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Graphical Enumeration of the Sextet Polynomials. Novel Identities of Resonant Sextet Numbers of Cata-condensed Benzenoid Hydrocarbons†

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Novel graph-theoretical identities of resonant sextet numbers of certain nonbranched and branched cata-condensed benzenoid hydrocarbons are given, which are based on transforming Kekulé valence-bond structures into the subspace of their double bonds. Analytic expressions are given which allow construction of sextet polynomials of certain types of benzenoid hydrocarbons of very large sizes in a few seconds without drawing any graphs.

A little more than a decade ago Hosoya introduced his concept of nonadjacent numbers[1] as the sum of a set of numbers $p(G,k)$'s defined as the number of ways in which k bonds in graph G are so chosen that no two of them are connected. Thus $p(G,2)$ *e.g.* would be the number of disconnected K_2 graphs in G. Hosoya correlated such numbers with boiling points of alkanes.[1] The concept is related to the so called bond eigenfunctions of many-electron molecules adopted in old resonance theory.[2] The reference polynomial[3] of benzenoid hydrocarbons, BH's is expressed as simple functions of such disconnected K_2 graphs.[4]

Some years later Hosoya and Yamaguchi[5] extended the "nonadjacent" concept to Clar's sextet theory[6] by defining a resonant sextet number, $r(G,k)$ for a BH graph G as the number of ways in which k disconnected but mutually resonant sextets are chosen from G. Such resonant sextet numbers are used to construct sextet polynomials, $B_G(X)$'s, as given by

$$B_G(X) = \sum_{k=0}^{m} r(G,k)X^k,$$

where $r(G,0)$ is defined as unity and m is the maximal number of disconnected sextets in G. Two years later, Gutman[7] correlated sextet polynomials with characteristic polynomials of certain trees, $P_T(X)$, corresponding to nonbranched cata-condensed BH's, where

$$P_T(X) = \sum_{k=0}^{(N/2)} (-1)^k p(T,k)X^{N-2k},$$

N is the number of vertices in the tree, and $p(T,k)$ is the number of ways in which k nonincident edges are selected from T. Gutman demonstrated and proved the equality of the two variables, *viz.*,

$$r(G,k) = p(T,k).$$

In quite a recent development, Gutman[8] constructed his so called C graphs associated with a BH composed of y hexagons, $h_1, h_2, \ldots, h_y$. The vertices of the C graph $v_1, v_2, \ldots, v_y$ correspond to the h's such that v_r and v_s are adjacent if and only if h_r and h_s in BH are mutually nonresonant. Gutman[8] discovered the interesting relation that such C graphs are actually the line graphs[9] corresponding to tree graphs associated with nonbranched cata-condensed BH's so that we may write:

$$L^{-1}(C) = T.$$

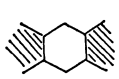
In a related development Aihara[10] defined a new polynomial based on the $r(G,k)$ numbers from which an expression was deduced for resonance energies of BH's. The above history of the sextet polynomial stimulated many people of deriving algorithms for its construction[11] due to its importance to both theorists and organic chemists.

In this work we analyze the sextet polynomial from a novel vent, namely from the permutation[12] of double bonds in Kekulé structures of BH's. First we cite some terms and their meanings.

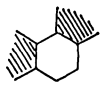
Definitions

Types of Benzenoid Hydrocarbons. We shall adopt the following terminology in this paper: A molecular network which is entirely composed of hexagons is called benzenoid. If all benzene rings in one of the Kekulé structures have an aromatic sextet the hydrocarbon is called all-benzenoid (in the opposite sense, a nonall benzenoid). If no three hexagons have a common atom, the system is called cata-condensed. If every hexagon of a cata-condensed system has at most two neighbouring hexagons, it is said to be nonbranched. If there is at least one hexagon in a cata-condensed hydrocarbon that is surrounded by three other hexagons, it is said to be branched.

Modes of Ring Annellation, the L,A-Sequence.[7] The nonterminal hexagons in a nonbranched cata-condensed system can be annellated in just two ways,[7] *viz.*,

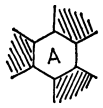


L-mode



A-mode

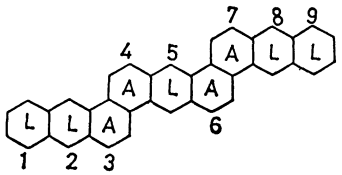
Furthermore we shall adopt an additional convention that a hexagon which is fused simultaneously to three other hexagons (*i.e.* a branched hexagon) will be assigned the symbol A, *viz.*,



