

THE DETERMINANT OF THE ADJACENCY MATRIX  
OF A MOLECULAR GRAPH

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ABSTRACT

A review of various graph-theoretical techniques for the calculation of the determinant  $D$  of the adjacency matrix of a molecular graph is presented. A recurrence relation and several simple topological expressions for  $D$  of benzenoid, alternant, non-alternant and heteroconjugated systems are obtained.

## 1. INTRODUCTION

There are two main reasons why the determinant  $D$  of the adjacency matrix of a molecular graph is of interest in theoretical chemistry of conjugated molecules. First, whenever  $D=0$ , there exist non-bonding molecular orbitals (NBMO's). Second, the total  $\pi$ -electron energy of a conjugated molecule is a monotonously increasing function of  $D$ .

The question how the determinant  $D$  of the adjacency matrix of a graph  $G$  depends on the structure of this graph was fully answered by a result of Harary<sup>1</sup>. However, in chemical literature Harary's theorem was hardly ever used. Moreover, Marcus<sup>2</sup> and Wilcox<sup>3</sup> 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 chemical literature<sup>4,5</sup> long before Harary's paper appeared.

The theoretical chemistry interest in  $D$  of molecular graphs begins with the discovery by Longuet-Higgins<sup>4</sup> that the presence of 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<sup>5</sup> and was elaborated in greater detail in Refs. 3, 6 and 7.

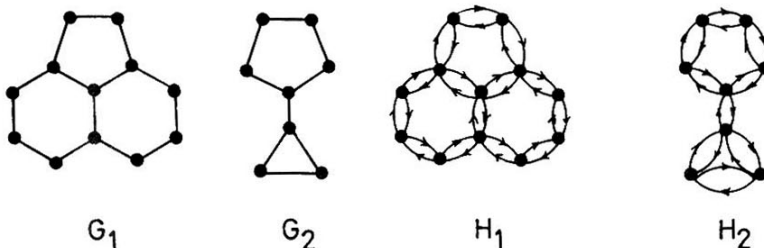
In addition to the simple fact<sup>4</sup> that  $D=0$  is a necessary and sufficient condition for the presence of NBMO's, the actual numerical value of  $D$  is shown to parallel the thermodynamic stability of the corresponding molecule (as given by HMO theory)<sup>3, 6, 8</sup>.  $D$  is one of the most important topological factors in bounds<sup>9</sup> and approximate formulas<sup>10</sup> for HMO total  $\pi$ -electron energy. The stability difference between two

isomeric conjugated hydrocarbon molecules is shown<sup>11</sup> to be roughly proportional to the difference in their  $\log D$  values. Evaluation of  $D$  is necessary also in connection with the determination of the number of bonding and antibonding molecular orbitals<sup>12</sup>.

In the present review we present a complete theory of the determinant of the adjacency matrix of a molecular graph. A part of the results presented in sections 2 and 3 was given previously in Ref. 13. In section 3 Harary's theorem is exposed together with a new recurrence formula and a graphical technique for calculation of  $D$ . Harary's theorem enables also the evaluation of the characteristic polynomial. In section 4 we consider the relations between  $D$  and the structure of the molecular graph. First the earlier known results for benzenoid (4.1.) and alternant (4.2.) systems are summarized and then a general formulation for non-alternant (4.3.) and heteroconjugated (4.4.) systems is given. Necessary graph-theoretical concepts and definitions as well as some previous results are introduced in section 2, where also a convenient notation is developed. Further details of graph theory and its application to chemistry can be found in Refs. 14, 15, 16, 17.

## 2. NOTATION AND DEFINITIONS

In the present work both graph<sup>16, 18</sup> and digraph<sup>19, 20</sup> representation of a molecular skeleton will be used. Thus for example acenaphthylene and calicene are presented by molecular graphs  $G_1$  and  $G_2$  and molecular digraphs  $H_1$  and  $H_2$ , respectively.

