

Directed toward the Development of a Unified Structure Theory of Polycyclic Conjugated Hydrocarbons: The Aufbau Principle in Structure/Similarity Studies

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This work introduces two new concepts applicable to structure/similarity studies of conjugated hydrocarbons: (1) The first concept deals with orthogonal strongly subspectral series of molecular graphs and their properties. (2) In the second concept, if a relationship exists among set of strongly subspectral molecular graphs, then an equivalent relationship exists among the complementary molecular graphs of that set. Two sets of triplet series having strongly subspectral molecular graphs are presented. Collections of subspectral molecular graphs and their eigenvalues are tabulated for the first time.

INTRODUCTION

The discovery of elementary substructures that are carriers of chemical information in compact form represents an important strategy in structure theory. Examples of well-known elementary substructures (subgraphs) are atoms (graph vertexes), bonds (graph edges), rings (graph cycles), excised internal structures (subgraphs spanned by the internal vertexes located at the juncture of three rings), elementary aufbau units (C_4H_2 , C_3H , and C_2), elementary capping units (C_6 , C_5 , C_2 , C , and edge), organic functional groups (subgraphs with a collection of weighted edges and vertexes), monomeric units (repeating subgraphs), 1-factor subgraphs, 2-factor subgraphs, Sachs graphs, Ulam subgraphs, embedding fragments (Hall subgraphs), and right-hand mirror-plane fragments (McClelland subgraphs).^{1–4} Excised internal structures and elementary aufbau units are important in the enumeration of polycyclic conjugated hydrocarbons and their constant-isomer series,⁵ and elementary capping units have been used in the generation of fullerene structures.⁶ 1-Factor subgraphs correspond to Kekulé structures^{3,4} and 2-factor subgraphs include Hamiltonian circuits and Clar sextets.⁷ Sachs, Ulam, Hall, and McClelland subgraphs have found application in the determination of characteristic polynomials and the eigenvalues (energy levels) and eigenvectors (wave functions) of molecular graphs (conjugated polyene hydrocarbon molecules). In this paper, recent new results in our study of infinite series having corresponding molecular graphs that are strongly subspectral (having a preponderance of common eigenvalues)^{8–10} and the first examples of strongly subspectral series of molecular graphs occurring in sets of three will be presented.

Three general theoretical approaches can be identified in the modeling of large π -electronic networks—study of infinitely long strips, belt-shaped rings, and a series of strips that are progressively incremented (i.e., a homologous series). This latter approach follows more closely the way experimentalists currently study very large molecules and is analogous to the standard methodology in which molecular systems are partitioned into smaller elementary substructures. The study of successive members of infinite series where

the initial members correspond to known chemical structures enhances our ability to recognize trends which will allow us to predict the properties of larger unknown member molecules using molecular modeling techniques.^{8–10}

BASIC CONCEPTS AND TERMINOLOGY

The C–C σ -bond skeleton representation of a fully conjugated polyene chemical structure is called a molecular graph and will be used herein. A molecular graph devoid of weighted edges and vertexes 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 $-H$ s to each carbon not having four covalent bonds. Since most polycyclic conjugated polyenes can have more than one arrangement of its $p\pi$ -bonds, the molecular graph representation avoids artificially representing these molecular systems by writing only one of these arrangements. Molecular energy level and eigenvalue are equivalent as are wave function and eigenvector. The highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) are called the frontier MOs (FMOs). An alternant hydrocarbon (AH) is a fully conjugated polyene structure without any odd size rings. In AHs every other carbon vertex can be starred so as no two starred or non-starred positions are adjacent. Functional groups are substructures (groups of interconnected atoms) having a characteristic set of properties that are conveyed to the whole structure with only minor perturbation. 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.^{8–10} Two strongly subspectral molecular graphs are *almost-isospectral* if their unique eigenvalues are zero or integer.⁸ Hall subgraphs (embedding fragments) and McClelland subgraphs (right-hand mirror-plane fragments) 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; if the FMOs are included, then this similarity is strengthened. The overlapping close proximity of energy

levels in infinitely large π -electronic networks result in bands bounded by singularities. We will show that many series of strongly subspectral molecular graphs approach the same density of states in the limit.

