Graph Theory and Molecular Orbitals. VIII[1]. Kekulé Structures and Permutations

I. Gutman and N. Trinajstić

Institute, »Ruđer Bošković«, P. O. B. 1016, 41001 Zagreb, Croatia, Yugoslavia

Received September 10, 1973

The relation between Kekulé structures and permutations is discussed. It is shown that Kekulé structures are permutations and that their number in alternant hydrocarbons is equal to the square root of the total number of permutations contained in the molecular graph.

As simple special cases of this result the Dewar-Longuet-Higgins equation[2] and the relation between the permanent of the adjacency matrix and the number of Kekulé structures[3] are obtained.

Generalizations for nonalternant hydrocarbons are also given.

INTRODUCTION

It has been shown in the preceeding papers of this series[1,4] that graph theory is a suitable mathematical technique for the study of electronic properties of conjugated systems.

The relation between the molecular orbital theory and the valence bond theory was established some 25 years ago[5] and thereafter numerous other results in this direction have been obtained[2,6]. In recent years a new impetus is given to these investigations due to an icreased interest for both simple molecular-orbital theory and valence-bond theory[7]. Namely, the Hückel and resonance theory are in fact both topological approximations where the application of graph theory can be justified[8].

A directed graph can be related to a conjugated molecule[4e] when carbon atoms are represented as small circles (vertices) and a pair of opposite oriented lines (edges) are drawn between two circles if and only if the corresponding atoms are connected. For example, the following directed graps I, II, and III are the representations of butadiene, fulvene, and benzene, respectively:


I II III
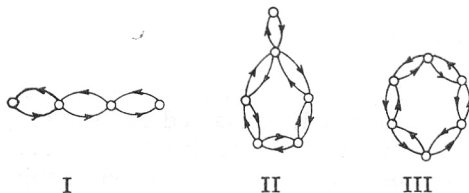
The adjacency matrix $\mathbf{A}(G) = \mathbf{A}$ of the graph G is defined as

$$A_{pq} = \begin{cases} 1 & \text{if there is a direct edge from p towards q} \\ 0 & \text{if there is not} \end{cases} \tag{1}$$

According to the above definition the adjacency matrix of the molecular graph is necessarily symmetric, *i. e.*

$$\mathbf{A} = \mathbf{A}^T \tag{2}$$

However, subgraphs of G do not need to possess both opposite directed edges at the same time. Thus, for example, IV and V are the subgraphs of the fulvene graph II:


IV   V
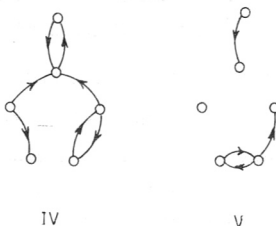
We are interested here only in subgraphs which contain all the vertices of the graph. The number of vertices in the graph G (and in all considered subgraphs) is N. We suppose that N is even since this is a necessary condition for the existence of at least one Kekulé structure in the corresponding molecule.

If the conjugated molecule is alternant, the related graph is bipartite[5a,9]. The starred vertices will be numbered with $1, 2, \ldots, u$ and the unstarred with $u + 1, u + 2, \ldots, u + v$ $(u + v = N)$. Then the adjacency matrix is of the form

$$\mathbf{A} = \begin{pmatrix} \mathbf{O} & \mathbf{B} \\ \mathbf{B}^T & \mathbf{O} \end{pmatrix} \tag{3}$$

We define a *starred Kekulé graph* as a subgraph of G with the property that only one edge starts from every starred vertex and only one ends at every unstarred one. The *unstarred Kekulé graph* is defined similarly, however, the edges start from unstarred and end at starred vertices.

For example, the benzene graph III has the following Kekulé graphs:

starred Kekulé graphs   unstarred Kekulé graphs   starring convention
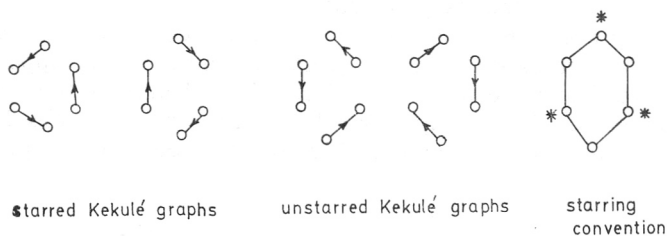
Let K be the number of Kekulé structures of the molecule. It is evident that there are exactly K starred and K unstarred Kekulé graphs of the molecular graph; they will be denoted by k_j^* and k_j^o $(j = 1, 2, \ldots, K)$. k_j^* and k_j^o are directed graphs and correspond to an undirected graph k_j.

