

Molecular Orbital Functional Groups. 3. Subspectrality in the Eigenvalues of Linear Polyene Molecules and Related Aspects

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Embedding and McClelland right-hand mirror-plane fragments are MO functional groups. Molecular graphs having common embedding and right-hand mirror-plane fragments are subspectral in those eigenvalues and have a greater degree of similarity. Collections of subspectral structures are tabulated.

INTRODUCTION

Two or more molecular graphs having one or more eigenvalues in common are said to be subspectral. While embedding and related subspectrality of linear polyenes, L_1 to L_5 , have been extensively investigated,^{1–3} little work on embedding of higher conjugated linear polyenes has been pursued. D'Amato, Gimarc, and Trinajstić have discussed the presence of the eigenvalues of 1,3,5-hexatriene, L_6 (1.80194, 1.24698, and 0.44504), in biphenylene, pyrene, and 5,12-quinodimethanetetracene (Figure 1), the latter which eluded explanation.⁴ Recently, we observed that 2-methylenylbutadiene is subspectral to heptatrienyl radical (L_7), and L_7 (1.84776, $\sqrt{2}$, and 0.76537) is subspectral to 1-methylenyl-2-vinylnaphthalene, *m*-terphenyl, and 2-naphthylmethylenyl-1-naphthalene. Also, L_8 (1.87939, 1.53209, 1.0, and 0.347296) is subspectral to 1,2,5,6-tetramethylenylcyclooctatetraene, and the eigenvalues of 2.53209, 1.347296, and 0.87939 which differ from the corresponding eigenvalues in L_8 by ± 1 are found in 2,3-bismethylenylbicyclo[2.2.0]-hexatriene, biphenylene, pyrene, triphenylene, and 5,12-quinodimethanetetracene. In this paper, embedding of L_6 to L_8 in larger molecular systems and the possible origin for these other subspectralities and related aspects will be discussed.

Eigenvalues and corresponding eigenvectors are quantum based topological indices, and the degree overlap between the eigenvalues of two or more molecules is one measure of similarity.⁵ Since eigenvalues have a structural origin, molecular graphs having common eigenvalues will invariably have common structural components or functional groups. Thus, the study of subspectrality is important in understanding the origin of certain chemical properties. Two types of quantum chemical based functional groups are embedding fragments and right-hand mirror-plane fragments.^{1–4}

SOME TERMINOLOGY

The line-dot pictures used herein are C–C σ -bond representations of conjugated polyenes called molecular graphs; molecular graph edges correspond to bonds and vertices correspond to atoms. Eigenvalues and eigenvectors of molecular graphs correspond to $p\pi$ energy levels and wave functions, respectively, of the associated molecules. The positive eigenvalues correspond to bonding and negative to antibonding orbitals.

MOLECULAR GRAPHS SUBSPECTRAL IN THE EIGENVALUES OF 1,3,5-HEXATRIENE (L_6)

Figure 1 lists some molecular graphs that are subspectral in the eigenvalues of L_6 . The first eight molecular graphs are alternant hydrocarbons (AHs) and the last four are nonAHs. AHs have no odd size rings. Cyclotetradecaheptaene (C_{14}) is doubly degenerate in these eigenvalues. Cyclooctacyclooctatetraene, pyrene, benzo[*ef*]heptalene, dicycloheptapentalene, acepleiadylene, and azupyrene (Figure 1) have C_{14} perimeters and have the eigenvalues of L_6 once; the last three polycyclics are isomers of pyrene and can not be embedded by L_6 . By the principle that those reactions involving a minimum amount of electronic reorganization will be more facile, it is expected that isomerization of azupyrene to pyrene should be relatively facile since both molecular graphs have 8 (out of 16) common eigenvalues. The thermal rearrangement of azupyrene to pyrene has been studied.⁶ Several mechanistic pathways were shown to be consistent with the data in hand.⁶ This rearrangement is analogous to the proposed Stone–Wales transformation for converting one fullerene isomer to another.⁷

Based on either the principle of minimum electronic reorganization or the site of highest electron density in the HOMO, one would expect that the preferred site for electrophilic substitution in azupyrene to be position-4 which is experimentally observed for nitration.⁸ However, in electrophilic substitution of azupyrene by weakly oxidizing electrophiles, like acylium ions, steric factors appear to intervene in such a way as to lead to an overall preference for position-2.⁸ Because of their similarity to pyrene, the trianions of dicycloheptapentalene, acepleiadylene, and azupyrene have been studied.⁹

