ENUMERATION OF KEKULÉ STRUCTURES IN BENZENOID HYDROCARBONS: "FLOUNDERS"*

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Abstract

Combinatorial formulas for Kekulé structure counts (K) of a class of benzenoids referred to as "flounders" are derived. They represent a generalization of the previously studied "pentagon-shaped" benzenoids. A special case of the K formula reproduces the well-known Catalan numbers.

1. Introduction

Many interesting combinatorial problems have been encountered in the studies of Kekulé structure counts of benzenoid systems; cf., e.g., the recent book by Cyvin and Gutman [1] with the bibliography therein, and a few additional references [2–6].

In the present work we define some new classes of benzenoids, in continuation of the previous works [1]. Combinatorial K formulas are derived, where K designates the Kekulé structure counts. We point out explicitly the connections with some classical mathematical problems.

The importance of the Fibonacci numbers in the enumeration of the Kekulé structures is well known [1,7–11]. Here, we shall also identify the K numbers for a certain class of benzenoids with the Catalan numbers.

*Part VI in the series Pentagon-Shaped Benzenoids. For parts I – V, see refs. [12 – 16].

2. Definitions of benzenoid classes

In a series of papers [12–16], the K numbers of some classes of "pentagon-shaped" benzenoids (or simply "pentagons") were treated. The studies include "triangle-shaped" benzenoids T [14] as special cases of the pentagons D. The pentagonal shape of the so-called prolate and oblate pentagons among straight t-tier strips [1,17] is fairly obvious. Through further generalizations [1,15] it is obscured, but nevertheless the name "pentagon" was retained together with the symbol D. All classes defined in the present work belong to D, the pentagons in the generalized sense. The corresponding special cases identified by the symbol T are considered in particular. These are generalizations of the triangle-shaped benzenoids studied previously, but which no longer have a triangular shape in general.

In conclusion, it does not seem appropriate to push the designations "pentagon" and "triangle" further. We have therefore invented the fancy name "flounders" for the benzenoids of the classes defined in the following.

A benzenoid $T(k, m; p)$ is defined as a parallelogram $L(k, m)$ from which a prolate triangle $T^{i}(p)$ is deleted, as shown in fig. 1. It belongs to the flounders.

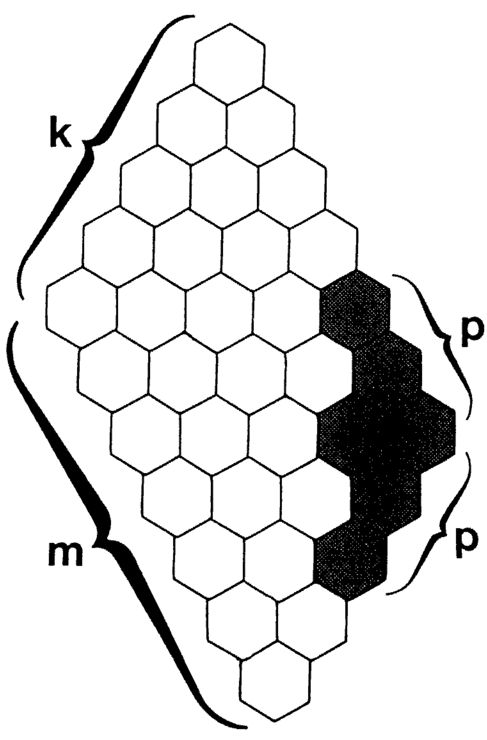

Fig. 1. Definition of the benzenoid (flounder) $T(k, m; p)$, the white part of the figure. The depicted example is $T(5,7; 3)$.

The systems $T(k, m; p)$ and $T(m, k; p)$ are isomorphic. The three types of triangles [1] are special cases of flounders:

$T^i(m) \equiv T(m, m; m-1)$ prolate triangle;

$T(m, m+1) \equiv T(m, m+1; m-1)$ problate triangle;

$T^j(m) \equiv T(m, m; m-2)$ oblate triangle.

