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Ordering Catacondensed Hexagonal Systems with Small Numbers of Kekulé Structures*

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Abstract

In this paper, we consider the problem of ordering catacondensed hexagonal systems with small numbers of Kekulé structures. Some order relations of elements in the union of three classes of catacondensed hexagonal systems with small numbers of Kekulé structures mentioned in [1] are obtained. Based on the above results, the catacondensed hexagonal systems with the fifth up to 12th smallest numbers of Kekulé structures are determined.

1. Introduction

Hexagonal systems are the natural graph representation of benzenoid hydrocarbons [3]. In the topological theory of hexagonal systems, the numbers of Kekulé structures or perfect matchings play an important role for computation of resonance energies and the Pauling bond orders of benzenoid hydrocarbons. A hexagonal system without internal vertex is called catacondensed hexagona system, written as CHS for short. The enumeration problems of Kekulé

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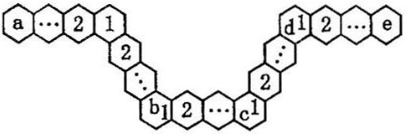
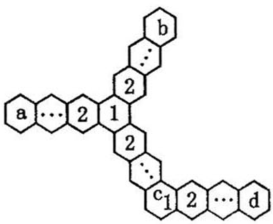
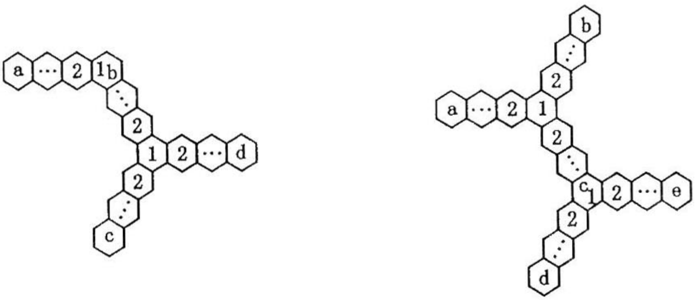
structures of hexagonal systems have been widely studied in several books and many papers[2-12], in which the enumeration of Kekulé structures of the CHSs is the topics of a whole chapter of book [3] and some other papers. In ref. [13], Gutman proved that in CHSs the linear polycene homologous series have the minimum numbers of Kekulé structures. In [1], J.S.Deogun et al. investigated three classes of CHSs, the unbranched CHSs with one kink and two kinks, and the branched CHS with exactly one branched hexagon, which have small numbers of Kekulé structures. They ordered the unbranched CHSs with one kink and determined the unbranched CHSs with two kinks and the branched CHSs with exactly one branched hexagon which have the smallest and largest numbers of Kekulé structures. Moreover, they gave the CHSs with the second, third, and the fourth smallest numbers of Kekulé structures. Our aim here is further to order CHSs with small numbers of Kekulé structures. Some order relations of elements in the union of three classes of CHSs mentioned in [1] are given. Meanwhile, we consider the unbranched CHS with n kinks which also have small numbers of Kekulé structures and give the order relations among the above three classes of CHSs together with the unbranched CHS with n kinks. Furthermore the CHSs with the fifth,..., up to the 12th smallest numbers of Kekulé structures are determined.



$L_4(a,b,c,d,e)$, $a,b,c,d,e \geq 2$, $h = a+b+c+d+e-4$



$BL(a,b,c,d)$, $a,b,c,d \geq 2$, $h = a+b+c+d-3$



$LB(a,b,c,d)$, $a,b,c,d \geq 2$,
$h = a+b+c+d-3$

$B_2(a,b,c,d,e)$, $a,b,c,d,e \geq 2$,
$h = a+b+c+d+e-4$

Fig. 1. Elements in M_h^4, YM_h, MY_h and Y_h^2.

In this paper, we follow the terminology and notations of [1]. For a hexagonal system H, we denote the number of Kekulé structures of H by $K(H)$. Let C_h be the set of CHSs with h hexagons. Clearly, the dualist graph of a CHS is a tree. Let $C_h^{'} \subseteq C_h$ denote the set of all hexagonal systems whose dualist graphs are paths. $C_h^{'}$ is also called the set of hexagonal chains, and $C_h \backslash C_h^{'}$ is the set of branched CHSs. For $H \in C_h$, a hexagon s of H is called a kink of H if s has exactly two consecutive vertices with degree 2 in H, and s is called a branched hexagon if s has no vertex with degree 2. The CHSs having no kinks and branched hexagons are called linear hexagonal chains. These represent the linear polycenes mentioned above. For two CHSs H_1 and H_2 with two adjacent vertices of degree 2, say u and v for H_1 and u' and v' for H_2, they can be fused to each other in the following two ways: (1) identify u and u' as well as v and v' to obtain a new CHS $H_1 : H_2$; (2) identify u and v' as well as v and u' to obtain another CHS $(H_1 : H_2)'$. Furthermore, if $H_1 : H_2$ and $(H_1 : H_2)'$ are not isomorphic, they are said to be isoarithmic. Conversely, two CHSs are said to be isoarithmic if they can be fused by a same pair of subsystems H_1 and H_2 in the previous way. We define M_h^n, $h \geq n+2$, to be the sets of the hexagonal chains with exactly n kinks, and Y_h^n, $h \geq 2n+2$, to be the set of the CHSs with exactly n branched hexagons and without kinks. We also define MY_h or YM_h, to be the sets of the hexagonal chains with exactly one kink and one branch. Denote by $L(a,b)$, $a+b=h+1$ and $a,b \geq 2$ (resp. $L(a,b,c)$, $a+b+c=h+2$ and $a,b,c \geq 2$), the elements of M_h^1 (resp. M_h^2). In general, we denote the elements of M_h^n by

