

CHEMICAL GRAPH POLYNOMIALS. PART 4.¹

NON-ISOMORPHIC GRAPHS WITH IDENTICAL ACYCLIC POLYNOMIALS

Ovidiu IVANCIUC

University "Politehnica" of Bucharest, Department of Organic Chemistry,
Faculty of Chemical Technology, Oficiul 12 CP 243, 78100 Bucharest, Roumania
E-mail: o_ivanciuc @ chim.upb.ro

Received May 5, 1997

The acyclic polynomial of molecular graphs representing cyclopropanes and cyclobutanes is investigated. Two non-isomorphic graphs with identical acyclic polynomial are termed matching isospectral graphs. A large number of matching isospectral graphs were found in the set of investigated graphs. Some of them are structurally related, and can be generated from graphs with matching endospectral vertices.

INTRODUCTION

The molecular graph polynomials, spectra (eigenvalues), eigenvectors, and spectral moments represent an important source of structural descriptors used in developing structure-property models. Also, they were studied extensively in connection with the molecular orbital theory of unsaturated compounds.²⁻⁵

The paper presents investigations on the acyclic polynomial of molecular graphs for a collection of cyclopropanes and cyclobutanes. Two non-isomorphic graphs with identical acyclic polynomial are termed matching isospectral graphs. A large number of matching isospectral graphs were found in the set of investigated graphs. Some of them are structurally related, and can be generated from graphs with matching endospectral vertices. The properties of matching endospectral graphs are presented.

THE ACYCLIC (MATCHING) POLYNOMIAL

The graph definitions used in this paper are presented below. A molecular graph is a representation of a molecule in which atoms are depicted as points (vertices), and chemical bonds are depicted as lines (edges) joining the vertices. All N vertices of a graph G form the vertex set V , and the M edges are elements of the edges set E . The subgraph $G-v_i$ is obtained from the graph G by deletion of vertex v_i , $v_i \in V(G)$. The subgraph $G-e_{ij}$ is obtained from the graph G by deletion of edge e_{ij} connecting two vertices v_i and v_j , $v_i, v_j \in V(G)$. The graph denoted $(G, v_i; a)$ is obtained from the graph G by inserting a loop of weight a to vertex v_i . The composite graph $(G \cdot H, v_g \cdot v_h)$, where $v_g \in V(G)$ and $v_h \in V(H)$, is obtained from graphs G and H by identifying their vertices v_g and v_h . A walk in a graph is a sequence of edges which can be continuously traversed, starting from any vertex and ending on any vertex. Repeated use of the same edge or edges is allowed. A self-returning walk is a walk starting and finishing at the same vertex. The length of a walk is the total number of edges that are traversed.

A k -matching of a graph G is a subgraph of G consisting of k independent (i.e. mutually non-incident) edges. If $m(G, k)$ denotes the number of k -matchings of a graph G with N vertices, then the acyclic (matching) polynomial of G is defined by the following equation:⁶⁻⁹

$$\text{Ac}(G, x) = \sum_{k=0}^{N/2} (-1)^k m(G, k) x^{N-2k} \quad (1)$$

This polynomial plays an important role in statistical physics (theory of monomer-dimer systems),⁶⁻⁸ in developing topological indices for quantitative structure-property relationships,⁹ and in quantum organic chemistry (topological resonance energy).^{10,11}

A widely used method for the computation of the acyclic polynomial is the decomposition of the graph in smaller subgraphs by the deletion of a vertex or of an edge. The idea behind the use of recurrence relationships is to reduce the graph G to smaller fragments for which the acyclic polynomials are known or easier to compute with other methods. The decomposition of the graph G at its edge e_{ij} gives the following equality in terms of acyclic polynomials of the graph G , $\text{Ac}(G)$, and its subgraphs:⁹

$$\text{Ac}(G) = \text{Ac}(G - e_{ij}) - \text{Ac}(G - v_i - v_j) \quad (2)$$

The expansion of the acyclic polynomial is given in the following equation in terms of the acyclic polynomials of its subgraphs, corresponding to the decomposition of the graph G at its vertex v_i .¹²

$$\text{Ac}(G) = x\text{Ac}(G - v_i) - \sum_{j=1}^{d_i} \text{Ac}(G - v_i - v_j) \quad (3)$$

where the summation goes over all d_i neighbours of vertex v_i .

