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The Number of *Kekulé* Structures of Hexagon-shaped Benzenoids and Members of Other Related Classes

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Some results from the enumeration of *Kekulé* structures are reviewed; they pertain to parallelogram-shaped, bent strips, chevrons and symmetrical hexagon-shaped benzenoids. The existing formulas are extended to the class of asymmetrical hexagons. Applications of the new formula reproduces a number of known results for three-tier and four-tier strips. In the latter case also some new formulas are achieved.

(Keywords: Kekulé structures; Benzenoids)

Die Anzahl der Kekulé-Strukturen von Benzenoiden mit sechseckigem Umriß und Mitgliedern anderer verwandter Klassen

Es wird ein Überblick über die Berechnung der Anzahl möglicher *Kekulé*-Strukturen von benzenoiden Verbindungen unterschiedlicher Formenklassen gegeben. Dabei werden die existierenden Formeln für die Klasse asymmetrischer Sechseckformen ausgeweitet und die neue Formel auch an bekannten Ergebnissen erprobt.

Introduction

The enumeration of *Kekulé* structures[1,2] in conjugated hydrocarbons has attained an increasing interest in modern times[3—6]. The present work deals with peri-condensed benzenoid systems only; they are represented by reticles of regular hexagons. The emphasis is laid on combinatorial formulas in closed form. The number of *Kekulé* structures of a benzenoid B is designated $K\{B\}$.

The main subject of this paper is a study of a class of benzenoids referred to as hexagonal. We prefer this designation[7] rather than the alternative[8] "circular", especially because we now are going to renounce much of the symmetry in these systems.

Results and Discussion

Previous Results

The combinatorial formula of K for the $m \times n$ parallelogram-shaped benzenoids, say $\mathrm{L}(m,n) = \mathrm{L}(n,m)$, is a classical result[7], which has been quoted frequently[4–6,8]:

$$K\{\mathrm{L}(m,n)\} = \binom{m+n}{n} \tag{1}$$

This class of benzenoids contains two parameters (m,n), which are the numbers of hexagons in a row or column. In general the parameters are

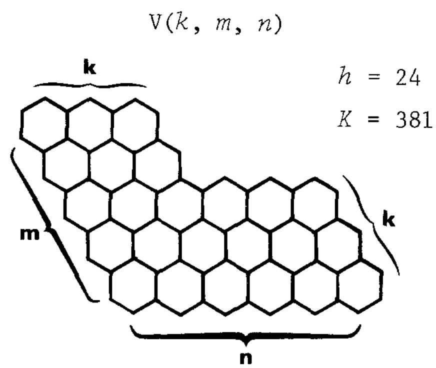


Fig. 1. The benzenoid $\mathrm{V}(k,m,n)$ with $k = 3$, $m = 5$, $n = 6$: $\mathrm{V}(3,5,6)$; the number of rings (h) and *Kekulé* structures (K) are indicated

positive integers, which however, usually may degenerate to zero. Classes of three-parameter benzenoids have also been studied:

1. *Bent strip.* This (V-shaped) benzenoid may be interpreted as a subbenzenoid of the $m \times n$ parallelogram; cf. Fig. 1. It is determined by three parameters $(k,\ m,\ n)$. A general formula for the number of *Kekulé* structures has recently been derived by *Cyvin* and *Gutman*[9];

$$K\{\mathrm{V}(k,m,n)\} = \sum_{i=0}^{k} \binom{m}{i}\binom{n}{i} \tag{2}$$

These authors[9] have also solved the problem for the bent strip of unequal thickness of the two branches, a four-parameter problem.

2. *Chevron-shaped benzenoids.* The classical paper of *Gordon* and *Davison*[7] contains a general formula for the K number of a three-parameter chevron-shaped benzenoid; cf. Fig. 2. The formula has since

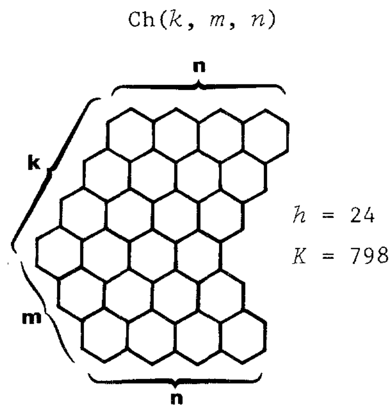


Fig. 2. The benzenoid Ch(4, 3, 4); the numbers of *h* and *K* are given (notice that *h* is the same as in Fig. 1)

