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Properties and derivation of the fourth and sixth coefficients of the characteristic polynomial of molecular graphs*—New graphical invariants

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Some previously unknown relationships for determining the a_4 and a_6 coefficients of the characteristic polynomial for polycyclic aromatic hydrocarbons are presented for the first time. The structural information contained in these coefficients is more fully revealed. The equations derived for a_4 and a_6 allow one to determine the characteristic polynomial by inspection for many small molecular graphs. Some relationships for a_8 and a_{10} are presented. The set of known graphical invariants (GI) or properties that remain unchanged in isomeric PAH6s is now shown to be $\mathrm{GI} = \{a_4, a_6 + n_0 + 2r_6, a_8^c, d_s + \mathrm{N}_{\mathrm{Ic}}, \mathrm{N}_c, \mathrm{N}_{\mathrm{H}}, \mathrm{N}_{\mathrm{Ic}} + \mathrm{N}_{\mathrm{Pc}}, q, r\}$.

Key words: Graph theory — Characteristic polynomials — Benzenoid hydrocarbons — Molecular topology — Graphical invariants

1. Introduction

Part of the intuitive modus operandi in the teaching of chemistry is that many molecular properties are topological in origin. Ingrained in this approach is the use of molecular graphs to represent pictures of chemical molecules. The mathematical relationships of graphs provide a powerful tool for interlinking molecular topology with molecular properties. Various numerical topological indices have been contrived seeking to give a general measure of molecular structure similarity and dissimilarity and have been presented via concepts of molecular complexity, connectivity, and information content [1, 2, 3]. An allied objective is to rank and numerically characterize various atomic positions within a single molecule as

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* Part VIII: A periodic table for polycyclic aromatic hydrocarbons

with random walks and canonical labeling of the various molecular positions [4, 5, 6]; summing up these individual numerical atomic ranks gives a molecular topological index. These topological indices can be used in structure/activity relationship studies both among different molecules and at different sites within a molecule, computer encoding for both storage and retrieval, and in computer recognition of identical structures or substructures [7, 8, 9, 10]. In more abstract form, the latter is a problem of graph and subgraph isomorphism [11]. An important goal related to the above objectives is the identification of graphical invariants. The characteristic polynomial represents the secular equation of a $p\pi$-electron system in the Hückel MO model of a conjugated polyene molecule, as well as being related to the eigenvalues of the mathematical graph [12]. As it will become evident from this paper, the coefficients of the characteristic polynomial are either graphical invariants in toto or contain graphical invariant components.

The unique organizational format of the Formula Periodic Table for Benzenoid Polycyclic Aromatic Hydrocarbons (Table 1) has led to a deeper understanding of the mathematical/structural relationships associated with polyhexes in general [13, 14]. After one carefully distinguishes between the sets of internal (Q_I, P_I) and peripheral (Q_P, P_P) edges and vertices of a polycyclic graph, an exceedingly simple relationship ($d_s + \mathrm{N_{Ic}} = r - 2$) evolves which is the basis of Table 1 [15]. If the peripheral edges of a polycyclic graph are cut away from its internal edges leaving a group of acyclic graphs, then d_s equals the number of acyclic subgraphs minus one. Alternatively, if this process leaves a polycyclic subgraph, then d_s equals the negative value of the number of rings; for an admix of these two possibilities d_s takes on a net value. The number of third degree vertices bounded by three rings is equal to $\mathrm{N_{Ic}}$. Every position on Table 1 has unique coordinates $[d_s, \mathrm{N_{Ic}}]$, and all PAH isomers of the same formula must obey the following equation: $d_s + \mathrm{N_{Ic}} = \frac{1}{2}[\mathrm{N}_c - \mathrm{N_H}] - 1$. Thus $d_s + \mathrm{N_{Ic}}$ is a graphical invariant of polycyclic graphs of considerable importance [13, 14, 15]. The broad utility of Table 1 will be exemplified by its key role in the derivation of additional graphical invariants in this paper associated with the characteristic polynomial of polycyclic graphs that were previously unknown.

The characteristic polynomial $P(G; X)$ can be obtained by reducing the secular determinant or enumerating all the Sachs subgraphs associated with a molecular graph G [16]. Factoring the characteristic polynomial gives the eigenvalues corresponding to the graph. It is well known that the coefficients of the characteristic polynomial convey graphical information [17]. Consider the following polynomial equation for a graph, G,

$$P(G; X) = \sum_{n=0}^{\mathrm{N}} a_n X^{\mathrm{N}-n} = X^{\mathrm{N}} - qx^{\mathrm{N}-2} - 2r_3 X^{\mathrm{N}-3} + a_4 X^{\mathrm{N}-4}$$
$$+ a_5 X^{\mathrm{N}-5} + \cdots + a_{\mathrm{N}-2} X^2 + a_{\mathrm{N}-1} X + a_{\mathrm{N}}. \tag{1}$$

From Eq. (1) it is evident that the values of the first four coefficients are $a_0 = 1$ (by definition), $a_1 = 0$, $a_2 = -q$ (q = No. of graph edges), and $a_3 = -2r_3$ (r_3 = No.

Table 1. Formula periodic table for benzenoid polycyclic aromatic hydrocarbons (PAH6)[a,b]

