Enumeration of Kekulé Structures for Multiple Zigzag Chains and Related Benzenoid Hydrocarbons

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The benzenoid classes of multiple zigzag chains, $A(n, m)$, and incomplete multiple zigzag chains, $A(n, m, l)$, are considered. Numerical numbers of Kekulé structures (K) are given for n up to 5 and m up to 10. A recurrence relation is developed for the K numbers of $A(n, m)$ with fixed values of n; a general formulation for arbitrary m values was achieved.

Six new benzenoid classes are studied in connection with the application of the John-Sachs theorem to double zigzag chains. A new approach to the K enumeration is introduced by non-linearly dependent recurrence relations.

Finally a new type of combinatorial K formulas in terms of determinants and based on the John-Sachs theorem, is introduced. The new enumeration techniques are applied to multiple zigzag chains.

Introduction

The research on Kekulé structures in conjugated hydrocarbons has been intensivated during the last years. Only in 1985 and 1986 more than 50 papers have appeared dealing with the enumeration of Kekulé structures and closely related topics. The references [1–7] provide only a representative sample. A great number of chemical applications of Kekulé structures is known and have been reviewed several times [8–10]; for an exhaustive list of references on this matter, see also [11].

The present work is a continuation of the analysis of the number of Kekulé structures for multiple zigzag chains [10, 12]. This class of benzenoid hydrocarbons was recognized as an important class from the beginning of the systematic enumeration of Kekulé structures for classes of benzenoids [13, 14]. The multiple zigzag chains were included in several later works [2, 15–17] before our previous systematic studies [12].

Let the multiple zigzag chain be designated [12] by $A(n, m)$; see Figure 1. Furthermore, the number of Kekulé structures (K) of $A(n, m)$ will be denoted by $Z_n(m)$.

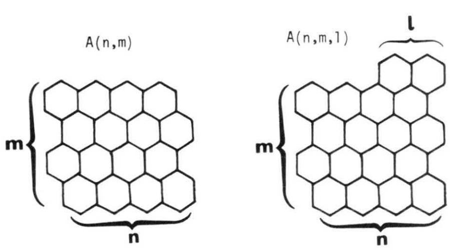

Fig. 1. Definition of the notation for the class of multiple zigzag chains and the auxiliary class of incomplete multiple zigzag chains.

In the previous studies [12] we derived by very laborious calculations the recurrence relations for $Z_n(m)$ with fixed values of n up to $n = 5$. In the present work we report an alternative form of the recurrence relations for $Z_n(m)$. A new expression of $Z_n(m)$ for arbitrary n is offered. In this analysis the very useful method of fragmentation due to Randić [18] was employed.

In the subsequent part of this work the newly developed enumeration techniques [11] based on the John-Sachs theorem [19] were applied to multiple zigzag chains in general and double zigzag chains in particular.

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Table 1a. Numerical values of $K\{A(n, m, l)\} = Z_n^{(l)}(m)$ for $n = 1, 2, 3$.

m	$Z_1^{(l)}(m)$		$Z_2^{(l)}(m)$			$Z_3^{(l)}(m)$			
	$l=0$	1	$l=0$	1	2	$l=0$	1	2	3
−3	1	0	1	0	0	1	0	0	0
−2	0	1	0	0	1	0	0	0	1
−1	1	1	1	1	1	1	1	1	1
0	1	2	1	2	3	1	2	3	4
1	2	3	3	5	6	4	7	9	10
2	3	5	6	11	14	10	19	26	30
3	5	8	14	25	31	30	56	75	85
4	8	13	31	56	70	85	160	216	246
5	13	21	70	126	157	246	462	622	707
6	21	34	157	283	353	707	1 329	1 791	2 037
7	34	55	353	636	793	2 037	3 828	5 157	5 864
8	55	89	793	1 429	1 782	5 864	11 021	14 849	16 886
9	89	144	1 782	3 211	4 004	16 886	31 735	42 756	48 620
10	144	233	4 004	7 215	8 997	48 620	91 376	123 111	139 997

Table 1b. Numerical values of $K\{A(n, m, l)\} = Z_n^{(l)}(m)$ for $n = 4$ and $n = 5$.

