match no. 20 pp. 181-195 1986

NUMBER OF KEKULÉ STRUCTURES FOR CONDENSED PARALLELOGRAMS AND RELATED BENZENOIDS WITH REPEATED UNITS

S. J. Cyvin and B. N. Cyvin

Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norway

(Received: June 1986)

Abstract: Different types of formulas for the number of Kekulé structures of benzenoid classes are summarized. Cases are treated where a new type is encountered, containing exponential functions of binomial coefficients. The enumeration problems are solved in terms of recurrence relations, and in some cases also explicit formulas. Benzenoid classes with repeated units are considered, containing condensed parallelograms or parallelograms without corners.

1. INTRODUCTION

The enumeration of Kekulé structures for classes of benzenoids[1] has been a subject of many investigations. These studies are not only interesting in organic and physical chemistry, but also from a purely mathematical viewpoint. Different types of formulas for the number of Kekulé structures (K) have been derived.

(1) *Binomial coefficients*. Gordon and Davison[2] identified the number of Kekulé structures for a parallelogram-shaped benzenoid with a binomial coefficient. They also reported formulas for hexagon, and chevron-shaped benzenoids in terms of binomial coefficients. A great number of such K formulas have been derived later.[3-8] Many of them contain only one parameter (say n), and are consequently equivalent to polynomials in n.

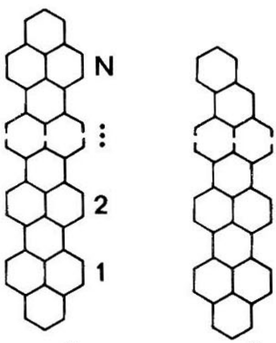
(2) *Repeated units*. Classes of benzenoids with repeated identical units have been studied.[9-12] Recurrence relations, and in some cases explicit

K formulas have been achieved for such systems. These explicit formulas are of a substantially different kind than those of the above paragraph:

(a) *Exponential functions of irrational numbers*. The leading example is Binet's formula for Fibonacci numbers, which is relevant for the K numbers of the well-known class of single zig-zag chains.[3,13] More advanced examples are found in later works.[8,11,12] Balaban and Tomescu[12] were the first who produced a formula of this type with an arbitrary parameter in the irrational numbers.

(b) *Exponential function of integer*. The cited work of Gutman[11] contains two benzenoid classes where the K formula is the exponential of an integer, viz. 3, occasionally multiplied by 2; cf. Fig. 1. This type of K formulas seems to occur very rarely. More precisely, it is so far the only known example, if we disregard the (trivial) cases of essentially disconnected benzenoids (see below).

(3) *Present work*. Here we encounter for the first time non-trivial benzenoid classes for which the K formulas contain exponentials of binomial coefficients. This is, in other words, a combination of the types under paragraphs (1) and (2) above. The present study throws some light on Gutman's[11] example (Fig. 1). Firstly, we obtain a straightforward generalization of Gutman's formulas. The integer 3 appears to be the binomial coefficient $\binom{2m-1}{m}$ for m=2. Secondly, we perform a further generalization, in which also exponentials of irrational numbers are invoked. The first



$K=2\cdot 3^N$ $K=3^N$

Fig. 1. Two benzenoid classes from I. Gutman, Match 17, 3 (1985).

example is found to represent an interesting singularity where the irrational numbers reduce to integers or cancel.

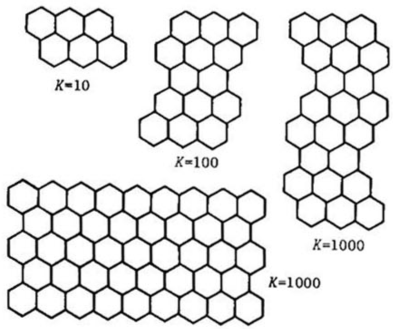


Fig. 2. Some benzenoids with decadic K numbers: one parallelogram (upper-left), otherwise essentially disconnected benzenoids.

