Distribution of K, the Number of Kekulé Structures, in Benzenoid Hydrocarbons: Normal Benzenoids with K to 110

S. J. CYVIN,* J. BRUNVOLL, and B. N. CYVIN

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

The importance of distinguishing between normal and essentially disconnected Kekuléan benzenoids is pointed out. The normal benzenoids have the fundamental property that their number is limited for a given K value, i.e., the number of Kekulé structures. All normal benzenoids for $K \leq K^*$ may be deduced by (a) the building-up principle, where normal benzenoids with $h + 1$ hexagons are generated from those with h hexagons, and (b) the sieve method, which successively eliminates the benzenoids with $K > K^*$. The methods were computerized. The distributions of K, i.e., the number of normal benzenoids with given K and different h values, are reported for $K = 2$–110. Actual forms of the benzenoids are depicted for $K \leq 30$.

The enumeration and classification of benzenoid (polycyclic aromatic) hydrocarbons has been treated several times and from different viewpoints.

(1) Given the number of hexagons, h, how many benzenoids can be constructed? Much effort has been put into studies of this mathematical enumeration problem[1–8] (not only for hexagon systems[1,2,6–8]). The problem so far remains unsolved. Especially the catacondensed systems have been studied extensively.[3–5,9] Computer programs have been devised and numerical solutions reported.[7,10–13] Some of these works include pericondensed systems.[7,11–13] One of them[13] gives a useful review. Recently a useful book by Knop et al.[14] has appeared; it contains a compilation of pictures of all benzenoids with h values to 9. In the work of the Düsseldorf–Zagreb group, which is contained in the above references,[11–14] the benzenoids with a given h are classified according to the number of internal vertices. In this way the catacondensed and pericondensed benzenoids are distinguished.

In recent years this research area has flared up. A number of works on enumeration and different classifications of benzenoids have appeared. A consolidated paper[15] by 14 authors summarizes the situation.

(2) A systematic chemical nomenclature for the benzenoids is a related problem.[3,4,16,17–25]

(3) The number of benzenoid isomers C_nH_m is another formulation of the problem 1 above. A periodic table of relevance to the benzenoid isomers (also including non-benzenoid systems) has been presented.[26–34]

(4) In the present work a new viewpoint is taken, classifying the benzenoids with respect to their number of Kekulé structures, which are recognized as playing an important role in chemical theories; see, e.g., references 35–37. This count is conventionally identified by the symbol K. The theory of relevance to the present viewpoint has been advanced in two previous papers.[38,39] In the latter work[39] the methods were used to deduce the number of normal benzenoids (for definition, see below), with $K = 2$–24. The actual forms for $K = 2$–14 are depicted therein. These results were obtained without the aid of computer programming. In the present work our programs[40] were extended by incorporating the computation of K numbers. With this aid all the normal benenoids with $K \leq 110$ were generated and classified according to the K values. This is a tremendous step forward since 1983 when a theorem[36,41] stated that only one benzenoid has $K = 2$ (viz., benzene). Furthermore, it was conjectured[41] that $K = 3$ is realized for one benzenoid (naphthalene) and also $K = 4$ for one benzenoid (anthracene), while $K = 5$ is realized for two benzenoids (tetracene and phenanthrene). A special conjecture

Table I. Numbers of Benzenoids with h Hexagons, Classified into Three Types (see Text)

h	n	e	o	total
1	1	0	0	1
2	1	0	0	1
3	2	0	1	3
4	6	0	1	7
5	14	1	7	22
6	48	3	30	81
7	167	23	141	331
8	643	121	671	1435
9	2531	692	3282	6505
10	10375	3732	15979	30086
11	42919	19960	78350	141229

was formulated[41] saying, "There is a finite number of benzenoid graphs for which $0 < K \leq 8$." It has also been said,[42] "It would be interesting to determine all benzenoid hydrocarbons which have 2, 3, 4, 5, 6, 7 and 8 Kekulé structures. We conjecture that their number is finite." And now we know the normal benzenoids that have 2–110 Kekulé structures.

By "normal" is meant Kekuléan benzenoids that are not essentially disconnected[43] (for definition, see below).

The quoted paragraph[42] continues: "On the other hand, there are infinitely many benzenoid systems with nine Kekulé structures." This feature was rigorously proved by Gutman,[44] who studied benzenoids annelated to a linear chain. He pointed out that perylene (P), zethrene (Z), etc., have $K = 9$ independently of the linear chain, which connects the two naphthalene units:
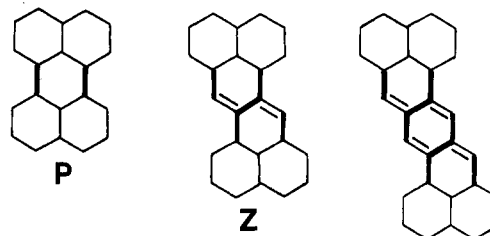
The fixed bonds are indicated by heavy and double lines. Naphthalene is known to have three Kekulé structures, and all of them fit the pattern of fixed bonds on both sides. Hence, the total number of Kekulé structures is $3 \times 3 = 9$ as stated above.

The above systems are the simplest examples of essentially disconnected benzenoids. Later it was demonstrated[45] that a multitude of other benzenoids with $K = 9$ may be constructed, where the connecting part may be a kinked chain

(also branched) or a pericondensed benzenoid, e.g.
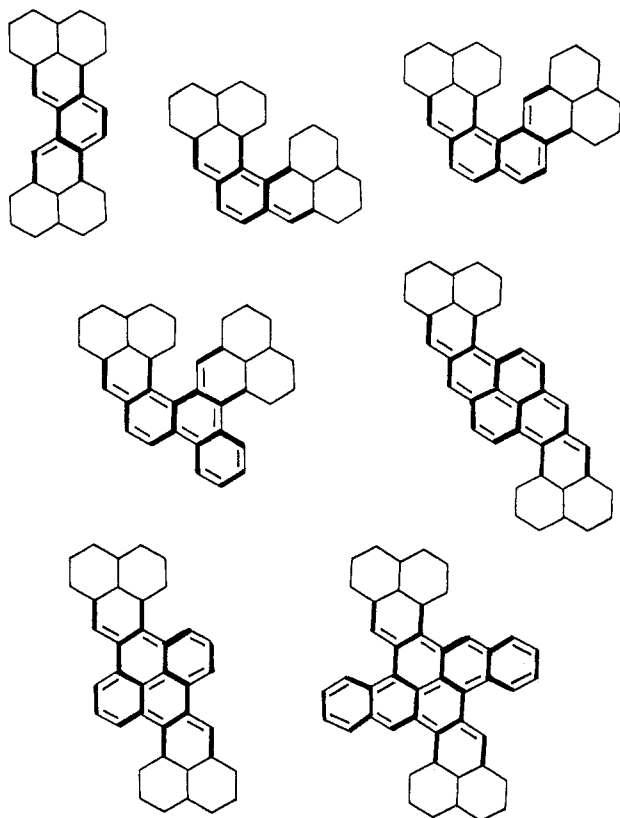
The effective units (not containing hexagons with fixed bonds) may be larger than naphthalene, catacondensed or pericondensed, as may be realized by simple extensions. Then, of course, the K number will be larger. If, for instance, one of the naphthalene units is expanded to pyrene, one obtains $K = 3 \times 6 = 18$.

In a way the knowledge of infinitely many benzenoids with $K = 9$ (as well as many K values greater than 9) blocked further thinking about the distribution of K numbers in general. In a sense it was a breakthrough when the distinction between normal and essentially disconnected benzenoids was considered seriously. That leads us naturally to the next paragraph, where these concepts are defined strictly.

RESULTS AND DISCUSSION

Definitions. The present work adheres to Gutman's[36] definition of a benzenoid. Accordingly, these systems should be planar. It is also significant that this definition excludes hexahelicene and its derivatives. It also excludes coronoid (corona-condensed) systems;[26,36,46] they do not occur before $h = 8$ when only the "true" systems with a corona hole of more than one hexagon are counted. When the distribution of K values is considered, the most important classifications of the benzenoids are as follows.

Non-Kekuléan benzenoids[47] (o) possess no Kekulé structures and are necessarily pericondensed.

Essentially disconnected benzenoids[43] (e), also pericondensed, have some of the bonds fixed[44] (single or double) in all Kekulé structures. A comprehensive treatise on such benzenoids, including a great variety of examples, has recently appeared.[48]

Normal pericondensed benzenoids[38,39] (np) are the Kekuléan pericondensed benzenoids not being essentially disconnected. A broader category is the normal benzenoids (n), which also includes all catacondensed systems (which invariably are Kekuléan).
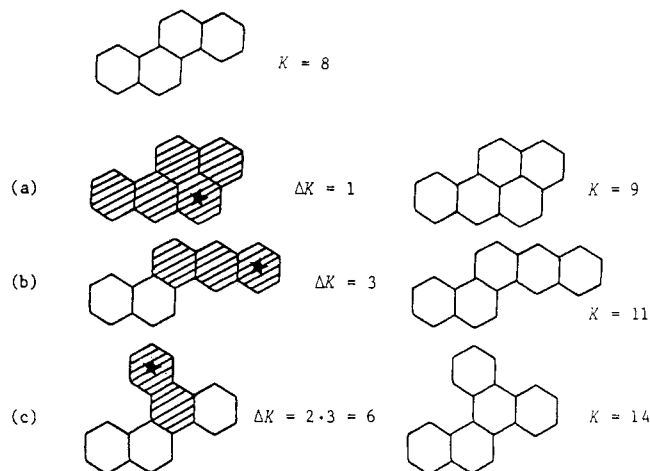
Figure 1. Effect on K of adding one hexagon (marked with asterisk) in three positions to a normal benzenoid (chrysene). The increment in K is the K number of the unhatched part (or unity if the whole benzenoid is hatched).

