

Chemical Graph Theory. II. On the Graph Theoretical Polynomials of Conjugated Structures

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Abstract

The graph theoretical polynomials of conjugated structures are examined, namely, the characteristic polynomial, the acyclic polynomial, the Hosoya polynomial, the sextet polynomial, the cyclic polynomial, and the Wheland polynomial. Several novel relationships among them have been obtained.

Introduction

There are several polynomials available for characterizing molecular (chemical) graphs [1], although they are not all equally efficient in so doing. Here we will examine the characteristic polynomial $P(G;x)$, the acyclic polynomial $P^{ac}(G;x)$, the Hosoya polynomial $P^h(G;x)$, the sextet polynomial $P^s(G;x)$, the cyclic polynomial $P^c(G;x)$, and the Wheland polynomial $P^w(G;x)$. We will consider only Hückel graphs [2,3], i.e., hydrogen-suppressed molecular graphs representing conjugated structures. (Hückel graphs are undirected, planar, and connected graphs with the maximal topological valency 3.)

Many of the above polynomials can be used, and are often used [4], for characterizing much wider families of graphs than the Hückel graphs. The graph theoretical polynomials depend on topological [5] properties of (Hückel) graphs and appear to be helpful devices for understanding the origin of such diverse characteristics of conjugated molecules as the number of Kekulé and Dewar valence structures and the pairing theorem.

The Characteristic Polynomial

When solving the eigenvalue problem for a graph G , the following determinant is considered:

$$P(G;x) = \det[x\mathbf{I} - \mathbf{A}] \quad (1)$$

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where I and A stand for the unit matrix and the (vertex) adjacency matrix [6] of G . $P(G;x)$ is called the characteristic polynomial of G and is of degree N (N being the number of vertices in a graph) [7],

$$P(G;x) = \sum_{n=0}^N a_n(G)x^{N-n} \quad (2)$$

where $a_n(G)$ ($n = 0, 1, 2, \dots, N$) are the coefficients of the polynomial. The characteristic polynomial is important for conjugated structures because of the identity of Hückel matrix, within the normalized Hückel theory, and adjacency matrix [8]. The Hückel Hamiltonian is a local operator [9] and is a unique function of the adjacency matrix [10]. The meaning of this result is that the roots of $P(G;x)$ are identical to the Hückel levels of a molecule [11]. Thus, the structure of $P(G;x)$ contains the information about the number of bonding (N_+), nonbonding (N_0), and antibonding (N_-) orbitals of a given conjugated system. These quantities are indeed readily available from the characteristic polynomial of the molecule by means of the following relations [12] (where Ch denotes the number of sign changes in the sequence of polynomial coefficients) [13]:

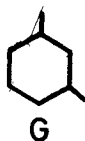
$$a_N(G) = a_{N-1}(G) = \dots = a_{N-N_0+1}(G) = 0 \quad (3)$$

$$a_{N-N_0}(G) \neq 0 \quad (4)$$

$$Ch[a_N(G), a_{N-1}(G), \dots, a_1(G), a_0(G)] = N_+ \quad (5)$$

$$N_+ + N_0 + N_- = N \quad (6)$$

As an example consider the characteristic polynomial of *m*-xylylene.



$$P(G;x) = x^8 - 8x^6 + 17x^4 - 10x^2$$

$$Ch(-10, +17, -8, +1) = N_+ = 3$$

Since $N = 8$ and $N_0 = 2[a_N(G) = a_{N-1}(G) = 0]$, $N_- = 3$. Thus, *m*-xylylene belongs to the class of conjugated structures [14] characterized by $N_+ = N_-$, and $N_0 > 0$, and it should be a reactive species. The spectrum of *m*-xylylene $\{-2.17533, -1.41421, -1.12603, 0, 0, 1.12603, 1.41421, 2.17533\}$ [15] is in accord with the above result.

A lot of research is done on generating the coefficients $a_n(G)$ of $P(G;x)$ from the structure of the graph [16–23a]. Most elegant, if not the most practical [21,24], is a method of Sachs [25], which can be best summarized in the following formula [26]:

$$a_n(G) = \sum_{s \in S_n} (-1)^{c(s)} 2^{r(s)}; \quad 0 \leq n \leq N \quad (7)$$

where s is a Sachs graph [26], S_n is a set of all Sachs graphs with exactly n vertices, while $c(s)$ and $r(s)$ denote, respectively, the total number of components and the total number of cycles (rings) in s . The components of a Sachs graph can be either K_2 (isolated bonds) or cycles C_m ($m = 3, 4, \dots, N$) or combinations of lK_2 and kC_m , with the restriction $2l + km = n$.

