DISTRIBUTION OF K, THE NUMBER OF KEKULÉ STRUCTURES

IN BENZENOID HYDROCARBONS. PART III:

KEKULÉ STRUCTURE STATISTICS

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Abstract: The material of K numbers for all benzenoids with h (number of hexagons) up to 9 is treated "statistically". The few existing coronoids with $h=8$ and $h=9$ are included. Average values of K, viz. $<K>$, are reported. The quantities $\ln<K>/h$ were found (empirically) to decrease fairly slowly with increasing h and apparently approach a limiting value. Finally the upper and lower bounds of K for normal pericondensed benzenoids are studied. A general conclusion about the lower limit is conjectured.

The present work does not deal with statistics in a strict sense. Although the terms "distribution" and "average value" are adapted from probability calculus and statistics, all the deduced numerical values are exact quantities (only

subjected to round-off errors in the decimals). They do not experience any kind of random fluctuations.

The definition of a benzenoid conforms with the usage of the Düsseldorf-Zagreb school;[1-3] see also Part II of this series.[4] A coronoid is defined similarly; it is equivalent to a "true" circulene[2,3] and has a hole larger than one hexagon.

CLASSIFICATION

The benzenoids are classified into[4] non-Kekuléan (o), which do not possess any Kekulé structures, normal (n) and essentially disconnected (e). The two latter classes are Kekuléan. An essentially disconnected benzenoid contains fixed (single or double) bonds in all Kekulé structures.

Similarly to the benzenoids the coronoids are classified into non-Kekuléan (o), normal (n) and essentially disconnected (e). The latter class will not be encountered here since we only are going to treat systems with h (number of hexagons) up to 9. The smallest essentially disconnected coronoid has $h=11$.

Table 1 shows the numbers of benzenoids and coronoids of

Table 1. Number of benzenoids and coronoids through $h=9$.*

h	Benzenoids				Coronoids		
	n	e	o	Total	n	o	Total
1	1	.	.	1	.	.	.
2	1	.	.	1	.	.	.
3	2	.	1	3	.	.	.
4	6	.	1	7	.	.	.
5	14	1	7	22	.	.	.
6	48	3	30	81	.	.	.
7	167	23	141	331	.	.	.
8	643	121	671	1435	1	.	1
9	2531	692	3282	6505	3	2	5

