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Isospectral and Subspectral Molecules

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Isospectral molecules are non-identical structures which possess the same spectrum of eigenvalues. Methods for recognizing isospectrality, procedures of Heilbronner, Herndon and Živković for constructing new isospectral mates, and the specification of the relationship among the eigenvectors of the adjacency matrix of isospectral pairs are discussed here.

Instances of isospectral graphs are relatively rare. There are many cases, however, in which the spectrum of one molecular graph contains the spectrum of a second, smaller graph. In such cases, the larger, composite, graph and the smaller, component graph are said to be subspectral. Methods of McClelland, Hall and D'Amato for determining subspectrality of graphs are reviewed in detail. It appears that all known cases of subspectral molecules, but one, can be explained by various decomposition or factorization schemes.

No chemical evidence is found so far that shows a relationship among the measured properties of isospectral or subspectral molecules. However, the existence of isospectral and subspectral molecules prevented the use of characteristic polynomial for the unique characterization of molecules in various classification schemes and in computerized chemical documentation.

1. INTRODUCTION

A chemical structural (constitutional) formula is a mathematical graph[1]. The former shows how bonds connect the different atoms in a molecule; the latter describes abstract vertices linked by edges[2]. Throughout this article we will be concerned only with hydrogen-suppressed molecular graphs. Several reviews discuss the applications of graph theory to a wide variety of chemical properties that depend on the internal connectivity of a molecule.[2-9] The connectivity of a graph is contained in its adjacency matrix.[10] If an edge links vertices i and j then the number *one* appears at the intersection of the i-th row and j-th column of the adjacency matrix. If no edge connects the two vertices then the ij-th matrix element is zero. For a graph of N vertices the adjacency matrix is an $N \times N$ symmetric array.[11] The determinant of the adjacency matrix can be expanded to produce the characteristic polynomial of the graph which can be solved for N roots called the eigenvalues or, collectively, the spectrum of the graph.[12] At one time[13-15] it was supposed that its spectrum and characteristic polynomial might be a unique property of a graph[16] and there-

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fore graphs with identical spectra would be identical or isomorphic, but demonstrated counterexamples have shown otherwise.[17-20] For some years now, examples have been known for which two or even more non-isomorphic graphs have identical characteristic polynomials and therefore identical spectra.[21] Non-identical graphs with identical spectra are called isospectral[2] or cospectral[10] graphs.

The eigenvalues of the adjacency matrix of a graph are related to the Hückel molecular orbital energy levels of planar conjugated hydro-carbons[2,8,11,22-26]. Therefore there must exist non-identical isomeric molecules which are isospectral. A classical example is provided by molecular graphs **1** and **2** corresponding to 1,4-divinylbenzene and 2-phenylbutadiene.

Their spectra are identical: Spectrum of **1** = spectrum of **2** = ($\pm$ 2.214, $\pm$ 1.675, $\pm$ 1.000, $\pm$ 1.000, $\pm$ 0.539). Such coincidences are at least very curious and they might be chemically significant.[27] However, there are strong opposing views based on the photoelectron spectra of isospectral molecules, depicted by **1** and **2** above, denying any relevance of this concept for chemistry.[28] On the other hand, isospectrality has found use in physics[29], not to mention applied mathematics.[30-33] We feel that it is important to investigate properties of iso-spectral molecules and to see how their occurrence is related to properties of molecules in order to trace those which might be strongly dependent on the isospectrality of molecular skeletons.

A much larger number of instances occur in which all of the eigenvalues of one graph appear among those of another, larger graph, and the two graphs are then said to be subspectral. The smaller graph can usually be recognized as a structural fragment or component of the larger, composite graph. There are still other examples in which two or more graphs share some, but not all, eigenvalues. These are examples of partially isospectral graphs. In many cases the partial isospectrality of two graphs occurs because they share a common subspectral component.

Although a large number of papers in the mathematical literature have been concerned with isospectral graphs,[12,13,20,21,30-34] only a few chemical papers have so far studied the properties of isospectral molecules.[27,35-42] In this review we will summarize the work previously reported on isospectral molecules and offer comments on the much larger group of subspectral molecules. We will not pursue the problem of partially isospectral molecules nor the interesting related question of why certain eigenvalues occur much more often than others.

2. ISOSPECTRAL MOLECULES

There are three problems we wish to address concerning isospectral mole-cules: (1) Given two non-identical molecules, how can one tell if they are

isospectral? (2) What are the available methods for generating isospectral molecules? (3) Given a particular molecule, is it possible to determine whether one or more isospectral mates exist and if so can one derive the isospectral partners?

2.1. Determination of Isospectrality

The first problem is the easiest to solve. Several methods exist for determining isospectrality of a pair of molecules. The obvious brute-force way is to calculate the eigenvalues of the adjacency matrix of each molecule and compare eigenvalues. If the two sets of eigenvalues match exactly, then the two molecules are isospectral. Another way is to work out the characteristic polynomial of the adjacency matrix of each molecule. If the coefficients of comparable terms in the characteristic polynomials are identical term by term then the molecules are isospectral.

The coefficients of the characteristic polynomial can be determined individually by the Coulson-Sachs procedure.[43,44] A graph G has the characteristic polynomial,

$$P(G; x) = \sum_{n=0}^{N} a_n x^{N-n} \tag{1}$$

The expressions for the first few coefficients are particularly simple.[15,33,43] For all graphs $a_0 = 1$ and $a_1 = 0$. Then,

$$a_2 = -e \tag{2}$$

where e is the number of edges in the graph or bonds in the molecule.

$$a_3 = -2 n_3 \tag{3}$$

where n_3 is the number of three-membered rings in the graph or molecule. Expressions for the coefficients of higher terms are more complicated,[33,43,45] but there is one important generalization: every term in the expressions for the odd-numbered coefficients a_{2k+1} contains a factor related to the number of odd-membered rings of size $2k+1$ or less in the graph. Thus, for graphs containing no odd-membered rings all the odd-numbered coefficients are zero. This result shows that systems containing only oven rings, such as **1** and **2**, will have necessarily the graph spectrum symmetric with respect to $x = 0$. This is, possibly, the simplest proof of the pairing theorem introduced by Coulson and Rushbrooke.[46]

The existence of Coulson-Sachs expressions for constructing the individual coefficients suggests that one could make a term-by-term calculation and comparison of characteristic polynomial coefficients for a pair of graphs; the first non-identical pair of comparable coefficients that arises would demonstrate non-isospectrality and further comparisons could be discontinued. The simplicity of the expressions for the coefficients a_2 and a_3 leads to the following simple counting rules that can quickly reveal basic differences between two graphs that prevent them being isospectral. These conditions are necessary but not sufficient for isospectrality.

1. Isospectral graphs must have the same number of vertices. The number of vertices determines the numbers of eigenvalues in the spectrum and graphs with different numbers of eigenvalues cannot be isospectral.

2. Isospectral graphs must have the same number of edges. Since $a_2 = -e$, graphs with different number of edges will have different values of a_2 and therefore cannot be isospectral.

3. An acyclic graph and a graph containing rings cannot be isospectral. To form a ring requires an additional edge beyond those present in the acyclic graph. Therefore, cyclic graphs necessarily have more edges and different coefficients a_n than acyclic graphs.

4. Isospectral graphs without fused rings must have the same number of rings. The same number of non-fused rings assures that the graphs will have the same number of edges and the same a_2. For graphs with fused rings the situation is more complicated because the number of fused rings is not related to the number of edges in a linear way.

5. Isospectral graphs must have the same number of three-membered rings. Since $a_3 = -2n_3$, graph with different numbers of three-membered rings will have different values of a_3 and therefore cannot be isospectral.

6. Graphs containing only even-membered rings cannot be isospectral with those containing any odd-membered rings. The Coulson-Sachs expressions for all the odd coefficients a_{2k+1} are zero for graphs containing no odd-membered rings. For a graph containing odd-membered rings at least one a_{2k+1} must be non-zero. Another justification for this rule is based on the fact that the alternant systems contain no odd-membered rings[25] and for every eigenvalue there is another eigenvalue of equal magnitude but opposite sign (the pairing theorem).[46] Non-alternant systems must contain at least one odd-membered ring and their energy levels are not paired. Therefore, alternant and non--alternant systems cannot be isospectral.

Rules 1 and 2 are specific statements of the fact that isospectral molecules must be isomers. Analysis of the Coulson-Sachs expressions for higher coefficients of the characteristic polynomial might lead to further conditions for isospectrality.

Heilbronner[47] has shown how to factor the secular determinant or characteristic polynomial of a composite molecule C composed of two fragments A and B linked by a bond between atom a in A and atom b in B. For normal homo-atomic molecules the characteristic polynomial of the composite molecule C can be expressed as

$$\text{C} = \text{A}\,\text{B} - \text{A}_a\,\text{B}_b \qquad (4)$$

where A and B represent the characteristic polynomials of fragments A and B, and A_a and B_b are the characteristic polynomials of fragments A and B with atoms a and b removed, respectively. Equation (4) is restated below in different notation.[8]

$$P(C; x) = P(A; x) P(B; x) - P(A(-a); x) P(B(-b); x) \qquad (5)$$

Factorization of this type can reduce the characteristic polynomial to smaller pieces which either can be immediately seen to be identical or else the polynomials of the fragments can be easily worked out, perhaps by the Coulson-

-Sachs procedure, and then compared for isospectrality. As an example, break up the acyclic graphs **3** and **4** across the bonds as indicated.


(6)

3   **4**

Applying the Heilbronner factorization formula for the characteristic polynomials we obtain,

(7)

where $[L_N]$ is the characteristic polynomial of the linear graph (chain) with N vertices and $[\rangle\!\!-\!\!\cdot]$ is the polynomial for the structure enclosed in brackets. The expressions C_3 and C_4 are identical hence the graphs **3** and **4** are isospectral mates.[29]

Randić[48] has proposed an interesting criterion for investigating whether two graphs are isospectral or not. He uses the fact that the characteristic polynomial is related to random walks[49]. (A random walk in a graph is a sequence of edges which can be continuously traversed, starting from any vertex and ending on any vertex, also permitting the use of the same edge several times.)[10,49] This relationship is reflected in the identity of the information given by the characteristic polynomial and spectral moments of a graph.[29] The random walks considered here are self-returning walks, i.e. random walks starting and ending at the same vertex. Self-returning walks starting at a vertex q are given by the q th diagonal elements of the adjacency matrix A raised to the powers n: $(A^n)_{qq}$, $n = 1, 2, \ldots, N$. For each n, the spectral moment of a graph is the trace of the matrix A^n. Two graphs are isospectral if they have identical sequences of spectral moments, $n = 1, 2, \ldots, N$.

As an example, we consider the Harary-Balaban isospectral pair:[17]

5   **6**
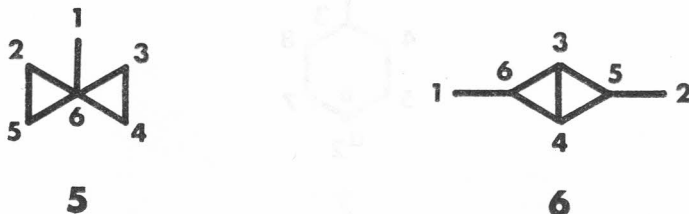
Graph 5

atom label	self-returning walks					
	n=1	2	3	4	5	6
1	0	1	0	5	4	29
2, 3, 4, 5	0	2	2	9	18	58
6	0	5	4	29	44	185
spectral moments						
	0	14	12	70	120	446

Graph 6

atom label	self-returning walks					
	n=1	2	3	4	5	6
1, 2	0	1	0	3	2	15
3, 4	0	3	4	17	36	115
5, 6	0	3	2	15	22	29
spectral moments						
	0	14	12	70	120	446

Graphs 5 and 6 have identical spectral moments and thus represent isospectral mates.

Another point of view is that of deciding whether identical spectra originate from identical graphs or non-identical graphs. Randić has proposed a procedure that he claims can establish the identity of two apparently different graphs.[50] It is based on a direct comparison of the adjacency matrices and hence he has developed a procedure for setting up these matrices uniquely.

Here we wish to mention that the procedure developed by Hall[38] for recognizing isospectral systems is really a method for tracing the subspectral systems.

2.2. Construction of Isospectral Systems

The generation of isospectral molecules is a more complex problem, but several methods are available and will be reviewed here.

2.2.1. Isospectral Graphs Derived from a Common Frame

Consider a graph which contains one or more pairs of vertices which have the property that the removal of each vertex in turn produces two identical or isospectral graphs. Vertices having this property may be called isospectral points[20] or active sites.[36,37] A graph containing isospectral points may serve as the common frame[36] in a newly-constructed isospectral pair of graphs, derived from the common frame by attaching two different graphical fragments to the isospectral points in a reciprocal relationship.

The isospectral points in the styrene graph 7, for example, are the vertices labeled a_1 and a_2 in the drawing below.

7
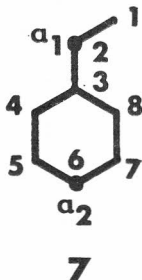
Randić[48] has produced a valuable criterion for detecting the isospectral points. The isospectral points always have identical sequences of atom self--returning walks. For the graph **7** the following list of self-returning walks for different atoms is derived from the powers of the adjacency matrix.

Self-Returning Walks

Atom label	n=1	2	3	4	5	6	7	8
1	0	1	0	2	0	6	0	22
2 (α_1)	0	2	0	6	0	22	0	90
3	0	3	0	12	0	52	0	235
4,8	0	2	0	7	0	30	0	135
5,7	0	2	0	6	0	23	0	98
6 (α_2)	0	2	0	6	0	22	0	90

As expected, the positions 2 (α_1) and 6 (α_2) have identical sequences of self-returning walks.

An examination of their tabulated eigenvalues[51-53] confirms the fact that the graph resulting from the removal of α_1, denoted by **7** $(-\alpha_1)$, and the graph resulting from the removal of α_2, denoted by **7** $(-\alpha_2)$, are isospectral.

**7**$(-a_1)$ ≡ **7**$(-a_2)$

(The symbol $"\equiv"$ is used here to signify an isospectral relationship.) Since α_1 and α_2 are isospectral points, two arbitrary graphical fragments A and B may be attached to α_1 and α_2 in a reciprocal manner (i. e., by an ordered replacement) to generate a new pair of isospectral graphs **8** and **9**.