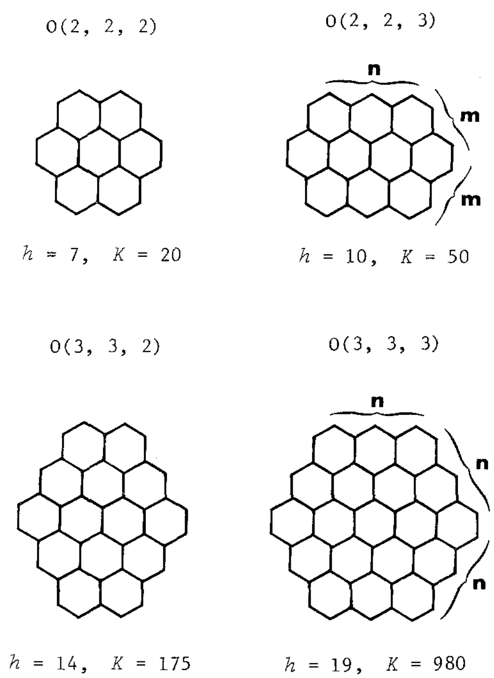


Fig. 3. Two regular, O(*n*, *n*, *n*), and two dihedral, O(*m*, *m*, *n*), hexagon-shaped benzenoids; values of *m*, *n*, *h* and *K* are given

passed unnoticed and seems therefore to be worth citing here. It reads (in a slightly modified form):

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

3. *Hexagon-shaped benzenoids*. The chevron is a sub-benzenoid in $O(k,m,n)$, presently referred to as the hexagon-shaped (or hexagonal) benzenoid. *Gordon* and *Davison*[7] have credited *R. M. Everett* for the equation of K for $O(n,n,n)$, the regular hexagon (a), and *M. Woodger* for the more general case $O(m,m,n)$, the dihedral hexagon (b). Fig. 3 shows some examples. The formulas[7,8] are given below in a slightly modified form.

a) The regular hexagon-shaped benzenoid (symmetry D_{6h}) has $2n-1$ rows (tier chains), and the number of rings is $h = 3n(n-1) + 1$. The number of *Kekulé* structures is

$$K\{O(n,n,n)\} = \prod_{i=0}^{n-1} \frac{\binom{2n+i}{n}}{\binom{n+i}{n}} \tag{4}$$

b) The dihedral hexagon (symmetry D_{2h}) has $2m-1$ rows, $h = m(m+2n)-2m-n+1$, and

$$K\{O(m,m,n)\} = \prod_{i=0}^{m-1} \frac{\binom{m+n+i}{n}}{\binom{n+i}{n}} \tag{5}$$

Notice that m and n are not interchangeable; Fig. 3 includes $O(2,2,3)$ and $O(3,3,2)$, which are not identical.

In the form eqns. (4) and (5) are written it is easy to put down the result: Start with n as the upper figure in the first binomial coefficient of the denominator; notice that these figures follow consecutively, and each product has the same number of factors, viz. m. Thus, for instance,

$$K\{O(3,3,2)\} = \frac{\binom{5}{2}\binom{6}{2}\binom{7}{2}}{\binom{2}{2}\binom{3}{2}\binom{4}{2}} = 175 \tag{6}$$

The asymmetrical hexagon-shaped benzenoids, $O(k,m,n)$, are the main subject of the present work. A simple (but not trivial) extension of eqn. (5) was achieved to make it applicable to this three-parameter case.

Asymmetrical Hexagon-Shaped Benzenoids

The asymmetrical hexagon with all parameters (k, m, n) different (cf. Fig. 4) belongs to the symmetry C_{2h}. The parameters are permutable; $O(k, m, n)$, $O(k, n, m)$, $O(m, n, k)$, etc., are all identical. If one of the

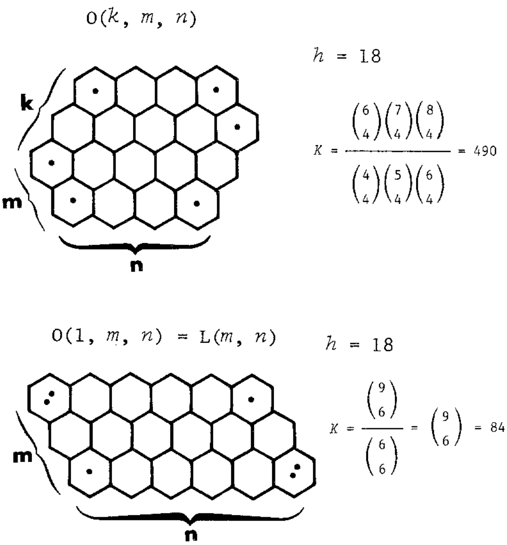


Fig. 4. The asymmetrical hexagon-shaped benzenoid with parameters 2, 3 and 4 (top part). The bottom part shows how the hexagon degenerates into a parallelogram when one of the parameters is unity. Corners are marked with dots