When an internal mirror plane of symmetry divides a molecular graph into two parts, the vertexes on the mirror plane remain with the left-hand fragment and vertexes in the right-hand fragment (McClelland subgraph) originally connected by a bisected edge have weights of -1 . Thus, the vertexes in the right-hand fragment are either normal or have weights of -1 ; the latter will be indicated on the fragment graphs by open circles. The McClelland mirror plane defines an antisymmetric relationship for the eigenvectors corresponding to the eigenvalues belonging to the right-hand mirror-plane fragments; in this case, the vertexes on the mirror plane have zero eigenvector coefficients. EAH (even alternant hydrocarbon) molecular graphs having at least one C_2 axis of symmetry can always be mirror-plane fragmented such that exactly half the vertexes are contained in the right-hand fragment.

If the two eigenvalues (X) within a single molecular graph or two related mirror-plane fragment graphs sum to zero ($X_1 + X_2 = 0$), they are said to be *paired*. The well-known pairing theorem^{3,4} states that all eigenvalues in a conjugated alternant hydrocarbon (AH) are either zero (nonbonding) or paired (bonding and antibonding). 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 unstarred 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 unstarred positions are zero.

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 *complementary*.² Two equal-sized right-hand mirror-plane fragments or molecular graphs are complementary if all their eigenvalues are mutually complementary. The normal vertexes of one of the complementary right-hand fragments correspond to -1 weighted vertexes in the other, and both have the same sets of normalized eigenvector coefficients, except for sign. Complementary molecular graphs of AHs have complementary right-hand mirror-plane fragments and will have the same number of vertexes. In the change from one molecular graph to its complementary analogue, all vertexes change by one degree; both degree-1 and degree-3 vertexes always go to degree-2 vertexes, and degree-2 vertexes go to either degree-1 or degree-3 vertexes depending on whether they are located on a edge that is bisected or not. Herein, we present two triplet sets of series having strongly subspectral molecular graphs that are complementary.

AUFBAU PRINCIPLE

Successive attachment of given aufbau units under prescribed rules can lead to families of molecular graphs having specific characteristics. This is the essence of the aufbau principle. The aufbau principle is a simple but very powerful concept having a broad range of applications in the analysis and understanding of chemical structures. The set of aufbau units, C_4H_2 , C_3H , and C_2 , are sufficient for the generation of all benzenoids, without exception; thus, they are called

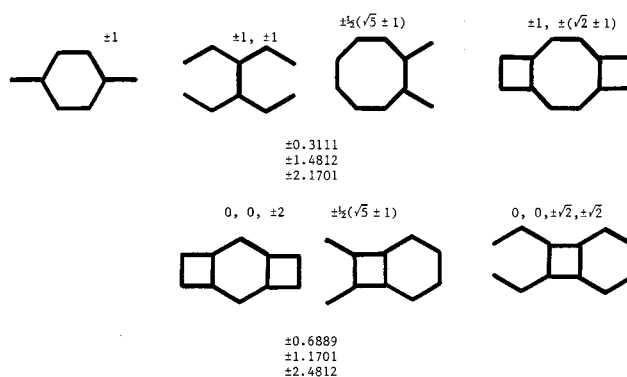


Figure 1. Two sets of strongly subspectral molecular graphs that are first generation members of related infinite series having special properties. Note that the 2nd and 5th, 3rd and 6th, and 4th and 7th molecular graphs are complementary with eigenvalues that have a correspondence to the relation of $X_1 + X_2 = \pm 1$.

