
TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY. SIMPLE ALTERNATIVE METHOD FOR DETERMINING PARITY OF KÉKULE STRUCTURES

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A simple alternative procedure for determining the parity of Kékule structures is presented. The procedure is based on the formalism of overlap determinant method.

Kékule structures are intuitively supposed to be related to the stability of cyclic conjugated hydrocarbons. Although their exact role in this respect is still unclear¹, several qualitative concepts have nevertheless been supported theoretically. Thus, for example, Longuet-Higgins has proved that hydrocarbons for which no Kékule structure can be written, are generally unstable². Similarly, the intuitive concepts explaining the stability of cyclic conjugated hydrocarbons by the existence of several Kékule structures have been supported on the basis of the so-called resonance theory³. Furthermore, for a limited class of benzenoid hydrocarbons, these concepts of resonance theory can be expressed even quantitatively, since — as shown already⁴⁻⁷ — the stabilization (resonance) energy is proportional to the number of corresponding resonance structures.

Unfortunately, such a simple relation cannot be extended to other types of conjugated hydrocarbons. This indicates that the number of Kékule structures itself does not represent likely the only universal quantity determining the stability of a given hydrocarbon. Further progress in the development of original simple resonance theory has been reached in the works by Wilcox^{8,9}, Herndon^{10,11} and by the Zagreb group¹²⁻¹⁵ who succeeded in generalizing the original ideas also to non-benzenoid systems. It has been shown that in such cases, the validity of the postulates of the resonance theory can be retained only if the so-called algebraic structure count (ASC)* and not the total number of Kékule structures is taken as the critical quantity determining the stability. In determining the ASC quantity, the concept of the parity of Kékule structure plays the decisive role. This concept has been introduced first to the chemistry by Dewar and Longuet-Higgins¹⁶ who proved for alternant hydrocarbons that the corresponding Kékule structures can be grouped into classes differing in the parity of permutations mutually converting the bonds of one structure to those of the other. Such a possibility has been regarded for a long time as an interesting algebraic property without any significant impact on chemistry. The deeper meaning of the parity of Kékule structure was disclosed by the above term ASC defined as a difference between the positive and negative Kékule structures.

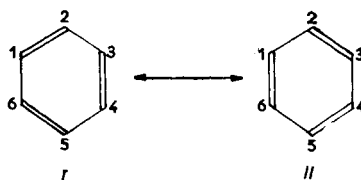
* Some authors use the term "corrected structure count" (CSC) (ref.¹¹) for the same quantity.

The original method for determining the parity proposed by Dewar and Longuet-Higgins was based on determination of the number of bonds, the permutation of which leads to the transformation of one Kékulé structure to another. If this number is odd, such as in *e.g.* benzene, both structures are of the same parity; if the number is even, as *e.g.* in cyclobutadiene, both structures are of the opposite parity. It has been, however, shown that this original method has some limitations. Therefore, the method has been generalized by Gutman and coworkers^{15,17} by the use of the so-called graph superposition technique.

The aim of this work is to present a simple alternative method for determining the parity of Kékulé structures based on the recently proposed overlap determinant method¹⁸.

THEORETICAL AND DISCUSSION

Similarly to our previous works, we believe that the use of the overlap determinant method can be best demonstrated by examples. Let us therefore analyze a simple example of benzene molecule, the structure of which is described as a resonance hybrid of two Kékulé structures *I* and *II* (Scheme 1). Despite the phenomenon of resonance



SCHEME 1

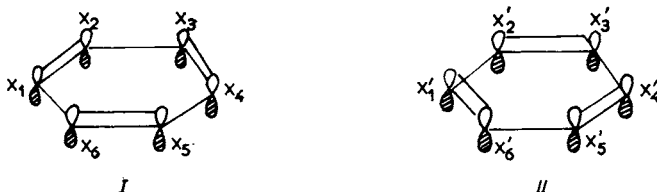
cannot be regarded as a “switching” of one structure to another, for purposes of our approach, such a simple analogy is nevertheless quite useful. In this sense, let us regard for a moment, the mutual transformation of structures $I \rightarrow II$ as “chemical reaction”. Formal reactant is then the hypothetical structure *I* while the structure *II* represents the “product”. In the sense of the overlap determinant method, these “reaction components” will be described by means of bond-functions Φ_I , Φ_{II} , constructed from the individual localized bonds corresponding to Kékulé structures (Eq. (1)).