m	$Z_4^{(l)}(m)$					$Z_5^{(l)}(m)$					
	$l=0$	1	2	3	4	$l=0$	1	2	3	4	5
−3	1	0	0	0	0	1	0	0	0	0	0
−2	0	0	0	0	1	0	0	0	0	0	1
−1	1	1	1	1	1	1	1	1	1	1	1
0	1	2	3	4	5	1	2	3	4	5	6
1	5	9	12	14	15	6	11	15	18	20	21
2	15	29	41	50	55	21	41	59	74	85	91
3	55	105	146	175	190	91	176	250	309	350	371
4	190	365	511	616	671	371	721	1 030	1 280	1 456	1 547
5	671	1 287	1 798	2 163	2 353	1 547	3 003	4 283	5 313	6 034	6 405
6	2 353	4 516	6 314	7 601	8 272	6 405	12 439	17 752	22 035	25 038	26 585
7	8 272	15 873	22 187	26 703	29 056	26 585	51 623	73 658	91 410	103 849	110 254
8	29 056	55 759	77 946	93 819	102 091	110 254	214 103	305 513	379 171	430 794	457 379
9	102 091	195 910	273 856	329 615	358 671	457 379	888 173	1 267 344	1 572 857	1 786 960	1 897 214
10	358 671	688 286	962 142	1 158 052	1 260 143	1 897 214	3 684 174	5 257 031	6 524 375	7 412 548	7 869 927

Auxiliary Benzenoid Class

Figure 1 includes the definition of auxiliary benzenoids [10, 12] referred to as incomplete multiple zigzag chains. The benzenoid $A(n, m, l)$ consists of the multiple zigzag chain $A(n, m)$ augmented by a row of l hexagons, where $0 \leqq l \leqq n$. For $l = 0$, $A(n, m, 0) = A(n, m)$. For $l = n$ the system becomes the "complete" multiple zigzag chain $A(n, m + 1)$. The number of Kekulé structures (K) of $A(n, m, l)$ will be denoted by $Z_n^{(l)}(m)$.

Note that $Z_n^{(0)}(m) = Z_n(m)$ and $Z_n^{(n)}(m) = Z_n(m + 1)$.

For the trivial case of $n = 0$ one has [10, 12] $Z_0^{(0)}(m) = 1$ for all m. For $n = 1, 2, 3, 4, 5$ we give the numerical values of $Z_n^{(l)}(m)$ for m up to 10; cf. Tables 1a and 1b. A part of these numbers are found in Table 1 of the previous work [12].

Two Schemes of Fragmentation

Figure 2 shows the scheme of fragmentation employed previously [10, 12]. It leads to the fundamental relation

$$Z_n^{(l)}(m) = Z_n^{(l-1)}(m) + Z_n^{(n-l)}(m - 1). \qquad (1)$$

A new scheme of fragmentation for multiple zigzag chains is indicated in Figure 3. It is a fragmentation procedure supposed to be applied l times

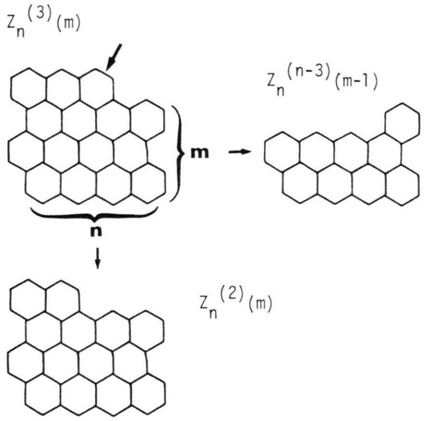

Fig. 2. The method of fragmentation applied to $Z_n^{(3)}(m)$. The example with $m = 3$ and $n = 4$ is depicted. Symbols for the K numbers of the fragments are indicated.

to $A(n, m, l)$. The final fragments are essentially disconnected. An analysis of the general case leads to

$$Z_n^{(l)}(m) = (l+1)\, Z_n^{(n-l)}(m-1) + \sum_{i=0}^{l-1} (i+1)\, Z_n^{(i)}(m-2). \tag{2}$$

New Recurrence Relation

Elimination of $Z_n^{(n-l)}(m-1)$ from (1) and (2) gives

$$l Z_n^{(l)}(m) = (l+1)\, Z_n^{(l-1)}(m) - \sum_{i=0}^{l-1} (i+1)\, Z_n^{(i)}(m-2). \tag{3}$$

