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Combinatorial Clar sextet theory

On valence-bond method of Herndon and Hosoya [9]*

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Clar structures recently used as basis-set to compute resonance energies [9] are identified as maximal independent sets of benzenoid hydrocarbons "colored" in a special way. Binomial properties of such objects are induced for several catafusenes and perifusenes (Eqs. 2-31). Novel polynomials, called Clar polynomials, are given for perifusens in terms of units of catafusenes which allow display and enumeration of the populations of their Clar structures. The work is particularly pertinent to that of [8] and [9].

Key words: Clar sextet theory — Benzenoid hydrocarbons — Graph theory

1. Introduction

During the past decade applications of graph theory to polycyclic aromatic hydrocarbons led to a revival of interest in resonance theory. Important developments in this direction include resonance theory of Herndon [1] and the conjugated circuits model introduced independently by Randić [2] and by Gomes [3]. The sextet polynomial discovered by Hosoya and Yamaguchi [4] provides a systematic combinatorial enumeration of Kekulé structures of aromatic hydrocarbons which shows that resonance theories independently proposed are related to each other. In another development, Clar's numerous works on the spectral properties of benzenoid systems [5], ripened into an amazingly simple formalism which reproduced many properties of these molecules.

Clar's notations [5, 6] when analyzed using the tools of graph theory became now known as *Clar sextet theory* [6]. In their recent studies Hosoya et al. [7, 8] (and Gutman [7]) defined the concept of generalized Clar formulas [6-8] and

* This paper is dedicated to Professor Eric Clar; the Doyen of aromatic chemistry.

discovered a far reaching algebra behind such Clar patterns [7]. In quite a recent development Herndon and Hosoya [9] adopted a novel valence-bond, VB, method using Clar structures as basis set. The resulting resonance energies were found to be almost identical with the "classical" values of Dewar and de Llano [10]. Such a result gave a strong impetus to further study of Clar's theory. The present paper deals with the combinatorial aspects of this latter theory. In particular methods will be given for the *display* and *enumeration* of all *Clar structures* (or *Clar bases*) of a given hydrocarbon. Although methods of finding the number of Kekulé structure *K*, are numerous [11], the literature seems to be lacking methods for finding the number of Clar structures [12]. Such methods would be particularly desirable in cases of large hydrocarbons for which the recent *VB* methods of Herndon and Hosoya [9] is most suitable. The present work is especially related to [8] and [9].

2. Definitions and procedures

Work on the Clar theory led to several related terms such as the Clar formula [6, 12], the generalized Clar formula [12], the Clar pattern [7], the *Clar graph* [13] and the *Clar structure* [9]. To avoid confusion the reader is referred to the appropriate reference. For the sake of the present work, however, we need the last two terms. Namely, a benzenoid system composed of hexagons $\{h_1, h_2, \ldots, h_r\}$ is transformed into a *Clar graph* [13] by replacing its set of hexagons by a set of vertices $\{v_1, v_2, \ldots, v_r\}$ such that two vertices are connected only if the corresponding hexagons are nonresonant. Every *Clar structure* is a generalized Clar formula but *not* vice-versa. Thus, if in the latter every "empty" hexagon is adjacent to at least one hexagon which contains a circle, it is called a *Clar structure.* Further if the latter contains maximum number of circles, it is called a Clar formula [6]. If this is the *only* Clar formula with a maximum number of circles it is called a unique Clar formula [6, 12].

Since this paper deals with Clar structures (which are the objects dealt with in [9]) we explicitly state the following three requirements that must be obeyed in every Clar structure.

(a) Two circles must not be drawn in neighboring hexagons.

(b) The circles must be arranged in a way so that a Kekulé structure can be written for the rest of the molecule.

(c) Every empty hexagon must be adjacent to at least one hexagon containing a circle.

