

From Small Polyradical Molecules to Infinitely Large π -Electronic Networks – Strongly Subspectral molecular Systems

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Series of polyradical systems having a preponderance of common eigenvalues (strongly subspectral) are identified, and their structural relationships studied. A framework for the analysis and molecular modeling of graphite-related polymers is provided by an infinite two-dimensional mapping. Some analytical expressions are derived. Aryl polyradical dendrimers form numerous strongly subspectral sets. Potential conductive/ferromagnetic properties are indicated. Collections of subspectral structures (molecular graphs) and their eigenvalues are tabulated for the first time.

Introduction

The first step toward general characterization of surface states at the boundary of crystals involves understanding how end states affect π -electronic properties of one- and two-dimensional polymers. These lower dimensional systems in themselves can occur as distinct systems or as boundary components of higher dimensional systems. Dangling bonds must necessarily occur at the surface and edges of newly formed crystals, and polymers and are invariably associated with radical sites. In addition, interest in polyradical molecular systems as magnetic materials of the future continues to stimulate experimental and theoretical investigations. Also, identifying the energetic/structural variables that prevent the pairing of radical sites to form bonds will contribute to our understanding of the very nature of bonding itself.

A pair of electrons can either have antiparallel spins ($S = 0$, antiferromagnetic spin coupling) or parallel spins ($S = 1$, ferromagnetic spin coupling) corresponding to a singlet or a triplet state, respectively. The energy difference between the singlet and triplet states (ΔE_{ST}) measures the strength of the spin coupling. A bonding pair of electrons can be regarded as an extreme case of antiferromagnetic coupling with ΔE_{ST} being a measure of bond strength.

Because singlet states prevail in the molecular universe, a limited number of polyradical molecules capable of experimental manipulation are

known. Fundamental studies of the archetypal diradicals, trimethylenemethane [1], tetramethyleneethane (bisallyl) [2], *m*-xylylene (*m*-benzoquinodimethane) [3] and 1,2,3,4-tetramethylenebenzene (2,3,5,6-tetrakis(methylene-1,4-cyclohexanedyl)) [4] continue to be reported in the literature. These simplest diradicals can be generated from appropriate precursor molecules by vapor phase thermolysis or low temperature matrix-immobilized irradiation. Experimentally, trimethylenemethane and tetramethyleneethane both have ground triplet states but only in the latter does the singlet state have a close proximity to the triplet state. Schlenk hydrocarbon, the most famous diradical, was synthesized in 1915 and also has a triplet ground state which is almost degenerate with the singlet state [5].

The two NBMOs in trimethylenemethane diradical have atoms in common, whereas the two NBMOs of tetramethyleneethane (bisallyl) diradical are confined to different sets of atoms. The NBMOs in the former are said to be nondisjoint, and in the latter disjoint. Thus, the two NBMOs trimethylenemethane are degenerate singly occupied MOs which are orthogonal but coextensive; exchange interaction in coextensive systems favors the high-spin state, in agreement with Hund's Rule. The bisallyl diradical can be derived by union of two allyl radicals at their central positions. In the NBMO of allyl, the 2-position is a node, that is, it has a π -electronic coefficient of zero. Under these circumstances, the exchange energy between the two halves of bisallyl is close to zero. Since it is the exchange energy that accounts for the separation between the triplet and lowest singlet, these

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two states will be almost degenerate. This means that Hund's Rule will not necessarily apply to π -electronic systems having disjoint NBMOs. All the molecular graph members of the strongly subspectral infinite series discussed in this work will have NBMOs that are orthogonal, singly occupied, and nondisjoint.

Related radical benzenoids have recently come to the forefront. Monoradical phenylenyl ($C_{13}H_9$) is easily formed by hydrogen-transfer reactions of phenylene ($C_{13}H_{10}$). Phenalenyl radicals ($C_{13}H_9$) tend to self-dimerize, and the product dimer subsequently undergoes further hydrogen-transfer reactions ultimately forming peropyrene ($C_{26}H_{14}$) [6]. Recent studies toward synthesis of a C_3 symmetrical derivative of phenalenyl, trinaphtho(8,1,2-*bcd*:8',1',2'-*fgh*:8'',1'',2''-*jkl*)phenalenyl, has been reported, and the synthesis of the corresponding cation has been accomplished [7]. According to cyclic voltammetric measurements, the LUMO-SOMO energy difference of the trinaphthophenalenyl radical is smaller than that of phenalenyl radical [7], which is consistent to their molecular graph eigenvalue differences of 0.649 and 1, respectively. The first examples of isospectral benzenoids (benzenoids with the same set of HMO energy levels or eigenvalues) have been reported [8]. These isospectral benzenoids are monoradical odd carbon isomeric ($C_{33}H_{17}$) hydrocarbons consisting of three fused phenalenyl units. Phenalenyl is the smallest odd carbon benzenoid and is the first generation member of the constant-one-isomer series discovered in [9]. A series of oxygen-containing phenalenyl monoradicals and their ESR measurements have been reported [10]. Diradicals based on oxygen-containing fused phenalenyl derivatives have been synthesized [11]. The Scheme 1 polyradical structures in [11] are progenitors to the constant-one-isomer series [9].

