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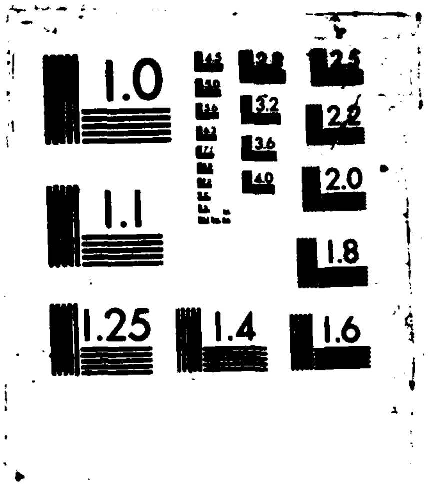

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On Global and Local Properties of Clar Pi-Electron Sextets

by

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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 from similar ring characterizations based on all Kekulé valence structures significantly in a number of cases. It is related to previously introduced quantities based on MO functions, but it can be obtained simply (i.e., without need for a computer). We have illustrated the new ring index for several families of compounds and report a number of regularities for homologous series of molecules.

Key Words
Graph Theory
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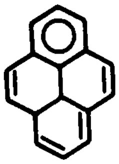
Introduction

Conjugated benzenoid hydrocarbons (such as depicted in Fig. 1) have been traditionally described by a set of Kekulé valence structures, which have been also widely used in the early quantum chemical contributions.[1] With revival of interest in chemical graph theory[2,3] 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 related to an innate degree of freedom of Kekulé valence structures.[5] Kekulé valence structrues which support a long range order (such as the selected structures in Fig. 2) can immediately be recognized by chemists as those structures which have little if any importance for descriptions and discussions of the aromaticity of compounds. On the other hand Kekulé valence structures shown in Fig. 3 can be recognized intuitively, or 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 which 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 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 novel structural formulas for these compounds. These, now so called Clar's structural formulas 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 pi-electron sextet, such as in benzene itself, or being "empty", i.e. without any pi-sextet character or any CC double bond; (b) Valence structures with some rings having sextets while other rings having 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 (Fig. 5), all possible combinations of pairs of structures of which are illustrated. By a superposition of two Kekulé valence structures one can identify a single conjugated circuit. Thus we find in pryene the conjugated circuits: as listed in Table 1.

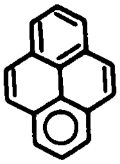
The expression for the molecular RE (resonance energy) is obtained by counting conjugated circuits of different size and dividing by K, the number of Kekulé structures. Hence:

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

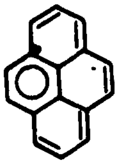
The factor of two enters because we considered only half of the possible pairs due to symmetry (i.e. superposition (A,B), e.g. gives the same result as superposition (B,A) and so on). The contribution of disjoint conjugated rings, here $R_1 \cdot R_1$, are neglected in numerical treatments due to their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



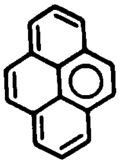
C+D



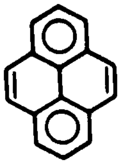
A+C



D+F



A+E

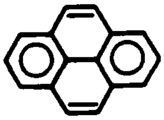


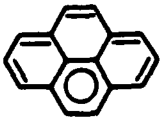
A+D+
B+C

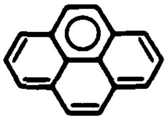
These have been called Clar-type valence structures or Clar patterns.[9] Only the last structure is that of Clar, i.e., only the last is the structure which Clar proposed to represent pyrene. Clar considered to have for a polycyclic conjugated hydrocarbon a single structural formula and in the case of pyrene the formula is the one designated as: A + B + C + D. Hence the new valence structure neglects two Kekule 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 that indeed 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 (c.f., Fig. 2) judged by chemical intuition.

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 system using 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):





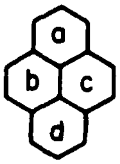


These are the only Clar-type structures which have a unique location for CC double bonds, once a sextet-circle is indicated. Observe also that by "broadening" the bases of Clar, i.e., by including the structures (D,F) and (A,E), Herndon and Hosoya[10] have recovered structural information carried by Kekulé valence structures E,F neglected by the single Clar's structures description of the system. In the approach of Herndon and Hosoya we find the valence structures A and D (of Fig. 5), which contribute $3R_1 + R_3$ each 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 of Herndon.[11]

All the above strongly suggest that Clar structural formulas and Clar-type valence structures contain important structural information and can form a basis for quantitative model of chemical stability of large benzenoid systems. We will therefore briefly review selected results concerning Clar structures.

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 sextet assignment (i.e. there is Clar-type formula with both rings having inscribed circles). In Clar's formulas such rings are disjoint. If we (arbitrarily) label the rings in pyrene as



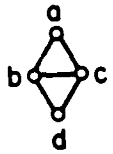
then, three Clar-type resonant structures are possible. They are the structures A + E, D + F and A + B + C + D shown before as the structures that uniquely determine the positions for all CC double bonds once Clar sextets are assigned. From the definition of the Clar graph one can construct a Clar matrix c_{ij} as:

$$c_{ij} = \begin{cases} 1 \text{ if rings } i,j \text{ are nonresonant} \\ 0 \text{ otherwise} \end{cases} \qquad (1)$$

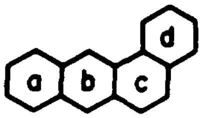
Observe that here adjacency means that rings are nonresonant and in Clar's qualitative description such (adjacent) rings were associated with pi-sextets "migration".[8] Hence for pyrene we obtain the following Clar matrix

$$\underline{C} = \begin{array}{c|cccc} & a & b & c & d \\ \hline a & 0 & 1 & 1 & 0 \\ b & 1 & 0 & 1 & 1 \\ c & 1 & 1 & 0 & 1 \\ d & 0 & 1 & 1 & 0 \end{array}$$

According to Gutman the Clar graph of pyrene is then the graph whose adjacency matrix is $\underline{C}$, i.e.



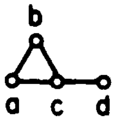
Observe that in this particular example the derived graph is the so called "inner dual"[13] of the molecular graph of pyrene, but this is not generally true as can be seen, e.g. by considering benz[a]anthracene:



B

$$\longrightarrow \begin{array}{c|cccc} & a & b & c & d \\ \hline a & 0 & 1 & 1 & 0 \\ b & 1 & 0 & 1 & 0 \\ c & 1 & 1 & 0 & 1 \\ d & 0 & 0 & 1 & 0 \end{array} \longrightarrow$$

$\underline{C}$



C

There is a bijective mapping between rings (hexagons) of a benzenoid hydrocarbon and the vertices of the corresponding Clar graph, such that 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 bases 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 before. For each Clar graph shown we illustrated the corresponding unique Clar structure.

Clar Polynomials

Polynomials provide simple bookkeeping of combinatorial enumerations and as such have been already used by Wheland[15] in connection with 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 polynomials 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. But the particular Wheland's approach, although of no consequence for his interest, has a disadvantage: By restricting the attention to canonical valence structures only (such as determined by Rumer's non-crossing rule[16]) the derived polynomials are not a structural invariant. 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 degree of excitation to canonical structures only, but one considers all valence structures, the counting polynomial named generalized Wheland polynomial,[17] becomes 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 it 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 powers, x^k, indicate k resonant rings. Hence the sextet polynomial of pryene is $1 + 4x + x^2$. In analogy a polynomial, the coefficients of its powers x^k indicate the number of Clar-type resonant structures with k inscribed circles[19] will be reflected to a CL(x) Clar polynomial. The Clar polynomial thus counts sets of maximally independent k vertices of the associated Clar graph. Thus we have:

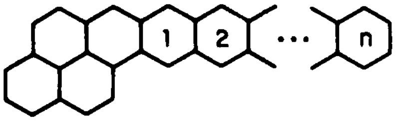
$$\mathrm{CR}\,(\text{pyrene}; x) = 2x + x^2 \qquad (2)$$

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

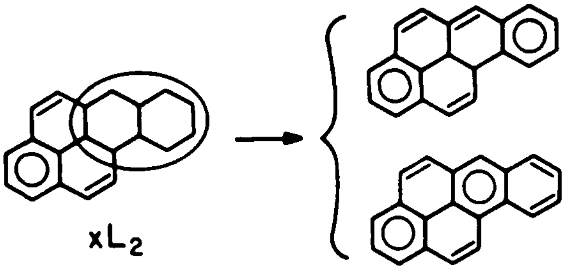
The Clar-resonant count, i.e., the number of Clar-type structures for a given benzenoid hydrocarbon is considerably smaller than Clar-sextet-structure count or the corresponding Kekulé count. For example for fulminene (Fig. 8) there are 21 Kekulé valence structures (as can be easily verified by following the elegant scheme of Gordon and Davison[20] for the count of Kekulé structures for catacondensed benzenoids). The number of Clar-sextet structures is 64 (as shown in Fig. 8 where only symmetry unrelated cases are illustrated), but only five of these 64 are Clar-resonant structures. These are the last five structures, four having three inscribed sextet circles and one having only two pi-sextets.

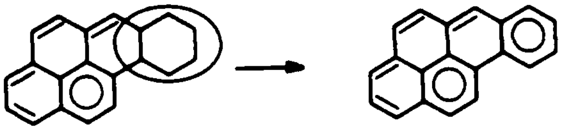
The structures can also be recognized as unique being the only structures in Fig. 8 in which all CC bonds have been assigned. The uniqueness of the five structures is seen also by the labels "1-structure" written underneath.

