ON GLOBAL AND LOCAL PROPERTIES OF CLAR Pi-ELECTRON SEXTETS

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Abstract

The individual rings in benzenoid systems are studied via a new structural index, called Clar's ring character. The new index, which is based on *selected* Kekulé valence structures, differs significantly in a number of cases from similar ring characterizations based on *all* Kekulé valence structures. It is related to previously introduced quantities based on MO functions, but it can be obtained simply (i.e. without the need of a computer). We have illustrated the new ring index for several families of compounds, and report a number of regularities for a homologous series of molecules.

1. Introduction

Conjugated benzenoid hydrocarbons (such as those depicted in fig. 1) have traditionally been described by a set of Kekulé valence structures, which have also been widely used in early quantum chemical contributions [1]. With the revival of interest in chemical graph theory [2], Kekulé valence structures received fresh attention, which resulted in numerous novel observations and results. For example, it was recognized that the individual Kekulé valence structures can themselves be decomposed into various $(4n + 2)$-size conjugated circuits [4], which then led to *expressions* for molecular resonance energy. Also, more recently it was found that Kekulé valence structures vary in their short- and long-range *order* characteristics, which can be
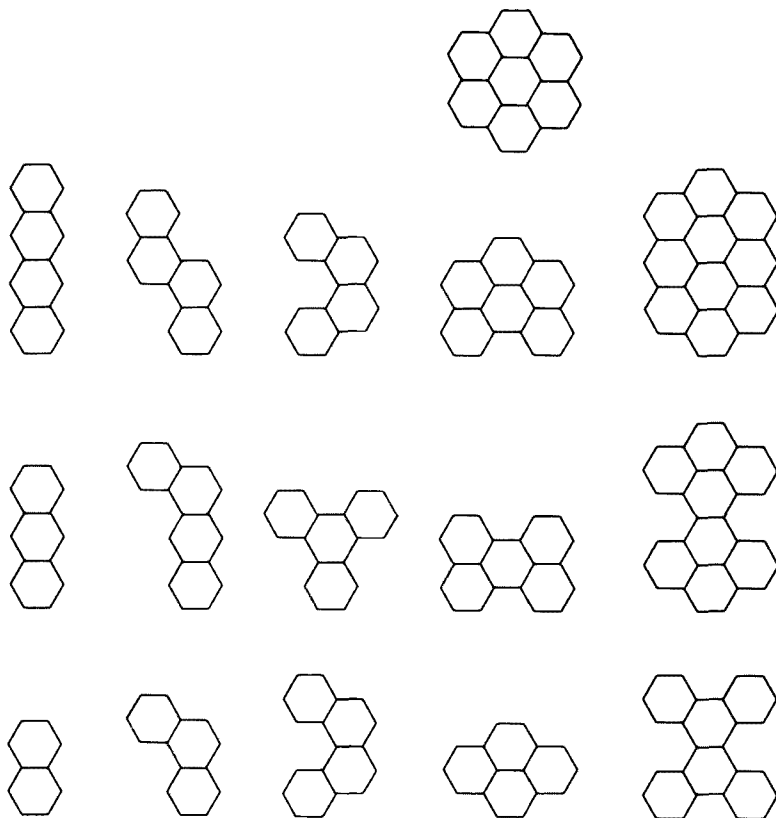
Fig. 1. Molecular graphs of some benzenoid hydrocarbons.

related to an innate degree of freedom of Kekulé valence structures [5]. Kekulé valence structures which support a long-range order (such as the selected structures in fig. 2) can immediately be recognized by chemists as those structures that have little, if any, importance for descriptions and discussions of the aromaticity of compounds. On the other hand, the Kekulé valence structures shown in fig. 3 can be recognized intuitively, or by using chemical logic and experience, as important. In fact, even before the early days of quantum chemistry, Fries [6] formulated an empirical rule describing the most important Kekulé valence structures. He recognized that those Kekulé valence structures that contain the largest number of formal Kekulé rings (i.e. rings with three double and three single bonds) are the most important. Hence, not all Kekulé valence structures have the same importance, but the difficult problem has been that of establishing which valence structures are important and which are not. Clar, the doyen of the chemistry of benzenoid hydrocarbons, accumulated impressive experience on the synthesis and properties of benzenoids [7,8] and was able, in a qualitative way, to resolve the problem of the relative importance of the individual Kekulé valence structures by an ingenious approach: by construction of
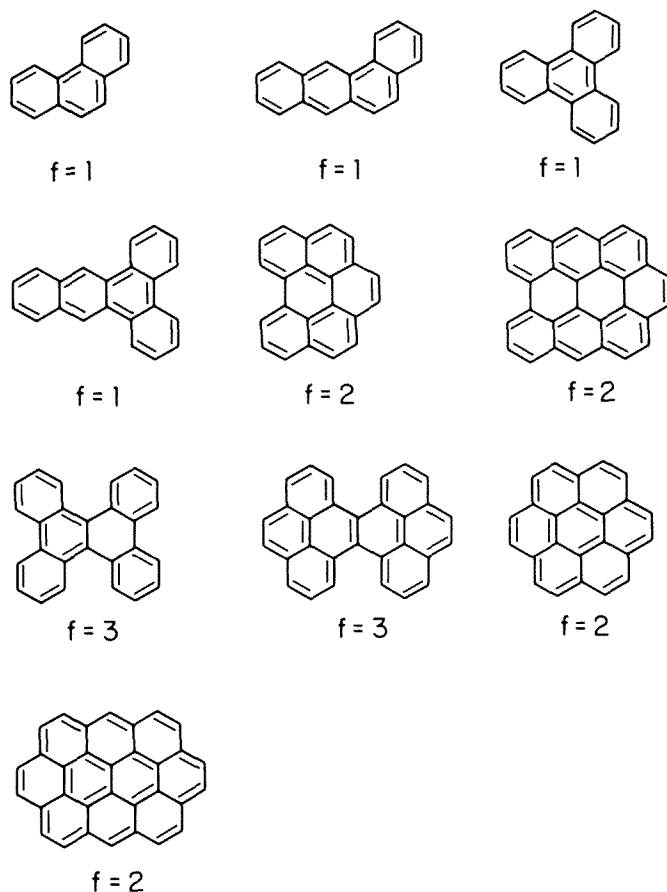
Fig. 2. Examples of Kekulé valence-bond structures that support a long-range order, i.e. have low innate degree of freedom values (f's). Such structures have a small contribution to the stability of the benzenoid system.

