

# Chemistry-Relevant Isospectral Graphs. Acyclic Conjugated Polyenes\*

Haruo Hosoya

Ochanomizu University, Bunkyo-ku, Tokyo 112-8610, Japan

Author's e-mail address: hosoya.haruo@ocha.ac.jp

RECEIVED: November 11, 2016 \* REVISED: February 23, 2017 \* ACCEPTED: February 27, 2017

THIS PAPER IS DEDICATED TO PROF. NENAD TRINAJSTIĆ ON THE OCCASION OF HIS 80<sup>TH</sup> BIRTHDAY

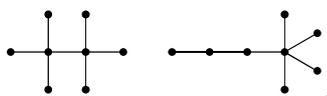
**Abstract:** By using the topological index  $Z$  and  $Z$ -counting polynomial proposed by the present author isospectral (IS) pairs of acyclic conjugated polyenes ( $C_{2n}H_{2n+2}$ ) were studied. Besides the hitherto known smallest pair of  $n = 6$ , four and twenty seven pairs of  $n = 7$  and 8, respectively, were first reported. Inspection of these results revealed several new features of IS tree graphs, i.e., appearance of two pairs of endospectral vertices in a tree graph and existence of several families of IS pair graphs whose  $Z$ -indices systematically grow up to infinity. Further several IS pairs were found to be closely related with each other topologically and called "intrinsic" IS pairs. Important role of the  $Z$ -index for analyzing the IS graphs is demonstrated.

**Keywords:** isospectral tree graph, cospectral tree graph, acyclic conjugated polyene, topological index  $Z$ ,  $Z$ -index, graph theory.

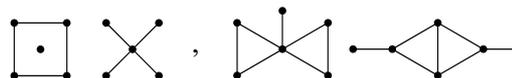
## INTRODUCTION

THE problem of isospectral (or cospectral) graphs<sup>[1–6]</sup> has been a continuous target in the graph theory. It is interesting to observe that almost all the contemporary mathematical chemists have at least once been involved in this problem but in vain.<sup>[7–22]</sup> The history of their unsuccessful endeavor including several behind stories can be traced in a recent paper<sup>[23]</sup> and book<sup>[24]</sup> by Randić. In a sense they might have been overwhelmed by Schwenk's finding, "almost all trees are cospectral."<sup>[25]</sup> Of course, several interesting features and concepts, such as isospectral point and endospectral graph, have been found for designing new isospectral (IS) pairs of graphs. However, these issues have nothing to do with general chemistry and never intrigue non-mathematical chemists at all.

Let us take our stance on the ground of chemistry but not on abstract mathematics. Although the very beginning of the problem of IS graphs is the discovery of the following pair of graphs,<sup>[1]</sup>



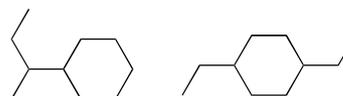
most graph theorists start their discussion from the following two pairs of IS graphs,<sup>[3,4]</sup>



It is difficult to find any chemical problem relevant to these pairs of graphs.

On the other hand, the question "Can one hear the shape of a drum?" cast by Kac from the standpoint of mathematical physics is a very important issue also in chemistry.<sup>[26]</sup> In a sense it is a problem arisen from non-tree graphs.

In this respect the IS pair of

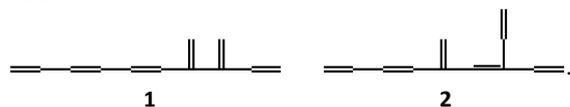


is introduced in many papers, but the present author could not find any chemically attractive discussion except for the one by Balasubramanian<sup>[18]</sup> who analyzes the relation between HMO and PPP. Then let us turn to acyclic conjugated polyene molecules to find more chemistry-relevant problem.