Both biphenylene and tetraphenylene have been shown to possess 1,3,5-hexatriene as one of their irreducible substructures.¹⁰ The trinaphthocoronene eigenvalue spectrum has been previously discussed.¹¹ It can be seen that the first and ninth AHs in Figure 1 are related. The first molecular graph, 4,5-dimethylenylcyclobutabenzene, has a McClelland right-hand mirror-plane fragment¹² listed in our book.² Recall that when a mirror-plane of symmetry divides a molecular graph into two parts, the vertices on the mirror-plane remain with the left-hand fragment and vertices in the right-hand fragment originally connected by a bisected edge (bond) have weights of -1 ; in other words, right-hand mirror-plane fragments are composed of either normal or -1 weighted vertices. It has been shown⁴ that two successive perpendicular mirror-plane fragmentations of biphenylene gives the right-hand

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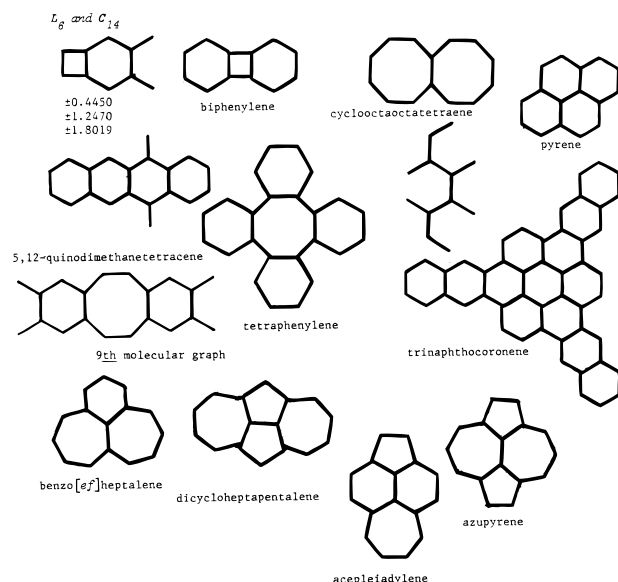
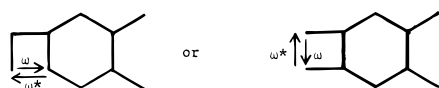


Figure 1. Molecular graphs possessing the paired eigenvalues of hexatriene (L_6).

mirror-plane fragment of L_6 . By submitting the ninth molecular graph in Figure 1 to two successive perpendicular mirror-plane fragmentations, it can be shown that it contains the same right-hand mirror-plane fragment that is present in the first molecular graph. Alternatively, one can see that the following general irreducible subgraph will give the first molecular graph by setting $n = 1$ and the eigenvalues of the ninth molecular graph by setting $n = 2$.^{2,13}



$$X^{10} - 11X^8 + 39X^6 - 52X^4 + 22X^2 - 1 - 2\cos\theta_k(X^6 - 5X^4 + X^2) = 0$$

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

Figure 2 presents molecular graphs of nonAHs that are subspectral in at least half (nonpaired) of the eigenvalues of L_6 . Molecular graphs having greater than twofold symmetry will invariably possess a doubly degenerate subset of eigenvalues.^{2,10-11} Tropyli (cycloheptatrienyl, C_7) has sevenfold symmetry and is doubly degenerate in the nonpaired half of the eigenvalues of L_6 . Many of the molecular graphs in Figure 2 possess a seven-membered ring. The first three molecular graphs, tropyli, heptafulvene, and 2,3-dimethylenylfulvene, are said to be semiembeddable² by L_6 . The fifth molecular graph (cyclohepta[*a*]naphthalene) is mixed embeddable by L_6 and C_7 and the sixth one (dicyclohepta[*a,d*]benzene) is embeddable by C_7 ; the relevant node positions are indicated by zero labels in Figure 2. The first (C_7), sixth, seventh [tris(cycloheptatrienyl)benzene], and ninth molecular graphs in Figure 2 are doubly degenerate (X2) in the unpaired eigenvalues of L_6 . The first, seventh, eighth (1,1-dicycloheptatrienylheptafulvene), and ninth (heptaradialene) molecular graphs have greater than twofold symmetry and must have at least a doubly degenerate subset of eigenvalues.^{2,10,11}