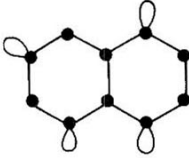


Both representations are equivalent, since a digraph H can be obtained by replacing every edge of the corresponding graph G by a pair of oppositely directed arcs, and vice versa.

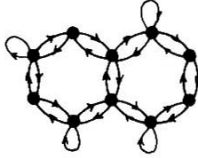
Let therefore G and H be a molecular graph and an equivalent molecular digraph with n vertices  $v_1, v_2, \dots, v_n$ . The adjacency matrix  $\underline{A}$  of them is defined for  $p \neq q$  as usual<sup>14-17</sup>.

$$A_{pq} = \begin{cases} 1 & \text{if there is an edge in G between } v_p \text{ and } v_q, \\ & \text{or if there is an arc in H from } v_p \text{ to } v_q, \\ 0 & \text{if there is no such an edge (arc)} \end{cases}$$

If  $A_{pp} = h_p \neq 0$ , we say that there is a loop of weight  $h_p$  on the vertex  $v_p$  of both G and H. 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<sup>21</sup>. For example  $G_3$  and  $H_3$  are the graph and digraphs respectively, of the molecular skeleton of pteridine.



$G_3$

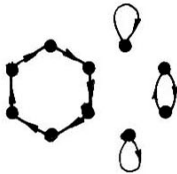


$H_3$

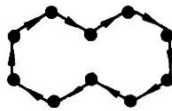
Evidently, the orientation of a loop in a digraph is for our discussion immaterial.

The determinant of  $\overset{A}{\sim} \underset{w}{w}$  will be denoted by  $D = D(G) = D(H)$ .

In the following we will consider spanning subgraphs\* of a digraph  $H$  (or of a graph  $G$ ) with the property that exactly one arc starts from and exactly one arc ends at every vertex. These are called<sup>1, 14, 22</sup> linear digraphs of  $H$  (or  $G$ ). It can be seen that a linear digraph consists of a number of directed, mutually disjoint cycles of length 1, 2, 3, 4 ... . For example  $L_1$  and  $L_2$  are two linear digraphs of  $H_3$ .  $L_1$  consists of two cycles of length 1, a cycle of length 2 and a cycle of length 6;  $L_2$  consists of a cycle of length 10.



$L_1$



$L_2$

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\* A spanning subgraph of a digraph contains all its vertices, but only some of its arcs.

Let the number of cycles of length  $t$  in a linear digraph  $L$  be  $c_t(L)$ , and  $c(L)$  be the total number of components<sup>\*\*</sup> of  $L$ . Then:

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

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

where, of course,  $n$  is the number of vertices in  $L$  (or  $G$  or  $H$ ).

In the forthcoming discussion we shall need the following quantities:

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

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

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

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

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

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

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

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);  $c_{\text{odd}}$  and  $c_{\text{even}}$  are the total number of odd and even cycles, respectively.

A linear graph<sup>1,22</sup>  $M$  of the graph  $G$  is obtained from a linear digraph  $L$  if

- a) loops in  $L$  are left unchanged,
- b) cycles of length two in  $L$  are changed into isolated edges,

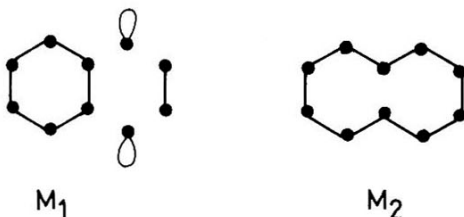
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<sup>\*\*</sup> Component is a subgraph which is not connected to other subgraphs.

and

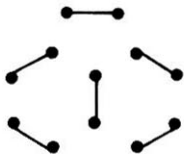
- c) directed cycles of length 3, 4, 5, ... in  $L$  are changed into undirected cycles.

For example,  $M_1$  and  $M_2$  are linear graphs obtained from  $L_1$  and  $L_2$ , respectively.