Although Godsil and McKay performed extensive computer-search for the IS graphs up to  $n = 14$ ,<sup>[2]</sup> they

\* To a street gang in Zagreb, Nenad, who grew up to the leader of mathematical chemists of Croatia in celebration of his 80<sup>th</sup> birthday dedicated from a gang of the same age in Tokyo, Haruo, who has not yet grown up enough but is still throwing stones to mathematics and chemistry.

published only two smallest pairs of “cospectral trees with a 1-factor,” among which only the following pair of graphs, **1** and **2**, were found to be useful for our discussion. Here double bonds are drawn in accordance with the chemical manner.



This is the smallest pair of IS acyclic conjugated polyenes,  $C_{12}H_{14}$ , which unfortunately, however, have not yet been synthesized nor isolated.

In this study isospectrality of larger acyclic conjugated polyenes was checked up to  $C_{16}H_{18}$ , and more than thirty IS pairs were discovered! Further, three kinds of such genealogy trees of IS polyene pairs were found that grow up to infinity.

## THEORY

It has been shown that the characteristic polynomial  $P_G(x)$  of tree graph  $G$  composed of  $N$  vertices, defined by the adjacency (**A**) and unit (**E**) matrices, can be obtained from the set of non-adjacent number  $p(G,k)$  as<sup>[27,28]</sup>

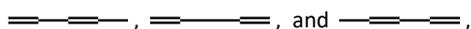
$$P_G(x) = (-1)^N \det(\mathbf{A} - x\mathbf{E}) = \sum_{k=0}^{\lfloor N/2 \rfloor} (-1)^k p(G,k) x^{N-2k} \quad (1)$$

( $G \in \text{tree}$ ).

The  $p(G,k)$  is the number of ways for choosing  $k$  disjoint edges from graph  $G$ . In mathematical terminology  $p(G,k)$  is the number of  $k$ -matchings.<sup>[2]</sup> For any graph  $p(G,0)$  is defined to be unity, and  $p(G,1)$  is nothing else but the number of edges of  $G$ . The topological index  $Z$  (or  $Z$ -index) of graph  $G$  is defined as the total sum of  $p(G,k)$ ,

$$Z = \sum_{k=0}^{\lfloor N/2 \rfloor} p(G,k). \quad (2)$$

Now instead of being bothered by the characteristic polynomial and its eigenvalues, we can only play with  $p(G,k)$ 's and  $Z$ . Let us explain a simple procedure for obtaining  $p(G,k)$  and  $Z$  by taking path graph  $P_5$ , or the carbon atom skeleton of  $n$ -pentane or pentadienyl radical, as an example. By definition  $p(G,0) = 1$ , and  $p(G,1) = 4$  for  $P_5$ , while  $p(G,2) = 3$  as enumerated from the following set of diagrams:



yielding  $Z = 1 + 4 + 3 = 8$  in this case.

If the  $Z$ -indices of a given pair of isomeric graphs are different, one can safely assert that they are not IS. If they happen to have a common  $Z$  value, their isospectrality can be checked just by comparing the set of  $p(G,k)$ 's without recourse to their spectra (the set of eigenvalues).

For this purpose the  $Z$ -counting polynomial  $Q_G(x)$ ,

$$Q_G(x) = \sum_{k=0}^{\lfloor N/2 \rfloor} p(G,k) x^k, \quad (3)$$

proposed by the present author is useful.<sup>[27]</sup> In the case of IS **1** and **2**, they have the common  $Q_G(x)$  as

$$Q_1(x) = Q_2(x) = 1 + 11x + 43x^2 + 73x^3 + 53x^4 + 14x^5 + x^6, \quad (4)$$

giving  $Z = 196 = 14^2$ .

As a matter of fact,  $Q_G(x)$  is essentially equivalent to the later-proposed matching polynomial,<sup>[29–31]</sup>

$$M_G(x) = \sum_{k=0}^{\lfloor N/2 \rfloor} (-1)^k p(G,k) x^{N-2k}, \quad (5)$$

using our  $p(G,k)$  numbers, and for tree graphs  $M_G(x)$  is identical to  $P_G(x)$ . Thus  $M_G(x)$  will not be treated here any more.

