

ON THE DEFINITION OF PARITY OF KEKULÉ
STRUCTURES OF BENZENOID HYDROCARBONS

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El-Basil's concept of parity of Kekulé structures of benzenoid hydrocarbons is analysed. A more precise formulation of this "parity" is given. General formulae for El-Basil's "algebraic structure count" (which we call here the EB-index) for several series of cata-condensed benzenoid molecules are derived. The EB-index may coincide with the number of Kekulé structures, may be slightly smaller than this number, but can have also zero or negative values.

Recently El-Basil¹ introduced a new concept in the topological theory of benzenoid hydrocarbons^{2,3}, namely a novel "parity" of the Kekulé structures.

Whereas the classical parity concept of Dewar and Longuet-Higgins⁴ predicts equal parity for all Kekulé structures of a benzenoid system, El-Basil permits structures of both parity. Whereas the Dewar - Longuet-Higgins parity concept results from a subtle algebraic analysis (of the adjacency matrix of the molecular graph and its determinant⁵ as well as of the relations between Kekulé structures and permutations⁶), the parity of El-Basil is just an ad hoc definition. El-Basil's parity (in its present formulation) can be applied only to benzenoid hydrocarbons, while no such limitation exists in the case of Dewar - Longuet-Higgins' concept. The novel parity concept has certainly some advantages, but its usefulness in practice remains still to be verified.

The aim of the present work is to offer a more precise approach to El-Basil's parity concept and to try to avoid some of its ambiguities. Since the actual computation of El-Basil's algebraic structure count is a rather cumbersome task, we shall present a few general formulae for certain series of cata-condensed benzenoid

systems.

Let B be a benzenoid system³ having $K = K(B)$ Kekulé structures. According to Ref. 1, an integer $p = p(k)$ can be associated to each Kekulé structure k of B , such that either $p = +1$ or $p = -1$ or $p = 0$. Although the name "parity" has been proposed for p , the mere fact that p can have three different values indicates that this name has not been chosen in a most appropriate manner. A detailed analysis shows that p should be understood rather as a weight than as the parity of the corresponding Kekulé structure.

The set of the Kekulé structures of B can be partitioned into "degenerate subsets" according to a construction which was described in Ref. 1. Let D_j symbolize a degenerate subset and let d_j be its cardinality, $j = 1, 2, \dots, m$. Then, of course,

$$d_1 + d_2 + \dots + d_m = K$$

Now, according to Ref. 1, if $d_j > 1$ then $p(k) = +1$ for all $k \in D_j$. If, on the other hand, $d_j = 1$ then either $p(k) = -1$ or $p(k) = 0$ for the (unique) Kekulé structure k , $k \in D_j$.

In order to distinguish between the cases $p(k) = -1$

and $p(k) = 0$, El-Basil uses the count of conjugated circuits⁷ of the corresponding Kekulé structure. He defines that

- $p(k) = -1$ for Kekulé structures "that have identical counts of conjugated circuits", and
- $p(k) = 0$ for Kekulé structures "with different conjugated circuit count than the rest of the set".

Since "the rest of the set", i.e. the Kekulé structures belonging to degenerate subsets need not necessarily possess equal conjugated circuit count, the above definition requires a slight modification.

Let $cc(k)$ be the number of conjugated circuits in the Kekulé structure k . Then we determine the weight $p(k)$ as follows.

Definition 1.

- (a) If $k \in D_j$ and $d_j > 1$ then $p(k) = +1$.
- (b) If $k \in D_j$ and $d_j = 1$ and there exists a Kekulé structure $k_0 \in D_1$, such that $d_1 > 1$ and $cc(k_0) = cc(k)$, then $p(k) = -1$.
- (c) If $k \in D_j$ and $d_j = 1$ and there exists no Kekulé structure k_0 having the properties described in (b), then $p(k) = 0$.

Definition 1 is a mathematically unambiguous reformulation of El-Basil's original parity concept. In a similar manner we can now introduce his "algebraic structure count". However, since the name "algebraic structure count" and its abbreviation ASC are nowadays used to denote a different, but related quantity⁸, in order to avoid confusion, we propose an alternative terminology.

Definition 2.

The EB-index of a benzenoid hydrocarbon B is

$$EB = EB(B) = \sum_k p(k)$$

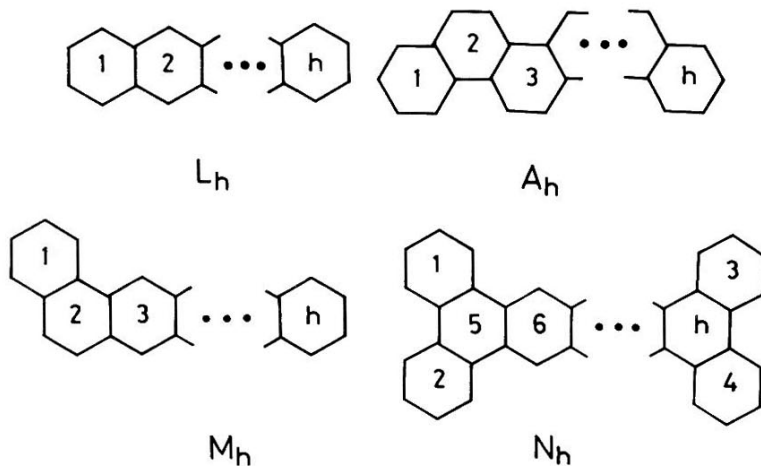
with the summation going over all Kekulé structures of the benzenoid system B.

