

# Properties and Relationships of Conjugated Polyenes Having a Reciprocal Eigenvalue Spectrum – Dendralene and Radialene Hydrocarbons\*

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RECEIVED APRIL 4, 2003; REVISED OCTOBER 13, 2003; ACCEPTED OCTOBER 15, 2003

*Key words*  
circumscribing with hexagonal rings  
characteristic polynomials  
comb molecular graphs  
complementary molecular graphs  
cross-conjugation  
reciprocal molecular graphs

While reviewing molecules corresponding to reciprocal graphs (graphs with all reciprocal eigenvalue pairs), new examples of reciprocal graphs are presented. Essential features of cross-conjugation are delineated, and how this phenomenon is important in the design of conducting and ferromagnetic polymers is discussed. Some recursion equations for determining characteristic polynomials of comb and ladder graphs are presented.

## INTRODUCTION

Three classes of graphs having reciprocal pairs of eigenvalues ( $|X|$ ,  $|1/X|$ ) in their complete eigenspectrum have been identified by Sarkar and Mukherjee.<sup>1</sup> Subsequently a Pascal's triangle-like approach for determining their characteristic polynomial coefficients was presented.<sup>2</sup> Two of these classes have graphs corresponding to conjugated polyenes of chemical interest – dendralenes<sup>3</sup> and radialenes.<sup>4</sup> This chemical interest derives, in part, from the fact that they are cross-conjugated systems.<sup>3,5</sup> Cross-conjugation is less effective in stabilization of acyclic (dendralene) and monocyclic (radialene)  $p\pi$  systems than is linear conjugation. All the  $p\pi$  orbitals in a linear conjugated system only overlap in two directions. Dendralenes have comb graphs that have been studied by a number of investigators.<sup>6–7</sup> The infinite limit member ( $x = \infty$ ) of the

dendralene series  $(C=CH_2)_x$  is isomeric to infinite polyacetylene  $(CH=CH)_x$ . This paper will present some new reciprocal molecular graphs and note additional properties of these molecular systems. The embedding and circumscribing characteristics dendralenes and radialenes will also be examined.

Molecular graphs correspond to conjugated polyenes and are vertex-line depictions having vertices of degree-1 to degree-3. The third class of reciprocal graphs comprise of star graphs having vertices greater than degree-3. Previously unidentified reciprocal graphs having vertices greater than degree-3 can be found in a compilation published by the Hosoya group<sup>8</sup> by noting that the characteristic polynomials of such graphs have coefficients symmetrically distributed about a center and that the first and last coefficients must be unity, which are necessary and sufficient conditions for reciprocal graphs.

\* Dedicated to Professor Nenad Trinajstić on the occasion of his 65<sup>th</sup> birthday.

