

PARITY OF KEKULÉ STRUCTURES REVISITED

Pavel KŘIVKA^a and Nenad TRINAJSTIĆ^b^a *Department of Mathematics, Institute of Chemical Technology, 532 10 Pardubice, Czechoslovakia and*^b *Department of Chemistry, University of South Carolina, Columbia, South Carolina 292 08, U.S.A.*

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A generalized definition of the parity of Kekulé structures is proposed.

In the last decade, several papers have appeared in which the concept of parity of Kekulé structures has been examined¹⁻⁷. The concept of parity is a rather important concept in the parametrized empirical valence-bond theory called structure-resonance theory⁸⁻¹⁶. For the structure-resonance theory to cover the whole set of conjugated structures, the concept of parity must be valid generally¹⁷.

The concept of parity was introduced by Dewar and Longuet-Higgins¹⁸ in their work on the correspondence principle between resonance theory and the MO method. They found that the Kekulé structures of alternant hydrocarbons may be partitioned into two classes of different parity: even and odd. In recent years some authors have tried to generalize the original concept of parity to non-alternant structures^{2-4,19}. In these reports, the original definition of Dewar and Longuet-Higgins¹⁸ (DLH definition) has been over-simplified and unfortunately misinterpreted (see, for example, Gutman and Trinajstić²: „Two Kekulé structures are of the same parity if one structures is obtained from the other by permutation of an odd number of double bonds.”, or Randić³: „Parity is determined by whether the number of permutations of double bonds required to transform one of the structures to the other is even or odd.”). As a result of this misunderstanding, it was deduced that the DLH definition predicts opposite parities for some Kekulé structures of pyrene², contradicting to the view that benzenoid systems all have structures of the same parity.

The original DLH definition¹⁸ is summarized below.

* Permanent address: The Rugjer Bošković Institute, P.O.B. 41001 Zagreb, Croatia, Yugoslavia.

RESULTS

Definition I

Let us number the n atoms ($n = \text{even}$) of an alternant hydrocarbon G in such a way that neither two odd-labelled nor two even-labelled atoms are directly linked. The Kekulé structure $((1, p(2)), (3, p(4)), (5, p(6)), \dots, (2n-1, p(2n)))$ is then defined to be positive or negative if atoms $1, 2, \dots, 2n-1$ are paired with an even or odd permutation of atoms $2, 4, \dots, 2n$ respectively (*i.e.*, if the permutation p is even or odd).

We recall that the permutation p (being even or odd) bears no direct relationship to the number of elements that are permuted. The permutation is even (odd) if and only if it can be obtained as a composition of an even (odd) number of transpositions. Transpositions are similar to "basic permutations", in that they keep all except two adjacent elements fixed, but these two are exchanged. For example, the cyclic permutation of an odd number of elements is always even. Thus, in the case of pyrene we see from Fig. 1 that the first Kekulé structure is given by $((1, 2), (3, 4), (5, 6), \dots, (15, 16))$ and the second by $((1, 6), (3, 2), (5, 4), (7, 8), (9, 10), (11, 16), (13, 12), (15, 14))$, so that the corresponding permutation is $p = (6, 2, 4, 8, 10, 16, 12, 14)$. It is composed from two cyclic permutations $(6, 2, 4)$ and $(16, 12, 14)$ while elements 8 and 10 are fixed.

p is thus an even permutation and both structures are of the same parity, as expected. We note that the assignment of a positive or negative value to one class of parity is arbitrary, because it depends on the initial numbering.

For alternant hydrocarbons (AHs) the following proposition holds.

Proposition 1

The DLH relationship to be of the same parity, defined for the set of all Kekulé structures by definition I, is equivalence relationship (*i.e.*, it is reflexive, symmetric, and transitive) and the set of Kekulé structures of a given AH splits up into exactly two classes of equivalence.