$L_n(a_1,a_2,\cdots,a_{n+1})$ or simply by $L(a_1,a_2,\cdots,a_{n+1})$, $a_1+a_2+\cdots+a_{n+1}=h+n$ and $a_i\geq 2$ for all $i\in\{1,2,\cdots,n+1\}$. Denote by $B(a,b,c)$, $a+b+c=h+2$ and $a,b,c\geq 2$ (resp. $B_2(a,b,c,d,e)$, $a+b+c+d+e=h+4$ and $a,b,c,d,e\geq 2$), the elements of Y_h^1 (resp. Y_h^2). Denote by $LB(a,b,c,d)$ (resp. $BL(a,b,c,d)$), $a+b+c+d=h+3$ and $a,b,c,d\geq 2$, the elements of MY_h (resp. YM_h). The elements in M_h^4, Y_h^2, MY_h and YM_h are shown in Figure 1.

2. Preparation

To give our main results we need the following lemmas.

Lemma 1 [3]. $K(L_h)=h+1$; $K(L(a,b))=ab+1$;
$K(L(a,b,c))=abc-(a-1)(c-1)+1$; $K(B(a,b,c))=abc+1$.

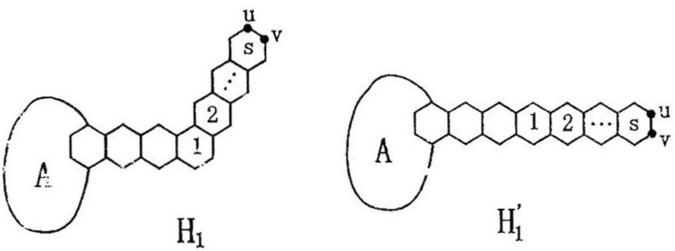
Lemma 2 [4]. Let G be a CHS, and $G+s$ the CHS obtained from G by fusing a hexagon s. Then $K(G+s)>K(G)$.

Lemma 3 [1]. The elements of $L(a,b)$, $a+b=h+1$, can be ordered by their numbers of Kekulé structures as follows:
$K(L(2,h-1))<K(L(3,h-2))<\cdots<K(L(\lfloor\frac{h}{2}\rfloor,\lceil\frac{h}{2}\rceil+1))$.

Lemma 4 [1]. The hexagonal chain in $C_h^{'}\setminus M_h^1$ with the minimum number of Kekulé structures is $L(2,2,h-2)$ in M_h^2.

Lemma 5 [1]. The branched CHS with the minimum number of Kekulé structures is $B(2,2,h-2)$ in Y_h^1.

Let $H_1,H_1^{'},H_2,H_2^{'}$ be the CHSs in Fig. 2. We say that $H_1^{'}$ (resp. $H_2^{'}$) is obtained from H_1 (resp. H_2) by an α-operation (resp. a β-operation).



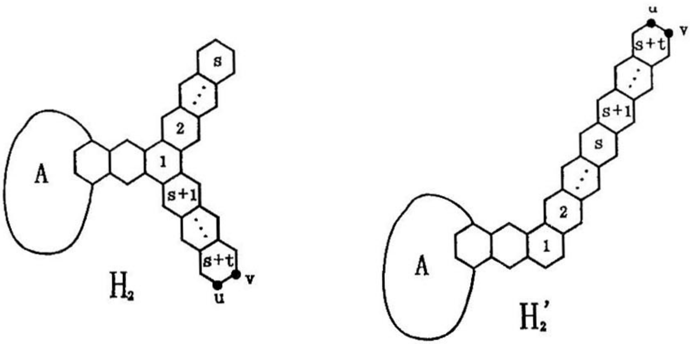


Fig. 2. An α-operation and a β-operation.

From the proof of Lemma 4 and Lemma 5 (see [1]), we have the following.

Corollary 1. Let H_1' (resp. H_2') be the CHS obtained from a CHS H_1 (resp. H_2) by an α-operation (resp. a β-operation). Then $K(H_1') < K(H_1)$ (resp. $K(H_2') < K(H_2)$).

Lemma 6 [1]. Let S_i, $i = 1,2,\cdots$, be the CHS with $h \geq 5$ hexagons and the ith smallest number of Kekulé structures. Then $S_1 = L(h)$, $S_2 = L(2,h-1)$, $S_3 = L(3,h-2)$, $S_4 = L(2,2,h-2)$.

