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A Periodic Table for Polycyclic Aromatic Hydrocarbons. Part V. 1-Factorable, 2-Factorable, and Dewar Graph Structures Associated with Benzenoid Hydrocarbons

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A Periodic Table for Polycyclic Aromatic Hydrocarbons. Part V. 1-Factorable, 2-Factorable, and Dewar Graph Structures Associated with Benzenoid Hydrocarbons

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ABSTRACT

Further properties of a Formula Periodic Table for Benzenoid PAH6s are presented. Whether the number of components of 1-factor and 2-factor subgraphs of benzenoid hydrocarbons are even or odd and the sign of the a_N coefficient of the characteristic polynomial is negative or positive are prescribed by this table. A method for computing the number of Dewar structures from the a^{ac}_{N-2} coefficient of the acrylic polynomial is reviewed. It is shown that a stronger correlation of resonance energy and ln a^{ac}_{N-2} of ln KN_c exists than for ln K where K = SC (structure count) = a_N^{ac}. It is conjectured that ethene is subspectral to all benzenoid PAH6 structures belonging to the $N_c \equiv 0 \pmod 4$ row series of the formula periodic table for benzenoid PAH6s.

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Previous research from this laboratory has evolved a formula periodic table for PAH6s which for the first time unified formula/structure relationships of benzenoid hydrocarbons into a systematic framework [1]. Herein additional correlations of this periodic table are presented. Also, structural relationships of the coefficients of the acyclic and characteristic polynomials within the frame of this table are reviewed.

DISCUSSION AND RESULTS

Throughout this paper only the σ-bond graph for PAHs will be drawn. The emphasis and correlations presented are for benzenoid polycyclic aromatic hydrocarbons (PAH6) or polyhexes. In the rows of the formula periodic table for benzenoid PAH6s (Table 1), the number of formula carbons (N_c) increases from left to right according to the even residue classes of congruent modulo 4. For example, in the $N_c = 2N_H - 6$ and $N_c = 2N_H - 4$ row series, the number of formula carbons follow $N_c \equiv 2(\mathrm{mod}\ 4)$ and $N_c \equiv 0(\mathrm{mod}\ 4)$, respectively; these two respective relationships are each applicable for every other row. In the columns of the formula periodic table for benzenoid PAH6s, the number of formula carbons increases from top to bottom according to the even residue classes of congruent modulo 6. In the $N_c = 3N_H - 14$, $N_c = 3N_H - 16$, and $N_c = 3N_H - 18$ column series, the number of formula carbons are given by $N_c \equiv 4(\mathrm{mod}\ 6)$, $N_c \equiv 2(\mathrm{mod}\ 6)$, and $N_c \equiv 0(\mathrm{mod}\ 6)$, respectively; this sequence of congruent modulo 6 relationships successively repeats for all the columns in Table 1. The basis for Table 1 is that all PAH structures having a common CH formula must comply with $d_s + N_{Ic}$ = constant where d_s is the net number of disconnections (or connections) of internal edges and N_{Ic} is the number of internal third degree carbon vertices. For example, anthracene/phenanthrene have two internal edges disconnected ($d_s = 1$) and no internal third degree vertices ($N_{Ic} = 0$), and anthanthrene/benzo(ghi)-perylene have all their internal edges connected ($d_s = 0$) and four internal third degree vertices ($N_{Ic} = 4$).

Graphical Properties of Polycyclic Aromatic Hydrocarbons

The minimum degree among the points (vertices) of graph G is denoted by $\delta(G)$ while $\Delta(G)$ is the maximum degree of G [2]. If all the points of a graph G have the same degree, then G is called a regular graph. A regular graph of degree 1 requires that every component contain exactly one line (edge); if a graph G is regular of degree 2, then every component is a cycle (ring). Regular graphs of degree 3 are called cubic; the planar isomorphic equivalents of the tetrahedron and cube are cubic graphs. Every cubic graph has an even number of points since $\Sigma d_i = 2q$; in any graph the number of odd degree points is even. The connectivity $\kappa = \kappa(G)$ of a graph G is the minimum number of points whose removal results in a disconnected or trivial graph. The connectivity of a connected graph with a cutpoint is 1. The complete graph K_p gives only a trivial graph upon removing p - 1 points $[\kappa(K_p) = p - 1]$. The line connectivity $\lambda = \lambda(G)$ of a graph G is the minimum number of lines whose removal results in a disconnected or trivial graph. The line connectivity of a connected graph with a bridge is 1 and $\lambda(K_1) = 0$. For any graph G, $\kappa(G) \leq \lambda\ (G) \leq \delta\ (G)$. A factor of a graph G is a spanning subgraph of G which is not totally disconnected. When G has a 1-factor, then p is even and the 1-factor lines are point disjoint. In general, the complete graph K_{2n} is 1-factorable. A graph is 2-factorable if it has spanning subgraphs that are regular of degree 2. The complete graph K_{2n+1} has n spanning cycles that are 2-factors. Girth g(G) of a graph G is the length of the shortest cycle of a graph, and circumference c(G) is the length of the longest cycle of G. Polycyclic conjugated hydrocarbon σ-bond graphs have only second and third degree carbon vertices; therefore, $\delta\,(PAH) = 2$ and $\Delta(PAH) = 3$. The $p\pi$ graphs of PAHs are regular graphs of degree 1 and can be derived by 1-factorization of the corresponding PAH σ-bond graph. All PAHs are 2-connected $[\kappa(PAH) = \gamma(PAH) = \delta\,(PAH) = 2]$. Biphenyl is 1-connected with $\kappa = \gamma = 1$. Triangulene is a diradical PAH6 and is not 1-factorable since it has no spanning, regular subgraph of degree 1. Chrysene, perylene, and benzo(ghi)perylene have the following 2-factorable subgraphs. The σ-bond graph of all cata-condensed PAH6s have a single 2-factor subgraph that corresponds to their circumference the length of which is given by $c(\text{cata-PAH6}) = q_p = 2N_H - 6$.

