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Original Scientific Paper

Graph Theory and Molecular Orbitals. II*

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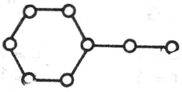
The total π-electron energy and chemical stability of conjugated hydrocarbons are discussed using the graph theoretical approach. A number of original theorems are presented and their relation with HMO theory is given. The main conclusion of this work is that some molecular properties can be obtained in a simple manner by inspection of the molecular topology.

The intimate relationship between HMO theory and Graph theory (GT) is now well known[1-3]. The mathematical apparatus of GT enables us to derive many useful *general* results of the HMO theory, and make in some cases direct calculation unnecessary. We will discuss some of this results from the point of view of *applicability of GT in chemistry.* More details about the algebra used are given earlier[3,4].

A binary relation on a (finite) set can be represented graphically as a *graph* if we draw the elements of the set as small circles (»vertices«)** and connect two vertices by a line (»edge«) only when the considered relation holds[5]. One property of molecules seems to be very closely to a binary relation, that is — two atoms in a molecule are either bonded or not bonded. Therefore, molecules can be represented by graphs when the only property considered is the existence or not of a chemical bond between two atoms. All other molecular properties (*e. g.* geometry, symmetry, type of bonding) are neglected. Especially, when GT is applied to HMO theory, we also neglect all bonds except carbon-carbon σ-bonds. So, for example, the graph representation of styrene is:



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* Part I: A. Graovac, I. Gutman, N. Trinajstić, and T. Živković, *Theoret. Chim. Acta* **26** (1972) 67.

** In Ref. 4 we did not use completely satisfactory terms »node«, »Spectre«, »partial subgraph« and »bichromatic graph«. Here and later we will use the generally adopted nomenclature[5] »vertex«, »spectrum«, »subgraph« and »bipartite graph.«

When graph representation is used, atoms are called »vertices« and bonds »edges« of the graph.

The *vertex adjacency matrix* A of the graph, defined as:

$$A_{pq} = \begin{cases} 1 & \text{if there is an edge between the vertices } p \text{ and } q \\ 0 & \text{if there is not} \end{cases} \qquad (1)$$

is related with the HMO Hamiltonian by:

$$H = \alpha I + \beta A \qquad (2)$$

where I is a unit matrix, α and β being the Coulomb and resonance integrals.

The left-hand side of the secular equation:

$$\det | H - E S | = 0 \qquad (3)$$

is a polynomial of x:

$$P_G(x) \equiv \det | x I - A | = \sum_{n=0}^{N} a_n x^{N-n} \qquad (4)$$

where

$$-x = \frac{E - \alpha}{\beta}, \quad S = I$$

and N is the number of vertices in the graph. (In the present work it is always assumed that N is even, therefore radicals are not considered here.)

The set of all roots of the polynomial $P_G(x)$ is called »the spectrum« of the graph.

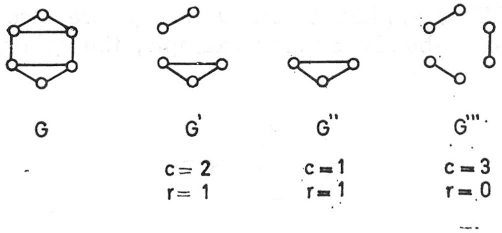
The coefficients a_n of the polynomial (4) can be calculated using a theorem originally given by Sachs[6,7]:

$$a_n = \sum_{s \varepsilon S_n} (-)^{c(s)} 2^{r(s)} \qquad (5)$$

$$a_0 = 1$$

where s is a Sachs graph and S_n is the set of all Sach graphs with n vertices contained in the considered graph. A Sachs graph s is defined as a subgraph* of the graph which possess only rings and complete graphs with two vertices as components. Then the total number of the components is c(s) and the number of rings is r(s).

Thus, for example, G′, G″, and G‴ are Sachs graphs of the graph G:



A Sachs graph without any ring we call »Kekulé graph«.

Because of eq. (2) all information which can be obtained from HMO theory are contained in the graph of the molecule. This gives us hope that some mo-

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* See remark about the graph terminology on page 365.

lecular properties are in a *simple* way determined by molecular topology and can be obtained by inspection of the graph. The most important properties of conjugated hydrocarbons which can be obtained using GT are

— total π-electron energy (E_π)
— chemical stability

There is no unambiguous deffinition of chemical stability because this concept is an intuitive one.

E_π correlates *in most cases* with stability, having higher values for more reactive molecules.