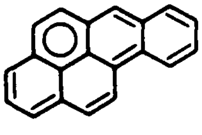
In Table 2 we have listed Clar and sextet polynomials for a number of smaller benzenoid systems. In Fig. 9 we illustrate recursive relation for Clar polynomial for a number of benzenoid familes shown in Fig. 10. Let us use the symbol L_n for Clar polynomial of a linearly fused chain of n-hexagons (polyacenes). If now we have a structure in which there is some "end" groups attached to one side of the linear chain, such as



we can obtain the corresponding Clar-resonant polynomial by successively assigning resonant pi-sextets to all possible sites. As an illustration we consider benzpyrene:


xL2

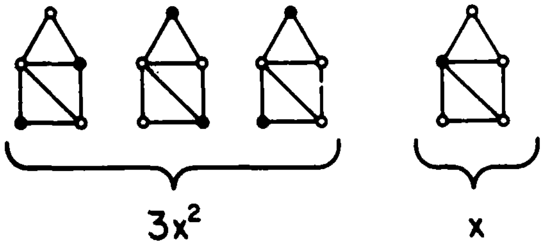

xL1


x

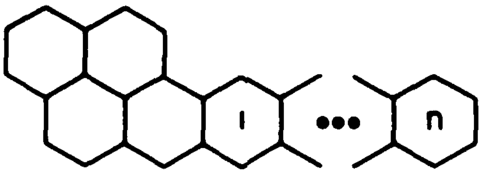
Among the structures at left only the last structure is complete and qualifies as Clar-resonant because all other bonds have unique bond-type assigned. Thus the last structure makes contribution to the polynomial with power x. The other two structures (at left) are not complete but when combined with the linear fragment produce the additional Clar resonant structures (shown at the right). 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 expression for the polynomial will depend on the chain length. We can summarize the result by writing the contributions as a product of x (in general case x^k) and L_n, where L_n respresents the pod arising from linear chain of length n.

Hence: $\mathrm{CR}(\text{benzopyrene}; x) = xL_2 + xL_1 + x$

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



Benzopyrene can be considered as the first member of the family



for which one can immediately construct the corresponding expressions for the individual members:

$$CR_1(x) = x(L_2 + L_1 + 1) \tag{4}$$

$$CR_2(x) = x(L_3 + L_2 + 1) \tag{5}$$

$$CR_3(x) = x(L_4 + L_3 + 1) \tag{6}$$

$$\cdot$$

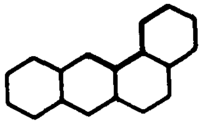
$$\cdot$$

$$CR_n(x) = x(L_{n+1} + L_n + 1) \tag{7}$$

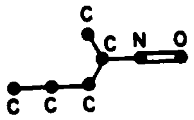
It can be shown that $L_n = nx$. Thus by substituting $x = 1$ in $CR_n(x)$ we obtain the Clar-resonant count $2n + 2$. In Table 2 we completed similar information for the other families of graphs depicted in Fig. 11.

Local Characteristics of Benzenoid Systems

The simplest local feature in polyatomic molecules disregarding atoms are bonds. For conjugated hydrocarbons, benzenoid hydrocarbons in particular, already at the beginning of quantum chemistry, Pauling[1] and Coulson[21] suggested, within 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 weighed orbital contributions in HMO for a bond (i,j) give valence bond order of Pauling. Other local parameters (including purely atomic descriptions) have been since considered. These include atomic free valencies,[23] para-localization energies[24] and consideration of special bonds or atoms, such as K and L regions in the earlier work of Pulman.[25] More recent experimental work[26] pointed, however to larger molecular fragment, the so called bay region as responsible for pro-carcinogenic potential of benzenoid hydrocarbons. Bay region is illustrated here for benz[a]anthracene.



Computer programs are available for 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 <u>fyord</u> was involved in discussion of shpaes and retention times of benzenoid hydrocarbons.[28] In quantitative approaches to structure-activity relations and drug designs and in pharmaceutical and medicinal chemistry for some time it has been recognized that larger molecular fragments are important for inducing particular biological effect. Empirically thus have been established "morphine" rule[29] and other similar rules which stipulate what molecular fragment is essential for considered biological, therapeutic and toxic response of such compounds. Recently a graph theoretical approach has been suggested[30] for a search of active fragments, and in the case of dozen nitrosamines it was found that the 7-atom fragment:



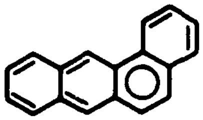
is the basis of the pronounced mutagenicity of these compounds.

Ring Indices

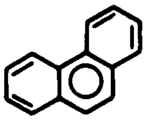
From the previous section it seems natural to consider individual rings in polycyclic conjugated hydrocarbons and try to differentiate between them. Stimulation for such studies came again from Clar[8] who in several of his publications was able to show how "ring aromatic character" is reflected in the magnitude of spin-spin couplings in NMR of attached hydrogens. Polansky and Derflinger,[31] using 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 relative role (i.e. weights) of individual rings in polycyclic structures. In a 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 or reflected in MO calculations. Subsequently Randić[3] restricted the considerations of the Kekulé index to individual rings, thus arriving to an alternative ring characterization which differs from the one of the scheme of ref. 30. All these approaches can be generally viewed as quantum chemical schemes, in the sense that refined calculations could be used when available and individual ring index values will be revised. But because they apply equally to HMO (and most of the results are of HMO origin) they can be viewed as graph-theoretical in view that 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 less convoluted graph-theoretical characterization of 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., 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, hence its ring index is 6/7. In order to derive the ring values for larger molecules one does not need to construct all Kekulé valence structures at all. As illustrated in Fig. 13, one selects the ring of interest, to which Clar's sextet is inscribed and completes assignment of all bonds possible. If for all bonds CC bond type has been thus assigned the ring index value is 2/K, K being the number of Kekulé structures for the system, and two arising from the fact that Clar's sextet (benzene ring) has two Kekulé structures. This is, for example the case of the central ring in benz[a]anthracene or phenanthrene:

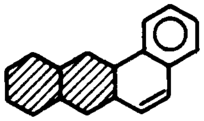


$R = 2/7$



$R = 2/5$

If, however, after completing 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:



$K' = 3$, $K = 7$

$R = 2 \cdot 3/7 = 6/7$

Here we have shaded the yet unassigned portion of the structure for better visibility of the not yet completed assignment. Additional examples are shown in Fig. 13. Hosoya and coworkers[19,37] have investigated this particular ring index, which they write as

$$R_{(i)} = \frac{K(B \ominus R_i)}{K(B)} \tag{8}$$

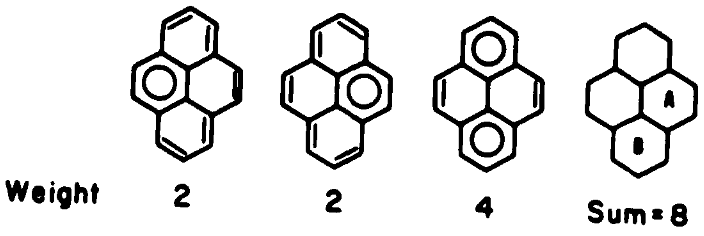
where B stands for benzenoid systems, $R_{(i)}$ for the selected ring and $B\theta R_i$ is the part of the molecular graph which is obtained after ring R_i and all connected CC bonds have been deleted.

Novel Ring Index

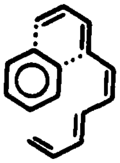
The ring index $R_{(i)}$ can be called Kekulé ring index, because it is based on the totality of Kekulé valence structures. Hence we will now use the symbol $KR_{(i)}$ in order to distinguish it from other ring indices. Now we want to define an anologous index, to be called Clar ring index, which will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

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

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.,



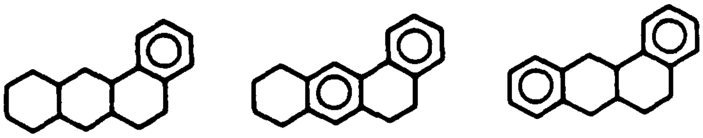
Consider rings A and B separately and each time erase the ring in question together will all edges incident with it. We obtain:



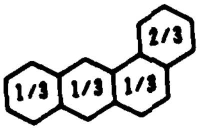
and

respectively, For $C_K R_A$ then we 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.

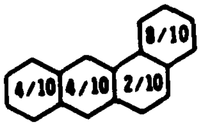
A Clar structure which contains k-disjoint pi-sextets is based on 2^k Kekulé valence structures, two structures per each pi-sextet. In Table 3 we report Clar's ring values for numerous smaller benzenoid structures. The proper weighting of the individual contributing $B\theta R_i$ graphs is essential 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):



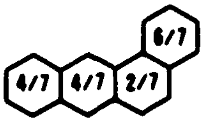
Then one obtains for all the three linearly fused rings the same index of 1/3, as they appear each once in the three structures, while the last ring has an index of 2/3 as it occurs in two of the three Clar structures. Hence



Such characterization is deficient, as we know that last linearly fused ring is different. .However with relative weights of 2:4:4 we obtain the following pattern;



Now the central ring at the "kink" site is found to have much lower ring value, hence 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 the experience. The revised values also parallel better the results based on Kekulé structures, viz.,



The parallelism 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 relevant data can also be found in Table 5 together with data on several additional systems shown previously in Fig. 10 and 11. From Table 4 we see a smooth monotonic relationship between the two quantities. This relationship is of considerable practical importance because computation of CR_i is very simple even for relatively large systems, while KR_i involves consideration of all Kekulé valence structures, which already in the case of modest-size compounds having a dozen benzene rings may approach thousand. True in some instances the powerful technique of the transfer matrices[38] can speed up the analysis, but in case of structures of little symmetry we have no simple way to by-pass tedious analysis. Yet Clar resonant structures are much fewer and can be easily analyzed. Because of the noted parallelism the choise between the different rug 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.

