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THE EXISTENCE OF KEKULÉ STRUCTURES IN HELICENES AND ENUMERATION OF CONCEALED NON-KEKULÉAN HELICENES WITH $h \leq 13$*

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Abstract

Helicenes are the simply connected helicenic (geometrically non-planar) polyhexes. In this paper, we give some necessary and sufficient conditions for a helicene to have Kekulé structures. For a helicene with $h \leq 14$, the necessary and sufficient conditions are simpler. By using the conditions, we give a construction method for all the concealed non-Kekuléan helicenes with $h \leq 13$, and rigorously prove that there are exactly one, seventeen, and two hundred and sixty-nine concealed non-Kekuléan helicenes with $h = 11$, 12, 13, respectively.

1. Introduction

A polyhex is a geometrical system consisting of congruent regular hexagons. Only the simply connected systems, that is, with no hole, are considered here. The simply connected polyhexes are divided into the (geometrically planar) benzenoids and (nonplanar) helicenic systems, for short referred to as helicenes. A helicene is a polyhex with overlapping edges if drawn in a plane (see fig. 1). However, it is not allowed that a vertex in a helicene has degree greater than three, or that two hexagons with a common edge overlap if drawn in a plane (see fig. 2). Under these restrictions, it is easy to see that three end points of any two incident edges in the dualist of a helicene form one of the three configurations: (a) a straight line, (b) an angle of 120°, (c) an equilateral triangle (see fig. 1).

Helicenes as chemical compounds have attracted much interest among organic and physical chemists, since the synthesis of the first such hydrocarbon, $C_{26}H_{16}$, hexahelicene or helicene with six hexagons [1,2] (see fig. 1(1)). Later, many unbranched helicenes as homologues to hexahelicene have been synthesized, actually up to helicene with fourteen hexagons [3]. A branched $C_{42}H_{24}$ helicene (see fig. 1(2)), which is also known chemically [4,5], is a fully benzenoid hydrocarbon [6]. On the other hand, graph-theoretical properties and the enumeration of helicenes have been

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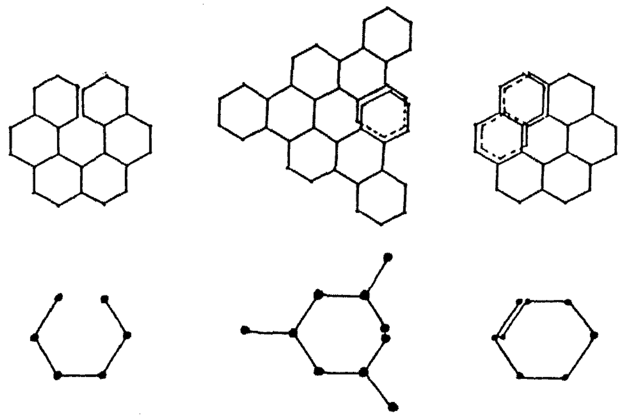


Fig. 1.

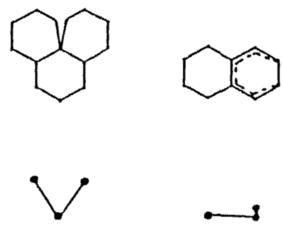


Fig. 2.

studied extensively by mathematical chemists. For example, Randić et al. [7,8] investigated the aromatic stability and Kekulé structure counts of helicenes; Herndon [9], Dias [10], Cyvin et al. [11–15] gave some results on the enumeration of helicenes.

A Kekulé structure of a polyhex G is a selection of independent edges of G which saturate all vertices of G. A polyhex is said to be Kekuléan if it has a Kekulé structure, otherwise non-Kekuléan. The existence of Kekulé structures of a simply connected polyhex is directly related to the chemical existence of the corresponding benzenoid or helicene molecule, so it is the first fundamental problem in topological theory of polycyclic aromatic hydrocarbons. Many investigations have been made in order to find necessary and sufficient conditions for the existence of Kekulé structures on a benzenoid system [16–21]. A recent survey [22] was given by

Zhang et al. However, for a helicene the problem of the existence of Kekulé structures has not been considered so far. In the present paper, we shall give a complete answer to the problem.

A polyhex is a bipartite graph, so it has a bipartition (V_1, V_2) of vertices, where each of V_1 and V_2 is an independent vertex set, coloured white and black, respectively. It is obvious that a Kekuléan polyhex must have the same number of white and black vertices, that is, the difference Δ of numbers of black and white vertices is equal to zero. At one time, it was even thought that a benzenoid system with $\Delta = 0$ was certainly Kekuléan. However, two smallest non-Kekuléan benzenoid systems with $\Delta = 0$ were found by Gutman [23] in 1974. Later, a non-Kekuléan benzenoid system with $\Delta = 0$ was said to be concealed non-Kekuléan. Similarly, we can speak about a concealed non-Kekuléan helicene or polyhex. Since 1974, many scientists [23–27] have been interested in hunting for concealed non-Kekuléan benzenoid systems, and in 1986, the eight smallest concealed non-Kekuléan benzenoid systems with $h = 11$ had been found. In 1987, by computer-aided generation, Brunvoll et al. [28] asserted that there are exactly eight smallest concealed non-Kekuléan benzenoid systems with $h = 11$, as had been found. In addition, by computer generation, He Wenchen et al. [29] found all the ninety-eight concealed non-Kekuléan benzenoid systems with $h = 12$. Quite differently, by using the necessary and sufficient conditions for the existence of Kekulé structures in a benzenoid system, the present authors [21,30] gave a graph-theoretical construction method for concealed non-Kekuléan benzenoid systems with $h \leq 13$ which does not depend on computer-aided generation. By this construction method, we rigorously proved the above results of computer-aided generation, and also proved for the first time that there are exactly 1097 concealed non-Kekuléan benzenoid systems with $h = 13$. Independently, Jiang and Chen [31] also found the numbers for $h = 12$ and 13, by an analytical deduction which is different from our method, and claimed the number for $h = 14$ to be 9781 without rigorous graph-theoretical proofs. However, their result of 9781 systems appears to deviate from the recent (so far unconfirmed) computer-generated number, viz. 9804, which was obtained by Cyvin et al. [32]. Quite recently, a rigorous graph-theoretical proof of the number for $h = 14$ has been completed by Guo Xiaofeng [33]. It is confirmed that the number is surely 9804, the same as the computer-generated number. On the other hand, for concealed non-Kekuléan helicenes, the parallel problem has not been widely studied up to now, although in 1982 Balaban [25] first found a concealed non-Kekuléan helicene with $h = 11$. In the present paper, based on our necessary and sufficient conditions for the existence of Kekulé structures in a helicene, we prove that the smallest concealed non-Kekuléan helicene has exactly 11 hexagons; furthermore, we give a construction method for concealed non-Kekuléan helicenes with $11 \leq h \leq 13$. By using the construction method, we first find and rigorously prove the numbers of all concealed non-Kekuléan helicenes with $h = 11$, 12, 13, which are 1, 17, 269, respectively. For $h = 14$, an improved construction method is going to be given by Guo Xiaofeng in ref. [33], in which all the concealed non-Kekuléan helicenes with $h = 14$ are also given.