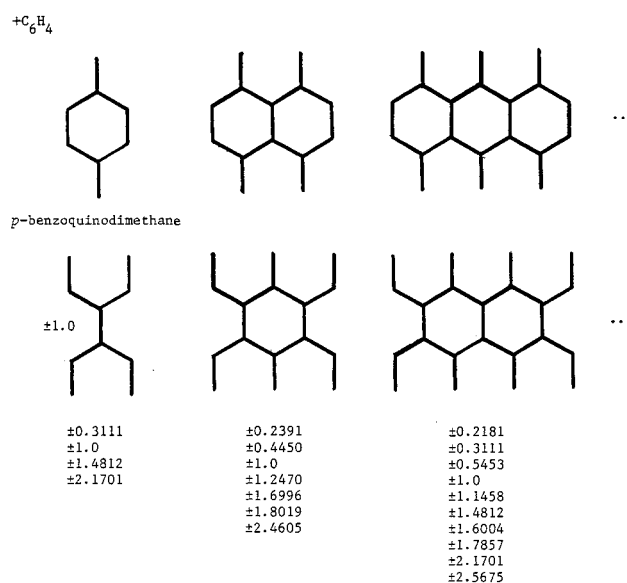


Figure 2. Two series of molecular graphs that are almost-isospectral. The unmatched ± 1 eigenvalues are indicated next to the first generation member of the lower series.

elementary aufbau units for the generation of benzenoids.⁵ In this paper, other aufbau units for the generation of pairs of infinite series that are strongly subspectral will be introduced.

FROM SMALL MOLECULES TO INFINITELY LARGE Π -ELECTRONIC SYSTEMS

Figure 1 presents two sets of strongly subspectral molecular graphs. The unique eigenvalues are indicated next to each molecular graph, and the common eigenvalues, below each set. The second molecular graph in the upper set and the fifth molecular graph in the lower set are complementary, as are the third and sixth and fourth and seventh molecular graphs. These seven molecular graphs will be used to illustrate two new concepts. The first and second molecular graphs are first generation members to two *orthogonal* almost-isospectral infinite series (Figures 2 and 3). Whenever one finds two pairs of orthogonal series, then this allows one to construct a pair of infinite two-dimensional arrays in which one can map from one to the other structurally related

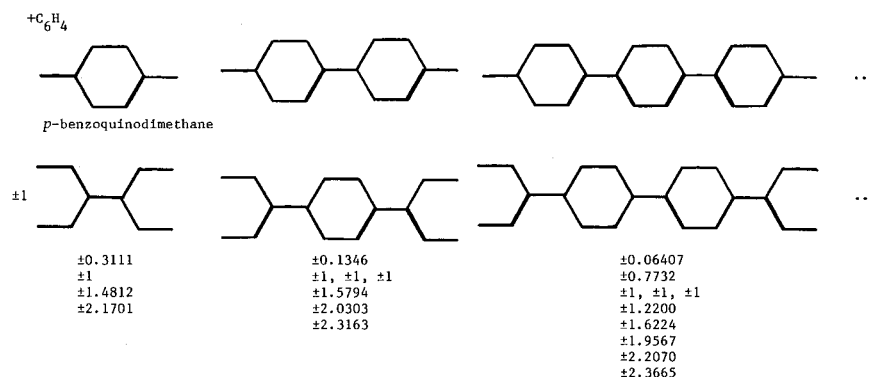


Figure 3. Two series of molecular graphs that are almost-isospectral. The unmatched eigenvalues are next to the lower first generation structure.

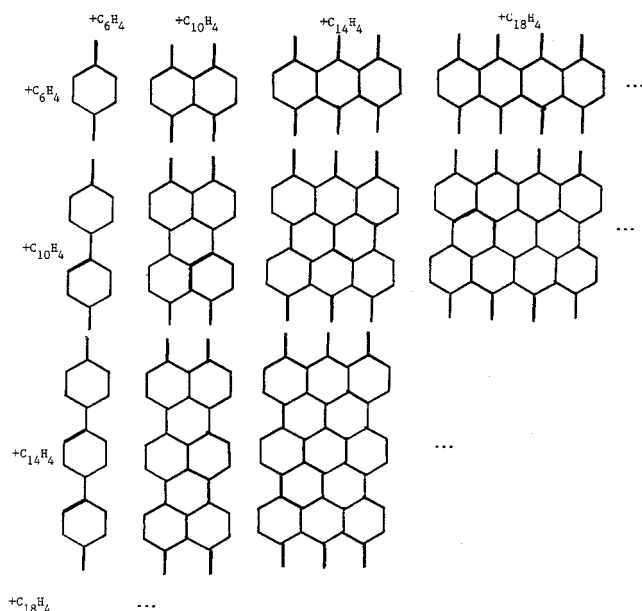


Figure 4. Two-dimensional array of molecular graphs that are almost-isospectral to the corresponding molecular graphs given in Figure 5.

molecular graphs that are pairwise strongly subspectral (Figures 4 and 5). This constitutes the essence of the first concept.

