

# Enumeration of Benzenoid and Coronoid Hydrocarbons

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This is a report on the present status of computer-aided enumeration and classification of benzenoids and coronoids (polyhexes). The existing data from previous works are displayed in comprehensive tables. Numerous data from papers in press are included, as well as original contributions.

## Introduction

The problem of “cell-growth” is a classical problem in mathematics [1–5]. When applied to hexagonal “animals” it has relevance to the studies of benzenoid (polycyclic aromatic) hydrocarbons, especially to their enumeration [6–27]. The research field is rapidly expanding, as is documented by the numerous papers in press or just appeared [28–34].

In works of this type it is important to define precisely the classes of systems which are subjected to enumeration. Here a benzenoid is defined in consistence with a review [35] and a book [36]. It is a planar system of identical regular hexagons, which are simply connected. The last restriction is released in the definition of coronoids. In those systems (also called “true” circulenes) a hole is recognized, which should have a size of at least two hexagons. Multiple coronoids with more than one hole are possible. It is emphasized that we adhere to the definitions which exclude helicene derivatives and similar systems.

A catacondensed system (benzenoid [35] or coronoid [28]) does not possess any vertex belonging to three hexagons [3, 35–40]. The feature is manifested by the absence of triangles in the dualist

graph. All other systems are referred to as peri-condensed. A system is non-Kekuléan when it does not possess any Kekulé structure; in the opposite case it is called Kekuléan. All catacondensed systems are known to be Kekuléan. Alternative designations for catacondensed benzenoids and pericondensed benzenoids are catafusenes and perifusenes, respectively.

The term polyhex seems to be a suitable designation for benzenoids and coronoids together.

In general it is noted that no terminology in this area has been established as a prevailing standard at present.

In the present work we summarize some previous results on enumeration of benzenoids and coronoids. Also new results are reported, where the ranges of computation have been extended with regard to the  $h$  value. Here  $h$  denotes the number of hexagons of a system.

The footnotes to tables (see below) are supposed to give the credit of priority to the different researchers. The quoted numbers are either found explicitly in the cited references or obtained simply by additions or subtraction of published numbers. Still the quotations do not give full justice to all researchers which have developed this field because of the special definitions of benzenoids and coronoids adhered to here. These conventions discriminate in particular the important works of

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Harary and Read [3] and of Lunnon [4]. These authors have included helicenes not covered by the definitions of the present work. Similarly the works of Balaban and Harary [6] and Balaban [7, 8] are discriminated due to the inclusion of helicenes.

In the present report the number of hexagons,  $h$ , is the leading parameter. As a consequence it makes the extensive works of Dias [13, 14, 17–19, 22] fall outside the present scope. This researcher concentrated upon the chemical isomerism, which is reflected by the chemical formula  $C_nH_s$ . For polyhexes  $n$  is the total number of vertices and  $s$  the number of vertices of second degree. The works of Cyvin [24] and Cyvin *et al.* [26, 31, 32], where the benzenoids are enumerated according to their Kekulé structure counts, fall also outside the scope of the present report.

## Benzenoids

### Catacondensed Benzenoids

Table 1 shows the results of enumeration for catacondensed benzenoids (catafusenes). The unbranched systems are classified according to their symmetries into [6]:

$a$  acenes (linear):  $D_{6h}$  for  $h = 1$ , otherwise  $D_{2h}$ ;  
 $m$  mirror-symmetrical,  $C_{2v}$ ;  
 $c$  centrosymmetrical,  $C_{2h}$ ;  
 $u$  unsymmetrical,  $C_s$ .

### Pericondensed Benzenoids

Table 2 shows the results of enumeration for pericondensed benzenoids (perifusenes). All non-Kekuléans ( $o$ ) are pericondensed. The Kekuléan pericondensed systems are divided into:

$np$  normal pericondensed;  
 $e$  essentially disconnected [41].

The latter systems ( $e$ ) possess edges which have fixed bonds (simple or double) in all Kekulé structures. All other Kekuléans are referred to as normal [23, 25].

### Coronoids (Single)

Multiple coronoids exist, the smallest one having  $h = 13$  [14]. They are not counted in this report.