novel structural formulae for these compounds. These, now called Clar's structural formulae or *Clar structures* [9], are illustrated for a number of benzenoid systems in fig. 4. Immediately we see three kinds of cases: (a) Valence structures with all rings either having a circle, signifying a pi-electron sextet, such as in benzene itself, or being "empty", i.e. without any pi-sextet character or any CC double bonds; (b) Valence structures with some rings having sextet, while other rings have CC double bonds; and finally (c) Molecules for which no unique Clar structure is possible. It is easy to see that Clar's circle can be obtained as a result of a superposition of a pair of Kekulé valence structures. Consider the case of pyrene, all possible combinations of pairs of structures of which are illustrated in fig. 5. By a superposition of two Kekulé valence structures, one can identify a single conjugated circuit. Thus, we find in pyrene the conjugated circuits listed in table 1.
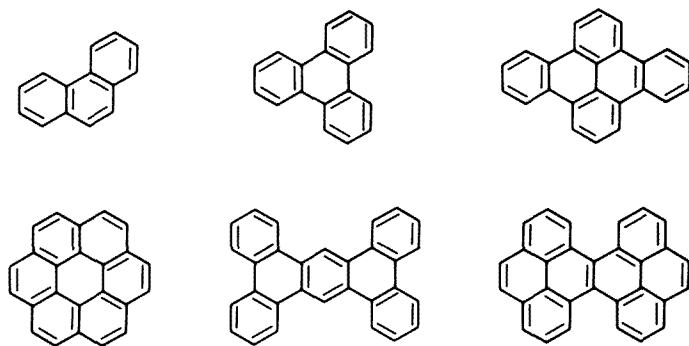
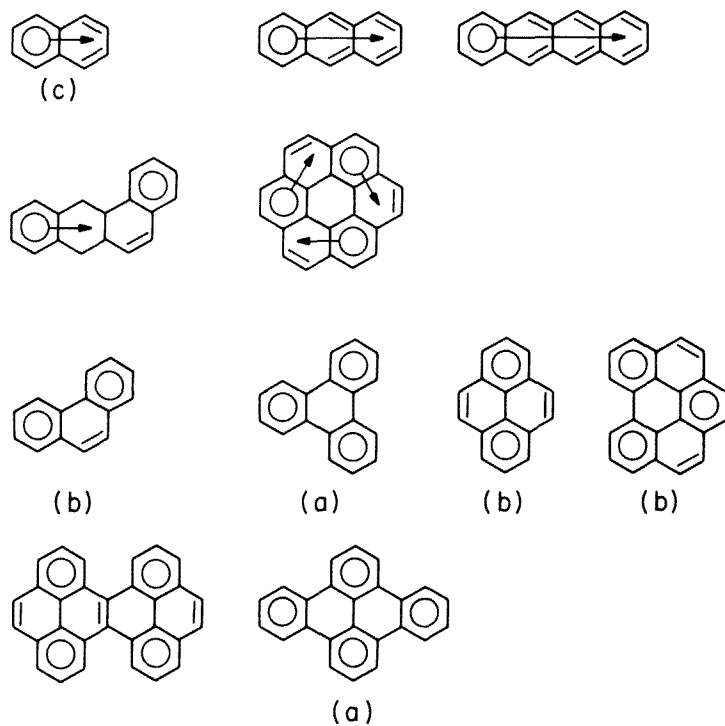Fig. 3. Examples of important Kekulé structures.

Fig. 4. Illustration of Clar structures (Clar structural formulae) of some benzenoid hydrocarbons.
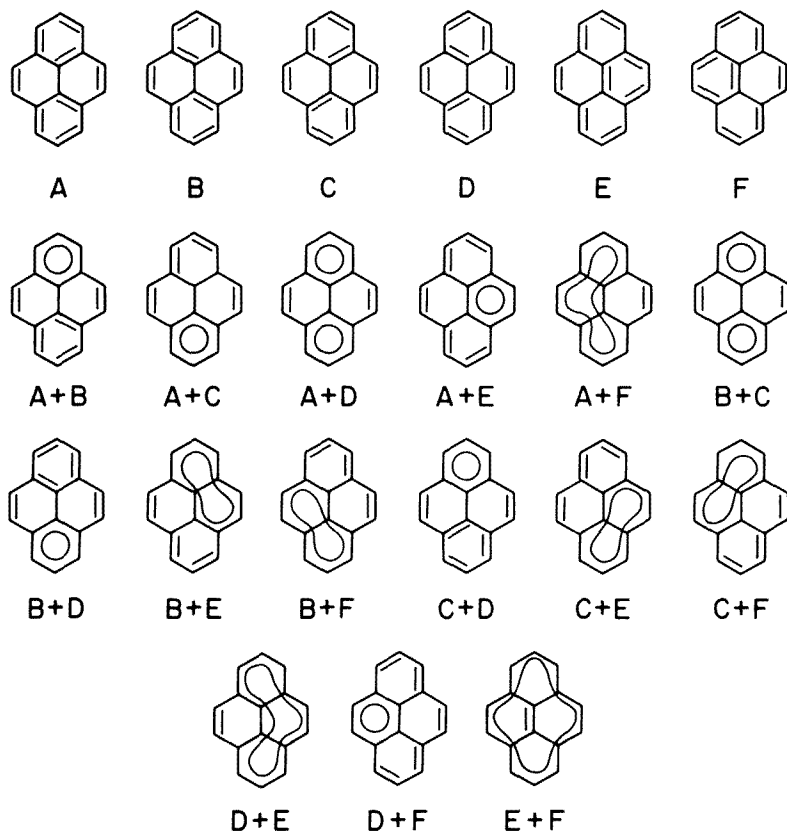
Fig. 5. Kekulé and Clar structures of pyrene. Structure A + B is obtained by superposition of structures A and B and so on.

The expression for the molecular resonance energy (RE) is obtained by counting conjugated circuits of different size and dividing by K, the number of Kekulé structures. Hence:

$$\text{RE (pyrene)} = 2(6R_1 + 4R_2 + 3R_3)/6.$$

The factor of two enters because we consider only half of the possible pairs due to symmetry, i.e. superposition (A, B), for example, gives the same result as superposition (B, A) and so on. The contribution of disjoint conjugated rings, here $R_1 \cdot R_1$, are neglected in numerical treatments due to their negligible role. Let us now restrict attention only to structures having R_1 conjugated circuits, some of which are shown below:
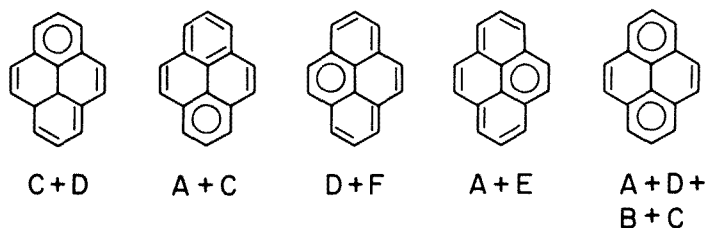
Table 1

Conjugated circuits of pyrene

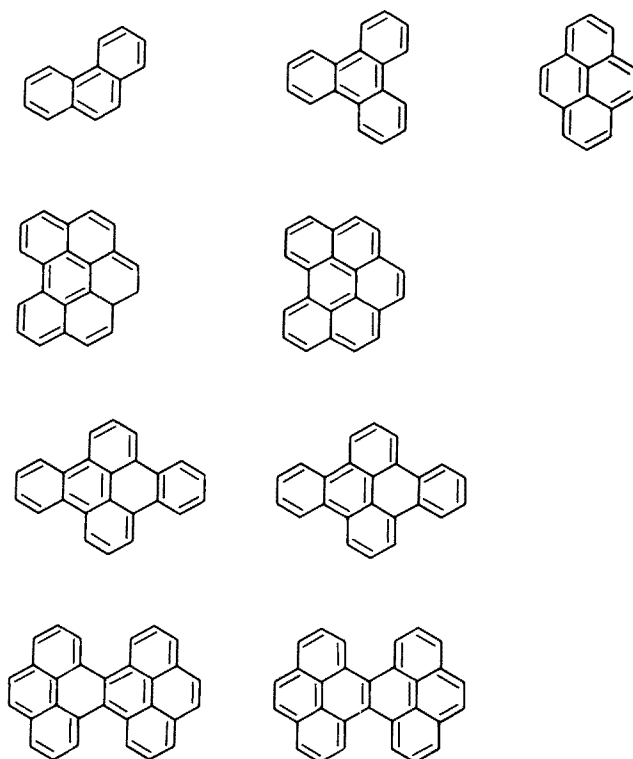| Number of pi-electrons	Size of circuits	Contributing structures	Total
6	R_1	A + B, A + C, A + E, B + D, C + D, D + F	6
10	R_2	B + E B + F C + E C + F	4
14	R_3	A + F D + E E + F	3
6.6	$R_1 \cdot R_1$ (disjoint)	A + D B + C	2

Fig. 6. Examples of Kekulé valence structures that are neglected by Clar formalism. All such structures are of minor importance.

These have been called Clar-type valence structures or *Clar patterns* [9]. *Only the last structure* is that of Clar, i.e. only the last is the structure by which Clar proposed to represent pyrene. Clar considered to have for a polycyclic conjugated hydrocarbon a single structural formula, and in the case of pyrene the formula is the one designated as: A + B + C + D. Hence, the new valence structure neglects two Kekulé structures of pyrene (the structures E and F of fig. 5). Observe that this is tantamount to neglecting numerous larger conjugated circuits (R_2, R_3, ...). However, if one focuses attention on the *dominant* factors involved in aromaticity, then one can see that Clar's intuitive approach can be justified because larger conjugated circuits (R_2, R_3, ...) make smaller and smaller contributions to the overall molecular thermodynamic stability. In fig. 6 we illustrate the Kekulé valence structures which are neglected by Clar's approach for selected benzenoid systems. The purpose of fig. 6 is to show that indeed these particular structures are of less importance (cf. fig. 2) judged by chemical intuition.