The second to fourth molecular graphs are complementary to the fifth to seventh molecular graphs, respectively. Whatever relationship exists between the second, third, and fourth molecular graphs will also result in an equivalent relationship between the fifth, sixth, and seventh molecular graphs. This constitutes the essence of the second concept, which will be illustrated by comparison of Figure 6 with Figure 7.

TWO-DIMENSIONAL MAPPING OF ORTHOGONAL STRONGLY SUBSPECTRAL SERIES

Figures 2 and 3 present two pairs of infinite series containing molecular graphs that are pairwise almost-isospectral. Both pairs of series have the same first generation members but oriented perpendicularly in going from Figure 2 to Figure 3, i.e., rotated 90° . In both pairs of series the molecular graphs increase one ring at a time and correspond to molecules that successively increase by the same amount (i.e., by C_6H_4); each molecular graph of the lower series in Figures 2 and 3 has the unique eigenvalue pair ± 1 .

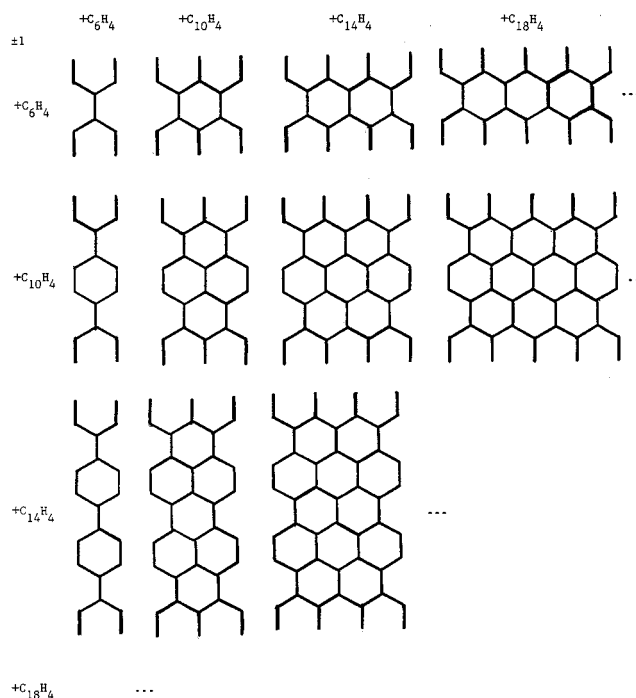


Figure 5. Two-dimension array of molecular graphs that are almost-isospectral to the corresponding molecular graphs given in Figure 4.

Subtraction of 1,3,5-hexatriene-2,3,4,5-tetrayl (C_6H_4) from *p*-benzoquinodimethane (C_8H_8) gives ethene (C_2H_4) and from tetravinylethylene ($C_{10}H_{12}$) gives two ethenes ($2 C_2H_4$) which may be regarded as zero generation members of the respective series in Figure 2; the one ethene excess in the latter explains the ± 1 unique eigenvalue pair common to all members of the lower series. This retro-aufbau example also illustrates how all the zero generation members were discovered for the series in Figures 6 and 7. Thus in general, once a set of two or more strongly subspectral molecular graphs are found, one then should search for a common aufbau unit which upon retro-aufbau gives zero generation molecular graphs containing the unique eigenvalues. Figure 8 illustrates how all members belonging to the pair of series in Figure 2 can be built-up starting from the zero generation members not shown but derived as explained above. This aufbau construction involves two steps. First, one transfers the 1,2-cis hydrogens from ethene to the 3,4-positions of 1,3,5-hexatriene-2,3,4,5-tetrayl. Second, the 1,2-cis positions of the ethene-1,2-diyl are attached to the 2,5-positions of

