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ENUMERATION OF BRANCHED CATACONDENSED BENZENOID HYDROCARBONS AND THEIR NUMBERS OF KEKULÉ STRUCTURES[†]

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Abstract - The computerized enumerations of unbranched catafusenes (catacondensed benzenoids) are summarized. The systems are classified according to symmetry. The numbers of helicenic systems are given explicitly. The results of enumerations for branched catafusenes are also reported, and the systems without helicenes for $4 \leq h \leq 12$ are classified according to symmetry. Here h denotes the number of hexagons. For the branched catafusenes without helicenes all Kekulé structure counts (K) were computed. Some characteristic values of K (K_{min}, $\langle K \rangle$, K_{abund}, K_{max}) are discussed. The subscripts refer to the minimum, most abundant and maximum value. $\langle K \rangle$ is the average. As one of the original results it was found $K_{max} = 504$ for $h=12$. This K number is realized in two isoarithmic branched catafusenes. Quantities of the type $(\ln K)/h$ display especially interesting behaviour.

INTRODUCTION

The enumeration and classification of benzenoid hydrocarbons (or simply benzenoids) in the chemical context started by the works of Balaban and Harary.[1-3] After a period of some years with apparently no activity in this area the problems were taken up again, in pace with the access to modern computers.[4-6] Suddenly, in the few last years, the research activity in this field has flared up. Twenty-one relevant works from 1984 or later are cited in a recent consolidated report by fourteen authors.[7] The report gives a survey of the topic and summarizes existing data from literature with supplements of many original contributions. However, the development in this field is so rapid that several further supplements were available as pre-publication data before the report went into print. The present work contains some of these supplementary data.

The enumeration of benzenoids of the present work are combined with the computation of the numbers of Kekulé structures (K). The significance of Kekulé structures of conjugated hydrocarbons in organic chemistry is well known. Also merely their numbers are important quantities in theoretical models for many chemical phenomena. It is sufficient to give the reference to a review by Herndon,[8] supplemented by some more recent publications.[9-17] Among these chemical phenomena we only mention as examples the total π-electron energy, heats of formation, interatomic carbon-carbon distances, photoelectron spectra, zero-field splitting parameters, reaction rate constants, resonance energies and aromaticity.

In a more qualitative way the number of Kekulé structures of a conjugated hydrocarbon is known to be a measure of its chemical stability; see, e.g. Herndon[18] or standard text-books. More precisely: of two conjugated hydrocarbons with the same number of carbon atoms the one with the

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[†] Part V of the series "Distribution of K, the number of Kekulé structures, in benzenoid hydrocarbons". For Parts I-VI, see References 19-22.

largest K number is the more stable one. The maximum K values considered in the present work are therefore of a great chemical interest.

The present work deals mainly with branched catacondensed benzenoid systems (or branched catafusenes). Triphenylene with four hexagons (or rings), i.e. $h=4$, represents the smallest example of this class. It is inferred as almost certain that the benzenoid system with the maximum K number ($K_{\max}$) among the class of benzenoids with a given $h \geq 4$, is a branched catafusene. It was conjectured explicitly by Cyvin,[19] and supported by (mostly empirical) evidence, that the benzenoid with $K = K_{\max}$ for a given h is a catafusene. Furthermore, all experience shows that kinks and branchings of the chain of hexagons contribute to large K numbers. Theoretical analyses and known combinatorial K formulas give support to these observations. The conjecture (that $K_{\max}$ occurs for a branched catafusene) has been verified by computer-aided enumerations of the benzenoids for all values of $h \leq 11$ during the studies of the distribution of K at given h values.[19-22]

DEFINITIONS

A benzenoid system (or benzenoid) is defined (in a strict sense[23]) as a planar system of identical regular hexagons, which are simply connected. This definition excludes (nonplanar) helicenic systems (or helicenes), which would possess overlapping edges if drawn in a plane. A benzenoid system, here defined mathematically as a graph, represents in an obvious way a benzenoid (polycyclic aromatic) hydrocarbon.

