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Note

On the Parity of Kekulé Structures

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The notion of the parity of Kekulé structures is discussed. A necessary and sufficient condition for the separability of Kekulé structures into *odd* and *even* is given. It is also shown that there are possible certain molecules with a non-alternant topology, the Kekulé structures of which cannot be separated. The synthesis of such compounds would be of interest.

The fact that for certain polycyclic conjugated molecules more than one structural formula (so called »Kekulé structure«) can be ascribed, has been known for over a century^{1,2}. It has also been known for some time³ that the number of Kekulé structures, K , is in close relation with »unexpected« thermodynamic and chemical stability of these compounds. However, the simple postulate³ that the stability of a conjugated molecule is proportional to its K number leads to false conclusions in many cases, in particular for cyclobutadiene-containing systems.

Some thirty years ago⁴ it was shown that in the case of *alternant* conjugated systems one can introduce the notion of the »parity« of Kekulé structures that is to separate all Kekulé structures of a conjugated molecule in two classes: »odd« and »even«. Thus, the total number of Kekulé structures (K) is equal to the sum of even (K^+) and odd (K^-) Kekulé structures:

$$K = K^+ + K^- \quad (1)$$

Similarly, a new quantity \tilde{K} can also be introduced:

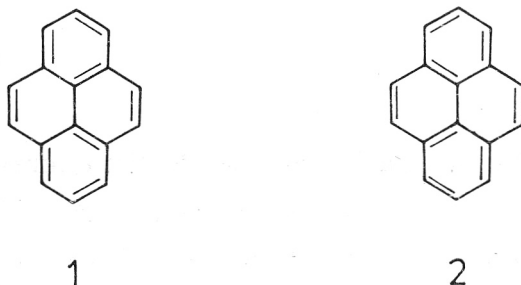
$$\tilde{K} = |K^+ - K^-| \quad (2)$$

\tilde{K} is called the »algebraic structure count« (ACS) by some authors⁵ and »corrected structure count« (CSC) by others⁶. Recent graph-theoretical analysis⁷ of alternant molecules produced a theoretical elucidation for the experimentally observed data that not K , but \tilde{K} determines the thermodynamic⁷ and chemical⁸ behaviour of alternant systems. For example, it is demonstrated⁷ that the total π -electron energy is proportional to $\ln \tilde{K}$.

Although the notion of the parity of Kekulé structures is relatively old⁴, there have been certain difficulties in establishing its theoretical foundation. The original concept⁴, that two Kekulé structures are of the *same* parity if,

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and only if, one structure is obtained from the other by transposing an *odd* number of double bonds, is not applicable in all cases. For example,



nevertheless that the structure 2 is obtained by transposition of 6 (= even) double bonds of 1, both Kekulé structures 1 and 2 are of the same parity.

The extensive use of graph theory in organic chemistry in the last couple of years⁹ made a simple definition of the parity of Kekulé structures possible¹⁰. Kekulé structures and Kekulé graphs⁹ will be denoted by k_a, k_b, k_c, \dots . Let the superposition of k_a and k_b give the graph S_{ab} ¹⁰⁻¹². Let also the number of ring components of the size $4m$ or $0 \pmod{4}$ ^{13,14} in the graph G be $R_o(G)$. Furthermore, let $p_a = +1$ if k_a is an even, and $p_b = -1$ if k_b is an odd Kekulé structure. Then, the equation

$$p_a p_b = (-1)^{R_o(S_{ab})} \quad (3)$$

completely determines the parity of Kekulé structures. Namely, two Kekulé structures k_a and k_b are of the *same* parity if, and only if, $R_o(S_{ab})$ is *even*¹⁰⁻¹².

In Refs. 5-12 and elsewhere, it is tacitly assumed that Eq. (3) can be satisfied for all pairs of k_a, k_b by an appropriate choice of the p_a -values. It will be shown here that this assumption is not generally true. Therefore, it is of interest to determine another necessary and sufficient condition for a set of Kekulé structures to be separable into two classes according their parity. This becomes even more important in the light of recent work on resonance theory, in connection with resonance energies of benzenoid and non-benzenoid π -systems^{15,16}, where it has been shown that a parametrized structure-resonance theory makes use of Kekulé structures of a proper parity *only*.

Since the numbers p_a will not generally exist, the desired condition should be independent of p_a 's. Because of $p_a^2 = 1$, it follows:

$$(-1)^{R_o(S_{ab})} + R_o(S_{bc}) + R_o(S_{ca}) = 1 \quad (4)$$

or

$$R_{abc} = R_o(S_{ab}) + R_o(S_{bc}) + R_o(S_{ca}) = \text{even} \quad (5)$$

Note that R_{abc} is completely determined with the Kekulé structures k_a, k_b , and k_c .