(4) *Essentially disconnected benzenoids.* Exponentials of integers or binomial coefficients are also achieved in a more trivial manner by essentially disconnected benzenoids. The first formula of this type, viz. $(n+1)^N$, was given by Yen.[3] It applies to prolate rectangles;[8] one example (n=9, N=3) is depicted in Fig. 2. Slightly more elevated (but still trivial) cases lead to $\binom{k+m}{m}^N$. Some examples are included in Fig. 2, where decadic K numbers were chosen for the sake of curiosity.

2. CONDENSED RHOMBS AND A RELATED CLASS

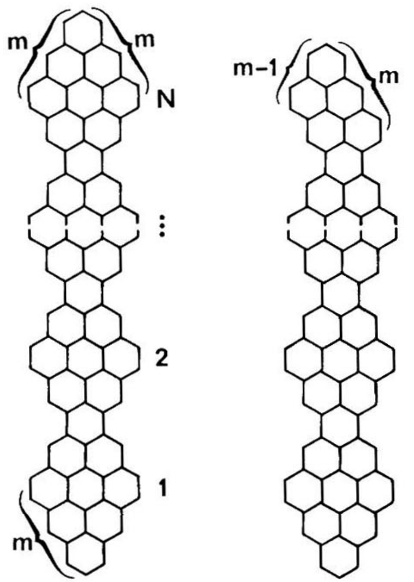
2.1. *Definitions*

Consider a number (N) of rhombic benzenoids, which are special cases of parallelograms, $L(m,m)$. Let them be condensed in a way that two neighbours overlap with one ring as shown in Fig. 3. The class may be designated $\langle L(m,m)\rangle^N$. Let the corresponding number of Kekulé structures be denoted

$$K\{\langle L(m,m)\rangle^N\} = S_N \tag{1}$$

A related class is obtained by deleting one row of m rings from an end rhomb (see Fig. 3). Let its K number be given by

$$K\{\langle L(m,m)\rangle^{N-1}\langle L(m-1,\ m)\rangle\} = S_N' \tag{2}$$



$K = S_N$ $K = S_N'$

Fig. 3. Condensed rhombs and a related class.

2.2. *K formulas*

By well-known enumeration methods for Kekulé structures[14] one obtains immediately the basic formula

$$S_N = 2S_N' \tag{3}$$

which connects the K numbers of the two classes (Fig. 3). A formula of a recursive nature reads

$$S_N = 2S_1' \, S_{N-1}' \; ; \qquad N \geq 1 \tag{4}$$

From eqns. (3) and (4):

$$S_N' = S_1' \, S_{N-1}' \, , \qquad S_N = S_1' \, S_{N-1} \; ; \qquad N \geq 1 \tag{5}$$

These are the recurrence relations for the two benzenoid classes in question. For the degenerate case of N=0 one has, in consistence with the above equations,

$$S_0' = 1, \qquad S_0 = 2 \tag{6}$$

As initial conditions to eqns. (5) we have:

$$S_1' = \binom{2m-1}{m}, \qquad S_1 = 2\binom{2m-1}{m} = \binom{2m}{m} \tag{7}$$

Consequently

$$S_2' = \binom{2m-1}{m}^2, \qquad S_2 = 2\binom{2m-1}{m}^2 \tag{8}$$

and in general:

$$S_N' = \binom{2m-1}{m}^N, \qquad S_N = 2\binom{2m-1}{m}^N \tag{9}$$

which holds for all $N \geq 0$.

The formulas of Gutman[11] - see Fig. 1 - are special cases of eqns. (9) for m=1.

2.3. *Decadic K numbers*

With m=3 eqns. (9) contain powers of 10. That gives rise to a non-trivial series of benzenoids with decadic K numbers, as shown in Fig. 4. This is of course only a modest contribution to the difficult problem: Produce all possible benzenoids (or their number) with a given number (K) of Kekulé structures. Fig. 4 includes two more examples with K=1000, of which one is essentially disconnected, and the other (the bottom drawing) not. The examples are by no means supposed to be exhaustive.

