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GRAPH-THEORETICAL ANALYSIS OF THE CLAR'S AROMATIC SEXTET

MATHEMATICAL PROPERTIES OF THE SET OF THE KEKULÉ PATTERNS AND THE SEXTET POLYNOMIAL FOR POLYCYCLIC AROMATIC HYDROCARBONS

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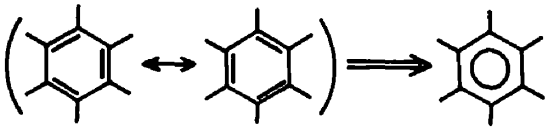
Abstract—The mathematical structure of a set of the Kekulé patterns for a polycyclic aromatic hydrocarbon has been analysed graph-theoretically. By defining the proper and improper sextets, sextet pattern, Clar transformation, and sextet rotation, one can prove the important property of the sextet polynomial $B_G(x)$ as $B_G(1) = K(G)$, where K(G) is the number of the Kekulé patterns for thin polyhex graph G. For fat polyhex graphs such as coronene the above relation is found to be also valid by introducing the concept of a super sextet. All the Kekulé patterns for a given G are shown to form a hierarchical tree structure by the sextet rotation. The theory developed in this paper gives a mathematical basis and interpretation for the concept of the Clar's aromatic sextet.

It has been established that the valence bond and molecular orbital methods are closely related through their simplest but mathematically neatest variants, namely, the resonance theory and Hückel MO method especially for conjugated hydrocarbons. In this respect the Kekulé pattern[a] plays one of the key roles in understanding the mathematical structure of the intimate relations between the resonance theory and MO method.

Various methods for enumerating the number K(G) of the Kekulé patterns for a polyhex graph G have been proposed and analysed from the graph-theoretical stand point.[1-5] The relation between K(G) and the stability of the π-electronic system have also been analysed. The numbers of the Kekulé patterns for the partial structures of the graph are good indices for the distribution of the π-electrons, e.g. bond orders, and the aromatic character of benzene rings.[6-9] However, very few studies have been done on the mathematical structure of the set of the Kekulé patterns.[9-13]

On the other hand, from a purely empirical stand point Clar has shown that various electronic properties of polycyclic aromatic hydrocarbons can be predicted by appropriately defining an aromatic sextet for their Kekulé patterns,[14]



aromatic sextet

(Clar) (1)

[a]We will use the term "Kekulé pattern" instead of the currently adopted term "Kekulé structure" from several reasons which will gradually be clear in the later discussion.

The present authors have proposed the sextet polynomial $B_G(x)$ and shown that through this polynomial many of the graph-theoretical quantities proposed so far by many authors are interrelated with one another and even with the Clar's postulate. The following important relation

$$B_G(1) = K(G)$$

was found for all the catacondensed and some groups of pericondensed aromatic hydrocarbons.[9]

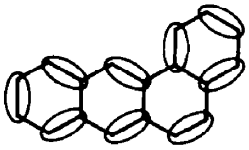
However, most of the above interesting relations have not yet fully been proved. The aim of the present paper is to analyse the mathematical structure of a set of the Kekulé patterns and to settle the mathematical interpretation for the concepts of the aromatic sextet and the related quantities.

DEFINITIONS

In this paper we will analyse the mathematical structure of the set of the Kekulé patterns of the polycyclic benzenoid aromatic hydrocarbons with a singlet ground state. As far as the π-electronic approximation is taken the graphs to be treated are the polyhex graphs corresponding to the C atom skeletons of unsaturated hydrocarbon molecules. Several important concepts will be defined first.

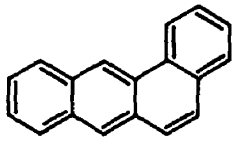
Polyhex graph and Kekulé pattern

A polyhex graph is a graph composed only of hexagons. Let us confine ourselves to those polyhex graphs which have even number, 2n, of points and can be spanned by n disjoint lines as in



1

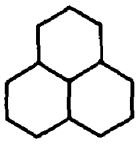
which will be denoted as



2 (k_3 in Fig. 1)

and called as a Kekulé pattern (k_i) composed of alternating single and double bonds. Let the number of the Kekulé patterns, or the maximum matching number, of a given polyhex graph G be denoted as $|\{k_i\}|$, or K(G).

The following graphs 3–6 will be excluded from our discussion, since 3 and 4 have odd number of points,



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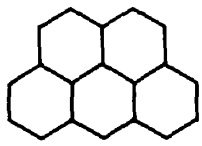

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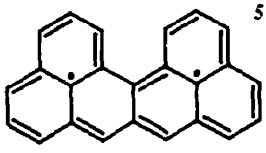
while for 5 and 6 we have K(G) = 0.



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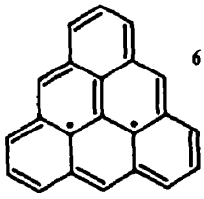
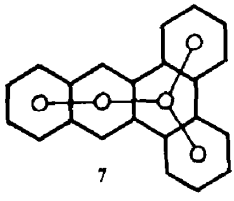


6

The dual graph of a polyhex graph G is defined as a graph obtained from G by joining the centers of the neighboring hexagons. A polyhex graph is called as catahex or perihex, depending that its dual graph is a tree or non-tree.[b] The following are some examples of a catahex (7) and perihexes (8, 9) on which their corresponding dual graphs are overlapped.



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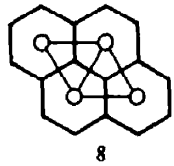

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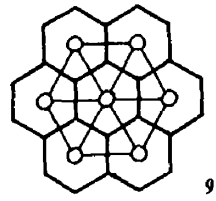
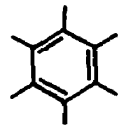


9

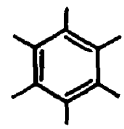
It may be worth noting here that although the number of the catafusene isomers can be enumerated by use of the counting polynomial,[15] it seems almost impossible to get systematically the counting polynomial for the perifusene isomers.[16] In the following discussion, it will be clear that for a polyhex graph which is "fat" enough to contain a coronene skeleton 9 one has to correct the theory developed for the "thin" polyhexes to some extent and the number of the correction terms gets larger as the graph swells.

