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CHEMICAL GRAPHS.XLI[1].NUMBERS OF CONJUGATED CIRCUITS AND KEKULÉ STRUCTURES FOR ZIGZAG CATAFUSENES AND (J,K)-HEXES;GENERALIZED FIBONACCI NUMBERS

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Abstract. The numbers $K_{j,k}$ of Kekulé structures in (j,k)-hexes (non-branched catafusenes formed by k strings of linearly condensed benzenoid rings with j rings in each linear portion) can be considered to be generalized Fibonacci numbers, because the sequence $K_{1,k}$ for increasing k values (k=1,2,...) is the Fibonacci sequence.Explicit and recurrent expressions are obtained for $K_{j,k}$. For the same (j,k)-hexes the numbers $R_{j,k}$ of conjugated 6-circuits are calculated by recurrence relations and explicit algebraic expressions in j and k,and are found to form an interesting numerical triangle if decomposed into polynomials in terms of j for each k value.

In (1,k)-hexes,i.e. helicenes and isoarithmic catafusenes, the numbers of 10-,14-,18-,...-membered circuits form the same numerical sequence $R_{j,k}$ as for conjugated 6-circuits , but with shifted j-values.General expressions are obtained for resonance energies of such (1,k)-hexes using Randić's approach. Sequences $R_{j,k}^{(4m+2)}$ in (j,k)-hexes are also discussed.

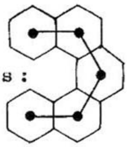
The ratio between the number $R_{j,k}$ of conjugated 6-circuits and the total number $(jk+1)K_{j,k}$ of benzenoid rings in (j,k)-hexes is calculated both by using explicit algebraic expressions,and recurrence relations;in addition,for facilitating the obtention of numerical data,a small computer program was devised.It was found that the asymptotic limit of the above ratio for $k \rightarrow \infty$ leads to a simple algebraic expression (47). A list of main symbols is appended.

1.Introduction

In previous papers[1,2] we have discussed the number of Kekulé structures for polycyclic aromatic hydrocarbons(polyhexes) having non-branched cata-condensation(non-branched catafusenes).We have called isoarithmic the systems whose L-transform[3] of the 3-digit code (3DC)[4,5] was identical;in other words, non-branched isoarithmic catafusenes have the same sequences of straightly-annelated benzenoid rings,irrespective of the direction of annelation.

Thus,pentahelicene (1) is isoarithmic with picene (2),and with (3);two other isomeric penta-catafusenes 4 and 5,form another isoarithmic pair,because their L-transform or two-

(1,4)-Hexes :



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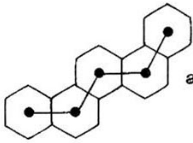

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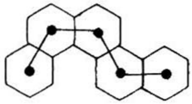
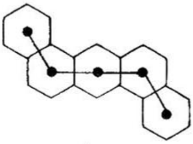
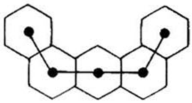


	1	2	3
3DC :	111	121	112
2DC :	111	111	111



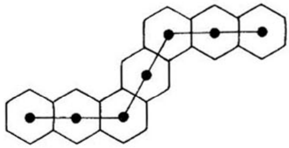


	4	5
3DC :	102	101
2DC :	101	101

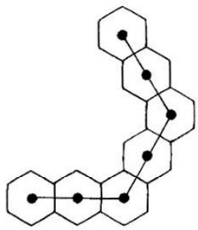
digit code (2DC) is identical.An equivalent of the L-transform is the LA-sequence[6].Isoarithmicity leads to closer physico-chemical similarity (e.g. electronic and photoelectronic spectra[8],chemical reactivity[9],etc.) than isospectrality[10],i.e. identity of characteristic polynomials and eigenvalues of the Hückel characteristic polynomial.All isoarithmic polyhexes have the same number of Kekulé structures,hence the same sextet polynomial and Kekulé polynomial.

The number of Kekulé structures for non-branched catafusenes may be found easily by using the Gordon-Davison algorithm[7] or by applying algebraic or recurrence formulas described in our previous papers[1,2].In the case when the numbers j in each linear portion of the non-branched catafusene are equal,these formulas take particularly interesting aspects.In the present paper we shall examine such catafusenes,composed of k linear portions,each containing j benzenoid rings,and shall call them (j,k)-hexes.Thus,1-3 are both (1,4)-hexes,6 and 7 are both (2,3)-hexes.

(2,3)-Hexes :



6



7

	6	7
3DC :	01020	01010
2DC :	01010	01010

One may consider the isoarithmic (j,k)-hexes as generalized catafusenes in complete analogy with helicenes or zigzag (fully benzenoid) catafusenes,which are (1,k)-hexes.

It should be noted that j is obtained by subtracting one from the number of condensed rings in any linear portion of (j,k)-hexes.We shall not discuss here systems such as 4 or 5 where j differs from one linear portion to another.

One can verify easily that the number n of benzenoid rings in (j,k)-hexes is

$$n = jk + 1 \qquad (1)$$

2.Numbers of Kekulé structures

It was shown[1,2] that the numbers $K_{j,k}$ of Kekulé structures for (j,k)-hexes obey the following recurrence relationship

$$K_{j,k} = jK_{j,k-1} + K_{j,k-2} \qquad (2)$$

When j = 1 (i.e.,for helicenes such as 1 and their isoarithmic catafusenes) the numbers $K_{1,k}$ of Kekulé structures form the Fibonacci sequence[1,2,7,8]:

$$K_{1,k} = F_{k+2} \qquad (3)$$

where $F_o = F_1 = 1$ are Fibonacci numbers,defined by

$$F_i = F_{i-1} + F_{i-2} = 2F_{i-2} + F_{i-3} = 3F_{i-3} + 2F_{i-4}, \text{etc.} \qquad (4)$$

For (j,k)-hexes the relationship (2) gives numbers of Kekulé structures $K_{j,k}$ which can be considered as generalized Fibonacci numbers.Table 1 presents some numerical data on such numbers.

