Partitioning of π-electrons in rings of polycyclic conjugated hydrocarbons. Part 4. Benzenoids with more than one geometric Kekulé structure corresponding to the same algebraic Kekulé structure

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A rigorous proof is provided for the theorem on the necessary and sufficient conditions for the algebraic Kekulé structure of a peri-condensed or corona-condensed benzenoid hydrocarbon to correspond to more than one geometric Kekulé structure.

KEY WORDS: polycyclic benzenoid hydrocarbons, algebraic vs. geometric Kekulé structures

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1.   Definitions and the main result

A geometric Kekulé structure is a normal structure as usually drawn to represent the two resonant structures of benzene, the three limiting structures of naphthalene, etc. As indicated in previous papers [1–4], an algebraic Kekulé structure inscribes in every possible Kekulé structure for a polycyclic benzenoid the count of π-electrons belonging to each ring by considering that a double bond shared by two condensed rings contributes by one π-electron.

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It was proved earlier [5] that catafusenes have a one-to-one correspondence between geometric and algebraic Kekulé structures, but that perifusenes and coronafusenes have exceptions from this rule. The simplest definitions of catafusenes, perifusenes and coronafusenes are based on their dualist (former name: characteristic) graphs [6,7]. This paper describes such exceptions in detail.

Denote by $V(G)$ the set of vertices of a connected graph G and by $E(G)$ the set of edges of G. Let S be a connected subgraph of G. Denote by $G - S$ the graph induced by the set of vertices $V(G) - V(S)$. By $E(H)$ denote the set of edges of a benzenoid ring H; by $E_1(H)$ the set of edges of hexagon H that are shared with another hexagon; by $E_2(H)$ the set of edges of H that belong only to hexagon H and by $\chi(K, H)$ the number of π-electrons that belong to hexagon H considering geometric Kekulé structure K. Denote the symmetric difference of the sets S_1 and S_2 (i.e., the set of elements that are contained in exactly one of the sets S_1 and S_2) by $S_1 \Delta S_2$. For a geometric Kekulé structure K, denote by $D(K)$ the set of double bonds.

Our main result reads

Theorem. A benzenoid system G does not have one-to-one correspondence between algebraic and geometric Kekulé structures if and only if it contains at least one graph C each of whose connected components is a cycle and such that edges of C can be divided in two classes C_1 and C_2 such that

(1) neither of classes C_1 and C_2 contains two consecutive edges of any cycle in C. In other words, C is a conjugated circuit.

(2) $G - V(C)$ has a Kekulé structure.

(3) For each hexagon H in the benzenoid G, we have

$$|E_1(H) \cap C_1| + 2 \cdot |E_2(H) \cap C_1| = |E_1(H) \cap C_2| + 2 \cdot |E_2(H) \cap C_2|.$$

Proof. First, suppose that benzenoid graph G does not have one-to-one correspondence between geometric Kekulé structures and algebraic Kekulé structures. Denote by A the algebraic Kekulé structure that corresponds to both Kekulé structures K_1 and K_2. Note that each vertex in the subgraph C of the graph G with the set of edges $D(K_1) \Delta D(K_2)$ has degree 0 or 2 (and at least one vertex has degree 2). Therefore C is the union of disjoint cycles. Denote $C_1 = C \cap D(K_1)$ and $C_2 = C \cap D(K_2)$. Note that neither of classes C_1 and C_2 contains two consecutive edges of any cycle in C. Also, note that the set of edges K_1/C_1 represents a Kekulé structure in G/C. It remains to prove (2). Let H be an arbitrary hexagon. Denote $D_1 = D(K_1)$ and $D_2 = D(K_2)$. Since K_1 and K_2 correspond to the same algebraic Kekulé structure, it follows that

$$|E_1(H) \cap D_1| + 2 \cdot |E_2(H) \cap D_1| = |E_1(H) \cap D_2| + 2 \cdot |E_2(H) \cap D_2|.$$