3. CONDENSED PARALLELOGRAMS AND RELATED CLASSES: PARALLEL CONDENSATION

3.1. *Definitions*

The generalization of the class of condensed rhombs (see preceding) section) to condensed parallelograms, L(k,m) where $k \neq m$, is not a trivial matter for several reasons. (a) In the present context a condensation of two parallelograms may be realized in two ways, say parallel and anti-parallel. The former kind is the subject of the present section, while the latter type of condensation is treated, more briefly, in the subsequent section. (b) The solution for k=m appears to be a kind of a singularity.

Figure 5 shows the definition of three classes. Their K numbers are:

$$\text{(i)} \quad K\{\langle \mathrm{L}(k,m)\rangle^{N}\} = P_N \tag{10}$$

$$\text{(ii)} \quad K\{\langle \mathrm{L}(k,m)\rangle^{N-1}\langle \mathrm{L}(k-1,\ m)\rangle\} = P_N^{(k)} \tag{11}$$

$$\text{(iii)} \quad K\{\langle \mathrm{L}(k,m)\rangle^{N-1}\langle \mathrm{L}(k,\ m-1)\rangle\} = P_N^{(m)} \tag{12}$$

In the modified classes (ii) and (iii) the parameters k and m, respectively, have been decreased by unity by deleting the appropriate rows from an end parallelogram.

3.2. *Recurrence formula*

The following equation holds.

$$P_N = P_N^{(k)} + P_N^{(m)} \tag{13}$$

It corresponds to eqn. (3) for the special case of k=m; in that case

$$P_N^{(k)} = P_N^{(m)} = S_N' \ ; \qquad k=m \tag{14}$$

As recursive formulas we now have

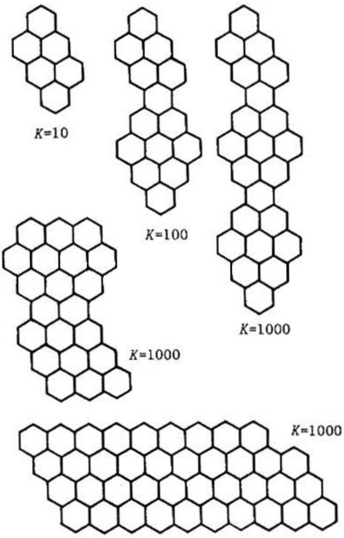


Fig. 4. Some benzenoids with decadic K numbers (see also Fig. 2).

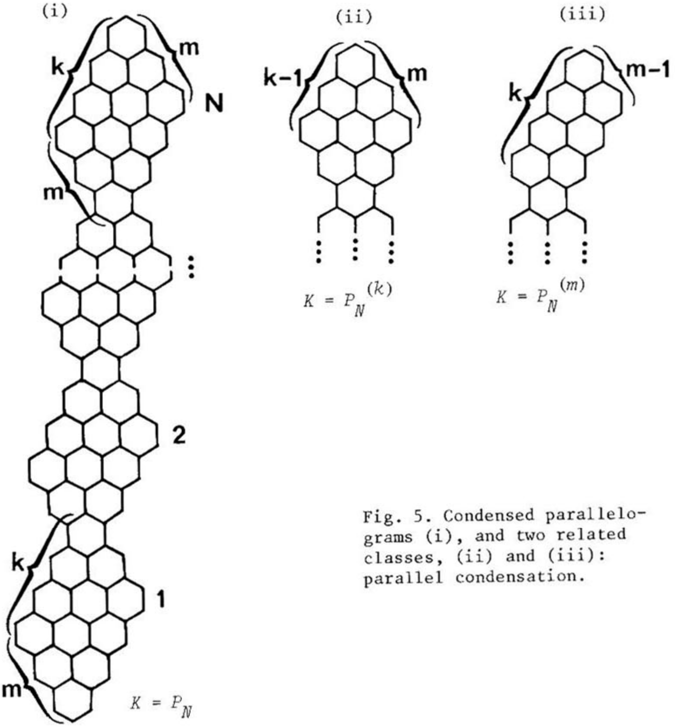


Fig. 5. Condensed parallelograms (i), and two related classes, (ii) and (iii): parallel condensation.

