Enumeration and Classification of Benzenoid Hydrocarbons. 17. Further Developments for Constant-Isomer Series

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The constant-isomer series of benzenoids are studied theoretically. General expressions for the pertinent formulas C_nH_s are reported. The number of benzenoid isomers associated with a formula C_nH_s is referred to as the cardinality of C_nH_s. A version of the Dias algorithm for the cardinalities in constant-isomer series is analyzed in detail. This analysis has led to explicit expressions for parts of the cardinalities.

INTRODUCTION

The interesting phenomenon of constant-isomer series was discovered by Dias[1] when he pointed out that coronene, circumcoronene, dicircumcoronene, ... have chemical formulas ($C_{24}H_{12}$, $C_{54}H_{18}$, $C_{96}H_{24}$, ...) representing one benzenoid isomer each. Later the other five one-isomer series of this kind were detected[2-4] and are summarized elsewhere.[5,6] The first constant-isomer series of benzenoids with formulas representing more than one isomer each was again detected by Dias.[3] They read $C_{22}H_{12}$, $C_{52}H_{18}$, $C_{94}H_{24}$, ..., where the first of them represents the three isomers anthanthrene, benzo[ghi]perylene, and triangulene. The subsequent formulas correspond to successive circumscribing of these three benzenoids and represent constantly three isomers each.

Recently Dias[6-8] revisited the area of constant-isomer series of benzenoids making use of the extensive enumeration data of Stojmenović et al.[5,9] These useful data, also exploited in the present work, shall be referred to as the STD (Stojmenović–Tošić–Doroslovački) data.

In the present work we have supplemented the existing data for numbers of benzenoid isomers and particularly for the constant-isomer series. But more significant is the contribution to the theoretical analysis of the constant-isomer series. We have achieved some general formulations and derived explicit expressions for parts of the numbers under consideration.

RESULTS AND DISCUSSION

Notation. Let the formula C_nH_s for a benzenoid hydrocarbon 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. This means the number of nonisomorphic benzenoid systems compatible with the formula in question. An alternative notation is

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

Ground Forms and Higher Members. The benzenoids that are the smallest members of a constant-isomer series are referred to as the ground forms.[5] They correspond to the base-excised internal structure,[6-8] but benzene and naphthalene are always reckoned among the ground forms.

Let $(n; s)$ be a formula for a set of ground forms. Then the formula for any higher members obtained by k-tuple circumscribing the benzenoids $(n; s)$, say $(n_k; s_k)$, is given by

$$(n_k; s_k) = (6k^2 + 2sk + n; s + 6k) \quad (1)$$

All these formulas are known to be found at the extreme-left ends of certain rows of the periodic table for benzenoid hydrocarbons.[1-4,10,11] All of the corresponding benzenoids, except benzene and naphthalene, are strictly peri-condensed[2-4,10] in the sense that all their internal vertices and edges are connected. They are also extremal benzenoids inasmuch as they have the maximum number of internal vertices for a given number of hexagons.

A constant-isomer series for benzenoids manifests itself by obeying the relation

$$|n; s| = |6k^2 + 2sk + n; s + 6k| \quad (2)$$

for all $k = 0, 1, 2, 3, ...$ Here $k = 0$ is assumed to correspond to the ground forms.

General Formulas for Constant-Isomer Series. Assume that C_nH_s is a formula for a set of ground forms. A general formula for $(n; s)$ was deduced with the result

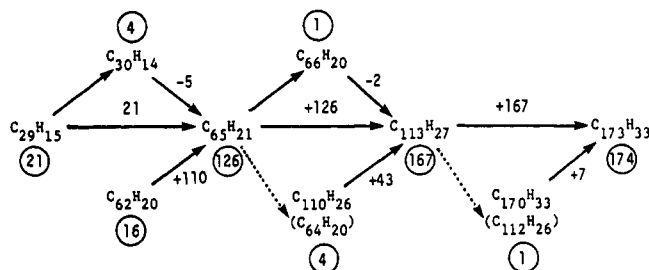$$(n; s) = \left(t + 1 + 2\left[\frac{t^2}{12} - \frac{t}{2} + 1\right]; t + 1\right) \quad (3)$$

where $[x]$ is the floor function, viz., the largest integer smaller than or equal to x. Here $t = 5, 7, 8, 9, 10, ...$, which gives consecutively all the possible numbers of hydrogens in a benzenoid, viz., $s = 6, 8, 9, 10, 11, ...$