From the last relationship, it follows that

$$|E_1(H) \cap (D_1 \cap D_2)| + 2 \cdot |E_2(H) \cap (D_1 \cap D_2)| + |E_1(H) \cap (D_1/D_2)|$$
$$+2 \cdot |E_2(H) \cap (D_1/D_2)|$$
$$= |E_1(H) \cap (D_1 \cap D_2)| + 2 \cdot |E_2(H) \cap (D_1 \cap D_2)| + |E_1(H) \cap (D_2/D_1)|$$
$$+2 \cdot |E_2(H) \cap (D_2/D_1)|.$$

From here, it follows that

$$|E_1(H) \cap (D_1/D_2)| + 2 \cdot |E_2(H) \cap (D_1/D_2)| = |E_1(H) \cap (D_2/D_1)|$$
$$+2 \cdot |E_2(H) \cap (D_2/D_1)|$$

or equivalently that

$$|E_1(H) \cap C_1| + 2 \cdot |E_2(H) \cap C_1| = |E_1(H) \cap C_2| + 2 \cdot |E_2(H) \cap C_2|.$$

Now, let us prove the opposite implication. Let C be the graph with properties required in the theorem. Let K be an arbitrary Kekulé structure of the graph $G - V(C)$. Note that $K \cup C_1$ and $K \cup C_2$ are two different geometric Kekulé structures of G. Let us prove that these two structures correspond to the same algebraic Kekulé structure. Let H be an arbitrary hexagon. We have

$$|E_1(H) \cap C_1| + 2 \cdot |E_2(H) \cap C_1| = |E_1(H) \cap C_2| + 2 \cdot |E_2(H) \cap C_2|.$$

It follows that

$$|E_1(H) \cap C_1| + 2 \cdot |E_2(H) \cap C_1| + |E_1(H) \cap K| + 2 \cdot |E_2(H) \cap K|$$
$$= |E_1(H) \cap C_2| + 2 \cdot |E_2(H) \cap C_2| + |E_1(H) \cap K| + 2 \cdot |E_2(H) \cap K|.$$

Therefore,

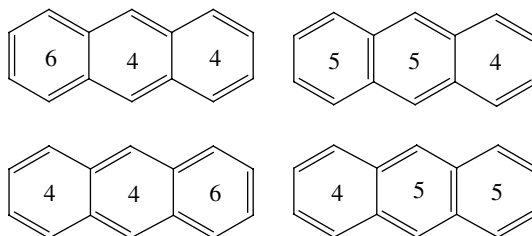$$|E_1(H) \cap (C_1 \cup K)| + 2 \cdot |E_2(H) \cap (C_1 \cup K)| = |E_1(H) \cap (C_2 \cup K)|$$
$$+2 \cdot |E_2(H) \cap (C_2 \cup K)|.$$

Therefrom, $\chi(C_1 \cup K, H) = \chi(C_2 \cup K, H)$, which proves the claim. □

We now illustrate the theorem with examples.

Example 1. Here, we give an example of a benzenoid graph (anthracene) with one-to-one correspondence between algebraic and geometric Kekulé structures, as for all catafusenes.

Example 2. Now, we give an example of another benzenoid graph (pyrene) which is peri-condensed and does not present a one-to-one correspondence between algebraic and geometric Kekulé structures: the outline of hexagons on the left-hand side with the algebraic count of π-electrons corresponds to two geometric Kekulé structures on the right.
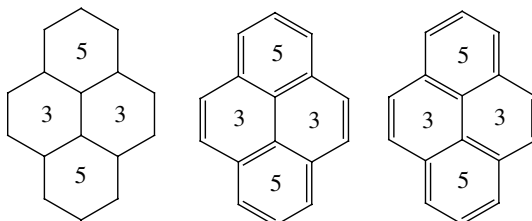

Of course, note that this graph has to have a subgraph described in our theorem. There are two such subgraphs presented in the following figure:
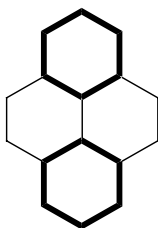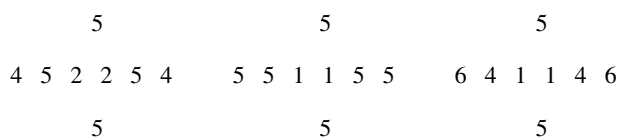

