Monatshefte für Chemie 118, 541—552 (1987)

Monatshefte für Chemie
Chemical Monthly

Topological Properties of Benzenoid Systems. XXXV. Number of *Kekulé* Structures of Multiple-Chain Aromatics

Ivan Gutman[a] and **Sven J. Cyvin**[b,*]

[a] Faculty of Science, University of Kragujevac, YU-34000 Kragujevac, Yugoslavia

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

(Received 12 March 1986. Accepted 5 May 1986)

Recurrence relations and explicit combinatorial expressions are derived for the number of *Kekulé* structures of certain multiple-chain condensed aromatics.

(Keywords: Aromatics; Kekulé structures)

Topologische Eigenschaften benzenoider Systeme, 35. Mitt.: Anzahl von Kekulé-Strukturen von Mehrfachketten-Aromaten

Es werden Beziehungen und explizite kombinatorische Ausdrücke für die Anzahl möglicher *Kekulé*-Strukturen bestimmter mehrfachkettiger kondensierter Aromaten abgeleitet.

Introduction

General

The enumeration of *Kekulé* structures of polycyclic aromatic (benzenoid) hydrocarbons has been studied by various authors over a quite long period of time [1–30]. This research field has accelerated tremendously during the last years. Notice that 73 percent of the references cited here are from 1980 or later. Combinatorial expressions are known for the number of *Kekulé* structures of numerous particular classes of aromatic hydrocarbons [3, 4, 10–13, 16, 17, 19, 21–30], yet a general solution of the enumeration problem (in terms of explicit formulas) has not been reached and is probably not to be expected. One of the present authors considered recently [19] the single-chain aromatics and offered a recursive technique

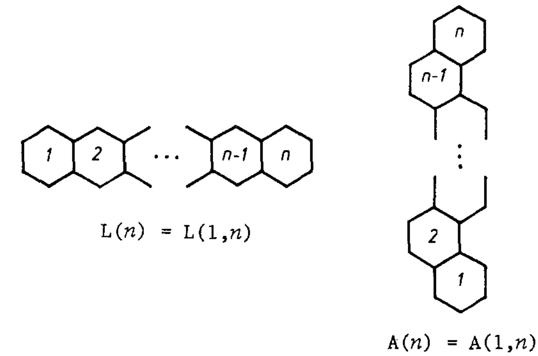


Fig. 1. Single-chain ($1 \times n$) aromatics

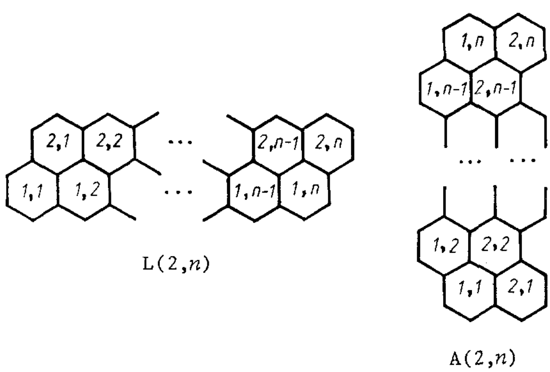


Fig. 2. Double-chain ($2 \times n$) aromatics

for the calculation of their *Kekulé* structure count; similar results have been reported also elsewhere [3, 7]. In the present work we wish to extend the previous results [19] to multiple-chain aromatics.

Previous Results

Consider for the beginning the following single-chain aromatics: the linear polyacene $L(n)$ and the zigzag polyacene $\mathrm{A}(n)$, which are presented on Fig. 1. It is well known that $\mathrm{L}(n)$ has $n+1$ *Kekulé* structures [3] whereas the number of *Kekulé* structures of $\mathrm{A}(n)$ is equal to F_{n+1} when F_n is the $(n+1)$-th *Fibonacci* number [3, 21]. (Recall that $F_0 = F_1 = 1$, $F_2 = 2, \ldots$, etc. and $F_{n+2} = F_{n+1} + F_n$.) We shall denote these facts as

$$K\{\mathrm{L}(n)\} = n + 1, \qquad K\{\mathrm{A}(n)\} = F_{n+1}.$$

By joining two L(n)-fragments we obtain the double-chain homologue of the linear polyacene, which will be denoted by L(2, n). The double chain homologue of A(n) is constructed analogously (see Fig. 2).