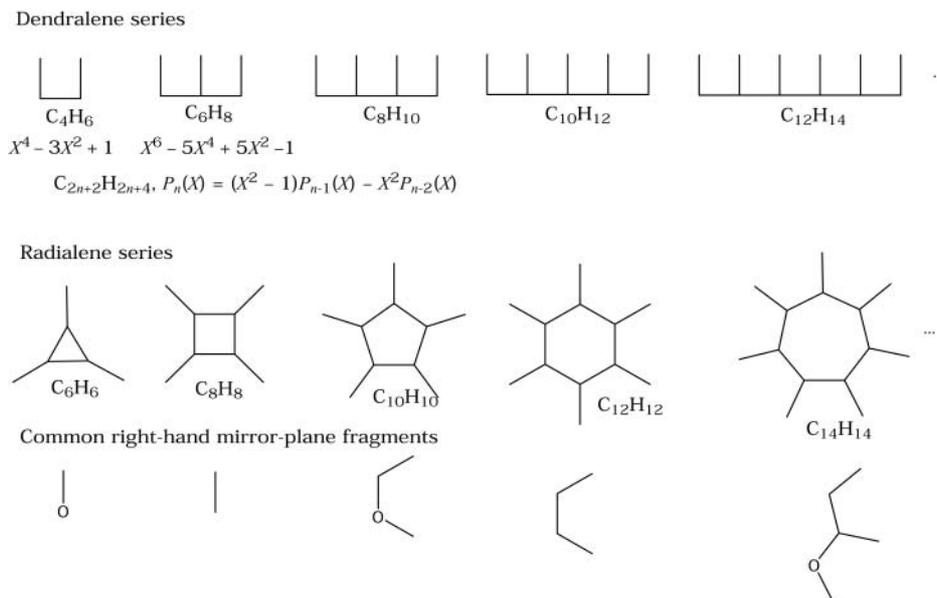


Figure 1. Two series of reciprocal molecular graphs with their common right-hand mirror-plane fragments (McClelland subgraphs) listed below.

## RESULTS AND DISCUSSION

### Dendralenes

Dendralenes are acyclic cross-conjugated polyenes having corresponding molecular graphs depicted in Figure 1. Though not cross-conjugated, ethene (not shown in Figure 1) and 1,3-butadiene can formally be regarded as [1]dendralene and [2]dendralene (first molecular graph in Figure 1), respectively. 3-Methylene-1,4-pentadiene, [3]dendralene (second molecular graph in Figure 1), and higher dendralene members are cross-conjugated. The first three dendralenes are known chemical species and derivatives of [4]dendralene have been reported.<sup>3,5</sup> *o*-Quinodimethane (*o*-xylylene) possesses the [4]dendralene  $\pi\pi$  framework. [2]Dendralene (1,3-butadiene) is known to undergo facile Diels Alder [4+2] reaction to form 4-vinylcyclohexene. When  $d_6$ -benzene solutions of [3]dendralene were heated to 90 °C in sealed tubes [4+2] dimerization to 1,4,4-trivinylcyclohexene occurred.<sup>5</sup>

The dendralene series in Figure 1 is constructed by starting with ethene and successively attaching the 1,1-ethenediyl aufbau unit. Ethene can be regarded as the zero generation member ( $n = 0$ ) of the dendralene series ( $C_{2n+2}H_{2n+4}$ ). The recursion relationship for the corresponding characteristic polynomials,  $P_n(X)$ , of the dendralene series is

$$P_n(X) = (X^2 - 1)P_{n-1}(X) - X^2P_{n-2}(X)$$

which allows one to determine the characteristic polynomial of a dendralene of any given generation ( $n$ ) from the known characteristic polynomials of the immediately consecutive two dendralenes ( $n-1$  and  $n-2$ ).<sup>9</sup> The zero roots ( $X$ ) of the characteristic polynomials are the eigenvalues (HMO energy levels) of the corresponding mole-

cular graphs. The characteristic polynomials for [2]dendralene and [3]dendralene are given in Figure 1.

Three important properties can be noted for dendralenes which have molecular (comb) graphs corresponding to reciprocal graphs. First, their characteristic polynomials have coefficients symmetrically distributed about a center and the first and last coefficients are unity.<sup>2</sup> Second, since three-connected graphs have a maximum possible eigenvalue of 3, the minimum possible eigenvalue of reciprocal molecular graphs must be 0.33333 (*i.e.*, 1/3). Third, the eigenvector coefficients for reciprocal eigenvalue pairs will be identical but in reverse order for adjacent degree-1 and degree-2 or degree-3 vertices. For example, consider 1,3-butadiene ([2]dendralene) and its reciprocal eigenvalue pair 1.61803 and 0.61803. For the eigenvalue of 1.61803, the eigenvector coefficients for the degree-1 vertex (position-1) is 0.3718 and for the adjacent degree-2 vertex (position-2) it is 0.6015. Whereas, for the eigenvalue of 0.61803, the eigenvector coefficients for the degree-1 vertex (position-1) is 0.6015 and for the adjacent degree-2 vertex (position-2) it is 0.3718.