2.   Quantitative approach to Clar's sextet model

The approach of Clar amounts to neglect of some Kekulé valence structures, but as Herndon and Hosoya [10] have recently demonstrated, one can base a quantitative description of conjugated systems on very few Clar-type structures. According to Herndon and Hosoya, in the case of pyrene it suffices to use only the following structures: (A + E), (D + F) and (A + B + C + D):
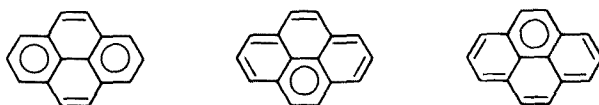

These are the only Clar-type structures that have a unique location for CC double bonds, once a sextet circle is indicated. Observe also that by "broadening" the bases of Clar, i.e. by including the structures (D, F) and (A, E), Herndon and Hosoya [10] have *recovered* structural information contained by Kekulé valence structures E, f that was neglected by the single Clar structure description of the system. In the approach of Herndon and Hosoya, we find the valence structures A and D (of fig. 5), which each contribute $3R_1 + R_3$ to pyrene's molecular RE, to have twice the weight of the other structures. Interestingly enough, the same two structures are precisely those that Fries' empirical rule [6] suggests as the most important. Alternatively, one sees that the same two structures make the largest relative contributions to the molecular RE in the conjugated circuit approach of Randić [4] and its valence bond counterpart: the resonance structure model by Herndon [11].

All the above strongly suggests that Clar structural formulae and Clar-type valence structures contain important structural information and can form a basis for

a quantitative model of chemical stability of large benzenoid systems. We will there-
fore briefly review selected results concerning Clar structures.

3.   Clar graphs

Gutman [12] considered the *resonance relations* among the individual hexagons
of a benzenoid hydrocarbon. Two rings are said to be resonant or resonance-related
if *simultaneously* both rings can have a sextet assignment (i.e. there is a Clar-type
formula with both rings having inscribed circles). In Clar's formulae, such rings are
disjoint. If we (arbitrarily) label the rings in pyrene as follows:
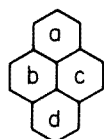
then three Clar-type resonant structures are possible. They are the structures A + E,
D + F and A + B + C + D shown before as the structures that uniquely determine the
positions for all CC double bonds once Clar sextets are assigned. From the definition
of the Clar graph, one can construct a *Clar matrix* c_{ij} thus:

$$c_{ij} = \begin{cases} 1 & \text{if rings } i, j \text{ are nonresonant} \\ 0 & \text{otherwise.} \end{cases} \tag{1}$$

Observe that here *adjacency* means that rings are nonresonant and in Clar's
qualitative description, such (adjacent) rings were associated with pi-sextet "migra-
tion" [8]. Hence, for pyrene we obtain the following Clar matrix:

$$\underline{C} = \begin{array}{c} \\ a \\ b \\ c \\ d \end{array} \begin{array}{cccc} a & b & c & d \\ \left(\begin{array}{cccc} 0 & 1 & 1 & 0 \\ 1 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{array} \right) \end{array}.$$

According to Gutman, the *Clar graph* of pyrene is then the graph whose adjacency
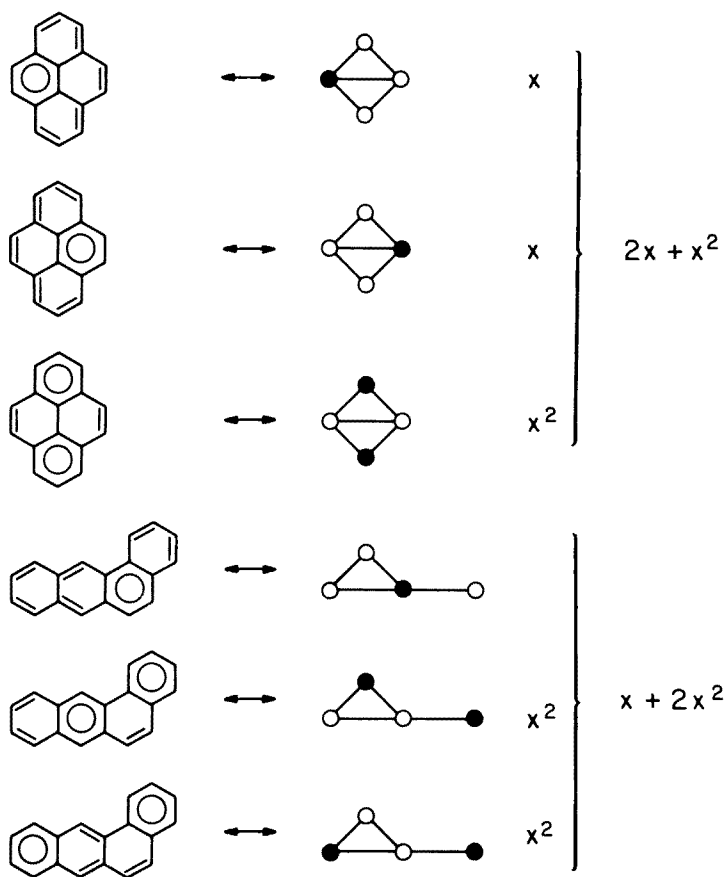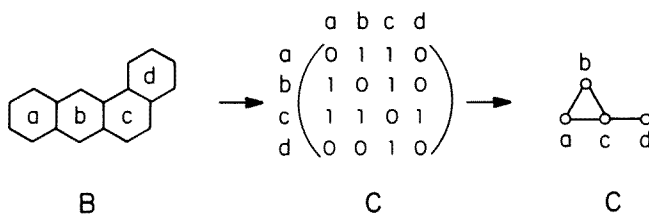matrix is $\underline{C}$, i.e.
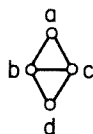
Fig. 7. Clar graphs of pyrene and of benz[a] anthracene. The colorings represent maximal independent sets of vertices.

Observe that in this particular example, the derived graph is the so-called "inner dual" [13] of the molecular graph of pyrene, although this is not generally true as can be seen, e.g. by considering benz[*a*]anthracene:

$$
\begin{array}{c}
\begin{array}{cccc}
a & b & c & d
\end{array} \\
\begin{array}{c} a \\ b \\ c \\ d \end{array}
\begin{pmatrix}
0 & 1 & 1 & 0 \\
1 & 0 & 1 & 0 \\
1 & 1 & 0 & 1 \\
0 & 0 & 1 & 0
\end{pmatrix}
\end{array}
$$

$$
\underline{C}
$$

There is a bijective mapping between the *rings* (hexagons) of a benzenoid hydrocarbon and the *vertices* of the corresponding Clar graph, such that the two vertices v_i, v_j of C are *adjacent* only if the corresponding rings in B are nonresonant. Given the Clar graph, one can *construct* the Clar-type *base* structures by following the rules for "coloring" vertices as follows:

(1)   No two colored vertices are adjacent.

(2)   Every non-colored vertex is adjacent to at least one colored vertex.

The above rules define the so-called "maximal independent sets of vertices" for a graph and appears in other graph-theoretical studies [14]. In fig. 7, we show the colorings for the selected two Clar graphs discussed previously. For each Clar graph shown, we illustrate the corresponding unique Clar structure.