Helicenes are also chemically important hydrocarbons inasmuch as a series of them have been synthesized[24] and their physical properties studied; cf., e.g. the work of Obenland and Schmidt[25] with references cited therein. We have included helicenes in a part of the enumerations. However, the numbers of Kekulé structures (K) for these systems were not considered in order to keep the present work within the frames of the previous studies[20-22] of K number distributions.

A catacondensed benzenoid is a benzenoid with no internal vertices. It displays an acyclic dualist graph.[1] All benzenoids which are not catacondensed, are referred to as pericondensed.[1,23] Here we are using the terms[1] catafusene and perifusene as abbreviations for catacondensed benzenoids and pericondensed benzenoids, respectively.

ENUMERATION AND CLASSIFICATION OF UNBRANCHED CATAFUSENES

Balaban and Harary[1] enumerated some benzenoids and classified the unbranched catafusenes according to their symmetries. They gave the data of unbranched catafusenes for $h \leq 8$ and branched for $h \leq 6$. The range for branched systems was supplemented with $h = 7$ and 8 by Balaban.[2] In these works[1,2] the catacondensed systems including helicenes were enumerated. The corresponding enumerations without helicenes were carried out through $h=9$ by Brunvoll et al.[26] Further supplements are found in the consolidated report:[7] unbranched catafusenes up to $h=20$ and branched up to $h=11$.

Table 1 shows the results of enumeration of catafusenes through $h=12$; the unbranched systems are classified according to symmetry as:

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

The main entries pertain to catafusenes without helicenes. The numbers for helicenic systems are given in parentheses.

The total numbers of unbranched catacondensed systems, i.e. for the systems including helicenes (not given explicitly in Table 1), follow simple combinatorial formulas.[1] Let a', m', c' and u' be the numbers pertaining to the appropriate columns of Table 1, while C_{ub}' denotes the total number of unbranched systems, viz.

$$C_{ub}' = a' + m' + c' + u' \tag{1}$$

Then[1]

Table 1. Numbers of catafusenes; helicenic systems in parentheses.

h	Unbranched ub					Total branched C_{br}	Total catacondensed
	a	m	o	u	Total C_{ub}		
1	1	0	0	0	1	0	1
2	1	0	0	0	1	0	1
3	1	1	0	0	2	0	2
4	1	1	1	1	4	1	5
5	1	4	1	4	10	2	12
6	1	3(1)	4	16	24(1)	12	36(1)
7	1	12(1)	4	50(2)	67(3)	51(2)	118(5)
8	1	10(3)	13	158(11)	182(14)	229(21)	411(35)
9	1	34(6)	13	472(48)	520(54)	969(146)	1489(200)
10	1	28(12)	39(1)	1406(194)	1474(207)	4098(914)	5572(1121)
11	1	97(24)	39(1)	4111(729)	4248(754)	16867(5165)	21115(5919)
12	1	81(40)	116(5)	11998(2643)	12196(2688)	68925(27821)	81121(30509)

$$a' = 1 \tag{2}$$

$$m' = \begin{cases} \frac{1}{2}(3^{(h-2)/2} - 1); & h = 2, 4, 6, \ldots. \\ \frac{1}{2}(3^{(h-1)/2} - 1); & h = 1, 3, 5, \ldots. \end{cases} \tag{3}$$

$$o' = \begin{cases} \frac{1}{2}(3^{(h-2)/2} - 1); & h = 2, 4, 6, \ldots. \\ \frac{1}{2}(3^{(h-3)/2} - 1); & h = 3, 5, 7, \ldots. \end{cases} \tag{4}$$

$$u' = \begin{cases} \frac{1}{4}(3^{(h-2)/2} - 1)^2; & h = 2, 4, 6, \ldots. \\ \frac{1}{4}(3^{h-2} - 3^{(h-1)/2} - 3^{(h-3)/2} + 1); & h = 3, 5, 7, \ldots. \end{cases} \tag{5}$$

$$C_{ub}' = \begin{cases} \frac{1}{4}(3^{(h-2)/2} + 1)^2; & h = 2, 4, 6, \ldots. \\ \frac{1}{4}(3^{h-2} + 3^{(h-1)/2} + 3^{(h-3)/2} + 1); & h = 3, 5, 7, \ldots. \end{cases} \tag{6}$$

