GRAPH-THEORETICAL ANALYSIS OF THE SEXTET POLYNOMIAL. PROOF OF THE CORRESPONDENCE BETWEEN THE SEXTET PATTERNS AND KEKULÉ PATTERNS*

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Abstract

Wenjie and Wenchen defined the sextet pattern and the super sextet and claimed to prove the one-to-one correspondence between the Kekulé and sextet patterns [1]. However, the set of sextet patterns of a polyhex G by their definition cannot be obtained unless we know all the Kekulé patterns of G. In this sense, their definition does not match the theory of the sextet polynomial. Here, the whole set of sextet patterns, including the super sextets of G, is defined from the properties of G, not from the Kekulé patterns. The one-to-one correspondence between the Kekulé and sextet patterns is thus proved.

1. Introduction

The sextet polynomial $B_G(x)$ has been defined by Hosoya and Yamaguchi as follows [2]:

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

where G is a graph representing a polycyclic aromatic hydrocarbon, $r(G, i)$ is the number of ways in which i mutually resonant sextets are chosen from G, and m is the maximum number of i for which $r(G, i)$ is non-zero. It was found that Clar's aromatic sextet theory [3] and the resonance theory are related mathematically through the following expressions [2]:

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

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

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where $K(G)$ is the number of Kekulé patterns for G, $B'_G(x)$ is the first derivative of $B_G(x)$, $G - (r)$ is the subgraph of G obtained by deleting hexagon r and all their adjacent edges from G, and the summation runs over all the hexagonal rings in G. These mathematical relations can be proved by the existence of the one-to-one correspondence between the Kekulé and sextet patterns [4]. So far, this correspondence has been proved only for "thin" polyhexes (fig. 1) [4]. For "fat" polyhexes (fig. 1), the theory of the sextet polynomial has included the ambiguity arising from the "super sextets" which was introduced without a proper definition in ref. [2] to keep (2) and (3).

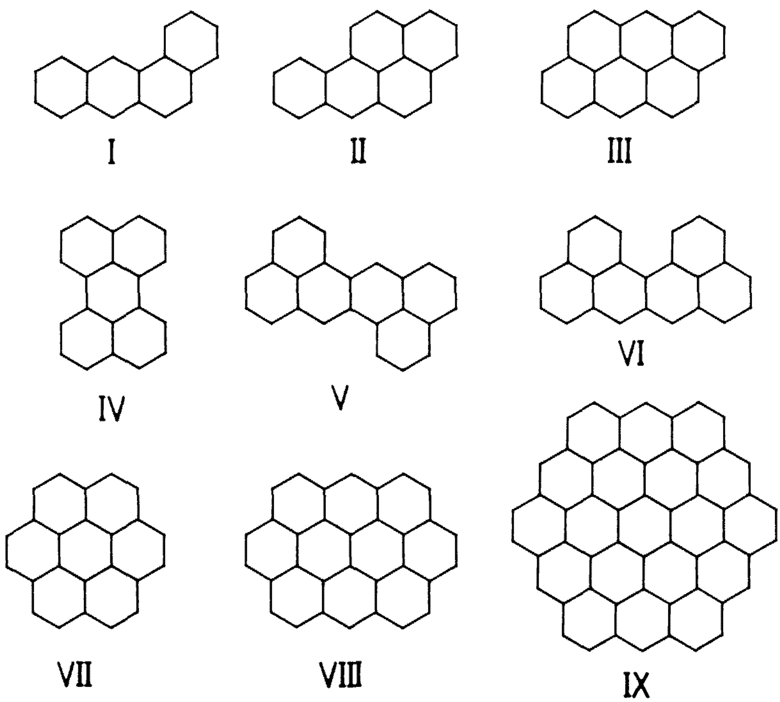


Fig. 1. Examples of holed polyhexes. Thin polyhexes (I, II, III, IV, and V) do not contain a coronene (VII) skeleton, while fat polyhexes (VII, VIII, and IX) do. Only graph VI is not a Kekulé polyhex. Among the Kekulé polyhexes, IV and V contain fixed edges, and they are not free polyhexes.

For any polyhex, Wenjie and Wenchen proposed the definitions of the sextet pattern and super sextet and claimed to prove the one-to-one correspondence between these sextet patterns and Kekulé patterns [1]. A sextet pattern by its definition is, however, derived from a Kekulé pattern. Hence, when we obtain the sextet polynomial of G, we must draw all the Kekulé patterns of G. Therefore, their approach is inappropriate to the theory of the sextet polynomial.

The aim of this paper is to reconstruct the theory of the sextet polynomial by explicitly defining the whole set of sextet patterns, including super sextets. Here, the sextet patterns are derived not from the Kekulé patterns but from the properties of the polyhex. Then, the one-to-one correspondence between the Kekulé and sextet patterns is proved in a way similar to that of ref. [4]. To perform this, polyhexes and their Kekulé patterns have to be examined in detail graph-theoretically.

2. Terms and notations

In the previous section, the terms "polyhex" and "ring" were introduced without definition. In this section, several terms and notations are defined explicitly to remove the ambiguity from the theory of the sextet polynomial.

$V(G)$:	the vertex set of graph G;
$E(G)$:	the edge set of graph G;
$D_G(u, v)$:	the distance between vertices u and v in graph G;
$d_G(v)$:	the degree of vertex v in graph G;
K_G:	the set of all Kekulé patterns for graph G. In this paper, each Kekulé pattern is denoted by the lower case letter k;
$K(G)$:	the number of Kekulé patterns of G;
Alternating path(cycle):	a path(cycle) whose edges are alternately single and double in a Kekulé pattern. A k-alternating path(cycle) is an alternating path(cycle) in a Kekulé pattern k;
Fixed edge:	an edge of graph G being double in any k in K_G or an edge being single in any k in K_G;
Free edge:	an edge being double not in all Kekulé patterns, i.e. a free edge is an edge not being a fixed edge;
$G - (G')$:	subgraph of G obtained by deleting G' and its adjacent edges from G (fig. 2);
$G - [G']$:	subgraph of $G - (G')$ obtained by deleting all the fixed edges from $G - (G')$ (fig. 2).

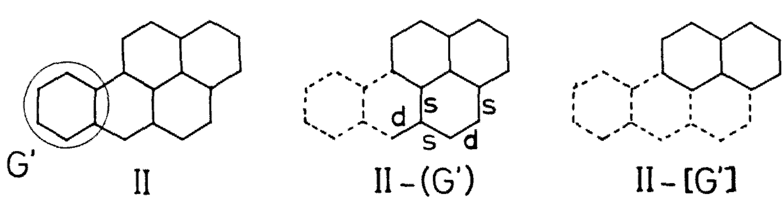


Fig. 2. Subgraphs of graph G. Edges labeled by s and d in $\text{II} - (G')$ are fixed single and fixed double edges, respectively.

For a planar graph, an area of the plane bounded by edges and containing neither edges nor vertices is called a finite region [5].

