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Contribution to the Techniques of Enumeration of *Kekulé* Structures

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Four auxiliary classes of benzenoids are introduced, and formulas are given for their number of *Kekulé* structures (*K*). An enumeration method for *K* of different important classes of benzenoids is illustrated by examples. The utilization of essentially disconnected benzenoids is a special feature of the method.

(Keywords: Benzenoid hydrocarbons; Kekulé structures)

Ein Beitrag zur Methodik der Bestimmung möglicher Kekulé-Strukturen

Es werden Hilfsklassen von benzenoiden Aromaten eingeführt und Formeln zur zahlenmäßigen Auswertung möglicher *Kekulé*-Strukturen angegeben (*K*). Die Auswertungsmethode für *K* wird an verschiedenen wichtigen Klassen benzenoider Verbindungen exemplarisch gezeigt. Die Verwendbarkeit essentiell abgekoppelter aromatischer Bauelemente ist eine spezielle Eigenschaft dieser Methode.

Introduction

The enumeration of *Kekulé* structures of polycyclic aromatic (benzenoid) hydrocarbons has been reviewed by *Trinajstić* [1]. A fairly complete bibliography is found elsewhere in this journal [2]. Here *Gutman* and *Cyvin* [2] pointed out the tremendous acceleration of the research in this field during the last few years.

Gutman [3] and later *Gutman* and *Cyvin* [2, 4] showed the usefulness of introducing auxiliary classes when studying the number of *Kekulé* structures. This is also an essential part of the enumeration techniques described in the present work. In addition, a special feature of the present method is the utilization of essentially disconnected benzenoids.

Let the number of *Kekulé* structures for a benzenoid B be denoted $K\{B\}$. Furthermore, let $B_1 \cdot B_2$ denote the essentially disconnected benzenoid consisting of the fragments B_1 and B_2. This means that B_1 and B_2 are joined by essentially single bonds, i.e. bonds which are single in all *Kekulé* structures. Then one has $K\{B_1 \cdot B_2\} = K\{B_1\} K\{B_2\}$.

Results and Discussion

Auxiliary Classes of Benzenoids

Gutman and *Cyvin* [2, 4] have defined $A(n, m, l)$ for $0 \leqslant l \leqslant n$ as a multiple zigzag chain, $A(n, m)$, augmented by a row of l hexagons. For the extremal values of l one has by virtue of definition:

$$A(n, m, n) = A(n, m + 1), \qquad A(n, m, 0) = A(n, m).$$

Here we will apply these classes with $m = 1$ and $m = 2$. In addition, we define some related classes designated $B(n, 2, l)$ and $B(n, 2, -l)$ for $0 \leqslant l \leqslant n$.

The Class $A(n, 1, l)$

For $n = 1$ the class $A(n, m, l)$ reduces to one single straight (linear acene) chain of n hexagons augmented by a row of l hexagons; cf. Fig. 1.

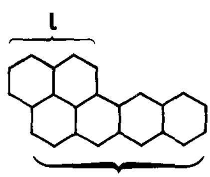

Fig. 1. The benzenoid class $A(n, 1, l)$, depicted for $n = 4$, $l = 2$

For the extremal values $l = n$ and 0 the benzenoids reduce to a parallelogram and a single chain, respectively;

$$A(n, 1, n) = A(n, 2) = L(n, 2), \qquad A(n, 1, 0) = A(n) = L(n).$$

An explicit formula for the number of *Kekulé* structures of $A(n, 1, l)$ for arbitrary values of n and l is known [2, 4]; it may be written in the form

$$K\{A(n, 1, l)\} = (n + 1)(l + 1) - \binom{l + 1}{2}; \qquad l \leqslant n \tag{1}$$

The Class A$(n, 2, l)$

Figure 2 shows the definition of A$(n, 2, l)$.