Normally, one has $0 < p < \min(m, n)$. The case of $p = 1$ is a parallelogram without corner [1]:

$La(k, m) \equiv T(k, m; 1)$.

Furthermore, there is no difficulty in extending the range of p to zero. In this case, the flounder simply degenerates to the corresponding parallelogram:

$L(k, m) \equiv T(k, m; 0)$.

In the following definition of a class of flounders, it is expedient to also define:

$T(k, m; t) \equiv L(k, m)$ when $t < 0$.

A class of flounders $T(k, m; p)$ may be defined so that $k - p$ and $m - p$ are constant for all members. In the example of fig. 1, one has $k - p = 2$ and $m - p = 4$. In fig. 2, the members of the corresponding class with decreasing p values are depicted, right down to the utterly degenerate case of "no hexagons", where $k = 0$ and $p = -2$.

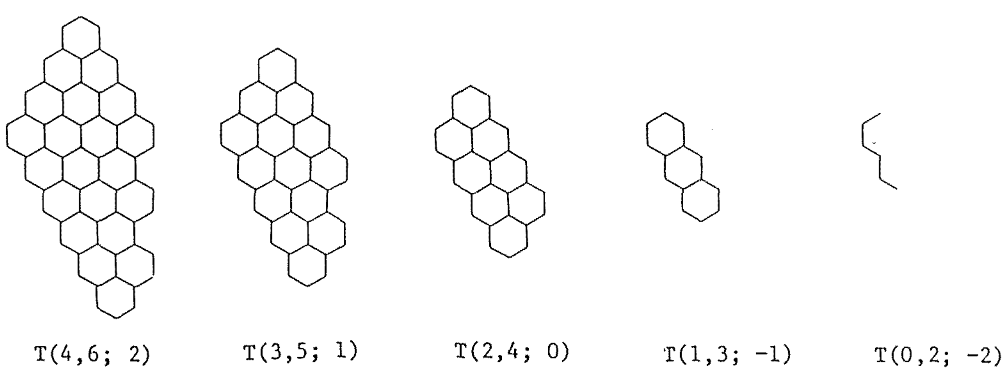

Fig. 2. A class of benzenoids (flounders) $T(k, m; p)$, where $k - p$ and $m - p$ are constant. In this example, $k - p = 2$, $m - p = 4$.

A flounder $T(k, m; p)$ may also be taken as a starting point of a class of regular $(k + m - 1)$-tier strips [1]. A member of such a class, also called a flounder,

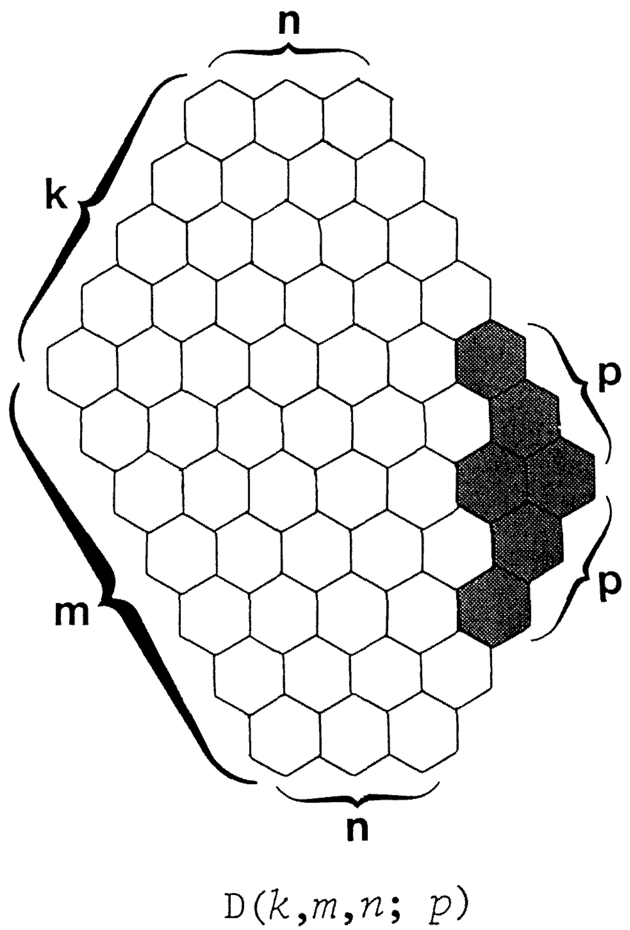

Fig. 3. Definition of the benzenoid (flounder) $D(k, m, n; p)$.
The depicted example: D(5,7,3;3).

