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Graph-Theoretical Treatment of Aromatic Hydrocarbons V*:

THE NUMBER OF KEKULÉ STRUCTURES IN AN ALL-BENZENOID AROMATIC HYDROCARBON

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Abstract

A general expression (2) for the number of Kekulé structures in an all-benzenoid aromatic hydrocarbon is obtained.

The determination of the number of Kekulé structures, K, in aromatic hydrocarbons is of certain interest to theoretical organic chemistry. This seems to be a rather difficult combinatorial problem and in spite of repeated attempts in the past [1], a general solution has not yet been obtained.

On the other hand, it is known [2] that the number of Kekulé structures is related in a simple manner to the adjacency matrix $\underset{\sim}{A}$ of the molecular graph of the aromatic hydrocarbon, namely

$$\det \underset{\sim}{A} = (-1)^{p/2} K^2$$

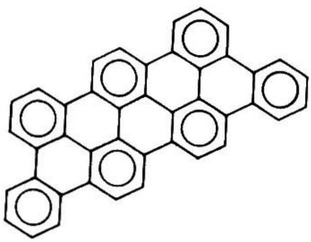
where p is the number of vertices of the molecular graph.

In the present work we shall consider all-benzenoid aromatic hydrocarbon (ABAH) systems. The number of Kekulé structures of such a hydrocarbon A is denoted by K = K(A).

We shall derive a general combinatorial expression for K of the ABAH systems. Our main result, which is summarized in Rule 2 and eq. (2) will be deduced in three steps. First we shall present Rule 1 and eq. (1) which are valid for a restricted class of ABAH systems. Then we modify Rule 1 into Rule 2 and thus extend the validity of eq. (1). Finally we modify eq. (1) to eq. (2) and thus obtain a generally valid expression for K of any ABAH.

The basic properties and the topological peculiarities of the all-benzenoid aromatic hydrocarbons have been considered in a previous paper [3].

Let A be an all-benzenoid aromatic hydrocarbon with n(A) six-membered rings. n(F) rings of A contain an aromatic sextet and will be called full rings; n(E) = n(A) - n(F) rings of A are empty. For example, the molecule A_1 has $n(A_1) = 12$, n(F) = 7 and n(E) = 5. Later we shall see that $K(A_1) = 227$.

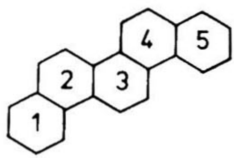


A_1

1. SOME TOPOLOGICAL PROPERTIES OF ALL-BENZENOID AROMATIC HYDROCARBONS

The rings of an ABAH can be partitioned into two parts. Those rings of A which contain an aromatic sextet (and which are as usual marked by a circle) form the full subsystem F(A), while the empty rings of A form the empty subsystem E(A).

The full subsystem F(A) has a trivial structure: it is always composed of n(F) disjoint benzene rings. In the following we shall be mainly interested in the empty subsystem of an ABAH. For example, $E(A_1)$ is given as follows.



$E(A_1)$

Of course, E(A) contains n(E) rings. We will label them 1,2,..., n(E).

The number of rings in E(A) and F(A) are related in the following manner:

$$n(F) = n(E) + 1 + c(E) - \gamma(E)$$

where c(E) is the number of disconnected parts of the empty subsystem, while $\gamma(E)$ is the number of those rings of F(A) which are adjacent* to six rings of E(A).

Since an ABAH can possess any number n(E) = 0,1,2,... of empty rings, from the above equation we conclude that there exist ABAH systems with n(A) = 1,4,6,7,8,... rings and that there exist ABAH systems with n(F) = 1,3,4,5,... full rings.

From the basic topological properties of an ABAH [3] it is evident that every ring from E(A) has exactly three neighbours from F(A). Therefore,

(a) no three rings in E(A) can be annelated in a linear mode, that is, the fragment X_1 cannot occur in E(A);

(b) no three rings in E(A) can be peri-condensed, that is, the fragment X_2 cannot occur in E(A);

(c) E(A) can be connected, but may also consist of an arbitrarily large number of components.

