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DISTRIBUTION OF K, THE NUMBER OF KEKULÉ STRUCTURES, IN BENZENOID HYDROCARBONS. PART I:

UPPER AND LOWER BOUNDS OF K

S. J. Cyvin

Division of Physical Chemistry, The University of Trondheim,
N-7034 Trondheim-NTH, Norway

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Abstract: The number of Kekulé structures (K) was computed for all benzenoids up to h (the number of hexagons) = 7. The lower limit of K, viz. $K_{\min} = h+1$ was recently proved to be valid for not only catacondensed, but all normal (also Kekuléan pericondensed which are not essentially disconnected) benzenoids. (The proof is not conducted here.) The upper limit of K in catacondensed benzenoids is improved. It is inferred that it also applies to all normal benzenoids. All normal benzenoids with K = 2, 3, 4, 5, 6, 7, 8 and 9 are depicted.

INTRODUCTION

Much work has been done on the number of Kekulé structures (K) for different classes of benzenoid hydrocarbons, especially during the last years. Therefore it seems timely to offer some thoughts to the distribution of K numbers for benzenoids with different numbers of hexagons (h) in more general terms.

It is adherred to a previous definition of benzenoids,[1] which excludes hexahelicene and its derivatives, as well as circulenes. By "normal" benzenoids we refer to (a) all catacondensed systems (which are Kekuléan[2]) and (b) "normal pericondensed" systems, i.e. Kekuléans without fixed bonds. A fixed (or localized) bond is present when a given edge in a benzenoid has the same character (single or double) in all Kekulé structures. Benzenoids not referred to as "normal" are pericondensed and (a) essentially disconnected (with fixed bonds)[3,4] or (b) non-Kekuléans.[2]

The present work contains a number of empirical findings about benzenoids and their number of Kekulé structures. More general rules are tentatively put forward with a varying degree of confidence. Other results are deduced in a more stringent way.

The basic definition of benzenoids[1] will not prevent us from including some considerations of helicenes.

PATTERNS OF K DISTRIBUTION

Figure 1 shows the distributions of K numbers for $h = 3$, 4, 5, 6 and 7. The patterns are seen to be very irregular, possessing sharp peaks between the minimum and maximum K values. The curves are damped when K numbers of isoarithmic[5] structures are counted only once; see the dotted curves. Isoarithmic benzenoids differ only in the way the kinks of angular annelation go in single chains, either isolated or annelated to a pericondensed system.

MINIMUM AND MAXIMUM K NUMBERS

Previous work

Of particular interest are the studies of the minimum and maximum K numbers for a given h, say $K_{\min}(h)$ and $K_{\max}(h)$. Gutman[6] has reported a significant result in this area. He demonstrated in a stringent way that any catacondensed benzenoid has a number of Kekulé structures (K) within the limits

$$h+1 \leq K \leq 2^{h-1} + 1 \qquad (1)$$

The lower limit of (1) is realized for linear polyacenes, say L(h). We may write

$$K_{\min}(h) = K\{L(h)\} = h+1 \tag{2}$$

The solution for the lower limit is therefore definite.