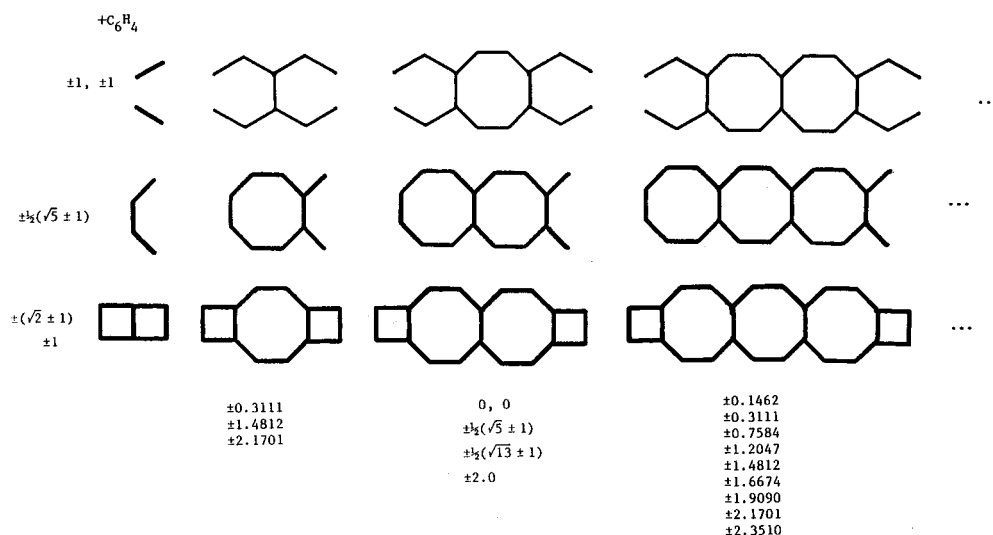


Figure 6. Three series of molecular graphs that are strongly subspectral. The unmatched eigenvalues are indicated next to the zero generation member of each series. These series are complementary to those in Figure 7.

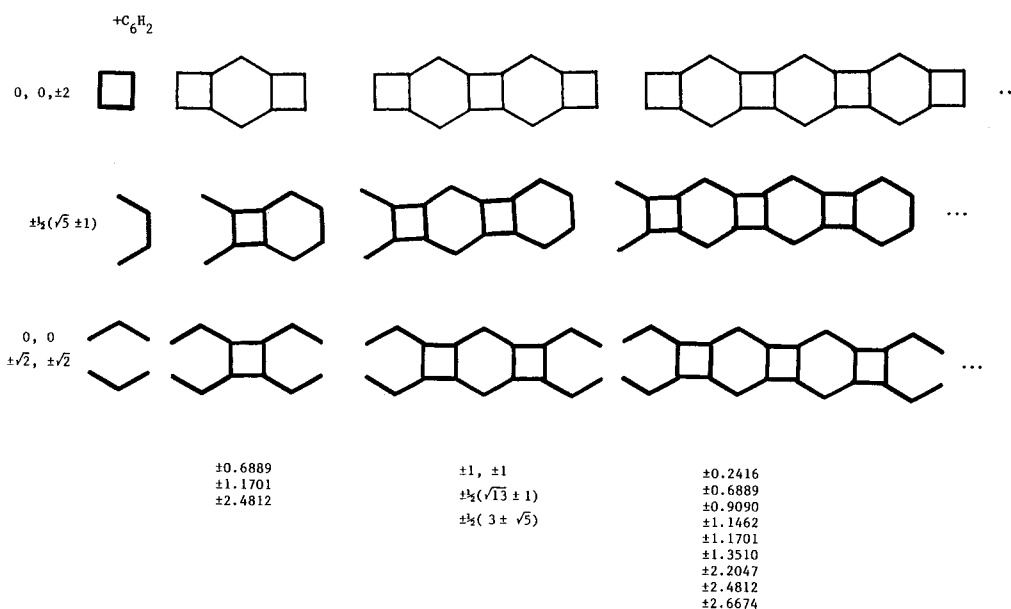


Figure 7. Three series of molecular graphs that are strongly subspectral. The unmatched eigenvalues are indicated next to the zero generation member of each series. These series are complementary to those in Figure 6.

the 1,3,5-hexatriene-2,5-diyl, both of which were formed in the first step. By repeating this process on each successive generation member, one generates the two series given in Figure 2. Analogously, Figure 9 illustrates how the series in Figure 3 were generated.