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 a time. Perhaps, at best it was viewed in some circles as controversial. It was unfortunate that Clar while the excellence of his 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 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[39] pre-quantum chemistry era. Herndon's work on resonance structure model[11,40] provided important stimuli and justification for models considering only sets of Kekulé valence structures.

Conjugated circuits[4] approach, perhaps, simplified and helped to visualize the underlying computational structure. Finally more recently Herndon and Hosoya[10] further reduced the basis of valence structures to what appears minimum: the set of Clar-resonant structures, meanwhile Živković[41] introduced highly accurate quantum chemical computations on benzenoid sytems 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 selected results of SCF-MO quality, one may need additional graph invariants. In this paper we advocate use of CR_i, Clar resonant ring indices, as potentially useful descriptors for local aromatic 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 with such assistance.

Acknowledgments

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TABLE 1

Conjugated Circuits of Pryene

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

TABLE 2

Clar and Sextet Polynomials of Some Families of Benzenoid Hydrocarbons. The number of Clar structures is $\mathcal{CR}(G;1)$ while the weighed structures is $\mathcal{CR}(G;2)$.

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)	$x + 4nx^3$	$1 + (n + 5)x + 4(n + 1)x^2 + 4nx^3$
$(2^2:n)$	$x + (2n + 1)x^2$	$1 + (n + 4)x + (2n + 1)x^2$
$(2^3:n)$	$x + 3(n + 1)x^2$	$1 + (n + 6)x + 3(n + 1)x^2$
$(2^4:n)$	$x + (4n + 6)x^2$	$1 + (n + 7)x + (4n + 6)x^2$
$(2:n:2^2)$	$3x^2 + (2n + 1)x^3$	$1 + (n + 6)x + (3n + 7)x^2 + (2n + 1)x^3$
$(2:n:2^3)$	$4x^2 + 3(n + 1)x^3$	$1 + (n + 7)x + (4n + 11)x^2 + 3(n + 1)x^3$
$(2^2:n:2^2)$	$4x^2 + 4(n + 1)x^3$	$1 + (n + 8)x + (4n + 14)x^2 + 4(n + 1)x^3$
$(2^2:n:2^3)$	$5x^2 + (6n + 9)x^3$	$1 + (n + 10)x + (5n + 22)x^2 + (6n + 9)x^3$

Table 3

Clar and Kekulé ring indices of some benzenoid systems. Numbers inside rings are Clar indices (Eqn. 9) while those outside are Kekulé indices (Eqn. 8).

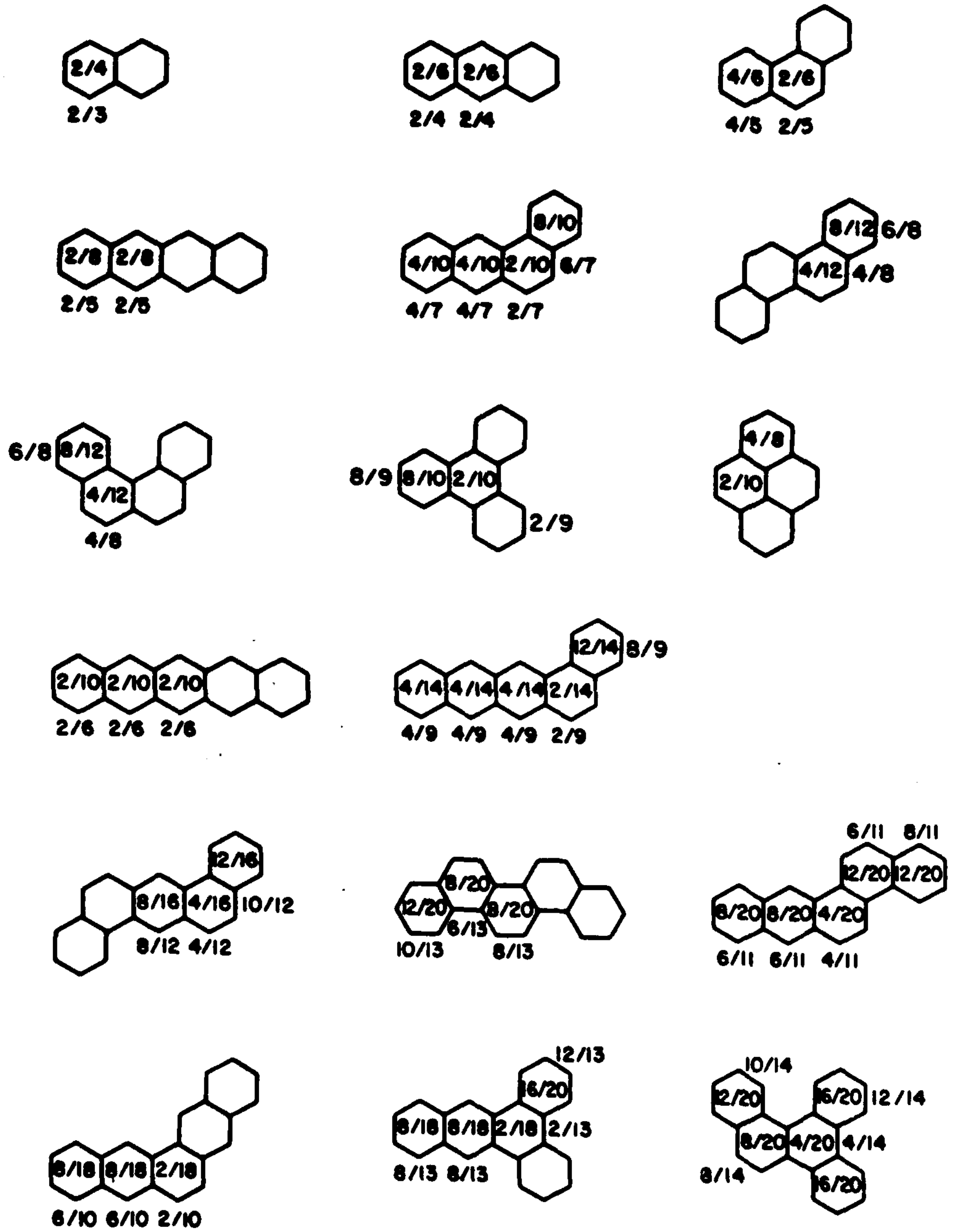


TABLE 4

Clar characters CR(i), Eqn. 9, and Kekulé ring indices, R(i), Eqn. 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 of 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
$(n:2)$	$2n + 3$	$n + 1$	$4n + 2$
$(n:3)$	$3n + 4$	$2n + 1$	$8n + 2$
$(n:4)$	$4n + 5$	$3n + 1$	$12n + 2$
$(2:n:2)$	$4n + 8$	$n + 2$	$8n + 8$
$(1:2:n)$	$3n + 5$	$2n + 1$	$8n + 4$
$(2:2:n)$	$4n + 7$	$3n + 2$	$12n + 8$
$(2:(1):n)$	$4n + 5$	$n + 1$	$8n + 2$
$(3:(2):n)$	$9n + 10$	$4n + 1$	$32n + 2$
$(2^2:n)$	$3n + 6$	$2n + 2$	$8n + 6$
$(2^3:n)$	$4n + 10$	$3n + 4$	$12n + 14$
$(2^4:n)$	$5n + 15$	$4n + 7$	$16n + 26$
$(2:n:2^2)$	$6n + 15$	$2n + 4$	$16n + 20$
$(2:n:2^3)$	$8n + 24$	$3n + 7$	$24n + 40$
$(2^2:n:2^2)$	$9n + 27$	$4n + 8$	$32n + 48$
$(2^2:n:2^3)$	$12n + 42$	$6n + 14$	$48n + 92$

Fig. Legends

Fig. 1 Molecular graphs of some benzenoid hydrocarbons.

Fig. 2 Examples of Kekulé valence-bond structures which support a long range order, i.e. have low innate degree of freedom values (f's). Such structures have small contribution to the stability of the benzenoid system.

Fig. 3 Examples of important Kekulé structures.

Fig. 4 Illustration of Clar structures (Clar structural formulas) 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.

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

Fig. 7 Clar graphs of pyrene and of benz[a]anthracene. The colorings represent maximal independent sets of vertices.

Fig. 8 Clar-sextet structures of fulminene. Only non-symmetry related structures are shown.

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

Fig. 10 Familes of cata-condensed benzenoid hydrocarbons studied in this work (c.f., Tables 2 and 5).

Fig. 11 Familes of peri-condensed benzenoid hydrocarbons studied in this paper (c.f. Tables 2 and 5).

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.

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, Tables 2,5).