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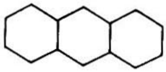
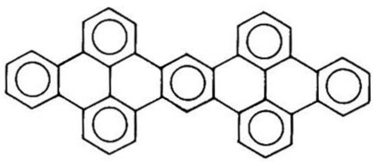
* Two rings are said to be adjacent if they possess a common bond. Otherwise they are disjoint.



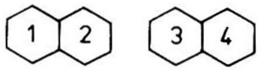
X_1

X_2

For example, the empty subsystem of A_2 consists of two components.

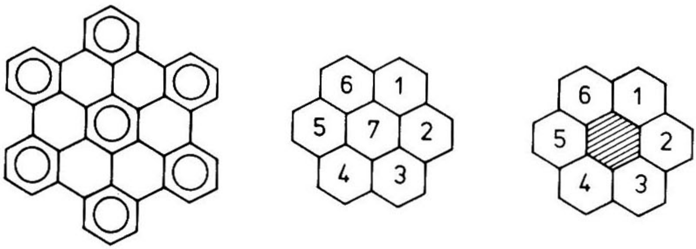


A_2



$E(A_2)$

In certain cases caution is necessary with the properties (a) and (b), namely when F(A) possesses rings which are adjacent to six rings of E(A). For example, if the empty subsystem of A_3 is presented as $E(A_3)^+$, then one may erroneously conclude that



A_3 $E(A_3)^+$ wrong $E(A_3)^{++}$ correct

n(E) = 7 and that fragments of both the type X_1 and X_2 occur in $E(A_3)$. In fact the central ring of this system belongs to $F(A_3)$ and therefore is to be left out of the consideration; this is indicated in $E(A_3)^{++}$.

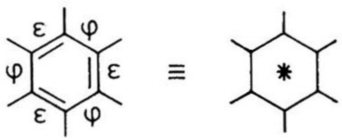
The properties (a), (b) and (c) fully characterize the empty subsystem. Namely, every benzenoid system with the properties (a), (b) and (c) can be understood as an empty subsystem of some ABAH. Moreover, every connected benzenoid system with the properties (a), (b) and (c) is the empty subsystem of a unique ABAH.

In the following we shall give a few additional definitions which will be necessary for the formulation of our results.

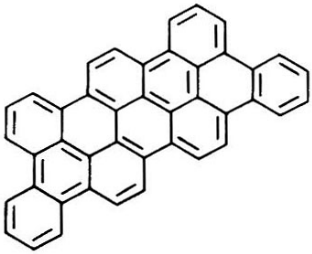
The bonds of A which belong to F(A) will be called ϕ-bonds. Some of them belong also to E(A). Every ring of F(A) possesses six ϕ-bonds; the total number of ϕ-bonds in A is thus 6n(F).

The bonds of A which belong exclusively to E(A) will be called ε-bonds. Every ring of E(A) possesses three ϕ- and three ε-bonds.

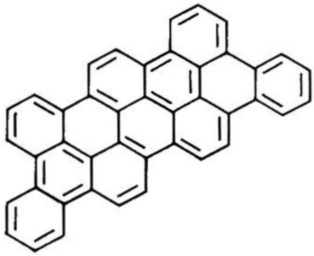
If in a given Kekulé structure of an ABAH, all three ε-bonds of an empty ring are double bonds, we will label this ring by a star and call it a "starred" ring.



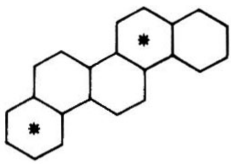
By definition, only rings from E(A) can be starred. Thus, for example, in the Kekulé structures k_1 and k_2 of A_1 the rings 1 and 4 are starred.



k_1



k_2



σ

In the following we shall say that the starring σ induces the Kekulé structures k_1 and k_2. We emphasize that σ induces exactly these two Kekulé structures.