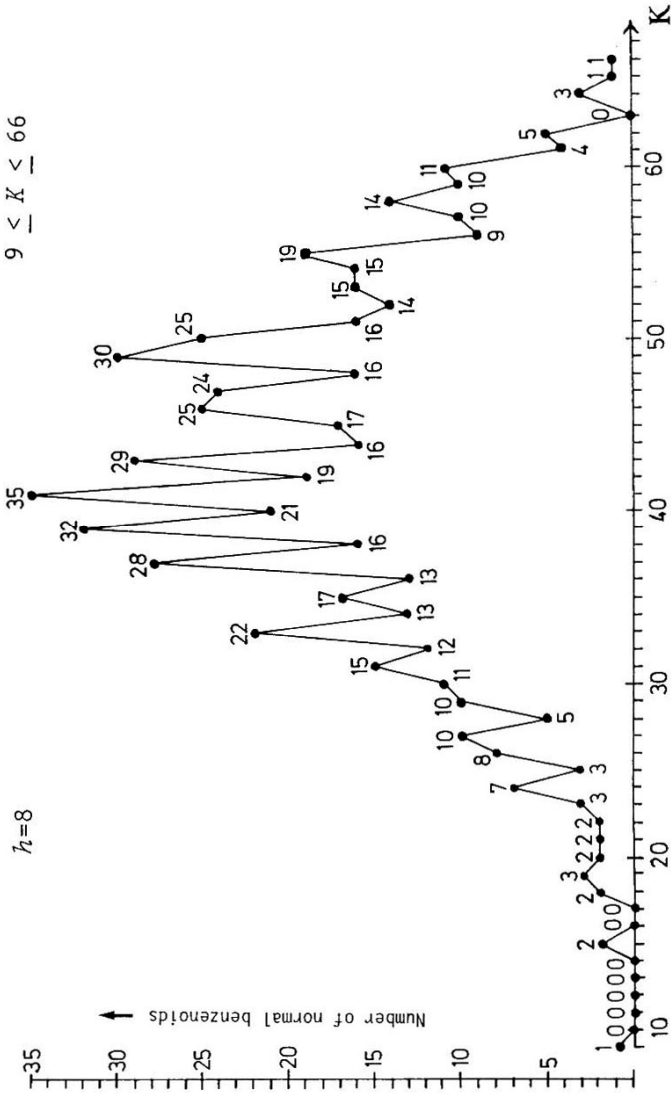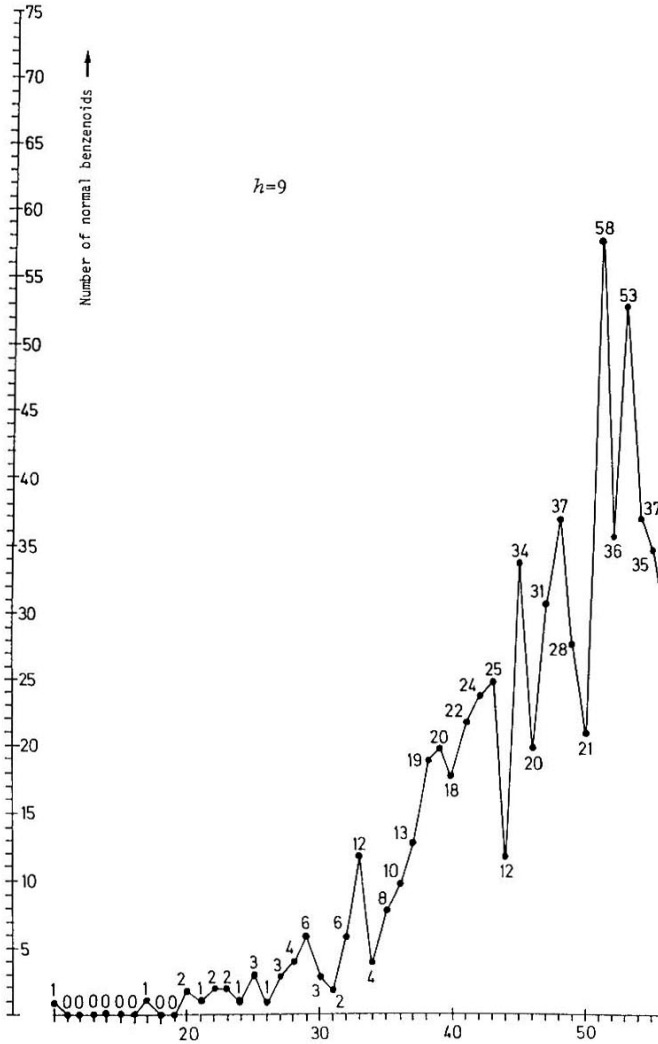*Dots indicate zeros. For abbreviations, see the text.

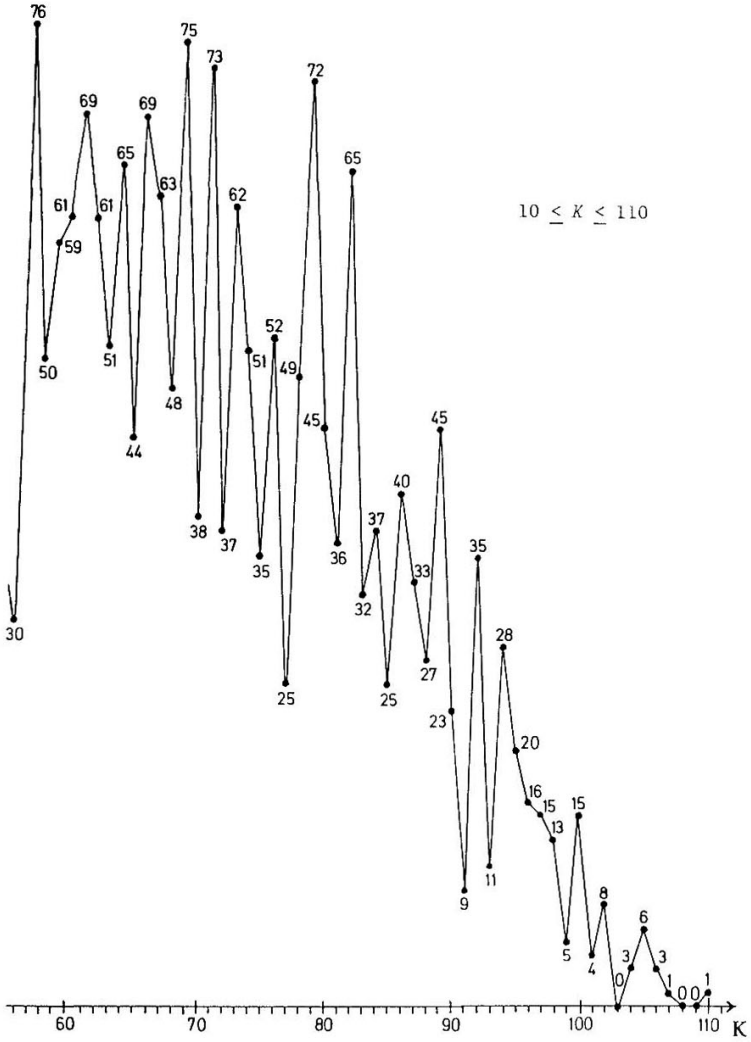Figure 1. Number of normal benzenoids with $h=8$ and different K values.