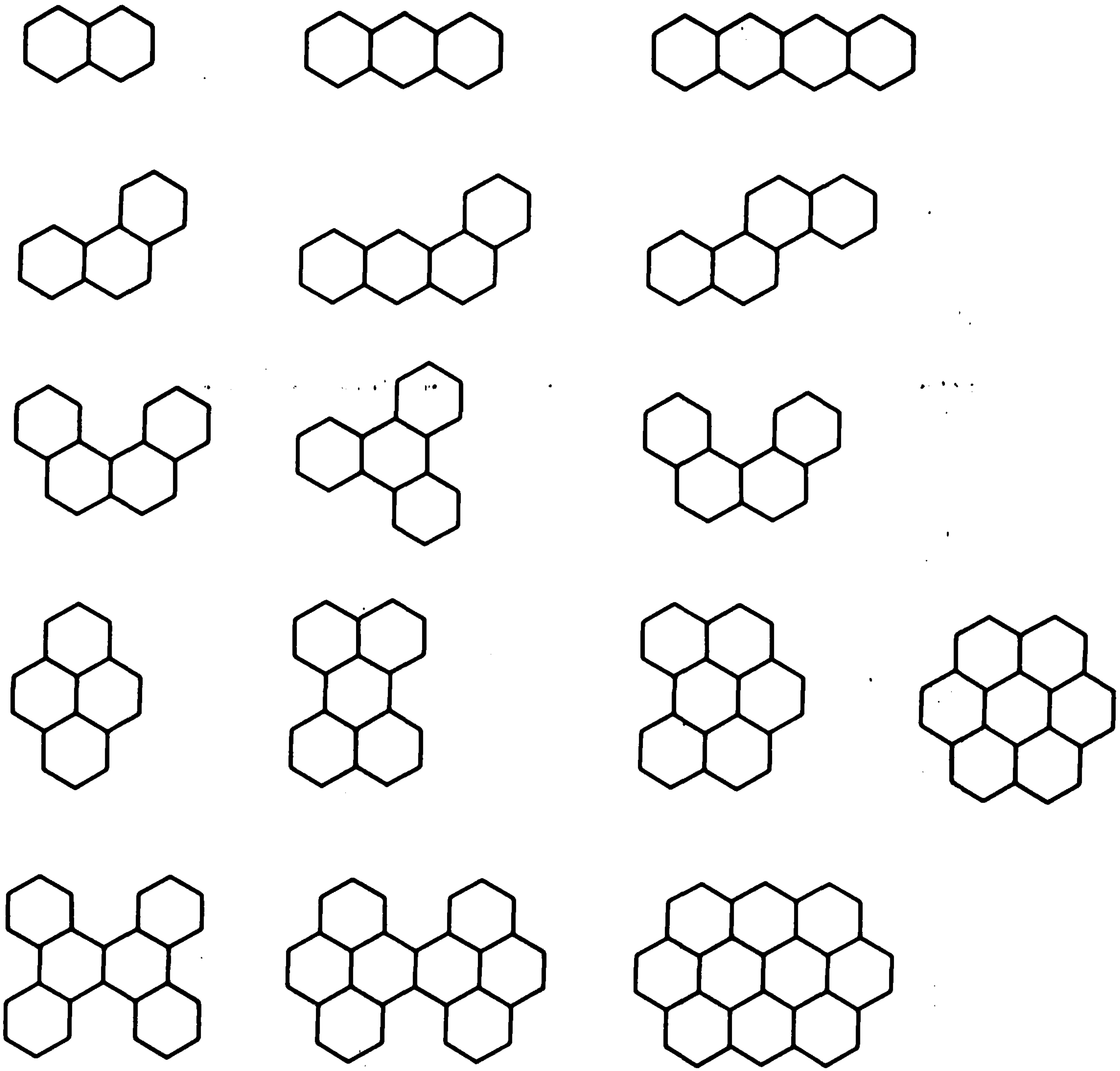
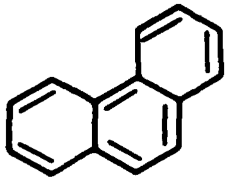


Fig 1



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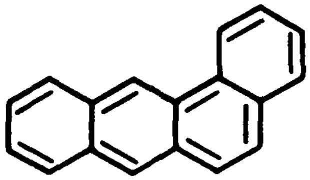

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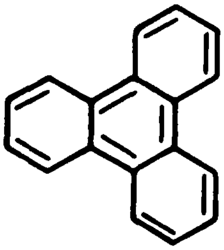

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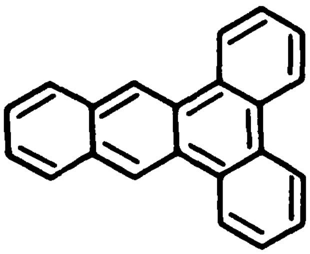

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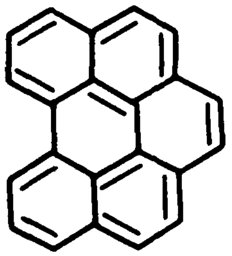

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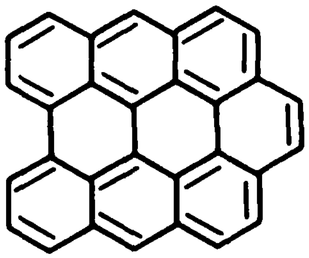

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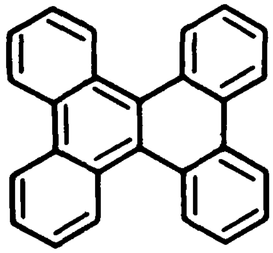

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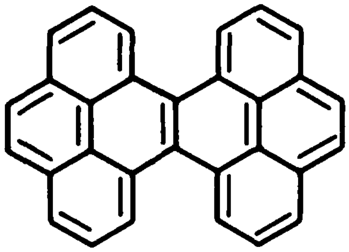

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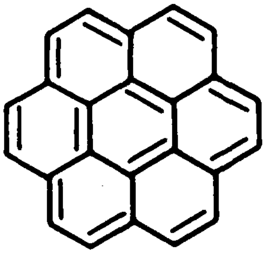

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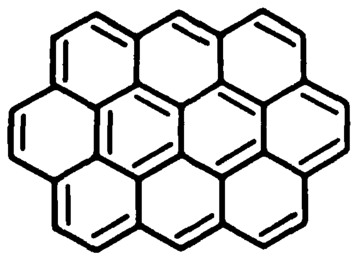