$$\begin{aligned}\Phi_I &= |\pi_{12}\bar{\pi}_{12}\pi_{34}\bar{\pi}_{34}\pi_{56}\bar{\pi}_{56}| \\ \Phi_{II} &= |\pi'_{23}\bar{\pi}'_{23}\pi'_{45}\bar{\pi}'_{45}\pi'_{16}\bar{\pi}'_{16}|.\end{aligned}\quad (1)$$

Individual bonds will be again described in terms of usual linear combination of atomic orbitals χ , χ' , where the primes distinguish the orbitals of the products from those of the reactant (Eq. (2)).

$$\begin{aligned}
 \pi_{12} &= \chi_1 + \chi_2 & \pi'_{23} &= \chi'_2 + \chi'_3 \\
 \pi_{34} &= \chi_3 + \chi_4 & \bar{\pi}'_{45} &= \chi'_4 + \chi'_5 \\
 \pi_{56} &= \chi_5 + \chi_6 & \pi'_{16} &= \chi'_1 + \chi'_6
 \end{aligned}
 \tag{2}$$

Mutual relation of functions Φ_I, Φ_{II} will be characterized by their overlap. Its calculation in terms of overlap determinant requires to transform the "product" bonds from the basis of primed AO χ' into the basis of the orbitals χ which are used also



SCHEME 2

for description of structure *I*. This transformation can be performed by using the so-called assigning tables, the construction of which based on simple geometrical concepts was reported in detail in our previous work⁸ and need not be repeated here. For our purposes it is sufficient to realize that in the transformation of the structures *I* \rightarrow *II*, there is no change in the orientation of the orbitals χ and χ' . This implies that the corresponding assigning tables (Eq. (3), Scheme 2) represent a simple identity.

$$\begin{aligned}
 \chi'_1 &\rightarrow \chi_1 & \chi'_4 &\rightarrow \chi_4 \\
 \chi'_2 &\rightarrow \chi_2 & \chi'_5 &\rightarrow \chi_5 \\
 \chi'_3 &\rightarrow \chi_3 & \chi'_6 &\rightarrow \chi_6
 \end{aligned}
 \tag{3}$$

From the foregoing discussion it follows that the transformation described by such tables does not change phase properties of linear combinations that describe individual bonds in structure *II* (Eq. (4)) so that in constructing the overlap determinant,

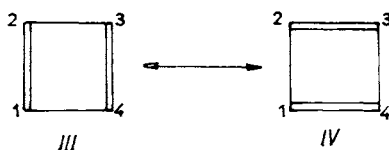
$$\begin{aligned}
 \pi'_{23} &= \chi'_2 + \chi'_3 & \xrightarrow{f} & \chi_2 + \chi_3 \equiv \pi_{23} \\
 \pi'_{45} &= \chi'_4 + \chi'_5 & \xrightarrow{f} & \chi_4 + \chi_5 \equiv \pi_{45} \\
 \pi'_{16} &= \chi'_1 + \chi'_6 & \xrightarrow{f} & \chi_1 + \chi_6 \equiv \pi_{16}
 \end{aligned}
 \tag{4}$$

the primes distinguishing orbitals χ and χ' can be omitted for the bonds describing the "product".

From the method of construction of the assigning tables it becomes clear that this result does not hold only for the just discussed transformation of structures *I* and *II* but that it is quite general. In our case, the set of bonds $\pi_{12}, \pi_{34}, \pi_{56}, \pi_{23}, \pi_{45}, \pi_{16}$ then leads to the following form of the overlap determinant (Eq. (5)).

$$D_{I \rightarrow II} = \begin{vmatrix} 1 & 0 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & 1 \end{vmatrix}^2 \neq 0 \quad (5)$$

Its non-zero value indicates that the transformation of hypothetical structures *I* and *II* has to be considered formally as allowed. This result cannot be, of course, interpreted too literally but rather it indicates that non-zero value of $D_{I \rightarrow II}$ implies the same nodal structure of the bond-functions Φ_I, Φ_{II} describing Kékulé structures of benzene. This result itself says, however, nothing about the parity of the corresponding structures. To interpret this result in this sense, it should be complemented by the empirical criterion according to which the same nodal structure of bond-functions implies also the same parity of the corresponding structures. This interpretation being an empirical one ensures, nevertheless, the compatibility of the results of the overlap determinant method with previous procedures. It is worthy of note that the same conclusions have been recently drawn also by Živković¹⁹ who used different approach.



