What do We Know about the Numbers of Benzenoid Isomers?

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The numbers of benzenoid chemical isomers, represented by the formulas C_nH_s, are reviewed. The data which have been deduced from the available literature are supplemented.

Introduction

The enumeration and classification of benzenoid hydrocarbons (or rather their molecular graphs or benzenoid systems) has become a significant part of molecular topology; see, e.g. the consolidated report by fourteen authors [1] with supplementary data [2, 3] and references cited therein. In most of these works the number of hexagons (or hexagonal rings) is taken as the leading parameter. It is usually identified by the symbol h. Another problem is to enumerate the benzenoids with a given number of carbon atoms (n) and hydrogen atoms (s) in the chemical formula, viz. C_nH_s. This is the enumeration of benzenoid isomers, the topic of the present work. Isomer enumerations have a long tradition, linked to works of more than hundred years ago. The enumeration of alkane isomers (C_NH_{2N+2}) is a relatively well known story; some of the key references should include Cayley from 1875 [4], Herrmann from 1880 [5], Henze and Blair from 1931 [6], and finally the more recent computer works of Davis et al. [7] and of Knop et al. [8].

The two problems, enumeration of benzenoids with h hexagons and the enumeration of C_nH_s isomers, are not so much contrasted to each other as it sometimes may seem, for instance when reading the statement of Dias [9]: "In this paper, the scope and framework for achieving this goal [systematically enumerate all possible polycyclic aromatic hydrocarbons] is defined. The basis for this framework is the molecular formula in contrast to the number of hexagonal rings [10]." As a matter of fact, all benzenoid isomers with a given molecular formula (C_nH_s) have the same number of hexagonal rings (h). Therefore the classes of benzenoid isomers form subclasses under the sets of benzenoids with the same h values. For instance, the benzenoids with $h=4$ comprise exactly the isomers of $C_{16}H_{10}$, $C_{17}H_{11}$ and $C_{18}H_{12}$. The subdivision leading to the classes of benzenoid isomers is treated in detail in a subsequent section.

So what do we know about the numbers of benzenoid isomers? Quite a lot, in fact. This knowledge is basically gained from three types of sources:

(a) The scriptures of Dias which contain: an article series in ten parts [9, 11–19], an early review [20], a monograph [21], and the most recent papers [22–24].

(b) Information from other works on classification and/or enumeration of benzenoids [1–3, 25–28], wherein the benzenoid isomers are not treated explicitly. Nevertheless, as we shall see, substantial amounts of data pertaining to C_nH_s may be "hidden" in such works.

(c) Own works: a note [29] to one of the Dias papers [24], and the original contributions of the present work.

In this paper it is attempted to summarize all the available knowledge about the numbers of benzenoid isomers. However, the existing specific enumerations of 2-factorable benzenoids (incorporating all-benzenoids) [14–16, 20–22, 24, 30, 31] are not included. We have also avoided the Dias [13, 15, 20, 21] concept of strictly pericondensed benzenoids. It should be noted specifically that helicenic systems are excluded from the data consistently.

Periodic Table for Benzenoid Hydrocarbons

By the invention of a periodic table, Dias [9] created, in an ingenious way, orderness in the chaotic myriads of chemical formulas for benzenoid hydrocar-

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* Part XI of the series "Enumeration and Classification of Benzenoid Hydrocarbons".

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bons, which may be written. This periodic table has been reproduced (to different extents) so many times [8, 9, 11–18, 20, 21] that only a short portion of it seems to be sufficient to show here; cf. Table 1. Usually the table is given only for even-numbered carbon atoms (n even), but we have also included formulas where n is odd. Thus our table is a fusion of the two periodic tables given separately in one of the Dias publications [18]. Furthermore, we have included benzene (C_6H_6). The table extends infinitely to the right and downwards. The formulas are listed in a coordinate system with respect to the number of internal vertices of the benzenoid system, n_i (corresponding to internal carbon atoms), and the Dias parameter, d_s (see below).

Some Topological Properties

When is a Formula C_nH_s Compatible with a Benzenoid Hydrocarbon?

Dias [9] has developed an algorithm for deciding whether a formula C_nH_s theoretically is compatible with a benzenoid hydrocarbon or not. This is not at all a trivial problem. The Dias algorithm seems to contain an element of empirical knowledge and not to be proved mathematically. An alternative method [29, 32] is based on the exact results from a mathematical analysis of Harary and Harborth [33] and outlined in the following.

(i) The possible integer values of n are, 6, 10, 13, 14, $\geqq 16$.

(ii) Either (a) both n and s are even, or (b) both n and s are odd.

(iii) When n is given, the possible integer values of s are

$$2\left\{\tfrac{1}{2}(n+\sqrt{6n})\right\}-n \leqq s \leqq n+2-2\left\{\tfrac{1}{4}(n-2)\right\}, \qquad (1)$$

when $\{x\}$ is used to denote the smallest integer larger than or equal to x.

Comments to the above rules: (i) The possible integer values of s turn out to be 6, $\geqq 8$. (ii) In case (a) the benzenoid may be Kekuléan (non-radicalic hydrocarbon) or non-Kekuléan (a radical). In case (b) the benzenoid must be non-Kekuléan. (iii) The upper bound of (1) may be written, when n is even,

$$s \leqq \begin{cases} (n/2)+3; & n=6, 10, 14, 18, \ldots, \\ (n/2)+2; & n=16, 20, 24, 28, \ldots. \end{cases} \qquad (2)$$

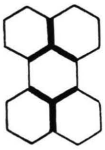
The Dias Parameter

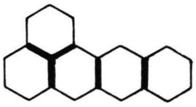
The Dias parameter d_s [9] (see Table 1) is an invariant for benzenoid systems and defined in terms of other invariants by

$$d_s = h - n_i - 2 = (n_e/2) - h - 3. \qquad (3)$$

Here n_i is the number of internal vertices (see also Table 1), while n_e is the number of external vertices, also equal to the length of the perimeter (boundary) of the benzenoid. Dias [9] interpreted the invariant d_s as the number of tree disconnections of internal edges. Examples:


$d_s = 0$


$d_s = 1$


$d_s = 2$

Negative values of d_s indicate tree connections. This phenomenon occurs for the first time (at $h=7$) for coronene, where six of the internal edges form a cycle (see the illustration below). It should be noted that d_s actually indicates the net number between disconnections and connections [20]; cf. the case of benzo[*a*]-coronene below.