In order to obtain  $Q_G(x)$  for a moderately large graph the following recursion relation is useful.

$$Q_G(x) = Q_{G-l}(x) + x Q_{G \ominus l}(x), \quad (6)$$

where  $G-l$  stands for the subgraph of  $G$  obtained by deleting an edge  $l$ , while  $G \ominus l$  is obtained by deleting  $l$  together with all the edges incident to  $l$ . In both the cases the  $Q_G(x)$ 's of all the isolated components arisen from this deleting process are to be multiplied. Let us explain this procedure by taking **1** as an example. See Figure 1, where  $l$  is chosen at the small arrow. Then we get the  $Q_G(x)$  which is identical to Eq. (4). The dotted circle demonstrates the process of getting  $Q_{G \ominus l}(x)$ . Note that in deriving  $Q_{G \ominus l}(x)$  the  $Q$  function for a vertex, or  $P_1$ , has been set to be unity. In the above process several other path graphs,  $P_n$ , can be seen, whose  $Z$ -values, or the sums of the coefficients of  $Q_G(x)$ , form the famous Fibonacci numbers, 1, 2, 3, 5, 8, 13, 21, etc.<sup>[27,28]</sup>

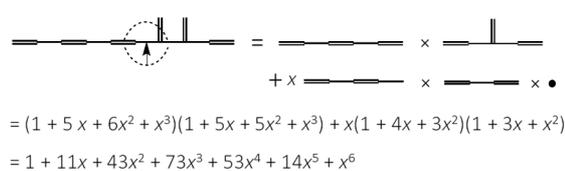
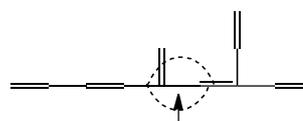
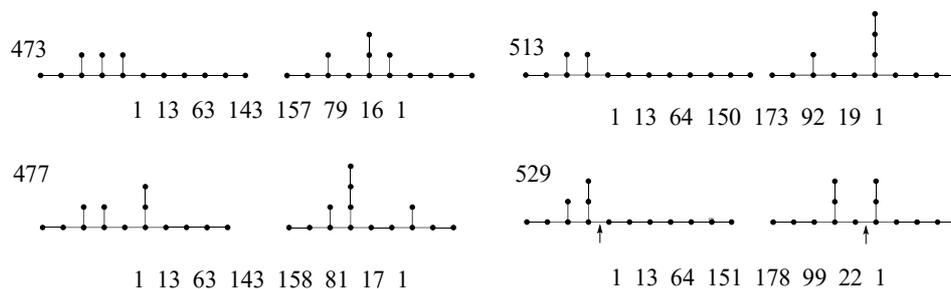


Figure 1. Procedure for obtaining the  $Q_G(x)$  of **1**.

Next, try to obtain the  $Q$  function of **2**, again by using the recursion relation (6). In this case, although any edge can be chosen for  $l$ , the wisest choice is found to be the small arrow as indicated below.



**Table 1.** Isospectral pairs of tetradecaheptaene.



Now the readers can realize that the same recursion formula can be obtained as in the case of **1**. Let us call such a pair of IS graphs as **1** and **2** “intrinsic IS graphs”, while other IS pairs of graphs may be called “fortuitous IS graphs”.

## RESULTS AND DISCUSSION

By using these techniques we could find four and twenty seven pairs of IS graphs, respectively, among the isomers of tetradecaheptaene and hexadecaheptaene, as shown in Tables 1 and 2.

The integers given to the left and below the top-left graphs in Table 1 mean, respectively,

$Z = 473$  and

$$Q_G(x) = 1 + 13x + 63x^2 + 143x^3 + 157x^4 + 79x^5 + 16x^6 + x^7.$$

Although it is not applied to this pair of graphs, the function of the pair of small arrows is the same as already explained above for **1** and **2**.