The elaborate floor function in eq 3 can be avoided by introducing two parameters (j, δ). We found the following alternative expression for the formulas of ground forms in general:

$$(n; s) = (6j^2 + 12j + \delta(2j + 3) + 7 + 2[\delta/6]; 6j + \delta + 7) \quad (4)$$

where $\delta = 1, ..., 6$, and $j = 0, 1, 2, 3, ...$, but also $j = -1$ for $\delta = 5$. In order to get the formulas in the sequence of ascending s values, one should take $j = 0$ with $\delta = 1, ..., 6$, then $j = 1$ with $\delta = 1, ..., 6$, and so on; the whole set preceded by $j = -1$, $\delta = 5$ (corresponding to C_6H_6 benzene). Table I summarizes the formulas according to eq 4 up to $j = 6$. They reproduce the first formulas in each column of the previous listings.[6-8]

Table I. Formulas for Ground Forms of Constant-Isomer Series for Benzenoids (C_nH_s)[a]

δ	j						
	0	1	2	3	4	5	6
1	$C_{10}H_8$	$C_{30}H_{14}$	$C_{62}H_{20}$	$C_{106}H_{26}$	$C_{162}H_{32}$	$C_{230}H_{38}$	$C_{310}H_{44}$
2	$C_{13}H_9$	$C_{35}H_{15}$	$C_{69}H_{21}$	$C_{115}H_{27}$	$C_{173}H_{33}$	$C_{243}H_{39}$	$C_{325}H_{45}$
3	$C_{16}H_{10}$	$C_{40}H_{16}$	$C_{76}H_{22}$	$C_{124}H_{28}$	$C_{184}H_{34}$	$C_{256}H_{40}$	$C_{340}H_{46}$
4	$C_{19}H_{11}$	$C_{45}H_{17}$	$C_{83}H_{23}$	$C_{133}H_{29}$	$C_{195}H_{35}$	$C_{269}H_{41}$	$C_{355}H_{47}$
5	$C_{22}H_{12}$	$C_{50}H_{18}$	$C_{90}H_{24}$	$C_{142}H_{30}$	$C_{206}H_{36}$	$C_{282}H_{42}$	$C_{370}H_{48}$
6	$C_{27}H_{13}$	$C_{57}H_{19}$	$C_{99}H_{25}$	$C_{153}H_{31}$	$C_{219}H_{37}$	$C_{297}H_{43}$	$C_{387}H_{49}$

[a] They are preceded by C_6H_6 (benzene) for $j = -1$, $\delta = 5$, which falls outside the scheme.

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Figure 1. The Dias algorithm applied to $C_{173}H_{33}$.

From eqs 1 and 4 one obtains the following expressions for the coefficients of any benzenoid belonging to a constant-isomer series:

$$n_k =$$
$$6(j + k)^2 + 2(j + k)(\delta + 6) + 2k + 3\delta + 7 + 2[\delta/6]$$

$$s_k = 6(j + k) + \delta + 7 \qquad (5)$$

These equations reproduce all the formulas for special constant-isomer series listed in the papers which are cited above.[12] Also some special cases of the present eq 5 have been given previously.[5,11]

Below we also give the expressions for the numbers of hexagons (h) and numbers of internal vertices (n_i) pertaining to the benzenoids (n_k; s_k) since some special cases of these equations have been reported.[5,13] They read as follows:

$$h_k = 3(j + k)^2 + (j + k)(\delta + 3) + k + \delta + 1 + [\delta/6]$$

$$(n_i)_k = 6(j + k)^2 + 2(j + k)\delta + 2k + \delta - 1 + 2[\delta/6] \qquad (6)$$

Dias Algorithm. An algorithm for determining the numbers of benzenoid isomers in constant-isomer series is described by Dias[7] in this Journal. In the present version of it the systems are broken down, successively making use of smaller constant-isomer series, so that it fully remains to add a number of isomers that may be known from the STD data or elsewhere.