is by definition a pentagon (although not always pentagon-shaped) and will therefore be identified by the symbol $D(k, m, n; p)$; see fig. 3 for a precise definition of the parameters. One has:

$$T(k, m; p) \equiv D(k, m, 1; p).$$

The three types of pentagons [1] are special cases of flounders as specified below:

$D^i(m, n) \equiv D(m, m, n; m - 1)$ prolate pentagon;

$D(m, m + 1, n) \equiv D(m, m + 1, n; m - 1)$ problate pentagon;

$D^j(m, n) \equiv D(m, m, n; m - 2)$ oblate pentagon.

The cases of $p = 1$ and $p = 0$ are a hexagon without corner and a hexagon [1], respectively:

$$\mathrm{Oa}(k, m, n) \equiv \mathrm{D}(k, m, n; 1);$$

$$\mathrm{O}(k, m, n) \equiv \mathrm{D}(k, m, n; 0).$$

In consistency with the above considerations for $\mathrm{T}(k, m; p)$, we also define:

$$\mathrm{D}(k, m, n; t) \equiv \mathrm{O}(k, m, n) \quad \text{when} \quad t < 0.$$

3. Recurrence relations for T flounders

For the flounders of fig. 1, which are of the T type, one finds straightforwardly the following recurrence relations for the K numbers (Kekulé structure counts) by means of the method of fragmentation [1,18]:

$$\begin{aligned} K\{\mathrm{T}(k, m; p)\} &= K\{\mathrm{T}(k-1, m; p-1)\} + K\{\mathrm{T}(k, m-1; p)\} \\ &= K\{\mathrm{T}(k, m-1; p-1)\} + K\{\mathrm{T}(k-1, m; p)\}. \end{aligned} \tag{1}$$

The special case of $p \leqslant 0$ gives the long known recurrence relation for parallelograms due to Randić [18]:

$$K\{\mathrm{L}(k, m)\} = K\{\mathrm{L}(k-1, m)\} + K\{\mathrm{L}(k, m-1)\}. \tag{2}$$

4. Explicit formula for T flounders

A combinatorial formula for the K numbers of T-type flounders is deduced in the following.

THEOREM

$$K\{\mathrm{T}(k, m; p)\} = \binom{k+m}{m} - \binom{k+m}{p-1}. \tag{3}$$

Proof

There is exactly one peak u and exactly one valley v in $\mathrm{T}(k, m; p)$ when it is posed as in fig. 1. The K number is equal to the number of monotonic paths from

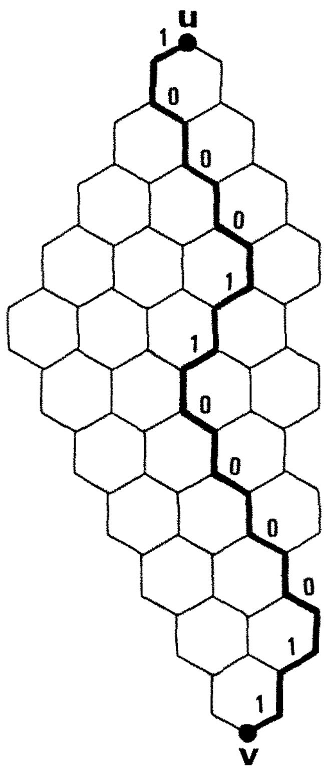

Fig. 4. A monotonic path in the flounder of fig. 1, and its labeling.

