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Original Investigations

Topological dependency of the aromatic sextets in polycyclic benzenoid hydrocarbons. Recursive relations of the sextet polynomial

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Mathematical meaning of the Clar's "aromatic sextet" is clarified by analysing the topological dependency of the sextet polynomial. Generalised recursive method for obtaining the sextet polynomial of a polyhex graph is presented. It is shown that the concept of the "super sextet" is necessarily introduced, if one-to-one correspondence between the Kekulé and sextet patterns is assumed. Topological dependency of the maximum number of resonant sextets is clarified and discussed in relation to the aromaticity and stability of polycyclic benzenoid hydrocarbons.

Key words: Polycyclic benzenoid hydrocarbon—Kekulé structure—Clar's aromatic sextet—Sextet polynomial—Graph theory.

1. Introduction

Recent studies have shown that the revived resonance theory successfully gives not only qualitative but also quantitative predictions on π-electronic properties of benzenoid hydrocarbons [1–4]. In this theory the carbon atom skeletons of these molecules are often treated as "graphs" from the graph-theoretical standpoint. The advantage of these studies lies in their predictability of the electronic properties of infinitely large networks, where the numbers of "Kekulé patterns" of graph G, $K(G)$, and its subgraphs play a key role. Thus various methods have been proposed to enumerate and analyse these numbers [5–8].

On the other hand, the concept of "aromatic sextet" has been proposed by Clar from the experimental standpoint [9]. Many π-electronic properties, e.g. relative

Fig. 1. Definition of aromatic sextet. Two aromatic sextets can mutually be resonant as in the right pattern

stabilities, aromaticities, and reactivities of isomeric benzenoid hydrocarbons, are shown to be explained by this concept rather quantitatively [2–4, 10, 10a].

To analyse the mathematical features of the aromatic sextet, the sextet polynomial $B_G(x)$ has been proposed for a "polyhex graph" G representing a benzenoid hydrocarbon [11]. According to Clar, if a set of three conjugated double bonds are drawn in a hexagon for one of the Kekulé patterns of the graph concerned, an aromatic sextet can be assigned to that hexagon [9]. Two or more aromatic sextets can be mutually resonant if the remainder of the graph has at least one Kekulé pattern (Fig. 1). Let us define the resonant sextet number, $r(G, k)$, as the number of ways in which k resonant aromatic sextets can be chosen from G. With a set of $r(G, k)$'s the sextet polynomial $B_G(x)$ is defined as follows:

$$B_G(x) = \sum_{k=0}^{\max} r(G, k) x^k, \tag{1}$$

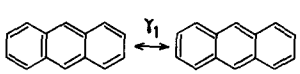
where x is simply a parameter to hold k. Define $r(G, 0) = 1$ for any G, and we get $B_\phi(x) = 1$ for a vacant graph ϕ.

It has been shown that the following two interesting relations hold for the sextet polynomial [11]:

$$B_G(1) = K(G), \tag{2}$$

$$B'_G(1) = \sum_{i}^{\text{all}} K(G - (r_i)), \tag{3}$$

where $B'_G(x)$ is the first derivative of $B_G(x)$, and $G-(r_i)$ [12] is the subgraph of G obtained from G by deleting the hexagon r_i and all its adjacent edges. Eq. (2) means that the counting up of all the sextet patterns of G is equivalent to the enumeration of the number of Kekulé patterns of G. It is clear that the value of the right hand side of Eq. (3) is equal to the value of $\sum \gamma_1$ proposed by Herndon and Ellzey [2], which is the number of resonance interactions among the Kekulé patterns as shown below.



Thus we can show that through the sextet polynomial many quantities in resonance theory are mathematically correlated with one another.

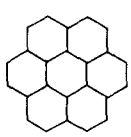
Although several recurrence relations for the sextet polynomial are known, most of the investigations reported so far are concerned only with "catafusenes" [13–16]. It is very tedious to get the sextet polynomial even for moderately large "perifusenes" [13], and further in many cases we should consider the correction terms arising from the "super sextets" in order to keep Eqs. (2) and (3) valid [17].

In this paper, the recursive method to get the sextet polynomial for any polyhex graph G has been proposed, and for some infinitely large networks general expressions for their sextet polynomials are obtained and discussed, through which the mathematical meaning of the "super sextet" was made clear. Further, systematic understanding was obtained for the relation between the topological structure of polyhex graphs and the maximum number of resonant sextets.

2. Definitions and notations

In this paper only the polycyclic benzenoid hydrocarbons are concerned. The carbon atom skeletons of these molecules are expressed by polyhex graphs. Discussions are limited to those polyhex graphs which have at least one Kekulé structure, or Kekulé pattern, in which all the component points belong to one and only one double bond spanning a pair of adjacent points; the number of points of the graph being even. As has been proposed in Ref. [17], let us draw all the polyhex graphs on a plane so that a pair of edges of each hexagon lie in parallel with the vertical line. It will be clear that this simplifies the later discussions without loss of generality.

The following are the necessary definitions and notations. Sextet pattern: If for a given Kekulé pattern a set of three conjugated double bonds are assigned on a hexagon, one can draw a circle representing an aromatic sextet in that hexagon. Once an aromatic sextet is drawn on a certain hexagon, no aromatic sextet is allowed to be drawn in the neighbouring hexagons [9]. As mentioned above, one can draw more than two resonant sextets as long as at least one Kekulé pattern is drawn for the remainder of the molecule [9, 17]. A sextet pattern is a pattern derived from a Kekulé pattern by transforming certain sets of aromatic sextets into circles and by wiping out the remaining double bonds [17].
Fixed bond (edge): If a bond e of G is a single (or double) bond in all the Kekulé patterns of G, it is called as an s-fixed (or a d-fixed) bond.
$G-(s)$: A subgraph of G obtained by deleting s and all the edges which are adjacent to s (Fig. 2).
$G-[s]$: A subgraph of $G-(s)$ obtained by deleting all the fixed bonds in $G-(s)$ (Fig. 2).
Thin polyhex: A polyhex graph which does not contain a coronene skeleton.