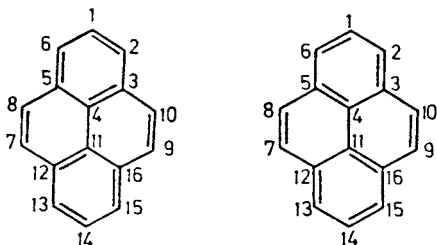


FIG. 1
Kekulé structure of pyrene

Proof

Reflexivity is trivial. Symmetricity follows from the fact that if p is an even (odd) permutation, so is p^{-1} (inverse permutation). Transitivity: Let K_a, K_b, K_c be three Kekulé structures of the same AH, with K_a and K_b , and K_b and K_c having the same parity. As K_a and K_b are of the same parity, K_b can be obtained from K_a by means of an even permutation p , and by the same reasoning K_c can be obtained from K_b by means of an even permutation p' . But the composition of two even permutations is itself an even permutation, so that K_a and K_c are again of the same parity. The last part of the proposition follows from the fact that each permutation has to be either even or odd (there is no other possibility), and composition of any two odd permutations is an even permutation.

On the basis of the seeming objections against the original DLH definition, a new definition has been proposed^{2,4}. Let us remind the reader that the Kekulé structures of a given conjugated molecule may be represented by Kekulé graphs^{19,20}. Kekulé graphs are isomorphic with 1-factors of a graph²¹.

Definition II

Two different Kekulé structures (1-factors) of a given polycyclic conjugated molecule (general graph G) are of the same parity if the number of the $4n$ -membered rings in their superposition graph is even.

This definition may be analyzed in the following way. Let the Kekulé structures and the corresponding Kekulé graphs be denoted by $K_a, K_b, \dots, K_n$ and $k_a, k_b, \dots, k_n$, respectively. Let the superposition of k_a and k_b give the graph G_{ab} . Let also the number of cycles (circuits) of length $4n$ (cyclic components of size $4n$, $n = 1, 2, \dots$) in the graph G be $R_{4n}(G)$. 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 relationship

$$p_a p_b = (-1)^{R_{4n}(G_{ab})} \quad (1)$$

determines the parity of the Kekulé structures. Thus, two Kekulé structures are of the same (opposite) parity if and only if $R_{4n}(G_{ab})$ is even (odd).

Proposition 2

For AHs, definition I and definition II are equivalent.

Proof

First note, that if K_b is obtained from K_a by means of just one cyclic permutation then their superposition is just one ring (this ring is of length $4n$ if the number of permuted elements is even, *i.e.* the permutation is odd, and of length $4n + 2$ if the number

of permuted elements is odd, *i.e.* the permutation is even). Recall also that any permutation can be obtained as a combination of cyclic permutations. Now let the Kekulé structure K_b be obtained from K_a by means of an even (odd) permutation p . This can be generally decomposed into several cyclic permutations of an odd number of elements (as these permutations are even), and an even (odd) number of cyclic permutations of an even number of elements. This means that the superposition of k_a and k_b gives several $4n + 2$ rings and an even (odd) number of $4n$ rings, *q.e.d.*

Hence, there are no problems with the definition of parity for Kekulé structures of alternant hydrocarbons.

We now investigate the generalization of the notion of parity of Kekulé structures to non-alternant hydrocarbons (NHs), or in graph theoretical language^{22,23} to all graphs having 1-factors. Thus, we attempt to define a relationship to be of the same parity for the set of all 1-factors (Kekulé structures) of a given planar graph (conjugated hydrocarbon). Thus, this relationship should be transitive and, of course, reflexive and symmetric (equivalence), since only then will the set of Kekulé structures split up into several classes of equivalence. When we have exactly two such classes we denote one of them by K^+ and the second by K^- , following the suggestion by Dewar and Longuet-Higgins. Thus, the total number of Kekulé structures K is equal to the sum of positive (even) and negative (odd) Kekulé structures,

$$K = K^+ + K^- \quad (2)$$

Similarly, the difference between even and odd Kekulé structures is introduced as the algebraic structure count,^{24,25} ACS , or the corrected structure count^{1,26} CSC ,

$$ASC = K^+ - K^- ; \quad K^+ < K^- \quad (3)$$

Unfortunately, neither definition I nor definition II can be used as a basis for the required generalization. Definition I cannot be used at all, because for NHs the desired labelling does not generally exist. Definition II can be extended to include NHs, but does not lead to equivalence.