Table 1.Fibonacci (first row) and generalized Fibonacci numbers $K_{j,k}$

j \ k	1	2	3	4	5	6
1	3	5	8	13	21	34
2	4	10	24	58	140	338
3	5	17	56	185	611	2018
4	6	26	110	466	1974	8362
5	7	37	192	997	5177	26882
6	8	50	308	1898	11696	72074

In order to obtain an explicit formula for generalized Fibonacci numbers, by analogy with Binet's formula

$$F_i = \left[\left(\frac{1+\sqrt{5}}{2}\right)^{i+1} - \left(\frac{1-\sqrt{5}}{2}\right)^{i+1}\right] \Big/ \sqrt{5} \qquad (5)$$

we look for the general solution of equation (2). We note that, in addition to (2), we know for acenes:

$$K_{j,1} = j + 2 \qquad (6)$$

and also for V-shaped (j,2)-hexes[1]:

$$K_{j,2} = (j+1)^2 + 1 = j^2 + 2j + 2 \qquad (7)$$

The general solution will be of the form

$$K_{j,k} = ar_1^k + br_2^k \qquad (8)$$

where r_1, r_2 verify the characteristic equation

$$r^2 - rj - 1 = 0, \qquad (9)$$

therefore $r_1 = (j+\sqrt{j^2+4})/2$; $r_2 = (j-\sqrt{j^2+4})/2$ (10)

It can be seen that $-1 < r_2 < 0$. In (8) we set successively $k = 1$, cf. (6), and $k = 2$, cf. (7):

$$ar_1 + br_2 = j + 2$$

$$ar_1^2 + br_2^2 = j^2 + 2j + 2$$

Hence by simple transformations using (10), we have

$$a(j+\sqrt{j^2+4}) + b(j-\sqrt{j^2+4}) = 2j + 4$$

$$a(j^2+2+j\sqrt{j^2+4}) + b(j^2+2-j\sqrt{j^2+4}) = 2j^2 + 4j + 4$$

We obtain the solutions

$$a = (\sqrt{j^2+4}+2) \Big/ \sqrt{j^2+4} \ ; \ b = (\sqrt{j^2+4}-2) \Big/ \sqrt{j^2+4}, \qquad (11)$$

therefore the generalized Fibonacci numbers are:

$$K_{j,k} = \frac{\sqrt{j^2+4}+2}{\sqrt{j^2+4}}\left(\frac{j+\sqrt{j^2+4}}{2}\right)^k + \frac{\sqrt{j^2+4}-2}{\sqrt{j^2+4}}\left(\frac{j-\sqrt{j^2+4}}{2}\right)^k \qquad (12)$$

This expression reduces to the Binet formula for $j = 1$, i.e., $K_{1,k} = F_{k+2}$, cf. (3).

3. Numbers of Kekulé structures and of conjugated circuits in (j,k)-hexes

For a given Kekulé structure in a polyhex, Randić on one hand[11a], and Gomes and Mallion[11b,11c] on the other hand have independently defined the conjugated circuits in a polycyclic conjugated system as being a cyclic array of alternating single and double bonds. In polyhexes, the numbers of conjugated 6-, 10-, 14- and 18-circuits play an important role for estimating the resonance energy (there are no smaller circuits in polyhexes, and the larger ones have negligible contributions).[12,13]

By means of these numbers of conjugated circuits, Randić[11a] obtained a parametrized formula for the resonance energy of the polyhex, which is in close agreement with Herndon's formula, as shown by Schaad and Hess in their excellent review.[14] Actually, Randić only considered in his formula the linearly independent conjugated circuits, but in Herndon's equivalent approach all circuits of a given size are considered, irrespective if they are linearly independent, or if they may be represented as a superposition of conjugated circuits of smaller size.

The number of conjugated 6-circuits is identical to the number of "perfect benzenoid rings" in Sahini's formulas[15] for the resonance energy; this number was shown to equal the number of zeroes in the three-digit code of a non-branched catafusene[16].The conjugated 6-circuits are relevant to Clar's theory of aromatic sextets[17].

We shall compute the number of conjugated 6-circuits in (j,k)-hexes.On increasing k by one,we have for each Kekulé structure three situations at the bond becoming annelated with a string of j+1 linearly condensed rings,illustrated by (i)-(iii) for the case when we add with kinked condensation a tetracene unit (j=4) to the existing (j,k)-hex.In each Kekulé structure the bond undergoing annelation will be termed "terminal bond" and the annelated Kekulé structures will be called "successors".In Fig.1 we denote a conjugated 6-ring by a central dot.Let r be the number of conjugated 6-circuits in the starting (j,k)-hex undergoing annelation.

(i) The terminal bond is single;in this situation one (iii)-type successor results,i.e. the next annelation at the new "terminal bond" will be of type (iii);the number r of conjugated 6-rings (dots) is conserved in the successor.

(ii) The terminal bond is double and belongs to a conjugated (dotted) 6-circuit;this situation leads to one (i)-type successor with r dots,one (ii)-type successor with r+1 dots and j-1 (iii)-type successors with r+1 dots each.

(iii) The terminal bond is double and belongs to a non-dotted 6-circuit;this situation leads to one (i)-type successor with r+1 dots,one (ii)-type successor with r+2 dots,one (iii)-type successor with r+1 dots,and j-2 successors of (iii)-type with r+2 dots each (Fig.1).