2. THE NUMBER OF KEKULÉ STRUCTURES IN AN ABAH: THE SIMPLE CASE

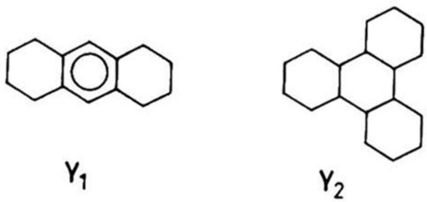
Let us first consider those Kekulé structures which have the property that all ε-bonds in them are single bonds. These correspond to the case when none of the empty rings is starred.

Since all the full rings in an ABAH are mutually independent, two different Kekulé structures can be drawn in each full ring without this influencing the arrangement of the double bonds in any other full ring. Therefore we have a total of $2^{n(F)}$ Kekulé structures of this type and in a given ABAH there must be $K - 2^{n(F)}$ Kekulé structures in which at least one ε-bond is a double bond. We proceed now to determine the number of Kekulé structures of this latter type.

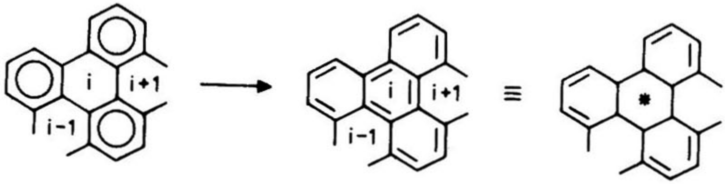
As a starting point we shall consider the simplest case when all the "disturbing" effects are avoided. Let A thus be an ABAH such that

(a) it possesses no fragment of the type Y_1, and

(b) E(A) possesses no fragment of the type Y_2.



Let us start to construct a Kekulé structure of A by choosing one of the ε-bonds of the ring i to be a double bond. It is immediately seen that then all the three ε-bonds of i must be double (and, hence, this ring becomes starred). Furthermore, the double bonds in all the three full rings which are adjacent to i become fixed. It is also evident that if i is starred, then i-1 and i+1 cannot be starred.



This double bond fixation terminates, however, on the rings which are adjacent to i and the positioning of the double bonds in the rest of the system is not influenced by the starring of the ring i. Consequently, there are $2^{n(F)-3}$ Kekulé structures of A such that the ring i is starred, but all other rings from E(A) are not starred.
Extending this argument we arrive at the following conclusion, which is the crucial one in the entire approach.

Assume that it is possible to make an arrangement of double bonds in A such that the rings k, l, m,..., q of E(A) are all simultaneously starred. Assume that a total of f rings of F(A) are adjacent to the collection of rings k, l, m,...,q. Then the starring of the rings k, l, m,...,q causes the fixation of the double bonds in f full rings and there remain $2^{n(F)-f}$ Kekulé structures of A, such that the rings k, l, m,...,q are starred, but all other rings from E(A) are not starred.

Definition. The "starring" σ is a selection of rings from E(A), with the property that it is possible to construct a Kekulé structure of A such that all rings from σ (and only these) are starred.

The set of all starrings is $\underset{\sim}{\sigma}$. By definition, $\underset{\sim}{\sigma}$ contains also the trivial starring σ_o which corresponds to the situation when no ring of E(A) is starred.

The rings from σ are adjacent to $f(\sigma)$ rings of $F(A)$. In particular, $f(\sigma_o) = 0$.

According to the above discussion, every starring σ will induce $2^{n(F)-f(\sigma)}$ Kekulé structures of the molecule A. Whenever $f(\sigma) = n(F)$, the starring σ induces a unique Kekulé structure.