The above requirements plus the definition of the Clar graph leads to the following important relation: Every Clar structure corresponds to a maximal set of independent vertices of the Clar graph (or the reduced Clar graph [9, 13]). An independent set of vertices $V(r)$ is said to be a maximal [14] set if every vertex of the graph not included in $V(r)$ is adjacent to at least one of the r vertices of $V(r)$. To avoid confusion between Clar structures and other Clar objects we suggest the name

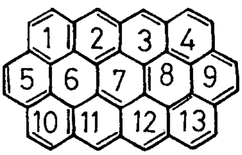
"*Clar bases*" in agreement with the *VB* effective Hamiltonian bases set adopted by Herndon and Hosoya [9].

Clar matrix: *construction of Clar graph*

As will become clear the combinatorial properties of Clar structures are most easily approached by studying the Clar graph of the corresponding benzenoid hydrocarbon. Unfortunately the required Clar graphs may be rather complicated. (This is especially true for fat polyhexes [7] and other types of pericondensed systems). A systematic (and non-error-prone) procedure to construct a Clar graph is approached by computing its *Clar matrix*, defined as follows: For a benzenoid system, B, composed of r hexagons define an $r \times r$ matrix, $\zeta(B)$, the elements of which are given by

$$\zeta_{ij} = \begin{cases} 1 & \text{if } h_i \text{ is nonresonant with } h_j \\ 0 & \text{otherwise,} \end{cases} \tag{1}$$

where h_i is a hexagon $\in B$. The adjacency relation of the Clar graph (which will be given the symbol ϕ (Benzenoid system) is then obtained from the elements ζ_{ij}. The procedure may seem too tedious as to require a display of all Kekulé structures of the benzenoid hydrocarbon. This is not so: consider, e.g. the system $C_{3,4}$ (we adopt almost similar nomenclature as in [8]. Using the formula given in [8], its Kekulé content, $K(C_{3,4}) = 105$ [1]. One of these Kekulé structures is shown below:



It is immediate the $\zeta_{ij} = 0$ for the following values of (i, j): (1, 7), (1, 8), (1, 10), (1, 11), (2, 5), (2, 8), (2, 10), (2, 11), (5, 7) and (5, 8). Consideration of symmetry, i.e. $h_1 \equiv h_4 \equiv h_{10} \equiv h_{13}$ etc. generates other obvious vanishing terms in $\zeta(C_{3,4})$. *Clar* "*coloring*" [15]: Clar structures might be represented by the corresponding Clar graph colored (arbitrarily) in the following way: *black* vertices corresponding to hexagons containing circles (i.e. aromatic sextets) and *white* vertices for empty hexagons. The black and white vertices must be arranged such that *no two black vertices are adjacent and that every white vertex must be* adjacent to at least one black vertex. The number of such "Clar colorings" is the number of Clar structures (=Clar bases) of the hydrocarbon, denoted by ζ (benzenoid system). For chrysene, e.g. we have the following facts:

ϕ (chrysene) = P_4; a path on 4 vertices,

K (chrysene) = 8

ζ (chrysene) = 3.

[1] The number of its Clar bases in *only* 29 (see Sect. 3.3)

The three Clar structures correspond to the following three Clar colorings:
●—○—●—○; ○—●—○—●; ●—○—○—●

Clar polynomial

It is convenient for the enumeration of Clar structures (=Clar bases) to define a Clar polynomial as follows. Let $\phi(B)$ be the Clar graph of a benzenoid system B. Let $V(r)$ be the number of Clar structures in which there are r black vertices, where $r \geq 1$ and let m be the maximal value of r. Then a Clar polynomial $\xi(\phi(B); x)$, might be given by Eq. (2), viz.,

$$\xi(\phi(B); x) = \sum_{r=1}^{m} V(r) x^r. \qquad (2)$$

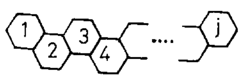
Naturally, the Clar count, $\zeta(B)$, would be defined as:

$$\zeta(B) = \xi(\phi(B); 1). \qquad (3)$$

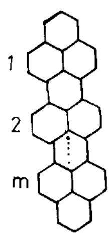
Equation (3) must take into account super-rings [8, 9] (see Sect. 3.3).

