RECURRENCE RELATIONSHIPS FOR THE COMPUTATION OF THE NUMBER OF KEKULÉ STRUCTURES

Ovidiu IVANCIUC and Alexandru T. BALABAN
Organic Chemistry Department, Polytechnic Institute, Splaiul Independentei 313, 77206 Bucharest, Roumania

Abstract

On the basis of expansions of the characteristic and acyclic polynomials of conjugated hydrocarbons, five recurrence relationships enabling the computation of the number of Kekulé structures are presented.

1. Introduction

Molecular topology determines a large number of physico-chemical properties of chemical compounds [1–10]. Among them, the determination of the number of Kekulé structures of benzenoid hydrocarbons has attracted the attention of theoretical chemists over a relatively long period of time. Explicit combinatorial expressions enabling the calculation of the Kekulé structure count have been derived for a large number of classes of benzenoid hydrocarbons [9–14].

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.

Some of the most important theorems concerning the computation of the number of Kekulé structures of benzenoids are summarized. Based on expansions of the characteristic and acyclic polynomials of the molecular graphs of conjugated hydrocarbons, in terms of the corresponding polynomials of certain subgraphs of the molecular graph, five recurrence relations enabling the computation of the number of Kekulé structures will be presented.

2. Notation and definitions

We shall use the standard graph notation and terminology [15]; G will denote a graph with N vertices: $v_1, v_2, \ldots, v_N$; the degree of the vertex v_i will be denoted by d_i. The edge connecting vertices v_i and v_j is denoted by e_{ij}. The subgraph $G - v_i$ is obtained from the graph G by deletion of the vertex v_i and its incident edges. The subgraph $G - e_{ij}$ is obtained from the graph G by deletion of the edge e_{ij}. The subgraph $G - C_i$ is obtained from the graph G by deleting all the vertices of the cycle C_i and their incident edges.

The adjacency matrix of a graph G with N vertices, $A = A(G)$, is the square $N \times N$ symmetric matrix which contains information about the connectivity of the vertices in G. Its entries are defined as

$$a_{ij} = \begin{cases} 1, & \text{for vertices } i, j \text{ adjacent,} \\ 0, & \text{otherwise.} \end{cases} \tag{1}$$

The characteristic polynomial of the graph G may be expressed as follows [15]:

$$\mathrm{Ch}(G, x) = \det(x\mathbf{I} - \mathbf{A}) = \sum_{n=0}^{N} a_n x^{N-n}, \tag{2}$$

where $\mathbf{I}$ is the unit matrix.

The acyclic (matching) polynomial was defined as [16]

$$\mathrm{Ac}(G, x) = \sum_{k=0}^{N} (-1)^k P(G, k) x^{N-2k}, \tag{3}$$

where $P(G, k)$ is the number of ways of choosing k disjoint edges from G.

It is known that the number $K(G)$ of Kekulé structures is related in a simple manner to the adjacency matrix A of the aromatic hydrocarbon, namely [17]

$$\det A(G) = (-1)^{N/2} K(G)^2. \tag{4}$$

$K(G)$ obeys the following known recurrence relationship [18]:

$$K(G) = K(G - e_{ij}) + K(G - \upsilon_i - \upsilon_j). \tag{5}$$

If the vertex υ_i is of degree one, we obtain

$$K(G) = K(G - \upsilon_i - \upsilon_j). \tag{6}$$

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

$$K(G) = K(G_1) K(G_2). \tag{7}$$

If G is a benzenoid graph with N vertices, then [19]

$$\mathrm{Ch}(G, 0) = (-1)^{N/2} K(G)^2. \tag{8}$$

If G is a graph with N vertices, then [20]

$$\mathrm{Ac}(G, 0) = (-1)^{N/2} K(G). \tag{9}$$

The free terms, i.e. the coefficients of x^0, of the characteristic and acyclic polynomials, are denoted by Ch(G, 0) and Ac(G, 0), respectively.

LEMMA 1 [14]

If B is a benzenoid graph and C_i is its cycle with nc vertices, then in the interior of C_i there is an odd number of vertices, whenever $nc \equiv 0 \pmod 4$.