If fragments Y_2 are absent from $E(A)$, then all Kekulé structures of A are induced by means of the starring procedure, and thus we conclude that

$$K(A) = \sum_{\sigma \in \underset{\sim}{\sigma}} 2^{n(F)-f(\sigma)} \qquad (1)$$

In order to make formula (1) applicable, we have to specify the construction of the set $\underset{\sim}{\sigma}$. For the case which we consider in this section, $\underset{\sim}{\sigma}$ is constructed in a rather simple way.

<u>Rule 1</u>. If fragments of the type Y_1 are not present in A, then $\underset{\sim}{\sigma}$ consists of all k-tuples ($k = 0,1,2,\ldots$) of mutually disjoint rings of $E(A)$.

<u>Example</u>: A_1. According to Rule 1, $\underset{\sim}{\sigma}$ contains the following 11 collections of mutually disjoint empty rings.

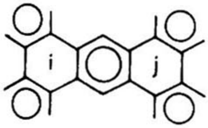
σ	$f(\sigma)$	σ	$f(\sigma)$
σ_o	0	1,3	5
1	3	2,4	5
2	3	3,5	5
3	3	1,4	6
4	3	1,5	6
5	3	2,5	6
		1,3,5	7

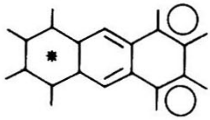
$$K(A_1) = 2^7 + 5 \cdot 2^{7-3} + 3 \cdot 2^{7-5} + 3 \cdot 2^{7-6} + 1 \cdot 2^{7-7} = 227$$

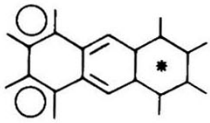
3. THE NUMBER OF KEKULÉ STRUCTURES IN AN ABAH: THE PRESENCE OF Y_1

When Y_1 fragments are present in an ABAH, then Rule 1, but not eq. (1) is to be modified. Contrary to this, when an ABAH contains Y_2 fragments, then Rule 1 holds and appropriate changes are necessary in eq. (1). The considerations in the present and the following section are aimed towards such modifications of eq. (1) & Rule 1.

The case when a fragment Y_1 is present in an ABAH is simple indeed. If the ring i is starred, then the ring j cannot be starred and vice versa.







Therefore we have the following straightforward extension of Rule 1, after which eq. (1) is applicable to all ABAH systems which have no fragments of the type Y_2.

Rule 2. $\underset{\sim}{\sigma}$ consists of all k-tuples (k = 0,1,2,...) of mutually disjoint rings of E(A), except of those which possess two empty rings annelated in a linear mode to a full ring.

Example: A_2. The rings 2 and 3 (which are annelated in a linear mode) cannot be simultaneously starred. According to Rule 2, $\underset{\sim}{\sigma}$ contains the following 8 collections of rings.

σ	$f(\sigma)$	σ	$f(\sigma)$
σ_o	0	1,3	6
1	3	1,4	6
2	3	2,4	6
3	3		
4	3		

$$K(A_2) = 2^7 + 4 \cdot 2^{7-3} + 3 \cdot 2^{7-6} = 198$$

Example: A_3. The following three pairs: 1,4; 2,5 and 3,6 cannot occur in any σ. According to Rule 2, $\underset{\sim}{\sigma}$ contains the following 15 selections of empty rings.

σ	f(σ)	σ	f(σ)
σ_o	0	1,3	5
1	3	1,5	5
2	3	2,4	5
3	3	2,6	5
4	3	3,5	5
5	3	4,6	5
6	3	1,3,5	7
		2,4,6	7

$$K(A_3) = 2^7 + 6 \cdot 2^{7-3} + 6 \cdot 2^{7-5} + 2 \cdot 2^{7-7} = 250$$

As is seen from the above two examples, fragments of the type Y_1 not only cause no serious difficulties, but are rather convenient and considerably reduce the number of starrings which have to be taken into account in the summation (1).