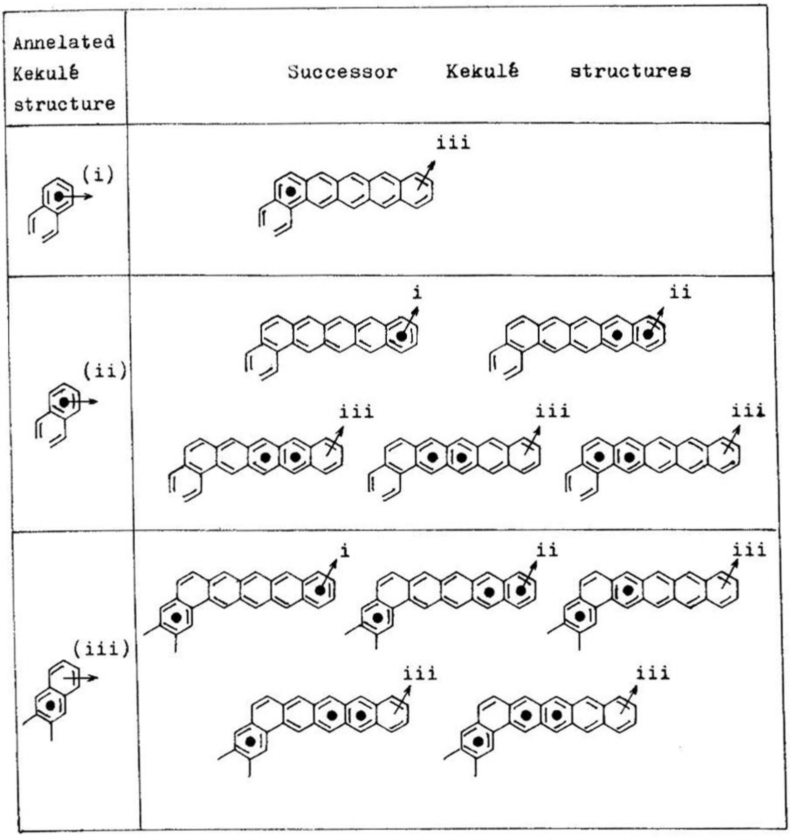


Fig.1.Annelation of Kekulé structures with tetracene units;terminal bonds are denoted by arrows.

Taking (6) into account for the first starting term in the series which is a (j,1)-hex,i.e.,a (j+1)-acene,from the j+2 Kekulé structures,one is (i)-type with one dot,one is (ii)-type with two dots,and the remaining j are of (iii)-type (one with one dot,the other with two dots each);the total number of dots is thus $R_{j,1} = 2j + 2$.

On the basis of the above data, the following recurrences hold, when the number of Kekulé structures is denoted by s_k, s_k', s_k'' and the number of conjugated 6-circuits by r_k, r_k', r_k'' for (i)-type, (ii)-type, and (iii)-type successors, respectively, at the k-th annelation with a string of j linearly condensed benzenoid rings:

$$K_{j,k} = s_k+s_k'+s_k'' = s_k''+2s_k' = K_{j,k-1}+js_k' \qquad (13)$$

$$R_{j,k} = r_k+r_k'+r_k'' = r_k''+2r_k'-s_k' \qquad (14)$$

$$s_k' = s_k \qquad (15)$$

$$r_k' = r_k+s_k = r_k+s_k' \qquad (16)$$

$$s_{k+1} = s_{k+1}' = s_k''+s_k' \qquad (17)$$

$$s_{k+1}'' = s_k'+(j-1)s_k'+s_k''+(j-2)s_k'' = js_k'+js_k''-s_k'' = js_{k+1}'-s_k'' \qquad (18)$$

$$r_{k+1} = r_k'+r_k''+s_k'' = r_{k+1}'-s_{k+1}' \qquad (19)$$

$$r_{k+1}' = r_k'+s_k'+r_k''+2s_k'' \qquad (20)$$

$$r_{k+1}'' = r_k+(j-1)(r_k'+s_k')+r_k''+s_k''+(j-2)(r_k''+2s_k'') = jr_k'+(j-2)s_k'+(j-1)r_k''+(2j-3)s_k'' \qquad (21)$$

From these relationships, and especially from (13), (17) and (18), one obtains the recurrence for $K_{j,k}$ in terms of j, k, s_k' and s_k'', by applying in order the following relations for any j:

$$s_k' = s_{k-1}'+s_{k-1}'' \; ; \; s_k'' = js_k'-s_{k-1}'' \; ; \; K_{j,k} = s_k''+2s_k'$$

wherefrom one obtains easily recurrence (2).

The general formula for $K_{j,k}$ is

$$K_{j,k} = (j+1)^k+1-P_j \tag{22}$$

where P_j is a polynomial in j of degree k-1,starting with $(k-2)j^{k-1}$.

Table 2.Expression for $K_{j,k}$ in terms of k and j

k	s_k''	$s_k'=s_k$	$K_{j,k}$
1	j	1	$(j+1)+1$
2	j^2	$j+1$	$(j+1)^2+1$
3	j^3+j	j^2+j+1	$(j+1)^3+1-j^2$
4	j^4+2j^2	j^3+j^2+2j+1	$(j+1)^4+1-(2j^3+2j^2)$
5	j^5+3j^3+j	$j^4+j^3+3j^2+2j+1$	$(j+1)^5+1-(3j^4+5j^3+4j^2)$
6	$j^6+4j^4+3j^2$	$j^5+j^4+4j^3+3j^2+3j+1$	$(j+1)^6+1-(4j^5+9j^4+12j^3+$ $+6j^2)$

The coefficients of this polynomial form a numerical triangle which may be calculated from Pascal's triangle.A detailed discussion of the former numerical triangle was presented in the earlier papers[1,2] from which it follows that

$$P_j = W_{k,k-1}j^{k-1}+W_{k,k-2}j^{k-2}+ \dots +W_{k,2}j^2 ,$$

where $$W_{k,r} = \binom{k}{r} - \binom{\lfloor (k+r)/2 \rfloor}{r} - \binom{\lfloor (k+r-1)/2 \rfloor}{r}$$

for every $k,r \geq 1$,and $\lfloor x \rfloor$ denotes the integer part of x.

4.Numbers of conjugated 6-circuits in (j,k)-hexes

For the number $R^{(6)}_{j,k}$ of conjugated 6-circuits in (j,k)-hexes the relationships (14)-(21) lead to the recurrence stated below (in this section we shall omit the upper index (6) from the notation for convenience): $R^{(6)}_{j,k} = R_{j,k}$.

Theorem 1.The following recurrence relation holds:

$$R_{j,k} = jR_{j,k-1} + R_{j,k-2} + 2(K_{j,k} - K_{j,k-1}) \qquad (23)$$

for $k \geqslant 3$ and

$$R_{j,1} = 2j + 2 ;$$

$$R_{j,2} = K_{2j,2} = (2j + 1)^2 + 1.$$

Proof: From (15),(17) and (18) we deduce that

$$s_{k+2} = js_{k+1}+s_k \qquad (24)$$

Taking into account (14),(13) and (15) it is clear that (23) is equivalent to

$$r_k''+2r_k'-s_k = jr_{k-1}''+2jr_{k-1}'-js_{k-1}+r_{k-2}''+2r_{k-2}'-s_{k-2}+2js_k, \text{or}$$

$$r_k''+2r_k' = jr_{k-1}''+2jr_{k-1}'+r_{k-2}''+2r_{k-2}'+2js_k , \qquad (25)$$

because (24) holds.