The two-dimensional array in Figure 4 is constructed from the upper series found in Figures 2 and 3; the first is placed in the uppermost horizontal row, and the latter, in the left-hand vertical column. In a similar manner, the two-dimensional array in Figure 5 is constructed using the lower series. The formulas of the relevant aufbau units head each row and column in Figures 4 and 5.

All the molecular graphs in Figures 4 and 5 correspond to conjugated hydrocarbons having one Kekulé structure ($K = 1$). The initial molecular graphs of the infinite series in Figures 2–5 correspond to known reactive compounds. *p*-Benzoquinodimethane (*p*-xylylene or *p*-quinodimethane) is formed by flash-vacuum pyrolysis of [2.2]paracyclophane,¹¹ and 3,4-diethenyl-1,3,5-hexatriene (tetravinylethyl-

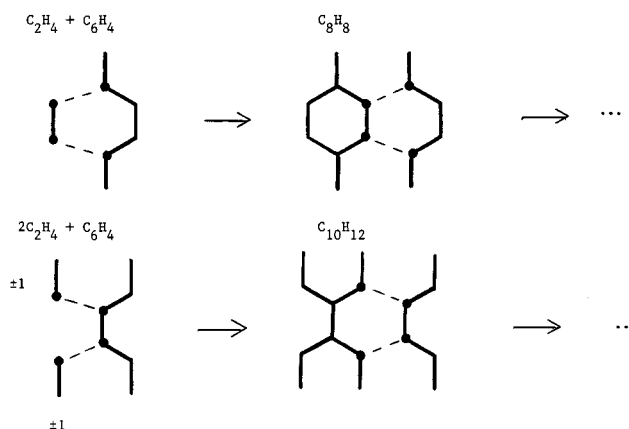


Figure 8. Aufbau construction of the first generation members of the series in Figure 2 by attaching 1,3,5-hexatriene-2,3,4,5-tetrayl to the ethene zero generation members.

ene) is formed by photolytic electrocyclic ring opening of 2,3-diethenyl-1,3-cyclohexadiene.¹² 1,4,5,8-Tetrameth-

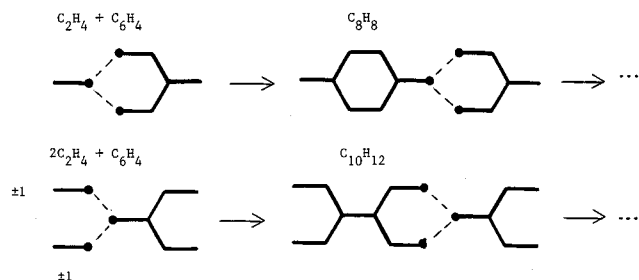


Figure 9. Aufbau construction of the first generation members of the series in Figure 3 by attaching 2-ethenyl-1,3-butadiene-1,1,4,2'-tetrayl to the ethene zero generation members.

glenylnaphthalene is the $\pi\pi$ -electronic substructure of 2,7-dihydropyrene which has been theoretically studied.¹³ The oxo analogues of the first two molecular graphs in Figure 4 are known oxidants—namely quinone and 1,4,5,8-naphthalenetetraone; the latter is the stronger oxidant.¹⁴ On the basis of this sampling of chemistry and other results,¹⁰ it is expected that large members of Figures 4 and 5 will have band gaps approaching zero and in the bulk phase are likely to be conductive.

STRONGLY SUBSPECTRAL SERIES AND THEIR COMPLEMENTARY ANALOGUES

We will now consider the aufbau construction of the molecular graphs members in the series in Figure 6 and how it corresponds to the aufbau construction of their complementary molecular graph members belonging to the series in Figure 7. While the zero generation molecular graph members are listed for the series in Figures 6 and 7 because of their usefulness in construction and structure analysis, it needs to be emphasized that they do not contribute directly to chemical property evaluation because the smallest members of homologous series are invariably more deviant. Figures 6 and 7 clearly show that zero generation members are not, as a rule, strongly subspectral and may even be disconnected molecular graphs. Zero generation members of strongly subspectral series are Hall subgraphs for the respective series and account for the unique eigenvalues.