The adjacency matrices of Kekulé graphs (which are obviously not symmetric) are of the form

$$\mathbf{A}(k^*) = \begin{pmatrix} \mathbf{O} & \mathbf{B}(k) \\ \mathbf{O} & \mathbf{O} \end{pmatrix} \quad \mathbf{A}(k^o) = \begin{pmatrix} \mathbf{O} & \mathbf{O} \\ \mathbf{B}(k)^T & \mathbf{O} \end{pmatrix} \tag{4}$$

Since there is just one unit in every row and every column of $\mathbf{B}$ (k) it is a permutation matrix. Therefore, every Kekulé graph can be considered as a permutation of N/2 elements.

However, there exists one less trivial relation between Kekulé graphs and permutations. We define[10] a (directed) Sachs graph as a subgraph of G with the property that one edge starts from and one edge ends at every vertex of G. For example, the graph III has the following four Sachs graphs:
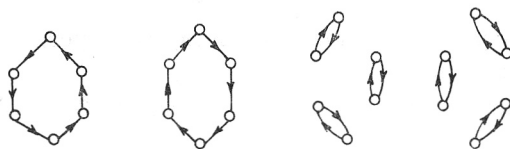
We will use the following notation. A Sachs graph is denoted as s. The set of Sachs graphs of the graph G is S (G) = S. The number of elements in S (G), or the number of Sachs graphs for a given graph G, is $|S|$. The number of components, or disconnected islands, of s is c (s) and among them there are r_{4m} (s) (4m)-membered cycles. The subset of S containing Sachs graphs with at least one odd-memberd cycle is S_{odd}. Evidently, $S_{odd} = \emptyset$ for bipartite graphs.

Note that in Ref. 4, where undirected graphs have been considered, the definition of Sachs graph is different.

Sachs graphs are the graphical representation of permutations. In order to realize this one should remember that a permutation is defined[11] as a one-to-one mapping of a set into itself. In the Sachs graph vertices represent the elements of the set and edges indicate the mapping. Thus if s ∈ S (G) we say that the permutation s is contained in the graph G.

BASIC THEOREMS

For bipartite graphs there is a relation between the permutations and the Kekulé structures.

Theorem 1

The number of permutations contained in a (bipartite) graph is equal to the square of the number of Kekulé structures of the corresponding molecule, i. e.

$$|S| = K^2 \tag{5}$$

In order to show this we will prove a more general statement.

It is obvious from (4) that the matrix $\mathbf{M} = \mathbf{A}(k^*) + \mathbf{A}(k^0)$ is an adjacency matrix, say of the graph h, because $M_{pq} = 1$ or 0. Therefore, let be $h = k^* + k^0$ if and only if $\mathbf{A}(h) = \mathbf{A}(k^*) + \mathbf{A}(k^0)$.

Theorem 2

Every $k_i^* + k_j^0$ is a Sachs graph. For a given s of a bipartite graph there are exactly one k^* and one k^0, and *vice versa*. I. e. there is a unique correspondence as

$$s_{ij} = k_i^* + k_j^0$$

Besides, $s_{ij} \neq s_{ji}$ for $i \neq j$.

Note that this implies *Theorem 1*. There are K^2 different graphs of the form $k_i^* + k_j^o$. Hence, eq. (5) follows from *Theorem 2*.

Proof

From eq. (4)

$$A(h) = \begin{pmatrix} O & B(k^*) \\ B(k^o) & O \end{pmatrix} \qquad (7)$$

Since $B(k)$'s are permutation matrices $A(h)$ is a permutation matrix too. Thus h is a Sachs graph.

Since G is bipartite graph every graph from S(G) is bipartite also. Therefore from (3)

$$A(s) = \begin{pmatrix} O & C(s) \\ D(s) & O \end{pmatrix} \qquad (8)$$

C and D are necessarily permutation matrices. The »starring process« in bipartite graphs is unique (except that the symbols * and ^{o} can be interchanged) hence (8) is unique and the two Kekulé graphs are uniquely defined by $B(k^*) = C(s)$ and $B(k^o) = D(s)$. This completes the proof of the *Theorem 2*.