The tricarocation of the seventh molecular graph, 1,3,5-tris(cycloheptatrienyl)benzene, and the dication of the eighth molecular graph in Figure 2 have been synthesized.^{2,14,15} Let N , N_+ , N_0 , N_- , n , n_+ , and n_- be the number

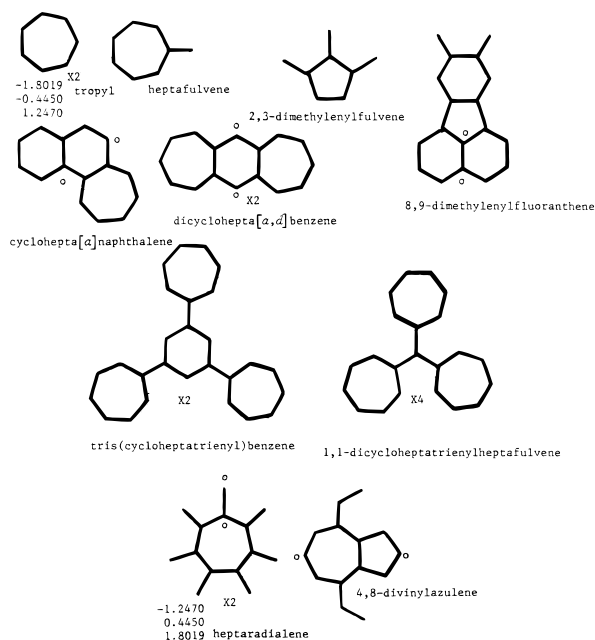


Figure 2. Nonalternant molecular graphs that are subspectral to hexatriene (L_6).

of carbon vertices ($p\pi$ centers), positive eigenvalues (bonding energy levels), zero eigenvalues (nonbonding energy levels), negative eigenvalues (antibonding energy levels), $p\pi$ -electrons, $p\pi$ -electrons occupying bonding energy levels, and $p\pi$ -electrons occupying antibonding energy levels, respectively. Molecular systems with $n = \text{odd}$ have open shell electronic configurations. According to Fowler's terminology for systems of even electronic configuration,¹⁶ there are four distinct types. If HOMO and LUMO are degenerate, it is open-shell. A molecular system will have a properly closed-shell configuration if all bonding orbitals are doubly occupied ($N_+ = n/2$), pseudo closed-shell if all electrons are in doubly occupied orbitals but some bonding orbitals are left empty ($N_+ > n/2$), meta closed-shell if all the electron are in doubly occupied orbitals but some electrons are forced to be in nonbonding or antibonding orbitals ($N_+ < n/2$). From this it is seen that if the seventh molecular graph with $N = 27$ and $N_+ = 12$ should easily go from the open-shell ($n = \text{odd}$) neutral species ($n_+ = 24$ and $n_- = 3$) to the properly closed-shell tricarocation form ($n_+ = 24$ and $n_- = 0$). The eighth molecular graph with $N = 22$ and $N_+ = 10$ should easily go from the open-shell (HOMO = LUMO = -0.4450) neutral species ($n_+ = 20$ and $n_- = 2$) to the properly closed-shell dication form ($n_+ = 20$ and $n_- = 0$); note that the neutral form of the eighth molecular graph is related to trimethylenemethane diradical. Based on these results and our work with indacenoids,¹⁷ the following generalization is put forth: molecular systems composed of pentagonal or pentagonal and hexagonal rings can have $N_+ > N_-$ and heptagonal or heptagonal and hexagonal rings can have $N_+ < N_-$. In other words, pseudo closed-shell configurations can occur in pentagonal and pentagonal/hexagonal even molecular systems and meta closed-shell configurations can occur in heptagonal and heptagonal/hexagonal even molecular systems.

