On a Graph-Theoretical Approach to Kekulé Structures*.
Novel Identities of Sextet Polynomials and a Relation
to Clar's Sextet Theory

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Kekulé structures are transformed into the subspace of their double bonds to yield the corresponding factor graphs, originally called submolecules (S. E l - B a s i l, *Internat. J. Quantum Chem.* 21 (1982) 771). A graph-theoretical analysis of factor graphs is presented for certain classes of benzenoid hydrocarbons. Such an analysis led to expressions for the construction of sextet polynomials of some types of benzenoid hydrocarbons containing as many as ten rings in a few seconds without drawing any graphs!.

1. INTRODUCTION

Although Kekulé structures are mathematical states of no »real« existence, their impact on chemistry[1] and mathematical chemistry[2] is obvious. Revival of interest in such VB structures arose in the early seventies[2] when it was realized that they are hidden in the detailed complexity of sophisticated MO calculations.[2,3] There are a number of interesting properties of Kekulé structures[4] such as their count,[5] usually given the symbol K, for a particular hydrocarbon. Naturally, K, being an integer, has many possible partitions. E.g. Gordon and Davidson[6] have demonstrated that K for a nonbranched catacondensed all-benzenoid hydrocarbon (see later for definitions) is composed of a partition of numbers that form a Fibonacci sequence. Recently Hosoya and Yamaguchi[7] partitioned K into a sum of what they called resonant sextet numbers, $r(G, K)$'s, defined as the number of ways in which k disconnected but mutually resonant sextets are chosen from G, the molecular graph of the hydrocarbon. Such numbers are used to construct sextet polynomials, $B_G(X)$'s given by:

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

where $r(G, O)$ is defined as unity and m is the maximum number of disconnected sextets. The combinatorial and chemical implications of

* This paper is dedicated to Professor Nenad Trinajstić.

the sextet polynomial led many people[8,9] to interesting discoveries of the topological properties of benzenoid hydrocarbons. This paper aims at analyzing Kekulé structures of certain types of benzenoid hydrocarbons for which novel identities of their sextet polynomials have recently been observed.[9]

<div align="center">2. PRELIMINARIES AND DEFINITIONS</div>

a) Factor-Graph, F(K), of a Kekulé Structure

When a Kekulé structure is transformed into the subspace of its double bonds a factor-graph,[10] $F(K)$ results. E.g. We consider K_I and $F(K_I)$:
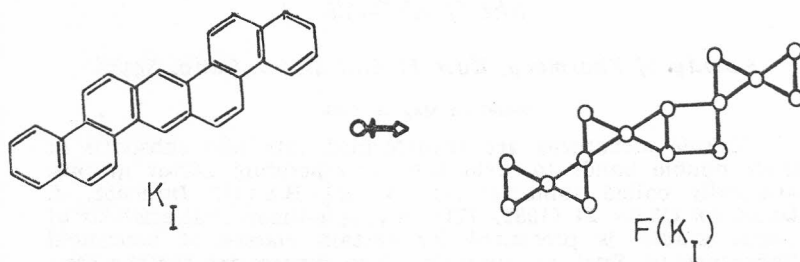
b) Partition Sequence, S(P)

The set of $F(K)$'s of a particular benzenoid hydrocarbon are partitioned according to the number of bivalent vertices,[11] v_2's. Thus, e.g., picene has thirteen $F(K)$'s shown in Figure 1. It turns out that just one of these $F(K)$'s has seven v_2's, there are five $F(K)$'s each containing six v_2's, six $F(K)$'s each possessing five v_2's and only one containing four v_2's. Thus a partition sequence, $S(P)$, might be defined for picene as given by eqn. 2, viz.,

$$S(P) = [7] + 5\,[6] + 6\,[5] + [4]$$

where, in general, $[j]$ is a partition of the $F(K)$'s for which $v_2 = j$.

c) Factor-graph vector, $\vec{V}\,[F(K)]$

Defined by

$$\vec{V}\,[F(K)] = (f_1, f_2, \ldots, f_R)$$

R, being the number of cycles in $F(K)$ (= number of hexagons in the benzenoid hydrocarbon). The f's are numbers of bivalent vertices in the individual cycles composing a particular $F(K)$, so that:

$$\sum_{i=1}^{R} f_i = \text{total number of bivalent vertices in } F(K) = v_2.$$