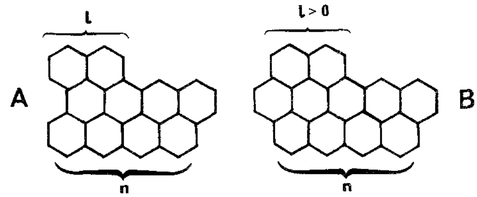

Fig. 2. The classes A$(n, 2, l)$ and B$(n, 2, l)$; see the text for a special definition of B$(n, 2, 0)$

Also in this case an explicit formula for the K number has been given previously [2, 4]; we write it by means of binomial coefficients in the following way.

$$K\{\mathrm{A}(n,2,l)\} = \binom{n+2}{2}(l+1) - \binom{l+2}{3}; \qquad l \leqslant n \qquad (2)$$

The Class B$(n, 2, l)$

Figure 2 also shows B$(n, 2, l)$ for $l > 0$. For $l = n$ we arrive at the rectangle- or hexagon-shaped benzenoid with three tier chains [5–7]. For $l = 0$ it is not expedient to define B$(n, 2, 0)$ merely by omitting the l hexagons, since this gives a non-*Kekuléan* structure. We remove also one of the end hexagons of the $(n + 1)$-row and attain at

$$\mathrm{B}(n,2,0) = \mathrm{A}(n,2,0) = \mathrm{A}(n,2) = \mathrm{L}(n,2).$$

We wish a formula for the K number of B$(n, 2, l)$ with arbitrary values of n and l. By means of the well-known method of partitioning of the benzenoid [8] we easily obtain the recurrence formula

$$K\{\mathrm{B}(n,2,l)\} = K\{\mathrm{B}(n-1,2,l-1)\} + K\{\mathrm{A}(n,2,l)\}; \qquad l \geqslant 1 \quad (3)$$

Together with the initial condition $K\{\mathrm{B}(n,2,0)\} = K\{\mathrm{A}(n,2,0)\}$ we arrive at the summation formula

$$K\{\mathrm{B}(n,2,l)\} = \sum_{i=0}^{l} K\{\mathrm{A}(n-l+i,2,i)\}; \qquad l \geqslant 0 \qquad (4)$$

On combining Eq. (4) with (2) we attained at

$$K\{B(n,2,l)\} = \frac{1}{2}\left[(n-l)(n-l+1)+\frac{1}{3}\right]\sum_{i=0}^{l}(i+1) + \left(n-l+\frac{1}{2}\right)\sum_{i=0}^{l}(i+1)^2 + \frac{1}{3}\sum_{i=0}^{l}(i+1)^3 \qquad (5)$$

By tedious, but elementary computations this expression was simplified to

$$K\{B(n,2,l)\} = \binom{n+2}{2}\binom{l+2}{2} - (n+2)\binom{l+2}{3}; \qquad l \leqslant n \qquad (6)$$

The Class B$(n, 2, -l)$

We introduce an auxiliary class of benzenoids denoted B$(n, 2, -l)$. It consists of two rows; (1) one of n hexagons and (2) one of $(n+1)$ hexagons with the hexagon number l (starting from $l = 0$) omitted. For the sake of clarity we have depicted the whole series of B$(4, 2, -l)$ for $l = 0, 1, \ldots, 4$ in Fig. 3. For $l = 0$ the appropriate benzenoid, viz. B$(n, 2, 0)$, coincides

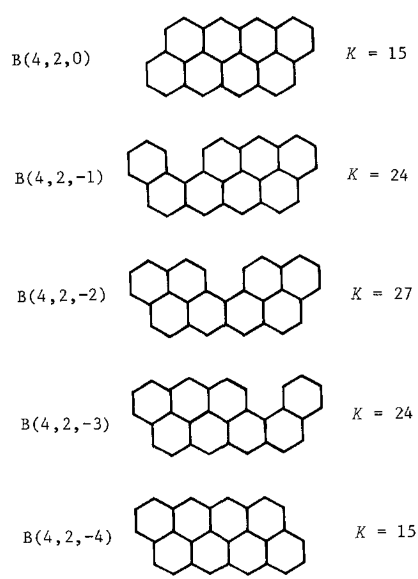

Fig. 3. The benzenoids B$(n, 2, -l)$ for $n = 4$ and $l = 0, 1, 2, 3, 4$

with the member of the preceding series ($l \geqslant 0$) denoted by the same symbol. We have obviously the symmetry property