A C_3 symmetrical trioxo derivative of diradical triangulene ($C_{22}H_{12}$) has been synthesized and studied [11 - 12]. From the ESR spectrum of this trioxy-triangulene trianion diradical and the molecular mechanics valence bond calculations on triangulene, it was concluded that the latter has a triplet ground state [13], and it is expected that all successors generated by successive circumscribing of triangulene [9] will also have triplet ground states consistent with nondisjoint diradicals. Tricornan is a tris ortho-bridged triphenylmethane analog of triangulene diradical. Trioxatricornan derivatives have been synthesized as keystones for the construction of rigid molecular cavities [14].

Herein, we investigate the trends that are associated with homologous series of conjugated polyradical systems that progressively increase by regular repeating structural units referred to as aufbau units. Two questions, germane to all molecular modeling studies of polymers arise [15]. How large must a finite molecule be in order for it to be reliably modeled by the infinite system assumption? How do terminal groups influence the infinite system assumption? In regard to these inquiries, pairs of strongly subspectral series will be examined. In particular, an answer to the second inquiry for some types of end groups will be given, resulting in some analytical expressions. At the HMO level, strongly subspectral series are homologous series of conjugated π -electronic molecular systems in which the corresponding successive member pairs (or, in some cases, larger sets) have a preponderance of eigenvalues ($p\pi$ -energy levels) in common [16]. From the regularities present in matching strongly subspectral series and the known chemistry of smaller member molecules, we expect to be able to extrapolate the properties of larger molecular members through molecular modeling methods. In addition, we have an interest in understanding end and edge effects associated with the terminal end of polymers which should have relevance to crystal surface effects.

Basic Concepts, Definitions, and Terminology

Molecular graph is the C-C σ -bond skeleton representation of a fully conjugated polyene chemical structure. Molecular graphs are presumed to be planar, whereas, the molecules they represent might be capable of rotating into nonplanar conformations. A molecular graph can be transformed to a chemical structure representation by converting each vertex to a C atom, adding as many $p\pi$ -bonds as possible, and then adding no more than two -Hs to each carbon not having four covalent bonds. Molecular graph eigenvalue and eigenvector are the mathematical terms that are equivalent to the chemical terms of HMO molecular energy level and wave function, respectively.

If two molecular graphs have at least one eigenvalue in common, they are said to be subspectral. Two molecular graphs are *strongly* subspectral if they have a preponderance of eigenvalues in common. Two strongly subspectral molecular graphs are *almost-isospectral* if their unique eigenvalues are zero or integer. Hall subgraphs (embedding fragments) and McClelland subgraphs (right-hand mirror-plane frag-

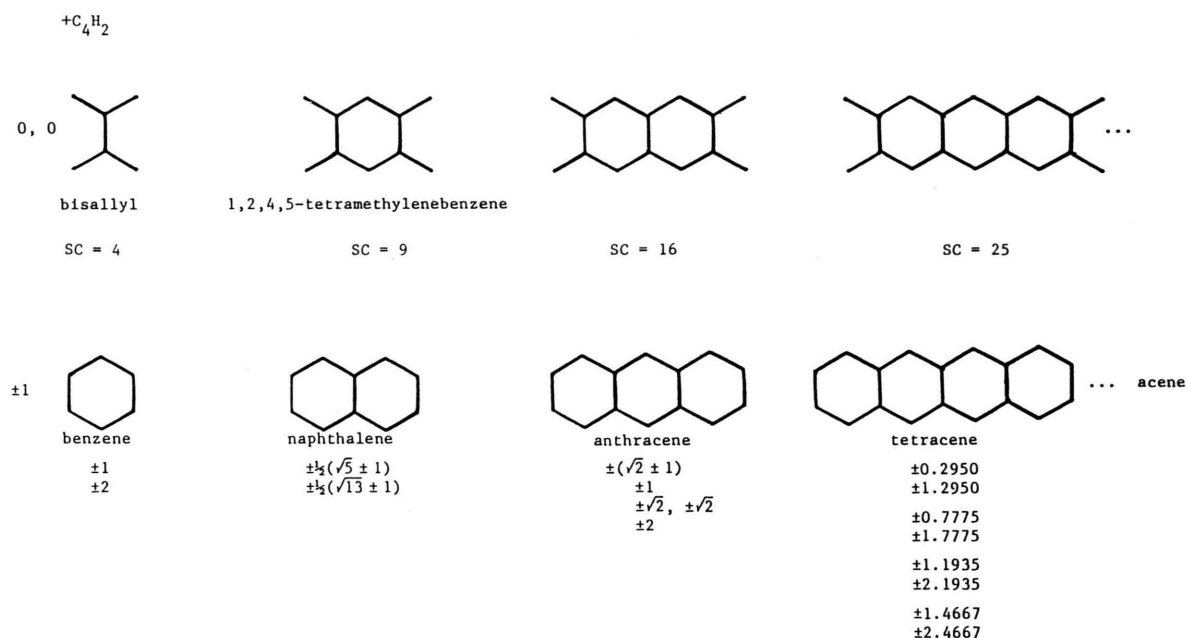


Fig. 1. Two series of complementary molecular graphs that are almost-isospectral. The unmatched eigenvalues are indicated at the beginning next to the first generation structures of each series.