Table I shows the so far available numbers of benzenoids with given h values and belonging to the three types n, e, and o. The numbers of benzenoids in total ($n + e + o$) are consistent with authorized values.[15] They also agree with other literature data[1-5,7,9] when the proper corrections are made for the differences in the definition of the counted systems.[49]

Two recent monographs[50,51] should be cited as pertinent to the topic of the present work.

Minimum and Maximum K Numbers. For a given h the K numbers for the normal benzenoids, $K(h)$, are limited. For $1 \le h \le 10$ have been found $K(1) = 2$, $K(2) = 3$, $K(3) = 4$, $5, 5 \le K(4) \le 9$, $6 \le K(5) \le 14$, $7 \le K(6) \le 24$, $8 \le K(7) \le 41$, $9 \le K(8) \le 66$, $10 \le K(9) \le 110$, and $11 \le K(10) \le 189$. The minimum values were definitely proved to be $h + 1$ and are realized in the linear acenes.[52] For the maximum values different upper bounds have been deduced.[39,42,53] The normal benzenoids with the maximum K are catacondensed systems and branched for $h \ge 4$.

Basic Principles. (1) It is inferred that all normal benzenoids with $h + 1$ hexagons may be generated by adding one hexagon each in selected positions of the normal benzenoids with h hexagons. This is referred to as the building-up process.[39]

(2) It was proved rigorously[39] that this kind of addition makes the K number increase.

The latter principle (2) is illustrated in Figure 1. One hexagon is added in three positions to an $h = 4$ benzenoid (chrysene). The example illustrates that the increment to K may be (a) unity, (b) K number of a normal benzenoid, or (c) K number of a disconnected system of benzenoids. This analysis is based on the well-known method of fragmentation due to Randić.[54]

Distribution of K. We are interested in all the normal benzenoids with $K = 2, 3, 4, ..., K^*$. Since K has the minimum value of $h + 1$, it is clear[38,39] that a normal benzenoid with K Kekulé structures cannot have more than $K - 1$ hexagons. The desired distribution may consequently be determined in principle by inspecting all the K numbers for benzenoids with $h = 1, 2, 3, ..., K^* - 1$. This shows that the numbers of the distribution are limited, but it would be hopeless to follow this procedure in practice. For $K^* = 10$ one would have to inspect 3413 systems (cf. Table I), which of course is feasible by computer aid. However, the number increases tremendously with increasing K^*; we estimate it roughly to be multiplied by 4 for every unit of some of the subsequent K^* values.

Classification of All Benzenoids with Seven Hexagons. Here we give an account of the 331 benzenoids with $h = 7$ (cf. Table
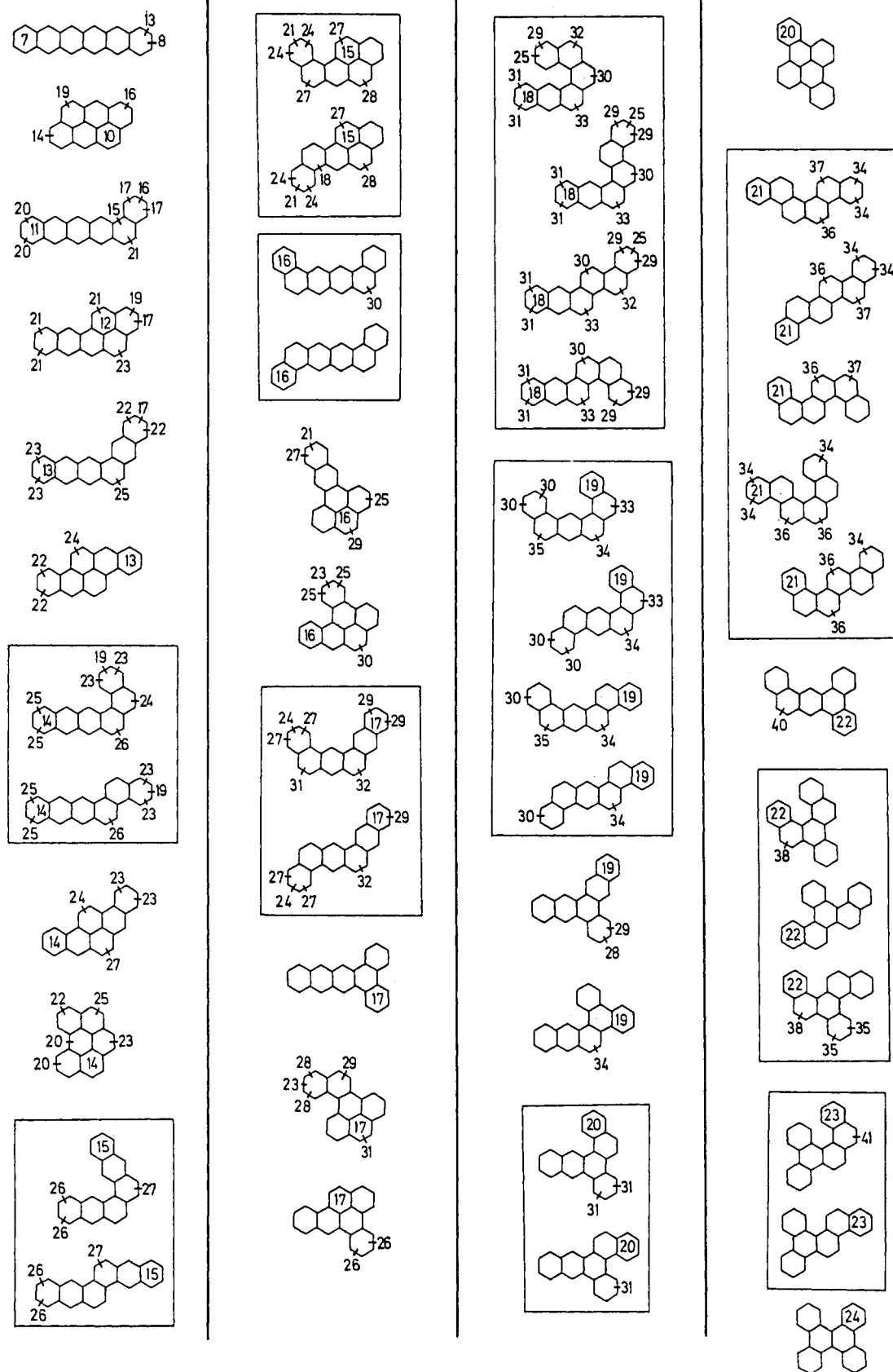
Figure 2. 48 normal $h = 6$ benzenoids with K numbers inside. Framed systems are isoarithmic. Each numeral outside these benzenoids indicates the K number of an $h = 7$ benzenoid generated by adding one hexagon in the appropriate position.

I). Emphasis is put on the normal systems and their numbers of Kekulé structures.

A previous paper[39] gives the K numbers for all normal benzenoids with $h = 2-5$. The distribution of K for $h = 6$ is

also reported therein, but does not specify all the actual forms. These 48 benzenoids are shown in Figure 2. They are ordered by increasing numbers of Kekulé structures (K). These K numbers are written into one of the hexagons, and every time

Table II. Distribution of K Numbers for $h = 7$ Benzenoids of Different Types

	catacondensed						pericondensed				grand total
K	a	m	c	u	b	total	np	e	o	total	
0	.	.	.	.	.	.	.	.	141	141	141
8	1	.	.	.	.	1	.	.	.	.	1
9	.	.	.	.	.	.	.	3	.	3	3
12	.	.	.	.	.	.	.	2	.	2	2
13	.	.	.	1	.	1	.	.	.	.	1
14	.	.	.	.	.	.	1	.	.	1	1
15	.	.	.	.	.	.	1	4	.	5	5
16	.	.	.	1	.	1	1	2	.	3	4
17	.	1	.	2	.	3	1	.	.	1	4
18	.	.	.	.	.	.	1	1	.	2	2
19	.	.	.	2	.	2	2	.	.	2	4
20	.	1	1	.	.	2	2	2	.	4	6
21	.	.	.	.	1	1	6	4	.	10	11
22	.	.	.	2	.	2	3	.	.	3	5
23	.	.	.	6	.	6	6	.	.	6	12
24	.	1	1	.	1	3	6	3	.	9	12
25	.	2	.	5	1	8	4	2	.	6	14
26	.	.	.	4	2	6	2	.	.	2	8
27	.	.	.	4	2	6	5	.	.	5	11
28	.	.	.	.	1	1	4	.	.	4	5
29	.	2	.	8	1	11	2	.	.	2	13
30	.	2	2	2	5	11	1	.	.	1	12
31	.	.	.	8	4	12	1	.	.	1	13
32	.	.	.	.	4	4	.	.	.	.	4
33	.	.	.	.	6	6	.	.	.	.	6
34	.	3	.	5	5	13	.	.	.	.	13
35	.	.	.	.	4	4	.	.	.	.	4
36	.	.	.	.	7	7	.	.	.	.	7
37	.	.	.	.	3	3	.	.	.	.	3
38	.	.	.	.	2	2	.	.	.	.	2
40	.	.	.	.	1	1	.	.	.	.	1
41	.	.	.	.	1	1	.	.	.	.	1
total	1	12	4	50	51	118	49	23	141	213	331

into a hexagon that can be removed to produce a normal h = 5 benzenoid. The structures in frames are isoarithmic.[51,55] They only differ in the way their kinks go, which does not affect the K number. Each of the marked edges shows a position where one hexagon was added to generate a new benzenoid with h = 7. The new K number (for the h = 7 benzenoid) is written in the appropriate place outside the marked edge. In this way Figure 2 contains in a compressed way the information about K numbers of all the existing 167 normal benzenoids with h = 7.