f = 2

Fig2

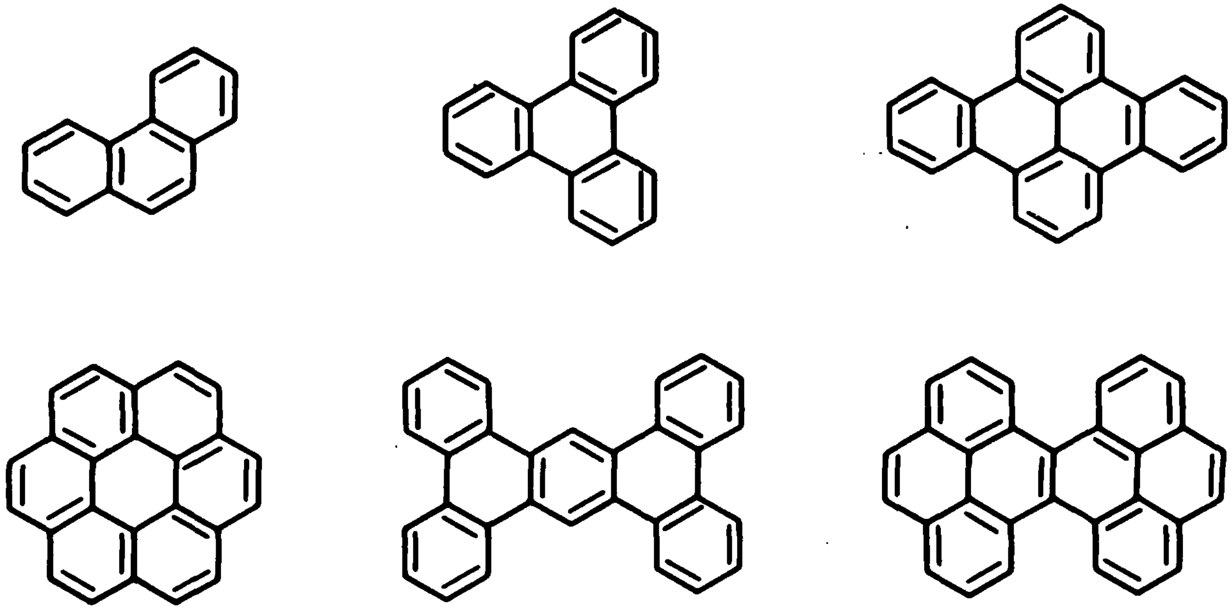


Fig 3

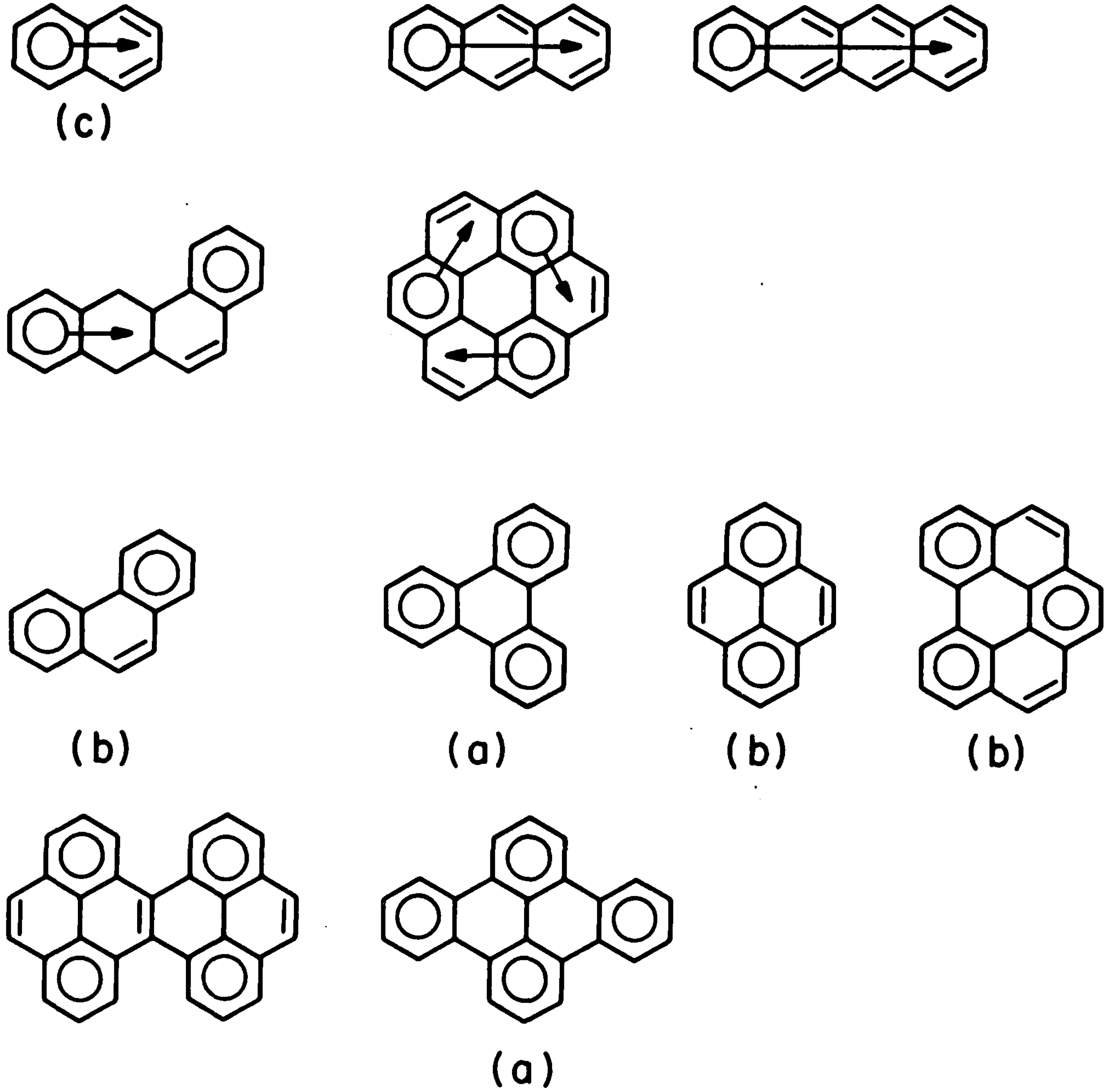


Fig4

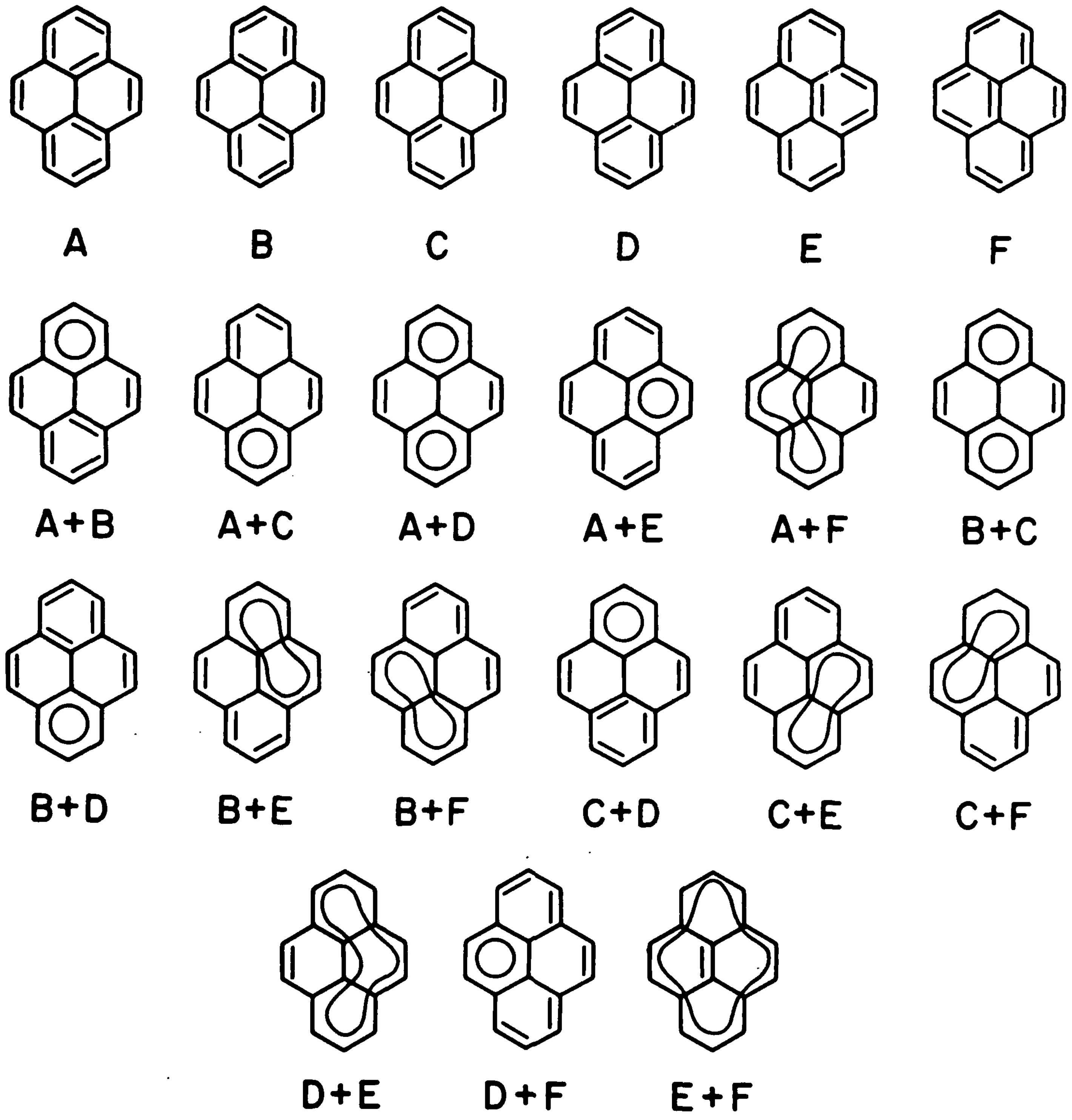


Fig 5

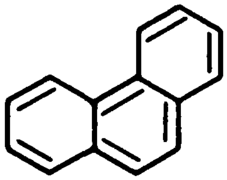
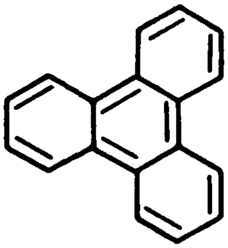
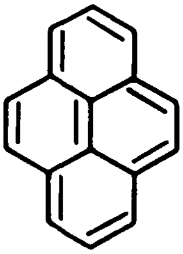
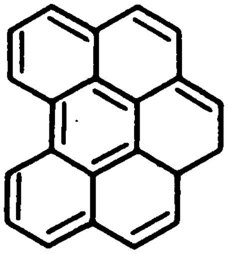
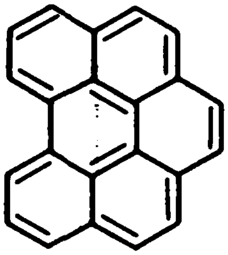
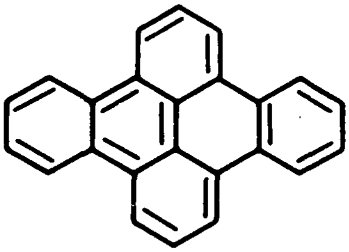
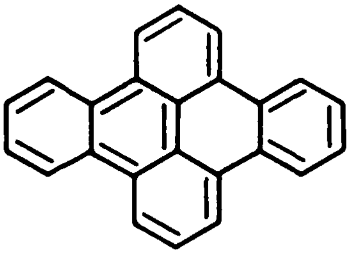
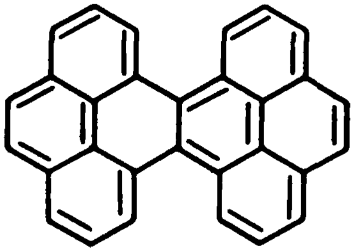
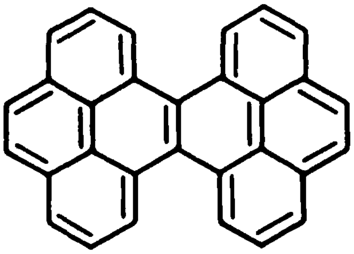