4.   Clar polynomials

Polynomials provide simple bookkeeping for combinatorial enumerations and as such have already been used by Wheland [15] in connection with the enumeration of valence structures of conjugated benzenoids. Wheland polynomials enumerate valence structures of different degrees of excitation for a set of *canonical* valence structures. The elegance and advantages of the polynomial approach have already been demonstrated in Wheland's pioneering work. This includes the use of recursions and graph-theoretical reduction of large systems to smaller ones. However, the particular Wheland approach, although of no consequence for his interest, has a disadvantage: By restricting attention to *canonical* valence structures only (as determined by Rumer's non-crossing rule [16]), the derived polynomials are not structural *invariants*. The form of the polynomial depends on the assumed labeling of the vertices, as illustrated amply by Randić et al. [17]. In graph-theoretical considerations, graph invariants play a more important role than quantities that are not invariant. Recently, it has been shown that if one does not restrict the count of structures of different degrees of
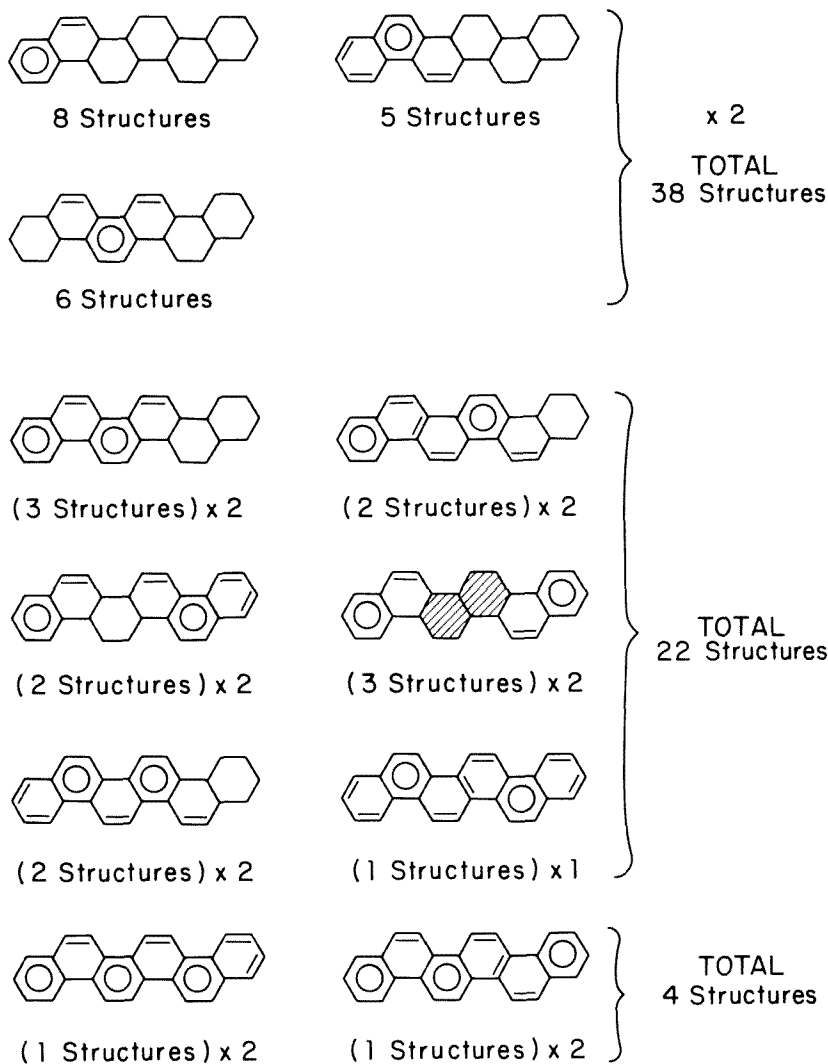
Fig. 8. Clar-sextet structures of fulminene. Only
non-symmetry-related structures are shown.

excitation to canonical structures only, but considers *all* valence structures, the
counting polynomial known as the generalized Wheland polynomial [17] becomes
a structural invariant. With respect to Clar structures, similarly one would like to
consider various invariants. The counting polynomial for Clar structures, called the
sextet polynomial, was introduced by Hosoya and Yamaguchi [18] and is structurally
invariant. The polynomial considers all Clar-like structures and counts resonance rings.
By definition, the coefficient corresponding to $k = 0$ is 1, and the coefficients of its
power, x^k, indicate k resonant rings. Hence, the sextet polynomial of pyrene is

$1 + 4x + x^2$. Analogously for a polynomial, the coefficients of its powers x^k indicate the number of Clar-type resonant structures with k inscribed circles [19] and will be reflected in a $CL(x)$ *Clar polynomial*. The Clar polynomial thus counts sets of maximally independent k vertices of the associated Clar graph. Thus we have:

$$CR \text{ (pyrene; } x) = 2x + x^2 \tag{2}$$

$$CR \text{ (benz}[a]\text{ anthracene; } x) = x + 2x^2. \tag{3}$$

The Clar resonant count, i.e. the number of *Clar-type structures* for a given benzenoid hydrocarbon, is considerably smaller than the *Clar-sextet-structure count* or the corresponding Kekulé count. For example, for fulminene (fig. 8) there are twenty-one Kekulé valence structures (as can be easily verified by following the elegant scheme by Gordon and Davison [20] for the count of Kekulé structures for catacondensed benzenoids). The number of Clar-sextet structures is sixty-four (as shown in fig. 8, where only symmetry-unrelated cases are illustrated), but only *five* of these sixty-four are Clar resonant structures. These are the last five structures, four having three inscribed sextet circles and one having only two pi-sextets. The structures can also be recognized as unique, being the only structures in fig. 8 in which all CC bonds have been assigned. The uniqueness of the five structures is seen also by the labels "1-structure" written underneath.

In table 2, we have listed Clar and sextet polynomials for a number of smaller benzenoid systems. In fig. 9, we illustrate recursive relations for the Clar polynomial of a number of benzenoid families shown in fig. 10. Let us use the symbol L_n for the Clar polynomial of a linearly fused *chain* of n-hexagons (polyacenes). If now we have a structure in which some "end" groups are attached to one side of the linear chain, as illustrated:
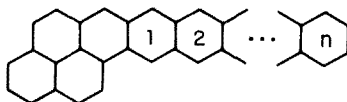
we can obtain the corresponding Clar-resonant polynomial by successively assigning resonant pi-sextets to all possible sites. As an illustration, we consider benzpyrene:
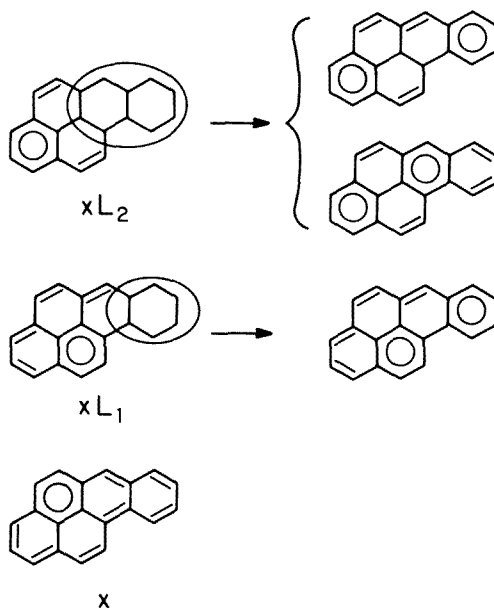
Among the structures on the left-hand side, the last structure is complete and qualifies as *Clar-resonant* because all other bonds have a unique bond-type assigned. Thus, the last structure makes a contribution to the polynomial with power x. The other two structures (to the left) are not complete, but when combined with the linear fragment produce the additional Clar resonant structures (shown on the right-hand side). Because linear chains already have one pi-sextet, we in this way obtain the coefficients of the x^2 term of the sought Clar polynomial. In more general graphs, expressions for the polynomial will depend on the chain length. We can summarize the result by writing the contributions as a product of x (in the general case x^k) and L_n, where L_n represents the characteristic polynomial arising from a linear chain of length n. Hence:

$$\text{CR (benzopyrene; } x) = xL_2 + xL_1 + x,$$

and in view of $L_1 = x$ and $L_2 = 2x$, etc., we finally obtain $\text{CR(benzopyrene; } x) = x + 3x^2$. Thus, there are four Clar structures of benzopyrene which correspond to the four "colored" Clar graphs shown below:
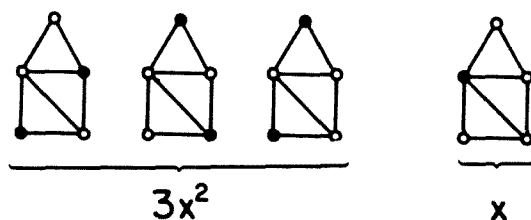
Table 2

Clar and sextet polynomials of some families of benzenoid hydrocarbons. The number of Clar structures is CR(G; 1), while that for the weighted structures is CR(G; 2).

