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Constant-isomer series of benzenoid hydrocarbons

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Summary. The constant-isomer series are studied in relation to the periodic table of benzenoid hydrocarbons. General properties of the table are formulated in terms of explicit expressions. In particular a general expression for the formulas (C_nH_s) of the ground forms of the constant-isomer series was achieved. The numbers of the isomers (cardinalities of C_nH_s) are divided into to parts. Explicit equations are given for the first part of the cardinalities.

Key words: Benzenoid hydrocarbons – Periodic table – Isomer enumeration

1. Introduction

A benzenoid (system) has a chemical counterpart in a polycyclic hydrocarbon (chemically known or unknown), for which the formula C_nH_s can be written. In the enumeration of benzenoid isomers one tries to find the number of non-isomorphic benzenoid systems corresponding to a given formula C_nH_s. The reader is referred to two recent monographs [1, 2] for a general background and the definitions adopted here.

A pioneering work on benzenoid isomers is due to Dias [3, 4], who invented the periodic table for benzenoid hydrocarbons [3–6]. His enumerations of benzenoid isomers were preceded by Elk [7]. The enumeration and classification of benzenoids according to their numbers of internal vertices, as executed by the Düsseldorf–Zagreb group [8, 9] is virtually a benzenoid isomer enumeration. This is also the case for the enumeration of Stojmenović et al. [10], who employed the perimeter length as the leading parameter and classified the generated systems according to their numbers of hexagons. Recently the works on benzenoid isomer generation and enumeration by Dias [3–5, 11–13] were supplemented and corrected for several errors [14–16].

Much of the enumeration work by Dias [3–6, 11–13] deals with special strictly pericondensed benzenoids which form constant-isomer series. This is to say that the number of isomers for certain formulas C_nH_s are preserved on circumscribing all the benzenoids belonging to such a formula. This topic was recently revisited [17–19].

In the present work some further studies have been done on the properties of the periodic table of benzenoid hydrocarbons. They led to new general formulations, especially in connection with the constant-isomer series. Also the enumeration data of benzenoid isomers were supplemented.

1. Periodic table for benzenoid hydrocarbons

The periodic table for benzenoid hydrocarbons is a scheme of the possible formulas C_nH_s, which are compatible with benzenoid systems. The formulas are arranged in a coordinate system (d_s, n_i). Here d_s denotes the number of tree disconnections with reference to the internal edges of the benzenoid [3, 4] and is also called the Dias parameter [14, 20]. The symbol n_i is used to denote the number of internal vertices.

Here we are using the version of the periodic table [14] which takes into account all benzenoids, both even-carbon and odd-carbon systems. They have both n and s even or both of these coefficients odd, respectively, in the C_nH_s formulas. Thus our table is a fusion of the two periodic tables given separately by Dias [5]. The formula C_6H_6 (for benzene) is not included in the table. The formulas are obtained recursively by the scheme:

$$\begin{tikzcd} C_nH_s(d_s, n_i) \arrow[r] \arrow[d] & C_{n+4}H_{s+2}(d_{s+1}, n_i) \\ C_{n+3}H_{s+1}(d_s, n_i+1) & \end{tikzcd}$$

As the initial condition one has $C_{10}H_8$ (0, 0), the formula for naphthalene, at the upper-left corner. The table extends infinitely to the right and downwards. To the left it is limited by a staircase-like boundary, which is fully determined by the maximum number of internal vertices, $(n_i)_{\max}$, for a given number of hexagons (h) of the benzenoids, viz. [21, 22]:

$$(n_i)_{\max} = 2h + 1 - \lceil (12h - 3)^{1/2} \rceil \tag{1}$$

3. Notation

Let the formula C_nH_s for a benzenoid be denoted alternatively as:

$$C_nH_s \equiv (n; s)$$

The cardinality of C_nH_s, written $|C_nH_s|$, is the number of benzenoid isomers or the number of nonisomorphic benzenoid systems with that formula. An alternative notation is:

$$|C_nH_s| \equiv |n; s|$$

4. Circumscribing

The generation of a (larger) benzenoid by circumscribing another (smaller) benzenoid by hexagons is an important process in the studies of benzenoid isomers [3–5]. Let B be a benzenoid which can be circumscribed and has the formula C_nH_s. Further, let $B' \equiv$ circum-B and have the formula $C_{n'}H_{s'}$. Then [14]:

$$(n'; s') = (n + 2s + 6; s + 6) \tag{2}$$

Repeated application of Eq. (2) is covered by the following explicit formula:

$$j\text{-circum-B:} \quad (6j^2 + 2sj + n; 6j + s)$$

5. Classes of benzenoids

It is useful to define new classes of benzenoids in connection with the staircase-like boundary of the periodic table for benzenoid hydrocarbons. But first we recall the well-known class of *extremal* benzenoids corresponding to the "extremal animals" of Harary and Harborth [21]. They are defined by having $n_i = (n_i)_{\max}$ for a given h, governed by Eq. (1). It is easily found that the extremal benzenoids, say A, have the formulas given by:

$$\text{A:} \quad (2h + 1 + \lceil (12h - 3)^{1/2} \rceil; 3 + \lceil (12h - 3)^{1/2} \rceil)$$

for $h = 1, 2, 3, \ldots$. Notice that benzene (C_6H_6) is reckoned among the extremal benzenoids.

Any formula for the extremal benzenoids (except benzene) is obviously situated on the staircase-like boundary so that it has no formula in the same row to the left of it. If it in addition has no formula in the same column above it, then the corresponding benzenoids shall be referred to as *protrusive*. All the pericondensed protrusive benzenoids are generated by circumscribing the extremal benzenoids. Consequently they have the formulas given by:

$$\text{circum-A:} \quad (2h + 13 + 3\lceil (12h - 3)^{1/2} \rceil; 9 + \lceil (12h - 3)^{1/2} \rceil)$$

In addition comes naphthalene ($C_{10}H_8$), which also by definition is a protrusive benzenoid, the only catacondensed system of this class.

The *extreme* benzenoids (or *extreme-left* if one wants to make it clearer) are defined as those benzenoids which have formulas on the staircase-like boundary so that in each case, there is no formula in the same row to the left. Hence all extremal benzenoids (except benzene) are also extreme. But there exist extreme-left benzenoids, say x, which are not extremal and may be of special interest. Their formulas are found one step up and one step to the right from every formula for the pericondensed protrusive benzenoids. Then, from the formula for circum-A given above one obtains readily:

$$\text{x:} \quad (2h + 14 + 3\lceil (12h - 3)^{1/2} \rceil; 10 + \lceil (12h - 3)^{1/2} \rceil)$$

The pericondensed extreme-left benzenoids constitute a subclass of the strictly pericondensed benzenoids in the sense of Dias [11, 19]; they are defined by having all their internal vertices connected and no catacondensed appendages. Phenalene, $C_{13}H_9$, which has only one internal vertex, is reckoned among the strictly pericondensed benzenoids. An equivalent definition in a most succint form reads:

A strictly pericondensed benzenoid is a benzenoid with all its internal edges connected.

6. Constant-isomer series

6.1. Preliminaries

Already in his early paper Dias [3] pointed out that the formulas $C_{24}H_{12}, C_{54}H_{18}, C_{96}H_{24}, \ldots$ correspond to a single isomer each. They pertain to coronene, circumcoronene, dicircumcoronene, ... This is a one-isomer series. Later the other five one-isomer series were detected [5, 11, 12] and are collected elsewhere [14, 17]. The first constant-isomer series with more than one isomer which was found, again due to Dias [11], consists of the formulas $C_{22}H_{12}, C_{52}H_{18}, C_{94}H_{24}, \ldots$. Here $C_{22}H_{12}$ comprises the three isomers anthanthrene, benzo[*ghi*]perylene and triangulene, while the subsequent formulas correspond to successive circumscribing of these three benzenoids. All the formulas in question describe constantly three isomers each.