A formal proof of this latter eigenvector/eigenvalue property of reciprocal eigenvalue pairs ( $X$  and  $1/X$ ) is the following. Let the two distinct vertices of any comb graph be assigned the eigenvector coefficients of  $a$  for the primary vertex and  $b$  the other vertex. Then the following equation may be written for the primary vertex for any given eigenvalue  $Y$ :  $-aY + b = 0$ . Substituting the eigenvalue of  $X$  into this equation gives  $-aX + b = 0$ . Repeating this process with its reciprocal  $1/X$  gives  $-a(1/X) + b = 0$ . Multiplying latter equation by  $-X$  gives  $a - bX = 0$  which shows that the order of the coefficients has been inverted. It should be evident from the above equations that for positive eigenvalues ( $X$ ) the corresponding eigenvector coefficients ( $a$  and  $b$ ) must have identical signs and for

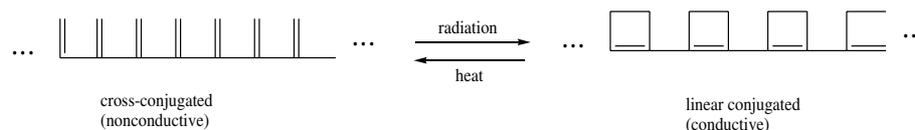


Figure 2. Possible design of a photo on/off switch.

negative eigenvalues the eigenvector coefficients should have opposite signs.

The density of states of infinite dendralene and polyacetylene will now be compared. Hosoya and coworkers have shown that the singular points to the density of states of a periodic polymer is given by the eigenvalues of the hypothetical cyclic dimer having the same recurring aufbau unit; if this cyclic dimer has NBMOs, then the corresponding polymer has a zero HOMO-LUMO band gap or isolated NBMOs between the valence and conduction bands.<sup>7,10</sup> The general expression for the infinite polymer ring of  $C_n$  symmetry ( $[n]$ radialene) having the same repetitive (aufbau) unit as the dendralene chain is obtained from its irreducible subgraph<sup>9-10</sup> which gives

$$X^2 - 2X \cos \theta_k - 1 = 0$$

$$\theta_k = 2k\pi/n, \text{ for } k = 0, 1, 2, \dots, n-1.$$

Solution of this equation for the cyclic dimer ( $n = 2$ ) gives the eigenvalues of  $\pm 0.41421$  and  $\pm 2.41421$  which correspond to the singularities for the density of states.<sup>7,9,10</sup> This result shows that infinite dendralene has a band gap between the valence and conduction bands of twice 0.41421 and is expected to be nonconductive;<sup>11</sup> note that above we already established that infinite dendralene would at least have a band gap of twice 0.33333. A similar solution for infinite polyacetylene gives eigenvalues of  $\pm 2$  for the singularities of its density of states. This means that infinite polyacetylene has a continuum of eigenvalues from  $+2$  to  $-2$ . Therefore, infinite polyacetylene has zero band gap and should be conductive.<sup>9,12</sup> Because

synthetic polyacetylene can never be infinitely extended and because of Peierls distortion, synthetic polyacetylene must be doped to make it conductive. Thus, if an infinite conjugated polymer has a zero band gap at the HMO level, it is predicted to be capable being made conductive by doping techniques. Otherwise, if it has a significant nonzero band gap, it is unlikely that it can be made conductive by doping.

The conduction of doped polyacetylene involves a mobile charged carrier called a soliton.<sup>12</sup> The soliton is thought to propagate down the polyacetylene chain *via* a valence bond-like mechanism which is not possible for cross-conjugated systems like dendralene polymers. While doping of polyacetylene increases its conductivity without an increasing its magnetic susceptibility, one might expect that doping dendralene polymers could lead to non-conducting polymers with an increase in magnetic susceptibility. Figure 2 presents a speculative photo transformation of an extended dendralene to a linear  $\pi$ -conjugated system analogous to that of polyacetylene. One might be able to use this dendralene-to-polyacetylene design as a framework for fabrication of organic on/off switches for electronic conduction devices by alternate application of light and heat to such a system.