Figure 1 shows an example of the application of the Dias algorithm to a formula for a constant-isomer series, viz., $C_{173}H_{33}$. The cardinalities of the different formulas are shown by the encircled numbers. The horizontal row represents successive circumscribing from left to right. The upper part represents the detection of systems with coves, which can not be circumscribed. Their numbers are therefore subtracted. The lower part represents the generation of systems by two-contact additions of hexagons (attachments of C_3H). This is equivalent to attachments of CH methylenyl groups to the corresponding excised internal structures. The latter description is preferred by Dias;[7] therefore, the parenthesized formulas of Figure 1 are those he would enter into his scheme. A benzenoid with a parenthesized formula when circumscribed is, namely, converted into a benzenoid with the formula above it. Example: circum-$C_{112}H_{26} \rightarrow C_{170}H_{33}$. It is noted that the parenthesized formulas are also very useful in our scheme; they give a check on the formulas through the correlation indicated by the broken-line arrows in Figure 1.

It is noted that we consider the algorithm as built up successively from right to left (in relation to Figure 1), which is the opposite way from the Dias version.

The Dias algorithm (in our version) can be truncated at any formula in the horizontal row if the cardinality of it is known, for instance from the STD numbers. For the formulas in Figure 1, the STD numbers are available for $|C_{29}H_{15}|$ and $|C_{65}H_{21}|$, but not for $|C_{113}H_{27}|$.

Detailed Analysis of the Dias Algorithm. Assume that (n; s) represents a formula for the ground state of a constant-isomer series for benzenoids. Then the formulas in the Dias algorithm are constructed recursively, from right to left, as
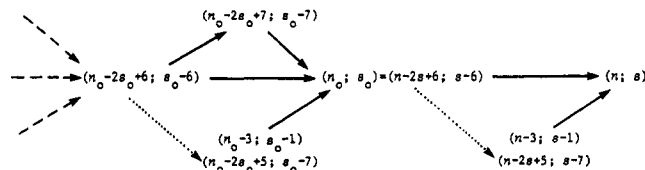

Figure 2. General scheme for constructing the formulas of the Dias algorithm.

Table II. Three-Parameter Codes of $(n - 3; s - 1)$

δ	$\{o, \delta', j'\}$	δ	$\{o, \delta', j'\}$
1	$\{0, 6, j - 1\}$	4	$\{0, 3, j\}$
2	$\{0, 1, j\}$	5	$\{0, 4, j\}$
3	$\{0, 2, j\}$	6	$\{-1, 5, j + 1\}$

shown in Figure 2. This formula (n; s) is determined by the two parameters j and δ which enter into eq 4. It also obeys eq 5 with $k = 0$. We shall identify the formula in question by a three-parameter code as

$$(n; s) \equiv \{j, \delta, 0\} \qquad (7)$$

First we concentrate upon the formula $(n - 3; s - 1)$ at the extreme right below the horizontal row (cf. Figure 2). It was found in the general case that

$$(n - 3; s - 1) \equiv$$
$$\left\{ 0 - \left[\frac{\delta}{6}\right], \delta - 1 + 6\left[\frac{7 - \delta}{6}\right], j + \left[\frac{\delta}{6}\right] - \left[\frac{7 - \delta}{6}\right] \right\} \qquad (8)$$

This somewhat awkward formula is a straightforward consequence of eq 5. Let us introduce three new parameters so that eq 8 transforms into the simpler form

$$(n - 3; s - 1) \equiv \{o, \delta', j'\} \qquad (9)$$

For the sake of brevity we shall demonstrate the relation 8 only under the "normal" behavior, viz., for $\delta = 2, 3, 4,$ and 5. In these instances one has $[\delta/6] = [(7 - \delta)/6] = 0$, and therefore

$$o = 0, \delta' = \delta - 1, j' = j \qquad (\delta = 2, 3, 4, 5) \qquad (10)$$

Hence it is inferred that

$$(n - 3; s - 1) \equiv \{0, \delta - 1, j\} \qquad (\delta = 2, 3, 4, 5) \qquad (11)$$

On inserting the three parameters from eq 11 as $\{j, \delta, k\}$ in eq 5 it is obtained

$$\{0, \delta - 1, j\} \equiv (6j^2 + 2j(\delta + 5) + 2j + 3(\delta - 1) + 7;$$
$$6j + \delta + 6)$$
$$= (6j^2 + 12j + \delta(2j + 3) + 4; 6j + \delta + 6) \qquad (12)$$

But this is exactly the expression also obtained from eq 4, or from eq 5 with $k = 0$, on subtracting three units from n and one unit from s. Table II gives a full account of the three-parameter codes of the formula $(n - 3; s - 1)$ in the bottom right position of the scheme under consideration (Figure 2). Notice that the δ values are cyclically permuted: $\delta \rightarrow \delta'$ follows $\delta \rightarrow \delta - 1$ for $\delta \neq 1$, while $\delta = 1 \rightarrow \delta' = 6$.