8   **9**
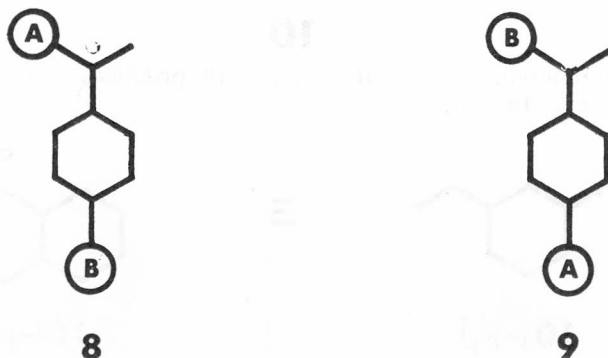
The graph **10**, shown below, contains a pair of vertices whose successive removal generates a pair of identical, rather than isospectral, graphs.
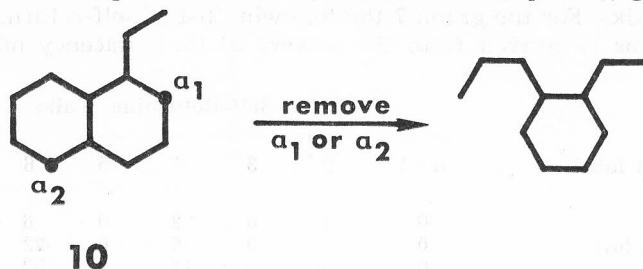

Since the vertices α_1 and α_2 are isospectral points in **10**, two isospectral graphs **11** and **12** may be constructed from **10** by the reciprocal attachment of two arbitrary fragments C and D at α_1 and α_2.
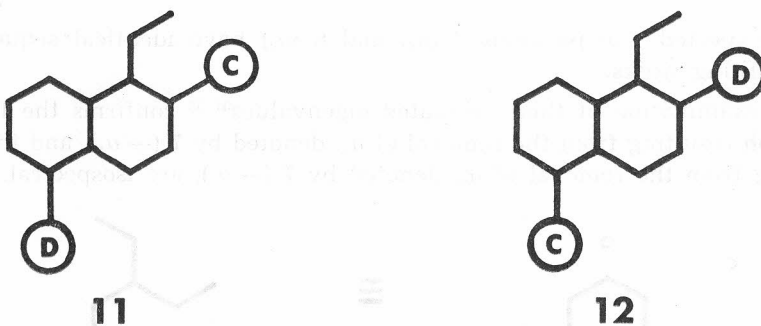

In many cases, the original graphical frame contains more than one pair of isospectral points. The graph **10**, for example, has as a second pair of isospectral points the vertices labeled β_1 and β_2 in the illustration below.
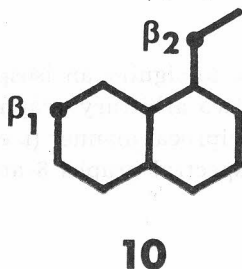

The successive deletion of β_1 and β_2 from **10** produces the two isospectral graphs **10** $(-\beta_1)$ and **10** $(-\beta_2)$.
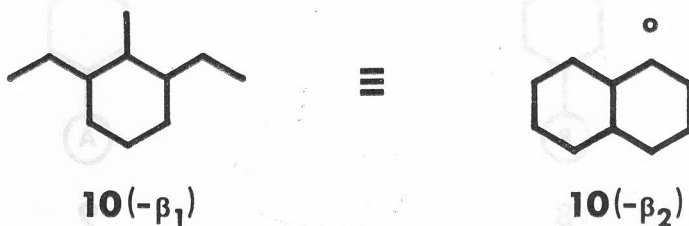
It is thus possible to construct an isospectral quartet **13**, **14**, **15**, and **16** by first attaching two fragments A and B to **10** at sites β_1 and β_2 then attaching two additional fragments C and D at sites α_1 and α_2.
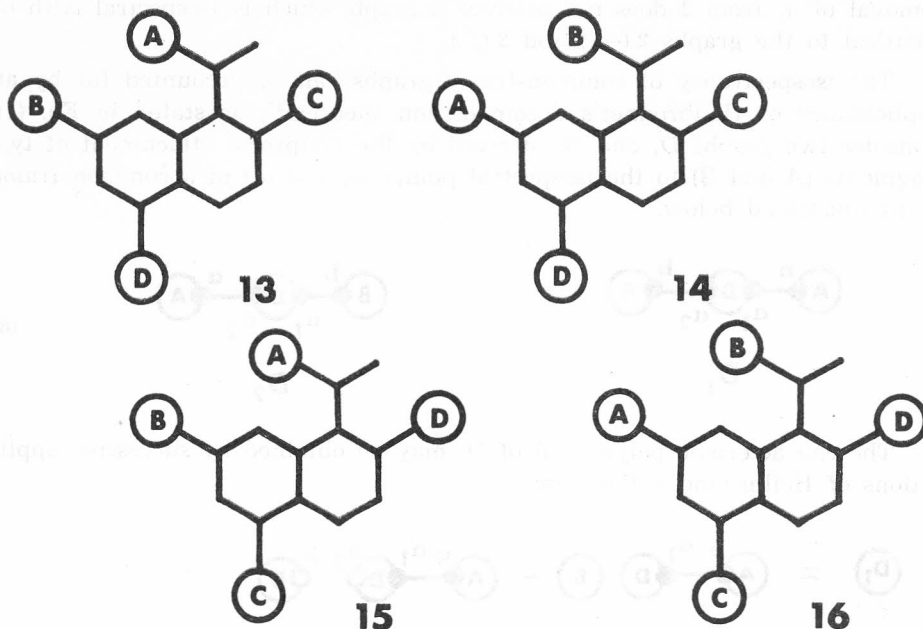
Frequently, one (or both) of the isospectral graphs derived from a common frame contain its own isospectral points at which additional fragments may be substituted in a reciprocal fashion to generate a new common-frame isospectral points, denoted here by β_1 and β_2.
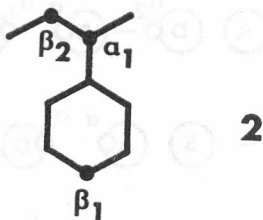
The vertices β_1 and β_2 are isospectral points by virtue of the fact that **2** ($-\beta_1$) and **2** ($-\beta_2$) are isospectral.
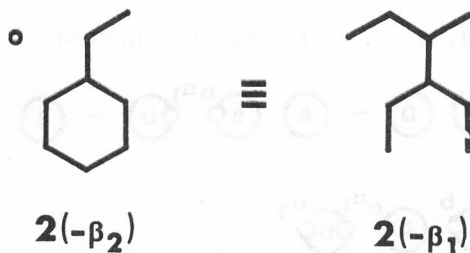
It should be noted at this point that, although β_1 in **2** is the same vertex as α_2 in the styrene frame, it is not generally true that isospectral points retain their unique properties in common-frame derivatives; here, for example, removal of α_1 from **2** does not produce a graph which is isospectral with or identical to the graphs **2** $(-\beta_1)$ and **2** (β_2).

The isospectrality of common-frame graphs can be accounted for by an application[39] of Heilbronner's decomposition theorem[47], as stated in Eq. (4). Consider two graphs D_1 and D_2, derived by the reciprocal attachment of two fragments (A and B) to the isospectral points (α_1 and α_2) of a common frame D, as illustrated below.

(8)

The characteristic polynomial of D_1 may be obtained by successive applications of Heilbronner's theorem:

(9)

The characteristic polynomial of D_2 may be obtained in the same manner:

(10)

Since the graphs $D(-a_1)$ and $D(-a_2)$ are either isospectral or identical, the characteristic polynomials of the graphs D_1 and D_2 are identical term-by-term; therefore D_1 and D_2 are isospectral.

2.2.2. *Isospectral Graphs Derived from an Isospectral Pair*

Consider a pair of graphs G_1 and G_2 which are known to be isospectral. (These graphs may be derived from a common frame, or they may be structurally unrelated). Suppose that it is possible to identify a vertex a_1 in G_1 and a vertex a_2 in G_2 such that the deletion of these vertices and their adjoining adges produces two identical or isospectral graphs. In such a case, a_1 and a_2 constitute a pair of substitution partners in the sense that a new pair of isospectral graphs may be generated by the substitution of an arbitrary graphical fragment R into G_1 at vertex a_1 and into G_2 at vertex a_2.

The isospectral graphs **17** and **18** have been studied extensively by Randić and co-workers,[37]

17   **18**

The vertices labeled a_1 and a_2 serve as substitution partners for these graphs, since the graphs **17** $(-a_1)$ and **18** $(-a_2)$ are identical.

17 $(-a_1)$
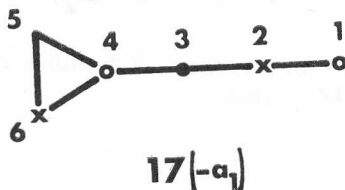
From the twofold symmetry of **17** and **18**, it is evident that these particular graphs contain a second pair of substitution partners equivalent to a_1 and a_2; these may be denoted by a_3 (in **17**) and a_4 (in **18**).

17   **18**
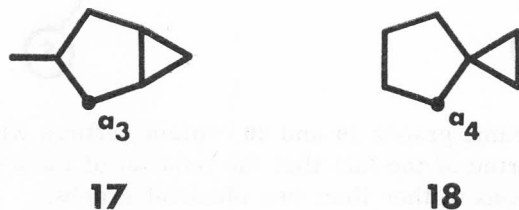
It is therefore possible to attach two arbitrary fragments R and S to **17** at vertices a_1 and a_3 and to **18** at vertices a_2 and a_4 to obtain two families of graphs which are isospectral for any given fragments R and S.
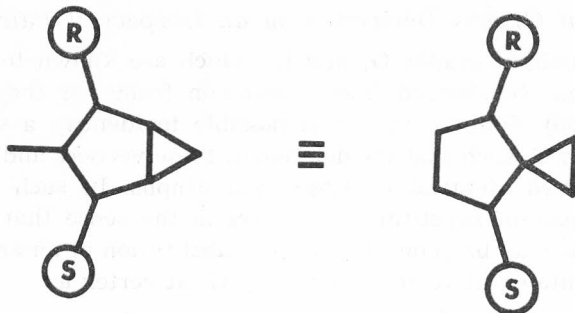
Further inspection of **17** and **18** reveals yet another pair of substitution partners, for deletion of the vertices labeled b_1 and b_2 produces the graph shown below.
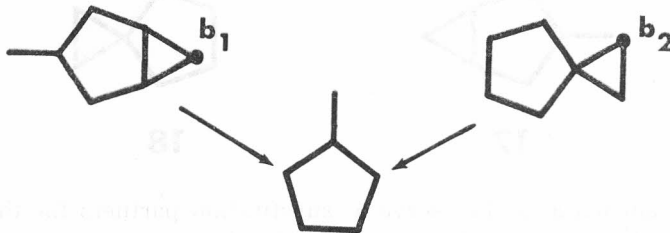
$$17(-b_1) = 18(-b_2)$$

The most general form of the isospectral families derivable by substitution from the graphs **17** and **18** is thus:
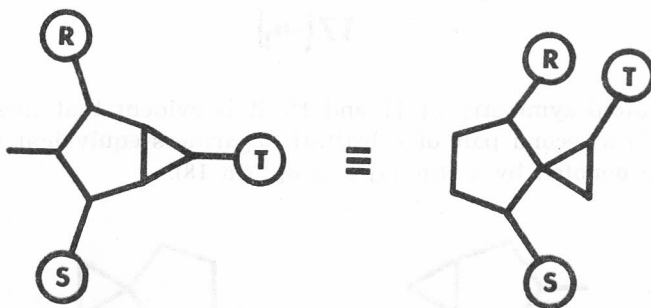
The common-frame graphs **19** and **20** contain vertices which are substitution partners by virtue of the fact that the removal of these vertices produces two isospectral graphs, rather than two identical graphs.
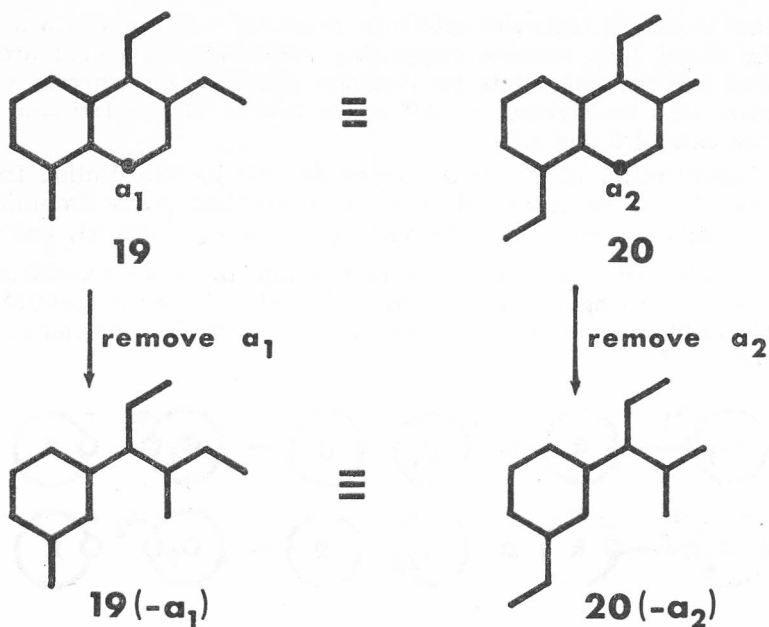
Attachment of a fragment R to the substitution partners of **19** and **20** leads to isospectral graphs of the form:

The generic styrene derivatives **8** and **9** have been studied at length both by Herndon and Ellzey[27] and by Živković et al.[36] These graphs contain two pairs of symmetry-equivalent substitution partners which may be used to construct isospectral families of the form:

(Recall that A and B represent arbitrary graphical fragments in **8** and **9**.) It should be noted that vertices comprising substitution partners are called unrestricted substitution points by Herndon and Ellzey,[27] whereas they are called active sites by Živković et al.[36] in the case of **17** and **18**[37] and inactive sites in the case of **8** and **9**.[36]

The isospectrality of a pair of graphs derived by substitution from isospectral parents can be accounted for by an application of the simplified form of Heilbronner's decomposition theorem[47] given in Equations (4) and (5).

Let $G_1(a_1)$——$R(r)$ and $G_2(a_2)$——$R(r)$ denote the graphs constructed by substitution of the fragment R at vertices a_1 and a_2 in the isospectral graphs G_1 and G_2. Heilbronner's formula gives as the characteristic polynomial of the substituted graphs:

$$\left(G_1 \!\!\bullet\!\!\!-\!\!\!\bullet\, R\right) = \left(G_1\right)\left(R\right) - \left(G_1 \circ\, \circ R\right) \tag{11}$$

$$\left(G_2 \!\!\bullet\!\!\!-\!\!\!\bullet\, R\right) = \left(G_2\right)\left(R\right) - \left(G_2 \circ\, \circ R\right) \tag{12}$$

Since the parent graphs G_1 and G_2 are known to be isospectral, and since $G_1(-a_1)$ and $G_2(-a_2)$ are either isospectral or identical, the characteristic polynomials of the substituted graphs are identical, and thus the substituted graphs are isospectral.

2.2.3. Properties of L_* and L_o

Heilbronner[34] has developed an elegant procedure which is useful both for accounting for observed instances of isospectrality between and among bipartite graphs and for constructing isospectral partners for certain bipartite graphs.

Suppose that the vertices of a bipartite graph (which may be considered the molecular graph of an alternant hydrocarbon)[2] are numbered in such a way that the »starred« vertices are numbered $1, 2, \ldots n_*$ and the »unstarred« vertices are numbered $(n_* + 1), \ldots (n_* + n_o)$, where n_* and n_o represent the number of starred and unstarred vertices and, for convenience, n_* is less than or equal to n_o. The adjacency matrix of a bipartite graph numbered in this manner has the form,[25,54,55]

$$A = \begin{pmatrix} O & B \\ B^{\mathrm{T}} & O \end{pmatrix}, \tag{13}$$

since vertices in the starred set are adjacent only to vertices in the unstarred set, and vice-versa. The eigenvector of A also assumes a partitioned form $(u\, v)^{\mathrm{T}}$, where u and v represent, respectively, the coefficients of the starred and unstarred vertices.

