CROATICA CHEMICA ACTA CCACCA 57 (3) 391—404 (1984)

YU ISSN 0011-1643
UDC .....
CCA-1452
Original Scientific Paper

Chemical Graphs. XL.[1] Three Relations Between the Fibonacci Sequence and the Numbers of Kekulé Structures for Non-branched cata-Condensed Polycyclic Aromatic Hydrocarbons

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Received November 15, 1983

For benzenoid or non-benzenoid catafusenes having a non-branched string of *cata*-condensed rings, the numbers K of Kekulé structures (perfect matchings) can be expressed via the recurrence relationship (1); as a corollary when each annelated segment has exactly two rings, the numbers of Kekulé structures form the Fibonacci sequence.

Corollary 2 presents a second relationship with Fibonacci numbers. Algebraic expressions for the number of Kekulé structures in non-branched catafusenes in terms of hexagon numbers in each linearly condensed segment can be obtained. The numbers of terms in such algebraic expressions lead to a new numerical triangle (Table I) which is related to Pascal's triangle, and which provides a third link with the Fibonacci numbers expressed either by relation (7) or by the equivalent relation (10).

INTRODUCTION

In hydrogen-depleted constitutional graphs of polycyclic benzenoid condensed hydrocarbon graphs, the degrees of all vertices are two, three or four. Two six-membered rings are said to be condensed if they share a bond, i.e. if they have in common two adjacent vertices.

There exist two modes of ring fusion (condensation): if no vertex is common to three six-membered rings, the structure is said to be *cata*--condensed; if there exist vertices common to three six-membered rings, the structure is *peri*-condensed. In this paper we shall discuss only cata--condensed polycyclic benzenoid hydrocarbons (polyhexes) which possess formula $C_{4n+2}H_{2n+4}$ when they have n benzenoid rings. Polyhexes are portions (subgraphs) of the honeycomb lattice which is one of the tesselations of the plane. To simplify the nomenclature, we shall use for *cata*-condensed polyhexes the name catafusenes (as mentioned above, we shall not discuss perifusenes).

If the centers of six-membered rings are marked by a point and if two points are joined by a line whenever the two respective rings are condensed, one obtains the dualist graph of the polyhex. An alternative definition[2] of *cata*-condensation considers the fact that dualist graphs of catafusenes contain no cycles (i.e. they are trees in graph-theoretical terminology). Dualist graphs differ in several respects from normal graphs; the most significant aspect is that their bond angles are important. Extension of a dualist graph from an endpoint may occur linearly (linear annelation) i.e. at an angle of 180°, or at angles 120° or 240° (kinked annelation). The structure may be coded numerically by using for angles of 180° or 120° (240°) the digits 0 and 1(2), respectively. Each line or bond in the molecular graph of the polyhex symbolizes an electron pair binding two carbon atoms; two such carbon atoms may share two electrons (symbolized by a single bond) or four electrons (symbolized by a double bond). Kekulé's well-known benzene formula contains alternatively single and double bonds in a six-membered ring; each vertex 1-6 stands for a CH group. Since atom 1 may be linked to atom 2 either by a single or by a double bond, benzene has two Kekulé structures.

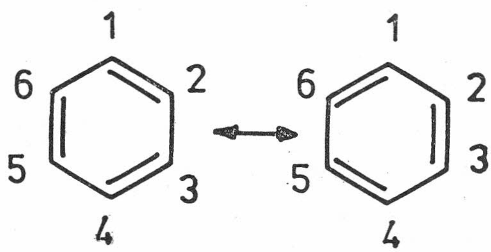

Figure 1. The two Kekulé structures of benzene.

Naphthalene has two condensed benzenoid rings. With three condensed benzenoid rings there exist two isomeric catafusenes, namely anthracene with linear annelation (a representative of the acene series possessing always linear annelation, whose dualist graphs are straight lines) and phenathrene with kinked annelation (see Figure 2 where dualist graphs G^* of these catafusenes are represented also).

The numbers of Kekulé structures for polyhexes can be correlated with their stability and with other properties of these hydrocarbons. There exist several methods for finding how many Kekulé structures exist for a given polyhex, which have been recently reviewed.[3,4]

Catafusenes differing only in the direction of kinks but having the same numbers of hexagons in linear segments (which are arranged in the same order and with the same branching topology) are called isoarithmic[4a] because they have the same Kekulé structure count. A different way of expressing the same idea is to associate with catafusenes a tree T (»isoarithmicity tree«) which is a homeomorphic contraction of the duailst graph

