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The Determinant of the Adjacency Matrix of the Graph of a Conjugated Molecule

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Various graph-theoretical techniques for the calculation of the determinant of the adjacency matrix of a molecular graph are discussed.

1. INTRODUCTION

The problem of the relations which exist between the structure of a graph G and the determinant D of its adjacency matrix was solved for the general case by Harary.[1] However, in chemical literature this result was hardly ever used. Moreover, Marcus[2] and Wilcox[3] have independently formulated rules for calculation of D of molecular graphs, which are rather close to Harary's result. Important contributions towards the understanding of the dependence of D on the structure of a graph were given in the chemical literature[4,5] much before Harary's paper appeared.

The theoretical chemistry interest in D of molecular graphs begins with the discovery by Longuet-Higgins[4] that the presence of non-bonding molecular orbitals (NBMO's) in Hückel theory is related to the absence of Kekulé structures in the molecule considered. The dependence of D on the number of Kekulé structures was established soon after that[5] and was elaborated in more detail in refs 3, 6 and 7.

In addition to the simple fact[4] that $D = 0$ is a necessary and sufficient condition for the presence of NBMO's, the actual numerical value of D is shown to parallel the thermodynamic stability of the corresponding molecule (as given within the HMO theory).[3,6,8] D is one of the most important topological factors in bounds[9] and approximate formulas[10] for total π-electron energy (as calculated within the HMO model). Evaluation of D is necessary also in connection with other problems of the topological theory of conjugated systems.[11]

In the present paper we shall present some graph-theoretical techniques for the calculation of the determinant of the adjacency matrix of a molecular graph.

Necessary graph-theoretical concepts and definitions are introduced in section 2, where a convenient notation is also developed. Further details of graph theory and its application to chemistry can be found in refs 12—14.

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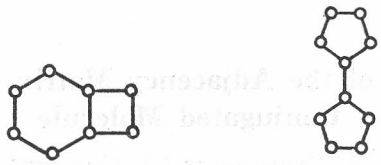
2. NOTATION AND DEFINITIONS

In the present work the graph representation of a molecular skeleton will be used.[13,15] Thus for example, benzcyclobutadiene and fulvalene are presented by molecular graphs G_1 and G_2, respectively.



G_1 G_2

Let G be a molecular graph with n vertices $v_1, v_2, \ldots, v_n$. Its adjacency matrix **A** is defined as usual.[11-14]

If $A_{pp} = h_p \neq 0$, we say that there is a loop of weight h_p on the vertex v_p of G. If $A_{pp} = 0$, there is no loop on the vertex v_p. The molecular graphs of hydrocarbons have no loops ($A_{pp} = 0$ for all p), while heteroatoms are represented by a loop on the corresponding vertex.[16]

The determinant of **A** wil be denoted by $D = D(G)$.

In the following we will consider linear graphs[1,17] of G. A linear graph consists of a number of mutually disjoint cycles of length 1, 2, 3, 4, ... Cycles of length 1 are called loops and cycles of length 2 are called edges.

Let the number of cycles of length t in a linear graph L be $c_t(L)$, and $c(L)$ be the total number of components* of L. Then

$$c_1(L) + c_2(L) + c_3(L) + \ldots = c(L)$$

$$c_1(L) + 2c_2(L) + 3c_3(L) + \ldots = n$$

where, of course, n is the number of vertices in L.

In the forthcoming discussion we shall need the following quantities:

$$c_3(L) + c_4(L) + c_5(L) + \ldots = r(L)$$

$$c_1(L) + c_5(L) + c_9(L) + \ldots = r_1(L)$$

$$c_2(L) + c_6(L) + c_{10}(L) + \ldots = r_2(L)$$

$$c_3(L) + c_7(L) + c_{11}(L) + \ldots = r_3(L)$$

$$c_4(L) + c_8(L) + c_{12}(L) + \ldots = r_4(L)$$

$$r_1(L) + r_3(L) = c_{odd}(L)$$

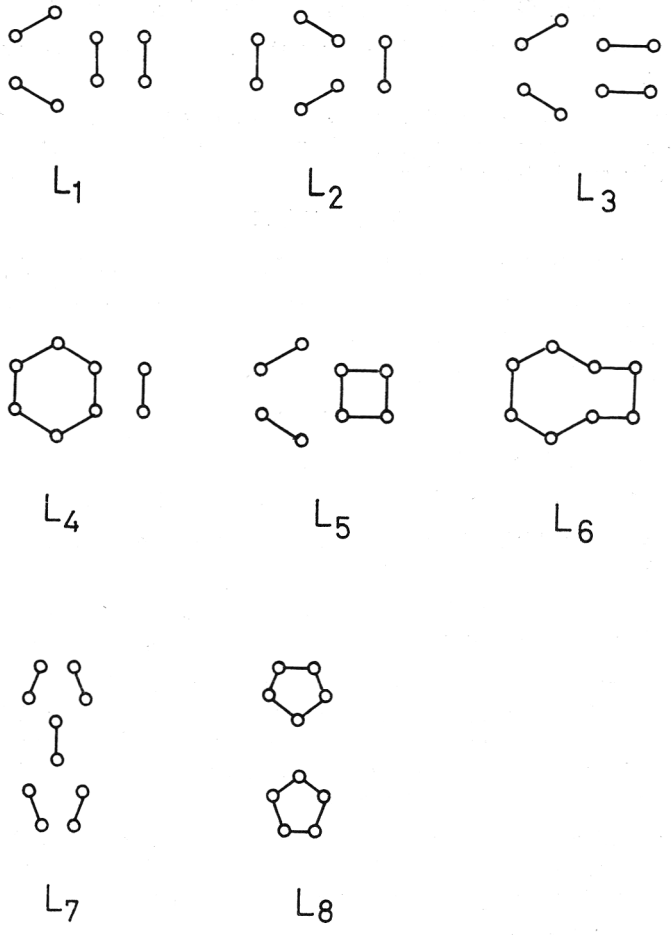
$$r_2(L) + r_4(L) = c_{even}(L)$$

Hence r is the number of cycles of length greater than two; r_1, r_2, r_3, r_4 are the total number of cycles of size $4m+1$, $4m+2$, $4m+3$, $4m$ (m = integer); c_{odd} and and c_{even} are the total number of odd and even cycles, respectively.

All linear graphs of graphs G_1 and G_2 are presented in Chart 1. The benzcyclobutadiene graph G_1 has 6 different linear graphs L (L_1 — L_6). The fulvalene graph G_2 has 2 linear graphs L (L_7, L_8).

* Component is a subgraph which is not connected to other subgraphs.

CHART 1



Linear graphs, the only components of which are isolated edges ($c_1 = c_3 = c_4 = \ldots = 0$, $c_2 = n/2$) are called[13,15,19] Kekulé graphs, since they are in an obvious manner related to the Kekulé structures of the corresponding molecule. For instance L_1, L_2, L_3 and L_7 in Chart 1 are Kekulé graphs.

Kekulé graphs, which play an important role in the subsequent considerations will be denoted by K_1, K_2, ..., K_k, with k being the number of Kekulé structures of the molecular skeleton G.

Let us define now certain sets of linear graphs. The set of all linear graphs of the molecular graph G is denoted by $\mathbf{L} = \mathbf{L}(G)$. The subsets of linear graphs from $\mathbf{L}$ with the property $c_{odd}(L) = 0$ and $c_{odd} > 0$ are denoted by $\mathbf{L}_{even}$ and $\mathbf{L}_{odd}$, respectively. Thus $\mathbf{L}_{even}$ contains the linear graphs which are composed entirely from even cycles and $\mathbf{L}_{odd}$ contains those with at least one odd cycle. Finally, the set of all Kekulé graphs of the molecular graph G is denoted by $\mathbf{K} = \mathbf{K}(G)$.

The *superposition*[7,15,18,20] $K_1 \oplus K_2$ of two Kekulé graphs K_1 and K_2 is the spanning subgraph of G which contains all edges from both K_1 and K_2.

Now we can formulate the following theorems, which are proved in refs 15, 18 and 20.

Theorem 1. The superposition of two Kekulé graphs K_i and K_j is a linear graph. Moreover, every linear graph $L \in \mathbf{L}_{\text{even}}$ can be presented in the form $L = K_i \oplus K_j$. In symbolic notation:

$$\mathbf{L}_{\text{even}} = \mathbf{K} \oplus \mathbf{K}$$

There are $2^{r(L)}$ distinct ordered pairs (K_i, K_j) such that $L = K_i \oplus K_j$.

If the molecule considered is alternant, the molecular graph G is bipartite and has no odd cycles. Then $\mathbf{L}_{\text{even}} = \mathbf{L}$.

Theorem 2. If G is bipartite,

$$\mathbf{L} = \mathbf{K} \oplus \mathbf{K}$$

Corollaries. Let G be a bipartite graph.

a) If $k = 0$, there exists no linear graph of G and $\mathbf{L} = \emptyset$.

b) If $k = 1$, the Kekulé graph is the unique linear graph of G, that is $\mathbf{L} = \{K_1\}$.

c) The existence of two Kekulé graphs in G is a necessary and sufficient condition for the existence of a linear graph L, such that $r(L) > 0$.