3. Method for ordering CHSs with small numbers of Kekulé structures

For the formula $K(L(a,b)) = ab+1$, where $a+b = h+1$ and $a,b \geq 2$, one of parameters a and b, say b can be expressed by a and h. Similarly, for the formula $K(L(a,b,c)) = abc-(a-1)(c-1)+1$ and $K(B(a,b,c)) = abc+1$, one of parameters a, b and c, say c, can be expressed by a, b and h. For a given h, we can express the formulas above as functions of first degree in h. It is clear that the value of a function of first degree depends on the values of its coefficients of degree one term and constant term. Hence, in order to order two different CHSs by the number of Kekulé structures, we only need to compare respective values of coefficients of degree one term and constant term in corresponding expressions for their numbers of Kekulé structures. For example, consider two distinct CHSs H_1 and H_2 with $K(H_i) = x_i h - y_i$, $i = 1,2$, respectively. We may compare them as follows.

Case 1: $x_1 \neq x_2$. We may assume $x_1 > x_2$ without loss of generality.

1) If $y_1 \leq y_2$ or $h \geq \left\lceil \frac{y_1 - y_2}{x_1 - x_2} \right\rceil$, then $K(H_1) \geq K(H_2)$;

2) If $h \leq \left\lfloor \frac{y_1 - y_2}{x_1 - x_2} \right\rfloor$, then $K(H_1) \leq K(H_2)$.

Case 2: $x_1 = x_2$.

1) If $y_1 \leq y_2$, then $K(H_1) \geq K(H_2)$;

2) If $y_1 \geq y_2$, then $K(H_1) \leq K(H_2)$.

When ordering a set of CHSs, we can first deal with CHSs which satisfy the condition in case 2 and then determine the whole order for a given h.

We will apply the above method to attain our main results in the following section.

4. Some order relations of CHSs in $M_h^1 \cup M_h^2 \cup Y_h^1$ on the numbers of Kekulé structures

By Lemma 1, we can see that the parameters a and b are symmetric in formula $K(L(a,b)) = ab+1$. Similarly, parameters a and c are symmetric in formula $K(L(a,b,c)) = abc-(a-1)(c-1)+1$ and parameters a, b, c are symmetric in formula $K(B(a,b,c)) = abc+1$. In this sense, we only need to consider CHSs of the four forms in $M_h^1 \cup M_h^2 \cup Y_h^1$ as follows: $L(a,b)$, $L(a,b,c)$, $L(a,c,b)$, $B(a,b,c)$. From Lemma 1 and the ordering method showed in Section 3, we have that

$$K(L(a_1,h+1-a_1)) = a_1h - [a_1(a_1-1)-1]$$

$$K(L(a_2,b_2,h+2-a_2-b_2)) = [a_2(b_2-1)+1)]h - [a_2(b_2-1)(a_2+b_2-2)+b_2-2]$$

$$K(L(a_3,h+2-a_3-b_3,b_3)) = a_3b_3h - [(a_3b_3-1)(a_3+b_3-1)-1]$$

$$K(B(a_3,h+2-a_3-b_3,b_3)) = a_3b_3h - [a_3b_3(a_3+b_3-2)-1]$$

When $a_1 = a_2(b_2-1)+1 = a_3b_3 = m+1$ for a given integer m, then $K(L(a_1,h+1-a_1))$, $K(L(a_2,b_2,h+2-a_2-b_2))$, $K(L(a_3,h+2-a_3-b_3,b_3))$ and $K(B(a_3,h+2-a_3-b_3,b_3))$ have the same coefficient $m+1$ of the term of degree one, and we say that these CHSs are the CHSs with the index $x(h) = m+1$. We can attain the order for CHSs in $M_h^1 \cup M_h^2 \cup Y_h^1$ with $x(h) = m+1$ by the numbers of Kekulé structures, which is called as m - *order*.

When $m=1$, from Lemma 6 we can see that $L(2,h-1)$ is the only one in $M_h^1 \cup M_h^2 \cup Y_h^1$ with $x(h)=m+1$. Hence we only need to consider $m \geq 2$. By Lemma 1 and a straightforward calculation, we can give Lemma 7, 8 and 9.

Lemma 7. If $ab=a'b'=m$, $a<b$, $b>2$ and $c \leq c'-1$, then

$K(L(a,b+1,c)) < K(L(b,a+1,c)) < K(L(a',b'+1,c'))$.

Proof. By Lemma 1, we have

$K(L(a,b+1,c)) = a(b+1)c - ac + a + c = abc + a + c < abc + b + c = K(L(b,a+1,c))$ since $a<b$. Similarly, $K(L(b,a+1,c)) = abc + b + c \leq a'b'(c'-1) + b + c' - 1$

$= a'b'c' + c' - a'b' + b - 1 = a'b'c' + c' - b(a-1) - 1 < a'b'c' + c' + a' = K(L(a',b'+1,c'))$

since $ab=a'b'$ and $c \leq c'-1$.

Then the desired inequalities follow. □

Lemma 8. If $ab=a'b'=m+1$ and $c \leq c'-1$, then

$K(L(a,c,b)) < K(B(a,c,b)) < K(L(a',c',b')) < K(B(a',c',b'))$.