It can be shown without difficulties that if Eq. (5) holds for all R_{abc} 's, it is possible to determine the parity of every Kekulé structure. If, however, there exists at least one triplet of Kekulé structures such that R_{abc} is *odd*, then it is *not* possible to assign the parity to these three structures in a logically coherent way. In order to demonstrate this one should remember that if R_{abc} is *odd* it is either

$$R_o(S_{ab}) = \text{even} \tag{6a}$$

$$R_o(S_{bc}) = \text{even} \tag{6b}$$

$$R_o(S_{ca}) = \text{odd} \tag{6c}$$

or

$$R_o(S_{ab}) = \text{odd} \tag{7a}$$

$$R_o(S_{bc}) = \text{odd} \tag{7b}$$

$$R_o(S_{ca}) = \text{odd} \tag{7c}$$

Other possible cases reduce easily to Eq. (6) or (7). Now, from Eqs. (6a) and (6b) it follows that k_a , k_b , and k_c are of the same parity. However, this is in direct contradiction with Eq. (6c). A similar contradiction can be obtained when an analogous reasoning is applied to Eqs. (7a)—(7c).

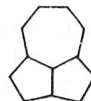
Although the relations (3) and (5) are mathematically equivalent, the latter has the advantage to give a deeper insight into the structural requirements for the separability of Kekulé structures. In Refs. 11 and 12 it was shown that Eq. (3) holds for *all* alternant conjugated molecules. However, an inspection of Eq. (5) shows that the non-alternant conjugated systems can be designed where the Kekulé structures cannot be separated into odd and even structures. In fact, it turns out that such structures *necessarily* contain three fused odd-membered rings. Examples are given in Fig. 1.



K = 3
(3)



K = 4
(4)



K = 3
(5)



K = 4
(6)

Fig. 1. Example of molecules with the non-separable Kekulé structures

The three Kekulé structures of 3 which fulfil the relation $R_{abc} = 3$ (odd), together with the corresponding superposition graphs S_{ab} , S_{bc} , and S_{ca} are presented in Fig. 2.

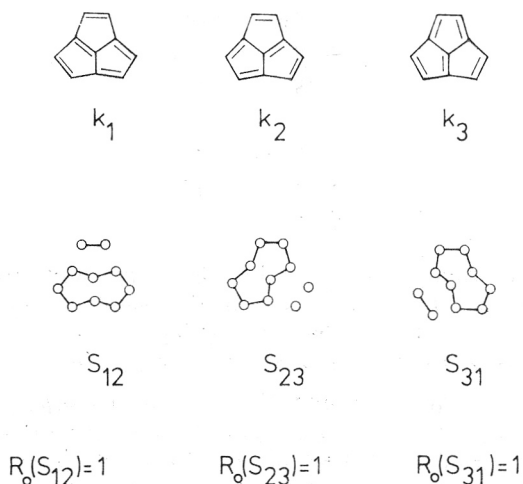
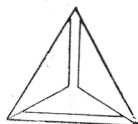


Fig. 2.

It would be of considerable interest to prepare some of these (or similar to these) compounds and to compare their properties with the number of Kekulé structures. In particular, it would be amusing to determine the »experimental«

In \tilde{K} value of such molecules. However, these molecules are expected to exhibit low stability and to be rather reactive compounds. It is interesting to note that the smallest example of this class of conjugated molecules is



although it is not expected to be prepared.

REFERENCES

1. A. Findlay, *A Hundred Years of Chemistry*, Duckworth, London 1948 (second edition).
2. C. R. Noller, *Textbook of Organic Chemistry*, Saunders, Philadelphia 1958 (second edition).
3. G. W. Wheland, *The Theory of Resonance and Its Application to Organic Chemistry*, Wiley, New York 1953.
4. M. J. S. Dewar and C. H. Longuet-Higgins, *Proc. Roy. Soc (London)* A **214** (1952) 482.
5. C. F. Wilcox, Jr., *Tetrahedron Lett.* (1968) 795.
6. W. C. Herndon, *Tetrahedron* **29** (1972) 1.
7. I. Gutman, N. Trinajstić, and C. F. Wilcox, Jr., *Tetrahedron* **31** (1975) 143.
8. C. F. Wilcox, Jr., I. Gutman, and N. Trinajstić, *Tetrahedron* **31** (1975) 147.
9. For review and basic definitions see: I. Gutman and N. Trinajstić, *Fortschr. Chem. Forsch.* **42/2** (1973) 49.
10. A. Graovac, I. Gutman, N. Trinajstić, and T. Živković, *Theoret. Chim. Acta* **26** (1972) 67.

11. I. Gutman and N. Trinajstić, *Croat. Chem. Acta* **45** (1973) 539.
12. D. Cvetković, I. Gutman, and N. Trinajstić, *J. Chem. Phys.* **61** (1974) 2700.
13. M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.* **93** (1971) 6193.
14. I. Gutman and N. Trinajstić, *Scientia Yugosl.* **1** (1974) 1.
15. W. C. Herndon, *J. Amer. Chem. Soc.* **95** (1973) 2404; *ibid.* **96** (1975) 7605.
16. W. C. Herndon and M. L. Ellzey, Jr., *J. Amer. Chem. Soc.* **96** (1975) 6631.

SAŽETAK

O parnosti Kekuléovih struktura

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U ovoj noti se diskutira o parnosti Kekuléovih struktura. Prikazan je potreban i dovoljan uvjet za razdvajanje Kekuléovih struktura na parne i neparne. Pokazano je također da su moguće neke nealternantne konjugirane molekule za koje se Kekuléove strukture *ne* mogu podijeliti po parnosti u dvije grupe. Priprema takovih spojeva i ispitivanje njihovih svojstava bilo bi od značaja za daljnja istraživanja o upotrebljivosti teorije rezonancije u kemiji konjugiranih molekula.

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