Table II gives a survey of the different types of benzenoids with h = 7 for every K number. For the sake of completeness the essentially disconnected benzenoids (and non-Kekuléans) are included in this listing. In addition to the abbreviations introduced above, are used (for the catacondensed systems) a, acene (linear), symmetry group D_{2h}; m, mirror-symmetrical, C_{2v}; c, centrosymmetrical, C_{2h}; u, unsymmetrical, C_s; and b, branched, different symmetries.

The essentially disconnected benzenoid systems with h = 7 are displayed in Figure 3 as dualist graphs.[3] K numbers are given therein.

For the 141 non-Kekuléan systems with h = 7,[16,34] see Figure 4 (dualist graphs). Most of these systems consist of annelations to the units

(i)   (ii)   (iii)   (iv)
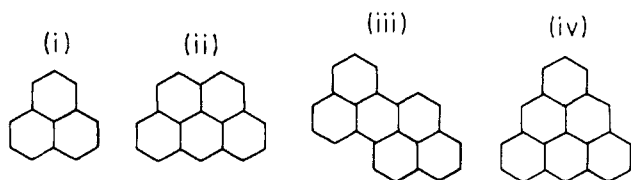
The annelated parts are mostly single chains of varying number and length (down to one hexagon), also branched. In three

systems a pyrene graph is annelated to unit i. Two units i may also be annelated to each other. The occurrence of the units i–iv is indicated in Figure 4. In four cases a system of seven pericondensed hexagons occurs; they are identified by (v). Otherwise, the systems are ordered according to (a) the number of hexagons of the longest linear chain within the systems and (b) the value of Δ, which is unity in the majority of the cases, but may be 2. This quantity is defined as the absolute magnitude of the difference between the numbers of black and white vertices with reference to coloring of vertices.[36,47] All the systems were built up by adding one hexagon each into selected positions of the 30 non-Kekuléans with h = 6.[40] It is supposed that the present systems of classifying non-Kekuléan benzenoids may be useful for similar studies of benzenoids with higher h values.

Sieve Method. Turning back to the distribution of K for normal benzenoids, it is fortunately not necessary to continue the described kind of a complete analysis for all h up to K^* − 1 to deduce the normal benzenoids with $K \leq K^*$. By virtue of the basic principles stated above, this tedious process is circumvented. The actual procedure is referred to as the sieve method:[39] (1) Assume for the sake of argument that K^* = 110, which is the maximum K for h = 9. (2) Consider all the normal benzenoids with h = 9 but the one with K = 110. (3) Use the building-up process to generate all possible normal benzenoids with h = 10 from them. (4) Discard all of these systems unless $K < 110$ and proceed to h = 11. (5) Continue the process as long as necessary. It tends to fade out, resulting in no benzenoids for several h values before the last one with $h = K^* - 1 = 109$. Here we have presupposed that the forms of all normal benzenoids with h = 9 are known. If not, they may be generated from those with lower h values by the building-up process as described in detail above.

Computer Programming. A computer program for generation of benzenoids with given h values is described elsewhere.[40] It has the special feature of an option to generate the normal benzenoids separately. This program was coupled with a procedure for computing the K numbers, following the methods of Brown.[56] It is based on the determinant of a matrix obtained from the adjacency matrix,[35,36] where all rows are compressed to half their original size by eliminating a number of zeros. Another procedure was built into the program to execute the sieve method automatically.

Results for the K Distributions. In a previous work[39] the numbers of normal benzenoids with $K \leq 24$ are reported. The actual forms are depicted for $K \leq 14$ only. These results were obtained without computer programming. In the present work the described program reproduced exactly all the previous numbers, and the process was carried on to $K \leq 110$. This number is the maximum K for h = 9. Table III shows the result.

The actual forms of the normal benzenoids with different K numbers are interesting, but space-consuming. It is important chemical information reflecting a new principle of ordering the benzenoids, namely, according to increasing K numbers. Figure 5 gives a survey for $2 \leq K \leq 30$.

Fading-Out Phenomenon. The sieve method (see above) tends to fade out in the sense that for a given K there are no normal benzenoids with h values above a certain limit until the table terminates with one system, the linear acene, for which $h = K - 1$; cf. Figure 6. For K = 100, for instance, there is one system at h = 35 and then nothing until h = 99 (cf. Table III here and in the following discussions). This feature was exploited in the tabulation by entering the horizontal line of unities, which actually represents a diagonal of unities (as seen at the beginning of the table).

The fading-out phenomenon goes far beyond the linear acenes, which possess the maximum h value for a given K.
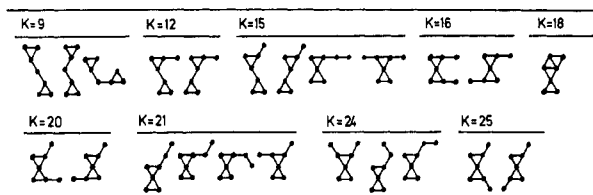
Figure 3. All essentially disconnected benzenoids with $h = 7$ as dualist graphs. K numbers are given.