3. Binomial properties of Clar structures

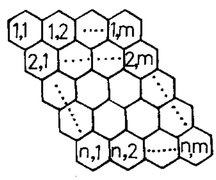
Four types of pericondensed systems are dealt with in this paper as well as a catacondensed system in which the hexagons are annelated in a zig-zag manner. (See Chart) Kekulé counts and sextet polynomials of these pericondensed systems are studied elsewhere [8].



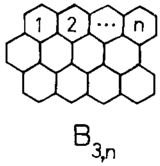
A_j



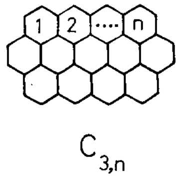
π_m



$P_{n,m}$



$B_{3,n}$



$C_{3,n}$

3.1. *Nonbranched cata-condensed all-benzenoid systems*

If benzene rings are annelated in a zig-zag way an all-benzenoid hydrocarbon results [15]. Lower members of this series are phenanthrene, chrysene, picene and fulminene; the latter contains six hexagons. Chemical and spectral properties of this system are studied and outlined in Clar's book [5]. Certain pericondensed systems contain this system as subunits and that is why it is included here (cf., $C_{3,n}$ system). The main combinatorial properties of this system which will be used later are the following: (other properties may be found elsewhere [16]).

3.1.1. The populations of Clar structures in periodic families of this system recur as follows:

$$\zeta(A_j)+\zeta(A_{j+1})=\zeta(A_{j+3}), \tag{4}$$

where $\zeta(A_i)$ is the number of Clar structures (=Clar bases [9]) of A_i, a non-branched zig-zag type benzenoid hydrocarbon containing i rings. Equation (4) is to be compared with the Fibonacci recursion [17], viz.,

$$F_j+F_{j+1}=F_{j+2}, \tag{5}$$

where F_i is the ith Fibonacci number when $F_0=F_1=1$. For this system one recalls that [18].

$$F_j=K(A_j) \tag{6}$$

and whence

$$K(A_j)+K(A_{j+1})=K(A_{j+2}) \tag{7}$$

where $K(A_i)$ is the Kekulé structure count of A_i. The real value of the VB method of Herndon and Hosoya [9] is now already clear. By comparing Eqs. (4) and (7) it is obvious that populations of Kekulé structures grow "much faster" than the corresponding populations of Clar structures. Because of Eqs. (5) and (6), Eq. (4) generates what might be called a "*delayed*" *Fibonacci sequence.* Chemical interpretations of Fibonacci-like progressions are known [18, 19].

3.1.2. The number of terms, τ, in Clar polynomials. We let r be the number of rings in A_r, then τ, the number of terms in $\xi(A_r; x)\equiv\xi(\phi(A_r), x)$ is given by:

$$\tau=\tfrac{1}{2}j+1 \tag{8}$$

where j is the *integral* value satisfying the equation

$$r=3j+a \tag{9}$$

where

$$a=\begin{cases}\{0,2,4\} & \text{for even value of } r\\ \{-3,-1,1\} & \text{for odd values of } r.\end{cases} \tag{10}$$

Here, the notation $\{k, l, m\}$ means either k, l or m which leads to an integral value of j. As an illustration: for A_8 we have $8=3j+a$ where $a=\{0,2,4\}$. Only $a=2$ leads to an integral value of $j(=2)$, and thus $\tau(A_8)=\frac{1}{2}\cdot 2+1=2$. Actually $\xi(A_8; x)=4X^3+5x^4$. Equation (8) will be used in the next property, viz., *3.1.3. Clar polynomials of A_i types.* The Clar graph of an A_i is simply a path, P_i. The following explicit expressions might be induced: (Throughout Eqs. (11–14) $n=0, 1, 2, \ldots$)

$$\xi(\phi(A_{4n}); x) = \binom{2n+1}{1}x^{2n} + \binom{2n}{3}x^{2n-1} + \binom{2n-1}{5}x^{2n-2} + \cdots + \binom{2n-\tau+2}{2\tau-1}x^{2n-\tau+1} \tag{11}$$