2. Some related results

Let H be a simply connected polyhex (a benzenoid or a helicenic system) drawn in a plane such that a pair of edges of every hexagon is parallel to the vertical line. A peak (valley) of H is a vertex in H which lies above (below) all its adjacent vertices. We denote the number of peaks and valleys of H by $p(H)$ and $v(H)$, respectively. For convenience, we colour the vertices of H black and white so that any two adjacent vertices have different colours, and the peaks of H are by convention coloured black. Let n_b and n_w be the numbers of black and white vertices, respectively. Then $\Delta = n_b - n_w = p(H) - v(H)$.

In a drawing of H, a broken line segment $C = p_1 p_2 p_3$ (possibly, $p_2 = p_3$) is called a horizontal g-cut segment of H if:

(1) $p_1 p_2$ is horizontal,

(2) each of p_1, p_3 is the center of an edge lying on the boundary of H; and if $p_2 \neq p_3$, p_2 is the center of a hexagon of H,

(3) every point of C is either an interior or a boundary point of some hexagon of H,

(4) if $p_2 \neq p_3$, the angle $p_1 p_2 p_3$ is $\pi/3$.

Let $C = p_1 p_2 p_3$ be a horizontal g-cut segment of H, and let C_{12} and C_{23} denote the sets of the edges of H intersected by straight line segments $C_{12} = p_1 p_2$ and $C_{13} = p_2 p_3$, respectively. Let $C = C_{12} \cup C_{23}$. C is called a horizontal g-cut of H. Clearly, $H - C$ has exactly two components, in which the component containing the white (black) end vertices of the edges in C_{12} is called the upper (lower) bank of C, denoted by $U(C)$ and $L(C)$, respectively (see fig. 3). Let X and Y denote the sets

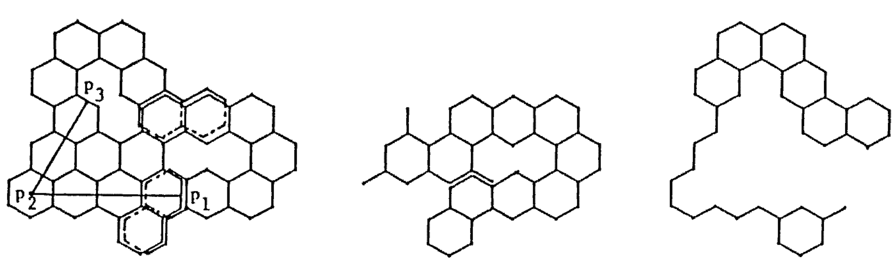


Fig. 3. A horizontal g-cut C of a simply connected polyhex H, and the upper ($U(C)$) and lower ($L(C)$) bank of C.

of the hexagons in $U(C)$ and $L(C)$, and let $H[X]$ and $H[Y]$ be the systems induced by X and Y, respectively. Let $p(H/U(C))$ ($v(H/U(C))$ denote the number of the peaks (valleys) of H that are in $U(C)$.

In particular, if $p_2 = p_3$, $C_{23} = \varnothing$, then C is called a horizontal cut segment and C is called a horizontal cut of H (see fig. 4).

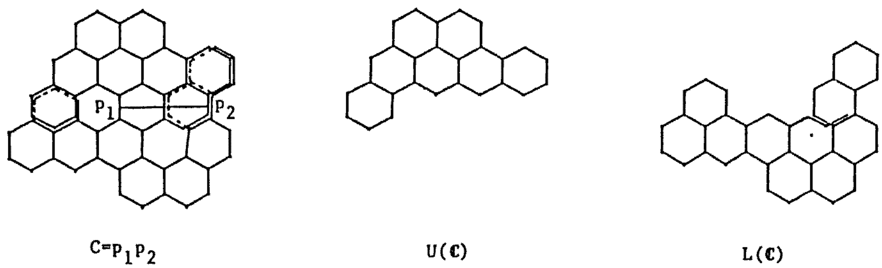


Fig. 4. A horizontal cut C of H, and $U(C)$ and $L(C)$.

For a benzenoid system, the following necessary conditions were given by Sachs [16].

THEOREM 2.1 [16]

Let H be a Kekuléan benzenoid system. Then for each of the six possible positions of H:

(1) $p(H) = v(H)$,

(2) $p(H/U(C)) - v(H/U(C)) \leq |C|$, where C runs through all horizontal cuts.

The above necessary conditions are not sufficient [17]. Some fairly simple necessary and sufficient conditions were given by Kostochka [18], and independently by Zhang Fuji and Chen Rongsi [19,20].

THEOREM 2.2 [19,20]

Let H be a benzenoid system. Then H has a Kekulé structure if and only if for each of the six possible positions of H:

(1) $p(H) = v(H)$,

(2) $p(H/U(C)) - v(H/U(C) \leq |C_{12}|$, where C runs through all horizontal g-cuts of H.