Not all of the isomers of the peri-condensed PAH6s are 2-factorable. A prerequisite for a nonsymmetrical peri-condensed PAH6 to be 2-factorable is that it must possess a concave bay region [e.g., like perylene or benzo(ghi)perylene]. The symmetrical graphs of the one isomer series of polycircumnaphthalene and polycircumcoronene have 2-factor subgraphs comprised of concentric rings, whereas the one isomer polycircumpyrene series give graphs that do not have 2-factor subgraphs [1]. Other symmetrical peri-condensed PAH6s having concave bay regions may or may not have 2-factor subgraphs. Table 2 summarizes the 1- and 2-factorable characteristics of some benzenoid PAHs. It is informative to examine the structures of $C_{22}H_{12}$ versus $C_{52}H_{18}$ (Fig. 1) and $C_{30}H_{14}$ versus $C_{64}H_{20}$ (Figs. 2 and 3). Anthathrene and benzo(ghi)perylene ($C_{22}H_{12}$) are the exised internal

TABLE 1. Formula Periodic Table for Polycyclic Aromatic Hydrocarbons (PAH6) ($N_c = 3N_H - 14 - 2d_s$)

$N_c = 3N_H + 4$	$N_c = 3N_H + 2$	$N_c = 3N_H$	$N_c = 3N_H - 2$	$N_c = 3N_H - 4$	$N_c = 3N_H - 6$	$N_c = 3N_H - 8$
	Forbidden region					
						$N_c/N_H < 2$
		$C_{00}H_{00}$				
					$2 < N_c/N_H < 3$	
$N_c/N_H > 3$						
						$C_{40}H_{16}$
					$C_{42}H_{16}$	$C_{46}H_{18}$
					$C_{48}H_{18}$	$C_{52}H_{20}$
				$C_{50}H_{18}$	$C_{54}H_{20}$	$C_{58}H_{22}$
			$C_{52}H_{18}$	$C_{56}H_{20}$	$C_{60}H_{22}$	. . .
		$C_{54}H_{18}$	$C_{58}H_{20}$	$C_{62}H_{22}$	. . .	
		$C_{60}H_{20}$	$C_{64}H_{22}$	. . .		
	$C_{62}H_{20}$	$C_{66}H_{22}$	. . .			
$C_{64}H_{20}$	$C_{68}H_{22}$	. . .				
$C_{70}H_{22}$	. . .					
. . .						

(continued)

TABLE 1 (continued)

$N_c = 3N_H - 10$	$N_c = 3N_H - 12$	$N_c = 3H_N - 14$	$N_c = 3N_H - 16$	$N_c = 3N_H - 18$	$N_c = 3N_H - 20$	$(N_c = 2N_H - 6 + N_{Ic})$
		$C_{10}H_8$	$C_{14}H_{10}$	$C_{18}H_{12}$	$C_{22}H_{14}$	$N_c = 2N_H - 6$
		$C_{16}H_{10}$	$C_{20}H_{12}$	$C_{24}H_{14}$	$C_{24}H_{14}$	$N_c = 2N_H - 4$
		$C_{22}H_{12}$	$C_{26}H_{14}$	$C_{30}H_{16}$	$C_{34}H_{16}$	$N_c = 2N_H - 2$
	$C_{24}H_{12}$	$C_{28}H_{14}$	$C_{32}H_{16}$	$C_{36}H_{18}$	$C_{40}H_{20}$	$N_c = 2N_H$
	$C_{30}H_{14}$	$C_{34}H_{16}$	$C_{38}H_{18}$	$C_{42}H_{20}$	$C_{46}H_{22}$	$N_c = 2N_H + 2$
$C_{32}H_{14}$	$C_{36}H_{16}$	$C_{40}H_{18}$	$C_{44}H_{20}$	$C_{48}H_{22}$	$C_{52}H_{24}$	$N_c = 2N_H + 4$
$C_{38}H_{16}$	$C_{42}H_{18}$	$C_{46}H_{20}$	$C_{50}H_{22}$	$C_{54}H_{24}$	$C_{58}H_{26}$	$N_c = 2N_H + 6$
$C_{44}H_{18}$	$C_{48}H_{20}$	$C_{52}H_{22}$	$C_{56}H_{24}$	$C_{60}H_{26}$	$C_{64}H_{28}$	$N_c = 2N_H + 8$
$C_{50}H_{20}$	$C_{54}H_{22}$	$C_{58}H_{24}$	$C_{62}H_{26}$	$C_{66}H_{28}$	. . .	$N_c = 2N_H + 10$
$C_{56}H_{22}$	$C_{60}H_{24}$	$C_{64}H_{26}$	$C_{68}H_{28}$	. . .		$N_c = 2N_H + 12$
. . .	. . .	. . .	. . .			$N_c = 2N_H + 14$
						$N_c = 2N_H + 16$
						$N_c = 2N_H + 18$
						$N_c = 2N_H + 20$
						$N_c = 2N_H + 22$
						$N_c = 2N_H + 24$
						$N_c = 2N_H + 26$
						. . .

(continued)

TABLE 1 (continued)

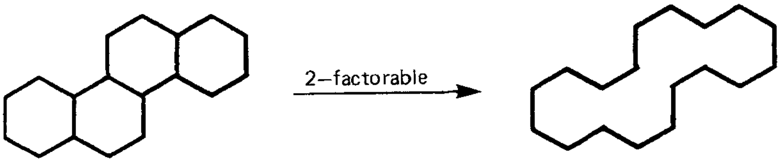
$N_c = 3N_H - 22$	$N_c = 3N_H - 24$	$N_c = 3N_H - 26$	$N_c = 3N_H - 28$	$N_c = 3N_H - 30$	$N_c = 3N_H - 32$	$N_c = 3N_H - 34$
$C_{26}H_{16}$	$C_{30}H_{18}$	$C_{34}H_{20}$	$C_{38}H_{22}$	$C_{42}H_{24}$	$C_{46}H_{26}$	$C_{50}H_{28}$
$C_{32}H_{18}$	$C_{36}H_{20}$	$C_{40}H_{22}$	$C_{44}H_{24}$	$C_{48}H_{26}$	$C_{52}H_{28}$	$C_{56}H_{30}$
$C_{38}H_{20}$	$C_{42}H_{22}$	$C_{46}H_{24}$	$C_{50}H_{26}$	$C_{54}H_{28}$	$C_{58}H_{30}$	$C_{62}H_{32}$
$C_{44}H_{22}$	$C_{48}H_{24}$	$C_{52}H_{26}$	$C_{56}H_{28}$	$C_{60}H_{30}$	$C_{64}H_{32}$	$C_{68}H_{34}$
$C_{50}H_{24}$	$C_{54}H_{26}$	$C_{58}H_{28}$	$C_{62}H_{30}$	$C_{66}H_{32}$	. . .	. . .
$C_{56}H_{26}$	$C_{60}H_{28}$	$C_{64}H_{30}$	. . .	. . .		
$C_{62}H_{28}$	$C_{66}H_{30}$	. . .				
$C_{68}H_{30}$	. . .					
. . .						