Figure 2. Number of normal benzenoids with $h=9$ and different K values.

the different categories up to $h=9$. All the numbers are in
principle obtainable from the useful compilations in the book
of Knop et al.,[3] if only the classes n and e are properly dis-
tinguished. In the present work this counting was actually
performed, with extensive assistance of computer programming.

DISTRIBUTION OF K FOR GIVEN h VALUES

   In Part I[5] the distributions of K numbers for normal
benzenoids up to $h=7$ are given. In Fig. 1 and Fig. 2 (prece-
ding pages) the corresponding distributions for $h=8$ and $h=9$
are shown.

   Figure 3 shows a corresponding distribution of K num-
bers for the essentially disconnected benzenoids with h up to
9. These diagrams are seen to have a substantially different
character from those of the normal benzenoids. First of all,

if K is the number of Kekulé structures of an essentially dis-
connected benzenoid, then $K = p \cdot q$, where p and q are integers
greater than two. Consequently, only the numbers 9, 12, 15, 16,
18, 20, 21 etc. are compatible with the K values of essentially
disconnected benzenoids.

   Let K_{min}^e and K_{max}^e be the minimum and maximum among the
K values of essentially disconnected benzenoids with a fixed
number h of hexagons. In accordance with the above observation,
$K_{min}^e = 9$ for all values of h. From Fig. 3 it is seen that K
may be any number from the interval $[K_{min}^e, K_{max}^e]$ having the
form $p \cdot q$.

   The results of this section are also contained impli-
citly in the cited book,[3] but not presented in such a form
that the information of Figures 1-3 could easily be extracted
from the relevant 7940 drawings without computer aid.

   The coronoid with $h=8$ has $K=40$. The three Kekuléan coro-
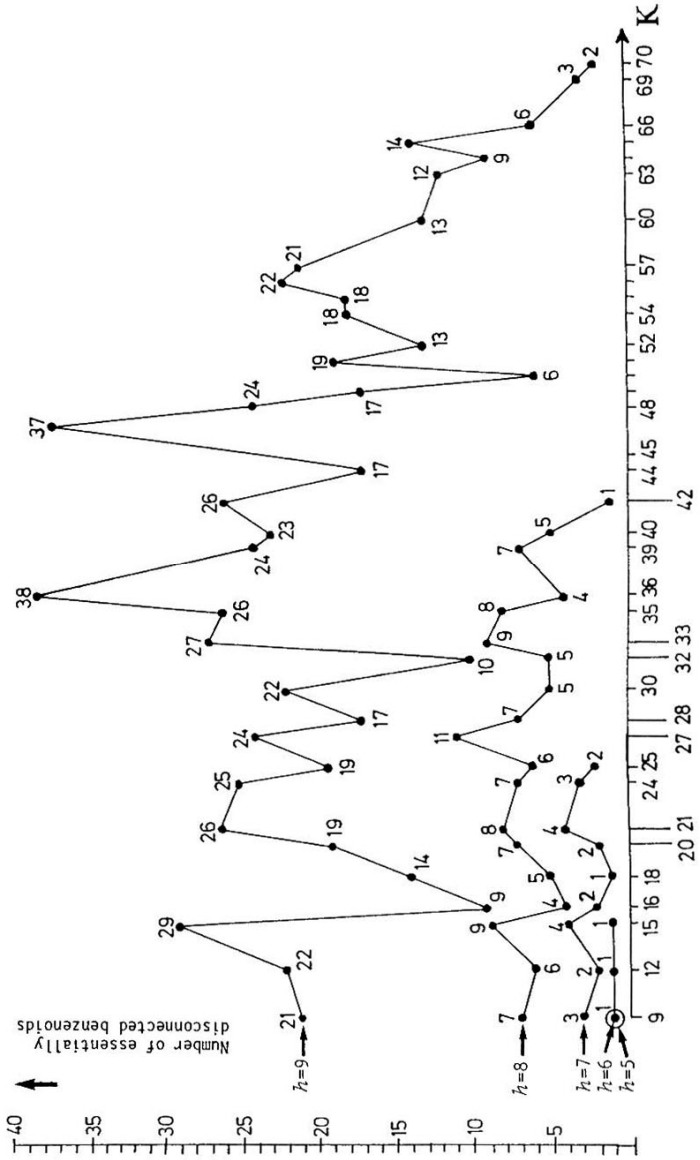noids of $h=9$ have $K = 54$, 66 and 72.