[6]Dendralene is unusual in that it not only has a reciprocal eigenvalue spectrum but it is also subspectral in the eigenvalues of 1,3,5-hexatriene ( $L_6$ ) which are either complementary or negatively complementary to the remaining eigenvalues (Figure 3).<sup>13</sup> This multi facet aspect of [6]dendralene is only partly understood. To briefly review, two graphs,  $M$  and  $\underline{M}$ , are complementary if the normal vertices of one correspond to the  $-1$  weighted vertices of the other (indicated by open circles in Figure 3).

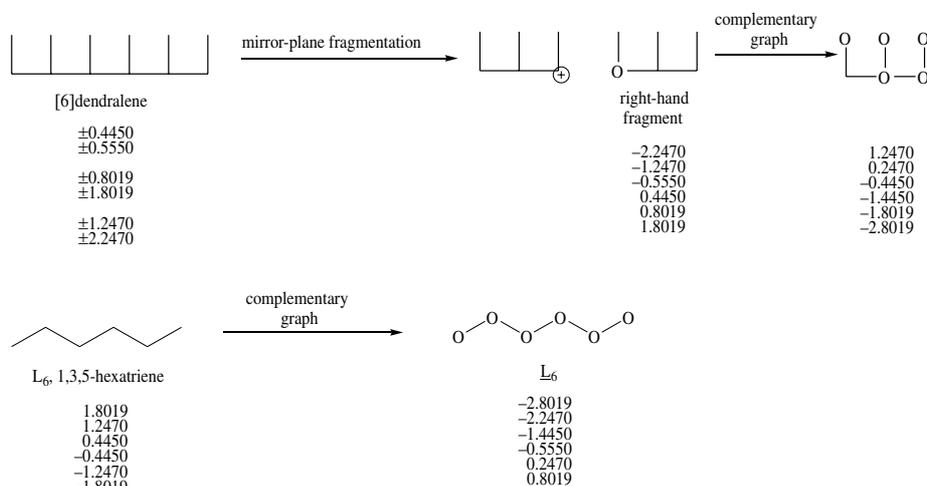


Figure 3. 1,3,5-Hexatriene is subspectral to [6]dendralene which is almost self-complementary. Two graphs,  $M$  and  $\underline{M}$ , are complementary if the normal vertices of one are weighted  $-1$  vertices in the other and vice versa. The eigenvalues ( $X$ ) of complementary graphs are related per  $X(M) + X(\underline{M}) = -1$

The associated eigenvalues ( $X$ ) of complementary graphs are related by  $X(\mathbf{M}) + X(\underline{\mathbf{M}}) = -1$ . Furthermore, if the eigenvector  $\Phi(\mathbf{M})$  of one complementary graph is given by

$$\Phi(\mathbf{M}) = \sum a_i^* \phi_i^* + \sum a_i^\circ \phi_i^\circ \text{ for eigenvalue } X(\mathbf{M})$$

where  $\phi_i^*$  is the p AO of a starred atomic vertex and  $\phi_i^\circ$  that of an unstarred atomic vertex, then the eigenvector of the other complementary one is given by

$$\Phi(\underline{\mathbf{M}}) = \sum a_i^* \phi_i^* - \sum a_i^\circ \phi_i^\circ \text{ for eigenvalue } X(\underline{\mathbf{M}})$$

All right-hand mirror-plane fragments (McClelland subgraphs)<sup>14-16</sup> have complementary graphs and all molecular graphs of linear conjugated polyenes have complementary graphs, *e.g.*, Figure 3 shows the molecular graph of 1,3,5-hexatriene and its complementary (vertex weighted) graph. The complementary graph ( $\underline{L}_n$ ) of a molecular graph ( $L_n$ ) of a linear polyene of  $n$  p $\pi$ -centers is the right-hand mirror-plane fragment of the ladder graph of  $n$  rungs. Most McClelland subgraphs up to six vertices have been listed.<sup>14</sup> The characteristic polynomial  $P(\underline{L}_n; X)$  has the following recursion

$$P(\underline{L}_n; X) = (X + 1)P(\underline{L}_{n-1}; X) - P(\underline{L}_{n-2}; X)$$

where  $P(\underline{L}_0; X) = 1$  and  $P(\underline{L}_1; X) = (X + 1)$ . This recursion should be compared with the recursion for the linear polyenes:  $P(L_n; X) = XP(L_{n-1}; X) - P(L_{n-2}; X)$  where  $P(L_0; X) = 1$  and  $P(L_1; X) = X$ .<sup>16</sup>