$d_s=-9$	$d_s=-8$	$d_s=-7$	$d_s=-6$	$d_s=-5$	$d_s=-4$	$d_s=-3$	$d_s=-2$	$d_s=-1$	$d_s=0$	$d_s=1$	$d_s=2$	$d_s=3$	N_{Ic}
									$C_{10}H_8$	$C_{14}H_{10}$	$C_{18}H_{12}$	$C_{22}H_{14}$	… 0
Forbidden Region							Most Reactive		$C_{16}H_{10}$	$C_{20}H_{12}$	$C_{24}H_{14}$	$C_{28}H_{16}$	… 2
					$N_c/N_H<2$				$C_{22}H_{12}$	$C_{26}H_{14}$	$C_{30}H_{16}$	$C_{34}H_{18}$	… 4
		$C_{00}H_{00}$—						$C_{24}H_{12}$—	$C_{28}H_{14}$—	$C_{32}H_{16}$—	$C_{36}H_{18}$—	$C_{40}H_{20}$—	… 6
					$2<N_c/N_H<3$			$C_{30}H_{14}$	$C_{34}H_{16}$	$C_{38}H_{18}$	$C_{42}H_{20}$	$C_{46}H_{22}$	… 8
							$C_{32}H_{14}$	$C_{36}H_{16}$	$C_{40}H_{18}$	$C_{44}H_{20}$	$C_{48}H_{22}$	$C_{52}H_{24}$	… 10
							$C_{38}H_{16}$	$C_{42}H_{18}$	$C_{46}H_{20}$	$C_{50}H_{22}$	$C_{54}H_{24}$	$C_{58}H_{26}$	… 12
						$C_{40}H_{16}$	$C_{44}H_{18}$	$C_{48}H_{20}$	$C_{52}H_{22}$	$C_{56}H_{24}$	$C_{60}H_{26}$	$C_{64}H_{28}$	… 14
$N_c/N_H>3$					$C_{42}H_{16}$	$C_{46}H_{18}$	$C_{50}H_{20}$	$C_{54}H_{22}$	$C_{58}H_{24}$	$C_{62}H_{26}$	$C_{66}H_{28}$	…	
					$C_{48}H_{18}$	$C_{52}H_{20}$	$C_{56}H_{22}$	$C_{60}H_{24}$	$C_{64}H_{26}$	$C_{68}H_{28}$	…		
				$C_{50}H_{18}$	$C_{54}H_{20}$	$C_{58}H_{22}$	…	…	…	…			
			$C_{52}H_{18}$	$C_{56}H_{20}$	$C_{60}H_{22}$	…							
Least Reactive		$C_{54}H_{18}$	$C_{58}H_{20}$	$C_{62}H_{22}$	…								
		$C_{60}H_{20}$	$C_{64}H_{22}$	…				Intermediate Reactive					
	$C_{62}H_{20}$	$C_{66}H_{22}$	…										
$C_{64}H_{20}$	$C_{68}H_{22}$	…											
$C_{70}H_{22}$	…												
…													

[a] Number of rings, $r=\frac{1}{2}(N_c+2-N_H)$

[b] For the row series $N_c=N_H-6+N_{Ic}$, and for the column series $N_c=3N_H-14-2d_s$

3-membered cycles or rings). Also, for benzenoid graphs it is known that $a_{N-2} = a_{N-2}(\text{cyclic}) + a_{N-2}(\text{acyclic}) = a_{N-2}(\text{cyclic}) + \frac{1}{2}N_cK + D$ (K is the number of Kekule' structures and D is the number of Dewar structures) and $a_N = \pm K^2$ [18, 19]. We will now present previously unknown relationships for a_4 and a_6 and illustrate the broad applications of the former.

2. Derivation of a_4

2.1. *Benzenoid graphs*

In the following molecular graphs, only the C-C σ-bond framework will be shown and all $p\pi$-bonds, C-H bonds, and C and H atoms will be omitted. All benzenoid isomers have the same a_4 values [20]. To determine the general form for the a_4 coefficient, we use Sachs' formula [21].

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

where s denotes a Sachs graph made up of K_2 and C_m components, S_n is a set of all such graphs with n vertices of a graph G, $c(s)$ is the total number of components in each, and $r(s)$ is the number of cyclic components. Thus Eq. (2) becomes

$$a_4 = \sum_i [2K_2]_i - 2r_4 \tag{3}$$

where r_4 is the number of different four-membered cycles (rings) in the graph G. To determine the number of pairs of K_2 subgraphs in benzenoid molecular graphs, we apply the following simple combinatorial relationship. All benzenoid graphs have three basic types of bonding neighborhoods illustrated with naphthalene in Fig. 1. Edge types are designated by $e(m, n)$ where m and n are the degrees of the vertices associated with the edge e. Bonds 1-2, 2-3, 3-4, 5-6, 6-7, and 7-8 comprise the first type $[e(2, 2)]$, bonds 4-4a, 4a-5, 8-8a, and 8a-1 the second type $[e(2, 3)]$, and bond 4a-8a the third type $[e(3, 3)]$. Placement of a double bond between bonds of the first type excludes three edges from accepting a second double bond, between bonds of the second type excludes four edges, and between bonds of the third type excludes five edges. Since all acenes have six bonds of the first type and q_I internal bond edges of the third type, we write the following simple combinatorial relationship for the number of pairs of K_2 subgraphs associated with the acenes

$$\frac{6(q-3) + (q - q_I - 6)(q-4) + q_I(q-5)}{2} \tag{4}$$

where q is the number of bond edges in the benzenoid graph and $(q-3)$, $(q-4)$, and $(q-5)$ are exclusion terms for the first, second, and third type of bonds, respectively. Since benzenoid hydrocarbons have no four-membered rings, inserting (4) into Eq. (3) gives the following equation which is valid for all benzenoid hydrocarbons.

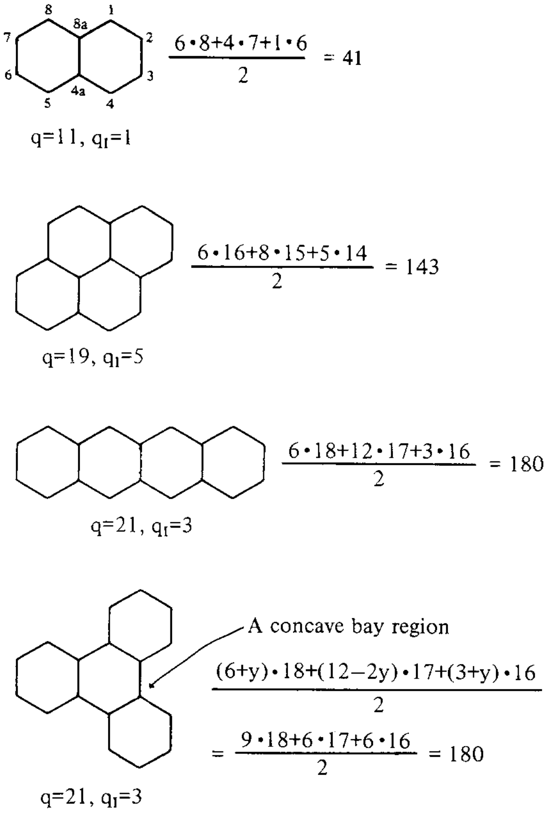


Fig. 1. Example computations of a_4 for representative benzenoid hydrocarbons

$$a_4(\mathrm{PAH6}) = \frac{6(q-3)+(q-q_I-6)(q-4)+q_I(q-5)}{2} = (\tfrac{1}{2})(q^2-9q+6\mathrm{N}_c) \qquad (5)$$

