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Note

Counting Kekulé Structures of Benzenoid Parallelograms Containing One Additional Benzene Ring*

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Formulas are given for counting Kekulé structures in a special class of benzenoids made up of benzenoid parallelograms to which a single benzene ring is added.

This note was stimulated by recent papers of Lukovits[1] and Došlić[2] on counting Kekulé structures in benzenoid parallelograms. Their works are rooted in earlier reports by Gordon and Davison[3] and Yen.[4] In the present note, we give the answer to the question how the number of Kekulé structures K changes when a single benzene ring is added to the benzenoid parallelogram. Note that a benzenoid in a parallelogram-like shape, called the benzenoid parallelogram and denoted by $B_{m,n}$, consists of $m \times n$ benzene rings, arranged in m rows, each row containing n benzene rings, shifted by a half benzene ring to the right from the row immediately below. In Figure 1, we give as an illustrative example a benzenoid parallelogram $B_{m,n}$ where $m = 3$ and $n = 4$.

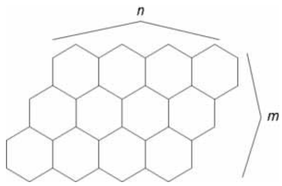

Figure 1. Benzenoid parallelogram $B_{m,n}$ where $m = 3$ and $n = 4$.

A single benzene ring can be added to a benzenoid parallelogram in two ways – it can be attached to $B_{m,n}$ either to its one bond or to its two adjacent bonds. However, in the latter case the obtained benzenoids possess no Kekulé structures. In the former case, three classes of benzenoids can be generated depending on to which bond in $B_{m,n}$ the benzene ring is attached. These three classes of benzenoids, denoted by $B'_{m,n}$, $B''_{m,n}$, and $B'''_{m,n}$, are depicted in Figure 2.

One can easily see that benzenoids $B'_{m,n}$, $B''_{m,n}$, and $B'''_{m,n}$ coincide in mn hexagons and differ only in the attached benzene ring. Hence, it may be expected that when

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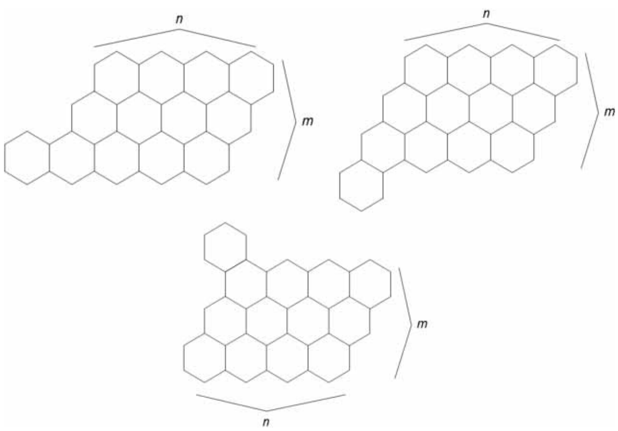

Figure 2. Three classes of benzenoids $B'_{m,n}$, $B''_{m,n}$, and $B'''_{m,n}$ obtained from a benzenoid parallelogram $B_{m,n}$ to which a benzene ring is added.

m and n are large, the numbers of Kekulé structures $K(B'_{m,n})$, $K(B''_{m,n})$, and $K(B'''_{m,n})$ are similar, *i.e.*:

$$\lim_{\substack{m\to\infty\\ n\to\infty}} \frac{K(B'_{m,n})}{K(B''_{m,n})} = \lim_{\substack{m\to\infty\\ n\to\infty}} \frac{K(B'_{m,n})}{K(B'''_{m,n})} = \lim_{\substack{m\to\infty\\ n\to\infty}} \frac{K(B''_{m,n})}{K(B'''_{m,n})} = 1 .$$

To derive expressions for computing $K(B'_{m,n})$, $K(B''_{m,n})$, and $K(B'''_{m,n})$, we will utilize the following result, which has been proved by Došlić.[2] In each row of $B_{m,n}$, there is exactly one vertical double bond. Let us denote vertical double bonds in a benzenoid by numbers $1,\ldots, m+1$ in each of the n rows and let denote rows by numbers $1,\ldots, n$. Then the double bonds define the function *db* from $\{1,\ldots, n\}$ to $\{1,\ldots, m+1\}$. An example of such correspondence is given in the following figure:

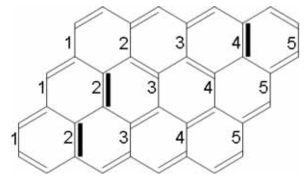

Figure 3. The Kekulé structure that corresponds to function ϕ given by $\phi(1) = 2$, $\phi(2) = 2$, $\phi(3) = 4$.

