Number of Kekulé Structures as a Function of the Number of Hexagons in Benzenoid Hydrocarbons

S. J. Cyvin
Division of Physical Chemistry, The University of Trondheim, Norway

I. Gutman
Faculty of Science, University of Kragujevac, Yugoslavia *

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The possible values of the number of Kekulé structures (K) of a benzenoid hydrocarbon with h hexagons are examined. For normal benzenoids the lowest possible value of K is $h+1$. Based on this result the benzenoid systems which have K up to 24 are determined. A number of results concerning enumeration and classification of benzenoid systems is reported.

Introduction

The enumeration of Kekulé structures has fascinated several researchers since the first systematic studies of benzenoids in terms of graph theory [1–9]. Apart from the recognized importance of Kekulé structures in organic and physical chemistry they also have purely mathematical interest. Reference is made to a recent article in the present journal [10] along with the bibliography therein. A considerable number of newly published papers on the enumeration of Kekulé structures [11–31] shows that the interest in this topic has increased substantially during the last few years.

In the present work the term benzenoid is applied in consistence with the definition of the review [32] and the book [33]. The problem of the determination of all benzenoid hydrocarbons with K Kekulé structures, $0 < K < 9$ was posed several times (see e.g. [34, 35]). It has been conjectured that this number is finite [35] and that only one benzenoid has $K = 3$ (naphthalene), one has $K = 4$ (anthracene) and two have $K = 5$ (tetracene and phenanthrene) [35]. In [35] it was demonstrated that $K = 2$ is obeyed only for the benzene graph.

It is known for a long time that there are infinitely many benzenoid systems with nine Kekulé structures. The case $K = 9$ refers to essentially disconnected benzenoids [10], where two naphthalene units (with three Kekulé structures each) behave independently and may be connected by arbitrarily large junctions of hexagons with fixed bonds [17].

In the present paper we show that the above mentioned conjectures are correct and determine all benzenoid systems with 2, 3, 4, 5, 6, 7 and 8 Kekulé structures. In addition to this we determine all normal benzenoids (i.e. those without fixed double or single bonds) for which $0 < K \leqq 24$.

Building-up Process

A successive generation of the benzenoids with increasing number of hexagons is an essential part of the present approach. Figure 1 shows the well-known [3, 32, 33] benzenoids with h (number of hexagons) equal to 1, 2 and 3 in the top row. In order to demonstrate the building-up process the $h = 4$ Kekuléan benzenoids [3] are placed in a column in the order of increasing K (number of Kekulé structures). Kekuléan (in contrast to non-Kekuléan) benzenoids possess Kekulé structures ($K > 0$). Framed structures are isoarithmic [36]; they only differ in the way their kinks go, which does not affect the number of Kekulé structures [1, 36]. The six existing Kekuléan benzenoids of $h = 4$ give rise to 14 Kekuléans of $h = 5$ as shown in Figure 1. One hexagon is added every time to generate a $h = 5$ Kekuléan structure. It is put down only if not already generated during the successive process. The K numbers are indicated on the figure. For the five-hexagon benzenoids they are written into the hexagons which have been added.

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* P.O. Box 60, YU-34000 Kragujevac.

Reprint requests to Prof. Dr. S. J. Cyvin, Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norwegen.