APPLICATIONS

It can be demonstrated[1] that *Theorem 1* is the basis for every case of congruity between simple valence bond and molecular-orbital theory. Here we would like to show that the Dewar-Longuet-Higgins formula[2]

$$\det A = (-)^{N/2}(K^+ - K^-)^2 \qquad (9)$$

is a simple corrolary of eq. (5). To do this one should remember that Sachs established[10] that

$$\det A = \sum_{s \in S} (-)^{c(s)} \qquad (10)$$

According to *Theorem 2* and eq. (10)

$$\det A = \sum_{i=1}^{K} \sum_{j=1}^{K} (-)^{c(k_i^* + k_j^o)} \qquad (11)$$

and if a »parity« P_j is attributed to every Kekulé structure k_j such that $P_j = +1$ or -1 and $(-)^{c(k_{1}^* + k_j^o)} = (-)^{N/2}P_iP_j$ eq. (9) follows, where K^+ and K^- are the numbers of »even« ($P_j = +1$) and »odd« ($P_j = -1$) Kekulé structures ($K^+ + K^- = K$). Thus

$$\left| \sum_{i=1}^{K} P_i \right| = |K^+ - K^-| \qquad (12)$$

It is, however, rather difficult to determine the parity of a Kekulé structure using the method of Dewar and Longuet-Higgins[2]. In order to overcome this difficulty a set of rules has been given by Wilcox[12] covering several special types of molecules of interest in chemistry. We show here that there exists a very simple procedure for obtaining the P_j-values. The idea of this algorithm has been first given in Ref. 4a.
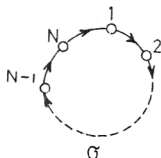
Theorem 3

If the Kekulé structures k_i and k_j are of the same parity the Sachs graph $s_{ij} = k_j{}^* + k_j{}^o$ contains even number of $(4m)$-membered **cycles**, *i. e.*

$$P_i P_j = (-)^{r_{4m} (k_i^* + k_j^o)} \qquad (13)$$

Proof

Let σ be a N-membered (directed) cycle.

Decompose σ by deleting edges in such a way that the remaining subgraph is a Kekulé graph. If N is even* the obtained Kekulé graph possesses N/2 components. Thus, the decomposition of a $(4m + 2)$-membered cycle will not alter the parity of the number of components while the decomposition of a $(4m)$-cycle will. Since every Sachs graph (of a bipartite graph) can be in the above manner decomposed to Kekulé graphs, it follows

$$(-)^{c(s)} = (-)^{N/2} (-)^{r_{4m}(s)} \qquad (14)$$

Applying *Theorem 2* and using the definition of P_j the *Theorem 3* follows.

Theorem 3 is the basis of the following simple algorithm: if the figure obtained by superposition of the double bonds in two Kekulé structures contains an even (odd) number of $(4m)$-membered **rings** the Kekulé structures have the same (opposite) **parity**.

Example
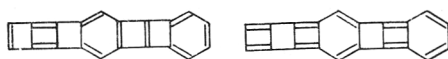
k_1 k_2

the superposition figure s

k_1 and k_2 are of the same parity since $r_{4m}(s) = 2$.

The application of eq. (9) for predicting chemical behaviour is discussed in details elsewhere[4b,12].

A corrolary of *Theorem 3* is that in the following formula:

$$(-)^{N/2} \det \mathbf{A} \leqslant K^2 \qquad (15)$$

* If N is odd it is, of course, not possible to obtain a Kekulé graph. This is the reason why Theorem 1 holds for bipartite graphs only.

the equality holds if and only if it is r_{4m} (s) $= 0$ for all s $\in$ S. In Ref. 1 it has been shown that the latter is fulfilled for a rather wide class of graphs including graphs of benzenoid hydrocarbons.

The relation between the permanent of the adjacency matrix[13] and the number K can be obtained quite easily from (5). A reasoning similar to that which has been used in Ref. 10 in order to obtain eq. (10) leads to

$$\text{per } \mathbf{A} = \sum_{s \in S} (+)^{c(s)} = |\,S\,| \tag{16}$$

Hence, from (5)

$$\text{per } \mathbf{A} = K^2 \tag{17}$$

This equation was proved without the knowledge of eq. (5) in Ref. 3. Recently a novel proof of (17) was presented in a paper of Lee, Herndon and Phan[14].