3. Graph polynomials recurrence relationships

The characteristic polynomial of a graph G, Ch(G), can be expressed as a linear function of the characteristic polynomials of its subgraphs obtained after the removal of an edge e_{ij}, the vertices v_i and v_j, and all r cycles C_k containing the edge e_{ij} [17]:

$$\mathrm{Ch}(G) = \mathrm{Ch}(G - e_{ij}) - \mathrm{Ch}(G - v_i - v_j) - 2\sum_{k=1}^{r} \mathrm{Ch}(G - C_k). \tag{10}$$

The decomposition of the graph G at its edge e_{ij} gives the following equality in terms of acyclic polynomials of the graph G, Ac(G), and its subgraphs [21]:

$$\mathrm{Ac}(G) = \mathrm{Ac}(G - e_{ij}) - \mathrm{Ac}(G - v_i - v_j). \tag{11}$$

The expansion of the characteristic polynomial is given in the following equation in terms of the characteristic polynomials of its subgraphs, corresponding to the decomposition of the graph G at its vertex v_i [22]:

$$\mathrm{Ch}(G) = x\,\mathrm{Ch}(G - v_i) - \sum_{j=1}^{d_i} \mathrm{Ch}(G - v_i - v_j) - 2\sum_{k=1}^{r} \mathrm{Ch}(G - C_k), \tag{12}$$

where the second summation goes over all r cycles which contain vertex v_i.

In a similar way, we obtain the expression of the acyclic polynomial of the graph G decomposed at its vertex v_i [22]:

$$\mathrm{Ac}(G) = x\,\mathrm{Ac}(G - v_i) - \sum_{j=1}^{d_i} \mathrm{Ac}(G - v_i - v_j). \tag{13}$$

Let G be a graph with g_1 and g_2 as two distinct vertices, and let H be another graph with h_1 and h_2 as two distinct vertices. We construct the composed graph $G\!:\!H$ by identifying g_1 with h_1 and g_2 with h_2.

The characteristic polynomial of the composed graph $G\!:\!H$ is expressed by the following equality [23]:

$$\begin{aligned}\mathrm{Ch}(G{:}H) &= \mathrm{Ch}(G)\mathrm{Ch}(H-h_1-h_2)+\mathrm{Ch}(G-g_1)\mathrm{Ch}(H-h_2)\\ &\quad+\mathrm{Ch}(G-g_2)\mathrm{Ch}(H-h_1)+\mathrm{Ch}(G-g_1-g_2)\mathrm{Ch}(H)\\ &\quad-x[\mathrm{Ch}(G-g_1)\mathrm{Ch}(H-h_1-h_2)+\mathrm{Ch}(G-g_2)\mathrm{Ch}(H-h_1-h_2)\\ &\quad+\mathrm{Ch}(G-g_1-g_2)\mathrm{Ch}(H-h_1)+\mathrm{Ch}(G-g_1-g_2)\mathrm{Ch}(H-h_2)]\\ &\quad+x^2\mathrm{Ch}(G-g_1-g_2)\mathrm{Ch}(H-h_1-h_2)-2\sum_g\sum_h \mathrm{Ch}(G-P_g)\mathrm{Ch}(H-P_h),\end{aligned} \tag{14}$$

where the summations are over all paths P_g and P_h from G and H, respectively, connecting vertices g_1 and g_2 with h_1 and h_2, respectively.

In a similar way, we express the acyclic polynomial of graph $G{:}H$, namely [23]

$$\begin{aligned}\mathrm{Ac}(G{:}H) &= \mathrm{Ac}(G)\mathrm{Ac}(H-h_1-h_2)+\mathrm{Ac}(G-g_1)\mathrm{Ac}(H-h_2)\\ &\quad+\mathrm{Ac}(G-g_2)\mathrm{Ac}(H-h_1)+\mathrm{Ac}(G-g_1-g_2)\mathrm{Ac}(H)\\ &\quad-x[\mathrm{Ac}(G-g_1)\mathrm{Ac}(H-h_1-h_2)+\mathrm{Ac}(G-g_2)\mathrm{Ac}(H-h_1-h_2)\\ &\quad+\mathrm{Ac}(G-g_1-g_2)\mathrm{Ac}(H-h_1)+\mathrm{Ac}(G-g_1-g_2)\mathrm{Ac}(H-h_2)]\\ &\quad+x^2\mathrm{Ac}(G-g_1-g_2)\mathrm{Ac}(H-h_1-h_2).\end{aligned} \tag{15}$$