Chemical stability has a kinetic background and the energy difference between highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) reflects the capability of a molecule to react[8]. Specially when this difference is zero, a triplet degenerate ground state and extreme instability is to be expected. Of course, the degenerate states are forbidden because of Jahn-Teller theorem[9], and such molecules either do not exist or are to a large extent nonplanar (and thus HMO theory is not applicable). Chemical stability includes the stability of the whole molecule, and other effects (*e. g.* steric effects) are to be considered separately.

For reasons which will be explained later we will consider separately alternant hydrocarbons (AH) and non-alternent hydrocarbons (NAH).

Alternant Hydrocarbons (AH)

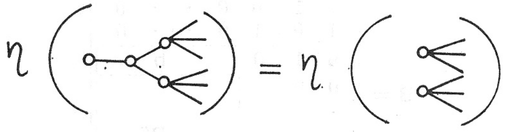
Because of the pairing theorem[10,11] there is an even number of zero's in the spectrum of AH. As a proper consequence of the pairing theorem (if there appears at least one zero in the spectrum), the ground state is degenerate because the nonbonding MO's (NBMO) play the role of the HOMO's[12]. Hence, the problem of the number of zero's in the spectrum of an AH is directly connected with chemical stability.

We will denote the number of zero's in the spectrum of the graph G as η (G).

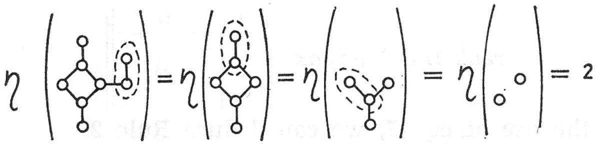
Using graph theoretical considerations a set of simple rules can be derived which enables us to determine η for a wide class of molecules. Proofs will be given only briefly, more details can be found in Ref. 3 and 4.

Rule 1

If there is a vertex of degree *one* (that is a vertex with only one neighbour), we can remove this vertex and its neighbour and all adjacent edges without changing the value of η:



Example



Proof

The vertices of a bipartite graph (alternant hydrocarbon) can be numbered so that the adjacency matrix has the following form:

$$A = \left\| \begin{array}{cc} O & B \\ B^T & O \end{array} \right\| \cdot \tag{6}$$

On the main diagonal there are square matrices and B is the adjacency matrix between two groups of vertices of the AH. It has been proved[12] that the relation

$$\eta(G) = N - 2 \text{ rank } B \tag{7}$$

holds.

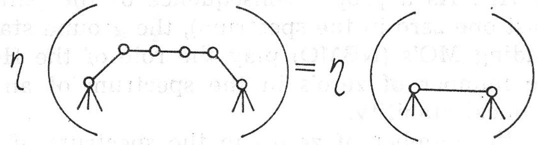
In our case the matrix B is of the form

$$B = \left\| \begin{array}{c|c} 1 & b \\ \hline 0 & \\ \cdot & \\ \cdot & B' \\ 0 & \end{array} \right\|, \tag{8}$$

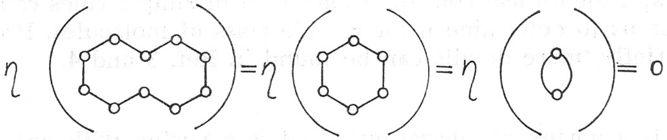
where B′ is the adjacency matrix of the molecule remaining after application of Rule 1 and *b* a vector with coordinates 0 and 1. Obviously, rank B = 1 + + rank B′, which together with (7) implies Rule 1.

Rule 2

A chain of four vertices can be replaced by an edge without changing the value of η



Example



Proof

In this case we have

$$B = \left\| \begin{array}{cc|c|c} 1 & 1 & 0 \;\; 0 & \cdots \;\; 0 \\ 1 & 0 & 1 \;\; 0 & \cdots \;\; 0 \\ \hline 0 & 1 & 0 & b \\ \cline{3-4} 0 & 0 & & \\ \cdot & & & \\ \cdot & & c & B'' \\ \cdot & & & \\ 0 & 0 & & \end{array} \right\| \tag{9}$$

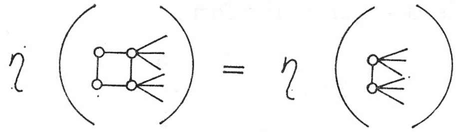
and

$$\text{rank } B = 2 + \text{rank} \left\| \begin{array}{c|c} 1 & b \\ \hline c & B'' \end{array} \right\| \tag{10}$$

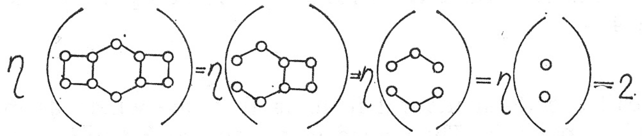
from which by the use of eq. (7) we can deduce Rule 2.