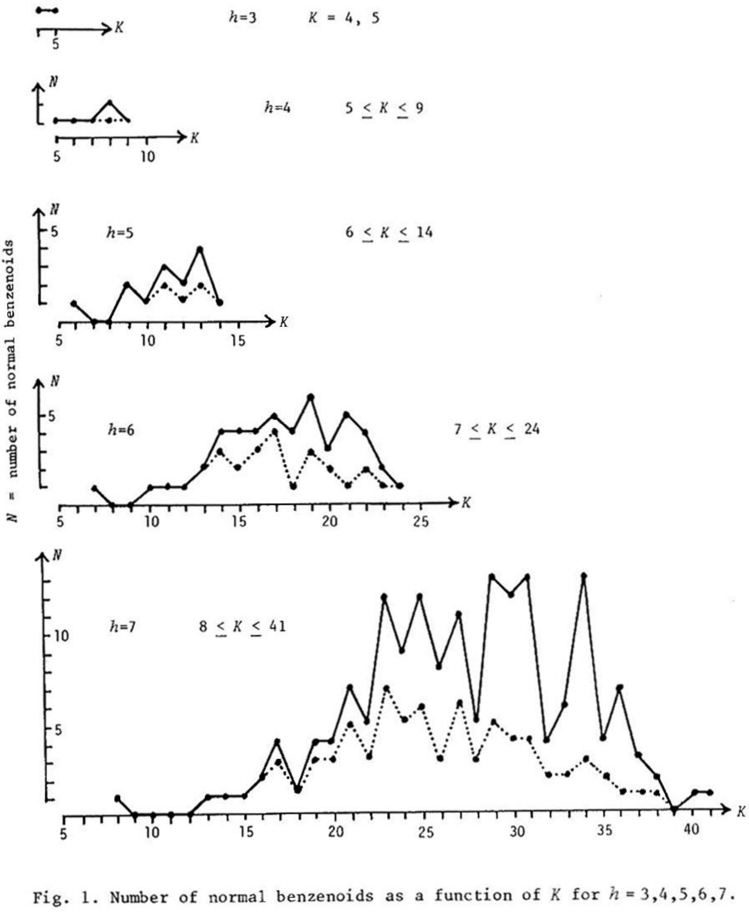


Fig. 1. Number of normal benzenoids as a function of K for $h = 3,4,5,6,7$.

The upper limit of (1) is realized for $h = 1, 2, 3$ and 4. With increasing h values this limit becomes more and more overestimated.

CATACONDENSED BENZENOIDS

Structures with maximum K

It is a general experience and supported by exact formulas, that (loosely speaking) a high K number for a catacondensed benzenoid is conditioned by (a) many branching hexagons in the first place and secondly (b) many angularly annelated hexagons rather than linearly. These criteria are not sufficient to depict with confidence a catacondensed benzenoid with a given h which has the maximum K value. Three mistakes are found in Gutman's[6] table. They do not change the conclusions of this pioneering work. Figure 2 shows catacondensed benzenoids with high K numbers in relation to the number of hexagons (h). All Gutman[6] K numbers emerge when each benzenoid is generated by adding a hexagon to the preceding one (see the top row and left column of Fig. 2). The h values are written into the added hexagons. But this principle is not always sound for $h > 6$, as shown by the present examples, which are supposed to give the real K maxima. The framed structures (h=11) are isoarithmic. Table 1 includes the three corrections ($h = 7, 9, 11$) of Gutman's[6] numbers.

Table 1. Maximal K values and upper bounds from Gutman[6]; corrected and extended.

h	maximal K value	upper bound (1)	h	maximal K value	upper bound (1)
1	2	2	7	41	65
2	3	3	8	66	129
3	5	5	9	110	257
4	9	9	10	189	513
5	14	17	11	302 (305)	1025
6	24	33	12	492 (510)	2049

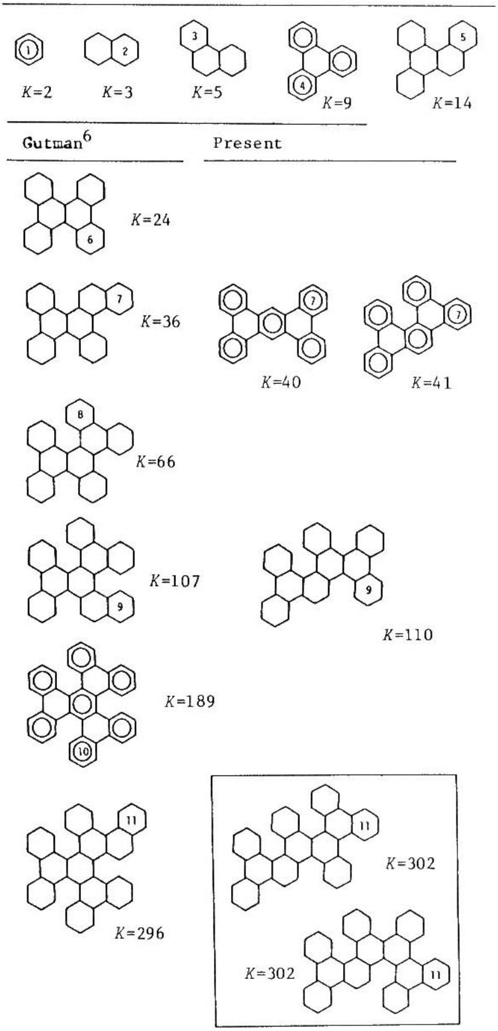


Fig. 2. Catacondensed benzenoids with $h = 1, \ldots, 11$ and the maximal or almost maximal K numbers.