Class	Clar polynomial	Sextet polynomial
	$CR(G; x)$	$\sigma(G; x)$
$(n:2)$	$x + nx^2$	$1 + (n+2)x + nx^2$
$(n:3)$	$x + 2nx^2$	$1 + (n+3)x + 2nx^2$
$(n:4)$	$x + 3nx^2$	$1 + (n+4)x + 3nx^2$
$(2:n:2)$	$2x^2 + nx^3$	$1 + (4+n)x + (2n+3)x^2 + nx^3$
$(1:2:n)$	$(2n+1)x^2$	$1 + (n+3)x + (2n+1)x^2$
$(2:2:n)$	$2x^2 + 3nx^2$	$1 + (n+4)x + 2x^2 + 3nx^2$
$(2:(1):n)$	$x + nx^3$	$1 + (n+3)x + (2n+1)x^2 + nx^3$
$(3:(2):n)$	$x + 4nx^3$	$1 + (n+5)x + 4(n+1)x^2 + 4nx^3$
$(2^2:n)$	$x + (2n+1)x^2$	$1 + (n+4)x + (2n+1)x^2$
$(2^3:n)$	$x + 3(n+1)x^2$	$1 + (n+6)x + 3(n+1)x^2$
$(2^4:n)$	$x + (4n+6)x^2$	$1 + (n+7)x + (4n+6)x^2$
$(2:n:2^2)$	$3x^2 + (2n+1)x^3$	$1 + (n+6)x + (3n+7)x^2 + (2n+1)x^3$
$(2:n:2^3)$	$4x^2 + 3(n+1)x^3$	$1 + (n+7)x + (4n+11)x^2 + 3(n+1)x^3$
$(2^2:n:2^2)$	$4x^2 + 4(n+1)x^3$	$1 + (n+8)x + (4n+14)x^2 + 4(n+1)x^3$
$(2^2:n:2^3)$	$5x^2 + (6n+9)x^3$	$1 + (n+10)x + (5n+22)x^2 + (6n+9)x^3$

Benzopyrene can be considered as the first member of the family
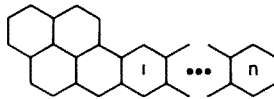
for which one can immediately construct the corresponding expressions for the individual members:

$$\text{CR}_1(x) = x(L_2 + L_1 + 1) \tag{4}$$
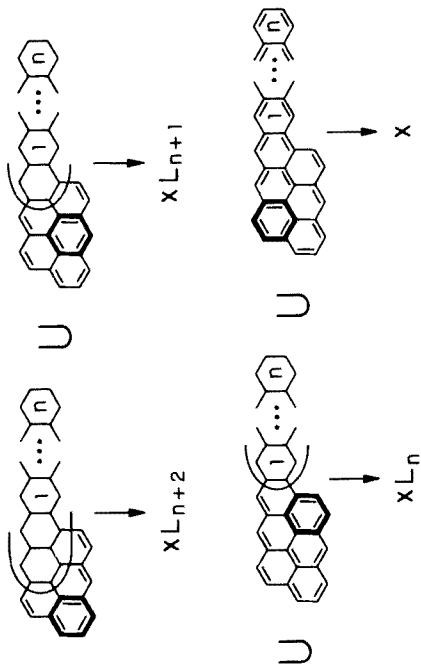
$$\text{CR}_2(x) = x(L_3 + L_2 + 1) \tag{5}$$

$$\text{CR}_3(x) = x(L_4 + L_3 + 1) \tag{6}$$

$$\begin{array}{c} \cdot \\ \cdot \\ \cdot \end{array}$$

$$\text{CR}_n(x) = x(L_{n+1} + L_n + 1). \tag{7}$$

It can be shown that $L_n = nx$. Thus, by substituting $x = 1$ in $\text{CR}_n(x)$ we obtain the Clar-resonant count $2n + 2$. In table 2, we present similar information for the other families of graphs depicted in fig. 11.

Fig. 10. Families of catacondensed benzenoid hydrocarbons studied in this work (cf. tables 2 and 5).

(n:3)

(2:n:2)

(2:2:n)

(3:(2):n)

(n:2)

(n:4)

(1:2:n)

(2:(1):n)

(1:1:1:1:····:1)

Family: 2³:n
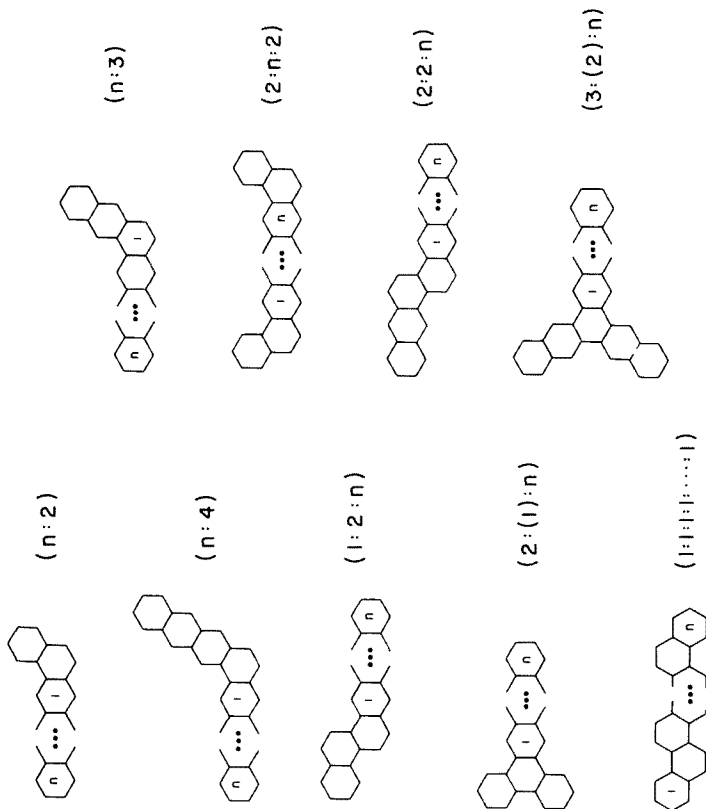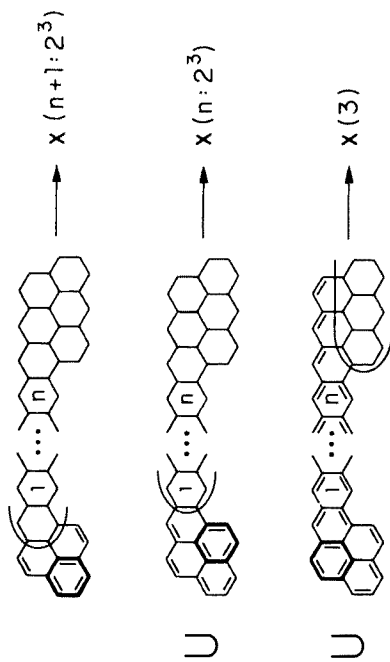
xL_{n+2}

xL_{n+1}

x

Family: 2²:n:2³

x(n+1:2³)

x(n:2³)

x(3)

Fig. 9. Illustration of the recursive relation to obtain the Clar polynomial of two families of benzenoid hydrocarbons (see figs. 10, 11).