Example 3. If one adds, on each side of the horizontal naphthalene fragment in the above formula of pyrene, any catafusene (benzene, naphthalene, etc.), then one obtains an infinity of pairs of geometric perifusene Kekulé structures with one and the same algebraic Kekulé structure. We will start by adding one benzenoid ring on each side.
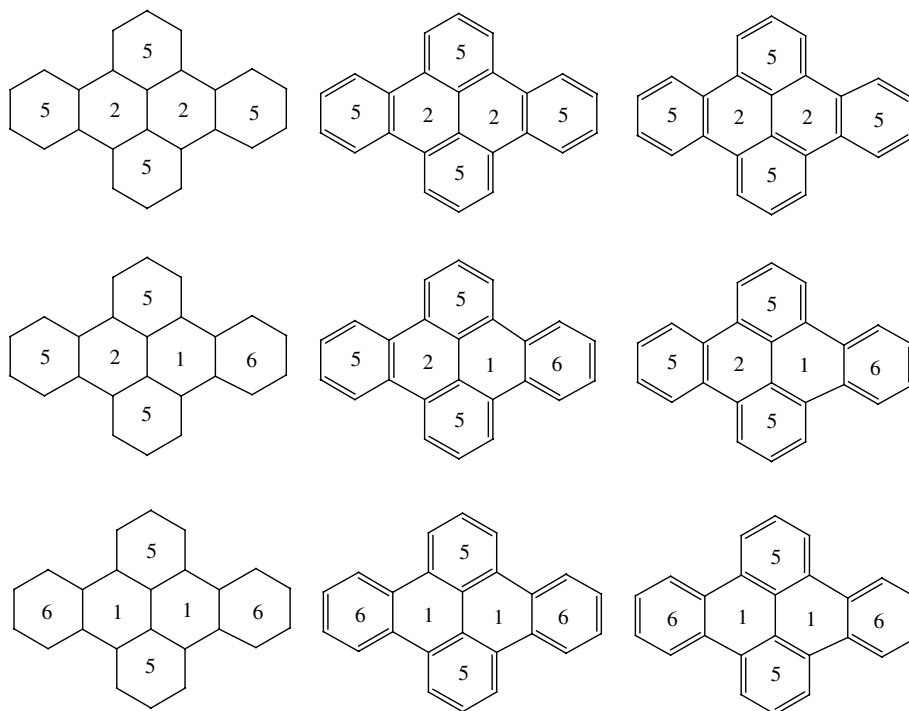
All these examples may be symbolized in condensed form by the following notation for the Kekulé structures:

```
    5           5              5               5

 3   3      5  2  2  5     5  2  1  6      6  1  1  6

    5           5              5               5
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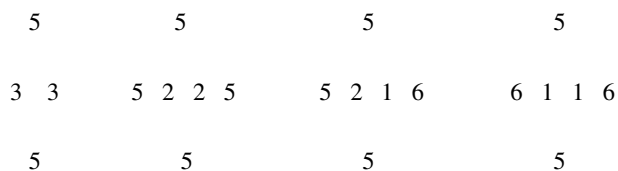
Example 4. In a similar manner, by adding on both sides of the two pyrene Kekulé structures from Example 2 naphthalene systems, one will obtain the following Kekulé structures that illustrate the present theorem:

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        5                    5                  5

 4  5  2  2  5  4      5  5  1  1  5  5    6  4  1  1  4  6

        5                    5                  5
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Example 5. Just as in the case of the system displayed in the middle formulas of Example 3 with non-symmetrical geometric Kekulé structures on the two sides of the two pyrene benzenoid rings, one obtains the following Kekulé structures