Although pyrene (Fig. 1), anthanthrene, and related benzenoid hydrocarbons also have six bonds of the first type $e(2,2)$ most of the other benzenoid hydrocarbons do not. Fig. 1 illustrates the application of Eq. (5) on naphthalene, pyrene, and naphthacene, all of which have only 6 bonds of first type $e(2,2)$. Why Eq. (5) works for benzenoid hydrocarbons having more than the minimum of six bonds of the first type $e(2,2)$ is revealed by examining what happens to triphenylene in Fig. 1. Comparing the computation of naphthacene which has six bond edges of the first type versus triphenylene with nine bonds of $e(2,2)$, in going from naphthacene to triphenylene one can see that the number of bond edges of the first $[e(2,2)]$ and third types $[e(3,3)]$ are increased by an equal quantity of $y=3$ and the number of bonds of the second type $[e(2,3)]$, is decreased by two times the same quantity of $2y=6$. Since the average of the associated multipliers (16 and 18) of first and third types of bonds is the average of the multiplier (17) of the second type of bond, it is evident that these changes always occur so as to preserve the magnitude of the overall expression as given by Eq.

(5). Thus for benzenoid hydrocarbon graphs a_4 is a graphical invariant having the same value for benzenoid isomers of the same formula.

2.2. *All graphs*

An expanded version of Eq. 5 is now presented without proof which gives the correct value of a_4 for all the characteristic polynomials of acyclic graphs [22, 23, 24], isospectral polyphenylpolyenes [25], and monocyclic and bicyclic graphs [23, 25, 26] conveniently tabulated. Using previous relationships [27] Eq. (5) becomes

$$a_4=\tfrac{1}{2}(q^2-9q+6\mathrm{N}_c)-2r_4-d_1-0d_2-0d_3-d_4-3d_5-6d_6-10d_7-\cdots \qquad (6)$$

where N_c is the number of carbon vertices, and d_i is the number of vertices of degree i. For alternative derivations of less comprehensive formulas for a_4, the reader is referred to the work of Gutman [28] and Türker [29].

3. Example application of Eq. (6)

3.1. *Graphs of six or less vertices*

The application of Eq. (6) will be illustrated using the graphs shown in Fig. 2. The characteristic polynomial of all graphs with six or less vertices can be written by inspection using the relationships provided herein; note that $a_5=-2r_5+2\sum_i(\mathrm{K}_2r_3)_i$. Consider the Balaban-Harary isospectral pair 1*a* and 1*b* [30]. Graph 1*a* can correspond to a conjugated olefinic hydrocarbon (or saturated one) but graph 1*b* cannot. Since 1*a* has a four-membered ring $(2r_4=2)$ and two vertices of degree 1 $(d_1=2)$ and 1*b* has a vertex of degree 5 $(3d_5=3)$ and one

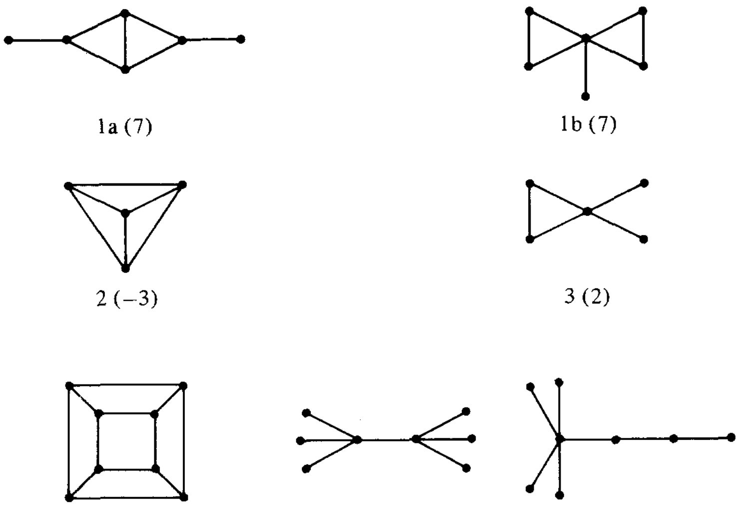
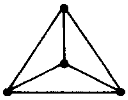


Fig. 2. Selected graphs and their corresponding a_4 values in parentheses

vertex of degree 1 ($d_1 = 1$), they both give a value of $a_4 = 7$. Thus the characteristic polynomial of 1*a* and 1*b* in Fig. 2 is given by $P(1a; X) = P(1b; X) = X^6 - 7X^4 - 4X^3 + 7X^2 + 4X - 1$ where the last term comes from the fact that 1*a* and 1*b* shown above have only one nonaromatic Kekule' structure. The tetrahedron planar isomorphic graph 2 [22] and graph 3 [26] in Fig. 2 provide other demonstrative examples, and their with corresponding characteristic polynomials are shown below.



2, C_4; $X^4 - 6X^2 - 8X - 3$

3, C_5H_5; $X^5 - 5X^3 - 2X^2 + 2X$

One can see that 2 has four three-membered rings (one for each tetrahedron face) giving $a_3 = 8$ and Eq. (6) gives $a_4 = -3$; note that the negative sign arises because there are four independent four-membered rings in a tetrahedron. Molecular graph 3 has five σ-bonds ($a_2 = -5$), one three-membered ring ($a_3 = -2$), and Eq. (6) gives $a_4 = 2$. Note that each vertex can only accommodate one double bond.

3.2. *Graphs with more than six vertices*

The planar isomorphic graph of the cube 4 [26] and the isospectral pair [30] of graphs 5*a* and 5*b* in Fig. 2 provide additional insights regarding the application of Eq. (6). The molecular graph of 4 gives $a_4 = 30$ after subtracting $2r_4 = 12$ from the first term in Eq. (6) since the six cube faces are four-membered rings. An acyclic graph with paths no longer than three bonds cannot have more than three terms in their associated characteristic polynomial; thus, $P(5a; X) = X^8 - 7X^6 + 9X^4$ where Eq. (6) gives directly $a_4 = 17 - 6 \times 1 - 2 \times 1 = 9$ for graph 5*a*.