At this stage we take into account structures with overlapping edges, viz. derivatives of hexahelicene and heptahelicene (but not a larger degree of overlapping, e.g. octahelicene). They are not genuine benzenoids.[1] Such a non-genuine benzenoid is isoarithmic with the one of $h=9$ ($K = 110$; Fig. 2); see Figure 3, where dualist graphs[7] are employed. For $h=11$ the figure shows four isoarithmic structures with $K = 302$, along with a new one having a slightly larger K number. The presumably maximal K values when overlapping edges are allowed, are given in parentheses in Table 1. The table is supplemented with $h=12$ in consistence with the illustration (Fig. 3). Parenthesized K numbers in the figure pertain to structures with overlapping edges.

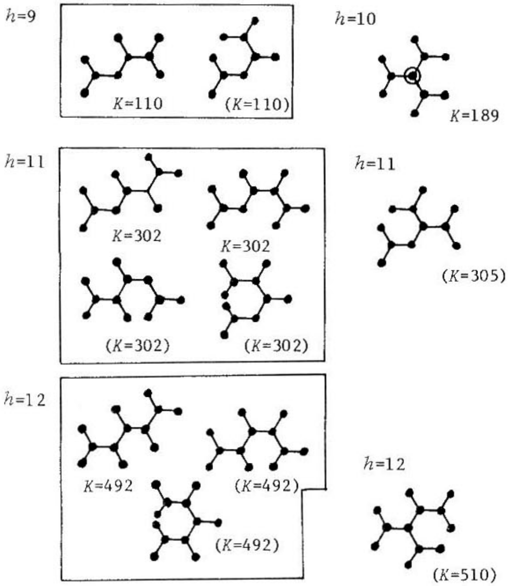
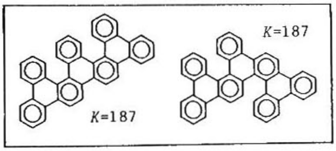


Fig. 3. Catacondensed benzenoids with h = 9, 10, 11, 12 and the maximal or almost maximal K numbers. Helicene derivatives are included.

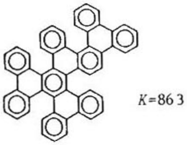
All-benzenoid systems

It is observed that all-benzenoid systems[8] (indicated by circles in the full rings) are among the benzenoids with maximum K. In the above examples it is seen to occur whenever possible, namely for $h = 1 + 3i$, where $i = 0, 1, 2$ and 3. It is also seen (cf. h=7; Fig. 2) that every catacondensed all-benzenoid is not represented. Again those with as many as possible branching hexagons and angular annelations are preferred. In supplement of this discussion we give the two isoarithmic h=10 all-benzenoids with a K number slightly below the maximum, $K_{\max}(10) = 189$, due to one branching hexagon less:

h=10



h=13



We believe that the next member of the list, i.e. for h=13, is the all-benzenoid depicted above.

It is tempting to conjecture that (at least if overlapping edges are allowed), for $h = 1 + 3i$, the structure with maximum K is an all-benzenoid also when $i \geq 5$.

Upper bounds of K

The upper bound (1) from Gutman[6], viz.

$$K_{\max}(h) \leq 2^{h-1} + 1 \tag{3}$$

is consistent with the recurrence formula:

$$K_{\max}(h) \leq 3K_{\max}(h-1) - 2K_{\max}(h-2); \qquad h \geq 2 \tag{4}$$

It may be "regionally" improved in the following way. The initial conditions $K_{\max}(1) = 2$ and $K_{\max}(2) = 3$ give exactly eqn. (3). The formula (4) may be adapted to other conditions, for instance $K_{\max}(6) = 33$ and $K_{\max}(7) = 41$. In that case the explicit equation reads

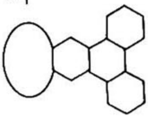
$$K_{\max}(h) \leq 17 \cdot 2^{h-6} + 7 \qquad (5)$$

The numerical values for h up to 12 are shown below.