Proper and improper sextets and sextet rotation

In order to simplify the discussion, a polyhex graph is to be placed on a plane so that a pair of edges of each hexagon lie in parallel with the vertical line. Let the sets of the circularly arranged three double bonds as shown below



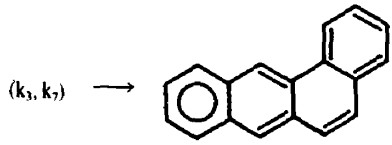
proper sextet



improper sextet

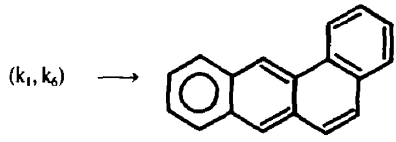
in a given Kekulé pattern be called, respectively, as proper and improper sextets.

Among the Kekulé patterns k_i–k_7 of graph 2 in Fig. 1, patterns k_3 and k_7 differ only in the left-end hexagon. According to Clar (eqn 1) one can draw a circle representing an aromatic sextet in the hexagon concerned,[14]



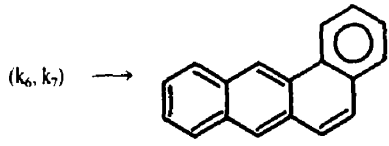
10a

Similarly one can get



10b

Different combinations among these Kekulé patterns gives



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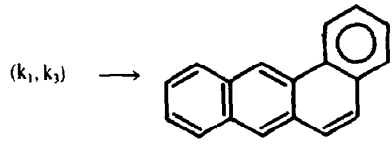
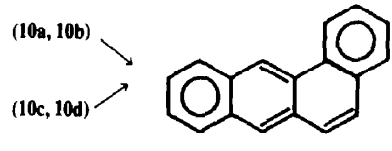


10d

Further by combining 10a–d we get the relation



10e

in which the two sextets are resonant.

In this way one can derive various patterns in which aromatic sextets are placed on the component hexagons. By transforming the remaining double bonds in these

[b]The catahex (catafusene) and perihex (perifusene), respectively, correspond to the catacondensed and pericondensed aromatic hydrocarbons.

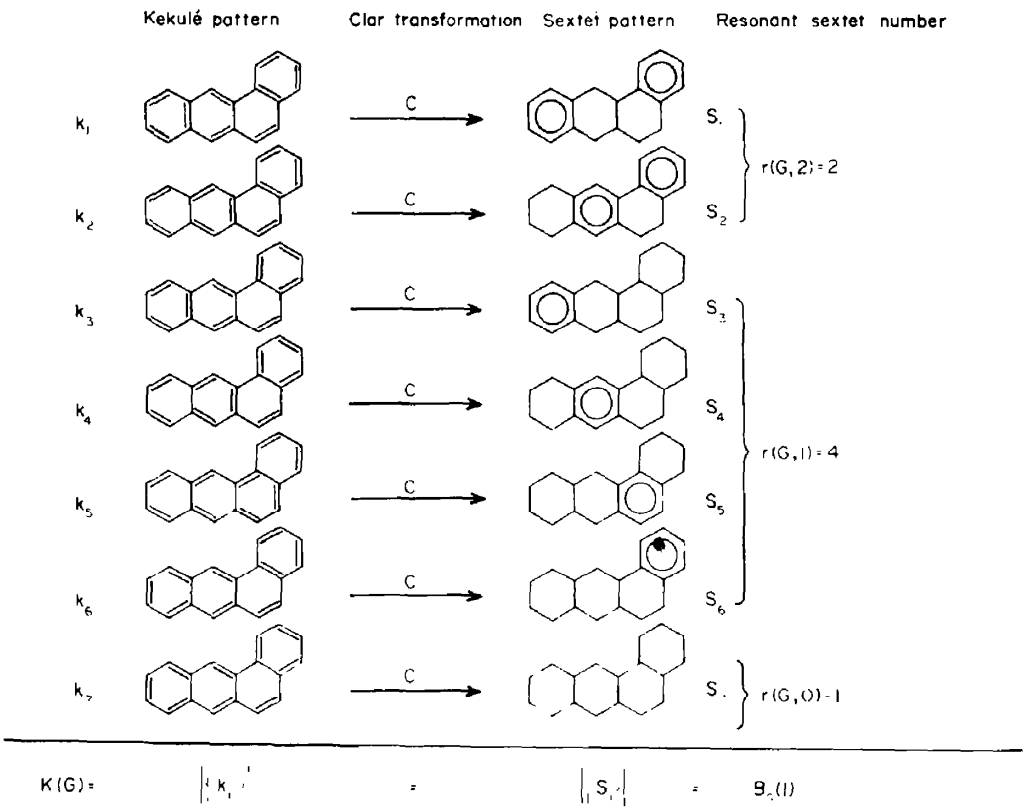
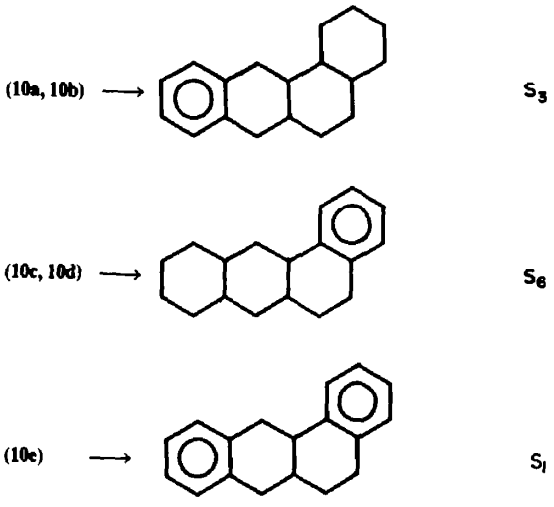
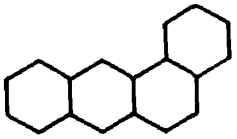


Fig. 1. One-to-one correspondence between the sets of the Kekulé $\{k_i\}$ and sextet $\{s_i\}$ patterns. These patterns are classified into classes with respect to the number of the resonant sextets to give the resonant sextet numbers.