$d_s = -1$

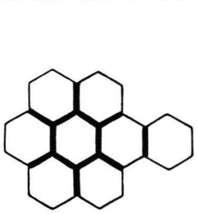

$d_s = 0$

Table 1. Periodic table for benzenoid hydrocarbons.

d_s …	−2	−1	0	1	…	n_i
		C_6H_6	$C_{10}H_8$	$C_{14}H_{10}$	…	0
			$C_{13}H_9$	$C_{17}H_{11}$	…	1
			$C_{16}H_{10}$	$C_{20}H_{12}$	…	2
			$C_{19}H_{11}$	$C_{23}H_{13}$	…	3
			$C_{22}H_{12}$	$C_{26}H_{14}$	…	4
			$C_{25}H_{13}$	$C_{29}H_{15}$	…	5
		$C_{24}H_{12}$	$C_{28}H_{14}$	$C_{32}H_{16}$	…	6
		$C_{27}H_{13}$	$C_{31}H_{15}$	$C_{35}H_{17}$	…	7
		$C_{30}H_{14}$	$C_{34}H_{16}$	$C_{38}H_{18}$	…	8
		$C_{33}H_{15}$	$C_{37}H_{17}$	$C_{41}H_{19}$	…	9
	$C_{32}H_{14}$	$C_{36}H_{16}$	$C_{40}H_{18}$	$C_{44}H_{20}$	…	10
	…	…	…	…	…	.
…	…	…	…	…	…	.

How to Find the Place of C_nH_s in the Periodic Table?

Known connections between different invariants of benzenoids [8, 9, 12, 21, 32, 33] give readily the coordinates (d_s, n_i) in terms of the numbers n and s of the chemical formula as

$$n_i = n - 2s + 6, \quad d_s = \tfrac{1}{2}(3s - n) - 7. \tag{4}$$

Other Relations Between Benzenoid Invariants

Other invariants for a benzenoid C_nH_s are given by

$$h = \tfrac{1}{2}(n - s) + 1, \quad n_e = 2s - 6. \tag{5}$$

If n_e is written as

$$n_e = s + t, \tag{6}$$

where t denotes the number of external vertices of degree 3 (tertiary carbon atoms on the perimeter), then the relation

$$t = s - 6 \tag{7}$$

emerges immediately on combining (6) and the last part of (5). Dias [9] conducted an inductive proof exclusively for (7).

It is also useful to have ready formulas for n and s in terms of other invariants. It is easily found that

$$n = 4h - n_i + 2, \qquad s = 2h - n_i + 4, \tag{8}$$

$$n = 2h + (n_e/2) + 1, \quad s = (n_e/2) + 3 \tag{9}$$

and

$$n = 3n_i + 4d_s + 10, \quad s = n_i + 2d_s + 8. \tag{10}$$

Finally we give the relation

$$h = n_i + d_s + 2, \tag{11}$$

cf. also (3).

The Three Sources for Numbers of Benzenoid Isomers

Here it is referred to the points (a), (b) and (c) of the Introduction.

(a) Scriptures of Dias

The relevant publications of Dias [9, 11–24] are a pioneering work in the treatment of benzenoid isomers and should be of great interest for chemists. However, the author has repeatedly stressed that his numbers are tentative, omissions may occur, or mistakes are unavoidable. We have found that the enumeration results in general should not be accepted without criticism.

An error in the Dias numbers for benzenoid isomers seems first to have been noticed by Knop et al. [35]. We have examined critically all the relevant data of Dias, and one of us [29] has specified a number of errors. In the present work these incorrect numbers are simply omitted from the subsequent tables.

(b) Hidden Information in Enumeration Data

An enumeration and classification of the benzenoids according to h and n_i gives precise information about numbers of C_nH_s isomers. Knop et al. [8] were perfectly well aware of this fact when they compared some Dias numbers to their own. Equation (8) gives the pertinent relations between the pairs of invariants (h, n_i) and (n, s).

The same information is obtained from an enumeration and classification according to h and n_e, as was pointed out elsewhere [32]. In this case (9) is relevant. In the extensive computations of Stojmenović et al. [27] the benzenoids are classified by (h, n_e).

(c) Present Work

A computer program was designed for the enumeration of benzenoid isomers (C_nH_s) on the basis of the invariants h and n_i. Furthermore, each set of isomers was subjected to the **neo** classification [1, 32, 36] (**n** = normal, **e** = essentially disconnected, **o** = non-Kekuléan benzenoids), where the non-Kekuléan systems were subdivided according to their color excess (Δ value). There are several possibilities to check the correctness of our results. First of all, we have the extensive data of Stojmenović et al. [27], which give total numbers of benzenoid isomers. These data are supposed to be completely reliable. They were obtained by computer programming, and all numbers for $h \leqq 10$ agree with those of Knop et al. [8, 25], who classified the benzenoids according to (h, n_i). Next, a substantial amount of data exists for the numbers of benzenoids with given values of h and Δ [1–3].

In addition, we have used some of the same methods as Dias [13, 15], taking advantage of the excised internal structures.