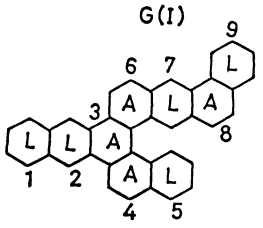
Therefore an ordered R-tuple of symbols L,A, the so called L,A-sequence,[7] might be associated with a cata-condensed BH containing R hexagons, thus: $S_1, S_2, \ldots, S_R$ where, by definition[7] $S_1 = S_R = L$ while S_n, $1 < n < R$, is assigned the symbol L or A depending on its mode of annellation. As an illustration we consider G(I)

† This paper is dedicated to Professor Nenad Trinajstić.

and G(II) representing molecular graphs of a non-branched and a branched cata-condensed BH and their L,A sequences



G(I)



G(II)

We distinguish three types of induced subgraphs[9] which might be partitioned out of the molecular graph of the BH, *viz*,

$$\langle g_1 \rangle = \mathrm{L}^{s_1}\mathrm{A}, \tag{1}$$

$$\langle g_2 \rangle = \mathrm{AL}^{s_2}\mathrm{A}, \tag{2}$$

$$\langle g_3 \rangle = \mathrm{AL}^{s_3}. \tag{3}$$

where L^s means L repeated s times (thus L^3 means L L L and so on). The values of s_1 and $s_3 \neq 0$ while s_2 may or may not be zero depending on the structure of G. As an illustration we consider all the induced subgraphs in G(I) and G(II). For G(I) we have:

$$\langle g_1 \rangle \supset \langle S_1, S_2, S_3 \rangle$$

$$\langle g_2 \rangle \supset \langle S_3, S_4 \rangle \; ; \; \langle S_4, S_5, S_6 \rangle \; ; \; \langle S_6, S_7 \rangle$$

$$\langle g_3 \rangle \supset \langle S_7, S_8, S_9 \rangle.$$

While G(II) is partitioned into:

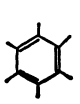
$$\langle g_1 \rangle \supset \langle S_1, S_2, S_3 \rangle$$

$$\langle g_2 \rangle \supset \langle S_3, S_6 \rangle \; ; \; \langle S_3, S_4 \rangle \; ; \; \langle S_6, S_7, S_8 \rangle$$

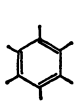
$$\langle g_3 \rangle \supset \langle S_8, S_9 \rangle \; ; \; \langle S_4, S_5 \rangle.$$

The number of induced subgraphs will be denoted as L. Thus $L(\mathrm{G(I)})=5$; $L(\mathrm{G(II)})=6$; L(linear acene)$=1$.

Clar Representation of Kekulé Structures, Dualist and Factor Graphs. In a recent graph-theoretical analysis of Clar sextet theory,[6] Hosoya *et al.*[13] distinguished two types of sextets proper and improper, *viz.*,

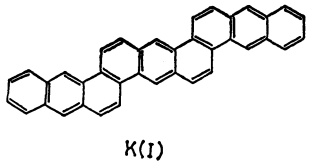


proper sextet

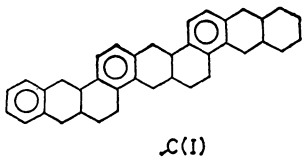


improper sextet

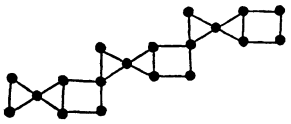
If, in a Kekulé structure circles are placed into hexagons containing proper sextets and then double bonds are replaced by single bonds a Clar formula, $\mathcal{C}$, results. When a Kekulé structure is transformed into the subspace of its double bonds, a factor graph,[14] $F(K)$ results. If the benzene rings of the benzenoid hydrocarbon are replaced by vertices and then connecting adjacent ones, a dualist,[15] D, results. As an illustration we consider a Kekulé structure for G(I), its Clar formula, factor graph and dualist:



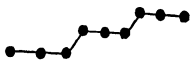
K(I)



$\mathcal{C}$(I)



F(K,I)



D(I)

Partition Sequence, $S(P)$ of the Factor Graphs

The factor graphs corresponding to the Kekulé structures of a BH might be partitioned according to the degrees of vertices composing them. Our treatment is restricted to BH's and the vertices of their factor graphs might have only degrees of 2, 3, and/or 4.[16] Figure 1 shows all $F(K)$'s of picene where the numbers in braces are populations of bivalent, tervalent and quadrivalent vertices respectively. We might, therefore, construct the following partition sequence for picene

$$S(P) = \{7,0,4\} + 5\{6,2,3\} + 6\{5,4,2\} + \{4,6,1\}.$$

One observes that the sextet polynomial of picene is given by $B_{\mathrm{G}}(X)=1+5X+6X^2+X^3$. The identity between the coefficients of our sequence and those of the polynomial is obvious.[17] In general one might define as ith partition, P_i as:

$$P_i = \{v_{2,i} \; ; \; v_{3,i} \; ; \; v_{4,i}\},$$

where $v_{2,i}$ is the number of bivalent vertices in ith partition and similarly for $v_{3,i}$ and $v_{4,i}$. Since, however, v_2, v_3, and v_4 for a BH are linearly related,[16] we might record only one variable, say v_2's. Thus our partition sequence takes the following general form for a set of $F(K)$'s with n partitions:

$$S(P) = a_{\bar{m}}[\bar{m}] + a_{\bar{m}-1}[\bar{m}-1] + \cdots + a_{\bar{m}-n+1}[\bar{m}-n+1], \tag{4}$$

where $[\bar{m}]$ is a partition for which v_2 is maximum and $a_{\bar{m}}$ is its population. The value $\bar{m}-n+1$ is minimum $v_2=\underline{m}$, and n is the number of partitions. Equation 4 might be written as:

$$S(P) = \sum_{j=0}^{n-1} a_{\bar{m}-j}[\bar{m}-j]$$

where

$$\sum_{j=0}^{n-1} a_{\bar{m}-j} = K,$$

being the Kekulé count. For picene we have

$$n = 4 \; ; \; a_{\bar{m}} = 1 \; ; \; a_{\bar{m}-1} = 5 \; ; \; a_{\bar{m}-2} = 6 \; ; \; a_{\bar{m}-3} = 1$$

whence $K(\mathrm{picene})=1+5+6+1=13$. One observes that the corresponding $r(\mathrm{G},k)$'s are:

$$r(G,0) = 1 \; ; \; r(\mathrm{G},1) = 5 \; ; \; r(\mathrm{G},2) = 6 \; ; \; r(\mathrm{G},3) = 1.$$

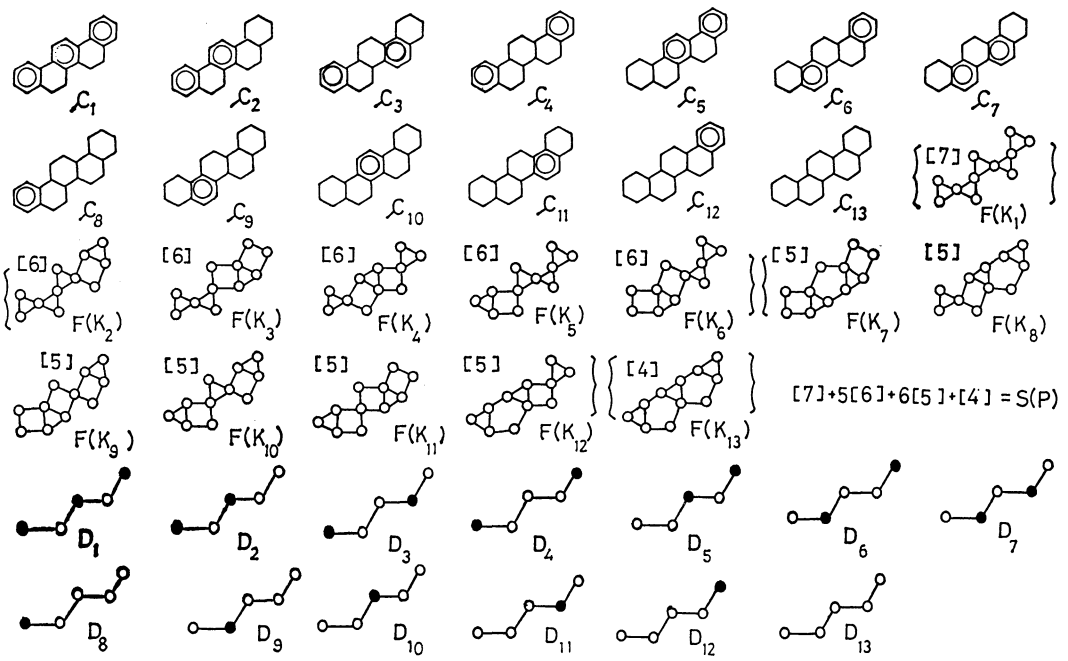


Fig. 1. Graphical illustration of Sextet Polynomial of pentaphene (a NBCCABH). The ⟋C's are Clar formulas, $F(K)$'s are the corresponding factor graphs while the D's being the corresponding dualists colored such that solid vertices correspond to hexagons containing circles. Thus dualists containing one solid vertex correspond to $r(G,1)$ or $N(1)$, those containing two solid vertices correspond to $r(G,2)$ or $N(2)$ and so on. Numbers in square brackets are v_2's in each $F(K)$.