4. The a_6 coefficient

4.1. *Linear and monocyclic polyenes*

Table 2 presents the characteristic polynomials for the linear polyenes (L_n) which are easily obtained by recursion [17]. Also it is well known that each coefficient in Table 2 follows a Fibonacci sequence comprised of the sum of the coefficient in the first row immediately above it plus the coefficient in the second row above and one column to the left. The coefficient (a_0) in the first column of Table 2 for the highest power of X is one. In the second column, the coefficients increase from L_2 by successive increments of one and are equal to the number of σ = bonds, $a_2 = -q$. The third coefficient column (a_4) increases from L_3 via the difference sequence of 1, 2, 3, ... and is given by Eq. (6). The characteristic polynomial for the monocyclic polyenes (C_n) follows the equation of $C_n = L_n - L_{n-2} - 2$. Except for the tail coefficients, the coefficients of the characteristic polynomial of the monocyclic polyenes have the same properties just described for the linear polyenes. The sixth coefficient (a_6) for both linear and monocyclic conjugated

Table 2. Characteristic polynomials (Chebyshev polynomials of $X/2$ argument) of linear polyenes[a]

$\mathrm{L}_0=1$
$\mathrm{L}_1=X$
$\mathrm{L}_2=X^2-1$
$\mathrm{L}_3=X^3-2X$
$\mathrm{L}_4=X^4-3X^2+1$
$\mathrm{L}_5=X^5-4X^3+3X$
$\mathrm{L}_6=X^6-5X^4+6X^2-1$
$\mathrm{L}_7=X^7-6X^5+10X^3-4X$
$\mathrm{L}_8=X^8-7X^6+15X^4-10X^2+1$
$\mathrm{L}_9=X^9-8X^7+21X^5-20X^3+5X$
$\mathrm{L}_{10}=X^{10}-9X^8+28X^6-35X^4+15X^2-1$
$\mathrm{L}_{11}=X^{11}-10X^9+36X^7-56X^5+35X^3-6X$
$\mathrm{L}_{12}=X^{12}-11X^{10}+45X^8-84X^6+70X^4-21X^2+1$
$\mathrm{L}_{13}=X^{13}-12X^{11}+55X^9-120X^7+126X^5-56X^3+7X$
$\mathrm{L}_{14}=X^{14}-13X^{12}+66X^{10}-165X^8+210X^6-126X^4+28X^2-1$
$\mathrm{L}_{15}=X^{15}-14X^{13}+78X^{11}-220X^9+330X^7-252X^5+84X^3-8X$
$\mathrm{L}_{16}=X^{16}-15X^{14}+91X^{12}-286X^{10}+495X^8-462X^6+210X^4-36X^2+1$
...

[a] Based on the recursion $\mathrm{L}_n=X\mathrm{L}_{n-1}-\mathrm{L}_{n-2}$ where $\mathrm{L}_0=1$ and $\mathrm{L}_1=X$

polyenes is given by the relationship of

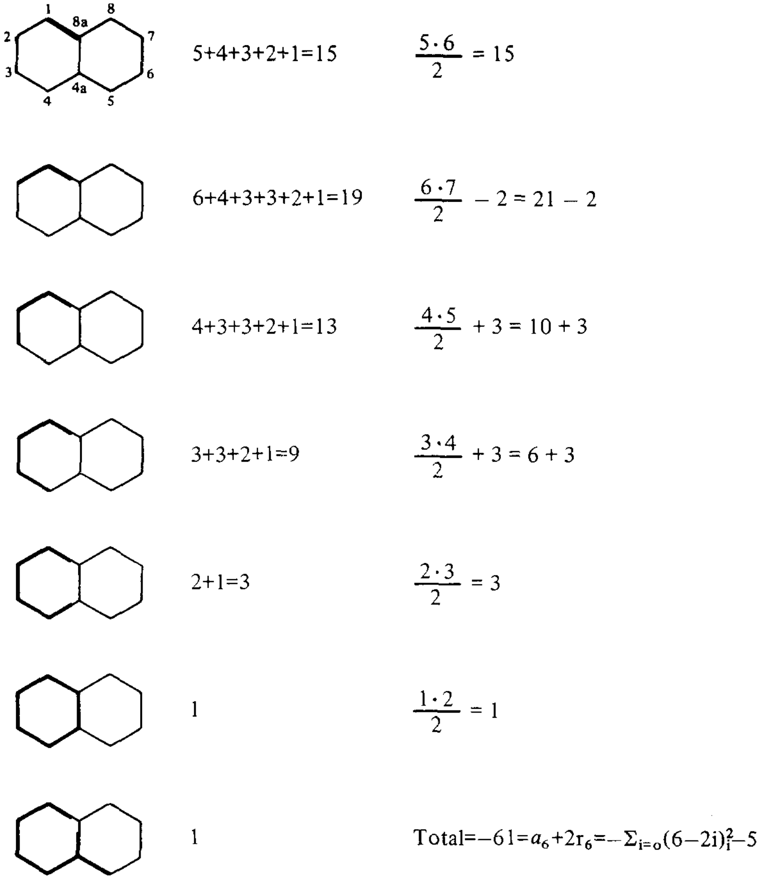
$$a_6(\mathrm{L}_n/\mathrm{C}_n)=-\sum_{i=0}(q-4-2i)_i^2+r(q-4)-2r_6$$

$$=-\frac{(q-4)(q-3)(q-2)}{6}+r(q-4)-2r_6 \qquad (7)$$

where $r=0$ for the linear polyenes and $r=1$ for the monocyclic polyenes and r_6 equals the number of 6-membered rings (i.e. $r_6=1$ for C_6). Thus, for L_9, $a_6=-(4^2+2^2+0)=-20$, and for C_9, $a_6=-(5^2+3^2+1)+5=-30$. Branched polyenes isomeric to a linear one will invariably have a smaller a_6 value.