Ring: a cycle that bounds a finite region;

Resonant ring: a ring r of G is resonant if $K(G-(r)) \neq 0$. When $K(G-(r_i)-(r_j)) \neq 0$ for two independent rings r_i and r_j, they are mutually resonant. Similarly, three of more mutually resonant rings can be defined if possible.

In this paper, we adopt the definition of polyhexes by Gutman [6] as follows.

Polyhex: let C_G be a cycle on the two-dimensional hexagonal lattice. Then, a polyhex G is a graph consisting of all the vertices and the edges which either lie on C_G or are enclosed by C_G (fig. 1).

Kekulé polyhex: a polyhex for which $K(G) \neq 0$ (fig. 1). The set of all Kekulé polyhexes is denoted as KP. A vacant graph ϕ is included in KP. When the sets of all the thin and fat polyhexes are denoted as TP and FP, respectively, $KP = TP + FP$.

Free polyhex: a polyhex consisting only of free edges (fig. 1). The set of all free polyhexes is denoted as FP. A vacant graph ϕ is included in FP.

The sextet polynomial for a polyhex that has no Kekulé pattern is trivial. The sextet polynomial for a Kekulé polyhex G with fixed edges is given by the product of the sextet polynomials for the free polyhexes which are obtained by deleting fixed edges from G [1,3]. So, it is enough to consider sextet patterns and the sextet polynomial only for free polyhexes. To simplify the later discussion, free polyhexes and their subgraphs are to be laid on the plane so that a pair of parallel edges of a ring are vertical. Then, for these graphs and/or their Kekulé patterns, the following is defined:

L-edge: the farthest left vertical edge of a cycle;

R-edge: the farthest right vertical edge of a cycle;

Proper cycle: an alternating cycle in which all R-edges are double and all L-edges are single (fig. 3);

Improper cycle: an alternating cycle in which all L-edges are double and all R-edges are single (fig. 3);

Proper(improper) ring: a proper(improper) cycle that bounds a finite region (fig. 3);

R: a set of rings mutually resonant in graph G.

For a fat polyhex G, $G-[R]$ may contain some components not belonging to FP and having "large" rings (fig. 4). This is the reason why the one-to-one correspondence was not proved for a general polyhex [4]. Here, such a graph that contains "large rings" is called a holed polyhex and is defined as follows:

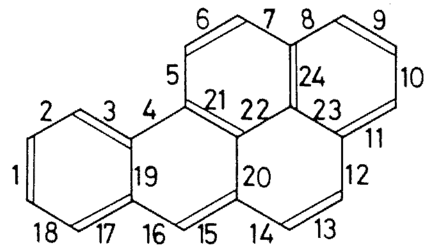


Fig. 3. Proper and improper cycles and rings. Each edge is labeled by a number as in the figure, and here, each cycle is denoted by the sequence of those numbers. Thus, (5,6,7,24,22,21) is a proper cycle and at the same time, a proper ring. Improper cycles are (1,2,3,19,17,18), (1,2,3,4,21,20,15,16,17,18), and (1,2,3,4,21,22,24,8,9,10,11,12,13,14,15,16,17,18). The first one is also an improper ring.

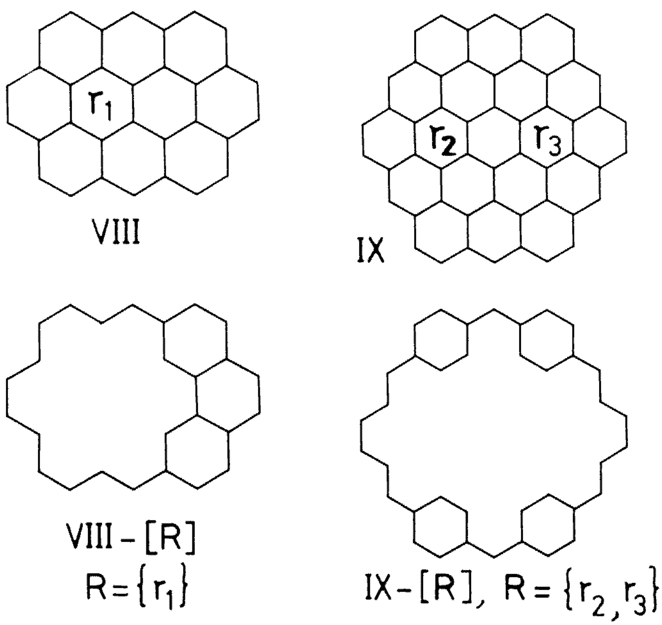


Fig. 4. Subgraphs not being free polyhexes.

Holed polyhex: a connected subgraph of a free polyhex having at least one Kekulé pattern, at least one ring with a length larger than six, and consisting only of free edges. The set of all holed polyhexes is denoted as *HP* (fig. 5).

Note here that for any R of a free polyhex G, each component of $G - [R]$ is either a free or a holed polyhex.

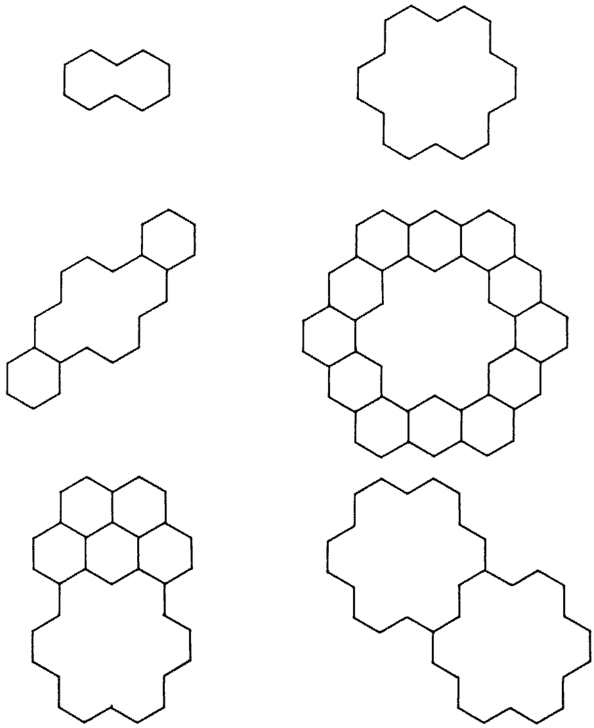


Fig. 5. Examples of holed polyhexes.

3. Preparation

Both free and holed polyhexes are bipartite graphs consisting only of free edges. The properties of these graphs play an important role in a later discussion; therefore, first of all, we will study these properties. Let us start with the theorem proved by Berge [7].

A matching M of G is a subset of $E(G)$ in which no two edges are adjacent to each other, and a maximum matching has the maximum number of edges among all the matchings of G. An unsaturated vertex is a vertex not incident with any edges in M.

THEOREM 1 (Berge [7])

An edge e is free if and only if, for an arbitrary maximum matching M, edge e belongs to an even alternating path beginning at an unsaturated vertex or to an alternating cycle.