Also, it is proved in the paper by Došlić[2] that this function is a non-decreasing function. Moreover, there is one-to-one correspondence between this set of non-decreasing functions and Kekulé structures of $B_{m,n}$. The following result is well known:[5]

Lemma 1. – There are $\binom{m+n}{n} = \binom{m+n}{m}$ non-decreasing functions from $\{1,\ldots, n\}$ to $\{1,\ldots, m+1\}$.

Let us prove the following:

Lemma 2. – There are $\binom{m+n-1}{n-1} = \binom{m+n-1}{m}$ non-decreasing functions f from $\{1,\ldots, n\}$ to $\{1,\ldots, m+1\}$ such that $f(1) = 1$.

Proof: Let F_1 be the set of all non-decreasing functions f from $\{1,\ldots, n\}$ to $\{1,\ldots, m+1\}$ such that $f(1) = 1$ and F_2 the set of all non-decreasing functions f from $\{1,\ldots, n-1\}$ to $\{1,\ldots, m+1\}$. Note that F_2 has $\binom{m+n-1}{n-1}$ elements; hence it is sufficient to define bijection ϕ: $F_1 \to F_2$. This bijection can be defined by $[\phi(f)](i) = f(i+1)$ for each $i = 1,\ldots, n-1$. ■

From Lemmas 1 and 2, it directly follows that:

Lemma 3. – There are $\binom{m+n-1}{m-1} = \binom{m+n-1}{n}$ non-decreasing functions f from $\{1,\ldots, n\}$ to $\{1,\ldots, m+1\}$ such that $f(1) > 1$.

Let us now calculate $K(B'_{m,n})$. Denote by H the hexagon that is added to $B_{m,n}$ to form $B'_{m,n}$. Carbon atoms of H can be covered by the double bonds in three different ways (see Figure 4).

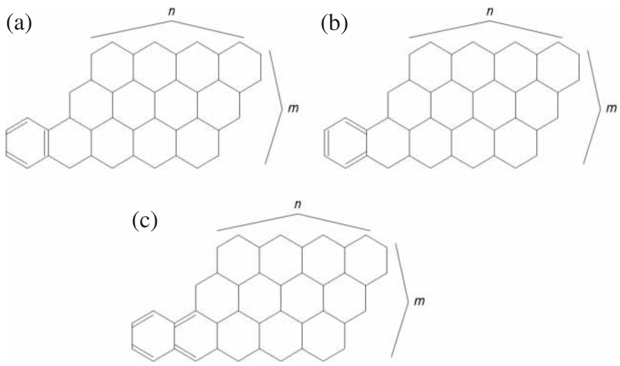

Figure 4. Three ways to cover the carbon atoms of H by double bonds in $B'_{m,n}$.

Denote by $K_1(B'_{m,n})$, $K_2(B'_{m,n})$, and $K_3(B'_{m,n})$, respectively, the number of Kekulé structures that cover carbon atoms of H as shown in Figures 4a, 4b, and 4c. Note that $K_1(B'_{m,n})$ and $K_2(B'_{m,n})$ are equal to the number of non-decreasing functions f from $\{1,\ldots, n\}$ to $\{1,\ldots, m+1\}$ such that $f(1) = 1$; hence (from Lemma 2):

$$K_1(B'_{m,n}) = K_2(B'_{m,n}) = \binom{m+n-1}{m}.$$

Note that $K_3(B'_{m,n})$ is equal to the number of non-decreasing functions f from $\{1,\ldots n\}$ to $\{1,\ldots m+1\}$ such that $f(1) > 1$; hence (from Lemma 3):

$$K_1(B'_{m,n}) = K_2(B'_{m,n}) = \binom{m+n-1}{m}.$$

Therefore:

$$K(B'_{m,n}) = 2\cdot\binom{m+n-1}{m}+\binom{m+n-1}{n}. \qquad (1)$$

Since $B'_{m,n}$ is isomorphic to $B''_{m,n}$, one has:

$$K(B''_{m,n}) = 2\cdot\binom{m+n-1}{m}+\binom{m+n-1}{n}. \qquad (2)$$

Now, let us calculate $K(B'''_{m,n})$. As above, denote by H the hexagon that is added to $B_{m,n}$ to form $B'_{m,n}$. Again, the carbon atoms of H can be covered by the double bonds in three different ways (see Figure 5).