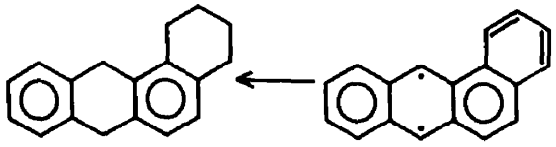
patterns into single bonds one can get various "sextet patterns" (Fig. 1) as



For the later discussion let us define the zero-sextet pattern with no sextet for any polyhex graph, as



Note, however, that the following sextet pattern is not allowed to draw, since its parent pattern does not belong to the family of the Kekulé patterns.



Sextet polynomial[9]

Now for a given polyhex graph one can draw a set of sextet patterns with various numbers of (resonant) sextets including the zero-sextet pattern. Let the number of the sextet patterns of G with k resonant sextets be denoted as r(G, k). The total number of the sextet patterns $\{s_i\}$ is

$$|\{s_i\}| = \sum_{k=0}^{m} r(G, k),$$

where m is the largest number of k. The sextet polynomial $B_G(x)$ for a polyhex graph G is defined as

$$B_G(x) = \sum_{k=0}^{m} r(G, k) \cdot x^k. \qquad (2)$$

It is obvious from the above definition that for any polyhex graph there is one and only one zero-sextet pattern, i.e.

$$r(G, 0) = 1. \qquad (3)$$

In Fig. 1 are shown the sets of the Kekulé patterns $\{k_i\}$ and sextet patterns $\{s_i\}$ for graph 2. At a first glance the relation between them seems to be rather entangled. However, generally for the thin polyhexes with $K(G) \neq 0$, it was found that

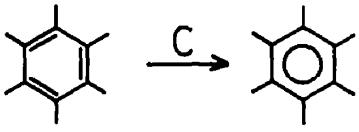
$$|\{k_i\}| = |\{s_i\}| \tag{4}$$

or

$$K(G) = B_G(1). \tag{4'}$$

Clar transformation and sextet rotation

Define the Clar transformation (C) as a simultaneous substitution of all the proper sextets by circles in a given Kekulé pattern k_i followed by the transformation of the remaining double bonds into single bonds,

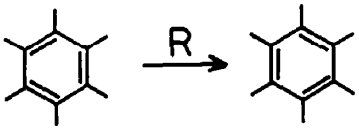


(5)

as exemplified for graph 2 in Fig. 1. It can symbolically be written as

$$C(k_i) = s_i. \tag{5'}$$

Define the sextet rotation (R) as a simultaneous rotation of all the proper sextets in a given Kekulé pattern k_i into the improper sextets to give another Kekulé pattern k_j,



(6)

or symbolically as

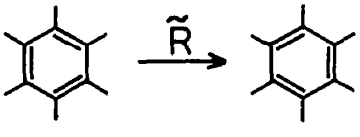
$$R(k_i) = k_j. \tag{6'}$$

For example, we get $R(k_1) = k_7$ for graph 2. Note that for such k_i with no proper sextet, e.g. k_7 in Fig. 1, one cannot operate the sextet rotation. In this case let us put it down as

$$R(k_i) = \phi,$$

and call such k_i as the root Kekulé pattern.

In the same way the counter-sextet rotation ($\tilde{R}$) is defined as follows:



(7)

Note that the operation R is not the inverse of $\tilde{R}$ and *vice versa*.

[c] Here *m* is the maximum number of the proper sextets. See eqn (2).

OBSERVATION

Since several patterns and operations have been defined for polyhex graphs, let us observe how all the Kekulé and sextet patterns are related to one another by taking graph 2 as an example. As evident from Fig. 1, by the Clar transformation, the one-to-one correspondence from k_i to s_i can be found, the relation (4) being satisfied. At this stage, however, it is not certain if one and only one k_i can be found for a given s_i.

Next try to operate the sextet and counter-sextet rotations to the set of the $\{k_i\}$. The resultant relationship among $\{k_i\}$ for graph 2 is a hierarchical structure and can be expressed by a directed rooted tree as shown in Fig. 2, where all the entries in $\{k_i\}$ can find the corresponding nodes including the root. It is to be noted here that the two trees obtained by the sextet and counter-sextet rotations are not necessarily isomorphic as exemplified in Fig. 2.

No exception to the above results could be found for all of the thin polyhexes studied. However, for fat polyhexes some difficulties have been observed. We will develop the theory on thin polyhexes first and then extend it to fat polyhexes.

THEOREMS

In this section the relation (4) and other results obtained for thin polyhex graphs are summarized as Theorems. It was found that the key of the proofs is what is stated as the lemma, whose proof will be given in Appendix.

Lemma

For each polyhex graph G, there exists one and only one root Kekulé pattern.

From Lemma the following Theorem can be obtained.

Theorem 1

$$B_G(1) = K(G).$$

Proof. Suppose the sets of k_i, $\{k_i | i = 1, 2, \ldots, K(G)\}$, and s_i, $\{s_i | i = 1, 2, \ldots, B_G(1)\}$, for a given polyhex graph G. The set $\{k_i\}$ can be classified into several, say, $m+1$ classes[c] with respect to the number of the proper sextets, and the set $\{s_i\}$ into the same number of classes with respect to the number of circles. Lemma ensures that for any graph there is a unique correspondence between such k, with no proper sextet (root Kekulé pattern) and such s_i with no circle (zero-sextet pattern). Then consider the class of $\{k_i\}$ with one proper sextet r_1 and the corresponding class of $\{s_i\}$. Choose k_i from the former class. Delete r_1 from G together with the bonds incident to it. The resultant graph is denoted as $G \ominus r_1$. Since k_i has only one proper sextet, there is no proper sextet in its $G \ominus r_1$ part, which is either a polyhex or a branched polyhex graph. In the latter case the terminal bonds are fixed to be double, and all the bonds adjacent to them should be single. Then delete all the fixed double and single bonds from $G \ominus r_1$. If the resultant truncated graph still has branches, repeat the above process until we get either a polyhex graph(s) or a vacant graph, for which there is one and only one root Kekulé pattern (including the case of a vacant graph) according to Lemma. Then by tracing back all the processes we get a unique Kekulé pattern which has a proper sextet in r_1 but nowhere else.