Now it is important to realize that the formula $(n - 3; s - 1)$ treated above invariably represents a member of one of the six one-isomer series. They have namely the ground forms given by $\{-1, 5, 0\}$ and $\{0, \delta, 0\}$, where $\delta = 1, 2, 3, 4, 6$. The formulas for these ground forms are (cf. Table I): C_6H_6, $C_{10}H_8$, $C_{13}H_9$, $C_{16}H_{10}$, $C_{19}H_{11}$, and $C_{27}H_{13}$, respectively. The third parameter indicates, in accordance with the general rule, the number of circumscribings around the ground forms. The members of the one-isomer series are (for $s = 12$ and $s \geq 14$) "protrusive" benzenoids; the formula of such a system has no other formula above it or to the left of it in the periodic table for benzenoid hydrocarbons.

Table III. Functions P and M^a

j	δ	$P(j, \delta, k)$		$M(j, \delta, k)$	
-1	5	$1/2(k + 1 - \epsilon)$		$1/2(k - 1 + \epsilon)$	
0	1	$1/2(3k + 1 + \epsilon)$		$1/2(3k - 1 - \epsilon)$	$(k > 0)$
0	2	$k + 1$		k	
0	3	$1/2(3k + 3 - \epsilon)$		$1/2(3k - 1 + \epsilon)$	
0	4	$3k + 3$		$3k$	
0	5	$7k + 7 - \epsilon$	$(k > 0)$	$7k - 1 + \epsilon$	$(k > 0)$
0	6	$3k + 4$		$3k + 1$	
1	1	$1/2(27k + 31 + \epsilon)$	$(k > 0)$	$1/2(27k + 5 - \epsilon)$	$(k > 0)$
1	2	$12k + 16$	$(k > 0)$	$12k + 4$	$(k > 0)$
1	3	$1/2(27k + 41 - \epsilon)$	$(k > 0)$	$1/2(27k + 13 + \epsilon)$	$(k > 0)$
1	4	$21k + 33$	$(k > 0)$	$21k + 12$	$(k > 0)$
1	5	$1/2(87k + 147 - 3\epsilon)$	$(k > 0)$	$1/2(87k + 57 + 3\epsilon)$	$(k > 0)$
1	6	$21k + 40$	$(k > 0)$	$21k + 19$	$(k > 0)$
2	1	$1/2(147k + 285 + \epsilon)$	$(k > 0)$		
2	2	$6k + 136$	$(k > 0)$		
2	3	$1/2(147k + 335 - \epsilon)$	$(k > 0)$		
2	4	$108k + 260$	$(k > 0)$		
2	5	$196k + 489 - 2\epsilon$	$(k > 0)$		
2	6	$108k + 296 + \epsilon$	$(k > 0)$		

$^a \epsilon = (1/2)[1 + (-1)^k]$.

Now we look at the next-to-extreme right-hand formula on the horizontal row in Figure 2. It is seen to have one more carbon atom and one more hydrogen in relation to $(n - 2s + 5; s - 7)$. The latter formula is the excised internal structure of $(n - 3; s - 1)$ and therefore also a member of a one-isomer series, provided that we have started with a sufficiently large system so that it still is a benzenoid. Therefore it should be clear that the formula $(n - 2s + 6; s - 6)$ represents benzenoids on an extreme-left edge of the periodic table except for some of the small s values. These special strictly peri-condensed benzenoids can always be circumscribed. It was found by inspection that also the pertinent benzenoids with the small s values can be circumscribed. In conclusion, therefore, there will never appear a formula at the extreme right above the horizontal row of the scheme under consideration (Figure 2).

Let us turn to the formula that appears as the extreme right above the horizontal row of Figure 2. Dias[7] stated without proof that it always belongs to the same one-isomer series as $(n - 2s + 5; s - 7)$ in the bottom-right corner. This interesting observation is just the kind of thing we are proving rigorously in this analysis. Again, for the sake of brevity, consider only the "normal" cases, for which it is inferred that

$$(n - 4s + 25; s - 13) \equiv \{0, \delta - 1, j - 2\} \qquad (\delta = 2, 3, 4, 5) \tag{13}$$

The left-hand side of this equation was obtained by substituting n_0 and s_0 in the expressions of Figure 2 with the appropriate functions of n and s. Then from eq 4 it follows

$$(n - 4s + 25; s - 13) =$$
$$(6j^2 - 12j + \delta(2j - 1) + 4; 6j + \delta - 6) \tag{14}$$

On the other hand, when the three parameters from the right-hand side of eq 13 are inserted into eq 5 one obtains:

$$\{0, \delta - 1, j - 2\} \equiv (6(j - 2)^2 + 2(j - 2)(\delta + 5) +$$
$$2(j - 2) + 3(\delta - 1) + 7; 6(j - 2) + \delta + 6) \tag{15}$$

This expression reduces indeed to the right-hand side of eq 14.