4. Kekulé structures recurrence relationships

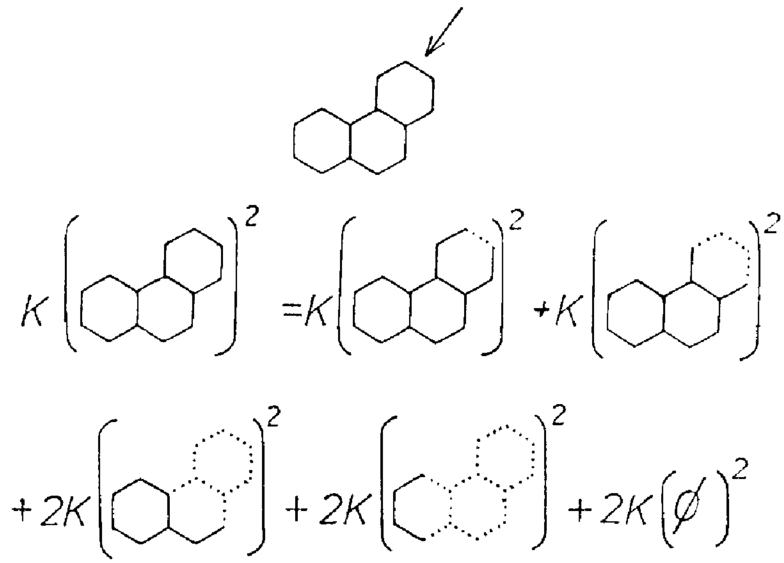
Based on the recurrence relationships (10)–(15) in terms of the characteristic and acyclic polynomials of conjugated hydrocarbons, we will derive five recurrence relationships enabling the computation of the number of Kekulé structures.

THEOREM 1

Let G be a benzenoid graph. Then $K(G)$ can be expressed as a function of the number of Kekulé structures of the subgraphs of G which do not contain the edge e_{ij}:

$$K(G)^2 = K(G-e_{ij})^2 + K(G-v_i-v_j)^2 + 2\sum_{k=1}^{r} K(G-C_k)^2, \tag{16}$$

where the summation goes over all r cycles in G which contain the edge e_{ij}.



Scheme 1.

The proof is straightforward by applying equality (8) to the recurrence relationship (10). An illustrative example (phenanthrene) is shown in scheme 1. On this and the following examples, the place of application of the theorems is indicated by an arrow pointing to the corresponding edge or vertex.

The graphical equation shown in scheme 1 gives the following equality expressed by the corresponding number of Kekulé structures:

$$5^2 = 3^2 + 2^2 + 2 \cdot 2^2 + 2 \cdot 1^2 + 2 \cdot 1^2.$$

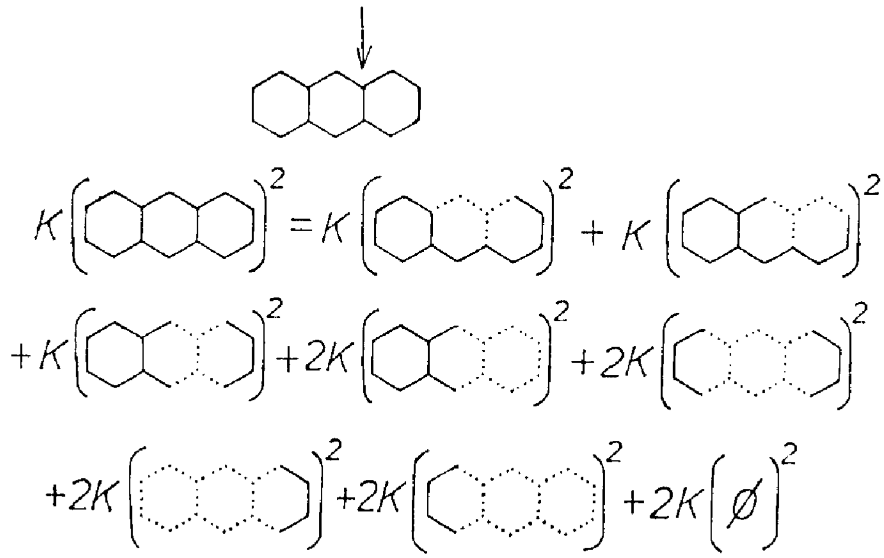
Using equality (9) in the corresponding decomposition in terms of acyclic polynomials (eq. (10)), we obtain the well-known equation (5).