The characteristic polynomial can now be expressed in a different form obtained by introducing Eq. (7) into Eq. (2):

$$P(G; x) = \sum_{n=0}^N \sum_{s \in S_n} (-1)^{c(s)} 2^{r(s)} x^{N-n} \quad (8)$$

This relation can help us to see, in a direct way, how the structure of $P(G; x)$ reflects the topology of a given graph (molecule). Below we summarize some results which support the above statement:

(i) Since the legal Sachs graphs are K_2 and C_m , there cannot be a Sachs graph of conjugated hydrocarbons with only one vertex. Therefore, it is always valid,

$$S_1 = \emptyset \quad (9)$$

$$a_1(G) = 0 \quad (10)$$

The meaning of the above is that the sum of the roots of $P(G; x)$ is always zero:

$$a_1(G) = \sum_{i=1}^N x_i = 0 \quad (11)$$

Nonvanishing values of a_1 coefficients appear only when heteroconjugated structures are considered. Heteroconjugated structures are represented by the vertex- and edge-weighted graphs G_{VEW} [27,28]. In these systems the heteroatoms and the connecting heterobonds are singled out by having "weights" h (vertices) and k (edges). These "weights" are equal to Hückel parameters used in heteroconjugated systems [8]. Thus,

$$-a_1(G_{\text{VEW}}) = \sum_i h_i \quad (12)$$

where h_i stands for i th heteroatomic parameter ("weight"). In addition, the sum of the whole spectrum (the set of all eigenvalues) of G_{VEW} is equal to the sum of the chosen parameters of the "weighted" vertices appearing in it:

$$\sum_{i=1} x_i = \sum_i h_i \quad (12a)$$

(ii) The computation of the characteristic polynomial, using formula (8) [26,29], reveals that the a_2 and a_3 coefficients are related to the number of bonds e and the three-membered rings C_3 , respectively, in G ,

$$-a_2(G) = e \quad (13)$$

$$-1/2 a_3(G) = C_3 \quad (14)$$

In addition, it can be shown that the sum of squares of polynomial roots is related to the a_2 coefficient and, consequently, to the number of bonds (edges) in a structure (graph),

$$-2a_2(G) = \sum_{i=1}^N x_i^2 = 2e \quad (15)$$

For heteroconjugated systems, with one heteroatom, Eq. (13) changes,

$$-a_2(G) = e + 2k^2 \quad (16)$$

where e stands for the number of the "normal" carbon-carbon bonds.

(iii) Alternant hydrocarbons [30] may be described as bipartite graphs. Bipartite graphs, by a theorem [31], do not contain odd-membered cycles. Hence it follows that for alternant structures $S_n = \emptyset$ and $a_n(G) = 0$ for $n = 2j + 1$. Therefore, the characteristic polynomial of an alternant hydrocarbon is necessarily of the form,

$$P(G;x) = \sum_{j=0}^{[N/2]} (-1)^j a_{2j}(G) x^{N-2j} \quad (17)$$

where the coefficients $a_{2j}(G)$ are the non-negative quantities for all j . The structure of the polynomial (17) is such that the corresponding spectrum *must* be symmetrically arranged with respect to $x = 0$, because if x is a root of Eq. (17), then $-x$ must be also a root. This is a simple demonstration of the pairing theorem [32].

(iv) For alternant heteroconjugated systems, like *s*-triazine, a theorem similar to the pairing theorem exists. The theorem states that the eigenvalues of alternant heteroconjugated structures, with the atoms in one set weighted, will be arranged symmetrically with respect to the vertex weight h , i.e.,

$$x_i + x_{N+1-i} = h \quad \text{for } 1 \leq i \leq N \quad (18)$$

To illustrate the use of the above theorem, consider 1,3-diazacyclobutadiene:



Its characteristic polynomial is given below,

$$P(G;x) = x^4 - 2hx^3 - (4k^2 - h^2)x^2 + 4hk^2x$$

If the parameter k equals unity the solutions of this polynomial are

$$\begin{aligned} x_1 &= \frac{h + (h^2 + 16)^{1/2}}{2} \\ x_2 &= h \\ x_3 &= 0 \\ x_4 &= \frac{h - (h^2 + 16)^{1/2}}{2} \end{aligned}$$

and are paired about h as predicted.