The ninth and tenth molecular graphs (heptaradialene and 4,8-divinylazulene, respectively) in Figure 2 can be derived from the seventh and only acyclic molecular graph in Figure 1 by the appropriate joining of vertices with eigenvector

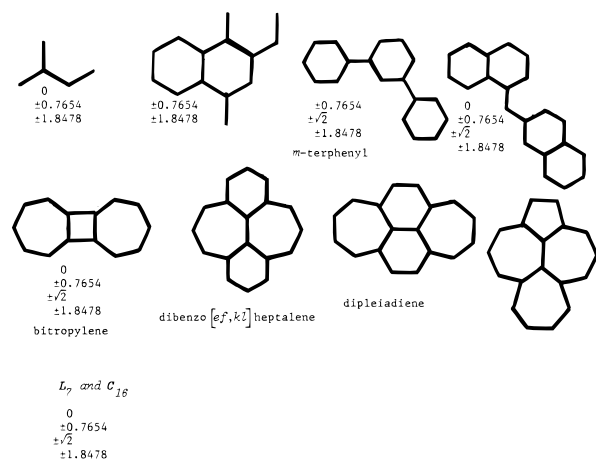


Figure 3. Molecular graphs that are subspectral in the eigenvalues of heptatrienyl radical, $\pm(2 \pm \sqrt{2})^{1/2}$.

coefficients of the same magnitude but opposite sign through node (zero coefficient) vertices.¹⁸ The fulfillment of these requirements is equivalent to compliance to the well-known zero-sum rule.²

It should be noted that embedding of L_6 and mirror-plane fragmentation of C_{14} and the third, fourth (pyrene), and tenth (benzo[ef]heptalene) molecular graphs in Figure 1 are equivalent where the embedding node positions of the former coincide with the mirror-plane of the latter. Mirror-plane fragmentation of the last three molecular graphs in Figure 1 will give the same right-hand mirror-plane fragment which contains the eigenvalues of L_6 . Mirror-plane fragmentation of the seventh molecular plane in Figure 1 and the last two molecular graphs, heptaradialene and 4,8-divinylazulene, in Figure 2 give the same right-hand mirror-plane fragment.² L_6 and the first three molecular graphs in Figure 2 can be mirror-plane fragmented to give the same vertex-weighted graph.²

MOLECULAR GRAPHS SUBSPECTRAL IN EIGENVALUES OF HEPTATRIENYL (L_7)

The number of molecular graphs that are subspectral in the eigenvalues of L_7 are less numerous. The first two molecular graphs in Figure 3 are uniquely subspectral to L_7 . Styrene and L_7 (except for the zero eigenvalue) are subspectral to m -terphenyl. L_7 is one of the irreducible subgraphs of bitropylene.¹⁰ The sixth (dibenzo[ef,kl]heptalene) molecular graph in Figure 3 can be embedded by L_7 or mirror-plane fragmented to give L_7 . C_{16} has greater than twofold symmetry and can be embedded by L_7 and is doubly degenerate in the eigenvalues of heptatrienyl. As a result of this, the sixth, seventh (dipleiadiene), and eighth molecular graphs can be generated from C_{16} . The last two molecular graphs in Figure 3 and C_{16} can be mirror-plane fragmented to give the same vertex-weighted graph which contain the eigenvalues of L_7 .

MOLECULAR GRAPHS SUBSPECTRAL IN EIGENVALUES OF 1,3,5,7-OCTATETRAENE (L_8)

The right-hand mirror-plane fragments to all the molecular graphs in Figure 4 are subspectral in the eigenvalues of L_8 . Both the first and seventh (dicyclopenta[α,ϵ]octatetraene) molecular graphs have the same right-hand fragment, and the third, fourth, fifth, sixth, and eighth (last) molecular graphs have the same right-hand fragment. Perylene can also

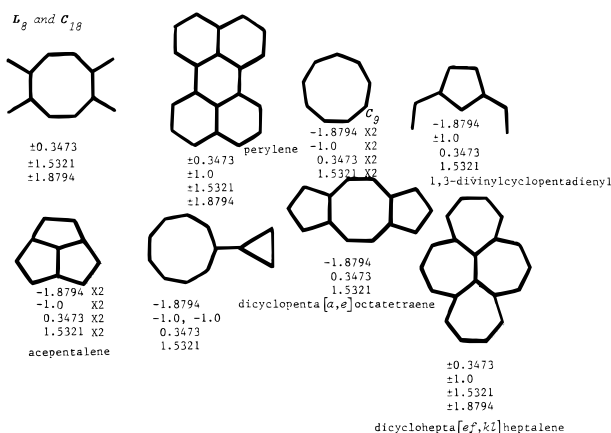


Figure 4. Molecular graphs that are subspectral to octatetraene (L_8).

be embedded, and the third (C_9), fourth (1,3-divinylcyclopentadienyl), fifth (acenaphthalene), and sixth molecular graphs can be semiembedded by L_8 .² Both perylene and the last molecular graph, dicyclohepta[ef,kl]heptalene, can be constructed from C_{18} , which is doubly degenerate in the eigenvalues of L_8 , by inserting the two internal vertices such that the zero-sum rule is obeyed.