Let g be a vertex in the graph G and let h be a vertex in the graph H . The composed graph $G \cdot H$ is obtained by identifying vertex g with vertex h . The acyclic polynomial of the composed graph $G \cdot H$ is expressed by the following equation:^{13,14}

$$\text{Ac}(G \cdot H) = \text{Ac}(G)\text{Ac}(H - h) + \text{Ac}(G - g)\text{Ac}(H) - x\text{Ac}(G - g)\text{Ac}(H - h) \quad (4)$$

The acyclic polynomial is identical with the characteristic polynomial for trees (graphs without cycles). This property and equation (2) were used by Ramaraj and Balasubramanian to develop an efficient algorithm for the computation of the acyclic polynomial.¹⁵

If graph G is modified by setting a loop with the weight a to vertex v_i , the following equality takes place:¹⁶

$$\text{Ac}(G, v_i; a) = \text{Ac}(G) - a\text{Ac}(G - v_i) \quad (5)$$

MATCHING ISOSPECTRAL GRAPHS

The characteristic polynomial is an important graph invariant, used to develop structural descriptors, aromaticity and reactivity indices. Although it was initially conjectured that the characteristic polynomial and its spectrum might be used as unique descriptors of graphs, nonisomorphic graphs with identical spectrum, spectral moments and characteristic polynomial were found, and called isospectral or cospectral graphs.¹⁷⁻²³

Self-returning walks of length k may be computed by considering the diagonal elements of the first k powers of the adjacency matrix \mathbf{A} , due to the fact that each diagonal element $(\mathbf{A}^k)_{ii}$ of the matrix \mathbf{A}^k can be interpreted as the sum of all self-returning walks of length k from/to vertex v_i . The sequence of integers $\{(\mathbf{A}^1)_{ii}, (\mathbf{A}^2)_{ii}, \dots, (\mathbf{A}^N)_{ii}\}$ defines the Self-Returning Walk Atomic Code (SRWAC) of the atom v_i in a molecule.²⁴ The SRWAC characterizes the environment of a given atom in a molecule.

In certain cases, nonequivalent vertices in a molecular graph have identical SRWACs. Such vertices are termed endospectral vertices, and the corresponding graph is termed an endospectral graph.²¹⁻²⁸ The concept of endospectral graphs is connected with the problem of isospectral graphs: in an endospectral graph with v and w as the endospectral vertices any subgraph attached to either vertex v or vertex w produces a pair of isospectral graphs.

In the case of the acyclic polynomial the existence of non-isomorphic cyclic graphs with identical acyclic polynomials is known. We designate such graphs as Matching Isospectral Graphs (MIGs). Because the problem of Matching Endospectral Graphs (MEGs) and Matching Endospectral Vertices (MEVs) was not investigated, we present here some results for molecular graphs representing cyclopropanes and cyclobutanes.

Table 1

Acyclic isospectral molecular graphs derived from cyclopropane and their degenerate acyclic polynomial