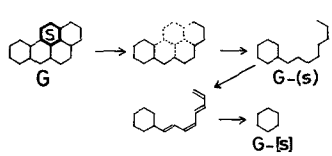


Fig. 2. Definitions of subgraphs $G-(s)$ and $G-[s]$

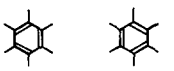


Fig. 3. Definitions of proper and improper sextets

Fat polyhex: A polyhex graph which includes at least one coronene skeleton.
Proper and improper sextets: If a set of three conjugated double bonds are arranged in a hexagon as shown in Fig. 3 for a given Kekulé pattern, they are called as proper and improper sextets respectively [17].

3. One-to-one correspondence between Kekulé and sextet patterns

In Ref. [17] we have shown the one-to-one correspondence between Kekulé and sextet patterns of thin polyhex graphs through the "Clar transformation." Consider a Kekulé pattern k_i for a given polyhex graph, such as pyrene (See Fig. 4). When we transform all the proper sextets in k_i into aromatic sextets and all the remaining double bonds into single bonds, we can get a sextet pattern s_i uniquely corresponding to k_i (Clar transformation). Conversely, when we transform all the aromatic sextets in a given sextet pattern s_j into proper sextets and draw the double bond(s) in the remaining subgraph so as to have no proper sextet (it is always possible), we can uniquely get k_j corresponding to s_j (See Ref. [17] in detail). From this correspondence Eqs. (2) and (3) are proved for thin polyhex graphs.

For fat polyhex graphs "super sextets" have been introduced to hold these equations (Fig. 5). Though we have not defined "super sextet" explicitly, we have found empirically the one-to-one correspondence between Kekulé and sextet patterns including super sextets by considering a "super proper sextet"

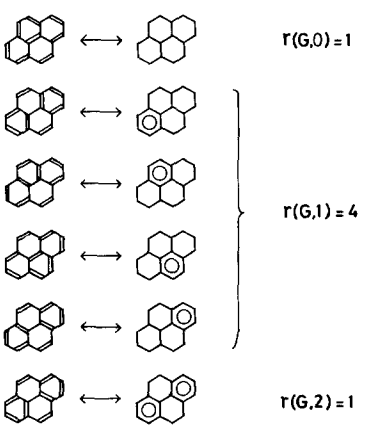


Fig. 4. One-to-one correspondence between Kekulé and sextet patterns

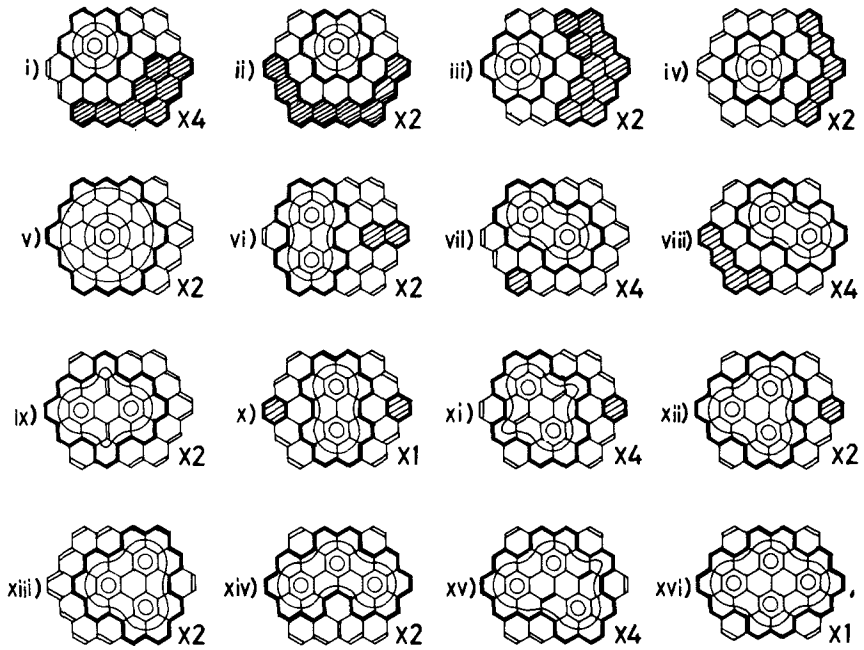


Fig. 5. Super sextets and their contribution to the sextet polynomial. The super sextet is represented by concentric circles and bold edges. The shaded polyhex can be resonant with the super sextet giving the following contributions: i) $x(1+8x+11x^2+2x^3)$, ii) $x(1+8x+16x^2+8x^3)$, iii) $x(1+10x+22x^2+12x^3+x^4)$, iv) $x(1+5x+4x^2)$, v) x, vi) $x^2(1+2x)$, vii) $x^2(1+x)$, viii) $x^2(1+4x+2x^2)$, ix) x^2, x) $x^2(1+x)^2$, xi) $x^2(1+x)$, xii) $x^3(1+x)$, xiii) x^3, xiv) x^3, xv) x^3, xvi) x^4. The total correction to $B_G(x)$ due to the super sextets can be obtained as $12x+96x^2+168x^3+60x^4+2x^5$ by adding these terms with weight given in the figure. The resultant $B_G(x)$ is $1+36x+306x^2+996x^3+1446x^4+984x^5+303x^6+42x^7+2x^8$, which is identical to what is obtained from Eq. (24) with $n=4$

(Fig. 6). Hereafter the term "sextet pattern" may include a super sextet. Then we propose the following Conjecture.