Fig. 3. Number of essentially disconnected benzenoids with $h = 5, 6, 7, 8, 9$ and different K values. The K values for which no essentially disconnected benzenoids exist are not indicated.

AVERAGE K VALUES AND RELATED QUANTITIES

Average values of K for every h up to 9 were calculated for:

(i) the normal benzenoids only (n);
(ii) the essentially disconnected benzenoids only (e);
(iii) Kekuléans $(n+e)$;
(iv) all benzenoids including non-Kekuléans $(n+e+o)$.

The results are found in Table 2.

	Benzenoids			
h	n	e	$n+e$	$n+e+o$
1	2	.	2	2
2	3	.	3	3
3	4.5	.	4.5	3
4	7.17	.	7.17	6.14
5	11.21	9	11.07	7.55
6	17.5	12	17.18	10.81
7	27.46	17.7	26.28	15.08
8	42.83	25.53	40.09	21.35
9	66.94	37.58	60.64	30.04

Table 2. Average K values.

Coronoids	
n	$n+o$
40	40
64	38.4

Bearing in mind that the number of Kekulé structures is related with various physical and chemical properties of benzenoid hydrocarbons (enthalpy, total π-electron energy, resonance energy, certain types of reactivities etc.),[6] we can use the data from Table 2 in the following manner. If a certain benzenoid molecule is given, we can compare its (K-dependent) properties with the same properties of an average benzenoid system. Thus we can answer to the question whether a given benzenoid molecule is more stable (more aromatic, more reactive etc.) than a "typical" benzenoid molecule of the same size.

h	$\langle K\rangle/h$	$\ln\langle K\rangle/h$
1	2	0.693
2	1.5	0.549
3	1.5	0.501
4	1.79	0.492
5	2.24	0.483
6	2.92	0.477
7	3.92	0.473
8	5.35	0.470
9	7.44	0.467

Table 3. Values of $\langle K\rangle/h$ and $(\ln\langle K\rangle)/h$ for the average K values based on normal (n) benzenoids.

In accordance with this we wish to inspect how the coronoids are placed in relation to the benzenoids with respect to their K numbers. It is seen (Table 2) that $K=40$ for the unique $h=8$ coronoid practically coincides with the average value for Kekuléan benzenoids. Also the average K for the three Kekuléan coronoids with $h=9$ is seen to be compatible with the corresponding benzenoid values (for n or $n+e$). This empirical material is too small to give a basis for a more general opinion about these averages. It is clear, however, that the average K with respect to all (also non-Kekuléan) coronoids does not fit the corresponding benzenoid data. It is mentioned by passing that the average K values of 88.96 and 49.65 were found for the $h=10$ coronoids with respect to the 24 (normal) Kekuléan and 43 total systems, respectively. No values for $h=10$ benzenoids are available for comparison.

Table 3 shows some quantities derived from the average K values for benzenoids. For the sake of brevity only the data pertaining to the normal benzenoids are given therein. The function $\langle K\rangle/h$ is seen to increase with increasing h. On the other hand, $\ln\langle K\rangle/h$ is a slowly decreasing function of h; it seems to approach a limiting value of about 0.47. On the

basis of the available numerical data one cannot, however, completely exclude the possibility that for large h, $\ln\langle K\rangle/h$ tends to zero. Similar behaviours (for $h \geq 4$) were found for $\ln\langle K\rangle/h$ based on the other average values, as illustrated in Figure 4.