parameters is 1, the hexagon degenerates into a parallelogram. The number of rings is

$$h = (k + m)(n - 1) + km - n + 1 \tag{7}$$

Number of *Kekulé* structures:

$$K = \prod_{i=0}^{k-1} \frac{\binom{m+n+i}{n}}{\binom{n+i}{n}} \tag{8}$$

Recurrence Relations

From eqn. (8) we obtain a recurrence relation when one of the parameters is increased by unity. Because of the permutation properties all cases are covered if only one of the parameters, say k, is chosen to undergo this change. The relation reads

$$\frac{K\{\mathrm{O}(k+1,m,n)\}}{K\{\mathrm{O}(k,m,n)\}} = \prod_{i=1}^{n} \frac{k+m+i}{k+i} = \frac{\binom{k+m+n}{n}}{\binom{k+n}{n}} \tag{9}$$

We also give a recurrence relation pertaining to the dihedral hexagon-shaped benzenoids:

$$\frac{K\{\mathrm{O}(m+1,m+1,n)\}}{K\{\mathrm{O}(m,m,n)\}} = \frac{(2m+n+1)\binom{2m+n}{n}^2}{(2m+1)\binom{m+n}{n}^2} \tag{10}$$

Finally we give the corresponding formula for regular hexagons:

$$\frac{K\{\mathrm{O}(n+1,n+1,n+1)\}}{K\{\mathrm{O}(n,n,n)\}} = \frac{(3n+1)^2(3n+2)\binom{3n}{n}^3}{(2n+1)^3\binom{2n}{n}^3} \tag{11}$$

Corners of a Hexagon-Shaped Benzenoid

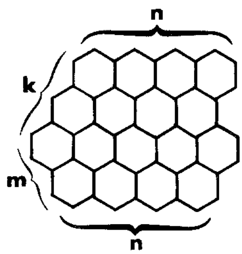
A hexagon-shaped benzenoid has six special positions at the corners; cf. Fig. 4. The number degenerates to four for the parallelograms. In this case two corners have collapsed together at the two acute-angle positions.

If we remove one hexagon from the boarder of $\mathrm{O}(k,m,n)$ we run into a non-*Kekulé*an structure in most cases; a *Kekulé*an structure is achieved only if we remove a corner. Let $\mathrm{Oa}(k,m,n)$ designate the structure where a corner is removed from $\mathrm{O}(k,m,n)$ and conventionally chosen at the meeting point of the k and m chains; cf. Fig. 5. (Notice that according to this convention the rows belonging to the last parameter, n, remain undisturbed.) For the K value it is easily found by familiar methods in enumeration of *Kekulé* structures[10]

$$K\{\mathrm{Oa}(k,m,n)\} = K\{\mathrm{O}(k,m,n)\} - K\{\mathrm{O}(k,m,n-1)\} \tag{12}$$

Notice that the removal of two corners in contact with each other again leads to a non-*Kekulé*an structure. Fig. 4 contains examples of this situation. The effect of removing one degenerate (acute-angle) double-corner from a parallelogram is the same. The removing of two diagonal corners may be treated in general terms. We define the benzenoid

Oa(k, m, n)

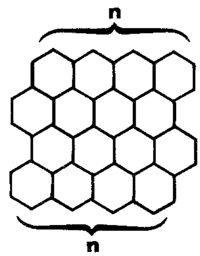


$h = 17$, $K\{Oa(3,2,4)\}$

$= K\{(3,2,4)\} - K\{O(3,2,3)\}$

$= 490 - 175 = 315$

Ob(k, m, n)



$h = 16$, $K\{Ob(3,2,4)\}$

$= K\{O(3,2,4)\}$

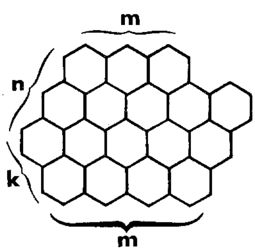
$- 2K\{O(3,2,3)\}$

$+ K\{O(3,2,2)\}$

$= 490 - 350 + 50 = 190$

Fig. 5. The hexagon-shaped benzenoid O(3, 2, 4) of Fig. 4 with some corners removed; the right-hand side benzenoid, Ob(3, 2, 4), is a zig-zag strip, also designated Z(4, 4)