In general a constant-isomer series is defined by the formulas $C_{6j^2+2sj+n}H_{s+6j}$ when, for the cardinalities:

$$|n; s| = |6j^2 + 2sj + n; s + 6j| \tag{3}$$

are equal for $j = 0, 1, 2, \ldots$. The formula for $j = 0$ is assumed to correspond to the set of the smallest benzenoids belonging to the constant-isomer series. They are referred to as the *ground forms* [14]. In the terminology of Dias [17–19] most of them are base excised internal structures. Only the ground forms benzene and naphthalene are the so-called ultimate excised internal structures.

Where are the formulas for the ground forms found in the periodic table for benzenoid hydrocarbons? It appears that they are extremal benzenoids (A) which do not fall under the circumscribed extremal benzenoids (circum-A). The latter classes contain the higher members of the constant-isomer series and are all protrusive benzenoids. In consequence, the ground form formulas are obtained by inserting $h = 1, 2, 3, 4, \ldots$ into the expression for A above, but skipping the formulas which coincide with circum-A. This occurs for the h values:

$$h' = h + 3 + \lceil (12h - 3)^{1/2} \rceil \tag{4}$$

viz. $h' = 7, 10, 12, 14, 16, 19, \ldots$ (an irregular sequence).

In order to inspect the ground forms more closely it is expedient to switch over from h to s as the leading parameter. Then, instead of the elaborate specification of the above paragraph, we shall be able to present explicitly the general formula for ground forms. But first some preparations are necessary.

6.2. Circular benzenoids

Let a *circular* benzenoid be defined by having $h = h_{\max}$ for a given s. These systems have, loosely speaking, the largest area in relation to the circumference; hence the term "circular". More precisely, they have the largest number of hexagons for a given perimeter length. These numbers of hexagons are selected values according to:

$$h_{\max} = \left\lfloor \frac{s^2}{12} - \frac{s}{2} + 1 \right\rfloor \tag{5}$$

where $s = 6, 8, 9, 10, 11, 12, \ldots$.

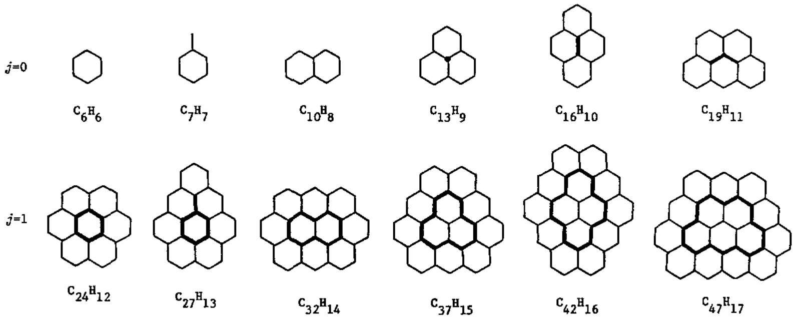

Fig. 1. Circular benzenoids (and one non-benzenoid). The excised internal structures of the strictly pericondensed systems are indicated in bold

All circular benzenoids are extremal. The first (smallest) such systems have the formulas C_6H_6, $C_{10}H_8$, $C_{13}H_9$, $C_{16}H_{10}$, $C_{19}H_{11}$, $C_{24}H_{12}$ and $C_{27}H_{13}$, of which $C_{24}H_{12}$ represents a protrusive benzenoid (coronene). All the higher circular benzenoids constitute a subset of the protrusive benzenoids.

The formulas for all circular benzenoids, say O, are now obtained as:

$$\text{O:}\quad \left(s-2+2\left[\frac{s^2}{12}-\frac{s}{2}+1\right];s\right)$$

where s has the same values as in Eq. (5).