A successive application of this reasoning leads to the conclusion that if any two k_i and k_j are chosen the corresponding $s_i (= C(k_i))$ and s_j should be different. That

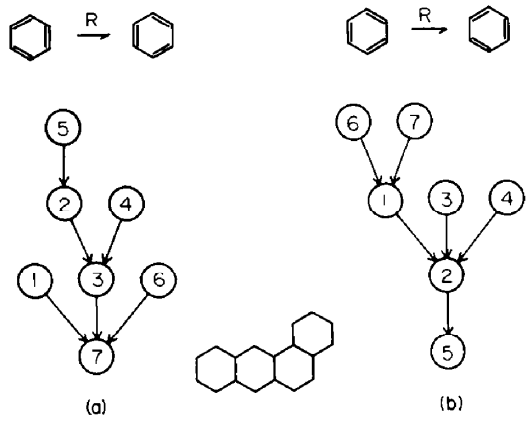


Fig. 2. Directed rooted trees of the Kekulé patterns of graph 2 derived from the sextet (a) and counter-sextet (b) rotations. The numbers refer to Fig. 1.

is

$$C(k_i) \neq C(k_j) \qquad \text{for } i \neq j, \tag{8}$$

which means

$$\{k_i\} \subseteq \{s_i\} \tag{9}$$

or

$$|\{k_i\}| \leq |\{s_i\}|. \tag{9'}$$

It follows from the definition of the sextet pattern that for any s_i there is at least one k_i leading to s_i. Further, it is apparent that for two different s_i and s_j the corresponding k_i and k_j should be different. For the zero-sextet pattern Lemma ensures the existence of the uniquely corresponding root Kekulé pattern which is different from any of the Kekulé patterns corresponding to the rest of the sextet patterns. Now we have

$$\{s_i\} \subseteq \{k_i\} \tag{10}$$

or

$$|\{s_i\}| \leq |\{k_i\}|. \tag{10'}$$

By combining the relations (9) and (10) Theorem 1 can be proved.

Although the variable x in the sextet polynomial $B_G(x)$ does not mean anything other than what holds the power k and the coefficient r(G, k), $B_G(x)$ can be differentiated formally with respect to x as

$$B_G'(x) = \frac{d}{dx} B_G(x).$$

Then it is easy to get the second Theorem:

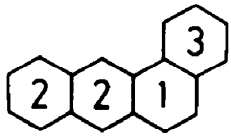
Theorem 2

$$B_G'(x) = \sum_{k=1}^{m} k \cdot r(G, k) = \sum_{\text{hexagon in G}} K(G \ominus r_i). \tag{11}$$

[d] As Herndon,[6] Randić[7] and Aihara[8] independently pointed out that the number $K(G \ominus r_i)$ can be used as a measure of aromatic character of the component hexagon.

Proof. Consider the graph $G \ominus r_i$. Theorem 1 ensures that $K(G \ominus r_i)$ is equal to the number of the sextet pattrns of $G \ominus r_i$, which is equal to the number of such sextet patterns of G that have a circle in ring r_i. If the sum of $K(G \ominus r_i)$ is to be taken over all the hexagons, r_i's of G, each sextet pattern s_i is counted just the same times as the number k of the aromatic sextets in s_i. Then the summation of $K(G \ominus r_i)$ over i is turned out to be the counting of all the circles in the set of $\{s_i\}$, which can be obtained by the sum of $k \cdot r(G, k)$ over k. Thus we get Theorem 2.

For graph 2 the $K(G \ominus r_i)$ value for each hexagon can be obtained from Fig. 1 as[d]



Make sure that each of these numbers $K(G \ominus r_i)$ can be exactly obtained by counting the number of such sextet patterns that have circles in a given hexagon r_i. The total sum of the circles are obtained either by adding these numbers as $2+2+1+3=8$ or by adding $k \cdot r(G, k)$ as $1 \times 4 + 2 \times 2 = 8$. These relations are generally valid for all the thin polyhexes.

The hierarchical tree of the set of the Kekulé patterns shown in Fig. 2 can be expressed as the third Theorem:

Theorem 3

The sextet rotation to the set of the Kekulé patterns $\{k_i\}$ gives a directed tree graph with a root (root Kekulé pattern) representing a hierarchical structure of $\{k_i\}$, where each point corresponds to a Kekulé pattern.

Proof. Let $\{k_i\}$ be the set of the Kekulé patterns of a given polyhex graph and k_1 be the root Kekulé pattern. If $R(k_i) = k_j$, draw an arrow from point p_i to p_j, and we get a directed graph. Since $R(k_i) = \phi$, the outdegree of p_1 is zero. As Lemma ensures the existence of one and only one root Kekulé pattern, the obtained graph should be a rooted graph. By the definition of the sextet rotation R, one and only one arrow starts from each point p_i ($i \neq 1$). Here we note that each hexagon in any thin polyhex graph has at least a peripheral edge. Let the hexagon r be a proper sextet in a Kekulé pattern k_i of a thin polyhex graph. If we operate the sextet rotation R on k_i to get another Kekulé pattern k_{i+1}, r should be an improper sextet in k_{i+1}. In the same way we can get Kekulé patterns k_{i+2}, k_{i+3}, etc. by operating R on k_{i+1}, k_{i+2}, etc. Without loss of generality we can suppose that one of the peripheral edges l of r is single in k_i, and double in k_{i+1}. As long as l is a double bond, r cannot be a proper sextet, and l belongs only to r. Then the sextet rotations to k_{i+1}, k_{i+2}, etc. cause no change in l. That is, for any j ($= 1, 2, 3, \ldots$), $k_i \neq k_{i+j}$. This means that the directed graph obtained by the sextet rotation to the set of the Kekulé patterns has no cycle, and therefore it is a directed rooted three.