When only odd K numbers are considered, the next-to-largest actual h value is $^1/_2(K + 1)$. These systems may be described as one hexagon annelated to a linear acene; cf. Figure 6. For $K = 9$ and $K = 15$ one pericondensed system in each case has the same K number (viz., for $h = 5$ and 8, respectively); cf. Figure 5. Otherwise, the benzoacenes are the unique systems where h assumes the next-to-largest value at a given odd K. Also, this feature was exploited in a space-saving way in Table III (for $K \geq 31$). This horizontal line of alternating unities and empty spaces represents a diagonal of unities that is less steep than the aforementioned diagonal pertaining to the linear acenes. This part of the fading-out phenomenon is not effective for even K numbers of 6 and 10. In each case one nonvanishing entry occurs below the appropriate diagonal of unities.
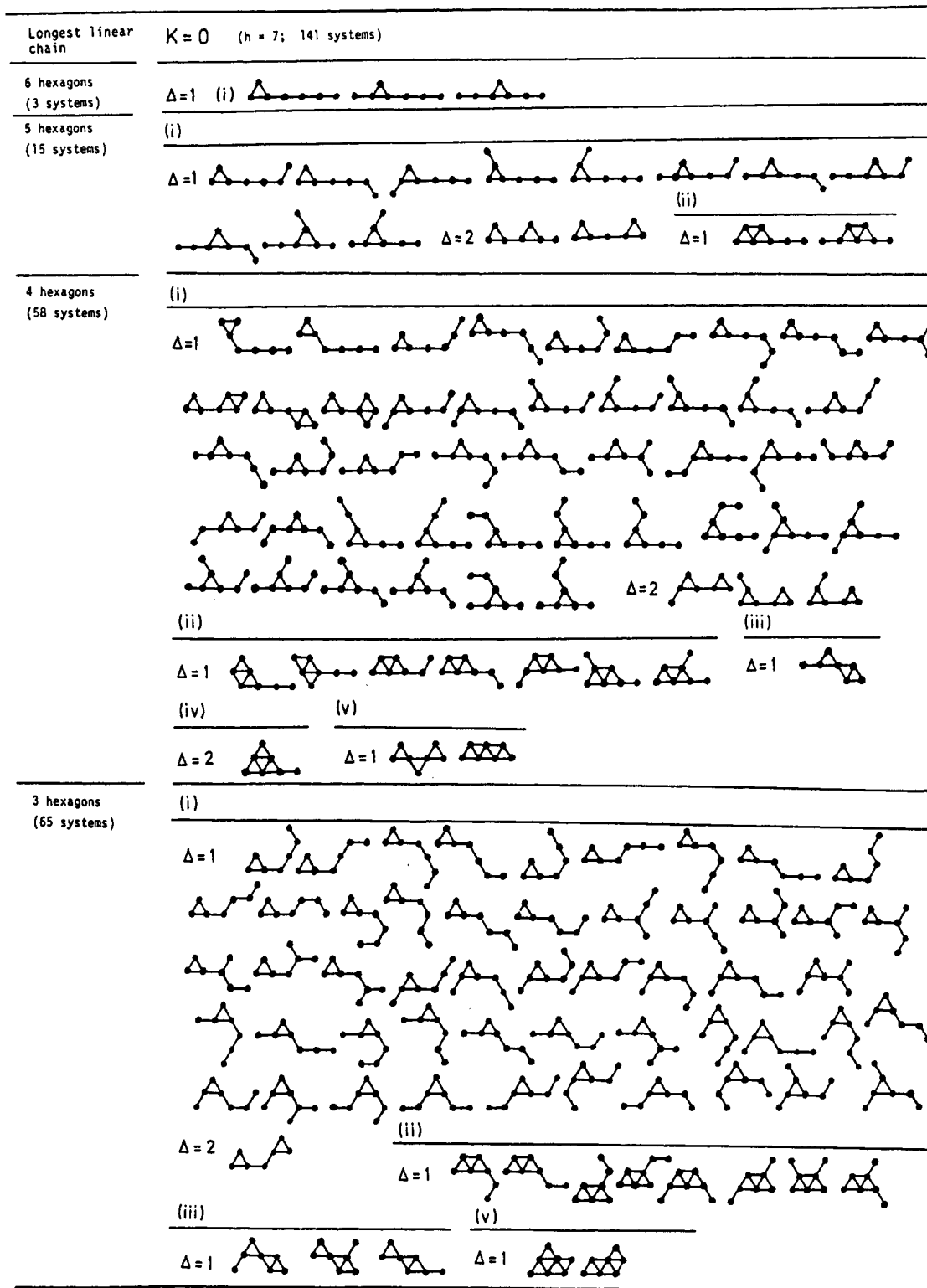
Figure 4. All non-Kekuléan ($K = 0$) benzenoids with $h = 7$ as dualist graphs. Δ values are given.
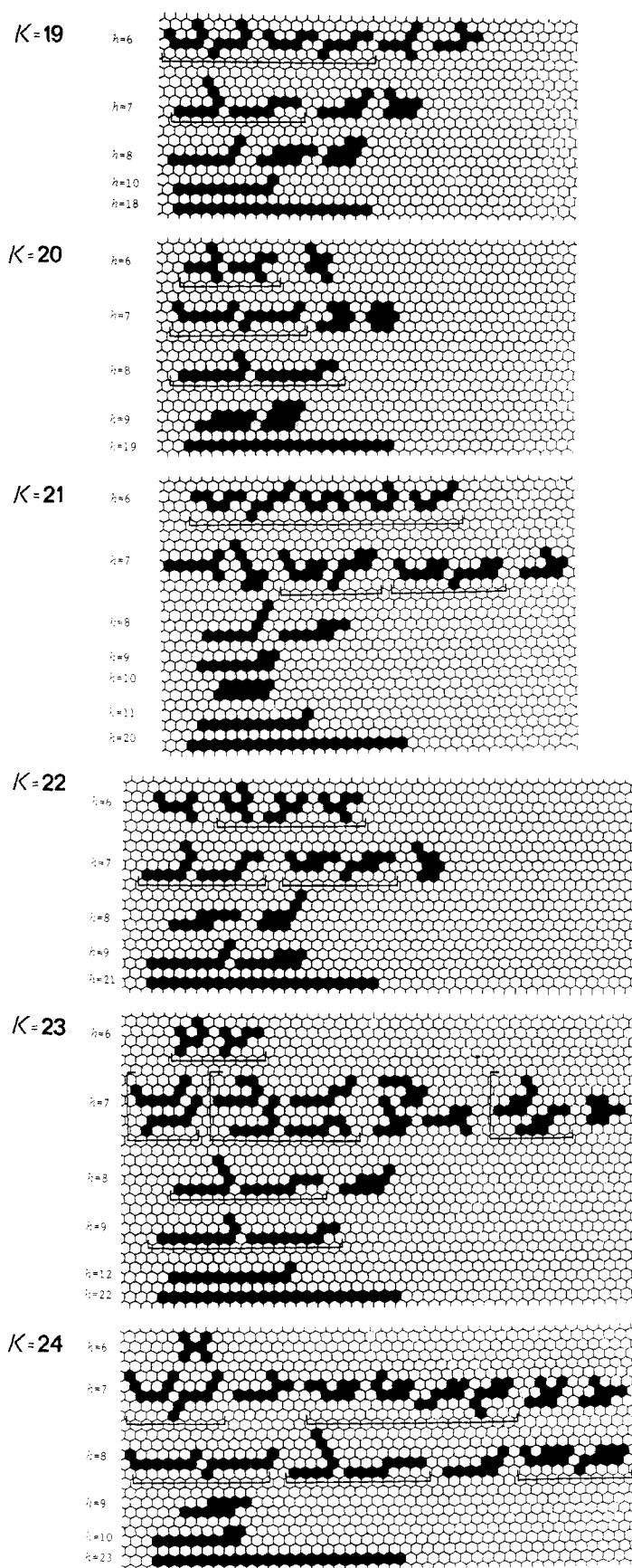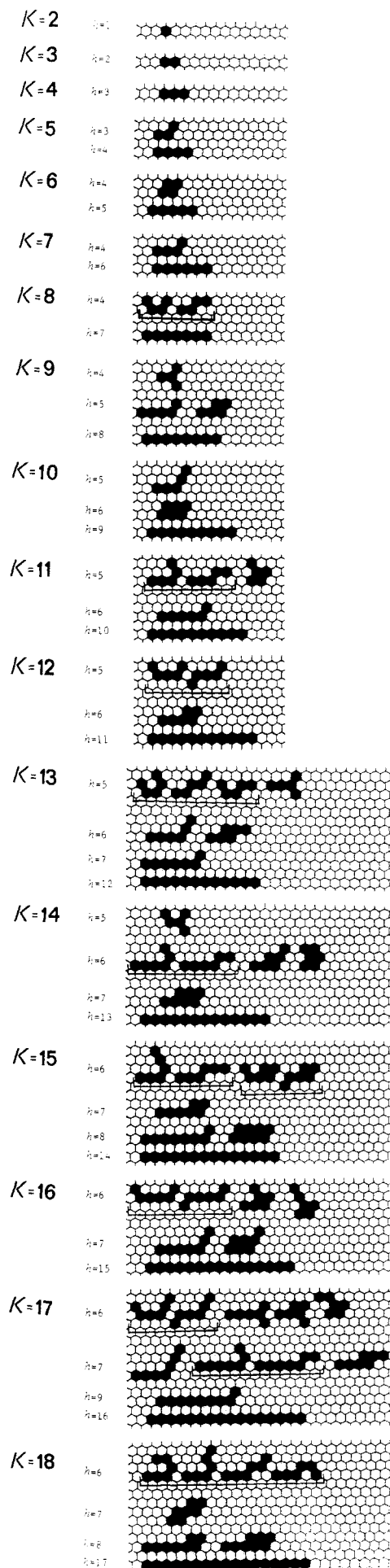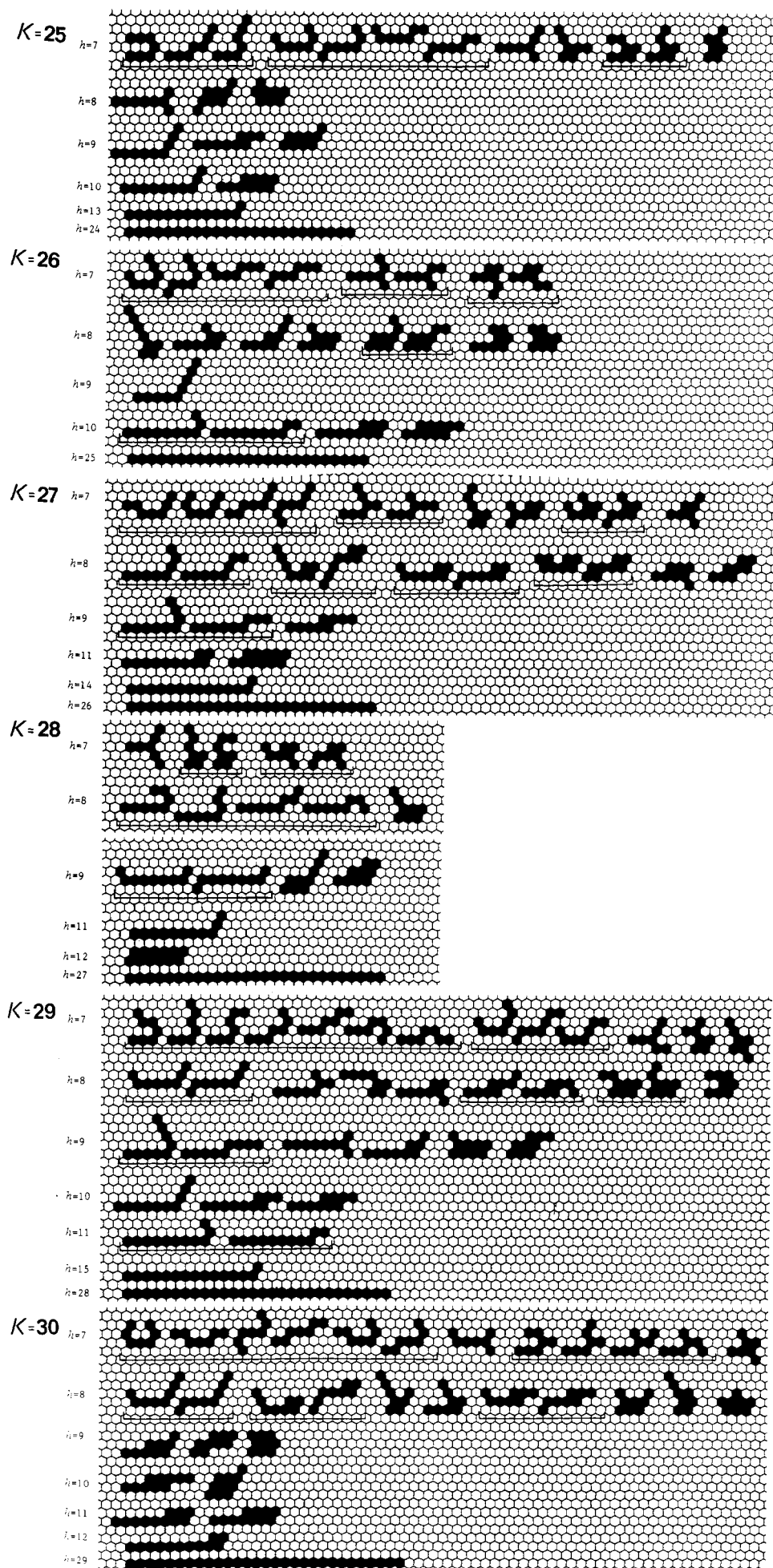
Figure 5. Forms of all normal benzenoids with $K \leq 30$.

$$K = h + 1$$

$$K = 2h - 1; \quad h \geq 2$$

$$K = 3h - 6; \quad h \geq 4$$

$$K = 3h - 5; \quad h \geq 3$$

$$K = 3h - 4; \quad h \geq 3$$

$$K = \frac{1}{8}(h+2)(h+4); \quad h = 4, 6, 8, \ldots$$

$$K = \frac{1}{8}(h+1)(h+7); \quad h = 5, 7, 9, \ldots$$
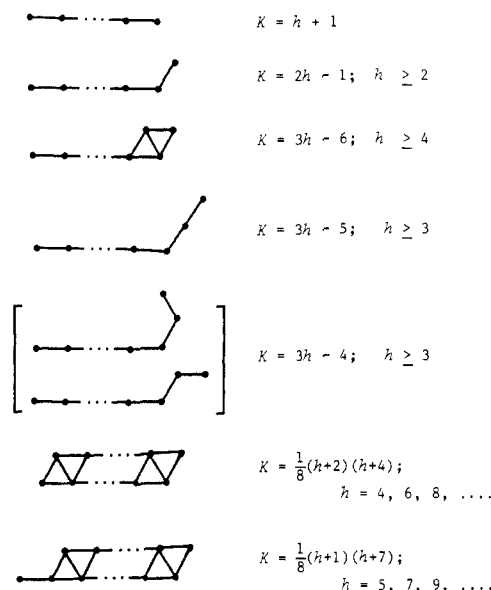
Figure 6. Classes of benzenoids with a single or double linear chain of hexagons. K formulas are given. Bracketed systems are isoarithmic.

