Journal of Mathematical Chemistry, Vol. 42, No. 3, October 2007 (© 2006)
DOI: 10.1007/s10910-006-9096-7

Unicyclic graphs possessing Kekulé structures with minimal energy

Wen-Huan Wang*
Department of Mathematics, Shanghai University, Shanghai 200444, China
E-mail: whwang@shu.edu.cn

An Chang
Department of Mathematics, Fuzhou University, Fujian 350002, China

Dong-Qiang Lu
Shanghai Institute of Applied Mathematics and Mechanics, Shanghai 200072, China

Received 2 February 2006; revised 15 February 2006

Unicyclic graphs possessing Kekulé structures with minimal energy are considered. Let n and l be the numbers of vertices of graph and cycle C_l contained in the graph, respectively; r and j positive integers. It is mathematically verified that for $n \geqslant 6$ and $l = 2r+1$ or $l = 4j+2$, S_n^4 has the minimal energy in the graphs exclusive of S_n^3, where S_n^4 is a graph obtained by attaching one pendant edge to each of any two adjacent vertices of C_4 and then by attaching $n/2-3$ paths of length 2 to one of the two vertices; S_n^3 is a graph obtained by attaching one pendant edge and $n/2-2$ paths of length 2 to one vertex of C_3. In addition, we claim that for $6 \leqslant n \leqslant 12$, S_n^4 has the minimal energy among all the graphs considered while for $n \geqslant 14$, S_n^3 has the minimal energy.

KEY WORDS: unicyclic graph, perfect matching, Kekulé structure, minimal energy

MSC 2000: 05C17, 05C35

1. Introduction

It is known that conjugated molecules in chemistry may be classified into two groups: Kekuléan and non-Kekuléan molecules, depending on whether or not they possess Kekulé structures, which are perfect matchings for a molecular graph corresponding to the carbon atom skeleton of a conjugated unsaturated hydrocarbon [1]. In the chemical graph theory, the extremal energy of molecular graphs systems has been a subject of interest [2–14]. In this paper, the minimal energy of the unicyclic graph with Kekulé structures, i.e., unicyclic graphs with

*Corresponding author.

perfect matchings, will be investigated. The set of these graphs is denoted by $\mathcal{K}_n^l$. For any graph in $\mathcal{K}_n^l$, n is the number of vertices of the graph and l the number of vertices of the cycle contained in the graph. We denote the cycle by C_l.

The heats of atomization of conjugated hydrocarbons can be determined by the total π-electron energy. The total energy of all π-electrons in conjugated hydrocarbons, within the framework of HMO approximation [15, 16], can be given by

$$E(G) = \sum_{i=1}^{n} |\lambda_i|, \tag{1}$$

where $\lambda_1, \ldots, \lambda_n$ are the eigenvalues of the corresponding graph G. $E(G)$ can also be expressed as the Coulson integral formula [6]

$$E(G) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{1}{x^2} \ln \left[\left(\sum_{j=0}^{[n/2]} b_{2j} x^{2j} \right)^2 + \left(\sum_{j=0}^{[n/2]} b_{2j+1} x^{2j+1} \right)^2 \right] \mathrm{d}x, \tag{2}$$

where $b_i(G) = |a_i(G)|$, $(i = 0, 1, 2, \ldots, n)$, and $a_0, a_1, \ldots, a_n$ are the coefficients of the characteristic polynomial of G. The property of the Coulson integral formula was discussed by Gutman and Mateljevic [17]. It can be seen from equation (2) that $E(G)$ is a strictly monotonously increasing function of $b_i(G)$. Consequently, if

$$b_i(G_1) \geqslant b_i(G_2) \tag{3}$$

holds for all $i \geqslant 0$ where G_1 and G_2 are unicyclic graphs, then

$$E(G_1) \geqslant E(G_2) \tag{4}$$

and the equality in formula (4) is attained only if relation (3) is an equality for all $i \geqslant 0$ [6].

2. Preliminaries

For any graph G, the number of the Kekulé patterns is simply called the Kekulé number, denoted by $K(G)$, i.e., the number of perfect matching. Thus, we have property 1.

Property 1. Let $G \in \mathcal{K}_n^l$. If at least one vertex v of C_l is attached by a forest of odd order, then $K(G) = 1$. Otherwise, $K(G) = 2$.