Table 1. Numbers of catacondensed benzenoids (catafusenes).

$h$	Unbranched				Total unbranched	Branched	Total catacondensed
	$a$	$m$	$c$	$u$			
1	1 <sup>a</sup>	0	0	0	1 <sup>a</sup>	0	1 <sup>a</sup>
2	1 <sup>a</sup>	0	0	0	1 <sup>a</sup>	0	1 <sup>a</sup>
3	1 <sup>a</sup>	1 <sup>a</sup>	0	0	2 <sup>a</sup>	0	2 <sup>a</sup>
4	1 <sup>a</sup>	1 <sup>a</sup>	1 <sup>a</sup>	1 <sup>a</sup>	4 <sup>a</sup>	1 <sup>a</sup>	5 <sup>a</sup>
5	1 <sup>a</sup>	4 <sup>a</sup>	1 <sup>a</sup>	4 <sup>a</sup>	10 <sup>a</sup>	2 <sup>a</sup>	12 <sup>a</sup>
6	1 <sup>a</sup>	3 <sup>b</sup>	4 <sup>a</sup>	16 <sup>a</sup>	24 <sup>c</sup>	12 <sup>c</sup>	36 <sup>d</sup>
7	1 <sup>a</sup>	12 <sup>b</sup>	4 <sup>a</sup>	50 <sup>b</sup>	67 <sup>c</sup>	51 <sup>c</sup>	118 <sup>d</sup>
8	1 <sup>a</sup>	10 <sup>b</sup>	13 <sup>a</sup>	158 <sup>b</sup>	182 <sup>c</sup>	229 <sup>c</sup>	411 <sup>d</sup>
9	1 <sup>b</sup>	34 <sup>b</sup>	13 <sup>b</sup>	472 <sup>b</sup>	520 <sup>b,e</sup>	969 <sup>b,c</sup>	1 489 <sup>d</sup>
10	1 <sup>b</sup>	28 <sup>b</sup>	39 <sup>b</sup>	1 406	1 474	4 098	5 572 <sup>d</sup>
11	1 <sup>b</sup>	97 <sup>b</sup>	39 <sup>b</sup>	4 111	4 248	16 867	21 115 <sup>f</sup>
12	1 <sup>b</sup>	81 <sup>b</sup>	116 <sup>b</sup>	11 998	12 196	†	†
13	1	271	115	34 781	35 168	†	†
14	1	226	339	100 660	101 226	†	†
15	1	764	336	290 464	291 565	†	†
16	1	638	988	837 137	838 764	†	†
17	1	2 141	977	2 408 914	2 412 033	†	†
18	1	1 787	2 866	6 925 100	6 929 754	†	†
19	1	6 025	2 832	19 888 057	19 896 915	†	†
20	1	5 030	8 298	57 071 610	57 084 939	†	†

<sup>a</sup> Balaban and Harary [6]. – <sup>b</sup> Brunvoll, Cyvin, and Cyvin [29]. – <sup>c</sup> He and He [20]. – <sup>d</sup> Knop, Szymanski, Jeričević, and Trinajstić [11]. – <sup>e</sup> He and He [33]. – <sup>f</sup> Stojmenović, Tošić, and Doroslovački [34]. – † Unknown.

Table 2. Numbers of pericondensed benzenoids (perifusenes).

<i>h</i>	Kekuléan		Total pericondensed Kekuléan*	Non-Kekuléan	Total pericondensed**
	<i>np</i>	<i>e</i>			
3	0	0	0	1 <sup>a</sup>	1
4	1 <sup>a</sup>	0	1	1 <sup>a</sup>	2
5	2 <sup>b</sup>	1 <sup>b</sup>	3	7 <sup>a</sup>	10
6	12 <sup>b</sup>	3 <sup>b</sup>	15	30 <sup>a</sup>	45
7	49 <sup>b</sup>	23 <sup>b</sup>	72	141 <sup>c</sup>	213
8	232 <sup>b</sup>	121 <sup>b</sup>	353	671 <sup>c</sup>	1024
9	1042 <sup>b</sup>	692 <sup>b</sup>	1734	3282 <sup>b</sup>	5016
10	4803 <sup>d</sup>	3732	8535	15979	24514
11	21804 <sup>d</sup>	19960	41764	78350	120114

\* The sums of numbers in the two first columns.