A perfect matching is a maximum matching with no unsaturated vertex. As is well known, all the double edges in a Kekulé pattern constitute a perfect matching. Thus, it is clear that:

LEMMA 2

Let G be a graph such that $K(G) \neq 0$. Then, an edge e of G is free if and only if, for an arbitrary $k \in K_G$, edge e belongs to an alternating cycle.

In a bipartite graph, vertices can be classified into two groups, say, starred and unstarred, so that no two vertices in the same group are adjacent. For a certain class of bipartite graphs, the following properties are proved.

THEOREM 3

Let G be a bipartite graph consisting only of free edges, and $K(G) \neq 0$. Then, for any Kekulé pattern $k \in K_G$, there is an alternating path between any starred and unstarred vertices in which both end edges are double in k.

Before proving this theorem, we should introduce the concept "alternating tree" [8]. An alternating tree J is defined as a tree graph J each of whose edges joins an inner vertex to an outer vertex so that each inner vertex of J meets exactly two edges of J. Therefore, an alternating tree is a bipartite graph whose vertices are classified into two groups, inner and outer (fig. 6).

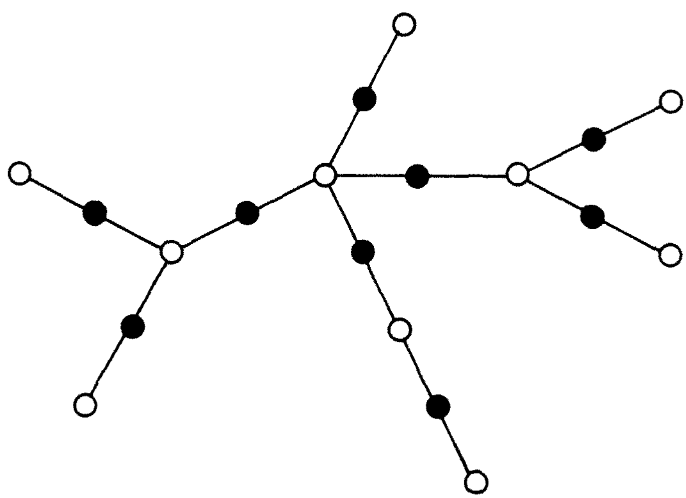


Fig. 6. An alternating tree. o: outer vertex; •: inner vertex.

Proof of theorem 3

Let x be a starred vertex of G. Construct an alternating tree J for k with the following procedure (fig. 7a):

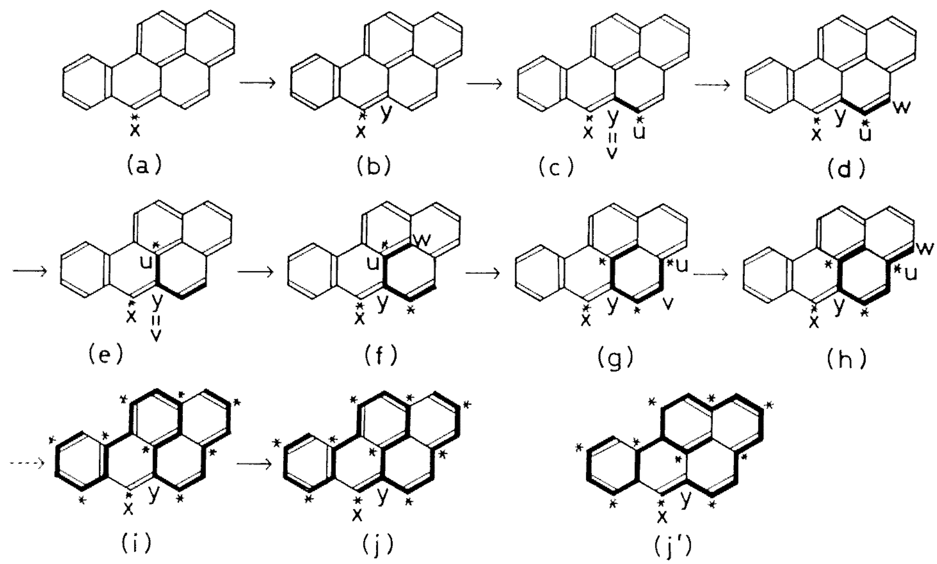


Fig. 7. Construction of a spanning tree subgraph $J + x$. (a) Kekulé pattern k of graph II and a starred vertex x is shown. Vertices labeled by * are starred. (b) By procedure 1, vertex y is determined. (c,d,...,h) and (i) J is extended by repeating procedures 2 and 3 until J contains all the vertices of graph II except x, as shown in (i). (j) By procedure 4, one can obtain the spanning tree $J + x$. (j') If one chooses the outer vertices u in a different way, one may obtain another spanning tree, as in (j').

(1) There is an unstarred vertex y such that the edge (x, y) is double in k. Let $J = y$, and y be an outer vertex (fig. 7b).

(2) Choose an outer vertex υ from $V(J)$. If there is a vertex $u(\neq x)$ in G such that $(u, \upsilon) \in E(G)$ and $u \notin V(J)$, extend J by $V(J) = V(J) + u$ and $E(J) = E(J) + (u, \upsilon)$ (fig. 7c, 7e, and 7g). Then go to (3). If there is not such a vertex u for any outer vertex (fig. 7i), go to (4).

(3) By definition, $d_J(u)$ must be two. Extend J by $V(J) = V(J) + w$ and $E(J) = E(J) + (u, w)$, where the edge (u, w) is double in k (fig. 7d, 7f, and 7h). Go to (2).

(4) Construct a tree subgraph $J + x$ such that $V(J + x) = V(J) + x$ and $E(J + x) = E(J) + (x, y)$ (fig. 7j).

The obtained subgraph $J + x$ is a spanning tree subgraph of G for the following reason: Suppose that in a Kekulé pattern k we cannot extend $J + x$ to a spanning tree of G any longer. Let G_a be a subgraph of G whose vertex set $V(G_a) = V(J + x)$ and whose edge set $E(G_a)$ includes all such edges in $E(G)$ that connect two vertices belonging to $V(J + x)$. Let G_b be $G - (G_a)$, and E_{ab} be the set of all the edges connecting G_a and G_b. Each edge in E_{ab} is denoted as $e_i = (u_i, \upsilon_i)$ $(i = 1, 2, \ldots)$, where $u_i \in G_a$ and $\upsilon_i \in G_b$. Note the following facts: (i) Each u_i is an inner vertex for, if u_i is outer, we can extend j by procedure (2). This means that all u_i's are incident to double edges belonging to $E(G_a)$ (see procedure (3)). Therefore, all e_i's are single. (ii) In J, each edge joins an inner vertex to an outer vertex by definition, and the root vertex y is outer and unstarred. So, in J, all the inner vertices are starred and all the outer vertices are unstarred.

Consider an edge $e_1 = (u_1, v_1)$. From lemma 2, there is a k-alternating cycle C including e_1. In C, there must be an edge $e_j = (u_j, v_j)$ for which $e_j \neq e_1$ and $e_j \in E_{ab}$. If not, C cannot be a cycle. As noted above, the vertex u_j is inner and starred. Then, the length of an alternating path between u_1 and u_j on C is even, and recall that both e_1 and e_j are single. Therefore, C cannot be an alternating cycle. This contradicts the assumption that all the edges of G are free.