4.2. Benzenoid hydrocarbons

For any set of benzenoid polycyclic aromatic hydrocarbon (PAH6) isomers, a_6 differs only by the difference in the number of concave bay regions (n_0). For example the anthracene molecule has no bay region ($n_0=0$) with $a_6=-296$ and the phenanthrene molecule has one bay region ($n_0=1$) with $a_6=-297$. Thus a_6+n_0 is a graphical invariant for PAH6s [11]. A general outline for the derivation of a_6(PAH6) will now be presented. An example algorithmic calculation of a_6 for naphthalene is presented in Fig. 3. Starting at the top of Fig. 3, if bonds 1-8a and 2-3 are covered, then the third bond can have five different locations; if bonds 1-8a and 3-4 are covered, then the third bond can be located at four different positions, and so forth. This gives the first summation series of $5+4+3+2+1$. Once the first bond 1-8a has been covered as above, it cannot be covered again. Repetition of this procedure for the other positions leads to the series of



5+4+3+2+1=15 $\frac{5\cdot 6}{2}=15$

6+4+3+3+2+1=19 $\frac{6\cdot 7}{2}-2=21-2$

4+3+3+2+1=13 $\frac{4\cdot 5}{2}+3=10+3$

3+3+2+1=9 $\frac{3\cdot 4}{2}+3=6+3$

2+1=3 $\frac{2\cdot 3}{2}=3$

1 $\frac{1\cdot 2}{2}=1$

1 Total$=-61=a_6+2r_6=-\Sigma_{i=o}(6-2i)^2_i-5$

Fig. 3. Algorithmic calculation of a_6 for naphthalene where the bonds once covered cannot be used again and are shown in bold

sums presented in Fig. 3 which give the total of $a_6+2r_6=-61$. If 2 is added to the second sum series starting with 6 and 3 is subtracted both from the sum series starting with 4 and 3 and noting the last extra bottom sum series of 1, the sum of the arithmetic series is given by $\sum_{k=0}^{n} k = n(n+1)$. Application of this relationship to the series of sums for naphthalene gives 56 to which a residue of 5 must be added.

$$\text{Series of sums} = \frac{(q-5)(q-4)}{2}+\frac{(q-6)(q-5)}{2}+\frac{(q-7)(q-6)}{2}$$
$$+\frac{(q-8)(q-7)}{2}+\dots+\frac{[q-(q-1)][q-(q-2)]}{2}$$
$$+\frac{[q-q][q-(q-1)]}{2}=\frac{(q-5)(q-4)(q-3)}{6}.$$

In general, then from each successive pairs of terms one can factor out the common factors as follows

$$\text{Series of sums} = \frac{(q-5)}{2}[(q-4)+(q-6)] + \frac{(q-7)}{2}[(q-6)+(q-8)] + \cdots$$
$$+ \frac{[q-(q-1)]}{2}[q-(q-2)+q-q].$$

The second factor in each term above is two times the first factor which upon simplification gives

$$\text{Series of sums} = (q-5)^2+(q-7)^2+\cdots+[q-(q-1)]^2 = \sum_{i=0} (q-5-2i)_i^2.$$

Thus, for PAH6s

$$a_6+2r_6 = -\sum_{i=0} (q-5-2i)_i^2\text{-residue-}n_0$$

which has the same form as Eq. (7). Using published data [20], the values for a, b, and c in the following equation were determined for the $N_c=2N_H$-6, $2N_H$-4, and $2N_H$-2 row series of Table 1.

$$a_6+2r_6+n_0 = -\sum_{i=0} (q-5-2i)_i^2 + aq_I^2 + bq_I + c.$$

The respective results obtained are as follows

$$a_6+2r_6+n_0 = -\sum_{i=0} (q-5-2i)_i^2 + (\tfrac{5}{2})q_I^2 - (\tfrac{13}{2})q_I - 1$$

and

$$a_6+2r_6+n_0 = -\sum_{i=0} (q-5-2i)_i^2 + (\tfrac{5}{2})q_I^2 - (\tfrac{25}{2})q_I + 13$$

and

$$a_6+2r_6+n_0 = -\sum_{i=0} (q-5-2i)_i^2 + (\tfrac{5}{2})q_I^2 - (\tfrac{37}{2})q_I + 27.$$

The $N_c=2N_H$-6, $2N_H$-4, $2N_H$-2 row series have benzenoid PAH6 structures with varying internal third degree vertices of $N_{Ic}=0$, 2, and 4, respectively. It is also evident that the last two terms in the above last three equations vary successively by $-(\tfrac{12}{2})q_I+14$. These facts were incorporated into the following Eq. (8) which then gives the correct solution for a_6 for all known published results on benzenoid PAH6s [20, 31].

$$\begin{aligned} a_6 &= -\sum_{i=0} (q-5-2i)_i^2 + (\tfrac{5}{2})q_I^2 - (\tfrac{13}{2}+3N_{Ic})q_I + (7N_{Ic}-1) - 2r_6 - n_0 \\ &= -(\tfrac{1}{6})(q-5)(q-4)(q-3) + (\tfrac{5}{2})q_I^2 - (\tfrac{13}{2}+3N_{Ic})q_I - (1-7N_{Ic}) - 2r_6 - n_0 \\ &= -(\tfrac{1}{6})(q^3-27q^2+146q+36) - N_c(3q-22) - n_0 - 2r_6. \end{aligned} \tag{8}$$

This equation is also valid for PAH6s having an odd number of carbon vertices.

Since Table 1 is based on the graphical invariant of $d_s + N_{Ic}$ = constant, a similar derivation using d_s and the column series of Table 1 should be possible. However, it turns out that recognizing the systematic change in the column equations in the last step is more difficult.

5. The a_8 coefficient

5.1. *Linear and monocyclic polyenes*

The eighth coefficient (a_8) for both linear and monocyclic conjugated polyenes is given by Eq. (9) as

$$a_8(L_n/C_n) = (\tfrac{1}{24})(q-6)(q-5)(q-4)(q-3) - (\tfrac{1}{2})r(q-6)(q-5) - 2r_8 \tag{9}$$

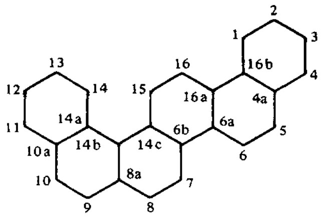
which has a similar form as Eq. (7); $r = 0$ for the linear polyenes (L_n) and $r = 1$ for the monocyclic polyenes (C_n) and $r_8 = 1$ only for C_8.