The circular benzenoids are members of one-constant isomer series, as is expressed by:

$$\left|s-2+2\left[\frac{s^2}{12}-\frac{s}{2}+1\right];s\right|=1 \tag{6}$$

As mentioned above there are six such series, each representing a characteristic shape. Their ground forms are C_6H_6, $C_{10}H_8$, $C_{13}H_9$, $C_{16}H_{10}$, $C_{19}H_{11}$ and $C_{27}H_{12}$. For the sake of systematization we assign the first five of these formulas to $j=0$, while the last formula is associated with $j=1$. Thence $C_{27}H_{12}$ is circum-C_7H_7, although C_7H_7 is not a benzenoid. For the sake of clarity the members for $j=0$ and $j=1$ are depicted in Fig. 1. All the higher members are obtained by further circumscribing.

Let now the six shapes of circular benzenoids be labeled by $\delta=0, 1, 2, 3, 4, 5$ going from left to right in Fig. 1. An alternative general expression was found for the formulas of circular benzenoids, which includes the information about their shapes. It reads:

$$\text{O:}\quad \left(6j^2+12j+\delta(2j+3)+4+2\left[\frac{6-\delta}{6}\right];6j+\delta+6\right)$$

The ground forms for the one-isomer series are associated with $j=1$ for $\delta=1$, otherwise $j=0$.

6.3. *Ground forms*

The ground forms for constant-isomer series of benzenoids in general appear to have their formulas just below those of the circular benzenoids. In addition comes C_6H_6. Altogether we attain at the following general expression for the formulas of the ground forms, say G.

$$\text{G:}\quad \left(t+1+2\left\lfloor\frac{t^2}{12}-\frac{t}{2}+1\right\rfloor; t+1\right)$$

where $t = 5, 7, 8, 9, 10, 11, \ldots$

Again we shall derive an alternative expression for the formulas of the ground forms making use of the label δ. However, it is convenient to switch from $\delta = 0$ to $\delta = 6$ so that $\delta = 1, 2, 3, 4, 5, 6$. The following result was derived.

$$\text{G:}\quad (6j^2+12j+\delta(2j+3)+7+2\lfloor\delta/6\rfloor; 6j+\delta+7)$$

By switching from $\delta = 0$ to $\delta = 6$ we achieve that the ground forms appear successively with monotonously increasing s (and h) values when j has a lexicographic preference before δ, but benzene (C_6H_6) is not covered by the expression. Thus we should start (after C_6H_6) with $j = 0$ and $\delta = 1, 2, \ldots, 6$, then take $j = 1$ with $\delta = 1, 2, \ldots, 6$, and so on.

7. Fundamental *aufbau* principle

Dias, in his seminal paper [3] on benzenoid isomers, suggested a principle for generating all isomers with a given formula (C_nH_s). He claimed that all these benzenoids can be generated by attachments of C_4H_2 to the $C_{n-4}H_{s-2}$ systems and C_6H_2 to the $C_{n-6}H_{s-2}$ systems. However, Dias [3] takes all proper precautions by saying: "... postulates which have been tested (but not proved) by a noncomputer method for sample formulas" ... "Although these examples do not provide unequivocal proof for the above postulates and the associated systematic procedure for enumerating the PAH6 isomers, they do, at the very least, provide an intuitive starting point for computer enumeration." Later Dias quotes the principle (without reservations) as if it was generally valid [4, 6, 23] and refers to it as the *aufbau* principle. When trying to use this *aufbau* principle of Dias we found quickly copious counterexamples beyond the test formulas he used for illustration. But a different principle is presented in the following, referred to as the *fundamental* aufbau *principle*. It has been proved rigorously; the proof is easy, but somewhat lengthy and therefore not included here.

The fundamental *aufbau* principle states that all benzenoid ($h > 1$) isomers with the formula C_nH_s are generated by the following three types of additions of one hexagon at a time:

(a) two-contact additions (C_3H attachments) to the $C_{n-3}H_{s-1}$ benzenoids;
(b) one-contact additions (C_4H_2 attachments) to the $C_{n-4}H_{s-2}$ benzenoids;
(c) three-contact additions (C_2 attachments) to the $C_{n-2}H_s$ benzenoids.