Proof. By Lemma 1, we have

$K(L(a,c,b)) = abc - ab + a + b = abc - (a-1)(b-1) + 1 < abc + 1 = K(B(a,c,b))$ and

$K(L(a',c',b')) < K(B(a',c',b'))$.

Similarly, $K(B(a,c,b)) = abc + 1 \leq ab(c'-1) + 1 = a'b'c' - a'b' + 1 < a'b'c' - a'b' + a' + b'$

$= K(L(a',c',b'))$ since then $ab = a'b$ and $c \leq c'-1$.

Then the desired inequalities follow. □

Lemma 9. If $a(b-1)+1 = a'b' = m+1$, then the order of $K(L(a,b,c))$, $K(L(a',c',b'))$, $K(B(a',c',b'))$ will be:

1) When $a+b \leq a'+b'$, we have $K(L(a',c',b')) < K(B(a',c',b')) < K(L(a,b,c))$;

2) When $a+b \geq a'+b'-1$, we have $K(L(a,b,c)) < K(L(a',c',b') < K(B(a',c',b'))$.

Proof: From Lemma 8, we know that $K(L(a',c',b')) < K(B(a',c',b'))$ holds in any case. It only remains for us to prove the second inequality in 1) and the first inequality in 2).

1) When $a+b \le a'+b'$, since $a+b+c=h+2$ and $a'+b'+c'=h+2$, we see that $c \ge c'$. Since $a \ge 2$, it follows that (by Lemma 1)

$$K(B(a',c',b'))=a'b'c'+1 \le a'b'c+1 < [a(b-1)+1]c+a = K(L(a,b,c)).$$

2) When $a+b \ge a'+b'+1$, since $b \ge 2$, we have (by Lemma 1)

$$K(L(a,b,c)) = [a(b-1)+1]c+a = [a(b-1)+1](h+2-a-b)+a$$

$$=[a(b-1)+1]h-a(b-1)(a+b-2)+2-b \le a'b'h-(a'b'-1)(a'+b'-1)+2-b$$

$$\le a'b'h-(a'b'-1)(a'+b'-1) < K(L(a',c',b')).$$

Now the proof is completed. □

Lemma 10. When $ab-(a-1)=a'b'=m+1$, then the CHS in $M_h^2 \cup Y_h^1$ with $x(h)=m+1$ and the minimum number of Kekulé structures is $L(m,2,h-m)$.

Proof. The proof is by contradiction. Suppose that there is another CHS H in $M_h^2 \cup Y_h^1$ with $x(h)=m+1$ and $K(H) < K(L(m,2,h-m))$. If $H \in M_h^2$, let $H=L(a,b,c)$, where $ab-(a-1)=m+1$, $b>2$, $a,c \ge 2$ and $a+b+c=h+2$.

By Lemma 1, we have

$$K(L(a,b,c))=(m+1)h-[m(a+b-2)+(b-2)] < (m+1)h-m^2 = K(L(m,2,h-m))$$

This implies that $b-2 > a(a-1)(b-1)(b-2)$. Now we deduce a contradiction since then $a \ge 2$ and $b>2$. When $H \in Y_h^1$, let $H=B(a',c',b')$, where $a'b'=m+1$, $a,b,c \ge 2$ and $a+b+c=h+2$. We can also deduce a contradiction in the same way. The lemma follows immediately. □

Note: The formula $K(L(a_1,h+1-a_1))=a_1h-[a_1(a_1-1)-1]=(m+1)h-[a_1(a_1-1)-1]$ implies that $L(m+1,h-m)$ is the only one in M_h^1 that may appear in $m-order$. From Lemma 10, we know that the CHS in $M_h^2 \cup Y_h^1$ with $x(h)=m+1$ and the minimum number of Kekulé structures is $L(m,2,h-m)$. And by Corollary 1, we have $K(L(m+1,h-m)) < K(L(m,2,h-m))$ for $m \ge 2$. Hence we can see that the CHSs in $m-order$ with the first and second smallest number of Kekulé structures must be $L(m+1,h-m)$ and $L(m,2,h-m)$ respectively. This means that we only need to consider the CHSs in $m-order$ after $L(m,2,h-m)$.

By our assumption $a_2(b_2-1)+1=a_3b_3=m+1$ i.e. $a_2(b_2-1)=m$ and $a_3b_3=m+1$, we need to distinguish the two cases depending on the parity of m and $m+1$ respectively. If m is prime, then, for $b_2>2$, there is no CHS $L(a_2,b_2,h+2-a_2-b_2)$ with $a_2(b_2-1)=m$, so we only need to order the CHSs in M_h^2 having the form of $L(a',c',b')$ and the CHSs in Y_h^1 having the form of

$B(a',c',b')$. If $m+1$ is prime, then there is no CHS in Y_h^1 with $x(h)=m+1$, and so we only need to order CHSs in M_h^2 having the form of $L(a,b,c)$. Otherwise, we need to order CHSs in $M_h^2 \cup Y_h^1$ having three forms as above. Now we can show $m-order$ after $L(m,2,h-m)$ as follows.