THEOREM 2

The number of Kekulé structures of a benzenoid graph G is related to the number of Kelulé structures of the subgraphs of G obtained after the removal of the vertex υ_i with each of its d_i neighbours and of each of the r cycles C_k containing vertex υ_i:

$$K(G)^2 = \sum_{j=1}^{d_i} K(G - \upsilon_i - \upsilon_j)^2 + 2\sum_{k=1}^{r} K(G - C_k)^2. \tag{17}$$

This can be easily shown using eqs. (8) and (12). In scheme 2, we give another example, anthracene.



Scheme 2.

From the graphical example of theorem 2, we obtain the following equality for the number of Kekulé structures of the corresponding graphs:

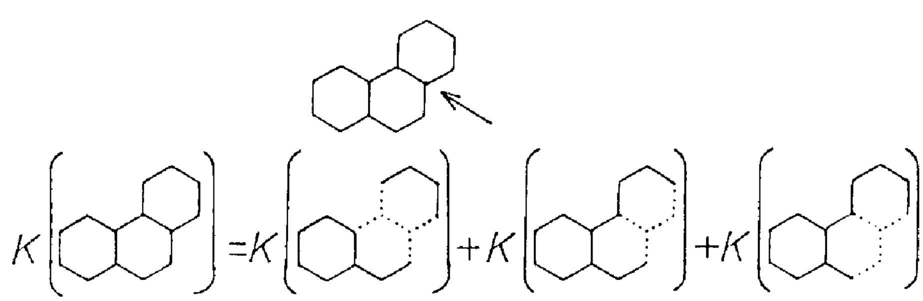
$$4^2 = 2^2 + 1^2 + 1^2 + 2\cdot 1^2 + 2\cdot 1^2 + 2\cdot 1^2 + 2\cdot 1^2 + 2\cdot 1^2.$$

THEOREM 3

The number of Kekulé structures of a graph G can be expressed in terms of the number of Kekulé structures of the subgraphs of G, corresponding to the deletion of the vertex v_i and each of its d_i neighbours in turn:

$$K(G) = \sum_{j=1}^{d_i} K(G - v_i - v_j). \tag{18}$$

The proof comes from eqs. (9) and (13). The theorem is illustrated for the same benzenoid hydrocarbon as above, phenanthrene.



Scheme 3.

The graphical example for theorem 3 gives the following expression for the number of Kekulé structures of the corresponding graphs:

$5 = 2 \cdot 1 + 2 + 1.$

For theorems 2 and 3 one must note that if G has an even number of vertices, then $G - v_i$ has an odd number of vertices and $K(G - v_i) = 0$. Obviously, the term corresponding to the subgraph $G - v_i$ was omitted.

