,n\}$, $1 \leq k \leq n$, such that $n-\ell_k = 0 \pmod 2$ and $\ell_{j+1} - \ell_j = 1 \pmod 2$, for $j = 1, 2, \ldots, k-1$ ($\ell_1 < \ell_2 < \ldots < \ell_k$).

Proof. Let H be the last kink of $[x_1,\ldots,x_{n-1},x_n]$. We denote by u and v the vertices belonging only to hexagon H (Figure 2). We apply the method of fragmentation (see [4,6]) by attacking the bond uv. Every perfect matching (Kekulé structure) with the double bond uv does not contain any other edge belonging only to H. The rest of such a perfect matching will be the perfect matching of the graph consisting of two components: $[x_n-1]$ and $[x_1,\ldots,x_{n-1}]$ (Figure 2a). The number of such perfect matchings is $K_1[x_1-1]\cdot K_{n-1}[x_1,\ldots,x_{n-1}]$, i. e., according to (1),

$$x_n K_{n-1}[x_1,\ldots,x_{n-1}]. \qquad (4)$$

On the other hand, each perfect matching with the single bond uv must contain all the double bonds indicated in Figure 2b. The

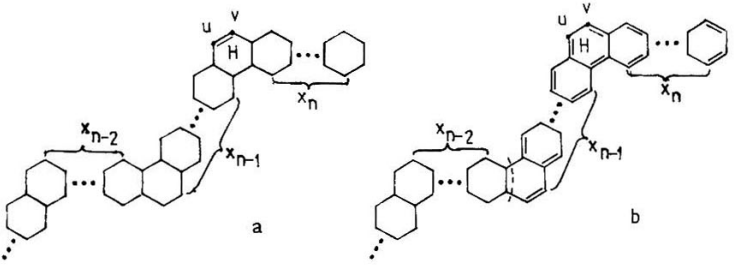

Figure 2

rest of such a perfect matching will be a perfect matching of $[x_1,\ldots,x_{n-2}]$ and the number of such perfect matching is

$$K_{n-2}[x_1,\ldots,x_{n-2}]. \qquad (5)$$

From (4) and (5) we obtain the following recurrence relation:

$$K_n[x_1,\ldots,x_n] = x_n K_{n-1}[x_1,\ldots,x_{n-1}] + K_{n-2}[x_1,\ldots,x_{n-2}]. \qquad (6)$$

Now the theorem will be proved by induction. First, the statement is true for $K_1[x_1]= 1 + x_1$ and $K_2[x_1,x_2]= x_2K_1[x_1]+ K_0 = 1 + x_2+ x_1x_2$.

Suppose now that the statement is true for all K_i, $i < n$, $n \geq 3$. Then, it easily follows from the recurrence relation (6) that the statement is also true for K_n.

The obtained expression for $K_n[x_1,\ldots,x_n]$ is a polynomial of degree n depending on variables $x_1,\ldots,x_n$. It is easy to see that the number of terms of this polynomial is F_{n+2}, where F_i is the ith member of Fibonacci sequence

$$F_0 = 0,\ F_1 = 1;\ F_i = F_{i-1}+ F_{i-2},\ \text{for } i \geq 2. \qquad (7)$$

Namely, $K_1[x_1]$ has $F_3 = 2$ terms and $K_2[x_1,x_2]$ has $F_4 = 3$ terms. Suppose that for $i \geq 3$, the numbers of terms of $K_{i-2}[x_1,\ldots,x_{i-2}]$ and $K_{i-1}[x_1,\ldots,x_{i-1}]$ are F_i and F_{i+1} respectively. Then, according to (6), it follows by induction that the number of terms of $K_i[x_1,\ldots,x_i]$ is F_{i+1} .

Taking into account that the zig-zag benzenoid chain with n hexagons may be considered as composed from segments of the length one each, we obtain as a direct consequence of our theorem the following very well known result.

Corollary. The number of Kekulé structures of a zig-zag benzenoid chain with n hexagons is F_{n+2} .

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