$$\mathrm{B}(n, 2, -l) = \mathrm{B}(n, 2, l - n).$$

By means of the standard techniques [8] it is found

$$K\{\mathrm{B}(n, 2, -l)\} = K\{\mathrm{B}(n, 2, l)\} - K\{\mathrm{B}(n, 2, l - 1)\}; \qquad l \geqslant 1 \tag{7}$$

Consequently, with the aid of Eq. (6)

$$K\{\mathrm{B}(n, 2, -l)\} = K\{\mathrm{B}(n, 2, l - n)\} = \binom{n+2}{2}(l + 1) - (n + 2)\binom{l+1}{2}; \quad 0 \leqslant l \leqslant n \tag{8}$$

Simple Example One

Consider the four-tier zigzag chain of arbitrary length (n hexagons); cf. Fig. 4. The method of fragmentation [8] is supposed to be applied n times, each time focusing the attention upon the bond marked by a thick arrow (Fig. 4). Consequently one obtains altogether

$$K\{\mathrm{A}(n, 4)\} = \sum_{i=0}^{n} K\{\mathrm{A}(n, 1, i)\} K\{\mathrm{L}(i)\}. \tag{9}$$

On inserting the expression from Eq. (1) along with the well known K formula for $\mathrm{L}(i)$ it is obtained

$$\begin{aligned} K\{\mathrm{A}(n, 4)\} &= \sum_{i=0}^{n} \left[(n + 1)(i + 1) - \binom{i+1}{2} \right] (i + 1) \\ &= (n + 1) \sum_{i=0}^{n} (i + 1)^2 - \sum_{i=1}^{n} (i + 1)\binom{i+1}{2} \\ &= (n + 1)\left[(n + 1)\binom{n+2}{2} - \binom{n+2}{3} \right] \\ &\quad - \left[\binom{n+1}{2}\binom{n+2}{2} - n\binom{n+2}{3} + \binom{n+2}{4} \right] \\ &= \binom{n+2}{2}^2 - \binom{n+3}{4}. \end{aligned} \tag{10}$$

This final expression is simpler than the binomial-coefficient form given previously by *Cyvin* [7]. A polynomial-form of Eq. (10) was first derived in a different way by *Gutman* and *Cyvin* [2, 4].