Presentation of Tables

Table 2 gives the full listing of the numbers of benzenoid isomers for $h \leqq 10$ with the classifications spec-

Table 2. Numbers of benzenoid chemical isomers; $h \leqq 10$.

h	n_i	d_s	Formula	$\Delta=0$			o (non-Kekuléan)				Total isomers*
				n	e	Total Kek.	$\Delta=1$	2	3	Total non-Kek.	
1	0	−1	C_6H_6	1[a]		1					1
2	0	0	$C_{10}H_8$	1[a]		1					1
3	0	1	$C_{14}H_{10}$	2[a]		2					2
	1	0	$C_{13}H_9$	0		0	1[b]			1[c]	1
4	0	2	$C_{18}H_{12}$	5[a]		5					5
	1	1	$C_{17}H_{11}$	0		0	1[b]			1[c]	1
	2	0	$C_{16}H_{10}$	1		1[d]	0			0	1
5	0	3	$C_{22}H_{14}$	12[a]		12					12
	1	2	$C_{21}H_{13}$	0		0	6[b]			6[c]	6
	2	1	$C_{20}H_{12}$	2	1	3[d]	0			0	3
	3	0	$C_{19}H_{11}$	0	0	0	1[b]			1[c]	1
6	0	4	$C_{26}H_{16}$	36[e]		36					36
	1	3	$C_{25}H_{15}$	0		0	24			24[c]	24
	2	2	$C_{24}H_{14}$	10	3	13[d]	0	1[b]		1[c]	14
	3	1	$C_{23}H_{13}$	0	0	0	4	0		4[c]	4
	4	0	$C_{22}H_{12}$	2	0	2[d]	0	1[b]		1[e]	3
7	0	5	$C_{30}H_{18}$	118[f]		118					118
	1	4	$C_{29}H_{17}$	0		0	106			106[c]	106
	2	3	$C_{28}H_{16}$	40	22	62[e]	0	6[b]		6[c]	68
	3	2	$C_{27}H_{15}$	0	0	0	25	0		25[c]	25
	4	1	$C_{26}H_{14}$	8	1	9[d]	0	1[b]		1[c]	10
	5	0	$C_{25}H_{13}$	0	0	0	3	0		3[c]	3
	6	−1	$C_{24}H_{12}$	1	0	1[d]	0	0		0	1
8	0	6	$C_{34}H_{20}$	411[f]		411					411
	1	5	$C_{33}H_{19}$	0		0	453			453[c]	453
	2	4	$C_{32}H_{18}$	180	107	287[c]	0	42[b]		42[c]	329
	3	3	$C_{31}H_{17}$	0	0	0	144	0		144[c]	144
	4	2	$C_{30}H_{16}$	45	13	58[e]	0	9[b]		9[c]	67
	5	1	$C_{29}H_{15}$	0	0	0	21	0		21[c]	21
	6	0	$C_{28}H_{14}$	7	1	8[d]	0	1[b]		1[e]	9
	7	−1	$C_{27}H_{13}$	0	0	0	1	0		1[c]	1
9	0	7	$C_{38}H_{22}$	1489[f]		1489					1489
	1	6	$C_{37}H_{21}$	0		0	1966			1966[c]	1966
	2	5	$C_{36}H_{20}$	777	575	1352[c]	0	249		249[c]	1601
	3	4	$C_{35}H_{19}$	0	0	0	823	0	2[b]	825[c]	825
	4	3	$C_{34}H_{18}$	225	108	333[e]	0	63	0	63[c]	396
	5	2	$C_{33}H_{17}$	0	0	0	153	0	1[b]	154[c]	154
	6	1	$C_{32}H_{16}$	37	9	46[e]	0	9	0	9[c]	55
	7	0	$C_{31}H_{15}$	0	0	0	15	0	0	15[c]	15
	8	−1	$C_{30}H_{14}$	3	0	3[d]	0	1	0	1[e]	4
10	0	8	$C_{42}H_{24}$	5572[f]		5572					5572
	1	7	$C_{41}H_{23}$	0		0	8395			8395	8395
	2	6	$C_{40}H_{22}$	3403	2853	6256	0	1396		1396	7652
	3	5	$C_{39}H_{21}$	0	0	0	4491	0	27[b]	4518	4518
	4	4	$C_{38}H_{20}$	1132	775	1907	0	433	0	433	2340
	5	3	$C_{37}H_{19}$	0	0	0	1007	0	11[b]	1018	1018
	6	2	$C_{36}H_{18}$	236	101	337	0	79	0	79	416
	7	1	$C_{35}H_{17}$	0	0	0	123	0	0	123	123
	8	0	$C_{34}H_{16}$	31	3	34[g]	0	8	0	8[g]	42
	9	−1	$C_{33}H_{15}$	0	0	0	8	0	1[b]	9[h]	9
	10	−2	$C_{32}H_{14}$	1	0	1[e]	0	0	0	0	1

* From Knop et al. (1983) [25].

[a] Catacondensed hydrocarbons without helicenic systems: Balaban and Harary (1968) [10]; [b] Brunvoll et al. (1988) [3]; [c] Knop et al. (1985) [8] ; [d] Dias (1982) [9], incorrect data are omitted; [e] Dias (1984) [15], incorrect data are omitted; [f] Catacondensed hydrocarbons without helicenic systems: Knop et al. (1983) [25]; [g] Cyvin in press [29]; [h] Dias (1986) [18], incorrect data are omitted.

ified above. Table 3 shows the total numbers of benzenoid C_nH_s isomers as far as they are known, without further classification. For many of these entries, when they are not too large, the classifications have been worked out (without computer aid). These results are presented in Table 4.

One-Isomer and Few-Isomer Series

One-Isomer Series

When certain forms of benzenoids are considered one may give the number of chemical isomers for infinitely large benzenoids.