EIGENVECTORS

A number of important relationships for determining eigenvectors for given eigenvalues have been presented. They include the Coulson–Rushbrooke pairing theorem,¹⁹ embedding fragments,¹ the path deleting procedure,²⁰ the vertex deleting procedure,²¹ the vertex adjacency relationship,¹⁸ and the relationship for complementary eigenvalue pairs.²² Per the Coulson–Rushbrooke pairing theorem, all eigenvalues in an AH (or a AH substructure within a nonAH structure) are either zero (nonbonding) or paired (bonding and antibonding). Every other carbon vertex in an AH can be starred so as no two starred or nonstarred positions are adjacent. Consider a maximally starred AH. The eigenvector coefficients for the starred positions of the AH are unchanged in going from one eigenvalue (X_1) to its paired partner (X_2), and for the nonstarred positions the sign (but not magnitude) changes in going from one eigenvalue to its paired partner; if an eigenvalue has no paired partner (i.e., $X = 0$), then the coefficients of the nonstarred positions are zero.

Whenever a smaller molecular graph can be embedded on a larger one, then the eigenvalues of the smaller one will be found among the eigenvalues of the larger one.¹ These eigenvalues in the larger molecular graph will have eigenvectors that coincide with the embedding pattern. The coefficients of these eigenvectors are the same as the embedded fragments but renormalized by multiplying by $1/\sqrt{n}$ where n is the number of embedded fragments.

For any vertex u with adjacent vertices of r , s , and t in any molecular graph, the (unnormalized) eigenvector coefficient C_{iu} for any eigenvalue X_i is given by

$$-X_i C_{iu} + C_{ir} + C_{is} + C_{it} = 0$$

This vertex adjacency relationship is more general than the zero-sum rule used in perturbation molecular orbital theory²³ and in embedding.¹

If two eigenvalues in a single molecular graph, two related molecular graphs, or right-hand mirror-plane fragments sum to minus one ($X_1 + X_2 = -1$), they are said to be

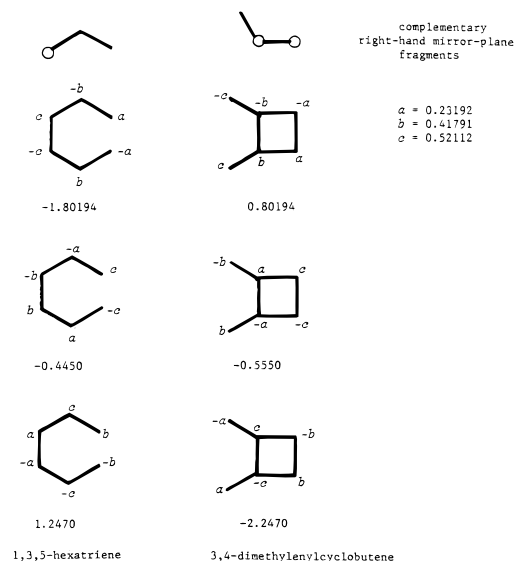


Figure 5. Corresponding eigenvectors for complementary eigenvalues belonging to complementary molecular graphs.

complementary.²² Two equal-sized right-hand mirror-plane fragments or molecular graphs are complementary if all their eigenvalues are mutually complementary. The normal vertices of one of the complementary right-hand fragments correspond to -1 weighted vertices in the other and both have the same set of normalized eigenvector coefficients, except for sign. Figure 5 illustrates this correspondence for the right-hand mirror-plane fragment of 1,3,5-hexatriene (L_6) and its complementary. Since L_6 and 3,4-dimethylenecyclobutene in Figure 5 correspond to AHs, the pairing theorem can be used to obtain their remaining eigenvalues and eigenvectors. A polycyclic analog of L_6 can be made by conjoining it through a methine carbon at positions 1, 3, and 6, and a polycyclic analog of 3,4-dimethylenecyclobutene can be made by cojoining its methylenyl groups through a methylene carbon; these two analogs are now C_7H_9 isomers and have been synthesized.²⁴ It was shown in this work²⁴ that the analog of L_6 (HOMO = 0.445β) was more labile than the analog of 3,4-dimethylenecyclobutene (HOMO = 0.555β) which is consistent with the frontier orbital results presented here (Figure 5).