that illustrate the present theorem; the first two are symmetrical, and the third one is not.

$$
\begin{array}{ccc}
5 & 5 & 5 \\
6\ 4\ 1\ 2\ 5\ 4 & 6\ 4\ 1\ 1\ 5\ 5 & 2\ 5\ 4\ 1\ 4\ 6 \\
5 & 5 & 5
\end{array}
$$

Example 6. On adding on both sides of the two pyrene Kekulé structures from Example 2 anthracene systems, it is possible to obtain the following Kekulé structures that illustrate the present theorem, as well as less symmetrical ones that are not shown:

$$
\begin{array}{ccc}
5 & 5 & 5 \\
6\ 4\ 4\ 1\ 1\ 4\ 4\ 6 & 5\ 5\ 4\ 1\ 1\ 4\ 5\ 5 & 4\ 5\ 5\ 1\ 1\ 5\ 5\ 4 \\
5 & 5 & 5
\end{array}
$$

Example 7. As a last variation on the pyrene theme, the following benzenoid combines all but one of the possible partitions of the π-electrons to illustrate the theorem (only zero is absent).
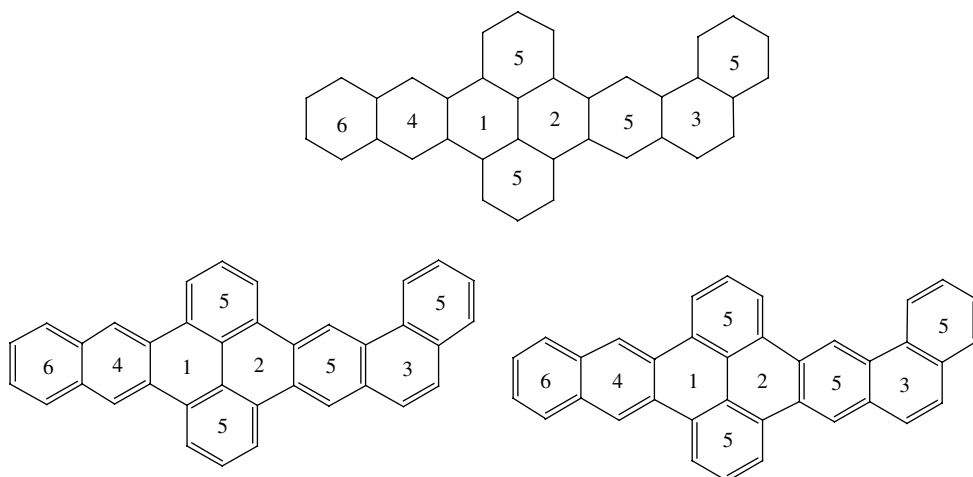
Example 8. Let us observe the following graph, which is again a perifusene (bis-perylene):
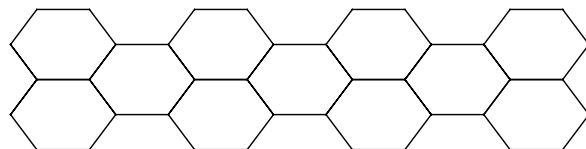

In this graph, we have a larger number of graphs with the properties described in the theorem as presented by the following figure:
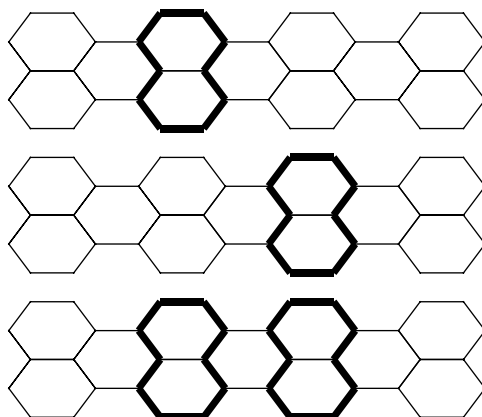

Obviously, this benzenoid does not have one-to-one correspondence between algebraic and geometric Kekulé structures as demonstrated by the following four geometric Kekulé structures corresponding to one and the same algebraic Kekulé structure.
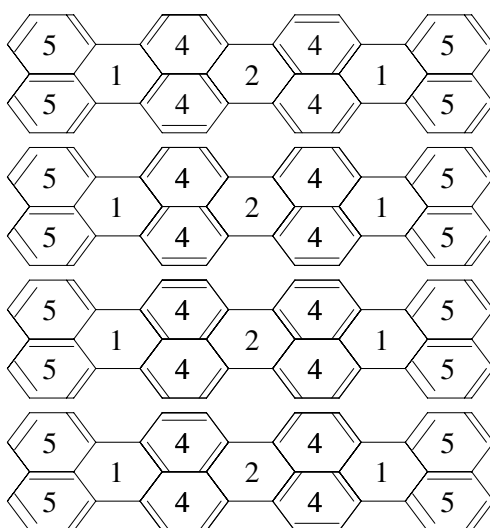
