Facile Calculations of the Characteristic Polynomial and π-Energy Levels of Molecules Using Chemical Graph Theory

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Using mathematical graph theory, which is a rigorous subdivision of mathematics, one can model chemical structural concepts within a mathematical framework (1–3). The advantages of this approach include computational speed and a different conceptual perspective which leads to insights not possible otherwise (4). The purpose of this paper is to illustrate the application of chemical graph theory in the rapid calculation of the characteristic polynomial and pπ-energy levels of many conjugated polyenes without solving the Hückel MO secular determinant (5–7). Like the PMO method, chemical graph theory adds to the armaments available to the practicing organic chemist (8–11).

Terminology

Throughout this paper only the σ-bond graph will be drawn where the carbon and hydrogen atoms and the C–H and pπ bonds are omitted (6). A graph edge (line) and σ bond are synonymous, and a vertex (point) is equivalent to a carbon atom (carbon vertex). A primary carbon has a degree of one, a secondary carbon has a degree of two, and a tertiary carbon has a degree of three. Both benzene and cyclohexane have the same σ-bond molecular graph, which is a hexagon that consists of only second-degree vertices joined by $e(2,2)$-type edges.

A factor of a graph G is a spanning subgraph (spans all the carbon atom vertices) that is not totally disconnected. When G has a 1-factor, then p (the number of carbon atom vertices) must be even and the 1-factor lines are point disjoint. The number of different 1-factors of a PAH σ-bond graph is equal to the number of Kekulé structures or structure count ($K = SC$). A graph is 2-factorable if it has spanning subgraphs that are regular of degree 2. Examples of a 1-factor and the only 2-factor of naphthalene is presented by the following.

naphthalene σ-bond molecular graph   2-factor   1-factor
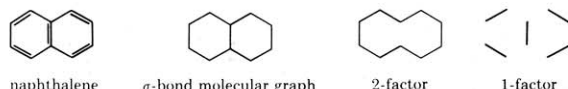
Each fragment in a 1-factor subgraph is a K_2 component. All the eigenvalues of a graph are collectively called the spectrum of the graph. If the eigenvalues of a smaller graph are contained among the eigenvalues of a larger graph, then the smaller graph is said to be subspectral to the larger one. A 2-factor subgraph on n vertices is called a cycle C_n on n vertices. The 2-factor subgraph of naphthalene has one C_{10} component and its 1-factor subgraph has five components.
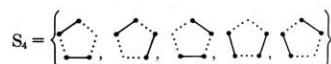
Characteristic Polynomial

Expansion of the Hückel molecular orbital (HMO) secular determinant for a PAH graph gives the characteristic polynomial $P(G; x) = \det |x\mathbf{I} - \mathbf{A}|$ of the corresponding conjugated system where $\mathbf{I}$ is the identity matrix, $x = (E - \alpha)/\beta$, and $\mathbf{A}$ is the adjacency matrix (5). The characteristic polynomial of N carbon atom system has the following form

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

where a_n are coefficients that can be alternatively obtained by the graphical Sachs method which is a formalized variant of the procedure first presented by Coulson (2, 12, 13). This method is summarized by the following formula

$$a_n = \sum_{s \in S_n} (-1)^{c(s)} 2^{r(s)}$$

where $0 \le n \le N$, s is a Sachs graph, S_n is a set of all Sachs graphs with exactly n vertices, $c(s)$ is the number of components, and $r(s)$ is the total number of rings (cycles) in s. The components of a Sachs graph can be either K_2 or cycles $C_m(m = 3, 4, \ldots, N)$ or combinations of lK_2 and kC_m such that $2l + km = n$. By definition $a_0 = 1$. Since only K_2 and C_m components are allowed, $S_1 = \phi$ and $a_1 = 0$. The set S_2 of all Sachs graphs on two vertices leads to the value of $a_2 = -q$ which is equal to the negative number of graph edges (σ bonds). Only C_m components or C_n components together with K_2 components are allowed for $m = $ odd. Consider the cyclopentadienyl system. The set of Sachs graphs of S_3 is zero since there are no trigonal rings in the cyclopentadienyl molecule. For S_4 the following enumerates all the Sachs graphs on four vertices

which gives $a_4 = 5 (-1)^2 2^0 = 5$. For S_5, $a_5 = (-1)2 = -2$. Thus the characteristic polynomial for the cyclopentadienyl molecule is $P(C_5H_5; x) = x^5 - 5x^3 + 5x - 2$.