Biphenylene and pyrene have a one-to-one matching in their eigenvectors belonging to the corresponding eigenvalues of L_6 . This can be seen by bisecting biphenylene through its central four-membered ring and pyrene through its central trio perimeter vertices and internal third-degree vertices with a mirror-plane; these mirror-planes define an antisymmetric relationship for the eigenvectors and vertices on the plane in pyrene are zero coefficients.

MOLECULAR GRAPHS SUBSPECTRAL IN THE COMPLEMENTARY EIGENVALUES OF L_6

Molecular graphs having eigenvalues complementary to L_6 are presented in Figure 6; those corresponding to AHs are listed in the first group and nonAHs in the last group. The first molecular graph in Figure 6 (also see Figure 5) is an isomer of benzene and has been studied both experimentally and theoretically.²⁵ The right-hand mirror-plane fragment of 3,4-dimethylenecyclobutene (Figure 5) is also present in the third, eighth (cyclobutacyclopentadienyl), and ninth molecular graphs in Figure 6. The first and third

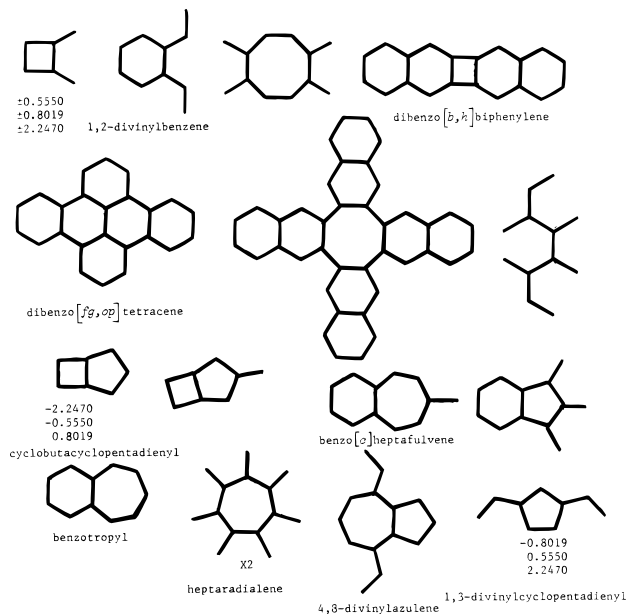


Figure 6. Molecular graphs having eigenvalues that are complementary to the eigenvalues present in hexatriene (L_6).

molecular graphs can be shown to be related by a general irreducible graph where the first one is obtained by setting $n = 1$ and the eigenvalues of the third by setting $n = 2$ as done for the first and ninth molecular graphs in Figure 1 (*vide supra*). By quenching the anion of the molecule corresponding to the eighth molecular graph with acids of various strength it has been shown it has a pK_a of ≈ 29 which is 11 units higher than that exhibited by cyclopentadienyl anion.²⁴ The difference in E_π energy for cyclopentadienyl anion and 1,3-butadiene is 2β units and for the anion of the eighth (cyclobutacyclopentadienyl) molecular graph and 3,4-dimethylenecyclobutene is 1.7β units. This is quite consistent with the above experimental results.