Suppose next that A is applied twice to its eigenvector. The equation may be written as

$$A^2 \begin{pmatrix} u \\ v \end{pmatrix} = \varepsilon^2 \begin{pmatrix} u \\ v \end{pmatrix} \tag{14}$$

or as

$$\begin{pmatrix} BB^\mathrm{T} & O \\ O & B^\mathrm{T}B \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \varepsilon^2 \begin{pmatrix} u \\ v \end{pmatrix}. \tag{15}$$

Notice that the submatrix BB^T of the block-diagonal matrix A^2 pertains only to the starred vertices and that the submatrix $B^\mathrm{T}B$ pertains only to the unstarred vertices. Performance of the matrix multiplication produces two equations, the first of which refers to the starred vertices alone and the second of which refers to the unstarred vertices alone.

$$BB^\mathrm{T} u = \varepsilon^2 u \tag{16}$$
$$B^\mathrm{T}B v = \varepsilon^2 v. \tag{17}$$

Consider now a graph L_* constructed in such a way that its adjacency matrix is given by BB^T. Such a graph must contain n_* vertices and must have n_* positive eigenvalues λ which are related to the eigenvalues of the original graph by $\lambda = \varepsilon^2$. Consider a graph L_o constructed in a similar fashion, so that its adjacency matrix is given by $B^\mathrm{T}B$. L_o must contain n_o vertices, and its spectrum must be identical to that of L_* except that the spectrum of the former contains zero as an eigenvalue $(n_o - n_*)$ times. It follows that the spectrum of the original graph may be obtained from the spectrum of L_* or from the spectrum of L_o by first listing the $2 n_*$ positive and negative square roots of λ, them listing zero $(n_o - n_*)$ times.[8]

Heilbronner has described a straightforward method for drawing the L_* and L_o graphs without actually writing out A and performing the matrix multiplication to obtain the matrices BB^T and $B^\mathrm{T}B$. His procedure is based on the graph theoretical theorem which states that the elements of the matrix A^2 identify all walks of length 2 in the graph described[2] by A. When A^2 is written in the partitioned form shown in equation (15), it is clear that the elements of BB^T describe the walks of length 2 from each starred vertex to each of the other starred vertices and that the elements of $B^\mathrm{T}B$ list the walks of length 2 from each unstarred vertex to each of the other unstarred vertices. Thus, the i, jth element of BB^T is equal to the number of different ways in which one may reach the jth starred vertex from the ith starred vertex in two steps (this can be done in only one way unless vertices i and j belong to a 4-membered cycle). The i, ith element of BB^T corresponds to the degree of the ith starred vertex, since one may describe a walk of length 2 by starting at vertex i, stepping out to each neighbor of i, then stepping back to i. The elements of $B^\mathrm{T}B$ are defined in an analogous manner.

These considerations give rise to a three-step procedure for constructing L_* and/or L_o for any bipartite graph G which contains no 4-membered cycles:

1) The vertices belonging to the starred and unstarred sets are re-written separately.
2) Those vertices which are connected by a walk of length 2 in G are linked by a single edge.
3.) A weight equal to its degree in G is assigned to each vertex in the new graphs.

Heilbronner's construction process is applied to the styrene graph in the illustration below.

$$\text{(18)}$$

7 $\mathbf{L_*(7)}$ $\mathbf{L_o(7)}$
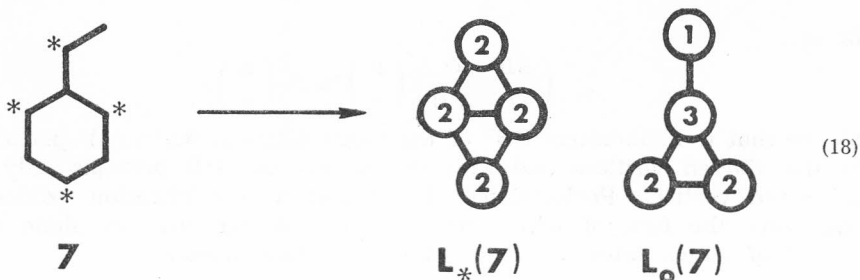
By constructing L_* and L_o, one may rapidly verify the existence of an isospectral relationship between two bipartite graphs having the same total number of vertices. If at least one of the two graphs L_*, L_o of a graph G is identical to or isospectral with at least one of the graphs L'_*, L'_o of G', then G and G' are isospectral. A comparison of the L_* and L_o graphs of the styrene derivatives **1** and **2**, for example, shows immediately that **1** and **2** are isospectral.

$$\text{(19)}$$

1 $\mathbf{L_o(1) = L_*(1)}$

$$\text{(20)}$$

2 $\mathbf{L_o(2)}$ $\mathbf{L_*(2)}$
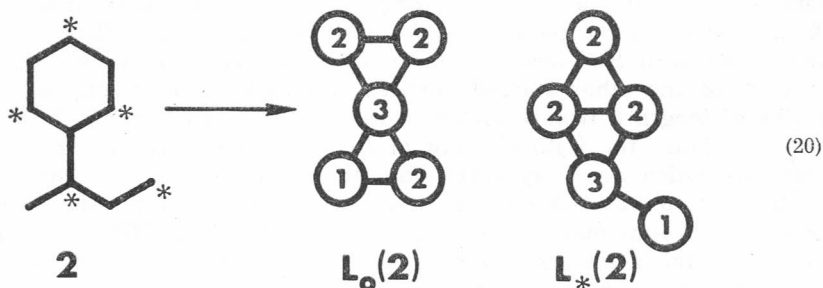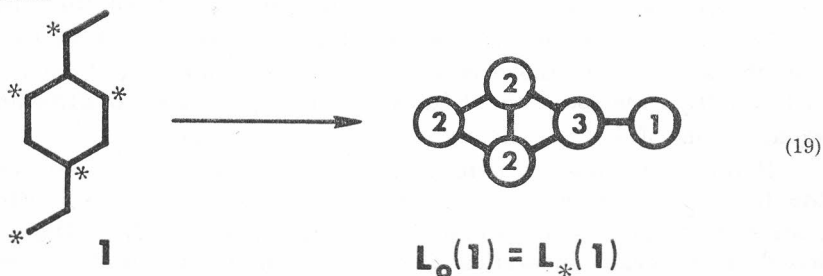
It is slightly more difficult to confirm the isospectrality of the graphs **21** and **22**, since neither of the graphs L_* (**21**), L_o(**21**) is identical to L_* (**22**) or L_o(**22**).

$$\text{(21)}$$

21 $\mathbf{L_*(21) = L_o(21)}$

**22** $L_*(22)$ $L_o(22)$ (22)
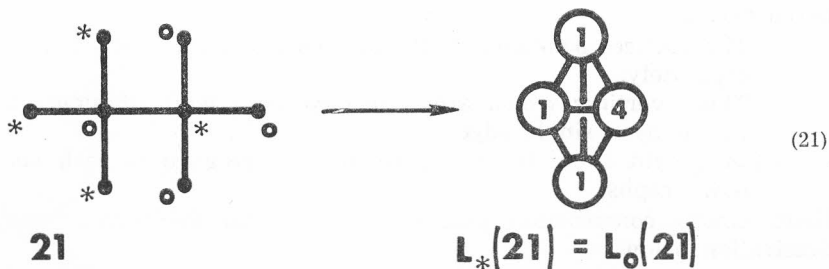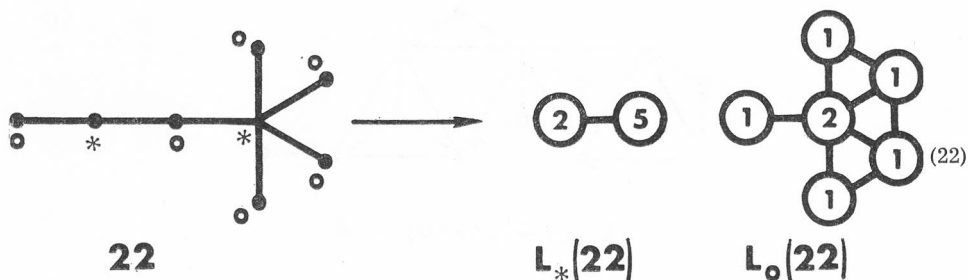
In this case, the spectra of the constructed graphs must actually be computed; nonetheless, the calculation involved is much simpler than that required to obtain the spectrum of **21** and **22**, since the determinants which must be expanded are of order 2×2 and 4×4, rather than 8×8 and 8×8 (recall that it is only necessary to compute the $2n_*$ positive and negative square roots of the n_* eigenvalues of L_* , then to list zero as an eigenvalue $n_o - n_*$ times).

Constructed starred and unstarred graphs (as L_* and L_o may be called) may also be used, in many cases, to construct an isospectral partner for a given bipartite graph by a wrapping procedure. Given a bipartite graph G containing n_* starred vertices and n_o unstarred vertices, it may be possible to wrap the L_* graph of G with n_o vertices in such a way that a new bipartite graph G' is produced, for which $L'_* = L_*$. In cases for which this procedure is possible, G' is necessarily isospectral with G.
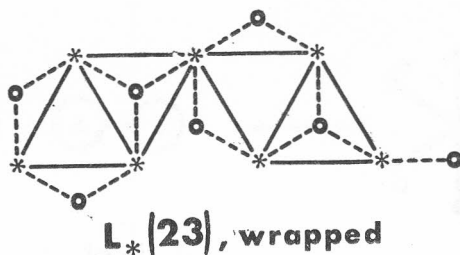
The wrapping process may be illustrated by its application to the molecular graph of 1,1-diphenylethylene **23**.

23
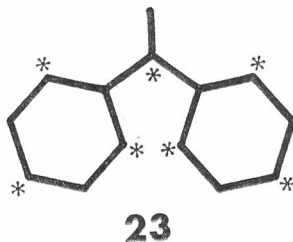
As a first step, the L_* and L_o graphs are constructed by inspection of **23**.

$L_*(23)$ $L_o(23)$
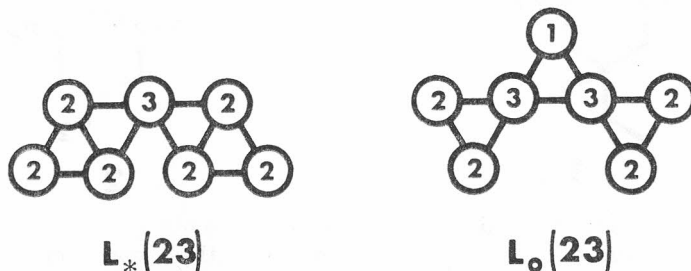
Next, seven unstarred vertices are placed among the vertices of L_* (**23**) in such a way that their edge pattern differs from that of L_o(**23**).

L_* (23), wrapped

A new graph **24** is now constructed by joining the starred and unstarred vertices in the wrapped form od L_* (**23**).


24
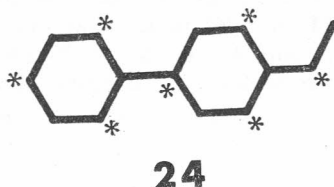
Since the L_* graph of **24** is identical to the L_* graph of 23, **24** must be an isospectral partner of **23**. An examination of compilations of pi electron eigenvalues reveals that the common-frame molecular graphs representing 1,1-diphenylethylene and vinylbiphenyl are, in fact, isospectral.[51-53]

2.2.4. Coefficient Regularities in Isospectral Graphs

Investigations of isospectral graphs have revealed many interesting regularities among the eigenvectors of the adjacency matrices of such graphs. Since the topological eigenvectors are identical to the molecular orbitals obtained by a simple Hückel LCAO treatment,[22] their observed regularities may be related to molecular properties, such as bond order, charge density, and free valence, which can be calculated from the Hückel MO's.

The eigenvectors of the 1,4-divinylbenzene (**1**) and 2-phenylbutadiene (**2**) graphs have been studied in detail by Živković et al.[36]

1

2
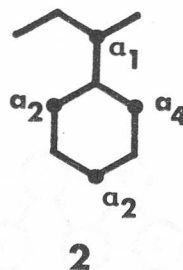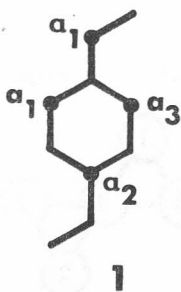
These authors have pointed out that the coefficients of the vertices (a_1, a_2, a_3, a_4) which serve as substitutition partners for these common frame isospectral graphs are identical (to within a sign) for a given eigenvalue. Furthermore, they note that the coefficients of the isospectral point of the common frame to which the ethylene fragment has been attached (a_2 in **1** and a_1 in **2**) are

equal, as are the coefficients of the unsubstituted isospectral points of the common styrene frame (a_1 in **1** and a_2 in **2**). Finally, the coefficients of the vertices within the ethylene fragment are identical in the two graphs. These relationships may be seen more clearly by examining the coefficients associated with the lowest common eingenvalue of **1** and **2** ($\varepsilon = 2.214$), as shown in the diagram below.

The relationships among the coefficients of the vertices in a generalized pair of isospectral styrene derivatives may be diagrammed, with arrows linking vertices whose coefficients are equal.
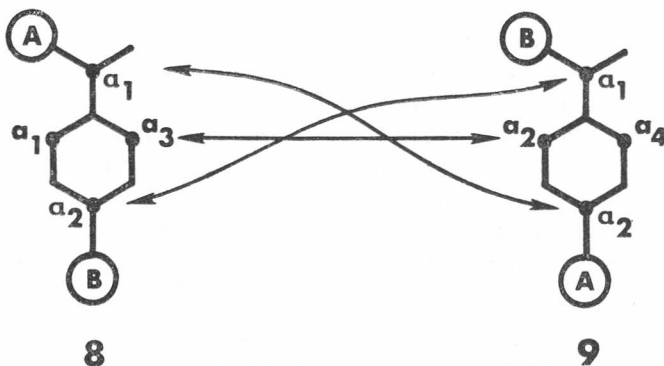

The alternation properties of the styrene frame (indicated in the diagram above by enlarged vertices) provide an explanation for the observed coefficient regularities. By applying Heilbronner's construction procedure to **8** and **9**, it is immediately evident that these graphs have the same L_* graph.
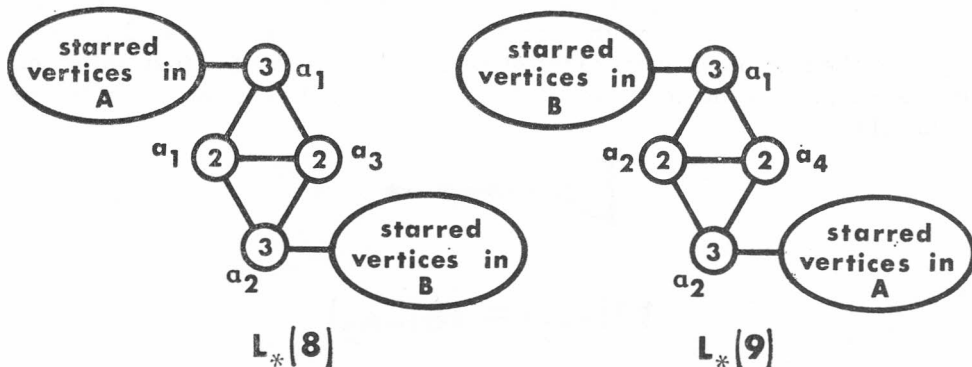
Clearly, the vertex a_1 (or a_3) in L_* (8) is equivalent to a_2 (a_4) in L (9), just as a_1 and a_2 in L_* (8) are respectively equivalent to a_2 and a_1 in L_*^* (9); thus these pairs of equivalent vertices necessarily have the same coefficient in μ, the eigenvector of the adjacency matrix of the L_* graph. Coefficient regularities in bipartite isospectral graphs sharing a frame other than styrene may be explained by a similar analysis.