Extention to "fat polyhex graphs"

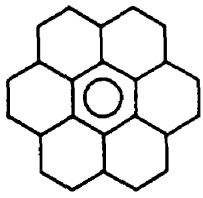
As mentioned above, Theorems 1 and 2 do not hold for fat polyhex graphs, i.e. the carbon atom skeletons of pericondensed aromatic hydrocarbons (perifusenes) which contain the coronene skeleton, 9. The sextet

polynomial of coronene would be

$$B_G(x) = 1 + 7x + 9x^2 + 2x^3$$

giving $B_G(1) = 19$ and $B_G'(1) = 31$, whereas $K(G) = 20$ and $\Sigma K(G \ominus r_i) = 32$ (Fig. 3, where the Kekulé and sextet patterns are overlapped).[c]

The failure of Theorems 1 and 2 can be remedied if the second term in $B_G(x)$ is corrected to 8x. See the patterns 2 and 3 in Fig. 3. Although the two Kekulé patterns are distinct, the Clar transformation on them gives the same sextet pattern



Note that for a given arrangement of the proper sextet in the central hexagon two different arrangements of the nine alternating double bonds around the peripheral 18-membered ring of coronene are possible. Let such an "octadecet" as in these two patterns be called as a "super sextet". Further, let such a super sextet as in pattern 3 in Fig. 3 be called as a "proper super sextet" and be denoted by the concentric double circles as shown in Fig. 4. Now if this twentieth sextet pattern is assumed to contribute a term x in $B_G(x)$, Theorems 1 and 2 are automatically satisfied for coronene skeleton (Fig. 4).

It can be shown that the concept of the super sextet may be extended to such a generalised "(4j + 2)-et" surrounding k disjoint but resonant sextets and contributes a term x^k to $B_G(x)$ as in Fig. 5. In Fig. 6 are shown how Theorems 1 and 2 hold for a large network as "super coronene" by introducing the concept of the super sextet.

It was found that for necklace-like molecules the one-to-one correspondence bwtween the Kekulé and sextet patterns can also be obtained if the definition of the sextet is extended to the generalised sextet as exemplified in Fig. 7. Formal application of the Clar transformation to any one of the three Kekulé patterns k_1–k_3 in Fig. 7 would yield the zero-sextet pattern s_1. However, the (4j + 2)-membered holes, or generalised hexagons in k_1 and k_2 can be regarded, respectively, as improper and proper sextets, and thus the set of the five alternating double bonds along the hole may be called to form an enlarged or a generalised sextet. Further, the Clar transformation can formally be extended to the transformation of k_3 in Fig. 7 to give the sextet pattern s_3 with a super sextet. Thus the three Kekulé patterns k_1–k_3 are transformed into distinct generalised sextet patterns s_1–s_3. Observe the one-to-one correspondence between k_1–k_3 in Fig. 7 and the patterns 1–3 in Fig. 3. The corrected sextet polynomial

$$B_G(x) = 1 + 10x + 18x^2 + 10x^3 + x^4$$

gives the correct values for K(G) and $K(G \ominus r_i)$ as in Fig. 8.

Similarly the $B_G(x)$ of graph 11 can be obtained as

$$B_G(x) = 1 + 14x + 48x^2 + 76x^3 + 48x^4 + 12x^5 + x^6$$

with a generalised sextet pattern **11a** and a super sextet

[c] The $K(G \ominus r_i)$ value for the central hexagon is two, and that for each of the peripheral hexagon is five (Fig. 3). Thus we get $K(G \ominus r_i) = 1 \times 2 + 6 \times 5 = 32$.

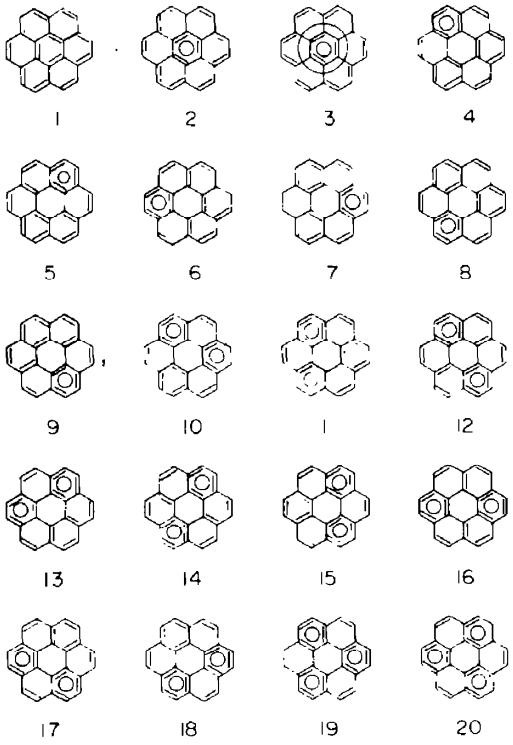


Fig. 3. Kekulé and sextet patterns of coronene. See Fig. 4 for the sextet polynomial and Fig. 9 for the hierarchical tree structure.

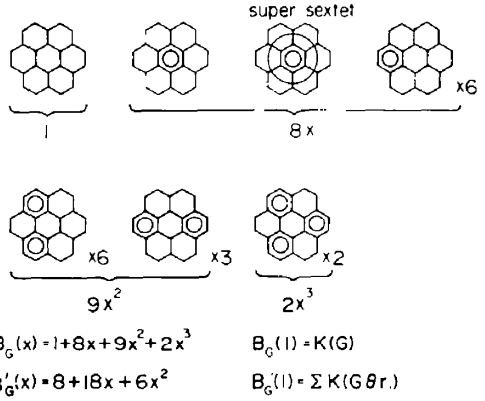


Fig. 4. Sextet polynomial and sextet patterns of coronene.