Already in his early paper Dias [11] described the one-isomer formulas C_6H_6, $C_{24}H_{12}$, $C_{54}H_{18}$, $C_{96}H_{24}$, $C_{150}H_{30}$, ... They pertain to benzene, coronene, circumcoronene, dicircumcoronene, tricircumcoronene, etc. Let us consider in a more general way the *j*-circumbenzenes, where $j=0$ corresponds to what we shall call the ground form (not being circumscribed), in the present case benzene; cf. Figure 1. Then $j=1$ gives coronene, $j=2$ circumcoronene, etc. A simple combinatorial analysis gave the general formula: (*j*-circumbenzene) $C_{6(j+1)^2}H_{6(j+1)}$; see also Dias [37]. The relevant invariants in terms of *j* were found to be

$$h^{(j)}=3j^2+3j+1, \quad n_i^{(j)}=6j^2, \tag{12}$$

$$d_s^{(j)}=-3j^2+3j-1. \tag{13}$$

Dias [12] observed that the d_s value (with negative sign) corresponds to the number of hexagons of the prior member of the series. In our notation this means $-d_s^{(j+1)}=h^{(j)}$. This feature is indeed verified on substituting j with $j+1$ in (13). We shall see in a subsequent section that this is a quite general phenomenon for circumscribed benzenoids.

Two additional one-isomer series were also detected by Dias [13, 15], in which the ground forms are naphthalene and pyrene; cf. Figure 1. In the former case one has $C_{10}H_8$, $C_{32}H_{14}$, $C_{66}H_{20}$, $C_{112}H_{26}$, $C_{170}H_{32}$, ... pertaining to naphthalene, ovalene (circumnaphthalene), circumovalene (dicircumnaphthalene), tricircumnaphthalene, tetracircumnaphthalene, etc. In the latter case, $C_{16}H_{10}$, $C_{42}H_{16}$, $C_{80}H_{22}$, $C_{130}H_{28}$, ... are the benzenoids pyrene, circumpyrene, dicircumpyrene, tricircumpyrene, etc. Also in these cases the general formula and expressions for the relevant invariants were worked out (see also Dias [37]):

(*j*-circumnaphthalene) $C_{2(3j^2+8j+5)}H_{2(3j+4)}$:

$$h^{(j)}=(j+1)(3j+2), \quad n_i^{(j)}=2j(3j+2), \tag{14}$$

$$d_s^{(j)}=-3j^2+j. \tag{15}$$

(*j*-circumpyrene) $C_{2(j+2)(3j+4)}H_{2(3j+5)}$:

$$h^{(j)}=(j+1)(3j+4), \quad n_i^{(j)}=2(j+1)(3j+1), \tag{16}$$

$$d_s^{(j)}=-3j^2-j. \tag{17}$$

The three one-isomer series described above yield Kekuléan benzenoids, which all are normal. Dias [18] found also three one-isomer series for non-Kekuléan benzenoids (with $\Delta=1$). They are the polycircumphenalenes ($C_{13}H_9$, $C_{37}H_{15}$, $C_{73}H_{21}$, $C_{121}H_{27}$, ...), polycircumnaphthanthrenes ($C_{19}H_{11}$, $C_{47}H_{17}$, $C_{87}H_{23}$, $C_{139}H_{29}$, ...) and polycircumbenzo[*bc*]coronenes ($C_{27}H_{13}$, $C_{59}H_{19}$, $C_{103}H_{25}$, $C_{159}H_{31}$). The ground forms are shown in Figure 1.

Few-Isomer Series

Dias [15] pursued the idea of circumscribing benzenoids in order to produce isomer series, but now with more than one form for each chemical formula. Figure 2 shows the ground forms of six such few-isomer series, listed systematically by increasing numbers of hexagons (h). Two of the series, viz. for $h=11$ and $h=15$, are supplements [18] to those which first were given by Dias [15]. The series are briefly described in the following.

$h=6$: $C_{22}H_{12}$, $C_{52}H_{18}$, $C_{94}H_{24}$, $C_{148}H_{30}$, ...;

each formula representing 2 Kekuléan (normal) benzenoids +1 non-Kekuléan ($\Delta=2$).

$h=9$: $C_{30}H_{14}$, $C_{64}H_{20}$, $C_{110}H_{26}$, $C_{168}H_{32}$, ...;

3 Kekuléan (normal) +1 non-Kekuléan ($\Delta=2$).

$h=11$: $C_{35}H_{15}$, $C_{71}H_{21}$, $C_{119}H_{27}$, ...;

2 non-Kekuléans ($\Delta=1$).

$h=13$: $C_{40}H_{16}$, $C_{78}H_{22}$, $C_{128}H_{28}$, ...;

3 Kekuléans (normal) +1 non-Kekuléan ($\Delta=2$).

$h=15$: $C_{45}H_{17}$, $C_{85}H_{23}$, $C_{137}H_{29}$, ...;

4 non-Kekuléans ($\Delta=1$).

$h=17$: $C_{50}H_{18}$, $C_{92}H_{24}$, $C_{146}H_{30}$, ...;

7 Kekuléans (normal) +2 non-Kekuléans ($\Delta=2$).

Table 3. Total numbers of benzenoid chemical isomers for $h \geqq 11$. The listing is incomplete for $h > 12$.