By substituting $s_k'' = s_{k+1}-s_k$ from (17) into (20) and (21) we infer that:

$$r_{k+1}' = r_k'+r_k''+2s_{k+1}-s_k \qquad (26)$$

$$r_{k+1}'' = jr_k'+(j-1)r_k''-(j-1)s_k+(2j-3)s_{k+1} \qquad (27)$$

Now we replace the values of r_k'' and r_k' deduced from (26) and (27) in the left-hand side of (25) to obtain after simplification:

$$r_{k-1}''-r_{k-2}''-(j-2)r_{k-1}'-(j+1)s_{k-1}-2r_{k-2}'+s_k = 0 \qquad (28)$$

Substituting again r_{k-1}' and r_{k-1}'' from (26) and (27),respectively,into (28) one finds

$$s_k-js_{k-1}-s_{k-2} = 0,$$

which is an identity by virtue of (24). □

We shall solve the recurrence (23) to obtain an analytical expression for $R_{j,k}$,analogous to (12) which is the general solution of (2).By substituting (8) into (23) we obtain

$$R_{j,k} = jR_{j,k-1}+R_{j,k-2}+2ar_1^k+2br_2^k-2ar_1^{k-1}-2br_2^{k-1} \tag{29}$$

where a and b are given by (11).

We look for a particular solution having the form

$$R_{j,k} = C_1kr_1^k + C_2kr_2^k \tag{30}$$

From (29) and (30), by equating the terms which contain r_1 and r_2, respectively, and then by dividing with r_1^{k-2} and r_2^{k-2}, respectively, we obtain the two equations

$$\begin{aligned} C_1kr_1^2 &= jC_1(k-1)r_1+C_1(k-2)+2ar_1^2-2ar_1 \\ C_2kr_2^2 &= jC_2(k-1)r_2+C_2(k-2)+2br_2^2-2br_2 \end{aligned} \tag{31}$$

Taking relation (9) into account, we obtain

$$r_1^2 = r_1j+1 \quad \text{and} \quad r_2^2 = r_2j+1 \ , \tag{32}$$

therefore by appropiate substitutions

$$C_1 = \frac{2ar_1^2-2ar_1}{2+jr_1} \quad \text{and} \quad C_2 = \frac{2br_2^2-2br_2}{2+jr_2} \tag{33}$$

and by using (32)

$$C_1 = \frac{2a(r_1(j-1)+1)}{2+jr_1} \quad \text{and} \quad C_2 = \frac{2b(r_2(j-1)+1)}{2+jr_2} \tag{34}$$

The general solution of recurrence (23) will be the sum of the particular solution (30) and the general solution of the homogeneous recurrence

$$\overline{R}_{j,k} = j\overline{R}_{j,k-1} + \overline{R}_{j,k-2} \tag{35}$$

which is obtained from (23) by converting $R_{j,k}$ into $\overline{R}_{j,k}$ and by omitting the non-homogeneous term.

The solution of (35) has the form

$$\overline{R}_{j,k} = cr_1^k + dr_2^k \tag{36}$$

where constants c and d depend upon the initial conditions of the problem, therefore the general solution of recurrence (23) is

$$R_{j,k} = cr_1^k + dr_2^k + C_1kr_1^k + C_2kr_2^k \qquad (37)$$

where C_1 and C_2 are given by (34).

Since the values of a and b are found from (11), a straightforward computation leads to the following expressions for C_1 and C_2:

$$C_1 = \frac{j(j+2+\sqrt{j^2+4})}{j^2+4}, \quad C_2 = \frac{j(j+2-\sqrt{j^2+4})}{j^2+4} \qquad (38)$$

In order to obtain the values of c and d we put k = 1 and k = 2, respectively, into (37) and use initial values $R_{j,1} = 2j+2$ and $R_{j,2} = 4j^2+4j+2$. We obtain the system

$$c\,\frac{j+\sqrt{j^2+4}}{2} + d\,\frac{j-\sqrt{j^2+4}}{2} = \frac{4j+8}{j^2+4}$$

$$c\,\frac{j^2+2+j\sqrt{j^2+4}}{2} + d\,\frac{j^2+2-j\sqrt{j^2+4}}{2} = \frac{2(3j^2+4j+4)}{j^2+4},$$

which has the solution

$$c = \frac{1}{(j^2+4)\sqrt{j^2+4}}\left[(j^2+4)\sqrt{j^2+4} - (j^3-8)\right]$$

$$d = \frac{1}{(j^2+4)\sqrt{j^2+4}}\left[(j^2+4)\sqrt{j^2+4} + j^3-8\right] \qquad (39)$$

Substituting (38) and (39) into (37) one sees that

$$R_{j,k} = \frac{1}{j^2+4}\left\{\left(\frac{j+\sqrt{j^2+4}}{2}\right)^k\left[\frac{(j^2+4)\sqrt{j^2+4}-(j^3-8)}{\sqrt{j^2+4}} + jk(j+2+\sqrt{j^2+4})\right]\right.$$

$$\left.+\left(\frac{j-\sqrt{j^2+4}}{2}\right)^k\left[\frac{(j^2+4)\sqrt{j^2+4}+j^3-8}{\sqrt{j^2+4}} + jk(j+2-\sqrt{j^2+4})\right]\right\} \qquad (40)$$

By a straightforward calculation, taking into account Newton's binomial formula, from (40) one finds that:

<u>Theorem 2.</u> The following equality holds

$$\left.\begin{aligned} R_{j,k} = \frac{1}{2^{k-1}}\Bigg[\sum_{s\geq 0}\binom{k}{2s} j^{k-2s}(j^2+4)^s-(j^3-8)\sum_{s\geq 1}\binom{k}{2s+1} j^{k-2s-1}\times \\ (j^2+4)^{s-1}+jk(j+2)\sum_{s\geq 1}\binom{k}{2s} j^{k-2s}(j^2+4)^{s-1} + \\ +jk\sum_{s\geq 0}\binom{k}{2s+1} j^{k-2s-1}(j^2+4)^s+2kj^{k-1}\Bigg] , \end{aligned}\right\} (41)$$

where, by definition, $\binom{k}{p} = 0$ whenever $p \geq k+1$.

