Number of Kekulé Structures of Five-Tier Strips

S. J. Cyvin and B. N. Cyvin
Division of Physical Chemistry, The University of Trondheim, Norway

I. Gutman
Faculty of Science, University of Kragujevac, Yugoslavia*

Z. Naturforsch. 40a, 1253–1261 (1985); received September 12, 1985

Benzenoid systems called regular t-tier strips are examined. 27 classes of benzenoids belonging to the regular 5-tier strips can be distinguished. Combinatorial formulas are developed for the number of Kekulé structures of all these classes.

Introduction

The enumeration of Kekulé structures in aromatic (benzenoid) hydrocarbons has found numerous chemical applications, which have been reviewed several times [1–4]. The research in this field has been intensified during the recent years. A part of these studies is concentrated upon peri-condensed (reticulate) benzenoids referred to as t-tier strips. In the ideal case explicit combinatorial formulas are developed for the number of Kekulé structures of different classes of these benzenoids. Three-tier strips are relatively simple and well known [5, 6]. A systematic study of four-tier strips, on the other hand, has been performed only very recently [7]. Somewhat more has previously been done for the most symmetrical five-tier strips [5, 6, 8], but far from a complete study. In the present work we wish to fill this gap. Firstly, however, we give, as a contribution to a systematic treatment, a precise definition of a regular t-tier strip. Next we present a derivation of explicit combinatorial formulas for all classes of benzenoids belonging to the regular five-tier strips. The paper illustrates several methods in the enumeration of Kekulé structures.

Definition

A regular t-tier strip is a benzenoid defined by the following two conditions.

(a) It consists of t tier fused chains (rows), conventionally drawn horizontally, where the bottom and top chain should have the same length in terms of the number of hexagons, say n.

(b) The (vertical) rims should each consist of a connected chain of t hexagons, of which any LA-sequence [9, 10] is permitted.

This definition sorts out a limited number of classes for every t value, and yet it embraces the conventional classes as parallelograms, hexagons, chevrons, etc. [5–8].

As a first illustration of this definition we give examples of (non-regular) five-tier strips, which do not obey the above conditions. Either (a) or (b) or both of them may be violated; cf. Figure 1.

Regular Five-Tier Strips

The regular five-tier strips consist of twenty-seven classes, which may be divided into three series (I–III) and derived from the classes of hexagons, say O(k, m, n); cf. Figure 2. If k = m the hexagon is referred to as dihedral; if all parameters (k, m, n) are different as centro-symmetrical.

Ohkami and Hosoya [8] were probably the first to suggest a study of the latter type. If k = 1 the hexagon degenerates into the m × n or L(m, n) parallelogram. For a t-tier strip

\[ k + m = t + 1. \]  

(1)

(I) \( k = m = 3 \). The leading class of hexagons is given by \( O(3, 3, n) \); a member of any other class of this series is a sub-benzenoid of \( O(3, 3, n) \). The top and bottom rows are unshifted.

---

* P.O. Box 60, Yu-34 000 Kragujevac.
Reprint requests to S. J. Cyvin, Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norway.

0340-4811 / 85 / 1200-1253 $ 01.30/0. – Please order a reprint rather than making your own copy.
Figures 3 and 4 show the ten plus six classes within the series (I). Figure 5 shows the ten classes within the series (II); they are analogous to the classes of Figure 3. Finally the parallelogram of the series (III) is depicted in Figure 6.

**General Formulas: Hexagons and Chevrons**

Within the regular $t$-tier strips the hexagon-shaped and chevron-shaped benzenoids are the only three-parameter classes for which the number of Kekulé structures ($K$) is known in terms of general explicit formulas.

When $K[B]$ denotes the $K$ number of the benzenoid $B$, one has

$$K[O(k, m, n)] = \prod_{i=0}^{k-1} \binom{m+n+i}{n+i} \binom{n+i}{n}.$$  (2)

This formula for the hexagon in the general case was first given by Cyvin [7] as a generalization of a formula pertaining to dihedral hexagons [5]. The three parameters $(k, m, n)$ in (2) are completely permutable.

For the chevron [5, 7] a general formula reads

$$K[Ch(k, m, n)] = \sum_{i=0}^{n} \binom{k+i-1}{i} \binom{m+i-1}{i}.$$  (3)

Here $k$ and $m$ are interchangeable, but $n$ is unique. Therefore an alternative formula is very useful, where the summation to $n$ is replaced by a summation to $k$. It is presented here for the first time:

$$K[Ch(k, m, n)] = \sum_{j=\max(1, k-n)}^{k} (-1)^{k-j} \binom{n+j-1}{n} \binom{n+m}{n-k+j}.$$  (4)

An application of (2) gives readily

(I-1) $K[O(3, 3, n)] = \frac{1}{40} \binom{n+3}{3} \binom{n+4}{3} \binom{n+5}{3}$

$$= \frac{1}{8640} (n+1)(n+2)^2(n+3)^2(n+4)^2(n+5).$$  (5)

The polynomial form in (5) was also derived by Ohkami and Hosoya [8]. Similarly we obtain

(II-1) $K[O(2, 4, n)] = \frac{1}{5} \binom{n+4}{4} \binom{n+5}{4}$

$$= \frac{1}{2880} (n+1)(n+2)^2(n+3)^2(n+4)^2(n+5).$$  (6)
Fig. 3. Ten classes of regular 5-tier strips belonging to the series (I). The drawings have $n = 4$.