\*\* Obtained as differences from published data (Grand total – Total catacondensed).

<sup>a</sup> Balaban and Harary [6]. – <sup>b</sup> Brunvoll, Cyvin, and Cyvin [29]. – <sup>c</sup> He and He [20]. <sup>d</sup> Cyvin, Brunvoll, and Cyvin [32].

Table 3. Numbers of catacondensed coronoids.

<i>h</i>	Primitive (unbranched)	Annelated (branched)	Total catacondensed*
8	1 <sup>a</sup>	0	1
9	1 <sup>a</sup>	2 <sup>a</sup>	3
10	3 <sup>a</sup>	12 <sup>a</sup>	15
11	2 <sup>a</sup>	60 <sup>a</sup>	62
12	11 <sup>a</sup>	301	312
13	12 <sup>a</sup>	1423	1435
14	40 <sup>a</sup>	†	†
15	68	†	†
16	192	†	†
17	395	†	†
18	1061	†	†
19	2432	†	†
20	6318	†	†

\* The sums of numbers of the two first columns.

<sup>a</sup> Brunvoll, Cyvin, and Cyvin [28]. – † Unknown.

Table 4. Numbers of pericondensed coronoids.

<i>h</i>	Kekuléan		Total pericondensed Kekuléan*	Non-Kekuléan	Total pericondensed**
	<i>np</i>	<i>e</i>			
9	0	0	0	2 <sup>a</sup>	2 <sup>a</sup>
10	9 <sup>a</sup>	0	9	19 <sup>a</sup>	28 <sup>a</sup>
11	64 <sup>a</sup>	2 <sup>a</sup>	66	155 <sup>a</sup>	221 <sup>a</sup>
12	508	34	542	1100 <sup>a</sup>	1642

\* The sums of numbers in the two first columns.

\*\* Sum Pericondensed Kekuléan + Non-Kekuléan.

<sup>a</sup> Brunvoll, Cyvin, and Cyvin [28].

Table 3 shows the numbers of catacondensed coronoids. Primitive [28] systems are defined as consisting of one single circular chain. The other catacondensed systems have at least one branching hexagon and are sometimes referred to as annelated.

Table 4 shows the number of pericondensed coronoids. The designations *np* and *e* refer to normal pericondensed and essentially disconnected systems in analogy with the benzenoids (see above, especially Table 2).

### The “neo” Classification

The usefulness of a distinction between normal (*n*) and essentially disconnected (*e*) benzenoids or coronoids among the Kekuléan systems has been pointed out previously [24, 26, 29]. Here the normal benzenoids or coronoids refer to the catacondensed systems together with the normal pericondensed. The inclusion of non-Kekuléan systems (*o*) gives the grand total (*n* + *e* + *o*). The concept *neo* classification refers to the *n*, *e* and *o* classes. The different numbers of the benzenoids and coronoids (in parentheses) within this classification are summarized in Table 5.

### More Special Classifications

#### Symmetry

The classification of unbranched catacondensed benzenoids according to symmetry was first undertaken by Balaban and Harary [6], and pursued by Brunvoll *et al.* [29]; cf. Table 1. It has been pointed out that the benzenoids in general can belong to one of the eight symmetries [42]:  $D_{6h}$ ,  $C_{6h}$ ,  $D_{3h}$ ,  $C_{3h}$ ,  $D_{2h}$ ,  $C_{2h}$ ,  $C_{2v}$  or  $C_s$ . The same is the case for coronoids. Table 6 summarizes the distribution into the different symmetries for all benzenoids (also pericondensed and branched catacondensed) and coronoids; the latter results are given in parentheses.

#### $\Delta$ Values

The positive integer  $\Delta$  is an important parameter for benzenoids and coronoids. It is defined as the absolute magnitude of the difference between the numbers of black and white vertices, referring to

Table 5. The “neo” classification for benzenoids and coronoids (numbers in parentheses).