Some numerical values are presented in Table 3.

Table 3. Numbers $R_{j,k}$ of conjugated 6-circuits

j \ k	1	2	3	4	5	6
1	4	10	20	40	76	142
2	6	26	86	266	782	2226
3	8	50	236	1016	4136	16238
4	10	82	506	2818	14794	74770
5	12	122	932	6392	41252	256062
6	14	170	1550	12650	97046	715682

From (41) it can be seen that $R_{j,k}$ is a polynomial of degree k in j, of the form:

$$R_{j,k} = A_{1,k}j^k + A_{2,k}j^{k-1} + \dots + A_{k+1,k} \qquad (42)$$

From (41) one can deduce easily that

$$A_{1,k} = \frac{1}{2^{k-1}}\Bigg[\binom{k}{0}+\binom{k}{2}+\binom{k}{4}+\dots-\binom{k}{3}-\binom{k}{5}-\dots+k\binom{k}{2}+ \\ +k\binom{k}{4}+\dots+k\binom{k}{1}+k\binom{k}{3}+\dots\Bigg] = \frac{1}{2^{k-1}}\Bigg[2^{k-1}-(2^{k-1}-k)+$$

$$+k(2^{k-1}-1)+k2^{k-1}\Big] = 2k \; ; \; A_{2,k} = \frac{1}{2^{k-1}}\left[2k+2k(2^{k-1}-1)\right] = 2k;$$

If $k = 2p$ then $A_{k+1,k} = \frac{4^p}{2^{k-1}} = 2$ and

$$A_{k,k} = \frac{1}{2^{k-1}}\left[8\binom{k}{k-1}4^{p-2} + 2k4^{p-1}\right] = \frac{k4^p}{2^{k-1}} = 2k.$$

If $k = 2p + 1$ one finds that

$$A_{k+1,k} = \frac{8\cdot 4^{p-1}}{2^{k-1}} = 2 \quad \text{and}$$
$$A_{k,k} = \frac{1}{2^{k-1}}\left[\binom{k}{k-1}4^p + k4^p\right] = \frac{2k4^p}{2^{2p}} = 2k.$$

It follows that $A_{k+1,k} = 2$ and $A_{k,k} = 2k$.

In complete analogy with Table 2, relations (20), (21) and (14), in this order, allow also the construction of Table 4. These recurrences make use of r_k, r'_k, s'_k and s''_k, but the expressions of s'_k and s''_k are the same as in Table 2 and are not repeated in Table 4.

Table 4. Expression of $R_{j,k}$ in terms of k and j

k	r'_k	r''_k	$R_{j,k}$
1	2	$2j-1$	$2j+2$
2	$4j+2$	$4j^2-3j-1$	$4j^2+4j+2$
3	$6j^2+2j+2$	$6j^3-5j^2+3j-1$	$6j^3+6j^2+6j+2$
4	$8j^3+2j^2+8j+2$	$8j^4-7j^3+11j^2-6j-1$	$8j^4+8j^3+14j^2+8j+2$
5	$10j^4+2j^3+18j^2+4j$	$10j^5-9j^4+23j^3-15j^2$	$10j^5+10j^4+26j^3+18j^2$
	$+2$	$+4j-1$	$+10j+2$

The coefficients $A_{x,k}$ of the polynomial $R_{j,k} = 2kj^k+2kj^{k-1}+\ldots+2k+2$ form an interesting numerical triangle presented in more detail and in a different format in Table 5.

The structure of this triangle is more complicated than of the one obtained for $K_{j,k}$ from Table 2.

Table 5. Numerical triangle of the coefficients $A_{x,k}$ of $R_{j,k} = A_{1,k}j^k + A_{2,k}j^{k-1} + \dots + A_{k,k}j + A_{k+1,k}$

k \ x	1	2	3	4	5	6	7	8	9
1	2	2							
2	4	4	2						
3	6	6	6	2					
4	8	8	14	8	2				
5	10	10	26	18	10	2			
6	12	12	42	32	30	12	2		
7	14	14	62	50	68	36	14	2	
8	16	16	86	72	130	80	52	16	2

Also from (41) we obtain that for $r \geq 1$ the following equalities hold:

$$A_{2r+1,k} = 2^{2r-k+1}\left[\sum_{s\geq r}\binom{k}{2s}\binom{s}{r} - \sum_{s\geq r+1}\binom{k}{2s+1}\binom{s-1}{r} + k\sum_{s\geq r+1}\binom{k}{2s}\binom{s-1}{r} + k\sum_{s\geq r}\binom{k}{2s+1}\binom{s}{r}\right] \text{ and}$$

$$A_{2r+2,k} = 2^{2r-k+2}\left[\sum_{s\geq r}\binom{k}{2s+1}\binom{s-1}{r-1} + k\sum_{s\geq r+1}\binom{k}{2s}\binom{s-1}{r}\right].$$

But standard binomial formulas[20] imply that

$$\sum_{s\geq r}\binom{k}{2s+1}\binom{s}{r} = 2^{k-2r-1}\binom{k-r-1}{r};$$

$$\sum_{s\geq r}\binom{k}{2s}\binom{s}{r} = 2^{k-2r-1}\frac{k}{r}\binom{k-r-1}{r-1};$$

$$\sum_{s\geq r+1}\binom{k}{2s+1}\binom{s-1}{r} = 2^{k-2r-1}\left[\binom{k-r-1}{r} - 2^2\binom{k-r}{r-1} + \right.$$
$$\left. + 2^4\binom{k-r+1}{r-2} - \dots + (-1)^{r-1}2^{2r-2}\binom{k-2}{1} + (-1)^r 2^{2r}\right] + (-1)^{r-1}k;$$
$$\sum_{s\geq r+1}\binom{k}{2s}\binom{s-1}{r} = k2^{k-2r-1}\left[\frac{1}{r}\binom{k-r-1}{r-1} - \frac{2^2}{r-1}\binom{k-r}{r-2} + \right.$$
$$\left. + \dots + (-1)^{r-1}2^{2r-2}\right] + (-1)^r(2^{k-1} - 1).$$