It turns out that the values and ordering of these f's are rather delicate functions of $F(K)$-topologies and lead to a graph-theoretical analysis of the individual Kekulé structures.
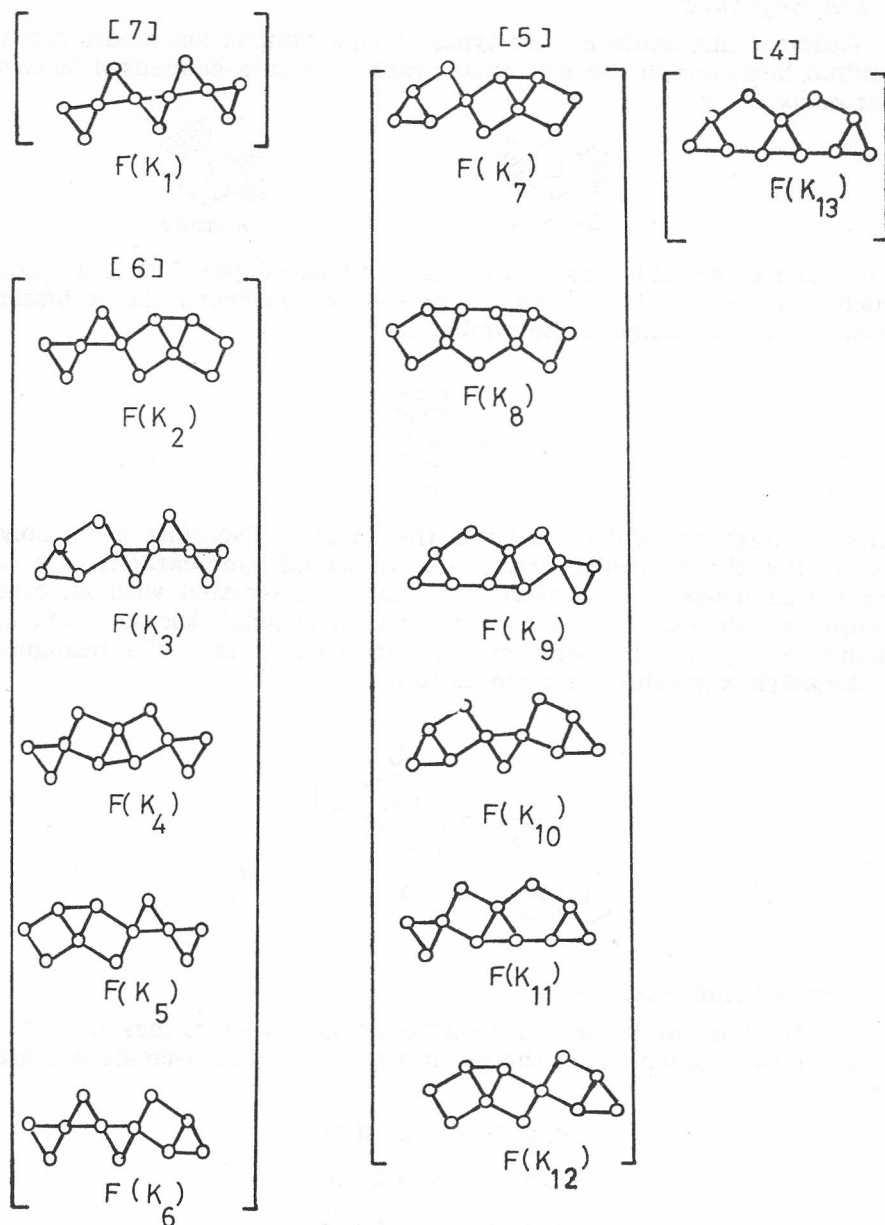
Figure 1. Factor graphs of picene grouped according to their vector degrees. Numbers in [] are v_2's.

d) L-A Sequence[8]

Gutman[8] distinguished two types of ring annellation modes for non-terminal hexagons in the molecular graph of a cata-condensed benzenoid hydrocarbon, viz.,

L-mode   A-mode

Furthermore the additional convention will be adopted[12] that a hexagon which is fused simultaneously to three other hexagons (i.e. a branched hexagon) will be assigned the symbol A, viz.

Terminal hexagons will be assigned the letter L. Therefore every polyhex graph[13] (i.e. the molecular graph of a benzenoid hydrocarbon) of a cata--condensed benzenoid hydrocarbon might be associated with an ordered R-tuple of symbols L, A (R = number of hexagons), the so-called L, A--sequence.[8] E.g. the following symbols are used to label the hexagons of G_1 the polyhex graph corresponding to K_1:
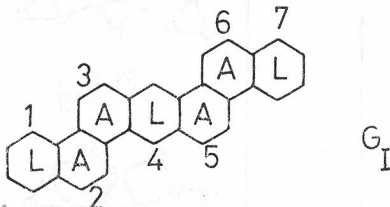
e) Induced Subgraph[14,15]

Three types of induced subgraphs composed of strings of hexagons might be partitioned out of the polyhex graph of a cata-condensed system viz.,

$$< g_1 > = < L^{s_1} A > \tag{1}$$

$$< g_2 > = < A L^{s_2} A > \tag{2}$$

$$< g_3 > = < A L^{s_3} > \tag{3}$$

where L^{s_1} e.g. means L repeated s_i times. In eqns. 1—3 the powers of the L symbols are maximum possible values corresponding to an induced subgraph of the maximum number of rings. The values of s_1 and $s_3 \neq 0$, while s_2 may or may not be zero depending on the structure of the poly-hex. As an illustration G_1 contains the following induced subgraphs:

$$< g_1 > \supset < 1, 2 >; \text{ or } < g_1 > \supset < LA >)$$
$$< g_2 > \supset < 2, 3 >, < 3, 4, 5 >, < 5, 6 >;$$
$$(\text{or } < g_2 > \supset < A^2 >, < ALA >, < A^2 >)$$
$$< g_3 > \supset < 6, 7 > \text{ or } < g_3 > \supset < AL >).$$

where the numbers in »brackets« are numerical labels of hexagons as shown in G_1. The total number of induced subgraphs in G will be denoted by L. E.g. $L(\text{Linear acene}) = 1$, $L(G_1) = 5$ and so on.

f) Some Definitions Regarding Benzenoid Hydrocarbons

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 allbenzenoid. Therefore an all-benzenoid hydrocarbon has one $F(K)$ which is composed of C_3 cycles only (C_3 is a cycle composed of three vertices). An allbenzenoid hydrocarbon containing R rings, therefore, has an L—A sequence given by $LA^{R-2}L$. Examples of allbenzenoids are given by the following polyhexes.

etc.
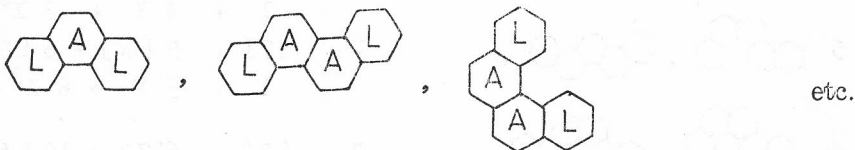
Thus, in an allbenzenoid system all induced subgraphs have orders* of two (i.e. composed of two rings). In the opposite sense to the above definition, a hydrocarbon is termed non-allbenzenoid. Examples are

etc.
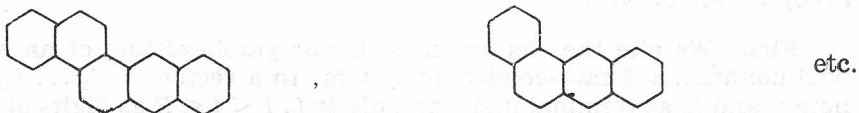
A necessary and sufficient condition for a non-allbenzenoid cata-condensed system is the existence of $< g_1 > = L^{S_1} A$ where $s_1 \geqq 2$ or $< g_3 > = A L^{S_3}$ $s_3 \geqq 2$. If every hexagon of a cata-condensed system has at most two neighboring hexagons it is said to be nonbranched.