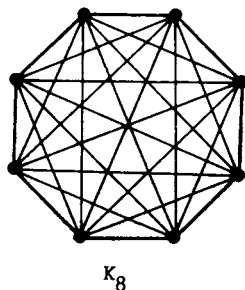
Proposition 3

The relationship to be of the same parity defined by the definition II is not transitive for the set of all graphs having 1-factors.

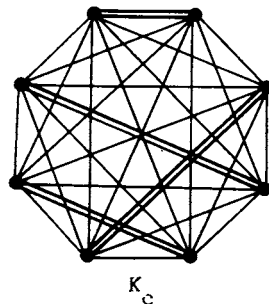
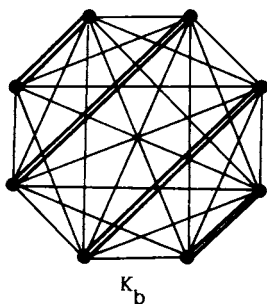
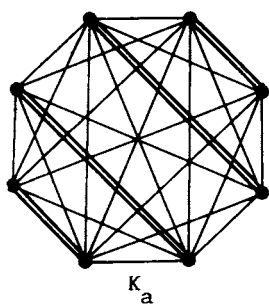
Proof

We will show that there exists a graph and its three 1-factors k_a, k_b, k_c such that

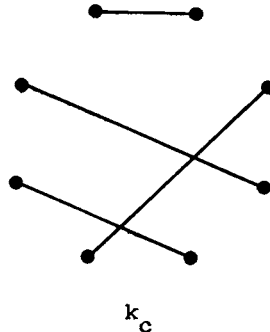
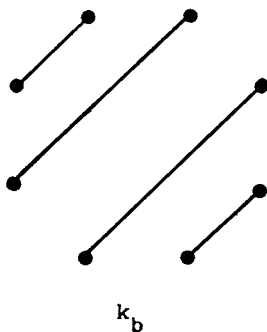
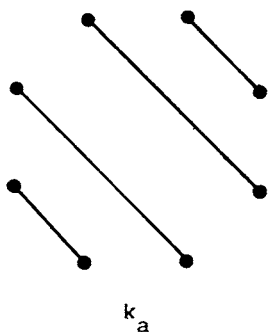
k_a and k_b are of the same parity, k_b and k_c are of the same parity, but k_a and k_c are opposite parity. Let us take K_8 (a complete graph on eight vertices)²⁷:



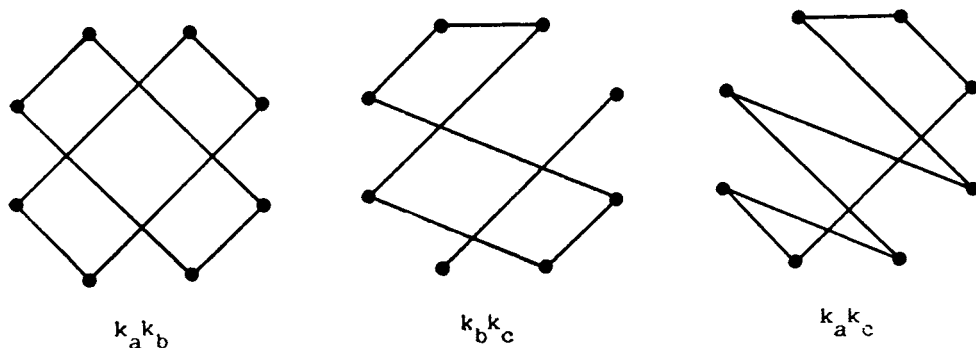
As an abstract structures, we can create among many the following three Kekulé structures of K_8 :



whose corresponding Kekulé graphs (1-factors) are given below:



For their superpositions we obtain the following structures:



In the superposition of k_a and k_b two $4n$ ($n=1$) rings are present, whilst in $k_a k_c$ there is one $4n$ ($n=2$) ring. The superposition structure $k_b k_c$ does not contain $4n$ rings.