Cyclopropanes with Identical Acyclic Polynomial		x^0	x^1	x^2	x^3	x^4	x^5	x^6	x^7	x^8	x^9	
1,2,3- M_3 - cC_3	1-E-1-M- cC_3	-1	0	6	0	-6	0	1				
1-E-2,2- M_2 - cC_3	1-iP-1-M- cC_3	0	-2	0	10	0	-7	0	1			
1-B-M- cC_3	1-sB-2-M- cC_3	0	-4	0	12	0	-7	0	1			
1-B-1-M- cC_3	1-sB-2-M- cC_3	1	0	-9	0	17	0	-8	0	1		
1,2-E ₂ -3-M- cC_3	1-E-1-P- cC_3	1	0	-11	0	17	0	-8	0	1		
1,2-M ₂ -2-P- cC_3	1-iP-2,3-M ₂ - cC_3	(1,1-M ₂ -P)- cC_3	0	0	-7	0	16	0	-8	0	1	
1-E-2-P- cC_3	(1-E-P)- cC_3	1	0	-12	0	18	0	-8	0	1		
1,2-P ₂ - cC_3	(1-E-B)- cC_3	0	5	0	-24	0	25	0	-9	0	1	
1-iP-2-P- cC_3	(1-E-2-M-P)- cC_3	0	2	0	-20	0	24	0	-9	0	1	
1,1,2-M ₃ -2-P- cC_3	1-tB-1-E- cC_3	0	0	0	-13	0	21	0	-9	0	1	
1,1,2-M ₃ -3-P- cC_3	1-E-2-iP-2-M- cC_3	0	2	0	-16	0	22	0	-9	0	1	
1,2-E ₂ -3,3-M ₂ - cC_3	1-E-1-iP-2-M- cC_3	0	2	0	-17	0	22	0	9	0	1	
1-iB-1,2-M ₂ - cC_3	1-tB-2-E- cC_3	0	0	0	-13	0	22	0	-9	0	1	
1-sB-2,2-M ₂ - cC_3	1-(1,2-M ₂ -P)-1-M- cC_3	1-(1,1-M ₂ -P)-2-M- cC_3	0	2	0	-14	0	22	0	-9	0	1
1-B-2,2-M ₂ - cC_3	1-E-1-iB- cC_3	0	2	0	-17	0	23	0	-9	0	1	
1-iB-2,3-M ₂ - cC_3	1-(1,2-M ₂ -P)-2-M- cC_3	0	2	0	-16	0	23	0	-9	0	1	
1-(3-M-B)-1-M- cC_3	(2,2-M ₂ -B)- cC_3	0	2	0	-15	0	23	0	-9	0	1	
1-(3-M-B)-2-M- cC_3	(2,3-M ₂ -B)- cC_3	0	2	0	-18	0	24	0	-9	0	1	
1-A-1-M- cC_3	(1,2-M ₂ -B)- cC_3	0	4	0	-20	0	24	0	-9	0	1	
1-(1-E-P)-1-M- cC_3	(1-E-1-M-P)- cC_3	0	4	0	-19	0	23	0	-9	0	1	
1-sB-2-E- cC_3	1-(1-E-P)-2-M- cC_3	0	5	0	-21	0	24	0	-9	0	1	

The acyclic polynomials of 142 cyclopropanes between C_3H_6 and C_9H_{18} were computed by decomposing the molecular graph in acyclic fragments with equation (2), followed by the computation of the characteristic polynomials of the fragments with the Le Verrier-Fadeev-Frame algorithm.²⁹ By comparing the acyclic polynomials we have identified the MIGs reported in Table 1 together with their corresponding polynomials. For such a small collection we have identified a fairly large number of degenerated polynomials: 19 pairs of MIGs and 2 triplets of MIGs.

Table 2

Acyclic isospectral molecular graphs derived from cyclobutane and their degenerate acyclic polynomial