We shall not pursue this kind of demonstration in detail but indicate the three-parameter forms for the formulas of the Dias algorithm in general; see Figure 3. The formulas above and below the horizontal row pertain to constant-isomer series. Those on the horizontal row, except for the one at the extreme right, do not pertain to constant-isomer series and have therefore no three-parameter codes.

Analysis of the Cardinalities. An ultimate goal to produce an explicit equation for the cardinalities of the constant-isomer
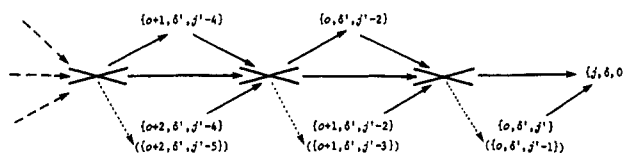

Figure 3. Three-parameter $\{j, \delta, k\}$ forms of the general scheme of the Dias algorithm.

series seems to be a very difficult problem and has not been solved in the present work. However, we have deduced some partial solutions of the problem.

In the scheme of the Dias algorithm every arrow pointing upward to the right toward the horizontal row is associated with a positive number, say P. Similarly every arrow pointing downward to the right toward the horizontal row is associated with a negative number, say M. Examples are found in Figure 1. Accordingly we introduce the plus and minus functions, viz., $P(j, \delta, k)$ and $M(j, \delta, k)$, respectively. The parameters of these functions should conform with the three-parameter representations of the formulas at the origins of the arrows; cf. Figure 3.

Table III shows the plus and minus functions for some values of j and δ while k is variable. The expressions were found by simple combinatorial methods in a somewhat tedious, but elementary way.

Let again $(n; s)$ represent a formula for a constant-isomer series. Then, according to the Dias algorithm, the corresponding cardinality is

$$|n; s| = P(o, \delta', j') + \sum_{\nu=1}^{x-1} [P(o + \nu, \delta', j' - 2\nu) -$$
$$M(o + \nu - 1, \delta', j' - 2\nu)] + |n_{-x}; s_{-x}| \tag{16}$$

The recursive process of the Dias algorithm should not be carried too far; this has implications for the upper index of summation in eq 16. Assume that it is carried out as far as possible before the scheme of Figure 3 breaks down. This means that ν should stop until $j' - 2\nu$ is 0 or 1, depending on whether j' is even or odd, respectively. However, the summation can be truncated any place before this limit. Since we wish to apply the expressions for P and M from Table III and most of them are not valid for $k = 0$, we shall assume that the summation stops when $j' - 2\nu$ is 2 for j' even. In conclusion, the number of terms will be determined by the ceiling function

$$x = \{j'/2\} \tag{17}$$

viz., the smallest integer larger than or equal to $j'/2$.

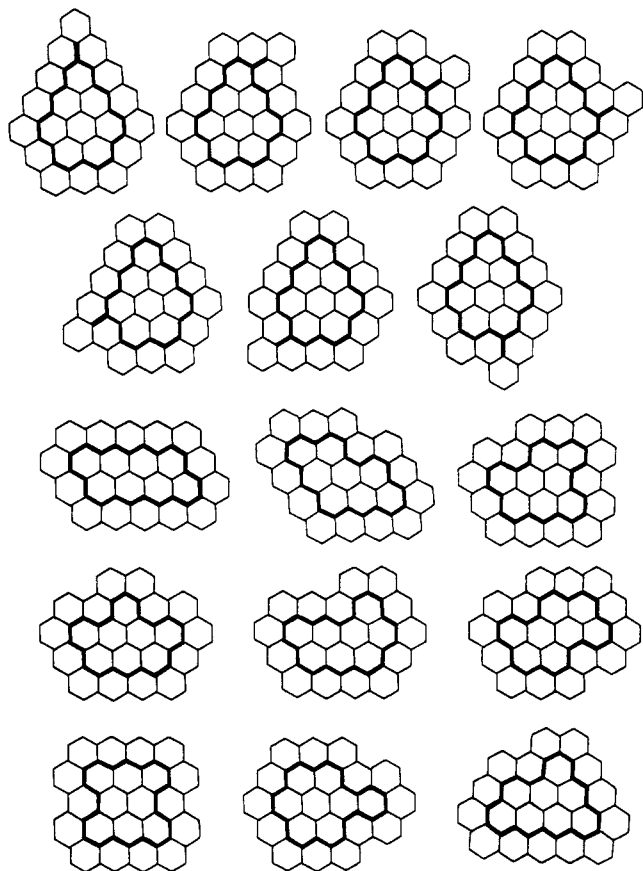**Figure 4.** The 16 benzenoid isomers $C_{62}H_{20}$. The boundaries of excised internal structures are indicated in bold.