5.2. *Benzenoid hydrocarbons*

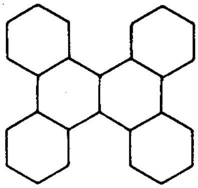
For any set of cata-condensed benzenoid isomers, a_8 differs only by the following relationship

$$\Delta a_8(\text{cata-PAH6 isomers}) = 5(r_6 - 2)n_0 + n_0' - 2(n_4 - 2) \tag{10}$$

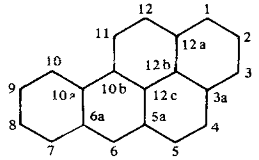
where n_0 is the number of bay regions, n_0' is the number of separate or isolated bay regions, and n_4 is the number of branches. The application of Eq. (10) for a selected number of representative PAH6s is presented in Fig. 4. Consider



Dibenzo[a, l]chrysene
$n_0=4$, $n_0'=3$, $n_{04}=2$, $n_1=0$, $n_2=4$
$n_3=0$, $n_4=2$



Dibenzo[g, p]chrysene
$n_0=6$, $n_0'=4$, $n_{04}=6$, $n_1=0$, $n_2=0$
$n_3=0$, $n_4=4$



Benzo[a]pyrene
$n_0=1$, $n_0'=1$, $n_{04}=1$, $n_1=1$, $n_2=2$
$n_3=1$, $n_4=1$

Fig. 4. Example benzenoid hydrocarbons and their associated perimeter topological descriptors

dibenzo[*a*, *l*]chrysene in Fig. 4; there are four bay regions between 6a, 6b, 14a, 14b, 14c, 16a, and 16b ($n_0 = 4$), but since the two bay regions between 14a, 14b, and 14c are adjacent, there are only three isolated (groups of) bay regions ($n'_0 = 3$). Two of these bay regions are adjacent to end rings (i.e. $n_{04} = 2$) and two of them are not. Similarly, for dibenzo[*g*, *p*]chrysene (Fig. 4) there are six bay regions ($n_0 = 6$), four isolated groups of bay regions ($n'_0 = 4$), and four end rings ($n_4 = 4$) with all the bay regions adjacent to the end rings ($n_{04} = 6$). Thus, for dibenzo[*a*, *l*]chrysene $\Delta a_8 = 83$ and $a_8 = 16\,305$ and for dibenzo[*g*, *p*]chrysene $\Delta a_8 = 120$ and $a_8 = 16\,342$ since Δa_8(hexacene) = 0 and a_8(hexacene) = 16 222.

Consider benzo[*a*]pyrene in Fig. 4, between the third degree-peripheral vertices 10b and 10a there are no points ($c_0 = 0$), between 5a and 6a there is a single second degree point ($c_1 = 1$) numbered 6, between 3a and 5a there are the two second degree points ($c_2 = 2$) of numbers 4 and 5, between 12a and 3a there are the three second degree points ($c_3 = 3$) of numbers 1, 2, and 3 and finally between the peripheral vertices of 6a and 10a there are four second degree points ($c_4 = 4$) of numbers 7, 8, 9, and 10; the quantity of each of these five different sequences of intervening second degree points between peripheral third degree vertices in a particular structure is designated by n_0, n_1, n_2, n_3, and n_4, respectively. The simple sum of the number of each of these five sequences is given by $n_0 + n_1 + n_2 + n_3 + n_4 = N_{Pc}$ which for benzo[*a*]pyrene (Fig. 4) is $1+1+2+1+1 = 6$, i.e., there is one sequence with no intervening second degree points (between 10a and 10b), one sequence with one intervening second degree point (between 5a and 6a), two sequences with two intervening points (between 3a and 5a and 10b and 12a), one sequence with three intervening points (between 12a and 3a), and one sequence with four intervening points (between 6a and 10a) and the sum of these sequences gives the number of peripheral third degree carbon atoms. When there are no intervening points $c_0 = 0$, one intervening point $c_1 = 1$, two intervening points $c_2 = 2$, three intervening points $c_3 = 3$, and four intervening points $c_4 = 4$. Since these intervening points correspond to second degree vertices between the outer third degree vertices, the total number of second degree vertices is given by $N_H = n_0c_0 + n_1c_1 + n_2c_2 + n_3c_3 + n_4c_4$ which for benzo[*a*]pyrene gives $12 = 1 \cdot 0 + 1 \cdot 1 + 2 \cdot 2 + 1 \cdot 3 + 1 \cdot 4$; note that $n_1 + n_3 =$ even number $\leq N_H$ since $N_H \geq n_1 + 3n_3$ for even PAH6s. The number of bay regions in a PAH6 is given by its n_0 value, and the number of branches is given by n_4; note that the definition of bay region used here is not restricted to n_0 regions adjacent to terminal rings. Adding the above equations gives $n_0 + 2n_1 + 3n_2 + 4n_3 + 5n_4 = N_{Pc} + N_H = N_c - N_{Ic} = 2N_H - 6 = q_p$ for PAH6s which says that benzenoid structures having the same number of formula hydrogens (N_H) have the same number of peripheral bonds (q_p) and are constrained by the same range of *n* values.