### Radialenes

The radialene series in Figure 1 is constructed by starting with [3]radialene and successively splicing in the 1,1-ethenediyl aufbau unit. Though not a cyclic molecule, the cumulene, 1,2,3-butatriene, can be formally considered to be a [2]radialene. In this case, the p $\pi$ -orbital of carbon vertex-2 in 1,2,3-butatriene can be visualized as interacting with the p $\pi$ -orbital of carbon vertex-3 *via* two pathways of a 2-membered ring, thus accounting for the value of  $\gg 2 \ll$  in the corresponding adjacency matrix. Because of nonbonded hydrogen interaction, the *exo* methylenyl groups in the radialenes can be slightly deformed from planarity. Derivatives of the first four members of the series and [3]-, [4]-, and [6]radialene themselves have been synthesized.<sup>4</sup> [3]Radialene (trimethylenecyclopropane) is isomeric to benzene and is sensitive to oxygen and prone to self-polymerization.<sup>17</sup> Clearly [3]radialene is the most strained member shown in Figure 1. [4]Radialene (tetramethylenecyclobutane) is also sensitive to oxygen.<sup>17</sup> According to *ab initio* calculations, [4]radialene is more stable than four acetylene molecules by 122.4 kcal/mol.<sup>18</sup>

Each radialene is subspectral (have common eigenvalues) to the dendralene above it in Figure 1. The McClelland subgraphs<sup>14-16</sup> common to each radialene and im-

mediately above dendralene is given in the lowest row with the corresponding characteristic polynomials and eigenvalues. Additionally, all the alternant hydrocarbon (AH, alternant hydrocarbons are devoid of odd-sized rings) radialenes and their corresponding dendralene can be embedded by ethene (Hall subgraphs)<sup>14,16,19</sup> and consequently have eigenvalues of  $X = \pm 1$ ; nonAH radialenes cannot be embedded by ethene because alternation of sign of the embedded fragment is precluded.<sup>14,16</sup> All radialenes have eigenvalues of  $X = 1 + \sqrt{2}$  and  $1 - \sqrt{2}$  which have corresponding symmetric eigenvectors (sets of wave function coefficients).<sup>20-21</sup> By the pairing theorem, [4]radialene, [6]radialene, and larger AH radialenes also have  $X = -1 - \sqrt{2}$  and  $-1 + \sqrt{2}$  where the latter eigenvalue is also the HOMO in the AH radialenes. The *ab initio* calculated IP energies have been determined to be 8.73, 7.86, 7.98, and 7.50 eV for [3]-, [4]-, [5]-, and [6]radialene,<sup>22</sup> respectively which coincides with their respective HOMO values of 0.6180, 0.41421, 0.4773, and 0.41421. The nonAH radialenes have doubly degenerate HOMOs.<sup>22</sup>