It is rather strange that almost no IS pair of acyclic conjugated polyene has ever been discussed irrespective of the keen continuous interest of mathematical chemists for almost half a century. In Table 3 the number of isomers and IS pairs of acyclic conjugated polyenes  $C_{2n}H_{2n+2}$  are given. Although systematic analysis for larger polyenes has not yet been tried, the number of IS pairs of octadecanonaenes ( $n = 9$ ) is whimsically estimated to be around 200 independently of Schwenk's assertion.<sup>[25]</sup>

By scrutinizing the  $Z$ -indices of the (re)discovered 31 pairs of IS graphs it was observed that there are so many square numbers. That is:  $196 = 14^2$ ,  $529 = 23^2$ ,  $1156 = 34^2$ ,  $1296 = 36^2$ , and  $1369 = 37^2$ . Further, it is curious to find  $14 + 23 = 37$ . Then after comparing the structures of these polyenes very interesting relation was found.

See Table 4, where a family of IS graphs is growing from the pair of **1** ( $A_6$ ) and **2** ( $B_6$ ) by stepwise addition of an edge at the pair of \* and # vertices, respectively. Reversely, if a pair of edges of  $A_6$  (or  $B_6$ ) marked with \* (or #) are deleted, one gets  $A_5$  (or  $B_5$ ). Note that the graphs  $A_5$  and  $B_5$  are equal, with  $Z_5 = 81 = 9^2$ . If this process is repeated to  $A_5$  (or  $B_5$ ), one gets a disjoint pair of  $P_4$  graphs yielding  $Z_4 = 5^2$ .

All the  $Z_n$ 's above  $n = 4$  are found to be square numbers and obey the following recursive relation,

$$Z_n = 2Z_{n-1} + 2Z_{n-2} - Z_{n-3}, \quad (7)$$

yielding

$$\lim_{n \rightarrow \infty} Z_{n+1} / Z_n = \tau^2 = (3 + \sqrt{5}) / 2 = 2.618 \dots, \quad (8)$$

where  $\tau$  is the golden ratio,  $(1 + \sqrt{5}) / 2 = 1.618 \dots$ , which is deduced from the following relation,

$$\sqrt{Z_n} = \sqrt{Z_{n-1}} + \sqrt{Z_{n-2}}. \quad (9)$$

Although detailed analysis has not yet been completed, the interesting feature of the genealogies observed here may be due to the appearance of two pairs of endospectral vertices<sup>[17,33,34]</sup> in a tree graph.