ENUMERATION OF BRANCHED CATAFUSENES

The numbers of branched catafusenes (without helicenes) are reported[7] previously for $h \leq 11$. A major contribution of the present work is the generation of the 68925 branched catafusenes with $h=12$. The very number was actually derived recently by He and He[27] during a complete enumeration of benzenoids (both catacondensed and pericondensed) with $h=12$. We have reproduced the mentioned number exactly by a computer program[26] based on entirely different principles from those of He and He.[28,29] In the present work the systems in question were generated specifically by starting with the triphenylene system and adding hexagons, one at a time, into properly restricted positions. Coded information of the forms of all nonisomorfic benzenoids generated in this way was stored in the computer files and used to deduce different properties (see below).

Now the numbers for all (branched + unbranched) catafusenes are known for $h \leq 12$. The total numbers of catacondensed systems including helicenes are known for the same h values.[30] Consequently also the numbers of helicenes among the catacondensed systems could be obtained by subtraction (cf. the parenthesized figures in the last column of Table 1). Finally, by a new subtraction, the branched helicenic systems were enumerated (cf. column C_{br} of Table 1).

SYMMETRY OF BRANCHED CATAFUSENES

Table 2 shows the distribution of all branched catafusenes (without helicenes) into the six possible symmetry groups. The D_{6h} and C_{6h} will never occur in this case because all benzenoids

Table 2. Classification of branched catafusenes according to symmetry.

h	D_{3h}	C_{3h}	D_{2h}	C_{2h}	C_{2v}	C_s
4	1	0	0	0	0	0
5	0	0	0	0	1	1
6	0	0	1	0	4	7
7	1	1	1	0	4	44
8	0	0	1	4	18	206
9	0	0	1	4	27	937
10	2	4	3	25	67	3997
11	0	0	4	26	118	16719
12	0	0	4	132	269	68520

belonging to these groups (for $h > 1$) are pericondensed.[31]

DISTRIBUTION OF K NUMBERS FOR BRANCHED CATAFUSENES

The numbers of Kekulé structures (K) for all the enumerated branched catafusenes were computed automatically by a program based on the principles of Brown.[32]

Figure 1 gives a complete account of the distribution of K numbers for the considered systems with $h = 6$, 7 and 8. For every h value the K numbers are found within a minimum ($K_{\min}$) and maximum ($K_{\max}$) value. The shapes of the diagrams are rather irregular, but there seems to be a tendency to