Oa(k, m, n)

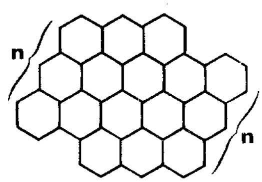


$h = 17$, $K\{Oa(2,4,3)\}$

$= K\{O(2,4,3)\} - K\{O(2,4,2)\}$

$= 490 - 105 = 385$

Ob(k, m, n)



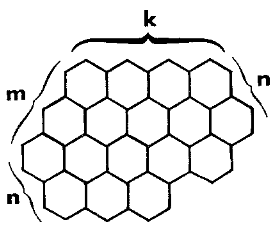
$h = 16$, $K\{Ob(2,4,3)\}$

$= K\{O(2,4,3)\}$

$- 2K\{O(2,4,2)\}$

$+ K\{O(2,4,1)\}$

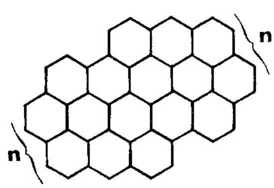
$= 490 - 210 + 15 = 295$



$h = 17$, $K\{Oa(4,3,2)\}$

$= K\{O(4,3,2)\} - K\{O(4,3,1)\}$

$= 490 - 35 = 455$



$h = 16$, $K\{Ob(4,3,2)\}$

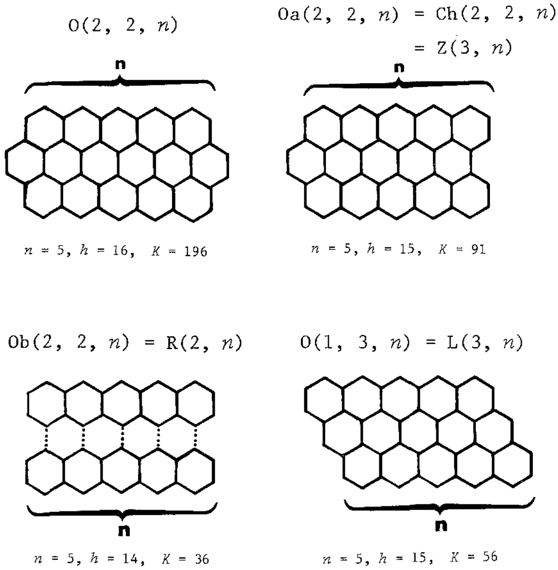
$= K\{O(4,3,2)\}$

$- 2K\{O(4,3,1)\}$

$+ K\{O(4,3,0)\}$

$= 490 - 70 + 1 = 421$

Fig. 6. The additional possibilities of removing one or two (diagonal) corners from O(3, 2, 4), which is identical with O(2, 4, 3) and O(4, 3, 2)



$$K\{O(2,\ 2,\ n)\} = \frac{1}{12}(n+1)(n+2)^2(n+3)$$

$$K\{Z(3,\ n)\} = \frac{1}{6}(n+1)(n+2)(2n+3)$$

$$K\{R(2,\ n)\} = (n+1)^2$$

$$K\{L(3,\ n)\} = \frac{1}{6}(n+1)(n+2)(n+3)$$

Fig. 7. Different types of regular benzenoids with three tier chains and algebraic formulas for the number of *Kekulé* structures; the dotted edges in $R(2, n)$ represent essentially single bonds

$Ob(k, m, n)$ with one more (diagonal) corner removed from $Oa(k, m, n)$ as shown in Fig. 5. Then we have

$$K\{Ob(k,m,n)\} = K\{O(k,m,n)\} - 2K\{O(k,m,n-1)\} + K\{O(k,m,n-2)\} \tag{13}$$

Fig. 6 shows (in addition to Fig. 5) the result of removing one or two (diagonal) corners from $O(3,2,4)$. Observe the conventions of notation.