The next step in the fading-out phenomenon manifests itself by three still less steep diagonals for every third K number. The pertinent forms of the benzenoids are found in Figure 6. In this case there are two distinct classes and one class of isoarithmic pairs. The first coefficient in the formula of the form $K = ah - b$ (see Figure 6) determines the steepness of the diagonal of numerals, in this case three parallel diagonals, two consisting of unities and one of the figures 2. The corresponding h values are $h = \frac{1}{3}(K + 6)$, $\frac{1}{3}(K + 5)$, and $\frac{1}{3}(K + 4)$, respectively. The pattern is completely regular for $K > 36$. At $K = 36$ the first "contamination" occurs inasmuch as a benzenoid not belonging to the considered classes shows up for $h = 14$. At this entry we have two forms instead of one. This part of the listing goes beyond Figure 5. We therefore specify the two forms below. Dualist graphs are invoked.

$$h = 14, \quad K = 36$$
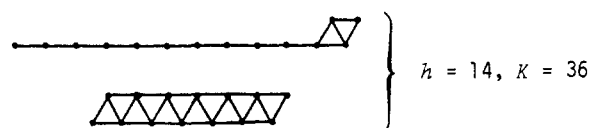
The next contamination occurs at the K value just before, viz., $K = 35$:

$$h = 13, \quad K = 35$$
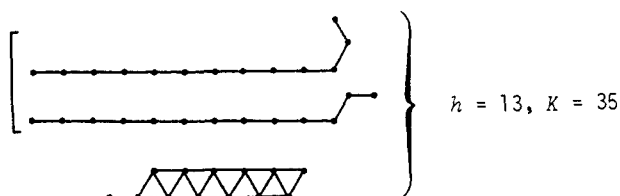
The first "serious contamination" is found at $K = 28$, where an alien form with $h = 12$ is present in addition to the standard member of the considered classes at $h = 11$. These forms are covered by Figure 5, but are also reproduced below (in terms of dualist graphs) for the sake of consistency.

$$h = 11, \quad K = 28$$

$$h = 12, \quad K = 28$$

$$K = \quad 39+6i \qquad 40+6i \qquad 41+6i$$

$$a_h = \frac{1}{3}(K+6)$$
$$b_h = \frac{1}{3}(K+5)$$
$$c_h = \frac{1}{3}(K+4)$$

$$h = \frac{1}{2}(K+1)$$

$$h = K-1$$

$$42+6i \qquad 43+6i \qquad 44+6i \ ; \quad i = 0, 1, 2, \ldots.$$

$$a_h = \frac{1}{3}(K+6)$$
$$b_h = \frac{1}{3}(K+5)$$
$$c_h = \frac{1}{3}(K+4)$$

$$h = \frac{1}{2}(K+1)$$

$$h = K-1$$
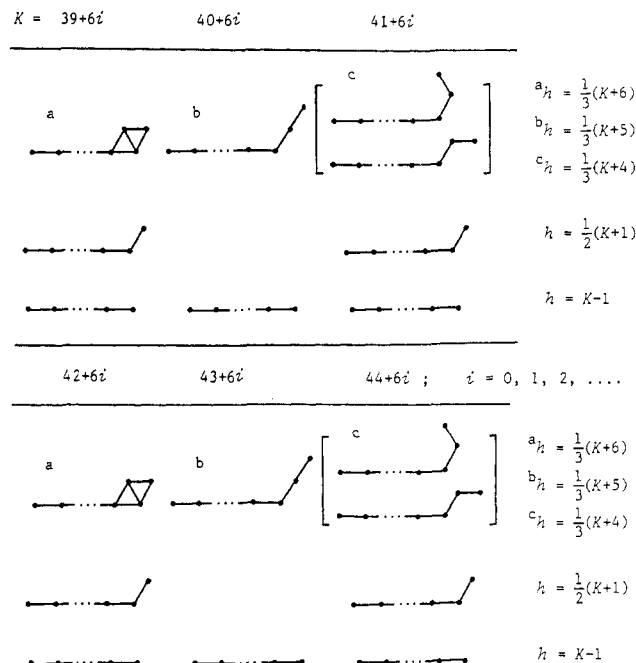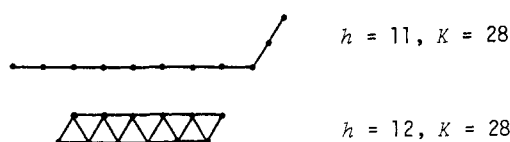
Figure 7. Illustration of the fading-out phenomenon.

$$K = 4h - 14; \quad h \geq 6$$

$$K = 4h - 11; \quad h \geq 4$$

$$K = 4h - 11; \quad h \geq 5$$

$$K = 4h - 9; \quad h \geq 4$$

$$K = 4h - 8; \quad h \geq 4$$

$$K = 4h - 7; \quad h \geq 3$$
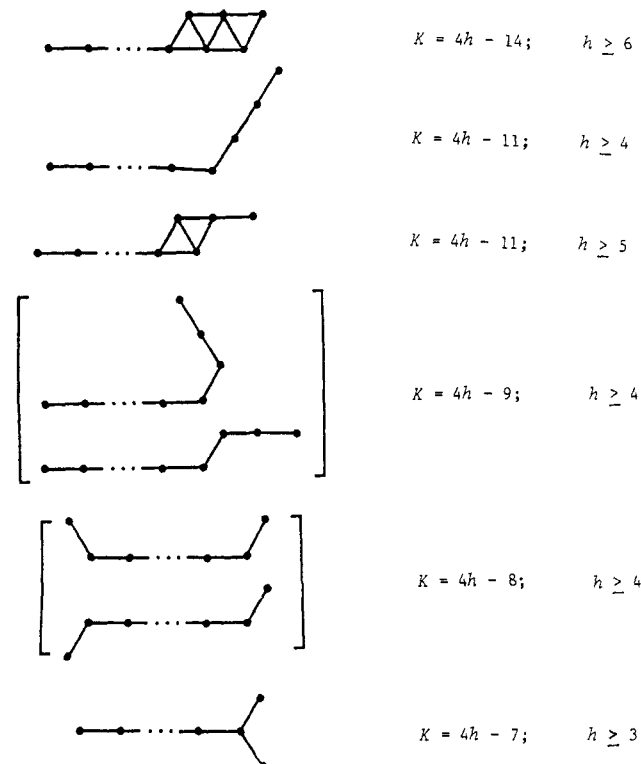
Figure 8. Classes of benzenoids with a single linear chain (see also Figure 6).

For the K value immediately before, we find again a duplication when $h = 11$:

$$h = 11, \quad K = 27$$
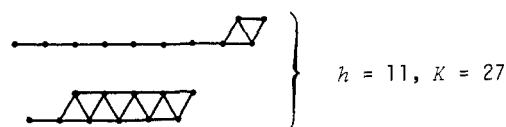
The contaminating forms discussed above may be attributed to two classes, which are included in Figure 6. In both cases the K formulas are polynomials of second degree in h, in contrast to the linear functions of the standard classes. Therefore, it is granted that no member of these two classes