$$P_N = P_1^{(k)}\ P_{N-1}^{(m)} + P_1^{(m)}\ P_{N-1}^{(k)}\ ; \qquad N \geq 1 \tag{15}$$

$$P_N = P_2^{(k)}\ P_{N-2}^{(m)} + P_2^{(m)}\ P_{N-2}^{(k)}\ ; \qquad N \geq 2 \tag{16}$$

Here eqn. (15) corresponds to (4). In this generalized case ($k \neq m$) a simple form like (5) does not exist. Another term, e.g. P_{N-2}, in addition to P_N and P_{N-1} has to be invoked. From eqns. (13), (15) and (16) a recurrence formula for P_N is obtained as follows.

$$P_N = \frac{P_2^{(k)} - P_2^{(m)}}{P_1^{(k)} - P_1^{(m)}}\, P_{N-1} + \frac{P_1^{(k)} P_2^{(m)} - P_1^{(m)} P_2^{(k)}}{P_1^{(k)} - P_1^{(m)}}\, P_{N-2}\ ; \qquad k \neq m, \quad N \geq 2 \tag{17}$$

Notice that this equation is not valid for k=m; both numerators and denominators vanish in that case.

Similarly to eqn. (6) we have

$$P_0^{(k)} = P_0^{(m)} = 1 , \qquad P_0 = 2 \tag{18}$$

Furthermore

$$P_1^{(k)} = \binom{k+m-1}{m} , \qquad P_1^{(m)} = \binom{k+m-1}{m-1} \tag{19}$$

and

$$P_1 = \binom{k+m}{m} \tag{20}$$

The quantities $P_2^{(k)}$ and $P_2^{(m)}$ are obtainable from the following recursive equations.

$$P_N^{(k)} = \binom{k+m-2}{m} P_{N-1}^{(m)} + \binom{k+m-2}{m-1} P_{N-1}^{(k)} \; ; \qquad N \geq 1 \tag{21}$$

$$P_N^{(m)} = \binom{k+m-2}{m-1} P_{N-1}^{(m)} + \binom{k+m-2}{m-2} P_{N-1}^{(k)} \; ; \qquad N \geq 1 \tag{22}$$

The result is:

$$P_2^{(k)} = \binom{k+m-1}{m}\binom{k+m-2}{m-1} + \binom{k+m-1}{m-1}\binom{k+m-2}{m} \tag{23}$$

$$P_2^{(m)} = \binom{k+m-1}{m}\binom{k+m-2}{m-2} + \binom{k+m-1}{m-1}\binom{k+m-2}{m-1} \tag{24}$$

One has also, in consistence with the given equations,

$$P_2 = 2 \binom{k+m-1}{m}\binom{k+m-1}{m-1} \tag{25}$$

With the aid of eqns. (19), (23) and (24) the recurrence formula (17) was rendered into the form

$$\boxed{P_N = \binom{k+m-2}{m-1}\left[2P_{N-1} - \frac{1}{k}\binom{k+m-1}{m} P_{N-2}\right] ; \quad k \neq m, \quad N \geq 2} \tag{26}$$

A more profound analysis shows that the same recurrence relation also applies to $P_N^{(k)}$ and $P_N^{(m)}$, but the initial conditions are different. The relations for these quantities were not pursued further, but it was concentrated upon P_N, for which an explicit equation was derived (see next paragraph).