v to u [7]; cf. the John–Sachs theorem [1,19], of which the present case pertains to a simple specialization. Consider such a path. Label each non-vertical edge of that path by 1 if it is going upwards to the right and by 0 if it is going upwards to the left. Vertical edges may be ignored. An example is shown in fig. 4. In this way, a bijection is established between all monotonic paths from v to u and all the words w of length $k + m$ over the alphabet L, $\{0, 1\}$, $w \in \{0, 1\}^{k+m}$, satisfying the following conditions:

(i) w contains exactly k unities and exactly m zeros;

(ii) for each prefix r of the word w ($w = rq$), $l_1(r) - l_0(r) \leqslant a = k - p$, where $l_1(r)$ and $l_0(r)$ denote the number of unities and zeros in r, respectively.

It is known [20,21] that the number of words w as specified above is

$$\binom{k+m}{m} - \binom{k+m}{k-a-1},$$

i.e.

$$\binom{k+m}{m} - \binom{k+m}{p-1}.$$

Hence follows the statement (3). □

5. Some special cases of equation (3)

When $p = k - 1$, we obtain a trapeze as shown in fig. 5. The pertinent K formula reads

$$K\{\mathrm{T}(k, m; k-1)\} = \binom{k+m}{m} - \binom{k+m}{k-2}. \quad (4)$$

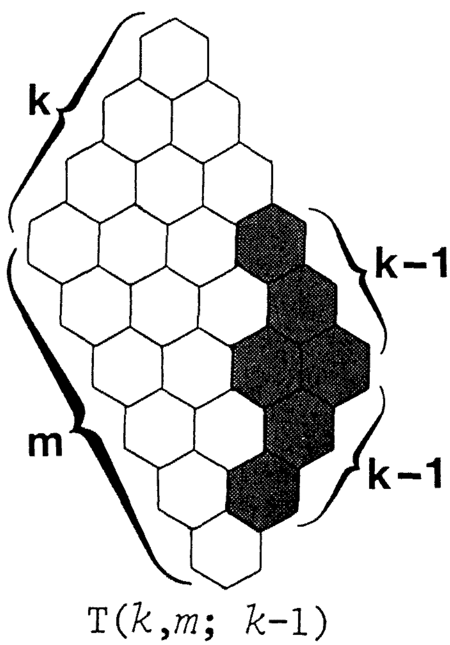

Fig. 5. The trapeze (special flounder) T(4,6;3).

The problate triangle [1] (see also above) is a typical trapeze. In this case, one has

$$K\{\mathrm{T}(m, m+1; m-1)\} = \binom{2m+1}{m} - \binom{2m+1}{m-2}. \quad (5)$$

By elementary computations, it is verified that this formula is equivalent to the previously given form [1], which was derived in a different way, viz.

$$K\{\mathrm{T}(m, m+1)\} = \frac{3}{m+3}\binom{2m+2}{m}. \tag{6}$$

Especially interesting is the case of $k = m$ and $p = m - 1$, which represents the prolate triangles [1] (see also above). From eq. (3) it is found

$$K\{\mathrm{T}(m, m, m-1)\} = \binom{2m}{m} - \binom{2m}{m-2}, \tag{7}$$

which is consistent with [1]. Hence,

$$K\{\mathrm{T}^i(m)\} = \frac{1}{m+2}\binom{2m+2}{m+1} = \frac{1}{m+1}\binom{2m+2}{m}. \tag{8}$$

These K numbers form a series (1,2,5,14,42,132,429,1430,4862,16796,...), which occurs very often in combinatorial counting problems. Leonhard Euler (1707–1783) discovered this series for counting triangulations. Nevertheless, it is named after Eugene Charles Catalan (1814–1894), who re-discovered the same series in connection with the problem: in how many ways can a product be parenthesized? Joseph Louis François Bertrand (1822–1900) solved the equivalent ballot problem. The history of that problem and some of its generalizations can be found in [20,21]. The Catalan numbers are usually written

$$C_n = \frac{1}{n+1}\binom{2n}{n}. \tag{9}$$

Hence,

$$K\{\mathrm{T}^i(m)\} = C_{m+1}. \tag{10}$$

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