We now state two theorems, illustrate them and prove them by graph analysis of factor graphs and their vectors.

3. THEOREM 1

Let $a_{\overline{m-j}}$ be the number of $F(K)$'s containing $(\overline{m-j})$ divalent vertices, where $\overline{m}$ is the maximum possible number of v_2's in an $F(K)$ in the set. Then for an all-benzenoid nonbranched cata-condensed system the following identity exists:

$$a_{\overline{m-j}} = r(G, j) \tag{4}$$

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* The order of an induced subgraph is defined here as the number of its rings.

where $r(G, j)$ is a resonant sextet number corresponding to j disconnected but mutually resonant sextets in G. i.e. $r(G, j)$ = number of selections of j disconnected but mutually resonant sextets in G.

Table I illustrates the application of eqn. (4) to some allbenzenoid nonbranched systems.

TABLE I

Partition Sequences, S(P)'s, (Above), and Sextet Polynomials, $B_G(X)$'s, (Below) of the First Few Members of Allbenzenoid Nonbranched Cata-condensed Hydrocarbons

R	Examples of G	$\overline{m}$	S(P), (above) and $B_G(X)$, (below)
3		5	[5] + 3 [4] + [3]
			1 + 3 X + x^2
4		6	[6] + 4 [5] + 3 [4]
			1 + 4 X + 3 x^2
5	, ...	7	[7] + 5 [6] + 6 [5] + [4]
			1 + 5 X + 6 x^2 + x^3
6	, ...	8	[8] + 6[7] + 10 [6] + 4 [5]
			1 + 6 X + 10 x^2 + 4 x^3

Proof of Theorem 1

First: We cite the characters of factor-graph-vectors of an allbenzenoid nonbranched cata-condensed system: In a vector $(f_1, f_2, \ldots f_R)$ we denote f_1 and f_R as terminal digits and digits f_i, $1 < i < R$ as digits of internal sequence. We state three rules: viz.,

Rule 1: The terminal digits may assume only values of 1 and 2. i.e. there are four possible combinations. Furthermore, digit 1 corresponds to C_3, while digit 2 to C_3 or C_4. Digits of internal sequence can assume values 0 or 1;

Rule 2: No two successive zeros are allowed;

Rule 3: When a terminal number is adjacent to the zero then it has to assume value 2 (the opposite, however, is not true).

E.g. $R = 5$ leads to five possibilities for internal sequence: $(1, 1, 1)$, $(1, 1, 0)$, $(1, 0, 1)$, $(0, 1, 1)$, $(0, 1, 0)$. Considering Rule 3, we have only 13 allowed combinations with the four combinations of terminal digits (not 20 as one might expect). These vectors are shown in Figure 1 for picene, an allbenzenoid zigzag cata-condensed system.
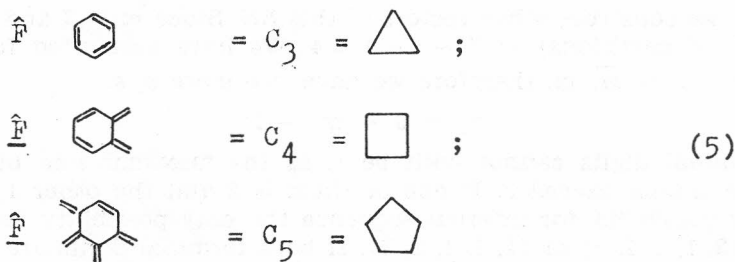
Second: We demonstrate the validity of eqn. 4 for $R = 5$. Similar

.   The maximum number of divalent vertices requires upper limits on both terminal and internal digits of $\vec{V}\,[F(K)]$. A partial vector structure would then be $(2, \quad, \quad, \quad, 2)$. There are still three digits to be accounted for, composed of zeros and/or ones and subject to rules 2 and 3. The upper limit to this internal combination is obviously 1, 1, 1 leading to a $\vec{V}\,[F(K)] = (2, 1, 1, 1, 2)$. There is no other configuration leading to a higher value of v_2. Thus $a_{\overline{m}} = 1$. But, by definition, $r(G, O) = 1$ for any G. Thus $a_{\overline{m}} = r(G, O)$ $(= a_7$ in this case).

$$\overline{m} : (\text{minimum } v_2).$$

The lower limit on the terminal numbers leads to $(1, \quad, \quad, \quad, 1)$. According to rule 3 we cannot have zeros adjacent to terminal ones, therefore vectors such as $(1, 0, f, g, 1)$ or $(1, g, f, 0, 1)$ are not allowed. This reduces our choice to $(1, 1, f, 1, 1)$. To have the lower limit on v_2, f must be zero, whence m generates the vector $(1, 1, 0, 1, 1)$ leading to v_2 (min.) = $\overline{m} = 4$. Therefore $a_4 = a_{\overline{m}-3} = r(G, 3) = 1$. This result depends on the value of R.