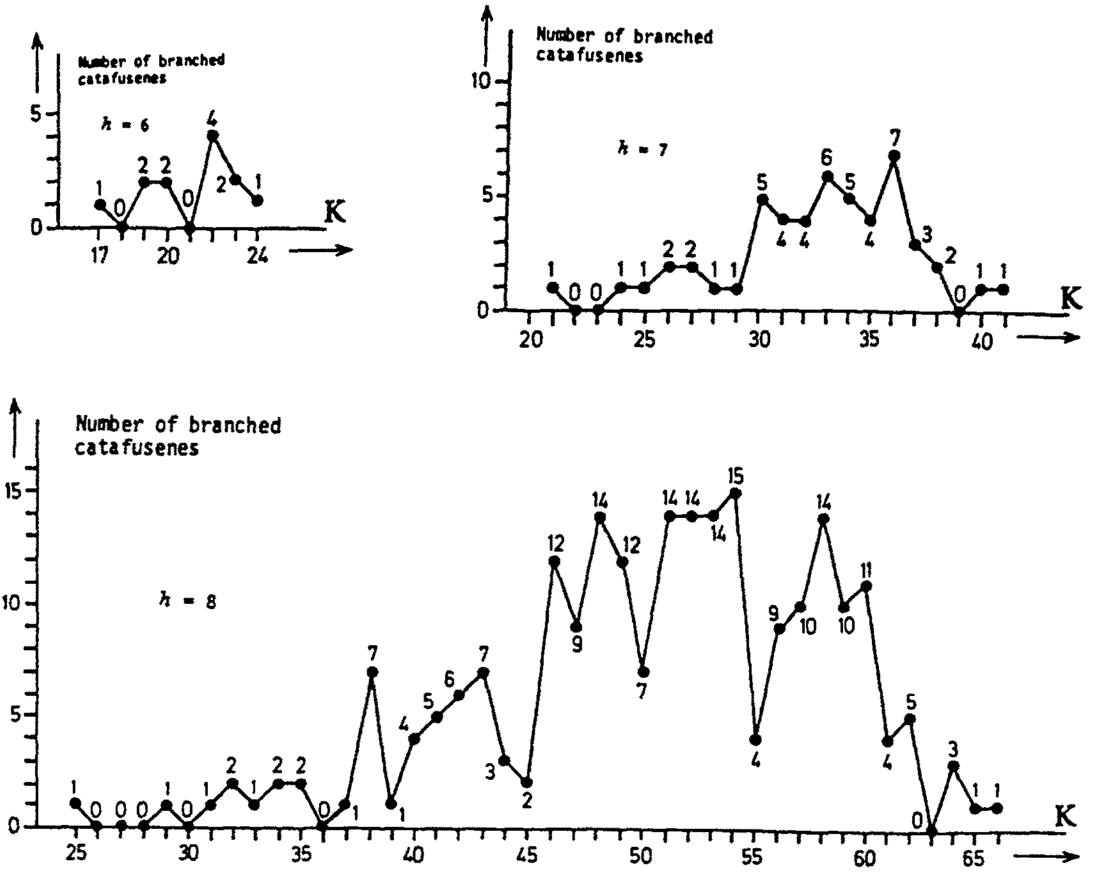


Fig. 1. Numbers of branched catafusenes with $h = 6$, 7 and 8 at given K numbers (Kekulé structure counts)

find the K numbers with largest abundancies in the second half, viz. $K > \frac{1}{2}(K_{max} - K_{min})$, of the region. This tendency continues throughout the present material ($h \le 12$), which is too voluminous to be reported here in details. Some characteristic values from the material are shown in Table 3: K_{min}, K_{max}, K_{abund} denoting the most abundant K number, and finally the average $\langle K\rangle$.

Table 3. Characteristic K values for branched catafusenes: minimum K_{min}, average $\langle K\rangle$, most abundant K_{abund}, maximum K_{max}.

h	K_{min}	$\langle K\rangle$	K_{abund}	K_{max}
4	9	9	9 (1)*	9
5	13	13.5	13-14	14
6	17	21.1	22 (4)	24
7	21	32.6	36 (7)	41
8	25	50.7	54 (15)	66
9	29	79.1	82 (61)	110
10	33	123.6	134 (119)	189
11	37	193.7	222 (320)	302
12	41	304.2	298 (602)	504

*Multiplicities, i.e. number of systems with the same K, in parentheses.

BRANCHED CATAFUSENES WITH h=12

It is of course not conceivable to give a full account of the 68925 forms of branched h=12 catafusenes. Figure 2 shows fourteen selected representatives. At the top of the figure the unique system (a) with $K = K_{min} = 41$ is displayed. It is a linear chain with a triphenylene-type branching at one end. The four existing systems with D_{2h} symmetry (cf. Table 2) are included as (b), (c) and (f). In the latter case (f) the two isoarithmic[33] systems are depicted. They only differ in the way some of the kinks go; that does not affect the numbers of Kekulé structures. In (d) one of the 602 systems with $K = K_{abund} = 298$, the most abundant K value, is shown. The average K value, $\langle K\rangle$, is close to 304 as the nearest integer value. One of the 486 systems with $K = 304$ is depicted in (e). The seven remaining systems, (g)-(j), are the branched catafusenes with the highest K numbers ($K \ge 492$); see also below.

MINIMUM OF K FOR BRANCHED CATAFUSENES

The catafusene with the minimum K number for a given h is the linear chain of h hexagons (polyacene), for which $K = h+1$.[34] It has recently been proved that this number in fact is the absolute minimum for all normal benzenoids (catacondensed and normal pericondensed) with a given h.[35]

For branched catafusenes (cf. Table 3) the value of K_{min} is evidently

$$K_{min}(h) = 4h - 7 \tag{7}$$

This value is realized, as we claim with great confidence, for the linear chain of h-2 hexagons to which two hexagons are added into a branch at one of the ends. Figure 2 (a) shows the example for h=12.