Cyclobutanes with Identical Acyclic Polynomial		x^0	x^1	x^2	x^3	x^4	x^5	x^6	x^7	x^8	x^9	
1-E-3-M- cC_4	iP- cC_4	0	-4	0	12	0	-7	0	1			
1-E-2,2-M ₂ - cC_4	1-iP-1-M- cC_4	0	0	-8	0	16	0	-8	0	1		
1-E-3,3-M ₂ - cC_4	tB- cC_4	0	0	-6	0	16	0	-8	0	1		
1-E-2,4-M ₂ - cC_4	1-M-1-P- cC_4	0	0	-10	0	17	0	-8	0	1		
1,3-E ₂ - cC_4	sB- cC_4	2	0	-12	0	18	0	-8	0	1		
1-E-2,3,4-M ₃ - cC_4	1,1-E ₂ -3-M- cC_4	0	4	0	-19	0	23	0	-9	0	1	
1-E-2,2,3-M ₃ - cC_4	1-iP-1,2-M ₂ - cC_4	0	2	0	-16	0	22	0	-9	0	1	
1-iP-1,3-M ₂ - cC_4	1-iP-2,2-M ₂ - cC_4	0	0	0	-14	0	22	0	-9	0	1	
1-P-3,3-M ₂ - cC_4	1-iB-1-M- cC_4	0	0	0	-16	0	23	0	-9	0	1	
1-P-2,3-M ₂ - cC_4	1-E-2-iP- cC_4	1-B-1-M- cC_4	0	4	0	-21	0	24	0	-9	0	1
1-P-1,3-M ₂ - cC_4	1-iP-2,4-M ₂ - cC_4	0	0	0	-17	0	23	0	-9	0	1	
1-E-3-iP- cC_4	1-sB-3-M- cC_4	(1,2-M ₂ -P)- cC_4	0	4	0	20	0	24	0	-9	0	1
1,3-E ₂ -1-M- cC_4	(1,1-M ₂ -P)- cC_4	0	4	0	-18	0	23	0	-9	0	1	
1-B-2-M- cC_4	(1-M-B)- cC_4	0	6	0	-24	0	25	0	-9	0	1	
1-iP-3,3-M ₂ - cC_4	1-tB-3-M- cC_4	0	0	0	-12	0	22	0	-9	0	1	

The acyclic polynomials of 93 cyclobutanes between C_4H_8 and C_9H_{18} were computed with the same method used in the case of cyclopropanes. By comparing the coefficients of the acyclic polynomials we have identified the MIGs presented in Table 2 together with their corresponding polynomials. The degeneracy phenomena are quite frequent for cyclobutanes also, and we have found 13 pairs of MIGs and 2 triplets of MIGs.

MATCHING ENDOSPECTRAL VERTICES

An inspection of the molecular graphs with identical acyclic polynomials presented in Tables 1 and 2 reveals that certain pairs of degenerate graphs are structurally related, and can be obtained from a common graph G which has two topologically nonequivalent vertices v and w with the property that any subgraph H connected in turn to v and w gives a pair of MIGs. We denote such vertices v and w as matching endospectral vertices. A graph containing a pair of MEVs is called a matching endospectral graph. Below we present the properties of matching endospectral vertices.

Two topologically nonequivalent vertices v_i and v_j , $v_i, v_j \in V(G)$, are matching endospectral, if the following three conditions are true:

(1) by deleting both vertices v_i and v_j in turn the graphs $G - v_i$ and $G - v_j$ are matching isospectral:

$$\text{Ac}(G - v_i) = \text{Ac}(G - v_j) \quad (6)$$

(2) by weighting both vertices v_i and v_j in turn with a loop with weight a the graphs $(G, v_i : a)$ and $(G, v_j : a)$ are matching isospectral:

$$\text{Ac}(G, v_i : a) = \text{Ac}(G, v_j : a) \quad (7)$$

(3) by connecting a graph H with its vertex v_h to both vertices v_i and v_j in turn the graphs $(G \cdot H, v_i \cdot v_h)$ and $(G \cdot H, v_j \cdot v_h)$ are matching isospectral:

$$\text{Ac}(G \cdot H, v_i \cdot v_h) = \text{Ac}(G \cdot H, v_j \cdot v_h) \quad (8)$$

Consider that equality (6) holds. Then from equation (5) we obtain equation (7), and from equation (4) we obtain equation (8). Equation (8) defines the general method of generating MIGs from an MEG.