On substituting l by $l+1$ in (3) it is obtained

$$\begin{aligned}(l+1)\, Z_n^{(l+1)}(m) &= (l+2)\, Z_n^{(l)}(m) - \sum_{i=0}^{l} (i+1)\, Z_n^{(i)}(m-2) \\ &= (l+2)\, Z_n^{(l)}(m) - (l+1)\, Z_n^{(l)}(m-2) \\ &\quad - \sum_{i=0}^{l-1} (i+1)\, Z_n^{(i)}(m-2).\end{aligned} \tag{4}$$

Here the last summation is eliminated by means of (3), and the result reduces to

$$Z_n^{(l+1)}(m) = 2 Z_n^{(l)}(m) - Z_n^{(l-1)}(m) - Z_n^{(l)}(m-2). \tag{5}$$

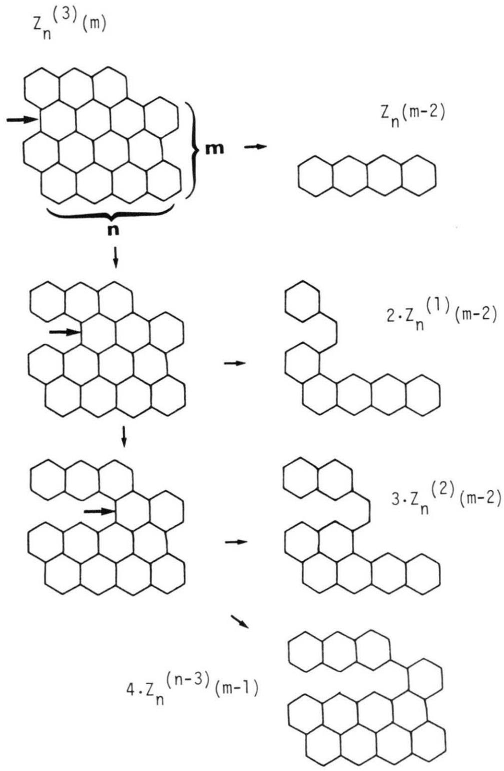

Fig. 3. The method of fragmentation applied three times to $Z_n^{(3)}(m)$. See also Figure 2.

Application of the New Relation

A special analysis reveals that $Z_n^{(-1)}(m) = 0$, which makes it possible to use (5) for $l = 0, 1, 2, \ldots$. Bearing in mind that $Z_n^{(0)}(m) = Z_n(m)$, a successive application of (5) enables one to express $Z_n^{(l)}(m)$ as a function of $Z_n(k)$, where $k \leqq m$. The first three of these formulas are

$$Z_n^{(1)}(m) = 2 Z_n(m) - Z_n(m-2), \tag{6}$$

$$Z_n^{(2)}(m) = 3 Z_n(m) - 4 Z_n(m-2) + Z_n(m-4), \tag{7}$$

$$\begin{aligned}Z_n^{(3)}(m) &= 4 Z_n(m) - 10 Z_n(m-2) \\ &\quad + 6 Z_n(m-4) - Z_n(m-6).\end{aligned} \tag{8}$$

It is a straightforward matter to set up the general form of these equations once the recipe is given by (5). It reads

$$Z_n^{(l)}(m) = \sum_{i=0}^{l} (-1)^i \binom{l+i+1}{2i+1} Z_n(m-2i). \tag{9}$$

Table 2. Coefficients in the expression for $Z_n(m+2)$ in terms of $Z_n(m-2j)$; cf. Eq. (12).

n	$Z_n(m)$	$Z_n(m-2)$	$Z_n(m-4)$	$Z_n(m-6)$	$Z_n(m-8)$	$Z_n(m-10)$	$Z_n(m-12)$	$Z_n(m-14)$	$Z_n(m-16)$
0	1								
1	3	−1							
2	6	−5	1						
3	10	−15	7	−1					
4	15	−35	28	−9	1				
5	21	−70	84	−45	11	−1			
6	28	−126	210	−165	66	−13	1		
7	36	−210	462	−495	286	−91	15	−1	
8	45	−330	924	−1287	1001	−455	120	−17	1

This form is proved to be sound by virtue of the identity

$$\binom{r+1}{s} = 2\binom{r}{s} + \binom{r-1}{s-2} - \binom{r-1}{s}, \qquad (10)$$

which holds for the binomial coefficients.