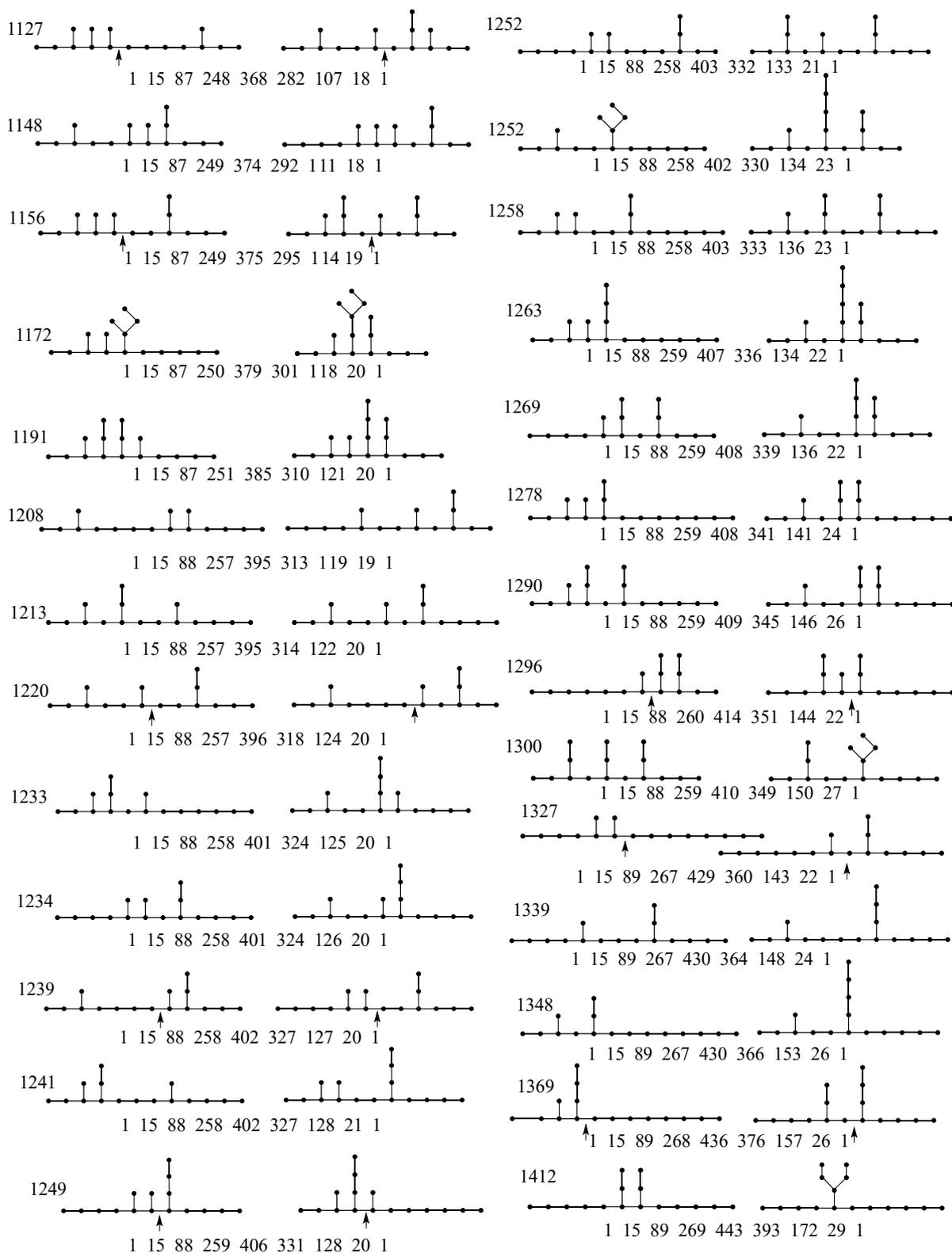
In Table 5 is given another genealogy of IS pairs of tree graphs originating from  $(C_7, D_7)$  which already appeared in Table 1. In this case also by “tracing-back” one can obtain  $(C_6, D_6)$  both of which are the pair of  $P_6$  graphs yielding  $Z_6 = 13^2$ . The  $Z$ -indices of this family are also square numbers and obey the same recursion relations, (7) and (9).

Finally a very interesting family of IS pairs were found as shown in Table 6, which starts from  $(E_8, F_8)$  but the next members  $E_9$  and  $F_9$  are identical and radicals. Further, pairs of polyene and radical alternately appear as  $n$  increases. The fact that both of  $E_7$  and  $F_7$  are the pairs of  $Z = 19$  graphs as well as the cases with  $(A_4, B_4)$  may suggest a plausible explanation of these three families of IS graphs whose  $Z$ -indices are all square numbers.

In Tables 4–6 we cannot find any family of IS pair graphs whose  $Z$ -indices are not square number, in spite of our expectation that the probability of finding IS pair graphs is rapidly increasing with the size of graphs. As the IS pairs in Tables 1 and 2 will play a key role for clarifying this problem, study in this direction is being in progress.

Here detailed accounts are not given, we have found a number of growing families of IS pairs of polyene radicals whose  $Z$  indices are not square numbers, which will be reported in other papers.

Table 2. Isospectral pairs of hexadecaoctaene.