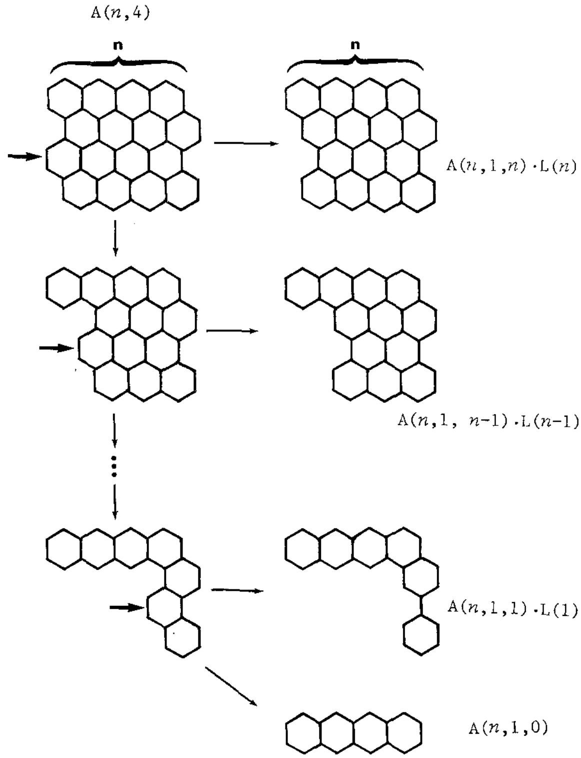

Fig. 4. Steps in the enumeration of *Kekulé* structures for A$(n, 4)$

Simple Example Two

Consider in the same way the four-tier pentagonal benzenoid designated D$(2, 3, n)$, and also referred to as a hexagon with one corner removed, 0a$(3, 2, n)$ = 0$(2, 3, n)$ [7]; cf. Fig. 5. Our method gives

$$K\{\mathrm{D}(2,3,n)\} = \sum_{i=0}^{n} K\{\mathrm{B}(n,2,-i)\}\, K\{\mathrm{L}(i)\}, \tag{11}$$

and by means of Eq. (8):

$$K\{\mathrm{D}(2,3,n)\} = \sum_{i=0}^{n} \left[\binom{n+2}{2}(i+1) - (n+2)\binom{i+1}{2}\right](i+1)$$
$$= \binom{n+2}{2}\binom{n+3}{3} - (n+2)\binom{n+3}{4}, \tag{12}$$

which is equivalent to the known polynomial-form [7] of this equation.

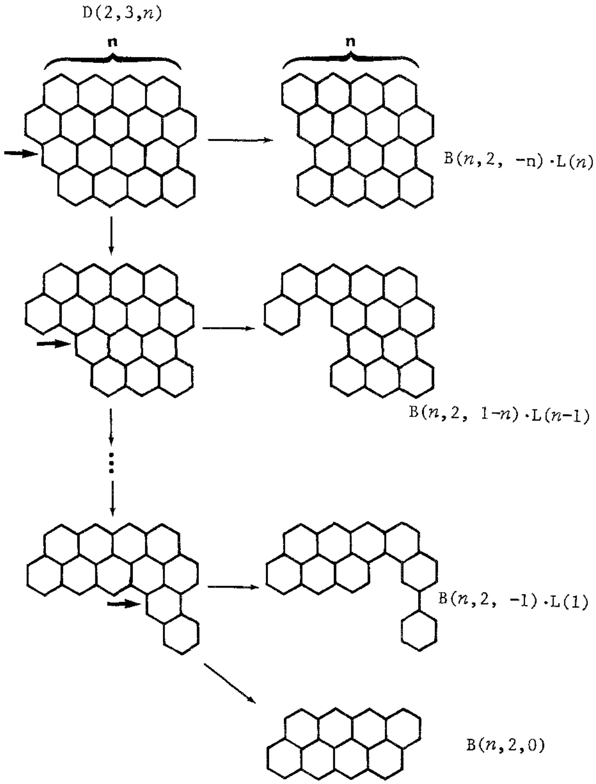

Fig. 5. Steps in the enumeration of *Kekulé* structures for D(2, 3, n)

Simple Example Three

The five-tier zig-zag chain, A(n, 5), is depicted in Fig. 6. The present method leads to

$$K\{\mathrm{A}(n,5)\} = \sum_{i=0}^{n} K\{\mathrm{A}(n,2,i)\}\, K\{\mathrm{L}(i)\}. \tag{13}$$

With the aid of Eq. (2) and a computation as in the preceding examples it was arrived at

$$K\{\mathrm{A}(n,5)\} = (n+2)\binom{n+2}{2}^2 - \left[\binom{n+2}{2} - (n+2)\right]\binom{n+3}{3} - (n+3)\binom{n+4}{4} + \binom{n+5}{5}. \tag{14}$$

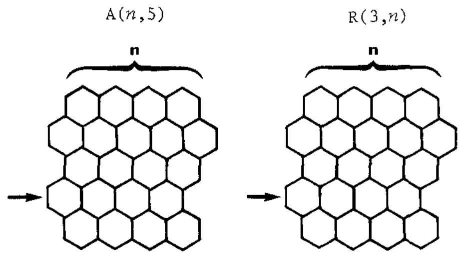

Fig. 6. The benzenoids A$(n, 5)$ and R$(3, n)$, pertaining to the simple examples three and four, respectively; the method of fragmentation starts with the bond marked by an arrow

This formula was first derived in a polynomial-form by *Gutman* and *Cyvin* [2,4].