A procedure which is similar to one given in the present paper leads to the generalization of eq. (5) for nonalternant hydrocarbons[15]:

$$|\,S\,| - |\,S_{\text{odd}}\,| = K^2 \tag{18}$$

Then, a completely analogous consideration gives

$$\det \mathbf{A} = (-)^{N/2} (K^+ + K^-)^2 + \sum_{s \in S_{\text{odd}}} (-)^{c(s)} \tag{19}$$

$$\text{per } \mathbf{A} = K^2 + |\,S_{\text{odd}}\,| \tag{20}$$

REFERENCES

1. Part VII: D. C v e t k o v i ć, I. G u t m a n, and N. T r i n a j s t i ć, *J. Chem. Phys.* in press.
2. M. J. S. D e w a r and H. C. L o n g u e t - H i g g i n s, *Proc. Roy. Soc. Ser. A* **214** (1952) 482.
3. D. C v e t k o v i ć, I. G u t m a n, and N. T r i n a j s t i ć, *Chem. Phys. Lett.* **16** (1972) 614.
4. a) Part I: A. G r a o v a c, I. G u t m a n, N. T r i n a j s t i ć and T. Ž i v k o v i ć, *Theor. Chim. Acta* **26** (1972) 67; b) Part II: D. C v e t k o v i ć, I. G u t m a n, and N. T r i n a j s t i ć, *Croat. Chem. Acta* **44** (1972) 365; c) Part III: I. G u t m a n and N. T r i n a j s t i ć, *Chem. Phys. Lett.* **17** (1972) 535; d) Part IV: I. G u t m a n and N. T r i n a j s t i ć, *Croat. Chem. Acta* **45** (1973) 257; e) Part V: I. G u t m a n and N. T r i n a j s t i ć, *Chem. Phys. Lett.* **20** (1973) 257; f) Part VI: I. G u t m a n, N. T r i n a j s t i ć, and T. Ž i v k o v i ć, *Tetrahedron* **29** (1973) 3449.
5. a) C. A. C o u l s o n and H. C. L o n g u e t - H i g g i n s, *Proc. Roy. Soc. Ser. A* **192** (1947) 16; b) H. C. L o n g u e t - H i g g i n s, *J. Chem. Phys.* **18** (1950) 265.
6. a) N. S. H a m, *J. Chem. Phys.* **29** (1958) 1229; b) E. H e i l b r o n n e r, *Helv. Chim. Acta* **45** (1962) 1722; c) Extensive bibliography is given by J. R. P l a t t in *Encyclopedia of Physics*, Vol. 37, ed. by. S. F l ü g g e, Springer-Verlag, Berlin 1961.
7. *e. g.* H. H o s o y a, *Bull. Chem. Soc. Japan* **44** (1971) 2332; *Theor. Chim. Acta* **25** (1972) 215; W. C. H e r n d o n, *J. Amer. Chem. Soc.* **95** (1973) 2404; *J. Chem. Educ.* in press.
8. For details of graph theory and further references see: I. G u t m a n and N. T r i n a j s t i ć, *Fortschr. Chem. Forsch.* **42** (1973) 49.
9. C. A. C o u l s o n and G. S. R u s h b r o o k e, *Proc. Cambridge Phil. Soc.* **36** (1940) 196.
10. H. S a c h s, *Publicationes Mathematicae (Debrecen)* **11** (1963) 119.
11. *e. g.* J. R i o r d a n; *An Introduction to Combinatorial Analysis*, Wiley, New York 1958.
12. C. F. W i l c o x, *Tetrahedron Lett.* (1968) 795. This work was later extended to nonalternant hydrocarbons in a work which has appeared in *J. Amer. Chem. Soc.* **91** (1969) 2732.

13. For the definition of the permanent see Refs. 3 and 8 or M. M a r c u s and H. M i n c, *Amer. Math. Monthly* **72** (1965) 577.
14. M. A. L e e, W. C. H e r n d o n, and V. T. P h a n, *Acta Math.* in press.
15. I. G u t m a n, *Thesis,* University of Zagreb (1973).

IZVOD

Teorija grafova i molekularne orbitale. VIII. Kekuléove strukture i permutacije

I. Gutman i N. Trinajstić

Analiziran je odnos između Kekuléovih struktura i permutacija i pokazano je da su Kekuléove strukture permutacije te da je njihov broj u alternantnim ugljikovodicima jednak drugom korijenu ukupnog broja permutacija sadržanih u molekularnom grafu. Kao jednostavni posebni slučajevi dobijena je formula Dewar-Longuet-Higginsa i odnos između permanente matrice susjedstva i broja Kekuléovih struktura. Također je dano i poopćenje za nealternantne ugljikovodike.