Coefficient regularities among structurally unrelated isospectral graphs have not previously been described. Several regularities appear among the coefficients of the vertices of the graphs **17** and **18** (see Table I).
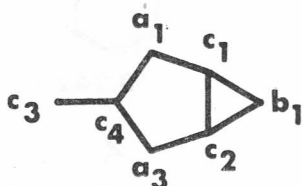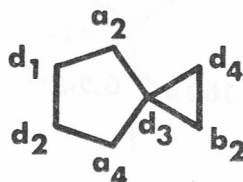
17   **18**

First, it may be noted that the coefficients of the vertices a_1 and a_3 in **17** are related by symmetry, as are the coefficients of a_2 and a_4 in **18**. Secondly, as in the case of the isospectral styrene derivatives, the coefficients of the vertices which function as substitution partners in **17** and **18** are equal; that is, the coefficient of a_1 (or a_3) equals the coefficient of a_2 (or a_4), and the coefficient of b_1 equals the coefficient of b_2. The explanation for the regularities observed in this case is not readily apparent, since Heilbronner's construction procedure is not applicable to **17** and **18**.

Another interesting feature of the coefficients of the two graphs may be noted. It has been observed by D'Amato[40] that several additivity relationships exist among the coefficients of vertices in **17** and **18** and that such relationships may be predicted from certain features of the graphs **17** $(-a_1) =$ $= $ **18** $(-a_2)$ and **17** $(-b_1) = $ **18** $(-b_2)$. These relationships and features will now be described in some detail.

Additivity relationships among coefficients in a single graph. In the graph **17** $(-a_1)$, it is observed that the sum of the coefficients of vertices 2 and 6 is equal to the sum of the coefficients of vertices 1 and 4 for the first, third and last eigenvalues. (The coefficients of all vertices in this graph are listed in Table II.)

$$\mathbf{17(-a_1) = 18(-a_2)}$$

TABLE I

Coefficients of the Vertices in Graphs 17 and 18

Vertex in 17	$\varepsilon = 2.473$	$\varepsilon = 1.463$	$\varepsilon = 0.618$	$\varepsilon = 0.000$	$\varepsilon = -1.000$	$\varepsilon = -1.618$	$\varepsilon = -1.935$
a_1	0.331	0.247	0.602	0.378	0.000	-0.372	0.432
a_3	0.331	0.247	-0.602	0.378	0.000	0.372	0.432
b_1	0.404	-0.373	0.000	-0.378	0.707	0.000	0.235
c_1	0.499	-0.273	0.372	0.000	-0.354	0.602	-0.227
c_2	0.499	-0.273	-0.372	0.000	-0.354	-0.602	-0.227
c_3	0.130	0.433	0.000	-0.756	-0.354	0.000	0.314
c_4	0.320	0.643	0.000	-0.000	0.354	0.000	-0.609
Vertex in 18							
a_2	0.331	0.247	0.602	-0.378	0.000	-0.372	-0.432
a_4	0.331	0.247	-0.602	-0.378	0.000	0.372	-0.432
b_2	0.404	-0.373	0.000	0.378	0.707	0.000	-0.235
d_1	0.225	0.534	0.372	0.378	0.000	0.602	0.147
d_2	0.225	0.534	-0.372	0.378	0.000	-0.602	0.147
d_3	0.594	-0.173	0.000	-0.378	0.000	0.000	0.688
d_4	0.404	-0.373	0.000	0.378	-0.707	0.000	-0.235

TABLE II

Coefficients of the Vertices in Graph **17** *(— a₁)*

Vertex	$\varepsilon = 2.228$	$\varepsilon = 1.360$	$\varepsilon = 0.186$	$\varepsilon = -1.000$	$\varepsilon = -1.000$	$\varepsilon = -1.775$
1	0.090	0.485	— 0.632	0.535	0.000	0.267
2	0.201	0.660	— 0.118	— 0.535	0.000	— 0.474
3	0.357	0.413	0.610	0.000	0.000	0.574
4	0.595	0.099	0.231	0.535	0.000	— 0.545
5	0.485	— 0.273	— 0.284	— 0.267	0.707	0.196
6	0.485	— 0.273	— 0.284	— 0.267	—· 0.707	0.196

The vertices whose coefficients are to be added together have been labeled with x's and o's for ready identification; the sum of the x-marked vertices equals the sum of the o-marked vertices.

In the graph **17**(-b_1), a similar relationship is found to exist between the sum of the coefficients of vertices 1 and 2 and the sum of the coefficients of vertices 4 and 5 for all but the second eigenvalue (see Table III).
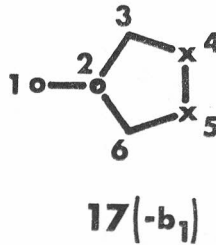

17(-b_1)

TABLE III

Coefficients of the Vertices in Graph **17** *(— b₁)*

Vertex	$\varepsilon = 2.115$	$\varepsilon = 1.000$	$\varepsilon = 0.618$	$\varepsilon = -0.254$	$\varepsilon = -1.618$	$\varepsilon = -1.861$
1	0.247	0.500	0.000	0.749	0.000	0.357
2	0.523	0.500	0.000	— 0.190	0.000	— 0.664
3	0.429	0.000	0.602	— 0.351	— 0.372	0.439
4	0.385	— 0.500	0.372	0.280	0.602	—· 0.153
5	0.385	— 0.500	— 0.372	0.280	— 0.602	— 0.153
6	0.429	0.000	— 0.602	— 0.351	0.372	0.439

The additivity relationships in both cases may be explained by an analysis of the matrix equation

$$A\,C = C\,\lambda, \tag{23}$$

where A represents the adjacency matrix of a given graph, C represents the matrix of its eigenvectors, and λ represents the diagonal matrix of its eigenvalues. Examining a particular element of the matrix product on each side of equation (23), one obtains:

$$(A\,C)_{ij} = \sum_m A_{im}\,C_{mj} \tag{24}$$

equations (24) and (25) may be combined to give

$$\sum_{m} A_{im} C_{mj} = C_{ij} \lambda_{jj}. \tag{26}$$

For a given value of j, equation (26) reduces to

$$\sum_{m} A_{im} c_{m} = c_{i} \lambda, \tag{27}$$

where c_i is the coefficient of vertex i in the jth eigenvector c_j. A particular term in the summation of the left-hand side of equation (27) is zero if no edge exists between vertices i and m, whereas it has the value $1 \cdot c_m$ if an edge does exist between vertices i and m. For every vertex in the graph of interest, then, there is an equation that relates the product of λ and the coefficient of that vertex to the sum of the coefficients of all the vertices adjacent to that vertex. (This sum rule has been exploited in previous cases.[39,46])

When the sum rule defined by equation (27) is applied to the graph 17 ($— a_1$), the following set of equations is obtained:

$$c_2 = c_1 \lambda \tag{28}$$
$$c_1 + c_3 = c_2 \lambda \tag{29}$$
$$c_2 + c_4 = c_3 \lambda \tag{30}$$
$$c_3 + c_5 + c_6 = c_4 \lambda \tag{31}$$
$$c_4 + c_6 = c_5 \lambda \tag{32}$$
$$c_4 + c_5 = c_6 \lambda \tag{33}$$

A comparison of the sum of equations (28) and (31) with the sum of equations (29) and (33)-or, equivalently, (29) and (32)-leads immediately to the conclusion that $c_1 + c_4 = c_2 + c_6$ (or $c_2 + c_5$).

$$(c_2 + c_6) + (c_3 + c_5) = \lambda (c_1 + c_4) \qquad (28) + (31)$$
$$(c_1 + c_4) + (c_3 + c_5) = \lambda (c_2 + c_6) \qquad (29) + (33)$$

The additivity relationships observed in the graph 17 ($— b_1$) may also be explained by, first, applying the sum rule to each vertex to generate six equations:

$$d_2 = d_1 \varepsilon \tag{34}$$
$$d_1 + d_3 + d_6 = d_2 \varepsilon \tag{35}$$
$$d_2 + d_4 = d_3 \varepsilon \tag{36}$$
$$d_3 + d_5 = d_4 \varepsilon \tag{37}$$
$$d_4 + d_6 = d_5 \varepsilon \tag{38}$$
$$d_2 + d_5 = d_6 \varepsilon \tag{39}$$

then comparing the sum of equations (34) and (35) with the sum of equations (37) and (38).

$$(d_1 + d_2) + (d_3 + d_6) = \varepsilon (d_1 + d_2) \qquad (34) + (35)$$
$$(d_4 + d_5) + (d_3 + d_6) = \varepsilon (d_4 + d_5) \qquad (37) + (38)$$

Clearly, $d_1 + d_2 = d_4 + d_5$.

Predicting additivity relationships within a graph. The question arises as to how the additivity relationships observed in the graphs **17** $(-a_1)$ and **17** $(-b_1)$ might be predicted on the basis of structural features alone. Several guidelines for making such a prediction may be stated.

Examine again the graph **17** $(-b_1)$. Notice that the x-marked vertices are connected to vertices 3 and 6, as are the o-marked vertices. Furthermore, the sum of the degrees of the x-marked vertice (four) is equal to the sum of the degrees of the o-marked vertices. These two conditions quarantee that the sum-rule equations (34) and (35) for vertices 1 and 2 together contain the same number of terms as the sum-rule equations (37) and (38) for vertices 4 and 5 and that, moreover, both sets of equations contain the terms d_3 and d_6.

In the case of **17** $(-a_1)$, the o-marked vertices are connected to vertices 2, 3, 5, and 6, and the x-marked vertices are connected to vertices 1, 3, 4, and 5. Again, the sums of the degrees of the x-marked and o-marked vertices are equal. In this instance, however, the x and o vertices are not only connected to a common pair of vertices, as was the case in **17** $(-b_1)$, but also connected in a reciprocal fashin to one another. The sum-rule equations for vertices 1 and 4 and the equations for vertices 2 and 6 thus contain c_3 and c_5 as common terms, and they contain the terms $(c_1 + c_4)$ and $(c_2 + c_6)$ in a reciprocal relationship.

Unfortunately, the process of searching a graph for the existence of vertices fulfilling these conditions is very tedious. The guidelines stated here may be more useful in explaining observed additivity relationships among coefficients than in predicting new ones.

Coefficient regularities in **17** *and* **18**. The additivity relationships in the graphs **17** $(-a_1)$ and **17** $(-b_1)$ may now be related to certain coefficient regularities in **17** and **18**.

Suppose that the x-marked vertices in **17** $(-a_1)$ are bridged through a single vertex to produce the graph **17** and that the o-marked vertices are bridged through a single vertex to produce the graph **18**.
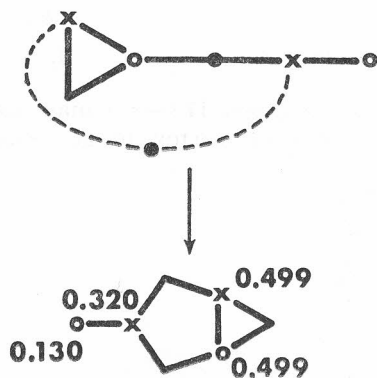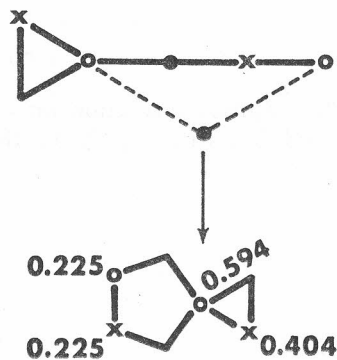
17   **18**

The values of the coefficients at the marked positions have been indicated. Notice that the sum of the coefficients of the x-marked vertices in **17** is identical to the sum of the coefficients of the o-marked vertices in **18** and that the reverse is also true.

The graphs **17** and **18** may also be generated by bridging, through a single vertex, the x-marked and o-marked vertices (respectively) of **17** ($-b_1$).

17   **18**
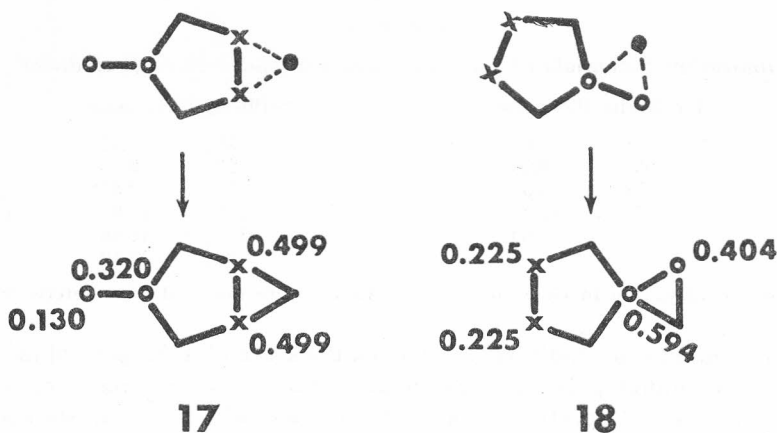
Again, the sum of the coefficients of the x-marked vertices in **17** equals the sum of the coefficients of the o-marked vertices in **18**, and vice versa.

These regularities observed here and in other cases have led D'Amato[40] to make the following conjecture:

> »Given the existence of additivity relationships such as those described for the graphs **17** ($-a_1$) and **17** ($-b_1$), it is possible to bridge the x-marked vertices through a single vertex to form a new graph G_x and to bridge the o-marked vertices in a similar fashion to form a new graph G_o. When this occurs, (1) G_x and G_o are either isospectral or identical; (2) the coefficient of the bridging vertex in G_x is equal to the coefficient of the bridging vertex in G_o; (3) the sum of the coefficients of the x-marked vertices in G_x is equal to the sum of the coefficients of the o-marked vertices in G_o, and vice-versa; (4) the bridging vertices serve as substitution partners for the graphs G_x and G_o.«

It is hoped that one or more of these conclusions may soon be verified.

2.2.5. *Chemical Behavior of Isospectral Molecules*

No survey of current research involving isospectral graphs would be complete without addressing the question of experimentally measured chemical similarities among isospectral molecules, that is, among molecules represented by isospectral graphs. One might expect to find that the topologically dependent properties (ionization potential, oxidation or reduction potential, and so on) of isospectral molecules are closely related. This is apparently not the case, however. Heilbronner and Jones[28] have measured the π ionization potentials of the isospectral molecules 1,4-divinylbenzene and 2-phenylbutadiene (see Table IV) and have reported that the measured values "differ at least as much as those of any other 'nonisospectral' pair having π systems of comparable size." Unfortunately, no other experimental evidence is available to support or refute the findings of Heilbronner and Jones, since instances of isospectrality among molecular graphs are fairly rare. Perhaps some relationship among the

measured properties of isospectral molecules will be discovered in the future. Research in this direction is in progress.[56]

1,4-Divinylbenzene		2-Phenylbutadiene	
$5a'' \pi$	8.60	$3b_g \pi$	8.11
$4a'' \pi$	9.28	$2b_g \pi$	9.18
$3a'' \pi$	9.5	$2a_u \pi$	9.80
$20a' \sigma$	11.2	$1 b_g \pi$	11.0
$2a' \pi$	11.54	$10a_g \sigma$	11.46
		$9a_g \sigma$	12.19

[a] Ionization potentials are in electron volts. All values were obtained from reference 28.

An intriguing side result has come from the search for isospectral molecules. Schmidt[57] has found polycyclic conjugated molecules that have remarkably similar experimental spectra. As an example, consider the pair shown below with their first and second ionization potentials.
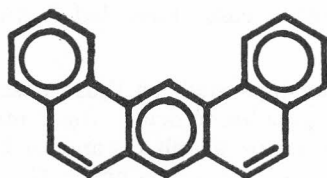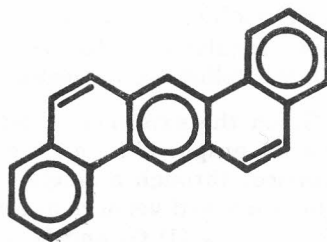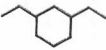

**7.40 / 7.79**   **7.38 / 7.80**

These molecules have different Hückel spectra i. e., are not isospectral. In order to avoid confusion with the term isospectral, Clar and Schmidt refer to these molecules as isotopic.