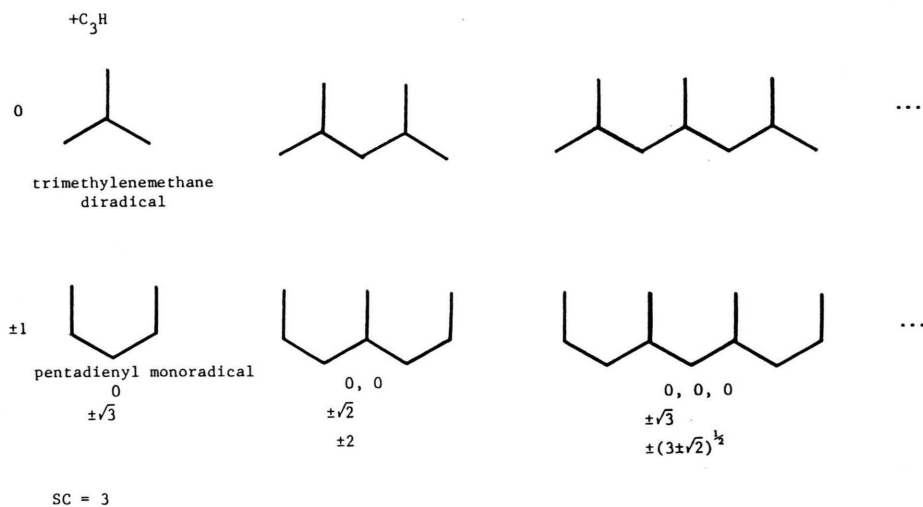


Fig. 2. Two series of molecular graphs that are almost-isospectral. The unmatched eigenvalues are indicated next to the first structure of each series.

ments) and other kinds of subspectrality are regarded as types of molecular orbital functional groups. The more functional groups two molecular graphs have in common, the more they are similar, other things being equal; if the FMOs (HOMO and LUMO) are included this similarity is even stronger. Members of

a homologous series of intermediate size are called oligomers, and larger members are called polymers, the latter being often modeled by assuming that they have reached infinite extent. The size of an oligomer can usually be precisely determined, whereas the size of a polymer cannot normally be precisely defined.

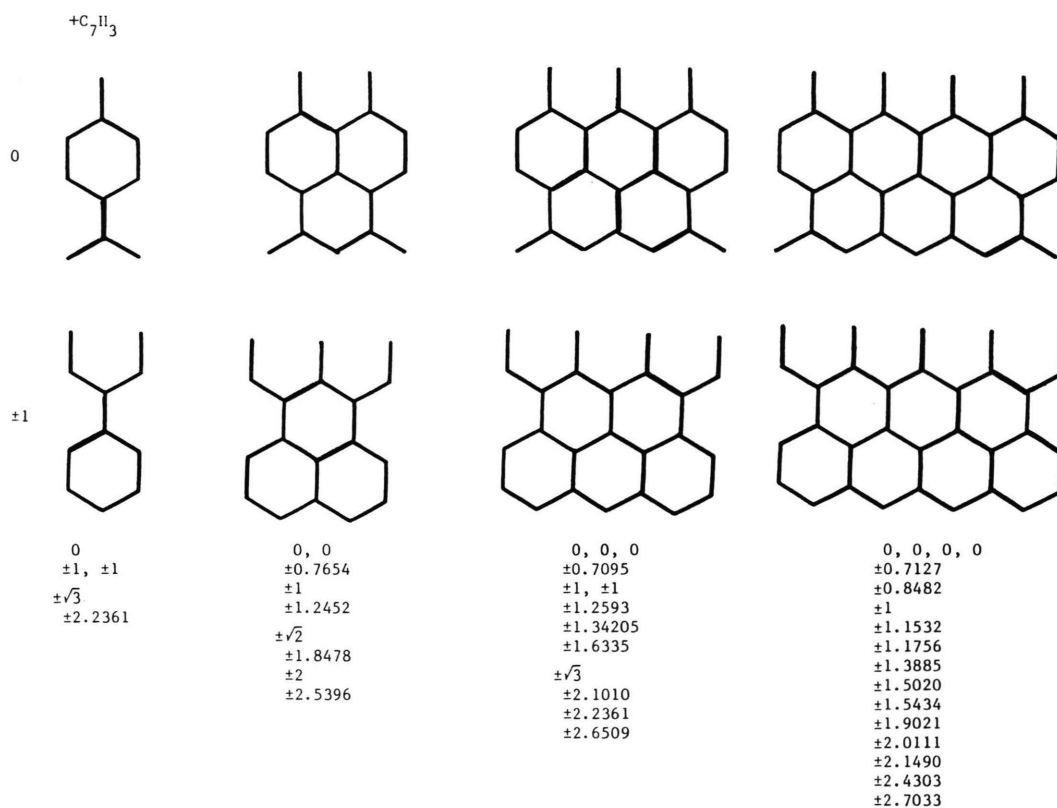


Fig. 3. Two series of molecular graphs that are almost-isospectral. The unmatched eigenvalues are indicated next to the first structure of each series.