In the same manner we define the m-chain homologues of L(n) and A(n) and denote them by L(m, n) and A(m, n), respectively (see Fig. 3).

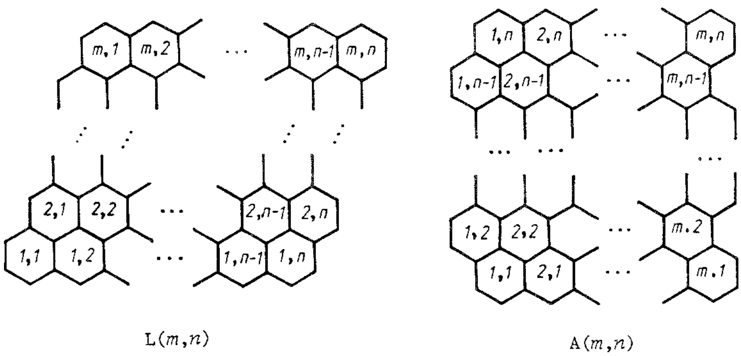


Fig. 3. Multiple-chain ($m \times n$) aromatics

It is a classical result of *Kekulé* structure enumeration that [3, 4]

$$K\{\mathrm{L}(m,n)\} = \binom{m+n}{m} = \binom{m+n}{n} = \frac{(m+n)!}{m!\,n!} \tag{1}$$

No combinatorial formula for $K\{\mathrm{A}(m,n)\}$ is known in the literature in spite of the fact that the class A(m, n) embraces a variety of important aromatic hydrocarbons. In the present paper we wish to contribute to this problem.

Results and Discussion

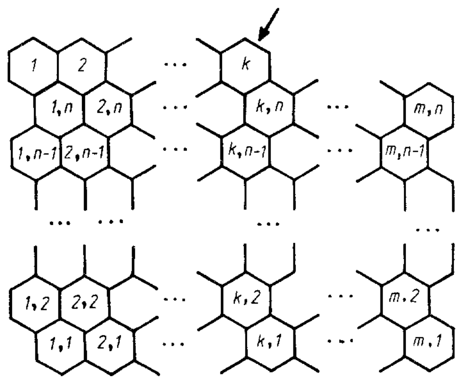
Auxiliary Class

In order to calculate $K\{\mathrm{A}(m,n)\}$ consider a more general (auxiliary) benzenoid system, namely A(m, n, k), obtained by attaching k hexagons to A(m, n). The way in which the hexagons of A(m, n, k) are labeled can be seen from Fig. 4.

By definition, $\mathrm{A}(m,n,0) = \mathrm{A}(m,n)$ and $\mathrm{A}(m,n,m) = \mathrm{A}(m,n+1)$.

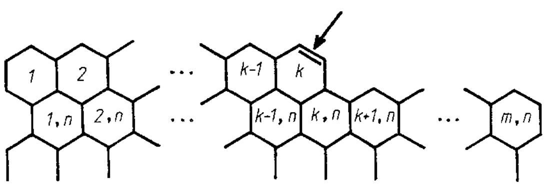
The Main Recurrence Relation

The *Kekulé* structures of A(m, n, k) can be divided into two groups. In the first group are those in which the edge indicated by an arrow in Fig. 4 is

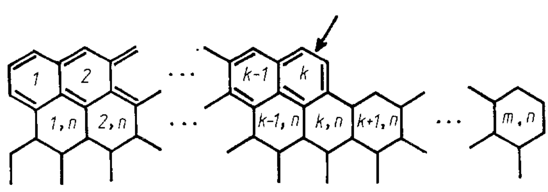


A(m,n,k)