From theorems 2.1 and 2.2, we have that there exist some concealed non-Kekuléan benzenoid systems which satisfy the conditions of theorem 2.1 but not (2) of theorem 2.2. We call them the concealed non-Kekuléan benzenoid systems of type I. The smallest concealed non-Kekuléan benzenoid system of type I was first found by the present authors [21] (see fig. 5).

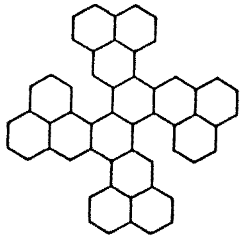


Fig. 5.

THEOREM 2.3 [21]

Let H be a smallest concealed non-Kekuléan benzenoid system of type I. Then,

(1) $h = 14$,

(2) H is unique, as shown in fig. 5.

Combining theorems 2.1, 2.2 and 2.3, we naturally have the following theorem.

THEOREM 2.4 [21]

Let H be a benzenoid system with $h < 14$. Then H has a Kekulé structure if and only if for each of six possible positions and every horizontal cut C of H:

(1) $p(H) = v(H)$,

(2) $p(H/U(C)) - v(H/U(C)) \leq |C|$.

As stated above, a smallest concealed non-Kekuléan benzenoid system has eleven hexagons. It implies the following theorem, which was rigorously proved by the present authors [21,22].

THEOREM 2.5 [21,22]

Let H be a benzenoid system with $h < 11$. Then H has a Kekulé structure if and only if $p(H) = v(H)$.

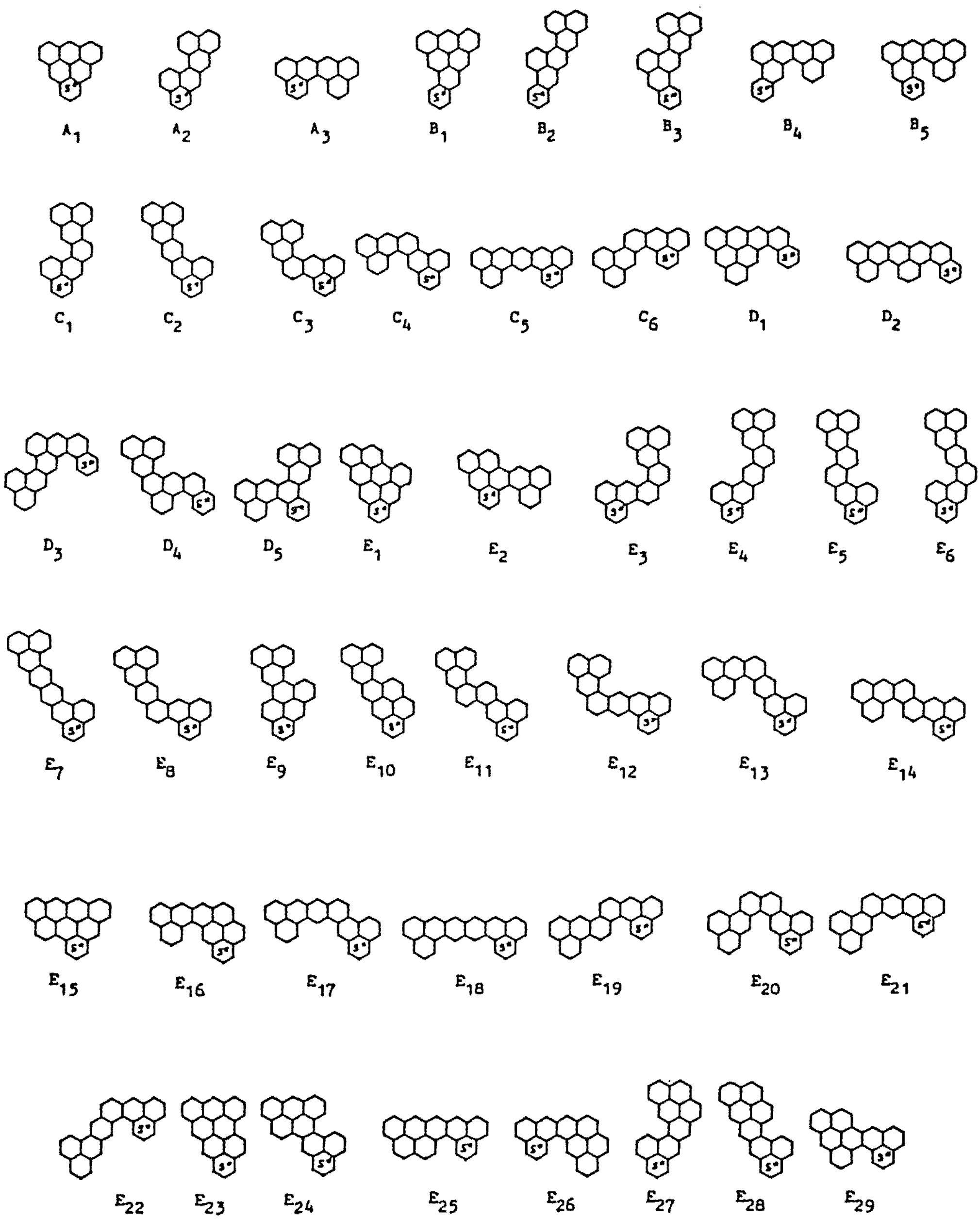
In ref. [30], Guo and Zhang further gave the following theorems.

THEOREM 2.6 [30]

Let H be a concealed non-Kekuléan benzenoid system with $h < 14$. Then there is a horizontal cut C in H such that

(1) $p(H/U(C)) - v(H/U(C)) > |C|$,

(2) $|C| = 2$.



A1 A2 A3 B1 B2 B3 B4 B5
C1 C2 C3 C4 C5 C6 D1 D2
D3 D4 D5 E1 E2 E3 E4 E5 E6
E7 E8 E9 E10 E11 E12 E13 E14
E15 E16 E17 E18 E19 E20 E21
E22 E23 E24 E25 E26 E27 E28 E29

Fig. 6.