$h$	$n$	$e$	$o^*$	Total benzenoids (coronoids)	Total benzenoids + coronoids
1	1 <sup>a</sup>	0	0	1 <sup>b</sup>	1 <sup>c</sup>
2	1 <sup>a</sup>	0	0	1 <sup>b</sup>	1 <sup>c</sup>
3	2 <sup>a</sup>	0	1 <sup>d</sup>	3 <sup>b</sup>	3 <sup>c</sup>
4	6 <sup>a</sup>	0	1 <sup>d</sup>	7 <sup>b</sup>	7 <sup>c</sup>
5	14 <sup>a</sup>	1 <sup>a</sup>	7 <sup>d</sup>	22 <sup>b</sup>	22 <sup>c</sup>
6	48 <sup>a</sup>	3 <sup>a</sup>	30 <sup>d</sup>	81 <sup>e</sup>	81 <sup>c</sup>
7	167 <sup>a</sup>	23 <sup>a</sup>	141 <sup>f</sup>	331 <sup>e</sup>	331 <sup>c</sup>
8	643 <sup>a</sup> (1 <sup>g</sup> )	121 <sup>a</sup>	671 <sup>f</sup>	1 435 <sup>e</sup> (1 <sup>h</sup> )	1 436 <sup>c</sup>
9	2 531 <sup>a</sup> (3 <sup>g</sup> )	692 <sup>a</sup>	3 282 <sup>a</sup> (2 <sup>g</sup> )	6 505 <sup>e</sup> (5 <sup>h</sup> )	6 510 <sup>c,i</sup>
10	10 375 <sup>j</sup> (24 <sup>g</sup> )	3 732	15 979 (19 <sup>g</sup> )	30 086 <sup>e</sup> (43 <sup>h,k</sup> )	30 129 <sup>i</sup>
11	42 919 <sup>j</sup> (126 <sup>g</sup> )	19 960 (2 <sup>g</sup> )	78 350 (155 <sup>g</sup> )	141 229 <sup>l</sup> (283 <sup>g</sup> )	141 512
12	† (820)	† (34)	† (1100 <sup>g</sup> )	† (1954 <sup>g</sup> )	†

\* Also Table 2 (coronoids Table 4).

<sup>a</sup> Brunvoll, Cyvin, and Cyvin [29].<sup>b</sup> Klarner [1].<sup>c</sup> He and He [33].<sup>d</sup> Balaban and Harary [6].<sup>e</sup> Knop, Szymanski, Jeričević, and Trinajstić [11].<sup>f</sup> He and He [20].<sup>g</sup> Brunvoll, Cyvin, and Cyvin [28].<sup>h</sup> Knop, Szymanski, Jeričević, and Trinajstić [16].<sup>i</sup> Ciosłowski [30].<sup>j</sup> Cyvin, Brunvoll, and Cyvin [32].<sup>k</sup> Correction: Knop, Müller, Szymanski, and Trinajstić [25].<sup>l</sup> Stojmenović, Tošić, and Doroslovački [34].

† Unknown.

Table 6. Numbers of benzenoids and coronoids (in parentheses) of different symmetries.

$h$	$D_{6h}$	$C_{6h}$	$D_{3h}$	$C_{3h}$	$D_{2h}$	$C_{2h}$	$C_{2v}$	$C_s$
1	1	0	0	0	0	0	0	0
2	0	0	0	0	1	0	0	0
3	0	0	1	0	1	0	1	0
4	0	0	1	0	2	1	1	2
5	0	0	0	0	2	1	9	10
6	0	0	1	1	3	7	12	57
7	1	0	1	1	3	7	39	279
8	0	0	0	0	6 (1)	35	61	1 333
9	0	0	1 (1)	5	7 (0)	36	178 (1)	6 278 (3)
10	0	0	4 (0)	5	11 (3)	169 (3)	274 (9)	29 623 (28)
11	0	0	0 (0)	0	14 (0)	177 (0)	796 (24)	140 242 (259)
12	0 (1)	0	3 (3)	21 (2)	21 (10)	807 (25)	† (79)	† (1834)
13	2 (0)	0	4 (0)	26 (0)	23 (0)	859 (0)	† (185)	† (†)
14	0 (0)	0	0 (0)	0 (0)	41 (†)	† (†)	† (†)	† (†)
15	0 (0)	0	3 (9)	95 (17)	50 (0)	† (0)	† (†)	† (†)
16	0 (0)	0	12 (0)	118 (0)	80 (†)	† (†)	† (†)	† (†)
17	0 (0)	0	0 (0)	0 (0)	94 (0)	† (0)	† (†)	† (†)
18	0 (3)	0 (1)	6 (23)	423 (102)	156 (†)	† (†)	† (†)	† (†)
19	2 (0)	2 (0)	19 (0)	543 (0)	189 (0)	† (0)	† (†)	† (†)
20	0 (0)	0 (0)	0 (0)	0 (0)	310 (†)	† (†)	† (†)	† (†)

