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Number of *Kekulé* Structures of Single-Chain Aromatics

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The number of *Kekulé* structures is derived for an arbitrary single-chain aromatic. This class of molecules consists of condensed aromatics where the line through the centers of the fused benzene rings is a single (unbranched) line.

(Keywords: Aromatics; Kekulé structures)

Die Anzahl der Kekulé-Strukturen von unverzweigt kettenförmig kondensierten Aromaten

Es wird die Anzahl der *Kekulé*-Strukturen für beliebige in unverzweigten Ketten linear kondensierte aromatische Systeme abgeleitet.

Introduction

The numbers of *Kekulé* structures for condensed aromatics and their symmetries have been studied to some extent[1,2]. Formulas have been derived for the number of *Kekulé* structures (K) of chain aromatics belonging to the classes of molecules: (a) straight chains (polyacenes)[1], (b) bent chains (polyphenes)[2], and (c) zig-zag chains (phenanthrene, chrysene, picene, etc.)[1]. These formulas read:

(a) $$K = Q + 1 \qquad Q = 1, 2, 3, \ldots$$

(b) $$K = \begin{cases} 1 + \frac{1}{4}(Q+1)^2; & Q = 1, 3, 5, \ldots \\ 1 + \frac{1}{4}Q(Q+2); & Q = 2, 4, 6, \ldots \end{cases}$$

(c) $$K = F_{Q+1}; \qquad Q = 1, 2, 3, \ldots$$

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Here Q denotes the number of benzene rings. The symbol F_n is used to denote the members of the *Fibonacci* series, viz.

$$F_1 = 1,\ F_2 = 2,\ F_n = F_{n-1} + F_{n-2};\ n = 3, 4, 5, \ldots$$

The different molecules in question up to $Q = 5$ are listed in Table 1.

Table 1. *Molecules with $Q = 1, \ldots, 5$ belonging to the* (a) *straight chain*, (b) *bent chain and* (c) *zig-zag chain aromatics. Number of Kekulé structures (K) in parentheses*

Q	(a)	(b)	(c)
1	benzene (2)	benzene (2)	benzene (2)
2	naphthalene (3)	naphthalene (3)	naphthalene (3)
3	anthracene (4)	phenanthrene (5)	phenanthrene (5)
4	naphthacene (5)	tetraphene (7)	chrysene (8)
5	pentacene (6)	pentaphene (10)	picene (13)

In the present work a prescription is given for the derivation of K for *any* single-chain aromatic. In a single-chain aromatic molecule the line through the centers of the fused benzene rings is a single (unbranched) line.

Theory

Assume the benzene rings in a single-chain aromatic to be numbered from one end to the other, the total number being Q as above. Let a and b be the numbers of *Kekulé* structures with a single or double bond, respectively, at a certain "critical" position.

For $Q = 1$ one has obviously $a_1 = b_1 = 1$.

For $Q > 1$ the critical position is defined as belonging to the Q'th ring and opposite to the bond connecting the rings number Q and $Q - 1$.

The *Kekulé* structures of a Q-membered single-chain aromatic may be derived by adding the Q'th ring to the *Kekulé* structures of the corresponding $(Q - 1)$-membered molecule. In this process one or two new *Kekulé* structures are generated depending on the nature of the bond to which the last ring is added; it may be a single or a double bond, respectively. These features are illustrated in Fig. 1.

By pursuing the lines of thought in the above paragraphs the following procedure was established for deriving the number of *Kekulé* structures, K_Q, for any single-chain aromatic with Q benzene rings.

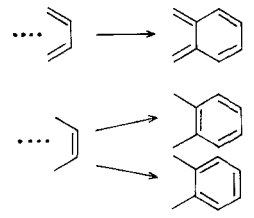


Fig. 1. Patterns for generating *Kekulé* structures by adding one benzene ring to a single-chain aromatic

1. The molecule is built up successively by adding one benzene ring at a time.

2. For every step the number of *Kekulé* structures is obtained as

$$K_Q = a_Q + b_Q$$

3. For $Q = 2$ one has the numbers

$$a_2 = 2,\ b_2 = 1$$

4. When the chain is extended in a straight line (defined by the last two rings), the new pair of numbers (a, b) are

$$a_Q = a_{Q-1} + b_{Q-1},\ b_Q = b_{Q-1}$$

5. When the new ring is added with a bend, one has

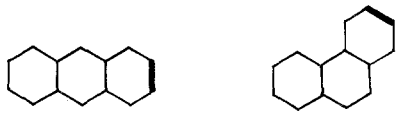
$$a_Q = a_{Q-1} + b_{Q-1},\ b_Q = a_{Q-1}$$

Examples

Fig. 2 shows the above rules applied to anthracene (straight chain) and phenanthrene (bent chain), both with $Q = 3$.

These chains are extended to the different single-chain aromatics with $Q = 4$ as shown in Fig. 3. Notice that tetraphene has been derived in two different ways. The resulting number pairs (a, b) are different, viz. (4, 3) and (5, 2), depending on the way the benzene rings are numbered. The number of *Kekulé* structures, $K = a + b$, is of course the same in the two cases. Notice also that chrysene and benzo(c)phenanthrene have the same number pairs, viz. (5, 3). It is immaterial, as far as the number of *Kekulé* structures is concerned, which way the chain is bent when a new ring is added.