Now we establish the correspondence between $a_{\overline{m}-3}$ and $r(G, 3)$: We let F be an operator that transforms a Kekulé structure into the subspace of its double bonds (to give a factor graph), hence we may write the following identities:

$$\hat{F} \quad \bigcirc \qquad = C_3 \quad = \triangle \quad ;$$

$$\underline{\hat{F}} \quad \bigcirc\!\!\!< \qquad = C_4 \quad = \square \quad ; \qquad\qquad (5)$$

$$\underline{\hat{F}} \quad >\!\!\!\bigcirc\!\!\!< \qquad = C_5 \quad = \pentagon$$

Whence we have the following inverse relations:

$$\underline{\hat{F}}^{-1}C_3 = \bigcirc \quad ; \quad \hat{F}^{-1}C_4 = \bigcirc\!\!\!< \quad ; \quad \hat{F}^{-1}C_5 = >\!\!\!\bigcirc\!\!\!< \qquad (6)$$
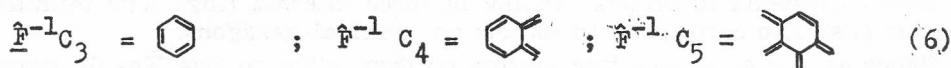
Furthermore we have the following cyclic interpretations of the elements of $\vec{V}\,[F(K)]$: (these cyclic interpretations are functions of the particular topology of an allbenzenoid nonbranched system)

i) Terminal digits:

$$1 = C_3 \qquad\qquad (7)$$
$$2 = C_3,\ C_4$$

ii) Internal sequence:

$$0 = C_3 \qquad\qquad (8)$$
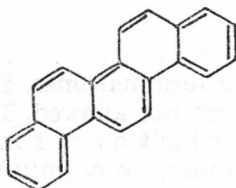$$1 = C_3;\ C_4;\ C_5$$

when we use (7) and (8) we get

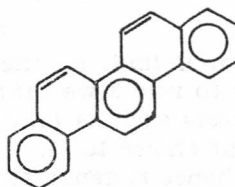$$F^{-1}(1, 1, 0, 1, 1) = F^{-1}(C_3, 1, C_3, 1, C_3)$$

The remaining ones might be C_j; $(j = 3, 4, 5)$.
It can be shown that an allbenzenoid nonbranched system requires the inetrnal 1 to be C_5 when the terminal cycles and middle one are C_3's. Thus we write, using (6) the following identity:

$$F^{-1}(C_3, C_5, C_3, C_5, C_3) = F^{-1} F(K_{13});$$
$$= K_{13}$$

(see Figure 1)

$$\underline{K_{13}}$$ (Clar's formula)
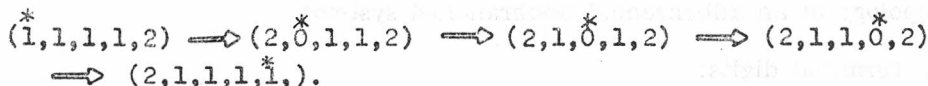
But K_{13} contains three disjoint and mutually resonant hexagons. Hence K_{13} corresponds to $r(G; 3)$; but K_{13} is derived from $V F(K) = (1, 1, 0, 1, 1)$, and the latter is deduced from $a_{\overline{m}-3}$. Therefore $r(G, 3) = a_{m-3} = 1$.

Now we construct other vectors of this BH. Since $\overline{m} = 7$ and $m = 4, n$ (number of partitions) $= 7 - 4 + 1 = 4$. We have accounted for two of them, viz., $v_2 = \overline{m}; m$, therefore we have two more v_2 s:

$$v_2 = 6 = \overline{m} - 1:$$

The terminal digits cannot both be 1, as the maximal sum of internal sequence cannot exceed 3. If one of them is 2 and the other 1, we have the only possibility for internal sequence the only possibility being three 1's, i.e. (2, 1, 1, 1, 1) or (1, 1, 1, 1, 2). If both terminal digits are 2, we get for internal sequence two 1's and 0, and that gives three possibilities: (2, 1, 1, 0, 2); (2, 1, 0, 1, 2) and (2, 0, 1, 1, 2). We observe that the zero moves over three positions. From Eqn. (8) and (6) we conclude that these zeros correspond to sextets existing in three internal rings. The terminal ones (1's) also correspond to sextets on terminal hexagons.

Hence $a_{\overline{m}-1} = a_6 \longrightarrow$ five vectors corresponding to five Kekulé structures with at least one resonant sextet per structure such that it moves successively from one ring to the other over the five structures. This is illustrated pictorially as follows:

$$(\overset{*}{1},1,1,1,2) \Longrightarrow (2,\overset{*}{0},1,1,2) \Longrightarrow (2,1,\overset{*}{0},1,2) \Longrightarrow (2,1,1,\overset{*}{0},2)$$
$$\Longrightarrow (2,1,1,1,\overset{*}{1},).$$

The sextet is shown by an asterisk above its corresponding code. Whence these vectors (which are derived from $a_{\overline{m}-1} = a_6$) correspond to the number of ways in which one sextet is chosen from a nonbranched cata-condensed allbenzenoid hydrocarbon for which $R = 5$ i.e. to $r(G, 1)$.

Therefore $a_{\overline{m}-1} = r(G, 1) = 5$

$$v_2 = 5 = \overline{m} - 2$$

We may easily generate these vectors as done with $v_2 = 6$. These vectors are: (1, 1, 1, 1, 1); (1, 1, 0, 1, 2); (2, 1, 0, 1, 1); (1, 1, 1, 0, 2); (2, 0, 1, 1, 1); (2, 0, 1, 0, 2). Applying Eqn. (7) and (8) to these vectors, they may be rewritten as $(C_3, 1, 1, 1, C_3)$; $(C_3, 1, C_3, 1, 2)$; $(2, 1, C_3, 1, C_3)$; $(C_3, 1, 1, C_3, 2)$; $(2, C_3, 1, 1, C_3)$ and $(2, C_3, 1, C_3, 2)$. These vectors, therefore correspond to Kekulé structures containing pairs of disjoint but mutually resonant sextets, i.e. to $r(G, 2)$. There are six such different pairs. One may apply (6), (7) and (8) to generate the actual Kekulé structures. We may thus write $a_{\overline{m}-2} = r(G, 2) = 6$.

Similar enumerative proofs might be written for higher (or lower) members).