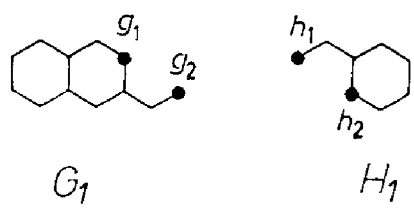
THEOREM 4

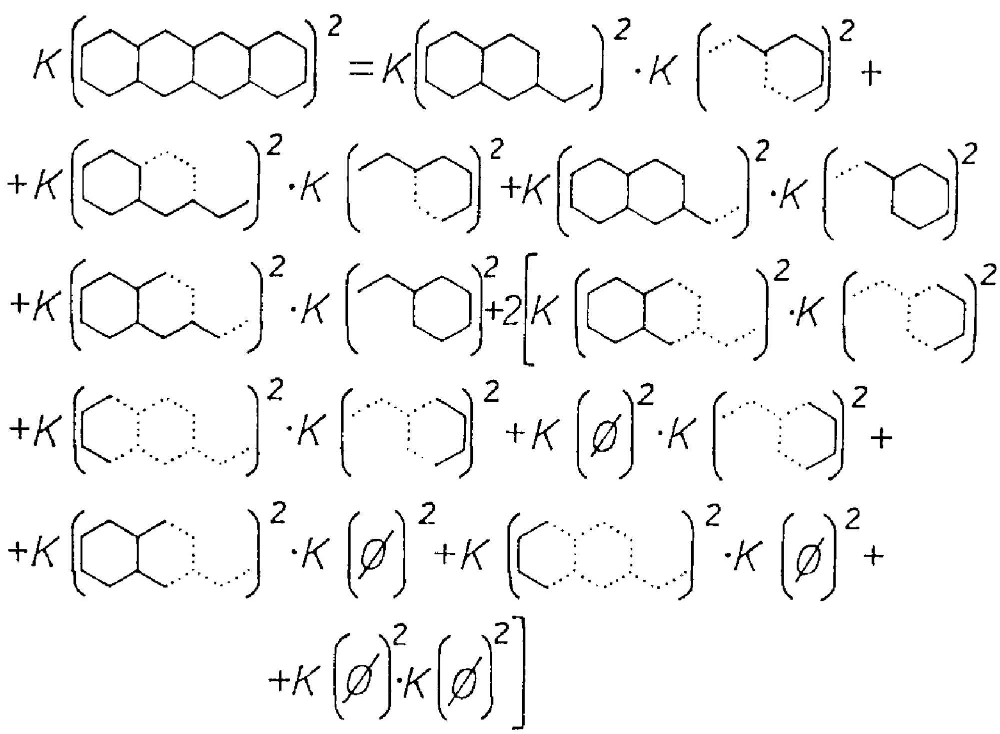
The number of Kekulé structures of the composed benzenoid graphs $G:H$ is equal to

$$K(G{:}H)^2 = K(G)^2 K(H - h_1 - h_2)^2 + K(G - g_1)^2 K(H - h_2)^2 + K(G - g_2)^2 K(H - h_1)^2 + K(G - g_1 - g_2)^2 K(H)^2 + 2\sum_g \sum_h K(G - P_g)^2 K(H - P_h)^2, \quad (19)$$

where the summations are over all paths P_g connecting vertices g_1 and g_2, and paths P_h connecting vertices h_1 and h_2, from G and H, respectively.

We prove this equality using eqs. (8) and (14) and lemma 1. An application of the theorem is illustrated in scheme 4 for the graphs G_1 and H_1, and $G_1{:}H_1$ is tetracene.





Scheme 4.

The graphical relation illustrated in scheme 4 can be translated in terms of the number of Kekulé structures of the graph $G:H$ and its subgraphs from eq. (19):

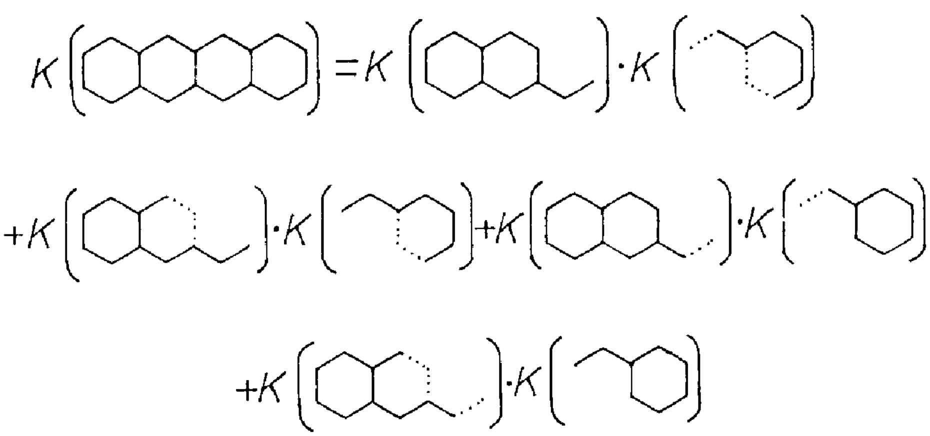
$$5^2 = 3^2 \cdot 1^2 + 0 \cdot 0 + 0 \cdot 0 + 1^2 \cdot 2^2 + 2 \cdot [1^2 \cdot 1^2 + 1^2 \cdot 1^2 + 1^2 \cdot 1^2 + 1^2 \cdot 1^2 + 1^2 \cdot 1^2 + 1^2 \cdot 1^2].$$

THEOREM 5

The number of Kekulé structures of the composed graph $G:H$ is equal to

$$K(G:H) = K(G)K(H - h_1 - h_2) + K(G - g_1)K(H - h_2)$$
$$+ K(G - g_2)K(H - h_1) + K(G - g_1 - g_2)K(H). \tag{20}$$

The proof comes from eqs. (9) and (15). The theorem is illustrated by the same graphs G_1, H_1 and G_1:H_1 as in the preceding case.