Rule 3

Two vertices and the four edges of a peripherial four-membered ring can be removed without changing the value of η as shown:



Example



Proof

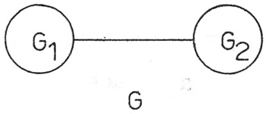
The proof is similar to previous one and is based on the fact that

$$\operatorname{rank} B = \operatorname{rank}\left\|\begin{array}{c:c:c} 1 & 1 & 0 \cdots 0 \\ \hdashline 1 & 1 & b \\ \hdashline 0 & & \\ \vdots & c & B''' \\ 0 & & \end{array}\right\| = 1 + \operatorname{rank}\left\|\begin{array}{c:c} 0 & b \\ \hdashline c & B''' \end{array}\right\| \tag{11}$$

where B and the last matrix are adjacency matrices of the graph prior and after application of Rule 3.

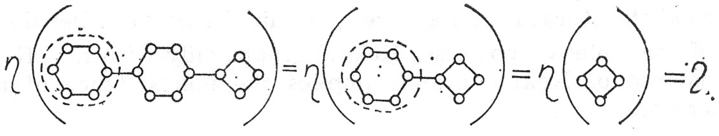
Rule 4

Let the graph G be of the form



and $\eta(G_1) = O$. Then $\eta(G) = \eta(G_2)$.

Example



Proof

The adjacency matrix B has now the form

$$B = \left\|\begin{array}{c:c:c} & 1 & 0 \cdots 0 \\ \cdashline{2-3} & 0 & 0 \qquad 0 \\ B_1 & \vdots & \\ & 0 & \\ & \cdot & 0 \qquad 0 \\ \hdashline 0 & \multicolumn{2}{c}{B_2} \end{array}\right\| \tag{12}$$

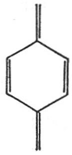
B_1 and B_2 are adjacency matrices of graphs G_1 and G_2. Since $\eta(G_1) = 0$, B_1 is a square regular matrix. Then we can add the columns corresponding to B_1, preliminarily multiplied by suitable numbers, to the column denoted by i so that after this B acquires the form

$$B^* = \left\| \begin{array}{c:c} B_1 & 0 \\ \hdashline 0 & B_2 \end{array} \right\| \tag{13}$$

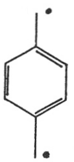
Now we have rank B = rank B^* = rank B_1 + rank B_2, which is sufficient for proving Rule 4.

Rule 5

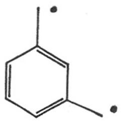
We will call »good« structural formula that one where as many electrons are paired as it is possible. Thus, good formulae are A and C but not B.



A



B



C

Then η is equal to the number of unpaired electrons in a good structural formula. This rule is valid only if there is no 4m-membered ring in the graph of the molecule.

Proof

If η is the exact number of zero's in the spectrum, then from eq. (4) follows:

$$a_N = a_{N-1} = \cdots = a_{N-\eta+1} = 0, \text{ and}$$

$$a_{N-\eta} \neq 0. \tag{14}$$

From eq. (5) follows that

$$a_n = 0 \Longleftrightarrow S_n = \emptyset \tag{15}$$

Hence, no Sachs graph with more than $N\text{-}\eta$ nodes can exist.

Let a good structural formula have $\bar{\eta}$ unpaired electrons. Per definitionem, the graph of the molecule possesses Kekulé graphs only with $n \leqslant N\text{-}\bar{\eta}$ vertices. The nonexistence of Kekulé graphs implies the nonexistence of any Sachs graph[4]. Therefore:

$$a_n = 0 \quad \text{for} \quad n > N - \bar{\eta} \tag{16}$$

It was shown in Ref. 4 that all terms in summation (5) have the same sign if there is no subgraph of the graph which is a 4m-membered ring. In this case is $a_n \neq 0$ for $n = N\text{-}\bar{\eta}$ and therefore:

$$\eta = \bar{\eta}. \tag{17}$$

Rule 6

Let the molecule have K Kekulé structures. The most general theorem for AH is given by Longuet-Higgins and Dewar[12–14] which enables us to calculate a_N (see eq. (5)):

$$(-)^{N/2} a_N = (\sum_{i=1}^{K} p_i)^2 \qquad (18)$$

where p_i is the parity of the Kekulé structure *i* (for details see Ref. 12). An interpretation of p_i in terms of Kekulé graph summation is given in Ref. 4.