Final Recurrence Relations

As a consequence of a previously derived [10, 12] summation formula (on the basis of the fragmentation scheme of Fig. 2) one has

$$Z_n(m+2) = \sum_{j=0}^{n} Z_n^{(j)}(m). \qquad (11)$$

By means of (9) one obtains

$$Z_n(m+2) = \sum_{j=0}^{n} (-1)^j \binom{n+j+2}{2j+2} Z_n(m-2j). \qquad (12)$$

This is a general form of a recurrence relation for the K number of $A(n, m)$ with fixed values of n. In Table 2 the numerical forms of the inherent coefficients are worked out up to $n = 8$.

Here a recurrence relation was developed for the K numbers of $A(n, m)$ when n is fixed (but otherwise arbitrary). The similar recurrence relations for n up to 5 of the previous work [12] are not identical with those of the present work. In the present case the m values constantly step by two units. This means that odd and even values of this parameter never mix with each other.

Note that recurrence relations of the same form (i.e. with identical coefficients) are valid for any of the quantities $Z_n^{(l)}(m)$ with an arbitrary (fixed) l value. This is a consequence of linear dependences between K numbers of these classes.

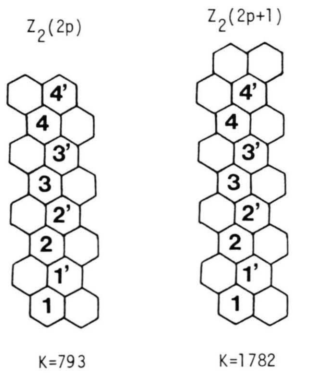

Fig. 4. Double zigzag chains. The symbols indicate K numbers. Numerical values are given for $p = 4$.

In the next section the particular case of $A(n, m)$ with the fixed value of n equal to 2 is considered. It is the double zigzag chain.

Double Zigzag Chain: Nonlinearly Coupled Recurrence Relations

The usefulness of considering linearly coupled recurrence relations in enumerations of K numbers has been pointed out previously [20] and employed several times since [6, 10, 12, 21–23]; see also the preceding section. In the present section we employ a new method of K enumeration [11], which is based on the John-Sachs theorem [19] and leads to nonlinearly coupled recurrence relations.

The K numbers of a double zigzag chain, $A(2, m)$, are denoted $Z_2(m)$. We have to distinguish between two cases, viz. $Z_2(2p)$ and $Z_2(2p+1)$, corresponding to even and odd m, respectively. The cases of $m = 8$ and $m = 9$ are depicted in Figure 4.

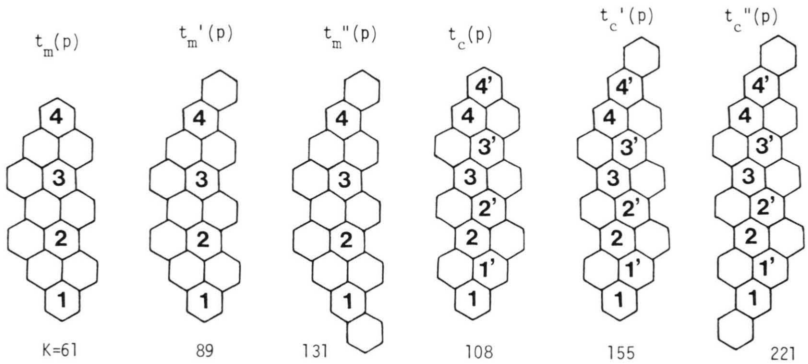

Fig. 5. Six benzenoid classes related to the double zigzag chain. The symbols indicate K numbers. Numerical values are given for $p = 4$.

Next we introduce six benzenoid classes related to $A(2, m)$ as shown in Fig. 5: t_m and t_c pertain to $A(2, m)$ with one hexagon condensed at each end, and m is odd or even, respectively. The resulting benzenoids are mirror-symmetrical (t_m) or centro-symmetrical (t_c), respectively. The classes with K numbers t'_m and t'_c emerge by annelating one hexagon to those of t_m and t_c, respectively. Finally t''_m and t''_c symbolize annelations of two hexagons, one at each end of the original benzenoids.