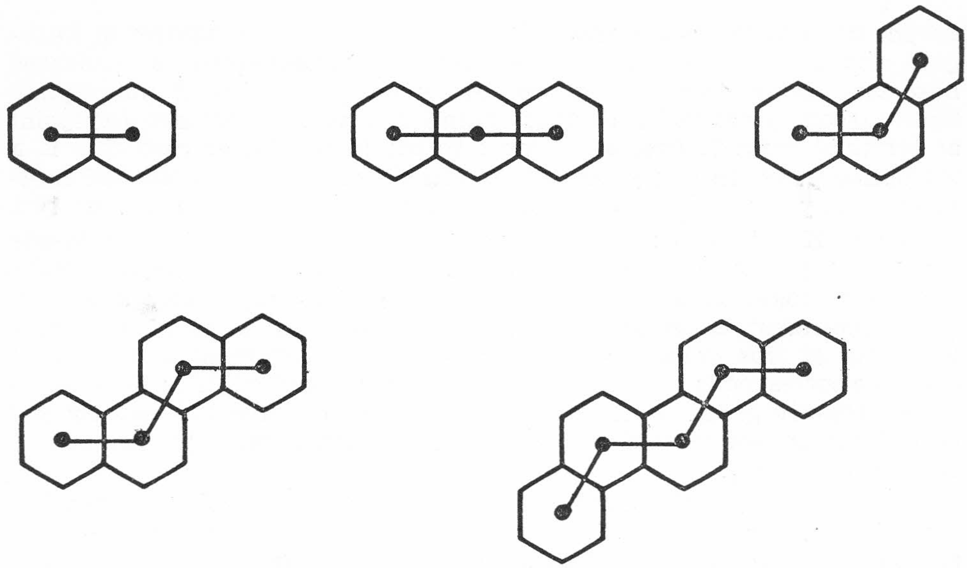

Figure 2. Ring structure and dualist graphs of naphthalene, anthracene, phenanthrene, chrysene, and picene.

by ignoring all vertices with linear annelation. Catafusenes with isomorphic trees T_1 and T_2 are isoarithmic if the corresponding linear segments of the catafusenes have the same number of hexagons.[4a]

A related concept, of isocannonical polyhexes, was proposed by Biermann and Schmidt[4b] for polyhexes having the same structure count ratio for product and reactant, according to Herndon's definition of this ratio as a reactivity index.[4c]

The kinked annelation of phenanthrene may be continued to form a zigzag catafusene (e.g. chrysene, picene). Alternatively, the kinked annelation of phenanthrene may be continued to afford a helix-shaped system called helicene. The helicenes with the same number of hexagons form a series whose terms are isoarithmic to the zigzag catafusenes.

NUMBERS OF KEKULÉ STRUCTURES FOR ZIGZAG CATAFUSENES

All catafusenes with the same number n of hexagons are isomeric i.e. they all have the same molecular formula $C_{4n+2}H_{2n+4}$. The molecular graph of a *cata*-condensed benzenoid hydrocarbon will be named here catafusene graph. Every such graph G with n hexagons has precisely $p = 4n + 2$ vertices and $q = 5n + 1$ edges. The vertices of G will be labeled by $v_1, v_2, \ldots, v_p$ and the edges by $e_1, \ldots, e_p$, $E_1, \ldots, E_{n-1}$ such that $e_i = v_i v_{i+1}$ for $1 \leq i \leq p-1$, $e_p = v_p v_1$ and the p-cycle of G: $v_1, v_2, \ldots, v_p, v_1$ is the perimeter of G. The edges $e_1, e_2, \ldots, e_p$ of G will be called external and the remaining n-1 edges $E_1, \ldots, E_{n-1}$ are said to be internal; the latter represent the bonds between neighbouring hexagons of the structure, and are intersected by edges of the dualist graph. To every catafusene graph G containing n hexagons we have associated its dualist graph G^* which is a tree having n vertices and n-1 edges. Hence dualist graphs of catafusenes are trees whose vertices represent centres of hexagons and whose edges link together vertices corresponding to condensed hexagons, i.e. vertices sharing two adjacent carbon atoms in the original hydrocarbon. A vertex in a dualist graph can have degree one (endpoint or terminal vertex), two, or at most three; in the latter case this is a branching point. In this paper we are concerned with non-branched catafusenes only, whose dualist graphs have vertices of degree one or two.

Every Kekulé structure of a catafusene molecule is in a one-to-one correspondence with a selection of $p/2$ independent, i.e. mutually non--adjacent, edges in the corresponding molecular graph. Any subset of $p/2$ independent edges in a graph with p vertices is called a perfect matching of this graph. Hence every Kekulé structure of a catafusene molecule corresponds to a selection of $p/2$ independent edges in its associated catafusene graph. Note that every catafusene graph has exactly two perfect matchings containing external edges only, namely $\{e_1, e_3, \ldots, e_{p-1}\}$ and $\{e_2, e_4, \ldots, e_p\}$.