If one or two of the classes $C_{n-3}H_{s-1}$, $C_{n-4}H_{s-2}$ and $C_{n-2}H_s$ do not exist, then the remaining one or two classes are sufficient for the *aufbau*. Therefore all catacondensed benzenoids ($h > 1$) are generated by the additions (b) alone, as has been pointed out previously [3]. Likewise all extreme-left benzenoids ($h > 3$) are obtained by the additions (a) and (b). Finally the protrusive benzenoid systems ($h > 2$) are all generated by the scheme (c) exclusively [23].

It should be clear that isomorphic benzenoids are often generated by two of the schemes or all three of them. Thus, for instance, benzo[*e*]pyrene ($C_{20}H_{12}$) is obtained by: (a) two-contact addition to benzophenalene ($C_{17}H_{11} + C_3H$); (b) one-contact addition to pyrene ($C_{16}H_{10} + C_4H_2$); (c) three-contact addition to triphenylene ($C_{18}H_{12} + C_2$).

8. Modified *aufbau* principle

In the present studies a *modified* aufbau *principle* is very useful. It is obtained from the fundamental *aufbau* principle by replacing the last point (c) with:

(c′) circumscribing the $C_{n-2s+6}H_{s-6}$ systems.

In the modified *aufbau* principle the schemes (a) and (b) may lead to isomorphic systems, of course, but the generation according to (c′) should be exclusive. It is a fact that none of the benzenoids generated by circumscribing other benzenoids are isomorphic with those obtained from (a) or (b). However, it is a danger with the modified *aufbau* principle, which must be emphasized. It may be necessary to include certain non-benzenoids among the $C_{n-2s+6}H_{s-6}$ systems to be circumscribed. The smallest example is biphenyl $C_{12}H_{10}$. Therefore the application of the modified *aufbau* principle is not a mere routine since the non-benzenoids of the biphenyl type have not been currently enumerated. Furthermore, one may also miss some non-strictly pericondensed benzenoids if special precautions are not taken.

On the other hand it is a great advantage that the application of the scheme (c′) rather than (c) may reduce substantially the number of hexagons in the benzenoids (and non-benzenoids) to be circumscribed. Assume that the benzenoids with the formula C_nH_s have h hexagons and n_i interval vertices each. In the $C_{n-2s+6}H_{s-6}$ benzenoids let these two invariants be denoted by h° and n_i°, respectively. Then one has:

$$h^\circ = n_i - h + 2, \qquad n_i^\circ = 3n_i - 4h + 10 \tag{7}$$

9. Cardinalities

9.1. Splitting in two parts

Now when we have identified and classified all ground forms of the constant-isomer series for benzenoids we turn to the prime problem of their cardinalities. We shall use the modified *aufbau* principle for the enumerations of benzenoid isomers.

Let C_nH_s represent the formula for a set of ground forms. Since the ground forms (for $h > 1$) invariably are extreme-left benzenoids the generation schemes (a) and (c′) of the modified *aufbau* principle are sufficient. The cardinality of C_nH_s is consequently split into two parts (where the second part may vanish);

$$|C_nH_s| = |C_nH_s|^a + |C_nH_s|^o \tag{8}$$

This equation does not cover the smallest benzenoid, viz. benzene, and should therefore be supplemented by:

$$|C_6H_6| = 1 \tag{9}$$

The next-smallest benzenoid, viz. naphthalene ($C_{10}H_8$) is compatible with Eq. (8) if we allow for a two-contact addition to the non-benzenoid C_7H_7 (cf. Fig. 1).