In Figure 10, the top three rows illustrate the aufbau construction of the initial members to the series in Figure 6 and the bottom three rows illustrate the aufbau construction of the initial members to the series in Figure 7. The zero generation molecular graphs of the upper three rows are complementary to the respective zero generation molecular graphs of the lower three series; two ethenes and cyclobutadiene are complementary, 1,3-butadiene is self-complementary, and butadiene and two allyls are complementary.² The aufbau unit for the upper three rows is 1,3,5-hexatriene-2,3,4,5-tetrayl, and the aufbau unit for the lower three rows is 3,4-bis(methylene)cyclobutene-1,2,5,6-tetrayl. 1,3,5-Hexatriene and 3,4-bis(methylene)cyclobutene are complementary.¹⁵ In Figure 10, the vertexes with matching numbers between the zero generation molecular graph and the aufbau unit of each row are connected to give the first generation molecular graph shown to the right of each arrow. The squiggly line passing through bonds in the zero generation molecular graphs of the third and sixth rows denotes a splicing-in operation. The parallelism between the constructions of the upper three and lower three rows is made quite evident in Figure 10.

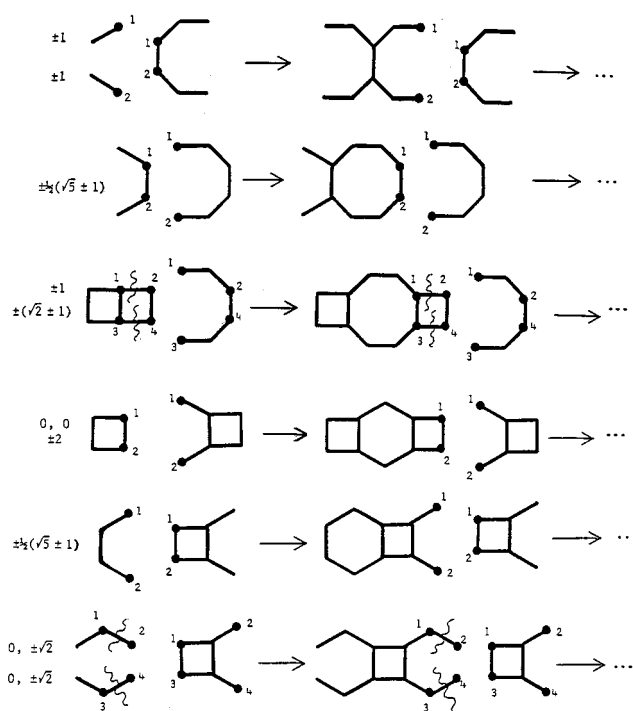


Figure 10. Aufbau construction of the first generation members of the complementary pairs of series in Figures 6 and 7. The 1,3,5-hexatriene-1,3,4,6-tetrayl aufbau unit in the upper three rows is complementary to the 3,4-bis(methylene)cyclobutene-1,2,5,6-tetrayl aufbau unit in the lower three rows, and the upper three zero generation members are complementary to the lower three zero generation members.

PROPERTIES OF STRONGLY SUBSPECTRAL SERIES

To summarize, molecular graph members of strongly subspectral series have the following general properties. They are all AHs, and their generation involves starting with different zero generation molecular graphs and the repeated attachment of the same aufbau unit but with different connections. The unique eigenvalues transmitted to every member of a series are present in the corresponding zero generation molecular graph, which is a Hall subgraph of that series. As the size increases, the members of strongly subspectral series begin to look more alike. Thus, the limit members to the series in Figure 6 look like the upper π -electronic polymer strip and the limit members to the series in Figure 7 look like the lower π -electronic polymer strip in Figure 11.