Example 9. The last example is a coronoid (kekulene). Two of its geometric Kekulé structures correspond to one and the same algebraic Kekulé structure. These have the lowest degree of freedom among all geometric Kekulé structures of kekulene.
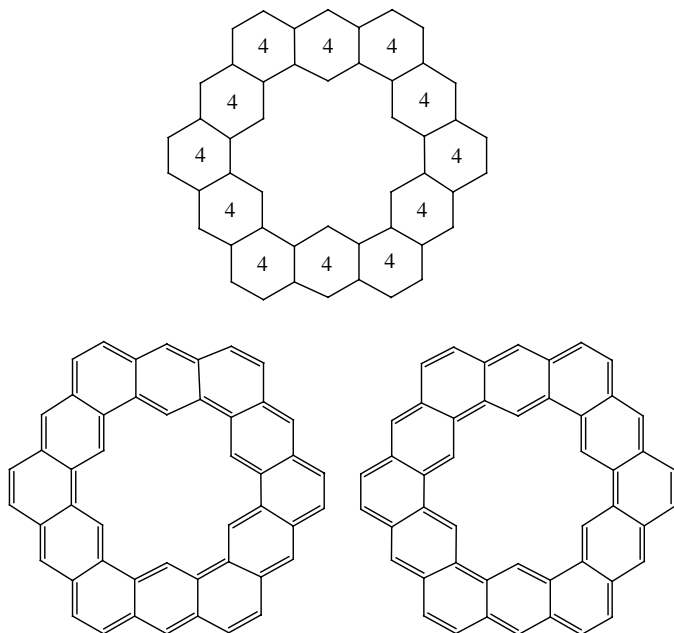
It is not difficult to realize that any coronoid (such as those examined in Part 2 of the present series, including the following two fibonacenic coronoids), have such a pair of geometric Kekulé structures with one outer and inner con-jugated circuit yielding an algebraic Kekulé structure that has for each ring a partition of four π-electrons, just as in kekulene. However, for fibonacenic cor-onoids (where there is no anthracenic subgraph) there is third geometric Kekulé structure whose rings have all the same partition with four π-electrons, namely the so-called Fries structure in which every benzenoid ring has a π-electron sex-tet, sharing two electron pairs with adjacent rings.
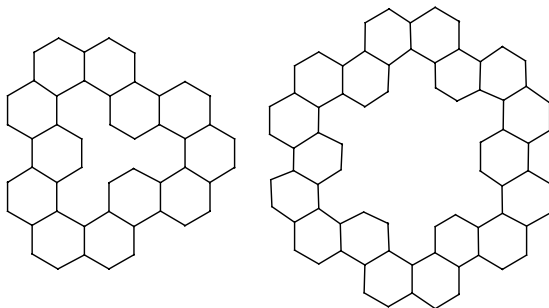
It is easy to see that for kekulene and similar coronoids, the benzenoid ring in the middle of the linear portion satisfies the condition of being a *C*-type ring. For fibonacenic coronoids, any single benzenoid ring satisfies that condition, and all alternate rings together satisfy that condition.

2.   Conclusion

The necessary and sufficient conditions for an algebraic Kekulé structure to correspond to two or more geometric Kekulé structures were described and exemplified for perifusenes and coronafusenes.

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