$2 < N_c/N_H < 3$

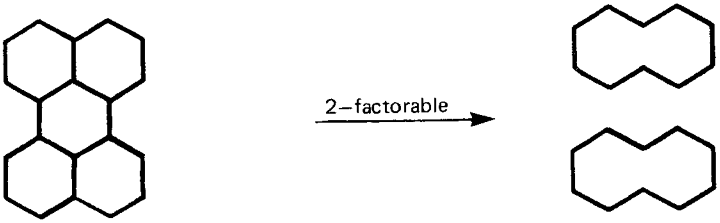
(continued)

TABLE 1 (continued)

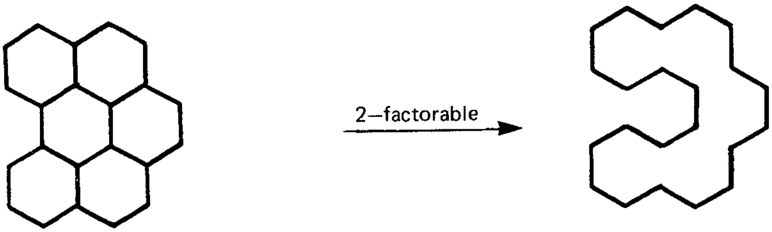
$N_c = 3N_H - 36$	$N_c = 3N_H - 38$	$N_c = 3N_H - 40$	$N_c = 3N_H - 42$	$N_c = 3N_H - 44$	. . .	
$C_{54}H_{30}$	$C_{58}H_{32}$	$C_{62}H_{34}$	$C_{66}H_{36}$	$C_{70}H_{38}$	. . .	$N_c = 2N_H - 6$
$C_{60}H_{32}$	$C_{64}H_{34}$	$C_{68}H_{36}$	$C_{72}H_{38}$	. . .	. . .	$N_c = 2N_H - 4$
$C_{66}H_{34}$	. . .	. . .	. . .		. . .	$N_c = 2N_H - 2$
$C_{72}H_{36}$					. . .	$N_c = 2N_H$
. . .					. . .	$N_c = 2N_H + 2$
					. . .	$N_c = 2N_H + 4$
					. . .	$N_c = 2N_H + 6$
					. . .	$N_c = 2N_H + 8$
					. . .	$N_c = 2N_H + 10$
						. . .



$C_{18}H_{12}$
Chrysene



$C_{20}H_{12}$
Perylene



$C_{22}H_{12}$
Benzo(ghi)perylene

structures of the structures of $C_{52}H_{18}$. Only benzo(ghi)perylene and its circumscribed derived $C_{52}H_{18}$ structure have one concave bay region and 2-factorable subgraphs. Similarly, dibenzo(bc,ef) coronene, naphtho(abc)coronene, and dibenzo(bc,kl)coronene ($C_{30}H_{14}$) are the excised internal structures of the structures of $C_{64}H_{20}$; only the first structures and their corresponding circumscribed derived $C_{64}H_{20}$ structures have one concave bay region and 2-factor subgraphs. In general, derived PAH6 structures made by circumscribing internal structures have the same number of concave bay regions as their excised internal structures. Also, derived structures have 2-factor subgraphs if their internal structures are 2-factorable, and the former have one more component than their corresponding excised internal

TABLE 2. 1-Factorable and 2-Factorable Benzenoid PAHs

Formula	No. of PAH6 isomers[a]	No. of concave bay regions	No. of isomers having 2-factor subgraphs	No. of isomers having two or more 2-factor subgraphs	No. of components in 2-factor subgraphs	SC range[b]
$C_{10}H_8$[c]	1	0	1	0	1	3
$C_{14}H_{10}$[c]	2	0-1	2	0	1	4-5
$C_{16}H_{10}$	1	0	0	0	0	6
$C_{18}H_{12}$[c]	5	0-3	5	1	1, 3	5-9
$C_{20}H_{12}$	3	1-2	2	0	2	9-11
$C_{22}H_{12}$	2	0-1	1	0	1	10-14
$C_{22}H_{14}$	12	0-4	12	2	1, 3	6-14
$C_{24}H_{12}$	1	0	1	0	2	20
$C_{24}H_{14}$	13	1-4	7	1	2, 4	9-20
$C_{26}H_{14}$	9	1-3	4	2	1, 3	14-25
$C_{26}H_{16}$[c]	37	0-6	37	12	1, 3	7-24
$C_{28}H_{14}$	8	0-2	5	0	2	15-34

(continued)

TABLE 2 (continued)

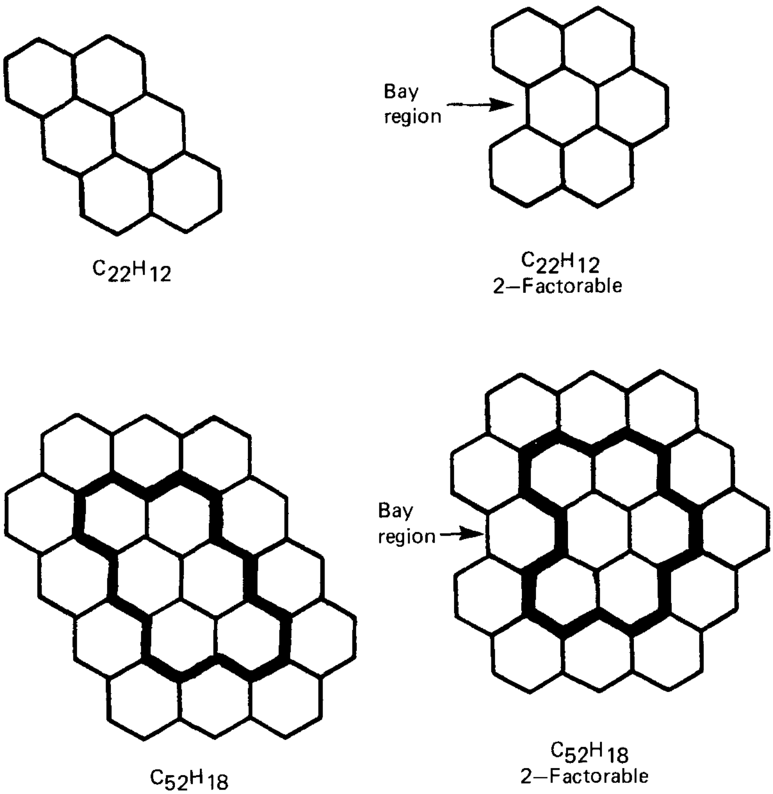
Formula	No. of PAH6 isomers[a]	No. of concave bay regions	No. of isomers having 2-factor subgraphs	No. of isomers having two or more 2-factor subgraphs	No. of components in 2-factor subgraphs	SC range[b]
$C_{28}H_{16}$	62	1-5	39	3	2	9-31
$C_{30}H_{14}$	3	0-1	2	0	1	20-30
$C_{30}H_{18}$[c]	123	0-7	123	53	1, 3, 5	8-41
$C_{32}H_{14}$	1	0	1	0	2	50
$C_{34}H_{16}$	37	0-4	21	14	1, 3	
$C_{34}H_{20}$[c]	446	0-9	446	250	1, 3, 5	9-66
$C_{38}H_{16}$	10	0-2	6	0	1, 3	35-136
$C_{40}H_{16}$	3	0-1	2	0	2	105-155
$C_{42}H_{16}$	1	0	0	0	0	175
$C_{48}H_{18}$	22	0-3	11	4	2, 4	70-585
$C_{50}H_{18}$	7	1-2	4	2	1, 3	
$C_{52}H_{18}$	2	0-1	1	1	2	