From Theorem 1 we can see that some cycles of G can be obtained by superposition of Kekulé graphs. These cycles are called by Randić[21] »*conjugated circuits*« and recently it was shown by the same author[21,22] that the number and size of conjugated circuits in a molecular graph are responsible for aromaticity (antiaromaticity) of the corresponding conjugated compound.

Of course, all cycles of a molecular graph are not conjugated circuits (e. g. odd circuits are never conjugated). In this respect the following statement summarizes an important property of benzenoid systems.[21,22]

Theorem 3. All conjugated circuits of benzenoid graphs are of size $4m+2$ (m = integer).

Another formulation of this theorem is

$$r_1(L) = r_3(L)) = r_4(L) = 0$$

$$\text{for all} \quad L \in \mathbf{L}$$

It is not possible to deduce the above statement without precisely knowing the conditions the molecule has to fulfill in order to be called »benzenoid«. Therefore, the proof of a result (Theorem 2 of ref 18), which is seemingly equivalent to our Theorem 3 cannot be assumed as satisfactory for the present approach. In the chemical literature there seems to be no generally accepted and mathematically consequent definition of benzenoid systems.[23] Moreover, according to Randić,[21,22] benzenoid graphs can be *defined* as those fulfilling the requirements of Theorem 3. We note, however, that in the great majority of cases there is no doubt whether a conjugated system is benzenoid or not.

3. HARARY'S THEOREM

The following result of Harary[1] gives a general answer to the problem of dependence of D on the structure of a graph G.

Theorem 4. For an arbitrary graph G,

$$D(G) = \sum_{\mathbf{L}} (-1)^{c_{even}(L)} \, 2^{r(L)} \tag{1}$$

where the summation in the above formula goes over the set of all linear graphs of the graph G.

Theorem 4 holds for G being an arbitrary graph including the case of graphs with loops of unit weight. However, if the loops in G have weights $h \neq 1$, Theorem 4 does not apply and the related formula is derived.

Theorem 5. Let the linear graph L contain t loops of weight $h_1, h_2, \ldots h_t$ and let $p(L)$ be the product of $h_1, h_2, \ldots, h_t$.

Then,

$$D(G) = \sum_{\mathbf{L}} (-1)^{c_{even}(L)} \, 2^{r(L)} \, p(L) \tag{2}$$

3.1. *Alternative Formulations of Harary's Theorem*

Theorem 6. For an arbitrary graph G,

$$D(G) = (-1)^n \sum_{\mathbf{L}} (-1)^{c(L)} \, 2^{r(L)} \tag{3}$$

$$D(G) = (-1)^{n/2} \sum_{\mathbf{L}} (-1)^{r_4(L) + \frac{r_3(L) - r_1(L)}{2}} \, 2^{r(L)} \tag{4}$$

The formulation of Harary's theorem in the form (3) was first given by Sachs[24], and later widely applied in chemistry.[13,15,18] From formula (4) the following corollary can be deduced.

If G is a bipartite graph, $r_3 = r_1 = 0$ for all linear graphs of G. Then eq 4 reads

$$D(G) = (-1)^{n/2} \sum_{\mathbf{L}} (-1)^{r_4(L)} \, 2^{r(L)} \tag{5}$$

3.2. *A Recursion Relation for D*

In this section we develop an algorithm for calculation of D based on a recursion relation. Let consider a graph G and the set $\mathbf{L}$ of its linear graphs. Let e be an arbitrary edge of G. Then the following three cases can occur: either a linear graph $L \in \mathbf{L}$ does not contain e, or e is an isolated edge of L, or e belongs to a cycle C_i of L. Accordingly, the set $\mathbf{L}$ can be partitioned as

$$\mathbf{L} = \mathbf{L}(\ddot{e}) \cup \mathbf{L}(e) \cup \bigcup_i \mathbf{L}(C_i)$$

where

- $\mathbf{L}(\ddot{e})$ is the set of those linear graphs of G which do not contain e,
- $\mathbf{L}(e)$ is the set of those linear graphs of G which contain e as an isolated edge,
- $\mathbf{L}(C_i)$ is the set of those linear graphs of G which contain e within the cycle C_i.