Previously the author derived the following general equations for the fourth and sixth coefficients of the characteristic polynomial

$$a_4 = (1/2)(q^2 - 9q + 6N_C) - 2r_4 - d_1 - d_4 - 3d_5 - 6d_6 - \ldots \quad (1)$$

$$a_6 = -(1/6)(q^3 - 27q^2 + 116q) - N_C(3q - 16)$$

$$- e(3,3) - 2r_6 + (q - 6)e(2,1)$$

$$+ (q - 5)e(3,1) + 2(q - 4 - \alpha_4)r_4 + r_3 \quad (2)$$

where $q = $ no. of C–C σ bonds, $N_C = $ no. of carbon vertices, $r_n = $ no. of rings of size n, $d_i = $ no. of carbon vertices of degree-i, $e(i, j) = $ no. of edges (C–C σ bonds) with end points of degree i and degree j, and $a_4 = $ no. of attachments or branches on the tetragonal ring (5). Equation 1 is valid for all graphs and eq 2 is valid for all graphs having vertices of degree 1 to 3 and having no more than one trigonal or one tetragonal ring. With eq 1 and eq 2 the characteristic of polynomial of small molecules can be quickly generated by inspection.

We will now illustrate with examples from Figure 1 how to generate the characteristic polynomial of small molecules
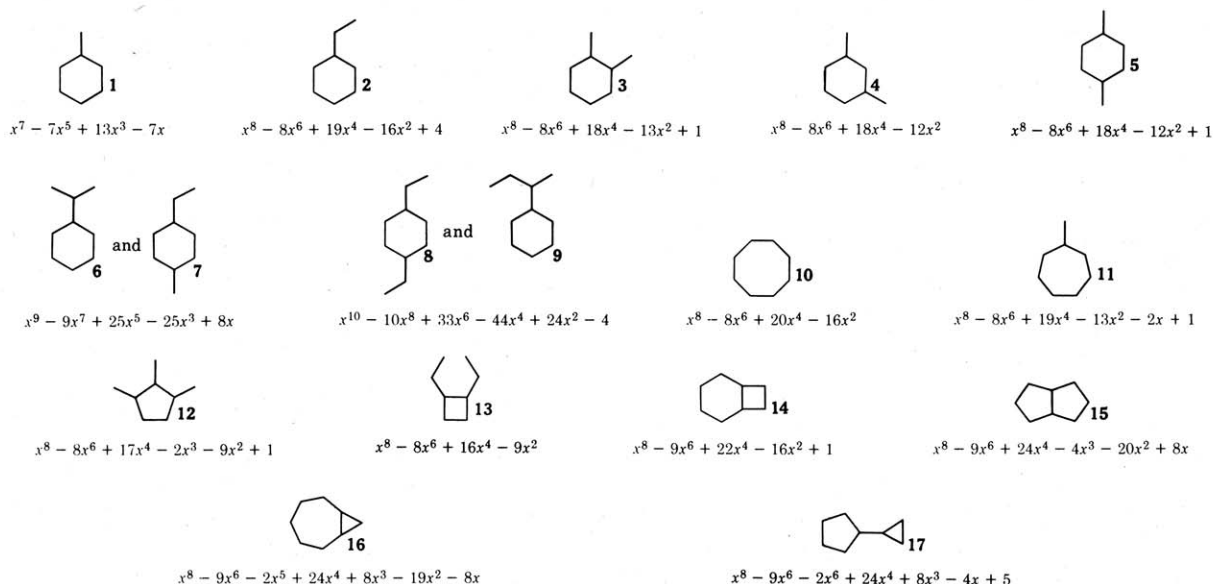
Figure 1. Representative small molecular graphs and their corresponding characteristic polynomials where $x = (E - \alpha)/\beta$.