Conjecture. For any polyhex graph G there exists one-to-one correspondence between Kekulé and sextet patterns.

In the next section this conjecture plays a key role together with the following Remark.

Remark. If a hexagon in a polyhex graph contains at least one fixed bond, neither a proper nor an improper sextet can be drawn in that hexagon.

This remark is proved by the fact that any proper sextet can always be transformed into an improper sextet leaving the rest of the Kekulé pattern unchanged.

4. Recurrence relations and general formulae of sextet polynomials

We will show that the sextet polynomial of a polyhex graph can be obtained as the sum of the sextet polynomials of smaller polyhex graphs. By using this

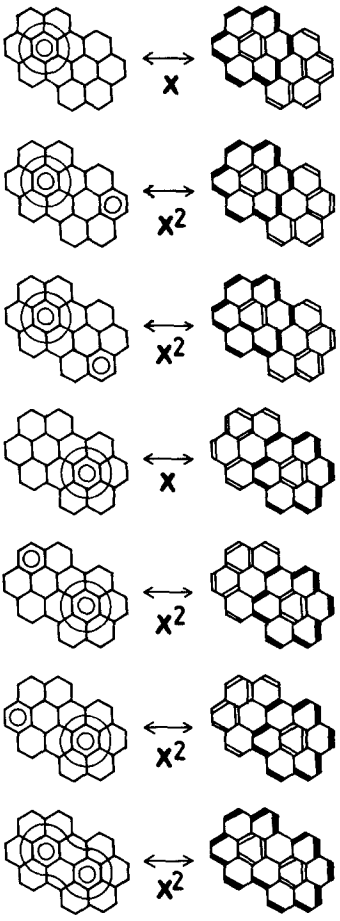


Fig. 6. One-to-one correspondence between Kekulé (right) and sextet (left) patterns containing a super sextet. In the Kekulé patterns the proper super sextets are marked with "solid" double bonds. Note the characteristic feature of the arrangement of the double bonds in the proper super sextet in phase with that of the proper sextet. The contribution of each pattern to the sextet polynomial is given below the arrows

recursive method, general expressions of sextet polynomials for several specific networks can be obtained as follows.

4.1. The parallelogram system $P_{m,n}$

First we will consider the parallelogram system constructed from $m \times n$ hexagons as shown in Chart. Let us denote this graph as $P_{m,n}$ and its sextet polynomial as $P_{m,n}(x)$. Further, each hexagon in $P_{m,n}$ is denoted as $r_{i,j}(i=1,2,\ldots,m,\ j=1,2,\ldots,n)$ as in Chart.

The $P_{1,n}$ series is known as the polyacene. The general expression of its sextet polynomial has already been obtained as

$$P_{1,n}(x)=1+nx[15]. \tag{4}$$

Obviously, $P_{1,n}(x)=P_{n,1}(x)$.

In the case of $m=2$, we can divide the set of the Kekulé patterns of $P_{2,n}$, $\{k\}$, into the following three distinctive subsets (Fig. 7). $\{k_A\}$: The subset of $\{k\}$ in

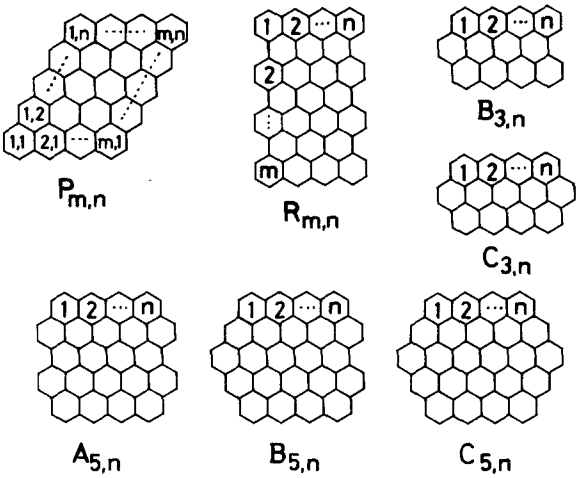


Chart.

which the left vertical bond of $r_{1,1}$, e_0, is double, $\{k_B\}$: the subset of $\{k\}$ in which e_0 is single and the right vertical bond of $r_{1,1}$, e_1, is double, and $\{k_C\}$: the subset of $\{k\}$ in which both e_0 and e_1 are single. Consider first the sextet patterns corresponding to the Kekulé patterns in $\{k_A\}$. In those Kekulé patterns $r_{1,1}$ cannot be a proper sextet because e_0 is fixed to be a double bond, and $r_{2,1}$ cannot also be a proper sextet because it has fixed bonds (i.e., from Remark). Then the sextet patterns derived from the Kekulé patterns in $\{k_A\}$ have a one-to-one correspondence with those of $P_{2,n-1}$ (Fig. 7). On the other hand all the sextet patterns corresponding to the Kekulé patterns in $\{k_B\}$ have a proper sextet in $r_{1,1}$, whereas $r_{1,i}$ $(i = 2, 3, \ldots, n)$ and $r_{2,1}$ cannot be a proper sextet from Remark. Then the sextet patterns derived from $\{k_B\}$ have an aromatic sextet in $r_{1,1}$ and have a one-to-one correspondence with those of $P_{1,n-1}$. In the third subset $\{k_C\}$, all the