MAXIMUM OF K

As mentioned in the introduction, we conjecture that the values of K_{max} for branched catafusenes, as they are presented in Table 3, are the absolute maxima as a function of h for all benzenoids.

Figure 2 (g) shows the branched h=12 catafusene with $K = 492$. This number was supposed to be the K_{max} value according to Cyvin.[19] Here we have generated not less than six additional h=12

K	(Multiplicity)	
41	(1)	(a)
120	(17)	(b)
261	(304)	(c)
298	(602)	(d)
304	(486)	(e)
315	(251)	(f)
492	(1)	(g)
494	(1)	(h)
502	(3)	(i)
504	(2)	(j)

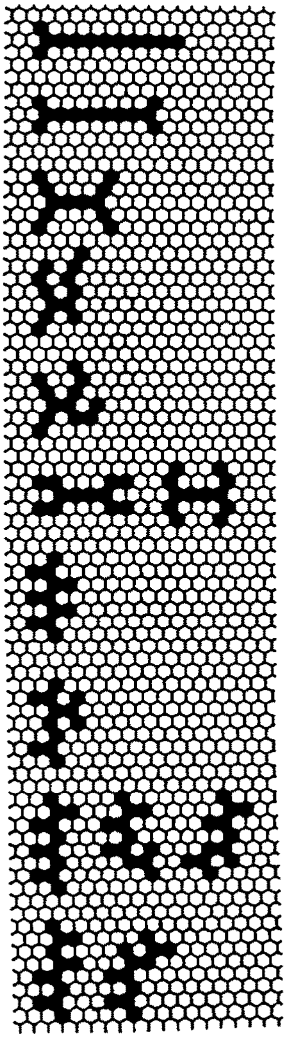
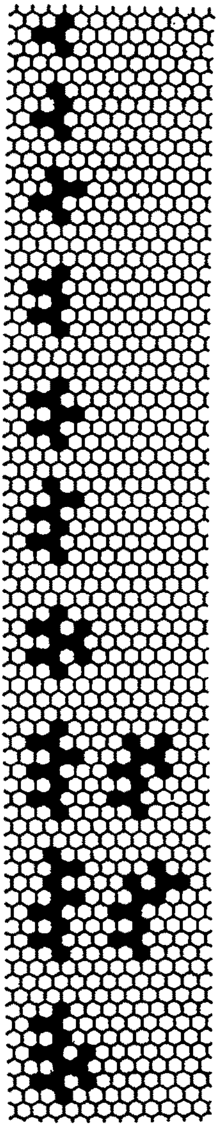


Fig. 2. Selected representatives of branched catafusenes with h=12. K numbers and their multiplicities (i.e. numbers of systems with the same K) are given

Fig. 3 (right). The benzenoids with $K = K_{max}$ for $4 \leq h \leq 13$

h	$K = K_{max}$	
4	9	⌬
5	14	
6	24	
7	41	⌬
8	66	
9	110	
10	189	⌬
11	302	
12	504	
13	863(?)	⌬



⌬ all-benzenoid

benzenoids with higher K (cf. Fig. 2) and proved that the real maximum value is K_{max} = 504 (but Cyvin[19] has reported an h=12 helicenic system with K = 510). Two isoarithmic forms have $K = K_{max}$ = 504, while K = 502 is realized by three isoarithmic forms; cf. Fig. 2 (j) and (i), respectively.

In Fig. 3 the benzenoids with $K = K_{max}$ for $4 \leq h \leq 13$ are summarized. The last system (h=13) is taken from Cyvin[19] and is still uncertain. All the others are ascertained by means of computer-generations of the benzenoids. It is noted that every third one of the systems, i.e. for h = 4, 7, 10, 13, is an all-benzenoid (or fully benzenoid).[36,37] These systems are defined by the property that it is possible to assign uniquely a constellation of aromatic sextets (hexagons with three double bonds as in benzene) throughout, so that the remaining hexagons do not possess any additional double bonds. Such systems are known to have large K numbers in relation to their number of hexagons, and it has been conjectured[19] that the system with $K = K_{max}$ is an all-benzenoid for all $h = 3i + 1$; i = 0, 1, 2, ...