Results

The Linear Acenes. $S(P)$'s and $B_G(X)$'s of the lower numbers of the linear acenes are listed below

Benzene	:	0[4] + 2[3] ; 1 + X,
Naphthalene	:	[4] + 2[3] ; 1 + 2X,
Anthracene	:	2[4] + 2[3] ; 1 + 3X,
Naphthacene:	:	3[4] + 2[3] ; 1 + 4X,
Pentacene	:	4[4] + 2[3] ; 1 + 5X.

The following relations hold for a linear acene

$$a_4 = a_{\bar{m}} = R - 1 = r(G,1) - 1, \tag{5}$$

$$a_{\underline{m}} = a_3 = 2, \tag{6}$$

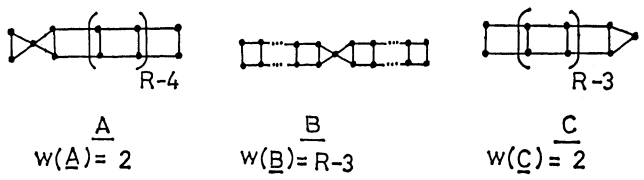
$$n = 2. \tag{7}$$

Theorem: The vertices of a set of $F(K)$'s of a linear acene partition themselves in only two distinct ways; such that two of these $F(K)$'s have only three bivalent vertices while the remaining factor graphs contain four bivalent vertices each. *i.e.*

$$S(P)_{\text{Linear acene}} = (R-1)[4] + 2[3]. \tag{8}$$

R being the number of benzene rings.

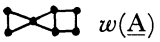
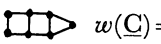
Proof: We consider the most general case first, of a linear acene containing R rings, $R \geqslant 4$. One can easily show that there are three types of factor graphs belonging to such a linear acene, A, B, and C, *viz.*,



Where w is the multiplicity of factor graph type. *E.g.* there are two forms of A *i.e.* A and its mirror image and similarly for C, while the B type generates $(R-3)$ $F(K)$'s. The number of cycles in B is, of course, R. We observe that the sum of w's is $2+R-3+2=R+1=K$. Furthermore types A and B lead to partition with maximum number of bivalent vertices, thus $a_{\bar{m}}=w(\underline{A})+w(\underline{B})=2+R-3=R-1$. Type C leads to $[\underline{m}]$, and since $w(\underline{C})=2$, $\bar{m}=4$ and $\underline{m}=3$ Eq. 8 is proved for $R \geq 4$.

The proof can easily be demonstrated for $R<4$. *E.g.* when $R=2$, A=B=  and w ( ) $=1$;

C=  $w(\underline{C})=2$. When $R=3$, $w(\underline{B})=0$ while

A=  $w(\underline{A})=2$, and C=  $w(\underline{C})=2$.

Again A and C lead to $[\bar{m}]$ and $[\underline{m}]$ respectively, where $\bar{m}=4$, $\underline{m}=3$. When the values of w's are used, Eq. 8 results.

Nonbranched Cata-condensed All-benzenoid Hydrocarbons NBCCABH's. An all-benzenoid cata-condensed hydrocarbon is defined above. In terms of Eqs. 1—3, only three types of induced subgraphs[9] might be factored out of the molecular graph of a NBCCABH, *viz.*,

$$\langle g_1 \rangle = \text{LA},$$

$$\langle g_2 \rangle = \text{A}^2,$$

$$\langle g_3 \rangle = \text{AL}.$$

Thus for a NBCCABH containing R rings the L,A sequence would be LA^{R-2}L. Consequently for this

TABLE 1. PARTITION SEQUENCES $S(P)$'s, (ABOVE), AND SEXTET POLYNOMIALS, $B_G(X)$'s, (BELOW), OF SOME NONBRANCHED ALLBENZENOID SYSTEMS

R	Example	$S(P)$; $B_G(X)$
3		$[5]+3[4]+[3]$ $1+3X+X^2$
4		$[6]+4[5]+3[4]$ $1+4X+3X^2$
5		$[7]+5[6]+6[5]+[4]$ $1+5X+6X^2+X^3$
6		$[8]+6[7]+10[6]+4[5]$ $1+6X+10X^2+4X^3$
7		$[9]+7[8]+15[7]+10[6]+[5]$ $1+7X+15X^2+10X^3+X^4$
10		$[12]+10[11]+36[10]+56[9]+35[8]+6[7]$ $1+10X+36X^2+56X^3+35X^4+6X^5$

class of BH's we may write:

$$R = L + 1. \tag{9}$$

Table 1 outlines $S(P)$'s and $B_G(X)$'s for some representative members of this topology. The following identity holds for NBCCABH's:

$$a_{\bar{m}-j} = r(G,j). \tag{10}$$

Equation 10 might easily be induced from observation of the results. The following relations hold for population coefficients:

$$a_{\bar{m}} = 1 = a_{R+2}\ ;\ (\bar{m}=R+2), \tag{11}$$
$$a_{\bar{m}-1} = R, \tag{12}$$
$$a_{\bar{m}-2} = 2^{-1}(R-2)(R-1), \tag{13}$$
$$a_{\bar{m}-3} = 6^{-1}(R-4)(R-3)(R-2), \tag{14}$$
$$a_{\bar{m}-4} = 24^{-1}(R-6)(R-5)(R-4)(R-3), \tag{15}$$
$$a_{\bar{m}-5} = 120^{-1}(R-8)(R-7)(R-6)(R-5)(R-4), \tag{16}$$
$$a_{\bar{m}-6} = 720^{-1}(R-10)(R-9)(R-8)(R-7)(R-6)(R-5). \tag{17}$$

Thus, a general expression is given by:

$$a_{m-j} = r(G,j) = (j!)^{-1}(R+1-j)\prod_{m=0}^{j-2}(R-j-m) \tag{18}$$
$$= \binom{R+1-j}{j}.$$

The algebraic properties of the above factorials make the derivation of higher populations possible. Naturally the sum of these coefficients will lead to K. The number of different partitions, n, is related to R in the following way:

R	n
3, 4	3
5, 6	4
7, 8	5
9, 10	6 ⋯ *etc.*

Thus

$$n = \frac{(R+1)}{2} + 1 \qquad (R \text{ odd})$$
$$= \frac{R}{2} + 1 \qquad (R \text{ even})$$

or by using the Gaussian brackets

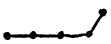
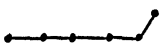
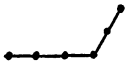
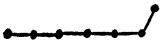
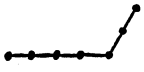
$$n = \left[\frac{(R+1)}{2}\right] + 1.$$

The value of $a_{\underline{m}} = a_{\bar{m}-n+1}$ is given by:

$$a_{\underline{m}} = 1 \qquad (R \text{ odd}) \tag{19}$$
$$a_{\bar{m}} = \frac{R}{2} + 1 \qquad (R \text{ even}) \tag{20}$$

Non-branched Cata-condensed Nonall-benzenoid Hydrocarbons for Which $L=2$, (NBCCNABH's)$_{L=2}$. Dualists of this class of BH's are characterised by having just one bend (kink),[18] *i.e.* $L=2$ (See Table 2 for some representative members). It is convenient to express their partition sequence as:

TABLE 2. PARTITION SEQUENCES, $S(P)$, (ABOVE), AND SEXTET POLYNOMIALS, $B_G(X)$, (BELOW), OF NONBRANCHED NONALL-BENZENOIDS CONTAINING TWO LINEAR SUBGRAPHS

R	Dualist	$S(P)$; $S_G(X)$
4		$[3]+4[4]+2[5]$; $1+4X+2X^2$
5		$[3]+5[4]+4[5]$; $1+5X+4X^2$
5		$[3]+5[4]+3[5]$ $1+5X+3X^2$
6		$[3]+6[4]+4[5]$ $1+6X+4X^2$
6		$[3]+6[4]+6[5]$; $1+6X+6X^2$
7		$[3]+7[4]+5[5]$; $1+7X+5X^2$
7		$[3]+7[4]+9[5]$; $1+7X+9X^2$
7		$[3]+7[4]+8[5]$; $1+7X+8X^2$

$$S(P)_{(\text{NBCCNABH})_{L=2}} = a_3[3] + a_4[4] + a_5[5], \quad (21)$$

i.e. $\underline{m}=3$; $\bar{m}=5$; $n=3$ for this class of BH's. Furthermore, their resonant numbers are identified with their population coefficients as given by:

$$a_{\underline{m}+i} = r(\text{G},i). \quad (22)$$

Equation 22 can easily be induced from observation of the results (Table 2). Equation 22 leads to three explicit expressions of the individual resonant numbers, .,*viz*

$$a_3 = r(\text{G},0) = 1, \quad (23)$$

$$a_4 = r(G,1) = R, \quad (24)$$

$$a_5 = r(\text{G},2) = e\langle g_1\rangle\, e\langle g_3\rangle, \quad (25)$$

where $e\langle g_1\rangle$ is size of $\langle g_1\rangle$ *i.e.* number of its edges and similarly for $e\langle g_3\rangle$. (*c.f.* Eqs. 1, 3). Thus for pentaphene, *e.g.* $e\langle g_1\rangle = e\langle g_3\rangle = 2$; whence $a_5=4$. An expression for K for this class of BH's is:

$$K_{(\text{NBCCNABH})_{L=2}} = \sum_{i=0}^{2} a_{\underline{m}+i} = 1 + R + e\langle g_1\rangle \cdot e\langle g_3\rangle. \quad (26)$$

Conjecture: The set of $F(K)$'s of a NBCCNABH for which $L=2$ (*i.e.* whose graph has only one hexagon with an A annellation mode) may partition themselves into three subsets only, in which the number of bivalent vertices may take on values of three, four, or five.