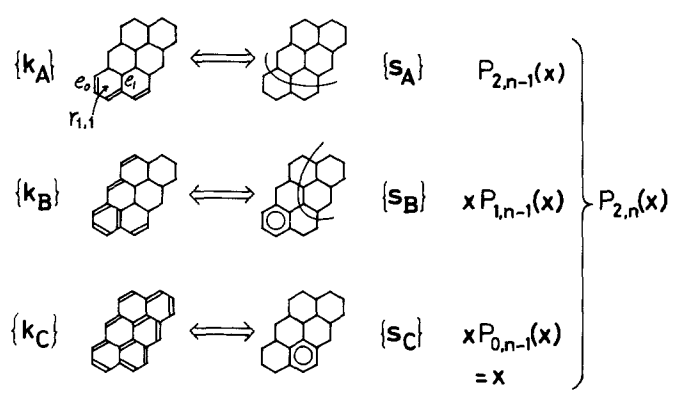


Fig. 7. Subsets of Kekulé patterns and the corresponding sextet patterns derived from the recursive process. See Eq. (5)

bonds are fixed by the first condition, and the sextet pattern corresponding to that Kekulé pattern has only one proper sextet on $r_{2,1}$. So we can get the recurrence relation of $P_{2,n}(x)$ as

$$P_{2,n}(x) = P_{2,n-1}(x) + xP_{1,n-1}(x) + x. \tag{5}$$

Note in the second term of the right hand side $P_{1,n-1}(x)$ is multiplied by x representing the aromatic sextet on $r_{1,1}$. By a successive application of this recurrence relation down to the initial condition, $P_{2,1}(x) = 1 + 2x$, and from Eq. (4), we get the general formula

$$\begin{aligned} P_{2,n}(x) &= 1 + 2nx + \frac{n(n-1)}{2}x^2 \\ &= 1 + \binom{2}{1}\binom{n}{1}x + \binom{2}{2}\binom{n}{2}x^2. \end{aligned} \tag{6}$$

In the case of $m = 3$, we can get the sextet polynomial, $P_{3,n}(x)$, by a similar way to $P_{2,n}(x)$. In this case we divide the whole set of the Kekulé patterns, $\{k\}$, into four subsets as follows: If we divide $\{k\}$ into three subsets as in the case of $P_{2,n}$, we obtain the three subsets $\{k_A\}$, $\{k_B\}$, and $\{k_C\}$ as shown in Fig. 8a. From Conjecture there exist three subsets of the sextet patterns $\{s_A\}$, $\{s_B\}$, and $\{s_C\}$ corresponding to $\{k_A\}$, $\{k_B\}$, and $\{k_C\}$, respectively. As in the case of $P_{2,n}(x)$ the sextet polynomial corresponding to the subsets $\{k_A\}$ and $\{k_B\}$ is expressed as $P_{3,n-1}(x) + xP_{2,n-1}(x)$. In $\{k_C\}$ a proper sextet cannot be placed on $r_{1,i}$ $(i = 1, 2, \ldots, n)$ nor $r_{2,i}$ $(i = 2, 3, \ldots, n)$. Contrary to the case of $P_{2,n}(x)$ a proper sextet may or may not be placed on $r_{2,1}$, since the right vertical bond e_2 of $r_{2,1}$ is not a d-fixed bond in $\{k_C\}$. Thus we further divide $\{k_C\}$ into two subsets depending that e_2 is double or single as shown in Fig. 8b. These subsets contribute $xP_{1,n-1}(x)$ and x, respectively, to $P_{3,n}(x)$. Consequently, the recurrence relation of $P_{3,n}(x)$ is expressed as

$$P_{3,n}(x) = P_{3,n-1}(x) + xP_{2,n-1}(x) + xP_{1,n-1}(x) + x, \tag{7}$$

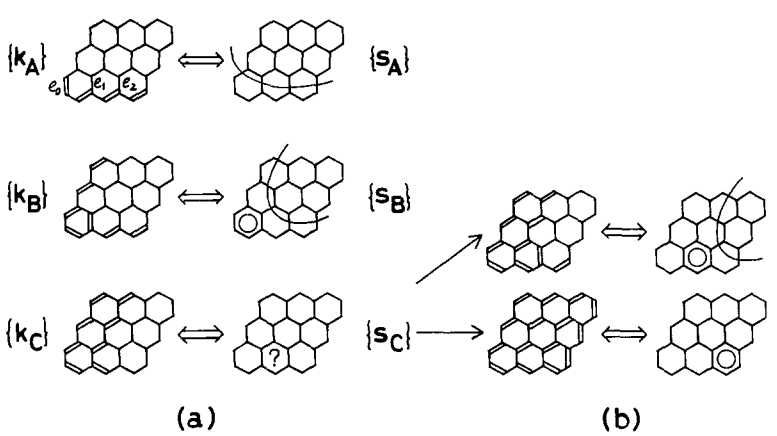


Fig. 8. Successive branching of the recurrence relation. See Eqs. (7) and (9)

and using the same method as in $P_{2,n}(x)$ we get the following general formula:

$$P_{3,n}(x) = 1 + \binom{3}{1}\binom{n}{1}x + \binom{3}{2}\binom{n}{2}x^2 + \binom{3}{3}\binom{n}{3}x^3. \tag{8}$$

Similarly we can obtain the general recurrence relation as follows:

$$P_{m,n}(x) = P_{m,n-1}(x) + x\sum_{i=0}^{m-1} P_{i,n-1}(x), \tag{9}$$

where we define $P_{0,n}(x) = 1$. And the general expression is obtained as

$$P_{m,n}(x) = \sum_{i=0}^{m}\binom{m}{i}\binom{n}{i}x^i, \qquad (m \le n) \tag{10}$$

which can be proved by induction.

