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Enumeration of *Kekulé* Structures: *Étagères* and Related Benzenoid Classes

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Formulas are developed for the number of *Kekulé* structures of some benzenoid classes, which are interpreted in terms of annelations of a multiple linear chain (parallelogram). One-sided and two-sided annelations are considered, the latter category leading to the definition of a benzenoid class referred to as *étagères*.

(Keywords: Kekulé structures; Benzenoids)

Ermittlung der Anzahl von Kekulé-Strukturen: „Étagère" und verwandte benzenoide Klassen

Es werden Formeln für die Ermittlung der Anzahl möglicher *Kekulé*-Strukturen für einige benzenoiden Klassen angegeben, wobei diese durch annelierte, mehrfache, lineare Ketten (Parallelogramme) charakterisiert werden. Dabei wird einseitige und zweiseitige Annelierung berücksichtigt, für die letztgenannte Gruppe wird der Ausdruck „*Étagère*" geprägt.

Introduction

The enumeration of *Kekulé* structures in benzenoid hydrocarbons has attained an increasing interest in recent years, as has been documented in a previous paper [1], which includes references up to 1983. Supplementary references from 1983 and later are included here [2–17]. The main subject of the present work is a class of benzenoids referred to as *étagères* and designated E. This is not only a bizzare class, for which it was succeeded to develop a combinatorial formula of $K\{E\}$, its number of *Kekulé* structures. The five-tier oblate rectangle, $Rj(3, n)$, is a special *étagère* and recognized as an important benzenoid, of which the number of *Kekulé* structures has been studied extensively [15, 17, 18–20]. Even more significant is the fact that the class of *étagères* is a non-trivial example of benzenoid annelation to multiple chains, which has been very little studied. In contrast, the annelations of single chains have been studied in numerous works; here we give references [21–24] only to those which explicitly contain formulas for the number of *Kekulé* structures.

Results and Discussion

Simple One-Sided Annelations

Fig. 1 shows four examples of benzenoid classes, which may be interpreted as annelations of a multiple linear chain (parallelogram). The

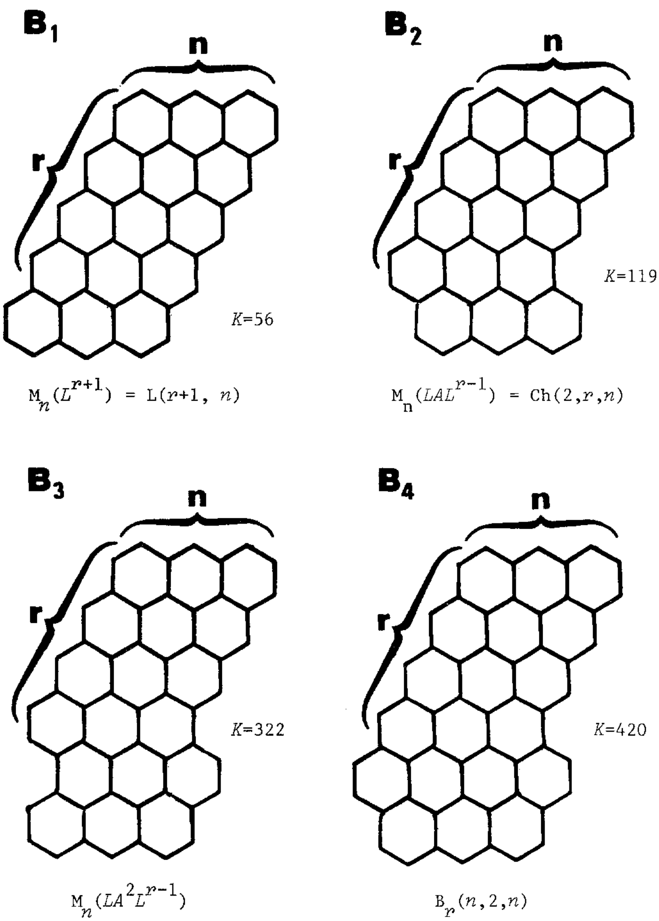


Fig. 1. Examples of one-sided annelation of a multiple linear chain; the K numbers pertain to the depicted examples for $n = 3$ and $r = 4$

length of this chain in terms of the number of hexagons is denoted by r. $\mathbf{B}_1$, $\mathbf{B}_2$ and $\mathbf{B}_3$ are n-tuple chains [17] (M_n), which are characterized by their *LA*-sequence[25,26]; cf. Fig. 1. The first example ($\mathbf{B}_1$) is rather trivial, being itself a parallelogram [1, 18] (L), while $\mathbf{B}_2$ is a chevron [1, 13, 18] (Ch). Explicit formulas of K for these three classes of multiple chains are obtainable by different methods [1, 13, 17] and are given in Table 1. The last example ($\mathbf{B}_4$) is less trivial, but may be treated conveniently in terms of auxiliary benzenoid classes [11, 27–29], if the theory is extended appropriately.