Numerical example, which pertains to Fig. 5 (k=4, m=3).

$$P_1 = \binom{7}{3} = 35,\ P_1^{(k)} = \binom{6}{3} = 20,\ P_1^{(m)} = \binom{6}{2} = 15$$

$$\boxed{P_N = 20P_{N-1} - 50P_{N-2}\ ; \qquad N \geq 2}$$

N	P_N	$P_N^{(k)}$	$P_N^{(m)}$
0	2	1	1
1	35	20	15
2	600	350	250
3	10250	6000	4250

3.3. *Explicit formula*

An explicit formula for P_N was worked out by standard methods from the recurrence relation (26) along with the initial conditions given by (18) and (20). It was attained at the form:

$$P_N = \binom{k+m-2}{m-1}^N \left\{ \left[1 + \frac{k(k-1) + m(m-1)}{2\sqrt{km(k-1)(m-1)}}\right]\left[1 + \sqrt{\frac{(k-1)(m-1)}{km}}\right]^N + \left[1 - \frac{k(k-1) + m(m-1)}{2\sqrt{km(k-1)(m-1)}}\right]\left[1 - \sqrt{\frac{(k-1)(m-1)}{km}}\right]^N \right\} \quad (27)$$

Numerical example (k=4, m=3):

$$P_N = \tfrac{1}{4}\left[(4 + 3\sqrt{2})(10 + 5\sqrt{2})^N + (4 - 3\sqrt{2})(10 - 5\sqrt{2})^N\right]$$

It is noteworthy that eqn. (27) also is valid for k=m. In that case:

$$P_N = \binom{2m-2}{m-1}^N \cdot 2 \cdot \left(\frac{2m-1}{m}\right)^N = 2\binom{2m-1}{m}^N \ ; \qquad k=m \quad (28)$$

in consistence with eqn. (9). A more detailed analysis with relevance to Gutman's[11] example - see Fig. 1 - seems to be warranted. It was foreshadowed in the introduction (Section 1). In this case k=m=2. For k=2 eqn. (27) takes the form:

$$P_N = \left[1 + \frac{m(m-1) + 2}{2\sqrt{2m(m-1)}}\right]\left[\frac{2m + \sqrt{2m(m-1)}}{2}\right]^N + \left[1 - \frac{m(m-1) + 2}{2\sqrt{2m(m-1)}}\right]\left[\frac{2m - \sqrt{2m(m-1)}}{2}\right]^N \ ; \qquad k=2 \quad (29)$$

If we now insert $m=2$ the second term on the right-hand side of eqn. (29) cancels, while the first term becomes $(1+1)3^N$.

4. CONDENSED PARALLELOGRAMS AND RELATED CLASSES: ANTI-PARALLEL CONDENSATION

4.1. *Definitions*

Figure 6 shows a class of condensed parallelograms, which like the one at the left-hand side of Fig. 5, could be designated $\langle L(k,m)\rangle^N$. We shall not elaborate this type of notation in order to distinguish between the different cases. The two classes differ, indeed: in two neighbouring parallelograms of the present case (Fig. 6) the k-rows and m-rows are not mutually parallel. This condensation, executed in a zig-zag manner, is referred to as anti-parallel. The figure includes two related classes obtained again by modifications of one of the end parallelograms. Also the notation for the K numbers is specified in the figure.

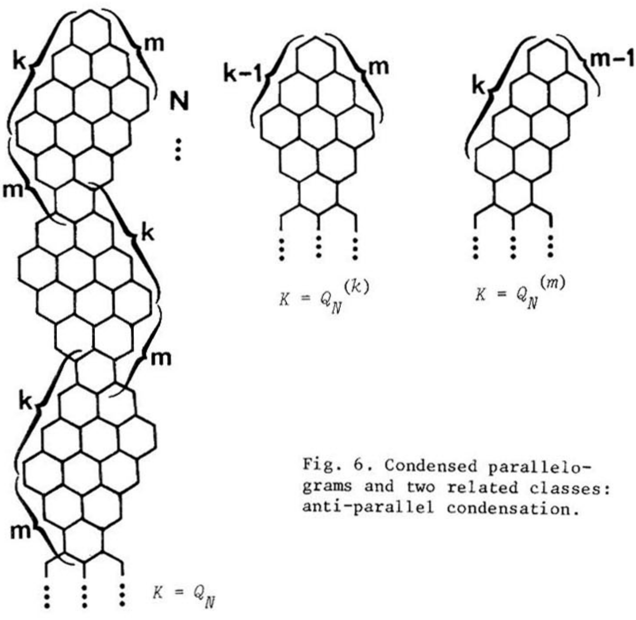


Fig. 6. Condensed parallelograms and two related classes: anti-parallel condensation.