$C_{52}H_{18}$	2	0-1	1	1	2	
$C_{54}H_{18}$	1	0	1	0	3	980
$C_{60}H_{20}$	20	1-3	13	8	2, 4	
$C_{62}H_{20}$	12	0-2	8	6	1, 3	
$C_{64}H_{20}$	3	0-1	2	2	2	

[a] Graphs that are 1-factorable.

[b] Structure count (SC) is the number of Kekulé structures which is equal to the number of 1-factor subgraphs.

[c] Cata-condensed benzenoid series.



$C_{22}H_{12}$

$C_{22}H_{12}$
2–Factorable

$C_{52}H_{18}$

$C_{52}H_{18}$
2–Factorable

FIG. 1. The two nonradical isomers of $C_{22}H_{12}$ and $C_{52}H_{18}$.

structures. From Table 2 it is evident that 2-factor subgraphs of structures having formulas falling in the alternate rows of $N_c = 2N_H - 6$, $N_c = 2N_H - 2$, . . . [i.e., $N_c \equiv 2 (\mathrm{mod}\ 4)$] of Table 1 have an odd number of components and an even number of components if they fall in the other set of alternate rows [i.e., $N_c \equiv 0 (\mathrm{mod}\ 4)$]. Many of the benzenoid graphs that are 2-factorable have only a single 2-factor subgraph. Examples of a few benzenoid graphs of this study that have three or more 2-factor subgraphs are shown in Fig. 4. In general, isomers having more concave bay regions are the more stable isomers and have more 2-factor subgraphs, and a PAH graph is 2-factorable if its excised internal structure is 2-factorable. The cata-condensed PAH6 isomers having two or more (odd component) 2-factor subgraphs were invariably branched (Table 2). Also, the most branched cata-condensed PAH6s have the largest number of 1-

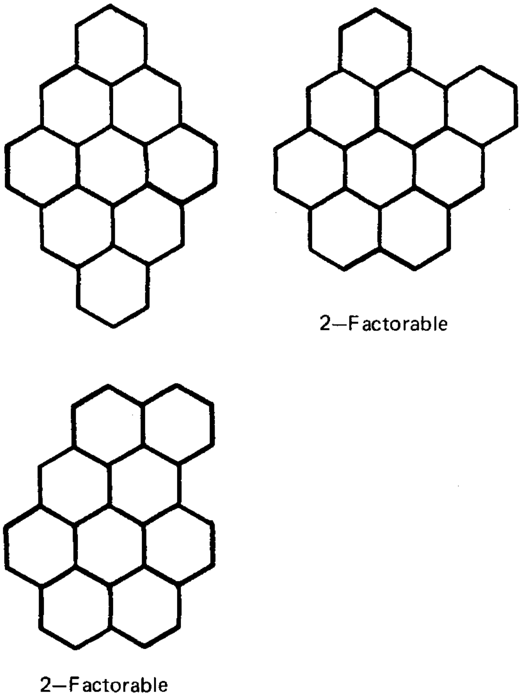
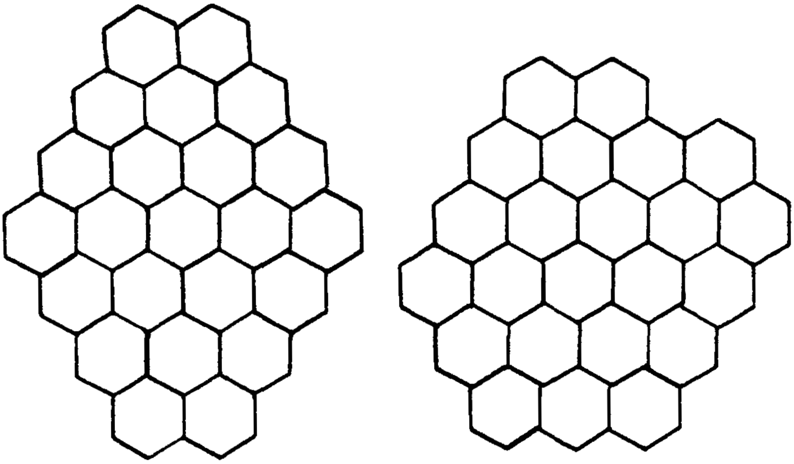


FIG. 2. The three nonradical isomers of $C_{30}H_{14}$.

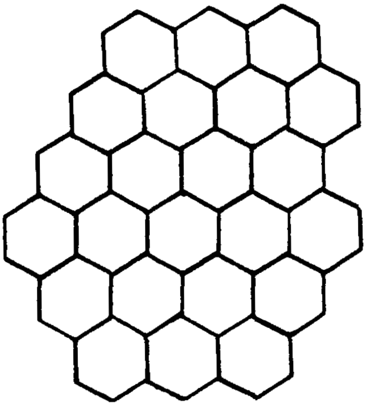
factor subgraphs (i.e., SC) whereas the acenes have the smallest number of 1-factor subgraphs.