Theorem 1. If $m+1$ is prime, let $m=p_iq_i$, $i=1,2,\cdots,r$,

$2=p_1<p_2<\cdots<p_r<\lfloor\sqrt{m}\rfloor$, then

$$K(L(p_1,q_1+1,h+1-p_1-q_1))<K(L(q_1,p_1+1,h+1-p_1-q_1))<$$
$$K(L(p_2,q_2+1,h+1-p_2-q_2))<K(L(q_2,p_2+1,h+1-p_2-q_2))<\cdots<$$
$$K(L(p_r,q_r+1,h+1-p_r-q_r))<K(L(q_r,p_r+1,h+1-p_r-q_r)). \qquad \text{..............(a)}$$

Proof. The inequalities in (a) are directly from Lemma 7. □

Theorem 2. If m is prime, let $m+1=p'_jq'_j$, $j=1,2,\cdots,t$,

$2=p'_1<p'_2<\cdots<p'_t<\lfloor\sqrt{m+1}\rfloor$, then

$$K(L(p'_1,h+2-p'_1-q'_1,q'_1))<K(B(p'_1,h+2-p'_1-q'_1,q'_1))<$$
$$K(L(p'_2,h+2-p'_2-q'_2,q'_2))<K(B(p'_2,h+2-p'_2-q'_2,q'_2))<\cdots<$$
$$K(L(p'_t,h+2-p'_t-q'_t,q'_t))<K(B(p'_t,h+2-p'_t-q'_t,q'_t)). \qquad \text{...............(b)}$$

Proof. The inequalities in (b) are directly from Lemma 8. □

Theorem 3. If both m and $m+1$ are not prime,
let $m=p_iq_i$, $i=1,2,\cdots,r$, $2=p_1<p_2<\cdots<p_r<\lfloor\sqrt{m}\rfloor$ and $m+1=p'_jq'_j$, $j=1,2,\cdots,t$, $2<p'_1<p'_2<\cdots<p'_t<\lfloor\sqrt{m+1}\rfloor$, then

i) When $p_i+q_i+1\le p'_j+q'_j$, $i=1,2,\cdots,r$, $j=1,2,\cdots,t$, we have
$$K(L(p'_j,h+2-p'_j-q'_j,q'_j))<K(B(p'_j,h+2-p'_j-q'_j,q'_j))<K(L(p_i,q_i+1,h+1-p_i-q_i))$$
$$<K(L(q_i,p_i+1,h+1-p_i-q_i));$$

ii) When $p_i+q_i>p'_j+q'_j$, $i=1,2,\cdots,r$, $j=1,2,\cdots,t$, we have
$$K(L(p_i,q_i+1,h+1-p_i-q_i))<K(L(q_i,p_i+1,h+1-p_i-q_i))<$$
$$K(L(p'_j,h+2-p'_j-q'_j,q'_j))<K(B(p'_j,h+2-p'_j-q'_j,q'_j)); \qquad \text{...............(c)}$$

where the order of $K(L(p_i,q_i+1,h+1-p_i-q_i))$ and $K(L(q_i,p_i+1,h+1-p_i-q_i))$ satisfies the inequalities in (a), and the order between $K(B(p'_j,h+2-p'_j-q'_j,q'_j))$ and $K(L(p'_j,h+2-p'_j-q'_j,q'_j))$ satisfies the inequalities in (b).

Proof. The inequalities in (a) and (b) have been proven in Theorems 1 and 2 respectively. The inequalities between $K(L(*,*,*))$'s and $K(B(*,*,*))$'s in (c) are obtained from Lemma 9. It completes the proof of Theorem 3. □

Consequently, for a given m, we can determine $m-order$ from Theorems 1, 2, and 3. We denote by $m*\text{-}order$ the order of the CHSs in $M_h^1 \cup M_h^2 \cup Y_h^1$ with the index $x(h)=2,3,\cdots,m+1$, with respect to the numbers of Kekulé structures. We can obtain the $m*\text{-}order$ of some CHSs in $M_h^1 \cup M_h^2 \cup Y_h^1$ as follows. First, we have known that $1-order$ only contains $L(2,h-1)$, and the $2-order$ must be $K(L(3,h-2)) < K(L(2,2,h-2))$. Hence, we can give $2*\text{-}order$ as follows: $K(L(2,h-1)) < K(L(3,h-2)) < K(L(2,2,h-2))$. Next we consider CHSs in $3-order$. For a given h, we can insert the CHSs in $3-order$ into $2*\text{-}order$ to expand $2*\text{-}order$ to $3*\text{-}order$. In general, suppose that we have obtained $m*\text{-}order$ $(m \geq 3)$. Then we can insert the CHSs in $(m+1)-order$ into $m*\text{-}order$ to obtain $(m+1)*\text{-}order$. This process can be continued according to the value of h. Meanwhile, we may find some CHSs that are not isomorphic and have the same numbers of Kekulé structures.

5. Other CHSs which have small number of Kekulé structures

Besides CHSs investigated in Section 4, there are other CHSs that also have small numbers of Kekulé structures. From the proofs of Lemma 4 and 5 (see [1]), it is valuable to consider CHSs in $M_h^n (n \geq 3)$.