The overlapping close proximity of energy levels (continuum) in infinitely large π -electronic networks result in bands bounded by singularities, where the continuum of occupied energy levels is called the valence band, and the continuum of unoccupied energy levels above the valence band is called the conduction band. If there is a zone containing no energy levels between the valence and conduction bands, then this zone is referred to as a bandgap. Electrical conductivity in a polymer network is associated with a zero bandgap. If a nonzero bandgap material contains isolated NBMOs (half-filled zero energy levels), then this polymer network will have a chance to be highly ferromagnetic.

Acene Polymer Strips and Related Strongly Subspectral Series

Figures 1 - 5 present series of strongly subspectral molecular graphs of chemical relevance. In Figs. 1 - 3,

the common eigenvalues are listed below the corresponding pairs of molecular graphs, and the unique eigenvalues associated with all molecular graphs of a given row are indicated next to the first generation member. There is a one-to-one matching of the eigenvalues between the corresponding molecular graphs in Figs. 4 and 5 with the unique eigenvalues of ± 1 in Fig. 4 and zero in Fig. 5, indicated in the upper left-hand corners. The formula of the aufbau unit used to construct the strongly subspectral series in a given figure is indicated in the upper left-hand corner.

Our previous work established an infinite two-dimensional mapping between two sets of molecular graphs that were pairwise strongly subspectral [16]. Herein, we present a new example of two sets of molecular graphs (Figs. 4 and 5) arranged in two-dimensional arrays in which there is a one-to-one correspondence in their associated eigenvalues. The specific eigenvalues for the first two rows of molecular graphs in Figs. 4 and 5 are tabulated in Figs. 2 and 3;

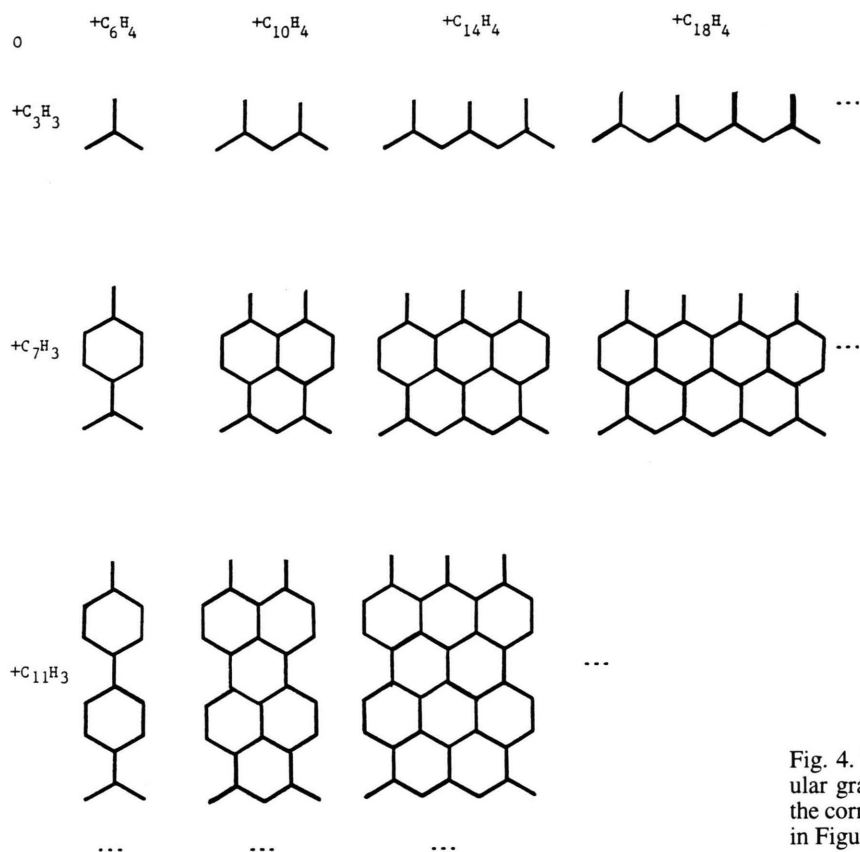


Fig. 4. Two-dimensional array of molecular graphs that are almost-isospectral to the corresponding molecular graphs given in Figure 5.

the strongly subspectral pair of molecular graphs in Fig. 2 correspond to those in the first rows of Figs. 4 and 5, and the strongly subspectral pair of molecular graphs in Fig. 3 correspond to those in the second rows of Figures 4 and 5.

Figure 1 presents two strongly subspectral series that devolve to the same ultimate infinite acene polymer strip [16], and the two series presented in Fig. 2 devolve to the same ultimate polymethyleneacetylene infinite polymer strip [17]. We will now demonstrate that the acene-related polymers in Fig. 1 are progenitors to the polymethyleneacetylene-related polymers in Figure 2. Deletion of two vertices from the molecular graph of tetramethyleneethane diradical (bisallyl) in Fig. 1 gives the molecular graph of trimethylenemethane diradical in Figure 2. Continuing this vertex deletion operation on the molecular graphs of this series, but successively incrementing the number of vertices deleted by one, leads to the upper molecular graph series in Figure 2. Similarly, deletion of one vertex from the molecular graph of benzene in Fig. 1 gives the molecular graph of pentadienyl monoradical

in Figure 2. Again, continuing this vertex deletion operation on the lower molecular graph series in Fig. 1, but successively incrementing the number of vertices deleted by one, leads to the lower series in Figure 2. From this realization, we performed the exact same vertex deletion operation on the strongly subspectral members of the series in Figs. 7 and 8 in [16] and obtained the new results presented in Figs. 4 and 5 of this work.

