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ON KEKULÉ STRUCTURE COUNT OF CATA-CONDENSED BENZENOID HYDROCARBONS

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Abstract: If a cata-condensed benzenoid hydrocarbon with h six-membered rings has K Kekulé structures, then $h + 1 \leq K \leq 2^{h-1} + 1$.

INTRODUCTION

In the present paper we denote the number of Kekulé structures (i.e. the Kekulé structure count) by K and the number of six-membered rings by h. The structure count of a benzenoid system with h hexagons will be sometimes denoted by K_h. The abbreviation CCB will be used for "cata-condensed benzenoid".

The calculation of Kekulé structure count of benzenoid molecules is a problem which attracted the attention of a large number of scientists over a long period[1-12]. Closed analytical formulas for K have been determined for various classes of benzenoid systems[1,2,7-10]. Different enumeration techniques have been proposed[1,3-6,8]. An efficient recursive method for the enumeration of K of non-branched cata-condensed benzenoid systems is long known[1]. According to this method,

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

in the case when all hexagons are annelated in a linear mode, and

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

if all hexagons are annelated in an angular mode[13]; the structure count of all other non-branched CCB systems lies between the above two extremes. Since in both eqs. (1) and (2), $K_1 = 2$ and $K_2 = 3$, we

obtain the bounds

$$h + 1 \leqslant K \leqslant \frac{1}{\sqrt{5}} \left[\left(\frac{1 + \sqrt{5}}{2} \right)^{h+2} - \left(\frac{1 - \sqrt{5}}{2} \right)^{h+2} \right] . \quad (3)$$

In the present paper we offer an extension and generalization of the result (3) to the case of all cata-condensed (that is, both non-branched and branched) benzenoid molecules. Namely, we prove that for all CCB systems,

$$h + 1 \leqslant K \leqslant 2^{h-1} + 1 . \quad (4)$$

It can be immediately verified that both the left and the right inequality (4) become equalities in the case of $h = 1$ and $h = 2$. Therefore in the following we shall assume that $h > 2$.

SOME PROPERTIES OF CATA-CONDENSED BENZENOID HYDROCARBONS AND THEIR KEKULÉ STRUCTURES

Cata-condensed benzenoid hydrocarbons have the general formula $C_{4h+2}H_{2h+4}$. ($h = 1$ stands for benzene, $h = 2$ for naphthalene, $h = 3$ for anthracene and phenanthrene, etc.) These hydrocarbons are characterized by the fact that all their carbon atoms lie on the perimeter. (For details on various topological characterizations of the CCB systems see refs. 14,15.)

The molecular graph of a CCB hydrocarbon will be called a cata-condensed benzenoid graph (CCB graph). Let G be a CCB graph. Then G has $n = 4\,h + 2$ vertices and $m = 5\,h + 1$ edges. The vertices of G will be labelled by $v_1, v_2, \ldots, v_n$ and the edges by $e_1, e_2, \ldots, e_n, E_1, \ldots, E_{h-1}$ in such a manner that the edge e_i connects the vertices v_i and v_{i+1} $(i = 1,2,\ldots,n-1)$, the edge e_n connects the vertices v_n and v_1 and the n-membered cycle $v_1 e_1 v_2 e_2 v_3 \ldots e_{n-1} v_n e_n v_1$ is just the perimeter of G.

The edges $e_1, e_2, \ldots, e_n$ of the graph G will be called external. The remaining $h - 1$ edges $E_1, \ldots, E_{h-1}$ are said to be internal.

Every Kekulé structure of a conjugated molecule is in a one-to-one correspondence with a certain selection of n/2 independent (i.e. mutually non-incident) edges in the pertinent molecular graph[16]. A selection of n/2 independent edges in a graph with n vertices is called a p e r f e/c t m a t c h i n g of this graph.

Hence every Kekulé structure of a CCB hydrocarbon corresponds to a choice of $2\,h + 1$ independent edges in the respective CCB graph. We will classify the perfect matchings of a CCB graph according to the number of internal edges they contain. A perfect matching of a CCB graph is said to be of type k if it is composed

of k internal and $2h + 1 - k$ external edges.

L e m m a 1. Every CCB graph has exactly two perfect matchings of type 0.

P r o o f. These two perfect matchings are $(e_1, e_3, \ldots, e_{n-1})$ and $(e_2, e_4, \ldots, e_n)$.

L e m m a 2. Every CCB graph has exactly $h - 1$ perfect matchings of type 1.

P r o o f. Let the edge E_i connects the vertices v_{p_i} and v_{q_i}. Then, obviously, $p_i - q_i$ is odd. If a perfect matching of the graph G contains the edge E_i, then the additional 2h edges cannot be incident to the vertices v_{p_i} and v_{q_i}. Hence we have to select 2h independent (external) edges from the graph $G - v_{p_i} - v_{q_i}$.