† Unknown.

the coloring of vertices (“black and white” is synonymous with “starred and unstarred”) [37, 40]. This number ( $\Delta$ ) is also equal to the absolute magnitude of the difference between the numbers of valleys and peaks [43, 44]. Furthermore,  $\Delta$  is also equal to the absolute magnitude of the difference between the numbers of upright and upset triangles [20, 45] in the dualist graph [6]. It is long known that

all Kekuléan systems have  $\Delta = 0$ , and that this is not a sufficient condition [37]. Non-Kekuléan benzenoids and coronoids with  $\Delta = 0$  exist; benzenoids when  $h \geq 11$  [37] and coronoids when  $h \geq 15$  [28]. They are called concealed non-Kekuléans [28, 44]. The others ( $\Delta > 0$ ) are referred to as obvious non-Kekuléan [44]. Table 7 shows the distribution of  $\Delta$  values for all benzenoids (and coronoids).

Table 7. Numbers of benzenoids and coronoids (in parentheses) with different  $\Delta$  values.

$h$	$\Delta = 0^*$	$\Delta = 1$	$\Delta = 2$	$\Delta = 3$	$\Delta = 4$
1	1	0	0	0	0
2	1	0	0	0	0
3	2	1 <sup>a</sup>	0	0	0
4	6	1 <sup>a</sup>	0	0	0
5	15	7 <sup>a</sup>	0	0	0
6	51	28 <sup>a</sup>	2 <sup>a</sup>	0	0
7	190	134 <sup>a</sup>	7 <sup>a</sup>	0	0
8	764(1 <sup>b</sup> )	619 <sup>a</sup>	52 <sup>a</sup>	0	0
9	3223(3 <sup>b</sup> )	2957(2 <sup>b</sup> )	322	3	0
10	14107(24 <sup>b</sup> )	14024(16 <sup>b</sup> )	1916(3 <sup>b</sup> )	39	0
11	62887(128 <sup>b</sup> )	67046(131 <sup>b</sup> )	10922(23 <sup>b</sup> )	374(1 <sup>b</sup> )	0
12	†(854 <sup>b</sup> )	†(906 <sup>b</sup> )	†(182 <sup>b</sup> )	†(12 <sup>b</sup> )	14

\* For benzenoids when  $h \leq 10$ : All Kekuléan, viz. catacondensed (Table 1) +  $np + e$  (Table 2). All coronoids when  $h \leq 14$  are Kekuléan, viz. catacondensed (Table 3) +  $np + e$  (Table 4).

<sup>a</sup> Brunvoll, Cyvin, and Cyvin [29]. – <sup>b</sup> Brunvoll, Cyvin, and Cyvin [28]. – † Unknown.

It was demonstrated by an inductive reasoning that the maximal  $\Delta$  value for a benzenoid is

$$\Delta_{\max} = \left\lfloor \frac{h}{3} \right\rfloor,$$

where  $\lfloor x \rfloor$  is used to designate the largest integer smaller than or equal to  $x$ .

#### Numbers of Internal and External Vertices

The computer program of Knop and Trinajstić with collaborators [11, 12, 16, 21] is based on the fact that a benzenoid is uniquely defined by its perimeter. For the purpose of identification these authors devised a boundary code given in terms of a six-letter alphabet, actually consisting of a sequence of integers. Basically the same idea was first used by Balaban [46], and was employed with modifications by Doroslovački and Tošić with collaborators [15, 23, 34].