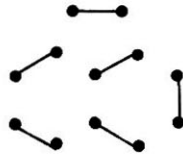


Similarly, linear digraphs can be generated from linear graphs by changing every isolated edge into a cycle of length two, and by directing any cycle of length 3, 4, 5, ... . Since cycles of length 3, 4, 5, ... can be directed in two different ways, we see that  $2^{r(M)}$  various linear digraphs can be generated from a single linear graph  $M$ . This observation will be of utmost importance in the following considerations. It enables the preformulation of statements valid for graphs into statements for digraphs and vice versa. Consequently, in the following considerations we use either graph or digraph terminology, depending on their adequacy for the particular problem we study.

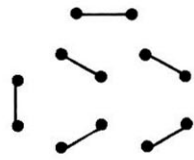
All linear graphs of the graphs  $G_1$  and  $G_2$  are presented in Chart 1. The acenaphthylene graph  $G_1$  has 6 different linear graphs ( $M_3 - M_8$ ) and consequently  $2^0 + 2^0 + 2^0 + 2^1 + 2^1 + 2^1 = 9$  different linear digraphs. The calicene graph  $G_2$  has 2 linear graphs ( $M_9, M_{10}$ ) or  $2^0 + 2^2 = 5$  linear digraphs.



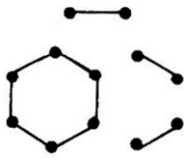
M3



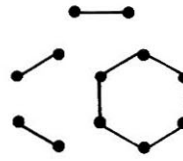
M4



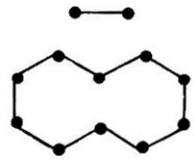
M5



M6



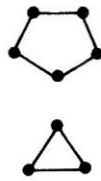
M7



M8



M9



M10

Chart 1



Linear graphs, whose only components are isolated edges ( $c_1=c_3=c_4=\dots=0$ ,  $c_2=n/2$ ) are called<sup>16, 18</sup> Kekulé graphs, since they are in an obvious manner related to the Kekulé structures of the corresponding molecule<sup>\*\*\*</sup>. For instance  $M_3, M_4, M_5$  and  $M_9$  in Chart 1 are Kekulé graphs.

Kekulé graphs are denoted by  $K_1, K_2, \dots, K_k$ , with  $k$  being the number of Kekulé structures of the molecular skeleton  $G$ . They play an important role in the subsequent considerations.

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

The superposition<sup>7, 18-20</sup>  $K_1 \oplus K_2$  of two Kekulé graphs  $K_1$  and  $K_2$  is the spanning subgraph of  $G$  which contains all edges from both  $K_1$  and  $K_2$ .

The following theorems are proved in Refs.<sup>18-20</sup>.

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\*\*\* One should notice that the concept of Kekulé graphs coincides with 1-factors in mathematical literature<sup>14</sup>.

Theorem 1. The superposition of two Kekulé graphs  $K_i$  and  $K_j$  is a linear graph. Moreover, every linear graph  $M \in M_{\text{even}}$  can be presented in the form  $M = K_i \oplus K_j$ .

In symbolic notation:  $M_{\text{even}} = K \oplus K$ . There are  $2^{r(M)}$  distinct ordered pairs  $(K_i, K_j)$  such that:  $M = K_i \oplus K_j$ . Therefore we have the following corollary of Theorem 1.

Theorem 2. There are  $k^2$  linear digraphs of the graph  $G$  without odd membered cycles. In symbolic notation:  $|L_{\text{even}}| = k^2$ .

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

Theorem 3. If  $G$  is bipartite,  $M = K \oplus K$ , and there are  $k^2$  linear digraphs of  $G$ .

Corollaries. Let  $G$  be a bipartite graph.

- If  $k=0$ , there exists no linear graph of  $G$  and  $L = M = \emptyset$ .
- If  $k=1$ , the Kekulé graph is the unique linear graph of  $G$ , that is  $L = M = \{K_1\}$ .
- The existence of two Kekulé graphs in  $G$  is a necessary and sufficient condition for the existence of a linear graph  $M$ , such that  $r(M) > 0$ .

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<sup>23</sup> "conjugated circuits" and recently it was shown by the same author<sup>23, 24</sup> that the number and size of conjugated circuits in a molecular graph are responsible for aromaticity (antiaromaticity) of the corresponding conjugated compound.