Without losing the generality of our proof we may set $p_i = 1$ and $q_i = q$, where q is an even integer. By deleting the vertices v_1 and v_q from G, the perimeter of G decomposes into two paths: $v_2 e_2 v_3 e_3 \cdots v_{q-1}$ and $v_{q+1} e_{q+1} v_{q+2} e_{q+2} \cdots v_{n-1}$. Both paths are of odd length and thus both have a unique perfect matching: $(e_2, e_4, \ldots, e_{q-2})$ and $(e_{q+1}, e_{q+3}, \ldots \ldots, e_{n-1})$. Therefore there exists a unique perfect matching of G possessing the edge E_i and 2h external edges.

Lemma 2 follows now from the fact that the above conclusion applies to all edges E_i, $i=1,\ldots,h-1$.

Combining Lemmas 1 and 2 we immediately obtain the left-hand side inequality in (4).

L e m m a 3. If $k \geqslant 2$, then every CCB graph has at most $\binom{h-1}{k}$ perfect matchings of the type k.

P r o o f. We shall use a similar argument as in the proof of Lemma 2. Let us consider a set of k internal edges of G $(1 < k < h)$. Without losing the generality of the proof, we may assume that the elements of this set are $E_1, E_2, \ldots, E_k$.

By deleting the vertices $v_{p_1}, v_{q_1}, v_{p_2}, v_{q_2}, \ldots, v_{p_k}$ and v_{q_k} from G, the perimeter of the graph G decomposes into a collection of paths. If the length of every path in this collection is odd, we will have a unique selection of $2h + 1 - k$ independent external edges in the graph $G - v_{p_1} - v_{q_1} - v_{p_2} - v_{q_2} - \ldots - v_{p_k} - v_{q_k}$. Then in the graph G there will be a unique perfect matching of the type k, possessing the internal edges $E_1, E_2, \ldots, E_k$. If, however, at least one path from the above collection has even length, then a perfect matching of type k, possessing the edges $E_1, E_2, \ldots, E_k$ can not exist.

Hence we proved that there exists at most one perfect matching of type k, possessing a given set of k internal edges. Since k internal edges in the graph G can be chosen in $\binom{h-1}{k}$ distinct ways, we arrive to Lemma 3.

L e m m a 4. Every CCB graph has at most $2^{h-1} - 1$ perfect matchings, containing at least one internal edge.

P r o o f. Lemma 4 follows from Lemmas 2 and 3 because of the identity

$$\sum_{k=1}^{h-1} \binom{h-1}{k} = 2^{h-1} - 1 \quad .$$

The right-hand side inequality in (4) is now a straightforward consequence of Lemmas 1 and 4.

This completes the proof of the relations (4).

DISCUSSION

The lower bound in (4) is the best possible since there exists a CCB hadrocarbon with h six-membered rings, having h+1 Kekulé structures (the linear polyacene). The upper bound, however, reproduces the greatest possible value of K only for h = 1,2,3 and 4. For larger values of h, the upper bound (4) significantly overestimates the actual Kekulé structure count of CCB hydrocarbons.

h	maximal K value	u p p e r bound (4)	h	maximal K value	u p p e r bound (4)
1	2	2	7	38	65
2	3	3	8	66	129
3	5	5	9	107	257
4	9	9	10	189	513
5	14	17	11	296	1025
6	24	33			

The finding that the linear polyacenes are the CCB hydrocarbons with minimal structure count is not a surprising result and was certainly anticipated by many authors. Nevertheless, the proof of this result (which is given here for the first time) seems to be not quite elementar.

The characterization of CCB hydrocarbons with greatest Kekulé structure count appears to be a much more difficult task. The results obtained in this paper are far from the final solution of the problem. We hope therefore that a better upper bound for K_h will be discovered in the future.

Concluding this paper we would like to point to some related, but still unsolved questions.

(a) Which is the maximal possible value for the Kekulé structure count in benzenoid hydrocarbons with h hexagons?

(b) Which is the minimal non-zero value of the Kekulé structure count in benzenoid hydrocarbons with h hexagons? We conjecture that if K is not zero, then $K \geqslant h + 1$ for $h \leqslant 7$ and $K \geqslant 9$ for $h \geqslant 8$.

(c) It would be interesting to determine all benzenoid hydrocarbons which have 2,3,4,5,6,7 and 8 Kekulé structures. We conjecture that their number is finite. On the other hand, there are infinitely many benzenoid systems with nine Kekulé structures.

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