4.2. *Results of the analysis*

One has

$$Q_0^{(k)} = Q_0^{(m)} = 1 , \qquad Q_0 = 2 \tag{30}$$

as in eqn. (18). Evidently one has also

$$Q_1^{(k)} = P_1^{(k)} , \qquad Q_1^{(m)} = P_1^{(m)} \tag{31}$$

and

$$Q_1 = P_1 \tag{32}$$

The relevant expressions (in terms of k and m) are given by eqns. (19) and (20). For N=2 it was found:

$$Q_2^{(k)} = \binom{k+m-1}{m}\binom{k+m-2}{m} + \binom{k+m-1}{m-1}\binom{k+m-2}{m-1} \tag{33}$$

$$Q_2^{(m)} = \binom{k+m-1}{m}\binom{k+m-2}{m-1} + \binom{k+m-1}{m-1}\binom{k+m-2}{m-2} \tag{34}$$

Furthermore,

$$Q_2 = \binom{k+m-1}{m}^2 + \binom{k+m-1}{m-1}^2 \tag{35}$$

The following recurrence relation holds for Q_N.

$$\boxed{Q_N = \binom{k+m-2}{m-1}\left[\left(\frac{k-1}{m} + \frac{m-1}{k}\right) Q_{N-1} + \frac{1}{k}\binom{k+m-1}{m} Q_{N-2}\right] ; \quad k \neq m, \quad N \geq 2} \tag{36}$$

It is equivalent to:

$$\boxed{Q_N = \left[\binom{k+m-2}{m} + \binom{k+m-2}{m-2}\right] Q_{N-1} + \frac{1}{k}\binom{k+m-1}{m}\binom{k+m-2}{m-1} Q_{N-2} ; \quad k \neq m, \quad N \geq 2} \tag{37}$$

Numerical example, which pertains to Fig. 6 (k=4, m=3).

$$Q_N = 15Q_{N-1} + 50Q_{N-2}\ ; \qquad N \geq 2$$

N	Q_N	$Q_N^{(k)}$	$Q_N^{(m)}$
0	2	1	1
1	35	20	15
2	625	350	275
3	11125	6250	4875

4.3. *Connection between P_N and Q_N numbers for N=1 and 2*

Equations (19), (25) and (35) give

$$P_2 = 2P_1^{(k)}\, P_1^{(m)}, \qquad Q_2 = [P_1^{(k)}]^2 + [P_1^{(m)}]^2 \tag{38}$$

Hence

$$P_2 + Q_2 = [P_1^{(k)} + P_1^{(m)}]^2 = P_1^{\,2} = Q_1^{\,2} = \binom{k+m}{m}^2 \tag{39}$$

The same result is obtained on combining the two recurrence relations (26) and (37) with N=2. Then

$$P_2 + Q_2 = \left[\binom{k+m-2}{m} + 2\binom{k+m-2}{m-1} + \binom{k+m-2}{m-2}\right]P_1 \tag{40}$$

which is consistent with eqn. (39).