DISTRIBUTION OF K

J. Chem. Inf. Comput. Sci., Vol. 29, No. 2, 1989 **87**

$K = 5h - 25;$ $h \geq 8$

$K = 5h - 21;$ $h \geq 7$

$K = 5h - 19;$ $h \geq 5$

$K = 5h - 18;$ $h \geq 6$

$K = 5h - 16;$ $h \geq 5$

$K = 5h - 16;$ $h \geq 5$

$K = 5h - 14;$ $h \geq 4$

$K = 5h - 14;$ $h \geq 5$

$K = 5h - 13;$ $h \geq 4$

$K = 5h - 12;$

$h \geq 4$
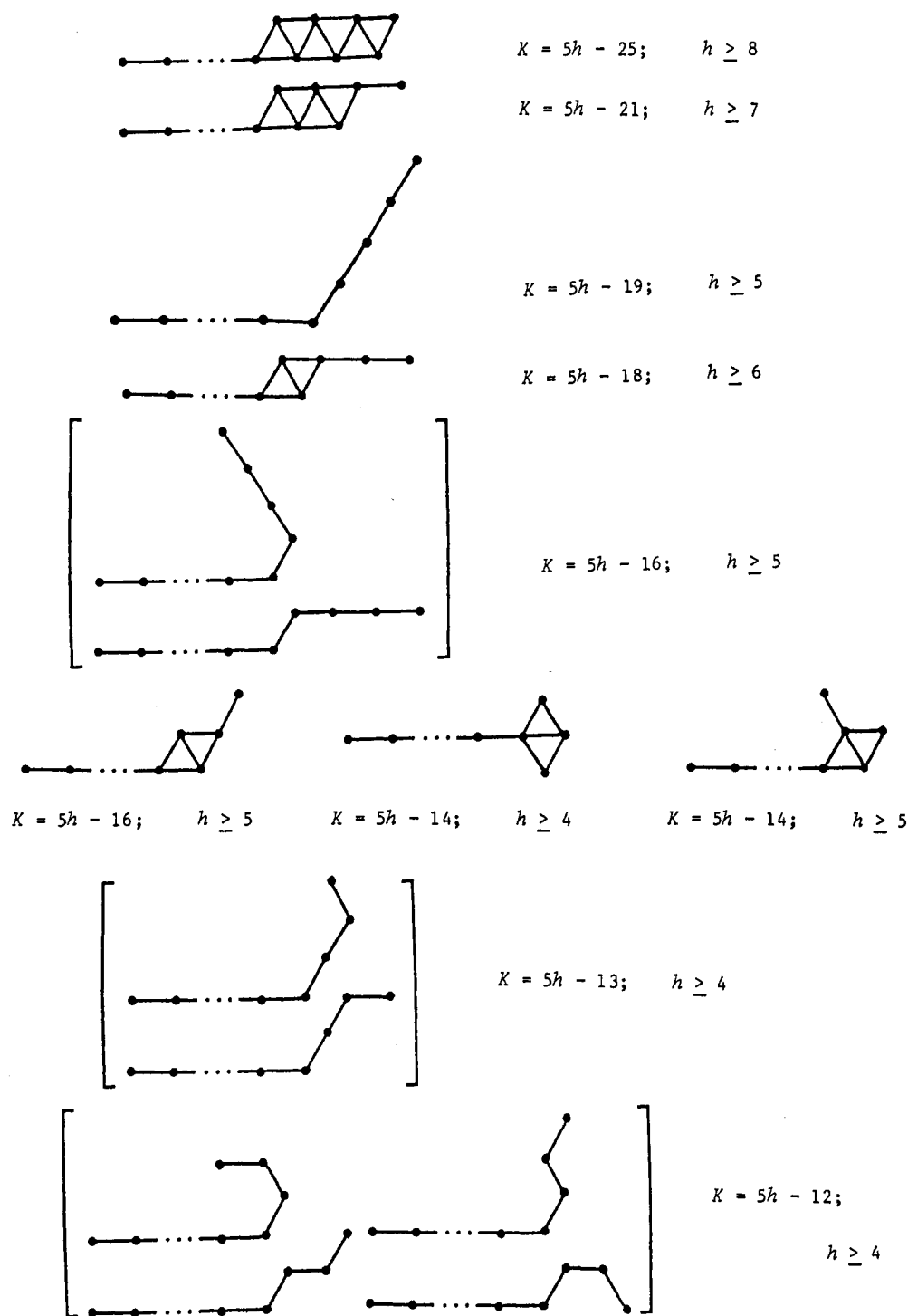
Figure 9. Classes of benzenoids with a single linear chain (see also Figures 6 and 8).

will cause any contamination with regard to the considered step of the fading-out phenomenon for higher K values, or precisely for $K > 36$.

We believe actually that the six standard classes (with linear dependencies between h and K) of Figure 6 cover all the forms of normal benzenoids for $K \geq 38$ and $h \geq {}^{1}/_{3}(K + 4)$. A more detailed account is given in Figure 7. According to the present analysis the figure takes into account all of the normal benzenoids with sufficiently high h values as indicated up to K = 110, which corresponds to $i = 11$. The sequence of $N(K)$ numbers, viz., 3, 2, 4, 2, 3, 2, repeats itself for every step in i. We believe with great confidence that this feature is sound for infinitely large i numbers.

Sequences of Numbers. The above description of the fading-out phenomenon implies a regular occurrence of sequences of numbers in Table III, viz., the numbers of normal benzenoids with given K values. These sequences (occasionally degenerating to one number) are attributed to classes of benzenoids that obey the formula for Kekulé structure counts

$$K = Ah - B$$

where A and B are constant integers.

(i) For the sequence {1} pertaining to $K = h + 1$, the unities appear on a diagonal:

$$\begin{matrix} 1 & \\ & 1 \end{matrix}$$

(ii) For the sequence {1} pertaining to $K = 2h - 1$, the unities appear on a less steep diagonal:

$$\begin{matrix} 1 & \\ & 1 \end{matrix}$$

Table III. Numbers of Normal Benzenoids with Given K Numbers at Different h Values

h	K=2	3	4	5	6	7	8	9	10
1	1								
2		1							
3			1	1					
4				1	1	1	2	1	
5					1	0	0	2	1
6						1	0	0	1
7							1	0	0
8								1	0
9									1
sum	1	1	1	2	2	2	3	4	3

h	K=11	12	13	14	15	16	17	18	19	20
5	3	2	4	1						
6	1	1	2	4	4	4	5	4	6	3
7	0	0	1	1	1	2	4	1	4	4
8	0	0	0	0	2	0	0	2	3	2
9	0	0	0	0	0	0	1	0	0	2
10	1	0	0	0	0	0	0	0	1	0
11		1	0	0	0	0	0	0	0	0
12			1	0	0	0	0	0	0	0
13				1	0	0	0	0	0	0
14					1	0	0	0	0	0
15						1	0	0	0	0
16							1	0	0	0
17								1	0	0
18									1	0
19										1
sum	5	4	8	7	8	7	11	8	15	12

h	K=21	22	23	24	25	26	27	28	29	30
6	5	4	2	1						
7	7	5	12	9	12	8	11	5	13	12
8	2	2	3	7	3	8	10	5	10	11
9	1	2	2	1	3	1	3	4	6	3
10	1	0	0	1	2	4	0	0	3	2
11	1	0	0	0	0	0	2	1	2	2
12	0	0	1	0	0	0	0	1	0	1
13	0	0	0	0	1	0	0	0	0	0
14	0	0	0	0	0	0	1	0	0	0
15	0	0	0	0	0	0	0	0	1	0
K − 1	1	1	1	1	1	1	1	1	1	1
sum	18	14	21	20	22	22	28	17	36	32

h	K=31	32	33	34	35	36	37	38	39	40
7	13	4	6	13	4	7	3	2	0	1
8	15	12	22	13	17	13	28	16	32	21
9	2	6	12	4	8	10	13	19	20	18
10	4	3	3	5	5	2	4	6	9	7
11	0	1	2	2	2	5	3	0	4	2
12	1	2	1	2	2	0	2	1	4	2
13	0	0	1	1	3	0	0	1	1	1
14	0	0	0	0	0	2	1	2	0	0
15	0	0	0	0	0	0	0	0	1	1
$\frac{1}{2}(K + 1)$	1		1		1		1		1	
K − 1	1	1	1	1	1	1	1	1	1	1
sum	37	29	49	41	43	40	56	48	73	54

h	K=41	42	43	44	45	46	47	48	49	50
7	1									
8	35	19	29	16	17	25	24	16	30	25
9	22	24	25	12	34	20	31	37	28	21
10	7	9	12	12	10	20	14	21	16	27
11	5	2	6	4	8	5	9	4	7	13
12	2	2	2	3	1	5	5	9	2	2
13	3	0	2	4	1	2	1	1	5	3
14	0	2	1	0	4	0	2	3	3	1
15	2	0	0	1	0	1	0	0	3	1
16	0	1	1	2	1	0	0	0	0	1
17	0	0	0	0	1	1	2	0	0	0
18	0	0	0	0	0	0	0	1	1	2
$\frac{1}{2}(K + 1)$	1		1		1		1		1	
K − 1	1	1	1	1	1	1	1	1	1	1
sum	79	60	80	55	79	80	90	93	97	97

h	K=51	52	53	54	55	56	57	58	59	60
8	16	14	15	15	19	9	10	14	10	11
9	58	36	53	37	35	30	76	50	59	61
10	33	19	32	31	25	27	45	27	38	29
11	8	7	9	25	14	15	20	20	31	23
12	7	2	7	3	11	6	6	7	8	13
13	3	4	7	2	4	1	4	2	4	3
14	1	1	1	5	2	2	5	6	3	1
15	4	2	1	1	1	3	2	0	3	2
16	0	1	3	0	3	3	2	0	2	1
17	0	0	0	2	0	0	2	0	2	4
18	0	0	0	0	1	0	0	1	0	0
19	1	1	2	0	0	0	0	0	0	0
20	0	0	0	1	1	2	0	0	0	0
21	0	0	0	0	0	0	1	1	2	0
22	0	0	0	0	0	0	0	0	0	1
$\frac{1}{2}(K + 1)$	1		1		1		1		1	
K − 1	1	1	1	1	1	1	1	1	1	1
sum	133	88	132	123	118	99	175	129	164	150