Let $|\sigma|$ denotes the number of rings in σ. Then

$$2|\sigma| \leq f(\sigma) \leq 3|\sigma|$$

The left inequality results from the fact that the starring of every ring in E(A) causes the fixation of the double bonds of at least two new full rings. The right inequality holds because just three full rings are adjacent to every empty ring.

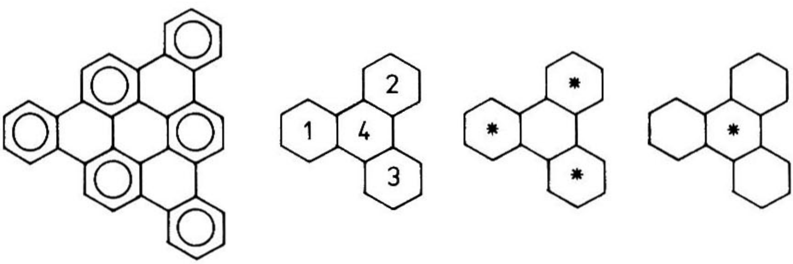
From the above inequalities we obtain the following bounds for K:

$$\sum_{k=o}^{m} r(E,k)\,2^{n(F)-3k} \leq K(A) \leq \sum_{k=o}^{m} r(E,k)\,2^{n(F)-2k}$$

where r(E,k) is the number of ways in which k rings can be starred in E(A); r(E,O) = 1. (One should note that the numbers r(E,k) play a central role in a recently developed "sextet theory" of aromatic hydrocarbons [4]).

4. THE NUMBER OF KEKULÉ STRUCTURES IN AN ABAH: THE PRESENCE OF Y_2

When Y_2 is present in an empty subsystem, eq. (1) does not reproduce the correct number of Kekulé structures. The reason for this is seen immediately from the example of A_4.

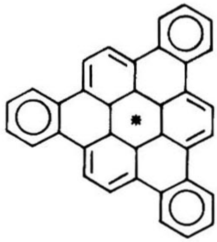


A_4 $E(A_4)$ σ σ'

The starring σ of the rings 1,2 and 3 has the property f(σ)=6=n(F) and thus leads to the fixation of the double bonds in all the six full rings of A_4. The corresponding (unique) Kekulé structure is k_3. However, without moving the double bonds in the full

k_3

k_4



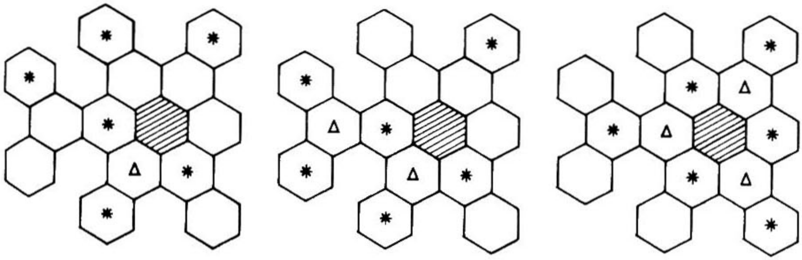
k_5

rings of A_4 one can construct another Kekulé structure k_4, which cannot be generated by the previously described starring procedure. (Note that ring 4 is formally starred in k_4, but k_4 contains ε-double bonds which are not in starred rings. According to our method, the starring σ would actually induce not k_4, but 2^3 Kekulé structures of the form k_5.)

Kekulé structures in which not all ε-double bonds belong to starred rings (e.g. k_4) will be called "anomalous", while those in which all double ε-bonds belong to starred rings will be called "normal" (e.g. k_1, k_2, k_3, k_5). Eq. (1) gives in fact the number of normal Kekulé structures, which in certain cases coincides with the total number of Kekulé structures.

A detailed examination shows that anomalous Kekulé structures necessarily occur whenever three starred (empty) rings are adjacent to a fourth empty ring.