(v) The analysis of the structural origin of the a_N coefficient of $[N]$ -annulenes may be used for rationalizing the Hückel $(4n + 2)$ rule [33]. A cycle with N ($=$ even) vertices, depicting $[N = \text{even}]$ -annulene, has *only* three Sachs graphs with N vertices, two of them consisting of K_2 components and the third a C_N cycle. Thus, the $a_N(G)$ coefficient is given by the following formula obtained from the use of relation (7):

$$a_N(G) = (-1)^{N/2} 2^0 + (-1)^{N/2} 2^0 + (-1)^1 2^1 = \begin{cases} 0 & \text{for } N = 4n \\ -4 & \text{for } N = 4n + 2 \end{cases} \quad (19)$$

An additional result arises from the above consideration. Since annulenes with $(4n + 2)$ or $(4n)$ atoms are alternant structures it follows that for $a_N(G) = 0$ there must be, at least, two zero elements in the spectrum of the corresponding annulene as required by the pairing theorem. It appears that such structures are rather unstable [34].

A polynomial tail $a_N(G)$ for $[N = \text{odd}]$ -annulenes is constructed from only one Sachs graph, and that is an odd-membered cycle,

$$a_N(G) = (-1)^1 2^1 = -2 \quad \text{for } \begin{cases} N = 4n + 1 \\ \text{or} \\ N = 4n + 3 \end{cases} \quad (20)$$

(vi) Another bit of information contained in the tail of $[N = \text{even}]$ -annulenes is significant in that it gives the number of Kekulé structures (1 factors) [7] of $[4n + 2]$ -annulene(s),

$$a_N(G) = -K^2 \quad (21)$$

However, the appearance of $a_{N(N=4n)}(G) = 0$ is connected with the parity of Kekulé structures [35]. Therefore, the more general expression for the annulene tail should be as follows:

$$a_N(G) = \begin{cases} -(K^+ + K^-)^2 & \text{for } N = 4n + 2 \\ +(K^+ + K^-)^2 & \text{for } N = 4n \end{cases} \quad (22)$$

where K^+ denotes Kekulé structures with *even* and K^- with *odd* parity. Since Kekulé structures can be represented by determinants [36], it appears that even permutations of columns (or rows) lead to the same parity of Kekulé structures, while odd permutations lead to structures with different parity [37]. For example, to convert one of the benzene Kekulé structures to the other an even number of column permutations in the Kekulé determinant is needed, while for the same process in the case of cyclooctatetraene an odd number of permutations is required. Consequently, both Kekulé structures of benzene have the same parity while Kekulé structures of cyclooctatetraene have the opposite parity. Therefore, for cycles with $N/2 = \text{odd}$, Kekulé's structures are of the same parity; while for cycles with $N/2 = \text{even}$, the Kekulé structures are of the opposite

parity.* This is the origin of the tail having in $[4n + 2]$ -annulene nonvanishing value while in $[4n]$ -annulenes it vanishes,

$$[4n + 2]\text{-annulenes: } a_N(G) = -(2 + 0)^2 = -4 \quad (23)$$

$$[4n]\text{-annulenes: } a_N(G) = +[1 + (-1)]^2 = 0 \quad (24)$$

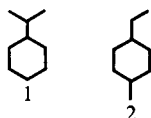
These considerations also reveal the intimate connection between the resonance theory and the simple (Hückel) molecular orbital theory.

(vii) The derivative of the characteristic polynomial of a graph G , $P'(G;x)$, is equal to the sum of the characteristic polynomials of subgraphs $G - v_i$ ($i = 1, 2, \dots, N$), $P(G - v_i;x)$, derived by excising a single vertex v_i from G at the time [37b,37c],

$$P'(G;x) = \sum_i P(G - v_i;x) \quad (24a)$$

The above result states that a collection of subgraphs obtained from G by a successive removal of a single vertex is unique to that graph. This is illustrated in Table I.