The six classes (Fig. 5) were studied by the methods of linearly coupled recurrence relations. The four classes pertaining to t_m, t'_m, t_c and t'_c appeared to constitute a self-consistent system. The K numbers for them are linearly dependent, and it was found in terms of t'_m:

$$t_m(p) = t'_m(p) - t'_m(p-1), \tag{13}$$

$$t_c(p) = 3t'_m(p) - 6t'_m(p-1) + t'_m(p-2), \tag{14}$$

$$t'_c(p) = 5t'_m(p) - 11t'_m(p-1) + 2t'_m(p-2), \tag{15}$$

while

$$t'_m(p) = \sum_{i=0}^{p} t_m(i). \tag{16}$$

The two remaining classes were coupled to this system with the result:

$$t''_m(p) = 5t'_m(p-1) - t'_m(p-2), \tag{17}$$

$$t''_c(p) = 9t'_m(p) - 22t'_m(p-1) + 4t'_m(p-2). \tag{18}$$

All the six classes obey recurrence relations of the same form, for which it was found:

$$t(p) = 5t(p-1) - 6t(p-2) + t(p-3). \tag{19}$$

We will see that the K numbers of $A(2, m)$, $Z_2(m)$, may also be expressed in terms of $t'_m(p)$, but the relations are nonlinear.

(a) *m even*

According to the new enumeration methods [11], the K number is found as the determinant of a matrix $\mathbf{W}$ with the dimension $d \times d$, where d designates the number of peaks and the (same) number of valleys. Let the double zigzag chain be oriented so that it acquires two peaks and two valleys. Figure 6 shows an example where m is an even number ($m = 8$). Then we are looking for 4 elements, viz. W_{11}, W_{12}, W_{21} and W_{22}. Each of them is to be identified with the K number for a smaller benzenoid (subgraph of the double zigzag chain). These benzenoids are painted black in Fig. 6 on the background of $A(2, 2p)$. The four (black) benzenoids belong to the classes considered in this section. Specifically it is found:

$$W_{11} = W_{22} = t'_m(p), \quad W_{12} = t''_c(p-1), \quad W_{21} = t_c(p). \tag{20}$$

With the abbreviated notation

$$\tau_p = t'_m(p) \tag{21}$$

the following expression for $Z_2(2p)$ results:

$$\begin{aligned} Z_2(2p) &= \tau_p^2 - (3\tau_p - 6\tau_{p-1} + \tau_{p-2}) \\ &\quad \cdot (4\tau_p - 11\tau_{p-1} + 2\tau_{p-2}) \\ &= -11\tau_p^2 + 57\tau_p\tau_{p-1} - 66\tau_{p-1}^2 - 10\tau_p\tau_{p-2} \\ &\quad + 23\tau_{p-1}\tau_{p-2} - 2\tau_{p-2}^2. \end{aligned} \tag{22}$$

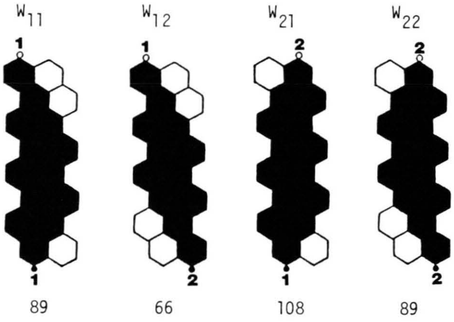

Fig. 6. Benzenoids (black) pertaining to the **W** matrix elements, W_{ij}. Numbering of the peaks (i) and valleys (j) is indicated. K numbers are given.

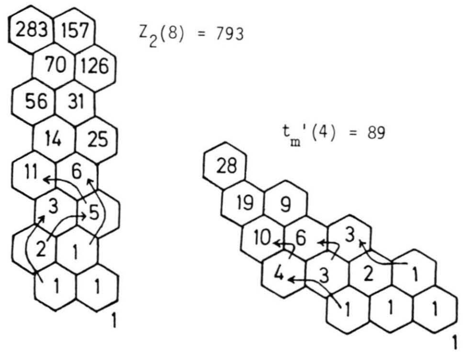

Fig. 7. An algorithm applied to two benzenoids. The K number (cf. also Figs. 4 and 5) is the sum of the algorithm numerals inside the hexagons including the outside unity.

(b) *m odd*

A corresponding analysis was performed for $Z_2(2p+1)$. It was obtained:

$$W_{11} = t_{\mathrm{m}}(p+1), \quad W_{12} = W_{21} = t'_{\mathrm{c}}(p), \quad W_{22} = t''_{\mathrm{m}}(p). \tag{23}$$

That gives the final result

$$\begin{aligned} Z_2(2p+1) &= (4\tau_p - 6\tau_{p-1} + \tau_{p-2})(5\tau_{p-1} - \tau_{p-2}) \\ &\quad - (5\tau_p - 11\tau_{p-1} + 2\tau_{p-2})^2 \\ &= -25\tau_p^2 + 130\tau_p\tau_{p-1} - 151\tau_{p-1}^2 \\ &\quad - 24\tau_p\tau_{p-2} + 55\tau_{p-1}\tau_{p-2} - 5\tau_{p-2}^2. \end{aligned} \tag{24}$$