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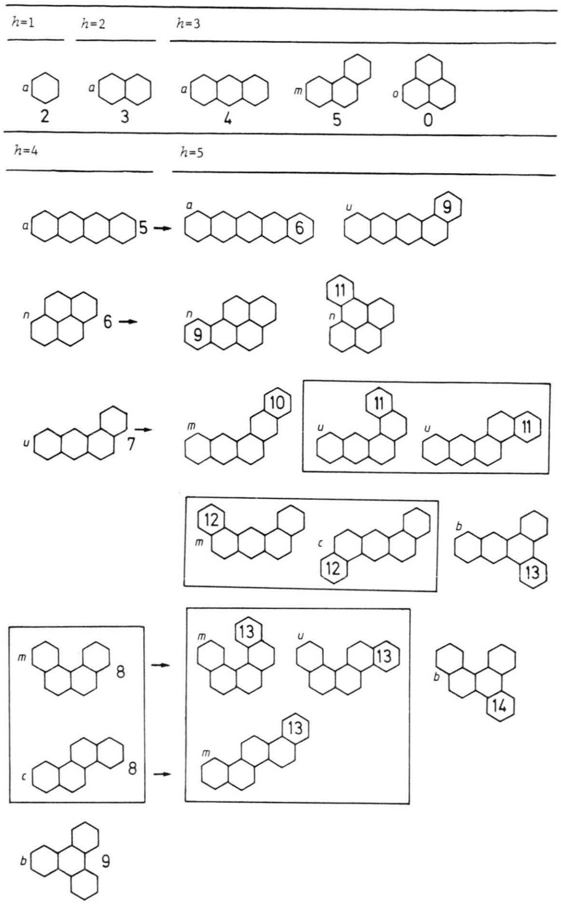


Fig. 1. Benzenoids with 1 through 5 hexagons. Numbers of Kekulé structures are indicated.

Classification

The benzenoids are classified by a slightly modified system from Balaban and Harary [3], viz:

Catacondensed

- **a** acene (linear);
- **m** mirror-symmetrical (unbranched);
- **c** centrosymmetrical (unbranched);
- **u** unsymmetrical (unbranched);
- **b** branched.

Pericondensed

- **n** normal Kekuléan (without fixed bonds);
- **e** Kekuléan with fixed bonds (essentially disconnected);
- **o** non-Kekuléan.

Normal benzenoid. By "normal" benzenoids we will refer to the (Kekuléan) catacondensed benzenoids and the normal pericondensed.

Discussion of the Building-up Process

It is evident that all benzenoids with h hexagons for $h > 1$ can be generated by adding one hexagon each to the benzenoids with $h - 1$ hexagons. Here we assume a stronger property.

Conjecture **A**. All normal benzenoids with h hexagons ($h > 1$) can be generated from the normal benzenoids with $h - 1$ hexagons.

By Fig. 1 this conjecture is empirically verified for h going from 4 to 5. It was also verified in the same way for $h = 5 \rightarrow 6$. All benzenoids with $h = 6$ are treated in a subsequent section.

Could it be that a normal benzenoid may elude the building-up process? It does not seem likely because of the plausibility of the following statement, from which **A** follows.

Conjecture **B**. From an arbitrary normal benzenoid with h hexagons ($h > 1$) one hexagon may be removed to yield another normal benzenoid with $h - 1$ hexagons.

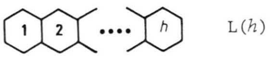
On the other hand the building-up process has an "intrinsic security". It means that an omission during the process often will be repaired automatically because many of the benzenoids may be generated in different ways. Suppose, for instance, that the two branched (**b**) five-hexagon benzenoids of Fig. 1 are omitted by mistake. Then there is a new chance to generate these benzenoids from the **b** four-hexagon structure. By a correct application of the method (as illustrated) the last benzenoid does not give any new structures.

Two Theorems

In [34] it was proved that

$$K \geqq h + 1 \tag{1}$$

for all catacondensed benzenoids. The lower limit of K is realized for linear acenes $L(h)$:



Thus one may write

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

Table 1. Numbers of normal benzenoids: distribution of K*.

K	1	2	3	4	5	6	7	8	9	10	11	12	13	Total
	Number of hexagons (h)													
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
9				1	2	0	0	1						4^+
10					1	1	0	0	1					3
11					3	1	0	0	0	1				5
12					2	1	0	0	0	0	1			4^+
13					4	2	1	0	0	0	0	1		8
14					1	4	1	0	0	0	0	0	1	7

K	6	7	8	9	10	11	12	13	14.........23	Total
	Number of hexagons (h)									
15	4	1	2	0	0	0	0	0	1	8^+
16	4	2	0	0	0	0	0	0	. 1	7^+
17	5	4	0	1	0	0	0	0	. . 1	11
18	4	1	2	0	0	0	0	0	. . . 1	8^+
19	6	4	3	0	1	0	0	0	 1	15
20	3	4	2	2	0	0	0	0	 1	12^+
21	5	7	2	1	1	1	0	0	 1	18^+
22	4	5	2	2	0	0	0	0	 1	14
23	2	12	3	2	0	0	1	0	 1	21
24	1	9	7	1	1	0	0	0	 1	20^+

* Dots and not entered numerals signify zeros.
$^+$ Not counting essentially disconnected benzenoids.