Table 1. *Combinatorial formulas of K (number of Kekulé structures) for the classes of Fig. 1*

Class	$K\{\mathbf{B}\}$
$\mathbf{B}_1$	$\binom{n+r+1}{n}$
$\mathbf{B}_2$	$(n+2)\binom{n+r}{n}-\binom{n+r+1}{n}$
$\mathbf{B}_3$	$\binom{n+2}{2}\binom{n+r}{n}-\binom{n+r+1}{n-1}$
$\mathbf{B}_4$	$\binom{n+2}{2}\binom{n+r+1}{n}-(n+2)\binom{n+r+1}{n-1}$

Auxiliary Benzenoid Classes

Consider a three-parameter structure, $B_r(n, 2, l)$, as depicted in Fig. 2; l is restricted to $0 \leqslant l \leqslant n$. It represents an auxiliary class of benzenoids, which is an extension of *Cyvin*'s [29] B $(n, 2, l)$:

$$B_1(n, 2, l) = B(n, 2, l)$$

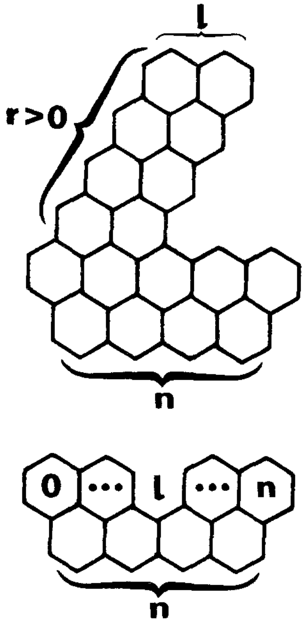
For $l = 0$ all the benzenoids (irrespective of r) degenerate to the $2 \times n$ parallelogram, which is a regular 2-tier strip [17]:

$$B_r(n, 2, 0) = L(2, n)$$

For $l = n$ the benzenoid becomes a regular $(r+2)$-tier strip, say b_r. The first of these benzenoids are:

$$B_1(n, 2, n) = b_1 = O(2, 2, n)$$
$$B_2(n, 2, n) = b_2 = D(2, 3, n)$$
$$B_3(n, 2, n) = b_3 = Di(2, 4, n)$$

They are named [1, 17] hexagon (O), pentagon (D) and prolate pentagon (Di), respectively. Hence it is reasonable to designate the three auxiliary



$B_r(n, 2, l)$

$B_0(n, 2, l)$

Fig. 2. Auxiliary benzenoid class

classes as: incomplete hexagon from parallelogram (B_1), double-incomplete pentagon from parallelogram (B_2) and triple-incomplete prolate pentagon from parallelogram (B_3).

A basic formula for the multiple-incomplete strips reads

$$K\{B_r(n, 2, l)\} = K\{B_r(n, 2, l-1)\} + K\{B_{r-1}(n, 2, l)\}; \quad l \geqslant 1 \qquad (1)$$

and consequently

$$K\{B_r(n, 2, l)\} = \sum_{i=0}^{l} K\{B_{r-1}(n, 2, i)\} \qquad (2)$$

The relation (1) is easily derived by means of the fragmentation method of *Randić* [30]. In order to make Eqns. (1) and (2) valid also for $r = 0$ one has to define [29]

$$B_0(n, 2, l) = B(n, 2, -l)$$

see also Fig. 2. *Cyvin* [29] has given the K formulas for $B(n, 2, l)$ and $B(n, 2, -l)$. When applied together with Eqn. (2) it was attained at the explicit formula

$$K\{B_r(n, 2, l)\} = \binom{n+2}{2}\binom{l+r+1}{r+1} - (n+2)\binom{l+r+1}{r+2} \qquad (3)$$

The expressions [29] for $\mathrm{B}(n, 2, l)$ and $\mathrm{B}(n, 2, -l)$ emerge as special cases for $r = 1$ and $r = 0$, respectively.

The final step in order to obtain $K\{\mathbf{B}_4\}$ amounts to inserting $l = n$ in Eqn. (3). The result is entered into Table 1.