(viii) In concluding this section we wish to mention that the characteristic polynomial does not uniquely determine the topology of a (conjugated) molecule because it has been found [11,18,22,23,38] that two or more graphs which are nonisomorphic may have the same characteristic polynomials. For example, molecules **1** and **2** are isospectral, because they have identical characteristic polynomials: $P(G_1;x) \equiv P(G_2;x) = x^9 - 9x^7 + 25x^5 - 25x^3 + 8x$.



The Acyclic Polynomial

The acyclic polynomial of a graph has been recently defined [39] as

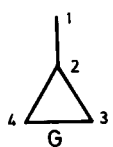
$$P^{ac}(G;x) = \sum_{n=0}^N a_n^{ac}(G)x^{N-n} \quad (25)$$

This polynomial is closely related to the characteristic polynomial of a graph and it is the essential quantity in the topological theory of aromaticity [40–43]. Coefficients $a_n^{ac}(G)$ of $P^{ac}(G;x)$ contain only acyclic contributions and can be constructed by means of the conveniently adapted Sachs formula (7),









$$a_n^{ac}(G) = \sum_{s \in S_n^{ac}} (-1)^{c(s)}; \quad 0 \leq n \leq N \quad (26)$$

* Parity is, of course, defined for a pair of valence structures and has significance only when the relative effects of such structures are discussed. It cannot be assigned to an individual structure, since it is not invariant to symmetry operations. It should be noted that the parity concept fails in some nonalternant systems [37a].

TABLE I



$P(G;x) = x^4 - 4x^2 - 2x + 1$
 $P'(G;x) = 4x^3 - 8x - 2$

	G	$G - v_i$	$P(G - v_i;x)$
$i = 1$			$x^3 - 3x - 2$
$i = 2$			$x^3 - x$
$i = 3$			$x^3 - 2x$
$i = 4$			$x^3 - 2x$
	$\sum_i P(G - v_i;x) = 4x^3 - 8x - 2$		

where S_n^{ac} is a set of all acyclic Sachs graphs with exactly n vertices. A Sachs graph s is called acyclic if $r(s) = 0$. Therefore, only K_2 components of a graph are used in building up the acyclic polynomial. It appears that $P^{\text{ac}}(G;x)$ is a fundamental combinatorial mathematical structure. For example, the identities between the acyclic polynomial and some special functions, e.g., Chebyshev, Hermite, and Laguerre polynomials, are established [44]. Below we list some properties of the acyclic polynomial:

(i) The tail of the acyclic polynomial is equal to the number of Kekulé structures,

$$a_N^{\text{ac}}(G) = -K \quad (27)$$

(ii) The characteristic and acyclic polynomials are related in the following way [42,45,46]:

$$\begin{aligned}
 P(G;x) - P^{\text{ac}}(G;x) = & -2 \sum_m P^{\text{ac}}(G - C_m;x) \\
 & + 4 \sum_{m < n} P^{\text{ac}}(G - C_m - C_n;x) \\
 & - 8 \sum_{m < n < p} P^{\text{ac}}(G - C_m - C_n - C_p;x) + \dots \quad (28)
 \end{aligned}$$

where the summations go over all pairs, triplets, etc., of mutually disjoint cycles which are contained in G . $G - C_m$, $G - C_m - C_n$, $G - C_m - C_n - C_p$, . . . , etc., are subgraphs obtained by removing successively the vertices of C_m ; C_m , and C_n ; C_m , C_n , and C_p ; . . . ; from G . The difference $P(G;x) - P^{\text{ac}}(G;x)$ is not, in general, linear and is suggestive that the aromatic stability of polycyclic systems depends only on the contributions of cycles to the total π -electron energy [47a].

In the case of annulenes the difference between $P(G;x)$ and $P^{\text{ac}}(G;x)$ is rather simple. The acyclic polynomial of $[N]$ -annulene, depicted by cycle C_N , can be given as

$$P^{\text{ac}}(C_N;x) = \sum_{k=0}^{[N/2]} (-1)^k p(C_N;k) x^{N-2k} \quad (29)$$

where $p(C_N;k)$ is the k number of ways in which K_2 graphs can cover the cycle C_N with the restriction that no two of them are connected. If we present the characteristic polynomial of $[N]$ -annulene in the similar way:

$$P(C_N;x) = \sum_{k=0}^{[N/2]} (-1)^k p(C_N;k) x^{N-2k} - 2 \quad (30)$$

then, the difference between $P(C_N;x)$ and $P^{\text{ac}}(C_N;x)$ is given by

$$P(C_N;x) - P^{\text{ac}}(C_N;x) = -2 \quad (31)$$

Since $P^{\text{ac}}(C_N - C_N;x) = 1$ by definition, Eq. (28) reduces straightforwardly to Eq. (31) for $[N]$ -annulenes.