The following results in Lemma 11 can be found in [2].

Lemma 11 [2]. The numbers $K(L_n(2,2,\cdots,2))$ are Fibonacci numbers i.e., $K(L_n(2,2,\cdots,2)) = F_{n+3}$ for every $n \geq 1$. ($F_0 = F_1$ and $F_n = F_{n-1} + F_{n-2}$ for every $n \geq 2$).

Lemma 12. $K(L_n(a_1,a_2,\cdots,a_{n+1})) \geq K(L_n(2,a_1+a_2-2,a_3,\cdots,a_{n+1}))$.

Proof. From Lemma 3, it is not difficult to see that

$$
\begin{aligned}
&K(L_n(a_1,a_2,\cdots,a_{n+1})) \\
&= K(L(a_1,a_2-1)) \cdot K(L_{n-2}(a_3-1,a_4,\cdots,a_{n+1})) + K(L(a_1-1)) \cdot K(L_{n-3}(a_4-1,a_5,\cdots,a_{n+1})) \\
&\geq K(L(2,a_1+a_2-3)) \cdot K(L_{n-2}(a_3-1,a_4,\cdots,a_{n+1})) + 2K(L_{n-3}(a_4-1,a_5,\cdots,a_{n+1})) \\
&= K(L_n(2,a_1+a_2-2,a_3,\cdots,a_{n+1})).
\end{aligned}
$$

□

Theorem 4. Let $L_n(a_1,a_2,\cdots,a_{n+1})$ be an element of M_h^n, where $a_1+a_2+\cdots+a_{n+1} = h+n$ and $h \geq n+2$. Then the hexagonal chain in M_h^n with the minimum number of Kekulé structures is $L_n(2,2,\cdots,2,h-n)$.

Proof: The proof is by induction on n.

For $n=1$ and 2, the results are easily seen to be true by Lemmas 3 and 4.

As an induction hypothesis, suppose that the result is true for $1 \le n \le k-1$.

Now we consider $n=k$.

From Lemma 12 and induction hypothesis, we have that

$K(L_n(a_1,a_2,\cdots,a_{n+1})) \ge K(L_n(2,a_1+a_2-2,a_3,\cdots,a_{n+1}))$

$= K(L_{n-1}(a_1+a_2-2,a_3,\cdots,a_{n+1})) + K(L_{n-2}(a_1+a_2-3,a_3,\cdots,a_{n+1}))$

$\ge K(L_{n-1}(2,2,\cdots,2,h-n)) + K(L_{n-2}(2,2,\cdots,2,h-n))$

$= K(L_n(2,2,\cdots,2,h-n))$. □

Theorem 5. Let $K(L_n(2,2,\cdots,2,h-n)) = \alpha_n h - \beta_n$, where $\alpha_n, \beta_n \in N$ for every $n \ge 1$. Then α_n are Fibonacci numbers, i.e., $\alpha_n = F_{n+1}$ for every $n \ge 1$.

Proof. It is not difficult to see that

$K(L_n(2,2,\cdots,2,h-n)) = K(L_{n-1}(2,2,\cdots,2)) + (h-n-1)\ K(L_{n-2}(2,2,\cdots,2))$.

By Lemma 11, we see that $K(L_{n-1}(2,2,\cdots,2)) = F_{n+2}$ and $K(L_{n-2}(2,2,\cdots,2)) = F_{n+1}$. Thus, $K(L_n(2,2,\cdots,2,h-n)) = F_{n+2} + (h-n-1)F_{n+1} = F_{n+1}\cdot h - [(n+1)F_{n+1} - F_{n+2}]$.

It completes the proof of Theorem 5. □

Notes: Theorems 4 and 5 indicate that $L_n(a_1,a_2,\cdots,a_{n+1})\ (n \ge 1)$ may begin to appear in $(F_{n+1}-1)$-*order* as defined in Section 4, where F_{n+1} are Fibonacci numbers. Hence, for a given h, the position which $L_n(a_1,a_2,\cdots,a_{n+1})\ (n \ge 1)$ may first insert into the order of some elements in $M_h^1 \cup M_h^2 \cup Y_h^1$ by the number of Kekulé structures can be determined.

6. The CHSs with the fifth up to 12$^{\text{th}}$ smallest numbers of Kekulé structures

We first determine the element of CHSs in $C_h \backslash (M_h^1 \cup M_h^2 \cup Y_h^1)$ with the smallest number of Kekulé structures.

Lemma 13. The CHS in $C_h \backslash (M_h^1 \cup M_h^2 \cup Y_h^1)$ with the smallest number of Kekulé structures is $L_3(2,2,2,h-3)$.

Proof. By Corollary 1, if $H \in C_h \backslash (M_h^1 \cup M_h^2 \cup Y_h^1)$ and $H \notin M_h^3 \cup MY_h \cup YM_h \cup Y_h^2$, then there is a CHS H^* in $M_h^3 \cup MY_h \cup YM_h \cup Y_h^2$ such that H^* can be obtained from H by a number of α-operations and β-operations, and so $K(H^*) < K(H)$. Hence, the element of CHSs in $C_h \backslash (M_h^1 \cup M_h^2 \cup Y_h^1)$ with the smallest number of Kekulé structures must be in $M_h^3 \cup MY_h \cup YM_h \cup Y_h^2$.