Two-Sided Annelations

1. Essentially Disconnected Benzenoid

The benzenoid class $\mathbf{B}_5$ of Fig. 3 is an example of a special multiple-chain annelation, where the resulting benzenoids are essentially disconnected. It is a regular $(r + 2)$-tier strip referred to as a goblet [17] (X). All bonds in the $r \times n$ parallelogram are localized, i.e. fixed as single or double in all *Kekulé* structures. The prolate rectangles [15, 19] represent another example of essentially disconnected benzenoids. The category has been treated most extensively by *Cyvin* and *Gutman* [24]. In the present case ($\mathbf{B}_5$) the formula for the number of *Kekulé* structures is simply

$$K\{\mathbf{B}_5\} = [K\{\mathrm{L}(n+1)\}]^2 \tag{4}$$

see also Table 2.

None of the classes to be treated in the following belong to essentially disconnected benzenoids and are consequently not so simple. For the sake of brevity we have chosen only symmetrical annelations; they consist of identical structures annelated symmetrically to a parallelogram.

2. Multiple Chains

The classes $\mathbf{B}_6$, $\mathbf{B}_7$ and $\mathbf{B}_8$ of Fig. 3 are two-sided annelations which correspond to $\mathbf{B}_1$, $\mathbf{B}_2$ and $\mathbf{B}_3$ (Fig. 1), respectively. All of them are multiple chains. The derived K formulas for $\mathbf{B}_6$, $\mathbf{B}_7$ and $\mathbf{B}_8$ are found in Table 2.

3. *Étagère*

The two-sided annelation corresponding to $\mathbf{B}_4$ (Fig. 1) inspired to the definition of a benzenoid class, *étagères*, designated $\mathrm{E}(3, m, n)$; cf. Fig. 4. *Étagères* belong to regular $(m + 2)$-tier strips [17]. The indices $(3, m, n)$ conform with the conventional system of notation [1, 17]; $\mathrm{E}(3, m, n)$ is a sub-benzenoid of the hexagon [1] $\mathrm{O}(3, m, n)$. The class might be generalized to $\mathrm{E}(k, m, n)$ with k different from 3 in one way or another; this question is presently left open. When r is the length of the multiple chain as in Fig. 3 the parameter m is given by

$$m = r + 2 \tag{5}$$

For the degenerate case of $r = 0$ ($m = 2$) it is expedient to define $\mathrm{E}(3, 2, n)$ as identical to the four-tier pentagon; cf. Fig. 4.

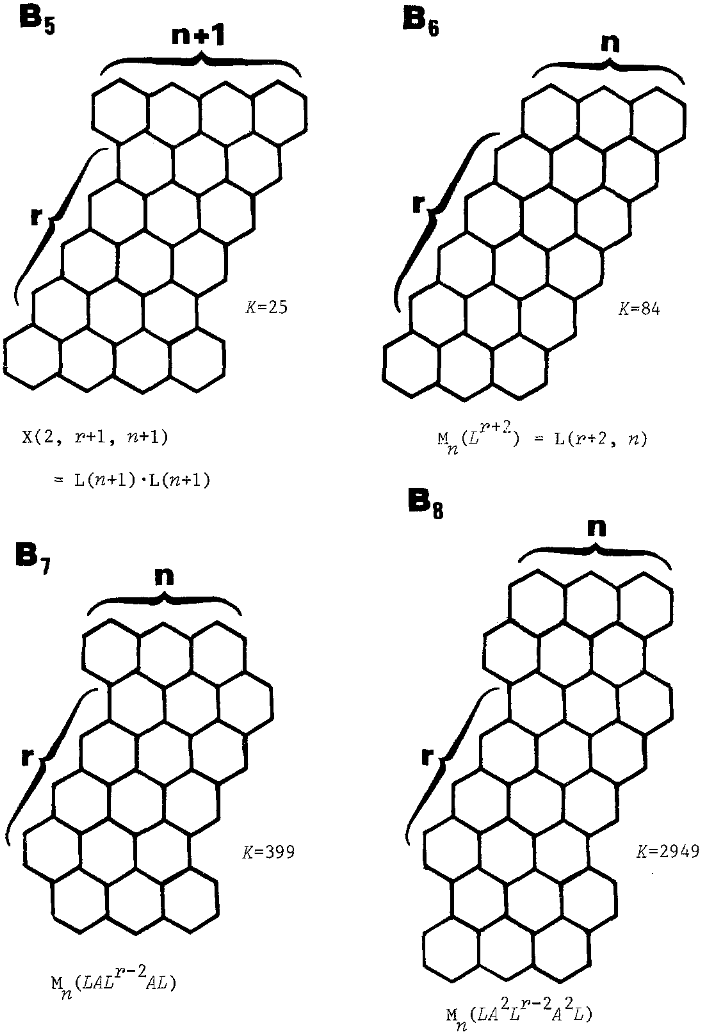


Fig. 3. Examples of two-sided annelation of a multiple linear chain; the K numbers pertain to the depicted examples for $n = 3$ and $r = 4$