Denote by $K_n(r)$ the number of Kekulé structures for a non-branched catafusene graph G consisting of n linear segments with r hexagons each and by $K_n^*(r)$ the number of these structures for the graph derived from G by deleting one of the two terminal hexagons.

Theorem 1. The numbers $K_n(r)$ verify the following recurrence relation:

$$K_n(r) = (r-1)K_{n-1}(r) + K_{n-2}(r) \tag{1}$$

$$\text{for } n \geq 3 \text{ and } K_1(r) = r + 1\ ;\ K_2(r) = r^2 + 1.$$

Proof: Since every Kekulé structure of a catafusene molecule is in a bijective correspondence with a perfect matching of the corresponding molecular graph G, it follows that $K_1(r) = r + 1$. Indeed, in this case G has exactly two perfect matchings containing external edges only and $r-1$ perfect matchings containing exactly one internal edge of G. Note that any subset of two internal edges E_s and E_t of G is not contained in any perfect matching of G because the paths on the perimeter of G connecting the extremities of E_s to those of E_t are both even paths of G. Similarly we find that $K_2(r) = 2 + 2(r-1) + (r-1)^2 = r^2 + 1$, since every perfect

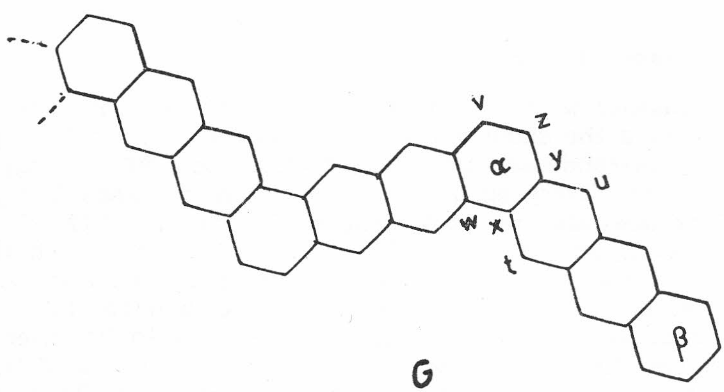

Figure 3. Terminal part of a non-branched catafusene with linear segments having r hexagons each (in the drawing, $r = 4$).

matching of G contains at most two internal edges, one on each linear portion of G.

Let now G be a catafusene graph consisting of n linear segments with r hexagons each, β be a terminal hexagon of this graph and x, y, z, t, u, v, w vertices of this graph, drawn in Figure 3 for $r = 4$.

Denote by L the linear segment of G with r hexagons lying between α and β in Figure 3. First observe that any perfect matching of G does not contain the pairs of external edges $\{wx,\ yu\}$ or $\{xt,\ yz\}$ since the paths on the perimeter of G arround β between t and y and between x and u are both even paths of length $4(r-1)$. Hence the set M of perfect matchings of G may be written as

$$M = M_{xy} \cup M_{wz} \cup M_{tu},$$

where M_{xy} is the set of perfect matchings of G containing xy, M_{wz} is the set of perfect matchings containing both xw and yz and M_{tu} corresponds to the choice of xt and yu. Note that M_{xy}, M_{tu} and M_{wz} are three pairwise disjoint sets.

It is clear that there exists a unique perfect matching of L such that this matching contains xy or both xw and yz. Since every perfect matching of α contains xy or both xw and yz, it follows that

$$|M_{xy}| + |M_{wz}| = K_{n-1}(r)$$

If a perfect matching of L includes both edges xt and yu, this matching may or may not contain any internal edge from the set of r-2 internal edges different from xy of L. Hence set $\{xt,\ yu\}$ may be completed to a perfect matching of L in r-1 ways, and any such matching contains also edge vz. If we delete linear segment L from G we obtain a catafusene graph which has exactly $K_{n-1}{}^*(r)$ perfect matchings, hence we can write

$$|M_{tu}| = (r-1)K^*_{n-1}(r)$$

which implies that

$$K_n(r) = |M| = K_{n-1}(r) + (r-1)K^*_{n-1}(r) \tag{2}$$

If we delete β from G, the corresponding linear segment L' includes only r-1 hexagons. Hence similarly as above we derive that

$$K_n{}^*(r) = K_{n-1}(r) + (r-2)K_{n-1}{}^*(r) \tag{3}$$

From (2) and (3) we obtain

$$K_n{}^*(r) = K_n(r) - K_{n-1}{}^*(r), \text{ or equivalently}$$
$$K_n(r) = K_n{}^*(r) + K_{n-1}{}^*(r) \tag{4}$$