The coefficients are found to have substantially different magnitudes from those of $Z_2(2p)$ in (22). If $Z_2(2p-1)$ is worked out instead, the coefficients of $Z_2(2p)$ become roughly halved, and roughly one fifth of those in (24):

$$\begin{aligned} Z_2(2p-1) &= (\tau_p - \tau_{p-1})(-\tau_p + 5\tau_{p-1} - \tau_{p-2}) \\ &\quad - (2\tau_p - 5\tau_{p-1} + \tau_{p-2})^2 \\ &= -5\tau_p^2 + 26\tau_p\tau_{p-1} - 30\tau_{p-1}^2 - 5\tau_p\tau_{p-2} \\ &\quad + 11\tau_{p-1}\tau_{p-2} - \tau_{p-2}^2. \end{aligned} \tag{25}$$

General Remarks

We wish to point out that still no explicit formula is known for $Z_n(m)$. Moreover, no explicit formula for $Z_n(m)$ is known for any given (fixed) value of n, except for $n = 1$ (the single zigzag chain). This applies in particular to the double zigzag chain $A(2, n)$.

Two versions are known for the recurrence relation of K numbers for the double zigzag chain, $Z_2(m)$, viz. [10, 12]

$$Z_2(m) = 2Z_2(m-1) + Z_2(m-2) - Z_2(m-3) \tag{26}$$

and

$$Z_2(m) = 6Z_2(m-2) - 5Z_2(m-4) + Z_2(m-6). \tag{27}$$

The relation (27) was derived in the present work; see especially Table 2. The known mathematical methods for deducing an explicit equation for $Z_2(m)$ from (26) or (27) lead to cubic equations, which have no integer solution. Therefore the derivation of an explicit equation is untractable in the present case, although feasible.

In the preceding section $Z_2(m)$ is expressed (non-linearly) in terms of the K numbers of a new class, viz. $t'_{\mathrm{m}}(p)$. These K numbers are governed by a different recurrence relation, viz.

$$t'_{\mathrm{m}}(p) = 5t'_{\mathrm{m}}(p-1) - 6t'_{\mathrm{m}}(p-2) + t'_{\mathrm{m}}(p-3); \tag{28}$$

cf. (19). Unfortunately neither the cubic equation associated with this recurrence relation is amenable for producing an explicit formula.

The K numbers $Z_2(m)$ and $t'_{\mathrm{m}}(p)$ are easily accessible by an algorithm [24, 25]. Figure 7 shows an example. In both cases the method of adding algorithm numerals in their general form has failed in the attempts to produce combinatorial formulas.

The other part of the enumeration problem for multiple zigzag chains, namely the development of K formulas for $A(n, m)$ with fixed values of m, is basically solved (cf. [12], and especially the note added in proof therein). In the next section this problem is attacked from an original point of view. A new, general formulation for $Z_n(m)$ with an arbitrary m is achieved.

New Type of Combinatorial K Formulas: Determinants

By the new method of K enumeration [11] a new type of combinatorial formulas in the form of determinants may be produced. The features are exemplified here for the multiple zigzag chain. For this purpose it is necessary to invoke an orientation of the benzenoids different from the one of Figure 4.

(a) *Single Zigzag Chain*

The appropriate orientations of a single zigzag chain with the K number $Z_1(m)$ are shown in Figure 8. It is clear that an arbitrary W_{ij} element of the $\mathbf{W}$ matrix equals either 3 (K for naphthalene), 2 (K for benzene), 1 (K for an acyclic chain), or it vanishes. For the examples depicted in Fig. 8 (upper row) it is found

$$Z_1(6) = \begin{vmatrix} 3 & 1 & 0 \\ 1 & 3 & 1 \\ 0 & 1 & 3 \end{vmatrix} = \begin{vmatrix} 2 & 1 & 0 & 0 \\ 1 & 3 & 1 & 0 \\ 0 & 1 & 3 & 1 \\ 0 & 0 & 1 & 2 \end{vmatrix} = 21 \qquad (29)$$

and

$$Z_1(7) = \begin{vmatrix} 2 & 1 & 0 & 0 \\ 1 & 3 & 1 & 0 \\ 0 & 1 & 3 & 1 \\ 0 & 0 & 1 & 3 \end{vmatrix} = 34. \qquad (30)$$

This is in fact nothing else than a representation of Fibonacci numbers ($F_7 = 21$, $F_8 = 34$ when $F_0 = F_1 = 1$), which is well known in mathematics. In general, this kind of representation may be described as a stripe of nonvanishing elements on and around the main diagonal of a determinant. The width of the stripe is tightly connected with the number of terms in the recurrence relation for the quantities in question. It is interesting to realize that a purely mathematical property of Fibonacci numbers has been derived "chemically" through the studies of Kekulé structures.