Proof. *Case* (i). At least one vertex v of C_l is attached by a forest of odd order.

Because the forest is of odd order and every vertex of G is saturated, v and one vertex of the forest are matched. The rest of the vertices at C_l is clockwise considered. Denote the vertex adjacent to v by u. If u is also attached by a forest of odd order, similarly, u and one vertex of the forest are matched. If u is attached either by a forest of even order or by no forest, u and its next adjacent vertex at C_l are matched. The analysis on the rest of the vertices at C_l is the same as that for u. Thus, it can be concluded that every vertex of C_l are matched with a fixed vertex. Because the perfect matching of tree is unique, we have $K(G) = 1$.

Case (ii). Each vertex of C_l is attached either by a forest of even order or by no forest.

Since the perfect matching of the forest is unique, each vertex of C_l should be matched with another vertex at C_l. Thus, the number of the vertices of C_l is even and $K(C_l) = 2$. We have $K(G) = 2$. Thus, property 1 has been proved.

Let $m(G,k)$ be the number of k-matchings in G. It is clear that $m(G,1) = n$. We define $m(G,0) = 1$. Let $Q(G) = L(G) - M(G)$, where $L(G)$ is the edge set of G and $M(G)$ the perfect matching of G. It is clear that $|M(G)| = |Q(G)| = n/2$, where $|M(G)|$ and $|Q(G)|$ are the numbers of edges in $M(G)$ and $Q(G)$, respectively. Let $\widehat{G}$ be the graph induced by $Q(G)$, that is, $\widehat{G} = G - M(G) - S_0$, where S_0 is the set of singletons in $G - M(G)$. We call $\widehat{G}$ the capped graph of G and G the original graph of $\widehat{G}$. Each k-matching Ω of G can be partitioned into two parts: $\Omega = \Phi \cup \Psi$, where Φ is a matching in $\widehat{G}$ and $\Psi \subseteq M(G)$. On the other hand, any i-matching Φ of $\widehat{G}$ and $k-i$ edges Ψ of $M(G)$ that are not adjacent to Φ form a k-matching Ω of G with partition $\Omega = \Phi \cup \Psi$. Thus, we have

$$m(G,k) = \sum_{i=0}^{n/2} m(\widehat{G}, i) \cdot \binom{n/2 - j}{k - i}, \tag{5}$$

where j is the number of edges in $M(G)$, which are adjacent to i-matching Φ [4].

To formulate the main results of the present paper, definitions of certain types of graphs and necessary lemmas are introduced.

Let S_n^4 is a graph obtained by attaching one pendant edge to each of any two adjacent vertices of C_4 and then by attaching $n/2 - 3$ paths of length 2 to one of the two vertices. For instance, S_{10}^4 and $\widehat{S_{10}^4}$ are shown in figure 1.

Let R_n^3 is a graph obtained by attaching one pendant edge to every vertex of C_3 and then by attaching $n/2 - 3$ paths of length 2 to a vertex of C_3. For instance, R_{10}^3 and $\widehat{R_{10}^3}$ are shown in figure 2.

Let S_n^3 is a graph obtained by attaching one pendant edge and $n/2-2$ paths of length 2 to one vertex of C_3. For instance, S_{10}^3 and $\widehat{S_{10}^3}$ are shown in figure 3.

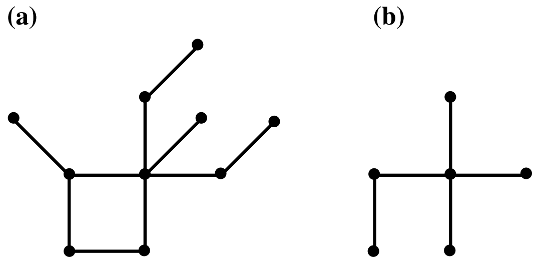

Figure 1. (a) S_{10}^{4}; (b) $\widehat{S}_{10}^{4}$.

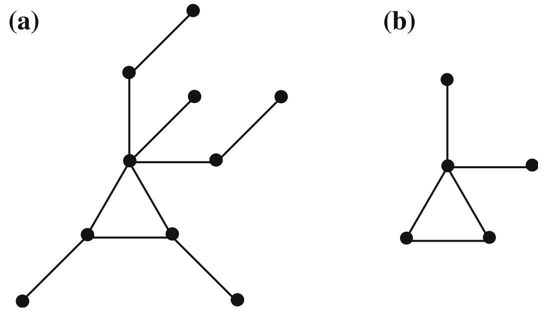

Figure 2. (a) R_{10}^{3}; (b) $\widehat{R}_{10}^{3}$.