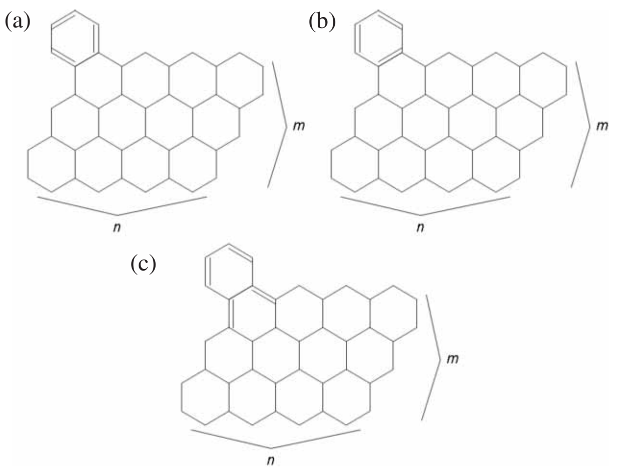

Figure 5. Three ways to cover the carbon atoms of H by double bonds $B'''_{m,n}$.

Denote by $K_1(B'''_{m,n})$, $K_2(B'''_{m,n})$, and $K_3(B'''_{m,n})$, respectively, the number of Kekulé structures that cover carbon atoms of H as shown in Figures 5a, 5b and 5c. Note that $K_3(B'''_{m,n})$ is equal to the number of non-decreasing functions f from $\{1,..., n\}$ to $\{1,..., m+1\}$ such that $f(n) = 1$. The only such function is the function $f(1) = f(2) = ... = f(n) = 1$; hence:

$$K_3(B'''_{m,n}) = 1.$$

Note that $K_1(B'''_{m,n})$ and $K_2(B'''_{m,n})$ are equal to the number of non-decreasing functions f from $\{1,..., n\}$ to $\{1,..., m+1\}$ such that $f(n) > 1$; hence:

$$K_1(B'''_{m,n}) = K_2(B'''_{m,n}) = \binom{m+n}{n} - 1.$$

Therefore:

$$K(B'''_{m,n}) = 2\binom{m+n}{n} - 1. \qquad (3)$$

Since $B'_{m,n}$ is isomorphic to $B''_{m,n}$ one has:

$$K(B''_{m,n}) = 2\cdot\binom{m+n-1}{n}+\binom{m+n-1}{m}=$$

$$2\cdot\binom{m+n-1}{m}+\binom{m+n-1}{m-1}=$$

$$2\cdot\frac{m+n-1-(m-1)}{m+n}\cdot\binom{m+n}{m}+\frac{m}{m+n}\cdot\binom{m+n}{m}=$$

$$\frac{2n+m}{m+n}\cdot\binom{m+n}{m} \qquad (4)$$

Analogously, we obtain:

$$K(B''_{m,n}) = \frac{2m+n}{m+n}\cdot\binom{m+n}{m}. \qquad (5)$$

Now, we can see that $\frac{K(B'_{m,n})}{K(B''_{m,n})} = \frac{2n+m}{2m+n}$ and hence $\lim_{\substack{m\to\infty \\ n\to\infty}} \frac{K(B'_{m,n})}{K(B''_{m,n})}$ is not equal to 1. Moreover, it does not exist. The value of $\frac{K(B'_{m,n})}{K(B''_{m,n})}$ is in the interval $\left(\frac{1}{2},2\right)$ and depends on the ratio m / n.

Also, limits $\lim_{\substack{m\to\infty \\ n\to\infty}} \frac{K(B'_{m,n})}{K(B'''_{m,n})}$ and $\lim_{\substack{m\to\infty \\ n\to\infty}} \frac{K(B''_{m,n})}{K(B'''_{m,n})}$ do not exist and $\frac{K(B'_{m,n})}{K(B'''_{m,n})}, \frac{K(B''_{m,n})}{K(B'''_{m,n})} \in \left(\frac{1}{2},1\right)$ and it also depends on the ratio m / n.

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SAŽETAK

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Prebrojavanje Kekuléovih struktura u benzenoidnim paralelogramima koji sadrže jedan dodatni benzenski prsten

Dane su formule za broj Kekuléovih struktura u posebnoj klasi benzenoida koja se sastoji od paralelograma kojemu je dodan još jedan jedini benzenoidni prsten.