The "stability index" S, proposed in Ref. 1, is simply the product of K and the EB-index. Since topological considerations are usually concerned with the number of Kekulé structures rather than with its square^{3,8}, there seems to be no reason to prefer the use of the stability index S over the EB-index.

In Ref. 1 arguments are given showing the advantage of the EB-index over the simple structure count K. It is clear that EB is necessarily smaller than or at

least equal to K . Hence EB may be a useful topological index in the cases where the structure count criterion provides an overestimate of the actual chemical stability of the benzenoid hydrocarbon considered⁹. Further work should answer to the question whether or not the EB-index correctly reproduces the chemical behaviour of all (or at least of the majority of) benzenoid hydrocarbons.

In the following we determine the EB-index of the cata-condensed benzenoid systems L_h , M_h , N_h and A_h , where h denotes the number of hexagons. The chemical formula of all the above four types of cata-condensed benzenoid hydrocarbons is $C_{4h+2}H_{2h+4}$. Hence L_h , M_h , N_h and A_h represent isomers.



It is long known that^{3,10}

$$K(L_h) = h + 1 \quad (1)$$

and

$$K(A_h) = K(A_{h-1}) + K(A_{h-2}) \quad (2)$$

with $K(A_0) = 1$ and $K(A_1) = 2$. The corresponding formulae for the number of Kekulé structures of the molecules M_h and N_h are¹¹

$$K(M_h) = 2h - 1 \quad (3)$$

and

$$K(N_h) = 16h - 72 \quad (4)$$

Theorem 1. If $h \geq 3$, then

$$EB(L_h) = 7 - h \quad (5)$$

In addition, $EB(L_1) = 2$ and $EB(L_2) = 3$.

Proof. All the $h + 1$ Kekulé structures of L_h have equal number of conjugated circuits, namely $cc(k) = h$ for all Kekulé structures. Hence $p(k) \neq 0$. There are only two pairs (= 4) of degenerate and $(h + 1) - 4$ non-degenerate Kekulé structures. Therefore $EB(L_h) = 4 \cdot (+1) + (h - 3) \cdot (-1)$.

Eq. (5) follows.

q. e. d.

C o r o l l a r y 1.1. Heptacene ($h = 7$) has zero EB-index. The higher homologues of the polyacene series L_h have negative EB-indices. The chemical meaning of a negative "algebraic structure count" needs explanation.

T h e o r e m 2. If $h \geq 5$, then

$$EB(A_h) = EB(A_{h-1}) + EB(A_{h-2})$$

with $EB(A_3) = 4$ and $EB(A_4) = 8$. In addition, $A_1 = L_1$ and $A_2 = L_2$ and thus $EB(A_1) = 2$ and $EB(A_2) = 3$.

P r o o f. Theorem 2 is an immediate consequence of the recursion relation (2) and the following Lemma.

L e m m a 2.1. If $h \geq 5$, then

$$EB(A_h) = 2 K(A_{h-2}) + 2 K(A_{h-5}) \quad (7)$$

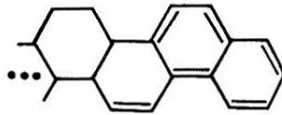
P r o o f. We will distinguish three types of Kekulé structures of A_h , viz. k_1 , k_2 and k_3 .



k_1



k_2

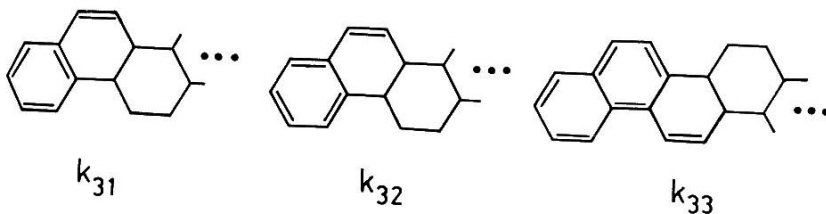


k_3

Since the double bonds in the last two hexagons in k_1 are fixed, there are just $K(A_{n-2})$ Kekulé structures of the type k_1 . For same reasons there are $K(A_{n-2})$ structures of the type k_2 and $K(A_{n-3})$ structures of the type k_3 .

The structures k_1 and k_2 belong to the same degenerate subset. Hence $p(k_1) = p(k_2) = +1$.