A concealed non-Kekuléan benzenoid system H is said to be reducible if it possesses a hexagon with four vertices of degree two in H, otherwise irreducible. The set of reducible (irreducible) concealed non-Kekuléan benzenoid systems with h hexagons is denoted by $\mathcal{N}_h$ ($\bar{\mathcal{N}}_h$).

By theorem 2.6, for a benzenoid system H in $\bar{\mathcal{N}}_h$, $h < 14$, there is a horizontal cut C such that $|C| = 2$ and $p(H/U(C)) - \upsilon(H/U(C)) \geq |C| + 1 = 3$. Let s^* be the unique hexagon of H not in $X \cup Y$, and let $H[X \cup \{s^*\}]$ and $H[Y \cup \{s^*\}]$ denote the benzenoid systems in H induced by $X \cup \{s^*\}$ and $Y \cup \{s^*\}$, respectively.

THEOREM 2.7 [30]

Let $H \in \bar{\mathcal{N}}_h$, $h < 14$, and let C be a horizontal cut of H which satisfies that (1) $|C| = 2$, (2) $p(H/U(C)) - \upsilon(H/U(C)) \geq 3$. Then, $H[X \cup \{s^*\}]$ ($H[Y \cup \{s^*\}]$) must be isomorphic to one of the benzenoid systems, as shown in fig. 6.

Based on the above theorems, a construction method [30] for concealed non-Kekuléan benzenoid systems with $h < 14$ was given by the present authors.

3. The existence of Kekulé structures in a helicene

From the proofs of the above theorems 2.1 and 2.2, it is not difficult to see that the proofs are still valid for helicenes. Hence, we can give the following theorems immediately.

THEOREM 3.1

Let H be a Kekuléan helicene. Then, for each of the six possible positions of H:

(1) $p(H) = \upsilon(H)$,

(2) $p(H/U(C)) - \upsilon(H/U(C)) \leq |C|$, where C runs through all horizontal cuts of H.

THEOREM 3.2

Let H be a helicene. Then H has a Kekulé structure if and only if for each of the six possible positions of H:

(1) $p(H) = \upsilon(H)$,

(2) $p(H/U(C)) - \upsilon(H/U(C)) \leq |C|$, where C runs through all horizontal g-cuts of H.

From theorems 3.1 and 3.2, we can similarly define a concealed non-Kekuléan helicene of type I which satisfies the conditions of theorem 3.1, but not (2) of theorem 3.2.

THEOREM 3.3

Let H be a smallest concealed non-Kekuléan helicene of type I. Then H has exactly fifteen hexagons.

Proof

From the proof od theorem 2.3, we can see that $h > 14$. On the other hand, we can construct such a helicene with $h = 15$ as shown in fig. 7, implying $h \leq 15$. So we have $h = 15$. □

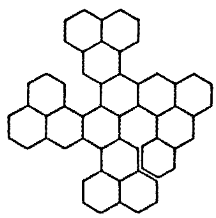


Fig. 7.

The following theorem is a natural corollary of theorems 3.1, 3.2 amd 3.3.

THEOREM 3.4

Let H be a helicene with $h < 15$. Then H has a Kekulé structure if and only if for each of the six possible positions and every horizontal cut C of H:

(1) $p(H) = \upsilon(H)$,

(2) $p(H/U(C)) - \upsilon(H/U(C)) \leq |C|$.

THEOREM 3.5

Let H be a helicene with $h < 11$. Then H has a Kekulé structure if and only if $p(H) = \upsilon(H)$.

Proof

The necessity is obvious. We need only prove the sufficiency. Suppose that $p(H) = \upsilon(H)$, but H has no Kekulé structure. By theorem 3.4, there is a horizontal cut C such that $p(H/U(C)) - \upsilon(H/U(C)) > |C| \geq 2$.

On the other hand, since $h < 11$, one of $U(C)$ and $L(C)$, say $U(C)$, contains at most four hexagons. So $p(H[X]) - \upsilon(H[X]) \leq 1$.

If $p(H[X]) - \upsilon(H[X]) \leq 0$, then $p(H/U(C)) - \upsilon(H/U(C)) \leq p(H[X]) - \upsilon(H[X]) + |C| \leq |C|$, a contradiction.

If $p(H[X]) - \upsilon(H[X]) = 1$, $3 \le h \le 4$ and $H[X]$ is as shown in fig. 8. Then we also have that $p(H/U(C)) - \upsilon(H/U(C)) \le p(H[X]) - \upsilon(H[X]) + |C| - 1 \le |C|$, again a contradiction. □

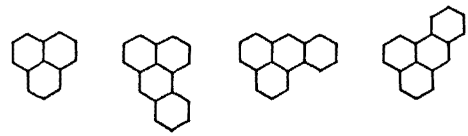


Fig. 8.

4. Enumeration of concealed non-Kekuléan helicenes with $h \le 13$

Let H be a concealed non-Kekuléan helicene; H is said to be h-reducible if there is a hexagon s in H such that the system obtained from H by deleting s, denoted by $H - s$, is still a helicene (not necessarily concealed non-Kekuléan); H is said to be c-reducible if there is a hexagon s with four vertices of degree two in H (clearly, $H - s$ is still concealed non-Kekuléan); the removable hexagon s is said to be an h-reducible hexagon or a c-reducible hexagon of H, respectively. In the other cases, H is said to be h-irreducible or c-irreducible.

If s is an h-reducible or c-reducible hexagon of H, let $H' = H - s$; then we also say that H is obtained from H' by one addition operation, denoted by $H = H' + s$, and the common edge of H' and s is called an attachable edge of H'. In general, for a benzenoid or helicenic system H, an edge with two end vertices of degree two in H is called an attachable edge of H. Particularly, if H is a benzenoid system and $H + s$ is a helicene, then the common edge of H and $H + s$ is called an h-attachable edge of H; if both H and $H + s_1$ are benzenoid systems and $(H + s_1) + s_2$ is a helicene, where s_1 and s_2 have a common edge, then the common edge of H and $H + s_1$ is called a $2 - h$-attachable edge of H.