$$\xi(\phi(A_{4n+2}); x) = \binom{2n+2}{1}x^{2n+1} + \binom{2n+1}{3}x^{2n} + \binom{2n}{5}x^{2n-1} + \cdots + \binom{2n-\tau+3}{2\tau-1}x^{2n-\tau+2} \tag{12}$$

$$\xi(\phi(A_{4n+1}); x) = \binom{2n+2}{0}x^{2n+1} + \binom{2n+1}{2}x^{2n} + \binom{2n}{4}x^{2n-1} + \cdots + \binom{2n-\tau+3}{2\tau-1}x^{2n-\tau+2} \tag{13}$$

$$\xi(\phi(A_{4n+3}); x) = \binom{2n+3}{0}x^{2n+2} + \binom{2n+2}{2}x^{2n+1} + \binom{2n+1}{4}x^{2n} + \cdots + \binom{2n-\tau+4}{2\tau-1}x^{2n-\tau+3}. \tag{14}$$

Evidently, Eqs. (11–14) lead to analytic expressions for the number of Clar structures when $x=1$. These results will be used in system $C_{3,n}$ (Sect. 3.3).

3.2. *The pyrene system*

We consider a pyrene system composed of n units, Π_n (see charrt). Obviously, Π_n contains $3n+1$ rings. A very little effort shows that Clar polynomials are simply given by:

$$\xi(\phi(\Pi_n); x) = x^{n+1} + (3^n - 1)x^{n+2} \tag{15}$$

and thus the Clar count is trivially:

$$\zeta(\Pi_n) = 3^n \tag{16}$$

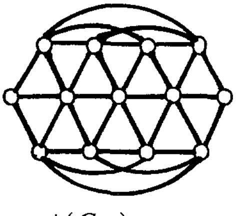
Equation (16) is to be compared with Gutman's formula [20]

$$K(\Pi_n) = 2.3^n \tag{17}$$

3.3. *The $C_{3,n}$ system*

The Kekulé counts of this system are considered in details in the recent work of Ohkami and Hosoya [8].

3.3.1. Clar graph of $C_{3,n}$; $\phi(C_{3,n})$. The ϕ graph of this system is composed of three rows of vertices derived from the skeletal graph [21] of the corresponding hydrocarbon. The vertices of both the upper and lower rows form complete graph [22] (i.e. every vertex is connected to all other vertices of the row). The vertices of the middle row has the connectivity of a path in relation to one another. I.e. is identical to $\phi(A_{n+1})$. Thus $\phi(C_{3,4})$ is shown below.



$\phi(C_{3,4})$

We might "losely" express $\phi(C_{3,n})$ as $\phi(K_n UA_{n+1} UK_n)$ where K_n is a complete graph on n vertices.

3.3.2. Clar counts and Clar polynomials. Clar polynomials of the $C_{3,n}$ system might conveniently be constructed if divided into three parts, viz.,

(1) Black colors assigned to vertices chosen from all three rows. We shall call this part of the polynomial $\xi(V(123); x)$.

(2) Black colors assigned to vertices chosen from middle row *only.* This part of the polynomial will be called $\xi(V(2); x)$. We now recall that the vertices of the middle row of a $\phi(C_{3,n})$ are attached to one another like the vertices of a path, i.e. form among themselves an A_{n+1} system. However out of the total of $\zeta(A_{n+1})$ *only two* "colors" form maximal independent sets with the rest of the vertices viz.,

$$\xi(V(2); x) = 2x \qquad (n \text{ odd}) \tag{18}$$

$$\xi(V(2); x) = x^{n/2} + x^{n/2+1} \qquad (n \text{ even}) \tag{19}$$

(3) Contribution from super-rings [8, 9] (super-sextets)

$= \xi(S; x) = (n-1)x.$

Thus for the $B_{3,n}$ system we have

$$\xi(\phi(B_{3,n}); x) \equiv \xi(B_{3,n}; x) = \xi(V(123); x) + \xi(V(2); x) + \xi(S; x) \tag{21}$$