Fig6

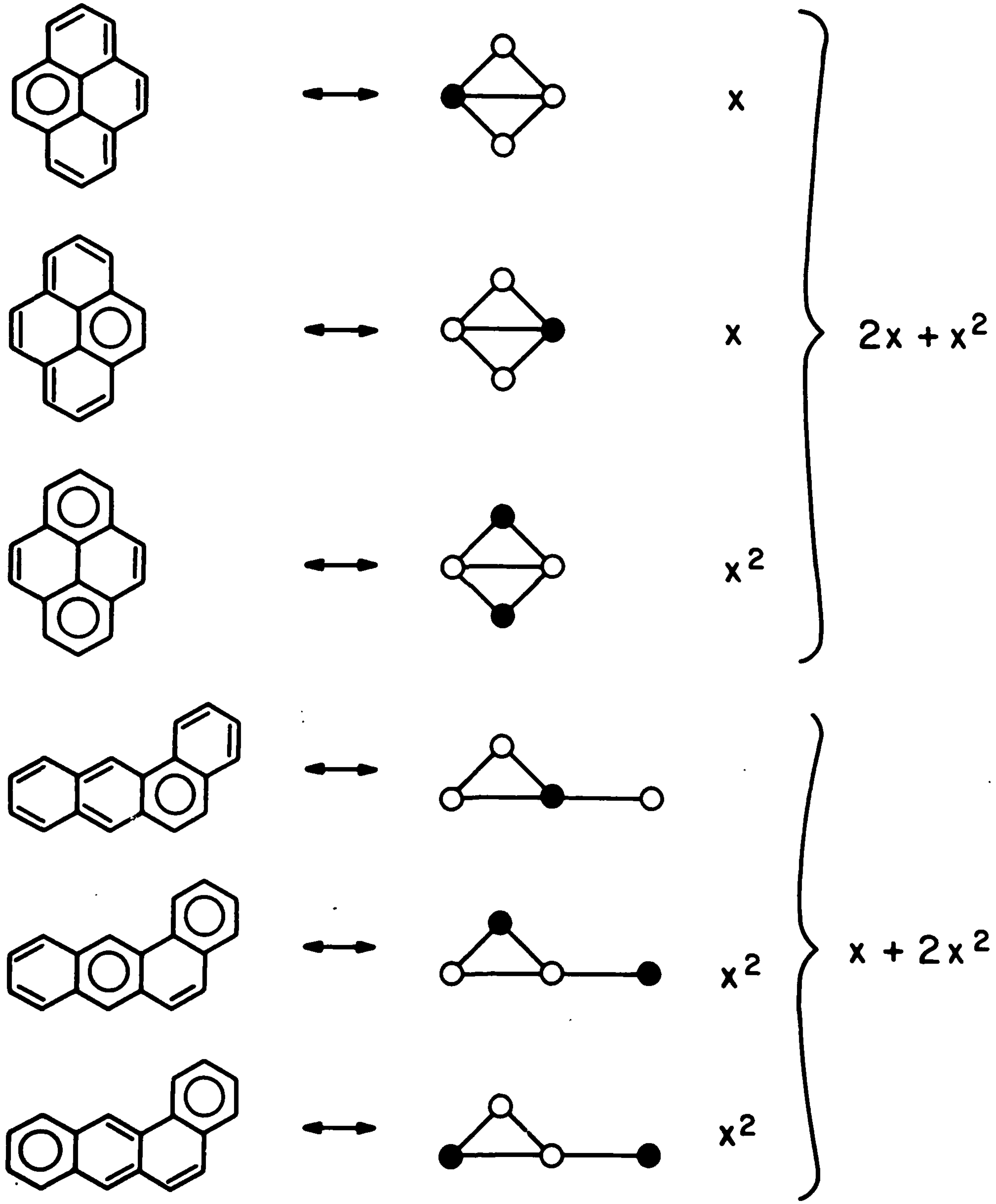
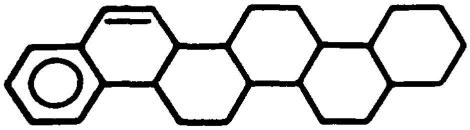
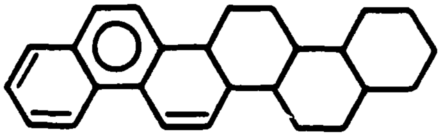