A point and a line are said to cover each other if and only if they are incident [3]. Two points or two lines cover each other if and only if they are adjacent. A set of points (lines) of a graph G which covers all the lines (points) of G is called a point (line) cover of G. The smallest number of points (lines) is a point (line) cover is the point (line) covering number $\alpha_0(\alpha_1)$ of G. A set of points (lines) of G is independent if no two of them are adjacent. The largest number of points (lines) in an independent set of points (lines) is the point (line) independence number of G and is denoted by $\beta_0(\beta_1)$. For any graph G, $\alpha_0(G) \geq S(G)$, $\alpha_0(G) \geq \beta_1(G)$, and $\alpha_1(G) \geq \beta_0(G)$. If G is bipartite, $\alpha_0(G) = \beta_1(G)$. For any nontrivial connected graph G, $\alpha_0 + \beta_0 = \alpha_1 + \beta_1$. A clique of a graph is a maximal complete subgraph. The clique graph of G, K(G), is the intersection graph of the set of cliques of G. For any G, $\beta_0(G) \leq \theta(G)$, where θ is the minimum number of cliques



$C_{26}H_{20}$

$C_{64}H_{20}$
2–Factorable



$C_{26}H_{20}$
2–Factorable

FIG. 3. The three nonradical isomers of $C_{64}H_{20}$.

the union of whose vertices is V(G). The density of G, ω(G), is the number of points in a maximum clique (maximum complete subgraph) or G. The chromatic number of G, χ(G), is the minimum coloring of G such that no two adjacent points have the same color. For any G, $\chi(G) \leq 1 + \Delta(G)$. If $\Delta(G) = 2$ and G does not have a component corresponding to an odd cycle or if $\Delta(G) \geq 3$ and G does not have $K_{\Delta+1}$ as

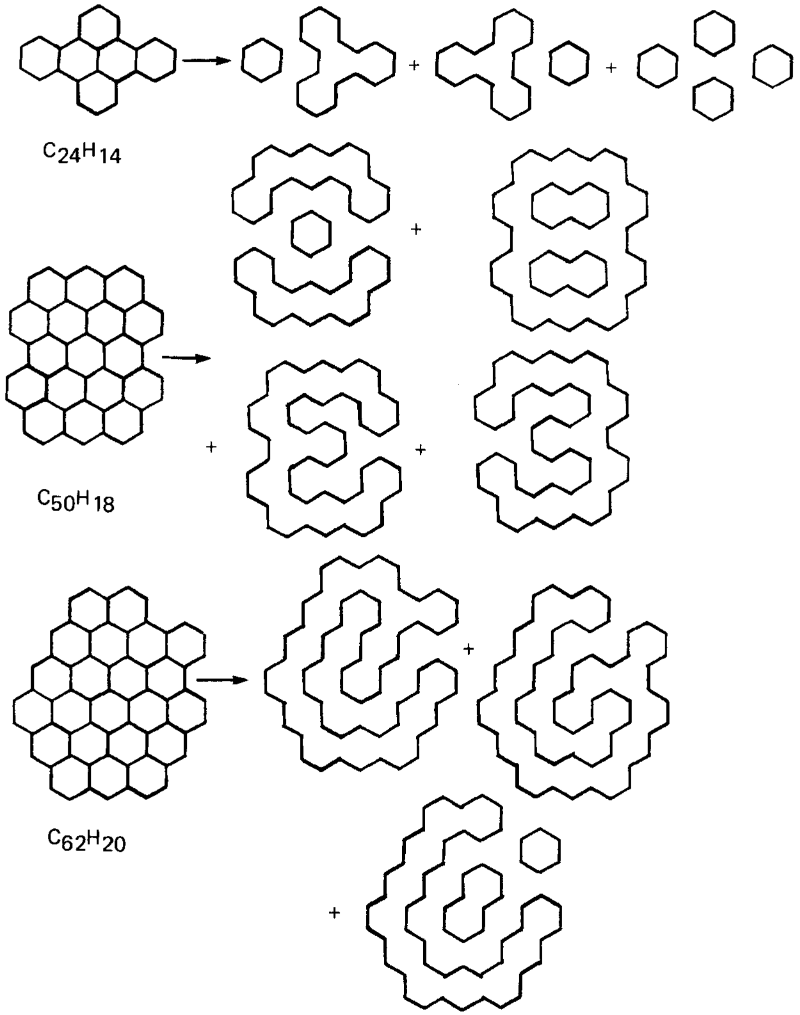
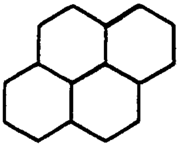


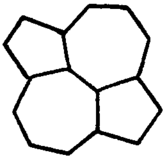
FIG. 4. Representative peri-condensed PAH6s and their 2-factor subgraphs.

a component, then $\chi(G) \leq \Delta(G)$. If G is connected, then $\chi(G) \leq 1 + \epsilon_{max}$, where ϵ_{max} is the maximum eigenvalue of the adjacency matrix of G. The genus of a graph G, $\gamma(G)$ is the minimum genus of a surface in which G can be embedded, i.e., surface curves can only intersect at points on the surface. Since planar graphs can be embedded on the surface of a sphere (or plane), $\gamma(G) = 0$ and $\chi(G) \leq 4$ for planar graphs. Hence, if a planar graph has an odd girth, g(G), $\chi(G) = 3$ or 4. If G cannot be embedded on a sphere but can be on a donut (torus) shaped surface, then $\gamma(G) = 1$, and $\chi(G) \leq 7$ if $g = 3$, $\chi(G) \leq 4$ if $g = 5$, and $\chi(G) \leq 3$ if $g \geq 6$. The line chromatic number of a graph G, $\chi_1(G)$, is the minimum number of colors that can be assigned to the lines of G such that no two adjacent lines have the same color. For any G, $\Delta(G) \leq \chi_1(G) \leq \Delta(G) + 1$. These graphical properties on PAHs are illustrated for the following σ-bond graphs of pyrene and azupyrene.