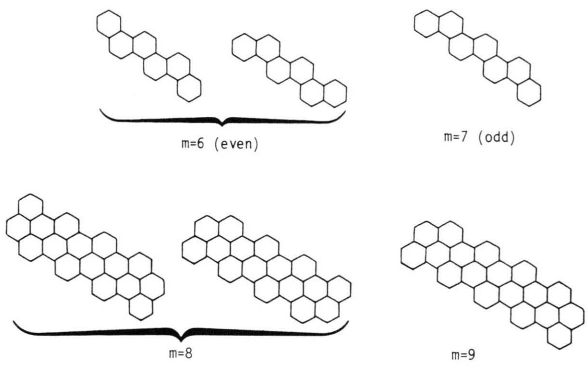

Fig. 8. The single (upper row) and double (lower row) zigzag chains in suitable orientations for the derivation of determinant formulas.

(b) *Multiple Zigzag Chain*

Let us approach this case by means of the double zigzag chain as an introductory example. Figure 8 (bottom row) shows the two appropriate orientations for $m = 8$ and one for $m = 9$ (corresponding to $p = 4$, the same as in Figure 4). The two alternatives obtained from the two orientations for even m (here $m = 8$) are presently referred to as the first and second version, respectively. For $m = 8$ they are:

$$Z_2(8) = \begin{vmatrix} 6 & 5 & 1 & 0 \\ 1 & 6 & 5 & 1 \\ 0 & 1 & 6 & 5 \\ 0 & 0 & 1 & 6 \end{vmatrix} = \begin{vmatrix} 3 & 4 & 1 & 0 & 0 \\ 1 & 6 & 5 & 1 & 0 \\ 0 & 1 & 6 & 5 & 1 \\ 0 & 0 & 1 & 6 & 4 \\ 0 & 0 & 0 & 1 & 3 \end{vmatrix} = 793 \qquad (31)$$

The nonvanishing stripes are separated from the zeros by dotted lines. The case of $m = 9$ (odd m) gives

$$Z_2(9) = \begin{vmatrix} 3 & 4 & 1 & 0 & 0 \\ 1 & 6 & 5 & 1 & 0 \\ 0 & 1 & 6 & 5 & 1 \\ 0 & 0 & 1 & 6 & 5 \\ 0 & 0 & 0 & 1 & 6 \end{vmatrix} = 1782. \qquad (32)$$

In the general case (arbitrary m) we distinguish between even and odd m. Figure 9 shows the

$$Z_n(2p) = \begin{vmatrix} \binom{n+2}{n} & \binom{n+3}{n-1} & \binom{n+4}{n-2} & \cdots & \binom{n+p+1}{n-p+1} \\ 1 & \binom{n+2}{n} & \binom{n+3}{n-1} & \cdots & \binom{n+p}{n-p+2} \\ 0 & 1 & \binom{n+2}{n} & \cdots & \binom{n+p-1}{n-p+3} \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ 0 & 0 & 0 & \cdots & \binom{n+2}{n} \end{vmatrix}$$

$$Z_n(2p+1) = \begin{vmatrix} \binom{n+1}{n} & \binom{n+2}{n-1} \quad \binom{n+3}{n-2} \quad \cdots \quad \binom{n+p+1}{n-p} \\ 1 & \\ 0 & \\ 0 & Z_n(2p) \\ \vdots & \\ 0 & \end{vmatrix}$$

$$Z_n(2p) = \begin{vmatrix} \binom{n+1}{n} & \binom{n+2}{n-1} \quad \binom{n+3}{n-2} \quad \cdots \quad \binom{n+p}{n-p+1} & \binom{n+p}{n-p} \\ 1 & & \binom{n+p}{n-p+1} \\ 0 & Z_n(2p-2) & \binom{n+p-1}{n-p+2} \\ \vdots & & \vdots \\ 0 & 0 \quad 0 \quad \cdots \quad 1 & \binom{n+1}{n} \end{vmatrix}$$