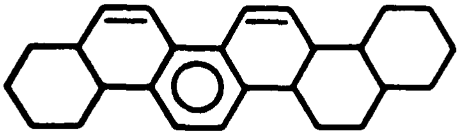
Fig 7



8 Structures



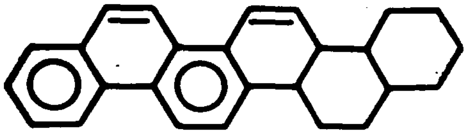
5 Structures



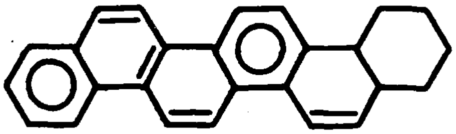
6 Structures

x 2

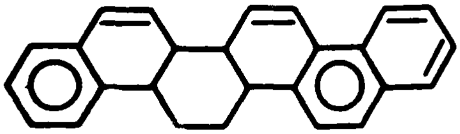
TOTAL
38 Structures



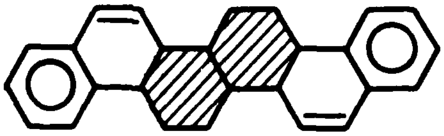
(3 Structures) x 2



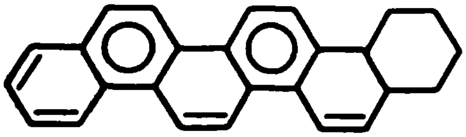
(2 Structures) x 2



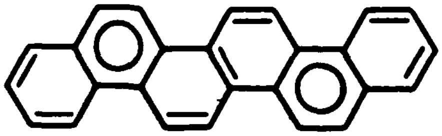
(2 Structures) x 2



(3 Structures) x 2

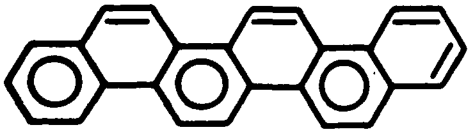


(2 Structures) x 2

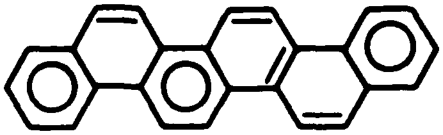


(1 Structures) x 1

TOTAL
22 Structures



(1 Structures) x 2

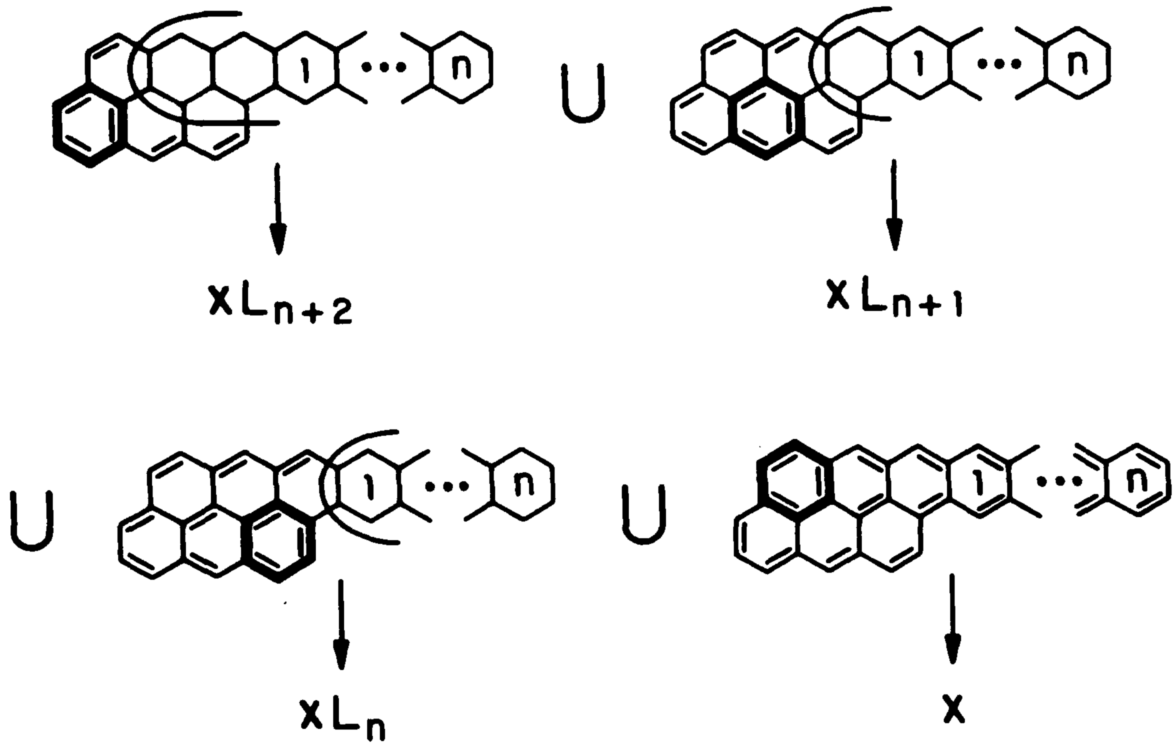


(1 Structures) x 2

TOTAL
4 Structures

Fig 8

Family: $2^3:n$



Family: $2^2:n:2^3$

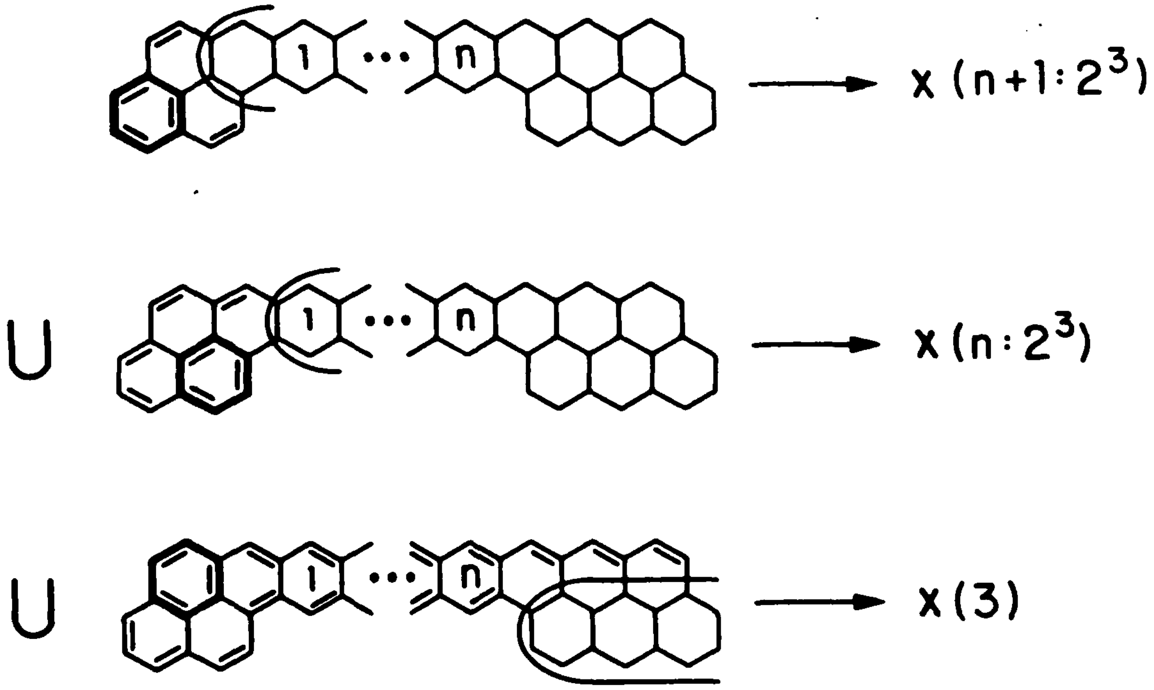
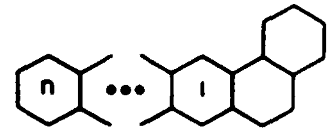
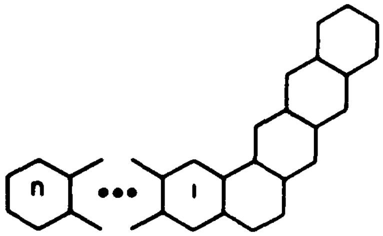


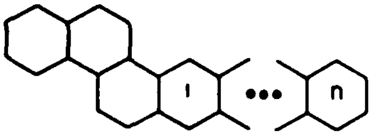
Fig 9



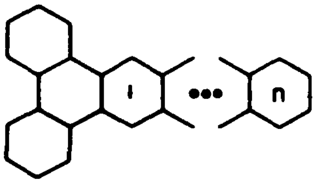
(n:2)



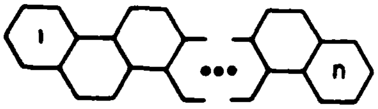
(n:4)



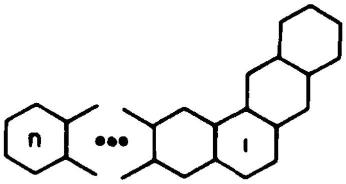
(1:2:n)



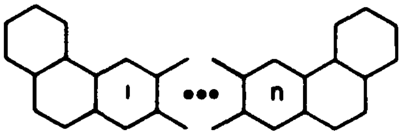
(2:(1):n)



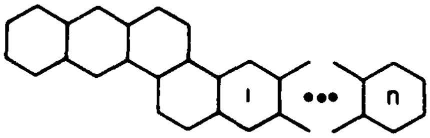
(1:1:1:1:····:1)



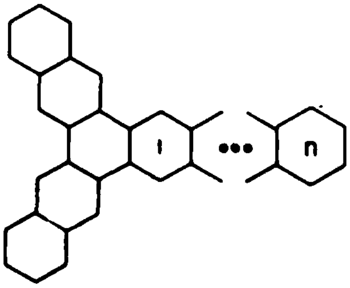
(n:3)



(2:n:2)

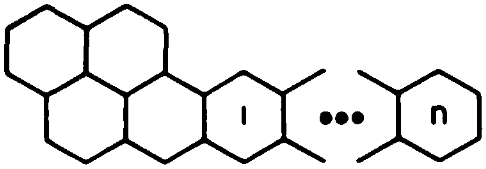


(2:2:n)

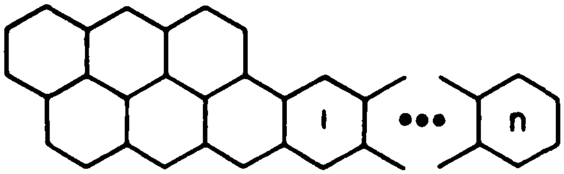


(3:(2):n)