By substituting these values in the expressions of $A_{s,k}$ $(s\geq 3)$ we infer that for $r\geq 1$ the following equalities hold:

$$\left.\begin{aligned} A_{2r+1,k} &= \left(\frac{2k^2}{r} - 2k+2\right)\binom{k-r-1}{r-1} + (-1)^r 2^{2r}(k-1) - 2^2\left(\frac{k^2-k}{r-1} + 2\right)\binom{k-r}{r-2} \\ &+ 2^4\left(\frac{k^2-k}{r-2} + 2\right)\binom{k-r+1}{r-3} - \dots + (-1)^{r-1}2^{2r-2}(k^2-k+2) = \\ &= \frac{2k^{r+1}}{r!} + P_1(k); \end{aligned}\right\} \quad (43)$$

$$\left.\begin{aligned} A_{2r+2,k} &= \frac{2k^2}{r}\binom{k-r-1}{r-1} + (-1)^r 2^{2r+1}(k-1) - 2^3\left(\frac{k^2-k}{r-1} + 2\right)\binom{k-r}{r-2} + \\ &+ 2^5\left(\frac{k^2-k}{r-2} + 2\right)\binom{k-r+1}{r-3} - \dots + (-1)^{r-1}2^{2r-1}(k^2-k+2) = \\ &= \frac{2k^{r+1}}{r!} + P_2(k), \end{aligned}\right\} \quad (44)$$

where $P_1(k), P_2(k)$ are polynomials of degree r in k. For example, from (43) and (44) we deduce

$A_{3,k} = 2k^2-6k+6$, $A_{4,k} = 2k^2-8k+8$,

$A_{5,k} = k^3-9k^2+28k-30$, $A_{6,k} = k^3-11k^2+40k-48$,

$A_{7,k} = (k^4-18k^3+122k^2-369k+420)/3$,

$A_{8,k} = (k^4-21k^3+164k^2-564k+720)/3$,and so on.

5. Ratios and asymptotic ratios between numbers of conjugated 6-circuits and numbers of benzenoid rings in (j,k)-hexes

In order to calculate the asymptotic ratio L_j between the number of conjugated 6-circuits $R_{j,k}$ and the total number of benzenoid rings $nK_{j,k}$ as $k \to \infty$, we need the analytic expression (37) for $R_{j,k}$. From (37) it follows that, irrespective of the initial conditions of the problem, when $k \to \infty$ we obtain for a given j ($j \geq 1$):

$$\lim_{k\to\infty} \frac{R_{j,k}}{C_1 k r_1^k} = 1 \text{ , i.e. } R_{j,k} \sim C_1 k r_1^k \qquad (45)$$

(by using symbol $\sim$ for denoting $f(n) \sim g(n)$ whenever $\lim_{n\to\infty} \frac{f(n)}{g(n)} = 1$).

On the other hand, for $k \to \infty$, from (8) we obtain:

$$K_{j,k} \sim a r_1^k , \qquad (46)$$

therefore, taking into account relations (10), (11) and (38), the following corollary may be obtained.

Corollary 1. We have

$$L_j = \lim_{k\to\infty} \frac{R_{j,k}}{(jk+1)K_{j,k}} = \frac{1}{j}\left(1 + \frac{j-2}{\sqrt{j^2+4}}\right) \qquad (47)$$

for any $j \geq 1$.

In fact, $\lim_{k\to\infty} \frac{R_{j,k}}{(jk+1)K_{j,k}} = \lim_{k\to\infty} \frac{C_1 k r_1^k}{(jk+1) a r_1^k} = \frac{C_1}{aj} =$

$$= \frac{j+2+\sqrt{j^2+4}}{\sqrt{j^2+4}\,(\sqrt{j^2+4}+2)} = \frac{1}{j}\left(1 + \frac{j-2}{\sqrt{j^2+4}}\right). \quad \square$$

Values of the ratio $R_{j,k}/nK_{j,k} = R_{j,k}/(jk+1)K_{j,k}$ are presented in Table 6, including the asymptotic value L_j.

Table 6. Ratio $R_{j,k}/nK_{j,k}$ between the number of conjugated 6-circuits and the total number of benzenoid rings in (j,k)-hexes

j \ k	1	2	3	4	5	...	L_j ∞
1	0.667	0.667	0.625	0.615	0.603	...	0.553
2	0.500	0.520	0.512	0.510	0.508	...	0.500
3	0.400	0.420	0.421	0.422	0.423	...	0.426
4	0.333	0.350	0.354	0.356	0.357	...	0.362
5	0.286	0.300	0.303	0.305	0.306	...	0.311
...	...	...	...	...	...	...	...
10	0.167	0.173	0.174	0.175	0.176	...	0.178
...	...	...	...	...	...	...	...

In a previous report[18], the asymptotic limit $L_1 = \lim_{k \to \infty} R_{1,k}/nK_{1,k} = 1 - 1/\sqrt{5} \cong 0.553$ was mentioned (in this case $n = j+1$) for helicenes and isoarithmic (1,k)-hexes.

It can be seen that, according to Table 4, for $j \to \infty$

$$\frac{R_{j,1}}{nK_{j,1}} = \frac{R_{j,1}}{(j+1)K_{j,1}} = \frac{2j+2}{(j+1)(j+2)} \sim \frac{2}{j} \qquad (48)$$

i.e., the same asymptotic value as that obtained from (47) for $j \to \infty$.

Table 6 shows that in the totality of Kekulé structures for (1,k)-hexes, i.e. helicenes and isoarithmic polyhexes, more than half of the benzenoid rings are conjugated 6-circuits, and that this ratio decreases slowly with increasing k towards $L_1 \cong 0.553$; for the (2,k)-hexes, a similar conclusion holds, i.e. the ratio decreases slowly towards L_2 = 1/2 (an exception is the ratio 0.5 for anthracene,i.e. for $R_{2,1}$).On the contrary,all other values for this ratio from Table 6 increase with increasing k values towards L_j.Globally,with increasing j,the ratio $R_{j,k}/nK_{j,k}$ decreases tending towards 2/j,according to relation No.(48),in agreement with the decreasing fraction of conjugated 6-circuits in linearly condensed systems of increasing magnitude.