From Eqs. (2) and (10), the number of the Kekulé patterns of $P_{m,n}$ is given by

$$P_{m,n}(1) = \sum_{i=0}^{m}\binom{m}{i}\binom{n}{i} = \sum_{i=0}^{m}\binom{m}{i}\binom{n}{m-i} = \binom{m+n}{m} \qquad (m \le n). \tag{11}$$

4.2. $R_{m,n}$ (*See Chart*)

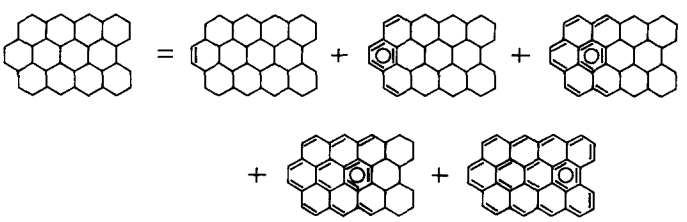
This system can be treated as m polyacenes being joined by $(n-1)$ rows of s-fixed bonds. Then,

$$R_{m,n}(x) = (1+nx)^m, \tag{12}$$

$$R_{m,n}(1) = (1+n)^m. \tag{13}$$

4.3. $B_{3,n}$ (*See Chart*)

The recurrence relation can be obtained by using the formula for $R_{2,n}$.



$$B_{3,n}(x) = R_{2,n}(x) + xR_{2,n-1}(x) + xR_{2,n-2}(x) + \cdots + xR_{2,1}(x) + x$$

$$= (1+nx)^2 + x\sum_{k=0}^{n-1}(1+kx)^2$$

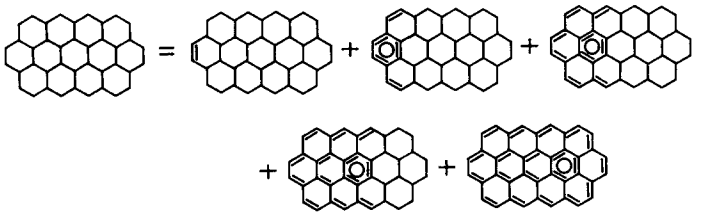
$$= 1 + 3nx + n(2n-1)x^2 + \frac{n(n-1)(2n-1)}{6}x^3, \tag{14}$$

and

$$B_{3,n}(1)=\frac{(n+1)(n+2)(2n+3)}{6}. \tag{15}$$

4.4. $C_{3,n}$ (See Chart)

Using the formula for $B_{3,n}$ series, we can obtain the general expression of $C_{3,n}(x)$ as follows:



$$\begin{aligned} C_{3,n}(x) &= B_{3,n}(x)+x(B_{3,n-1}(x)+B_{3,n-2}(x)+\cdots+B_{3,1}(x)+1) \\ &= B_{3,n}(x)+x\sum_{k=0}^{n-1} B_{3,k}(x) \\ &= 1+4nx+\frac{n(7n-5)}{2}x^2+n(n-1)^2x^3+\frac{n(n-1)^2(n-2)}{12}x^4, \end{aligned} \tag{16}$$

where $B_{3,0}(x)=1$, and

$$C_{3,n}(1)=\frac{(n+1)(n+2)^2(n+3)}{12}. \tag{17}$$

4.5. $C_{5,n}$ (See Chart)

In this large system, the recurrence relation is obtained by using those of two other systems, $A_{5,n}$ and $B_{5,n}$ (See Chart), in the same way as 4.2.–4.4.

$$C_{5,n}(x)=B_{5,n}(x)+x\sum_{i=0}^{n-1} B_{5,i}(x), \tag{18}$$

$$B_{5,n}(x)=A_{5,n}(x)+x\sum_{i=0}^{n-1} A_{5,i}(x). \tag{19}$$

The general expressions for $A_{5,n}$ and $B_{5,n}$ are obtained as follows [18]:

$$\begin{aligned} A_{5,n}(x) &= 1+7nx+3n(5n-2)x^2+\frac{n(41n^2-51n+13)}{3}x^3 \\ &\quad+\frac{n(n-1)(75n^2-103n+32)}{12}x^4 \\ &\quad+\frac{n(n-1)(89n^3-251n^2+214n-76)}{60}x^5 \end{aligned}$$

$$+\frac{n(n-1)(n-2)(21n^3-52n^2+47n-20)}{120}x^6$$

$$+\frac{n(n-1)^3(n-2)(n^2-2n+2)}{120}x^7, \tag{20}$$

$$A_{5,n}(1)=\frac{(n+1)(n+2)^3(n+3)(n^2+4n+5)}{120}. \tag{21}$$

$$B_{5,n}(x)=1+8nx+\frac{n(37n-19)}{2}x^2+\frac{n(112n^2-165n+59)}{6}x^3$$

$$+\frac{n(n-1)(29n^2-53n+23)}{3}x^4$$

$$+\frac{n(n-1)(82n^3-293n^2+337n-128)}{30}x^5$$

$$+\frac{n(n-1)(n-2)(152n^3-564n^2+679n-285)}{360}x^6$$

$$+\frac{n(n-1)(n-2)(12n^4-74n^3+168n^2-163n+63)}{360}x^7$$

$$+\frac{n(n-1)^2(n-2)^2(n-3)(3n^2-9n+8)}{2880}x^8, \tag{22}$$

$$B_{5,n}(1)=\frac{(n+1)(n+2)^2(n+3)^2(n+4)(3n^2+15n+20)}{2880}. \tag{23}$$

After rather complicated calculations we can get the following general expression.

