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On the anti-Kekulé number and anti-forcing number of cata-condensed benzenoids

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Previously introduced concepts the anti-Kekulé number and anti-forcing number (Vukicevic et al., J. Math. chem., in press) are applied to cata-condensed benzenoids. It is shown that all cata-benzenoids have anti-Kekulé number either 2 or 3 and both classes are characterized. The explicit formula for anti-forcing number of chain (unbranched) cata-benzenoids is given. It is also shown that anti-forcing number of any cata-benzenoid goes up to $h/2$ where h is the number of hexagons in a cata-benzenoid.

KEY WORDS: anti-forcing number, anti-Kekulé number, cata-condensed benzenoids, chain cata-benzenoids

AMS SUBJECT CLASSIFICATIONS: 05C35, 05C90

1. Introduction

The *anti-Kekulé number* and *anti-forcing number* are recently introduced in this journal [1]. The roots of these concepts can be traced to reports by Randić and Klein [2] and Harary et al. [3]. Randić and Klein introduced the term the innate degree of freedom or the forcing number of a Kekulé structure. Later Harary et al. discussed the concept of forcing number in more detail. Zhang and Li [4] also contributed early to the discussion on the forcing number of hexagonal systems. The concept has been revived in recent years and the global (or total) forcing number [5–7] is introduced.

The forcing number is defined as the smallest number of double bonds that completely determine the Kekulé structure of a benzenoid [8]. A quantity that is opposite to the forcing number is called the anti-forcing number. The anti-Kekulé number of a benzenoid is the smallest number of edges that have to

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be removed from a benzenoid in order that it remains connected, but without any Kekulé structure.

The aim of this paper is to analyze the anti-Kekulé number and the anti-forcing number of cata-condensed benzenoids (it is assumed that benzene is not cata-condensed benzenoid).

2. Results and discussion

Let G be a graph with at least one Kekulé structure. Anti-Kekulé set S is the set of edges such that $G - S$ is connected, but has no Kekulé structures. The cardinality of the smallest such set is called anti-Kekulé number and it is denoted by $\mathrm{akn}(G)$. Anti-forcing set S is the set of edges such that $G - S$ has only one Kekulé structure. The cardinality of the smallest such set is called anti-forcing number and it is denoted by $\mathrm{afn}(G)$.

We will show that all cata-condensed benzenoids have anti-Kekulé number either 2 or 3, where "more-branched" cata-condensed benzenoids have akn equal to 3, while "less-branched" cata-condensed benzenoids have akn equal to 2. These concepts will be defined below more formally. The hexagon H in the cata-condensed benzenoid B is called the *branched hexagon* if it has three neighbors. Otherwise, H is the *non-branched hexagon*.

Definition 1. Cata-condensed benzenoid B is a *more-branched* benzenoid if it has no two adjacent non-branched hexagons. Otherwise, it is a *less-branched* cata-condensed benzenoid.

Definition 2. Chain cata-condensed benzenoid is a cata-condensed benzenoid in which every hexagon has at most two neighbors.

Chain cata-condensed benzenoids can be *linear* or *kinky*. For example, the kinky cata-condensed benzenoid with five kinks is given below (figure 1).

Let us prove the following theorems.

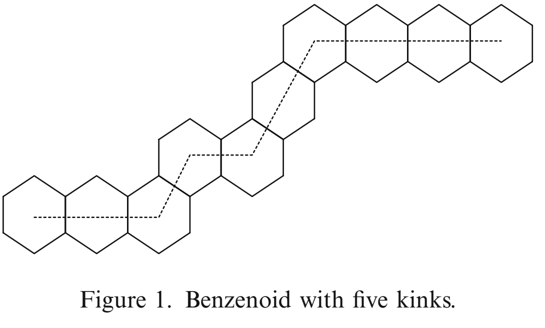

Figure 1. Benzenoid with five kinks.