It can be shown that the above results hold for all normal benzenoids. We summarize this in the following theorem whose proof (which is quite lengthy) will be reported elsewhere [37].

Theorem 1. A normal benzenoid with h hexagons has at least $h+1$ Kekulé structures. $L(h)$ is the unique benzenoid with h hexagons for which $K = h + 1$.

Corrolary. Let $h_{\max}(K)$ be the maximum value of h which can occur at a given number of K. Then,

$$h_{\max}(K) = K - 1 \,. \tag{3}$$

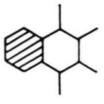
Table 1 includes the complete distributions of K numbers at $h \leqq 6$. The benzenoids up to $h = 5$ are presented in Fig. 1; for $h = 6$ see below. Theorem 1 and its corrolary are manifested in the table in the way that a diagonal of numerals 1 forms an absolute boarder; there are no non-vanishing numbers above it.

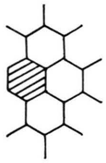
Theorem 2. Let B and B′ be two normal benzenoids where B′ is generated from B by adding to it one hexagon. Then

$$K\{B'\} > K\{B\} \,. \tag{4}$$

In other words, the addition of a hexagon when only normal (Kekuléan) benzenoids are involved strictly increases the number of Kekulé structures.

Proof. There are exactly three modes in which a new hexagon can be added to B, so as to form a normal benzenoid. These modes are denoted **L, C** and **F**:

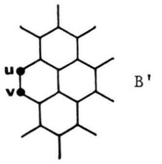

L-mode


C-mode


F-mode

We prove Theorem 2 only for the case of a **C**-mode addition. The proofs for the **L**- and the **F**-mode additions are fully analogous.

Let **u** and **v** be the newly added vertices in B′:



Denote by K_- and $K_=$ the number of Kekulé structures of B′ in which the bond between **u** and **v** is single and double, respectively. Of course, $K\{B'\} = K_- + K_=$. It is also clear that $K_= = K\{B\}$. Hence

$$K\{B'\} = K\{B\} + K_- \,. \tag{5}$$

Since B′ is supposed to be normal, it must have at least one Kekulé structure in which the bond between **u** and **v** is single, i.e. $K_- > 0$. Theorem 2 follows now by taking into account the identity (5).

Notes on the Benzenoids with $h \leqq 6$

Table 2 gives a survey of the numbers of existing benzenoids with $h = 1, \ldots, 6$. These numbers have been previously determined and discussed by various authors (see [3, 38, 39] and references cited therein).

Figure 1 includes all benzenoids with $h \leqq 3$ and all normal benzenoids with $h = 4$ and $h = 5$. For

Table 2. Number of benzenoids of the different types and with h up to 6.

	Catacondensed						Pericondensed				Total normal	Grand total
h	**a**	**m**	**c**	**u**	**b**	Total	**n**	**e**	**o**	Total		
1	1	.	.	.	.	1	.	.	.	.	1	1
2	1	.	.	.	.	1	.	.	.	.	1	1
3	1	1	.	.	.	2	.	.	1	1	2	3
4	1	1	1	1	1	5	1	.	1	2	6	7
5	1	4	1	4	2	12	2	1	7	10	14	22
6	1	3	4	16	12	36	12	3	30	45	48	81

Table 3. Distribution of K numbers for $h = 6$ benzenoids of the different types.