$$C_{5,n}(x)=1+9nx+\frac{9n(5n-3)}{2}x^2+\frac{n(149n^2-249n+106)}{6}x^3$$

$$+\frac{n(n-1)^2(86n-103)}{6}x^4+\frac{n(n-1)^2(28n^2-89n+72)}{6}x^5$$

$$+\frac{n(n-1)(n-2)(316n^3-1464n^2+2201n-1059)}{360}x^6$$

$$+\frac{n(n-1)(n-2)(236n^4-1784n^3+4921n^2-5749n+2430)}{2520}x^7$$

$$+\frac{n(n-1)(n-2)(n-3)(105n^4-838n^3+2427n^2-2918n+1272)}{20160}x^8$$

$$+\frac{n(n-1)^2(n-2)^3(n-3)^2(n-4)}{8640}x^9. \tag{24}$$

This equation gives the correct sextet polynomial of the polyhex graph in Fig. 5. And the number of Kekulé patterns of $C_{5,n}$ is expressed by the following simple form:

$$C_{5,n}(1)=\frac{(n+1)(n+2)^2(n+3)^3(n+4)^2(n+5)}{8640}. \tag{25}$$

Note that the denominators of the right hand sides of Eqs. (17) and (25) are factored, respectively, as $1\cdot 2^2\cdot 3$ and $1\cdot 2^2\cdot 3^3\cdot 4^2\cdot 5$, and thus one can expect the next series

$$C_{7,n}(1)=\frac{(n+1)(n+2)^2(n+3)^3(n+4)^4(n+5)^3(n+6)^2(n+7)}{1\cdot 2^2\cdot 3^3\cdot 4^4\cdot 5^3\cdot 6^2\cdot 7} \tag{26}$$

and so on. These expressions are shown to be identical to the results obtained by Woodger [19] for a more general case as

$$C_{m,n}(1)=\prod_{k=(m+1)/2}^{m}\binom{n+k}{n}\Big/\prod_{k=1}^{(m-1)/2}\binom{n+k}{n}. \tag{27}$$

In these large systems containing super sextets, the expressions of $B_G(1)$'s as functions of n are found to be identical to what were obtained by other methods [5, 6, 8]. This suggests that the conjecture we have proposed without rigorous proof is generally valid. Further the concept of the supersextet can be well extended to the "enlarged aromatic sextet" in necklace-like benzenoid hydrocarbons such as kekulene [17], where a super proper sextet is modified to an "enlarged proper sextet".

The recursive method exemplified above may be formulated as follows:
1) For a given polyhex graph G choose a row of hexagons as the $\{r_{n,1}|n=1,2,\cdots,m\}$ hexagons in the case of $P_{m,n}$ series.
2) Denote the series of vertical lines in $\{r_{n,1}\}$ consecutively as $\{e_n|n=0,\ 1,\ 2,\cdots m\}$.
3) Fix e_0 to be double and enumerate the $B_G(x)$ for $G-[e_0]$. Put $k=1$.
4) Fix $\{e_n|n=0,1,2,\ldots k-1\}$ to be single but e_k double, and enumerate $B_G(x)$ for $G-[r_{k,1}]$ which should be multiplied by x corresponding to the fixed proper sextet on $r_{k,1}$. Go to 3) until $k=m$ [20].
5) The recurrence formula of $B_G(x)$ for the given graph G is the sum of all the terms obtained in 3) and 4).

We should note here that the one-to-one correspondence between the Kekulé and sextet patterns is also obtained alternatively by transforming the improper sextets into aromatic sextets [17]. Then we can get the same recurrence relation by dividing the Kekulé patterns according to this alternative criterion (Fig. 9).

In Table 1 are given the recurrence relations of the sextet polynomials obtained for several typical series of graphs. In deriving these results we used the newly proposed operator technique for obtaining effectively the recurrence relations [21]. The advantage of the sextet polynomial is not only in obtaining the number of the Kekulé patterns easily but also in getting useful information on the aromatic

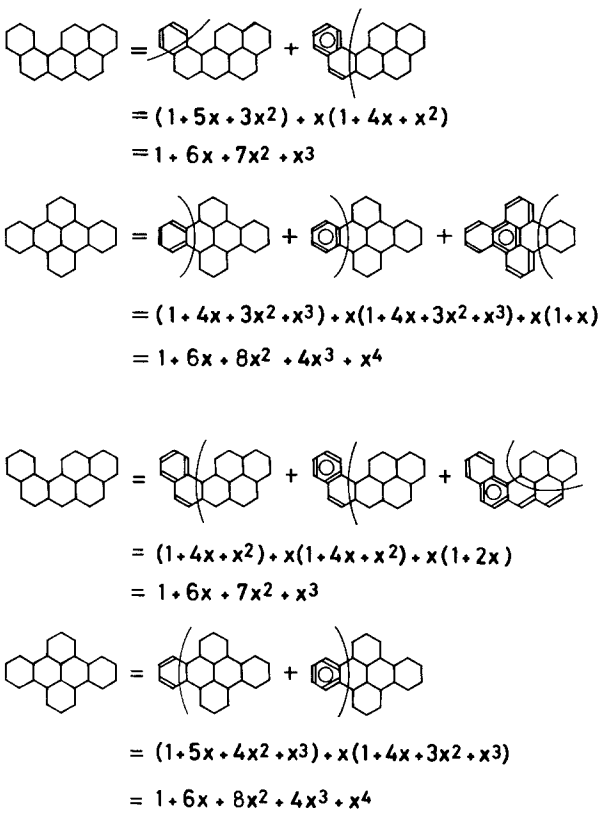


Fig. 9. Examples showing that the alternative choices of (a) proper and (b) improper sextets give the identical sextet polynomials

character of these molecules. For example, the over-all-index of aromaticity (OIA) proposed by Randić [22] and Aihara [10] can readily be obtained by the following relation

$$\mathrm{OIA} = 2B'_G(1)/B_G(1). \tag{28}$$

The general forms of OIA of several series of polyhex graphs are given in Table 2. These expressions are especially valuable for analysing the topological aspects of the aromaticity of infinitely large polyhex networks.