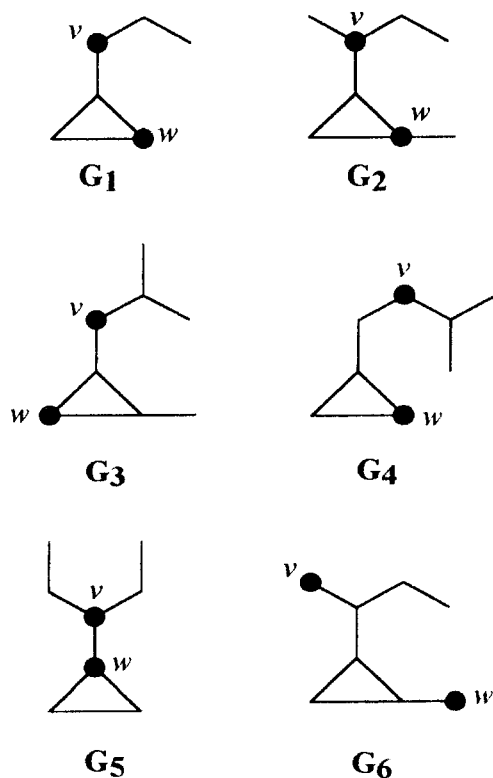


Fig. 1. Matching endospectral graphs derived from cyclopropane. Endospectral vertices v and w are depicted as black circles.

A search in the collection reported in Table 1 of MIGs derived from cyclopropane gives the set of MEGs presented in Fig. 1. Equation (6) is verified for all graphs G_1 - G_6 :

$$\text{Ac}(G_1 - v) = \text{Ac}(G_1 - w) = x^5 - 4x^3 + 3x$$

$$\text{Ac}(G_2 - v) = \text{Ac}(G_2 - w) = x^7 - 5x^5 + 5x^3 - x$$

$$\text{Ac}(G_3 - v) = \text{Ac}(G_3 - w) = x^7 - 6x^5 + 9x^3 - 2x$$

$$\text{Ac}(G_4 - v) = \text{Ac}(G_4 - w) = x^7 - 6x^5 + 9x^3 - 2x$$

$$\text{Ac}(G_5 - v) = \text{Ac}(G_5 - w) = x^7 - 5x^5 + 7x^3 - 3x$$

$$\text{Ac}(G_6 - v) = \text{Ac}(G_6 - w) = x^7 - 7x^5 + 12x^3 - 4x$$

The MEG G_1 can generate MIGs by using the constructive method defined by condition (3) when a graph H is connected in turn with its vertex v_h to both vertices v and w from G_1 : when H is methyl, one obtains MIGs 1-M-2-P-cC₃ and sB-cC₃; when H is ethyl, the generated MIGs are 1-E-2-P-cC₃ and (1-E-P)-cC₃; when H is propyl, the corresponding MIGs are 1,2-P₂-cC₃ and (1-E-B)-cC₃; when H is isopropyl, the resulting MIGs are 1-iP-2-P-cC₃ and (1-E-2-M-P)-cC₃.

The MEG G_2 is obtained from MEG G_1 by connecting a methyl group to both MEVs v and w and retaining the endospectral vertices. When H is methyl G_2 generates MIGs 1-sB-2,2-M₂-cC₃ and 1-(1,1-M₂-P)-2-M-cC₃.

By connecting in turn a methyl group to the two MEVs in G_3 one obtains the MIGs 1-iB-2,3-M₂-cC₃ and 1-(1,2-M₂-P)-2-M-cC₃. The same procedure applied to MEG G_4 gives MIGs 1-(3-M-B)-2-M-cC₃ and (2,3-M₂-B)-cC₃, while from G_5 one obtains MIGs 1-(1-E-P)-1-M-cC₃ and (1-E-1-M-P)-cC₃.