Figure 5. Excised internal structures of the seven first benzenoids of Figure 4 and the methylenyl attachments to them.

The remainder in eq 16 is the cardinality of the formula $(n_{-x}; s_{-x})$. It pertains to x times excising or "decircumscribing", the opposite process of circumscribing. The notation is especially adequate inasmuch as eq 1 appears to be valid also for negative k values. The formula in question is therefore

$$(n_{-x}; s_{-x}) = (6x^2 - 2sx + n; s - 6x) \qquad (18)$$

An example of the application of eq 16 seems to be warranted here. Consider Figure 1, where the target formula $C_{173}H_{33}$ has $\{4, 2, 0\}$ as its three-parameter code in consistancy with eq 4; see especially Table I. Then, according to eq 8—see especially Table II—the first term on the right-hand side of eq 17 is

$$P(0, 1, 4) = 7 \qquad (19)$$

The numerical value of this function is found from Table III. The same table also gives the value of the first term in the summation:

$$P(1, 1, 2) = 43, \qquad M(0, 1, 2) = 2 \qquad (20)$$

If we adhere to the upper index of summation given by eq 17, which gives $x = 2$ in the present case, the summation should stop with this only term. The remainder then becomes the cardinality of $C_{65}H_{21}$, as is obtained by inserting $x = 2$ together with $n = 173$, and $s = 33$ (from the target formula) into eq 18. For this cardinality, $|C_{65}H_{21}|$, 126 is an STD number. The algorithm can be extended by one step, for which we need

$$P(2, 1, 0) = 110, \qquad M(1, 1, 0) = 5 \qquad (21)$$

Now $x = 3$, and the remainder becomes $|C_{29}H_{15}| = 21$, another STD number. However, since the functions in eq 21 correspond to $k = 0$, the formulas in Table III are not valid. Below we show how these two numbers can be derived, since this will shed some light into the construction of the plus and minus functions (Table III) and hence the nature of the Dias algorithm.
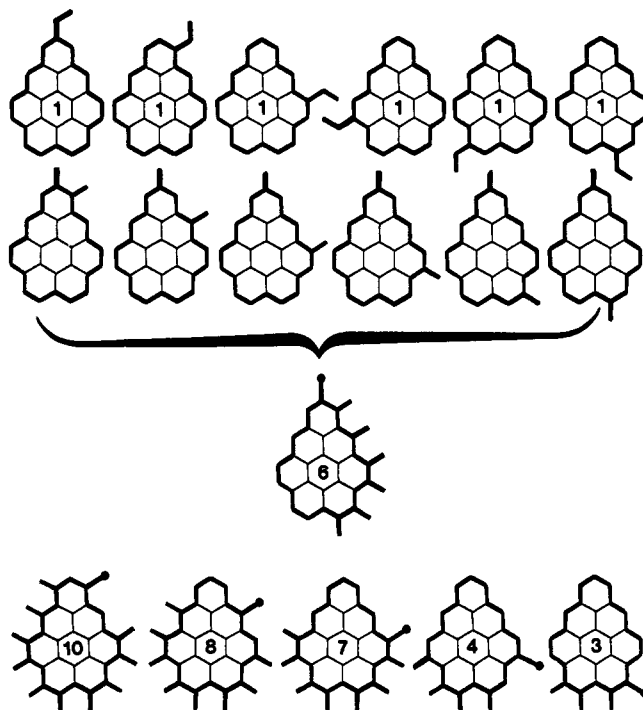
Figure 4 shows the 16 forms of the $C_{62}H_{20}$ isomers, which have the code $\{2, 1, 0\}$. In Figure 5 the two-contact additions to the first seven of them (two top rows of Figure 4) are illustrated. Only the excised internal structures are depicted. On adding the numbers that are inscribed in the different structures of Figure 5, one arrives at the number of 44 non-isomorphic systems generated in this way. The pertinent numbers generated from the remaining nine systems of Figure 4 are listed below.