(iii) Characteristic polynomial $P(L;x)$ and acyclic polynomial $P^{\text{ac}}(L;x)$ of polyenes are identical,

$$P(L;x) \equiv P^{\text{ac}}(L;x) \quad (32)$$

where the chain graphs corresponding to polyenes are denoted by L .

The conjecture that the zeros of the acyclic polynomial are real is shown by various authors [47b] to be true.

The Hosoya Polynomial

The Hosoya polynomial or the Z -counting polynomial of a graph is defined [48] as

$$P^{\text{h}}(G;x) = \sum_{k=0}^{[N/2]} p(G;k) x^k \quad (33)$$

where the nonadjacent numbers $p(G;k)$ for a graph G represent a k number of ways in which K_2 graphs can cover G in such a fashion that no two of them are joined. Note, $p(G;0) = 1$ by definition.

The sum of $P(G;k)$ numbers is the Hosoya topological index,

$$Z(G) = \sum_{k=0}^{[N/2]} p(G;k) \quad (34)$$

which appears to correlate well with physical properties of (conjugated) hydrocarbons [49]. $Z(G)$ may be, of course, also obtained from the Hosoya polynomial for $x = 1$,

$$Z(G) \equiv P^h(G; x = 1) \quad (35)$$

The Z -counting polynomial has some interesting features. Thus,

$$p(G; 1) = e \quad (36)$$

$$p(G; N/2) = K \quad (37)$$

As an example we construct the Hosoya polynomial of benzene.



$$p(G; 0) = 1,$$

$$p(G; 1) = 6 = e$$

$$p(G; 2) = 9$$

$$p(G; 3) = 2 = K$$

$$P^h(G; x) = 1 + 6x + 9x^2 + 2x^3$$

$$Z(G) \equiv P^h(G; X = 1) = 18$$

The Hosoya polynomial and the acyclic polynomial of G are connected in a simple way. If we present the acyclic polynomial of a graph in a convenient form for our discussion,

$$P^{ac}(G; x) = \sum_{k=0}^{[N/2]} (-1)^k p(G; k) x^{N-2k} \quad (38)$$

then $P^{ac}(G; x)$ and $P^h(G; x)$ are related by

$$P^{ac}(G; x) = x^N P^h(G; -x^{-2}) \quad (39)$$

Because of the relation (39), the connection between the Z -counting polynomial and the characteristic polynomial is rather simple: (i) for polyenes, because of identity (32), it is the same as Eq. (39),

$$P(L; x) = x^N P^h(L; -x^{-2}) \quad (40)$$

(ii) for annulenes, it is given by

$$P(C_N; x) = x^N P^h(C_N; -x^{-2}) - 2 \quad (41)$$

(iii) for polycyclic systems it is somewhat more complicated,

$$P(G;x) = x^N P^h(G;-x^{-2}) - 2x^{N-m} \sum_m P^h(G - C_m;-x^{-2}) \\ + 4x^{N-(m+n)} \sum_{m < n} P^h(G - C_m - C_n;-x^{-2}) - \dots \quad (42)$$

Naphthalene can serve as a convenient bicyclic structure for illustrating (42).



$$P(G;x) = x^{10} P^h(G;-x^{-2}) - 4x^4 + 12x^2 - 6$$

where

$$P^h(G;-x^2) = 1 - 11x^{-2} + 41x^{-4} - 61x^{-6} + 31x^{-8} - 3x^{-10}$$

$$P^h(G - C_6;-x^{-2}) = 1 - 3x^{-2} + x^{-4}$$

$$P^h(G - C_{10};-x^{-2}) = 1$$

The Sextet Polynomial

The sextet polynomial has been introduced by Hosoya and Yamaguchi [50] for the enumeration of Clar's sextets [51]. The Clar's sextets are considered to be the main origin of aromatic stabilization in benzenoid hydrocarbons [52-55].