By replacing in (2) the values of $K_n(r)$ and $K_{n-1}(r)$ from (4), we find

$$K_n{}^*(r) = (r-1)K_{n-1}{}^*(r) + K_{n-2}{}^*(r) \tag{5}$$

Now (4) implies

$$\begin{aligned} K_n(r) &= (r-1)K_{n-1}{}^*(r) + K_{n-2}{}^*(r) + (r-1)K_{n-2}{}^*(r) + K_{n-3}{}^*(r) = \\ &= (r-1)(K_{n-1}{}^*(r) + K_{n-2}{}^*(r)) + K_{n-2}{}^*(r) + K_{n-3}{}^*(r) = \\ &= (r-1)K_{n-1}(r) + K_{n-2}(r). \end{aligned}$$

The theorem is proved.

Corollary 1. The numbers $K_n(2)$ are Fibonacci numbers, i.e.

$$K_n(2) = F_{n+2}$$

Indeed, $K_n(2) = K_{n-1}(2) + K_{n-2}(2)$ and $K_1(2) = 3$; $K_2(2) = 5$ (We consider here that $F_0 = F_1 = 1$ and $F_{n+2} = F_{n+1} + F_n$ for any $n \geq 0$).
It follows that for isoarithmic helicenes or zigzag catafusenes consisting of linear segments with two hexagons each the numbers of Kekulé structures form the Fibonacci sequence, as mentioned by Cyvin,[5] and earlier first by Gordon and Davison,[6] and then by Yen.[7]

GENERALIZATION FOR NON-BENZENOID EVEN-MEMBERED SYSTEMS

What was demonstrated above for benzenoid catafusenes can be generalized for non-branched non-benzenoid *cata*-condensed systems formed from even-membered rings all having the same size. We define an annelation angle character φ as even or odd as seen in Figure 4 by means of dualist graphs: linear annelation corresponds to an even annelation angle character, i.e. $\varphi = 0$, and so on.

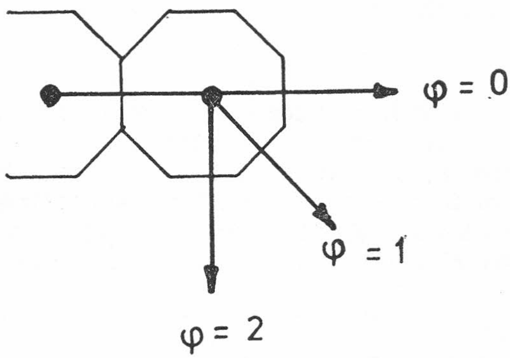

Figure 4. Annelation angle characters for a non-benzenoid *cata*-condensed system having an eight-membered terminal ring.

Even-membered rings ($4m$-membered, or 0 (mod 4) and $4m+2$-membered, or 2(mod 4)) are assigned with a size index λ which is either $\lambda = 0$ for 0(mod 4)-rings or $\lambda = 1$ for 2(mod 4)-rings, i.e. again an even/odd index.

All the preceding (and the following) formulas which refer to benzenoid systems having $m = 1$, .e. to 2(mod 4)-rings, may be converted into relationships which apply to 0(mod 4)-rings if one replaces »segments of linearly condensed rings« by »segments consisting of condensed 0(mod 4)-rings such that the annelation angle character φ is odd«.
Therefore in a non-branched *cata*-condensed system the segments are delimitated by annelation points where $\lambda + \varphi$ is odd.

The generalization is as follows: If the sum $\lambda + \varphi$ is even, then the non-branched string of *cata*-condensed rings arranged in n segments with two rings each has F_{n+2} Kekulé structures.

KEKULÉ STRUCTURE COUNT OF CATAFUSENES AND THE NUMBER OF SOME SEQUENCES OF INTEGERS

Corollary 1 has an interesting application to the enumeration, in terms of the Fibonacci numbers, of some sequences of integers satisfying parity conditions, as follows.

Corollary 2. The number of all sequences of integers

$$1 \leq i_1 < i_2 < \ldots < i_k \leq n$$

such that $i_{s+1} - i_s \equiv 1 (\mathrm{mod}\ 2)$ for $s = 1, \ldots, k-1$ $(1 \leq k \leq n)$ is equal to $F_{n+2} - 2$.

Proof. Let G be a zigzag catafusene graph composed of n linear segments with two hexagons each. It follows that G has $n+1$ hexagons and n internal edges $E_1, E_2, \ldots, E_n$, which are numbered such that E_i lies between E_{i-1} and E_{i+1} for $i = 2, \ldots, n-1$.