Fig. 4. The multiple $(m \times n)$ zigzag chain aromatics augmented by a row of k benzenoid rings



I



II

Fig. 5. Definition of two types of *Kekulé* structures for A(m,n,k)

a double bond (see formula I of Fig. 5). In the second group are those *Kekulé* structures of A (m, n, k) in which the edge indicated by the arrow is a single bond. In that case a number of double bonds must be located at certain positions of A (m, n, k), as shown by formula II of Fig. 5. The total *Kekulé* structure count of A (m, n, k) is equal to the sum of the number of *Kekulé* structures of these two kinds. From formula I it is evident that the number of *Kekulé* structures of the first kind is equal to the number of *Kekulé* structures of the system obtained by deleting the k-th hexagon from $A(m,n,k)$. Similarly, formula II implies that the number of *Kekulé* structures of the second kind is equal to the number of *Kekulé* structures of the system obtained by deleting from $A(m,n,k)$ the hexagons, $1, 2, \ldots, k$, $(1,n)$, $(2,n), \ldots, (k,n)$. It is not difficult to see that the latter deletion process leads to $A(m, n-1, m-k)$.

Hence we arrive at the recurrence relation

$$K\{A(m,n,k)\} = K\{A(m,n,k-1)\} + K\{A(m,n-1,m-k)\} \quad (2)$$

which holds for $m \geqslant k > 0$ and $n \geqslant 1$. In the case when $k = 0$ and $n \geqslant 2$, instead of (2) we have

$$K\{A(m,n,0)\} = K\{A(m,n-1,m-1)\} + K\{A(m,n-2,0)\} \quad (3)$$

As a matter of fact, because $A(m,n,0) = A(m,n-1,m)$, formula (3) is a special case of (2).

The recurrence relations (2) and (3) together with the initial conditions

$$K\{A(m,0,k)\} = K\{L(k)\} = k+1 \quad (4)$$

and

$$K\{A(m,1,0)\} = K\{L(m)\} = m+1 \quad (5)$$

enable the calculation of $K\{A(m,n,k)\}$ and $K\{A(m,n)\}$ for all values of m, n and k.

We wish to make the subsequent formulas also valid for m, n, k equal to zero. Then it is expedient to define $K\{L(0)\} = 1$ in consistence with (4) and (5). Furthermore, we define for all m and n: $A(m,0) = A(0,n) = L(0)$. This is the trivial case of "no hexagons".

Summation Formulas

By a repeated application of (2) and (3) we obtain a series of identities relating $K\{A(m,n)\}$ with $K\{A(m,n-j,i)\}$, $i = 0, 1, \ldots, m$. Here j is a fixed parameter. For $j = 2, 3, 4$ and 5 these identities read as follows.

$$K\{A(m,n)\} = \sum_{i=0}^{m} K\{A(m,n-2,i)\} \quad (n \geqslant 2) \quad (6)$$

$$K\{A(m,n)\} = \sum_{i=0}^{m} (i+1)\, K\{A(m,n-3,i)\} \quad (n \geqslant 3) \quad (7)$$

$$K\{A(m,n)\} = \sum_{i=0}^{m} (i+1)\left(m+1-\frac{i}{2}\right) K\{A(m,n-4,i)\} \quad (n \geqslant 4) \quad (8)$$

$$K\{A(m,n)\} = \sum_{i=0}^{m} \frac{1}{2}(i+1)\left[(m+1)(m+2)-\frac{i}{3}(i+2)\right] K\{A(m,n-5,i)\} \quad (n \geqslant 5) \quad (9)$$

With increasing values of j, the above equations become more and more complex. The analogous identities for $j > 5$ have not been derived.