The sextet polynomial is defined as

$$P^s(G;x) = \sum_{k=0}^L p(G;k) x^k \quad (43)$$

where $p(G;k)$ is the resonant sextet number of the graph G . The sextet number $p(G;k)$ for a graph G is defined as the number of ways in which k disconnected sextets are chosen from G . Note, $p(G;0) = 1$ by definition.

The sextet polynomial has a number of interesting properties:

(i) Sextet polynomial can be used for enumeration of Kekulé structures of catafusenes, i.e., polycyclic aromatic hydrocarbons in which no three hexagons have a common carbon atom,

$$P^s(G;x = 1) = K(G) \quad (44)$$

(ii) The derivative of $P^s(G;x)$ with respect to x , $P'^s(G;x = 1)$ is equal to the number of Kekulé structures for the subgraphs $G - b_i$, obtained from the graph G by deleting the benzene rings b_i and the adjacent bonds,

$$P'^s(G;x = 1) = \sum_i K(G - b_i) \quad (45)$$

It appears that $\sum_i K(G - b_i)$ is equal to the Herndon value $\sum_i \gamma_i$ used in his theory of aromaticity [56].

(iii) The ratio of $K(G - b_i)$ and $K(G)$ is a measure of the aromaticity of the individual six-membered rings. This ratio is identical to the local aromaticity index LAI of Randić [55],

$$(\text{LAI})_i = \frac{2K(G - b_i)}{K(G)} \quad (46)$$

(iv) The ratio of $\sum_i K(G - b_i)$ and $K(G)$, or $P^s(G; x = 1)$ and $P^s(G; x = 1)$, is a measure of total molecular aromaticity. It is identical to the total aromaticity index TAI of Randić [55],

$$\text{TAI} = \sum_i (\text{LAI})_i = \frac{2 \sum_i K(G - b_i)}{K(G)} = \frac{2P^s(G; x = 1)}{P(G; x = 1)} \quad (47)$$

(v) Aihara [57] has proposed a polynomial,

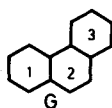
$$P^A(G; x) = \sum_{k=0}^L (-1)^k p(G; k) x^{2(L-k)} \quad (48)$$

The meaning of symbols in Eq. (48) is the same as in the case of the Hosoya polynomial. Polynomial (48) is used for estimating the degree of aromaticity in benzenoids.

The sextet polynomial can be converted in the Aihara polynomial by the relation,

$$P^A(G; x) = x^{2L} P^s(G; -x^{-2}) \quad (49)$$

Let us illustrate the use of the sextet polynomial on phenanthrene:

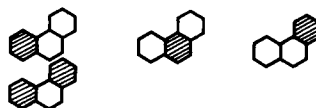


(a) Construction of the sextet polynomial

$$P(G; 0) = 1$$

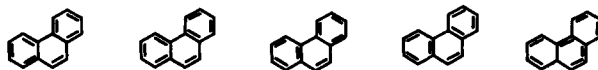
$$P(G; 1) = 3$$

$$P(G; 2) = 1$$



$$P^s(G; x) = 1 + 3x + x^2$$

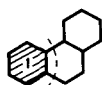
(b) Enumeration of Kekulé structures: $P^s(G; x = 1) = 5$



(c) Enumeration of Kekulé structures of subgraphs $G - b_i$

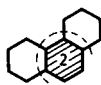
$$P'^s(G;x) = 3 + 2x$$

$$P'^s(G;x = 1) = 5$$



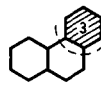
$$G - b_1$$

$$K(G - b_1) = 2$$



$$G - b_2$$

$$K(G - b_2) = 1$$



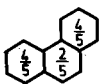
$$G - b_3$$

$$K(G - b_3) = 2$$

$$\sum_i K(G - b_i) = 5$$

(d) Evaluation of the local aromaticity index

$$(\text{LAI})_1 = \frac{4}{5}, \quad (\text{LAI})_2 = \frac{2}{5}, \quad (\text{LAI})_3 = \frac{4}{5}$$