h	n_i	d_s	Formula	Total isomers
11	0	9	$C_{46}H_{26}$	21 115[a]
	1	8	$C_{45}H_{25}$	35 885
	2	7	$C_{44}H_{24}$	36 109
	3	6	$C_{43}H_{23}$	24 020
	4	5	$C_{42}H_{22}$	13 415
	5	4	$C_{41}H_{21}$	6 405
	6	3	$C_{40}H_{20}$	2 811
	7	2	$C_{39}H_{19}$	1 008
	8	1	$C_{38}H_{18}$	333
	9	0	$C_{37}H_{17}$	100
	10	−1	$C_{36}H_{16}$	26
	11	−2	$C_{35}H_{15}$	2
12	0	10	$C_{50}H_{28}$	81 121[a, b]
	1	9	$C_{49}H_{27}$	152 688[b]
	2	8	$C_{48}H_{26}$	168 318
	3	7	$C_{47}H_{25}$	124 119
	4	6	$C_{46}H_{24}$	74 985
	5	5	$C_{45}H_{23}$	38 727
	6	4	$C_{44}H_{22}$	18 306
	7	3	$C_{43}H_{21}$	7 375
	8	2	$C_{42}H_{20}$	2 713
	9	1	$C_{41}H_{19}$	878
	10	0	$C_{40}H_{18}$	279
	11	−1	$C_{39}H_{17}$	61
	12	−2	$C_{38}H_{16}$	13
	13	−3	$C_{37}H_{15}$	1
13	4	7	$C_{50}H_{26}$	408 785
	5	6	$C_{49}H_{25}$	226 837
	6	5	$C_{48}H_{24}$	114 326
	7	4	$C_{47}H_{23}$	50 405
	8	3	$C_{46}H_{22}$	20 119
	9	2	$C_{45}H_{21}$	7 253
	10	1	$C_{44}H_{20}$	2 459
	11	0	$C_{43}H_{19}$	708
	12	−1	$C_{42}H_{18}$	187
	13	−2	$C_{41}H_{17}$	35
	14	−3	$C_{40}H_{16}$	4
14	6	6	$C_{52}H_{26}$	691 933
	7	5	$C_{51}H_{25}$	328 592
	8	4	$C_{50}H_{24}$	141 268
	9	3	$C_{49}H_{23}$	55 124
	14	1	$C_{56}H_{24}$	148 430
	15	0	$C_{55}H_{23}$	46 166
	16	−1	$C_{54}H_{22}$	13 286
	17	−2	$C_{53}H_{21}$	3 414
	18	−3	$C_{52}H_{20}$	763
	19	−4	$C_{51}H_{19}$	117
	20	−5	$C_{50}H_{18}$	9
18	14	2	$C_{60}H_{26}$	1 262 442
	15	1	$C_{59}H_{25}$	424 429
	16	0	$C_{58}H_{24}$	133 713
	17	−1	$C_{57}H_{23}$	39 143
	18	−2	$C_{56}H_{22}$	10 587
	19	−3	$C_{55}H_{21}$	2 437
	20	−4	$C_{54}H_{20}$	471
	21	−5	$C_{53}H_{19}$	53
	22	−6	$C_{52}H_{18}$	3
19	16	1	$C_{62}H_{26}$	1 223 950
	17	0	$C_{61}H_{25}$	388 180
	18	−1	$C_{60}H_{24}$	116 648
	19	−2	$C_{59}H_{23}$	32 042
	20	−3	$C_{58}H_{22}$	7 885
	21	−4	$C_{57}H_{21}$	1 647
	22	−5	$C_{56}H_{20}$	256
	23	−6	$C_{55}H_{19}$	18
	24	−7	$C_{54}H_{18}$	1
20	18	0	$C_{64}H_{26}$	1 140 529
	19	−1	$C_{63}H_{25}$	345 834
	20	−2	$C_{62}H_{24}$	97 607
	21	−3	$C_{61}H_{23}$	25 050
	22	−4	$C_{60}H_{22}$	5 726
	23	−5	$C_{59}H_{21}$	1 009
	24	−6	$C_{58}H_{20}$	129
	25	−7	$C_{57}H_{19}$	4
21	20	−1	$C_{66}H_{26}$	1 029 521
	21	−2	$C_{65}H_{25}$	296 025
	22	−3	$C_{64}H_{24}$	79 472
	23	−4	$C_{63}H_{23}$	18 876
	24	−5	$C_{62}H_{22}$	3 838
	25	−6	$C_{61}H_{21}$	587
26	30	−6	$C_{76}H_{26}$	414 305
	31	−7	$C_{75}H_{25}$	89 288
	32	−8	$C_{74}H_{24}$	16 114
	33	−9	$C_{73}H_{23}$	2 146
	34	−10	$C_{72}H_{22}$	156
	35	−11	$C_{71}H_{21}$	2
27	32	−7	$C_{78}H_{26}$	319 258
	33	−8	$C_{77}H_{25}$	63 732
	34	−9	$C_{76}H_{24}$	10 313
	35	−10	$C_{75}H_{23}$	1 105
	36	−11	$C_{74}H_{22}$	53
	37	−12	$C_{73}H_{21}$	1
28	34	−8	$C_{80}H_{26}$	240 218
	35	−9	$C_{79}H_{25}$	43 833
	36	−10	$C_{78}H_{24}$	6 214
	37	−11	$C_{77}H_{23}$	509
	38	−12	$C_{76}H_{22}$	16
29	36	−9	$C_{82}H_{26}$	174 603
	37	−10	$C_{81}H_{25}$	29 029
	38	−11	$C_{80}H_{24}$	3 456
	39	−12	$C_{79}H_{23}$	207
	40	−13	$C_{78}H_{22}$	4
30	38	−10	$C_{84}H_{26}$	123 790
	39	−11	$C_{83}H_{25}$	18 198
	40	−12	$C_{82}H_{24}$	1 799
	41	−13	$C_{81}H_{23}$	68
	42	−14	$C_{80}H_{22}$	1
31	40	−11	$C_{86}H_{26}$	84 207
	41	−12	$C_{85}H_{25}$	10 886
	42	−13	$C_{84}H_{24}$	825
	43	−14	$C_{83}H_{23}$	20
32	42	−12	$C_{88}H_{26}$	55 451
	43	−13	$C_{87}H_{25}$	6 042
	44	−14	$C_{86}H_{24}$	344
	45	−15	$C_{85}H_{23}$	4