Recurrence Relations for $K\{A(m,n)\}$ with Fixed Values of m

First we have the trivial "recurrence" relation for $m = 0$:

$$K\{A(0,n)\} = K\{A(0,0)\} \tag{10}$$

In the case of the single zigzag chains ($m = 1$), Eq. (3) gives immediately

$$K\{A(1,n,0)\} = K\{A(1,n-1,0)\} + K\{A(1,n-2,0)\}$$

i.e.

$$K\{A(1,n)\} = K\{A(1,n-1)\} + K\{A(1,n-2)\}$$

i.e.

$$K\{A(n)\} = K\{A(n-1)\} + K\{A(n-2)\} \quad (n \geqslant 2) \tag{11}$$

which is the well-known *Fibonacci* recurrence relation [3, 21].

In the case of the double zigzag chains ($m = 2$), Eqs. (2) and (3) result in

$$K\{A(2,n,1)\} = K\{A(2,n,0)\} + K\{A(2,n-1,1)\} \tag{11 a}$$

and

$$K\{A(2,n,0)\} = K\{A(2,n-1,1)\} + K\{A(2,n-2,0)\} \tag{11 b}$$

Eq. (11 b) can be rewritten as

$$K\{A(2,n-1,1)\} = K\{A(2,n,0)\} - K\{A(2,n-2,0)\} \tag{11 c}$$

which immediately gives

$$K\{A(2,n,1)\} = K\{A(2,n+1,0)\} - K\{A(2,n-1,0)\} \tag{11 d}$$

Substitution of (11 c) and (11 d) back into (11 a) gives

$$K\{A(2,n)\} = 2K\{A(2,n-1)\} + K\{A(2,n-2)\} - K\{A(2,n-3)\} \quad (n \geqslant 3) \tag{12}$$

An analogous, yet much more laborious calculation results in recurrence relations for the *Kekulé* structure count of $A(m,n)$ for higher values of m. For $m = 3, 4$ and 5 these relations are:

$$K\{A(3,n)\} = 2K\{A(3,n-1)\} + 3K\{A(3,n-2)\} - K\{A(3,n-3)\} - K\{A(3,n-4)\} \quad (n \geqslant 4) \tag{13}$$

$$K\{A(4,n)\} = 3K\{A(4,n-1)\} + 3K\{A(4,n-2)\} - 4K\{A(4,n-3)\} - K\{A(4,n-4)\} + K\{A(4,n-5)\} \quad (n \geqslant 5) \tag{14}$$

$$K\{A(5,n)\} = 3K\{A(5,n-1)\} + 6K\{A(5,n-2)\} - 4K\{A(5,n-3)\} - 5K\{A(5,n-4)\} + K\{A(5,n-5)\} + K\{A(5,n-6)\} \quad (n \geqslant 6) \tag{15}$$

The benzennoid members of relevance to Eqs. (11) and (12) were studied extensively by *Randić* [9] under the names of the phenanthrene-chrysene and pyrene-benzoperylene family, respectively. Eqs. (11)–(13) are special cases of recurrence formulas involving certain polynomials as given by *Ohkami* and *Hosoya* [23], while (14) and (15) are given here for the first time.

Combinatorial Expressions for $K\{\mathrm{A}(m,n)\}$ with Fixed Values of n

In this section we deduce explicit analytical expressions for the number of *Kekulé* structures of $\mathrm{A}(m,n)$, where n has a fixed value.

For $n = 1$ we have

$$K\{\mathrm{A}(m,1)\} = m + 1 \tag{16}$$

which is an obvious corollary of (5).

In order to enumerate the *Kekulé* structures of $\mathrm{A}(m,2)$, set $n = 2$ into (6). Then because of (4),

$$K\{\mathrm{A}(m,2)\} = \sum_{i=0}^{m} K\{\mathrm{A}(m,0,i)\} = \sum_{i=0}^{m} (i+1)$$

which gives

$$K\{\mathrm{A}(m,2)\} = \frac{1}{2}(m+1)(m+2) \tag{17}$$

This is consistent with the known (and previously mentioned) result

$$K\{\mathrm{L}(m,2)\} = \binom{m+2}{2}$$

since $\mathrm{A}(m,2) = \mathrm{L}(m,2)$.