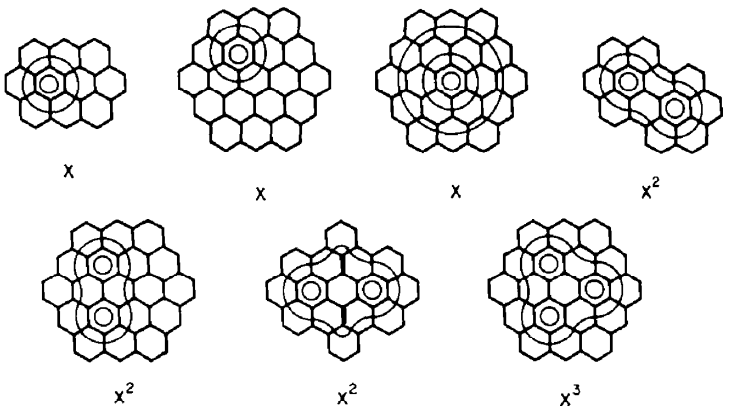


Fig. 5. Examples of super sextets and the correction terms for the sextet polynomial.

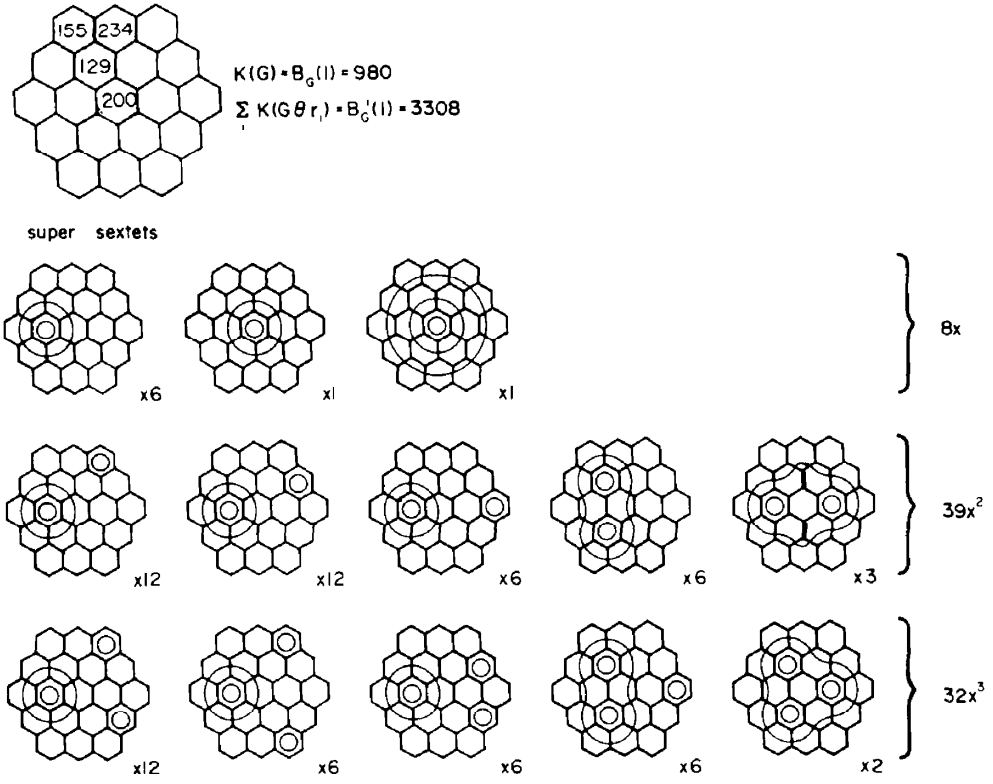
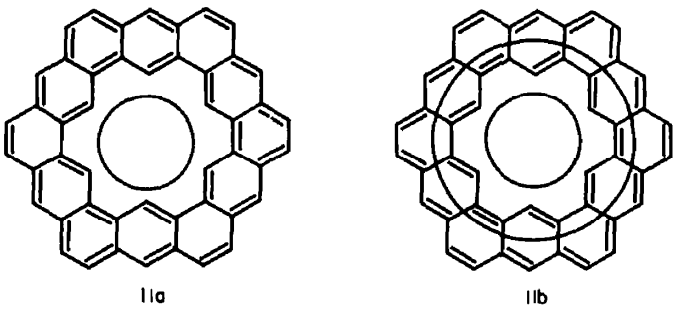


Fig. 6. Super sextets of "super coronene" and the corresponding correction terms to give the sextet polynomial $B_G(x) = 1 + 27x + 162x^2 + 350x^3 + 310x^4 + 114x^5 + 15x^6 + x^7$.

pattern **11b**,



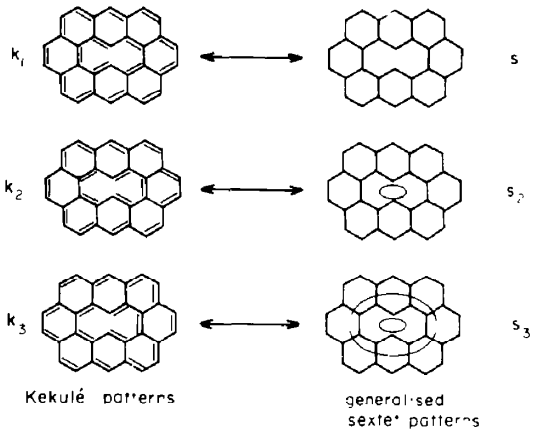


Fig. 7. Generalised sextet patterns including the enlarged (s_2) and super (s_3) sextets for the necklace-like molecule. See also Fig. 8.

unambiguous definition of the super sextet. However, as has been demonstrated in the several examples, one can uniquely assign the super sextet patterns for a given fat polyhex graph so that all of Theorems 1–3 hold. It should be pointed out here that the mathematical properties of polyhex graphs discussed in this paper not only are very useful for interpreting the various resonance-theoretical analyses on the aromatic characters for the benzenoid hydrocarbons,[9,17] but also have a close resemblance with those of the king and domino polynomials for the square lattice.[18]

APPENDIX

Proof of Lemma[1]

Let {P} be the set of polyhex graphs. If a certain bond is fixed to be single or double in the whole set of the Kekulé patterns of a graph G ∈ {P}, let it be called as an F-bond. The following remark can be obtained from the fact that any proper sextet can always be transformed into an improper sextet.