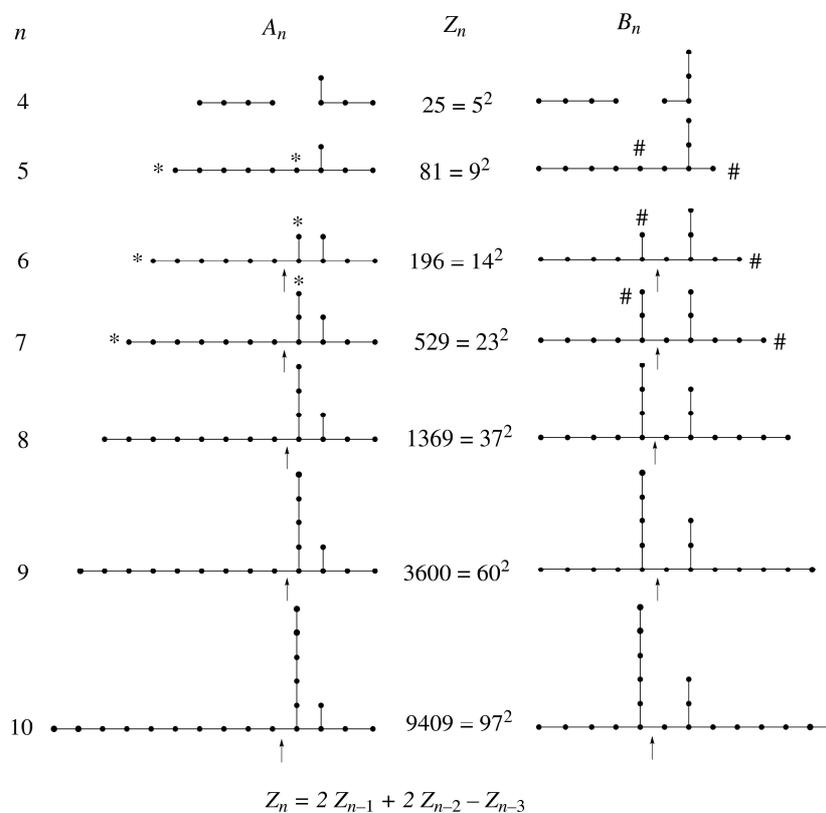
**Table 3.** The numbers of isomers<sup>[32]</sup> and IS pairs of acyclic conjugated polyenes  $C_{2n}H_{2n+2}$ .

$n$	1	2	3	4	5	6	7	8	9	10
Isomers	1	1	2	4	11	30	96	319	1135	4150
IS pairs	0	0	0	0	0	1	4	27	~200	?

Finally a serious question will be hurled to us: "Why are you playing with non-existing polyene isomers?" Yes, except for very limited cases actually almost no isomer above  $n > 4$  in Table 3 has ever been isolated, and until recently "polyene chemistry" has been left barren as a desert amongst the flourishing organic chemistry, simply due to scarce isolation of conjugated polyenes except for several limited number of groups, such as carotene, linear polyene, and dendralene. However, thanks to the rapid development of organic synthesis many interesting polyenes and polyynes begin to be synthesized or isolated,<sup>[35,36]</sup> but not enough. At present the chemistry of acyclic polyenes is still

uncultivated both experimentally and theoretically, although this area is in between the chemistry of aromatic and anti-aromatic compounds and thus ought to have a very important role in organic chemistry.

On the other hand, in the area of aromaticity and anti-aromaticity various properties of a vast number of hypothetical compounds have also been analyzed and discussed to establish and enlarge the real world of chemical compounds by the extensive use of chemical thinking and technique. This is the reason why the present author is now cultivating the polyene chemistry by reexamining the concept of cross-conjugation.<sup>[37]</sup>

**Table 4.** A genealogy of pairs of IS graphs ( $A_n, B_n$ ) of  $C_{2n}H_{2n+2}$  isomers, which grow up from  $n = 6$ . Crucial vertices are marked with \* and #, where edge-growing occurs.  $Z$  indices and their recursive formula are also given.  $A_6 = \mathbf{1}$  and  $B_6 = \mathbf{2}$ . See text for more explanation.


**Table 5.** A genealogy of another pairs of IS graphs ( $C_n, D_n$ ) of  $C_{2n}H_{2n+2}$  isomers, which grow up from  $n = 7$ . Crucial vertices are marked with \* and #, where edge-growing occurs.