Fig. 5. The existing ten classes of regular 5-tier strips belonging to the series (II). The drawings have $n = 4$. 

Fig. 4. Additional six classes of regular 5-tier strips belonging to the series (I). The drawings have \( n = 4 \).

Fig. 6. The parallelogram \( 5 \times n \), where \( n = 4 \). It constitutes the series (III) of regular 5-tier strips.

Boldface figures in parentheses, as in front of (5) and (6), refer to Figures 3–6.

The application of the general formulas to chevrons (4) renders an elucidating example. On application of (3) one obtains

\[
\begin{align*}
(\text{I-4}) \quad K'\{\text{Ch}(3,3,n)\} &= \sum_{i=0}^{n} \left( \frac{i+2}{2} \right)^2 \\
&= \frac{1}{4} \sum_{i=0}^{n} (i+1)^2(i+2)^2 \\
&= \frac{1}{60} (n+1)(n+2)(n+3)(3n^2+12n+10).
\end{align*}
\]

From (4), on the other hand, one obtains

\[
\begin{align*}
(\text{I-4}) \quad K'\{\text{Ch}(3,3,n)\}' &= \binom{n+2}{2} \binom{n+3}{3} - (n+1) \binom{n+3}{4} + \binom{n+3}{5}, \\
&= \left( \frac{n+2}{2} \right) \left( \frac{n+3}{3} \right) - (n+1) \left( \frac{n+3}{4} \right) + \left( \frac{n+3}{5} \right).
\end{align*}
\]

which already is an explicit formula, although in terms of binomial coefficients. It reduces indeed to the same polynomial form as in (7). For the chevron of series (II), (4) is again much easier to apply than (3) and gives

\[
(\text{II-4}) \quad K'\{\text{Ch}(2,4,n)\} = (n+1) \binom{n+4}{4} - \binom{n+4}{5} \\
= \frac{1}{120} (n+1)(n+2)(n+3)(n+4)(4n+5).
\]

Parallelograms and Essentially Disconnected Benzenoids

**Parallelogram**

For the parallelogram-shaped benzenoid, \( L(m,n) \), the number of Kekulé structures is one of the classical results [5]:

\[
K'\{L(m,n)\} = \binom{m+n}{n}.
\]

Hence

\[
(\text{III}) \quad K'\{L(5,n)\} = \binom{n+5}{5} \\
= \frac{1}{120} (n+1)(n+2)(n+3)(n+4)(n+5).
\]

**Essentially Disconnected Parallelograms**

A number of classes of the regular five-tier strips contain essentially single bonds and may be referred to as essentially disconnected. First we consider the benzenoids whose fragments are parallelograms, occasionally reduced to single chains. For the latter case

\[
K'\{L(n)\} = K'\{L(1,n)\} = n+1.
\]

This is a special case of (10) for \( m=1 \). The \( K' \) numbers are obtained by (10) and (12), and multiplication of the individual \( K' \)’s for the fragments. In summary we obtain:

\[
(\text{I-7}) \quad K'\{\Sigma j(3,3,n)\} = \binom{n+2}{2} \\
\]

\[
= \frac{1}{4} (n+1)^2(n+2)^2, \quad (13)
\]

\[
(\text{I-8}) \quad K'\{\text{Ri}(3,n)\} = (n+1)^3, \quad (14)
\]

\[
(\text{I-9}) \quad K'\{\Sigma \ i(3,3,n)\} = (n+1)^2, \quad (15)
\]
Number of Kekulé Structures of Five-Tier Strips

Other Essentially Disconnected Benzenoids

In two instances we encounter essentially disconnected benzenoids with fragments other than parallelograms, viz. three-tier hexagon, O(2, 2, n) and chevron, Ch(2, 2, n). The K numbers for the classes of these fragments are well known [5], and also (2)–(4) are applicable. Our result is:

(I-13) \[ K|L(n) \cdot O(2, 2, n)| = \frac{1}{3} (n + 1) \left( \frac{n + 2}{2} \right) \left( \frac{n + 3}{2} \right) = \frac{1}{12} (n + 1)^2 (n + 2)^2 (n + 3). \]

(I-15) \[ K|L(n) \cdot Ch(2, 2, n)| = (n + 1) \left( \frac{n + 1}{2} \right) \left( \frac{n + 2}{3} \right) = \frac{1}{6} (n + 1)^2 (n + 2)(2n + 3). \]

Non-Kekuléan Structures

The principal difference between (I-10) and (II-10) should be noticed: while X(2, 4, n) is essentially disconnected and Kekuléan, X(3, 3, n) is non-Kekuléan:

(I-10) \[ K|X(3, 3, n)| = 0 \]