9.2. *First part of the cardinalities*

It is a simple combinatorial problem to derive the numbers $|C_nH_s|^a$ explicitly. The following result was obtained by considering the different two-contact additions to the circular benzenoids.

$$(\delta = 1) \quad |6j^2 + 14j + 10;\ 6j + 8|^a = 3j + 1 \tag{10}$$

$$(\delta = 2) \quad |6j^2 + 16j + 13;\ 6j + 9|^a = j + \left[\frac{j+1}{2}\right] = \frac{1}{2}\left[3j + 1 + \frac{1 + (-1)^j}{2}\right] \tag{11}$$

$$(\delta = 3) \quad |6j^2 + 18j + 16;\ 6j + 10|^a = j + 1 \tag{12}$$

$$(\delta = 4) \quad |6j^2 + 20j + 19;\ 6j + 11|^a = j + 1 + \left[\frac{j}{2}\right] = \frac{1}{2}\left[3j + 3 - \frac{1 + (-1)^j}{2}\right] \tag{13}$$

$$(\delta = 5) \quad |6j^2 + 22j + 22;\ 6j + 12|^a = 3j + 3 \tag{14}$$

$$(\delta = 6) \quad |6j^2 + 24j + 27;\ 6j + 13|^a = \left[\frac{j+1}{2}\right] = \frac{1}{2}\left[j + 1 + \frac{1 + (-1)^j}{2}\right] \tag{15}$$

9.3. *Second part of the cardinalities*

In the present work it was not achieved to derive explicit expressions for $|C_nH_s|^o$ in general, which seems to be a very difficult problem. In any case, however, the first part of the problem is to identify the formulas of the benzenoids to be circumscribed.

Let G^o be a benzenoid which, if it can be circumscribed, gives G; i.e. circum-G^o = G. Then, from the expressions for the formulas of G given above it is readily found:

$$G^o\colon \quad \left(2\left[\frac{t^2}{12} - \frac{t}{2} + 1\right] - t + 6;\ t - 5\right); \quad t > 10$$

and

$$G^o\colon \quad (6j^2 + \delta(2j + 1) - 1 + 2\lfloor \delta/6 \rfloor;\ 6j + \delta + 1); \quad j > 0$$

in terms of different parameters, viz. t and (j, δ), respectively.

By inspection of the smallest benzenoids it was found that the circumscribing of G^o is not effective for $t < 15$. This means, in precise terms:

$$|C_nH_s|^o = 0; \qquad s < 16 \tag{16}$$

The parameter value $t = 15$ (or $s = 16$) corresponds to $j = 1$, $\delta = 3$. From now on, however, the second parts of the cardinalities never vanish.

Where in the periodic table are the formulas for G^o located in relation to G? The following procedure gives the answer. Look up the formula for the benzenoids with the same δ as in G, but one unit less for j. Then one arrives at:

$$(6j^2 + \delta(2j + 1) + 1 + 2\lfloor \delta/6 \rfloor;\ 6j + \delta + 1)$$

Table 1. Enumeration of constant-isomer series of benzenoids; C_nH_s is the formula for the ground form(s)