In order to find a formula for K the method of fragmentation [30] was employed. Here it is in the version where the fragments are essentially disconnected benzenoids consisting of members from auxiliary classes [29]. Fig. 5 shows the different fragments obtained from E(3, 5, n) when the row indicated by the arrow in Fig. 4 is attacked. In general it is found

$$K\{E(3, m, n)\} = \sum_{i=0}^{n} K\{B_0(n, 2, i)\} \cdot K\{B_{m-3}(n, 2, i)\}; \quad m \geqslant 3 \qquad (6)$$

Table 2. *Combinatorial formulas of K (number of Kekulé structures) for the classes of Fig. 3, and* $\mathbf{B}_9 = \mathrm{E}(3, r+2, n)$; *cf. Fig. 4*

Class	$K\{\mathbf{B}\}$
$\mathbf{B}_5$	$(n+2)^2$
$\mathbf{B}_6$	$\binom{n+r+2}{n}$
$\mathbf{B}_7$	$(n+2)^2\binom{n+r}{n} - 2(n+2)\binom{n+r+1}{n} + \binom{n+r+2}{n}$
$\mathbf{B}_8$	$\binom{n+2}{2}^2\binom{n+r}{n} - 2\binom{n+2}{2}\binom{n+r+1}{n-1} + \binom{n+r+1}{n-2}$
$\mathbf{B}_9$	$\binom{n+3}{2}^2\binom{n+r+2}{n} - 2(n+2)\binom{n+3}{2}\binom{n+r+3}{n} +$ $(n+2)^2\binom{n+r+4}{n}$

The type of auxiliary classes appearing in Eqn. (6) is found in Fig. 2, and their K numbers are given by Eqn. (3). Consequently

$$K\{\mathrm{E}(3,m,n)\} = K\{\mathrm{E}(3,r+2,n)\} = \binom{n+2}{2}^2 \sum_{i=0}^{n} (i+1)\binom{i+r}{r}$$
$$-(n+2)\binom{n+2}{2}\sum_{i=1}^{n}\left[(i+1)\binom{i+r}{r+1} + \binom{i+1}{2}\binom{i+r}{r}\right] +$$
$$(n+2)^2 \sum_{i=1}^{n}\binom{i+1}{2}\binom{i+r}{r+1} \tag{7}$$

The summations were expressed as K formulas for chevrons [13, 17] with the result

$$K\{\mathrm{E}(3,r+2,n)\} = \frac{1}{2}(n+2)(n+5)\binom{n+2}{2}K\{\mathrm{Ch}(2,r+1,n)\}$$
$$-(n+2)\binom{n+2}{2}[K\{\mathrm{Ch}(2,r+2,n)\} + K\{\mathrm{Ch}(3,r+1,n)\}]$$
$$+(n+2)^2\left[K\{\mathrm{Ch}(3,r+2,n)\} - \binom{n+2}{2}\binom{n+r+1}{n}\right] \tag{8}$$

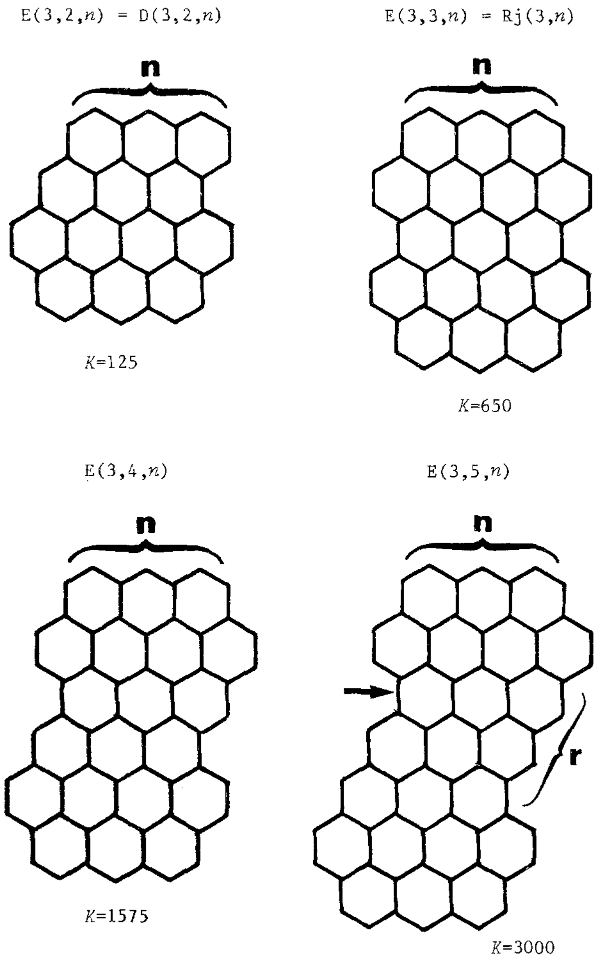


Fig. 4. Examples of ***étagères,*** E$(3, m, n)$ with $m = 2, 3, 4$ and 5 ($r = 0, 1, 2$ and 3)