h	K=61	62	63	64	65	66	67	68	69	70
8	4	5	0	3	1	1				
9	69	61	51	65	44	69	63	48	75	38
10	48	48	69	48	57	61	63	58	95	48
11	27	30	25	14	28	37	41	28	49	32
12	12	15	10	9	19	27	16	17	26	34
13	11	4	2	7	9	5	8	8	11	11
14	1	4	8	1	7	5	0	6	2	5
15	3	3	5	5	3	1	1	1	8	0
16	1	3	0	3	1	4	4	4	2	3
17	1	1	2	1	0	1	2	1	5	0
18	2	0	3	3	2	0	0	1	2	1
19	0	1	0	0	3	0	2	2	1	1
20	0	0	0	0	0	2	0	0	2	0
21	0	0	0	0	0	0	0	0	0	1
22	1	2	0	0	0	0	0	0	0	0
23	0	0	1	1	2	0	0	0	0	0
24	0	0	0	0	0	1	1	2	0	0
25	0	0	0	0	0	0	0	0	1	0
$\frac{1}{2}(K + 1)$	1		1		1		1		1	
K − 1	1	1	1	1	1	1	1	1	1	1
sum	182	178	178	161	178	215	203	177	281	176

h	K=71	72	73	74	75	76	77	78	79	80
9	73	37	62	51	35	52	25	49	72	45
10	68	102	97	73	130	74	78	118	110	62
11	50	45	55	53	66	37	44	82	55	53
12	21	21	22	34	35	26	30	25	32	41
13	7	10	9	16	25	15	23	28	22	23
14	2	8	6	9	11	6	4	8	10	7
15	7	1	5	3	4	1	2	4	6	8
16	5	0	1	3	5	2	6	1	9	7
17	2	3	6	2	2	1	2	3	0	2
18	2	2	0	4	1	3	2	6	3	0
19	0	1	0	2	1	2	2	0	3	2
20	2	2	1	0	2	1	0	0	1	0
21	0	0	2	0	2	2	2	0	0	1

h	K=81	82	83	84	85	86	87	88	89	90
9	36	65	32	37	25	40	33	27	45	23
10	142	84	134	119	105	87	191	96	133	130
11	79	79	74	62	84	94	124	96	102	151
12	56	27	44	46	55	43	68	42	56	72
13	16	20	24	27	27	33	30	16	36	34
14	13	9	16	13	21	22	20	15	14	27
15	5	6	5	4	4	6	7	4	12	16
16	0	3	0	0	3	5	4	8	4	3
17	7	2	7	1	6	3	3	0	5	0
18	3	1	2	3	3	2	4	1	6	4
19	2	3	6	2	1	0	2	2	4	0
20	3	1	0	6	1	3	2	4	2	2
21	0	0	0	1	1	1	3	0	3	1

Table III (Continued)

h	71	72	73	74	75	76	77	78	79	80
22	0	0	0	1	0	0	2	1	2	2
23	0	0	0	0	0	0	0	1	0	0
24	0	0	0	0	0	0	0	0	0	0
25	2	0	0	0	0	0	0	0	0	0
26	0	1	1	2	0	0	0	0	0	0
27	0	0	0	0	1	1	2	0	0	0
28	0	0	0	0	0	0	0	1	1	2
$\frac{1}{2}(K+1)$	1		1		1		1		1	
$K-1$	1	1	1	1	1	1	1	1	1	1
sum	243	234	269	254	322	224	226	328	328	256

h	81	82	83	84	85	86	87	88	89	90
22	1	0	0	0	1	0	0	1	2	0
23	2	0	2	2	1	0	0	0	0	2
24	0	1	0	0	2	0	2	2	1	0
25	0	0	0	0	0	1	0	0	2	0
26	0	0	0	0	0	0	0	0	0	1
27	0	0	0	0	0	0	0	0	0	0
28	0	0	0	0	0	0	0	0	0	0
29	1	1	2	0	0	0	0	0	0	0
30	0	0	0	1	1	2	0	0	0	0
31	0	0	0	0	0	0	1	1	2	0
32	0	0	0	0	0	0	0	0	0	1
$\frac{1}{2}(K+1)$	1		1		1		1		1	
$K-1$	1	1	1	1	1	1	1	1	1	1
sum	368	303	350	324	343	343	496	316	431	468

h	91	92	93	94	95	96	97	98	99	100
9	9	35	11	28	20	16	15	13	5	15
10	121	119	185	116	129	184	178	113	146	107
11	89	94	173	160	103	138	150	118	168	136
12	43	45	80	67	72	80	81	77	116	73
13	28	26	46	36	55	47	41	32	41	48
14	11	14	29	19	26	22	23	36	27	27
15	13	6	17	19	15	18	14	15	17	11
16	6	2	2	8	8	9	7	5	15	8
17	0	2	4	4	4	8	5	1	1	3
18	6	2	3	1	2	3	1	3	6	4
19	0	3	5	1	6	0	8	4	0	4
20	2	1	2	1	3	1	2	1	7	1
21	3	4	4	2	0	2	2	1	2	1
22	1	1	1	3	1	2	2	7	3	1
23	0	0	0	1	0	1	1	0	5	0
24	1	0	0	0	1	0	0	0	1	0
25	2	2	1	0	0	0	0	0	0	1
26	0	0	2	0	2	2	1	0	0	0
27	0	0	0	1	0	0	2	0	2	2
28	0	0	0	0	0	0	0	1	0	0
29	0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0	0
31	0	0	0	0	0	0	0	0	0	0
32	1	2	0	0	0	0	0	0	0	0
33	0	0	1	1	2	0	0	0	0	0
34	0	0	0	0	0	1	1	2	0	0
35	0	0	0	0	0	0	0	0	1	1
$\frac{1}{2}(K+1)$	1		1		1		1		1	
$K-1$	1	1	1	1	1	1	1	1	1	1
sum	338	359	568	469	451	535	536	430	565	444

h	101	102	103	104	105	106	107	108	109	110
9	4	8	0	3	6	3	1	0	0	1
10	166	166	140	114	166	160	135	142	171	101
11	139	211	168	142	217	180	208	227	206	198
12	81	115	84	89	124	118	95	131	114	135
13	61	55	58	44	57	61	60	47	85	64
14	29	32	38	23	39	25	45	54	20	44
15	15	17	21	18	20	14	20	16	22	31
16	13	16	11	15	19	21	10	8	8	9
17	3	6	3	5	14	6	9	10	12	12
18	3	4	4	4	0	2	2	0	3	9
19	2	1	4	1	1	2	7	3	7	4
20	4	3	5	4	2	2	2	0	2	3
21	2	2	0	2	6	2	4	0	7	3
22	0	1	1	2	1	1	5	1	1	1
23	3	2	4	2	2	0	0	3	2	0
24	1	2	1	3	1	2	2	4	1	2
25	0	0	0	2	0	1	1	0	3	0
26	0	0	0	0	1	0	0	0	1	0
27	1	0	0	0	0	0	0	0	0	1
28	2	0	2	2	1	0	0	0	0	0
29	0	1	0	0	2	0	2	2	1	0
30	0	0	0	0	0	1	0	0	2	0
31	0	0	0	0	0	0	0	0	0	1
32	0	0	0	0	0	0	0	0	0	0
33	0	0	0	0	0	0	0	0	0	0
34	0	0	0	0	0	0	0	0	0	0
35	2	0	0	0	0	0	0	0	0	0
36	0	1	1	2	0	0	0	0	0	0
37	0	0	0	0	1	1	2	0	0	0
38	0	0	0	0	0	0	0	1	1	2
$\frac{1}{2}(K+1)$	1		1		1		1		1	
$K-1$	1	1	1	1	1	1	1	1	1	1
sum	533	644	547	478	682	603	612	650	671	622

(iii) For the sequence {1, 1, 2} corresponding to $K = 3h - B$, where $B = 6, 5, 4$, and 4 (see Figure 6), the steepness of the pertinent diagonals is given by

$$\begin{matrix} 1 & 1 & 2 & . & . & . \\ & 1 & 1 & 2 \end{matrix}$$

(iv) A new sequence is recognized, viz.

$$\{1, 0, 0, 2, 0, 2, 2, 1\}$$

that corresponds to $K = 4h - B$, where $B = 14, 11, 11, 9, 9, 8, 8$, and 7. The forms of the benzenoids governed by this formula are shown (as dualist graphs) in Figure 8. For two consecutive h values the sequence is shifted (four units):

$$\begin{matrix} 1 & 0 & 0 & 2 & 0 & 2 & 2 & 1 & . & . & . & . \\ & 1 & 0 & 0 & 2 & 0 & 2 & 2 & 1 \end{matrix}$$

The last contamination in this sequence was found for $h = 22$.
(v) Another sequence is identified as

$$\{1, 0, 0, 0, 1, 0, 1, 1, 0, 3, 0, 2, 2, 4\}$$

It corresponds to $K = 5h - B$, where the constants B are specified in the formulas of Figure 9, which gives the pertinent benzenoid forms. Two sequences for consecutive h values are shifted by five units. Table III (for $K \leq 110$) does not go far enough to exhibit this sequence without contamination. The last complete set of numbers occurs at $h = 24$ and reads

$$1\ 0\ 0\ 0\ 1\ 0\ \underline{1}\ \underline{2}\ 1\ \underline{3}\ \underline{1}\ 2\ 2\ 4$$

This set contains three contaminations, as indicated by the underlined figures.

Number of Normal Benzenoids as a Function of K. Let $N(K)$ denote the title quantity (as in Figure 10). The $N(K)$ numbers for $K = 2\text{–}110$ are found in Table III. In Figure 10 they are presented graphically.