j	δ	C_nH_s	$\lvert C_nH_s\rvert^a$	$C_{n-2s+6}H_{s-6}$	$\lvert C_nH_s\rvert^{\circ}$	$\lvert C_nH_s\rvert$
—	—	C_6H_6	1	—	0	1^a
0	1	$C_{10}H_8$	1	—	0	1^a
	2	$C_{13}H_9$	1	—	0	1^a
	3	$C_{16}H_{10}$	1	—	0	1^a
	4	$C_{19}H_{11}$	1	—	0	1^a
	5	$C_{22}H_{12}$	3	—	0	3^b
	6	$C_{27}H_{13}$	1	—	0	1^b
1	1	$C_{30}H_{14}$	4	—	0	4^b
	2	$C_{35}H_{15}$	2	—	0	2^c
	3	$C_{40}H_{16}$	2	$C_{14}H_{10}$	2^a	4^c
	4	$C_{45}H_{17}$	3	$C_{17}H_{11}$	1^a	4^c
	5	$C_{50}H_{18}$	6	$C_{20}H_{12}$	3^a	9^c
	6	$C_{57}H_{19}$	1	$C_{25}H_{13}$	3^b	4^c
2	1	$C_{62}H_{20}$	7	$C_{28}H_{14}$	9^b	16^c
	2	$C_{69}H_{21}$	4	$C_{33}H_{15}$	9^b	13^c
	3	$C_{76}H_{22}$	3	$C_{38}H_{16}$	13^c	16^c
	4	$C_{83}H_{23}$	4	$C_{43}H_{17}$	16^c	20^c
	5	$C_{90}H_{24}$	9	$C_{48}H_{18}$	30^c	39^c
	6	$C_{99}H_{25}$	2	$C_{55}H_{19}$	18^c	20^c
3	1	$C_{106}H_{26}$	10	$C_{60}H_{20}$	47^c	57^c
	2	$C_{115}H_{27}$	5	$C_{67}H_{21}$	43^c	48^{d-f}
	3	$C_{124}H_{28}$	4	$C_{74}H_{22}$	53^c	$57^{e,f}$
	4	$C_{133}H_{29}$	6	$C_{81}H_{23}$	68^c	74^{d-f}
	5	$C_{142}H_{30}$	12	$C_{88}H_{24}$	121^c	$133^{e,f}$
	6	$C_{153}H_{31}$	2	$C_{97}H_{25}$	72^c	74^{d-f}
4	1	$C_{162}H_{32}$	13	$C_{104}H_{26}$	186^c	$199^{e,f}$
	2	$C_{173}H_{33}$	7	$C_{113}H_{27}$	167	$174^{e,f}$
	3	$C_{184}H_{34}$	5	$C_{122}H_{28}$	194^e	$199^{e,f}$
	4	$C_{195}H_{35}$	7	$C_{131}H_{29}$	251	$258^{e,f}$
	5	$C_{206}H_{36}$	15	$C_{140}C_{30}$	413	$428^{e,f}$
	6	$C_{219}H_{37}$	3	$C_{151}H_{31}$	255	$258^{e,f}$
5	1	$C_{230}H_{38}$	16	$C_{160}H_{32}$	600	$616^{e,f}$
	2	$C_{243}H_{39}$	8	$C_{171}H_{33}$	542	$550^{e,f}$
	3	$C_{256}H_{40}$	6	$C_{182}H_{34}$	610	$616^{e,f}$
	4	$C_{269}H_{41}$	9	$C_{193}H_{35}$	787	$796^{e,f}$
	5	$C_{282}H_{42}$	18	$C_{204}H_{36}$	1247	$1265^{e,f}$
	6	$C_{297}H_{43}$	3	$C_{217}H_{37}$	793	$796^{e,f}$

[a] Elk (1980) [7]
[b] Knop, Szymanski, Jeričević, Trinajstić (1983) [8]
[c] Stojmenović, Tošić, Doroslovački (1986) [10]
[d] Dias (1990) [17]
[e] Dias (1990) [18]
[f] Dias (1990) [19]

On comparing with the formula for G^o given in terms of (j, δ) it is seen that it remains to lower n by two units, but maintain s. This last process moves the formula one step to the right and two steps upwards in the periodic table. In conclusion it is arrived at the interesting result that the benzenoids to be circumscribed, G^o for $h > 6$ and $h \neq 8$, are selected extreme-left benzenoids which are not extremal; they belong to the class denoted by x above. In addition come (for $h < 6$ and $h = 8$) $C_{14}H_{10}$, $C_{17}H_{11}$, $C_{20}H_{12}$ and $C_{28}H_{14}$. Another description, which is generally valid, reads: the formulas for the G^o benzenoids are found one step to the right and one step upwards (i.e. one step in the diagonal up-right direction) from the formulas for the circular benzenoids (O) with $h > 2$.

