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A NEW RECURRENCE RELATIONSHIP FOR THE COMPUTATION OF THE NUMBER OF KEKULÉ STRUCTURES OF BENZENOID HYDROCARBONS

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Using a recently published relationship which expresses the characteristic polynomial of a molecular graph as a function of the characteristic polynomials of its subgraphs a new recurrence relationship is demonstrated for the computation of the number of Kekulé structures of benzenoid hydrocarbons.

INTRODUCTION

A Kekulé structure of an unsaturated conjugated hydrocarbon is a structural formula including hydrogens in which every carbon atom is tetravalent, sp^2-hybridized, and incident to exactly one double bond. The number of Kekulé structures (Kekulé Structure Count, **KSC**) of a benzenoid hydrocarbon gives information on the thermodynamic stability and chemical reactivity. Explicit combinatorial expressions enabling the calculation of the **KSC** have been derived for a large number of classes of benzenoid hydrocarbons.[1–5]

In this paper we will use the standard graph notation and termonology: G will denote a graph with N vertices: v_1, v_2, ..., v_N. The edge connecting vertices v_i and v_j are denoted by e_{ij}. The subgraph $G - v_i$ is obtained by deleting from the graph G the vertex v_i and its incident edges. The subgraph $G - e_{ij}$ is obtained by deleting from the graph G the edge e_{ij}.

The characteristic polynomial of the graph G may be expressed as follows:[6,7]

$$\mathbf{Ch}(G, x) = \mathbf{det}(x\mathbf{I} - \mathbf{A}) = \sum_{n=0}^{N} c_n x^{N-n}$$

where **I** is the unit matrix.

It is known that **KSC** is related in a simple manner to the adjacency matrix **A** of a benzenoid hydrocarbon, namely:

$$\mathbf{det\ A}(G) = (-1)^{N/2}\ \mathbf{KSC}(G)^2$$

The number of recurrence relationships which allow the computation of **KSC** for general conjugated molecular graphs is small. **KSC** obeys the following recurrence relationship:[8]

$$\mathbf{KSC}(G) = \mathbf{KSC}(G - e_{ij}) + \mathbf{KSC}(G - v_i - v_j)$$

When the vertex v_i is of degree one, we obtain:

$$\mathbf{KSC}(G) = \mathbf{KSC}(G - v_i - v_j) \tag{1}$$

If the conjugated system G is an essentially disconnected benzenoid composed of two non-interacting fragments G_1 and G_2, then:

$$\mathbf{KSC}(G) = \mathbf{KSC}(G_1)\mathbf{KCS}(G_2)$$

If G is a benzenoid graph with N vertices, then:[9]

$$\mathbf{Ch}(G, 0) = (-1)^{N/2}\mathbf{KSC}(G)^2 \tag{2}$$

The free term, i.e. the coefficients of x^0, of the characteristic polynomial is denoted by $\mathbf{Ch}(G, 0)$.

Rosenfeld and Gutman[10] reported the following recurrence relationship for the computation of the characteristic polynomial:

$$\mathbf{Ch}(G) = \frac{1}{\mathbf{Deg}(v_i) - 2}\left[\sum_{v_j}\mathbf{Ch}(G - e_{ij}) + \sum_{v_j}\mathbf{Ch}(G - v_i - v_j) - 2x\mathbf{Ch}(G - v_i)\right] \tag{3}$$

where the summations go over all $\mathbf{Deg}(v_i)$ vertices v_j that are adjacent to the vertex v_i. This formula is not applicable to a vertex v_i whose degree is two, but because, with the exception of monocyclic graphs, all other molecular graphs possess vertices of degree different than two this recurrence relationship is general and simplifies the decomposition of the molecular graph for the computation of the characteristic polynomial. In the present paper this recurrence relationship is used to demonstrate a new theorem for the computation of the Kekulé structure count for benzenoid hydrocarbons.

A NEW KEKULÉ STRUCTURE COUNT RECURRENCE RELATIONSHIP

THEOREM.

The number of Kekulé structures of a benzenoid graph G is related to the number of Kekulé structures of the subgraphs of G obtained after the removal of vertex v_i and its adjacent vertices:

$$\mathbf{KSC}(G)^2 = \frac{1}{\mathbf{Deg}(v_i) - 2}\left[\sum_{v_j}\mathbf{KSC}(G - e_{ij})^2 - \sum_{v_j}\mathbf{KSC}(G - v_i - v_j)^2\right]$$

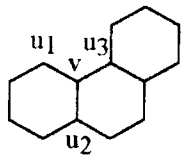
where the summations go over all $\mathbf{Deg}(v_i)$ vertices v_j which are adjacent to the vertex v_i.

The proof is straightforward by applying the equality (2) to the recurrence relationship for the characteristic polynomial (3). One must note that if $\mathbf{KSC}(G) \neq 0$ the molecular graph has an even number of vertices and $G - v_i$ has an odd number of vertices, resulting that $\mathbf{KSC}(G - v_i) = 0$. Obviously, the term corresponding to the subgraph $G - v_i$ was omitted.

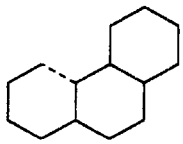
If the degree of the vertex v_i is one then this new recurrence relationship reduces to equation (1). Because the Theorem is not applicable to a vertex whose degree is two, its field of use is represented by vertices with degree three from polycyclic benzenoid hydrocarbons.

An illustrative example (phenanthrene, $\mathbf{G}_1$) for the theorem is presented below; the theorem is applied to vertex v which has three adjacent vertices, $\mathbf{u}_1$, $\mathbf{u}_2$, and $\mathbf{u}_3$.

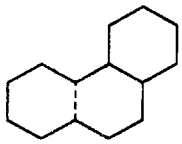
Graphs $\mathbf{G}_2$, $\mathbf{G}_3$, and $\mathbf{G}_4$ are obtained from graph $\mathbf{G}_1$ by eliminating the bond connecting vertex v and its neighbors $\mathbf{u}_1$, $\mathbf{u}_2$, and $\mathbf{u}_3$, in turn. Graphs $\mathbf{G}_5$, $\mathbf{G}_6$, and $\mathbf{G}_7$ are obtained from graph $\mathbf{G}_1$ by eliminating vertex v and its neighbors $\mathbf{u}_1$, $\mathbf{u}_2$, and $\mathbf{u}_3$, in turn.



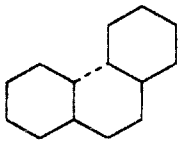
G_1



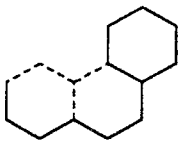
G_2



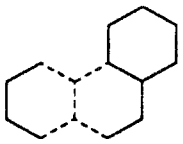
G_3



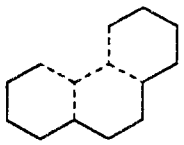
G_4



G_5



G_6



G_7

For the above example the Theorem gives the equality:

$$\mathbf{KSC(G_1)^2 = KSC(G_2)^2 + KSC(G_3)^2 + KSC(G_4)^2 - KSC(G_5)^2 - KSC(G_6)^2 - KSC(G_7)^2}$$

The above equality is expressed below by the corresponding number of Kekulé structures:

$$5^2 = 3^2 + 3^2 + 4^2 - 2^2 - 2^2 - 1^2$$

The new recurrence relationship for the computation of the Kekulé structure count can be applied to all classes of benzenoid hydrocarbons, providing a very efficient way of computation of **KSC** and of the reactivity indices based on **KSC**.

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