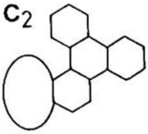
h	upper bound for K (5)	h	upper bound for K (5)
1	$\sim$7.27	7	41
2	$\sim$8.06	8	75
3	$\sim$9.13	9	143
4	11.25	10	279
5	15.50	11	551
6	24	12	1095

A more significant improvement is achieved by a fresh approach as outlined in the following. Consider a catacondensed benzenoid with h hexagons and the maximum number of Kekulé structures, $K_{\max}(h)$. Assume that one end is branched so that the whole benzenoid may be interpreted as C_1, C_2 or C_3:

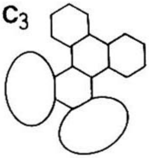
C_1



C_2



C_3

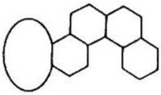


The fragmentation method[9] applied to any of these possibilities gives

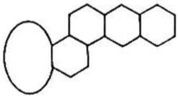
$$K_{\max}(h) = K(h-1) + 2K(h-3); \qquad h \geq 4 \qquad (6)$$

(a) The examples of Fig. 2 for $h \geq 6$ show the necessity to consider a branched end as depicted above. In any case we are on the safe side as far as the upper limit of $K_{\max}(h)$ is concerned because any unbranched configuration, like for instance C_4 and C_5, would give a result smaller than (6).

C_4



C_5



(b) The benzenoids associated with the right-hand side of eqn. (6) are in general unknown. However, if we substitute their K numbers by the maximum values, we have certainly

$$K_{\max}(h) \leq K_{\max}(h-1) + 2K_{\max}(h-3); \qquad h \geq 4 \tag{7}$$

Also in this case regional adjustments may be imposed, as is exemplified in the following table.

h	upper bound for K (7)		
1	2		initial conditions
2	3		
3	5		
4	9		
5	15		
6	25	24	new initial conditions
7	43	41	
8	73	66	
9	123	114	
10	209	196	
11	355	328	
12	601	556	

A new recurrence relation for the upper bound was obtained on combining (4) and (7):

$$\boxed{K_{\max}(h) \leq K_{\max}(h-2) + 3K_{\max}(h-3); \qquad h \geq 4} \tag{8}$$

This relation showed to be superior to all the preceding ones; see Table 2.

By means of Gutman's[6] result (1) we derive

$$K_{\max}(h) \leq 5 \cdot 2^{h-4} + 4 \tag{9}$$

This is the best explicit formula found for $K_{\max}$ when $h \geq 4$. Still the recurrence formula (8) is the best result.

Further application of eqn. (8)

Figure 4 shows a continuation of Fig. 3. All the depicted structures for $h > 13$ have overlapping edges. The K values for each h are the maximal values which were found. The subsequent application of eqn. (8) supports

Table 2. Maximal K values and upper bounds for catacondensed benzenoids. Parenthesized values pertain to helicenes.

h	maximal K value	upper bound (8)		upper bound (9)
1	2	2		∿4.6
2	3	3	initial conditions	5.25
3	5	5		6.5
4	9	9		9
5	14	14		14
6	24	24		24
7	41	41		44
8	66	66		84
9	110	113		164
10	189	189		324
11	302 (305)	311		644
12	492 (510)	528		1284