To illustrate further how Figs. 4 and 5 in this work and Figs. 10 and 11 in [16] can be obtained from Figs. 7 and 8 in [16], consider the vertex deletion and addition complementary operations performed on bisallyl and benzene summarized in Figure 6. Deletion of vertices 1 and 2 of the bisallyl molecular graph gives trimethylenemethane, and deletion of vertex 1 in the benzene molecular graph gives the pentadienyl molecular graph. In the reverse mode, attachment of vertices to positions 1,2,3,4 of bisallyl gives tetravinylethylene (3,4-diethenyl-1,3,5-hexatriene), and attachment of the vertices to positions 1 and 4 of benzene gives *p*-benzoquinodimethane

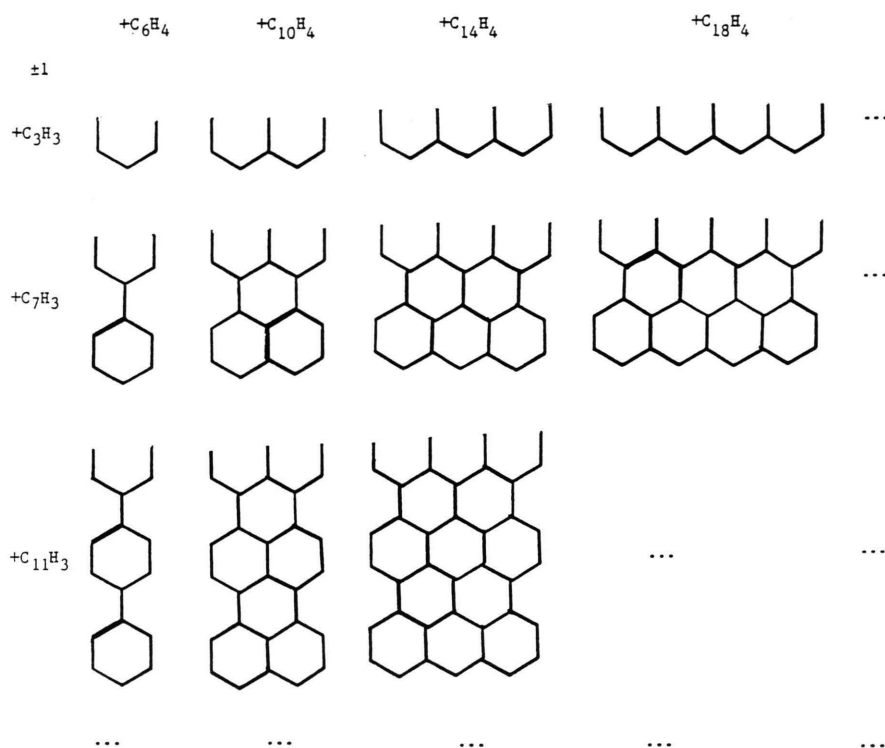


Fig. 5. Two-dimensional array of molecular graphs that are almost-isospectral to the corresponding molecular graphs given in Figure 4.

(*p*-xylylene). Note that in these initial generations, the number of vertices deleted or added on bisallyl is double that on benzene, and that the number of vertices added are double the number deleted.

Some Analytical Expressions obtained by the Method of Hosoya

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 (sometimes cyclic monomer) having the same recurring aufbau unit (unit cell); if this cyclic dimer has NBMOs, then the corresponding periodic polymer has a zero HOMO-LUMO bandgap or isolated NBMOs between the valence and conduction bands [18, 19]. To illustrate, consider the infinite acene and polymethyleneacetylene polymers which are the infinite limit members to the series in Figs. 1 and 2, respectively. The general expression for the infinite acene polymer ring [19, 20] is

$$X^4 - (5 + 4 \cos \theta_k)X^2 + 4(1 + \cos \theta_k)^2 = 0,$$

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

Solution of this equation for the cyclic dimer ($n = 2$) gives the eigenvalues of 0, 0, ± 1 , ± 1.56155 , ± 2.56155 which correspond to the location of the singularities for the density of states. For the eigenvalue of $X = 0$, $\cos \theta_k = 1$. These results show that the infinite acene strip has a zero bandgap and should be conductive. In contrast, the general expression for the infinite polymethyleneacetylene strip is

$$X^3 - (3 + 2 \cos \theta_k)X = 0,$$

which gives eigenvalues of 0, 0, ± 1 , $\pm \sqrt{5}$ for $n = 2$. Here X can be factored out and polymethyleneacetylene must have NBMOs, but for $X = 0$ we obtain $\cos \theta_k = -3/2$, which has no real solutions. Thus the infinite polymethyleneacetylene polymer has a nonzero bandgap with isolated NBMOs and is expected to be nonconductive but possibly ferromagnetic. Hosoya and coworkers [18] studied the polymethyleneacety-