SCHEME 3

Let us demonstrate now on a number of examples the use of the proposed criterion. A simple example of a hydrocarbon in which Kékulé structures are of the opposite parity is *e.g.* cyclobutadiene. We shall demonstrate that this assignment can be reproduced also by the overlap determinant method. The cyclobutadiene is described by Kékulé structures *III* and *IV* (Scheme 3) and the corresponding bonds are specified by the linear combination of atomic orbitals (Eq. (6)). For the reasons mentioned above,

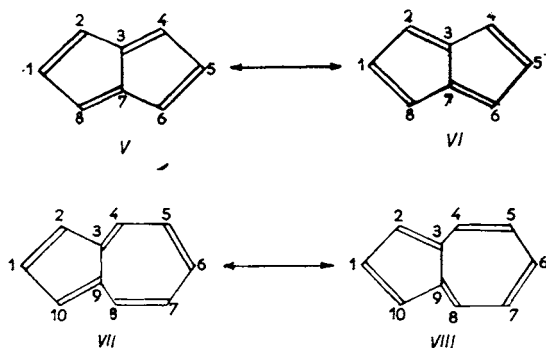
$$\begin{aligned} \pi_{12} &= \chi_1 + \chi_2 & \pi_{23} &= \chi_2 + \chi_3 \\ \pi_{34} &= \chi_3 + \chi_4 & \pi_{41} &= \chi_1 + \chi_4 \end{aligned} \quad (6)$$

the primes formally distinguishing the "reactant" and the "product" are already omitted in the bonds describing the structures *IV*. The overlap determinant characterizing formal transformation of structures *III* \rightarrow *IV* is then given by Eq. (7).

$$D_{III \rightarrow IV} = \begin{vmatrix} 1 & 1 \\ 1 & 1 \end{vmatrix}^2 = 0 \quad (7)$$

In accordance with the proposed empirical classification, its non-zero value confirms the opposite parity of the corresponding structures.

As another example demonstrating the applicability of the proposed criterion not only to alternant but also to non-alternant hydrocarbons let us analyze the mutual transformation of Kékulé structures of pentalene and azulene (*V*, *VI* and *VII*, *VIII*) (Schemes 4 and 5, respectively).



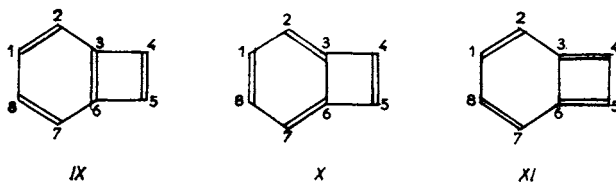
SCHEMES 4, 5

The overlap determinants (8) and (9) constructed in the usual way show that for azulene, both structures are of the same, while for pentalene of the opposite parity.

$$D_{V \rightarrow VI} = \begin{vmatrix} 1 & 0 & 0 & 1 \\ 1 & 1 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 1 & 1 \end{vmatrix}^2 = 0 \quad (8)$$

$$D_{VII \rightarrow VIII} = \begin{vmatrix} 1 & 0 & 0 & 0 & 1 \\ 1 & 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 & 1 \end{vmatrix}^2 \neq 0 \quad (9)$$

In all the cases analyzed so far, only such hydrocarbons were discussed, the structure of which was described by only two Kékulé structures. Such a condition does not represent, however, any restriction and the same procedure can be applied also in cases requiring the use of several Kékulé structures. As a simple example of such a situation let us determine now the parity of three Kékulé structures *IX*–*XI* of benzo-



SCHEME 6

cyclobutadiene (Scheme 6) on the basis of comparison of nodal properties of the pairs of structures *IX*–*X* and *IX*–*XI*. By comparing these structures, the irreducible core for both above pairs can be determined. In the former case this core is formed by the set of bonds of the benzene skeleton ($\pi_{12}, \pi_{36}, \pi_{78}, \pi_{23}, \pi_{67}, \pi_{81}$). On the basis of non-zero value of the corresponding overlap determinant (10), the structures *IX* and *X* can be assigned the same parity.