	Catacondensed						Pericondensed				Total normal	Grand total
h	**a**	**m**	**c**	**u**	**b**	Total	**n**	**e**	**o**	Total		
0	.	.	.	.	.	.	.	.	30	30	.	30
7	1	.	.	.	.	1	.	.	.	.	1	1
9	.	.	.	.	.	.	.	1	.	1	.	1
10	.	.	.	.	.	.	1	.	.	1	1	1
11	.	.	.	1	.	1	.	.	.	.	1	1
12	.	.	.	.	.	.	1	1	.	2	1	2
13	.	.	.	1	.	1	1	.	.	1	2	2
14	.	.	.	2	.	2	2	.	.	2	4	4
15	.	1	1	.	.	2	2	1	.	3	4	5
16	.	1	1	.	.	2	2	.	.	2	4	4
17	.	.	.	2	1	3	2	.	.	2	5	5
18	.	.	.	4	.	4	.	.	.	.	4	4
19	.	.	.	4	2	6	.	.	.	.	6	6
20	.	.	.	.	2	2	1	.	.	1	3	3
21	.	1	2	2	.	5	.	.	.	.	5	5
22	.	.	.	.	4	4	.	.	.	.	4	4
23	.	.	.	.	2	2	.	.	.	.	2	2
24	.	.	.	.	1	1	.	.	.	.	1	1
Total	1	3	4	16	12	36	12	3	30	45	48	81

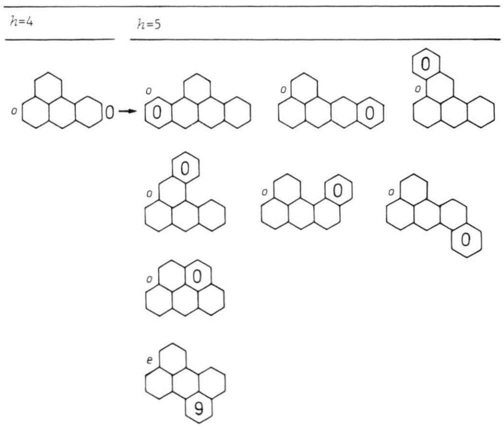


Fig. 2. Non-Kekuléan benzenoids (**o**) with $h = 4$ and 5. One essentially disconnected benzenoid (**e**) with $h = 5$.

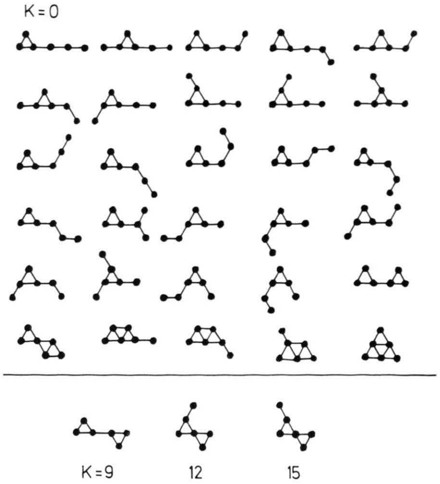


Fig. 3. Dualist graphs of the 30 non-Kekuléans and 3 essentially disconnected benzenoids with $h = 6$.

$h = 4$ one non-Kekuléan benzenoid exists; see Figure 2. This figure shows how the 7 existing $h = 5$ non-Kekuléans may be generated from it, as well as the unique $h = 5$ essentially disconnected benzenoid (perylene).

For $h = 6$ Table 2 indicates 30 non-Kekuléans in consistence with Balaban and Harary [3] (28 radicals and 2 diradicals). The actual shapes are shown in Fig. 3 in terms of dualist graphs [3]. Among the pericondensed Kekuléans the mentioned authors [3] listed zethrene separately, being aware of its "abnormal" nature. It is essentially disconnected, but two additional essentially disconnected benzenoids exist for $h = 6$; cf. Figure 3. This leaves 48 normal benzenoids, 36 catacondensed and 12 pericondensed. The distribution of K numbers from $K_{\min}(6) = 7$ until its maximum, viz. $K_{\max}(6) = 24$, is apparent from Table 1. Table 3 gives more details, specifying the different types of benzenoids. The 12 normal pericondensed benzenoids ($h = 6$) consist of anthranthene, benzo(g, h, i)perylene and ten substituted pyrenes. They are specified with their K numbers in Figure 4.