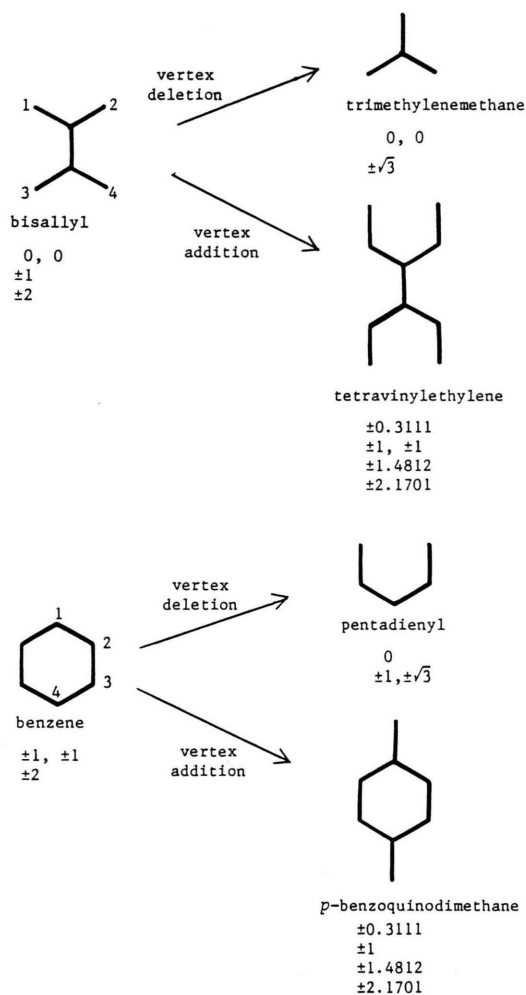


Fig. 6. Illustration of the relationships between subspectral molecular graphs in Figs. 4 and 5 of this work and Figs. 7, 8, 10 and 11 in [16].

lene in Fig. 2 as one member of a family of π -network polymers.

The two series in Fig. 3 devolve to the same infinite π -network polymer somewhat related to the one that Klein studied in regard to edge states [21]. The pair of series in Fig. 3 illustrates end effects which disappear in the infinite limit, and edge effects due to the presence of the upper methylenyl groups, the latter being of lasting influence. The discovery of strongly subspectral series suggests that at least some types of end effects only cause slight perturbations in the π -electronic properties.

Through this latter assumption, the general solution to the infinite polymer strip belonging to the series in

Fig. 3 is

$$X^7 - 9X^5 + 23X^3 - 15X \\ - 2 \cos \theta_k (3X^5 - 16X^3 + 17X) \\ + 4 \cos^2 \theta_k (3X^3 - 7X) - 8X \cos^3 \theta_k = 0,$$

which gives singularities at eigenvalues of 0, 0, ± 1 , ± 1 , ± 1 , ± 1.4736 , ± 2.2361 , ± 2.7979 for the density of states as determined by setting $n = 2$. Factoring out X from this equation and setting $X = 0$ for those X remaining within the parentheses gives

$$8 \cos^3 \theta_k + 28 \cos^2 \theta_k + 34 \cos \theta_k + 15 = 0$$

which has no real solutions. Based on these results, the infinite polymer strip corresponding to the limit member of the series in Fig. 3 has a nonzero bandgap with isolated NBMOs and is expected to be nonconductive but possibly ferromagnetic. In conclusion, Figs. 4 and 5 list structures having potential ferromagnetic properties.

Polymer End Group Effects

Two types of π -electronic polymer strips are possible. Type I occurs when the end-groups cause all the bonds along the strip to localize, and Type II occurs when the end-groups do not cause (extensive) bond localization throughout the total polymer strip. The pair of series in Figs. 1 and 2 are examples of the latter. In Fig. 1 the infinite limit member to the lower acene series has been established by Hosoya and coworker [18, 19, 22] to have its density of states determined by solution of the unit cell structure of the cyclic dimer, and in [16], it has been argued that the upper series is strongly subspectral to the acene series and that the infinite limit members of both series must become *virtually* identical. Therefore, the infinite limit member to the upper series in Fig. 1 should be also capable of being modeled by the same unit cell as the lower one, even though it has different end groups. Clearly the infinite limit member belonging to the two series in Fig. 2 must have the same unit cell, even though the two series have different end groups. Based on these results, we propose that polymer strips of a given type must approach the same density of states in the infinite limit regardless of the exact nature of the end-groups. By virtue of this assumption, the singularities for the density of states for the infinite limit member to the