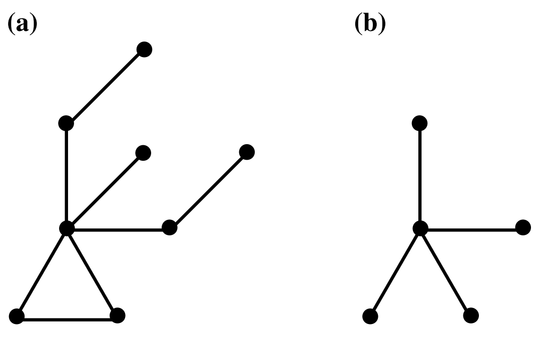

Figure 3. (a) S_{8}^{3}; (b) $\widehat{S}_{8}^{3}$.

Lemma 1 [16]. If u and v are adjacent vertices of G and e is the edge connecting u and v, then for $k \geqslant 1, m(G,k) = m(G-e,k) + m(G-u-v,k-1)$.

Lemma 2 [6]. Let G be a unicyclic graph with cycle C_l. Then

$$b_{2k}(G) = m(G,k) + 2(-1)^{r+1}m(G-C_l,k-r)$$

and $b_{2k+1}(G) = 0$ for $l = 2r$ while $b_{2k}(G) = m(G,k)$ and

$$b_{2k+1}(G) = \begin{cases} 0, & 2k+1 < l, \\ 2m(G-C_l,k-r), & 2k+1 \geqslant l \end{cases}$$

for $l = 2r+1$, where $k = 0, 1, \ldots, n/2$.

3. Main results

Next, some properties of $\widehat{G}$ are given. $\widehat{G}$ can be classified into three categories: (i) connected unicyclic graphs, (ii) trees, and (iii) unconnected graphs whose components are trees and C_l or trees only. If $\widehat{G}$ is a connected unicyclic graph, every vertex of $\widehat{G}$ is incident with a distinct edge of $M(G)$ since it is saturated. Obviously, we have property 2 as follows.

Property 2. If $\widehat{G}$ is a connected unicyclic graph, any 2-matchings of $\widehat{G}$ are adjacent to four edges of $M(G)$. Otherwise, any 2-matchings of $\widehat{G}$ are adjacent to at most four edges of $M(G)$.

Lemma 3. Let $G \in \mathcal{K}_n^l \backslash \{S_n^3\}$ and $n \geqslant 8$, then $m(\widehat{G}, 2) \geqslant n/2 - 3$.

Proof. It is clear that $m(\widehat{S_n^3}, 2) = 0$. $\widehat{G}$ is classified into three cases.

Case (i) $\widehat{G}$ is a connected unicyclic graph.

When $n \geqslant 8$ and $G = R_n^3$, it is obvious that $m(\widehat{R_n^3}, 2) = n/2 - 3$. Next we consider $G \neq R_n^3$.

From Lemma 1, we have $m(\widehat{G}, 2) = m(\widehat{G} - e, 2) + m(\widehat{G} - u - v, 1)$. We can choose an edge from $Q(G)$ at C_l in such a way that the edge, denoted by $e = uv$, satisfies $m(\widehat{G} - u - v, 1) \geqslant 1$ and $\widehat{G} - e \neq K_{1,n/2-1}$, where $K_{1,n/2-1}$ is a star graph. Obviously, $\widehat{G} - e$ is a tree with $n/2$ vertices. Therefore, $\widehat{G} - e$ has two non-empty trees, denoted by T_1 with a edges and T_2 with $n/2 - a - 2$ edges, which are connected by an edge of $\widehat{G} - e$. The edges in T_1 are disjoint with those in T_2. $\widehat{G} - e$ has at least $n/2 - 3$ 2-matchings since each edge in one tree along with another in the other tree forms a 2-matching. Thus, we obtain $m(\widehat{G}, 2) \geqslant (n/2 - 3) + 1 = n/2 - 2$.

Case (ii) $\widehat{G}$ is a tree.