Classes of Three-Tier Strip Benzenoids

Consider the removal of a corner from $O(2,2,n)$ as shown in Fig. 7. Equation (12) gives

$$\begin{aligned} K\{Oa(2,2,n)\} &= K\{O(2,2,n)\} - K\{O(2,2,n-1)\} \\ &= K\{O(2,n,2)\} - K\{O(2,n-1,2)\} \end{aligned} \tag{14}$$

On application of eqn. (8) one obtains

$$K\{\mathrm{Oa}(2,2,n)\} = \frac{1}{3}\binom{n+2}{2}\left[\binom{n+3}{2} - \binom{n+1}{2}\right] =$$

$$= \frac{1}{6}(n+1)(n+2)(2n+3) \tag{15}$$

By means of eqn. (3) for the chevron one obtains

$$K\{\mathrm{Ch}(2,2,n)\} = \sum_{i=0}^{n}\binom{i+1}{i}^2 = \sum_{i=0}^{n}(i+1)^2 = \frac{1}{6}(n+1)(n+2)(2n+3) \tag{16}$$

The identity of the results of eqns. (15) and (16) is not surprising inasmuch as the two benzenoids are identical; cf. Fig. 7. The result of these equations has been obtained several times by different methods[7,8,11,12].

Assume two diagonal corners to be removed from O(2, 2, n) as shown in Fig. 7. Equation (13) gives

$$K\{\mathrm{Ob}(2,2,n)\} = K\{\mathrm{O}(2,2,n)\} - 2K\{\mathrm{O}(2,2,n-1)\} + K\{\mathrm{O}(2,2,n-2)\}$$
$$= K\{\mathrm{O}(2,n,2)\} - 2K\{\mathrm{O}(2,n-1,2)\} + K\{\mathrm{O}(2,n-2,2)\} \tag{17}$$

and on inserting from eqn. (8):

$$K\{\mathrm{Ob}(2,2,n)\} = \frac{1}{3}\left[\binom{n+2}{2}\binom{n+3}{2} - 2\binom{n+1}{2}\binom{n+2}{2} + \binom{n}{2}\binom{n+1}{2}\right] = (n+1)^2 \tag{18}$$

This result can be obtained much easier; the benzenoid is in fact a special case of a well known class of rectangular-shaped benzenoids[7,8].

For the sake of completeness also the hexagon- and parallelogram-

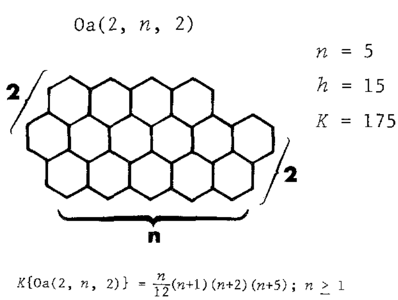


Fig. 8. One corner removed from O(2, 2, n) or O(2, n, 2)

shaped benzenoids of three-tier strips are included in Fig. 7. The list of K-value formulas of Fig. 7 may be supplemented by another class of three-tier strips, where a corner has been removed from $O(2,2,n)$ or $O(2,n,2)$; cf. Fig. 8. The formula therein is new, but supposed to be too special to be really important.

All the other formulas (given in Fig. 7) for three-tier strips are already well known. Also different classes of five-tier strips have been studied[7,8,12], taking advantage of the $O(3,3,n)$ benzenoids, for which eqn. (5) is relevant. These benzenoids, viz. $O(3,3,n)$, are here referred to as dihedral-hexagonal. The four-tier strips represent a gap in these investigations. With the knowledge of eqn. (8) for the asymmetrical-hexagonal benzenoids also these classes may be studied by the same methods.

Classes of Four-Tier Strip Benzenoids

Here the four-tier strips are treated systematically. Only the regular classes are considered in the sense that the bottom and top rows should have the same length of n hexagons. Consequently the example of Fig. 8 falls outside the system.

1. *Hexagons*

The only possibility for a non-degenerate hexagonal benzenoid with four tier chains is $O(3,2,n)$, which also may be written $O(2,3,n)$, and belongs to the asymmetrical type (unless $n = 2$ or 3); Fig. 4 depicts the example with $n = 4$. In this case one has according to eqn. (8):

$$K\{O(3,2,n)\} = K\{O(2,n,3)\} = \frac{1}{4}\binom{n+3}{3}\binom{n+4}{3} = \frac{1}{144}(n+1)(n+2)^2(n+3)^2(n+4) \tag{19}$$

2. *Pentagons*

A sub-benzenoid of $O(3,2,n)$ is obtained on removing one corner as depicted in Fig. 9. It has a pentagonal shape with one of the sides indented. The chevron $Ch(3,2,n)$ is a sub-benzenoid of this pentagon. Equations (12) and (8) lead to

$$K\{Oa(3,2,n)\} = K\{O(2,n,3)\} - K\{O(2,n-1,3)\} = \frac{1}{4}\binom{n+3}{3}\left[\binom{n+4}{3} - \binom{n+2}{3}\right] = \frac{1}{24}(n+1)(n+2)^3(n+3) \tag{20}$$