Table 8 includes the data from Knop *et al.* [11] concerning the classification of benzenoids according to their number of internal vertices, say  $n_i$ .

Stojmenović *et al.* [34] performed a classification according to the length of the perimeter. Actually their material contains the enumeration of all benzenoids with the perimeter length up to 46 edges and classified according to the  $h$  values. The length of the perimeter amounts to the same as the number of external vertices, say  $n_e$ . This number, being one of the invariants of a benzenoid, is closely related to

the invariant  $n_i$ . From the known connections between invariants of a benzenoid [35, 38] it is obtained

$$n_i = 2h - (n_e/2) + 1.$$

Hence also the data of Stojmenović *et al.* [34] contain the information about the numbers of internal vertices. As such most of these data are entered into Table 8. The table would be too voluminous if all the available data [34] were included. They cover all benzenoids up to  $n_e = 46$ , which makes the highest entry of  $h$  equal to 44. Actually a unique benzenoid with  $h = 44$  and  $n_e = 46$  is listed: it has 66 internal vertices ( $n_i = 66$ ).

The open spaces to the right and above the figures in Table 8 are equivalent to zeros. They reflect the fact that  $n_i$  has a maximal value for a given  $h$ . According to Harary and Harborth [5] this maximum is

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

where  $\{x\}$  is used to denote the smallest integer greater than or equal to  $x$ . We also deduce straightforwardly that the length of the perimeter is bounded as

$$2\{(12h - 3)^{1/2}\} \leq n_e \leq 4h + 2.$$

As an example, the formulas give for  $h = 44$ :  $(n_i)_{\max} = 66$ ,  $(n_e)_{\min} = 46$ , both figures in consistency with the above quoted case.

#### The ABCDEF Classification

He and He [20, 33] have classified the benzenoids and coronoids into the following six classes. A are the Kekuléans, B + C cover the catacondensed benzenoid systems: B unbranched and C branched. D + F cover the pericondensed benzenoids, D not possessing any end hexagon and F possessing at least one end hexagon, i.e. one with five free edges and manifested by a vertex of degree one in the dualist graph. The class E is coincident with the primitive coronoids. The rest of the coronoids come under D and F depending on whether they have not or have end hexagons, respectively. The classes D and F are separated into Kekuléans and non-Kekuléans. It is referred to Table 9 for enumeration results.

This classification is conveniently performed by means of (a)  $\Delta$  values equal to  $|U - D|$  and (b)  $(U + D)$  values, where  $U$  and  $D$  are the respective numbers of upright and upset triangles in the

Table 8. Numbers of benzenoids with different numbers of internal vertices,  $n_i$ .