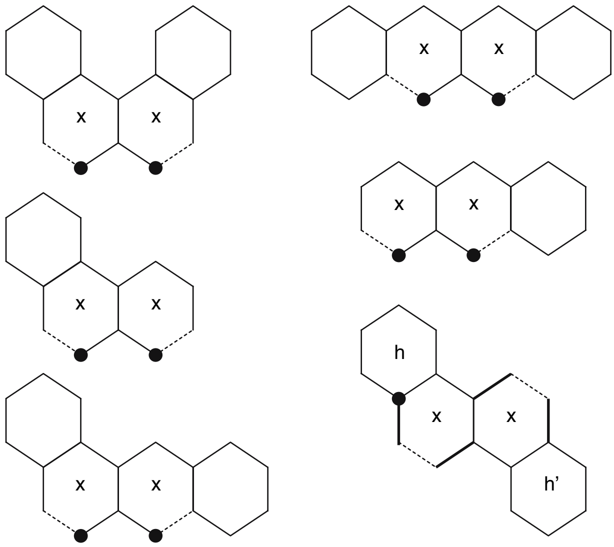

Figure 2. Six possible segments of B.

Theorem 3. Let B be less-branched benzenoid. Then, $\text{akn}(B) = 2$.

Proof. First, let us prove that $\text{akn}(B) \geqslant 2$. It can be easily seen that there are two Kekulé disjoint structures κ_1 and κ_2 such that union of their edges is border of B. Obviously, each anti-Kekulé set has to contain at least one edge from κ_1 and one edge from κ_2. Hence, indeed $\text{akn}(B) \geqslant 2$. Now let us prove that $\text{akn}(B) \leqslant 2$. If B is naphthalene, the claim is simple. Hence, suppose otherwise. Note that B has (up to symmetry) one of the segments presented below, where hexagons denoted by x have no additional neighboring hexagons (figure 2).

Denote by S edges drawn by dotted lines. In the first five cases, it can be easily seen that $B - S$ is connected graph without Kekulé structures (two vertices denoted by black circles cannot be covered by double bonds). Let us prove that same holds for the sixth case. Suppose to the contrary that there is Kekulé structure κ on $B - S$. Note that edges drawn by bold lines have to be covered by double bonds. Elimination of hexagons denoted by x (without edges incident to h and h') from B gives two cata-condensed hexagons B_1 (that contains h) and B_2 (that contains h'). Note that restriction of κ to B_1 coveres all vertices, but vertex denoted by black circle. The number of these vertices is odd (because number of vertices of B_1 is even). This is contradiction. Hence, indeed $\text{akn}(B) = 2$. □

Theorem 4. Let B be more-branched benzenoid. Then, $\text{akn}(B) = 3$.

Proof. First, let us prove that $\text{akn}(B) \leqslant 3$. Note that B has (up to symmetry) the segments presented below, where hexagons denoted by x have no additional neighboring hexagons (figure 3).

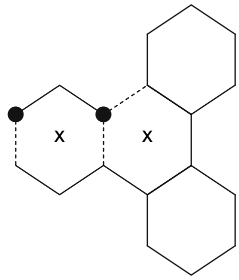

Figure 3. Segment of B.

It can be easily seen that $B-S$ is the connected graph without Kekulé structures (two vertices denoted by black circles cannot be covered by double bonds). Now let us prove that $\mathrm{akn}(B) \geqslant 3$. Suppose to the contrary, that $\mathrm{akn}(B) \leqslant 2$. Then, there is anti-Kekulé set S with two elements. As before, note that there are Kekulé structures κ_1 and κ_2 which union is border of B. Obviously, B contains one edge from κ_1 and other from κ_2. Observe the system of Kekulé structures K such that each non-branched hexagon has three double bonds and each edge between two branched-hexagons is covered by double bond. An example is given below (figure 4).