$n$	$C_n$	$Z_n$	$D_n$
6		169 = 13 <sup>2</sup>	
7		529 = 23 <sup>2</sup>	
8		1296 = 36 <sup>2</sup>	
9		3481 = 59 <sup>2</sup>	

$$Z_n = 2 Z_{n-1} + 2 Z_{n-2} - Z_{n-3}$$

**Table 6.** A genealogy of IS pair graphs ( $E_n, F_n$ ) of  $C_{2n}H_{2n+2}$  isomers, which grow up from  $n=8$ . Crucial vertices are marked with \* and #, where edge-growing occurs.

$n$	$E_n$	$Z_n$	$F_n$	
7		361 = 19 <sup>2</sup>		
8		1156 = 34 <sup>2</sup>		○
9		2809 = 53 <sup>2</sup>		identical radical
10		7569 = 87 <sup>2</sup>		○
11		19600 = 140 <sup>2</sup>		radical
12		51529 = 227 <sup>2</sup>		○

○ : isospectral polyene

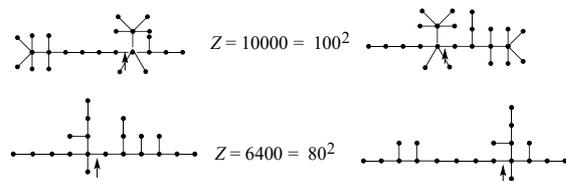
$$Z_n = 2 Z_{n-1} + 2 Z_{n-2} - Z_{n-3}$$

## CONCLUSION

From the analysis of isospectrality of conjugated polyenes (incidentally including radicals) quite new features of IS tree graphs were discovered, namely, appearance of two pairs of endospectral vertices in a tree graph and genealogy of pairs of IS tree graphs whose Z-indices are systematically growing. Further, several "intrinsic" IS pairs were shown to be decomposed into an identical set of fragmental tree components which are combined to give the same Z-counting polynomial. Although many IS pairs of square Z's are reported here, "square" does not seem to be the essence of this problem. These new features of IS tree graphs observed here may suggest that "topological scrutinization" by the aid of the Z-index is necessary for analyzing the chemico-mathematical features of IS graphs.

## APPENDIX

We have discovered many other interesting IS pairs of tree graphs with square Z's, among which two of them will be given below as a present to my old friend, Nenad Trinajstić. With  $A_9$  and  $B_9$  in Table IV they form a beautiful intrinsic IS tree trio with the property,  $60^2 + 80^2 = 100^2$ , in which 80 is our celebrated age.



**Acknowledgment.** The present author thanks Nenad Trinajstić and the editorial board of CCA for giving a nice chance to write this paper. He also thanks Umpei Nagashima for giving a good suggestion to improve this manuscript. Special thanks are due to the anonymous referee who gave the author many useful suggestions and references, especially Ref. [2].