We note in passing that there exists a linear dependence between $\ln K$ and the resonance energies of benzenoid hydrocarbons,[6,7] namely

$$RE = 114.3 \ln K \text{ [kJ mol}^{-1}\text{]}.$$

Bearing this in mind, the above observations can be interpreted so that the resonance energy of an average ("typical") benzenoid hydrocarbon increases with the increasing size of the molecule and is proportional to h. This also means that the average resonance energy per hexagon is a constant and can be estimated as $114.3 \times 0.47 = 53.7$ kJ/hexagon. Those benzenoid
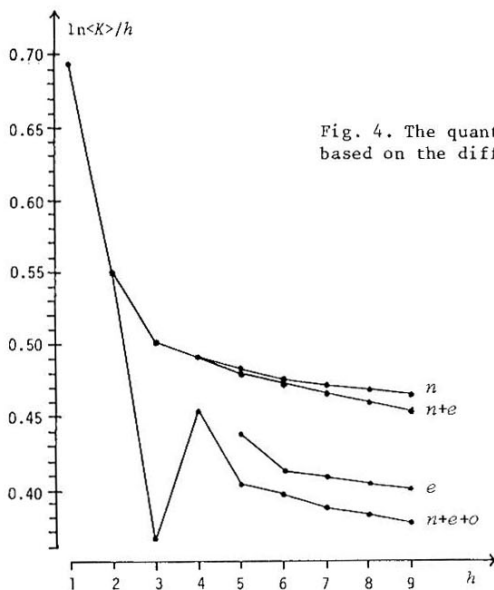

Fig. 4. The quantities $(\ln\langle K\rangle)/h$ based on the different K values.

hydrocarbons whose resonance energy per hexagon is above
(resp. below) 53.7 kJ can be characterized as unusually stable
(resp. unstable).

MAXIMAL AND MINIMAL K NUMBERS OF NORMAL BENZENOIDS

The maximum (K_{max}) and minimum (K_{min}) numbers of Kekulé
structures in normal benzenoids with given h are treated in Part
I.[5] It has been found definitively that $K_{min} = h+1$, while K_{max}
is most probably realized for a catacondensed benzenoid. The
latter statement was verified by inspection for $h \leq 9$, and is
conjectured to be true in general.[5] Here we are primarily inte-
rested in the extremal K values for normal pericondensed benze-
noids.

By inspection it is found that the maximal K numbers in
normal pericondensed benzenoids occur for annelated pyrenes when
$5 \leq h \leq 9$. These systems have only two internal vertices and are
therefore among the Kekuléans which come closest to the catacon-
densed systems.

Figure 5 gives a survey, where also basic benzenoids are
considered separately. This class consists of special normal
pericondensed benzenoids, which cannot be separated into two
fused benzenoid units. In this context two benzenoids are said
to be fused when they are combined so that exactly one edge
from each coalesce.

In the remaining part of this section we are treating the
minimal value of the normal pericondensed benzenoids, denoted
by K_{min}^{np}, as a function of h. It is inferred that:
    (i) the value of K_{min}^{np} is equal to 6, 9, 10, 14, 15, 20,
21, 27, 28 for h = 4, 5, 6, ..., 12;
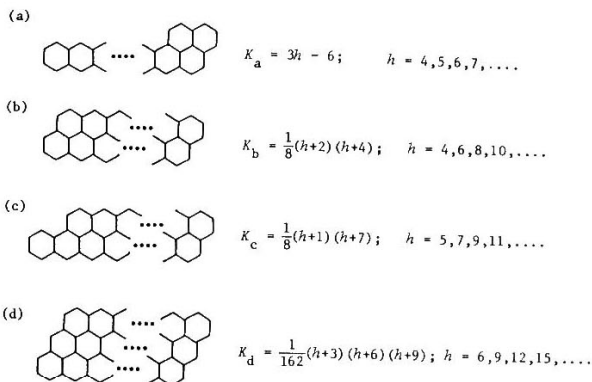   (ii) one has $K_{min}^{np} = 3h - 6$ for $h \geq 13$.

The first statement (i) was deduced by inspection. The
actual benzenoids up to $h=9$ with their K numbers are found in
Fig. 5. Those up to $h=15$ were determined by the sieve method.[4]
The second statement (ii) has not been proved rigorously, but

some considerations to its support are reported in the fol-
lowing.

Fig. 5. Benzenoids with extremal K numbers entered into hexagons, which
(for $h > 1$) can be removed without changing the property of being nor-
mal.

It was observed empirically that the normal pericondensed benzenoids with minimal K values up to $h=15$ may be classified into four types (a)-(d). They are shown in the below figure, which includes the appropriate combinatorial formulas of K numbers.