We denote by $\mathcal{H}_h$ ($\bar{\mathcal{H}}_h$) the set of c-reducible (c-irreducible) concealed non-Kekuléans with h hexagons.

By theorem 3.4, we can establish a construction method for all c-irreducible helicenes in $\bar{\mathcal{H}}_h$, $h \le 14$. Theorem 3.5 means that a smallest concealed non-Kekuléan helicene possesses at least eleven hexagons. So we need only to consider the cases for $11 \le h \le 14$. Furthermore, all c-reducible helicenes in $\mathcal{H}_h$, $h \le 14$, can be recursively obtained from systems in $\bar{\mathcal{N}}_{h-i}$ and $\bar{\mathcal{H}}_{h-i}$, $i \ge 1$, $h - i \ge 11$. In the present paper, we will first give $\bar{\mathcal{H}}_h \cup \mathcal{H}_h$, for $h = 11, 12, 13$.

THEOREM 4.1

Let $H \in \bar{\mathcal{H}}_h$, $h \le 13$. Then there is a horizontal cut C, for some position of H, such that (1) $|C| = 2$, (2) $p(H/U(C)) - \upsilon(H/U(C)) \ge |C| + 1 = 3$.

The proof of the theorem is similar to that of theorem 2 in ref. [30].

THEOREM 4.2

Let $H \in \bar{\mathcal{H}}_h$, $h \leq 13$, and let C be a horizontal cut of H which satisfies that (1) $|C| = 2$, (2) $p(H/U(C)) - v(H/U(C)) \geq 3$. Let s^* be the unique hexagon of H not in $X \cup Y$. Then $H[X \cup \{s^*\}]$ (also $H[Y \cup \{s^*\}]$) must be isomorphic to one of the benzenoid and helicenic systems, as shown in fig. 6 and fig. 9.

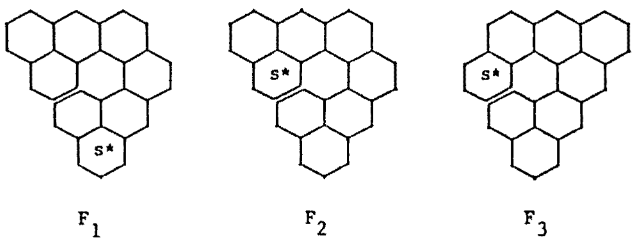


Fig. 9.

Proof

If $H[X \cup \{s^*\}]$ is not a helicene, then it must be isomorphic to one of the benzenoid systems in fig. 6, by the proof of lemma 8 in ref. [30]. In the other cases, $H[X \cup \{s^*\}]$ is a helicene.

Since $p(H/U(C)) - v(H/U(C)) \geq |C| + 1 = 3$, $p(H[X \cup \{s^*\}]) - v(H[X \cup \{s^*\}]) = p(H/U(C)) - v(H/U(C)) - (|C| - 1) \geq 2$. So $|X| \geq 5$, $|Y| \geq 5$. On the other hand, $h \leq 13$, so $|X| \leq 7$, $|Y| \leq 7$, and $6 \leq |X \cup \{s^*\}| \leq 8$. Then $p(H[X \cup \{s^*\}]) - v(H[X \cup \{s^*\}]) = 2$, thereby the dualist $D(H[X \cup \{s^*\}])$ of $H[X \cup \{s^*\}]$ contains two triangles pointing downwards.

It is easy to see that an h-irreducible helicene must be a cata-helicene, so a smallest h-irreducible subhelicene of $H[X \cup \{s^*\}]$ has at most six hexagons, and it can only be the helicene as shown in fig. 10 [19]. Note that $H \in \bar{\mathcal{H}}_h$, so $D(H[X \cup \{s^*\}])$ has at most one vertex of degree one, and if it has exactly one vertex of degree one, the vertex must correspond to s^*. It is not difficult to verify that $H[X \cup \{s^*\}]$ must be isomorphic to one of the three helicenes in fig. 9. □

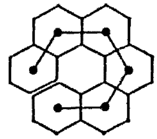


Fig. 10.

Now we are in a position to enumerate all helicences in $\bar{\mathcal{H}}_h \cup \mathcal{H}_h$, for $h \leq 13$. For convenience, we define some notations.

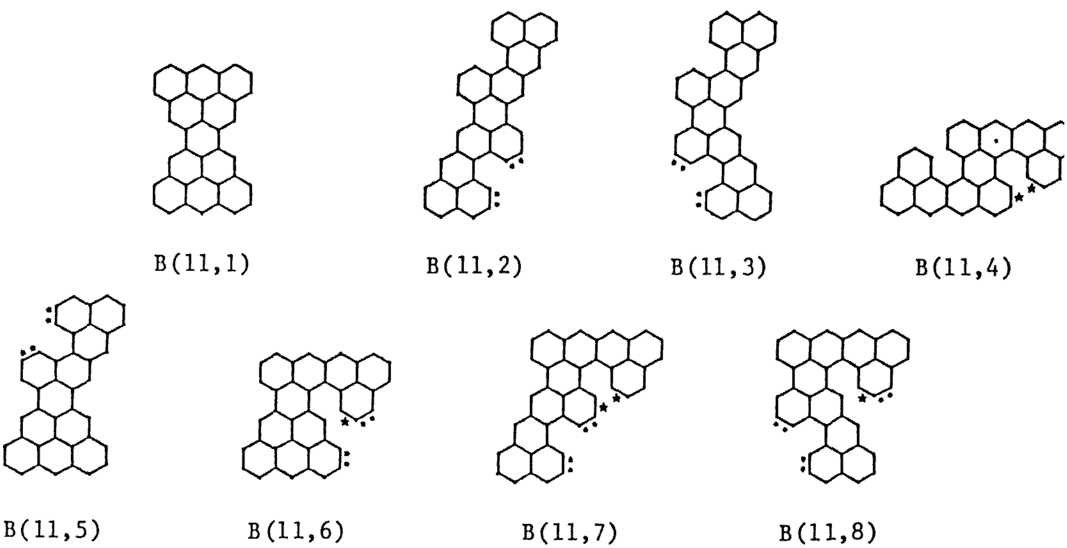


Fig. 11.