$(2^2 : n)$

$(2^3 : n)$

$(2^4 : n)$

$(2 : n : 2^2)$

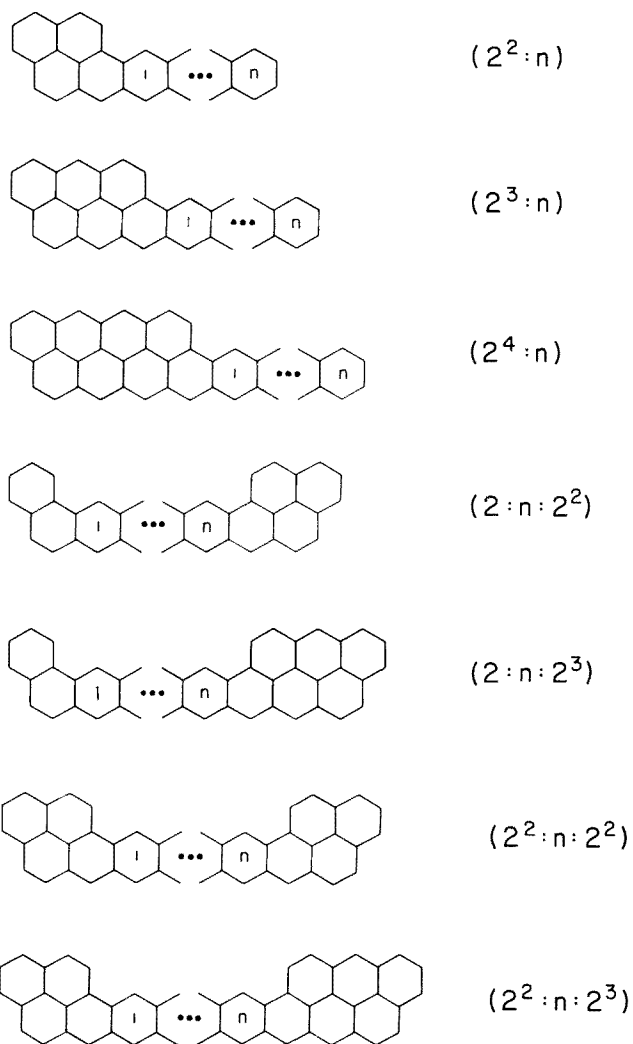$(2 : n : 2^3)$

$(2^2 : n : 2^2)$

$(2^2 : n : 2^3)$

Fig. 11. Families of peri-condensed benzenoid hydro-carbons studied in this paper (cf. tables 2 and 5).

5.   Local characteristics of benzenoid systems

The simplest local features in polyatomic molecules, diregarding atoms, are bonds. For conjugated hydrocarbons (benzenoid hydrocarbons in particular), even in the early days of quantum chemistry, Pauling [1] and Coulson [21] suggested, using Valence-Bond and Molecular Orbital methods, respectively, how to derive useful bond descriptors, known as Pauling and Coulson Bond Orders. A dozen years later, Ruedenberg and Ham [22] found an intriguing relationship between the two quantities: suitably weighted orbital contributions in HMO for a bond (i, j) give the valence bond order of Pauling. Other local parameters (including purely atomic descriptions) have since been considered. These include atomic free valencies [23], para-localization energies [24] and consideration of special bonds or atoms, such as the K and L regions in the work of Pullman [25]. More recent experimental work [26] pointed, however, to a larger molecular fragment, the so-called bay region, as being responsible for the pro-carcinogenic potential of benzenoid hydrocarbons. The bay region is illustrated here for benz[a]anthracene.
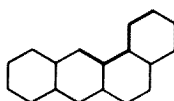
Computer programs are available for the construction and count of Kekulé structures, conjugated circuits and bay regions in large polycyclic structures [27]. Other molecular fragments may also be of interest. Recently, for example, a larger section called a fjord was involved in a discussion of shapes and retention times of benzenoid hydrocarbons [28]. In quantitative approaches to structure-activity relations and drug design and in pharmaceutical and medicinal chemistry, for some time it has been recognized that larger molecular fragments are important for inducing particular biological effects. Empirically, workers have established the "morphine" rule [29] and other similar rules which stipulate which molecular fragment is essential for the biological, therapeutic and toxic responses of such compounds. Recently, a graph-theoretical approach has been suggested [30] for the search for active fragments, and in the case of a dozen nitrosamines it was found that the 7-atom fragment:
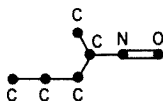
is the basis for the pronounced mutagenicity of these compounds.

6.   Ring indices

From the previous section, it seems natural to consider individual rings in polycyclic conjugated hydrocarbons and try to differentiate between them. Stimulation for such studies again came from Clar [8], who in several of his publications was able to show how "ring aromatic character" is reflected in the magnitude of spin-spin couplings in the NMR of attached hydrogens. Polansky and Derflinger [31], using the results of molecular orbital (MO) calculations, were able to assign an MO-ring value to individual rings of polycyclic hydrocarbons. Hence, MO results allow one to discuss the relative role (i.e. weights) of individual rings in polycyclic structures. In somewhat related work, Graovac et al. [32], using available MO results, assigned an index to individual Kekulé valence structures, the so-called Kekulé index. This index determines the relative weights of the individual Kekulé valence bond structures as reflected in MO calculations. Subsequently, Randić [3] restricted considerations of the Kekulé index to individual rings, thus arriving at an alternative ring characterization which differs from the one of the scheme in ref. [30]. All these approaches can generally be viewed as quantum chemical schemes in the sense that refined calculations could be used when available and individual ring index values are to be revised. However, because they apply equally to HMO (and most of the results are of HMO origin), they can be viewed as graph-theoretical because the adjacency matrix and the Hückel matrix (which in turn is based on Bloch's approximation of nearest-neighbor interaction [34]) are mathematically equivalent [35].

The question is: Can we have a less convoluted graph-theoretical characterization of the local ring features of polycyclic conjugated hydrocarbons? Can we arrive at simple ring indices that result from some graph-theoretical *enumeration*, rather than being a result of solving an eigenvalue problem?

These questions were first addressed by Randić [36], who proposed a ring index as the count of the number of Kekulé structures in which the selected ring appears formally as a benzene ring, i.e. it has three single and three double bonds alternating. In fig. 12, this is illustrated on benz[a]anthracene having seven Kekulé structures. We see that rings A and B are in four Kekulé structures, represented by R_1: the smallest conjugated circuit (which is equivalent to being represented by a Kekulé valence structure of benzene). The central ring appears only twice as a benzene ring, while the "exposed" terminal ring D appears in six out of seven, being represented as benzene, and hence its ring index is 6/7. In order to derive the ring values for larger molecules, one does not need to construct all the Kekulé valence structures. As illustrated in fig. 13, one selects the ring of interest, into which Clar's sextet is inscribed, and then completes assignment of all bonds possible. If for all bonds the CC bond type has been assigned, the ring index value is $2/K$, K being the number of Kekulé structures for the system, and 2 arising from the fact that Clar's sextet (benzene ring) has two Kekulé structures. This is, for example, the case for the central ring in benz[a]anthracene or phenanthrene:
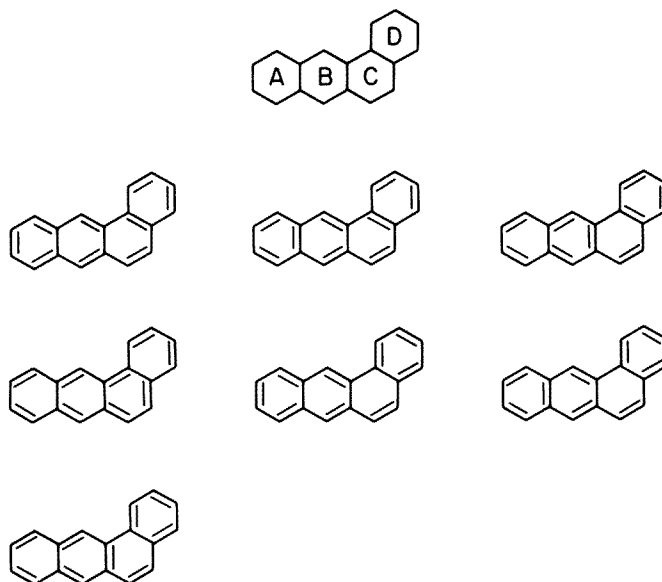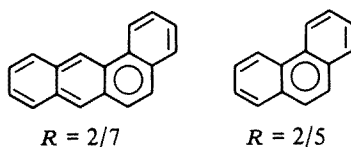
Fig. 12. The seven Kekulé structures of benz[a]anthracene. Rings A and B are represented by R_1 (a conjugated circuit containing 6 pi-electrons) in four of the structures. The "kink" ring appears only twice as a benzene ring, while ring D appears in six out of the seven structures as R_1.