Let further $G - e$, $G - (e)$ and $G - C_i$ denote the graphs obtained by deletion from G of the edge e, of the edge e and both vertices incident to it, and of the cycle C_i, respectively. Then from eq 3,

$$D(G) = (-1)^n \sum_{\mathbf{L}(G)} (-1)^{c(L)} \, 2^{r(L)} = (-1)^n \sum_{\mathbf{L}(\ddot{e})} + \sum_{\mathbf{L}(e)} + \sum_{i} \sum_{\mathbf{L}(C_i)} (-1)^{c(L)} \, 2^{r(L)}$$

$$= (-1)^n \left[\sum_{\mathbf{L}(G-e)} (-1)^{c(L)} \, 2^{r(L)} + \sum_{\mathbf{L}(G-(e))} (-1)^{c(L)+1} \, 2^{r(L)} + \right.$$

$$\left. \sum_{i} \sum_{\mathbf{L}(G-C_i)} (-1)^{c(L)+1} \, 2^{r(L)+1} \right]$$

By taking into account that the graphs $G - e$, $G - (e)$ and $G - C_i$ contain n, $n - 2$ and $n - |C_i|$ vertices, respectively, we get finally the recurrence formula

$$D(G) = D(G-e) - D(G-(e)) - 2 \sum_{i} (-1)^{|C_i|} D(G - C_i) \tag{6}$$

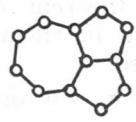
where $|C_i|$ is the size of the cycle C_i and $\sum_i$ denotes the summation over all cycles C_i which contain the edge e.

If C_i is a Hamiltonian cycle of G, $G - C_i$ is the graph $\emptyset$ without vertices. By definition, $D(\emptyset) = 1$.

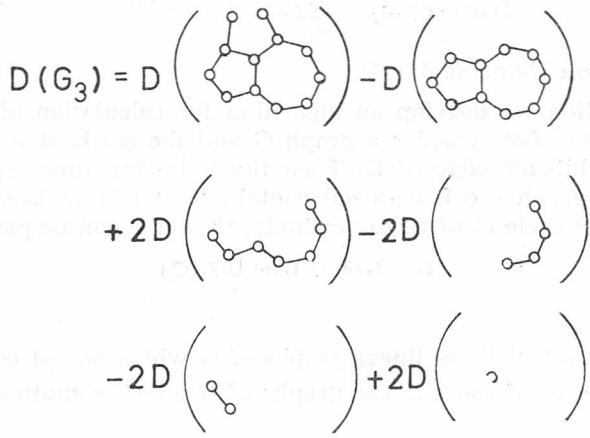
A simple special case of eq 6 is to be noted. Namely, if e is a terminal edge of G (that is an edge incident to a vertex of degree one), $G - e$ has an isolated vertex and therefore $D(G - e) = 0$. Moreover, e belongs to no cycles of G. Therefore, if e is a terminal edge

$$D(G) = -D(G - (e)) \tag{7}$$

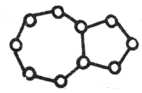
Let us now illustrate the applicability of eqs 6 and 7 on the example of aceazulene graph G_3.



G_3

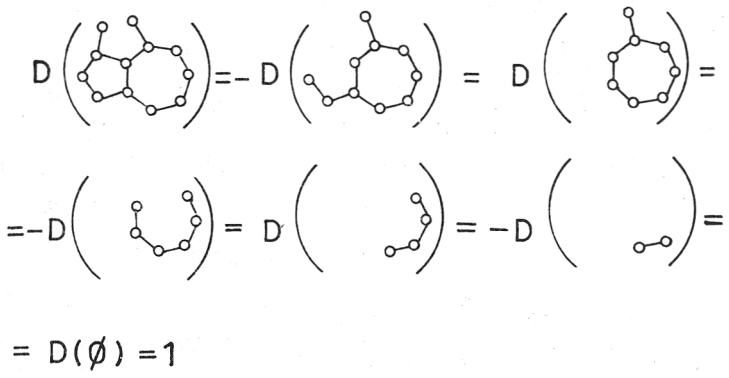


It can be established separately, that the determinant of the azulene graph G_4 is -4. Now we apply eq 7



G_4

several times. For instance,



Finally we have

$$D(G_3) = 1 - (-4) + 2 \cdot 0 - 2 \cdot 1 - 2 \cdot (-1) + 2 \cdot 0 = 5$$

Calculations of the above type are essentially simplified if one takes into account that the determinant of a path with n vertices fulfills the simple relation: $D = (-1)^{n/2}$ if n is even and $D = 0$ if n is odd.

The same way of reasoning which led to formula 6 can be applied also in the case of graphs containing (weighted) loops. Let the edge e be a loop of weight h on the vertex v of the graph $G(h)$. Let further G and $G - v$ be the graphs obtained by deletion of this loop from $G(h)$ (by formally seting $h = 0$) and by deletion of the vertex v from G, respectively. Then by applying Theorem 5, eq 6 becomes

$$D(G(h)) = D(G) - h\,D(G - v) \tag{8}$$

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SAŽETAK

Determinanta matrice susjedstva za graf konjugirane molekule

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Diskutirane su različite graf-teorijske tehnike izračunavanja determinante matrice susjedstva molekulskog grafa.

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