Let $B(11, i)$, $i = 1, 2, \ldots, 8$, denote the eight benzenoid systems in $\bar{\mathcal{N}}_{11}$ as shown in fig. 11, and let $B(12, j)$, $j = 1, 2, \ldots, 40$, denote the forty benzenoid systems in $\bar{\mathcal{N}}_{12}$ (see fig. 12). Let $H(h, i)$, $i = 1, 2, \ldots,$ denote the helicenes in $\bar{\mathcal{H}}_h$. Let $\mathcal{H}_{h_2}(\bar{\mathcal{H}}_{h_1})$ denote the set of helicenes in $\mathcal{H}_{h_2}$, each of which is obtained from a helicene in $\bar{\mathcal{H}}_{h_1}$ by $h_2 - h_1$ addition operations. Let $\mathcal{H}_{h_2}(\bar{\mathcal{N}}_{h_1})$ denote the set of helicenes in $\mathcal{H}_{h_2}$, each of which is obtained from a benzenoid system in $\bar{\mathcal{N}}_{h_1}$ by $h_2 - h_1$ addition operations.

For the systems in fig. 6 and fig. 9, let $A = \{A_1, A_2, A_3\}$, $B = \{B_1, B_2, \ldots, B_5\}$, $C = \{C_1, C_2, \ldots, C_6\}$, $D = \{D_1, D_2, \ldots, D_5\}$, $E = \{E_1, E_2, \ldots, E_{29}\}$, and $F = \{F_1, F_2, F_3\}$. Let $P, Q \in \{A, B, C, D, E, F\}$, $N' \subset P$, $N'' \subset Q$, and let $\bar{\mathcal{H}}_h(N', N'') \subset \bar{\mathcal{H}}_h$, $h \leq 13$, be the set of helicenes for which $H \subset \bar{\mathcal{H}}_h(N', N'')$ if $H[X \cup \{s^*\}]$ ($H[Y \cup \{s^*\}]$) is isomorphic to one system in N' (N''). In particular, for $H', H'' \in A \cup B \cup C \cup D \cup E \cup F$, we denote $\bar{\mathcal{H}}_h(\{H'\}, N'') = \bar{\mathcal{H}}_h(H', N'')$, $\bar{\mathcal{H}}_h(\{H'\}, \{H''\}) = \bar{\mathcal{H}}_h(H', H'')$.

THEOREM 4.3

There is exactly one smallest concealed non-Kekuléan helicene with $h = 11$, as shown in fig. 13 (found by Balaban [25]).

Proof

Since $h = 11$, $|X| = |Y| = 5$, and $H[X \cup \{s^*\}]$ and $H[Y \cup \{s^*\}]$ must be isomorphic to one of A_1, A_2, A_3 in fig. 6, by theorem 4.2. Obviously, only one helicene as in fig. 13 can be obtained. □

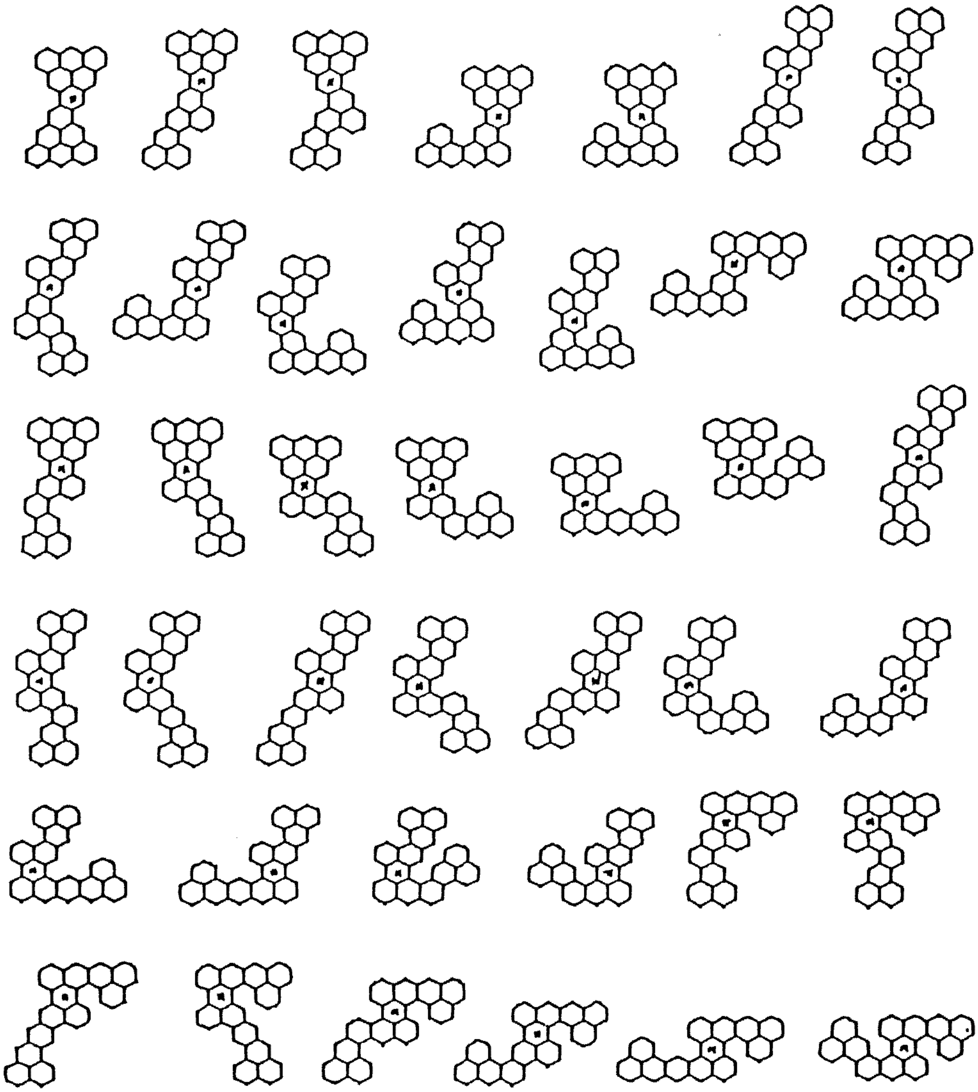


Fig. 12.