Sieve Method

All normal benzenoids with K up to 8

All the K numbers of the existing benzenoids with h up to 6 have been inspected (see above).

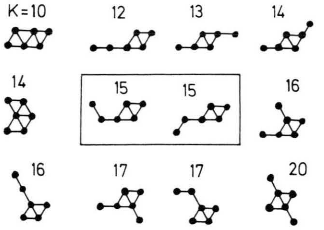


Fig. 4. Dualist graphs of the 12 normal pericondensed benzenoids with $h = 6$. Framed structures are isoarithmic. K numbers are indicated.

Having Theorem 1 in mind it is then clear that Table 1 covers all the existing benzenoids for $0 > K \leqq 8$. Their actual shapes are found in Figure 5. Hereby the question quoted in the introduction is answered.

All normal benzenoids with K up to 14

In order to derive all the normal benzenoids with $K \leqq 14$ (viz. upper part of Table 1) it is fortunately not necessary to inspect all the thousands of existing benzenoid structures for $h < 13$, if we in addition to the above reasoning take resort to Theorem 2 and Conjecture **A**.

Figure 6 contains the particular steps of the building-up procedure from $h = 5$ to $h = 6$ which gave "successful" K numbers, i.e. $K \leqq 14$. However, all five-hexagon normal benzenoids with $K < 14$ should be inspected in principle, as actually has been done. Further on, when passing from $h = 6$ to $h = 7$, it is sufficient to proceed with the six structures of $K < 14$ (Figure 6). All the others give K numbers larger than 14 by virtue of Theorem 2. Conjecture **A** assures (provided it is correct) that no $h = 7$ benzenoids have been missed. The actual inspection detected only two "successful" benzenoids in addition to the linear acene: (i) one with $K = 13$ emerging from the general scheme of Fig. 7 and (ii) one with $K = 14$ obtained by addition of one hexagon to anthranthene (cf. Figure 8).

The procedure continues by additions to the two remaining $h = 7$ benzenoids with $K < 14$ (viz. $K = 8$ and $K = 13$), for which the general schemes of Fig. 7 are applicable. Right after that it fades out to leave us with the linear acenes.

The described procedure will presently be referred to as the sieve method.