$$R = 2/7 \qquad R = 2/5$$

If, however, after completing the assignment of CC bond types some molecular fragment remains unassigned, the ring index is given by the ratio $R = 2K'/K$, where K' is the number of Kekulé structures for the fragment for which CC bond types are undecided. Hence, the ring value of 6/7 for one of the terminal rings in benz[a]anthracene:
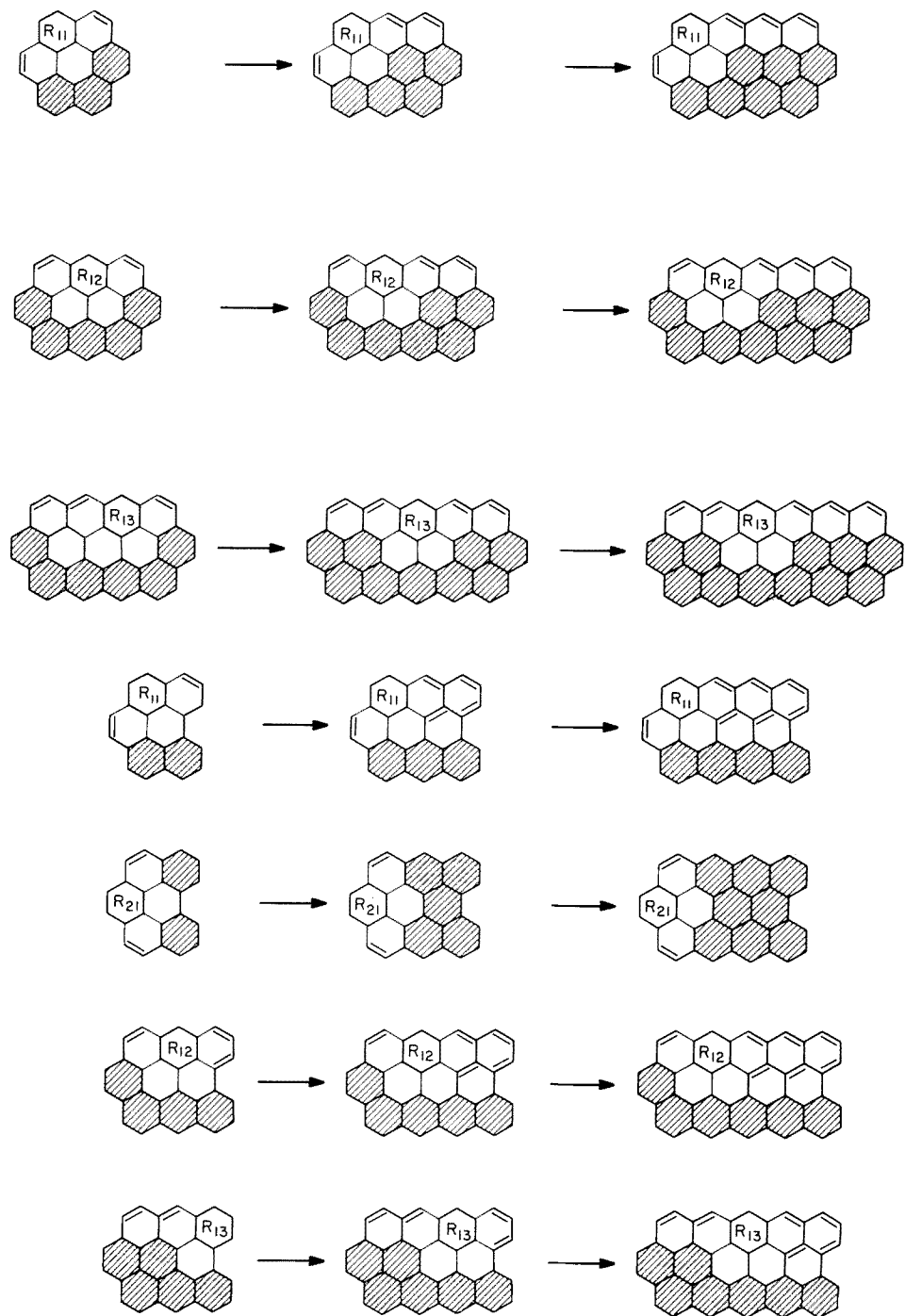

$$K' = 3, K = 7$$
$$R = 2 \cdot 3/7 = 6/7$$
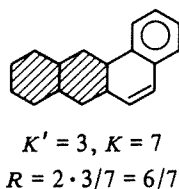
Fig. 13. Pictorial illustration of the topological environments of several selected families of rings in peri-condensed systems. The shaded parts represent hydrocarbons already studied here (figs. 10, 11 and tables 2, 5).

Here, we have shaded the as yet unassigned portion of the structure for better visibility of the presently incomplete assignment. Additional examples are shown in fig. 13. Hosoya and coworkers [19, 37] have investigated this particular ring index, which they write as:

$$R_{(i)} = \frac{K(B\theta R_i)}{K(B)} ,$$
(8)

where B denotes the benzenoid systems, $R_{(i)}$ the selected ring, and $B\theta R_i$ is part of the molecular graph obtained after ring R_i and all connected CC bonds have been deleted.

7. Novel ring index

The ring index $R_{(i)}$ can be called the *Kekulé ring index* because it is based on the totality of Kekulé valence structures. We use the symbol $KR_{(i)}$ in order to distinguish it from *other* ring indices. We also wish to define an analogous index, to be called the *Clar ring index,* which will be obtained in a similar way but by considering only Clar-resonance structures. Formally, we may write:

$$CR(i) = \frac{2C_K(B\theta R_i)}{C_K(B)} .$$
(9)

The factor of 2 arises because it takes two Kekulé structures to generate a Clar circle. Here, $C_K(B)$ represents the number of Kekulé valence structures involved in the superposition process which leads to Clar-resonant structures, and similarly $C_K(B\theta R_i)$ indicates the part of the molecular graph which is obtained after ring R_i has been deleted. Let us again consider pyrene, in which there are only three Clar structures, viz.,

Weight   2   2   4   Sum = 8
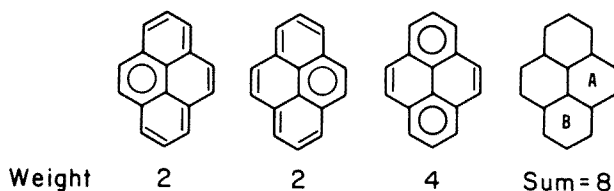
Consider rings A and B separately and each time erase the ring in question, together with all edges incident with it. We obtain:
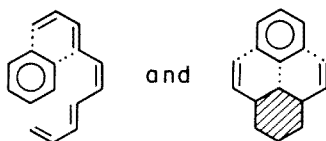
respectively. For $C_K R_A$ we then have 2/8 and for $C_K R_B$ we have 4/8, the denominator is $C_K(B)$, which is eight, because it takes eight Kekulé valence structures to obtain the three Clar structures.