For higher values of n the procedure is the same: one has to set $n = 3$ into (7), $n = 4$ into (8) or $n = 5$ into (9), etc. An elementary, but somewhat more complex calculation gives then

$$K\{\mathrm{A}(m,3)\} = \frac{1}{3!}(m+1)(m+2)(2m+3) \tag{18}$$

$$K\{\mathrm{A}(m,4)\} = \frac{1}{4!}(m+1)(m+2)(5m^2+15m+12) \tag{19}$$

$$K\{\mathrm{A}(m,5)\} = \frac{4}{5!}(m+1)(m+2)(2m+3)(2m^2+6m+5) \tag{20}$$

Note that formula (18) has been first obtained by *Gordon* and *Davison* [3] and recently deduced in another manner by *Ohkami* and *Hosoya* [23]. Three further results of the same type are obtained by combining the identities (6)–(9) with the combinatorial expressions (25)–(27) of the subsequent section. They read:

$$K\{\mathrm{A}(m,6)\} = \frac{1}{6!}(m+1)(m+2)(61m^4+366m^3+845m^2+888m + 360) \quad (21)$$

$$K\{\mathrm{A}(m,7)\} = \frac{2}{7!}(m+1)(m+2)(2m+3)(68m^4+408m^3+949m^2 + 1\,011m+420) \quad (22)$$

$$K\{\mathrm{A}(m,8)\} = \frac{1}{8!}(m+1)(m+2)(1\,385m^6+12\,465m^5+47\,517m^4 + 98\,127m^3+115\,810m^2+74\,136m+20\,160) \quad (23)$$

Contrary to (16)–(18), the formulas (19)–(23) have not been known previously. It is noted that all the polynomials of (17)–(23) have the common factor $(m+1)(m+2)$. For the odd-number m values 3, 5 and 7 they have $(2m+3)$ in addition.

Combinatorial Expressions for $K\{\mathrm{A}(m,n,k)\}$ with Fixed Values of n

It can be shown that the following identity holds for $m \geqslant k \geqslant 0$ and $n \geqslant 1$.

$$K\{\mathrm{A}(m,n,k)\} = \sum_{i=0}^{k} K\{\mathrm{A}(m,n-1,m-i)\} \quad (24)$$

Setting $n=1$ into (24) and using (4) one attains at

$$K\{\mathrm{A}(m,1,k)\} = \sum_{i=0}^{k} K\{\mathrm{A}(m,0,m-i)\} = \sum_{i=0}^{k} (m-i+1)$$

which finally results in

$$K\{\mathrm{A}(m,1,k)\} = (k+1)\left(m+1-\frac{k}{2}\right) \quad (25)$$

In a similar manner we deduce

$$K\{\mathrm{A}(m,2,k)\} = \frac{1}{2}(k+1)\left[(m+1)(m+2)-\frac{k}{3}(k+2)\right] \quad (26)$$

and

$$K\{\mathrm{A}(m,3,k)\} = \frac{1}{6}(k+1)\left\{\frac{k}{4}(k+1)(k+2) + \left[(m+1)(m+2)-\frac{k}{2}(k+2)\right](2m+3)\right\} \quad (27)$$

Conclusion for Multiple Zigzag Chain

Concluding the consideration of the multiple zigzag chain aromatics we may summarize that the derived formulas enable us to enumerate the *Kekulé* structures for quite sizable aromatics of the type $A(m,n)$, in addition to the auxiliary type $A(m,n,k)$. As far as the cases with $k = 0$ are concerned we have listed the K values in numerical form in Table 1. The second column constitutes the *Fibonacci* numbers. The eight first numerals of the third column have also been reported by *Randić* [9]. The values below the staircase-line (Table 1) are obtainable by (a) the recurrence relations (10)–(15), if the values above the staircase are known. All K values above the bottom line ($n \leqslant 8$) are available through (b) the explicit formulas (16)–(23). The values between the two lines were calculated by both methods (a) and (b). The identity of the results gives a convincing check of the correctness of our formula apparatus.