## REFERENCES

- [1] V. L. Collatz, U. Sinogowitz, *Abh. Math. Sem. Univ. Hamburg* **1957**, 21, 63.
- [2] C. D. Godsil, B. D. McKay in *Lecture Notes in Math. 560* (Eds.: L. R. A. Casse, W. D. Wallis), Springer Verlag, **1976**, pp. 73–92.
- [3] D. M. Cvetković, M. Doob, H. Sachs, *Spectra of Graphs*, 1<sup>st</sup> Ed., Academic Press, New York, **1980**; 2<sup>nd</sup> Ed., Academic Press, New York, **1982**; 3<sup>rd</sup> Ed., Johann Ambrosius Barth Verlag, Heidelberg, **1995**.
- [4] D. Cvetković, P. Rowlinson, S. Simić, *An Introduction to the Theory of Graph Spectra*, Cambridge Univ. Press, Cambridge, **2010**.
- [5] *Chemical Applications of Graph Theory* (Ed.: A. T. Balaban), Academic Press, London, **1976**.
- [6] N. Trinajstić, *Chemical Graph Theory*, 1<sup>st</sup> Ed., CRC Press, Boca Raton, Florida, **1983**; 2<sup>nd</sup> Ed., CRC Press, Boca Raton, Florida, **1992**.
- [7] A. T. Balaban, F. Harary, *J. Chem. Doc.* **1971**, 11, 258.
- [8] K. Mizutani, K. Kawasaki, H. Hosoya, *Natl. Sci. Rept. Ochanomizu Univ.* **1971**, 22, 39.
- [9] W. C. Herndon, *J. Chem. Doc.* **1974**, 14, 150.
- [10] W. C. Herndon, *Tetrahedron Lett.* **1974**, 15, 671.
- [11] M. Randić, N. Trinajstić, T. Živković, *J. Chem. Soc., Faraday Trans. II* **1976**, 72, 244.
- [12] I. Gutman, *J. Chem. Phys.* **1978**, 68, 1321.
- [13] M. Randić, *J. Comput. Chem.* **1980**, 1, 386.
- [14] Y. S. Jiang, *Sci. Sinic. (B)* **1984**, 27, 236.
- [15] W. C. Herndon, M. L. Ellzey, Jr., *MATCH* **1986**, 20, 53.
- [16] J. Knop, W. R. Müller, K. Szymanski, N. Trinajstić, A. F. Kleiner, M. Randić, *J. Math. Phys.* **1986**, 27, 2601.
- [17] M. Randić, A. F. Kleiner, *Ann. New York Acad. Sci.* **1989**, 555, 320.
- [18] K. Balasubramanian, *J. Math. Chem.* **1991**, 7, 353.
- [19] H. Hosoya, U. Nagashima, S. Hyugaji, *J. Chem. Inf. Comput. Sci.* **1994**, 34, 428.
- [20] Y. Jiang, C. Liang, *Croat. Chem. Acta* **1995**, 68, 343.
- [21] J. R. Dias, *Chem. Phys. Lett.* **1996**, 253, 305.
- [22] M. Randić, W. R. Müller, J. V. Knop, N. Trinajstić, *J. Chem. Inf. Comput. Sci.* **1997**, 37, 1072.
- [23] M. Randić, B. Horvat, T. Pisanski, *MATCH* **2010**, 63, 737.
- [24] M. Randić, M. Novič, D. Plavšić, *Solved and Unsolved Problems of Structural Chemistry*, CRC Press, Boca Raton, **2016**, pp. 72–83.
- [25] M. Schwenk, in *New Directions in the Theory of Graphs* (Ed.: F. Harary), Academic Press, New York, **1973**, pp. 275–307.
- [26] M. Kac, *Amer. Math. Monthly* **1966**, 73, 1.
- [27] H. Hosoya, *Bull. Chem. Soc. Jpn.* **1971**, 44, 2332.
- [28] H. Hosoya, *Fibonacci Quart.* **1973**, 11, 255.
- [29] I. Gutman, M. Milun, N. Trinajstić, *J. Am. Chem. Soc.* **1977**, 99, 1692.
- [30] J.-I. Aihara, *J. Am. Chem. Soc.* **1976**, 98, 2750.
- [31] E. J. Farrell, *J. Combin. Theory* **1979**, B27, 75.
- [32] L. Bytautas, D. J. Klein, *Theor. Chem. Acc.* **1999**, 101, 371.
- [33] W. C. Herndon, M. L. Ellzey, Jr., *Tetrahedron* **1975**, 31, 99.
- [34] Y. Jiang, C. Liang, *Croat. Chem. Acta* **1995**, 68, 343.
- [35] M. Gholami, R. R. Tykwinski, *Chem. Rev.* **2006**, 106, 4997.
- [36] *Cross Conjugation: Modern Dendralene, Radialene and Fulvene Chemistry* (Eds.: H. Hopf, M. S. Sherburn), Wiley-VCH Verlag, Weinheim, **2016**.
- [37] H. Hosoya, *Curr. Org. Chem.* **2015**, 19, 293.