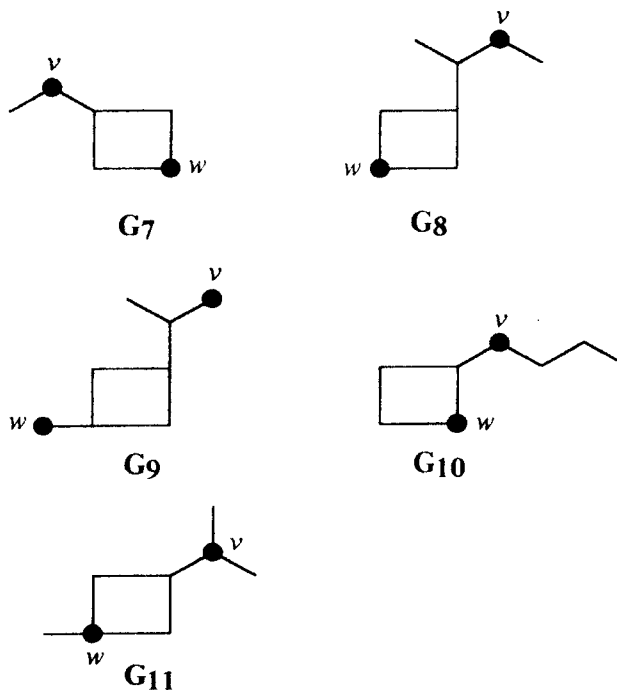


Fig. 2. – Matching endospectral graphs derived from cyclobutane. Endospectral vertices v and w are depicted as black circles.

The MEG G_6 is obtained from MEG G_1 by connecting a methyl group to both MEVs and considering the new endospectral vertices v and w situated on the primary carbon atoms. When H is methyl G_6 generates MIGs 1-sB-2-E-cC₃ and 1-(1-E-P)-2-M-cC₃.

In order to identify MEGs derived from cyclobutane we have investigated the collection of MIGs reported in Table 2, and five MEGs are presented in Fig. 2. Equation (6) holds for all graphs G_7 - G_{11} :

$$\text{Ac}(G_7 - v) = \text{Ac}(G_7 - w) = x^5 - 4x^3 + 2x$$

$$\text{Ac}(G_8 - v) = \text{Ac}(G_8 - w) = x^7 - 6x^5 + 8x^3 - 2x$$

$$\text{Ac}(G_9 - v) = \text{Ac}(G_9 - w) = x^7 - 7x^5 + 12x^3 - 4x$$

$$\text{Ac}(G_{10} - v) = \text{Ac}(G_{10} - w) = x^7 - 6x^5 + 10x^3 - 4x$$

$$\text{Ac}(G_{11} - v) = \text{Ac}(G_{11} - w) = x^7 - 5x^5 + 4x^3$$

The MEG G_9 is obtained from MEG G_7 by connecting a methyl group to both endospectral vertices and considering the new endospectral vertices v and w situated on the primary carbon atoms. The MEG G_{11} is obtained from MEG G_7 by a similar procedure, but with the retention of the the endospectral vertices v and w .

Condition (3) applied to MEG G_7 can generate a series of structurally related MIGs: when H is methyl, the resulting MIGs are 1-E-3-M-cC₄ and iP-cC₄; when H is dimethyl, the corresponding MIGs are 1-E-3,3-M₂-cC₄ and tB-cC₄; when H is ethyl, the generated MIGs are 1,3-E₂-cC₄ and sB-cC₄.

By connecting in turn a methyl group to the two MEVs in G_8 one obtains the MIGs 1-sB-3-M-cC₄ and (1,2-M₂-P)-cC₄. The same procedure applied to MEG G_9 gives MIGs 1-E-3-iP-cC₄ and 1-sB-3-M-cC₄, from G_{10} one obtains MIGs 1-B-2-M-cC₄ and (1-M-B)-cC₄, while from G_{11} the corresponding MIGs are 1-iP-3,3-M₂-cC₄ and 1-tB-3-M-cC₄.

ACKNOWLEDGEMENT. We acknowledge the partial financial support of this research by the Ministry of Research and Technology under Grant 381 TA10 and by the Ministry of Education under Grant 5001 TB10.