C_s symmetry − 1 bay (2 systems)	12 × 2
C_s − 2 bays (1 system)	10
C_{2v}(a) − 1 bay (1 system)	6
C_{2v}(a) or C_{2h} − 2 bays (2 systems)	5 × 2
C_{2v}(b) − 2 bays (1 system)	6
C_{2h} − no bays (1 system)	7
D_{2h} − 2 bays (1 system)	3

These numbers (together with 44) indeed add up to 110 in consistancy with the left-hand part of eq 21.

For the right-hand part of eq 21 we need the number of benzenoids with the formula $C_{29}H_{15}$ and which can be circumscribed. Figure 6 shows the pertinent 21 forms, of which five can not be circumscribed. They are the ones with coves, indicated by arrows in the figure. This number five can, however, be determined easier, without having the 21 depictions. Following the Dias algorithm, we look up the forms of the $C_{30}H_{14}$ isomers (cf. Figure 1). They are the ground forms of the constant-isomer series with the code $\{1, 1, 0\}$. There are only four of these isomers as displayed in Figure 7. The desired number is now obtained by counting the symmetrically nonequivalent P_4-mode hexagons. They are indicated by asterisks in Figure 7 and correspond to solo (meso-anthracenic) positions of carbon atoms on the boundary (perimeter). When the starred hexagons in the systems of Figure 7 are removed, one at a time, one arrives exactly at the $C_{29}H_{15}$ isomers with coves (cf. Figure 6).

Explicit Expressions for Parts of the Cardinalities. When eq 16 is applied in more general terms, the cardinality of a formula for the ground forms of a constant-isomer series of benzenoids emerges as

$$|n; s| = F_x(j, \delta) + |n_{-x}; s_{-x}| \qquad (22)$$
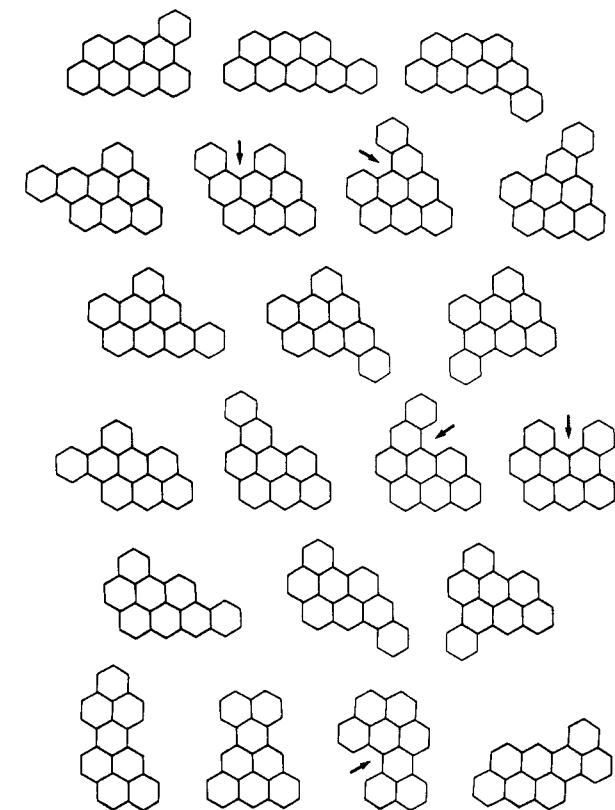
Figure 6. The 21 benzenoid isomers $C_{29}H_{15}$.
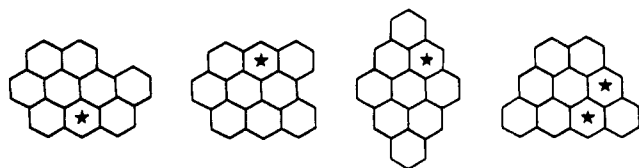
Figure 7. The 4 benzenoid isomers $C_{30}H_{14}$.

where the functions F_x are obtainable, up to certain parameter values, from the expressions in Table III. All the deduced F_x functions up to $x = 3$ (and $x = 4$ for $\delta = 6$) are listed in Table IV.