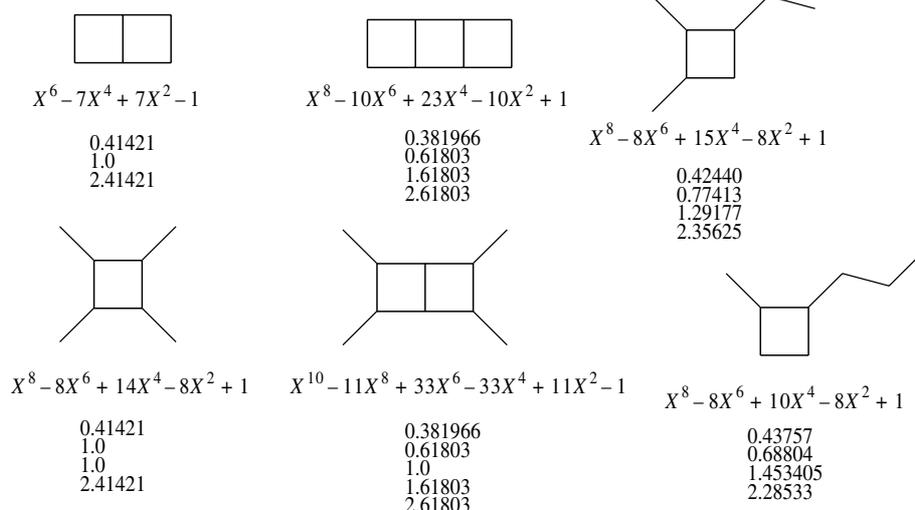
Besides its irregularity in IP energy above, [5]radialene appears to be somewhat anomalous in other respects. It is the only radialene whose parent has not yet been synthesized and so far only a couple of substituted derivatives have been prepared.<sup>4</sup> It is perhaps significant that [5]radialene substructures occur in buckminsterfullerene. The origin of the greater stability of buckminsterfullerene has been attributed to the fact that amongst the 1812 structural C60 fullerene isomers, it is the only isomer that has a Fries Kekule' structure where all the hexagons contain three double bonds and all pentagons none, *i.e.*, all the double bonds are *exo* to the 12 pentagons.<sup>23</sup> While benzene is the prototype structure for the sextet in benzenoids, one might regard that [6]radialene as the prototype for the empty rings in Clar structures.

It needs to be noted that while the characteristic polynomials and matching polynomials are identical for the dendralenes, the matching polynomials for the radialenes, which are different from their characteristic polynomials, still possess reciprocal eigenvalue pairs in their complete eigenspectrum.

### New Reciprocal Molecular Graphs

Figure 4 presents some new reciprocal graphs. A number of interesting features can be noted. So far reciprocal graphs correspond to conjugated molecules with either cyclobutadiene or multiple methylene groups. The HOMO-LUMO gap for dendralenes and radialenes are larger than  $2 \times 0.41421$  and in Figure 4 only two reciprocal graphs have smaller HOMO-LUMO gaps but even these are larger than the  $2 \times 0.33333$  which is absolutely the smallest band gap theoretically possible. From the new reciprocal graphs in Figure 4, one should expect that angle strain will be a dominant destabilization factor.

Figure 4. Reciprocal molecular graphs.



### Circumscribing Dendralenes and Radialenes

In this section, we suggest that there are two groups of (comb) polyenes – those that can be circumscribed by hexagonal rings and those that cannot. The group that can be circumscribed are necessarily less sterically congested than those that cannot. Thus, circumscribing can be used as a qualitative, graph theoretical measure of steric congestion.

Circumscribing [6]radialene with a polyene perimeter in such a way as to form only hexagonal rings generates hexabeno[*bc,ef,hi,kl,no,qr*]coronene which is the first generation member of the  $D_{6h}$  one-sextet-isomer series of the total resonant sextet benzenoids.<sup>24</sup> When a dendralene can be properly circumscribed, it becomes placed in a benzenoid system so that all the internal benzenoid vertices are covered only by the circumscribed graph. Similarly, circumscribing ethene with hexagonal rings generates pyrene and *s-cis*- and *s-trans*-1,3-butadiene gives benzo[*ghi*]perylene and anthanthrene (see the first and fourth molecular graphs in Figure 5), respectively; these are the first generation members of respective constant-isomer series which have the recursion of  $C_nH_s \Rightarrow C_{n+2s+6}H_{s+6}$  ( $n = N_C$  and  $s = N_H$ ) for each successive circumscribing step.<sup>25</sup> To properly circumscribe with hexagonal rings the conjugated polyene should have two or more carbon gaps, *i.e.*, pentadienyl in an all *cis* conformation or a benzenoid with a cove (two adjacent bay regions) can not be properly circumscribed with hexagonal rings.<sup>25</sup> Figure 5 shows an attempt to circumscribe [5]dendralene which possesses an all *cis* pentadienyl substructure with the one carbon gap circled. Thus, the molecular graph of [5]dendralene and larger comb graphs can not be circumscribed with hexagonal rings to generate benzenoid molecular graphs. This steric limitation to circumscribing coincides with the cutoff to the synthetically known dendralenes discussed above. This observation suggests that steric inhibition of coplanarity of  $p\pi$ -conjugation of larger dendralenes needs