On expanding these ***K*** formulas it was finally attained at the result of the **bottom line of Table** 2. With the parameter m it reads

$$K\{\mathrm{E}(3,m,n)\} = \binom{n+3}{2}^2\binom{m+n}{n} - 2(n+2)\binom{n+3}{2}\binom{m+n+1}{n} + \\ + (n+2)^2\binom{m+n+2}{n}; \\ m \geqslant 2 \tag{9}$$

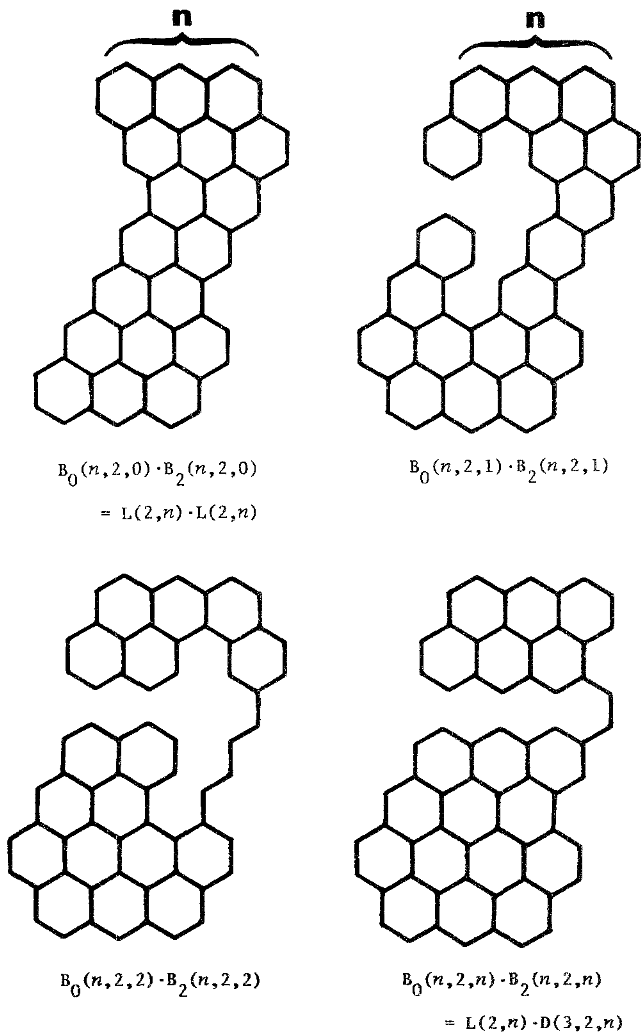


Fig. 5. The method of fragmentation applied n times to E(3, 5, n); the example with $n = 3$ is depicted

4. Connection with Annelation to Pyrene

Consider the special case of *étagères* with $n = 1$. They correspond to a two-sided annelation of a single linear chain with pyrene units at the two ends. Eqn. (9) gives

$$K\{E(3, m, 1)\} = 9(m-1) \quad (10)$$

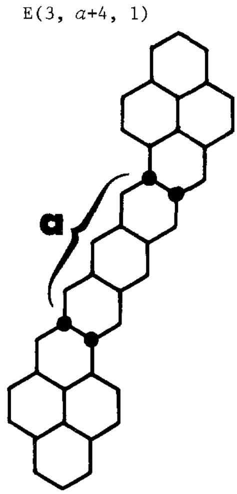


Fig. 6. Two pyrene units annelated to a linear chain as a special case of *étagère*

The case may be interpreted as two pyrenes annelated to a linear chain of the length of a hexagons as shown in Fig. 6. Here

$$a = m - 4 \tag{11}$$

Hence on inserting into Eqn. (10):

$$K\{\mathrm{E}(3, a+4, 1)\} = 9a + 27 \tag{12}$$

The result is consistent with the formula of *Gutman* [23] for this type of annelation.

Annelations to pyrene have been studied in a variety of branches of physical and organic chemistry. An extensive study of the number of *Kekulé* structures for such systems is in progress.

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