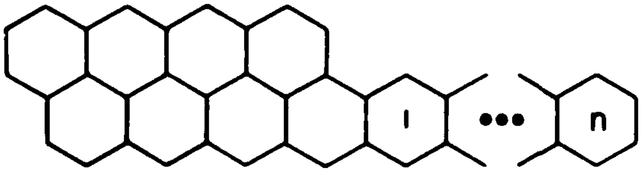
Fig 10



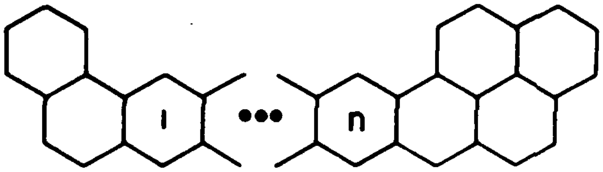
$(2^2 : n)$



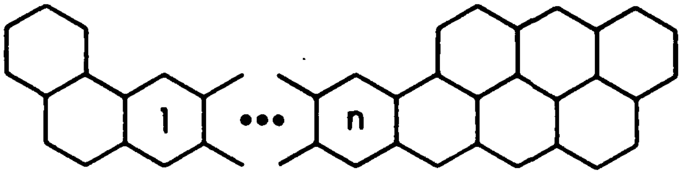
$(2^3 : n)$



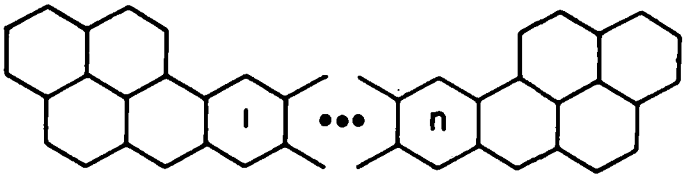
$(2^4 : n)$



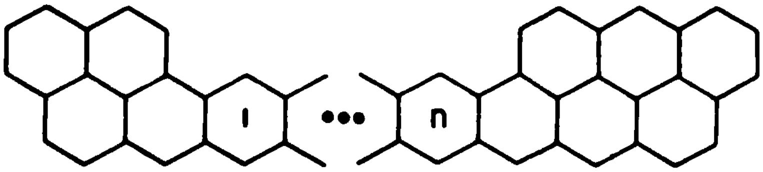
$(2 : n : 2^2)$



$(2 : n : 2^3)$



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



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

Fig 11

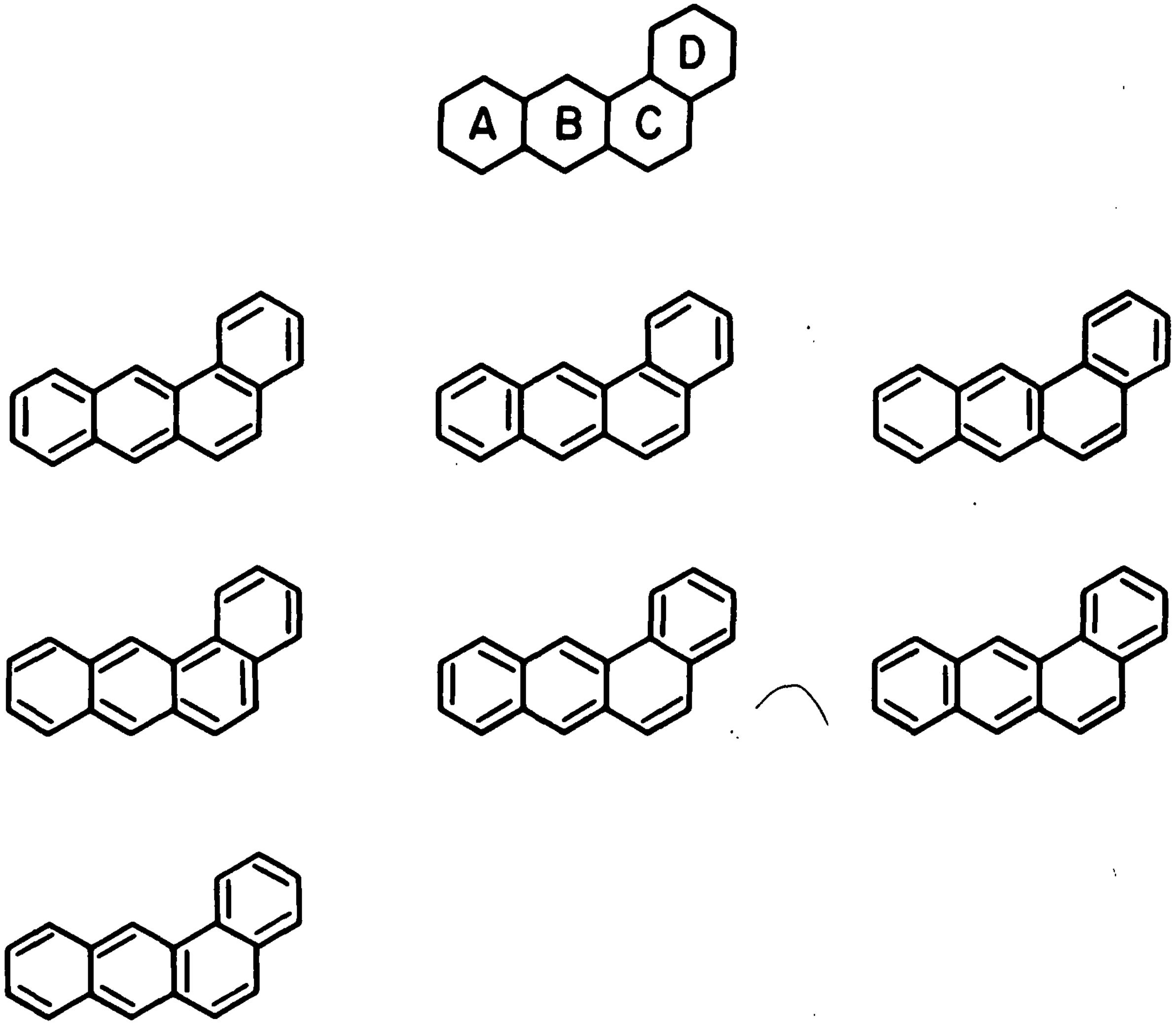


Fig 12

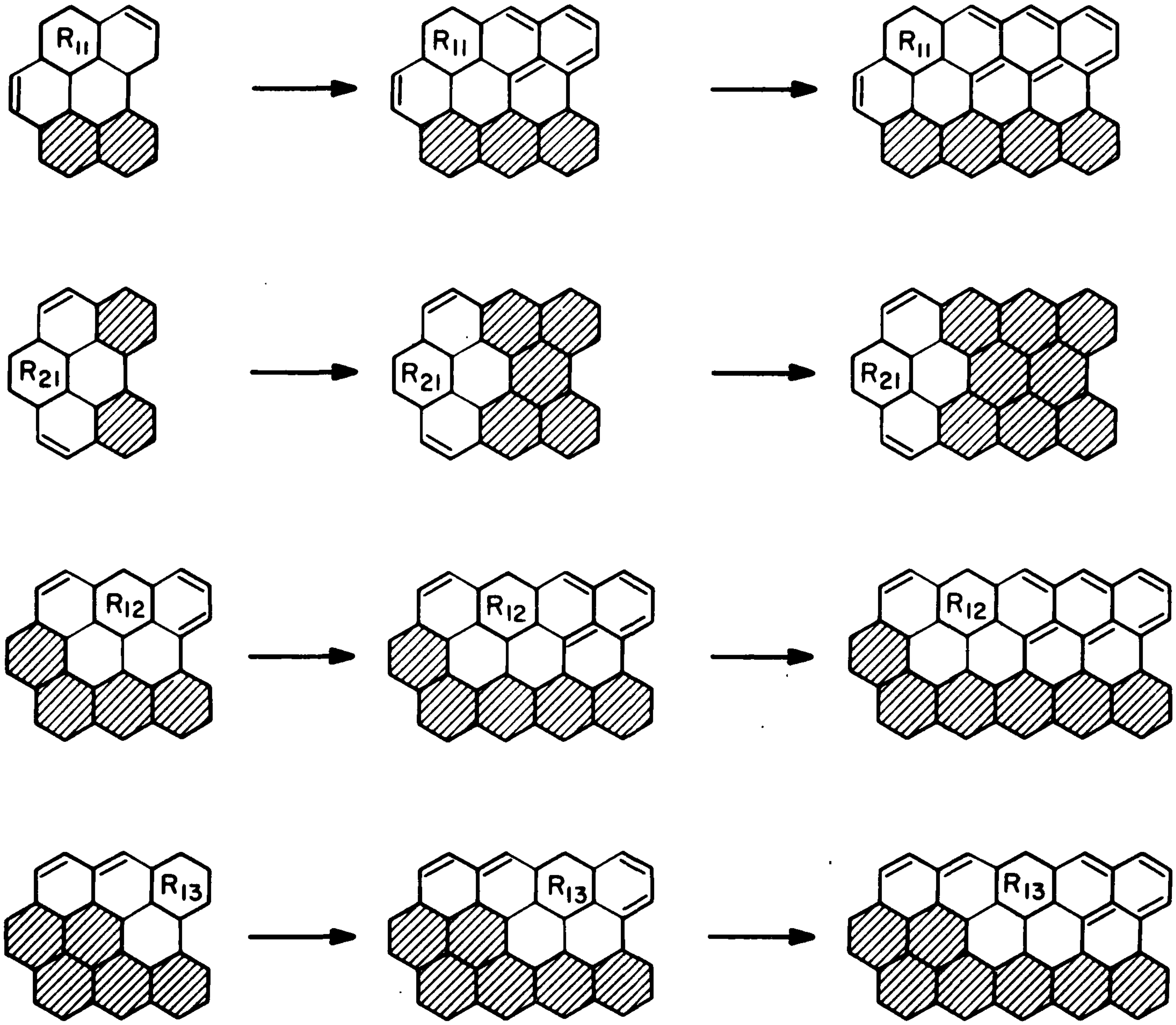


Fig13

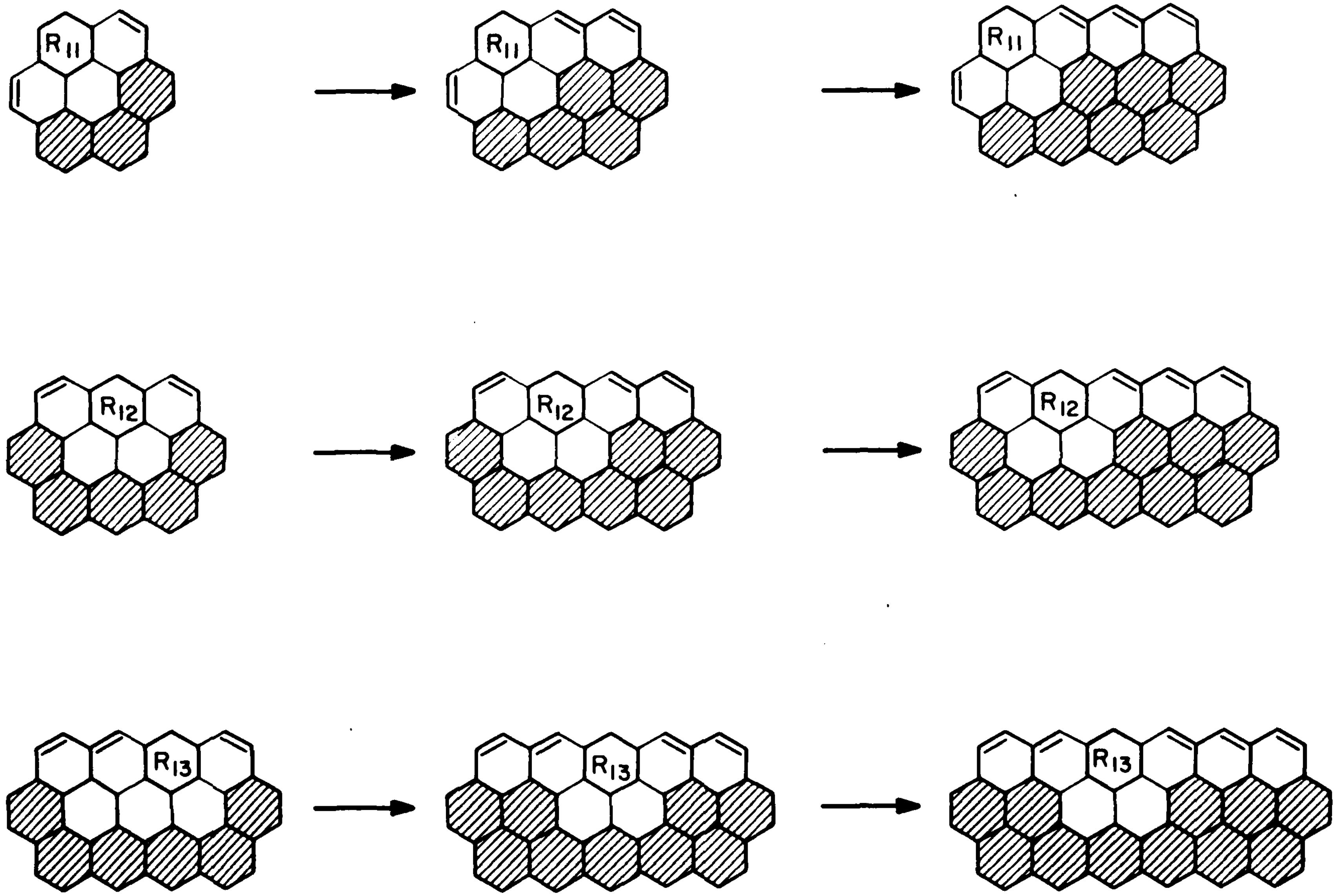


Fig 13 (Cont.)

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