	10	2	$C_{48}H_{22}$	20 321
	11	1	$C_{47}H_{21}$	6 594
	12	0	$C_{46}H_{20}$	2 001
	13	−1	$C_{45}H_{19}$	533
	14	−2	$C_{44}H_{18}$	120
	15	−3	$C_{43}H_{17}$	16
	16	−4	$C_{42}H_{16}$	1
15	8	5	$C_{54}H_{26}$	947 291
	9	4	$C_{53}H_{25}$	395 860
	10	3	$C_{52}H_{24}$	155 656
	11	2	$C_{51}H_{23}$	55 857
	12	1	$C_{50}H_{22}$	18 396
	13	0	$C_{49}H_{21}$	5 612
	14	−1	$C_{48}H_{20}$	1 570
	15	−2	$C_{47}H_{19}$	347
	16	−3	$C_{46}H_{18}$	70
	17	−4	$C_{45}H_{17}$	4
16	10	4	$C_{56}H_{26}$	1 132 642
	11	3	$C_{55}H_{25}$	436 698
	12	2	$C_{54}H_{24}$	156 434
	13	1	$C_{53}H_{23}$	51 691
	14	0	$C_{52}H_{22}$	16 234
	15	−1	$C_{51}H_{21}$	4 501
	16	−2	$C_{50}H_{20}$	1 121
	17	−3	$C_{49}H_{19}$	223
	18	−4	$C_{48}H_{18}$	30
	19	−5	$C_{47}H_{17}$	1
17	12	3	$C_{58}H_{26}$	1 236 839
	13	2	$C_{57}H_{25}$	440 491
	26	−7	$C_{60}H_{20}$	47
	27	−8	$C_{59}H_{19}$	1
22	22	−2	$C_{68}H_{26}$	903 415
	23	−3	$C_{67}H_{25}$	247 989
	24	−4	$C_{66}H_{24}$	62 027
	25	−5	$C_{65}H_{23}$	13 652
	26	−6	$C_{64}H_{22}$	2 467
	27	−7	$C_{63}H_{21}$	290
	28	−8	$C_{62}H_{20}$	16
23	24	−3	$C_{70}H_{26}$	771 061
	25	−4	$C_{69}H_{25}$	200 545
	26	−5	$C_{68}H_{24}$	47 167
	27	−6	$C_{67}H_{23}$	9 349
	28	−7	$C_{66}H_{22}$	1 448
	29	−8	$C_{65}H_{21}$	126
	30	−9	$C_{64}H_{20}$	4
24	26	−4	$C_{72}H_{26}$	643 859
	27	−5	$C_{71}H_{25}$	157 989
	28	−6	$C_{70}H_{24}$	34 324
	29	−7	$C_{69}H_{23}$	6 124
	30	−8	$C_{68}H_{22}$	789
	31	−9	$C_{67}H_{21}$	43
	32	−10	$C_{66}H_{20}$	1
25	28	−5	$C_{74}H_{26}$	522 218
	29	−6	$C_{73}H_{25}$	120 524
	30	−7	$C_{72}H_{24}$	24 118
	31	−8	$C_{71}H_{23}$	3 735
	32	−9	$C_{70}H_{22}$	377
	33	−10	$C_{69}H_{21}$	13
33	44	−13	$C_{90}H_{26}$	34 739
	45	−14	$C_{89}H_{25}$	3 129
	46	−15	$C_{88}H_{24}$	121
	47	−16	$C_{87}H_{23}$	1
34	46	−14	$C_{92}H_{26}$	20 811
	47	−15	$C_{91}H_{25}$	1 461
	48	−16	$C_{90}H_{24}$	39
35	48	−15	$C_{94}H_{26}$	11 719
	49	−16	$C_{93}H_{25}$	616
	50	−17	$C_{92}H_{24}$	9
36	50	−16	$C_{96}H_{26}$	6 155
	51	−17	$C_{95}H_{25}$	228
	52	−18	$C_{94}H_{24}$	3
37	52	−17	$C_{98}H_{26}$	2 979
	53	−18	$C_{97}H_{25}$	72
	54	−19	$C_{96}H_{24}$	1
38	54	−18	$C_{100}H_{26}$	1 324
	55	−19	$C_{99}H_{25}$	20
39	56	−19	$C_{102}H_{26}$	525
	57	−20	$C_{101}H_{25}$	4
40	58	−20	$C_{104}H_{26}$	186
	59	−21	$C_{103}H_{25}$	1
41	60	−21	$C_{106}H_{26}$	57
42	62	−22	$C_{108}H_{26}$	16
43	64	−23	$C_{110}H_{26}$	4
44	66	−24	$C_{112}H_{26}$	1

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[a] Catacondensed benzenoids.

[b] From He et al. [2]; all other data are from Stojmenović et al. [27].

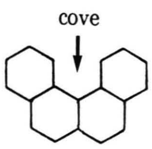
Table 4. Numbers of selected benzenoid isomers for $h \geqq 11$.