Construction of $B_G(X)$'s of Allbenzenoid Nonbranched Cata-condensed Systems

The graph-theoretical properties of $\overrightarrow{V}[F(K)]$'s of this class of hydrocarbons (c.f. rules 1—3) allow a systematic synthesis of sextet polynomials of very large systems from the vectors of phenanthrene; the five vectors of which are (2, 1, 2); (2, 1, 1); (1, 1, 2); (2, 0, 2); and (1, 1). Higher vectors are built up from smaller ones. Each time the terminal number (arbitrarily to the right) is suppressed by one and then both a one and a two are added. As a result of this operation vectors might result ending (to the right) at one preceded by zero. These are excluded by virtue of rule 3. E.g. a vector such as (2, 0, 1, 1, 1) might only be expanded into (2, 0, 1, 1, 0, 2): the alternative; (2, 0, 1, 1, 0, 1) is not consistent with the topological features of this class (allbenzenoid, nonbranched) of hydrocarbons. This consideration can be formulated generally as follows: If we have the vectors, $\overrightarrow{V}[F(K)]$'s, for some value of R, let us denote by $R_1(R)$ the number of vectors with the last digit 1 and $R_2(R)$ the number of vectors with the last digit 2. Then we get for $R + 1$: $R_1(R + 1) = R_2(R)$; $R_2(R+1) = R_1(R)+R_2(R)$. E.g. if we have for $R = 3$, $R_1=2$, $R_2=3$, then we get for $R=4$: $R_1(4)=3$; $R_2(4)=5$, for $R=5$: (5, 8), for $R=6$: (8, 13) etc. Partition sequences and sextet polynomials are thus most easily constructed. This result is outlined below:

R	R_1	R_2
3	2	3
4	3	5
5	5	8
6	8	13
.	.	.
.	.	.
.	.	.

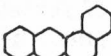We observe that both R_1 and R_2 define Fibonacci numbers.[16]
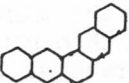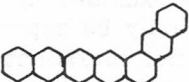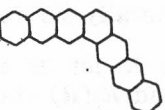
4- *Theorem 2*

Let a_{m+j} be the number of $F(K)$'s containing $(m + j)$ divalent vertices, where m is the minimum possible number of v_2's in an $F(K)$ in the set. Then for a nonallbenzenoid nonbranched cata-condensed system for which $L = 2$, the following identity exists:

$$a_{m+j} = r(G, j) = a_{3+j} \qquad (9)$$

before proving eqn. (9) we illustrate it with some examples:

TABLE II

Partition Sequences, S(P)'s, (Above), and Sextet Polynomials, $B_G(X)$'s, (Below), of a Few Members of Nonallbenzenoid Nonbranched Cata-condensed Systems for which $L = 2$

G	S(P), (above) and $B_G(X)$, (below)
	$[3] + 4[4] + 2[5]$ $1 + 4X + 2X^2$
	$[3] + 5[4] + 4[5]$ $1 + 5X + 4X^2$
	$[3] + 7[4] + 8[5]$ $1 + 7X + 8X^2$
	$3 + 7[4] + 9[5]$ $1 + 7X + 9X^2$

First we consider some graph-theoretical characters of $\overrightarrow{V}[F(K)]$'s of this class of hydrocarbons which are essential for the proof. A general representation of a nonallbenzenoid nonbranched hydrocarbon for which $L = 2$ is shown below
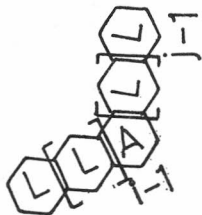
Thus the general form of the L, A-sequence would be $L^i AL^j$ where i and j are 1, 2, ... Such a sequence is consistent with only two types of vectors given by (10), (11), viz.

i) $$(f_1, 0^{i-1}, 1, 0^{j-1}, f_R) \tag{10}$$

ii) $$(f_1, 0^{i+j-1}, f_R) \tag{11}$$

where a zero raised to an integer, say 0^m, means a zero repeated m times, so instead of writing e.g., 0, 0, 0 we write 0^3 and so on. For type i) vectors, the terminal digits might have four combinations, viz.,

1) $f_1 = f_R = 1$ (2) $f_1 = 1; f_R = 2$

3) $f_R = 1; f_1 = 2$ (4) $f_1 = f_R = 2$

For type ii) vectors only one value can be assumed, viz., $f_1 = f_R = 2$. These bounds are simply dictated from the nature of the Kekulé permutations[2] (i.e. double-bond matchings) in such polyhex graphs. When eqns. (10) and (11) are used together with the bounds of the numerical values of the terminal digits only three values of v_2's become possible, viz., 3, 4 and 5 and whence the $S(P)$'s of these benzenoid systems have the general form: (c.f. Table II).

$$S(P)_{L=2} = a_3[3] + a_4[4] + a_5[5] \tag{12}$$

We need two more characters of such types of $V[F(K)]$'s

(a) Cyclic interpretations (codes) of vector elements:

    a) An internal zero $= C_3; C_4$
    b) An internal 1 $= C_3; C_4; C_5$
    c) A terminal 1 $= C_3$
    d) A terminal 2 adjacent to 1 $= C_3$
    e) A terminal 2 adjacent to zero $= C_3; C_4$.

It must be observed that by a terminal digit is meant a number which is located at either terminal of the vector. We now define a novel quantity:

(b) Vector multiplicity, w

The terminal cycles in $\overrightarrow{V}[F(K)]$'s are either C_3 and/or C_4. For the topology of nonbranched nonallbenzenoid graphs several $F(K)$'s might generate the same vector. Table III outlines vector structures and their multiplicities, w's i.e. the number of $F(K)$'s consistent with one, vector structure.