The π -electronic polymer strips in Figure 11 are complementary in their density of states. Hosoya and co-workers have shown that the energy levels of the cyclic dimer determine the singular points of the density of states of infinitely large polymers.¹⁶ Using this method, the singular points for the density of states of the polymer strips in Figure 11 were determined. As it is evident from the values listed in Figure 11, the relationship $X_1 + X_2 = \pm 1$ exists between the two sets of values. The infinite acene polymer strip is self-complementary with its singular points at ± 2.56155 , ± 1.56155 , ± 1 , 0 , 0 .^{8,9}

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 are unable to cause extensive bond localization throughout the total polymer strip.¹⁶ The series in Figures 6 and 7 are

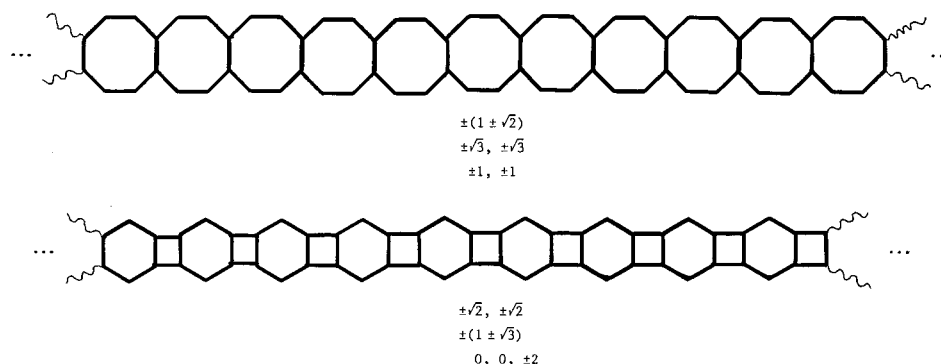


Figure 11. Two different types of π -electronic polymer strips that are complementary to each other. The singular points of the density of states are given below the respective polymer strips.

examples of the latter. The two different zigzag polymer strips discussed by Hosoya and co-workers are examples of type I and type II π -electronic polymer strips.¹⁶ On the basis of the results of this work, 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 as the polymer strips in Figures 6 and 7. In Figure 11, the upper and lower polymer strips are calculated to have nonzero and zero band gaps, respectively.

If a limited subset of the molecular graphs belonging to two or more strongly subspectral series correspond to known molecules or close analogues, then the relationships and trends defined by these series can be used as the framework for predicting properties of the unknown molecules corresponding to remaining molecular graphs. Many of the initial members to the series in Figures 6 and 7 correspond to known molecules or related chemical species. The tetravinylethene series in Figure 6 (top row) and the tetravinylcyclobutadiene series in Figure 7 (bottom row) are expected to undergo facile thermal electrocyclization to form six-membered rings. In Figure 7, both benzodicyclobutadiene and bis(methylene)benzocyclobutane and several substituted analogues have been synthesized.¹⁷ Benzodicyclobutadiene (second molecular graph in the upper row of Figure 7) was shown to be the more reactive, and its tetravinyl analogue (third molecular graph in the bottom row) is expected to have a similar reactivity. The bis(methylene)-benzocyclobutane substructure is found in 7,8-dihydro-6H-benzo[3,4]cyclobuta[1,2]cycloheptenyl.¹⁸ The general pattern of chemistry of known molecules is in agreement with the energy/structure information present in Figures 6 and 7. While many of the molecular graphs in this work correspond to reactive molecules, one can study the smaller molecules by trapping experiments, by mass spectrometric methods,¹⁹ in low-temperature glassy matrixes, and by complexing with metal ions as done with cyclobutadiene which forms a stable iron tricarbonyl complex²⁰ and cyclooctatetrene which forms a stable nickel bis(triphenylphosphine) complex.²¹ On the basis of the results of this work, we expect the properties of the polymer networks in Figure 11 to be complementary in that the upper polymer with a nonzero band gap should be nonconductive and the lower polymer with a zero band gap should be conductive.

SUMMARY

By the unique coupling of the aufbau principle and strongly subspectral relationship, a new tool for similarity

evaluation of π -electronic molecular systems has been developed. End effects of some types of π -electronic polymer strips have been interpreted, and examples of infinite polymer strips that are complementary² have been presented.

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