The only remaining possibility of formulating a general definition of parity to include non-alternant hydrocarbons is to investigate the simplified DLH definition^{2,4}. Why does it fail in the case of pyrene²?

When we look at two Kekulé structures of pyrene in Fig. 1, we see that the permutation of bonds can be performed in two independent steps: first we permute three bonds in the upper hexagon and then three bonds in the lower hexagon. Since both of these operations are parity preserving, it is natural to assume that their composition should also be parity preserving. The above may be rephrased as follows: Even if we have permuted an even number of bonds, the original and final Kekulé structures are of the same parity, providing we can perform the permutation in several independent steps, each of them involving an odd number of bonds.

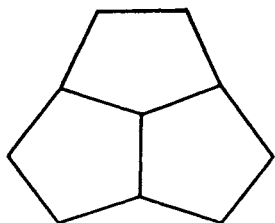
From the above considerations, we propose a general definition as follows:

Definition III

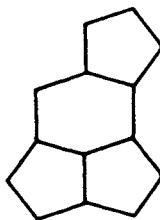
Two different Kekulé structures K and K' of a conjugated molecule (graph) G are said to be of the same parity if there exists a sequence $K_1, K_2, \dots, K_n$ of Kekulé structures of G such that $K = K_1$ and $K' = K_n$ and for every $i = 1, 2, \dots, n-1$ the number of transpositions of double bonds required to transform K_i into K_{i+1} is odd. Otherwise, K and K' are said to be of different parity.

The relationship to be of the same parity, according to Definition III, is transitive (*i.e.* equivalence), without any internal inconsistencies, and is applicable to any graph G having 1-factors. (It is therefore applicable to any conjugated system that possesses Kekulé structures).

There is also the question of there being more than just two classes of parity to be considered⁴. Examples of such molecules are tricyclic systems with fused odd-membered rings² such as acepentylene(I) or polycyclic systems with fused rings such as ace-as-indacene (II).

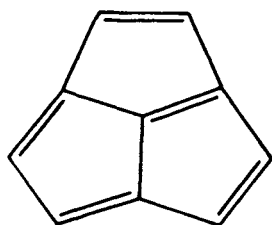
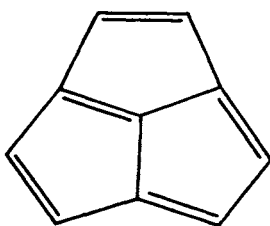
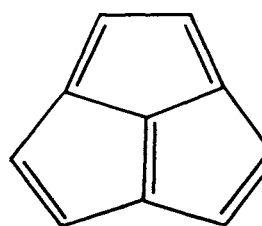


I

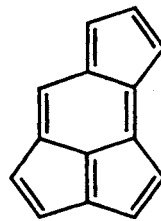
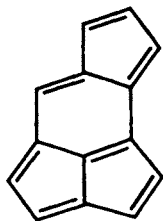
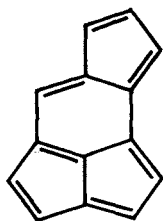


II

In such cases we could either include complex numbers and deal with several different parities (*e.g.*, the roots of the equation $x^n = -1$) or abandon the concept of parity completely²⁸. Actually, in the case of acepentylene, its three Kekulé structures (see below) are equivalent (since they can be obtained one from another by turning around the central point for 120°). But, there already are some other molecules possessing Kekulé structures of different parity in spite of their equivalency, *e.g.* cyclobutadiene and pentalene.

 K_a  K_b  K_c

In the case of ace-as-indacene, the Kekulé structures are even non-symmetric⁴.



It is easy to see that the first structure can be transformed to the second one by permuting the even number (4) of double bonds, the second one to the third again by permuting the even number (6) of double bonds and the third one to the first one also by permuting the even number (6) of double bonds. So there is no contradiction but in spite of internal consistency we have three classes of different parity.

There is another definition of the parity of Kekulé structures available in the literature³. However, this is actually the definition of the parameter called the algebraic circuit count, *ACC*, attributed to individual Kekulé structures, not a relationship definition. The parameter *ACC* of an individual Kekulé structure represents the sum of the $(4m + 2)$ - and $(4m)$ -conjugated circuits^{19,29-36} belonging to this valence structure. Each $(4m + 2)$ -conjugated circuit contributes +1 to *ACC*, while each $(4m)$ -conjugated circuit contributes -1.