Simple Example Four

Another five-tier benzenoid, R$(3, n)$, is shown in Fig. 6. In this case one finds

$$K\{\mathrm{R}(3,n)\} = \sum_{i=0}^{n} K\{\mathrm{B}(n,2,i)\} K\{\mathrm{L}(i)\}, \tag{15}$$

where we need Eq. (6). By a computation as in the preceding examples we arrived at

$$\begin{aligned} K\{\mathrm{R}(3,n)\} &= (n+2)\left[\binom{n+3}{2}\binom{n+3}{3} + \binom{n+5}{5}\right] \\ &\quad - \left[(n+2)^2 + \binom{n+3}{2}\right]\binom{n+4}{4} \\ &= \frac{1}{240}(n+1)(n+2)^2(n+3)(7n^2+23n+20). \end{aligned} \tag{16}$$

It should not be surprising to find relations between the K values of some of the benzenoids treated above, since also the auxiliary benzenoid classes are inter-related. Actually it was found

$$K\{\mathrm{R}(3,n)\} = \sum_{i=0}^{n} K\{\mathrm{A}(i,5)\} + \sum_{i=0}^{n-1} K\{\mathrm{D}(2,3,i)\}. \tag{17}$$

This relation may be employed in an alternative derivation of Eq. (16).

A More Advanced Example

Here we show an application of the described method to a benzenoid, say H(n), for which the K value has not been achieved by any other method previously. It is a six-tier benzenoid as shown in Fig. 7, which also indicates the steps of the partitioning procedure. In this case we have

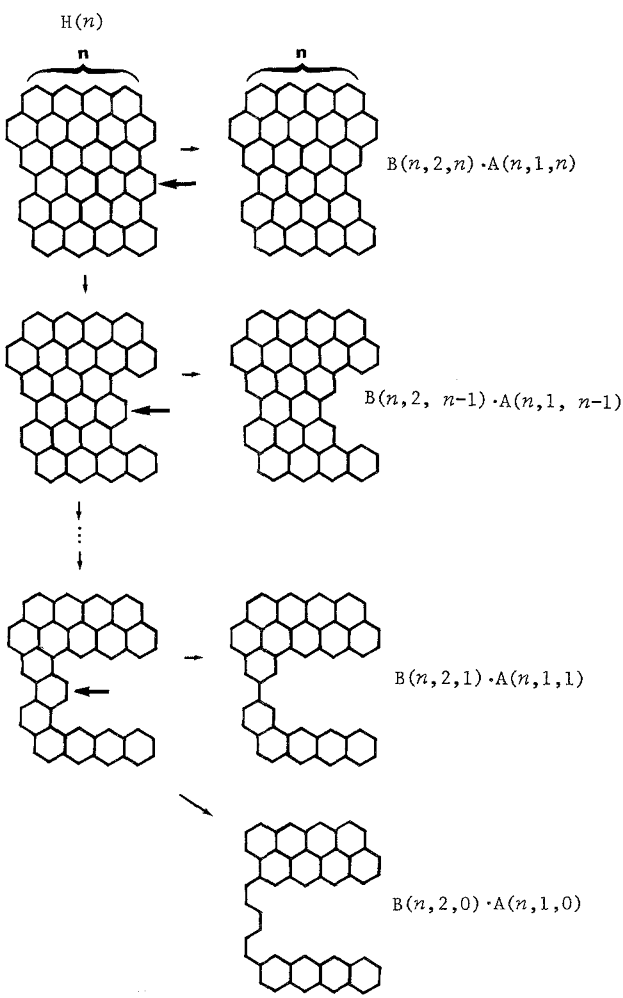

Fig. 7. Steps in the enumeration of *Kekulé* structures for H(n)