It follows that S consists of two edges in the same hexagon h both on the border of the benzenoid one in κ_1 and other in κ_2. Hexagon h has one or two neighbours, hence up to isomorphism, we have three possible cases (figure 5).

In the first case, S is one of the following sets: $\{e_1, e_2\}$, $\{e_1, e_4\}$, $\{e_2, e_3\}$, and $\{e_3, e_4\}$, but in each case $B - S$ is disconnected, which is contradiction. In the second case, E is one of the following sets: $\{e_5, e_6\}$, $\{e_5, e_7\}$, and $\{e_5, e_8\}$, but in each case $B-E$ is disconnected, which is contradiction. Similar analyses give the contradiction in the third case. □

Denote by $\lceil x \rceil$ the smallest integer not less then x. Then we have:

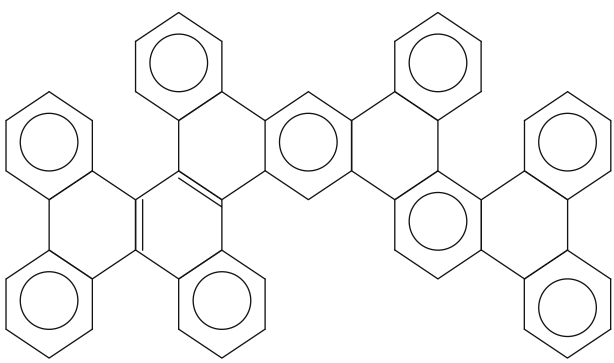

Figure 4. System of Kekulé structures on more-branched benzenoid.

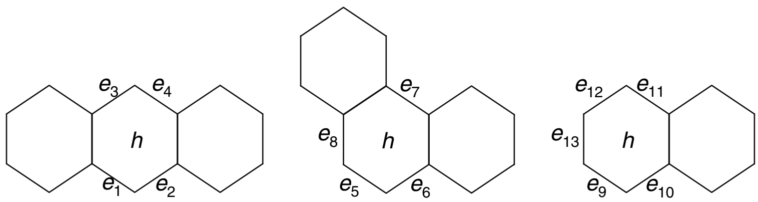

Figure 5. Three possible cases of neighbors of h.

Theorem 5. Let B be chain cata-benzenoid with k kinks. Then, $\mathrm{afn}(B) = \lceil k/2 \rceil$.

Proof. First, let us prove that $\mathrm{afn}(B) \leqslant \lceil k/2 \rceil$ by induction on k. Consider the case when $k = 1$ exemplified below (figure 6).

If $S = \{e_1\}$, then obviously this chain cata-benzenoid possess only one Kekulé structure. Similarly, consider the case when $k = 2$ exemplified below (figure 7).

Therefore, if $S = \{e_2\}$, then cata-condensed benzenoid possesses only one Kekulé strcture. Now, suppose that claim holds for all values smaller then k and let us prove it for k. Let us present this case by figure 8.

Note that edge e_3 fixes double bonds depicted in the figure. Eliminating vertices covered by these double bonds, we get chain cata-benzenoid-benzenoid B' with $k - 2$ kinks. Hence there is (by induction hypothesis) set S' with $\lceil (k-2)/2 \rceil$ elements that fixes all double bonds on B'. But then set $S' \cup \{e_3\}$ with $\lceil k/2 \rceil$ elements fixes all double bonds on B. Now, let us prove that $\mathrm{afn}(B) \geqslant \lceil k/2 \rceil$ by induction on k. If $k = 1, 2$, the claim is obvious. Hence, suppose that $k \geqslant 3$ and that claim holds for the smaller values. Let this case be presented

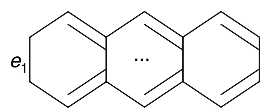

Figure 6. Chain benzenoid without kinks.

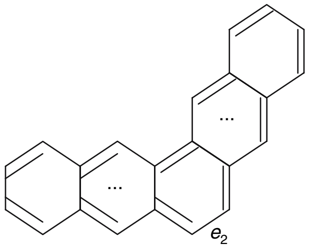

Figure 7. Chain benzenoid with only one kink.