$\alpha_0 = 8,\ \beta_0 = 8,\ \alpha_1 = 8,\ \beta_1 = 8$

$\theta = 8,\quad \omega = 2,\quad \chi = 2,\ \chi_1 = 3$



$\alpha_0 = 9,\ \beta_0 = 7,\ \alpha_1 = 8,\ \beta_1 = 8$

$\theta = 8,\quad \omega = 2,\quad \chi = 3,\ \chi_1 = 3$

The smallest number of points in a point cover of pyrene ($\alpha_0 = 8$) or azupyrene ($\alpha_0 = 9$) consists of their starred vertices; note that $\alpha_0(P) = 8 > \delta(P) = 2$. Since both pyrene and azupyrene are isomeric and both can be represented by Kekulé structures [$\alpha_1(P) = \alpha_1(A)$ and $\beta_1(P) = \beta_1(A)$] and only pyrene is bipartite [$\alpha_0(P) = \beta_1(P)$ and $\alpha_0(A) > \beta_1(A)$], azupyrene has $\alpha_0(A) = 9 > \beta_1(A) = 8$ and $\alpha_1(A) = 8 > \beta_0(A) = 7$. The only complete subgraphs of PAHs are K_2 components and the minimum number of cliques the union of whose vertices is V(PAH) is given by the union of the vertices of the K_2 components belonging to the 1-factor subgraph of the PAH. Thus $\beta_0(P) = \theta(P) = 8$ and $\beta_0(A) = 7 < \theta(A) = 8$. For all PAHs $\omega = 2$, and for all even alternate PAHs $\chi = 2$. Since pyrene is bipartite $\chi(P) = 2$, but for azupyrene which is not bipartite $\chi(A) = 3$; in both cases $\chi \leq \Delta(G) = 3$. For pyrene and azupyrene, $\chi(P) = 2 \leq 1 + \epsilon_{\max} = 3.5321$ and $\chi(A) = 3 \leq 1 + \epsilon_{\max} = 3.5321$. All PAHs are planar graphs of genus $\gamma = 0$ and colorability of $\chi \leq 3$ where the equality in the latter is applicable when the PAH graph has an odd girth like azupyrene. The line chromatic number of PAHs is $\chi_1 = \Delta(G) = 3$. All PAH graphs consisting of only even membered rings are bipartite and bichromatic. If a benzoid PAH6 σ-bond graph is not 1-factorable (i.e., is a diradical), then it cannot be 2-factorable. Conversely, if a PAH graph is 2-factorable, then it is also 1-factorable. All benzenoid PAH6 σ-bond graphs with $N_{Ic} = 0$ (i.e., cata-condensed) are 1-factorable and 2-factorable, and all PAH graphs with N_{Ic} = 1, 2, 3, . . . and N_c = odd number are not 1-factorable or 2-factorable. PAHs with N_c = even number and N_{Ic} = odd number cannot have spanning 2-factor subgraphs. Whether the number of components in 1-factor subgraphs of benzenoid of PAH6s are even or odd is also determined by Table 1. All benzenoid PAH6s in the row series of $N_c \equiv 2 \pmod 4$ will have an odd number of K_2 components, and all benzenoid PAH6s in the row series belonging to the $N_c \equiv 0 \pmod 4$ row series will have an even number K_2 components. In general, Fig. 5 illustrates that for any spanning subgraph composed of an admix of K_2 and C_{2n} components, whether there is an even or odd number of components is determined by the above rule.

Structural Relationships of Coefficients of the Acyclic and Characteristic Polynomials

Expansion of the Hückel molecular orbital (HMO) secular determined for a PAH graph gives the characteristic polynominal P(G; X) = det|XI-A| of the corresponding conjugated system where I is the identity matrix ans A is the adjacency matrix [4]. The characteristic polynomial of N carbon atom system has the following form

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

where a_n are coefficients that can be alternatively obtained by the graphical Sachs' method. This method is summarized by the following formula

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

where $0 \leq n \leq N$, 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, . . ., 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

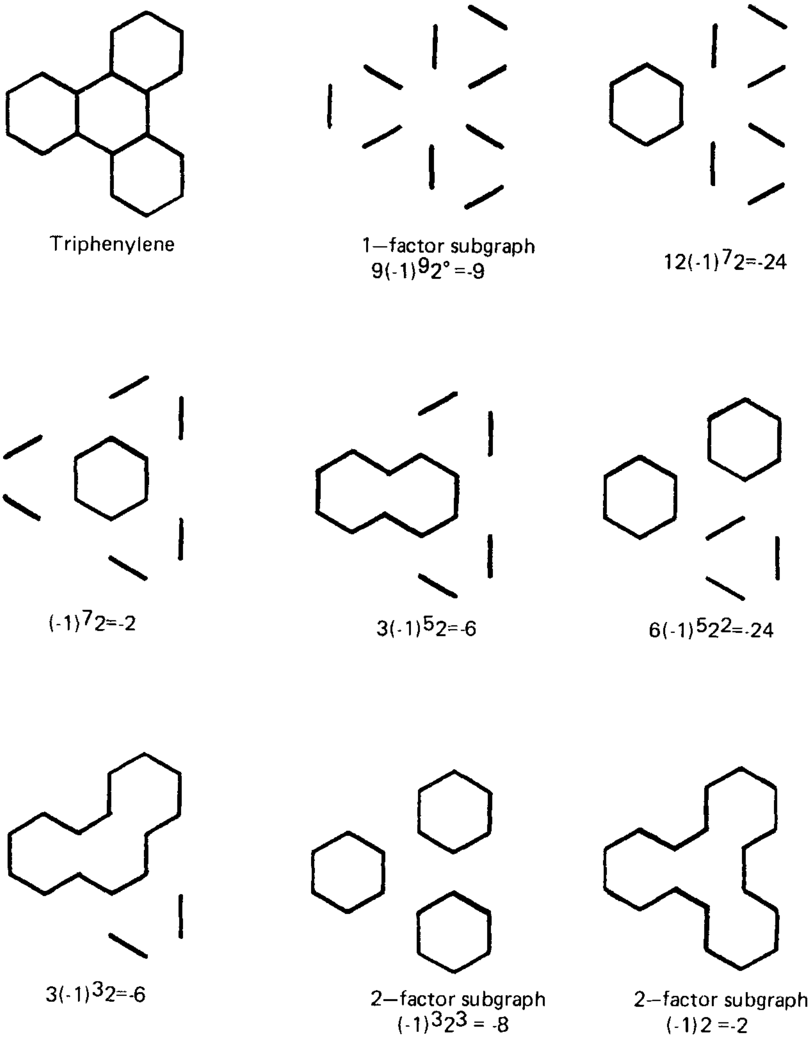


FIG. 5. Representative spanning subgraphs of triphenylene with corresponding contribution factors to $a_{18} = -K^2 = -81$.

of all Sachs graphs leads to the value of $a_2 = -q$ which is equal to the negative number of graph edges. For PAH6 $a_N = \pm K^2$, where K is the number of Kekulé structures (1-factors); for the PAH6s in the Table 1 row series of $N_c = 2N_H - 6$ (cata-condensed PAH6s), $N_c =$

$2N_H - 2$, $N_c = 2N_H + 2$, . . . the negative sign applies ($a_N = -K^2$) and for the remaining row series of $N_c = 2N_H - 4$, $N_c = 2N_H$, . . . the positive sign applies ($a_N = K^2$).