3.3.3. Computation of $\xi(V(123); x)$. This is not a trivial term to compute. A systematic method involves the construction of a "multiplication table or matrix". Thus we denote the vertices of the first row in $\phi(C_{3,n})$ by $(V_{11}, V_{12}, \ldots, V_{1n})$ and those of its third row by $(V_{31}, V_{32}, \ldots, V_{3n})$. We define a *color integral,* say, $\langle V_{1j} | V_{3k} \rangle$, where $j, k = [1, n]$, to give all Clar colorings which result when vertex V_{1j} and vertex V_{3k} are assigned black colors. Obviously, the resulting (Clar) colorings will come from the "path moiety" (from second row) which is *not* adjacent to V_{1j} or to V_{3k}. E.g., in $C_{3,7} \langle V_{11} | V_{31} \rangle = \zeta(A_6)$. (See Fig. 1). Thus the contribution of $\langle V_{11} | V_{31} \rangle$ to $\xi(V(123); x)$ will simply be $X^2 \xi(\phi(A_6))$. The factor of x^2 comes from assigning black colors to V_{11} and to V_{31}. Thus we realize this

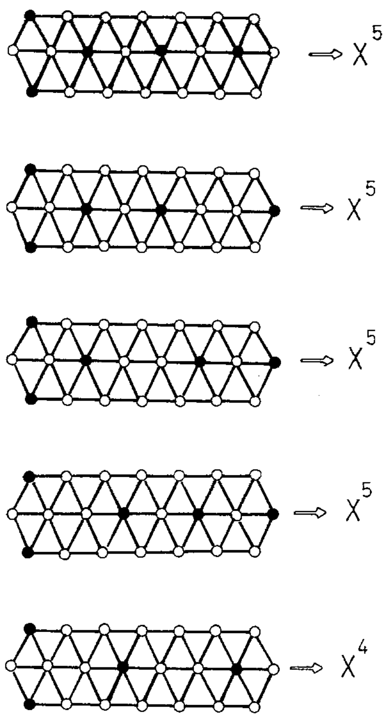


Fig. 1. All five Clar colors of $C_{3,7}$ resulting when black colors are assigned to V_{11} and V_{31}: computation of $\langle V_{11}|V_{31}\rangle$. Only skeletal graphs are shown. The total number of colors of this perifusene is 164 = the number of its Clar structures (see Appendix 1 and Table 1)

part of the Clar polynomial to be function of Clar polynomials of zig-zag polyacenes. In general one might write:

$$\langle V_{1j}|V_{3k}\rangle = x^2\xi(\langle V_{1j}|V_{3k}\rangle'; x). \tag{22}$$

Where the primed "bra-ket" indicates that part of the path (which may be disconnected) not connected with the subgraph $\{V_{1j}UV_{3k}\}$. Because of the particular topology of this system all $\langle V_{1j}|V_{3k}\rangle$''s are paths. (These might be called *here*, "complementary" paths). Thus we may write

$$\xi(V(123); x) = x^2 \sum_{j,k\in C_{3,n}} \xi(\langle V_{1j}|V_{3k}\rangle', x); \quad j, k = [1, n]. \tag{23}$$

where the summation is taken over all j and k for both $j = k$ and $j < k$. In the appendix the multiplication table of a lower member of $C_{3,n}$ is given.

Table 1 lists Clar polynomials of a few $C_{3,n}$ members in the units of zig-zag polyacenes. Polynomials of the latter are listed in the appendix.