Consequently, along the edges of $J + x$ one can find an alternating path from a starred vertex x to any unstarred vertex in which both end edges are double in k. ■

THEOREM 4

Let G be a bipartite graph consisting only of free edges, and $K(G) \neq 0$. Then, all the rings of G are resonant, namely, for an arbitrary ring r in G, $K(G - (r)) \neq 0$.

Proof

Suppose that for a ring r of G, $K(G - (r)) = 0$. Let $G' = G - (r)$ and E_r be the set of all edges connecting G' and r. Consider a Kekulé pattern $k \in K_G$. In k, if all the edges in E_r are single, $K(G - (r)) \neq 0$. Therefore, there are double edges in E_r. Let us denote one of these edges as $e_1 = (u_1, u_1')$, where $u_1 \in r$ and $u_1' \in G'$ (chart 1). Denote the vertices

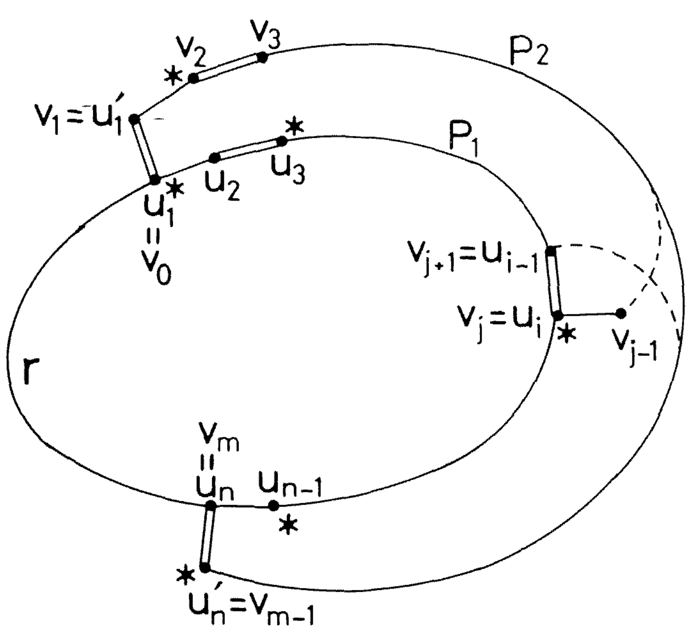


Chart 1.

on r as u_i ($i = 1, 2, 3, \ldots$), consecutively. One can choose a k-alternating path P_1 on r from u_1 to a vertex u_n that is incident on a double edge $e_n = (u_n, u'_n) \in E_r$ (chart 1). If there is no such vertex u_n, the length of r is odd and this is contradictory to G being a bipartite graph. Let u_1 be starred. As both end edges of P_1 are single, the length of P_1 is odd. Then, u_n is unstarred. From theorem 3, there is a k-alternating path P_2 in G from u_1 to u_n, both ends of which are double.

No vertex in P_2 is included in P_1 for the following reason: Let us denote $P_2 = (v_0(= u_1), e_1, v_1(= u'_1), e_2, v_2, \ldots, v_{m-1} (= u'_n), v_m(= u_n))$. Suppose that $v_j(=u_i) \in P_2$ and $v_i \notin P_2$ ($i = 1, 2, \ldots, j-1$). As the edge $e_j = (v_{j-1}, v_j)$ should belong to E_r, it is single. Then, the distance between $v_0(=u_1)$ and v_j on P_2 is even, and $v_j(= u_i)$ is starred. This means that the suffix i is odd and P_2 includes a double edge $(v_j(= u_i), v_{j+1}(= u_{i-1}))$. So, any path from $v_{j+1}(= u_{i-1})$ to $v_{m-1}(= u'_n)$ must come across the path $(v_0(= u_1), e_1, v_1(= u'_1), e_2, v_2, \ldots, v_{j-1}, e_j, v_j(= u_i))$. This contradicts that P_2 is an alternating path (chart 1). Therefore, $P_1 + P_2$ constructs a k-alternating cycle C.

Replace all the double edges on C into single and all the single edges into double. By repeating similar replacements, one can find a Kekulé pattern in which all the edges belonging to E_r are single. Then, $K(G - (R)) \neq 0$. ■

4. Sextet patterns and super sextets

Theorem 4 is the reason why the coefficient of the term x of the sextet polynomial for a thin polyhex G is equal to the number of hexagonal rings of G [1,6,9,10], and why the super sextet should be introduced for some fat polyhexes.

Now, the set of sextet patterns of a free polyhex G, S_G, is defined as the set obtained by the following procedure:

(1) Choose a set of mutually resonant rings from G, and draw circles in these rings to obtain a sextet pattern. Let S_G be the set of all these possible distinct sextet patterns. A sextet pattern with no circle must be included in S_G. This set can be obtained by considering combinations of resonant rings systematically (fig. 8a). Let A_i be the set of all aromatic rings in a sextet pattern s_i.

(2) Choose a sextet pattern $s_i \in S_G$ for which a component(s) of $G - [A_i]$ belongs to HP (s_i in fig. 9). If there is no such sextet pattern, go to (4).

(3) Choose a ring r_h of $G - [A_i]$ which is not a ring in G. Obtain a sextet pattern s_j by drawing circles on G in all rings and cycles belonging to A_i and in the cycle corresponding to r_h (s_j in fig. 9). If $s_j \notin S_G$, then add s_j to S_G. $A_j = A_i + r_h$. Go to (2).

(4) End.

A ring with a circle in the sextet pattern is called an aromatic ring. The explicit definition of a super sextet is no longer necessary, because the explicit definition of the set of sextet patterns is given. A super sextet is a cycle (not a ring) with a circle surrounding some mutually resonant rings and cycles in the sextet pattern (fig. 10).