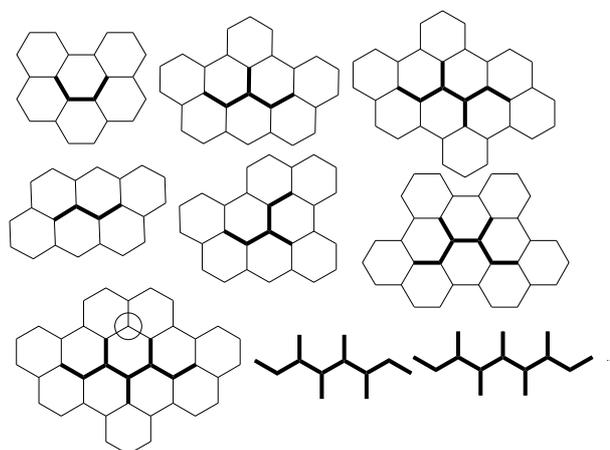


Figure 5. Two different conformations of [2]dendralene, [3]dendralene, and [4]dendralene can be circumscribed by hexagonal rings but no conformation of higher dendralenes can be circumscribed.

to be overcome for synthesis of [5]dendralene and larger members to be successful. In comparison, synthesis of increasing larger linear polyenes becomes progressively more difficult because the HOMO-LUMO gap rapidly decreases resulting in increasing reactivity which is not the case for dendralenes.

Inspection of the molecular graph of [7]dendralene in Figure 5 (last bold graph) suggests that nearest neighboring *syn* methylenyl groups in an extended dendralene will engage in a mutual deflection resulting in a twisting undulation along each side of an otherwise rigid chain. Overall, extended dendralenes represent intriguing systems to study.

### CONCLUSION

While planar dendralene molecules are cross-conjugated with lower  $p\pi$ -electronic energy than linear conjugated polyene molecules, they also tend to be less reactive be-

cause of their larger HOMO-LUMO gaps. At the same time, dendralenes and radialenes are sterically congested and strained polyene systems which result in some enhanced reactivity not foretold by the HOMO-LUMO gap. Comb molecular graphs correspond to polyenes in which cross-conjugation has been maximized and linear molecular graphs correspond to polyenes with no cross-conjugation. Thus, the comparative study of comb and linear molecular graphs provide us with a marked contrast in regard to the topological variables affecting  $\pi$ -electronic stability *versus* HOMO-LUMO gap in polyene molecules.<sup>11,26</sup>