Non-branched Cata-condensed Nonall-benzenoid Hydrocarbons for which $L=3$; $(NBCCNABH's)_{L=3}$. We report results for only two types of this class as illustrations, *viz.*,

Class i for which the size of the middle subgraph is unity, *i.e.* $e\langle g_2\rangle = 1$ (Table 3).

Class ii for which $e\langle g_2\rangle = 2$ (Table 4).

We conjecture that for both types, the partition sequence is described by Eq. 27, *viz.*

$$S(P)_{(\text{NBCCNABH})_{L=3}} = a_4[4] + a_5[5] + a_6[6]. \quad (27)$$

Table 3. Partition sequences, $S(P)$, (above), and sextet polynomials, $B_G(X)$, (below), of nonbranched nonall-benzenoids containing three G_L's such that the middle G_L has only one edge *i.e.*, $e(G_{L_2})=1$

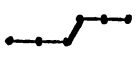
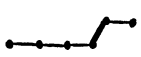
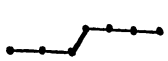
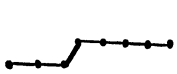
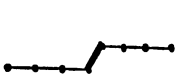
R	Dualist	$S(P)$; $B_G(X)$
5		3[4]+6[5]+2[6]; $1+5X+5X^2$
6		3[4]+8[5]+4[6]; $1+6X+8X^2$
6		3[4]+8[5]+3[6]; $1+6X+7X^2$
7		3[4]+10[5]+6[6]; $1+7X+11X^2$
8		3[4]+12[5]+8[6]; $1+8X+14X^2$
8		3[4]+12[5]+9[6]; $1+8X+15X^2$

Table 4. Partition sequences, $S(P)$, (above), and sextet polynomials, $B_G(X)$, (below), of nonbranched nonallbenzenoid systems containing three linear subgraphs, in which the middle one contains two edges *i.e.* $e(G_{L_2})=2$

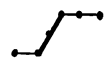
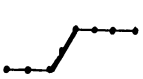
R	Dualist	$S(P)$; $B_G(X)$
5		4[4]+6[5]+2[6]; $1+5X+5X^2+X^3$
6		4[4]+9[5]+4[6]; $1+6X+8X^2+2X^3$
7		4[4]+12[5]+8[6]; $1+7X+12X^2+4X^3$
8		4[4]+14[5]+12[6]; $1+8X+16X^2+6X^3$

Table 5. Topological properties of $(\text{NBCCNABH's})_{L=3}$

Property	Class i	Class ii
$e\langle g_2\rangle$	1	2
a_4	3	4
a_5	$2(R-2)$	$3(R-3)$
a_6	$e\langle g_1\rangle \cdot e\langle g_3\rangle$	$2e\langle g_1\rangle \cdot e\langle g_3\rangle$
$a_5(R+1)-a_5(R)$ [a]	2	3
$r(\text{G},2)$	$a_6+(R-2)$	$\frac{1}{2}a_6+2(R-3)$
$r(\text{G},3)$	0.00	$e\langle g_1\rangle \cdot e\langle g_3\rangle$
K	$2R+e\langle g_1\rangle \cdot e\langle g_3\rangle - 1$	$3R+2e\langle g_1\rangle \cdot e\langle g_3\rangle - 5$

a) $a_5(R)$ is population coefficient of partition whose $v_2=5$ of a BH containing R rings and similary for $a_5(R+1)$.

We outline the following useful topological properties for these two classes of graphs:

Branched Cata-condensed Benzenoid Hydrocarbons. The structure of the sextet polynomials of branched cata-condensed systems depends on the mode of growth of the hexagons on the triphenylene unit. We consider the two modes of ring annellation *viz.* linear and angular ways as illustrated below on dualists of some triphenylene derivatives:

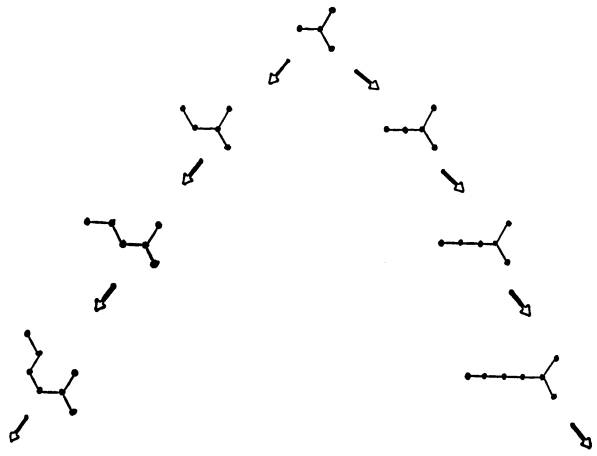
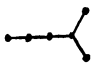
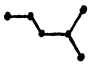
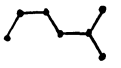