Fig. 9. Determinants for the number of Kekulé structures of multiple zigzag chains, $K\{A(n, m)\} = Z_n(m)$, where $m = 2p$ ($p > 0$) or $m = 2p + 1$ ($p \geqq 0$).

$$Z_n(1) = n + 1, \qquad Z_n(2) = \binom{n+2}{2}$$

$$Z_n(3) = \begin{vmatrix} (n+1) & \binom{n+2}{3} \\ 1 & \binom{n+2}{2} \end{vmatrix}, \qquad Z_n(4) = \begin{vmatrix} \binom{n+2}{2} & \binom{n+3}{4} \\ 1 & \binom{n+2}{2} \end{vmatrix},$$

$$Z_n(5) = \begin{vmatrix} (n+1) & \binom{n+2}{3} & \binom{n+3}{5} \\ 1 & \binom{n+2}{2} & \binom{n+3}{4} \\ 0 & 1 & \binom{n+2}{2} \end{vmatrix}, \quad Z_n(6) = \begin{vmatrix} \binom{n+2}{2} & \binom{n+3}{4} & \binom{n+4}{6} \\ 1 & \binom{n+2}{2} & \binom{n+3}{4} \\ 0 & 1 & \binom{n+2}{2} \end{vmatrix}.$$

Fig. 10. Determinants for the number of Kekulé structures of multiple zigzag chains $Z_n(m)$, where $m = 1, 2, 3, 4, 5, 6$.

general formulation of the $p \times p$ determinant for $m = 2p$ in the first version. In order to produce the determinant for $Z_n(2p + 1)$, where m is odd, follow the rules: Transfer the determinant for $Z_n(2p)$ of the first version. Augment it with a 0th row and 0th column as shown in Figure 9. The 0th column has only two nonvanishing elements. The result is a $(p + 1) \times (p + 1)$ determinant as specified in Figure 9. Finally we give the rules for constructing the $(p + 1) \times (p + 1)$ determinant for $Z_n(2p)$ in the second version. Start with $Z_n(2p - 2)$. It may be found as any $(p - 1) \times (p - 1)$ connected subdeterminant symmetrical about the main diagonal in $Z_n(2p)$ of the first version. Augment it with a frame as shown in Figure 9. The first row and last column are the same in reverse order. The same is true for the first column and last row. Correspondingly for all rows and columns, in fact, both in the first and second version. In other words, the determinants (for even m) are symmetrical about the secondary diagonal (from top-right to bottom-left). Notice especially that the top row of $Z_n(2p)$ in the second version is almost the same as the top row of $Z_n(2p + 1)$; only the last element may differ. In general (both even and odd m) the determinants are symmetrical with respect to the main diagonal.

Application of the Determinant Formulas

Figure 10 shows an application of the determinant forms (Fig. 9) for some of the lowest m values. For even m, only the determinant of this first version was applied. On expanding these determinants one obtains combinatorial formulas for K numbers of $A(n, m)$ with fixed values of m. Thus for $m = 3$:

$$Z_n(3) = (n + 1)\binom{n+2}{2} - \binom{n+2}{3}. \tag{33}$$

This form is simpler than the expression in terms of binomial coefficients given elsewhere [17]. That is also true for the next parameter value ($m = 4$);

$$Z_n(4) = \binom{n+2}{2}^2 - \binom{n+3}{4}. \tag{34}$$

For $m = 5$ we obtain an expression identical to a previously given formula [2], which was derived in a completely different way. It reads

$$Z_n(5) = (n+1)\left[\binom{n+2}{2}^2 - \binom{n+3}{4}\right] - \binom{n+2}{2}\binom{n+2}{3} + \binom{n+3}{5}. \tag{35}$$

For $m = 6$ no expression in terms of binomial coefficients has been given before. Here it is readily obtained:

$$Z_n(6) = \binom{n+2}{2}\left[\binom{n+2}{2}^2 - 2\binom{n+3}{4}\right] + \binom{n+4}{6}. \tag{36}$$

The combinatorial formulas of $Z_n(m)$ for m up to 6, given before [12] in the polynomial form, are equivalent to the present expressions in terms of binomial coefficients. The results were achieved far more easily according to the present methods, and there is no principal hindrance against an extension to higher m values.

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