A number of correlations exist between Table 1 and the n_0, n_2, n_2, n_3, and n_4 values for PAH6s. For the cata-condensed benzenoids ($N_c = 2N_H - 6$ row series of Table 1), $n_3 = 0$. Strictly peri-condensed PAH6s have formulas lying on the left-hand diagonal boundary of Table 1 and have connected excised internal structures; $n_4 = 0$ for all strictly peri-condensed benzenoid PAH6s. By subtracting the first two equations in the prior paragraph, it can be easily shown that for

PAH6s the following four-variable equation is obtained:

$$-n_0+n_2+2n_3+3n_4=6.$$

For the $N_c=2N_H-4$ row series, $n_3 \leq 4$ for all PAH6 structures with $N_{Ic}=2$. In general, $n_3 \leq 2N_{Ic}$ for all benzenoid structures where the equality occurs only when $N_{Ic}=1$ or 2 (e.g., in perylene). From the first equation presented in the previous paragraph n_0, n_1, n_2, n_3, and $n_4 \leq N_{Pc}$ where the equality is only applicable for coronene having $n_2=N_{Pc}$. Thus, $n_3=0$ for cata-condensed and $n_4=0$ for strictly peri-condensed PAH6s are necessary but not sufficient topological requirements for these classes of polyhexes. If any three values for n_0, n_2, n_3, and n_4 are known for polyhexes, then the fourth is known via the above equation; if n_1 and any three of the remaining topological perimeter parameters are known, then N_H and N_{Pc} are also known. While n_1 may have any value by the above equation, if $n_0=n_2=n_3=0$, then n_4 must equal two which is the case for the acenes. Similarly, if $n_0=n_2=n_4=0$, then n_3 must equal three which is the case for the perinaphthyl monoradical ($C_{13}H_9$). For $n_0=n_3=n_4=0$, n_2 must equal six which is the case for coronene. One must conclude from the negative sign before n_0 in the above equation that no benzenoid PAH6 structure can exist with $n_2=n_3=n_4=0$.

The coefficients of the characteristic polynomial are made up of acyclic (a_n^{ac}) and cyclic (a_n^c) contributions: $a_n=a_n^{ac}+a_n^c$. The first two even coefficients (a_0 and a_2) of characteristic polynomial have no cyclic contributions, and for benzenoid PAH6s $a_4(\text{PAH6})=a_4^{ac}(\text{PAH6})$ and $a_6(\text{PAH6})=a_6^{ac}-2r_6$ where r_6 is the number of hexagonal rings. The cyclic contribution to the eighth coefficient for PAH6s comprises of all the combinations of one K_2 and one C_6 graph components. All benzenoid isomers of a particular PAH6 formula have the same a_8^c value. For the acene cata-condensed PAH6s, if the C_6 component occupies one of the two end rings, then 8 edges are unavailable for the K_2 component; similarly if the C_6 component occupies one of the inner rings then 10 edges are unavailable for the K_2 component. Thus the cyclic contribution to the eighth coefficient of the characteristic polynomial for all cata-condensed benzenoid PAH6s must be given by

$$a_8^c(\text{cata-PAH6})=2^2(q-8)+2(q-10)(r_6-2) \tag{11}$$

where q is the total number of edges in the PAH6. Why this equation is also valid for the branched cata-condensed benzenoids is revealed by comparing naphthacene and triphenylene in Fig. 1. For naphthacene, there are two outer rings excluding 8 edges and two inner rings excluding 10 edges giving $a_8^c=2\cdot 2(21-8)+2(21-10)(4-2)=2\cdot 2\cdot 13+2\cdot 11\cdot 2=52+44=96$; whereas, triphenylene has three outer rings excluding 8 edges and one inner ring excluding 12 edges giving $a_8^c=2(2+1)(21-8)+2(21-12)(4-2-1)=2\cdot 3\cdot 13+2\cdot 9\cdot 1=78+18=96$. Thus it is evident that these combinatorial changes always occur so as to preserve the overall magnitude of a_8^c between benzenoid isomers of the same formula. By the same reasoning, it can be shown that for all squared peri-condensed benzenoid PAH6s (naphthalene, pyrene, anthanthrene, etc.) in the $N_c = 3N_H$-14 column series of Table 1, the value of a_8^c is given by

$$a_8^c(\text{squared-PAH6}) = 2^2(q-10) + 2^2(q-9) + 2(q-11)(r_6-4).$$

Using the periodicity of Table 1, it can be shown that these equations, can be generalized to the following which is valid for all odd and even carbon PAH6s.

$$\begin{aligned} a_8^c(\text{PAH6}) &= 2^2(q-8) + 2(q-10)(r_6-2) - 2N_{Ic} \\ &= 2^2(q-10) + 2^2(q-9) + 2(q-11)(r_6-4) + 2d_s. \end{aligned} \tag{12}$$

Refer to Gutman's work for an alternative derivation of Eq. (12) [19].

By analogy to the previous method used to determine the topological relationship for a_6, the following relationship is constructed for a_8(acenes):

$$\begin{aligned} a_8(\text{acenes}) &= a_8^c + a_8^{ac} \\ &= a_8^c + (\tfrac{1}{24})(q-7)(q-6)(q-5)(q-4) + aq_I^3 + bq_I^2 + cq_I + d. \end{aligned}$$

Using known data to solve for *a*, *b*, *c*, and *d* and combining the results with Eqs. (10) and (11) gives

$$\begin{aligned} a_8(\text{cat-PAH6}) = {} & 4(q-8) + 2(q-10)(r_6-2) + 5(r_6-2)n_0 \\ & + n_0' - 2(n_4-2) + (\tfrac{1}{24})(q-7)(q-6)(q-5)(q-4) - (\tfrac{50}{3})q_I^3 \\ & + 22q_I^2 - (\tfrac{34}{3})q_I + 2 \end{aligned} \tag{13}$$

which is valid for all cata-condensed benzenoid hydrocarbons.

Other row series can yield equations similar to Eq. (13) but the sparse data available has inhibited solution of a comprehensive equation for a_8 comparable to that of Eq. (8) for a_6. Also, a more general form of Eq. (10) needs to be discovered. Currently the following relationship of $\Delta a_8(\text{PAH6 isomers}) = 5(r_6-2)n_0 + n_0' - 2(n_4-2) + (n_4-n_0)N_{Ic}$ appears to predict 88% of the known data [20] with the remaining 12% of the data being off by ±1. Whether this indicates that current set of perimeter descriptors are inadequate or that this computer generated data incorporates a ±1 round-off error needs to be determined, and work is currently in progress in our laboratory to generate more characteristic polynomial data for PAH6s.

Utilization of relationships previously derived [27] converts Eq. (12) to

$$\begin{aligned} a_8^c = {} & 2(q^2 - 13q - 12) - 2N_c(q-15) - 2r_8 - 4d_1 - 2d_{2_b} \\ & + 0d_3 + 2d_4 + 4d_5 + 6d_6 + \cdots \end{aligned}$$

where d_{2_b} is the number of second degree vertices in a conjugated polyene branch (*b* for branch) of a σ-bond graph. This equation is valid for all benzenoid hydrocarbons with and without conjugated polyene substituents [25]; it is also valid for all acyclic conjugated polyenes for which this equation always gives $a_c^8 = 0$. All molecular graphs containing less than eight vertices or no rings have $a_c^8 = 0$, and the addition of other parameters can broaden the applicability of this equation to other classes of molecular graphs.