TABLE 6. PARTITION SEQUENCES, $S(P)$'s (ABOVE), AND SEXTET POLYNOMIALS, $B_G(X)$'s, (BELOW), OF SOME BRANCHED CATACONDENSED BENZENOID HYDROCARBONS

R	Dualist	$S(P)$; $B_G(X)$
4		$2[6]+3[5]+3[4]+[3]$ $1+4X+3X^2+X^3$
5		$3[6]+5[5]+4[4]+[3]$ $1+5X+5X^2+2X^3$
6		$4[6]+7[5]+5[4]+[3]$ $1+6X+7X^2+3X^3$
5		$2[7]+5[6]+5[5]+2[4]$ $1+5X+6X^2+2X^3$
6		$2[8]+7[7]+8[6]+5[5]+[4]$ $1+6X+10X^2+5X^3+X^4$
7		$2[9]+9[8]+13[7]+10[6]+3[5]$ $1+7X+15X^2+11X^3+3X^4$

The group of dualists to the right are derived from triphenylene by linear annellation of hexagons while those to the left by angular annellation. Table 6 lists $S(P)$'s and $B_G(X)$'s of these dualists. We now list some of the mathematical properties of these branched systems.

i) Systems Derived by Linear Ring Annellation: Throughout the following equations, by definition of a branched cata-condensed system, $R \geqslant 4$:

$$a_{\bar{m}} = R-2 = a_6, \tag{28}$$

$$a_{\bar{m}-1} = 2R-5 = a_5 = r(G,2), \tag{29}$$

$$a_{\bar{m}-2} = R-1 = a_4, \tag{30}$$

$$a_{\bar{m}-3} = a_{\underline{m}-3} = a_3 = 1, \tag{31}$$

$$r(G,3) = R-3. \tag{32}$$

One can easily deduce an expression for the Kekulé count of branched cata-condensed benzenoid hydrocarbons whose dualists have the general formula:

, $m=0, 1, 2, \cdots$

as:

$$K = a_6 + a_5 + a_4 + a_3 = 4R-7. \tag{33}$$

ii) Systems Derived by Angular Ring Annellation:

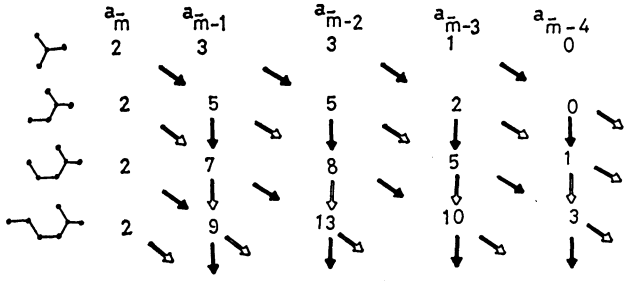
$$a_{\bar{m}} = 2 = a_{R+2}, \tag{34}$$

$$a_{\bar{m}-1} = 2R-5, \tag{35}$$

$$a_{\bar{m}-2}(R) + a_{\bar{m}-2}(R+1) = a_{\bar{m}-2}(R+2), \tag{36}$$

where $a_{\bar{m}-2}(R)$ is population of the partition $[\bar{m}-2]$ for an allbenzenoid benzenoid hydrocarbon containing R rings and one branched ring (*i.e.* a ring which is fused simultaneously to three other rings) and similarly for $a_{\bar{m}-2}(R+1)$ and $a_{\bar{m}-2}(R+2)$. *I.e.* the coefficients of $[\bar{m}-2]$ in a homologous series of this class of branched systems define a Fibonacci sequence.[19]

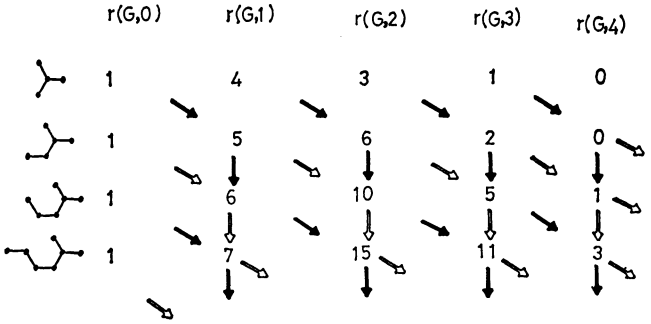
The relation among the coefficients of the partition sequences of this class of hydrocarbons is best shown in the following diagram (see Table 6) where the first row corresponds to triphenylene:



The above relation might be expressed as:

$$a_{\bar{m}}(R) + a_{\bar{m}-1}(R+1) = a_{\bar{m}-1}(R+2). \tag{37}$$

A similar relation holds for the resonant numbers as diagramed below: (the first row correspond to triphenylene).