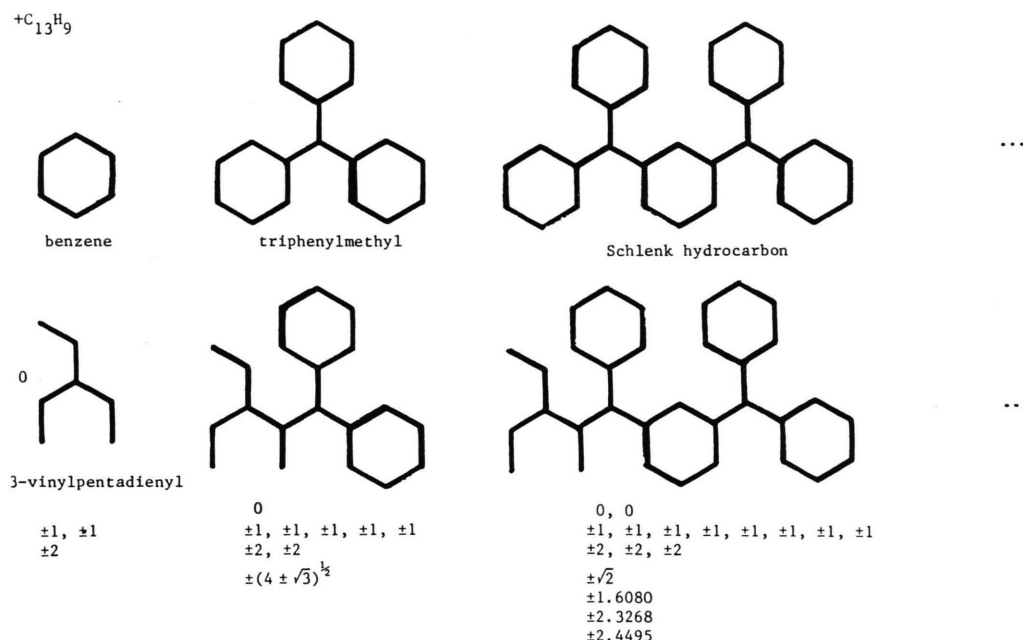


Fig. 7. Two series of molecular graphs that are almost isospectral. The unmatched zero eigenvalue is indicated next to the zero generation molecular graph of 3-vinylpentadienyl (lower series).

series given in Figs. 2 and 3 were determined above using Hosoya's method [19, 22].

Strongly Subspectral Series Containing Schlenk Diradical Hydrocarbon

Figure 7 presents two strongly subspectral series where there is a one-to-one matching of the eigenvalues between corresponding molecular graphs with the lower members having one additional zero eigenvalue. Triphenylmethyl radical can be derived (conceptually) by the joining of benzene to biphenylmethyl radical. Alternatively, benzene could be replaced by 3-vinylpentadienyl (trivinylmethyl) radical in this process to give the second molecular graph in the lower series (Figure 7). For all corresponding eigenvalues of benzene and 3-vinylpentadienyl, the associated eigenvector coefficients at the point of attachment (position-2) of 3-vinylpentadienyl and benzene are identical; for the extra zero eigenvalue in the former, the eigenvalue coefficient is zero (i. e., it is a node in the wavefunction). The union of two triphenylmethyl radicals at their m and m' positions produces the Schlenk Hydrocarbon [23], and in a similar fashion its strongly subspectral mate in the lower

series can be derived. In fact, one can take all combinations of this construction process to generate the six linear series molecular graphs given in Fig. 8 that are strongly subspectral in the same eigenvalues listed in Figure 7. The almost-isospectral series given in Fig. 8 are only representative of the uniformly constructed series. Using random combinations of the nuclei and aufbau units shown in Fig. 9, one can obtain innumerable subspectral series with the same set of eigenvalues.

Instead of successively connecting the aufbau units given in Figs 9 in a linear fashion as done in Figs. 7 and 8, one can connect them in a spiral fashion to generate strongly subspectral dendrimers, as shown in Figs 10 and 11. Growth of these dendrimers by attachment of random combinations of the aufbau units in Fig. 9 will lead to innumerable sets of successor dendritic molecular graphs that are also strongly subspectral. 1,3,5-Tris(diphenylmethyl)benzene triradical, which corresponds to the first molecular graph in Fig. 10, has been synthesized and studied [5, 24]. Larger aryl dendrimers, like the ones in Fig. 11, have been prepared and their intra ferromagnetic properties determined [25]. The dendrimers in Fig. 10 are benzene ring centric, and the ones in Fig. 11 are carbon vertex centric. A strong subspectrality between related aryl

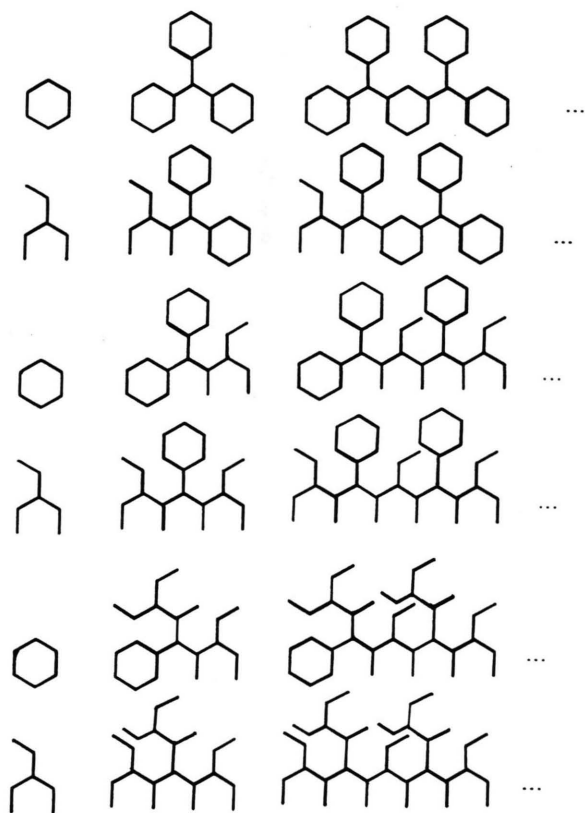


Fig. 8. Six series of molecular graphs that are almost-isospectral, differing only in the number of zero eigenvalues.