TABLE III

Vectors and Their Multiplicities, w's of Nonbranched Nonallbenzenoids

V $[F(K)]$'s	w
$(C_3, \ 0^i, \ 1, \ 0^j, \ C_3)$	1
$(C_3, \ 0^i, \ 1, \ 0^j, \ C_4)$	j
$(C_4, \ 0^i, \ 1, \ 0^j, \ C_3)$	i
$(C_4, \ 0^i, \ 1, \ 0^j, \ C_4)$	$(i.j)$
$(C_4, \ 0^k, \ C_4)$	1

As an illustration we consider L^3AL^4 and all its $\overrightarrow{V}$ $[F(K)]$'s whose configuration is $(2, 0, 0, 1, 0, 0, 0, 2) = (2, 0^2, 1, 0^3, 2)$. Using the cyclic codes (a—e) we have the following structures:

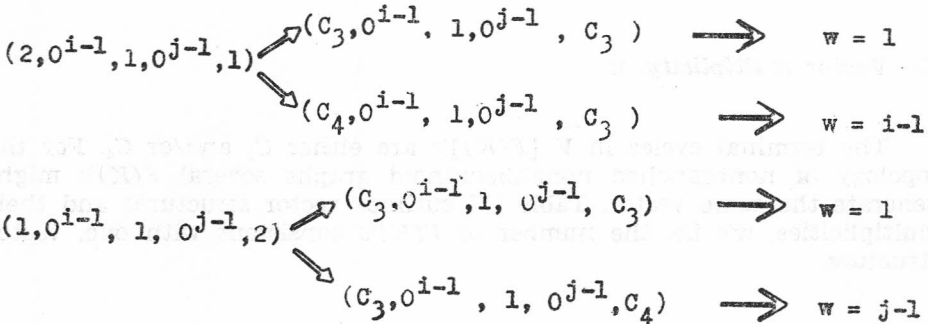| $V \ F(K)$	w
$(C_3, \ 0^2, \ 1, \ 0^3, \ C_3)$	1
$(C_3, \ 0^2, \ 1, \ 0^3, \ C_4)$	3
$(C_4, \ 0^2, \ 1, \ 0^3, \ C_3)$	2
$(C_4, \ 0^2, \ 1, \ 0^3, \ C_4)$	$2 \times 3 = 6$
	Total $= 12$ $F(K)$'s

Figure 2 contains these twelve factor graphs.

An Inductive Proof of eqn. 2

Consider an L^iAL^j polyhex graph. The lower limit on its v_2 i.e. m comes from the vector $(1, 0^{i-1}, 1, 0^{j-1}, 1)$ which must have two terminal C_3's (c.f. cyclic code, C), and whence $a_m = a_3 = 1 = r(G, 0)$, (by definition). Now we consider the other two partions, viz.,

$$v_2 = 4 = m + 1$$

We make use of Table III and cyclic codes derived above for this topology. We have the following vectors:

$(2, 0^{i+j-1}, 2)$ ⟶ $w = 1$

$(2, 0^{i-1}, 1, 0^{j-1}, 1)$ $\Bigg\langle$
  $(C_3, 0^{i-1}, 1, 0^{j-1}, C_3)$ ⟶ $w = 1$
  $(C_4, 0^{i-1}, 1, 0^{j-1}, C_3)$ ⟶ $w = i-1$

$(1, 0^{i-1}, 1, 0^{j-1}, 2)$ $\Bigg\langle$
  $(C_3, 0^{i-1}, 1, 0^{j-1}, C_3)$ ⟶ $w = 1$
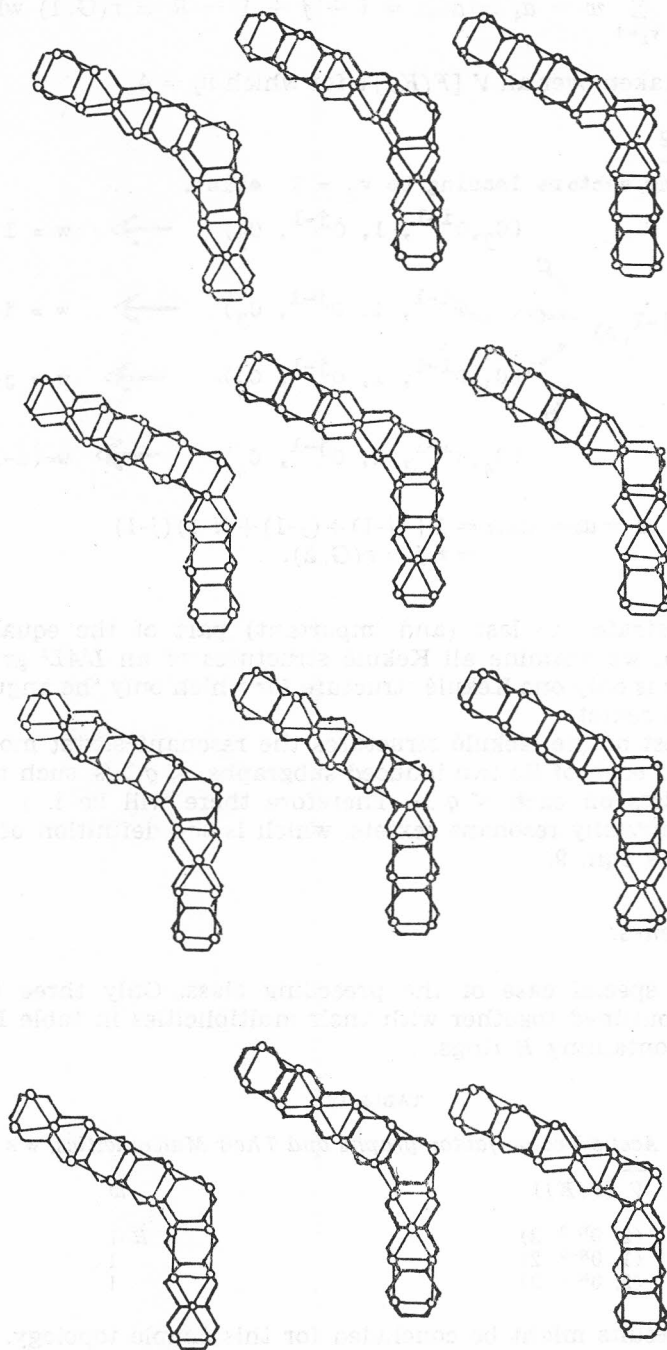 $(C_3, 0^{i-1}, 1, 0^{j-1}, C_4)$ ⟶ $w = j-1$

Figure 2. Factor graphs of L^3AL^4 which have $v_2 = 5$ i.e. whose configuration is given by $(2, 0^2, 1, 0^3, 2)$. (Table III). The factor graphs are implanted into the polyhex graphs.