When $n \geqslant 8$ and $G \neq S_n^3$, we have $\widehat{G} \neq K_{1,n/2}$. Furthermore, $\widehat{G}$ is obviously a tree with $n/2 + 1$ vertices. Therefore, $\widehat{G}$ has two non-empty trees, denoted by

T_3 with b edges and T_4 with $n/2-b-1$ edges, which are connected by an edge of $\widehat{G}$. The edges in T_3 are disjoint with those in T_4. $\widehat{G}$ has at least $n/2-2$ 2-matchings since each edge in one tree along with another in the other tree forms a 2-matching. Thus, we have $m(\widehat{G},2) \geqslant n/2-2$.

Case (iii) $\widehat{G}$ is a unconnected graph whose components are trees and C_l or trees only.

If $\widehat{G}$ is composed of trees and C_l, we might concatenate them together into a connected unicyclic graph, denoted by $\widehat{G}_1$. It is obvious that $m(\widehat{G},2) > m(\widehat{G}_1,2)$. By the approach similar to Case (i), we have $m(\widehat{G}_1,2) \geqslant n/2-3$. Therefore, $m(\widehat{G},2) > n/2-3$.

If $\widehat{G}$ is composed of trees only, we might concatenate them together into a tree, denoted by $\widehat{G}_2$, in such a way that $\widehat{G}_2 \neq \widehat{S}_n^3$. It is obvious that $m(\widehat{G},2) > m(\widehat{G}_2,2)$. By the approach similar to Case (ii), we have $m(\widehat{G}_2,2) \geqslant n/2-2$. Therefore, $m(\widehat{G},2) > n/2-2$.

Lemma 3 is readily attained by combining Cases (i)–(iii).

From lemma 3, we have theorem 1 as follows.

Theorem 1. Let $G \in \mathcal{K}_n^l \backslash \{S_n^3\}$ and $n \geqslant 6$. When $l = 2r+1$ or $l = 4j+2$ (r and j are non-negative integers), $E(G) > E(S_n^4)$.

Proof. When $n = 6$, $G \neq S_n^3$ and $l = 3, 5, 6$, by a straightforward calculation on $E(G)$, we verify that S_6^4 has the minimal energy.

It is noted that $m(\widehat{S}_n^4, 2) = n/2-2$. Since one 2-matching of $\widehat{S}_n^4$ are adjacent to three edges of $M(S_n^4)$ and the other 2-matchings of $\widehat{S}_n^4$ to four edges of $M(S_n^4)$, and $m(\widehat{S}_n^4, i) = 0$ when $3 \leqslant i \leqslant n/2$, we have

$$\begin{aligned} m(S_n^4,k) &= \sum_{i=0}^{n/2} m(\widehat{S}_n^4,i)\cdot\binom{\frac{n}{2}-j}{k-i} \\ &= \binom{\frac{n}{2}}{k} + \frac{n}{2}\cdot\binom{\frac{n}{2}-2}{k-1} + \binom{\frac{n}{2}-3}{k-2} + \left(\frac{n}{2}-3\right)\cdot\binom{\frac{n}{2}-4}{k-2}. \end{aligned}$$

From lemma 2 and the fact that $S_n^4 - C_4$ is composed of $n/2-3$ independent edges and two isolated vertices, we obtain

$$\begin{aligned} b_{2k}(S_n^4) &= m(S_n^4,k) - 2m(S_n^4 - C_4, k-2) \\ &= m(S_n^4,k) - 2\cdot\binom{\frac{n}{2}-3}{k-2} \\ &= \binom{n/2}{k} + \frac{n}{2}\cdot\binom{n/2-2}{k-1} - \binom{\frac{n}{2}-3}{k-2} + \left(\frac{n}{2}-3\right)\cdot\binom{\frac{n}{2}-4}{k-2}. \end{aligned} \tag{6}$$

When $n \geqslant 8$ and $G \neq S_n^3$, G is classified into two cases as follows.

Case (i) $l = 2r + 1$.