For example, for each Kekulé structure of acepentylene, $ACC = -2$. Randić's *ACC* parameter is also invariant under a symmetry operation but does not possess the generality of definition III, i.e., it is not applicable to graphs with 1-factors outside the set of graphs representing polycyclic conjugated molecules. However, it is sufficient for applications to the chemistry of conjugated structures.

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REFERENCES

1. Herndon W. C.: *Tetrahedron* 29, 3 (1973).
2. Gutman I., Trinajstić N.: *Croat. Chem. Acta* 47, 35 (1975).
3. Randić M.: *Mol. Phys.* 34, 849 (1977).
4. Gutman I., Randić M., Trinajstić N.: *Rev. Roum. Chim.* 23, 383 (1978).
5. El-Basil S.: *Math. Chem. (Mülheim/Ruhr)* 13, 199 (1982).
6. Gutman I.: *Math. Chem. (Mülheim/Ruhr)* 14, 139 (1983).
7. Živković T. P.: *Croat. Chem. Acta* 56, 525 (1983).
8. Herndon W. C.: *J. Amer. Chem. Soc.* 95, 2404 (1973).
9. Herndon W. C.: *Thermochim. Acta* 8, 225 (1974).
10. Herndon W. C.: *J. Chem. Educ.* 51, 10 (1974).
11. Herndon W. C., Ellzey M. L. jr: *J. Amer. Chem. Soc.* 96, 6631 (1974).
12. Swinborne-Sheldrake R., Herndon W. C., Gutman I.: *Tetrahedron Lett.* 755, (1975).
13. Herndon W. C.: *J. Amer. Chem. Soc.* 98, 887 (1976).
14. Herndon W. C., Párkányi C.: *J. Chem. Educ.* 53, 689 (1976).
15. Herndon W. C.: *Isr. J. Chem.* 20, 270 (1980).
16. Herndon W. C.: *J. Phys. Chem.* 85, 3041 (1981).
17. Randić M., Rushchic B., Trinajstić N.: *Croat. Chem. Acta* 54, 275 (1981).
18. Dewar M. J. S., Longuet-Higgins H. C.: *Proc. Roy. Soc. (London) A* 214, 482 (1962).

19. Trinajstić N.: *Chemical Graph Theory*, Vol. II, Chapter 2. CRC Press, Boca Raton, Florida 1983.
20. Cvetković D., Gutman I., Trinajstić N.: *Chem. Phys. Lett.* **16**, 614 (1972).
21. Harary F.: *Graph Theory*, Addison-Wesley Reading, second printing, p. 84. Massachusetts, 1971.
22. Gutman I., Trinajstić N.: *Topics Curr. Chem.* **42**, 49 (1973).
23. Trinajstić N.: *Chemical Graph Theory*, Vol. I, CRC Press, Boca Raton, Florida, 1983. Chapters 1 and 2.
24. Wilcox C. F. jr: *Tetrahedron Lett.* **795** (1968).
25. Wilcox C. F. jr: *J. Amer. Chem. Soc.* **91**, 2732 (1969).
26. Knop J. V., Trinajstić N., Živković T.: *This Journal* **39**, 2431 (1974).
27. Ref. 1, p. 16.
28. Randić M.: Private communication.
29. Radić M.: *Chem. Phys. Lett.* **38**, 68 (1976).
30. Randić M.: *J. Amer. Chem. Soc.* **99**, 444 (1977).
31. Randić M.: *Tetrahedron* **33**, 1905 (1977).
32. Graovac A., Gutman I., Randić M., Trinajstić N.: *This Journal* **43**, 1375 (1978).
33. Randić M.: *J. Phys. Chem.* **86**, 3970 (1982).
34. Seibert J., Trinajstić N.: *Int. J. Quantum Chem.* **23**, 1829 (1983).
35. Ref. 19, Chapter 3.
36. Randić M., Trinajstić N.: *J. Amer. Chem. Soc.*, in press.