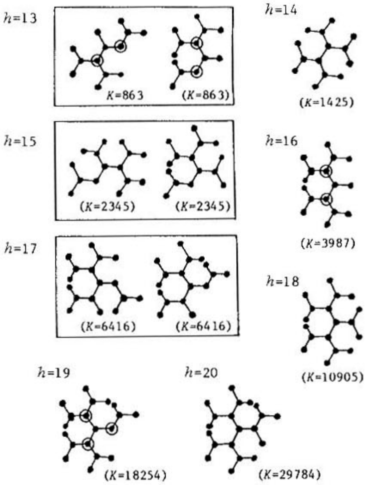


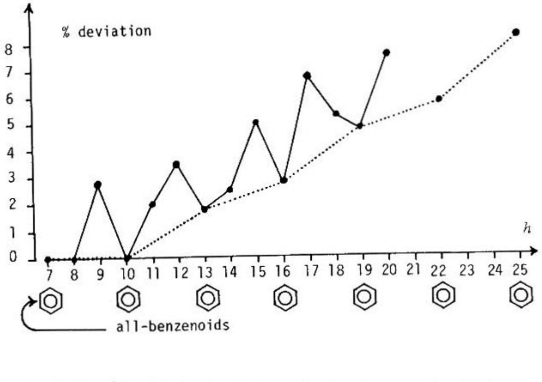
Fig. 4. Catacondensed benzenoids (mostly helicene derivatives) with h = 13, ... 20, and presumably maximal K values.

the belief that they may be the absolute maxima. All-benzenoid systems among the dualist graphs (Figs. 3 and 4) are recognized by the white circles for full non-terminal hexagons.

All the above equations for upper bounds are also valid when overlapping edges are allowed. The below table shows the results from eqn.(8) along with percentage deviations based on the (not guaranteed) maximal *K* values from Figs. 3 and 4.

h	maximal *K* value (?)	upper bound (8)	Deviation
9	110	113	∿2.7%
10	189	189	0%
11	(305)	311	(∿2.0%)
12	(510)	528	(∿3.5%)
13	863	878	∿1.7%
14	(1425)	1461	(∿2.5%)
15	(2345)	2462	(∿5.0%)
16	(3987)	4095	(∿2.7%)
17	(6416)	6845	(∿6.7%)
18	(10905)	11481	(∿5.3%)
19	(18254)	19130	(∿4.8%)
20	(29784)	32016	(∿7.5%)

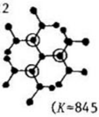
A graphical representation of these deviations (see below) displays a steadily, but not monotonously, ascending curve. It has local minima for every all-benzenoid with $h \geq 10$. The dotted curve drawn through these minima is fairly regular and approximately linear.



The diagram was supplemented by means of the two next all-benzenoids, for which the structures depicted on the next page are assumed to give the maximum *K* numbers.

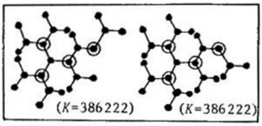
For as high *h* values as this the other estimates of upper bounds are quite out of order. As an example, we have for h=22 from (a) eqn. (7) with the original initial conditions K = 118113, (b) eqn. (9) K = 1310724, and (c) from eqn. (1) or (4) K = 2097153.

$h=22$



($K=84546$)

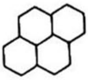
$h=25$



NORMAL BENZENOIDS

A detailed inspection of the normal pericondensed benzenoids with $h = 4, 5, 6$ and 7 revealed the following maximal numbers of Kekulé structures. All of the systems are annelated pyrenes (or pyrene itself):

$h=4$

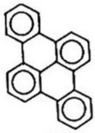


$K=6$

$h=5$

$K=11$

$h=6$



$K=20$

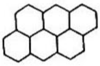
$h=7$

$K=31$

A higher degree of pericondensation gives lower K values for the same h:

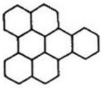
$h=6$

$K=14$

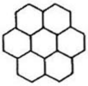


$K=10$

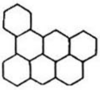
$h=7$



$K=23$

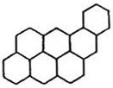


$K=20$

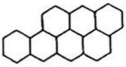


$K=19$

$K=18$



$K=15$



$K=14$

On the basis of these considerations, along with all empirical data, it is conjectured that the maximum K number for a given h occurs for a catacondensed benzenoid.

With regard to the minimum K it has recently been proved rigorously[10] that $h+1$ applies not only to the catacondensed, but to all normal benzenoids.

DISTRIBUTION OF h

It is of great interest to investigate the number of benzenoids with a fixed number of Kekulé structures (K). In the already frequently cited paper[6] Gutman says: "It should be interesting to determine all benzenoid hydrocarbons which have 2, 3, 4, 5, 6, 7 and 8 Kekulé structures."