The polynomials shown are:

1: $x^7 - 7x^5 + 13x^3 - 7x$

2: $x^8 - 8x^6 + 19x^4 - 16x^2 + 4$

3: $x^8 - 8x^6 + 18x^4 - 13x^2 + 1$

4: $x^8 - 8x^6 + 18x^4 - 12x^2$

5: $x^8 - 8x^6 + 18x^4 - 12x^2 + 1$

6 and 7: $x^9 - 9x^7 + 25x^5 - 25x^3 + 8x$

8 and 9: $x^{10} - 10x^8 + 33x^6 - 44x^4 + 24x^2 - 4$

10: $x^8 - 8x^6 + 20x^4 - 16x^2$

11: $x^8 - 8x^6 + 19x^4 - 13x^2 - 2x + 1$

12: $x^8 - 8x^6 + 17x^4 - 2x^3 - 9x^2 + 1$

13: $x^8 - 8x^6 + 16x^4 - 9x^2$

14: $x^8 - 9x^6 + 22x^4 - 16x^2 + 1$

15: $x^8 - 9x^6 + 24x^4 - 4x^3 - 20x^2 + 8x$

16: $x^8 - 9x^6 - 2x^5 + 24x^4 + 8x^3 - 19x^2 - 8x$

17: $x^8 - 9x^6 - 2x^6 + 24x^4 + 8x^3 - 4x + 5$

quickly without having to solve any secular determinant. The benzyl radical (**1**) is an odd-alternant hydrocarbon with $-a_2 = q = 7$, $a_4 = 13$, and $a_6 = -7$; $a_3 = a_5 = a_7 = 0$ because **1** has no trigonal, pentagonal, or heptagonal rings. Styrene (**2**) is an even-alternant hydrocarbon with $a_8 = 4$ because styrene has two Kekulé structures ($K = 2$) and $|a_N| = K^2$ for alternant hydrocarbons without antiaromatic components. Similarly, **3** and **5** have $a_8 = 1$ because they have only one Kekulé structure. Since **4** is a diradical with no Kekulé structures, $a_8 = 0$. Structures **10** and **13** are even-alternant hydrocarbons that are antiaromatic and therefore $a_8 = 0$. Even nonalternant hydrocarbons characteristically have odd rings with a tail coefficient of one, if they also possess pendant bonds like **11** and **12**. Thus all molecules with six or fewer vertices can unequivocally have their characteristic polynomial reproduced by inspection, and molecules with 7, 8, 9, or 10 vertices can have their characteristic polynomials reproduced by inspection if some other information is available. This information could be knowledge of one or more eigenvalue by virtue of the molecule's symmetry, embedding, or alternant characteristics, such as $a_N = \pm K^2$ where K is the number of Kekulé structures (1-factors). Thus, since naphthalene has $K = 3$ and $\epsilon = \pm 1$, its characteristic polynomial is easily computed to be $P(C_{10}H_8; x) = x^{10} - 11x^8 + 41x^6 - 65x^4 + 43x^2 - 9$ from eq 1 and eq 2. A method for determining select eigenvalues (or subspectral components) in many alternant hydrocarbons by embedding will now be described.

Subspectral Components

Benzenoid hydrocarbons having a plane of symmetry perpendicular to the molecular plane and passing through carbon atoms can be decomposed into smaller molecular fragments having eigenvalues that are present in the undecomposed parent molecule (7). Thus benzene can be decomposed into ethene, and both possess $\epsilon = \pm 1.0\beta$ (Fig. 2). That is, ethene is subspectral to benzene. Similarly, butadiene is subspectral to naphthalene and has the eigenvalues of 1.161803, 0.61803, −0.61803, and −1.61803β; note that the golden ratio is $\phi = 2/(\sqrt{5} - 1) = 1.61803 = 1/0.61803$. Benzene is subspectral to anthracene which in turn is subspectral to heptacene and, therefore, all these PAH6's have eigenvalues of $\epsilon = \pm 1.0, \pm 1.0$, and $\pm 2.0\beta$.

In a series of papers, Hall provided the basis for recognition of the HMO eigenvalues of $\epsilon = \pm 1.0$ and $\pm 2.0\beta$ by inspection of the molecular topology of alternant hydrocar-
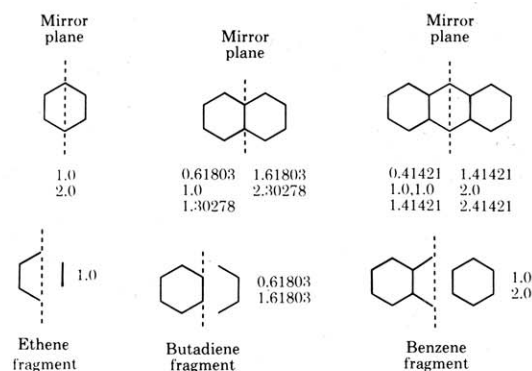

Figure 2. Mirror plane decomposition of representative benzenoids into smaller fragments possessing common eigenvalues.

bons (7, 14). His rules derive immediately from the eigenvector equations themselves and were translated into descriptive form that will now be reviewed. Molecules with a unit eigenvalue will have a corresponding MO such that the coefficients at each atom equals the sum of coefficients of its nearest neighbors.