The number of perfect matchings of G is equal to $K_n(2) = F_{n+2}$. Among these there are two perfect matchings containing external edges only, hence the number of perfect matchings which include at least one internal edge equals $F_{n+2} - 2$. We shall prove that a selection $\{E_{i_1}, E_{i_2}, \ldots, E_{i_k}\}$ of internal edges with $1 \leq i_1 < i_2 < \ldots < i_k \leq n$; $k \geq$ is the set of internal edges of a unique perfect matching of G if and only if all differences $i_{s+1} - i_s$ are odd for $1 \leq s \leq k-1$.

Note that if $E_s = v_i v_j$ is an internal edge of G, then both paths P_1 and P_2 connecting v_i and v_j on the perimeter of G (composed of external edges only) are odd. To see this, consider a hexagon corresponding to a terminal vertex of the graph G^*. If we delete this hexagon from G, exactly one of the paths P_1 and P_2 decreases its length by 4, hence it conserves its parity. We may repeat this procedure until we find a graph consisting of two hexagons only, and E_s is the unique internal edge of this catafusene graph, hence the two paths between v_i and v_j have both a length equal to five. Since both paths P_1 and P_2 have odd length, it follows that both odd paths P_1' and P_2' derived from P_1 or P_2, respectively, by deleting their extremities v_i and v_j and the edges incident to v_i and v_j have a unique perfect matching M_1, respectively M_2. Therefore there exists a unique perfect matching of G containing edge E_s and $2n+2$ external edges, namely $M_1 \cup M_2 \cup \{E_s\}$.

Now if we consider two internal edges E_s and E_t of G with $1 \leq s < t \leq n$, there exist exactly two paths P_1 and P_2 on the perimeter of G connecting the extremities of E_s to those of E_t and having in common with E_s and E_t only their extremities. It is clear that if we are going from E_s to E_t, P_1 and P_2 contain four edges each on the first linear segment composed of two hexagons of G. After this, these paths always turn to left or to right, hence the number of edges of P_1 and P_2 increases by 1 or by 3, i.e. they always change the parity. Hence P_1 and P_2 have the same parity in G, equal to the parity of the difference $t - s$.

Consequently, the perimeter of G is decomposed by E_s and E_t into four paths: P_1 and P_2 having the parity of $t - s$, P_3 between the extremities of E_s, and P_4 between the extremities of E_t. We have proved in the case of a single internal edge that P_3 and P_4 are both odd. Hence there exists a unique perfect matching of G containing both E_s and E_t if and only if P_1 and P_2 are both odd, or equivalently if $t - s \equiv 1 \pmod 2$.

We can use a similar argument for a set of $k \leq n$ internal edges $\{E_{i_1}, E_{i_2}, \ldots, E_{i_k}\}$ of G. Indeed, by deleting the vertices of these edges we obtain a subgraph G_k of G and the perimeter of G decomposes into a collection of paths. If the length of every path in this collection is odd, i.e. all differences $i_{s+1} - i_s$ are odd, there exists a unique perfect matching in G_k which together with $E_{i_1}, \ldots, E_{i_k}$ yields a unique perfect matching in G containing these internal edges. If at least one path from the above collection has even length, i.e. at least one of the differences $i_{s+1} - i_s$ is even, then a perfect matching of G containing all the edges $E_{i_1}, \ldots, E_{i_k}$ cannot exist. The proof is complete.

FIBONACCI NUMBERS AND A POLYNOMIAL COUNTING TECHNIQUE FOR THE KEKULÉ STRUCTURES

Let G be a non-branched catafusene graph consisting of n linear segments having the labels $a_1, a_2, \ldots, a_n$, such that every linear segment with label a_i lies between linear segments having labels a_{i-1}, respectively a_{i+1} for $i = 2, \ldots, n-1$.

With a such graph G in [4] is associated the polynomial

$$P(G; a_1, \ldots, a_n) = 1 + \prod_{i=1}^{n} (a_i + 1) - W(G)\,, \tag{6}$$

where $W(G)$ is a polynomial expression involving products of a_i's having all coefficients equal to one. By grouping these products according to the number k of a_i's, one obtains Table I. Note that $W(G) = 0$ only for $n = 1$ or $n = 2$.

The number $K(G)$ of Kekulé structures of G is then equal to $P(G; A_1, \ldots, A_n)$, i.e. to the numerical value of the polynomial associated with G for $a_1 = A_1, \ldots, a_n = A_n$, if every linear segment of G with label a_i contains $A_i + 1$ hexagons for $1 \leq i \leq n$.