The observation was made that, loosely speaking, systems with odd numbers of Kekulé structures are more abundant than those with even numbers of Kekulé structures. This feature is especially pronounced in the region $8 < K < 64$. In
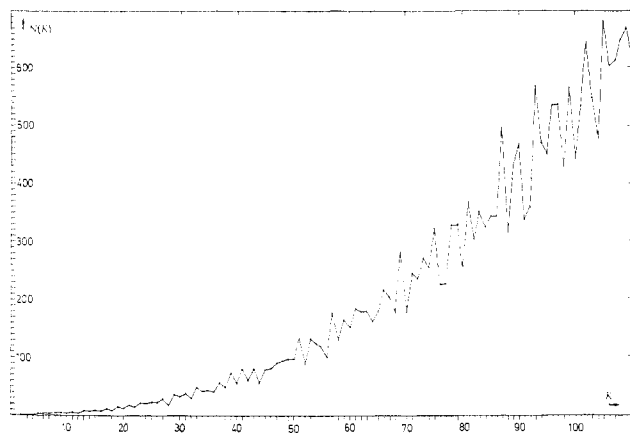
90 *J. Chem. Inf. Comput. Sci., Vol. 29, No. 2, 1989*

CYVIN ET AL.

Figure 10. Number of normal benzenoids as a function of the Kekulé structure count.

most cases $N(2p) < N(2p - 1)$ and $N(2p) < N(2p + 1)$, but there are exceptions. One finds $N(26) = N(25)$, $N(46) = 1 + N(45)$, $N(50) = N(49)$, and $N(62) = N(63)$, but these small discrepancies do not violate the general observation as we shall put it in precise terms in the following.

Suppose a red curve of linear segments is drawn through the points of $N(K)$ when K is odd and a blue curve is drawn when K is even. Then the red curve is situated above the blue curve in the whole region of $8 < K < 64$. (The blue curve is slightly above the red curve at $6 < K < 8$.)

It is interesting to study this trend for K values above 64. The first substantially "anomalous" feature occurs when $N(66) > N(65)$ as well as when $N(66) > N(67)$. This violation of the trend causes the red and blue curves to cross, so that the blue one is highest in a region around $K = 66$. More of such regions are observed up to $K = 110$, situated at shorter and shorter intervals. Actually the blue curve rises above the red one at $K = 7, 66, 78, 90, 96, 102$, and 108. The material available at present does not allow us to suggest an extrapolation of the curve. As a whole the main observation is still valid for $K < 110$, but a more general conclusion cannot be drawn.

ACKNOWLEDGMENT

REFERENCES AND NOTES

(1) Klarner, D. A. *Fibonacci Q.* **1965**, *3*, 9.
(2) Harary, F. *Graph Theory and Theoretical Physics*; Harary, F., Ed.; Academic Press: London, 1967; Chapter 1.
(3) Balaban, A. T.; Harary, F. *Tetrahedron* **1968**, *24*, 2505.
(4) Balaban, A. T. *Tetrahedron* **1969**, *25*, 2949.
(5) Harary, F.; Read, R. C. *Proc. Edinburgh Math. Soc.* **1970**, *17*(II), 1.
(6) Balaban, A. T. *Rev. Roum. Chim.* **1970**, *15*, 1251.
(7) Lunnon, W. F. *Graph Theory and Computing*; Read, R. C., Ed.; Academic Press: New York, 1972; p 87.
(8) Harary, F.; Harborth, H. *J. Comb. Inf. Syst. Sci.* **1976**, *1*, 1.
(9) Balaban, A. T. *MATCH* **1976**, *2*, 51.
(10) Balasubramanian, K.; Kaufman, J. J.; Koski, W. S.; Balaban, A. T. *J. Comput. Chem.* **1980**, *1*, 149.
(11) Knop, J. V.; Szymanski, K.; Jeričević, Ž.; Trinajstić, N. *J. Comput. Chem.* **1983**, *4*, 23.
(12) Trinajstić, N.; Jeričević, Ž.; Knop, J. V.; Müller, W. R.; Szymanski, K. *Pure Appl. Chem.* **1983**, *55*, 379.
(13) Knop, J. V.; Szymanski, K.; Jeričević, Ž.; Trinajstić, N. *MATCH* **1984**, *16*, 119.
(14) Knop, J. V.; Müller, W. R.; Szymanski, K.; Trinajstić, N. *Computer Generation of Certain Classes of Molecules*; Association of Chemists and Technologists of Croatia: Zagreb, 1985.
(15) Balaban, A. T.; Brunvoll, J.; Cioslowski, J.; Cyvin, B. N.; Cyvin, S. J.; Gutman, I.; He, W. C.; He, W. J.; Knop, J. V.; Kovačević, M.; Müller, W. R.; Szymanski, K.; Tošić, R.; Trinajstić, N. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1987**, *42A*, 863.
(16) He, W. C.; He, W. J. *Theor. Chim. Acta* **1985**, *68*, 301.
(17) Hellwinkel, D. *Chem.-Ztg., Chem. Appar.* **1970**, *94*, 715.
(18) Elk, J. B. *MATCH* **1980**, *8*, 121.
(19) Elk, J. B. *MATCH* **1982**, *13*, 239.
(20) Bonchev, D.; Balaban, A. T.; Mekenyan, O. *J. Chem. Inf. Comput. Sci.* **1980**, *20*, 106.
(21) Bonchev, D.; Balaban, A. T. *J. Chem. Inf. Comput. Sci.* **1981**, *21*, 223.
(22) Bonchev, D. *Pure Appl. Chem.* **1983**, *55*, 221.
(23) Bonchev, D.; Mekenyan, O.; Balaban, A. T. *Mathematical and Computational Concepts in Chemistry*; Trinajstić, N., Ed.; Ellis Horwood: Chichester, U.K., 1986; p 34.
(24) Cioslowski, J.; Turek, A. M. *Tetrahedron* **1984**, *40*, 2161.
(25) Cioslowski, J.; Turek, A. M. *Comput. Chem.* **1985**, *9*, 247.
(26) Dias, J. R. *J. Chem. Inf. Comput. Sci.* **1982**, *22*, 15.
(27) Dias, J. R. *J. Chem. Inf. Comput. Sci.* **1982**, *22*, 139.
(28) Dias, J. R. *MATCH* **1983**, *14*, 83.
(29) Dias, J. R. *Can. J. Chem.* **1984**, *62*, 2914.
(30) Dias, J. R. *J. Chem. Inf. Comput. Sci.* **1984**, *24*, 124.
(31) Dias, J. R. *Acc. Chem. Res.* **1985**, *18*, 241.
(32) Dias, J. R. *J. Macromol. Sci., Chem.* **1985**, *A22*, 335.
(33) Dias, J. R. *Nouv. J. Chim.* **1985**, *9*, 125.
(34) Dias, J. R. *J. Mol. Struct.* **1986**, *137*, 9.
(35) Herndon, W. C. *J. Chem. Educ.* **1974**, *51*, 10.
(36) Gutman, I. *Bull. Soc. Chim. Beograd* **1982**, *47*, 453.
(37) Trinajstić, N. *Chemical Graph Theory*; CRC Press: Boca Raton, FL, 1983; Vol. I, II.
(38) Cyvin, S. J. *MATCH* **1986**, *20*, 165.
(39) Cyvin, S. J.; Gutman, I. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1986**, *41A*, 1079.
(40) Brunvoll, J.; Cyvin, S. J.; Cyvin, B. N. *J. Comput. Chem.* **1987**, *8*, 189.
(41) Gutman, I. *Croat. Chem. Acta* **1983**, *56*, 365.
(42) Gutman, I. *MATCH* **1982**, *13*, 173.
(43) Cyvin, S. J.; Cyvin, B. N.; Gutman, I. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1985**, *40A*, 1253.
(44) Gutman, I. *Croat. Chem. Acta* **1982**, *55*, 371.
(45) Cyvin, S. J.; Gutman, I. *J. Serb. Chem. Soc.* **1985**, *50*, 443.
(46) Brunvoll, J.; Cyvin, B. N.; Cyvin, S. J. *J. Chem. Inf. Comput. Sci.* **1987**, *27*, 14.
(47) Gutman, I. *Croat. Chem. Acta* **1974**, *46*, 209.
(48) Brunvoll, J.; Cyvin, B. N.; Cyvin, S. J.; Gutman, I. *MATCH* **1988**, *23*, 209.
(49) One apparent controversy should be explained. The grand total for *h* = 6 is 81 according to our definition. When hexahelicene is added, it becomes 82.[2,3,7] Lunnon[7] makes a point of having corrected the number 83 reported by Klarner[1] and the same by Read (see the bibliography of Lunnon[7]). Knop et al.[13] have not adopted this view, but quoted Klarner's number 83 in support of their grand total including helicenes and circulenes (coronoids). The explanation is that Knop et al.[13] (and Klarner[1]) have included coronene as a circulene among the *h* = 6 systems. When the listing is continued to *h* = 7, this feature may be confusing because coronene also is counted as a pericondensed benzenoid under *h* = 7. The dualist graphs of [6]circulene and coronene are indeed different, but the graphs by hexagons are not, and also the corresponding hydrocarbons are chemically indistinguishable. As a minor detail, the numbers 210 and 1002 in Table 2 of ref 4 are meaningless.
(50) Dias, J. R. *Handbook of Polycyclic Hydrocarbons. Part A, Benzenoid Hydrocarbons*; Elsevier: Amsterdam, 1987.
(51) Cyvin, S. J.; Gutman, I. *Kekulé Structures in Benzenoid Hydrocarbons*; Lecture Notes in Chemistry 46; Springer-Verlag: Berlin, 1988.
(52) Gutman, I.; Cyvin, S. J. Unpublished data.
(53) Chen, R. S.; Cyvin, S. J. *MATCH* **1987**, *22*, 175.
(54) Randić, M. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 232.
(55) Balaban, A. T.; Tomescu, I. *MATCH* **1983**, *14*, 155.
(56) Brown, R. L. *J. Comput. Chem.* **1983**, *4*, 556.