(e) Evaluation of the total aromaticity index

$$\text{TAI} = \sum_i (\text{LAI})_i = 2$$

$$(f) \quad P^A(G;x) = x^4 - 3x^2 + 1$$

$$P^s(G;-x^{-2}) = 1 - 3x^{-2} + x^{-4}$$

$$x^{2L}P^s(G;-x^{-2}) = x^4 - 3x^2 + 1$$

The Cyclic Polynomial

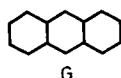
The cyclic polynomial $P^c(G;x)$ is a more general polynomial than the sextet polynomial because it not only enumerates 6-membered circuits (rings), but also 10-membered, 14-membered, ..., etc., circuits (rings) in the benzenoid hydrocarbons. It is defined as

$$P^c(G;x) = \sum_{m=0}^R \sum_{k=m}^L p(G - C_m;k) x_m^k \quad (50)$$

where $m = 0, 1, 2, 3$, denotes $0, C_6, C_{10}, C_{14}, \dots$, cycles, R stands for a total number of rings in a molecule, while $p(G - C_m;k)$ represents the circuit number of the graph G . The circuit number of G enumerates the number of Kekulé structures (1 factors) in the subgraph $G - C_m$ obtained after eliminating k -disconnected conjugated circuits. Note that $G - 0 \equiv G - C_0 \equiv G$ and $p(G - 0;k) = P^s(G;x = 1) = K$. If $x_m = 2C_{4m+2}$ is substituted in (50) the expression is obtained for the enumeration of conjugated circuits,

$$\sum_{m=0}^R \sum_{k=m}^L p(G - C_m;k) (2C_{4m+2})^k \quad (51)$$

Let us consider, as an illustrative example, anthracene (see Table II).



$$P^c(G;x) = 4 + 3x_1 + 2x_2 + x_3$$

By substituting $x_m = C_{4m+2}$ ($m = 1, 2, 3$) into the above relation we obtain,

$$6C_6 + 4C_{10} + 2C_{14}$$

and this is exactly the number of C_6 , C_{10} , and C_{14} circuits in anthracene which could be obtained by considering each Kekulé structure of anthracene separately [58]. The expression for the resonance energy RE of anthracene in the conjugated circuits theory of aromaticity [58–63] is given by

$$\text{RE (anthracene)} = \frac{1}{4} (6R_1 + 4R_2 + 2R_3)$$








where R_m ($m = 1, 2, 3$) are parametric values for C_6 , C_{10} , and C_{14} circuits. Thus, the cyclic polynomial contains all of the necessary data for calculating the resonance energies of benzenoid hydrocarbons.

The Wheland Polynomial

The Wheland polynomial of a given conjugated molecule enumerates the canonical structures of each degree of excitation [64,65a]. It is defined as

$$P^w(G;x) = \sum_{k=0}^M W(G;k)x^k \quad (53)$$

TABLE II

m	$G - C_m$	k	$p(G - C_m; k)$	x_m^k
0		0	4	1
1		1	1	x_1
		1	1	x_1
		1	1	x_1
2		1	1	x_2
		1	1	x_2
3		1	1	x_3

where $W(G;k)$ is the number of the k th excited structures for a given set of canonical resonance structures of the conjugated molecule. Therefore, the sum of $W(G;k)$ values gives the total number of resonance structures of a molecule,

$$P^w(G;x=1) = \sum_{k=0}^M W(G;k) = \frac{(2n)!}{n!(n+1)!} \quad (54)$$

where n is the number of double bonds in a system.

The coefficients of the Wheland polynomials can be obtained by using the graph-theoretical rules which depend on whether we study linear or cyclic structures.

Linear Structures

The Wheland polynomials for linear polyenes can be generated by the recurrence formula [64],

$$P^w(L_n;x) = P^w(L_{n-1};x) + x \sum_{k=2}^n P^w(L_{k-1};x)P^w(L_{n-k};x) \quad (55)$$

If we adopt for $P^w(L_0;x) = 1$ and $P^w(L_1;x) = 1$ then the higher Wheland polynomials can be easily obtained. Several $P^w(L_n;x)$ are given below.

$$\sum_{k=0}^{n-1} W(L_n;k)$$

$P^w(L_2;x) = 1 + x$	2
$P^w(L_3;x) = 1 + 3x + x^2$	5
$P^w(L_4;x) = 1 + 6x + 6x^2 + x^3$	14
$P^w(L_5;x) = 1 + 10x + 20x^2 + 10x^3 + x^4$	42
$P^w(L_6;x) = 1 + 15x + 50x^2 + 50x^3 + 15x^4 + x^5$	132