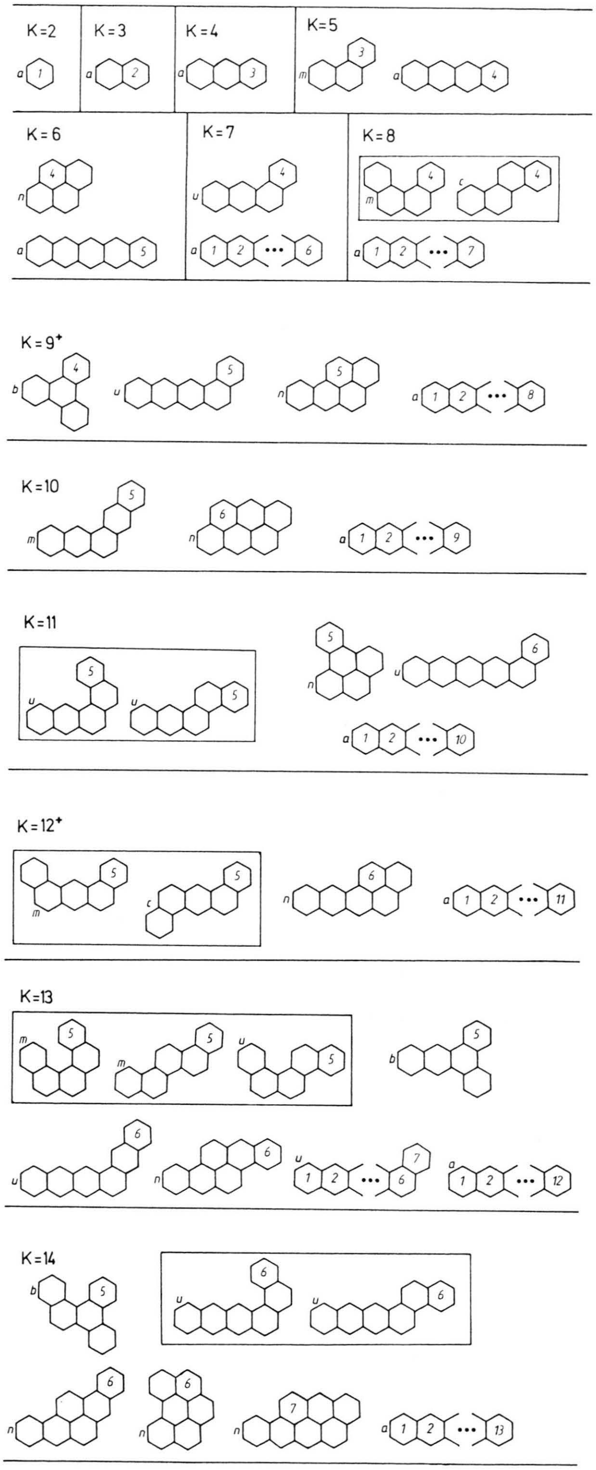


Fig. 5. Normal benzenoids with K up to 14. ⁺Infinitely many essentially disconnected benzenoids with this K number exist.

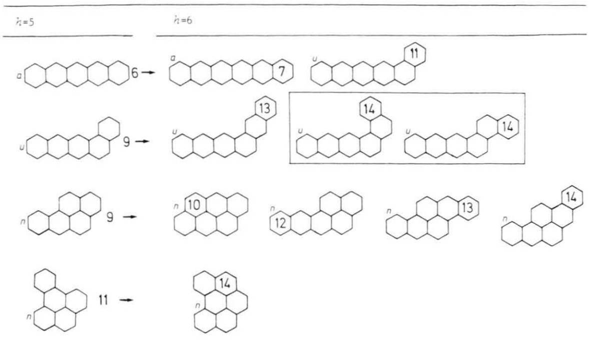


Fig. 6. Selected steps in the generation of normal benzenoids from $h = 5$ to $h = 6$. Numbers of Kekulé structures are indicated.

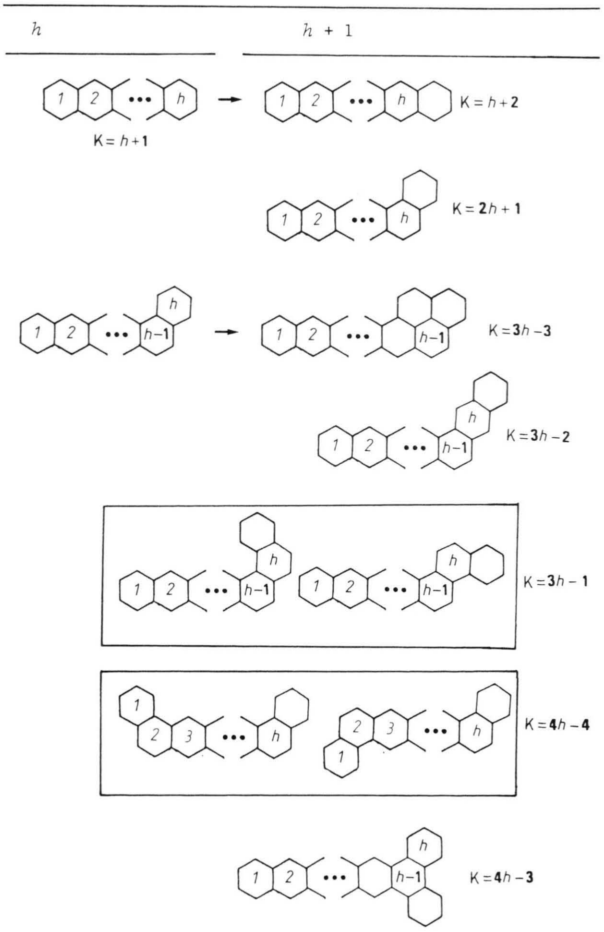


Fig. 7. Schemes for generating some benzenoids with low h values in relation to the K number. Framed structures are isoarithmic.