This question may be approached by a representation of part of the material underlying the diagrams of Fig. 1 the other way around. In other words we search the distribution of h for given K values. Table 3 shows the figures up to K=9. Apart from

Table 3. Number of benzenoids with given K and different numbers of hexagons (h).

K	**Number of hexagons (h)**										
	1	2	3	4	5	6	7	8	. . .	Total	
2	1									1	
3		1								1	
4			1							1	
5			1	1						2	
6				1	1					2	
7				1	0	1				2	
8				2	0	0	1			3	not counting essentially disconnected benzenoids
9				1	2	0	0	1		4	not counting essentially disconnected benzenoids
9					1	1	3	6	. . .	∞	only essentially disconnected

the extraordinary bottom line (for essentially disconnected benzenoids) these figures are all available when (a) having all K values for the h=7 normal benzenoids at hand and (b) adding the unity for $K\{L(8)\} = 9$. The table really embraces all normal benzenoids up to K=9. That is understood because of the theorem[10]

$$K \geq h+1, \qquad K_{\min}(h) = h+1 \tag{10}$$

Consequently

$$h \leq K-1, \qquad h_{\max}(K) = K-1 \tag{11}$$

which gives the upper limit of h for a given K. Hence it is evident that there will be no figures beyond (above and to the right of) the diagonal of unities in Table 3. In general

$$h_o \leq h \leq K-1 \tag{12}$$

for a normal benzenoid. The lower bound h_o, or more precisely $h_{\min}(K)$, is evidently larger than 1 for $K \geq 3$. By inspection it is found, for instance (see Table 3), $h_{\min}(K) = 4$ for K = 6, 7, 8 and 9.

The right-hand column of Table 3 answers Gutman's[6] question (see above) as far as the number of the benzenoids with $2 \leq K \leq 8$ are concerned. The actual structures are shown in Fig. 5. Table 3 gives furthermore the details for K=9. It confirms that the total number of benzenoids is unlimited,[6] but says also that only 4 normal benzenoids with K=9 exist.

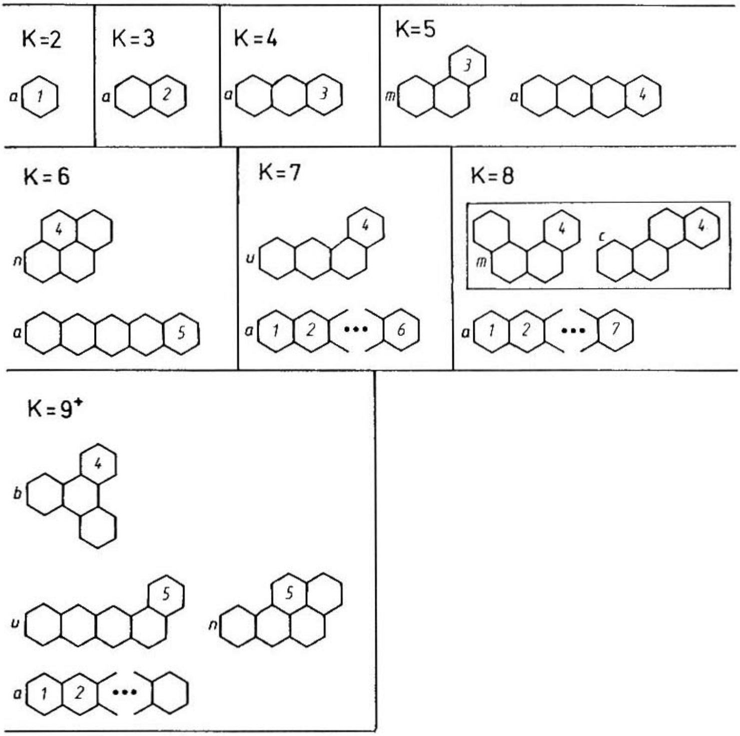


Fig. 5. All normal benzenoids with $K = 2, 3, \ldots, 9$. Abbreviations: *a* acene (linear); *b* bridged; centrosymmetrical; *m* mirror-symmetrical; *n* normal pericondensed; *u* unsymmetrical.

[+] Not counting essentially disconnected benzenoids.

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