3.4. *The $B_{3,n}$ system*

3.4.1. Clar graph of $B_{3,n}$; $\phi(B_{3,n})$. The skeletal graph [21] of $B_{3,n}$ is composed of three rows of vertices. If we keep the arrangement of hexagons of a $B_{3,n}$ as shown in chart, the three rows of vertices of its skeletal graph are numbered from left

Table 1. Clar polynomials of the first lower members of $C_{3,n}$ type in the units of the zig-zag polyacene polynomials [23]. Throughout the following $A_k=\xi(A_k;x)$, Appendix 2; $C_{3,k}=\xi(C_{3,k};x)$. Parts of the polynomials in parentheses are values of $\xi(V(2);x)$ while parts in braces represent contributions from super-rings; $\xi(S,x)$, see Eq. (21)

$C_{3,2}$ (coronene)
$2X^2+2A_2+(X+X^2)+\{X\};\ \zeta(C_{3,2})=7$

$C_{3,3}$
$2X^2+4X^2A_1+2X^2A_2+X^2A_1A_1+(2X^2)+\{2X\};\ \zeta(C_{3,3})=15$

$C_{3,4}$
$6X^2A_1+4X^2A_2+2X^2A_3+2X^2A_1A_2+2X^2A_1A_2+(X^3+X^2)+\{3X\};\ \zeta(C_{3,4})=29$

$C_{3,5}$
$6X^2A_2+4X^2A_3+2X^2A_4+6X^2A_1A_1+4X^2A_1A_2+2X^2A_1A_3$
$+X^2A_2A_2A_2+(2X^3)+\{4X\};\ \zeta(C_{3,5})=54$

$C_{3,6}$
$6X^2A_3+4X^2A_4+2X^2A_5+12X^2A_1A_2+4X^2A_1A_3+2X^2A_1A_4$
$+2X^2A_1A_1A_1+2X^2A_2A_2+2X^2A_2A_3+(X^4+X^3)+\{5X\};$
$\zeta(C_{3,6})=95$

$C_{3,7}$
$6X^2A_4+4X^2A_5+2X^2A_6+12X^2A_1A_3+4X^2A_1A_4+2X^2A_1A_5$
$+6X^2A_2A_2+4X^2A_2A_3+2X^2A_2A_4+6X^2A_1A_1A_2+X^2A_3A_3+(2X^4)+\{6X\};$
$\zeta(C_{3,7})=164.$

to right as follows $V_{11}, V_{12}, \ldots, V_{1n}$; $V_{21}, V_{22}, \ldots, V_{2n}$; $V_{31}, V_{32}, \ldots, V_{3n}$. To form the ϕ graph every vertex in each row is attached to all other vertices in the same row so that every row becomes a complete graph. In addition every vertex in the second row is connected to all other vertices to its left. This means that v_{2n} is adjacent to *all* vertices in $\phi(B_{3,n})$, i.e. $\{v'_{2n}\}=\{\varnothing\}$ (=the empty set), where, as before, $\{V'_j\}$ is, in general, the set of vertices *not* connected with V_j. Similarly $\{V'_{2,n-1}\}=\{V_{1n}UV_{3n}\}$. We can write analogous equations such as $\{V'_{2,(n-2)}\}=\{V_{1n}UV_{1,n-1}UV_{3n}UV_{3,n-1}\}$ and so on.

3.4.2. Clar polynomials of $B_{3,n}$. In this case all Clar colorings except one involve black vertices chosen from all three rows. Because V_{2n} is attached to all other vertices, a black V_{2n} leaves the rest of the vertices white. There is no super-ring [8, 9] correction. Using the technique of multiplication table explained in the previous case one can express the required Clar polynomial as follows

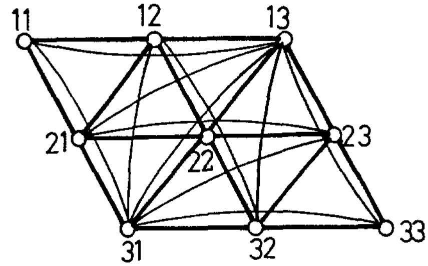
$$\xi(\phi(B_{3,n});x)\equiv\xi(B_{3,n};x)$$
$$=x^2\left[\sum_{j=1}^{n}(2(n-j)+1)\xi(L_{j-1};x)\right]+x, \qquad (24)$$

where $\xi(L_k;x)$ = Clar polynomial of a linear acene containing k hexagons ($=kx$) and $\xi(L_0;x)=1$. The factor of x comes from the maximal independent set containing a black V_{2n}. In the appendix a multiplication table is given for $B_{3,6}$.