A Clar structure that contains k-disjoint pi-sextets is based on 2^k Kekulé valence structures, two structures for each pi-sextet. In table 3, we report Clar's ring values for numerous smaller benzenoid structures. The proper weighting of the individual contributing $B\theta R_i$ graphs is essential if one is to obtain correct discrimination among chemically very different rings. Consider benz[a]anthracene and let us ignore the proper relative weights of the three Clar structures (which are 2, 4 and 4, respectively):
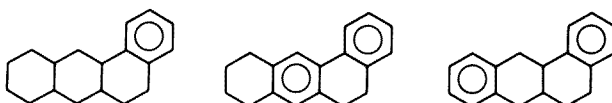
Then one obtains for all the three linearly fused rings the same index of 1/3, as each appears once in the three structures, while the last ring has an index of 2/3 as it occurs in two of the three Clar structures. We thus obtain the pattern:
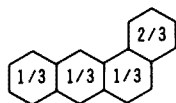
Such characterization is deficient, as we know that the last linearly fused ring is different. However, with relative weights of 2 : 4 : 4 we obtain the following:
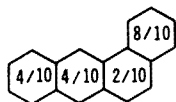
Now, the central ring at the "kink" site is found to have a much lower ring values, and thus much less local similarity to benzene. Meanwhile, the similarity of the adjacent terminal ring has increased from 2/3 to 8/10, in agreement with experience. The revised values also better parallel the results based on Kekulé structures, viz.,

Table 3

Clar and Kekulé ring indices of some benzenoid systems. Numbers inside rings are Clar indices [eq. (9)], while those outside are Kekulé indices [eq. (8)].
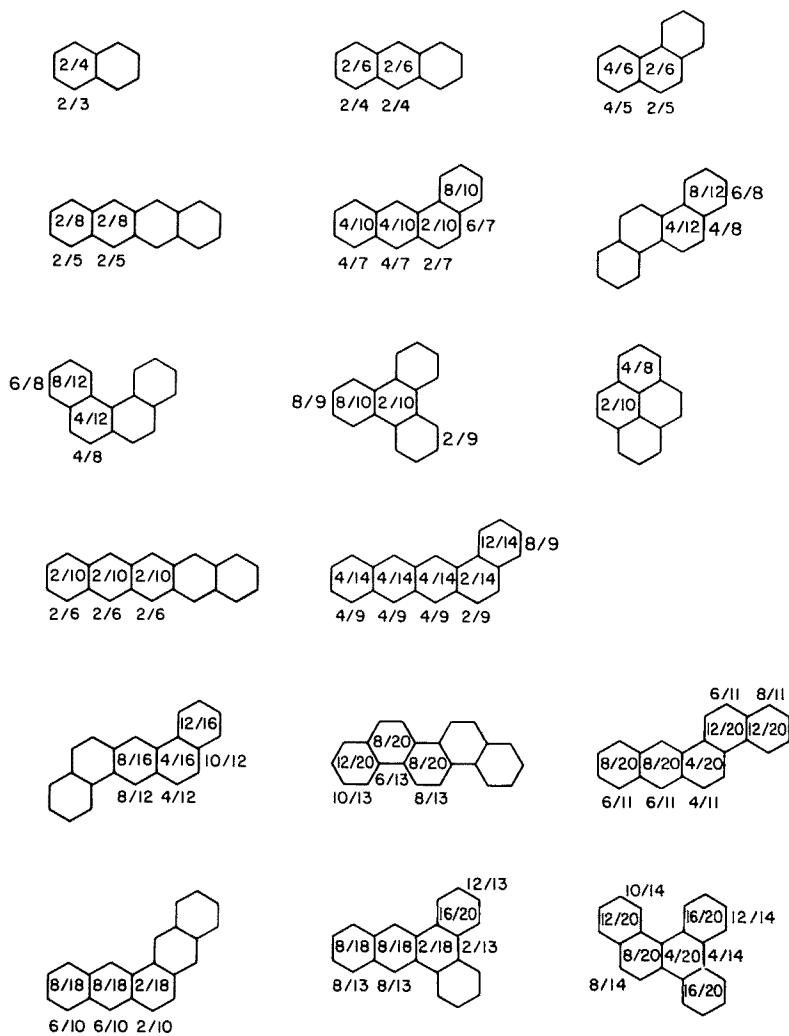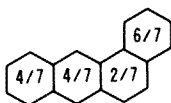
The parallelism of CR_i and KR_i (i.e. ring indices based on Clar and Kekulé structures, respectively) is illustrated in table 4 for several families of catacondensed benzenoids, for which all relevent data can also be found in table 5 together with data on several additional systems shown previously in figs. 10 and 11. From table 4, we see a smooth monotonic relationship between the two quantities. This relationship is of considerable practical importance because the computation of CR_i is very simple even for relatively large systems, while KR_i involves consideration of all Kekulé valence structures which, even in the case of modest-size compounds having a dozen benzene rings, may approach a thousand. In some instances, the powerful technique based on transfer matrices [38] can spped up the analysis, but in the case of structures of little symmetry, we have no simple way to by-pass tedious analysis. Clar resonant structures are much fewer in number and can be easily analyzed. Because of the noted parallelism, the choice between the different ring indices becomes the choice of convenience and here CR_i has an obvious advantage. In fig. 13, we show the topological dependency of ring environment for several ring types of pericondensed systems.

8.   Concluding remarks

It appears that Clar's qualitative approach, advanced well over a quarter of a century ago, has been deliberately overlooked by most quantum chemists for too long. At best, it was viewed in some circles as controversial. It is unfortunate that, while the excellence of Clar's experimental work was not questioned, his speculations apparently had to wait for recognition. The revived interest in chemical graph theory combined with a "novel view on old things" by Polansky and Derflinger together resulted in a full appreciation of Clar's outstanding pioneering results, at least in the chemical graph theory community. The theoretical origin of sextets can be traced to Armitt and Robinson's [39] pre-quantum chemistry era. Herndon's work on the resonance structure model [11,40] provided important stimuli and justification for models considering only sets of Kekulé valence structures.

The conjugated circuits [4] approach, simplified and helped one to visualize the underlying computational structure. Finally, more recently, Herndon and Hosoya [10] further reduced the basis of valence structures to what appears to be a minimum: the set of Clar-resonant structures. Živković [41] introduced highly accurate quantum-chemical computations on benzenoid systems by broadening the concept of valence structural incorporate valence orbitals that can be associated with the set of valence structures. In order to fully digest these theoretical capabilities, which can generate

Table 4

Clar characters CR(i) [eq. (9)], and Kekulé ring indices $R(i)$ [eq. (8)], of some families of benzenoid hydrocarbons.

Family	n	CR(i)	$R(i)$
$(n:2)$	1	2/3	4/5
	2	2/5	4/7
	3	2/7	4/9
	4	2/9	4/11
$(2:n:2)$	1	1/2	1/3
	2	1/3	1/4
	3	1/4	1/5
$(2:2:n)$	1	3/8	3/11
	2	3/14	3/15
	3	3/20	3/19
	4	3/26	3/23

Table 5

Expressions for the number of Kekulé structures K, number of Clar structures C, and the number of weighted Clar structures C_K, of families of benzenoid hydrocarbons

Family	K	C	C_K
$(n:2)$	$2n+3$	$n+1$	$4n+2$
$(n:3)$	$3n+4$	$2n+1$	$8n+2$
$(n:4)$	$4n+5$	$3n+1$	$12n+2$
$(2:n:2)$	$4n+8$	$n+2$	$8n+8$
$(1:2:n)$	$3n+5$	$2n+1$	$8n+4$
$(2:2:n)$	$4n+7$	$3n+2$	$12n+8$
$(2:(1):n)$	$4n+5$	$n+1$	$8n+2$
$(3:(2):n)$	$9n+10$	$4n+1$	$32n+2$
$(2^2:n)$	$3n+6$	$2n+2$	$8n+6$
$(2^3:n)$	$4n+10$	$3n+4$	$12n+14$
$(2^4:n)$	$5n+15$	$4n+7$	$16n+26$
$(2:n:2^2)$	$6n+15$	$2n+4$	$16n+20$
$(2:n:2^3)$	$8n+24$	$3n+7$	$24n+40$
$(2^2:n:2^2)$	$9n+27$	$4n+8$	$32n+48$
$(2^2:n:2^3)$	$12n+42$	$6n+14$	$48n+92$

selected results of SCF-MO quality, we may need additional graph invariants. In this paper, we advocate use of CR_i, Clar resonant ring indices, as potentially useful descriptors for the local atomatic characteristics of benzenoid systems, not necessarily to replace currently used descriptors [42], but to supplement them and thus extend the applications to systems which are too large for analysis without such assistance.

Acknowledgements

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