3. SUBSPECTRAL MOLECULES

An examination of tabulated graph spectra[51-53] reveals that the occurrences of isospectral molecular graphs are rare. A much more common situation is that in which the spectra of two different molecules have one or more common eigenvalues. In some cases, the spectrum of one molecular graph contains the complete spectrum of a second, smaller (component) graph. The two graphs are then said to be subspectral.[39] Such a relationship does not require that the two molecules have the same number of vertices or edges or the same number of rings. The most important examples for chemistry would be those in which the highest occupied molecular orbitals (HOMO's) are the same in two molecules and the lowest unoccupied molecular orbitals (LUMO's) also match each other. Because of the pairing of bonding and antibonding energy levels in alternant hydrocarbons,[46] the coincidence of the LUMO is guaranteed if the HOMO levels match. A survey of the compilation of Hückel MO calculations reveals many examples.[51-53]

Consider the eigenvalues of the bonding orbitals of butadiene, metadivinyl-benzene, naphthalene, and cyclodecapentaene (**25—28**).

| 25 | 26 | 27 | 28 |

0.61803	0.61803	0.61803	0.61803, 0.61803
	0.72606	1.0	
	1.23992	1.30278	
1.61803	1.61803	1.61803	1.61803, 1.61803
	2.22158	2.30278	2.0

Structures **26—28** have an equal number of vertices and an equal number of eigenvalues, but they are not isospectral. They are, however, partially iso-spectral because their spectra contain the eigenvalues of butadiene, with which each is subspectral. In many, but not all, cases, we can identify the smaller molecule as a fragment of the larger one, just as **25** is a fragment in **26—28**, with all the eigenvalues of the fragment appearing in the spectrum of the larger molecule. The trivial example of partially isospectral molecules whose spectra share only the zero eigenvalues of the non-bonding molecular orbitals will not be discussed here. Methods for enumerating the number of zeros in the graph spectrum have been reported elsewhere.[58-62]

Chemically interesting cases of subspectrality are those in which both the fragment and the larger composite molecule are non-radicals and in which neither has non-bonding MO's. Therefore, we will consider only those examples in which both fragment and composite molecule have an even number of vertices.

There are several general schemes by which the spectrum of the fragment can be shown to be a part of that of the larger molecule.

3.1. Linear and Cyclic Polyenes

The energy levels of the linear system of N vertices appear in the spectrum of the cyclic system containing $2N + 2$ vertices. Compare, for example, structures **25** and **28**. The energy levels of linear and cyclic polyenes are known in analytical form.[63,64]

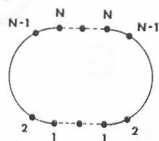*i. Linear polyenes*

$$m_j = 2 \cos \left(\frac{j \pi}{N + 1} \right) ; \; j = 1, 2, \ldots, N \tag{40}$$

ii. Cyclic polyenes

$$m_j = 2 \cos \left(\frac{2 j \pi}{K} \right) ; \; j = 1, 2, \ldots, K \tag{41}$$

Suppose we connect two linear polyenes of degree N with two additional vertices plus adjoining edges to form a cyclic polyene of the size $K = 2N + 2$,

The energy levels of this cyclic system are

$$m_j = 2 \, \cos \left(\frac{2 \, j \, \pi}{2 \, N + 2} \right) = 2 \, \cos \left(\frac{j \, \pi}{N + 1} \right) ; \; j = 1, 2, \ldots, 2N + 2 \qquad (42)$$

Thus, the spectrum of the $2N + 2$ cyclic system will contain all the eigenvalues of the N linear system.

3.2. *Symmetric Singly Bridged Fragments*

Živković and co-workers[39] have used the Heilbronner factorization procedure[47] to show why the eigenvalues of a fragment in some cases appear in the spectrum of the larger composite molecule. Consider the composite molecule G formed from two identical fragments A linked through a single vertex,
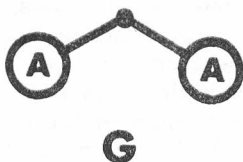
Using equation (4), the characteristic polynomial of G can be written as,

$$(43)$$

The characteristic polynomial of fragment A factors out of that for G and therefore the eigenvalues of A will appear in the spectrum of G. This example is not very interesting because G has an odd number of vertices and therefore a non-bonding MO or a zero in its spectrum. The situation can be remedied by introducing the modification G' in which the substituent B contains an odd number of vertices and A has an even number,
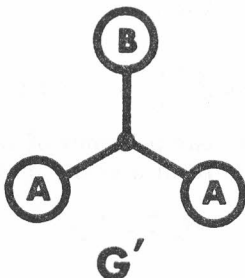
Then, the characteristic polynomial of G' is given by,

$$(44)$$

The polynomial of A factors out of that for G', and, therefore, the spectrum of A will be contained by the spectrum of G'. An example is structure **23**, in which the fragment A is benzene and B is a single vertex.

23
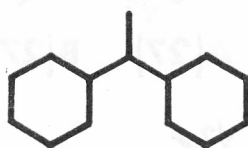
0.56451	
1.0, 1.0, 1.0	1.0, 1.0
1.53555	
2.0	2.0
2.30725	

Although the benzene spectrum is a component of that of **23**, the HOMO's of the two molecules do not match.

3.3. *Fragments Linked by Multiple Bridges*

Using the same reasoning as that employed in the earlier work of Heilbronner,[47] McClelland[65] has developed the following simple rules for the decomposition of a molecule with a plane of symmetry into simpler fragments for the purpose of simplifying the characteristic polynomial or secular determinant. McClelland's approach allows one to draw two component graphs by fragmenting the composite graph along its plane of symmetry. The rules for the fragmentation process may be stated as follows:

1) The symmetry plane perpendicular to the plane of the graph divides the composite graph into two fragments or component graphs, A and B.

2) Vertices lying on the plane of symmetry are included in the A fragment.

3) The weight of the edge[66] between a vertex lying on the plane of symmetry and a vertex not on the plane is $\sqrt{2}$.

4) If the symmetry plane bisects an edge between vertices μ and μ', then vertex μ (in A) is weighted $+1$ and vertex μ' (in B) is weighted[67] -1. All other edge and vertex weights remain unchanged.

5) The eigenvalues of the composite graph may be obtained by finding the eigenvalues of the component graphs A and B, which, should symmetry allow, might also be factorable by the application of rules 1 through 4.

McClelland's procedure may be ilustrated by the application of these rules to the naphthalene (27) and cyclopentadienyl (29) graphs, as shown below.
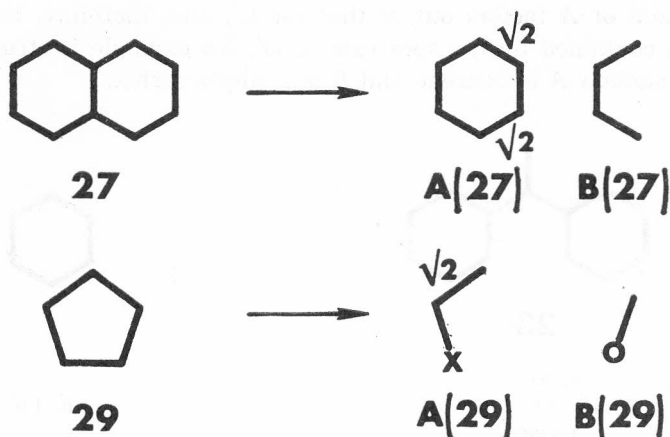

In the diagram above, X indicates an atom of weight $+1$ (or Coulomb integral of $\alpha + \beta$) while 0 denotes an atom of weight -1 (or Coulomb integral of $\alpha - \beta$). The quantity $\sqrt{2}$ written next to a bond indicates that the bond has a weight of $\sqrt{2}$ (the resonance integral for the bond is $\sqrt{2}\,\beta$). The factorization scheme described above is derived from a standard group theoretical approach the HMO theory. McClelland demonstrated that the character table for the C_2 point group may be used to generate, from the N $2p_z$ atomic orbitals $\Theta_1, \Theta_2, \ldots, \Theta_N$ comprising the molecular skeleton, N symmetry-adapted orbitals $\Phi_1, \Phi_2, \ldots, \Phi_N$, which belong to either the A or B representation.

Let atomic orbitals paired by the symmetry operation be denoted by Θ_μ and $\Theta_{\mu'}$, and let the orbitals self-equivalent under the operation (that is, the orbitals lying on the symmetry plane) be denoted by Θ_k. The symmetry orbitals belonging to the A-representation then have the form Θ_k or $1/\sqrt{2}\,(\Theta_\mu + \Theta_{\mu'})$; the symmetry orbitals belonging to the B-representation have the form $1/\sqrt{2}\,(\Theta_\mu - \Theta_{\mu'})$. Notice that, if atoms μ and ν are adjacent, then so are μ' and ν'; furthermore, $\langle \Theta_\mu | H | \Theta_\nu \rangle = 0$ unless μ and ν represent the same atom or adjacent atoms. From these facts it follows that the matrix components of the Hamiltonian on the symmetry-adapted basis are given by: $\langle \Phi_\mu | H | \Phi_\nu \rangle = \langle \Theta_\mu | H | \Theta_\nu \rangle = \beta$ if both or neither of the adjacent atoms μ and ν lie on the plane of symmetry; $\langle \Phi_\mu | H | \Phi_\nu \rangle = \langle \Theta_k | H | 1/\sqrt{2}\,(\Theta_\nu + \Theta_{\nu'}) \rangle = \sqrt{2}\,\beta$ if one of a pair of adjacent atoms lies on the plane of symmetry; and

$$\langle \varphi_\mu | H | \varphi_\mu \rangle = \langle \Theta_\mu | H | \Theta_\mu \rangle \pm \langle \Theta_\mu | H | \Theta_{\mu'} \rangle$$

$$= \left\{ \begin{array}{ll} \alpha & \text{if } \mu \text{ and } \mu' \text{ are non-adjacent,} \\ \alpha \pm \beta & \text{if } \mu \text{ and } \mu' \text{ are adjacent.} \end{array} \right. \tag{45}$$

Given the relationship between the Hückel parameters and the elements of the adjacency matrix of an edge- and vertex-weighted graph,[66-73] the origin of McClelland's factorization rules is apparent.

Let us now consider fragments linked by multiple bridges. Consider the molecule M formed from a pair of identical fragments R linked across a plane of symmetry by n vertices,

M
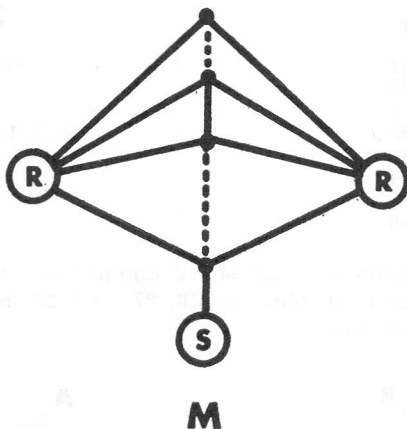
The bridging vertices may be bonded pairwise or they many have attached substituents S which if present must be symmetrical with respect to the symmetry plane. Now divide M into two fragments A and B subject to the rules (2) and (3) above.
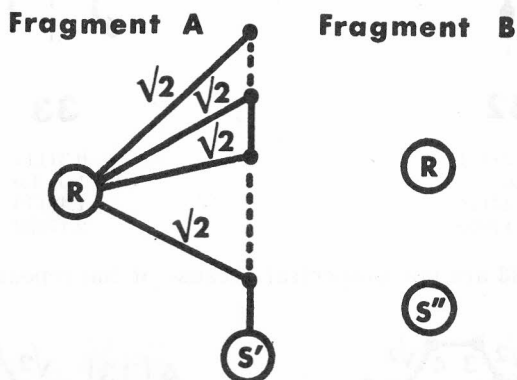
The eigenvalues of fragments ⓡ and ⓢ″ , assuming S is properly divided will, therefore, appear in the spectrum of the composite molecule M. Structures **30** and **31** serve as an example.
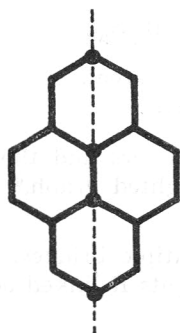
30

0.44504
0.87938
1.0, 1.0
1.24698
1.34730
1.80194
2.0
2.53209

31

0.44504

1.24698

1.80194

Two different composites may share eigenvalues because they share the same fragments. Simple examples are **26**, **27**, and **28**, but the situation in the pair **32** and **33** is less obvious.
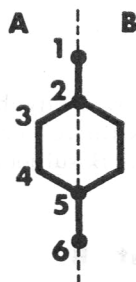
32

0.31111
1.0
1.48119
2.17009
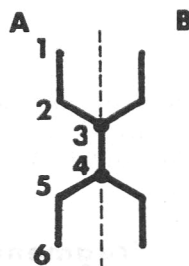
33

0.31111
1.0, 1.0
1.48119
2.17009

Structures **32** and **33** are not isospectral because of the repeated ethylene roots in **33**
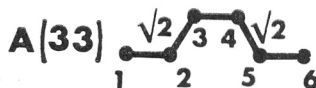
The B fragments of **32** and **33** are, respectively, one and two ethylenes. There-fore, one set of ± 1.0 eigenvalues appears in the spectrum of **32** and two sets in **33**. The A fragments of **32** and **33** are identical. They are related to hexatriene, but with resonance integrals for 2—3 and 4—5 connections increased by the factor $\sqrt{2}$.

The preceding examples all involve molecules in which vertices lie on the symmetry plane and no bonds cross the symmetry plane. These requirements ensure that at least the smaller B fragment will be obtained from the division with Coulomb and resonance integrals unchanged from those of the parent molecule.

If the symmetry plane cuts through bonds, then Coulomb integrals on both sides of the plane are changed (Rule 4) and the resulting pieces are no longer simple fragments of the composite. Consider **31** and **34**.
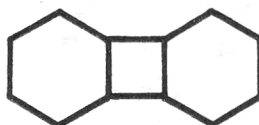
31	**34**
0.44504	0.44504
	0.87938
1.24698	1.24698
	1.34730
1.80194	1.80194
	2.53209

Structure **31** is clearly a fragment of **34** but decomposition of **34** with the horizontal symmetry plane according to Rule 4 does not yield a simple hexa-triene fragment.
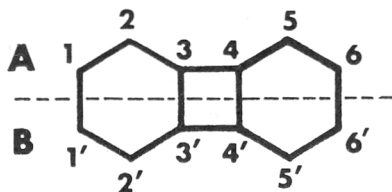
In the diagram X signifies an atom with weight $+1$ (for atoms 1, 3, 4, and 6 of A (**34**)) while 0 denotes — 1 weight (as in $1'$, $3'$, $4'$ and $6'$ of B (**34**)). Neither A (**34**) nor B (**34**) is identical to **31**.