$h$	$n_i = 0^*$	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1													
2	1													
3	2	1 <sup>a</sup>												
4	5	1 <sup>a</sup>	1 <sup>a</sup>											
5	12	6 <sup>a</sup>	3 <sup>a</sup>	1 <sup>a</sup>										
6	36	24 <sup>a</sup>	14 <sup>a</sup>	4 <sup>a</sup>	3 <sup>a</sup>									
7	118	106 <sup>a</sup>	68 <sup>a</sup>	25 <sup>a</sup>	10 <sup>a</sup>	3 <sup>a</sup>	1 <sup>a</sup>							
8	411	453 <sup>a</sup>	329 <sup>a</sup>	144 <sup>a</sup>	67 <sup>a</sup>	21 <sup>a</sup>	9 <sup>a</sup>	1 <sup>a</sup>						
9	1 489	1 966 <sup>a</sup>	1 601 <sup>a</sup>	825 <sup>a</sup>	396 <sup>a</sup>	154 <sup>a</sup>	55 <sup>a</sup>	15 <sup>a</sup>	4 <sup>a</sup>					
10	5 572	8 395 <sup>a</sup>	7 652 <sup>a</sup>	4 518 <sup>a</sup>	2 340 <sup>a</sup>	1 018 <sup>a</sup>	416 <sup>a</sup>	123 <sup>a</sup>	42 <sup>a</sup>	9 <sup>a</sup>	1 <sup>a</sup>			
11	21 115	35 885 <sup>b</sup>	36 109 <sup>b</sup>	24 020 <sup>b</sup>	13 415 <sup>b</sup>	6 405 <sup>b</sup>	2 811 <sup>b</sup>	1 008 <sup>b</sup>	333 <sup>b</sup>	100 <sup>b</sup>	26 <sup>b</sup>	2 <sup>b</sup>		
12	†	†	168 318 <sup>b</sup>	124 119 <sup>b</sup>	74 985 <sup>b</sup>	38 727 <sup>b</sup>	18 306 <sup>b</sup>	7 375 <sup>b</sup>	2 713 <sup>b</sup>	878 <sup>b</sup>	279 <sup>b</sup>	61 <sup>b</sup>	13 <sup>b</sup>	1 <sup>b</sup>
$h$	$n_i = 4$	5	6	7	8	9	10	11	12	13	14	15		
13	408 785	226 837	114 326	50 405	20 119	7 253	2 459	708	187	35	4			
14	†	† 691 933	328 592	141 268	55 124	20 321	6 594	2 001	533	120	16			
15	†	†	†	† 947 291	395 860	155 656	55 857	18 396	5 612	1 570	347			
16	†	†	†	†	†	† 1 132 642	436 698	156 434	51 691	16 234	4 501			
17	†	†	†	†	†	†	†	† 1 236 839	440 491	148 430	46 166			
18	†	†	†	†	†	†	†	†	† 1 262 442	424 429				
$h$	$n_i = 16$	17	18	19	20	21	22	23	24	25	26	27	28	
14	1													
15	70	4												
16	1 121	223	30	1										
17	13 286	3 414	763	117	9									
18	133 713	39 143	10 587	2 437	471	53	3							
19	1 223 950	388 180	116 648	32 042	7 885	1 647	256	18	1					
20	†	† 1 140 529	345 834	†	97 607	25 050	5 726	1 009	129	4				
21	†	†	†	† 1 029 521	296 025	79 472	18 876	3 838	587	47	1			
22	†	†	†	†	†	† 903 415	247 989	62 027	13 652	2 467	290	16		
23	†	†	†	†	†	†	†	† 771 061	200 545	47 167	9 349	1 448		
24	†	†	†	†	†	†	†	†	† 643 859	157 989	34 324			
25	†	†	†	†	†	†	†	†	†	†	† 522 218			

\* Catacondensed benzenoids; see Table 1. – † Unknown.

<sup>a</sup> Knop, Szymanski, Jeričević, and Trinajstić [11].<sup>b</sup> Stojmenović, Tošić, and Doroslovački [34]. All data for  $h > 10$  are taken from this reference.

Table 9. Numbers of benzenoids and coronoids (numbers in parentheses) according to the ABCDEF classification.

$h$	A Kekuléan					Non-Kekuléan	
	B*	C*	D	E**	F	D	F
1	1	0	0	0	0	0	0
2	1	0	0	0	0	0	0
3	2	0	0	0	0	1 <sup>a</sup>	0
4	4	1	1 <sup>a</sup>	0	0	0 <sup>a</sup>	1 <sup>a</sup>
5	10	2	1 <sup>a</sup>	0	2 <sup>a</sup>	1 <sup>a</sup>	6 <sup>a</sup>
6	24	12	3 <sup>a</sup>	0	12 <sup>a</sup>	3 <sup>a</sup>	27 <sup>a</sup>
7	67	51	6 <sup>a</sup>	0	66 <sup>a</sup>	9 <sup>a</sup>	132 <sup>a</sup>
8	182	229	22 <sup>a</sup>	(1)	331 <sup>a</sup>	27 <sup>a</sup>	644 <sup>a</sup>
9	520	969	60 <sup>b</sup>	(1)	1 674 (2)	117 (2)	3 165 <sup>b</sup>
10	1 474	4 098	224 (9)	(3)	8 311 (12)	437 (6)	15 542 (13)
11	4 248	16 867	806 (13)	(2)	40 958 (113)	1 778 (52)	76 572 (103)

\* See Table 1 (catacondensed); B unbranched, C branched.