For AH

$$a_N = 0 \qquad (19)$$

is a sufficient condition for degenerate ground state, but

$$\left|\frac{a_N}{N}\right| \ll 1 \qquad (20)$$

implies low chemical stability because of small HOMO-LUMO separation. It can be shown[4,13] that:

$$(-)^{N/2} a_N = K^2 \qquad (21)$$

if there is no 4m-membered ring in the molecule, and:

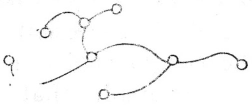
$$|a_N| < K^2 \quad (\text{often} \ll K^2) \qquad (22)$$

when 4m-membered rings are contained in the molecule.

Specially, if there is no Kekulé structure (K=O) the molecule is non-existing or a highly reactive species.

We applied these rules to chemically interesting families of compounds. Molecules (graphs) are represented using ribbons (as in Ref. 15).

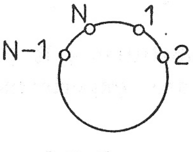
i) Linear and Branched Polyenes



Using rule 1 η can be easily determined. Chemically relevant species are those with one Kekulé structure (K = 1). These molecules are stable (see eq. (21)) but stability decreases when the number of atoms increases (see eq. (20)).

E_π and chemical stability are little influenced by the branching of the chain, linear polyenes (nonbranched chains) being most stable.

ii) Annulenes (rings)



As the consequence of rules 2 and 3 there are only two possibilities

A. $N = 4m + 2$

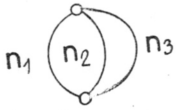
B. $N = 4m$

Molecules of type A are stable and those of type B are not. E_π correlates with chemical stability too. Detailed discussion is given elsewhere[16].

This is the well known Hückel (4m + 2)-rule. It can be extended on polycyclic systems if E_π is considered only[17]. So, every (4m + 2)-membered ring gives an energy gain and every (4m)-membered ring an energy loss, the 6- and 4-membered rings having the strongest effect.

The extension of Hückel rule to polycyclic systems in terms of chemical stability is not simple and is not solved up to date. The importance of HOMO's and LUMO's is shown in Ref. 15.

iii) Bicyclic Systems



Ribbons n_1, n_2 and n_3 have even numbers of vertices. There are three different rings in the graph (rings are subgraphs of the graph) and only two possibilities can arise:

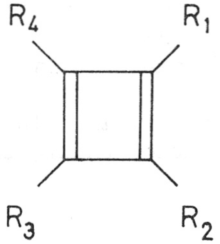
A. All three rings are of 4m + 2 type

B. One ring is of 4m + 2 type and two are of 4m type.

In both cases there is no zero in the spectrum of the graph[3], so both types of graphs correspond to stable molecules. The E_π is (because of Hückel rule) large only in the case A, so only molecules of type A are aromatic.

iv) Conjugated Molecules Joined by an Essential Single Bond

We apply rule 4. If G_1 and G_2 represent stable molecules, G is stable too. But if at least one of the components is not stable, the whole molecule is not stable too. It means, for example, that molecules

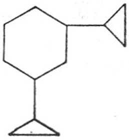


are unstable regardless the substituents R (if planarity is, at least approximately, conserved). There are experimental supports of this general conclusion[18].

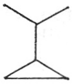
Nonalternant Hydrocarbons (NAH)

HMO's for NAH are not satisfactory in many cases. It is because they are not self-consistent[19]. Eqs. (18), (19) and even (20) do not hold necessarily.

Using Sachs theorem, structures can be easily found where stable singlet ground states and relatively large E_π can be expected from HMO calculations, while there is no chemical reason to ever obtain real molecules as in the following cases.



$a_{12} = -16$ and, hence, there are no NBMO's.



$a_6 = 0$ but $a_5 = 4$ and, hence, there is only one NBMO.

Therefore, the results of calculations for NAH should be interpreted cautiously. Rule 4, which is completely in agreement with chemical experience, cannot be extended onto the NAH's. The usual case that the existence of zero's in the spectrum (*i. e.* the existence of NBMO's) is followed by poorer chemical stability it is not necessarily fulfilled in NAH. Nevertheless, methods of estimating the number of zero's in the spectrum of graphs corresponded to NAH are recently developed by Živković[20].

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IZVOD

Teorija grafova i molekularne orbitale

D. Cvetković, I. Gutman i N. Trinajstić

Totalna π-elektronska energija i kemijska stabilnost konjugiranih ugljikovodika studirane su upotrebom teorije grafova. Izneseno je nekoliko originalnih teorema i diskutiran je njihov odnos prema HMO teoriji. Glavni je zaključak rada da se neka molekularna svojstva mogu dobiti na jednostavan način ispitivanjem molekularne topologije.

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