(a)

$$K_a = 3h - 6; \qquad h = 4,5,6,7,\ldots$$

(b)

$$K_b = \frac{1}{8}(h+2)(h+4); \qquad h = 4,6,8,10,\ldots$$

(c)

$$K_c = \frac{1}{8}(h+1)(h+7); \qquad h = 5,7,9,11,\ldots$$

(d)

$$K_d = \frac{1}{162}(h+3)(h+6)(h+9); \; h = 6,9,12,15,\ldots$$

The four systems are either parallelograms or incomplete parallelograms. In this respect they correspond to chains without kinks. It is well known from single chains that the kinks increase the K number. This feature has a parallel in multiple chains, complete or incomplete.[8] The following illustration is supposed to explain this point (K numbers are written into hexagons).

L(3) A(3) L(2,3) A(2,3) L(2,2,1) A(2,2,1)

$K\{L(3)\}<K\{A(3)\}$ $K\{L(2,3)\}<K\{A(2,3)\}$ $K\{L(2,2,1)\}<K\{A(2,2,1)\}$
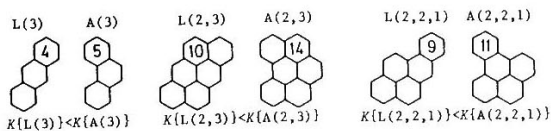
In general the type (a) is a strong candidate for a benzenoid where $K_{\min}^{np}$ is realized. For all values of h it comes closest to a catacondensed benzenoid inasmuch as it has only two internal vertices, and it simulates as best as possible the linear acene. For small and moderate values of h, however, the K_a number is sometimes underbid by K numbers of the other types. An analy-

sis was performed, which gives a complete account of the minimal K numbers as far as the four types (a)-(d) are concerned. (1) $K_a \leq K_b$ $(h \geq 4)$ is equivalent to $(h-4)(h-14) \geq 0$; hence $K_a = K_b$ for $h=4$ and $h=14$, and $K_a < K_b$ for $h > 14$. (2) $K_a \leq K_c$ $(h \geq 5)$ is equivalent to $(h-5)(h-11) \geq 0$; hence $K_a = K_c$ for $h=5$ and $h=11$, and $K_a < K_c$ for $h > 11$. (3) It was also found $K_b = K_d$ for $h=6$ and $K_b < K_d$ for $h > 6$; $K_c = K_d$ for $h=9$ and $K_c < K_d$ for $h > 9$; in conclusion $K_a < K_d$ for $h > 9$. The main conclusion is summarized by the statements (i) and (ii) above. Details are displayed in the below table.

h	Types	K_{min}^{np}	h	Types	K_{min}^{np}
4	$K_a = K_b$	6	10	K_b	21
5	$K_a = K_c$	9	11	$K_a = K_c$	27
6	$K_b = K_d$	10	12	K_b	28
7	K_c	14	13	K_a	33
8	K_b	15	14	$K_a = K_b$	36
9	$K_c = K_d$	20	≥ 15	K_a	$3h-6$

A FINAL OBSERVATION

The final speculation deals with the average K values for normal benzenoids (see Table 2). The orders of magnitude for $\langle K \rangle$ at $h \leq 9$ are found to be the same as $K_{max}(h-1)$; cf. Fig. 5. This feature is illustrated in Figure 6. It is an open question whether this tendency continues for $h > 9$.
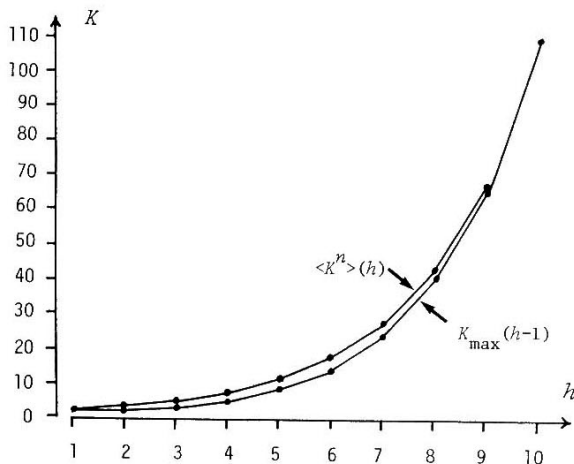
Fig. 6. The average values of K for normal benzenoids at h, and the maximum K at one hexagon less.

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