From Theorem 4, the CHS in M_h^3 with the smallest number of Kekulé structures is $L_3(2,2,2,h-3)$. To finish the proof, we only need to prove that $K(BL(a,b,c,d)) > K(L_3(2,2,2,h-3))$, $K(LB(a,b,c,d)) > K(L_3(2,2,2,h-3))$ and $K(B_2(a,b,c,d,e)) > K(L_3(2,2,2,h-3))$.

From Lemma 1, it is clear that

$$K(BL(a,b,c,d)) = K(L(a-1)) \cdot K(L(b-1)) \cdot K(L(c-1,d)) + K(L(d-1))$$

$$= ab \cdot K(L(c-1,d)) + d$$

and $K(L_3(a,b,c,d)) = K(L(a,b-1)) \cdot K(L(c-1,d)) + K(L(a-1)) \cdot K(L(d-1))$

$$= [a(b-1)+1] \cdot K(L(c-1,d)) + ad .$$

Hence, $K(BL(a,b,c,d)) - K(L_3(a,b,c,d)) = (a-1)K(L(c-1,d)) - (a-1)d$

$$= (a-1)[(c-1)d + 1 - d] = (a-1)[(c-2)d+1] \geq 0,$$

and so $K(BL(a,b,c,d)) > K(L_3(a,b,c,d)) \geq K(L_3(2,2,2,h-3))$.

In addition, $K(LB(a,b,c,d)) = K(BL(d,c,b,a)) > K(L_3(2,2,2,h-3))$.

Finally, we have that
$K(B_2(a,b,c,d,e)) = K(BL(a,b,c,d)) + K(B(a,b,c-1)) \cdot K(L(d-1)) \cdot (e-1)$, and so
$K(B_2(a,b,c,d,e)) > K(BL(a,b,c,d)) > K(L_3(2,2,2,h-3))$.

The proof is thus completed. □

Now we can assert that all the CHSs with the numbers of Kekulé structures less than $K(L_3(2,2,2,h-3))$, except for the single linear hexagonal chain, must be elements in $M_h^1 \cup M_h^2 \cup Y_h^1$.

Now, from the results in Section 4 and 5, we can easily extend Lemma 6 to the following result:

Theorem 6. For $h \geq 18$, we have $S_5 = L(4,h-3)$, $S_6 = L(3,2,h-3)$, $S_7 = L(2,h-2,2)$, $S_8 = B(2,h-2,2)$, $S_9 = L(5,h-4)$, $S_{10} = L(4,2,h-4)$, $S_{11} = L(2,3,h-3)$, $S_{12} = L_3(2,2,2,h-3)$.

Proof. From Lemma 6, we know that $S_4 = L(2,2,h-2)$.

By Theorems 1,2,3, we have
$K(L(4,h-3)) < K(L(3,2,h-3)) < K(L(2,h-2,2)) < K(B(2,h-2,2))$,
$K(L(5,h-4)) < K(L(4,2,h-4)) < K(L(2,3,h-3))$ and that the first C. S in $5-order$

is $L(6,h-5)$. Hence, we only need to compare $K(L(2,2,h-2))$ and $K(L(4,h-3))$, $K(B(2,h-2,2))$ and $K(L(5,h-4))$, $K(L(2,3,h-3))$, $K(L_3(2,2,2,h-3))$ and $K(L(6,h-5))$.

By Lemma 1, $K(L(2,2,h-2))=3h-4$, $K(B(2,h-2,2))=4h-7$, $K(L(5,h-4))=5h-19$, $K(L(2,3,h-3))=5h-13$ and $K(L(6,h-5))=6h-29$. Clearly, $K(L(2,2,h-2))<K(L(4,h-3))$ for $h\geq 8$, $K(B(2,h-2,2))<K(L(5,h-4))$ for $h\geq 13$ and that $K(L(2,3,h-3))<K(L(6,h-5))$ for $h\geq 17$. Hence, we can deduce that, for $h\geq 17$, $S_5=L(4,h-3)$, $S_6=L(3,2,h-3)$, $S_7=L(2,h-2,2)$, $S_8=B(2,h-2,2)$, $S_9=L(5,h-4)$, $S_{10}=L(4,2,h-4)$ and $S_{11}=L(2,3,h-3)$.
And by Theorem 5, we have $K(L_3(2,2,2,h-3))=5h-12$.
Clearly, $K(L_3(2,2,2,h-3))<K(L(6,h-5))$ for $h\geq 18$.

Now it is not difficult to complete the proof. □

Meanwhile, for $5\leq h\leq 17$, we can list the CHSs with the first, …, up to the 12th smallest numbers of Kekulé structures as follows.

We denote the set of CHSs with $h\geq 5$ hexagons and the ith smallest number of Kekulé structures by $S_i{}^*$, $i=1,2,\cdots$.