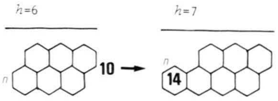


Fig. 8. One step in the generation of a benzenoid from $h = 6$ to $h = 7$.

Further Application of the Sieve Method

The described sieve method was carried further in order to derive all normal benzenoids with K up to 24. This is the maximal K number for six-hexagon benzenoids. The obtained numbers of benzenoids are collected in Table 1 (lower part).

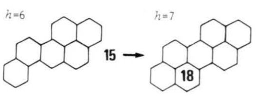
The actual forms of the 133 benzenoids with $14 < K \leqq 24$ (in continuation of Fig. 5) are too voluminous to be reproduced here. This material is available on request to one of the authors (SJC).

Discussion of the Sieve Method

The above results have demonstrated the practical applicability of the sieve method and its efficiency.

Assume that a set of benzenoids with h hexagons each are ordered by increasing K numbers as exemplified for $h = 4$ by Figure 1. The new benzenoids with $h + 1$ hexagons generated from them are then naturally found to occur roughly with increasing K numbers too. A warning against taking this rule in a strict sense is warranted. An example will illustrate how deceiving it may be.

Consider the generation of normal benzenoids of $h = 7$ from $h = 6$. When we arrive at $K = 14$ (for $h = 6$) the resulting new benzenoids have K values seldom below 20. Figure 9 shows a part of this process, using the two $K = 14$ structures of Figure 4. Then it was a surprise, when continuing the process, to find that one of the $K = 15$ structures resulted in peropyrene with $K = 18$:



All the other structures generated from the same benzenoid ($h = 6$, $K = 15$) possess the K numbers 21, 24, 27 and 28. Peropyrene is an especially elusive structure in this context. It can be generated from

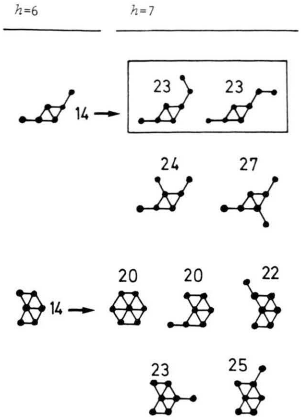


Fig. 9. Generation of new benzenoids from selected $h = 6$ systems (see Fig. 4); dualist graphs are employed. K numbers are indicated.

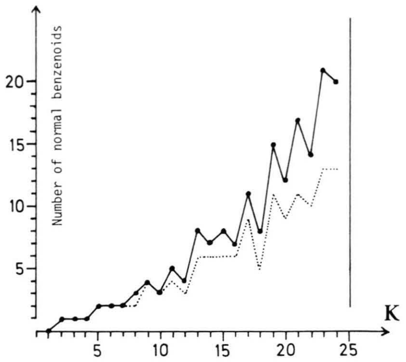


Fig. 10. Diagram of the number of normal benzenoids as a function of K (number of Kekulé structures). The dotted curve applies when isoarithmic structures are counted only once.

only one normal $h = 6$ benzenoid; the above scheme is unique. This means that the "intrinsic security" of the building-up process (see above) does not work in this case. Peropyrene is the only normal benzenoid with $h = 7$ and $K = 18$.

Conclusion

Figure 10 shows a graphical representation of the number of normal benzenoids with $K \leqq 24$. The curve is steadily ascending, but not monotonously. The results were obtained by a simple procedure referred to as the sieve method. It has given the answer to questions which have been considered as hardly soluble problems until now.

The method is amenable for computer programming, and some steps have already been taken in that direction. Also without computer aid it is possible to carry these studies beyond $K = 24$, although the analysis rapidly becomes rather tedious with increasing K values.

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