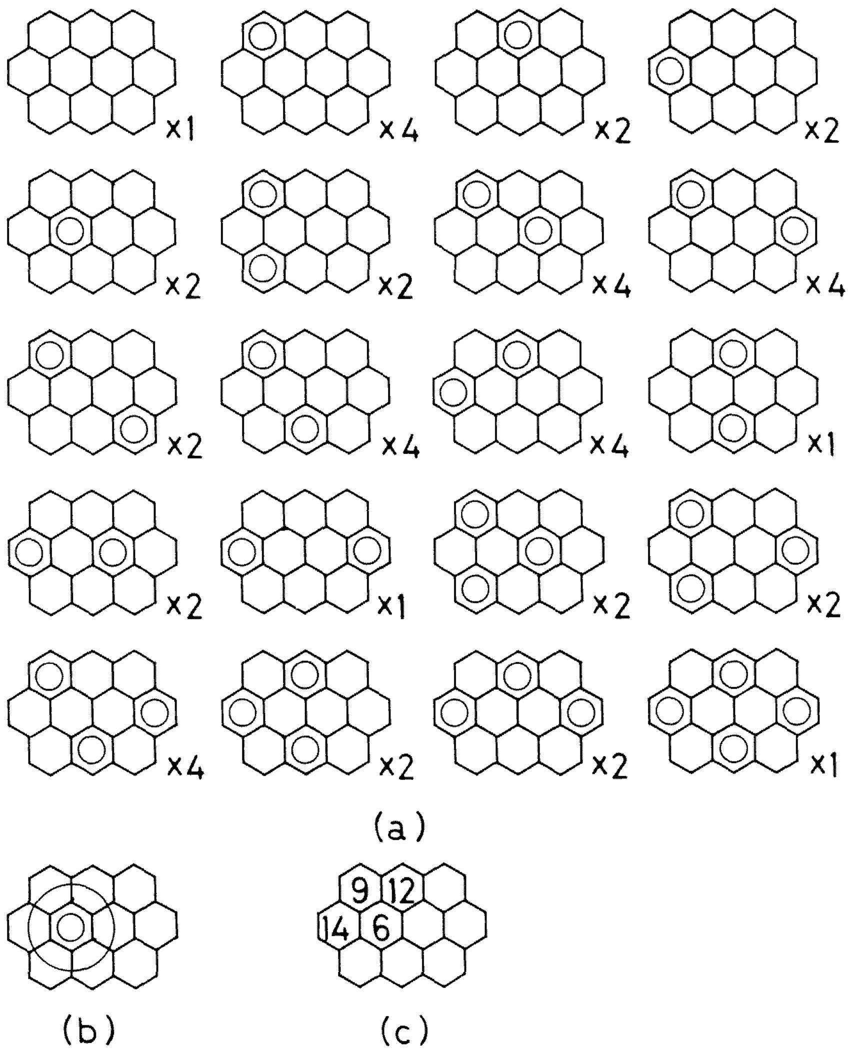


Fig. 8. All the sextet patterns of VIII. (a) Sextet patterns without super sextets. (b) Sextet patterns with super sextets. (c) The number in ring r_i denotes $K(G-(r_i))$. $B_{\mathrm{VIII}}(x) = 1 + 12x + 24x^2 + 12x^3 + x^4$. Then, $B_{\mathrm{VIII}}(1) = 50$ and $B'_{\mathrm{VIII}}(1) = 100$. Independently, we can obtain $K(\mathrm{VIII}) = 50$ and $\sum K(G-(r_i)) = 9 \times 4 + 12 \times 2 + 14 \times 2 + 6 \times 2 = 100$ from (c).

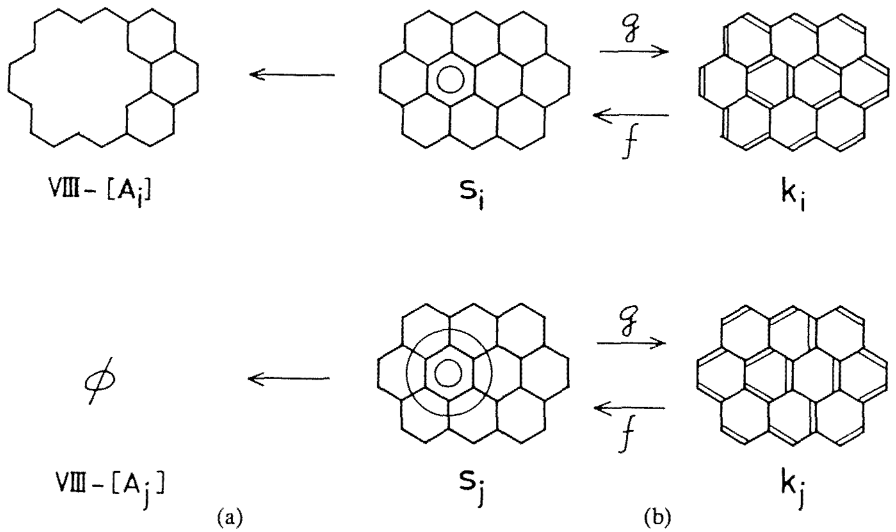


Fig. 9. Sextet patterns with and without a super sextet of VIII. (a) For s_i, VIII – $[A_i]$ is a holed polyhex. Then, a sextet pattern s_j is added to S_{VIII}. Subgraph VIII – $[A_j]$ is the vacant graph belonging to FP. (b) The one-to-one correspondence between s_i, s_j and k_i, k_j.

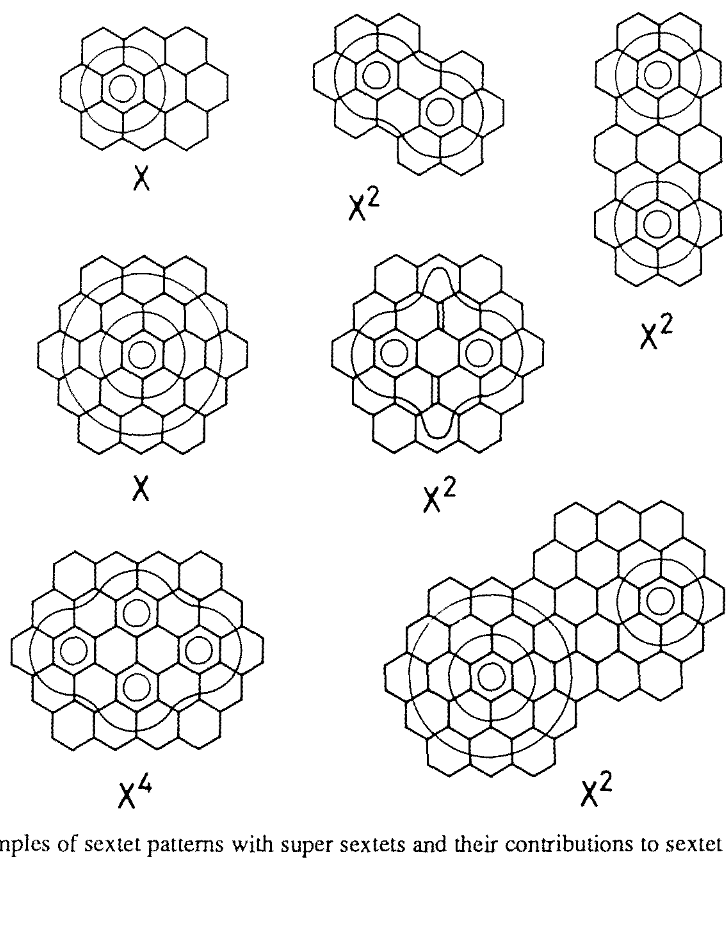


Fig. 10. Examples of sextet patterns with super sextets and their contributions to sextet polynomials.

Recall that the coefficients of the sextet polynomial, the $r(G, i)$'s, have been defined as the number of ways in which i mutually resonant sextets are chosen from G (eq. (1)), where the sextets obviously mean rings in the above discussion. Thus, the sextet polynomial is defined rigorously as follows.

For a free polyhex G, the sextet polynomial $B_G(x)$ is defined by eq. (1), where $r(G, i)$ is the number of ways of choosing i mutually resonant "rings" from G. $r(G, 0)$ is defined as unity. Therefore, the sextet polynomial for the vacant graph ϕ is unity.