To see the relationship between the spectra of **31** and **34**, divide **31**, A (**34**) and B (**34**) vertically, cutting the 3—4 bond. Use the symbols Y and P to denote atoms with Coulomb integrals $\alpha + 2\beta$ (weight $+2$) and $\alpha - 2\beta$ (weight -2), respectively.
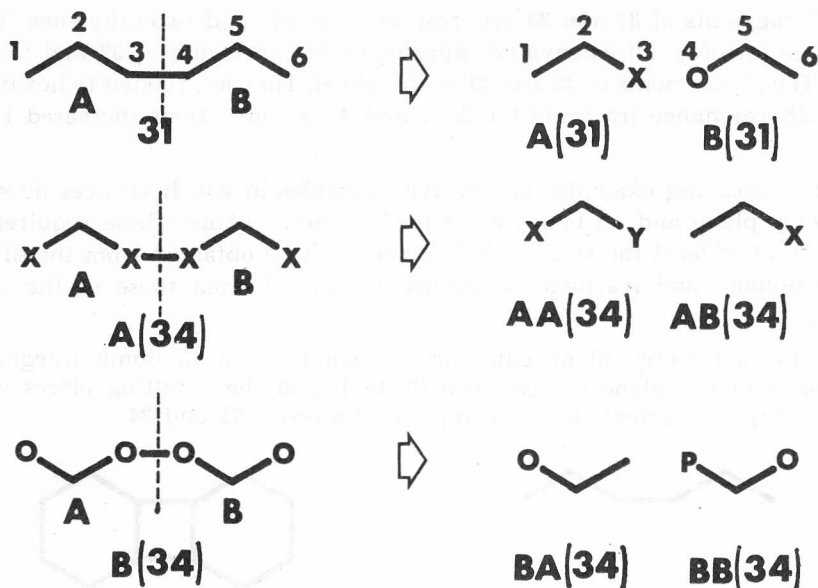
Fragments A (**31**) and AB (**34**) are identical, while B (**31**) matches BA (**34**). Since each member of the two pairs has three vertices, there should be six eigenvalues that coincide between the spectra of **31** and **34**, and exactly that many matchings actually occur.

3.4. Hall's Method for Determining Subspectral Graphs

Hall[38] has demonstrated that, in the case of a bipartite graph for which a twofold symmetry operation exchanges starred and unstarred vertices, one may construct a component graph which is a contraction of the composite graph in the sense that its eigenvalues, together with their negatives, constitute the complete spectrum of the composite graph.

The mathematical basis for the construction of such a contraction graph lies in the twofold symmetry properties of the adjacency matrix of the composite graph. Suppose that the $2N$ vertices of the composite graph are numbered in such a way that the starred vertices are numbered 1 through N and the unstarred vertices are numbered $N + 1$ through $2N$. The adjacency matrix of the composite graph then has the form

$$A = \begin{pmatrix} 0 & B \\ B^T & 0 \end{pmatrix}. \tag{46}$$

In order for the twofold symmetry operation, represented by

$$S = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tag{47}$$

to commute with A, the submatrix B must be symmetrical, that is, $B = B^T$.

Consider the eigenvalue equation for A:

$$\begin{pmatrix} 0 & B \\ B & 0 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \varepsilon \begin{pmatrix} u \\ v \end{pmatrix}. \tag{48}$$

The subvectors u and v represent the coefficients of the starred and unstarred vertices, respectively. Performance of the matrix multiplication gives two equations:

$$B\,v = \varepsilon\,u \tag{49}$$

$$B\,u = \varepsilon\,v. \tag{50}$$

Since S commutes with A, $(u\ v)^{\mathrm{T}}$ must also be an eigenvector of S; furthermore, the eigenvalues of S are $+1$, and -1, since $S^2 = 1$. Thus the eigenvalue equation for S:

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \pm \begin{pmatrix} u \\ v \end{pmatrix} \tag{51}$$

implies that $u = \pm v$. Substitution of this relation into equations (49) and (50) produces a new eigenvalue equation:

$$B\,u = \pm\,\varepsilon\,u. \tag{52}$$

It is clear from equation (52) that $u = \pm v$ is an eigenvector of B with eigenvalue $+\varepsilon$ and that $u = -v$ is an eigenvector of B with eigenvalue $-\varepsilon$. Hall concludes from this result that the graph containing N vertices whose adjacency matrix is given by B has eigenvectors identical to the u eigenvectors of the original graph (to within a normalization constant) and eigenvalues which, together with their negatives, give the spectrum of the original graph. This smaller graph Hall designates as the contraction of the original graph.

Although Hall has not explicitly described the procedure by which a contraction graph may be constructed by mere inspection of a twofold symmetric composite graph, construction rules may easily be derived upon consideration of the form of the submatrix B.

Suppose that a twofold symmetry operation exchanges starred and unstarred vertices in a given composite graph. Let the set m of starred vertices be numbered 1 through N, and let the set n of unstarred vertices be numbered in such a way that the number assigned to each vertex in n is N greater than the number assigned to its symmetry partner in m, that is, let the vertex n_i which is the symmetry partner of m_i be numbered $N + i$. As a consequence of this numbering procedure, the elements of B will be given by:

$$B_{ii} = \begin{cases} 1 & \text{if } m_i \text{ and } n_i \text{ are adjacent in the composite graph,} \\ 0 & \text{otherwise;} \end{cases} \tag{53}$$

$$B_{ij} = B_{ji} = \begin{cases} 1 & \text{if } m_i \text{ and } n_j \text{ (and therefore } n_i \text{ and } m_j\text{) are adjacent} \\ & \text{in the composite graph,} \\ 0 & \text{otherwise.} \end{cases} \tag{54}$$

The rules for constructing a contraction graph may therefore be stated as follows:

1) Distinguish between the starred and unstarred vertices of the composite graph by some means, then sketch the twofold symmetry operation (reflection in a plane of symmetry, rotation about a C_2 axis, or inversion trough a center of symmetry) which divides the composite graph into two symmetry-equivalent sets of vertices.

2) Number the starred and unstarred vertices by the procedure outlined above.

3) To draw the contraction graph, first draw the N vertices belonging to one of the symmetry-equivalent sets, preserving the adjacency relationships among the vertices in the set.

4) If a vertex m_i (or n_i) is adjacent to its symmetry partner n_i (m_i) in the original graph, then m_i (n_i) is weighted $+1$ in the contraction graph.

5) If a vertex m_i (n_i) is adjacent to a vertex n_j (m_j) in the original graph, then m_i and m_j $(n_i$ and $n_j)$ are joined by an edge of unit weight in the contraction graph.

These rules can be illustrated by the construction of two different contraction graphs for the naphthalene graph, as shown in Figure 1. In Figure 1 (a), the symmetry operation which exchanges starred and unstarred vertices is a twofold rotation around an axis perpendicular to the plane of the molecule,
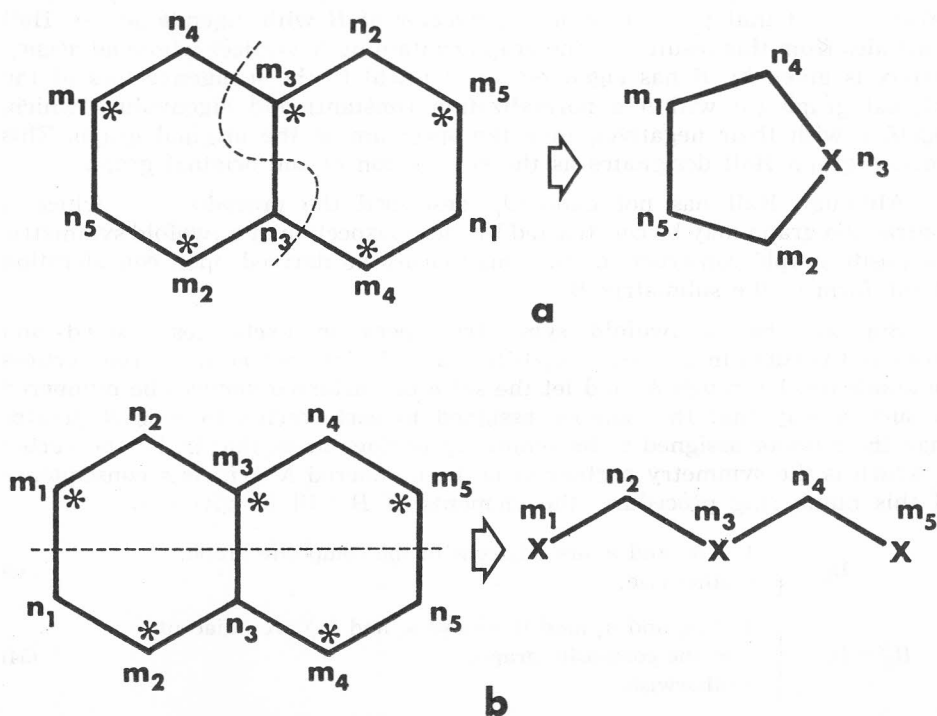

Figure 1. Two contractions of the naphthalene graph, constructed by Hall's procedure. In (a), the symmetry operation which exchanges starred and unstarred vertices is a twofold rotation; in (b), the twofold operation is reflection through a plane of symmetry.

whereas in Figure 1 (b), the twofold operation is reflection through a plane of symmetry perpendicular to the plane of the molecule. Notice that the contraction graph in (b) is identical to the A-fragment of naphthalene as derived by McClelland's procedure. It is clear that Hall's contraction process reduces to McClelland's fragmentation scheme in the case of composite graphs for which the twofold symmetry operation is a plane passing through one or more edges of the graph.

3.5. Factorization of Graphs with n-fold Symmetry

A third factorization procedure has been developed by D'Amato[40-42] which incorporates both McClelland's and Hall's procedures as special instances of a more general scheme for constructing the subspectral components of composite graphs possessing n-fold symmetry. The mathematical origin of this scheme is a unitary transformation upon the eigenvalue equation of the adjacency matrix of the composite graph by the matrix which represents the operation of n-fold rotation. King has reported a similar factorization procedure for graphs corresponding to polyhedra.[74] The factorization of twofold- and threefold-symmetric planar composite graphs by this procedure will now be described in detail.

3.5.1. Factorization of Graphs with Twofold Symmetry

Consider a bipartite or nonbipartite graph G characterized by a twofold symmetry operation which defines two equivalent sets of vertices r and s and, possibly, a set of vertices q which are self-equivalent under the twofold operation. The operation, which may be rotation about a twofold axis, inversion through a center of symmetry, or reflection through a plane perpendicular to the plane of the graph, need not exchange starred and unstarred vertices if G is a bipartite graph. The following rules may be used to construct the two graphs G_+ and G_-, which are the factors of G.

1) Draw the r set of vertices and all the edges connecting the members of the set. Then examine in G the vertices through which r and s are connected; for convenience, these may be called the bridging vertices.

2) If a bridging vertex r_1 is connected to its symmetry-equivalent partner s_1, then r_1 is weighted $+1$ in G_+ and -1 in G_-.

3) If r_1 is connected to a vertex s_2 which is symmetry-equivalent to a second bridging vertex r_2 in r, then the weight of the edge between r_1 and r_2 in G ($+1$ if they are adjacent, zero if they are not) is increased by one unit in G_+ and decreased by one unit in G_-.

4) If any bridging vertex in r is connected to a q vertex in G, then the weight of the edge between the adjacent r and q vertices is $\sqrt{2}$ in G_+. The q vertices and their adjacent edges are omitted entirely in G_-.

This factorization procedure is applied to the graphs corresponding to 1,2,5,6-dibenzanthracene (35), 1,2,5,6-dibenzopentalene (36), and 1,2,4,5-dibenzopentalene (37) in Figure 2. As used earlier, the symbols X and Y refer to atoms with weights $+1$ and $+2$, respectively, while 0 and P refer to atom weights -1 and -2, respectively.
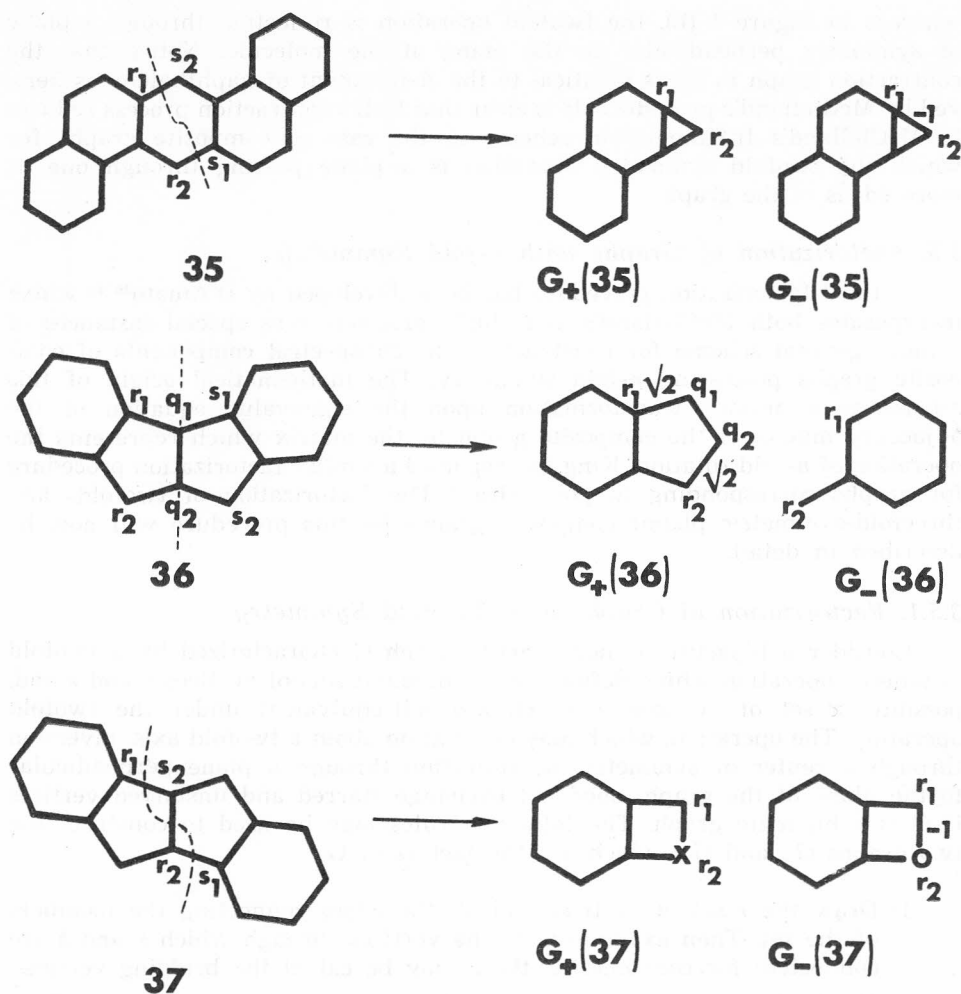
Figure 2. Factorization of the twofold-symmetric graphs representing 1,2,5,6-dibenzanthracene (35), 1,2,5,6-dibenzopentalene (36), and 1,2,4,5-dibenzopentalene (37) by the procedure of D'Amato.[40-42]

The rules for constructing the component graphs by inspection of the composite graph originate in the symmetry properties of the adjacency matrix of the composite graph.

Consider first a twofold-symmetric composite graph which contains $2N$ vertices, N vertices in each of the equivalent sets r and s. (Exclude, for the present, any graph containing a set of vertices q which are self equivalent under the twofold operation.) Let such a graph be denoted by G_1. The vertices of G_1 may be numbered in such a way that the number assigned to each vertex in s is N greater than the number assigned to its symmetry-equivalent partner in r. As a consequence of this numbering procedure, the adjacency matrix of G_1 takes the form:

$$A(G_1) = \begin{pmatrix} B_1 & B_2 \\ B_2 & B_1 \end{pmatrix}. \tag{55}$$

The elements of the $N \times N$ submatrix B_1 correspond to adjacency relationships within the r set and within the s set; the elements of the $N \times N$ symmetric submatrix B_2 represents the adjacency relationship between sets r and s.