We then have $\sum\limits_{v_2=4} w = a_4 = a_{m+1} = i + j + 1 = R = r(G, 1)$ where the summation is taken over all $\overrightarrow{V}[F(K)]$'s for which $v_2 = 4$.

$\underline{v_2 = 5 = \underline{m}+2}$

The following vectors leading to $v_2 = 5$ exist.

$$(C_3, 0^{i-1}, 1, 0^{j-1}, C_3) \implies w = 1$$

$$(2, 0^{i-1}, 1, 0^{j-1}, 2) \implies \begin{cases} (C_4, 0^{i-1}, 1, 0^{j-1}, C_3) \implies w = i-1 \\ (C_3, 0^{i-1}, 1, 0^{j-1}, C_4) \implies w = j-1 \\ (C_4, 0^{i-1}, 1, 0^{j-1}, C_4) \implies w=(i-1)(j-1) \end{cases}$$

Therefore $\sum\limits_{v_2=5} w = a_5 = a_{m+2} = 1 + (i-1) + (j-1) + (i-1) \cdot (j-1)$
$$= i \cdot j = r(G, 2).$$

To demonstrate the last (and important) part of the equality (i.e. $r(G, 2) = i \cdot j$), we examine all Kekulé structures of an $L^i A L^j$ graph. We find that there is only one Kekulé structure for which only the angular ring has a resonant sextet.

For the rest of the Kekulé structures the resonant sextet moves over i and j rings of each of its two induced subgraphs, $<g>$'s, such that just one sextet exists on each $<g>$. Therefore there will be i. j. pairs of disjoint and mutually resonant sextets, which is the definition of $r(G, 2)$. This establishes eqn. 9.

The linear acenes:

This is a special case of the preceding class. Only three types of vectors exist, outlined together with their multiplicities in table IV, for a linear acene containing R rings.

TABLE IV

Linear Acene Vector-factor-graphs and Their Multiplicities, w's

$\overrightarrow{V}[F(K)]$	w
$(2, 0^{R-2}, 2)$	$R-1$
$(1, 0^{R-2}, 2)$	1
$(2, 0^{R-2}, 2)$	1

Two obvious results might be concluded for this simple topology, viz.,

    1) For a linear acene: $S(P) = (R-1)[4] + 2[3]$ (13)

    2) $K = R-1+1+1 = R+1$ (14)

Eqn. (14) is a well-known fact.

Such graph-theoretical analysis might be extended to other types of polyhexes. However, we feel the above types considered are detailed enough to make other analyses, at least in principle, straightforward.

5) Expressions for Populations of Partitions: Restricted Disjoint Interactions, RDI's

To obtain expressions for the populations of the factor graph partitions and thus for the individual resonant sextet numbers we introduce the concept of a restricted disjoint interaction among the rings of a polyhex. A duplet of rings selected from the rings of the polyhex graph such that no two rings in the duplet belong to the same induced subgraph is called a restricted disjoint interaction, RDI, between the rings of such subset duplet of rings. We let P define the set of all rings composing an arbitrary polyhex graph i.e. $P = \{r_j : 1 \leq i \leq R\}$ where r_i is ith ring in P and R is total number of rings in graph. We define:

$$N(0) = 1, \tag{15}$$
$$N(1) = P = R \tag{16}$$

Furthermore pairs of RDI's, $N(2)$'s, are defined as all possible pairs of rings such that no two of them in each pair belong to the same induced subgraph; thus:

$$N(2) = \{(r_j r_j): r_i \; \epsilon < g_i >, r_j \; \epsilon \; < g_j >,$$
$$r_m \; \notin \; < g_n > \text{ for all } m \neq n\} \tag{17}$$

where $< g_i >$ is an induced subgraph (defined by eqns. 1, 2 and/or 3) such that $< g_i > \supset \; r_j$, other symbols are similarly defined. Analogously triplets of RDI's, $N(3)$'s are defined as all possible subsets composed of three rings such that no two rings in any subset belong to the same $< g >$. Thus:

$$N(3) = \{(r_i r_j r_k): r_j \; \epsilon \; < g_i >, r_j \; \epsilon \; < g_i >, r_k \; \epsilon \; < g_k >,$$
$$r_m \; \notin \; < g_n > \text{ for all } m \neq n\} \tag{18}$$

Similarly Quartets, $N(4)$'s, Quintets, $N(5)$'s, etc. might be defined depending on the size and topology of the polyhex graph. As an illustration we consider $G_I(p)$ and write down the following RDI's:

$$N(0) = 1 \qquad \text{(By definition)}$$
$$N(1) = \{r_1, r_2, r_3, r_4, r_5, r_6, r_7\} = 7$$

A simplified notation might be written by dropping r and writing only the numerical label of the ring thus:

$$N(1) = \{1, 2, 3, 4, 5, 6, 7\} = 7,$$

Then, $N(2) = \{(1, 3); (1, 4); (1, 5); (1, 6); (1, 7); (2, 4); (2, 5); (2, 6);$
$$(2, 7); (3, 6); (3, 7); (4, 6); 4, 7); (5, 7)\} = 14;$$
$$N(3) = \{(1, 3, 6); (1, 3, 7); (1, 4, 6); (1, 4, 7); (1, 5, 7);$$
$$(2, 4, 6); (2, 4, 7); (2, 5, 7)\} = 8;$$
$$N(\geq 4) = 0$$

It is convenient to define an RDI polynomial, $R(G, X)$, thus

$$R(G, X) = \sum_{j=0}^{m} N(j) \, X^j \tag{19}$$

where m = maximal value of j.