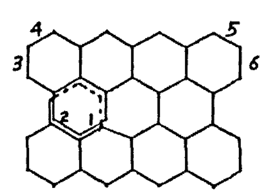


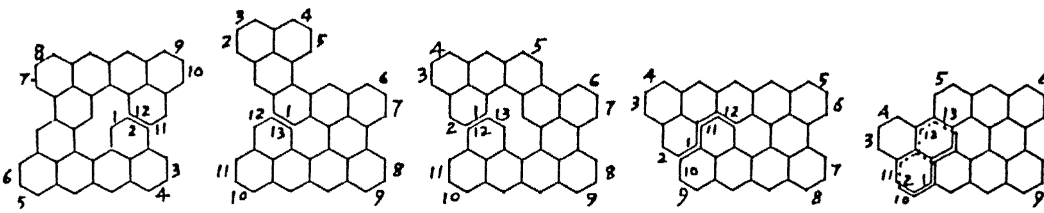
Fig. 13.

THEOREM 4.4

There are exactly seventeen concealed non-Kekuléan helicenes with $h = 12$.

Proof

For $H \in \bar{\mathcal{H}}_{12}$, by theorem 4.1, there is a horizontal cut C satisfying the conditions of theorem 4.2, and $|X| + |Y| = 11$. So one of $|X|$ and $|Y|$, say $|X|$, is equal to five, and $|Y|$ is equal to six. By theorem 4.3, $H[X \cup \{s^*\}]$ is isomorphic to one in A, and $H[Y \cup \{s^*\}]$ is isomorphic to one in $B \cup C$. It is easy to verify that $|\bar{\mathcal{H}}_{12}| = |\bar{\mathcal{H}}_{12}(A, B \cup C)| = 5$, and the five helicenes in $\bar{\mathcal{H}}_{12}$ are as shown in fig. 14.



H(12,1) H(12,2) H(12,3) H(12,4) H(12,5)

Fig. 14.

For $\mathcal{H}_{12}(\bar{\mathcal{N}}_{11})$, we need only to consider the h-attachable edges of every benzenoid system in $\bar{\mathcal{N}}_{11}$. By counting the number of symmetrical equivalence classes of h-attachable edges of each in $\bar{\mathcal{N}}_{11}$ and summing the numbers, we have that $|\bar{\mathcal{H}}_{12}(\bar{\mathcal{N}}_{11})| = 6$.

For $\mathcal{H}_{12}(\bar{\mathcal{H}}_{11})$, the number of symmetrical equivalence classes of attachable edges of the unique system in $\bar{\mathcal{H}}_{11}$ is just equal to six, implying $|\mathcal{H}_{12}(\bar{\mathcal{H}}_{11})| = 6$.

Now we have proved that $|\mathcal{H}_{12} \cup \bar{\mathcal{H}}_{12}| = 17$. □

THEOREM 4.5

There are exactly two hundred and sixty-nine concealed non-Kekuléan helicenes with $h = 13$.

Proof

For $H \in \bar{\mathcal{H}}_{13}$, let C be a horizontal cut of H satisfying the conditions of theorem 4.2. By theorem 4.2, either (1) $|X| = |Y| = 6$, and $H[X \cup \{s^*\}]$ ($H[Y \cup \{s^*\}]$) is isomorphic to one in $B \cup C$, or (2) $|X| = 5$, $|Y| = 7$, and $H[X \cup \{s^*\}]$ is isomorphic to one in A, and $H[Y \cup \{s^*\}]$ is isomorphic to one in $D \cup E \cup F$. It is easy to verify that

$$|\bar{\mathcal{H}}_{13}(B, B)| = 0, \ |\bar{\mathcal{H}}_{13}(B, C)| = |\bar{\mathcal{H}}_{13}(\{B_4, B_5\}, \{C_5, C_6\})| = 3,$$

$|\bar{\mathcal{H}}_{13}(C,C)|$
$= |\bar{\mathcal{H}}_{13}(C_3,C_6) \cup \bar{\mathcal{H}}_{13}(C_4,\{C_5,C_6\}) \cup \bar{\mathcal{H}}_{13}(C_5,\{C_5,C_6\}) \cup \bar{\mathcal{H}}_{13}(C_6,C_6)| = 6,$

$|\bar{\mathcal{H}}_{13}(A,D)| = |\bar{\mathcal{H}}_{13}(A_3,D)| = 5,$

$|\bar{\mathcal{H}}_{13}(A,E)|$
$= |\bar{\mathcal{H}}_{13}(A_3,\{E_i \mid i = 2,3,8,12,14,15,16,18,19,20,21,22,25,26,29\})| = 15,$

$|\bar{\mathcal{H}}_{13}(A,F)| = 15.$

Note that $\bar{\mathcal{H}}_{13}(A_3,\{D_1,D_2,D_3,D_4\}) \cup \bar{\mathcal{H}}_{13}(A,F_3)$, $|\bar{\mathcal{H}}_{13}(A,D) \cap \bar{\mathcal{H}}_{13}(A,F)| = 4$, and any pair of the above sets other than $\bar{\mathcal{H}}_{13}(A,D)$ and $\bar{\mathcal{H}}_{13}(A,F)$ are disjoint. So $|\bar{\mathcal{H}}_{13}| = 44 - 4 = 40$.