A unitary transformation on $A(G_1)$ and its eigenvector $(u\ v)^T$ (where the subvectors u and v contain the coefficients of the r and s vertices, respectively) may be performed by the $2N \times 2N$ matrix representing twofold rotation:

$$C_2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = C_2\dagger. \tag{56}$$

The transformed eigenvalue equation is

$$C_2\dagger A(G_1) C_2 C_2\dagger \begin{pmatrix} u \\ v \end{pmatrix} = \varepsilon C_2\dagger \begin{pmatrix} u \\ v \end{pmatrix}. \tag{57}$$

From the facts that (1) C_2 commutes with $A(G_1)$; (2) $C_2^2 = 1$; and (3) the eigenvalues of C_2 are $+1$ and -1, equation (57) can be written as

$$A(G_1) C_2\dagger \begin{pmatrix} u \\ v \end{pmatrix} = \varepsilon C_2\dagger \begin{pmatrix} u \\ v \end{pmatrix} = \pm\varepsilon \begin{pmatrix} u \\ v \end{pmatrix} \tag{58}$$

or

$$\begin{pmatrix} B_1 & B_2 \\ B_2 & B_1 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \varepsilon \begin{pmatrix} v \\ u \end{pmatrix} = \pm\varepsilon \begin{pmatrix} u \\ v \end{pmatrix} \tag{59}$$

Performance of the matrix multiplication in equation (59) gives

$$B_1 v + B_2 u = \varepsilon v = \pm\varepsilon u \tag{60}$$

$$B_2 v + B_1 u = \varepsilon u \quad \pm\varepsilon v \tag{61}$$

Clearly, $u = \pm v$, and therefore equation (60) and (61) reduce to a single equation

$$(B_1 \pm B_2) u = \varepsilon u \tag{62}$$

or its equivalent

$$(B_1 \pm B_2) v = \varepsilon v. \tag{63}$$

Thus it can be seen that $u = +v$ is an eigenvector of $B_1 + B_2$, and $u = -v$ is an eigenvector of $B_1 - B_2$; furthermore, the N eigenvalues of $B_1 + B_2$ and the N eigenvalues of $B_1 - B_2$ together comprise the spectrum of G_1. The graph G_1 may be factored, then, by constructing the two graphs G_+ and G_-, each containing N vertices, which have as their respective adjacency matrices $B_1 + B_2$ and $B_1 - B_2$.

The relationship between the forms of B_1 and B_2 and the rules given earlier for constructing the component graphs may best be clarified by means of an example. Consider the 1,2,4,5-dibenzopentalene graph (37) shown in Figure 2.

The nonzero elements of B_1 (37) correspond to the adjacency relationships between and among the eight vertices within the r set (or within the s set); the nonzero elements of B_2 (37) represent the adjacency of vertices r_1 and s_1, r_1 and s_2, and r_2 and s_1.

$$B_1(VII) = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \tag{64}$$

$$B_2(VII) = \begin{pmatrix} 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & & & & & & & \\ 0 & & & & & & & \\ 0 & & & & & & & \\ 0 & & & & 0 & & & \\ 0 & & & & & & & \\ 0 & & & & & & & \\ 0 & & & & & & & \end{pmatrix} \tag{65}$$

It can be seen that the only nonzero diagonal element of $B_1 \pm B_2$ will be that corresponding to r_1:

$$(B_1 \pm B_2)_{11} = \pm 1. \tag{66}$$

Thus r_1 will be weighted $+1$ in G_+ and -1 in G_-; all other vertices will remain unweighted. All off-diagonal elements of $B_1 \pm B_2$ will be identical to the corresponding elements of B_1 except for those elements which represent the edge between r_1 and r_2:

$$(B_1 \pm B_2)_{12} = (B_1)_{12} \pm 1 \tag{67}$$

$$(B_1 \pm B_2)_{21} = (B_1)_{21} \pm 1. \tag{68}$$

Therefore, the weight of the edge between r_1 and r_2 in G_1 (zero in this case) will increase by one unit in G_+ and decrease by one unit in G_-; the weights of all other edges will be unchanged. The origin of rules 1 through 3 (given at the beginning of this section) for constructing the subspectral components of a graph of the form of G_1 should now be apparent.

Suppose the composite graph of interest is identical to a graph of the form of G_1 except that it contains, in addition to the r and s vertices, a set of n vertices (denoted by q) which are self-equivalent under the twofold operation. Let this graph be denoted by G_1'. The adjacency matrix of G_1' can be written in the form

$$A(G_1') = \begin{pmatrix} 0 & D & D \\ D^T & B_1 & B_2 \\ D^T & B_2 & B_1 \end{pmatrix} \tag{69}$$

The nonzero elements of the $n \times N$ submatrices D represent the edges between the q vertices and the r and s vertices; the elements of the $N \times N$ submatrices

B_1 and B_2 represent the adjacency relationships within and between sets r and s, as previously described. (In the case of molecular graphs, B_2 is generally the zero matrix, since r and s vertices are adjacent only to q vertices and not to each other.)

The matrix representing twofold rotation must now be written as

$$C_2' = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = (C_2')^\dagger \tag{70}$$

since rotation about a twofold axis leaves the q vertices unaffected. The eigenvalue equation for $A(G_1')$ becomes, under unitary transformation,

$$[(C_2')^\dagger A(G_1') C_2'] (C_2')^\dagger \begin{pmatrix} p \\ u \\ v \end{pmatrix} = \varepsilon (C_2')^\dagger \begin{pmatrix} p \\ v \\ u \end{pmatrix}, \tag{71}$$

where the subvector p represents the coefficients of the q vertices. Equation (71) may be written as

$$\begin{pmatrix} 0 & D & D \\ D^\mathrm{T} & B_1 & B_2 \\ D^\mathrm{T} & B_2 & B_1 \end{pmatrix} \begin{pmatrix} p \\ v \\ u \end{pmatrix} = \varepsilon \begin{pmatrix} p \\ u \\ v \end{pmatrix}, \tag{72}$$

since C_2' commutes with $A(G_1')$ and since $(C_2')^2 = 1$. By performing the matrix multiplication in (72), one obtains equations (73) through (75):

$$D\,v + D\,u = \varepsilon\,p \tag{73}$$

$$D^\mathrm{T} p + B_1 v + B_2 u = \varepsilon\,v \tag{74}$$

$$D^\mathrm{T} p + B_2 v + B_1 u = \varepsilon\,u. \tag{75}$$

The behavior of the eigenvector under transformation by $(C_2')^\dagger$ implies that, once again, $u = \pm v$. Therefore, equations (73) through (75) may be simplified in one of two ways, according to whether u is equal to $+v$ or $-v$.

If $u = +v$, then equations (73) and (74) reduce to

$$2D\,u = \varepsilon\,p \tag{76}$$

$$D^\mathrm{T} p + (B_1 + B_2)\,u = \varepsilon\,u. \tag{76}$$

From equations (76) and (77), one may reconstruct the matrix equation

$$\begin{pmatrix} 0 & 2D \\ D^\mathrm{T} & B_1 + B_2 \end{pmatrix} \begin{pmatrix} p \\ u \end{pmatrix} = \varepsilon \begin{pmatrix} p \\ u \end{pmatrix}, \tag{78}$$

which implies that $(N + n)$ of the $(2N + n)$ eigenvalues of G_1' are also eigenvalues of a graph G_+' which has as its adjacency matrix

$$\begin{pmatrix} 0 & 2D \\ D^\mathrm{T} & B_1 + B_2 \end{pmatrix}. \tag{79}$$

It is evident from the form of this matrix that G_+' is identical to the G_+ factor of a graph of the form of G_1 except that the former contains a directed edge of weight 2 from each q vertex to its adjacent vertex in r and a directed edge of unit weight from the r vertices to their neighboring q vertices. Since these directed edges between r and q vertices do not belong to a cycle in G_+', only the product of their weights is of interest, and therefore they can be replaced by two directed edges weighted $\sqrt{2}$ each, or, equivalently, by a single undirected edge weighted $\sqrt{2}$.[8]

Referring again to equations (73) through (75), consider the second alternative, that is, that $u = -v$. In this case, the left-hand side of equation (73) reduces to zero, and the difference between equations (74) and (75) becomes

$$(B_1 - B_2)\, u = \varepsilon\, u. \tag{80}$$

The second factor of G_1' is the graph whose adjacency matrix is given by $B_1 - B_2$; it is therefore identical to the G_- factor of G_1. Rules 1 through 4 for constructing the subspectral components of a graph of the form of G_1' follow immediately from this analysis.

It should be noted that, in the case of a bipartite graph for which a twofold symmetry operation exchanges starred and unstarred vertices, the G_+ component constructed by the rules exposed earlier in this section is identical to Hall's contraction graph; compare, for example, the graph G_+ (35), shown in Figure 2, to the contraction graph for 1,2,5,6-dibenzanthracene drawn according to Hall's rules. In the case of graphs for which the symmetry element is a plane perpendicular to the plane of the graph, G_+ and G are identical to McClelland's A-fragment and B-fragment, respectively; see, for example, G_+ (36) and G_- (36) in Figure 2. The present method is thus the most general method yet developed for factoring an arbitrary twofold-symmetric composite graph into its subspectral components.

3.5.2. Factorization of Graphs with Threefold Symmetry

A procedure for factoring an arbitrary threefold-symmetric composite graph into its subspectral components has been developed by means of mathematical manipulations which are exactly analogous to those employed in the case of twofold-symmetric composite graphs, that is, by performance of a unitary transformation on the eigenvalue equation of the adjacency matrix of the composite graph after numbering the vertices of the composite graph in a manner consistent with its threefold symmetry. The factorization procedure and its derivation will now be described.

Consider a graph G characterized by a threefold rotational operation which defines three equivalent sets of vertices r, s, and t and, possibly, a self-equivalent vertex q lying on the axis of rotation. The following rules may be used to construct two graphs, G_a and G_e, such that the eigenvalues of G_a and the eigenvalues of G_e taken twice comprise the complete spectrum of G.

1) First, draw the vertices in set r, together with all the edges connecting members of the set. Then examine in G the vertices through which r is connected to s, t, and possibly q (the bridging vertices of r).

2) If a bridging vertex r_1 is connected to a vertex t_2 which is symmetry--equivalent to a second bridging vertex r_2, then the weight of the undirected edge between r_1 and r_2 in G (+ 1 if they are adjacent, zero if

they are not) is increased by one unit in G_a. In G_e, the weight of the directed edge from r_2 to r_1 is increased by $\omega = \exp(2\pi i/3)$, and the weight of the directed edge from r_2 to r_1 is increased by $\omega^* = \exp(-2\pi i/3)$. Furthermore, if these directed edges do not belong to a cycle in G_e, they may be replaced by an undirected edge whose weight is equal to the square root of the product of the weights of the directed edges, i. e., either $\sqrt{\omega\omega^*} = 1$ or $\sqrt{(1+\omega)(1+\omega^*)} = 1$.

3) If a bridging vertex r_1 is connected to its own symmetry partners s_i and t_1 in G, then r_1 is weighted $+2$ in G_a and $(\omega + \omega^*) = -1$ in G_e.

4) If r_1 is connected to q in G, then the weight of the undirected edge between r_1 and q in G_a is $\sqrt{3}$; in G_e, this edge and the vertex q are omitted.

The application of these rules may be illustrated by the examples given in Figure 3.

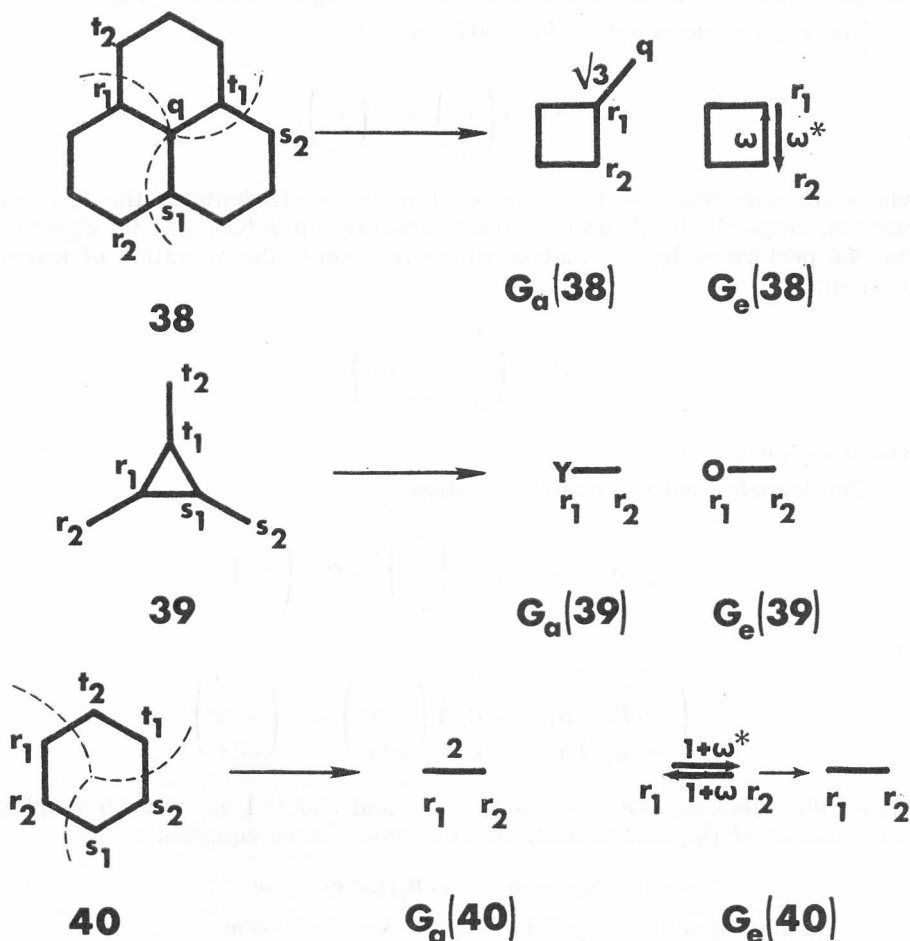
Figure 3. Factorization of the graphs representing acenaphthenyl (38), trimethylene-cyclopropenyl (39), and benzene (40) by the procedure of D'Amato.[40-42]

The derivation of these rules will first be given for the type of threefold--symmetric graph which contains $3N$ vertices, N vertices in each of the equivalent sets r, s, and t (graphs containing a vertex lying on the threefold rotational axis will be discussed in a later section). Let a graph of this type be denoted by G_2. If the vertices of G_2 are numbered in such a way that the number assigned to each vertex in s is N greater than the number assigned to its symmetry partner in r and N less than the number assigned to its symmetry partner in t, then the adjacency matrix of G_1 has the form:

$$A(G_2) = \begin{pmatrix} B_1 & B_2 & B_3 \\ B_3 & B_1 & B_2 \\ B_2 & B_3 & B_1 \end{pmatrix}. \tag{80}$$

The elements of the symmetric submatrix B_1 represent the adjacency relationships within a single set, r, s, or t; the elements of B_2 and $B_3 = (B_2)^{\mathrm{T}}$ represent the adjacency relationships between r and s, r and t, and s and t.

The eigenvalue equation for $A(G_2)$ is

$$A(G_2) \begin{pmatrix} u \\ v \\ w \end{pmatrix} = \varepsilon \begin{pmatrix} u \\ v \\ w \end{pmatrix}, \tag{81}$$

where the subvectors u, v, and w contain the coefficients of the r, s, and t vertices, respectively. A unitary transformation on $A(G_2)$ and its eigenvector may be performed by the matrix which represents the operation of threefold rotation:

$$C_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & \omega 1 \\ 0 & \omega^* 1 & 0 \end{pmatrix} = C_3{}^\dagger \tag{82}$$

where $\omega = \exp(2\pi i/3)$.