For the numerical data from Tables 1, 3 and 5,a simple computer program with 111 statements was devised and implemented on an HP-97 calculator.The listing of this program is presented in Fig.2.The upper part indicates how the initially selected data (j and k) are fed in.The program starts by pressing key A and ends by displaying the ratio $R_{j,k}/nK_{j,k}$. For retrieving the values $R_{j,k}$ and $K_{j,k}$ one recalls keys D and E,respectively.By simple modifications,one may change the program so as to print these three numbers for the final pair of selected j,k values. Statement LBL B should be ignored. Alternatively,taking into account that the program uses recurrences (13)-(21) for the given j value starting from k = 1 to the given k values one may include printing instructions for the values k, $R_{j,k}/nK_{j,k}$,$R_{j,k}$ and $K_{j,k}$ which are to be executed in each loop till the final selected k value is reached.

```
k  STO0
   P⇄S
   STO0
j  STO1
   P⇄S
   STO1

*LBLA
1
STOI
STO3
P⇄S
STO3
2
STO2
P⇄S
STO2
RCL1
STO5
P⇄S
STO5
RCL1
2
x
1
-
STO4
P⇄S
STO4
*LBLB
RCL5
RCL3
+
P⇄S
STO3
P⇄S
RCL1
RCL3
x
RCL1
RCL5
x
+
RCL5
-
P⇄S
STO5
P⇄S
RCL1
RCL2
x
RCL1
2
-
RCL3
x
+
RCL1
1
-
RCL4
x
+
RCL1
2
x
3
-
RCL5
x
+
P⇄S
STO4
P⇄S
RCL2
RCL3
+
RCL4
+
RCL5
2
x
+
P⇄S
STO2
RCL5
RCL3
2
x
+
STOE
RCL4
RCL3
-
RCL2
2
x
+
STOD
ISZI
RCLI
RCL1
x
1
+
RCLE
x
1/X
RCLD
x
STOC
RCLI
RCL0
X>Y?
GTOB
RCLC
RTN
R/S

R_j,k  RCLD
K_j,k  RCLE
```

Fig.2.Computer program for $R_{j,k}/nK_{j,k}$, $R_{j,k}$, and $K_{j,k}$.

6.Numbers of conjugated circuits in (1,k)-hexes and corresponding resonance energies

In the case when $j = 1$, the (j,k)-hexes become $(1,k)$-hexes isoarithmic with helicenes, zigzag catafusenes, etc., e.g. 1-3 for k = 4. Such systems were also called "fully benzenoid", because in each case one of their Kekulé structures has all rings as conjugated 6-circuits.

The numbers of Kekulé structures in this case form the Fibonacci sequence when k increases. We shall now examine the numbers of conjugated 6-, 10-, 14-, 18-circuits, etc. of such systems. The numbers of conjugated 6-circuits can be seen in Table 3 for $R_{1,k}$.

The numbers $R_{1,k}^{(t)}$ of conjugated t-circuits in (1,k)-hexes are presented in Table 7 (including all such circuits, not only the linearly independent ones).

Table 7. Numbers $R_{1,k}^{(t)}$ of conjugated t-circuits in (1,k)-hexes (upper part) and terms of their circuit polynomial (lower part)

t \ k	1	2	3	4	5
6	4	10	20	40	76
10	2	4	10	20	40
14	-	2	4	10	20
18	-	-	2	4	10
22	-	-	-	2	4
24	-	-	-	-	2
$K_{1,k}$	3	5	8	13	21
Circuit polynomial	$2x_1$	$5x_1$	$10x_1$	$20x_1$	$38x_1$
	x_2	$2x_2$	$5x_2$	$10x_2$	$20x_2$
	-	x_3	$2x_3$	$5x_3$	$10x_3$
	-	-	x_4	$2x_4$	$5x_4$
	-	-	-	x_5	$2x_5$
	-	-	-	-	x_6

The structure of Table 7 is quite simple: the same sequence is repeated, but with shifted k values, for various t values.

The circuit polynomial[11,12,19] $P_k^{(c)}$ is seen to bear a close relationship to the upper part of Table 7: it consists of the sum of all terms under the double line in Table 7. All coefficients of x_i's are half the values of $R_{1,k}^{(t)}$ from the upper part.

With Randić's parametrization of Dewar resonance energy values[11a], one can calculate with good results the resonance energy (RE) of conjugated hydrocarbons by adding contributions for conjugated (4m+2)-circuits and by subtracting contributions for conjugated 4m-circuits. In (1,k)-hexes there are no conjugated 4m-circuits. For any given k, the numbers $R_{1,k}^{(6)}$, $R_{1,k}^{(10)}$, $R_{1,k}^{(14)}$, and $R_{1,k}^{(18)}$ of conjugated 6-, 10-, 14-, and 18-circuits, respectively, can be easily calculated by recurrence, according to Table 7:

$$R_{1,k+1}^{(4(k+1)+1)} = R_{1,k}^{(4k+1)}$$

According to Randić's parametrization, for any given k in such (1,k)-hexes the resonance energy RE in eV is:

$$RE = (0.869R_{1,k}^{(6)} + 0.246R_{1,k}^{(10)} + 0.100R_{1,k}^{(14)} + 0.041R_{1,k}^{(18)})/K_{1,k}$$

We can calculate the asymptotic value of ΔRE for the difference between (1,k+1)- and (1,k)-hexes when $k \rightarrow \infty$, taking into account that $K_{1,k}/K_{1,k-1} \cong (1+\sqrt{5})/2 = z$ and that

$$\lim_{k \rightarrow \infty} (R_{1,k}/(k+1)K_{1,k}) = L_1 = 1 - 1/\sqrt{5}.$$

We obtain

$$\lim_{k \rightarrow \infty} \Delta RE = \frac{1}{zK_{1,k}} \lim_{k \rightarrow \infty} \Big[0.869(R_{1,k+1} - zR_{1,k}) + 0.246(R_{1,k} -$$

$$- zR_{1,k-1}) + 0.1(R_{1,k-1} - zR_{1,k-2}) + 0.041(R_{1,k-2} - zR_{1,k-3})\Big] =$$

$$= L_1(0.869 + 0.246z^{-1} + 0.100z^{-2} + 0.041z^{-3}) \cong 0.591 \text{ eV}.$$

The ratio RE/k has thus an asymptotic value of 0.591eV which is the increment in resonance energy on one further kinked annelation with an extra benzenoid ring.Actually,this limit is reached quite soon;on going from tetra- to pentahelicene already the increment in RE is 0.59eV,and it remains constant for succeeding kinked annelations with one benzenoid ring.