From lemma 2, we have

$$b_{2k}(G) = m(G, k)$$
$$= \binom{n/2}{k} + \frac{n}{2} \cdot \binom{\frac{n}{2} - 2}{k - 1} + m(\widehat{G}, 2) \cdot \binom{\frac{n}{2} - j}{k - 2} + \sum_{i=3}^{n/2} m(\widehat{G}, i) \cdot \binom{\frac{n}{2} - j}{k - i}.$$

From lemma 3 and property 2, we have

$$b_{2k}(G) \geqslant \binom{\frac{n}{2}}{k} + \frac{n}{2} \cdot \binom{n/2 - 2}{k - 1} + \left(\frac{n}{2} - 3\right) \cdot \binom{\frac{n}{2} - 4}{k - 2}. \quad (7)$$

Formula (7) subtracted from equation (6) gives

$$b_{2k}(G) - b_{2k}(S_n^4) \geqslant \binom{\frac{n}{2} - 3}{k - 2} \geqslant 0. \quad (8)$$

The second equality in formula (8) holds if and only if $k = n/2$. From formula (8), we have

$$b_{2k}(G) \geqslant b_{2k}(S_n^4). \quad (9)$$

It is clear that the equality in formula (9) does not hold for all k.

From lemma 2, we have $b_{2k+1}(S_n^4) = 0$ and $b_{2k+1}(G) = 2m(G - C_l, k - r)$. We get

$$b_{2k+1}(G) \geqslant b_{2k+1}(S_n^4). \quad (10)$$

The equality in formula (10) does not hold for all k. For example, $b_{2r+1}(G) = 2$.

From formulae (9) and (10), we have $E(G) > E(S_n^4)$ when $l = 2r + 1$.

Case (ii) $l = 4j + 2$ and $r = 2j + 1$.

From lemma 2, we have $b_{2k}(G) = m(G, k) + 2m(G - C_l, k - r)$. By the approach similar to Case (i), we have

$$b_{2k}(G) \geqslant b_{2k}(S_n^4). \quad (11)$$

The equality in formula (11) does not hold for all k.

From lemma 2, we have

$$b_{2k+1}(G) = b_{2k+1}(S_n^4) = 0. \quad (12)$$

From formulae (11) and (12) we have $E(G) > E(S_n^4)$ when $l = 4j + 2$.

From Cases (i) and (ii), theorem 1 has been proved.

3.1. Beyond theorem 1

By the method for calculating the characteristic polynomials [15], we obtain

$$\phi(S_n^3) = (\lambda^2 - 1)^{n/2-2}[\lambda^4 - (2 + n/2)\lambda^2 - 2\lambda + 1],$$
$$\phi(S_n^4) = (\lambda^2 - 1)^{n/2-4}[\lambda^8 - (4 + n/2)\lambda^6 + (2 + 3n/2)\lambda^4 - (3 + n/2)\lambda^2 + 1] .$$

For S_n^3, some absolutes of the odd coefficients, b_{2k+1}, of the characteristic polynomials of S_n^3 are non-zero. Thus, formulae (3) and (4) can not be used to compare the energies of S_n^3 and S_n^4. The sum of absolutes of eigenvalues of $\phi(S_n^3)$ can exactly be obtained as an algebraic expression, so is that of $\phi(S_n^4)$. However, it is extremely difficult to compare the algebraic expressions obtained so that the direct comparison between $E(S_n^3)$ and $E(S_n^4)$ remains a formidable mathematical task. Numerical calculations clearly indicate that for even $n, 6 \leqslant n \leqslant 12$, the energy of S_n^3 is greater than that of S_n^4. However, when $14 \leqslant n \leqslant 40$, the energy of S_n^3 is smaller than that of S_n^4. This is inferred by the data shown in table 1, where $\Delta_n = E(S_n^4) - E(S_n^3)$. It should be noted that Δ_n increases monotonically as n increases. Therefore, it is plausible to expect that $E(S_n^3) < E(S_n^4)$ for $n \geqslant 14$. Furthermore, the graphical representations for $\Delta_n = E(S_n^4) - E(S_n^3)$ with large n are shown in figures 4 and 5. The numerical and graphical evidences are sufficiently convincing to allow the formulation of the following improvement of theorem 1.

Assertion Let $G \in \mathcal{K}_n^l$. When $l = 2r + 1$ or $l = 4j + 2$ (r and j are non-negative integers), $E(G) > E(S_n^4)$ for $6 \leqslant n \leqslant 12$ while $E(G) > E(S_n^3)$ for $n \geqslant 14$.

A rigorous mathematical proof of the above assertion remains a task for the future.