The polynomial $W(G)$ has a purely combinatorial characterisation as follows: There exists a one-to-one mapping between the set of all products $a_{i_1} a_{i_2} \ldots a_{i_k}$ in the development of $W(G)$ as a sum of products and the set of all sequences of k natural numbers

$$1 \leq i_1 < i_2 < \ldots < i_k \leq n$$

such that at least one of the differences $i_{s+1} - i_s$ $(1 \leq s \leq k-1)$ is an even number.

The lower part of this Table I is a numerical triangle of the numbers $W_{n,k}$, where $W_{n,k}$ denotes the number of products containing exactly $k \geq 2$ variables a_i in the development of $W(G)$ as a sum of products of variables. The total number of terms in $W(G)$, denoted by $W_n = \sum_{k \geq 2} W_{n,k}$, may be obtained from (6) for all variables $a_i = 1$. Hence

$$W_n = 2^n + 1 - P(G; 1, \ldots, 1),$$

where $P(G; 1, \ldots, 1) = K_n(2)$ and Corollary 1 implies

TABLE I

The Terms of W(G), Above the Thick Line, and the Numbers of Such Terms for Given n and k (Below the Thick Line)

$n \setminus k$	5	4	3	2
3	—	—	—	a_1a_3
4	—	—	$a_1a_2a_4$ $a_1a_3a_4$	a_1a_3 a_2a_4
5	—	$a_1a_2a_3a_5$ $a_1a_2a_4a_5$ $a_1a_3a_4a_5$	$a_1a_2a_4$ $a_1a_3a_4$ $a_1a_3a_5$ $a_2a_3a_5$ $a_2a_4a_5$	a_1a_3 a_2a_4 a_1a_5 a_3a_5
6	$a_1a_2a_3a_4a_6$ $a_1a_2a_3a_5a_6$ $a_1a_2a_4a_5a_6$ $a_1a_3a_4a_5a_6$	$a_1a_2a_3a_5$ $a_1a_2a_4a_5$ $a_1a_3a_4a_5$ $a_1a_2a_4a_6$ $a_1a_3a_4a_6$ $a_1a_3a_5a_6$ $a_2a_3a_4a_6$ $a_2a_3a_5a_6$ $a_2a_4a_5a_6$	$a_1a_2a_4$ $a_1a_3a_4$ $a_1a_3a_5$ $a_2a_3a_5$ $a_2a_4a_5$ $a_1a_2a_6$ $a_1a_3a_6$ $a_1a_4a_6$ $a_1a_5a_6$ $a_2a_4a_6$ $a_3a_4a_6$ $a_3a_5a_6$	a_1a_3 a_2a_4 a_1a_5 a_3a_5 a_2a_6 a_4a_6
3	—	—	—	1
4	—	—	2	2
5	—	3	5	4
6	4	9	12	6

$$W_n = 2^n + 1 - F_{n+2} \tag{7}$$

Theorem 2. The numbers $W_{n,k}$ verify the following recurrence relation:

$$W_{n,k} = W_{n-1,k} + W_{n-1,k-1} + \binom{\lfloor (n+k-3)/2 \rfloor}{k-1} \tag{8}$$

where $\lfloor x \rfloor$ denotes the integer part of x.

Proof. The set of all sequences of k natural numbers $1 \leq i_1 < i_2 < \ldots < i_k \leq n$ such that at least one of the differences $i_{s+1} - i_s$ $(1 \leq s \leq k-1)$ is an even number may be written as the union of three pairwise disjoint sets A, B and C, where:

A is the set of all sequences of k natural numbers

$$1 \leq i_1 < i_2 < \ldots < i_k \leq n - 1$$

which satisfy the same condition;

B is the set of all sequences of k natural numbers

$$1 \leq i_1 < i_2 < \ldots < i_k = n$$

such that at least one of the differences $i_{s+1} - i_s$ $(1 \leq s \leq k-2)$ is an even number;

C is the set of sequences

$$1 \leq i_1 < i_2 < \ldots < i_k = n$$

which satisfy $i_2 - i_1 \equiv i_3 - i_2 \equiv \ldots \equiv i_{k-1} - i_{k-2} \equiv 1 \pmod 2$ and $i_k - i_{k-1} \equiv 0 \pmod 2$. It is clear that $|A| = W_{n-1,k}$ and $|B| = W_{n-1,k-1}$. If we denote $|C| = f(n,k)$ it remains to prove that

$$f(n,k) = \binom{\lfloor (n+k-3)/2 \rfloor}{k-1} \tag{9}$$

For $k = 1$ we deduce $f(n, 1) = 1$ and for $k = 2$ we have $i_2 = n$ and $i_2 - i_1$ is an even number, hence $f(n, 2) = \lfloor (n-1)/2 \rfloor$.
We shall prove (9) by induction on n.