REFERENCES

1. Part 3: O. Ivanciuc, *Rev. Roum. Chim.*, **1993**, *38*, 1499-1508.
2. J. V. Knop and N. Trinajstić, *Int. J. Quantum Chem.: Quantum Chem. Symp.*, **1980**, *14*, 503-520; H. Hosoya, *Discr. Appl. Math.*, **1988**, *19*, 239-257; H. Hosoya, in: *Computational Chemical Graph Theory*, Ed. D. H. Rouvray, Nova Science Publishers, New York, 1990, pp. 105-126.
3. M. V. Diudea and O. Ivanciuc, *Molecular Topology*, Complex, Cluj, Roumania, 1995.
4. O. Ivanciuc and A. T. Balaban, *Graph Theory in Chemistry*, in: "The Encyclopedia of Computational Chemistry", Eds.: P.v.R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, and P. R. Schreiner, John Wiley & Sons, Chichester, 1998, pp. 1169-1190.
5. O. Ivanciuc, T. Ivanciuc and M. V. Diudea, *Roum. Chem. Quart. Rev.* in press.
6. O. J. Heilman and E. H. Lieb, *Phys. Rev. Lett.*, **1970**, *24*, 1412-1414.
7. O. J. Heilman and E. H. Lieb, *Commun. Math. Phys.*, **1972**, *25*, 190-232.
8. H. Kunz, *Phys. Lett.*, **1970**, *32A*, 311-312.
9. H. Hosoya, *Bull. Chem. Soc. Japan*, **1971**, *44*, 2332-2339.
10. J. Aihara, *J. Am. Chem. Soc.*, **1976**, *98*, 2750-2758.
11. I. Gutman, M. Milun and N. Trinajstić, *J. Am. Chem. Soc.*, **1977**, *99*, 1692-1704.
12. O. E. Polansky, *MATCH (Commun. Math. Chem.)*, **1985**, *18*, 71-81.
13. I. Gutman and O. E. Polansky, *Theor. Chim. Acta*, **1981**, *60*, 203-226.
14. I. Gutman, *MATCH (Commun. Math. Chem.)*, **1986**, *19*, 127-137.
15. R. Ramaraj and K. Balasubramanian, *J. Comput. Chem.*, **1985**, *6*, 122-141.
16. O. Ivanciuc, *Rev. Roum. Chim.*, **1988**, *33*, 709-717.
17. L. Collatz and U. Sinogowitz, *Abh. Math. Sem. Univ. Hamburg*, **1957**, *21*, 63-67.

18. C. A. Baker, *J. Math. Phys.*, **1966**, *7*, 2238–2242.
19. A. T. Balaban and F. Harary, *J. Chem. Doc.*, **1971**, *11*, 258–259.
20. F. Harary, C. King, A. Mowshowitz and R. C. Read, *Bull. London Math. Soc.*, **1971**, *3*, 321–328.
21. W. C. Herndon and M. E. Ellzey, Jr., *Tetrahedron*, **1975**, *31*, 99–107.
22. W. C. Herndon, *Tetrahedron Lett.*, **1974**, 671–674.
23. T. Zivković, N. Trinajstić and M. Randić, *Mol. Phys.*, **1975**, *30*, 517–533.
24. M. Randić, *J. Comput. Chem.*, **1980**, *1*, 386–399.
25. J. V. Knop, W. R. Müller, K. Szymanski, M. Randić and N. Trinajstić, *Croat. Chem. Acta*, **1983**, *56*, 405–409.
26. M. Randić, W. L. Woodworth and A. Graovac, *Int. J. Quantum Chem.*, **1983**, *24*, 435–452.
27. J. V. Knop, W. R. Müller, K. Szymanski, N. Trinajstić, A. F. Kleiner and M. Randić, *J. Math. Phys.*, **1986**, *27*, 2601–2612.
28. C. Rücker and G. Rücker, *J. Math. Chem.*, **1992**, *9*, 207–238.
29. P. Krivka, Ž. Jeričević and N. Trinajstić, *Int. J. Quantum Chem.: Quantum Chem. Symp.*, **1986**, *19*, 129–147.