Table 1. *Number of Kekulé structures (K) for the $A(m,n)$ aromatics with $m \leqslant 5$ and $n \leqslant 10$*

	$m=0$	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$
$K\{A(m,0)\}$	1	1	1	1	1	1
$K\{A(m,1)\}$	1	2	3	4	5	6
$K\{A(m,2)\}$	1	3	6	10	15	21
$K\{A(m,3)\}$	1	5	14	30	55	91
$K\{A(m,4)\}$	1	8	31	85	190	371
$K\{A(m,5)\}$	1	13	70	246	671	1 547
$K\{A(m,6)\}$	1	21	157	707	2 353	6 405
$K\{A(m,7)\}$	1	34	353	2 037	8 272	26 585
$K\{A(m,8)\}$	1	55	793	5 864	29 056	110 254
$K\{A(m,9)\}$	1	89	1 782	16 886	102 091	457 379
$K\{A(m,10)\}$	1	144	4 004	48 620	358 671	1 897 214

Combinatorial Expression for $K\{L(m,n,k)\}$

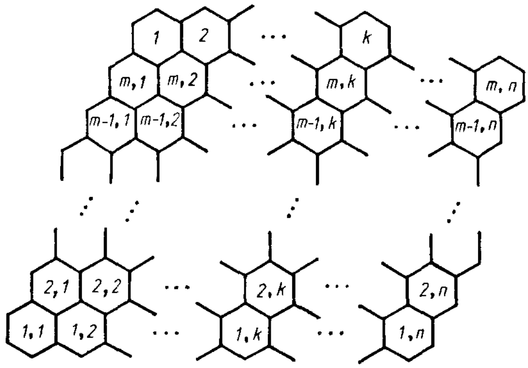
In full analogy to the benzenoid system $A(m,n,k)$ we may define the classes $L_0(m,n,k)$ and $L(m,n,k)$, which are obtained by attaching k hexagons to $L(m,n)$; see Fig. 6.

Since $L_0(m,n,k)$ has an odd number of atoms, we immediately see that

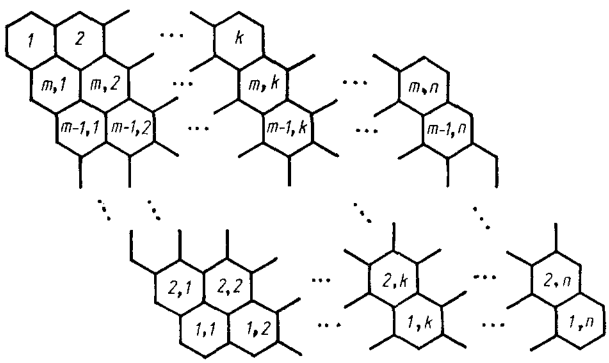
$$K\{L_0(m,n,k)\} = 0$$

provided that $0 < k < n$.

The number of *Kekulé* structures of $L(m,n,k)$ is non-zero. By definition $L(m,n,0) = L(m,n)$ and $L(m,n,n) = L(m+1,n)$. Note also that $L(m,n,n-1) = L(n-1,m+1,m)$.