Formula (9) is true for $n = 2$ and $n = 3$ for all $k \geq 1$, if we define $\binom{0}{0} = 1$. Suppose (9) to be true for $n \leq m - 1$.
It is clear that $f(m, k) = N_1(m, k) + N_2(m, k)$, where $N_1(m, k)$ is the number of sequences verifying the above conditions from C, for which $i_1 = 1$ and $N_2(m, k)$ is the number of such sequences with $i_1 \geq 2$. It follows that $N_2(m, k) = f(m-1, k)$ because the sequence

$$1 \leq i_1' < i_2' < \ldots < i_k' = m - 1,$$

where $i_j' = i_j - 1$ for $1 \leq j \leq k$ verifies the same conditions and this mapping is one-to-one.

For $m - k \equiv 0 \pmod 2$ we have $N_1(m, k) = 0$ and for $m - k \equiv 1 \pmod 2$ we deduce in a similar way that $N_1(m, k) = f(m-1, k-1)$.

We shall consider two cases:

i) $m - k \equiv 0 \pmod 2$. We derive

$$f(m, k) = f(m-1, k) = \binom{\lfloor (m+k-4)/2 \rfloor}{k-1}$$

by induction hypothesis. If $m - k \equiv 0 \pmod 2$ it follows $m + k \equiv 0 \pmod 2$, hence $\lfloor (m+k-4)/2 \rfloor = \lfloor (m+k-3)/2 \rfloor$ and $f(m, k) = \binom{\lfloor (m+k-3)/2 \rfloor}{k-1}$.

ii) $m - k \equiv 1 \pmod 2$, hence $m + k \equiv 1 \pmod 2$. In this case

$$f(m, k) = f(m-1, k) + f(m-1, k-1) = \binom{\lfloor (m+k-4)/2 \rfloor}{k-1} + \binom{\lfloor (m+k-5)/2 \rfloor}{k-2} = \binom{\lfloor (m+k-3)/2 \rfloor - 1}{k-1} + \binom{\lfloor (m+k-3)/2 \rfloor - 1}{k-2} = \binom{\lfloor (m+k-3)/2 \rfloor}{k-1},$$

hence (9) is true for $n = m$ also. The proof is complete.
It follows that Table I can be easily constructed from Pascal's triangle of binomial coefficients presented in Table II in a slightly modified form: its last column of 1's has been deleted, and zigzag lines have been marked. All entries in Pascal's triangle are bracketed in order to distinguish them from the entries of $W(G)$ in Table I.

Table III shows how one can obtain the entries in the lower part of Table I from the bracketed binomial coefficients displayed in Table II. Each non-bracketed number in Table III is the sum of one or two non-bracketed numbers (directly above and/or above-right) and of one bracketed number (directly above). The bracketed numbers are those following the zigzag lines in Table II (for illustration purposes, the same types of lines have been employed in Tables II and III).

TABLE II

Pascal's Triangle of Binomial Coefficients Depleted of the Last Column of 1's

(1)					
(1)	(2)				
(1)	(3)	(3)			
(1)	(4)	(6)	(4)		
(1)	(5)	(10)	(10)	(5)	
(1)	(6)	(15)	(20)	(15)	(6)

TABLE III

The Numerical Triangle for the Number of Terms in W(G) from Table I (Non-bracketed Values)

n	Triangle entries $W_{n,k}$	W_n
3	1 (1) (1)	1
4	2 2 (1) (1) (2)	4
5	3 5 4 (1) (1) (3) (2)	12
6	4 9 12 6 (1) (1) (4) (3) (3)	31
7	5 14 25 21 9 (1) (1) (5) (4) (6) (3)	74

Hence the numbers $f(n, k)$ for $k \geq 1$ generate the zigzag lines in Table II. Denote their sum for $k \geq 1$ by G_n, or

$$G_n = \sum_{k \geq 1} \binom{\lfloor (n+k-3)/2 \rfloor}{k-1}$$

From Pascal's triangle in both cases when n is even or odd we deduce that $G_{n+2} = G_{n+1} + G_n$ for any $n \geq 2$, taking into account the recurrence relation for the binomial numbers. We find also $G_2 = 1 = F_1$ and $G_3 = 2 = F_2$, which implies that $G_n = F_{n-1}$ for any $n \geq 2$.

This property and relation (8) imply a recurrence relation for the numbers W_n, which contains again Fibonacci numbers:

$$W_n = 2W_{n-1} + F_{n-1} - 1 \tag{10}$$

Relationship (10) can be deduced directly from (7), therefore formulas (7) and (10) are equivalent.