Of course, not all cycles of a molecular graph are conjugated circuits (e.g. odd circuits are never conjugated). In this respect the following state-

ment summarizes an important property of benzenoid systems<sup>23, 24</sup>.

Theorem 4. All conjugated circuits of benzenoid graphs are of size  $4m + 2$  ( $m = \text{integer}$ ).

Another formulation of this theorem is  $r_1(L) = r_3(L) = r_4(L) = 0$  for all  $L \in \underline{L}$ . It is not possible to deduce the above statement without precisely knowing the conditions the molecule must to fulfil in order to be called "benzenoid". Therefore, the proof of a result (Theorem 2 of Ref.19), which is seemingly equivalent to our Theorem 4 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<sup>x</sup>. Moreover, according to Randić,<sup>23,24</sup> benzenoid graphs can be defined as those fulfilling the requirements of Theorem 4. 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<sup>1</sup> gives a general answer to the problem of dependence of  $D$  on the structure of a graph  $G$ .

Theorem 5. For an arbitrary graph  $G$ ,

$$D(G) = \sum_{\underline{L}} (-1)^{c_{\text{even}}(L)} = \sum_{\underline{M}} (-1)^{c_{\text{even}}(M)} r(M) \quad (1)$$

where the summation in the above formulas goes over the set of all linear digraphs or graphs of the graph  $G$ .

Let us, for example, determine  $D(G_1)$  and  $D(G_2)$ . Using Chart 1 we have:

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x) The authors thank Professor M. Randić for helpful discussion on this problem.

$$\begin{aligned}
 D(G_1) &= \sum_{j=3}^8 (-1)^{c_{\text{even}}(M_j)} 2^{r(M_j)} = \\
 &= (-1)^6 2^0 + (-1)^6 2^0 + (-1)^6 2^0 + (-1)^4 2^1 + \\
 &+ (-1)^4 2^1 + (-1)^2 2^1 = 9
 \end{aligned}$$

$$\begin{aligned}
 D(G_2) &= (-1)^{c_{\text{even}}(M_9)} 2^{r(M_9)} + (-1)^{c_{\text{even}}(M_{10})} 2^{r(M_{10})} = \\
 &= (-1)^4 2^0 + (-1)^2 2^2 = 5
 \end{aligned}$$

Theorem 5 holds for  $G$  being an arbitrary graph (or digraph) including the case of graphs with loops of unit weight. However, if the loops in  $G$  have weights  $h \neq 1$ , Theorem 5 does not apply and a related formula is derived.

Theorem 6. Let the linear graph  $L$  contains  $t$  loops of the weight  $h_1, h_2, \dots, h_t$  and let  $p(L) = p(M)$  be the product of  $h_1, h_2, \dots, h_t$ . Then

$$D(G) = \sum_{\underline{L}} (-1)^{c_{\text{even}}(L)} p(L) = \sum_{\underline{M}} (-1)^{c_{\text{even}}(M)} 2^{r(M)} p(M)$$

This is a special case of a formula (2) for the determinant of an arbitrary matrix, which can be formally treated as an adjacency matrix of an arbitrary weighted digraph  $H$ . This formula reads

$$D(H) = \sum_{\underline{L}(H)} (-1)^{c_{\text{even}}(L)} p(L) \tag{2}$$

where  $p(L)$  is the product of weights of all arcs which are contained in  $L$ .