(1) $5\leq h\leq 7$.

Then $S_i(i=1,2,3,4)$ is similar to the results in Lemma 6.

When $h=5$, we only have $S_5=L(2,h-2,2)$, $S_6{}^*=\{B(2,h-2,2),L_3(2,2,2,h-3)\}$, $S_7=BL(2,2,2,h-3)$, since there exist no other class of CHSs.

When $h=6$, we have $S_5=L(3,2,h-3)$, $S_6=L(2,h-2,2)$, $S_7{}^*=\{B(2,h-2,2),L(2,3,h-3)\}$, $S_8=L_3(2,2,2,h-3)$, $S_9{}^*=\{BL(2,2,2,h-3),\ B(2,h-3,3),L_3(2,2,h-3,2)\}$, $S_{10}=BL(2,h-3,2,2)$, $S_{11}=L_4(2,2,2,2,h-4)$, $S_{12}=BL(2,2,h-3,2)$.

When $h=7$, we have $S_4{}^*=\{L(2,2,h-2),L(4,h-3)\}$, $S_5=L(3,2,h-3)$, $S_6=L(2,h-2,2)$, $S_7=B(2,h-2,2)$, $S_8=L(2,3,h-3)$, $S_9{}^*=\{L_3(2,2,2,h-3),\ L(2,h-3,3)\}$, $S_{10}=BL(2,2,2,h-3)$, $S_{11}{}^*=\{B(2,h-3,3),L_3(2,2,h-3,2),L_3(3,2,2,h-4)\}$, $S_{12}{}^*=\{BL(2,h-3,2,2),L_3(3,2,h-4,2)\}$.

(2) If $h: 8\leq h\leq 10$, then $S_i(i=1,2,3,4,5)$ is similar to the results in Lemma 6 and Theorem 6.

When $h=8$, we have $S_6=L(3,2,h-3)$, $S_7{}^*=\{L(2,h-2,2),L(4,2,h-4)\}$,

$S_8 = B(2,h-2,2)$, $S_9 = L(2,3,h-3)$, $S_{10} = L_3(2,2,2,h-3)$,

$S_{11}* = \{BL(2,2,2,h-3),\ L(2,h-3,3)\}$, $S_{12} = L(2,4,,h-4)$.

When $h=9$, we have $S_6 = L(5,h-4)$, $S_7 = L(3,2,h-3)$, $S_8 = L(2,h-2,2)$,

$S_9* = \{B(2,h-2,2), L(4,2,h-4)\}$, $S_{10} = L(2,3,h-3)$, $S_{11} = L_3(2,2,2,h-3)$,

$S_{12} = BL(2,2,2,h-3)$.

When $h=10$, we have $S_6* = \{L(3,2,h-3), L(5,h-4)\}$, $S_7 = L(2,h-2,2)$,

$S_8 = B(2,h-2,2)$, $S_9 = L(4,2,h-4)$, $S_{10} = L(5,2,h-5)$, $S_{11} = L(2,3,h-3)$,

$S_{12} = L_3(2,2,2,h-3)$.

(3) If $h: 11 \le h \le 12$, then $S_i (i=1,2,3,4,5,6,7)$ is similar to the results in Lemma 6 and Theorem 6.

When $h=11$, we have $S_7* = \{L(2,h-2,2), L(5,h-4)\}$,

$S_8* = \{B(2,h-2,2), L(6,h-5)\}$, $S_9 = L(4,2,h-4)$, $S_{10} = L(5,2,h-5)$, $S_{11} = L(2,3,h-3)$, $S_{12} = L_3(2,2,2,h-3)$.

When $h=12$, we have $S_8* = \{B(2,h-2,2), L(5,h-4)\}$, $S_9 = L(6,h-5)$,

$S_{10} = L(4,2,h-4)$, $S_{11}* = \{L(2,3,h-3), L(5,2,h-5)\}$,

$S_{12}* = \{L_3(2,2,2,h-3), L(6,2,h-6)\}$.

(4) If $h: 13 \le h \le 17$, then $S_i (i=1,2,\cdots,10)$ is similar to the results in Lemma 6 and Theorem 6.

When $h=13$, we have $S_{10}* = \{L(4,2,h-4), L(6,h-5)\}$, $S_{11} = L(7,h-6)$,

$S_{12} = L(2,3,h-3)$.

When $h=14$, we have $S_{11} = L(6,h-5)$, $S_{12}* = \{L(2,3,h-3), L(7,h-6)\}$.

When $h=15$, we have $S_{11} = L(6,h-5)$, $S_{12} = L(2,3,h-3)$.

When $h=16$, we have $S_{11}* = \{L(6,h-5), L(2,3,h-3)\}$, $S_{12} = L_3(2,2,2,h-3)$.

When $h=17$, we have $S_{11} = L(2,3,h-3)$, $S_{12}* = \{L_3(2,2,2,h-3), L(6,h-5)\}$.

Remark: From the above list, we can find the CHSs in $S_i * (i=1,2,\cdots,12)$, which are non-isomorphic, have the same numbers of Kekulé structures for a given h.

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