The remaining $K(A_{n-3})$ Kekulé structures can be further classified into three types, viz. k_{31} , k_{32} and k_{33} .



In k_{31} and k_{32} the double bonds in the first two (as well as in the last three) hexagons are fixed. Consequently, there are $K(A_{n-5})$ Kekulé structures of the

type k_{31} and the same number of Kekulé structures of the type k_{32} . Every structure of the type k_{31} belongs to the same degenerate subset as the corresponding structure of the type k_{32} . Hence $p(k_{31}) = p(k_{32}) = +1$.

The structures of the type k_{33} have a fixed configuration of double bonds on both ends. Therefore they cannot have degenerate pairs. This means that it must be either $p(k_{33}) = 0$ or $p(k_{33}) = -1$.

Now, an inspection of k_3 and k_{33} shows easily that the structures of the type k_{33} have more conjugated circuits than the Kekulé structures of A_n , being of any other type. This means that $cc(k_{33}) > cc(k)$ for k being of type k_1, k_2, k_{31} or k_{32} . Therefore by Definition 1 (c), $p(k_{33}) = 0$.

We conclude that only the structures of the type k_1, k_2, k_{31} and k_{32} contribute to the BA-index of A_n . Since their number is $K(A_{n-2}), K(A_{n-2}), K(A_{n-5})$ and $K(A_{n-5})$, respectively, we reach formula (7).

q. e. d.

C o r o l l a r y 2.2. From (2) it follows

$$K(A_n) = 2 K(A_{n-2}) + 2 K(A_{n-5}) + K(A_{n-6})$$

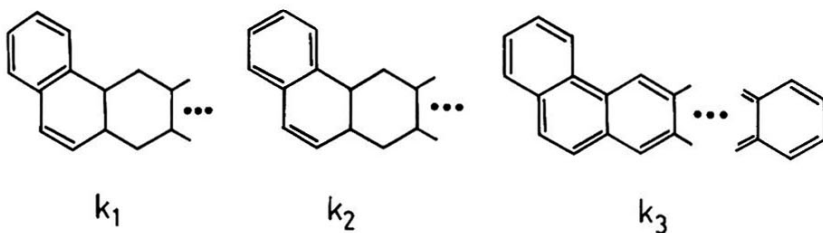
Hence

$$EB(A_n) = K(A_n) - K(A_{n-6}) \quad (8)$$

Theorem 3. If $n \geq 3$, then

$$EB(M_n) = 2n - 2 \quad (9)$$

Proof. The $2n - 1$ Kekulé structures of M_n can be classified into three types, viz. k_1 , k_2 and k_3 .



The number of Kekulé structures of the types k_1 and k_2 is equal and is equal to $K(L_{n-2})$. (According to eq. (1), $K(L_{n-2}) = n - 1$.) There is obviously only one Kekulé structure of the type k_3 . It is easy to see (using the techniques of Ref. 1) that k_1 and k_2 belong

to the same degenerate subset. Consequently, $p(k_1) = p(k_2) = +1$.

For all Kekulé structures of the type k_1 and k_2 , $cc(k) = h$. On the other hand, $cc(k_3) = 2h - 2$. Since $cc(k_1) \neq cc(k_3)$ and $cc(k_2) \neq cc(k_3)$, we conclude that $p(k_3) = 0$.

Eq. (9) follows.

q. e. d.

C o r o l l a r y 3.1. Comparing (3) and (9) we get

$$EB(M_h) = K(M_h) - 1 \quad (10)$$

From Corollaries 2.2 and 3.1, eqs. (8) and (10), one can see that the difference between the EB-index and the Kekulé structure count is negligible in the case of the compounds A_h and M_h . In the following theorem we point out a case where the EB-index and the Kekulé structure count fully coincide.

T h e o r e m 4. If $h \geq 5$, then

$$EB(N_h) = K(N_h) \quad (11)$$

P r o o f is analogous to that of Theorems 2 and 3. The Kekulé structures of N_h are classified in several groups and then one verifies that every Kekulé

structure has a degenerate pair. This means that $p(k) = +1$ for all k .

q. e. d.

C o r o l l a r y 4.1.

$$EB(M_h) = 16 h - 72$$

As a concluding remark we would like to emphasize the following. Eqs. (5) and (9) show that the EB-indices of the molecules L_h and M_h (i.e. of linear polyacenes and their monobenzo derivatives) differ drastically. Whereas $EB(L_h)$ vanishes with increasing h and then becomes negative (!), $EB(M_h)$ is only slightly different than $K(M_h)$ and increases as a linear function of h . This means that the EB-index, used as a criterion of stability of benzenoid hydrocarbons, predicts a dramatic difference in the chemical behaviour of the isomers L_h and M_h , especially when the number of hexagons is sufficiently large ($h = 5$ or more). This prediction may serve as an illustration of the practical value and predictive power of the novel EB-index.

R E F E R E N C E S

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