Two other reccurence relations can be obtained from (7) and (10), respectively, by using the adapted recurrence relations for Fibonacci numbers ($F_n = F_{n-1} + F_{n-2}$):

$$W_n = W_{n-1} + W_{n-2} + 2^{n-2} - 1 \tag{11}$$

$$W_n = 3\, W_{n-1} - W_{n-2} - 2\, W_{n-3} + 1 \tag{12}$$

An explicit formula for numbers $W_{n,k}$ can be deduced as follows.

Theorem 3. The following relation holds

$$W_{n,k} = \binom{n}{k} - \binom{\left\lfloor \frac{n+k}{2} \right\rfloor}{k} - \binom{\left\lfloor \frac{n+k-1}{2} \right\rfloor}{k} \tag{13}$$

for every $n, k \geq 1$.

Proof. From (13) we can conclude that $W_{n,1} = W_{n,n} = 0$ for every $n \geq 1$ and also that $W_{n,k} = 0$ for $k > n$. Then the proof follows by induction on n. Suppose that (13) holds for every $n \leq m - 1$ and every $k \geq 1$. By (8) we obtain that

$$W_{n,k} = \binom{m-1}{k} + \binom{m-1}{k-1} - \binom{\left\lfloor \frac{m+k-1}{2} \right\rfloor}{k} - \binom{\left\lfloor \frac{m+k-2}{2} \right\rfloor}{k} -$$

$$- \binom{\left\lfloor \frac{m+k-2}{2} \right\rfloor}{k-1} - \binom{\left\lfloor \frac{m+k-3}{2} \right\rfloor}{k-1} + \binom{\left\lfloor \frac{m+k-3}{2} \right\rfloor}{k-1} =$$

$$= \binom{m}{k} - \binom{\left\lfloor \frac{m+k}{2} \right\rfloor}{k} - \binom{\left\lfloor \frac{m+k-1}{2} \right\rfloor}{k},$$

by applying the recurrence relation for binomial coefficients, since $\left\lfloor \frac{m+k-2}{2} \right\rfloor = \left\lfloor \frac{m+k}{2} \right\rfloor - 1$. Thus (13) holds for every $n, k \geq 1$.

Corollary 3. For any fixed k, $k \geq 1$ the numbers $W_{n,k}$ verify that

$$\lim_{n \to \infty} \frac{W_{n,k}}{n^k} = \frac{1}{k!} \left(1 - \frac{1}{2^{k-1}}\right)$$

This follows from (13).

Corollary 4. The following equality holds:

$$\lim_{n \to \infty} \frac{W_n}{2^n} = 1$$

The proof follows from (7) since

$$F_n = \frac{1}{\sqrt{5}}\left[\left(\frac{1+\sqrt{5}}{2}\right)^{n+1} - \left(\frac{1-\sqrt{5}}{2}\right)^{n+1}\right] < 1.62^{n+1} \quad \text{for every } n \geq 0.$$

This indicates that for a non-branched catafusene consisting of n linear segments the number of products in the development of $W(G)$ from (6) has an exponential character as n tends towards infinity. The last corollary also indicates that the term 2^{n-2} in (11) represents asymptotically 1/4 from W_n.

The three links between the Fibonacci sequence and the numbers of Kekulé structures for non-branched *cata*-condensed polycyclic hydrocarbons (benzenoid or conjugated even-membered non-benzenoid) presented in this paper are supplementing the previous relationships between chemistry and Fibonacci numbers described by Hosoya.[8]

Acknowledgements. — Thanks are addressed to Profesor H. Hosoya for having suggested relation (12), and to Teodor-Silviu Balaban for stimulating discussions.

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SAŽETAK

Kemijski grafovi. 40. Tri relacije između Fibonaccijevog niza i brojeva Kekuléovih struktura za nerazgranate katakondenzirane policikličke aromatske ugljikovodike

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Određene su rekurentne relacije za *K* brojeve Kekuléovih struktura kod benzenoidnih i nebenzenoidnih katafuzena koji imaju nerazgranatu vrpcu katakondenziranih prstena. Odatle proizlazi da u slučaju aneliranih segmenata koji imaju dva prstena brojevi Kekuléovih struktura formiraju Fibonaccijev niz. Korolar 2 daje drugu relaciju s Fibonaccijevim brojevima. Dobivene su algebarske formule pomoću kojih se brojevi Kekuléovih struktura mogu dobiti iz brojeva šesterokuta za svaki linearno kondenzirani segment. Brojevi članova u ovim algebarskim izrazima formiraju numerički trokut koji je povezan s Pascalovim trokutom i koji daje treću relaciju s Fibonaccijevim brojevima.