### 3.1. ALTERNATIVE FORMULATIONS OF HARARY'S THEOREM

Theorem 7. For an arbitrary graph G

$$D(G) = (-1)^n \sum_L (-1)^{c(L)} = (-1)^n \sum_M (-1)^{c(M)} 2^{r(M)} \quad (3)$$

and

$$\begin{aligned} D(G) &= (-1)^{n/2} \sum_L (-1)^{r_4(L)} + \frac{r_3(L) - r_1(L)}{2} = \\ &= (-1)^{n/2} \sum_M (-1)^{r_4(M)} + \frac{r_3(M) - r_1(M)}{2} 2^{r(M)} \end{aligned} \quad (4)$$

The formulation of Harary's theorem in the form (3) was first given by Sachs<sup>26</sup> and later widely used in chemical applications<sup>16, 18, 19</sup>. 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

$$D(G) = (-1)^{n/2} \sum_L (-1)^{r_4(L)} = (-1)^{n/2} \sum_M (-1)^{r_4(M)} 2^{r(M)} \quad (5)$$

### 3.2. THE COEFFICIENTS OF THE CHARACTERISTIC POLYNOMIAL

When solving the eigenvalue problem for a graph G, the following determinant needs to be considered

$$P(G, x) = \det (xI - A)$$

where  $I$  is a unit matrix.  $P(G, x)$  is called the characteristic polynomial of the graph  $G$  and is of degree  $n$ . It can be written as

$$P(G, x) = \sum_{j=0}^n a_j x^{n-j}$$

We derive now an expression enabling the calculation of the coefficients  $a_j$  from the structure of the graph  $G$ . This result (usually called in chemical literature "the Sachs theorem") is an immediate consequence of Harary's theorem.

In linear algebra is known<sup>27</sup> that the coefficient  $a_j$  equals to the sum of all principal minors of  $j$ -th order of the determinant  $D(G)$  multiplied by the factor  $(-1)^j$ .

As the principal minors of the  $j$ -th order correspond (in an obvious way) to graphs with  $j$  vertices obtained from a graph  $G$  by deletion of  $(n-j)$  vertices, we can write, using eq. (3), the following formula for the coefficient  $a_j$ :

$$a_j = \sum_{L_j} (-1)^{c(L)} = \sum_{M_j} (-1)^{\frac{c(M)}{2} r(M)}$$

where  $L_j$  and  $M_j$  are the set of all linear digraphs and all linear graphs of  $G$  with  $j$  vertices, respectively. (When  $j=n$ , we will denote  $L_n$  and  $M_n$  simply by  $L$  and  $M$ , respectively).

The above formula was first explicitly given by Sachs<sup>26</sup>. It can be immediately generalized for graphs with loops and/or weighted edges<sup>21, 28</sup>. The discussion along the chemical significance of such generalizations goes beyond the scope of the present review.

3.3. A RECURSION RELATION FOR  $D^{29}$

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

$$\underline{M} = \underline{M}(\bar{e}) \cup \underline{M}(e) \cup \underline{M}(C_i)$$

where

$\underline{M}(\bar{e})$  is the set of those linear graphs of  $G$  which do not contain  $e$ ,

$\underline{M}(e)$  is the set of those linear graphs of  $G$  which contain  $e$  as an isolated edge,

$\underline{M}(C_i)$  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 (3),

$$\begin{aligned} D(G) &= (-1)^n \sum_{\underline{M}(G)} (-1)^{c(M)} 2^{r(M)} = (-1)^n \sum_{\underline{M}(\bar{e})} + \sum_{\underline{M}(e)} + \\ &+ \sum_i \sum_{\underline{M}(C_i)} (-1)^{c(M)} 2^{r(M)} = (-1)^n \left[ \sum_{\underline{M}(G-e)} (-1)^{c(M)} 2^{r(M)} + \right. \\ &\left. + \sum_{\underline{M}(G-(e))} (-1)^{c(M)+1} 2^{r(M)} + \sum_i \sum_{\underline{M}(G-C_i)} (-1)^{c(M)+1} 2^{r(M)+1} \right] \end{aligned}$$

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<sup>29</sup>

$$D(G) = D(G-e) - D(G-(e)) - 2 \sum_i (-1)^{|C_i|} D(G-C_i) \quad (6)$$

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  $e$ .