## REFERENCES

1. J. Sarkar and A. K. Mukherjee, *Mol. Phys.* **90** (1997) 903–907.
2. B. Mandal, K. Datta, A. K. Mukherjee, and M. Banerjee, *Mol. Phys.* **96** (1999) 1609–1611.
3. H. Hopf, *Angew. Chem. Int. Ed. Engl.* **23** (1984) 948–959.
4. (a) H. Hopf and G. Maas, *Angew. Chem., Int. Ed. Engl.* **31** (1992) 931–954; (b) F. Geneste and A. Moradpour, *Org. Prep. Proced. Int.* **31** (1999) 507–557.
5. W. S. Trahanovsky and K. A. Koeplinger, *J. Org. Chem.* **57** (1992) 4711–4716.
6. I. Gutman, B. Rušćić, N. Trinajstić, and C. F. Wilcox, *J. Chem. Phys.* **62** (1975) 3399–3405.
7. H. Hosoya and A. Tsuchiya, *J. Mol. Struct. (Theochem)* **185** (1989) 123–137.
8. K. Mizutani, K. Kawasaki, and H. Hosoya, *Nat. Sci. Rep., Ochanomizu Univ.* **22** (1971) 39–58.
9. J. R. Dias, *J. Quantum Chem.* **74** (1999) 721–733.
10. H. Hosoya, H. Kumazaki, K. Chida, M. Ohuchi, and Y.-D. Gao, *Pure Appl. Chem.* **62** (1990) 445–450.
11. P. W. Fowler, P. Hansen, G. Caporossi, and A. Soncini, *Chem. Phys. Lett.* **342** (2001) 105–112.
12. L. M. Tolbert, *Acc. Chem. Res.* **25** (1992) 561–568.
13. J. R. Dias, (a) *Mol. Phys.* **88** (1996) 407–417; (b) *J. Mol. Struct. (Theochem)* **417** (1997) 49–67; (c) *J. Chem. Inf. Comput. Sci.* **39** (1999) 197–203. (d) J. R. Dias, R. Carbo-Dorca, and P. G. Mezey (Eds), *Advances in Molecular Similarity*, Vol. 2, JAI Press, Stamford, Connecticut, 1998, pp. 245–258.
14. J. R. Dias, *Molecular Orbital Calculations Using Chemical Graph Theory*, Springer-Verlag, Berlin, 1993.
15. B. J. McClelland, *J. Chem. Soc., Faraday Trans. 2* (a) **70** (1974) 1453–1456; (b) **78** (1982) 911–916; (c) *Mol. Phys.* **45** (1982) 189–190.
16. J. R. Dias and G. A. Guirgis, *Croat. Chem. Acta* **75** (2002) 621–632.
17. P. A. Waitkus, E. B. Sanders, L. I. Peterson, and G. W. Griffen, *J. Am. Chem. Soc.* **89** (1967) 6318–6327.
18. R. Gleiter, I. Hyla-Kryspin, and K.-H. Pfeifer, *J. Org. Chem.* **60** (1995) 5878–5883.
19. G. G. Hall, (a) *Trans. Faraday Soc.* **53** (1957) 573–581; (b) *Inst. Bull. Math. Appl.* **17** (1981) 70–72; (c) *J. Math. Chem.* **13** (1993) 191–203.
20. J. R. Dias, *MATCH (Math. Chem. Commun.)* **48** (2003) 55–61.
21. J. R. Dias, *Mol. Phys.* **85** (1995) 1043–1060.
22. V. Galasso, *J. Mol. Struct. (Theochem)* **281** (1993) 253–257.
23. S. J. Austin, P. W. Fowler, P. Hansen, D. E. Manolopoulos, and M. Zheng, *Chem. Phys. Lett.* **228** (1994) 478–484.
24. J. R. Dias, (a) *Thermochim. Acta* **122** (1987) 313–337; (b) *J. Chem. Inf. Comput. Sci.* **31** (1991) 89–96.
25. J. R. Dias, (a) *Can. J. Chem.* **62** (1984) 2914–2922; (b) *J. Chem. Inf. Comput. Sci.* **30** (1990) 61–64.
26. J. R. Dias, *J. Chem. Inf. Comput. Sci.* **43** (2003) 1494–1501.

## SAŽETAK

### Svojstva i relacije konjugiranih poliena koji posjeduju recipročan spektar svojstvenih vrijednosti – dendraleni i radialeni

Jerry Ray Dias

Navedeni su novi primjeri recipročnih grafova, tj. grafova s recipročnim parovima svojstvenih vrijednosti. Ukratko su prikazane bitne odlike unakrižne konjugacije. Autor raspravlja o tome zašto je takva konjugacija važna kod oblikovanja vodljivih i feromagnetičnih polimera. Također su dane rekurzivne formule za računanje karakterističnih polinoma nekih specijalnih grafova, kao što su graf-češalj i graf-ljestve.