Multiple Chains

A multiple chain is defined as fused parallel chains, which may have kinks in alternating left-right-left-… manner. The concept of LA-sequences [9, 10] is applicable to multiple chains. In our context (t-tier strips) the multiple chains reveal themselves by having all rows of the equal length (n hexagons). There are six classes of multiple chains in our collection (5-tier strips): the parallelogram (III), the chevrons (I-4) and (II-4), the zig-zag chain (I-6), along with (II-6) \[ M_n(ALAL) \] and (I-14) \[ M_n(ALAAL). \] In this notation, particularly designed for multiple chains, one has

(III) \[ L(5, n) = M_n(LLLLL), \]

(II-4) \[ Ch(2, 4, n) = M_n(LLLAL), \]

(I-4) \[ Ch(3, 3, n) = M_n(LLALL), \]

(I-6) \[ Z(5, n) = M_n(ALAAL). \]

A general theory for the K numbers of multiple chains has not been developed. Preliminary (so far unpublished) findings have resulted in the following formulas:

(I-6) \[ K|Z(5, n)| = (n + 1) \left[ \left( \frac{n + 2}{2} \right)^2 - \left( \frac{n + 3}{4} \right) \right] - \left( \frac{n + 2}{2} \right) \left( \frac{n + 2}{3} \right) + \left( \frac{n + 3}{5} \right) \]
\[ = \frac{1}{30} (n + 1)(n + 2)(2n + 3)(2n^2 + 6n + 5), \]
The polynomial form of (24) was deduced in a different way by Gutman and Cyvin [13], while (25) and (26) are new.

**Summation- and Recurrence Formulas**

**General**

Many of the considered classes of benzenoids are inter-connected with respect to their number of Kekulé structures. The underlying theory is well known in the enumeration techniques of Kekulé structures [14], and has been applied previously to t-tier strips specifically by Yen [6]. If we, for instance, focus the attention upon the utter-most right- (or left-) hand bond in (I-1) we arrive at

\[ K'(O(3, 3, n)) = K'(O(3, 3, n - 1)) + K'(Dj(3, 3, n)). \] (27)

By successive application of this recurrence formula and the initial conditions

\[ K'(O(3, 3, 0)) = K'(Dj(3, 3, 0)) = 1 \]

we obtain the summation formula

\[ K'(O(3, 3, n)) = \sum_{i=0}^{n} K'(Dj(3, 3, i)). \] (28)

Altogether we have derived the following equations of the types (27) and (28):

\[ K_n[1] = \sum_{i=0}^{n} K_i[4], \] (29)

\[ K_n[2] = K_{n-1}[1], \] (30)

\[ K_n[2] = \sum_{i=0}^{n} K_i[5], \] (31)

\[ K_n[3] = \sum_{i=0}^{n} K_i[6], \] (32)

\[ K_n[4] = \sum_{i=0}^{n} K_i[7], \] (33)

\[ K_n[5] = K_{n-1}[2] - K_{n-1}[2], \] (34)

\[ K_n[6] = K_{n-1}[3] - K_{n-1}[3], \] (35)

\[ K_n[7] = K_{n-1}[4] - K_{n-1}[4]. \] (36)

Here the boldface figures refer to Fig. 3 or 5. The equations apply to both series (I) and (II). Thus, for instance, when (29) is used for (I-1) and (I-2) it coincides with (28). Finally we have a connection between two of the classes from Fig. 4:

\[ K_n[I-11] = \sum_{i=0}^{n} K_i[I-12], \] (37)

\[ K_n[I-12] = K_n[I-11] - K_{n-1}[I-11]. \] (38)

**Application of Hexagons**

The K formulas for the hexagons (I) are known; cf. (5) and (6). When they are applied in (30) we obtain first

\[ K_n[4] = \frac{1}{40} \binom{n+3}{3} \binom{n+4}{3} - \frac{1}{40} \binom{n+2}{3} \binom{n+3}{3} \binom{n+4}{3} = \frac{1}{2880} (n+1)(n+2)(n+3)^2(n+4) \cdot (3n^2+15n+20). \] (39)

For this class Yen [6] has given a considerably more complicated equation in terms of binomial coefficients, while Ohkami and Hosoya [8] arrived at the polynomial form of (39) by a different method involving laborious algebraic computations, which were executed by a computer program. In the series (II) we obtain a new formula, viz.

\[ K_n[4] = \frac{1}{5} \binom{n+4}{4} \binom{n+5}{4} - \frac{1}{5} \binom{n+3}{4} \binom{n+4}{4} = \frac{1}{720} (n+1)(n+2)^2(n+3)^2(n+4)(2n+5). \] (40)
Equation (37) together with (51) gives

\[ K_i D(3, 3, n) = \sum_{i=0}^{n} K_i R(3, i) \]

\[ = \frac{1}{720} (n + 1)(n + 2)^2 \cdot (3n^4 + 35n^3 + 149n^2 + 273n + 180). \]

Acknowledgements

Financial support to BNC from The Norwegian Research Council for Science and the Humanities is gratefully acknowledged.