6. The a_{10} coefficient

The cyclic contribution to the tenth coefficient a_{10}^c of the characteristic polynomial for cata-condensed benzenoid hydrocarbons differs among a set of PAH6 isomers according to $\Delta a_{10}^c(\text{cata-PAH6 isomers}) = 4n_0 + 8(n_4 - 2)$. A straightforward combinatorial derivation of a_{10}^c for the acenes can be easily accomplished by considering all possible combinations of one C_6 and two K_2 components, and combining this result with the above relationship leads to

$$\begin{aligned}-a_{10}^c(\text{cata-PAH6}) = {} & 10(q-11)+2(q_I-1)(5q-61)\\ & +2(r_6-1)+2(q-13)[5(r_6-3)+1]+4(q-14)(r_6-3)\\ & +4(q-14)[2(r_6-4)q_I-(r_6-2)(r_6-1)+6]\\ & +(q-15)(r_6-2)(q_I-2)+4n_0+8(n_4-2).\end{aligned} \tag{14}$$

7. Conclusion

An isomeric set of graphs has the same number of edges ($a_2 = -q$), rings (r) and vertices (p) which are graphical invariants. In this work, it has been shown that for an isomeric set of polycyclic graphs composed of only second and third degree vertices and no internal second degree vertices that $d_s + N_{Ic} = \text{constant}$ is also a graphic invariant. For such an isomeric set of polycyclic graphs without tetragonal rings, a_4 and $a_6 + n_0 + 2r_6$ (the latter without trigonal rings) of the characteristic polynomial are also graphical invariants.

From the contents of what has been presented, it should be apparent that Eq. (6) is almost universal in applicability to graphs in general. The explicit inclusion of d_2 and d_3 with zero coefficients in Eq. (6) is to emphasize the difference series of −1, 0, 1, 2, 3, 4,... between the coefficients of d_i.

Eq. (8) appears to be valid for benzene and all polycyclic aromatic hydrocarbons not possessing trigonal or tetragonal rings. The derivations presented herein emphasize the broad utility of Table 1.

If one compares the values (in parentheses) of a_4 for graphs corresponding to 2,2-dimethylbutane (6), 2,3-dimethylbutane (7), 2-methylpentane (8), 3-methylpentane (8), and *n*-hexane (9), one notes that the relative magnitude of a_4 parallels the boiling points and heats of vaporizations of these compounds where 2-methylpentane and 3-methylpentane have the smallest differences in these physical properties. This correlation emphasizes the relationship of a_4 to graph connectivity [2, 4]. Eqs. (6) and (8) not only allow us to determine the characteristic polynomial of small molecules by inspection but they are useful in checking computer HMO calculations of larger molecules.

Although, two less general equations have been previously presented for a_4 [28, 29], one after submission of this paper, this work emphasizes the utility of the relationship for a_4 in determining the characteristic polynomial for small molecules of interest to organic chemists by inspection [12, 26]. The usefulness of a_4 in determining an upper bound for the E_π energy for alternate conjugated hydrocarbons has been delineated [29]. Eqs. (8), (10), (13), and (14) have been derived in toto in this work for the first time, and alternative derivations for Eqs. (6) and (12) have been presented.

The perimeter topology of polyhexes has been detailed herein, and the perimeter topological parameters of n_0, n_0', n_1, n_2, n_3, and n_4 are useful descriptors. From this work our intuition that the bay region and branching parameters (n_0 and n_4, respectively) are the more important ones has been corroborated [cf. Eqs. (8), (10), and (14)]. By equating the two sides of Eq. (12), it can be easily shown that $d_s + \mathrm{N}_{\mathrm{Ic}} = r - 2$ is obtained; thus $a_8^c(\mathrm{PAH6})$ is also a graphical invariant. Topological equations for polyhexes in terms of perimeter descriptors have been derived for the first time. An independent derivation of a more comprehensive relationship for a_4 has been presented, and equations for a_6 and a_8 have been derived for the first time. The set of known graphical invariants (GI) for PAH6s is summarized as follows

$$\mathrm{GI} = \{a_4, a_6 + n_0 + 2r_6, a_8^c, d_s + \mathrm{N}_{\mathrm{Ic}}, \mathrm{N}_c, \mathrm{N}_{\mathrm{H}}, \mathrm{N}_{\mathrm{Ic}} + \mathrm{N}_{\mathrm{Pc}}, q, r\}.$$

Although the unavailability of more extensive characteristic polynomial data has thwarted the solution of comprehensive relationships for $a_8(\mathrm{PAH6})$ and $a_{10}(\mathrm{PAH6})$, the results thus far obtained suggest that the approach presented in this paper has further potential in identifying other structural parameters associated with the molecular topology of PAH6s. Before this approach can be fully manifested, a set of mathematical descriptors may be required which would allow one to totally differentiate each isomer from a set of PAH6s. While it is evident from this work that the perimeter topological parameters of n_0, n_0', n_{04}, n_1, n_2, n_3, and n_4 are useful descriptors, they do not allow one to clearly distinguish between all PAH6 isomers.

Since $n_3 = 0$ for the cata-condensed benzenoid hydrocarbons, one can deduce from the relationship of $-n_0 + n_2 + 3n_4 = 6$ that there are only two independent perimeter topological parameters for the cata-condensed PAH6s, and this is consistent with the qualitative observation that the more bay regions and branching possessed by a cata PAH6 isomer, the more stable it is relative to its other isomers. Since $n_4 = 0$ for strictly peri-condensed PAH6s, a similar argument can, likewise, be presented for these PAH6s. For PAH6s that are neither cata-condensed nor strictly peri-condensed, there are three independent perimeter topological parameters. From the relationship of $d_s + \mathrm{N}_{\mathrm{Ic}} = r - 2$, it must be deduced that there are also two independent internal topological parameters for PAH6s.

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