Let $g(\sigma)$ be the number of rings of E(A) which in a given starring σ are adjacent to three starred rings. We shall mark these rings by Δ. For example,



$g(\sigma_1) = 1$ $g(\sigma_2) = 2$ $g(\sigma_3) = 3$

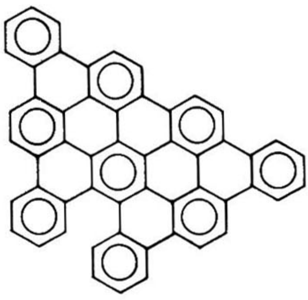
Let k be a normal Kekulé structure of A, which is induced by σ. Analysis shows that starting from k we can construct $2^{g(\sigma)} - 1$ anomalous Kekulé structures without moving the double bonds in the full subsystem. Since a starring σ induces $2^{n(F)-f(\sigma)}$ normal Kekulé structures, σ will induce additional $2^{n(F)-f(\sigma)}[2^{g(\sigma)} - 1]$ anomalous structures, that is a total of $2^{n(F)-f(\sigma)+g(\sigma)}$ structures. This leads to the equation

$$K(A) = \sum_{\sigma \in \underset{\sim}{\sigma}} 2^{n(F)-f(\sigma)+g(\sigma)} \qquad (2)$$

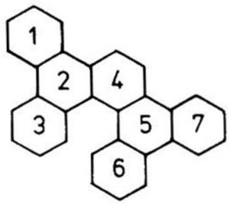
which together with Rule 2 provides a general combinatorial expression for the number of Kekulé structures in an all--benzenoid aromatic hydrocarbon.

The case $g(\sigma) > 0$ can, of course, occurs only if E(A) contains Y_2 fragments. Therefore in the absence of Y_2 fragments in E(A), $g(\sigma) = 0$ for all $\sigma \in \underset{\sim}{\sigma}$ and eq. (2) reduces to eq. (1).

<u>Example</u>: A_5.



A_5



$E(A_5)$

The pairs 2,6 and 3,5 cannot be present in any σ. Therefore the set $\underset{\sim}{\sigma}$ contains the following 37 elements.

σ	$f(\sigma)$	$g(\sigma)$	σ	$f(\sigma)$	$g(\sigma)$	σ	$f(\sigma)$	$g(\sigma)$
σ_o	0	0	1,5	6	0	1,3,4,6	8	1
1	3	0	1,6	6	0	1,3,4,7	8	1
2	3	0	1,7	6	0	1,4,6,7	8	1
3	3	0	2,7	6	0	3,4,6,7	8	1
4	3	0	3,7	6	0	1,3,6,7	9	0
5	3	0	1,3,4	6	1	1,3,4,6,7	9	2
6	3	0	4,6,7	6	1			
7	3	0	1,3,6	7	0			
1,3	5	0	1,4,6	7	0			
1,4	5	0	1,4,7	7	0			
2,5	5	0	3,4,6	7	0			
3,4	5	0	3,4,7	7	0			
3,6	5	0	3,6,7	7	0			
4,6	5	0	1,3,7	8	0			
4,7	5	0	1,6,7	8	0			
6,7	5	0						

Application of eq. (2) gives

$$K(A_5) = 2^9 + 7\cdot 2^{9-3+0} + 8\cdot 2^{9-5+0} + 5\cdot 2^{9-6+0} + 2\cdot 2^{9-6+1} + 6\cdot 2^{9-7+0} + 2\cdot 2^{9-8+0} + 4\cdot 2^{9-8+1} + 1\cdot 2^{9-9+0} + 1\cdot 2^{9-9+2} = 1209$$

The determination of $\underset{\sim}{\sigma}$ from the inspection of E(A) is an elementary combinatorial task. The determination of $f(\sigma)$ and $g(\sigma)$ is also straightforward. The four examples which we have worked out demonstrate that eq. (2) & Rule 2 provide a relatively easy and reliable way for the calculation of the number of Kekulé structures even in extremely large ABAH systems. The previously known methods [1] appear to be considerably less efficient.

Acknowledgement

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