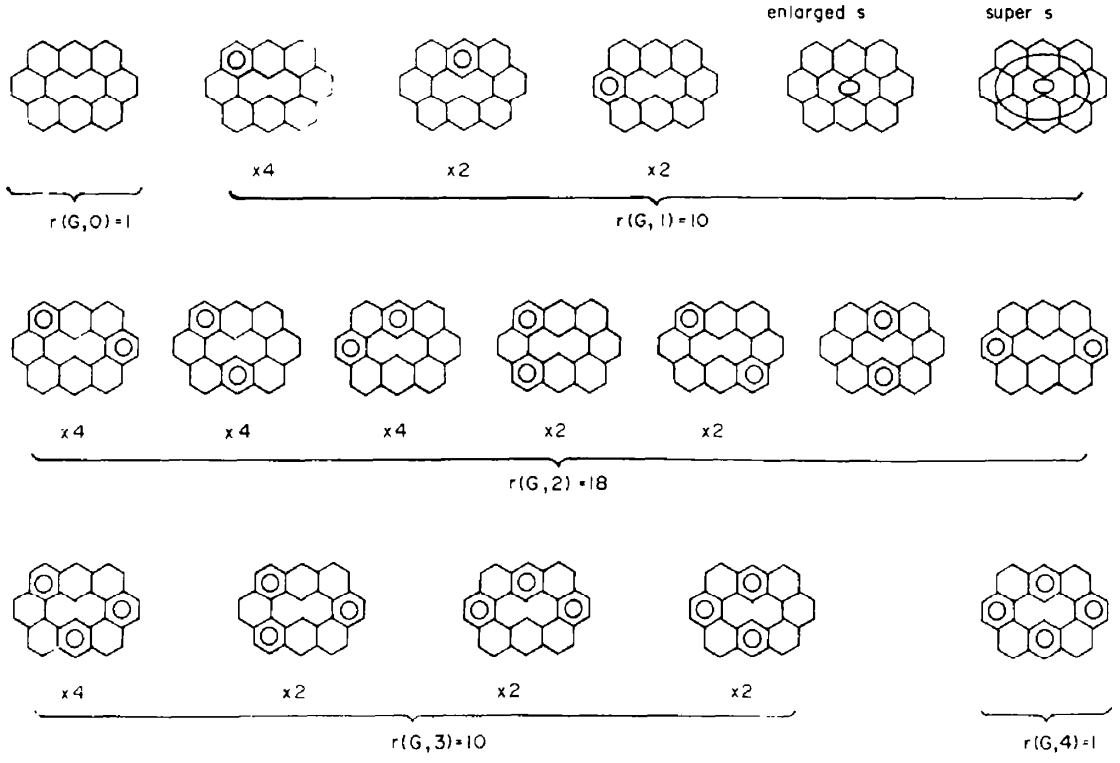


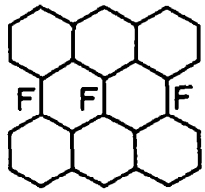
Fig. 8. Sextet patterns and r(G, k)'s of the molecule in Fig. 7.

Although the definition of the Clar transformation had to be extended to the super and generalised sextets, the sextet rotation need not be modified even in the case where super and/or generalised sextets are introduced. Theorem 3 has not been proved for fat polyhex graphs rigorously, but its validity is believed by the present authors from an extensive experience and reasoning. This is exemplified in Fig. 9 where the set of the twenty Kekulé patterns of coronene form a hierarchical tree by the sextet rotation.

At the present stage it is very difficult to give an

Remark 1. If a hexagon in G contains at least one F-bond, neither a proper nor an improper sextet can be drawn in the hexagon.

This is exemplified for graph 12, where all of the central bonds are single F-bonds, and no Kekulé pattern can be drawn with a sextet in the central two hexagons.



12

[1]Contribution by the Ochanomizu group.

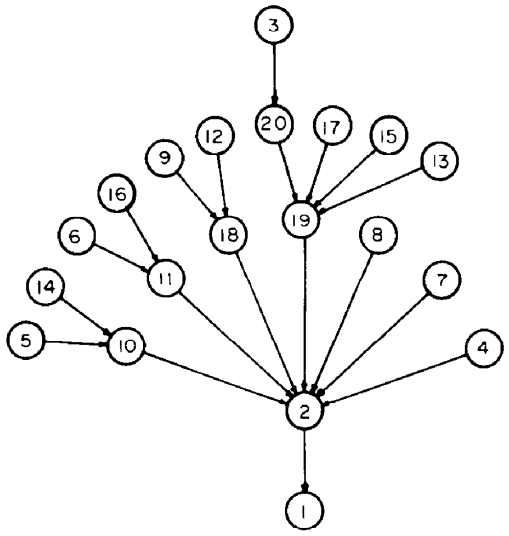
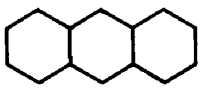


Fig. 9. Hierarchical tree of the Kekulé patterns for cononene obtained by the sextet rotation. The numbers refer to Fig. 3.

Let us consider the subgraph G–F of a polyhex graph G obtained by deleting all those hexagons which contain at least one F-bond. The resultant graph G–F may have one or more polyhex components. Let $\{\tilde{P}\}$ be the set of such polyhex graphs that have no F-bond. From this definition $\{\tilde{P}\} \subset \{P\}$. Graph 12 ($\in\{P\}$) is reduced to a couple of graphs



belonging to $\{\tilde{P}\}$. The following two remarks can easily be inferred from the above argument but deserve to be noticed.