The right-hand mirror-plane fragment of 1,2-divinylbenzene (second molecular graph in Figure 6) is complementary to the right-hand mirror-plane fragment of 4,5-dimethylenecyclobutabenzene (first molecular graph structure in Figure 1). By allyl embedding, one can easily show that 1,2-divinylbenzene is doubly degenerate in the eigenvalues of $\pm\sqrt{2}$ besides the eigenvalues given in Figure 6. The fact that 1,2-divinylbenzene (HOMO = 0.555) is the least reactive of its isomers (1,3- and 1,4-divinylbenzene) to polymerization, contrary to its intermediate HOMO value, suggests that the chain propagation reaction steps of the *ortho* isomer are subordinated by intramolecular cyclization leading to premature termination. Both the fourth (dibenzo[b,h]biphenylene) and sixth molecular graphs have 1,2-divinylbenzene as one of their irreducible subgraphs.^{2,10,13} By either mirror-plane fragmentation or embedding, it can be shown that dibenzo[fg,op]tetracene (fifth molecular graph) contains the eigenvalues 1,2-divinylbenzene. The right-hand mirror-plane fragments to benzo[c]heptafulvene, the 11th molecular graph, and benzotropyli in Figure 6 are identical to the right-hand mirror-plane fragment of 1,2-divinylbenzene.

The eigenvalues of L_6 and its complementary, 3,4-dimethylenecyclobutene, occur together in 3,4,5,6-tetramethylenecyclooctatetraene (seventh molecular graph in Figures 1 and 6); the same is true for the nonpaired eigenvalues present in heptaradialene and 4,8-divinylazulene (Figures 1 and 6). The molecular graph of 1,2,5,6-tetramethylenecyclo-

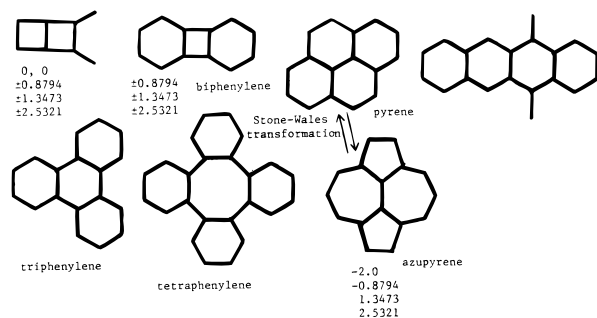


Figure 7. Molecular graphs having eigenvalues complementary to the eigenvalues present in octatetraene.

clooctatetraene is found in Figures 4 (first molecular graph) and 6 (third molecular graph) and, therefore, has eigenvalues of L_8 and the complementary eigenvalues of L_6 ; also see the molecular graph of 1,3-divinylcyclopentadienyl in Figures 4 (fourth molecular graph) and 6 (last molecular graph). 1,2,5,6-Tetramethylenecyclooctatetraene and biphenylene (Figures 1 and 7) are mutually complementary molecular graphs.

MOLECULAR GRAPHS SUBSPECTRAL IN THE COMPLEMENTARY EIGENVALUES OF L_8

The right-hand mirror-plane fragment to the first molecular graph in Figure 7 is complementary to the right-hand mirror-plane fragment of L_8 . Biphenylene, triphenylene, and tetraphenylene in all have a common irreducible subgraph ($k = 0$)² which is the carrier of the complementary eigenvalues of L_8 . Pyrene and its Stone–Wales isomer,⁷ azupyrene, biphenylene, 5,12-quinodimethanetetracene, and tetraphenylene are all subspectral in the eigenvalues of L_6 (see Figure 1) and in the eigenvalues complementary to L_8 (Figure 6). This latter was not recognized by prior workers.⁴ Two isomeric molecular graph that have identical characteristic polynomials (and therefore eigenvalues) are said to be isospectral.^{4,5,26} It should be noted that biphenylene and pyrene are almost isospectral, except pyrene has the additional eigenvalues of ± 1 and ± 2 . The chemistry of biphenylene and pyrene is very similar. For example, the first ionization potentials of biphenylene and pyrene are within a tenth of an electron volt to each other; the major differences in the chemistry of biphenylene and pyrene most likely have their origin in the strain induced by the cyclobutadiene substructure present in the former. All the eigenvalues of pyrene, except ± 2 , are found among the eigenvalues of 5,12-quinodimethanetetracene. The coincidences of the eigenvalues among the molecular graphs in Figure 7 have only been partially explained by this work.

CONCLUSIONS

Embedding and mirror-plane fragments are components of a functional group-like approach in the study molecular graphs corresponding to molecules of chemical interest. Numerous new examples of subspectral molecules have been presented. Some chemical and topological consequences have been illustrated. When experimental results are contrary to HMO theory, then this discrepancy leads one to examine variables not incorporated in the theory which may be dominating the chemistry.

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