From the above definition, the contribution of s to the sextet polynomial is x^i, where i is the number of aromatic rings regardless of the existence of super sextets as in fig. 10. Therefore, the sextet polynomial can be understood as a counting polynomial of sextet patterns classified by the number of aromatic rings (fig. 8).

5. Definition of a root Kekulé pattern and its properties

The one-to-one correspondence between the Kekulé and sextet patterns will be proved in a way similar to that in ref. [4], where the root Kekulé pattern played an important role. In ref. [4], the root Kekulé pattern was defined only for free polyhexes. Here, the definition is modified as follows.

For a free or holed polyhex, a root Kekulé pattern is a Kekulé pattern that has no proper rings.

The uniqueness of a root Kekulé pattern will be proved using the following theorems.

THEOREM 5

Let C be an alternating cycle in a Kekulé pattern k of a graph G ($FP \cup HP$). If an L-edge is single, C is a proper cycle, and if double, C is an improper cycle. If an R-edge of C is single, C is an improper cycle, and if double, C is a proper cycle.

Proof

Part 1: Without loss of generality, one can assign to each of all the vertices in G either a starred or an unstarred vertex so that each vertical edge in G connects an "upper" starred vertex with a "lower" unstarred one (chart 2). Let $k \in K_G$, and $C = (v_0, e_1, v_1, e_2, \ldots, v_{n-1}, e_n, v_0)$ be a k-alternating cycle. Suppose that $e_1 = (v_0, v_1)$ is an L-edge of C and that v_0 is unstarred. If $e_i = (v_{i-1}, v_i)$ is an R-edge of C, v_{i-1} is starred and v_i is unstarred, for, if v_{i-1} is unstarred, C cannot be a cycle or e_i cannot be an R-edge, as shown in chart 2. Since both v_0 and v_i are unstarred, $D_C(v_0, v_i)$ is even. In C, therefore, when e_1 (an L-edge) is single, e_i (an R-edge) is double, and when e_1 is double, e_i is single.

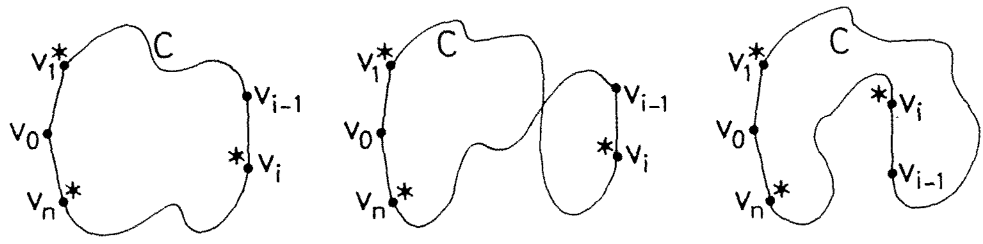


Chart 2.

Part 2: Let $e_i = (v_{i-1}, v_i)$ and $e_j = (v_{j-1}, v_j)$ be L-edges of C and both v_i and v_j be upper starred vertices. Note that in a polyhex, two vertical edges cannot be adjacent. So, v_{i-1} and v_j are connected by a path P. The length of P is odd, for v_{i-1} is unstarred and v_j is starred (chart 3). Then, if one of the L-edges of C is single (or double), all the L-edges are single (or double). The same is true for R-edges.

Parts 1 and 2 complete the proof.

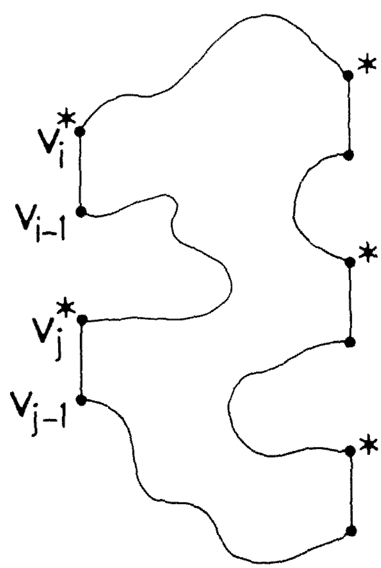


Chart 3.

THEOREM 6

In a Kekulé pattern $k \in K_G$ $(G \in (FP \cup HP))$, an arbitrary proper cycle contains a proper ring.

Proof

Let C be a proper cycle and denote $C = (v_0, v_1, \ldots, v_j, v_{j+1}, \ldots, v_n, v_0)$, where $e_1 = (v_0, v_1)$ is a single L-edge and $e_{j+1} = (v_j, v_{j+1})$ is a double R-edge of C (chart 4).

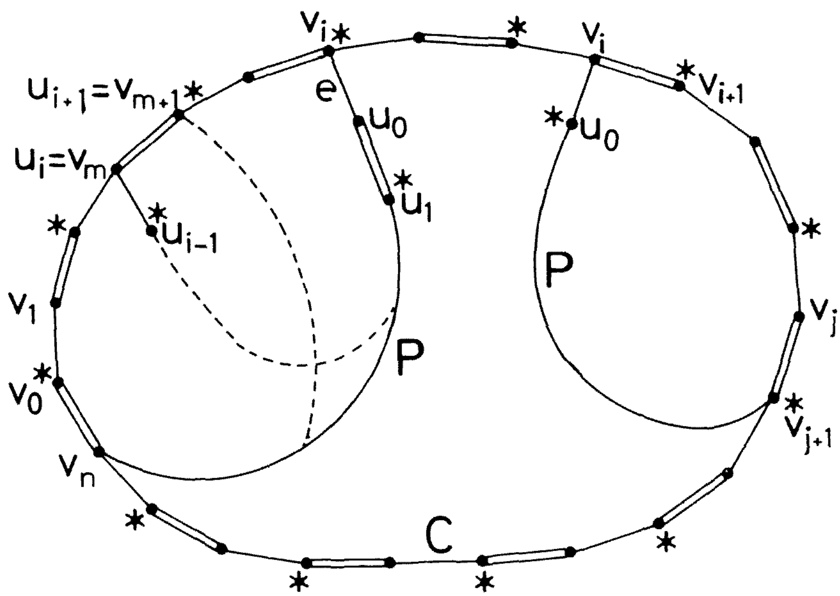


Chart 4.

Let v_0 be starred. If C is a ring, the proof is trivial. Then, consider a case where C is not a ring.

There is an edge $e = (v_i, u_0)$, where $v_i \in C$ and $u_0 \notin C$ (chart 4).