The transformed eigenvalue equation is

$$[C_3{}^\dagger A(G_2) C_3] C_3{}^\dagger \begin{pmatrix} u \\ v \\ w \end{pmatrix} = C_3{}^\dagger \begin{pmatrix} u \\ v \\ w \end{pmatrix} \tag{83}$$

or

$$\begin{pmatrix} B_1 & \omega^* B_2 & \omega B_2 \\ \omega B_2 & B_1 & \omega^* B_3 \\ \omega^* B_3 & \omega B_3 & B_1 \end{pmatrix} \begin{pmatrix} u \\ \omega w \\ \omega^* v \end{pmatrix} = \varepsilon \begin{pmatrix} u \\ \omega w \\ \omega^* v \end{pmatrix}, \tag{84}$$

where the identities $\omega^2 = \omega^*$, $(\omega^*)^2 = \omega$, and $\omega\omega^* = 1$ have been employed. Performance of the matrix multiplication gives three equations:

$$B_1 u + (\omega^* B_3)(\omega w) + (\omega B_2)(\omega^* v) = \varepsilon u \tag{85}$$

$$(\omega B_2) u + (\omega B_2) u + (\omega^* B_3)(\omega^* v) = \varepsilon \omega w \tag{86}$$

$$(\omega^* B_3) u + (\omega B_2)(\omega w) + B_1(\omega^* v) = \varepsilon \omega^* v. \tag{87}$$

These equations may be combined in several ways. The linearly independent combinations $(85) + \omega^* (86) + \omega (87)$, $(85) + \omega (86) + \omega^* (87)$, and $(85) + (86) + + (87)$ lead respectively to equations (88), (89), and (90):

$$(B_1 + \quad B_2 + \quad B_3)(u + \quad v + \quad w) = \varepsilon (u + \quad v + \quad w) \qquad (88)$$

$$(B_1 + \omega^* B_2 + \quad \omega B_3)(u + \omega^* w + \quad \omega v) = \varepsilon (u + \omega^* w + \quad \omega v) \qquad (89)$$

$$(B_1 + \quad \omega B_2 + \omega^* B_3)(u + \quad \omega w + \omega^* v) = \varepsilon (u + \quad \omega w + \omega^* v). \qquad (90)$$

Clearly, the N eigenvalues of the matrix $(B_1 + B_2 + B_3)$, the N eigenvalues of $(B_1 + \omega^* B_2 + \omega B_3)$, and the N eigenvalues of $(B_1 + \omega B_2 + \omega^* B_3)$ together constitute the complete spectrum of $A(G_2)$. Furthermore, since equation (90) is the complex conjugate of equation (89) and ε is real, the eigenvalues of the matrices $(B_1 + \omega^* B_2 + \omega B_3)$ and $(B + \omega B_2 + \omega^* B_3)$ are identical. Thus the graphs which have as their respective adjacency matrices $(B_1 + B_2 + B_3) = = B_a$ and $(B_1 + \omega B_2 + \omega^* B_3) = B_e$ are the subspectral components of G_2

The relationship between the forms of B_a and B_e and the rules for constructing the component graphs $G_{a,2}$ and $G_{e,2}$ may be clarified by means of the following examples. Consider first the benzene graph (40, shown in Figure 3) and its adjacency matrix,

$$A(40) = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} B_1 & B_2 & B_3 \\ B_3 & B_1 & B_2 \\ B_2 & B_3 & B_1 \end{pmatrix}. \qquad (91)$$

Notice that $(B_1)_{12} = (B_1)_{21} = 1$, since r_1 is adjacent to r_2, and that $(B_2)_{21} = = (B_3)_{12} = 1$, since r_1 is adjacent to t_2 and r_2 to s_1. B_a and B_e thus have the form,

$$B_a = (B_1 + B_2 + B_3) = \begin{pmatrix} 0 & 2 \\ 2 & 0 \end{pmatrix} \qquad (92)$$

$$B_e = (B_1 + \omega B_2 + \omega^* B_3) = \begin{pmatrix} 0 & 1 + \omega^* \\ 1 + \omega & 0 \end{pmatrix}. \qquad (93)$$

These matrices can be considered the adjacency matrices of the edge-weighted graphs G_a (40) and G_e (40), shown in Figure 3.

As a second example, the graph 39 in Figure 3 has the adjacency matrix,

$$A(39) = \begin{pmatrix} 0 & 1 & 1 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} B_1 & B_2 & B_3 \\ B_3 & B_1 & B_2 \\ B_2 & B_3 & B_1 \end{pmatrix}. \qquad (94)$$

The nonzero elements of B_1 are $(B_1)_{12} = 1$, since r_1 is connected to r_2; the nonzero elements of B_2 and B_3 are $(B_2)_{11} = (B_3)_{11} = 1$, because r_1 is connected to both s_1 and t_1. B_a and B_e are therefore given by

$$B_a = (B_1 + B_2 + B_3) = \begin{pmatrix} 2 & 1 \\ 1 & 0 \end{pmatrix} \tag{95}$$

$$B_e = (B_1 + \omega B_2 + \omega^* B_3) = \begin{pmatrix} \omega + \omega^* & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} -1 & 1 \\ 1 & 0 \end{pmatrix} \tag{96}$$

Again, these may be considered the adjacency matrices of the vertex-weighted graphs G_a (30) and G_e (39), also shown in Figure 3. The origin of rules 1 through 3 for constructing the component graphs of composite graphs of the form of G_2 should now be apparent.

Suppose that the composite graph of interest is identical to a graph of the form of G_2 except that it contains an additional vertex q which lies on the axis of rotation. Let this graph be denoted by G_2'. The adjacency matrix of G_2' can then be written in the form

$$A(G_2) = \begin{pmatrix} 0 & D & D & D \\ D^T & B_1 & B_2 & B_3 \\ D^T & B_3 & B_1 & B_2 \\ D^T & B_2 & B_3 & B_1 \end{pmatrix}. \tag{97}$$

The nonzero element of the $1 \times N$ vector D represents the edge between q and each of the sets r, s, and t; the $N \times N$ submatrices B_1, B_2, and B_3 represent the adjacency relationships within and among the sets r, s, and t, as previously described.

The matrix representing threefold rotation must now be written as

$$C_3' = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & \omega 1 \\ 0 & 0 & \omega^* 1 & 0 \end{pmatrix} = (C_3')^\dagger, \tag{98}$$

since rotation about the threefold axis leaves q unaffected. The eigenvalue equation for $A(G_2')$,

$$A(G_2') \begin{pmatrix} p \\ u \\ v \\ w \end{pmatrix} = \varepsilon \begin{pmatrix} p \\ u \\ v \\ w \end{pmatrix} \tag{99}$$

(where p is the coefficient of the vertex q), becomes under unitary transformation:

$$\begin{pmatrix} 0 & D & \omega^* D & \omega D \\ D^T & B_1 & \omega^* B_3 & \omega B_2 \\ \omega D^T & \omega B_2 & B_1 & \omega^* B_3 \\ \omega^* D^T & \omega^* B_3 & \omega B_2 & B_1 \end{pmatrix} \begin{pmatrix} p \\ u \\ w \\ {}^*v \end{pmatrix} = \varepsilon \begin{pmatrix} p \\ u \\ w \\ {}^*v \end{pmatrix} \tag{100}$$

Performance of the multiplication gives

$$D\ u + \ (\omega^* D)\,(\omega\,w) + \ \ (\omega\,D)\,(\omega^* v) = \varepsilon\,p \tag{101}$$

$$D^{\mathrm{T}} p + \ \ \ B_1 u + (\omega^* B_3)\,(\omega\,w) + \ \ (\omega\,B_2)\,(\omega^* v) = \varepsilon\,u \tag{102}$$

$$\omega\,D^{\mathrm{T}} p + \ (\omega\,B_2)\,u + \ \ \ B_1\,(\omega\,w) + (\omega^* B_3)\,(\omega^* v) = \varepsilon\,\omega\,w \tag{103}$$

$$\omega^*\,D^{\mathrm{T}} p + (\omega^* B_3)\,u + \ (\omega\,B_2)\,(\omega\,w) + \ \ \ B_1\,(\omega^* v) = \varepsilon\,\omega^* v. \tag{104}$$

Once again, equations (101) through (104) my be combined in several ways. Consider first a simplified form of equation (101) and the linear combination $(102) + \omega^* (103) + \omega\,(104)$:

$$D\,(u + v + w) = \varepsilon\,p \tag{105}$$

$$3\,D^{\mathrm{T}} p + (B_1 + B_2 + B_3)\,(u + v + w) = \varepsilon\,(u + v + w). \tag{106}$$

From (105) and (106) can be reconstructed the matrix equation:

$$\begin{pmatrix} 0 & D \\ 3\,D^{\mathrm{T}} & B_1 + B_2 + B_3 \end{pmatrix} \begin{pmatrix} p \\ u + v + w \end{pmatrix} = \varepsilon \begin{pmatrix} p \\ u + v + w \end{pmatrix} \tag{107}$$

which implies that $(N + 1)$ of the $(3N + 1)$ eigenvalues of G_2' are also eigenvalues of a graph $G_{\mathrm{a},2}'$ which has as its adjacency matrix the first matrix on the left-hand side of equatoin (107). It is evident from the form of this matrix that $G_{\mathrm{a},2}'$ is identical to $G_{\mathrm{a},2}$ except that the former contains a directed edge of unit weight from an r vertex to q and a directed edge of weight 3 from q to the r vertex. Since these directed edges between r and q do not belong to a cycle in $G_{\mathrm{a},2}'$, only the product of their weights is of interest, and therefore they may be replaced by a single undirected edge weighted $\sqrt{3}$.

Consider next a second, linearly independent combination of equations (102) through (104), $(102) + (103) + (104)$:

$$(1 + \omega + \omega^*)\,D^{\mathrm{T}} p + (B_1 + \omega\,B_2 + \omega^* B_3)\,(u + \omega\,w + \omega^* v) = \varepsilon\,(u + \omega\,w + \omega^* v). \tag{108}$$

Since $(\omega + \omega^*) = -1$, equation (108) reduces to equation (90); the second subspectral component of G_2' has as its adjacency matrix $(B_1 + \omega\,B_2 + \omega^* B_3) = B_e$ and is therefore identical to $G_{e,2}$. Rules 1 through 4 for constructing the subspectral components of a composite graph of the form of G_2' follow immediately from this analysis.

It should be noted that the mathematical manipulations employed here for the case of graphs with twofold and threefold symmetry can be applied to the treatment of planar graphs with higher-fold rotational symmetry. By numbering the vertices of such graphs in a manner consistent with their symmetry properties, and by choosing an appropriate matrix by which to perform the unitary transformation, rules may easily be developed for factoring symmetric composite graphs into their subspectral components. The general treatment presented here should prove useful for future investigations of graph spectral regularities.

3.6. Other Cases

Although most examples of subspectral coincidences can be explained by the various decomposition or factorization schemes described here, a few

others cannot. For instance, the eigenvalues of **31** are contained in the spectrum of **41**.

31   **41**
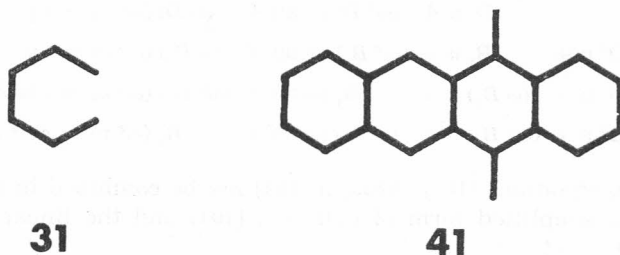
But decomposition of **41** along its plane of symmetry produces neither fragments directly related to **31** nor pieces that can be further reduced by the symmetry rules. Randić[78] has recently shown that a molecular orbital coefficient sum rule, based on nodal properties of the molecular orbitals, can explain the subspectral coincidences of **31** and **41**. Furthermore, the sum rule scheme can be used to construct other cases of subspectrality for which the methods described earlier do not apply.

3.7. *Chemical Behavior of Subspectral Molecules*

As in the case of isospectral molecules, the topologically-dependent properties of subspectral molecules seem to bear little relationship to one another. As shown in Table V, the ionization potentials of the subspectral molecules pentacene, naphthalene, and butadiene are quite dissimilar, as are the ionization potentials of ethylene, benzene, anthracene, and 1,1-diphenylethylene. Even those molecules which share HOMO/LUMO eigenvalues differ widely in their

TABLE V

Ionization Potentials of Several Subspectral Molecules[a]

Common HMO Eigenvalue	Pentacene	Naphthalene	Butadiene	Ethylene	Benzene	Anthracene	1,1-diphenyl-ethylene
$\varepsilon = 0.6180$	A_{1u} 7.93	A_{1u} 8.12	B_g 8.12				
$\varepsilon = 1.0000$	B_{2g} 8.35 B_{1g} 9.00	B_{3u} 8.91		A_u 10.50	B_{2g} 9.24 B_{1g}	B_{2g} 8.52 A_{1u} 9.16	B_1 A_2 9.05 A_2
$\varepsilon = 1.3028$	A_{1u} 9.80	B_{1g} 10.08					
$\varepsilon = 1.6180$	B_{2g} —	B_{2g} 10.85	A_u 11.25				
$\varepsilon = 2.0000$	B_{3g} —				B_{3u} 11.50	B_{2g} 11.9	A_2 10.25
$\varepsilon = 2.3028$	B_{2g} 10.26	B_{3u} 13.5					

UV-visible absorption characteristics and in their oxidation and reduction potentials, as shown in Table VI.

TABLE VI

Physicochemical Properties of Molecules Sharing HOMO/LUMO Eigenvalues

Subspectral Pair	Common Eigenvalue	λ_{max} (nm)[a]	Reduction Half-Cell[b] Potential (volts)	Oxidation Half-Cell[b] Potential (volts)
benzene	$\varepsilon = 1.0000$	$\lambda^{al} = 261$	< -2.5	2.30
ethylene		$\lambda^{gas} = 174$	$\ll -2.5$	2.90
naphthalene	$\varepsilon = 0.6180$	$\lambda^{al} = 311$	-2.50	1.54
1,3-butadiene		$\lambda^{al} = 217$	-2.64	2.03
pyrene	$\varepsilon = 0.4450$	$\lambda^{cy} = 335$	-2.11	1.16
1,3,5-hexatriene		$\lambda^{hx} = 266$	-2.65	—

[a] Values were obtained from reference 76.
[b] Values were obtained from reference 77.

A. Concluding Remarks

The fact that the characteristic polynomial does not uniquely represent the topology[79] of a molecule[17,80] ended attempts[14-16] to produce a sorting device, based on either the characteristic polynomial or the connectivity (adjacency) matrix for coding and retrieving chemical structures in computer oriented systems. One can see clearly how a notation system based on the adjacency matrix would have had excellent storage characteristics. However, the failure of this approach triggered attempts to find other graph-theoretical polynomials or topological indeces which could perhaps distinguish isospectral molecules[81-88].

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SAŽETAK

Izospektralne i subspektralne molekule

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Izospektralne molekule su strukture, koje posjeduju identične Hückelove spektre. Opisane su različite graf-teorijske metode za prepoznavanje izospektralnosti i za konstrukciju novih izospektralnih struktura.

Subspektralne molekule su različite strukture, kod kojih Hückelov spektar veće strukture sadrži cijeli ili dio spektra manje strukture. Prikazani su vrlo detaljno graf-teorijski pristupi za studiranje subspektralnosti. Pokazalo se da se svi poznati slučajevi subspektralnih molekula, osim jednoga, mogu objasniti pomoću metoda dekompozicije odgovarajućih grafova.

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