The results of Figs. 2 and 3 are consistent with the K numbers given in Table 1. The procedure may be extended to $Q = 5$ for additional



ANTHRACENE

$a_3 = a_2 + b_2 = 3$

$b_3 = b_2 = 1$

$K = 3 + 1 = 4$

PHENANTHRENE

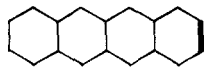
$a_3 = a_2 + b_2 = 3$

$b_3 = a_2 = 2$

$K = 3 + 2 = 5$

Fig. 2. Three-membered chains: anthracene and phenanthrene. Here and in subsequent figures the critical positions are marked by heavy lines

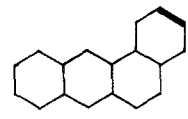
From ANTHRACENE - $(a,b) = (3,1)$:



NAPHTHACENE

$a_4 = 3 + 1 = 4$

$b_4 = 1 \quad K = 5$

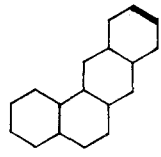


TETRAPHENE

$a_4 = 3 + 1 = 4$

$b_4 = 3 \quad K = 7$

From PHENANTHRENE - $(a,b) = (3,2)$:

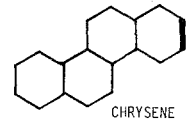


TETRAPHENE

$a_4 = 3 + 2 = 5$

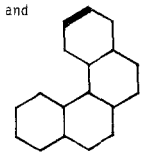
$b_4 = 2$

$K = 7$



CHRYSENE

and



BENZO(c)PHENANTHRENE

$a_4 = 3 + 2 = 5$

$b_4 = 3 \quad K = 8$

Fig. 3. Four-membered single chains generated from anthracene and phenanthrene (see Fig. 2)

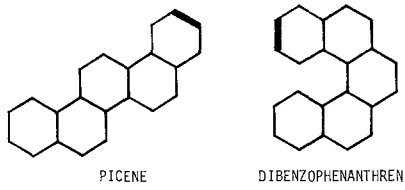


Fig. 4. Two aromatics with the same numbers: $a_5 = 8$, $b_5 = 5$, $K = 13$

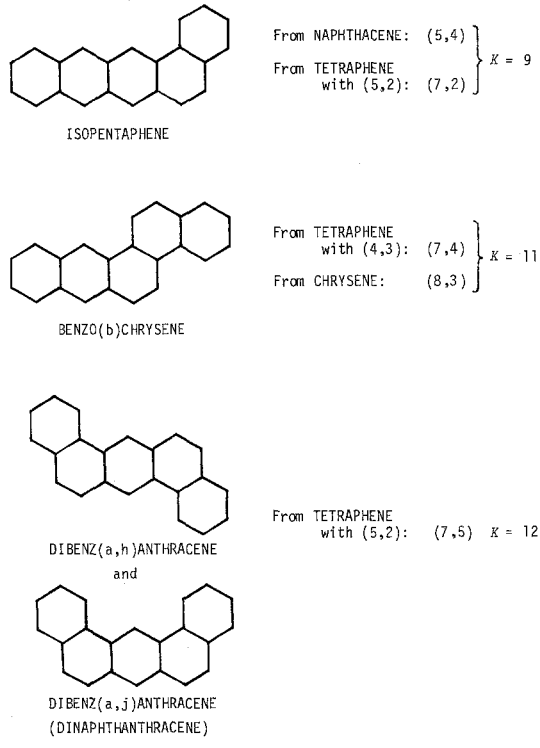


Fig. 5. Number pairs (a, b) and number of *Kekulé* structures (K) for some single-chain aromatics with $Q = 5$

confirmation of the results in Table 1. It is found from naphthacene: pentacene with the number pair (5, 1) and consequently $K = 6$; from tetraphene with (4, 3): pentaphene (7, 3), $K = 10$; from chrysene: picene (8, 5), $K = 13$; cf. Fig. 4. The latter numbers, viz. (8, 5) and $K = 13$ occur also for dibenzophenanthrene (see Fig. 4), which may be derived from benzo(c)phenanthrene.

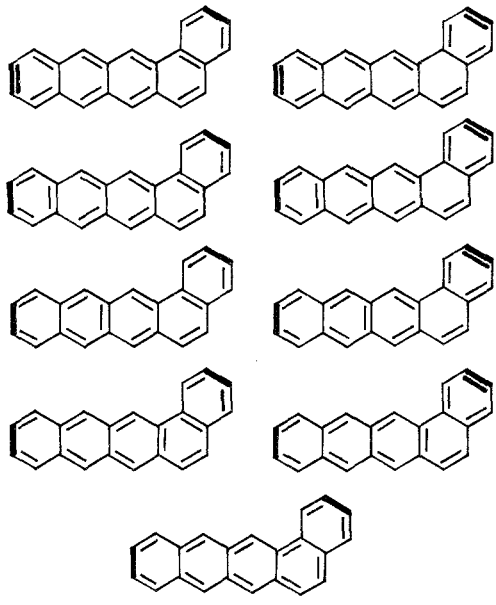


Fig. 6. The nine *Kekulé* structures of isopentaphene. The critical positions are marked by heavy lines

For further illustration we take some examples with $Q = 5$, where the molecules do not belong to any of the classes listed in Table 1. The results for isopentaphene, benzo(b)chrysene, dibenz(a,h)anthracene and dibenz(a,j)anthracene are summarized in Fig. 5. The nine *Kekulé* structures of isopentaphene are shown in Fig. 6. When derived from naphthacene the critical position occurs at the right-hand side of the chain. The *Kekulé* structures posses 5 single bonds and 4 double bonds at this position. That is consistent with the number pair (5, 4); cf. Fig. 5. When the *Kekulé* structures are derived from those of tetraphene with (5, 2), the number pair (7, 2) is obtained. It is consistent with the 7 single bonds and 2 double bonds found at the critical position, this time at the left-hand side of the chain.

References

[1] *Cyvin S. J.*, Acta Chim. Hung., in press.
[2] *Cyvin S. J.*, Monatsh. Chem. **113**, 1127 (1982).