It is realized that all benzenoids of the class G^o are strictly pericondensed and can be circumscribed. Furthermore, there will never occur non-benzenoids with the same formula as G^o which should be taken into account. Therefore the second part of the cardinality $|C_nH_s|$ in Eq. (8), where C_nH_s represents a ground form, is given by:

$$|C_nH_s|^o = |C_{n-2s+6}H_{s-6}| \tag{17}$$

9.4. *Comments*

The splitting of $|C_nH_s|$ is nothing else than a part of the algorithm of Dias [17, 18], but formalized in a different way and supported by theorems. It is also supplemented by new explicit expressions of Eqs. (10)–(15) for a part of the cardinalities.

9.5. *Numerical values*

With the data from Stojmenović et al. at hand [10, 14] one obtains readily together with Eqs. (10)–(15), the numbers down to $C_{162}H_{32}$ ($j = 4, \delta = 1$) in Table 1. This is already more than is contained in one of the Dias papers [17]. The computation was continued, using the Dias algorithm [17, 18], with results that all are consistent with his later values [18, 19].

10. Conclusion

The present work gives an original contribution to the studies of constant-isomer series of benzenoids, inspired by the recent work of Dias [17–19]. There is still much more to be done in this area. Dias observed, for instance, a pattern in the numbers for these series, which he referred to as a new topological paradigm [18]. It is manifested in the last column of Table 1 by the following pattern of the numbers – $a, b, c, b, d, e, d, f, g, f, \ldots$. The pattern is still more striking when the table is divided into two, as Dias did [17–19], for even-carbon and odd-carbon benzenoids separately. Dias [18, 19] has also provided an interesting characterization of the isomer series according to symmetry and other properties, but the paradigm remains essentially unexplained.

It is planned to devise a computer program for the numbers of benzenoid isomers and particularly for the constant-isomer series. This seems, however, to be a very complicated task.

References

1. Cyvin SJ, Gutman I (1988) Kekulé structures in benzenoid hydrocarbons (Lecture Notes in Chemistry). Springer, Berlin Heidelberg New York
2. Gutman I, Cyvin SJ (1989) Introduction to the theory of benzenoid hydrocarbons. Springer, Berlin
3. Dias JR (1982) J Chem Inf Comput Sci 22:15
4. Dias JR (1987) Handbook of polycyclic hydrocarbons, part A. Elsevier, Amsterdam
5. Dias JR (1986) J Mol Struct (Theochem) 137:9
6. Dias JR (1990) Topics Current Chem 153:123
7. Elk SB (1980) Match (Mülheim) 8:121
8. Knop JV, Szymanski K, Jeričević Ž, Trinajstić N (1983) J Comput Chem 4:23
9. Knop JV, Müller WR, Szymanski K, Trinajstić N (1985) Computer generation of certain classes of molecules. SKTH/Kemija u industriji, Zagreb
10. Stojmenović I, Tošić R, Doroslovački R (1986) In: Tošić R, Acketa D, Petrović V (eds) Graph theory, Proceedings of the sixth Yugoslav seminar on graph theory, Dubrovnik, April 18–19, 1985. University of Novi Sad, Novi Sad
11. Dias JR (1984) Can J Chem 62:2914
12. Dias JR (1984) J Chem Inf Comput Sci 24:124
13. Dias JR (1989) J Mol Struct (Theochem) 185:57
14. Brunvoll J, Cyvin SJ (1990) Z Naturforsch 45a:69
15. Cyvin SJ (1990) J Mol Struct (Theochem) 208:173
16. Cyvin SJ, Brunvoll J (1990) Chem Phys Letter 170:364
17. Dias JR (1990) J Chem Inf Comput Sci 30:61
18. Dias JR (1990) J Chem Inf Comput Sci 30:251
19. Dias JR (1990) Theor Chim Acta 77:143
20. Cyvin SJ, Brunvoll J (1989) Chem Phys Lett 164:635
21. Harary F, Harborth H (1976) J Combinat Inf System Sci 1:1
22. Gutman I (1982) Bull Soc Chim Beograd 47:453
23. Dias JR (1989) Z Naturforsch 44a:765