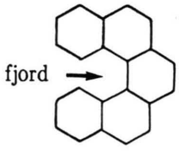
h	n_i	d_s	Formula	$\Delta=0$			o (non-Kekuléan)				
				n	e	Total Kek.	$\Delta=1$	2	3	4	Total non-Kek.
11	10	−1	$C_{36}H_{16}$	18	2	20[a]	0	6	0		6
	11	−2	$C_{35}H_{15}$	0	0	0	2	0	0		2[b]
12	12	−2	$C_{38}H_{16}$	10	0	10[c]	0	3	0	0	3[b]
	13	−3	$C_{37}H_{15}$	0	0	0	1	0	0	0	1[b]
13	13	−2	$C_{41}H_{17}$	0	0	0	34	0	1	0	35
	14	−3	$C_{40}H_{16}$	3	0	3[c]	0	1	0	0	1[b]
14	15	−3	$C_{43}H_{17}$	0	0	0	15	0	1	0	16
	16	−4	$C_{42}H_{16}$	1	0	1[c]	0	0	0	0	0
15	16	−3	$C_{46}H_{18}$	47	2	49	0	20	0	1	21
	17	−4	$C_{45}H_{17}$	0	0	0	4	0	0	0	4
16	18	−4	$C_{48}H_{18}$	22	0	22[c]	0	8	0	0	8[b]
	19	−5	$C_{47}H_{17}$	0	0	0	1	0	0	0	1[b]
17	20	−5	$C_{50}H_{18}$	7	0	7[c]	0	2	0	0	2[b]
18	22	−6	$C_{52}H_{18}$	2	0	2[c]	0	1	0	0	1[c]
19	23	−6	$C_{55}H_{19}$	0	0	0	17	0	1	0	18
	24	−7	$C_{54}H_{18}$	1	0	1[d]	0	0	0	0	0
20	25	−7	$C_{57}H_{19}$	0	0	0	4	0	0	0	4[b]
21	26	−7	$C_{60}H_{20}$	32	0	32	0	15	0	0	15
	27	−8	$C_{59}H_{19}$	0	0	0	1	0	0	0	1[b]
22	28	−8	$C_{62}H_{20}$	12	0	12[c]	0	4	0	0	4
23	30	−9	$C_{64}H_{20}$	3	0	3[c]	0	1	0	0	1[c]
24	32	−10	$C_{66}H_{20}$	1	0	1[c]	0	0	0	0	0
25	33	−10	$C_{69}H_{21}$	0	0	0	12	0	1	0	13
26	35	−11	$C_{71}H_{21}$	0	0	0	2	0	0	0	2
27	37	−12	$C_{73}H_{21}$	0	0	0	1	0	0	0	1[b]
28	38	−12	$C_{76}H_{22}$	12	0	12	0	4	0	0	4
29	40	−13	$C_{78}H_{22}$	3	0	3[c]	0	1	0	0	1[c]
30	42	−14	$C_{80}H_{22}$	1	0	1[c]	0	0	0	0	0
31	43	−14	$C_{83}H_{23}$	0	0	0	19	0	1	0	20
32	45	−15	$C_{85}H_{23}$	0	0	0	4	0	0	0	4
33	47	−16	$C_{87}H_{23}$	0	0	0	1	0	0	0	1[b]
34	48	−16	$C_{90}H_{24}$	27	0	27	0	12	0	0	12
35	50	−17	$C_{92}H_{24}$	7	0	7[c]	0	2	0	0	2[c]
36	52	−18	$C_{94}H_{24}$	2	0	2[c]	0	1	0	0	1[c]
37	54	−19	$C_{96}H_{24}$	1	0	1[d]	0	0	0	0	0
38	55	−19	$C_{99}H_{25}$	0	0	0	19	0	1	0	20
39	57	−20	$C_{101}H_{25}$	0	0	0	4	0	0	0	4[b]
40	59	−21	$C_{103}H_{25}$	0	0	0	1	0	0	0	1[b]
41	60	−21	$C_{106}H_{26}$	38	0	38	0	19	0	0	19
42	62	−22	$C_{108}H_{26}$	12	0	12	0	4	0	0	4
43	64	−23	$C_{110}H_{26}$	3	0	3[c]	0	1	0	0	1[c]
44	66	−24	$C_{112}H_{26}$	1	0	1[c]	0	0	0	0	0

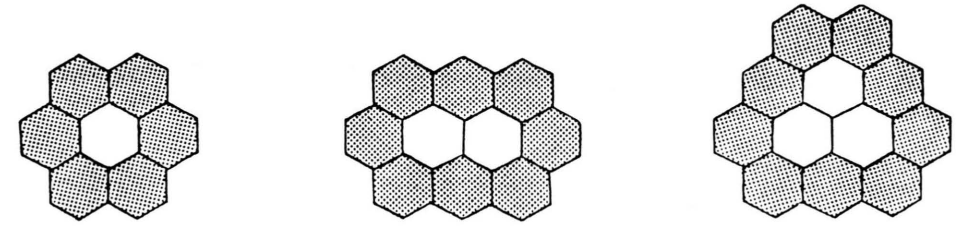
[a] Dias (1987) [21]; [b] Dias (1986) [18]; [c] Dias (1984) [15]; [d] Dias (1982) [11].

General Formulations

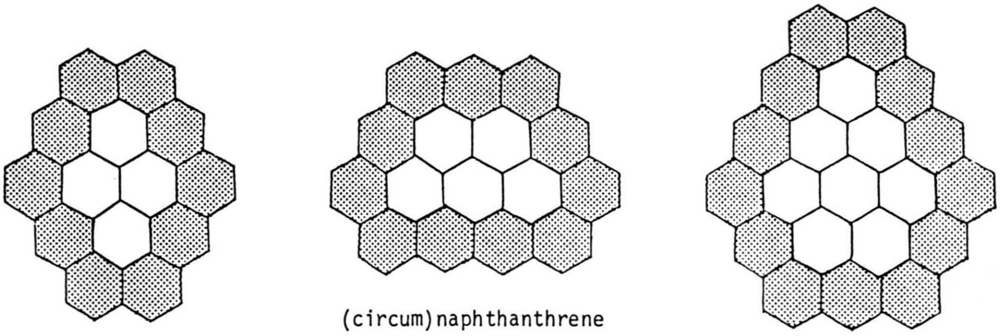
We shall give formulas of invariants for benzenoids during their circumscribing with hexagons in a quite general sense. But first we wish to point out that an arbitrary benzenoid B can not always be circumscribed to give a larger circumbenzenoid. The most obvious cases are those when B has a cove or a fjord [32, 38]. The two smallest benzenoids of this kind are depicted below.







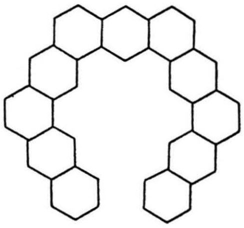
(circum)benzene (circum)naphthalene (circum)phenalene



(circum)pyrene (circum)naphthanthrene (circum)benzo[*bc*]coronene

Fig. 1. Ground forms of the one-isomer benzenoid series as white hexagons, circumscribed by grey hexagons.