If the components of a Sachs graph are restricted to only K_2, then one obtains the following formula

$$a_n^{ac} = \sum_{s \in S_n} (-1)^{c(s)} \tag{3}$$

where $0 \leq n \leq N$ and S_n^{ac} is the set of all acyclic Sachs graphs of exactly N vertices. The corresponding acyclic polynomial $P^{ac}(G; X)$ is devoid of cyclic contributions and has been used to compute topological resonance energies (TRE) through the use of

$$\text{TRE} = E_\pi\,(\text{PAH}) - E_\pi\,(\text{acyclic reference}) = \sum_{j=1}^{N} g_i\,(X_j - X_j^{ac}) \tag{4}$$

It turns out that using Heilbronner's formula $[P(G; X) = P(G - e; X) - P(G - (e); X)]$, which is valid only for polyenes along with the recursion formula $[L_n = XL_{n-1} - L_{n-2}]$, which enables one to compute the characteristic polynomial of linear polyenes starting with $L_0 = 1$ and $L_1 = X$, one can easily calculate the acyclic polynomial corresponding to any polycyclic structure [5]. The characteristic and acyclic polynomials are related as follows:

$$P(G; X) - P^{ac}(G; X) = -2\sum_{m} P^{ac}(G - C_m; X) + 4 \sum_{m \leq n} P^{ac}(G - C_m - C_n; X) - 8 \sum_{m \leq n \leq p} P^{ac}(G - C_m - C_n - C_p; X) + \cdots \tag{5}$$

where $G - C_m$, $G - C_m - C_n$, $G - C_m - C_n - C_p$, . . . are subgraphs obtained by removing successively the vertices of the cycles C_m, $C_m + C_n$, $C_m + C_n + C_p$, . . . from G and the summations are over mutually disjoint cycles contained in G. Equation (5) allows one to simplify the computation of the characteristic polynomial of any polycyclic structure from the acyclic polynomial and enumeration Sachs graphs having cyclic components only. The last term in the acyclic polynomial is $a_N^{ac} = \pm K$

TABLE 3. Comparison of the Characteristic and Acyclic Polynomials of Isomers of Naphthalene ($C_{10}H_8$)

Compound	P(G; X) =									
Naphthalene	X^{10}	$- 11X^8$		$+ 41X^6$		$- 65X^4$		$+ 43X^2$		$- 9$
Azulene	X^{10}	$- 11X^8$		$+ 41X^6$	$- 2X^5$	$- 61X^4$	$+ 6X^3$	$+ 31X^2$	$- 2X$	$- 4$
Bicyclo[6.2.0] decapentaene	X^{10}	$- 11X^8$		$+ 39X^6$		$- 51X^4$		$+ 18X^2$		$- 1$
Bicyclo[7.1.0] decapentaene	X^{10}	$- 11X^8$	$- 2X^7$	$+ 41X^6$	$+ 12X^5$	$- 60X^4$	$- 20X^3$	$+ 29X^2$	$+ 6X$	$- 4$
Compound	$P^{ac}(G; X) =$									
Naphthalene	X^{10}	$- 11X^8$		$+ 41X^6$		$- 61X^4$		$+ 31X^2$		$- 3$
Azulene	X^{10}	$- 11X^8$		$+ 41X^6$		$- 61X^4$		$+ 31X^2$		$- 2$
Bicyclo[6.2.0] decapentaene	X^{10}	$- 11X^8$		$+ 41X^6$		$- 61X^4$		$+ 32X^2$		$- 3$
Bicyclo[7.1.0] decapentaene	X^{10}	$- 11X^8$		$+ 41X^6$		$- 60X^4$		$+ 29X^2$		$- 2$

where the sign is determined by the rule cited above for a_N. Thus the last term in (5) is $\pm(K^2 - K) = \pm K(K - 1)$. All the spanning 1-factor and 2-factor subgraphs and other subgraphs containing both K_2 and C_{4n+2} components are presented in Fig. 5 for triphenylene. From the results presented in these last paragraphs, it is evident that important graph theoretical information of PAHs is transmitted by their 1-factor and 2-factor subgraphs.

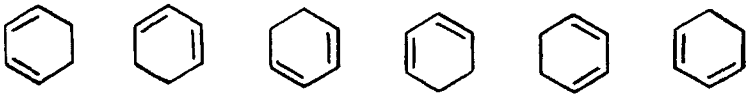
A comparison of the characteristic and acyclic polynomials of representative PAH6s is presented in Table 3 and reveals a number of topological generalizations that will now be discussed [6, 7]. The coefficient

$$a_4 = \sum_i [(K_2)_2]_i - 2\sum_j (C_4)_j$$

is graphically insensitive to structural changes in isomers having no tetragonal rings (C_4). Thus the $C_{14}H_{10}$ isomers of anthracene and phenanthrene have the same $a_4 = 98$ and the $C_{18}H_{12}$ isomers have the same $a_4 = 180$ [6]. In general, for benzenoid PAH6s,

$$a_4(\mathrm{PAH6}) = \sum_i [(K_2)_2]_i = a_4^{ac}$$

The difference in the polynomial coefficients of various PAH iosmers progressively increases for lower powers of X and are, therefore, more sensitive to structural changes among isomers. Differences in the a_{N-2} coefficient of various isomeric structures are significant and convey important structural information. This coefficient is made up of two primary contributions; an acyclic contribution (a^{ac}_{N-2}) and a cyclic one (a^{c}_{N-2}); $a_{N-2} = a^{ac}_{N-2} + a^{c}_{N-2}$. An outline for the inductive derivation for the acyclic contribution now follows. Consider the two Kekulé structures for benzene (K = 2). Deletion of one of the double bonds, one at a time for each Kekulé structure, gives the following six graphs which are equal to $K(N_c/2) = 2(6/2) = 6$.



The following additional graphs correspond to Dewar structures.

Thus, in general, the acyclic polynomial a^{ac}_{N-2} coefficient is given by

$$a^{ac}_{N-2} = K\left[\frac{N_c}{2}\right] + D = |a^{ac}_{N-2}|\left[\frac{N_c}{2}\right] + D \tag{6}$$

where K is the number of unexcited or Kekulé structures (structure count) and D is the number of first excited or Dewar structures [7]. Equation (6) is important and shows that excited graph structures make contributions to the polynomial coefficients. The Wheland Polynomial can be employed to determine the canonical structures of each degree of excitation, including the values of K and D, for polyenes, cata-condensed PAHs, and related composite structures [8]. However, determination of these quantities on peri-condensed PAHs is not obvious and considerably more difficult. Instead, determination of a^{ac}_{N-2} and $a_N{}^{ac}$ via the acyclic polynomial and using Eq. (6) to determine the value of D is far more expeditious; in this computational procedure one can immediately discard all terms having powers larger than two, thereby vastly reducing the arithmetic. By this method the number of Dewar structures associated with pyrene, a peri-condensed PAH6, was quickly determined to be D = 87. The characteristic and acyclic polynomials for the isomers of naphthalene are listed in Table 3. From their $a_8{}^{ac}$ and $a_{10}{}^{ac}$ values, it was determined that D = 16, 21, 17, and 19 for naphthalene, azulene, bicyclo-[6.2.0]decapentaene, and bicyclo[7.1.0]decapentaene, respectively, which was verified by manually writing out all these Dewar structures. Annulenes also obey Eq. (6).