Table 4. Some quantities of (ln$K$)/h.

h	$\frac{1}{h}\ln\langle K\rangle$	$\frac{1}{h}\ln K_{\max}$
4	0.5493	0.5493
5	0.5205	0.5278
6	0.5081	0.5297
7	0.4978	0.5305
8	0.4908	0.5237
9	0.4856	0.5222
10	0.4817	0.5242
11	0.4788	0.5191
12	0.4765	0.5185
13	?	0.5200(?)

QUANTITIES OF (ln$K$)/h

The resonance energy[38] has been related to K numbers of benzenoids as proportional to ln$K$. Hence the title quantity, which has been introduced into the "Kekulé structure statistics" by Cyvin et al.,[21] represents the resonance energy per hexagon.

Some of the quantities of (ln$K$)/h for the branched catafusenes are given in Table 4. Figure 4 shows a graphical representation of (ln$\langle K\rangle$)/h and (ln$K_{\max}$)/h from Table 4, supplemented with the curve for (ln$K_{\min}$)/h. The latter (steepest) curve is a representation of the function $(1/h)\ln(4h - 7)$ and tends to zero. The curve for $\langle K\rangle$ is remarkably smooth and monotonic, and it seems to approach a nonvanishing value when h increases, but this feature has not been proved. Similar behaviours have been observed for other averages of K numbers.[21] Finally we find that the curve for $K_{\max}$ (Fig. 4) is not monotonic, but the ripples of it seem to be regular in such a way that a smooth curve can be drawn through every third of the points. The local maxima correspond to the all-benzenoid systems. The size of the ripples tends to decrease when h increases, and also this curve seems to approach a nonvanishing limit value.

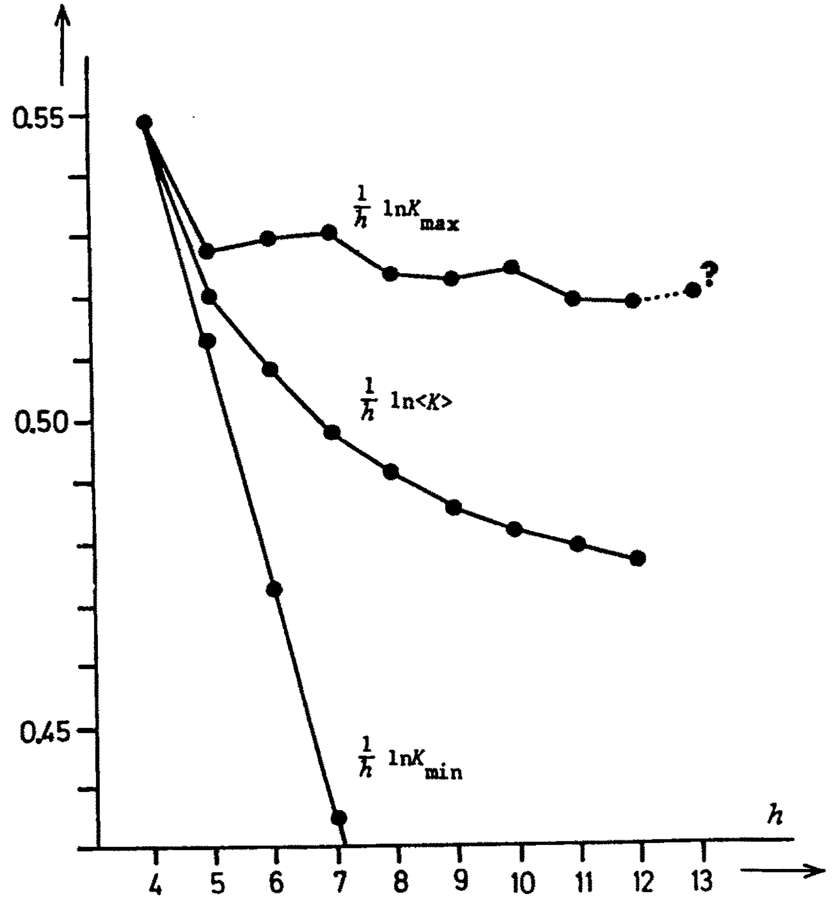


Fig. 4. Diagrams of the indicated (ln$K$)/h quantities

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