Case 1, where v_i is starred. In this case, u_0 is unstarred. From theorem 3, one can choose a k-alternating path P between u_0 and v_0 in which both end edges are double. All the vertices in C except v_0 and v_n cannot be included in P, for the following reason: Since both terminal edges of P are double, edge (v_n, v_0) is contained in P. Let us denote P by $P = (u_0, u_1, u_2, \ldots, v_n, v_0)$. Suppose that there is such a vertex $u_i (= v_m)$ that belongs to both P and C, and $u_j \notin C$ for $j = 1, 2, \ldots, i-1$. As u_i is incident on a double edge on C, edge (u_{i-1}, u_i) is single. Therefore, the length of an alternating path $P_1 = (u_0, u_1, \ldots, u_{i-1}, u_i(= v_m))$ is even. This means that $u_i(= v_m)$ is unstarred. Then, a double edge $(v_m(= u_i), v_{m+1})$ must be included in P. An alternating path from $v_{m+1}(= u_{i+1})$ to v_n must come across P_1. This contradiction ensures that $(v_0, v_1, \ldots, v_i, u_0) + P$ is an alternating cycle. Further, it is a proper cycle, for it includes a single L-edge (v_0, v_1).

Case 2, where v_i is unstarred. In this case, u_0 is starred. From theorem 3, one can choose a k-alternating path P between u_0 and v_j in which both end edges are double. v_j is incident on a double edge (v_j, v_{j+1}). Then, (v_j, v_{j+1}) is in P. A cycle $(u_0, v_i, v_{i+1}, \ldots, v_j) + P$ is an alternating cycle which can be proved in a similar way to that of case 1. Further, it is a proper cycle, for it includes a double R-edge (v_j, v_{j+1}).

In both cases, the new cycle has a smaller length than that of C. By repeating the reduction of a proper cycle according to cases 1 or 2, one can find a proper ring contained in the proper cycle. ■

THEOREM 7

For any free and holed polyhex, there exists exactly one root Kekulé pattern.

Proof

For any free and holed polyhex consisting of one cycle, theorem 7 is true.

Let G be a graph belonging to $FP \cup HP$ consisting of the smallest number of rings for which theorem 7 is not true, and e_0 be an L-edge of G. Let K_s and K_d be the sets of Kekulé patterns in each of which e_0 is single and double, respectively (figs. 10a,b). Obviously, $K_G = K_s + K_d$.

Case 1. Consider a Kekulé pattern k belonging to K_s. Since e_0 is free, there is an alternating cycle C containing e_0. C is a proper cycle, from theorem 5. Then, k has a proper ring inside C, from theorem 6. Therefore, k cannot be the root Kekulé pattern (fig. 11a).

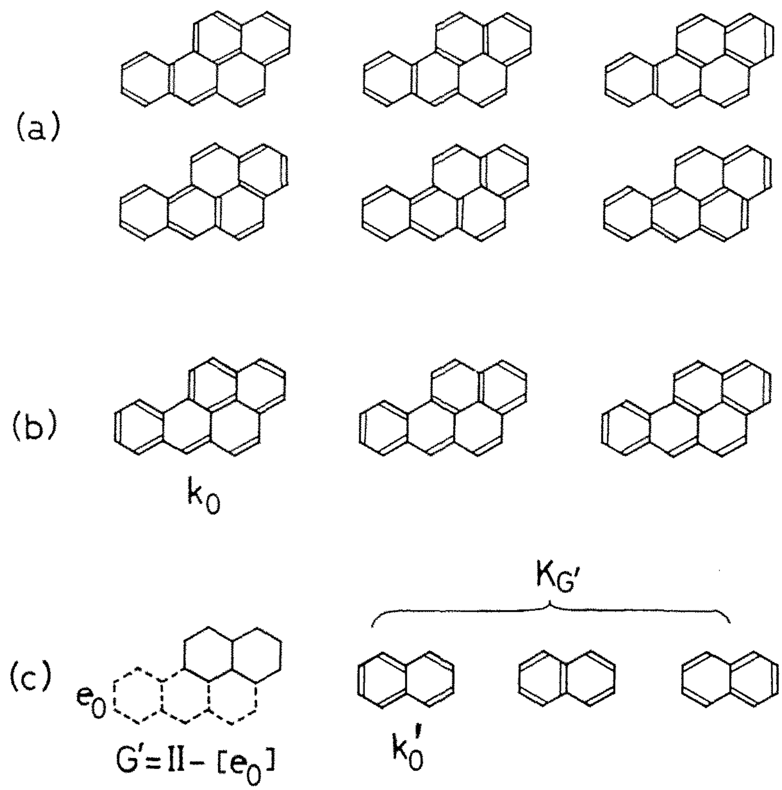


Fig. 11. Kekulé patterns of graphs II and II $-$ [e_0]. (a) Six Kekulé patterns in K_d. (b) Three Kekulé patterns in K_s. Among them, k_0 is the root Kekulé pattern of II. (c) Edges denoted by dashed lines are deleted from G to obtain G'. k'_0 is the root Kekulé pattern of G'.

Case 2. Consider K_d. Let $G' = G - [e_0]$, and E_{del} be the set of all edges being fixed in $G - (e_0)$ and of e_0. When we delete all the edges belonging to E_{del} from every Kekulé pattern in K_d, we can obtain $K_{G'}$ (fig. 11c). Since each component of G' is either a free or a holed polyhex containing a smaller number of rings than that of G, there is exactly one root Kekulé pattern for G', from the assumption. By tracing back e_0 and the deleted edges to the root Kekulé pattern, one obtains exactly one root Kekulé pattern k_0 of G (fig. 11b). Note here that all edges belonging to E_{del} cannot contribute to a proper ring of k_0, for the following reason: Suppose that in k_0 there is a proper ring r_i which contains the edge e_f belonging to E_{del}. From theorem 5, all the L-edges of r_i are single. So, the double L-edge e_0 cannot be contained in r_i. Therefore, we can obtain a Kekulé pattern belonging to K_d in which r_i is an improper ring and all other edges are unchanged. This contradicts that e_f is fixed in K_d.

Cases 1 and 2 complete the proof.

6. One-to-one correspondence between the Kekulé and sextet patterns

Here, mappings f and g are defined as follows.

$f: K_G \to S_G$: For any Kekulé pattern $k \in K_G$, $f(k)$ is determined by the following procedures (figs. 9b, 12):

*f*1. Let R be the set of all rings which are proper rings in a Kekulé pattern $k \in K_G$. If all components of $G - [R]$ belong to FP, go to *f*4. Otherwise, put $i = 1$.

*f*2. Let $G_i = G - [R]$. If k has proper cycles on holes of G_i, add those cycles to R. Otherwise, go to *f*4.

*f*3. Put $i = i + 1$ and go to *f*2.

*f*4. For G, put a circle in each ring or cycle belonging to R.

$g: S_G \to K_G$: For any sextet pattern $s \in S_G$, $g(s)$ is determined by the following procedures (figs. 9b, 12):

*g*1. For G, draw proper cycles in all the rings and cycles which have circles in s.

*g*2. In the remaining part of G, draw a Kekulé pattern so that no proper ring appears.

THEOREM 8

Let G be a free polyhex. For any $k \in K_G$, there exists $f(k)$ in S_G, and $f(k_i) \neq f(k_j)$ for $k_i \neq k_j$.

Proof

The definition of mutually resonant rings and theorem 4 ensures the existence of $f(k_i)$.