$$K\{\mathrm{H}(n)\} = \sum_{i=0}^{n} K\{\mathrm{A}(n,1,i)\} K\{\mathrm{B}(n,2,i)\}$$

$$= \sum_{i=0}^{n} \left[(n+1)(i+1) - \binom{i+1}{2}\right]\left[\binom{n+2}{2}\binom{i+2}{2} - (n+2)\binom{i+2}{3}\right]. \tag{18}$$

In the subsequent computations we made use of

$$\sum_{i=0}^{n} (i+1)\binom{i+2}{2} = (n+1)\binom{n+3}{3} - \binom{n+3}{4}, \tag{19}$$

$$\sum_{i=0}^{n} (i+1)\binom{i+3}{2} = (n+1)\binom{n+4}{4} - \binom{n+4}{5}, \tag{20}$$

$$\sum_{i=0}^{n} \binom{i+2}{2}^2 = \binom{n+3}{5} - (n+1)\binom{n+3}{4} + \binom{n+2}{2}\binom{n+3}{3}, \tag{21}$$

and

$$\sum_{i=0}^{n} \binom{i+2}{2}\binom{i+3}{3} = \binom{n+4}{6} - (n+1)\binom{n+4}{5} + \binom{n+2}{2}\binom{n+4}{4}. \tag{22}$$

It was finally attained at:

$$K\{\mathrm{H}(n)\} = \binom{n+2}{2}\left[\binom{n+5}{5} - (n+3)\binom{n+4}{4}\right.$$

$$\left. + \binom{n+3}{2}\binom{n+3}{3} + \frac{1}{30}\binom{n}{2}\binom{n+4}{3} - \frac{1}{5}\binom{n+1}{2}\binom{n+4}{3}\right]$$

$$= \frac{1}{720}(n+1)(n+2)^3(n+3)(13n^2+37n+30). \tag{23}$$

Conclusion

Two classes of zigzag chains are among the examples used to illustrate the application of the auxiliary benzenoids introduced in the present work. These classes have been studied in general by *Gutman* and *Cyvin* [2, 4], who solved in a different way the two particular problems treated here. The virtue of the present method is demonstrated by the more advanced example, but the class of benzenoids treated may seem too special to be of real importance.

In addition to the zigzag chains the rectangular benzenoids are recognized as important classes [9]. Here it is essential to distinguish between prolate rectangles, say Ri (with indentation inwards) and oblate rectangles, say Rj (with indentation outwards). The case of $K\{\mathrm{Ri}\}$ is completely solved [9], while $K\{\mathrm{Rj}\}$ causes serious problems. For the five-tier oblate rectangles, viz. $\mathrm{Rj}(3, n)$, the present method is applicable. One has actually

$$K\{\mathrm{Rj}(3, n)\} = \sum_{i=0}^{n} [K\{\mathrm{B}(n, 2, -i)\}]^2. \tag{24}$$

However, this problem has been solved previously by other methods [5, 7, 9]. An extension of the present method would make it feasible to attack the so far unsolved, difficult problem of the K number of seven-tier oblate rectangles, viz. $\mathrm{Rj}(4, n)$.

The applications of the present method are far from exhausted by the examples quoted here. Furthermore, there are several ways which suggest themselves for extensions of the techniques; they would undoubtedly increase the field of applicability to a great extent. One obvious extension is the exploitation of $K\{\mathrm{A}(n, 3, l)\}$, for which *Gutman* and *Cyvin* [2, 4] have given an explicit formula. In this connection additional auxiliary benzenoids as $\mathrm{B}(n, 3, l)$ and $\mathrm{B}(n, 3, -l)$ may be defined in analogy with $\mathrm{B}(n, 2, l)$ and $\mathrm{B}(n, 2, -l)$, respectively.

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