So that we may write

$$r(G,j)_R + r(G,j+1)_{R+1} = r(G,j+1)_{R+2}, \tag{38}$$

where $r(G,j)_R$ is $r(G,j)$ for a member of this set of branched hydrocarbons containing R rings and similarly for other notations. Diagrams like the ones shown above allow the systematic synthesis of sextet polynomials of very large graphs. Furthermore we have:

$$r(G,2) = \sum_{j=2}^{R-1} (R-j)\ ;\ R \geqslant 4. \tag{39}$$

Restricted Disjoint Interactions, RDI's

A pair of RDI is defined between two dualist vertices v_r and v_s such that:

i) v_r and v_s are not part of the same induced subgraph defined by Eqs. 1—3.

ii) v_r and v_s are never adjacent.

i) and ii) are equivalent to saying that v_r and v_s form a pair of RDI if and only if the corresponding hexagons, h_r and h_s, in BH are resonant. We now recall that the so called C(Clar) graph recently introduced by Gutman[8] has its v_r and v_s adjacent only if the corresponding h_r and h_s are nonresonant. We might, there-

fore, call the elements of our RDI's "non-Clar graphs". Examples of such pairs of RDI's are shown as solid circles in dualists of pentaphene (Fig. 1). The number of such pairs of RDI's will be denoted as $N(2)$.

Analogously we define $N(3)$ as triplet of RDI's *e.g.* $N(3)$ for pentaphene=1 (Fig. 1).

Quartets, Quintets *etc.* might similarly be defined. It can be shown that for any type of cata-condensed BH. The following identity holds:

$$N(j) = r(G,j). \tag{40}$$

The validity of the above identity is a result of the definition of RDI's and the fact that in a cata-condensed BH every induced subgraph (Eqs. 1—3) might have only one resonant sextet. This topology makes $N(j)$ identical with the number of ways in which j mutually resonant but disconnected sextets are selected from BH graph. For NBCCABH's the sextet numbers are related to population coefficients by:

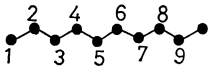
$$r(G,j) = a_{\bar{m}-j}. \tag{41}$$

Whence

$$a_{\bar{m}-j} = r(G,j) = N(j). \tag{42}$$

Therefore finding expressions for $N(j)$'s allows construction of sextet polynomials and generation of partition sequences of nonbranched allbenzenoid hydrocarbons without actually writing any Kekulé structures.

For the purpose of illustration we consider a NBCCABH containing ten rings. One such dualist is shown below:



We would like to compute, *e.g.* $r(G,5)$ *i.e.* coefficient of X^5 in sextet polynomial or $a_{\bar{m}-5}$ and since $\bar{m}=R+2$ (for NBCCABH) we are looking for $a_{12-5}=a_7$ *i.e.* population of [7] (that is the number of factor graphs for which $v_2=7$). We simply list the following quintets of RDI's (1,3,5,7,9); (1,3,5,8,10); (1,3,5,7,10); (1,3,6,8,10); (1,4,6,8,10); and (2,4,6,8,10). Therefore there are six Kekulé structures containing each, five disconnected but mutually resonant sextets. Alternatively, we say, there are six $F(K)$'s containing, each, seven bivalent vertices. Actually we do not have to "synthesize" these RDI's we may use Eq. 16, *viz.*,

$$a_{m-5} = 120^{-1}(R-8)(R-7)(R-6)(R-5)(R-4)$$
$$= 120^{-1}(2)(3)(4)(5)(6) = 6.$$

Obviously to use the approach originally suggested by Hosoya and Yamaguchi[5] would be rather a formidable task, especially for higher tuplets. Also, Gutman's method[7,8] requires the construction of the C graph and its $L^{-1}C$ as well as knowledge on characteristic polynomials of trees. To our knowledge our method is simple enough to be carried out by an "average" chemistry student !.

I wish to thank Professor Nenad Trinajstić for correcting some of my mathematical terms, namely dualist instead of dual graph and K_2 subgraphs for non-adjacent numbers. I am also indebted to Professor Ivan Gutman for sending me his recent work on the subject (Ref. 8).

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12) Although Kekulé structures are mathematical states that represent permutation of double bonds, this fact was explicitely stated only recently; D. Cvetkovic, I. Gutman, and N. Trinajstic, *J. Chem. Phys.*, **61**, 2700 (1974).
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