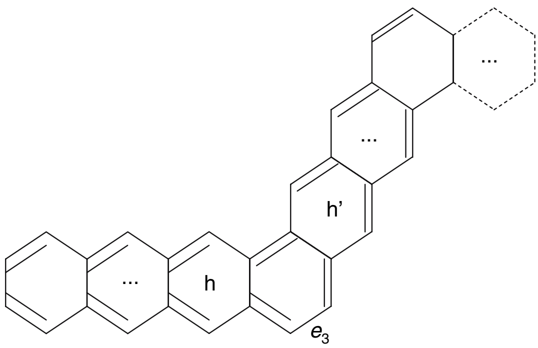

Figure 8. Chain benzenoid with at least two kinks.

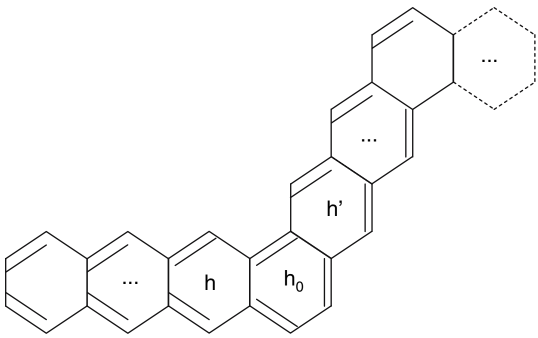

Figure 9. Fragment of Kekulé structure of the chain benzenoid with at least two kinks.

as in the last figure. Denote by B'' cata-benzenoid consisting of h hexagon and "before h" hexagons and denote by B''' cata-benzenoid consisting of h' hexagon and "after h'" hexagons. Distinguish three cases:

Case 1. $e_3 \in S$.
This fixes double bonds presented in the above figure. By induction hypothesis $\mathrm{afn}(B') \geqslant \lceil (k-2)/2 \rceil$. Hence, $\mathrm{afn}(B') \geqslant \lceil k/2 \rceil$.

Case 2. $e_3 \notin S$ and restricting the only Kekulé structure κ (of B) to B'' to be the Kekulé structure of B''.
In this case, $e_3 \in \kappa$. Hence, restriction of κ to B''' is Kekulé structure of B'''. Therefore:

$$\mathrm{afn}\,(B) \geqslant \mathrm{afn}\,(B'') + \mathrm{afn}\,(B''') \geqslant \{\text{by induction hypothesis}\} \geqslant 1 + \left\lceil \frac{k-2}{2} \right\rceil = \left\lceil \frac{k}{2} \right\rceil .$$

Case 3. $e_3 \notin S$ and restriction of the only Kekulé κ (of B) structure to B'' is not Kekulé structure of B'' (figure 9).

Let B_0 be benzenoid consisting of hexagon h_0 and hexagons "before" h_0. From the uniqueness of κ, it follows that there is at least one edge of B_0 in S.

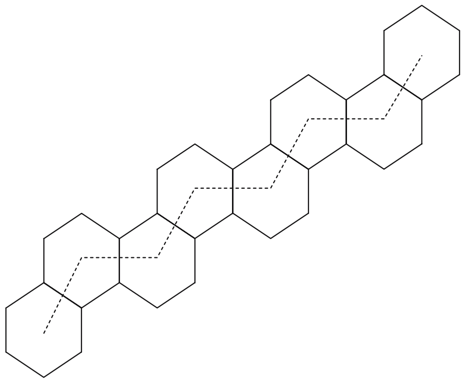

Figure 10. Zig-zag benzenoid.