Remark 2. For a given bond l of $G \in \{\tilde{P}\}$ there exists at least one Kekulé pattern in each of the cases where l is chosen as double and single.

Remark 3. If Lemma is valid for $G \in \{\tilde{P}\}$, it is valid also for $\{P\}$.

Let us call as the row of bonds the set of all the vertical bonds like F-bonds in Graph 12. Then we have.

Remark 4. If all the bonds belonging to one row of bonds are single in a Kekulé pattern of a polyhex graph, they are single F-bonds.

Proof. Consider a Kekulé pattern for a polyhex graph G in which all the bonds belonging to one row of bonds are single. Let the set of those single bonds be $L = \{l_i | i = 1, 2, \ldots\}$ and the subgraphs of G obtained by deleting all l_i's from G be g and g', both of which are even bipartite graphs. The numbers of the starred and unstarred atoms are the same for each of g and g'. Suppose that l_i connects atom a_i in g with b_i in g'. Without loss of generality one can assign a_i as starred and b_i as unstarred. Then it is observed that all the a_i's and b_i's are, respectively, starred and unstarred (Fig. A1).

Consider another Kekulé pattern in which l_i is chosen as double. Since $g - a_i$ has an odd number of atoms, in $\{l_j\}$ an odd number of l_j's should be double besides l_i. Let the set of such a_j's that are incident to the double bonded l_j's be A. Since all the a_j's are starred, the number of the starred atom in the subgraph g–A is less than that of the unstarred. Thus no Kekulé pattern would be drawn in g–A when l_i is double. This contradiction completes the proof.

In the following discussion let us prove Lemma by disproving its reciprocal. If Lemma is not true, there exists the smallest graph G_0 for which Lemma does not hold. Then there are two possible cases in which i) G_0 has no root Kekulé pattern, and ii) G_0 has more than one root Kekulé patterns. From Remarks 1 and 3 one can assume without loss of generality that $G_0 \in \{\tilde{P}\}$. Let l_0 be one of the farthest (vertical) left bonds of G_0.

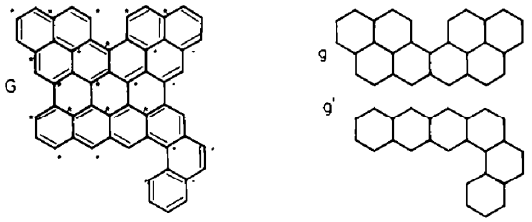


Fig. A1. An example of polyhex with a row of single bonds.

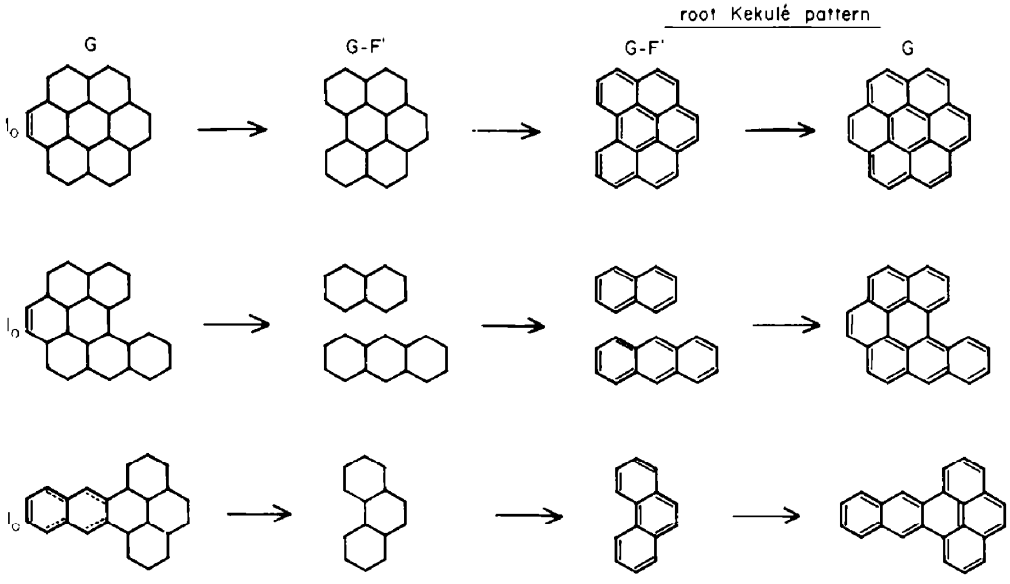
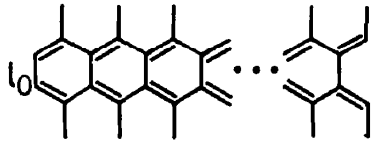


Fig. A2. Examples of polyhexes and their root Kekulé patterns.

Consider a case in which l_0 is fixed to be double. From Remark 2, we can draw at least one Kekulé pattern with l_0 as double, but in whatever case a proper sextet cannot be drawn in the hexagon r_1 containing l_0. If certain bonds in G_0 become to be fixed as double or single when l_0 is fixed to be double, let us call them as F'-bonds. Then delete from G_0 those hexagons which contain at least one F'-bond. The resultant subgraph $G_0 - F'$ is obviously composed of polyhexes which belong to $\{\tilde{P}\}$, and are smaller than G_0. Thus one can draw one and only one root Kekulé pattern for G_0–F', and by tracing back the deleted F'-bonds we can get one and only one root Kekulé pattern for G_0 (Fig. A2).

Now if Lemma is not true, we are left with only the possibility that there exists the smallest graph $G_0 \in \{\tilde{P}\}$ for which a root Kekulé pattern can be drawn with l_0 as single. If this is the case, any root Kekulé patterns for G_0 should have the following structure in which all the bonds in the



row of bonds including l_0 are single so as not to have any proper sextet. Then from Remark 4, G_0 would have F-bonds in contradiction to the assumption that $G_0 \in \{\tilde{P}\}$. Now the proof of Lemma is completed.

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