Table 1

n	Δ_n	n	Δ_n	n	Δ_n
6	−0.1347390	18	0.0757261	30	0.1616500
8	−0.0795080	20	0.0945098	32	0.1715100
10	−0.0358839	22	0.1110570	34	0.1805550
12	−0.0003988	24	0.1257690	36	0.1888890
14	0.0291360	26	0.1389520	38	0.1965970
16	0.0541752	28	0.1508490	40	0.2037540

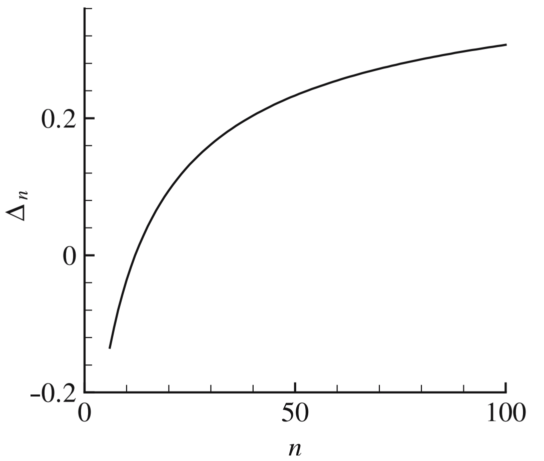

Figure 4. Δ_n for $6 \leqslant n \leqslant 10^2$.

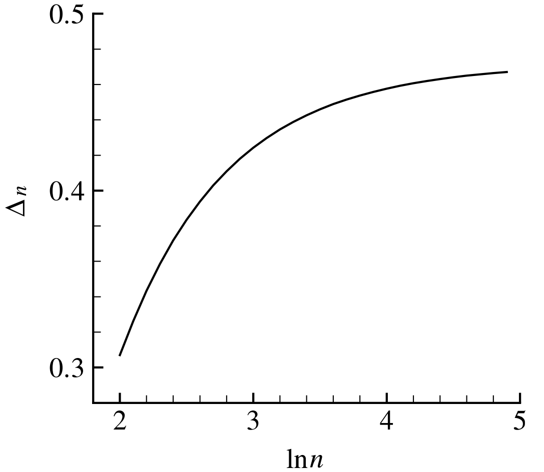

Figure 5. Δ_n for $10^2 \leqslant n \leqslant 10^5$.

Acknowledgments

The work was partially supported by the National Natural Science Foundation of China under Grant Numbers 10571117 and 10371019.

References

[1] H. Hosoya, Introduction to graph theory, in: *Graph Theoretical Approaches to Chemical Reactivity*, eds. D. Bonchev and O. Mekenyan (Kluwer Academic Publishers, Dordrecht, 1994), p. 30.

[2] I. Gutman, Theoret. Chim. Acta 45 (1977) 79–87.

[3] H. Li, J. Math. Chem. 25 (1999) 145–169.
[4] F. Zhang and H. Li, Discrete Appl. Math. 92 (1999) 71–84.
[5] I. Gutman and Y.P. Hou, MATCH-Commun. Math. Comput. Chem. 43 (2001) 17–28.
[6] Y.P. Hou, J. Math. Chem. 29 (2001) 163–168.
[7] F.J. Zhang, Z.M. Li and L. Wang, Chem. Phys. Lett. 337 (2001) 125–130.
[8] F.J. Zhang, Z.M. Li and L. Wang, Chem. Phys. Lett. 337 (2001) 131–137.
[9] Y.P. Hou, Linear Multilinear Algebra 49 (2002) 347–354.
[10] J. Rada, Discrete Appl. Math. 145 (2005) 437–443.
[11] J.B. Zhang and B. Zhou, J. Math. Chem. 37 (2005) 423–431.
[12] W.G. Yan and L.Z. Ye, Appl. Math. Lett. 18 (2005) 1046–1052.
[13] W.H. Wang, A. Chang, L.Z. Zhang and D.Q. Lu, J. Math. Chem. 39 (2006) 231–241.
[14] B. Zhou and F. Li, J. Math. Chem. 39 (2006) 465–474.
[15] D.M. Cvetković, M. Doob and H. Sachs, *Spectra of Graphs-Theory and Application* (Academic Press, New York, 1980).
[16] I. Gutman and O.E. Polansky, *Mathematical Concepts in Organic Chemistry* (Springer-Verlag, Berlin, 1986), p. 37.
[17] I. Gutman and M. Mateljevic, J. Math. Chem. 39 (2006) 259–266.