5. Maximum number of aromatic sextets

Deduced from a huge number of experimental data Clar postulated that the π-electronic properties of the ground state of a benzenoid hydrocarbon are well represented by a so-called Clar structure (or pattern) in which the maximum number of mutually resonant aromatic sextets are drawn [9]. It it is possible to draw two or more such patterns for a molecule, the set of those aromatic sextets are thought to migrate over the part or whole of the molecule (Fig. 10). Local

Table 1a. Recursion formulae and m/N values for some series of polyhexes

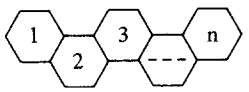
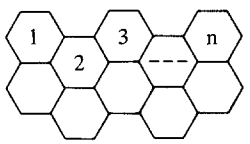
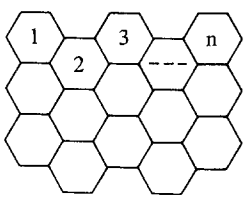
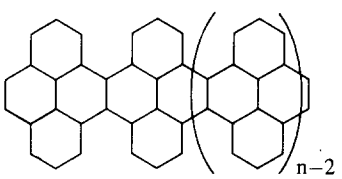
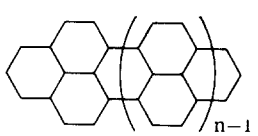
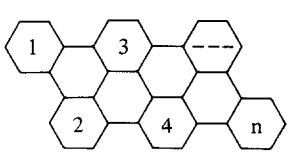
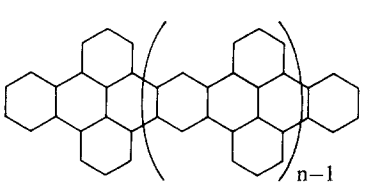
Series	Recursion Formula	$\frac{m}{N}$
W		$W_n(x) = W_{n-1}(x) + xW_{n-2}(x)$	$\frac{[(n+1)/2]}{n}$
D		$D_n(x) = (1+x)D_{n-1}(x) + xD_{n-2}(x) - x^2 D_{n-3}(x)$	$\frac{n}{2n}$
V		$V_n(x) = (1+x)V_{n-1}(x) + (2x+x^2)V_{n-2}(x) - x^2 V_{n-3}(x) - x^3 V_{n-4}(x)$	$\frac{n}{3n}$
E		$E_n(x) = (1+4x+x^2)E_{n-1}(x) - x^2 E_{n-2}(x)$	$\frac{2n}{4n}$
F		$F_n(x) = (1+2x)F_{n-1}(x) + x(1-x)F_{n-2}(x)$	$\frac{n+1}{3n+1}$
O		$O_n(x) = (1+x)O_{n-1}(x) + xO_{n-2}(x) - x^2 O_{n-3}(x)$	$\frac{2n}{4n-2}$
Q		$Q_n(x) = (1+5x+3x^2+x^3)Q_{n-1}(x) - x^2 Q_{n-2}(x)$	$\frac{3n+1}{5n+1}$

Table 1b. The sextet polynomials for the lower members of the series of graphs in Table 1a

$W_1(x) = 1 + x$	$E_1(x) = 1 + 4x + x^2$
$W_2(x) = 1 + 2x$	$E_2(x) = 1 + 8x + 17x^2 + 8x^3 + x^4$
$D_1(x) = 1 + 2x$	$F_1(x) = 1 + 4x + x^2$
$D_2(x) = 1 + 4x + x^2$	$F_2(x) = 1 + 7x + 9x^2 + x^3$
$D_3(x) = 1 + 6x + 6x^2 + x^3$	
	$O_1(x) = 1 + x$
$V_1(x) = 1 + 3x$	$O_2(x) = 1 + 2x + x^2$
$V_2(x) = 1 + 6x + 3x^2$	$O_3(x) = 1 + 4x + 3x^2 + x^3$
$V_3(x) = 1 + 9x + 15x^2 + 5x^3$	
$V_4(x) = 1 + 12x + 36x^2 + 28x^3 + 8x^4$	
$Q_1(x) = 1 + 6x + 8x^2 + 4x^3 + x^4$	
$Q_2(x) = 1 + 11x + 40x^2 + 62x^3 + 51x^4 + 25x^5 + 7x^6 + x^7$	

Note that $W_0(x) = D_0(x) = V_0(x) = E_0(x) = F_0(x) = O_0(x) = 1$, but $Q_0(x) = 1 + x$.

aromaticity of these molecules is thus expressed by the Clar pattern. Recently one of the present authors has shown that partial π-electron density maps of aromatic hydrocarbons well represent the local aromaticity of the molecule, supporting the Clar's postulate [23, 24]. It is worth while discussing the topological dependency of the maximum number of resonant aromatic sextets representing the Clar's pattern.