3.5. *The parallelogram system* $P_{n,m}$

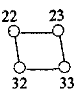
We consider a parallelogram of *mn* hexagons arranged in *n* rows and *m* columns. This is identical to Ohkami–Hosoya [8] $P_{m,n}$ (Actually, if the latter is reflected by a mirror at the bottom our system results: We prefer to call it $P_{n,m}$ in keeping with the matrix notation of listing the number of rows followed by the number of columns).

3.5.1. The Clar graph of $P_{n,m}$, $\phi(P_{n,m})$. This is a rather involved graph. To illustrate the pattern of this family we consider $\phi(P_{3,3})$ shown below.

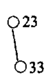


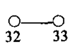
$\phi(P_{3,3})$

Higher members generate much more complicated relations. A convenient method to envisage the structures of these graphs is to list what is called *here* "complement subgraphs". Thus $\{v'_{ij}\}$ is such a subgraph of vertex v_{ij}. It is defined to be the subgraph of vertices *not* adjacent (i.e., not connected) with v_{ij}. For $\phi(P_{3,3})$. We have the following relations:

$\{v'_{11}\} =$  $= P_{2,2}$

Similarly;

$\{V'_{12}\} =$  $= P_{2,1};$

$\{V'_{21}\} =$  $= P_{1,2};$

$\{V'_{13}\} = \{V'_{31}\} = \{\varnothing\}.$

Analogously for $\phi(P_{3,4})$ one might write:

$\{V'_{11}\} = P_{2,3};\ \{V'_{12}\} = P_{2,2};\ \{V'_{13}\} = P_{2,1};$
$\{V'_{21}\} = P_{1,3};\ \{V'_{31}\} = \{V'_{14}\} = \{\varnothing\}.$

3.5.2. Clar counts of $P_{n,m}$. With some effort one can induce the following property of the number of clar structures of a $P_{n,m}$ in terms of smaller (complement) subgraphs of the vertices of the first row and those of the first column of $\phi(P_{n,m})$

$$\begin{aligned}\zeta(P_{n,m}) = \zeta(P_{n-1,m-1})\,U\zeta(P_{n-1,m-2})\,U\cdots U \\ \times\zeta(P_{n-1,1})\,U\zeta(\emptyset)\,U\zeta(P_{n-2,m-1})\,U \\ \zeta(P_{n-3,m-1})\,U\cdots U\zeta(P_{1,m-1})\,U\zeta(\emptyset).\end{aligned} \tag{25}$$

where $\zeta(\emptyset)=1$. Evidently $P_{1,j}=P_{j,1}=L_j=$ a linear acene on j hexagons. Of course $\zeta(P_k)=k$.

3.5.3. Recursive relations of Clar polynomials. The general recursion is given by

$$\begin{aligned}\xi(\phi(P_{n,m});x) \equiv \\ \xi(P_{n,m};x) = 2x + x\left[\sum_{i=1}^{m-1}\zeta(P_{n-1,i},x) + \sum_{j=1}^{n-2}\xi(P_{j,m-1};x)\right].\end{aligned} \tag{26}$$

Equation (26) is a result of property (25).

Explicit expressions of some of the lower members are given below.

$$\xi(\phi(P_{1,m});x) = \binom{m}{1}x \tag{27}$$

$$\xi(\phi(P_{2,m});x) = \binom{m}{2}x^2 + 2x \tag{28}$$

$$\xi(\phi(P_{3,m});x) = \binom{m}{3}x^3 + 3(m-1)x^2 + 2x \tag{29}$$

$$\xi(\phi(P_{4,m});x) = \binom{m}{4}x^4 + \binom{4}{1}\binom{m-1}{2}x^3 + 3mx^2 + 2x \tag{30}$$

$$\begin{aligned}\xi(\phi(P_{5,m});x) = \binom{m}{5}x^4 + \binom{5}{1}\binom{m-1}{3}x^4 + 2(m+2)(m-2)x^3 + \\ +3(m+1)x^2 + 2x.\end{aligned} \tag{31}$$

There are no super-rings [8, 9] in this system. Such expressions are to be compared with those of Ohkami and Hosoya [8] for the corresponding Kekulé counts.