To embed a fragment into a molecule repetitively the following rules must be followed: (1) all atoms connected directly to the fragment must be nodes; (2) on the other side of each of these nodes will be the repetition of the fragment with the opposite sign; and (3) other branches at these nodes will also be nodes since at all nodes the sum of nearest neighbor fragments must be zero in regard to their signs. Ethene, allyl, butadiene, and benzene are the most common fragments embedded in benzenoid hydrocarbons. All notes are designated in the figures by open circles. Thus by embedding (Fig. 3), it is predicted that all acenes have the eigenvalues of ethene ($\epsilon = \pm 1\beta$) and all odd ring acenes have the eigenvalues of benzene ($\epsilon = \pm 1$ and $\pm 2\beta$). Furthermore, anthracene, heptacene, etc. have eigenvalues of $\epsilon = \sqrt{2}\beta$ by allyl embedding and naphthalene, pentacene, octacene, etc. have the eigenvalues of butadiene. Note that in the embed-

a) Ethene embedding of acenes

b) Benzene embedding acenes

c) Allyl Embedding of acenes
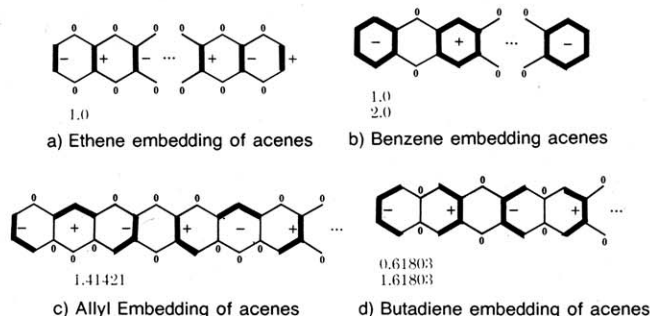

d) Butadiene embedding of acenes

Figure 3. Repetitive embedding of small fragments in acene molecules.

ding of allyl and butadiene fragments in Figure 3, corresponding fragment positions always align through each node.

Embedding of methyl radicals on 1,3-cyclobutadiene or 1,3,5,7-cyclooctatetraene explains why these conjugated monocyclic systems are diradicals since the signs of the embedded fragments must alternate.

$\epsilon = 0$

$\epsilon = 0$

Phenalenyl monoradical can be embedded by two pentadienyl radicals or three and four ethene units as shown by the following.

$\epsilon = 0, \pm 1, \pm \sqrt{3}$

$\epsilon = \pm 1$

$\epsilon = \pm 1$
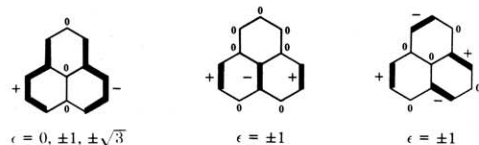
Because of the *pairing theorem* and since embedding has demonstrated that $\sqrt{2}$, $\sqrt{3}$, and 2 are frequent eigenvalues, then 2, 3, and 4 should be frequent factors of $|a_N| = K^2$ for even carbon benzenoids. Note that mixed embedding with more than one type of substructure without common eigenvalues is not allowed. Embedding is a sufficient but not a necessary requirement for the presence of a set of eigenvalues. The embedding of fragments with different kinds of vertices should be done in such a manner that equivalent positions on different fragments always match up through each node position. The following illustrates an improper and a proper embedding of 1,3-butadiene.