Scheme 5.

From the graphical expression of theorem 5, we obtain the following equality for the number of Kekulé structures of the graphs depicted in scheme 5:

$$5 = 3 \cdot 1 + 0 \cdot 0 + 0 \cdot 0 + 1 \cdot 2.$$

Obviously, if G and H contain even numbers of vertices, eq. (19) reduces to

$$K(G:H)^2 = K(G)^2 K(H - h_1 - h_2)^2 + K(G - g_1 - g_2)^2 K(H)^2$$
$$+ 2\sum_g \sum_h K(G - P_g)^2 K(H - P_h)^2, \tag{21}$$

while eq. (20) becomes

$$K(G:H) = K(G)K(H - h_1 - h_2) + K(G - g_1 - g_2)K(H). \tag{22}$$

If G and H contain odd numbers of verties, eq. (19) reduces to

$$K(G{:}H)^2 = K(G - g_1)^2 K(H - h_2)^2 + K(G - g_2)^2 K(H - h_1)^2 + 2\sum_g \sum_h K(G - P_g)^2 K(H - P_h)^2 \quad (23)$$

and eq. (20) gives

$$K(G{:}H) = K(G - g_1)K(H - h_2) + K(G - g_2)K(H - h_1). \quad (24)$$

If G has an even and H has an odd number of vertices, we have

$$K(G:H) = 0. \quad (25)$$

References

[1] A.T. Balaban, *Chemical Applications of Graph Theory* (Academic Press, London, 1976).
[2] N. Trinajstić, *Chemical Graph Theory* (CRC Press, Boca Raton, 1983).
[3] I. Gutman and O.E. Polansky, *Mathematical Concepts in Organic Chemistry* (Springer, Berlin, 1986).
[4] K. Balasubramanian, Chem. Rev. 85(1985)599.
[5] N. Trinajstić, D.J. Klein and M. Randić, Int. J. Quant. Chem. Quant. Chem. Symp. 20(1986)699.
[6] A.T. Balaban, Pure Appl. Chem. 54(1982)1075.
[7] A.T. Balaban, J. Mol. Struct. 120(1985)117.
[8] A.T. Balaban, J. Chem. Inf. Comput. Sci. 25(1985)334.
[9] S.J. Cyvin and I. Gutman, Comp. Math. Appl. 12B(1986)859.
[10] S.J. Cyvin and I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons*, Lecture Notes in Chemistry, Vol. 46 (Springer, Berlin, 1988);
I. Gutman and S.J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons* (Springer, Berlin, 1989); *Advances in the Theory of Benzenoid Hydrocarbons*, Topics in Current Chemistry, Vol. 153 (Springer, Berlin, 1990);
S.J. Cyvin, J. Brunvoll and B.N. Cyvin, *Theory of Coronoid Hydrocarbons*, Lecture Notes in Chemistry, Vol. 54 (Springer, Berlin, 1991).
[11] A.T. Balaban and I. Tomescu, MATCH 14(1983)155; 17(1985)91.
[12] A.T. Balaban and I. Tomescu, Croat. Chem. Acta 57(1984)391.
[13] A.T. Balaban, C. Artemi and I. Tomescu, MATCH 22(1987)77.
[14] D. Cvetković, I. Gutman and N. Trinajstić, J. Chem. Phys. 61(1974)2700.
[15] F. Harary, *Graph Theory* (Addison–Wesley, Reading, MA, 1971).
[16] I. Gutman, M. Milun and N. Trinajstić, MATCH 1(1975)171.
[17] D. Cvetković, M. Doob and H. Sachs, *Spectra of Graphs – Theory and Application* (Academic Press, New York, 1980).
[18] M. Randić, J. Chem. Soc. Faraday Trans. II 72(1976)232.
[19] M.J.S. Dewar and H.C. Longuet-Higgins, Proc. Roy. Soc. (London) A214(1952)482.
[20] I. Gutman, MATCH 6(1979)75.
[21] I. Gutman and H. Hosoya, Theor. Chim. Acta 48(1978)279.
[22] O.E. Polansky, MATCH 18(1985)71.
[23] I. Gutman, MATCH 19(1986)127.