Also note that the restriction of κ to B' is the Kekulé structure of B' and then it follows that $\mathrm{akn}(B) \geqslant 1 + \mathrm{akn}(B') \geqslant$ {by induction hypothesis} $\geqslant 1 + \lceil \frac{k-2}{2} \rceil = \lceil \frac{k}{2} \rceil$.
All the cases are exhausted and the theorem is proved. □

Theorem 6. Let B be the cata-condensed benzenoid with h hexagons. Then, $\mathrm{afn}(B) \leqslant \lfloor h/2 \rfloor$. There is a benzenoid B_h with h hexagons such that $\mathrm{afn}(B_h) = \lfloor h/2 \rfloor$.

Proof. Let benzenoid B_h be depicted below (figure 10).

From the theorem 5, it follows that, $\mathrm{afn}(B_h) = \lceil k/2 \rceil = \lceil (h-1)/2 \rceil = \lfloor h/2 \rfloor$. Now let us prove that for each cata-condensed benzenoid h with h vertices, we have $\mathrm{afn}(B) \leqslant \lfloor h/2 \rfloor$. We prove the claim by induction on h. Note that from theorem 5, it follows that claim holds for all chain cata-condensed benzenoids. Hence, the claim holds for $h = 2, 3$. Now suppose that $h \geqslant 4$ and that B has at least one hexagon H with three neighbors as on the following figure 11.

Denote by B_i benzenoid "starting" with hexagon H_i and denote by h_i number of hexagons in H_i (put $h_i = 0$ if there is no hexagon H_i in B). Note that $h_1 + h_2 + \cdots + h_6 \leqslant h - 4$. Let S_i be the smallest anti-forcing set of B_i. Note that S_i has (by inductive hypothesis) at most $\lfloor h_i/2 \rfloor$ elements. Set $S = \{e', e''\} \cup S_1 \cup S_2 \ldots \cup S_6$ has $2 + \lfloor h_1/2 \rfloor + \lfloor h_2/2 \rfloor + \cdots + \lfloor h_6/2 \rfloor \leqslant \lfloor h/2 \rfloor$ elements. It is sufficient to show that S is anti-forcing set of B. Note that elimination of edges e' and e'' fix all double bonds depicted in the above cata-condensed besnenoid. Hence, it is sufficient to fix all edges in benzenoids B_i, $i = 1, \ldots, 6$, but this is done by edges in S_i. Therefore, S is indeed the anti-forcing set with at most $2 + \lfloor h_1/2 \rfloor + \lfloor h_2/2 \rfloor + \cdots + \lfloor h_6/2 \rfloor \leqslant \lfloor h/2 \rfloor$ elements which proves the theorem.

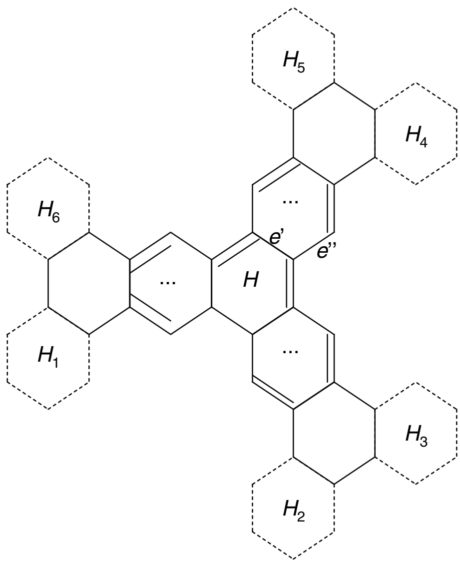

Figure 11. Benzenoid B.

3. Conclusion

The analysis of cata-condensed benzenoids shows that these benzenoids possess only two values of the anti-Kekulé number: 2 or 3, depending where the cata-benzenoid is unbranched or branched.

The anti-forcing number of chain (unbranched) cata-benzenoids is computed. It is also shown that this number of any cata condensed benzenoid is at most $h/2$ if h is even and $(h-1)/2$ if h is odd, where h is the number of hexagons in a cata-benzenoid.

Acknowledgments

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