Not a proper embedding

$\epsilon = \bullet 0.61803, \pm 1.61803$
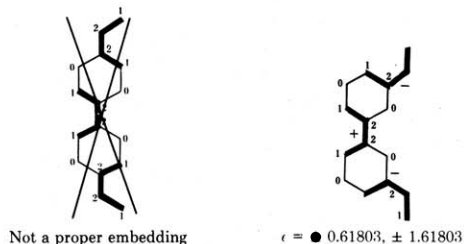
Structures **1, 2, 5, 6, 7,** and **8** all have either a plane or pseudoplane of symmetry perpendicular to the molecular plane and passing through two carbon vertices giving an ethene fragment, and thus they all have $\epsilon = \pm 1\beta$ as an eigenvalue pair (Fig. 1). Note that the two pairs of structures, **6** and **7** and **8** and **9**, each have identical characteristic polynomials (Fig. 1) and are therefore isospectral (*15*). Both **8** and **9** can be embedded by ethene substructures with para

ring nodes. Neither **3** nor **4** can be embedded by ethene. Structures **4, 10,** and **15** have a plane of symmetry giving an allyl fragment, but only the former two structures are alternant hydrocarbons capable of being prescribed by embedding with allyl; note that **15** appears to be embeddable by allyl fragments even if it is not an alternant hydrocarbon. Structure **13** has an eigenvalue pair of $\epsilon = \pm 1\beta$ but cannot be embedded by ethene. If the symmetry plane bisects an edge between vertices k and l, then the weight of the vertex in the separated fragment increases by one in the reduced determinant associated with the fragment (Fig. 4). Thus structures **11, 12,** and **16** have the same fragment and at least three common eigenvalues ($\epsilon = 1.2470, -0.44504,$ and -1.8019β). Styrene (**2**) can be embedded by allyl fragments as follows and, therefore, has $\epsilon = \pm \sqrt{2}\beta$ as eigenvalues.

Although embedding is a trial-and-error process, with some practice the reader will note that certain general structural patterns will emerge. For example, placement of heteroatoms or polyene substituents at node positions in any of the example structures presented in this paper does not change the embedding or associated HMO eigenvalues where $\alpha_X = \alpha_C + h\beta_{CC}$ and $\beta_{CX} = k\beta_{CC}$. Consider anthracene which can be embedded by allyl, benzene, and ethene substructures giving it eigenvalues of $\epsilon = \pm 1, \pm 1, \pm \sqrt{2}$, and $\pm 2\beta$; if a carbon atom is substituted by a heteroatom X at position 9, then these eigenvalues remain unchanged while the others change. If a carbon atom at position 1 in anthracene is substituted by a heteroatom, then the resulting structure can be embedded only by allyl and ethene substructures where the heteroatom is located at a node position giving eigenvalues of $\epsilon = \pm 1$ and $\pm \sqrt{2}\beta$. If a heteroatom is located at position 2 in the anthracene skeleton, then the resulting structure can only be embedded by ethene where the heteroatom is located at a node position giving $\epsilon = \pm 1\beta$. Replacement of two carbon atoms by heteroatoms at positions 9 and 10 in anthracene leads to a structure that can be embedded by ethene and benzene giving eigenvalues of $\pm 1, \pm 1,$ and
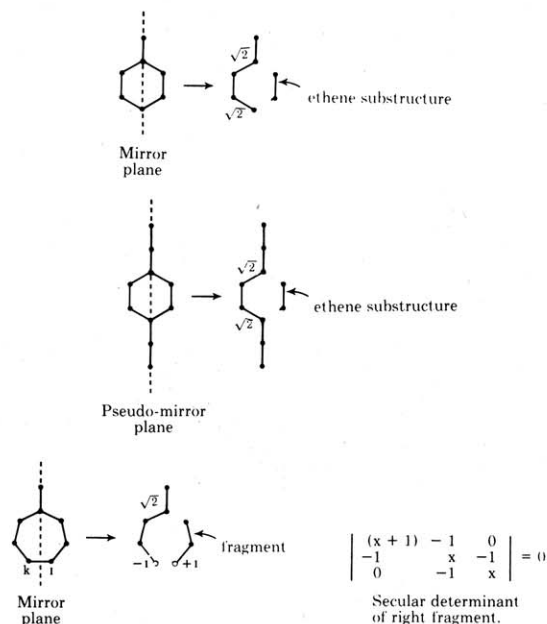

Figure 4. Mirror plane fragmentation of some representative small molecules.

$\pm 2\beta$. Similarly, placing ethenyl substituents at these various positions in anthracene leads to equivalent results. This process just described has features making it similar to Dixon's construction method, which appears to be equivalent to retro-embedding (16).

Summary

Graph theory is mathematically rigorous and exact. Part of the intuitive *modus operandi* in teaching of organic chemistry is that many molecular properties are topological in origin and can be represented by chemical (molecular) graphs. Because this aspect is ingrained in the method by which we approach chemistry, graph theory appeals more directly to the way chemists think and perceive chemical fundamentals.

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