It has been shown that a strong correlation between ln K and resonance energy (RE) exists [9]. It is now shown that an even better correlation between ln a_{N-2} and RE exists. Table 4 compares the RE of representative PAH6s with the various logarithm quantities. The correlation coefficient for comparison of the Hückel molecular orbital RE for ln a_{N-2}, ln a^{ac}_{N-2}, and ln $[KN_c/2]$ are all better than the correlation coefficient for ln K versus HMO-RE. The correlation coefficient for ln K versus SCF-MO-RE is artificially higher because ln K does not differentiate between the compounds biphenyl or anthracene and phenanthrene or naphthacene having the largest disparity in RE values between the HMO and SCF-MO computational methods. The higher correlation associated with ln a^{ac}_{N-2} and RE is in agreement with one's intuition. Structure count (SC = K) multiplied by the size of the pπ-system ($KN_c/2$) should be a better relative measure than just structure count for the ability of a molecular species to disperse electron density. Also, it is reasonable to expect that the number of first ex-

TABLE 4. Comparison of Resonance Energy (RE) Calculations

Compound	SC = K	HMO(β)[a]	SCF-MO (eV)[b]	1.85 ln K (eV)[c]	ln a_{N-2}	ln a^{ac}_{N-2}	ln $[KN_c/2]$
Benzene, C_6H_6	2	2.000	0.869	0.821	2.197	2.197	1.792
Naphthalene, $C_{10}H_8$	3	3.683	1.323	1.302	3.761	3.434	2.708
Biphenyl, $C_{12}H_{10}$	4	4.383	1.699	1.643	4.394	3.807	3.178
Anthracene, $C_{14}H_{10}$	4	5.314	1.600	1.643	4.997	4.331	3.332
Phenanthrene, $C_{14}H_{10}$	5	5.448	1.933	1.907	5.112	4.407	3.555
Naphthacene, $C_{18}H_{12}$	5	6.931	1.822	1.907	6.028	5.043	3.807
Benzo(a)anthracene, $C_{18}H_{12}$	7	7.101	2.291	2.306	6.225	5.220	3.989
Benzo(c)phenanthrene, $C_{18}H_{12}$	8	7.188	2.478	2.464	6.342	5.236	4.277
Chrysene, $C_{18}H_{12}$	8	7.192	2.483	2.464	6.358	5.242	4.277
Triphenylene, $C_{18}H_{12}$	8	7.275	2.654	2.604	6.474	5.289	4.394
				$\rho = 0.956$[d]	$\rho = 0.997$[d]	$\rho = 0.995$[d]	$\rho = 0.981$[d]
				$\rho = 0.997$	$\rho = 0.940$[e]	$\rho = 0.929$[e]	$\rho = 0.971$[e]

[a] Hückel molecular orbital resonance energy.

[b] Self-consistent-field molecular orbital resonance energy.

[c] Herndon's structure count (SC) resonance energy.

[d] Correlation coefficient against HMO column.

[e] Correlation coefficient against SCF-MO column.

cited state structures (D) would be an additional but lesser factor in pπ electronic processes. Though the correlation of ln $[KN_c/2]$ versus RE is less than ln a_{N-2} versus RE, it represents a compromise which still retains the simplicity and computation speed associated with ln K versus RE but with an improved correlation coefficient when comparing molecular systems of different sizes. For example, a recent application of SC resonance theory in correlating partial rate factors of protodetritiation of helicenes of different molecular size can give a noticeable improvement in the correlation coefficient by using ln $[KN_c/2]$ instead of ln K [10].

Isospectral molecular graphs are nonidentical isomeric structures which possess the same spectrum of eigenvalues [11]. Although isospectral molecules have the same characteristic polynomial, they were found to have different acyclic polynomials with nonidentical a_{N-2}^{ac} coefficients [12]. This suggests that the acyclic polynomial of PAH molecules might be used as unique topological index for correlation of corresponding molecular properties and for computer storage and retrieval. Since the SC of the isospectral molecules studied were identical, it is now apparent that the difference in a_{N-2}^{ac} arises from a different number of Dewar structures associated with isospectral molecules.

The acyclic and characteristic polynomials are monic polynomials ($a_o^{ac} = a_o = 1$) with integral coefficients over the field of real numbers [12]. All rational zeros of the acyclic and characteristic polynomials must be integral and divisors of a_N^{ac} and a_N, respectively. Thus the only integers possible for the eigenvalues of PAHs graphs are -2, -1, 1, 2. Since all values of the a_N^{ac} and a_N coefficients are divisible by 1 (and -1) whereas only even values are divisible by 2 (and -2), there is a greater likelihood of 1 occurring as a rational zero for those polynomials. All the acenes of the cata-condensed PAH6s have at least one pair of eigenvalues $\epsilon = \pm 1$ but most of the other cata-condensed isomers do not [13]. Benzo(ghi)perylene has one pair of eigenvalues of $\epsilon = \pm 1$ whereas anthanthrene does not. All of PAH6s structures of the formulas $C_{16}H_{10}$, $C_{20}H_{12}$, $C_{24}H_{14}$, $C_{24}H_{12}$, $C_{28}H_{14}$, and $C_{32}H_{14}$ found in the $N_c = 2N_H - 4$, $N_c = 2N_H$, and $N_c = 2N_H + 4$ row series were found to have at least one pair of eigenvalues of $\epsilon = \pm 1$ [6, 13]. These empirical observations suggest that all benzenoid PAH6s belonging to the $N_c \equiv 0 \pmod 4$ row series in Table 1 will always have eigenvalues of $\epsilon = \pm 1$.

CONCLUSION

The formula periodic table for polycyclic aromatic hydrocarbons (Table 1) prescribes that the number of components of 1-factorable and 2-factorable graphs of PAH6s belonging to the row series $N_c \equiv 2 \pmod 4$ or $N_c \equiv 0 \pmod 4$ will be odd or even, respectively. This table also prescribes the sign of the coefficients in the acyclic and characteristic polynomials; for example, the sign of the a_N^{ac} and a_N coefficients are negative or positive for PAH6s belonging to the $N_c \equiv 2 \pmod 4$ or $N_c \equiv 0 \pmod 4$ row series, respectively. Based on empirical observations, it is conjectured that all benzenoid PAH6 graphs belonging to the row series of $N_c \equiv 0 \pmod 4$ of Table 1 must have at least one pair of eigenvalues associated with the corresponding adjacency matrix having values of $\epsilon = \pm 1$. Dewarlike structures have been shown to make a contribution to the a_{N-2}^{ac} and a_{N-2} coefficients [7], and there is a strong correlation between resonance energy and the logarithm of these quantities.

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