The above results (Eqs. 4–31) as well as the method of "multiplication table" are certainly useful for the enumeration *and* display (respectively) of Clar structures. This is of value from several aspects, viz.

(1) The work of Herndon and Hosoya [9]: Clar structures form the bases of their effective *VB* Hamiltonian.

(2) The work of Ohkami and Hosoya [8]: Clar polynomials are to be compared with sextet polynomials, i.e., $\zeta(B)$ with $K(B)$.

(3) The work of Aida and Hosoya [21]: Clar structures may provide a novel *VB*-benzene character which may be of value in the analysis of mode of distribution of pi-electrons in the individual hexagons of a polycyclic aromatic hydrocarbon. Our work is in progress in this direction.

Appendix 1

Multiplication table of $C_{3,7}$: computation of $\xi(C_{3,7}(V(123); x)$. Table (matrix) elements are in units of $\xi(A_k; x) \equiv A_k$.

	V_{11}	V_{12}	V_{13}	V_{14}	V_{15}	V_{16}	V_{17}
V_{31}	A_6	A_5	A_4	A_1A_3	A_{22}	A_1A_3	A_4
V_{32}		A_1A_5	A_1A_4	A_1A_3	$A_1A_1A_2$	$A_1A_1A_2$	A_1A_3
V_{33}			A_2A_4	A_2A_3	A_2A_2	$A_2A_1A_1$	A_2A_2
V_{34}				A_3A_3	A_3A_2	A_3A_1	A_3A_4
V_{35}					A_4A_2	A_4A_1	A_4
V_{36}						A_5A_1	A_5
V_{37}							A_6

When $\zeta(A_k)$'s are used (from Appendix 2) the above table yields 156 maximal independent sets. The total number of $\zeta(C_{3,7}) = 156+2+6 = 164$ (cf. Eq. 21).

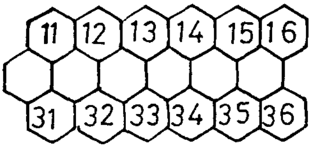
Appendix 2

Clar polynomials of the lower members of the zig-zag polyacenes. Throughout, the symbol A_k will be used to indicate $\zeta(A_k; x)$.

$A_1 = X$
$A_2 = 2X$
$A_3 = X^2+X$
$A_4 = 3X^2$
$A_5 = X^3+3X^2$
$A_6 = 4X^3+X^2$
$A_7 = X^4+6X^3$
$A_8 = 5X^4+4X^3$
$A_9 = X^5+10X^4+X^3$
$A_{10} = 6X^5+10X^4$
$A_{11} = X^6+15X^5+5X^4$
$A_{12} = 7X^6+20X^5+X^4$
$A_{23} = X^7+21X^6+15X^5$
$A_{14} = 8X^7+35X^6+6X^5$
$A_{15} = X^8+28X^7+35X^6+X^5$
$A_{16} = 9X^8+56X^7+21X^6$
$A_{17} = X^9+36X^8+70X^7+7X^6$
$A_{18} = 10X^9+84X^8+56X^7+X^6$
$A_{19} = X^{10}+45X^9+126X^8+28X^7$
$A_{20} = 11X^{10}+120X^9+126X^8+8X^7$

Appendix 3

Multiplication table of $B_{3,6}$



	11	12	13	14	15	16
31	∅	∅	∅	∅	∅	∅
32		L_1	L_1	L_1	L_1	L_1
33			L_2	L_2	L_2	L_2
34				L_3	L_3	L_3
53					L_4	L_4
36						L_5

∅: the empty set
L_k: Clar polynomial of a linear polyacene containing k hexagons

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This work is of value in the graph-recognition problem.