$$D_{IX \rightarrow X} = \begin{vmatrix} 1 & 0 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & 1 \end{vmatrix}^2 \neq 0 \quad (10)$$

Similarly, the pair of structures *IX* and *XI* can be analyzed. In this case the topological reduction leads to the irreducible core formed by the set of cyclobutadiene skeleton bonds ($\pi_{36}, \pi_{45}, \pi_{34}, \pi_{56}$). The corresponding overlap determinant (11) then implies the opposite parity of the structures *IX* and *XI*.

$$D_{IX \rightarrow XI} = \begin{vmatrix} 1 & 1 \\ 1 & 1 \end{vmatrix}^2 = 0 \quad (11)$$

Despite the above procedure allows to determine the parity of all three structures, it is nevertheless necessary to check the consistency of the above assignment by an independent determination of the parity of structures *X* and *XI* in terms of overlap determinant that describes their mutual transformation.

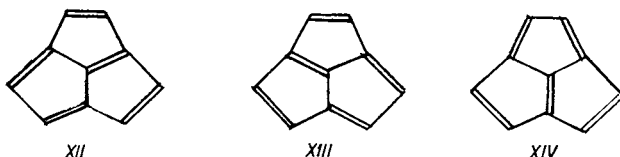
Comparison of both structures shows that the irreducible core contains in this case the set of bonds ($\pi_{23}, \pi_{45}, \pi_{67}, \pi_{81}, \pi_{12}, \pi_{34}, \pi_{56}, \pi_{78}$); the overlap determinant (12) constructed on the basis of this set does confirm the consistency of previous

assignments (Eq. (13)).

$$D_{X \rightarrow XI} = \begin{vmatrix} 1 & 1 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 1 & 1 \\ 1 & 0 & 0 & 1 \end{vmatrix}^2 = 0 \quad (12)$$

$$\begin{aligned} k_X &= k_{IX} \\ k_{XI} &= -k_{IX} \end{aligned} \quad \rightarrow \quad k_X = -k_{IX} \quad (13)$$

Summarizing, of three Kékulé structures *IX–XI*, structures *IX* and *X* are of the same parity while the structure *XI* has the opposite parity. ASC thus equals to 1. The requirement of mutual consistency of the assignment is not a redundant, automatically fulfilled condition but, as shown by the following example, it allows to discover a class of interesting hydrocarbons with the so-called nonseparable structures^{20,21}. In view of theoretical interest in these compounds, let us analyze in more detail the hydrocarbon acepentylene, the structure of which is described by three Kékulé structures *XII*, *XIII* and *XIV* (Scheme 7). The assignment based



SCHEME 7

on comparison of the structures *XII*, *XIII* and *XII*, *XIV* shows that the parity of structures *XIII* and *XIV* is opposite to the parity of structure *XII*. From this result one can expect the overlap determinant which describes nodal properties of *XIII* and *XIV* to be non-zero, in order to ensure the same parity of structures *XIII* and *XIV* (Eq. (14))

$$\left. \begin{aligned} k_{XIII} &= -k_{XII} \\ k_{XIV} &= -k_{XII} \end{aligned} \right\} \quad ? \quad k_{XIII} = k_{XIV} \quad (14)$$

However, the actual value of this determinant assigns the opposite parity to structures *XIII* and *XIV*. This discrepancy indicates that the concept of parity has obviously a more complex internal structure which manifests itself in the case of nonseparable structures. It has not yet been proved whether the phenomenon of nonseparability affects specifically the stability, properties and reactivity of the corresponding hydrocarbons²¹.

CONCLUSIONS

The examples discussed above have shown that the method of overlap determinant is not only a simple and efficient tool for analyzing the chemical reactivity but that this method also proves to be successful in determining the parity of Kékulé structures. It is encouraging that the method reproduces the results of other procedures not only in trivial cases but it describes correctly also specific cases such as are nonseparable structures. From the practical point of view, the proposed procedure can be used as a simple alternative approach for determination of the important characteristics such as ASC, in terms of which the stability of benzenoid and non-benzenoid hydrocarbons can be discussed.

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