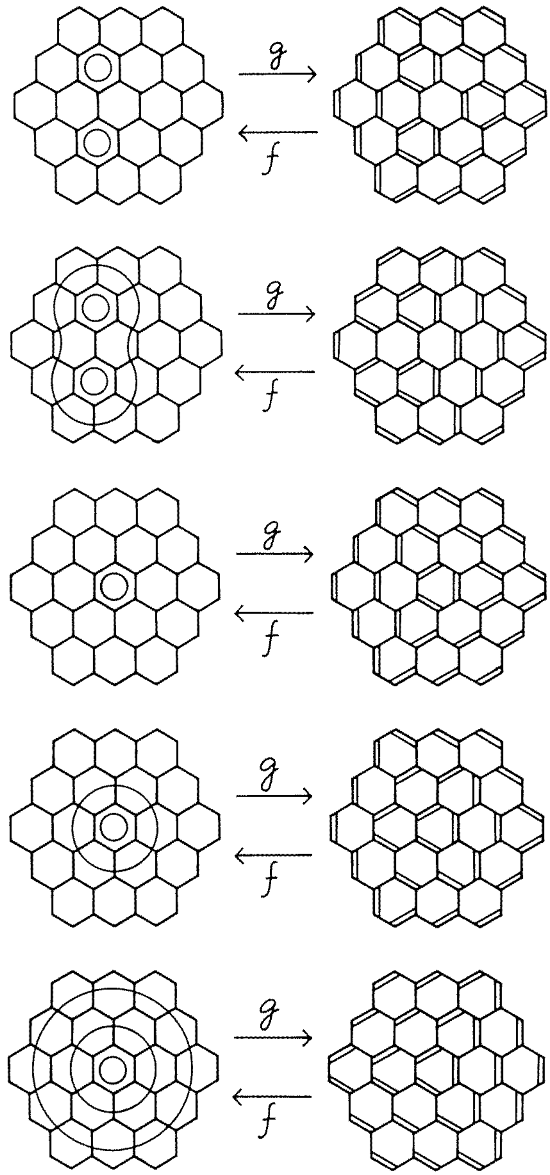


Fig. 12. Examples of the one-to-one correspondence between the Kekulé and sextet patterns through mappings f and g.

For k_i, let us denote R_i as the set obtained by $f1$–$f4$. Obviously, $k_i \neq k_j$ for $i \neq j$. Therefore, from theorem 7, there must be differences between R_i and R_j if $k_i \neq k_j$. This leads to the conclusion that $f(k_i) \neq f(k_j)$ for $k_i \neq k_j$. ■

THEOREM 9

Let G be a free polyhex. For any $s \in S_G$, there exists $g(s)$ in K_G, and $g(s_i) \neq g(s_j)$ for $s_i \neq s_j$.

Proof

From the definition of resonant rings and from theorem 4, $K(G - [A_i]) \neq 0$, where A_i is the set of all rings and cycles having circles in s_i. From theorem 7, procedure $g2$ is always possible, i.e. there is $g(s_i)$ in K_G. From the definition, $s_i \neq s_j$ for $i \neq j$. This means $A_i \neq A_j$ for $s_i \neq s_j$. Therefore, $g(s_i) \neq g(s_j)$ for $s_i \neq s_j$. ■

Theorems 8 and 9 complete the proof of the one-to-one correspondence between the Kekulé and sextet patterns and relation (2). Relation (3) is easily proved by (2) and the definition of the contribution of a sextet pattern to the sextet polynomial given above.

7. Concluding remarks

In this paper, the definition of sextet patterns is derived from graph-theoretical properties of free and holed polyhexes. So, for example, we can obtain fifty sextet patterns of VIII without the list of fifty Kekulé patterns of VIII (figs. 8a,b). It is straightforward to obtain all the 980 sextet patterns of S_{IX}. A sextet pattern of a graph G does not represent a Kekulé pattern, but represents some properties concerning perfect matchings of G.

The definitions of the sextet pattern and the sextet polynomial given above can be extended straightforwardly to holed polyhexes (fig. 13). The proof of the one-to-one correspondence is also valid for holed polyhexes, because theorems 4 and 7 are true for them.

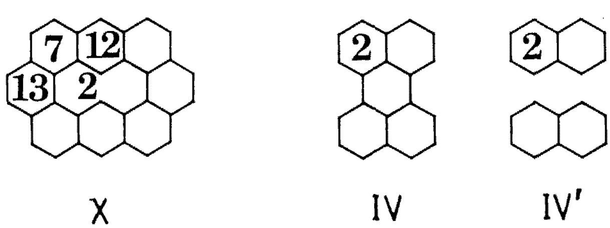
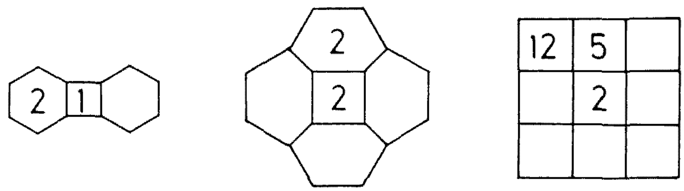


Fig. 13. Examples of sextet polynomials of holed and Kekulé polyhexes. The number in ring r_i denotes $K(G - (r_i))$. For a holed polyhex X, $S_X = 1 + 10x + 18x^2 + 10x^3 + x^4$, while $K(X) = 40$ and $\Sigma K(X - (r_i)) = 80$. Subgraph IV′ of IV is obtained by deleting all the fixed edges from IV. It contains two components of free polyhexes. The sextet polynomial $S_{IV}(x)$ is given as the product of sextet polynomials for components of IV′. $S_{IV}(x) = (1 + 2x)^2 = 1 + 4x + 4x^2$. $K(IV) = 9$ and $\Sigma K(IV - (r_i)) = 8$.

Kekulé polyhexes with fixed edges such as IV and V in fig. 1 are considered as sets of some independent free and holed polyhexes obtained by deleting all the fixed edges. Then, the combinations of resonant rings are given as the product of these free and holed polyhexes (fig. 13). This means that theorems 8 and 9 are true for any Kekulé polyhex.



XI XII XIII

Fig. 14. Sextet polynomials for bipartite graphs consisting only of free edges and having Kekulé patterns. The number in a ring r_i denotes $K(G - (r_i))$. For each case, relations (2) and (3) are valid. For a square lattice graph like XIII, see ref. [11]. $S_{XI}(x) = 1 + 3x + x^2$. $K(XI) = 5$ and $\Sigma K(XI - (r_i)) = 5$. $S_{XII}(x) = 1 + 6x + 2x^2$. $K(XII) = 9$ and $\Sigma K(XII - (r_i)) = 10$. $S_{XIII}(x) = 1 + 10x + 16x^2 + 8x^3 + x^4$. $K(XIII) = 36$ and $\Sigma K(XIII - (r_i)) = 70$.

Further, sextet patterns and the sextet polynomial can be applied to a general bipartite graph consisting only of free edges and having Kekulé patterns from theorem 4 (fig. 14). The proof of relations (2) and (3) for them will be completed if the dependency on the orientation of graphs in the above discussion is removed.

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