Let us see a few applications of eq 22 together with eq 18.

For the example $C_{173}H_{33}$ ($j = 4$, $\delta = 2$) treated above, one has (with $x = 2$):

$$|C_{173}H_{33}| = F_2(4, 2) + |C_{65}H_{21}| = 48 + 126 = 174 \quad (23)$$

Here the F_2 function was determined by means of Table IV, while 126 is an STD number. Alternatively (for $x = 1$):

$$|C_{173}H_{33}| = F_1(4,2) + |C_{113}H_{27}| \quad (24)$$

where Table IV gives $F_1(4, 2) = 7$, but the cardinality of $C_{113}H_{27}$ is unknown. Now, when using the result from eq 23, we obtain the new number

$$|C_{113}H_{27}| = 174 - 7 = 167 \quad (25)$$

In the next example we adhere to the same δ value, but increase j with one unit. In other words, we consider $C_{243}H_{39}$ ($j = 5$, $\delta = 2$). With $x = 3$ one obtains:

$$|C_{243}H_{39}| = F_3(5, 2) + |C_{63}H_{21}| = 260 + 290 = 550 \quad (26)$$

where again an STD number (for $C_{63}H_{21}$) was employed. Similar to the previous example we now obtain two new numbers with $x = 2$ and $x = 1$, by means of $F_2(5, 2) = 60$ and $F_1(5, 2) = 8$, respectively. They are

$$|C_{111}H_{27}| = 550 - 60 = 490 \quad (27)$$

$$|C_{171}H_{33}| = 550 - 8 = 542 \quad (28)$$

Table IV. Functions $F_x(j, \delta)^a$

δ	x	$F_x(j, \delta)$
1	1	$3j + 1$
	2	$21j - 14$
	3	$108j - 171 - \epsilon$
2	1	$1/2(3j + 1 + \epsilon)$
	2	$1/2(27j - 15 + 3\epsilon)$
	3	$1/2(147j - 215 + 5\epsilon)$
3	1	$j + 1$
	2	$12j - 5$
	3	$64j - 81$
4	1	$1/2(3j + 3 - \epsilon)$
	2	$1/2(27j - 3 - 3\epsilon)$
	3	$1/2(147j - 161 - 5\epsilon)$
5	1	$3j + 3$
	2	$21j$
	3	$108j - 100$
6	1	$1/2(j + 1 + \epsilon)$
	2	$7j + 2\epsilon$
	3	$1/2(87j - 75 + 9\epsilon)$
	4	$196j - 343 + 8\epsilon$

^{a} See footnote a, Table III.

In this way we have reproduced all the numbers for constant-isomer series of benzenoids reported by Dias.[6-8] In particular we have confirmed the value $|C_{297}H_{43}| = 796$, which was a predicted value based on induction.[7] We have also computed $|C_{310}H_{44}|$, for which the approximate value ~ 1800 was given.[8]

Let the formula $C_{310}H_{44}$ be our last example. It is identified by $j = 6$, $\delta = 1$. It follows (for $x = 3$):

$$|C_{310}H_{44}| = F_3(6, 1) + |C_{100}H_{26}| = 476 + 1324 = 1800 \quad (29)$$

Here an STD number (for $C_{100}H_{26}$) was used, and the Dias value for $C_{310}H_{44}$ was obtained exactly.

CONCLUSION

This work gives an original contribution to the studies of constant-isomer series of benzenoids, inspired by the recent work of Dias.[6-8] There is still more to be done in this area. Dias observed, for instance, a pattern in the cardinalities for the constant-isomer series and referred to it as a new topological paradigm.[7,13] This paradigm is so far not proved or disproved, and neither has the present analysis explained its origin. Dias has also defined a topological equivalence[7,8] between members of the constant-isomer series that are governed by the paradigm. So far also this one-to-one correspondence between certain sets of benzenoids is a mystery.

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(12) It is supposed to be very useful to have the expressions (eq 5) in order to assert that a formula C_nH_s really pertains to a constant-isomer series. Dias[4] has, for instance, given wrong formulas for the higher members of the isomer series starting with $C_{35}H_{15}$ and $C_{45}H_{17}$; these formulas are corrected in the later publications.[6-8] Furthermore, in the first publication[4] Dias stated erroneously that $C_{33}H_{15}$ and $C_{43}H_{17}$ are the first formulas in constant-isomer series.
(13) Dias, J. R. *Acta. Cryst.* Submitted for publication.