5. CONDENSED RHOMBS WITHOUT CORNERS

An analysis like the one of Section 2 was carried out for rhombic benzenoids without corners; cf. the left-hand part (i) of Fig. 7. A corner is here defined as a ring with three free edges (i.e. on the perimeter). With the notation of Fig. 7 (T for the number of Kekulé structures) it was attained at

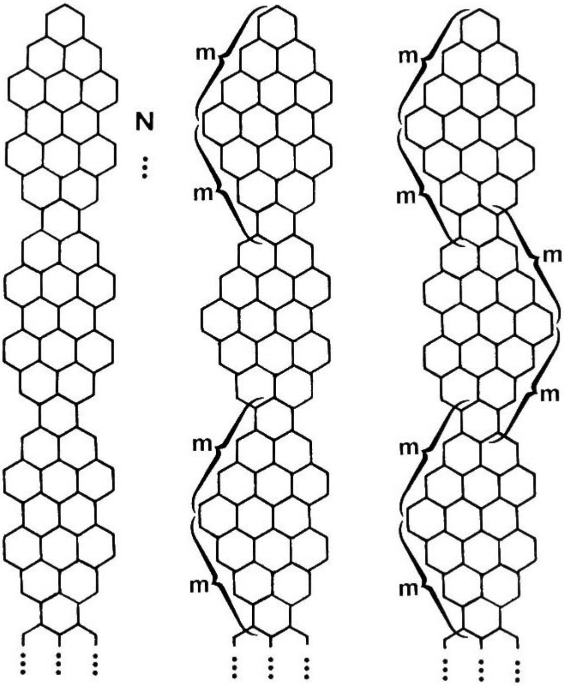
$$T_N = \left[\binom{2m-1}{m} - 1\right]T_{N-1} = \left[\frac{1}{2}\binom{2m}{m} - 1\right]T_{N-1}\ ; \qquad N \geq 1 \tag{41}$$

and explicitly:

$$T_N = 2\left[\binom{2m-1}{m} - 1\right]^N \tag{42}$$

The depicted examples (Fig. 7) pertain to m=4. Consider instead m=3. Then one unit, viz. L(3,3) without corners, corresponds to two units of condensed pyrenes, L(2,2); cf. Fig. 1. Equation (42) with m=3 gives

(i) (ii) (iii)



$K = T_N$ $K = U_N$ $K = V_N$

Fig. 7. Condensed rhombs without corners (i), and condensed rhombs without one corner each (ii), (iii).

$$T_N = 2 \cdot 9^N = 2 \cdot 3^{2N}$$

The result is indeed identical with the appropriate K formula of Fig. 1, if N is replaced by $2N$.

Figure 7 includes two classes, where the rhombs have been deprived of only one corner each. In one case (ii) the indentations after deleted corners are on the same side, while in the other (iii) they alternate in a zig-zag manner. The figure includes the symbols used to designate numbers of Kekulé structures. In these cases, (ii) and (iii), it appears again that the recurrence formulas consist of three terms, e.g. with subscripts N, N-1 and N-2. It was found:

$$U_N = \left[2\binom{2m-2}{m-1} - 1\right] U_{N-1} - \left\{\binom{2m-1}{m}\left[\binom{2m-2}{m-1} - 1\right] - \binom{2m-2}{m}\left[\binom{2m-1}{m} - 1\right]\right\} U_{N-2} \; ; \quad N \geq 2 \tag{43}$$

and

$$V_N = 2\binom{2m-2}{m} V_{N-1} + \left\{\binom{2m-1}{m}\left[\binom{2m-2}{m-1} - 1\right] - \binom{2m-2}{m}\left[\binom{2m-1}{m} - 1\right]\right\} V_{N-2} \; ; \quad N \geq 2 \tag{44}$$

The initial conditions are:

$$U_0 = V_0 = 2 \tag{45}$$

and

$$U_1 = V_1 = 2\binom{2m-1}{m} - 1 = \binom{2m}{m} - 1 \tag{46}$$

Hence for N=2:

$$U_2 = \binom{2m-1}{m}^2 + \left[\binom{2m-1}{m} - 1\right]^2 \tag{47}$$

$$V_2 = 2\binom{2m-1}{m}\left[\binom{2m-1}{m} - 1\right] \tag{48}$$

There is a connection between the numbers U_N and V_N for N=1 and 2 (compare with the treatment in Section 4.3). It was found

$$U_2 + V_2 = U_1{}^2 = V_1{}^2 = \left[\binom{2m}{m} - 1\right]^2 \tag{49}$$

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

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