The occurrence of a cove or a fjord is sufficient to make that B can not be circumscribed. However, it is not a necessary condition. Benzenoids without coves and fjords can be constructed so that they can not be circumscribed. This feature is demonstrated by the below example. The two-carbon gap criterion given by Dias [15, 18] is a sufficient and necessary condition.



Assume now that a benzenoid B can be circumscribed with hexagons, yielding the larger benzenoid B′. We shall find the relevant invariants of B′ in terms of those of B. The clue to the solution of this problem emerges from two facts: (i) the totality of vertices (corresponding to carbon atoms) in B become the internal vertices of B′; (ii) the number of vertices of degree 2 (corresponding to hydrogen atoms) increase by 6 from B to B′.

As a result one obtains the recursive formulas

$$h' = 3h - n_i + 4, \quad n'_i = n = 4h - n_i + 2, \tag{18}$$

$$d'_s = -h. \tag{19}$$

Equation (19) proves the phenomenon which was described under "polycircumbenzenes"; see after (13). The chemical formulas may be derived in a recursive way according to

$$C_{n's'} \equiv C_{n+2s+6}H_{s+6},$$

$$C_{n''s''} \equiv C_{n'+2s'+6}H_{s'+6} \equiv C_{n+4s+24}H_{s+12}.$$

Conclusion

The present paper shows the state of art with regard to benzenoid isomer enumerations. Much more work can still be done in this field. A quotation from Knop et al. [8] is relevant in this connection:

"The Dias method obviously becomes very complicated for systems with many isomeric forms because of the enormous combinatorial possibilities. However, if combined with our computer procedure [25], it can be

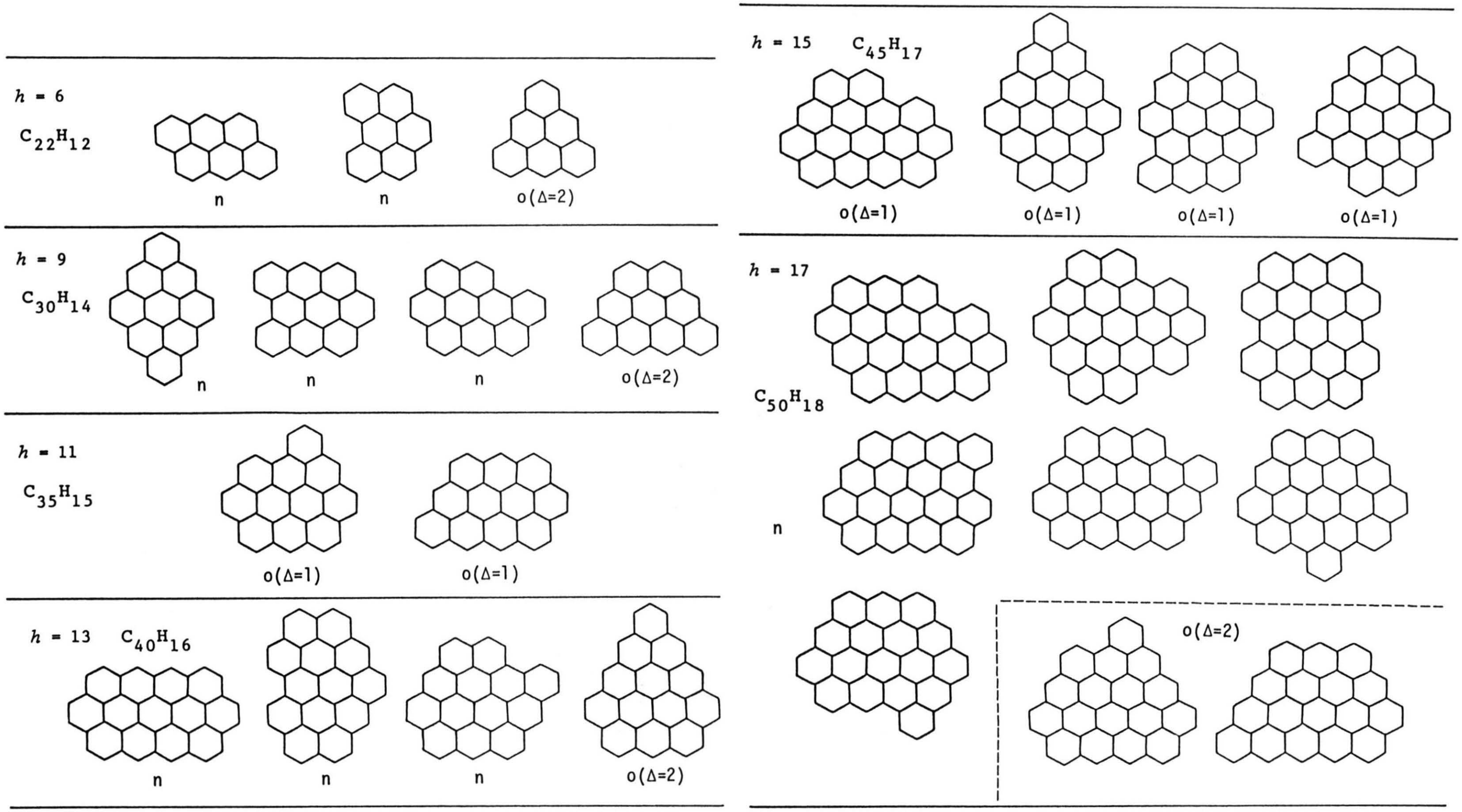


Fig. 2. Ground forms of some few-isomer benzenoid series. Abbreviations: n normal; o non-Kekuléan.

used for an efficient generation of all isomeric catafused and peri-fused (with an even number of internal vertices) benzenoid hydrocarbons of a particular CH composition."

The restriction about an even number of internal vertices is, to our opinion, not necessary. Anyhow, a computerization of the generation and enumeration methods of Dias has so far not been done.

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