It should be mentioned that Randić's scheme[11] of calculating RE considers only the linearly independent circuits; however,Schaad and Hess[14] as well as Herndon[13] showed that inclusion of all circuits,as it was done in the present paper, gives small differences from Randić's treatment and that the resulted values improve slightly Randić's values.

7.Numbers of conjugated circuits in (j,k)-hexes

The sequence of conjugated 6-,10-,14-,...,-membered circuits in (j,k)-hexes with $j>1$ was investigated;the corresponding numbers are denoted by $R^{(6)}_{j,k}$,$R^{(10)}_{j,k}$,$R^{(14)}_{j,k}$,etc.,respectively,and in general by $R^{(4m+2)}_{j,k}$.

Two examples will illustrate the result;in addition to the data for (1,k)-hexes discussed above,we present numbers $R^{(4m+2)}_{2,k}$ and $R^{(4m+2)}_{3,k}$ in Table 8.

It may be seen that in all cases,irrespective of the j value,the sequence of $R^{(4m+2)}_{j,k}$ contains all values for lower k: for a given pair of j,k values,the numbers of conjugated (4m+2) -circuits where $m = 1,2,\ldots,jk+1$ take values from one and the

Table 8. Numbers of conjugated circuits $R_{2,k}^{(4m+2)}$ and $R_{3,k}^{(4m+2)}$ in (2,k)- and (3,k)-hexes.

j	k \ m	1	2	3	4	5	6	7	8	9	10
2	1	6	4	2							
	2	26	16	6	4	2					
	3	86	52	26	16	6	4	2			
	4	266	160	86	52	26	16	6	4	2	
3	1	8	6	4	2						
	2	50	36	22	8	6	4	2			
	3	236	168	100	50	36	22	8	6	4	2

same sequence. It will suffice therefore to analyze these sequences of $R_{j,k}^{(4m+2)}$ in terms of j and m, taking into account that k has a lower importance.

Table 9 presents the sequences $R_{j,k}^{(4m+2)}$ in a different arrangement, without repetitions for the same j value, in terms of decreasing m values: the parameter $y = jk+1-m$ is an increasing integer starting with zero.

It may be noted that the values $R_{j,k}^{(6)}$ are at the corners of the steps, and that on each horizontal line, increments are constant (cf. Table 9). A formula for these increments in terms of j, k and m, or of j, k and y, remains to be found. The formula for these increments $D_k(j)$ is similar to that of $r'_k(j)$ as presented in Table 4 : $D_1 = 2$, $D_2 = 4j+2$ (exactly as r'_k), $D_3 = 6j^2+4j+2$, $D_4 = 8j^3+6j^2+8j+2$ (differences are at the coefficient of j^{k-2}, i. e. the second term), etc.

Table 9. Numbers $R_{j,k}^{(4(jk-y)+6)}$ of conjugated circuits in (j,k)-hexes. Symbol " means ditto (vertically).

j	k \ y	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	1	2	4														
	2	"	"	10													
	3	"	"	"	20												
	4	"	"	"	"	40											
	5	"	"	"	"	"	76										
	6	"	"	"	"	"	"	142									
2	1	2	4	6													
	2	"	"	"	16	26											
	3	"	"	"	"	"	52	86									
	4	"	"	"	"	"	"	"	160	266							
3	1	2	4	6	8												
	2	"	"	"	"	22	36	50									
	3	"	"	"	"	"	"	"	100	168	236						
4	1	2	4	6	8	10											
	2	"	"	"	"	"	28	46	64	82							
	3	"	"	"	"	"	"	"	"	"	164	278	392	506			
5	1	2	4	6	8	10	12										
	2	"	"	"	"	"	"	34	56	78	100	122					
	3	"	"	"	"	"	"	"	"	"	"	"	244	416	588	760	932

In Table 9 all numerical values of $R_{j,k}^{(4m+2)} = R_{j,k}^{(4(jk-y)+6)}$ are the same for j = 1 as in Table 7, and for j = 2 or 3 as in Table 8.

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8. List of main symbols

$A_{x,k}$	= coefficients of polynomial $R_{j,k} = A_{1,k}j^k + .. + A_{k+1,k}$
2DC	= two-digit code (L-transform) for catafusenes
3DC	= three-digit code for catafusenes in terms of 0,1,2
F_i	= i-th Fibonacci number ($F_0 = F_1 = 1$), i. e. number of Kekulé structures in [i-2]helicene and in all isoarithmic catafusenes ($F_i = K_{1,i-2}$)
j	= number of benzenoid rings in each linear portion of (j,k)-hexes
k	= number of linear portions of (j,k)-hexes
$K_{j,k}$	= number of Kekulé structures in (j,k)-hexes, or generalized Fibonacci numbers
L_j	= asymptotic ratio $R_{j,k}/nK_{j,k}$ for $k \rightarrow \infty$

m	= natural integer for conjugated $(4m+2)$-circuits
n	= total number ($n = jk + 1$) of benzenoid rings in (j,k)-hexes
r_k, r'_k, r''_k	= numbers of conjugated 6-circuits for (i)-, (ii)-, and (iii)-type successors, respectively, in the annelation of (j,k)-hexes with another linear portion on going from k to $k+1$
$R_{j,k}$ or $R^{(6)}_{j,k}$	= number of conjugated 6-circuits in (j,k)-hexes
$R^{(4m+2)}_{j,k}$	= number of conjugated $(4m + 2)$-circuits in (j,k)-hexes
RE	= resonance energy
s_k, s'_k, s''_k	= number of Kekulé structures for (i)-, (ii)-, and (iii)-type successors, respectively, in the annelation of (j,k)-hexes with another linear portion of j benzenoid rings (from k to $k+1$)
t	= natural integer ($t = 4m + 2$)
y	= parameter for Table 9 ($y = jk + 1 - m$)
z	= asymptotic ratio of successive Fibonacci numbers $K_{1,k}/K_{1,k-1} = F_{k+2}/F_{k+1}$ for $k \rightarrow \infty$