Now we state the important fact that for any cata-condensed benzenoid hydrocarbon there is exactly a 1:1 correspondence between $R(G, X)$ and the sextet polynomial, $B_G(X)$; i.e.

$$r(G, j) = N(j)$$

(20)

Eqn. (20) follows immediately from the definition of $r(G, j)$ and the fact that for any cata-condensed benzenoid hydrocarbon, there is only one sextet in each $<g>$, defined by eqns. 1—3 From eqns. (2) and (4) we write

$$a_{m-1}^- = N(j)$$

Therefore to derive expressions for the population coefficients, a's, we derive expressions for $N(j)$'s. Consider, e.g. an all-benzenoid nonbranched cata-condensed hydrocarbon containing seven rings, viz.,
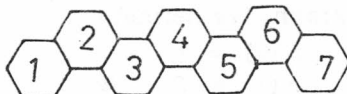
$$N(2) = \{(1, 3); \ (1, 4); \ (1, 5); \ (1, 6); \ (1, 7);$$
$$(2, 4); \ (2, 5); \ (2, 6); \ (2, 7);$$
$$(3, 5); \ (3, 6); \ (3, 7);$$
$$(4, 6); \ (4, 7);$$
$$(5, 7)\} = 15$$

Each pair has two integers, say i and j, varying as follows: i from 1 to 5 and j from 3 to 7. I.e. for the above polyhex i and j have the closed intervals $[1, 5]$ and $[3, 7]$ respectively or in general $[1, (R-2_1)]$ and $[3, R]$ for an all-benzenoid nonbranched cata-condensed hydrocarbon containing R rings, thus:

$$N(2) = \sum_{i=1}^{R-2} \sum_{j=i+2}^{R} 1 = \sum_{i=1}^{R-2} R-(i+1)$$

(22)

where we made use of the identity $\sum_{a}^{b} 1 = b-a+1$.

Thus,

$$N(2) = \sum_{i=1}^{R-2} R - \sum_{i=1}^{R-2} i - \sum_{i=1}^{R-2} 1$$
$$= R(R-2) - \frac{(R-2)(R-1)}{2} - (R-2)$$

Where we used the identity: $\sum_{i=1}^{R-2} i = 2^{-1}(R-2)(R-1)$

Thus $N(2) = 2^{-1}(R-2)(R-1) \ (= r(G, 2))$

(23)

Derivation of $N(3)$ is a little more involved but straight-foward, thus:

$$N(3) = \sum_{i=1}^{R-4} \sum_{j=i+2}^{R-2} \sum_{k=j+2}^{R} 1 = \sum_{i=1}^{R-4} \sum_{j=i+2}^{R-2} R-j-1$$
$$= \sum_{i=1}^{R-4} \left\{ \sum_{j=i+2}^{R-2} R - \sum_{j=i+2}^{R-2} j - \sum_{j=i+2}^{R-2} 1 \right\}$$

Using known algebraic identities we write:

$$N(3) = 6^{-1}(R-4)\,(R-3)\,(R-2) \quad (=r(G,3)) \tag{24}$$

Analogus expressions might be derived for higher duplets, viz

$$N(4) = 24^{-1}(R-6)\,(R-5)\,(R-4)\,(R-3) \tag{25}$$

$$N(5) = 120^{-1}(R-8)\,(R-7)\,(R-6)\,(R-5)\,(R-4) \tag{26}$$

$$N(6) = 720^{-1}(R-10)\,(R-9)\,(R-8)\,(R-7)\,(R-6)\,(R-5) \tag{27}$$

A more compact from of the above factorials is

$$N(j) = \binom{R+1-j}{j} \tag{28}$$

E.g. $N(3)$ for G_1 would be $6^{-1}(3)(4)(5) = 10$

These are $(1,3,5)$; $(1,3,6)$; $(1,3,7)$; $(2,4,6)$; $(2,4,7)$; $(2,5,7)$; $(3,5,7)$; $(1,4,6)$; $(1,4,7)$; $(1,5,7)$.

Eqn. (28) might be used to construct $r(G,j)$'s of the hydrocarbons shown in Table I. Furthermore the partition sequences might be easily computed from the eqn. (21) and the identity:

$$\overline{m} = R + 2$$

$$\tag{29}$$

which might be induced from inspection of the results. (c.f. Table I). For nonallbenzenoid nonbranched cata-condensed systems, the situation is much simpler. The following relations might most easily be induced for the case where $\alpha = 2$:

$$a_3 = r(G,0) = N(0) = 1 \tag{30}$$

$$a_4 = r(G,1) = N(1) = R \tag{31}$$

$$a_5 = r(G,2) = N(2) = e <g_1> e <g_3> \tag{32}$$

where $e <g>$ is the size of $<g>$ i.e. the number of its rings less one. As an illuultration eqns. 30—32 might be used to check the numbers in Table II.

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SAŽETAK

O graf-teorijskom pristupu Kekuléovim strukturama. Novi identiteti sekstetnih polinoma i veza s Clarovom teorijom seksteta

S. El-Basil

Kekuléove strukture prevedene su u potprostor njihovih dvostrukih veza dajući odgovarajuće faktor-grafove, izvorno nazvane submolekulama (S. E l - B a s i l, *Internat. J. Quantum Chem.* **21** (1982) 771). Graf-teorijska analiza faktor-grafova prikazana je za određene klase benzenoidnih ugljikovodika. Takva analiza dovela je do izraza koji omogućuje konstrukciju sekstetnih polinoma nekih tipova benzenoidnih ugljikovodika, koji sadrže i do deset prstenova, u nekoliko sekundi bez crtanja ijednog grafa.