\*\* See Table 3 (primitive). – <sup>a</sup> He and He [20]. – <sup>b</sup> He and He [33].

dualist graph, and (c)  $V_1$ ,  $V_2$  and  $V_3$ , designating numbers of vertices of the dualist graph with degree one, two and three, respectively.

These values are easily obtained from the He-matrix [20]. It is noted that in the graph generation program of He and He [20], considering the connectivity of the graph and using the properties of the He-matrix, the coronoids are automatically included into the classification. In particular the He-matrix can be used to classify the systems according to  $A$  values. A He-matrix is also suited for the studies of the rotation and reflection transformations. Thus it may be used to determine the symmetry groups of the benzenoid and coronoid systems.

### Estimates for the Number of Benzenoids

As the number  $h$  of hexagons increases, the direct enumeration of benzenoids becomes extremely difficult and even with the use of the most powerful computing devices one cannot expect the solution of this task for the totality of benzenoids with, say,  $h = 20$  or  $h = 30$ . Another approach to this problem would be the application of Pólya's theory, which provides general mathematical techniques for enumerations of combinatorial objects of various types [47]. Unfortunately, the enumeration of benzenoids by means of Pólya's method could not be realized until now and is considered as an open problem of combinatorics. From a mathematician's point of view, the enumeration of benzenoid systems is an unsolved problem.

If helicenes and other non-planar systems are not disregarded, then for large values of  $h$  an exact asymptotic behaviour of the number of catacondensed benzenoids is known [3] and has the form

$$N \approx a h^p b^h,$$

where  $p$ ,  $a$  and  $b$  are specified constants. This result does not apply for catacondensed systems as defined in the present paper. Nevertheless, it has been attempted [27] to reproduce an approximate asymptotic behaviour of catacondensed benzenoids with helicene-type systems disregarded by the same mathematical form, but other values of the parameters  $p$ ,  $a$  and  $b$ . By a fitting procedure, using the known numbers for  $h \leq 11$ , Gutman [27] determined  $p = -5/4$ ,  $a = 0.049$  and  $b = 4.27$ . In an analogous way he also determined a set of parameters, viz.  $p = -3/2$ ,  $a = 0.045$

Table 10. Comparison between exact and estimated numbers of catacondensed benzenoids and all benzenoids.

$h$	Catacondensed benzenoids		Total benzenoids	
	Exact	Estimate <sup>a</sup>	Exact	Estimate <sup>b</sup>
6	36	32	81	76
7	118	111	331	325 ± 10
8	411	402	1 435	1 440 ± 40
9	1 489	1 480 ± 30	6 505	6 510 ± 180
10	5 572	5 550 ± 120	30 086	30 000 ± 900
11	21 115	21 050 ± 500	141 229	140 400 ± 4 400
12	†	80 600 ± 2 000	†	666 000 ± 22 000
13	†	311 000 ± 8 000	†	3 190 000 ± 110 000
14	†	1 212 000 ± 32 000	†	15 400 000 ± 570 000
15	†	4 750 000 ± 130 000	†	75 000 000 ± 2 900 000

<sup>a</sup> The constants  $a$  and  $b$  (see the text for definitions) are assumed to have the values  $0.049 \pm 0.0005$  and  $4.27 \pm 0.005$ , respectively. <sup>b</sup>  $a = 0.045 \pm 0.0005$ ,  $b = 5.4 \pm 0.01$ .

† Unknown.

and  $b = 5.4$ , for the total number of benzenoids (both catacondensed and pericondensed). A corresponding analysis for normal benzenoids is due to Cyvin *et al.* [32].

In Table 10 the exact and estimated numbers of catacondensed benzenoids and benzenoids in total are given for  $6 \leq h \leq 15$ .

### Conclusion

The present report does not imply an end to the enumeration and classification of polyhexes. On the contrary, the activity in this research area has apparently been intensivated during the last years, and not least during the preparation of this report. New results are to be awaited, further extensions to higher  $h$  values on one hand and new types of classifications on the other.

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