The inspection of these polynomials indicate a regularity which leads to the general expression for construction of the Wheland polynomials for linear polyenes [64],

$$P^w(L_n;x) = \frac{1}{n} \sum_{k=0}^{n-1} \binom{n}{k} \binom{n}{k+1} x^k \quad (56)$$

Cyclic Structures

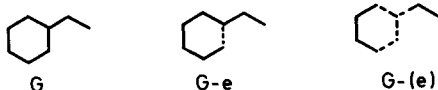
The Wheland polynomials for cyclic structures can be obtained by using the convenient recursion formula,

$$P^w(G;x) = P^w(G-e;x) + (1-x)P^w[G-(e);x] \quad (57)$$

G stands for a graph of a given (poly)cyclic structure, $G-e$ denotes a subgraph obtained by deletion of the edge e from G , while $G-(e)$ represents one or more subgraphs obtained by removing K_2 and all adjacent edges from G . The de-

composition of G continues until it reduces only to components corresponding to linear polyenes for which the Wheland polynomials are easily obtainable.

The use of relation (57) is illustrated on the styrene graph.



$$P^w(\text{styrene}; x) = P^w(L_4; x) + (1 - x)\{P^w(L_2; x)P^w(L_1; x)\}$$

$$= 2 + 6x + 5x^2 + x^3$$

Several Wheland polynomials of (poly)cyclic structures are given below.

	$\sum_{n=0}^{n-2} W(G; k)$
$P^w(\text{benzene}) = 2 + 3x$	5
$P^w(\text{naphthalene}; x) = 3 + 16x + 19x^2 + 4x^3$	42
$P^w(\text{anthracene}; x) = 4 + 48x + 150x^2 + 163x^3$ $+ 58x^4 + 6x^5$	429
$P^w(\text{phenanthrene}; x) = 5 + 47x + 148x^2 + 165x^3$ $+ 59x^4 + 5x^5$	429
$P^w(\text{triphenylene}; x) = 9 + 117x + 645x^2 + 1557x^3$ $+ 1659x^4 + 744x^5 + 125x^6 + 6x^7$	4862

The inspection of the coefficients reveals the following relationships:

$$W(G; 0) = K \quad (58)$$

$$W(G; 1) = D \quad (59)$$

where the symbol D is the number of Dewar structures. Higher coefficients are related to higher canonical structures, like double Dewar structures, etc. To our knowledge this is the only procedure which allows partition of resonance structures into sets containing Kekulé's structures, Dewar structures, double Dewar structures, etc.

It should be noted that the sum of all coefficients in the Wheland polynomials is the same for the isomers (e.g., anthracene and phenanthrene). This result also follows from the use of the Rumer diagrams [65b]. However, the use of Rumer diagrams soon becomes unwieldy with the increase of size of the systems studied.

Concluding Remarks

The graph theoretical polynomials of conjugated structures discussed in this work are a few of many polynomials in which theoretical chemistry and pure mathematics merge. Hence, they represent the important quantities in both fields. However, in theoretical chemistry they help to understand the origin of

regularities in chemistry of specific classes of compounds. For example, it can be shown that the polynomials discussed are closely related to π -electron energy of conjugated systems, because π energy can be approximately expressed in terms of a given polynomial [64–68]. π -Electron energy is, of course, a very important parameter, since it is related in a direct way with the stability of the molecule [69]. Thus, the stability of a given conjugated system can be predicted from the properties of polynomials. It is our belief that there are many more properties of these polynomials which remain to be discovered. Furthermore, there may be as yet unknown or unappreciated polynomials which have many important properties for structural chemistry [70].

Acknowledgments

One of the authors (N.T.) is thankful to Professor B. M. Gimarc (Columbia, SC) for kind hospitality, financial support during the stay in his laboratory, and for critical, but helpful, comments on the manuscript. Financial support, which has allowed N.T. to attend the Sanibel Palm Coast Symposium 1980, was obtained, in part, from the NSF Grant No. F6F006-Y.

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Received March 14, 1980

Revised June 3, 1980