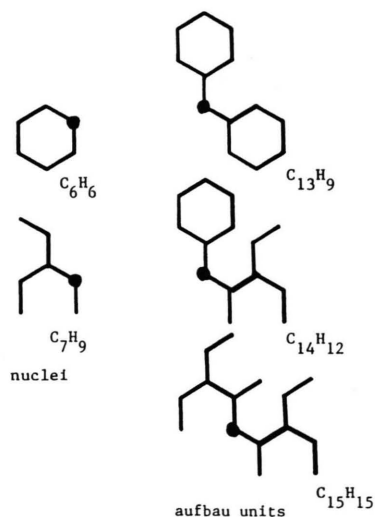


Fig. 9. Any combination of the above nuclei and aufbau units can lead to strongly subspectral series of molecular graphs by joining at the dotted vertices as illustrated by the infinite series shown in Figure 8.

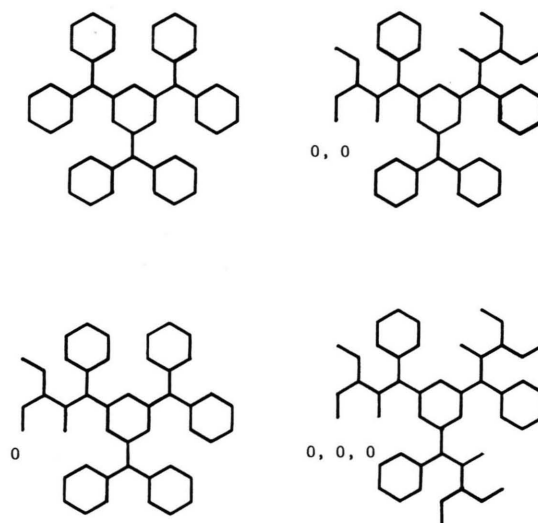


Fig. 10. Strongly subspectral dendrimers differing only in the number of zero eigenvalues. The additional zero eigenvalues are indicated next to the relevant molecular graph. The eigenvalues of the last molecular graph are: 0 (3 \times), ± 1 (11 \times), ± 1.3281 (1 \times), ± 1.6080 (2 \times), ± 2 (4 \times), ± 2.3268 (2 \times), ± 2.4972 (1 \times).

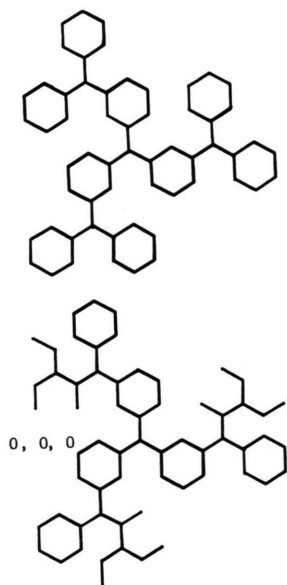


Fig. 11. Strongly subspectral vertex centric dendrimers differing only in the number of zero eigenvalues. 0 (4 \times), ± 1 (14 \times), ± 1.3508 (1 \times), ± 1.5060 (2 \times), ± 1.6953 (1 \times), ± 2 (5 \times), ± 2.2641 (1 \times), ± 2.3942 (2 \times), ± 2.4850 (1 \times).

dendrimers was indicated previously for monoradical analogs [26]. The consequence of replacing benzene

by 3-vinylpentadienyl offers some intriguing possibilities because the latter has more conformational flexibility and increases the number of unpaired electrons with very little increase in molecular size. As an example of the last point, in going from the first molecular graph in Fig. 10 to the last one, the number unpaired electrons goes from three to six. The related experimental work on nonradical polyphenylene dendrimers and their conformational mobility by Mullen and coworkers deserves note here [27].

Conclusion

Three pairs of two-dimensional arrays of strongly subspectral systems, that are derivable from any of the

other pair, have been identified, and these results attest to the uniqueness of the graphite (polyhex) motif. This uniqueness is also manifested by the existence of a benzenoid periodic table and constant-isomer series [9, 26]. The pair of two-dimensional arrays presented herein (Figs. 4 and 5) for the first time suggest that graphite might be made ferromagnetic, if the appropriate edge configuration could be manufactured. Planar aryl polyradical dendrimers that are strongly subspectral appear to be commonplace. All the molecular graph series in Figures 2, 5, 7, 8, 10 and 11 have nondisjoint NBMOs that are increasing in number with increasing membership size. It is expected that the member molecular graphs of these series will have escalating spin multiplicities.

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