$L_0(m,n,k)$



$L(m,n,k)$

Fig. 6. Two ways in which the multiple linear ($m \times n$) chain aromatics can be augmented by a row of k benzenoid rings

A method equivalent to that used for the derivation of (2) results now in

$$K\{L(m,n,k)\} = K\{L(m,n,k-1)\} + K\{L(m,n-k,0)\} \qquad (k \geqslant 1)$$

Taking into account Eq. (1), we have

$$K\{L(m,n,k)\} = K\{L(m,n,k-1)\} + \binom{m+n-k}{m} \tag{28}$$

A repeated application of (28) leads to the following summation formula

$$K\{\mathrm{L}(m,n,k)\} = \sum_{i=0}^{k} \binom{m+n-i}{m} \tag{29}$$

For $k=0$, Eq. (29) gives correctly the old result (1). For $k=n$ the summation gives

$$K\{\mathrm{L}(m,n,n)\} = K\{\mathrm{L}(m+1,n)\} = \binom{m+n+1}{m+1}$$

in accord with (1). A novel formula emerges for $0<k<n$, viz.

$$K\{\mathrm{L}(m,n,k)\} = \binom{m+n+1}{m+1} - \binom{m+n-k}{m+1} \tag{30}$$

Acknowledgement

We wish to thank Prof. *Milan Randić* (Ames, Iowa) for helpful suggestions for improvements in the manuscript.

References

[1] *Wheland GW* (1935) J Chem Phys 3: 356
[2] *Pullman A* (1946) Compt Rend 222: 736
[3] *Gordon M, Davison WHT* (1952) J Chem Phys 20: 428 (1952)
[4] *Yen TF* (1971) Theoret Chim Acta 20: 399
[5] *Herndon WC* (1973) Tetrahedron 29: 3
[6] *Herndon WC* (1974) J Chem Educ 51: 10
[7] *Cvetković D, Gutman I* (1974) Croat Chem Acta 46: 15
[8] *Randić M* (1976) J Chem Soc Faraday II 72: 232
[9] *Randić M* (1980) Internat J Quant Chem 17: 549
[10] *Biermann D, Schmidt W* (1980) Israel J Chem 20: 312
[11] *Polansky OE, Gutman I* (1980) Match (Mülheim) 8: 269
[12] *Jiang Y* (1980) Sci Sinica 23: 847
[13] *Eilfeld P, Schmidt W* (1981) J Electron Spectr Rel Phenom 24: 101
[14] *Džonova-Jerman-Blažič B, Trinajstić N* (1982) Comp Chem 6: 121
[15] *Džonova-Jerman-Blažič B, Trinajstić N* (1982) Croat Chem Acta 55: 347
[16] *Cyvin SJ* (1982) Monatsh Chem 113: 1127
[17] *Gutman I* (1982) Croat Chem Acta 55: 371
[18] *Brown RL* (1983) J Comput Chem 4: 556
[19] *Cyvin SJ* (1983) Monatsh Chem 114: 13
[20] *Cyvin SJ* (1983) Monatsh Chem 114: 525
[21] *Cyvin SJ* (1983) Acta Chim Hung 112: 281
[22] *Balaban AT, Tomescu I* (1983) Match (Mülheim) 14: 155
[23] *Ohkami N, Hosoya H* (1983) Theoret Chim Acta 64: 153
[24] *El-Basil S, Křivka P, Trinajstić N* (1984) Croat Chem Acta 57: 339
[25] *Balaban AT, Tomescu I* (1984) Croat Chem Acta 57: 391

[26] *Gutman I* (1985) Match (Mülheim) 17:3
[27] *Gutman I* (1985) Coll Sci Papers Fac Sci Kragujevac 6: 35
[28] *Balaban AT, Tomescu I* (1985) Match (Mülheim) 17: 91
[29] *Cyvin SJ* (1985) J Mol Struct (Theochem) 133: 211
[30] *Cyvin SJ* (1986) Monatsh Chem 117: 33

Note added in proof: Further studies have resulted in (a) a convenient recursive method for deducing $K\{A(m, n, k)\}$ and $K\{A(m, n)\}$, (b) formulas for the latter quantities with $n = 9$ and $n = 10$, (c) a proof about the existence of the common factors $(m + 1)$, $(m + 2)$ and $(2m + 3)$.