3. *Zig-zag strip*

On removing two (diagonal) corners from O(3, 2, *n*) as shown in Fig. 5 we attain at the Z(4, *n*) zig-zag strip or multiple zig-zag chain. Equations (13) and (8) give

$$K\{Z(4,n)\} = K\{Ob(3,2,n)\} = K\{O(2,n,3)\} - 2K\{O(2,n-1,3)\} + + K\{O(2,n-2,3)\} = \frac{1}{4}\left[\binom{n+3}{3}\binom{n+4}{3} - -2\binom{n+3}{3}\binom{n+2}{3} + \binom{n+2}{3}\binom{n+1}{3}\right] = = \frac{1}{24}(n+1)(n+2)(5n^2+15n+12) \tag{21}$$

This result was derived in an other way by *Gutman* and *Cyvin*[11].

4. *Parallelograms*

Equation (1) gives

$$K\{L(4,n)\} = \frac{1}{24}(n+1)(n+2)(n+3)(n+4) \tag{22}$$

For $n = 4$ as an example, $h = 16$ and $K = 70$.

5. *Chevrons*

For the Ch(3, 2, *n*) benzenoid, which has four tier chains, one obtains from eqn. (3)

$$K\{Ch(3,2,n)\} = \sum_{i=0}^{n}\binom{i+2}{i}\binom{i+1}{i} = \frac{1}{2}\sum_{i=0}^{n}(i+1)^2(i+2) = \frac{1}{24}(n+1)(n+2)(3n^2+13n+12) \tag{23}$$

For Ch(3, 2, 4) as an example, one has $h = 16$ and $K = 140$.

6. *Chevrons without apex*

Let the corner where the *k* and *m* rows of a chevron meet be defined as the apex. Then consider the sub-benzenoid Ch(3, 2, *n*) where the apex is removed, say Ca(3, 2, *n*); cf. Fig. 9. The familiar methods[10] combined with eqn. (3) give

$$K\{\mathrm{Ca}(3,2,n)\} = K\{\mathrm{Ch}(3,2,n)\} - K\{\mathrm{Ch}(3,2,n-1)\}$$
$$= \binom{n+2}{2}\binom{n+1}{1} = \frac{1}{2}(n+1)^2(n+2) \quad (24)$$

The result is easily understood by observing the essentially single bonds; cf. Fig. 9. It is equivalent with

$$K\{\mathrm{Ca}(3,2,n)\} = K\{\mathrm{L}(2,n)\} \cdot K\{\mathrm{L}(1,n)\} \quad (25)$$

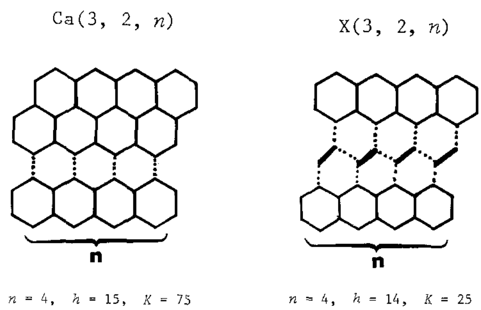


Fig. 9. The chevron Ch(3, 2, n) without apex (left), and a goblet (right); essentially single bonds are dotted, double bonds heavy

7. *Goblets*

Fig. 9 shows how we arrive at a (skew) goblet-shaped benzenoid on removing one hexagon from Ca(3, 2, n). The effect on the number of *Kekulé* structures is reflected by the following equations.

$$K\{\mathrm{X}(3,2,n)\} = K\{\mathrm{Ca}(3,2,n)\} - K\{\mathrm{B}\} \quad (26)$$

where

$$K\{\mathrm{B}\} = K\{\mathrm{Ca}(3,2,n-1)\} + K\{\mathrm{L}(2,n-1)\} \quad (27)$$

Consequently

$$K\{\mathrm{X}(3,2,n)\} = \binom{n+2}{2}\binom{n+1}{1} - \binom{n+1}{2}\binom{n}{1} - \binom{n+1}{2} = (n+1)^2 \quad (28)$$

The result could be reached easier, inasmuch as this special type of goblets are zethrene-type benzenoids with a number of essentially single bonds; cf. Fig. 9.

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