Using a similar argument it can be shown<sup>29</sup> that

$$P(G, x) = P(G-e, x) - P(G-(e), x) - 2 \sum_i (-1)^{|C_i|} P(G-C_i, x)$$

If  $C_i$  is a Hamiltonian cycle<sup>14</sup> of  $G$ , then  $G-C_i$  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

$$D(G) = -D(G-(e)) \quad (7)$$

As a first application of eqs. (6) and (7) we determine  $D(P_n)$  and  $D(C_n)$ , where  $P_n$  and  $C_n$  are the path and the cycle with  $n$  vertices. From (7),  $D(P_n) = -D(P_{n-2})$ . Since  $D(P_1) = 0$ ,  $D(P_2) = -1$  we conclude that  $D(P_n) = (-1)^{n/2}$  if  $n$  is even and  $D(P_n) = 0$  if  $n$  is odd. From (6),  $D(C_n) = D(P_n) - D(P_{n-2}) - 2(-1)^n D(\emptyset)$ . Therefore,  $D(C_n) = 2$  if  $n$  is odd,  $D(C_n) = 0$  if  $n=4m$  and  $D(C_n) = -4$  if  $n=4m+2$ .

As another example,  $D(G_2)$  will be determined. This is an occasion to compare the adequacy and practical value of our recursion relation (6) with the direct use of Theorem 5. According to our experience, eq. (6) is much more appropriate for the actual evaluation of  $D$ , but Theorem 5 enables a deeper insight into the dependence of  $D$  on graph structure. Thus



$$D(G_2) = D \left( \begin{array}{c} \text{C}_5 \\ \text{C}_3 \end{array} \right) - D \left( \begin{array}{c} \text{C}_5 \\ \text{C}_2 \end{array} \right) = D(C_5) D(C_3) - \\ - D(P_4) D(P_2) = 2 \cdot 2 - 1 \cdot (-1) = 5$$

where we have used the previously deduced results for  $D(P_n)$  and  $D(C_n)$ .

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 setting  $h=0$ ) and by deletion of the vertex  $v$  from  $G$ , respectively. Then by applying Theorem 6, eq. (6) becomes

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

#### 4. THE DETERMINANT OF SPECIAL MOLECULAR GRAPHS

##### 4.1. THE DETERMINANT OF BENZENOID GRAPHS

If  $G$  is a benzenoid graph, then by Theorem 4,  $r_4(L)=0$  for all  $L \in \underline{\underline{L}}(G)$ . Then from eq. (4) it follows

$$D(G) = (-1)^{n/2} \sum_{\underline{\underline{L}}} (-1)^0 = (-1)^{n/2} |\underline{\underline{L}}|$$

where  $|\underline{\underline{L}}|$  is the number of elements of the set  $\underline{\underline{L}}$ . But Theorem 3 guarantees that  $|\underline{\underline{L}}| = k^2$ . As a final result we have

$$D(G) = (-1)^{n/2} k^2 \quad (9)$$

Eq. (9) was first obtained by Dewar and Longuet-Higgins<sup>5</sup>. Its numerous consequences have been discussed elsewhere<sup>3, 5, 6, 8, 19</sup>.

One of the proper consequences of eq. (9) is that benzenoid systems, for which no Kekulé structure can be written, have NBMO's and are therefore species of rather low chemical stability<sup>4, 7, 30</sup>. Conversely, systems with at least one Kekulé structure cannot have NBMO's. Moreover, the thermodynamic stability of benzenoid hydrocarbons is found<sup>8, 31</sup> to be proportional to  $k$ .

These conclusions, which are in complete agreement with classical resonance theory, cannot, however, be simply extended to non-benzenoid molecules.

#### 4.2. THE DETERMINANT OF BIPARTITE MOLECULAR GRAPHS

A graph is bipartite if, and only if it contains no odd-membered cycles<sup>14</sup>. Bipartite graphs represent the so called "alternant molecules"<sup>25</sup>

Let us consider a bipartite graph  $G$ . Then Theorem 3 is applied and eq. (5) can be written in the form

$$D(G) = (-1)^{n/2} \sum_{i=1}^k \sum_{j=1}^k (-1)^{r_4(K_i \oplus K_j)} \quad (10)$$

We can distinguish two cases. Either  $r_4(K_i \oplus K_j)$  is an even number (including  $r_4(K_i \oplus K_j)=0$ ) or it is odd. In the first case we say that  $K_i$  and  $K_j$  are of equal parity; in the latter case  $K_i$  and  $K_j$  are said to be of opposite parity.