The maximum number m of the resonant aromatic sextets is, by definition, equal to the power of the last term of the sextet polynomial. The series of polyhex graphs studied here are classified into two depending that m stays constant or increases with N, the number of hexagons. Let us call the former class as 1-type (after linear acenes), while the latter as z-type (zigzag). As N goes to infinity, the ratio of m/N converges to zero and non-zero values, respectively, for 1- and z-types, indicating the difference in the stability of large π-electronic systems. The convergence limit of m/N for the z-type varies from series to series as shown

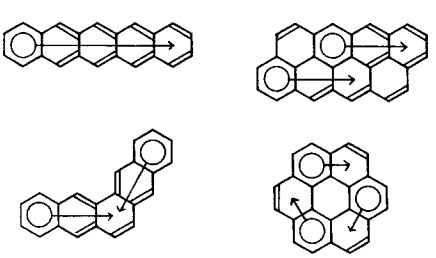
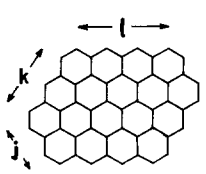


Fig. 10. Migration of aromatic sextets over a molecule

Table 2. The formulae of OIA's as a function of n

$P_{m,n}$	$P_{m,n}(1)=\binom{m+n}{n}$	$P'_{m,n}(1)=m\binom{m+n-1}{m}$	$\mathrm{OIA}=\dfrac{2mn}{m+n}$
$R_{m,n}$	$R_{m,n}(1)=(1+n)^m$	$R'_{m,n}(1)=mn(1+n)^{m-1}$	$\mathrm{OIA}=\dfrac{mn}{1+n}$
$B_{3,n}$	$B_{3,n}(1)=\dfrac{(n+1)(n+2)(2n+3)}{6}$		$\mathrm{OIA}=\dfrac{6n}{n+2}$
	$B'_{3,n}(1)=\dfrac{n(n+1)(2n+3)}{2}$		
$C_{3,n}$	$C_{3,n}(1)=\dfrac{(n+1)(n+2)^2(n+3)}{12}$		$\mathrm{OIA}=\dfrac{8n}{n+3}$
	$C'_{3,n}(1)=\dfrac{n(n+1)(n+2)^2}{3}$		
$A_{5,n}$	$A_{5,n}(1)=\dfrac{(n+1)(n+2)^3(n+3)(n^2+4n+5)}{120}$		
	$A'_{5,n}(1)=\dfrac{n(n+1)(n+2)(n+3)(7n^3+35n^2+60n+38)}{120}$		
	$\mathrm{OIA}=\dfrac{2n(7n^3+35n^2+60n+38)}{(n+2)^2(n+4n+5)}$		
$B_{5,n}$	$B_{5,n}(1)=\dfrac{(n+1)(n+2)^2(n+3)^2(n+4)(3n^2+15n+20)}{2880}$		
	$B'_{5,n}(1)=\dfrac{n(n+1)(n+2)(n+3)(n^4+10n^3+37n^2+60n+37)}{120}$		
	$\mathrm{OIA}=\dfrac{48n(n^4+10n^3+37n^2+60n+37)}{(n+2)(n+3)(n+4)(3n^2+15n+20)}$		
$C_{5,n}$	$C_{5,n}(1)=\dfrac{(n+1)(n+2)^2(n+3)^3(n+4)^2(n+5)}{8640}$		
	$C'_{5,n}(1)=\dfrac{n(n+1)(n+2)(n+3)(n+4)(21n^4+252n^3+1115n^2+2136n+1516)}{20160}$		
	$\mathrm{OIA}=\dfrac{6n(21n^4+252n^3+1115n^2+2136n+1516)}{7(n+2)(n+3)^2(n+4)(n+5)}$		

in Table 1, among which the so-called "fully benzenoid" hydrocarbons have the largest value of $\frac{3}{5}$, again supporting the Clar's intuition. The series of all the rest polyhexes, A, B, C, P, and R have the zero limiting value for m/N. As the last example of this 1-type the result of the following series of graphs $H_{j,k,l}(j \leq k \leq l)$



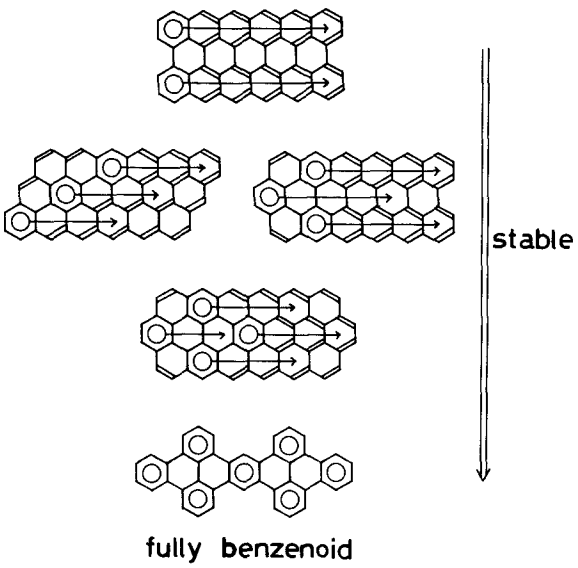


Fig. 11. Illustrative examples of the topological dependence of the maximum number m of resonant sextets. Note that stability and the value m for various "3-row polyhexes" increase as the direction of the vertical arrow up to the "fully benzenoid" hydrocarbons

will be given as

$$\frac{m}{N}(H_{j,k,l}) = jk/(jk+kl+lj-j-k-l+1) \quad (l \geq j+k-1) \tag{29}$$

$$= \left(jk - \sum_{i=l}^{j+k-2} [(j+k-l)/2]\right) \Big/ (jk+kl+lj-j-k-l+1)$$
$$(l < j+k-1). \tag{30}$$

These informations are useful for discussing the topological origin of the relative stability of these polyhex molecules as exemplified in Fig. 11, where the number of the resonant sextets in the Clar pattern represents the order of the stability reasonably well [25]. This line of analysis can be further extended by the supplemental combination of the results obtained with the molecular orbital methods [26] and other graph-theoretical considerations [23–28].

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