For $\bar{\mathcal{H}}_{13}$, we calculate $|\mathcal{H}_{13}(\bar{\mathcal{H}}_{12})|$, $|\mathcal{H}_{13}(\bar{\mathcal{N}}_{12})|$, $|\mathcal{H}_{13}(\bar{\mathcal{H}}_{11})|$, $|\mathcal{H}_{13}(\bar{\mathcal{N}}_{11})|$, respectively.

By counting the numbers of symmetrically equivalent attachable edges of every element in $\bar{\mathcal{H}}_{12}$ and then summing them (see fig. 14), we have that

$|\mathcal{H}_{13}(\bar{\mathcal{H}}_{12})| = 12 + 13 + 12 + 13 + 13 = 63.$

For $\mathcal{H}_{13}(\bar{\mathcal{N}}_{12})$, we count the number of symmetrical equivalence classes of h-attachable edges of $B(12,i)$, $i = 1, 2, \dots, 40$ (see fig. 12), and then take this sum, resulting in $|\mathcal{H}_{13}(\bar{\mathcal{N}}_{12})| = 23$.

For $H \in \mathcal{H}_{13}(\bar{\mathcal{H}}_{11})$, H is constructed from $H(11,1)$ by attaching a new hexagon s_1 to an attachable edge of $H(11,1)$ and then s_2 to an attachable edge of $H(11,1) + s_1$.

We divide the helicenes constructed in this way as six subsets $T_1, T_2, \dots, T_6$ according to the symmetrical equivalence classes $E_1, E_2, \dots, E_6$ of attachable edges of $H(11,1)$ such that $H \in T_i$ if an edge in E_i is attached by s_1 and any edge in $E_1 \cup \dots \cup E_{i-1}$ is not attached by s_2. So $|\mathcal{H}_{13}(\bar{\mathcal{H}}_{11})| = \cup_{i=1}^{6} |T_i| = 13 + 12 + 9 + 8 + 5 + 4 = 51$.

For $H \in \mathcal{H}_{13}(\bar{\mathcal{N}}_{11})$, H is constructed from $B(11,i)$, $i = 1, 2, \dots, 8$, by two addition operations. Let s_1, s_2 be the two attached hexagons. We consider the following two cases.

(1) s_1 and s_2 have an edge in common.

Then for every h-attachable edge of $B(11,i)$, s_1 and s_2 can be attached to it in three ways. Counting the number of symmetrically equivalent h-attachable edges of every $B(11,i)$ and taking three times their sum, we obtain eighteen helicenes in $\mathcal{H}_{13}(\bar{\mathcal{N}}_{11})$. For $2-h$-attachable edges of $B(11,i)$, we count the number of the numbers of symmetrical equivalence classes of them and then take the summation of the numbers for every i, obtaining three helicenes in $\mathcal{H}_{13}(\bar{\mathcal{N}}_{11})$.

(1) s_1 and s_2 have no common edge.

We first consider the case that H is constructed from $B(11,i)$ by attaching s_1 to an h-attachable edge of $B(11,i)$ and then attaching s_2 to an h-attachable edge of $B(11,i) + s_1$ which is not in s_1. The helicenes constructed in this way can be divided into t subsets $T_1, T_2, \ldots, T_t$ according to the symmetrical equivalence classes $E_1, E_2, \ldots, E_t$ of h-attachable edges of $B(11,i)$, for which $H \in T_i$ if an edge in E_i is attached by s_1, and any edge in $E_1 \cup \ldots \cup E_{i-1}$ is not attached by s_2. So from $B(11,i)$, $i = 4, 6, 7, 8$, eighteen, eight, nineteen, and ten helicenes in $\mathcal{H}_{13}(\bar{\mathcal{N}}_{11})$ can be obtained, respectively, resulting in fifty-five such helicenes (see fig. 15).

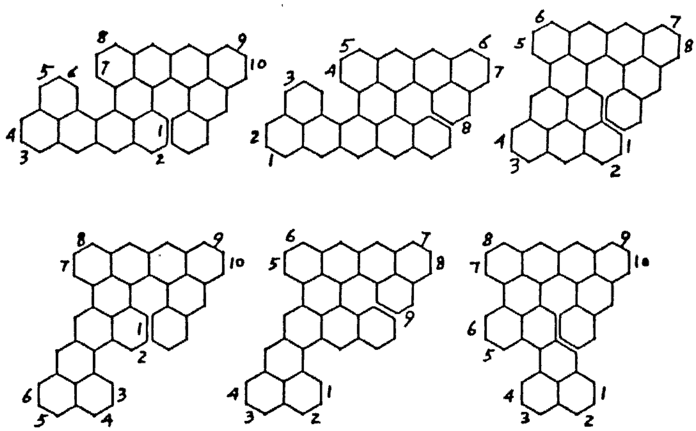


Fig. 15.

In the other case, H is constructed from $B(11,i)$ by attaching s_1 and s_2, respectively, to a pair of $2-h$-attachable edges of $B(11,i)$ such that $(B(11,i) + s_1) + s_2$ is a helicene. This gives six helicenes in $\mathcal{H}_{13}(\bar{\mathcal{N}}_{11})$.

Now it follows that $|\mathcal{H}_{13}(\bar{\mathcal{N}}_{11})| = 18 + 13 + 55 + 6 = 92$, $|\mathcal{H}_{13}| = 63 + 23 + 51 + 92 = 229$, and $|\mathcal{H}_{13} \cup \bar{\mathcal{H}}_{13}| = 229 + 40 = 269$.

5. Conclusion

Hunting for concealed non-Kekuléan benzenoid systems has an interesting history, as described in a paper by Cyvin et al. [32]. Several authors participated in this "hunting". However, a graph-theoretical approach has been developed only in recent years [21,30], based on the necessary and sufficient conditions for the existence of Kekulé structures in a benzenoid system.

Since we have the basic theory already available, the process of hunting for concealed non-Kekuléan helicenes is faster than the same process for benzenoids. In fact, this paper gives the numbers for $h = 11, 12, 13$, simultaneously. This perhaps shows the power of theoretical considerations. It would be interesting to compare the numbers obtained by analytical methods in the present work to a result obtained eventually by computer programming.

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