If  $G$  is a bipartite graph, the set  $K$  can be partitioned into subsets

$\underline{K}^+$  and  $\underline{K}^-$  in such a way that  $K_i$  and  $K_j$  are of opposite parity only if they belong to different subsets<sup>3, 32</sup>. Let  $|\underline{K}^+| = k^+$  and  $|\underline{K}^-| = k^-$ ,  $k^+$  and  $k^-$  are called the number of Kekulé structures of even and odd parity, respectively ( $k^+ + k^- = k$ ). The difference  $k^+ - k^-$  has been named the algebraic structure count<sup>5,6</sup> or corrected structure count<sup>33</sup>; recent investigations<sup>34</sup> confirmed the importance of this quantity.

Thus for alternant systems we obtain

$$D(G) = (-1)^{n/2} (k^+ - k^-)^2 \quad (11)$$

#### 4.3. THE DETERMINANT OF NON-BIPARTITE GRAPHS

Because of Theorem 1, in the case of non-alternant systems eq. (10) is to be modified as

$$D(G) = (-1)^{n/2} \sum_{i=1}^k \sum_{j=1}^k (-1)^{r_4(K_i \oplus K_j)} + (-1)^n \sum_{\underline{L}_{\text{odd}}} (-1)^{c(L)} \quad (12)$$

Further if one assumes that a partitioning of  $\underline{K}$  into  $\underline{K}^+$  and  $\underline{K}^-$  is possible, one deduces from (12)

$$D(G) = (-1)^{n/2} (k^+ - k^-)^2 + (-1)^n \sum_{\underline{L}_{\text{odd}}} (-1)^{c(L)} \quad (13)$$

a formula first proposed by Wilcox<sup>3</sup>. Eq. (13) applies the majority of chemically relevant non-bipartite graphs.

However, eq. (13) is not generally correct. Namely, the assumption that a particular "parity" can be associated with every Kekulé graph

holds not in the general case<sup>35</sup>. Then eq. (12) should be applied, which is indeed a generalization of both (13) and (11).

#### 4.4. CALCULATION OF D OF HETEROCONJUGATED SYSTEMS

The basis of a procedure for calculation of D of heteroconjugated systems is given in Theorem 6. However, in practice it is much more convenient to reduce this problem to the finding of D's of simple graphs (i.e. graphs without loops). This is enabled by eq. (8), which is deduced in section 3.3.

If the graph  $G(h_1, h_2)$  has two loops of weight  $h_1$  and  $h_2$  on the vertices  $v_1$  and  $v_2$ , respectively, a two-fold application of eq. (8) gives

$$D(G(h_1, h_2)) = D(G) - h_1 D(G-v_1) - h_2 D(G-v_2) + h_1 h_2 D(G-v_1-v_2)$$

Analogously,

$$D(G(h_1, h_2, \dots, h_t)) = D(G) - \sum_i h_i D(G-v_i) + \sum_{i,j} h_i h_j D(G-v_i-v_j) - \sum_{i,j,k} h_i h_j h_k D(G-v_i-v_j-v_k) + \dots$$

For example, the determinant of the pteridine graph  $G_3$  can be evaluated as given in Chart 2.

$$\begin{aligned}
 D(G_3) = & D \left( \text{Diagram 1} \right) - h \left[ D \left( \text{Diagram 2} \right) + \right. \\
 & + D \left( \text{Diagram 3} \right) + D \left( \text{Diagram 4} \right) + D \left( \text{Diagram 5} \right) \left. \right] + \\
 & + h^2 \left[ D \left( \text{Diagram 6} \right) + D \left( \text{Diagram 7} \right) + D \left( \text{Diagram 8} \right) + \right. \\
 & + D \left( \text{Diagram 9} \right) + D \left( \text{Diagram 10} \right) + D \left( \text{Diagram 11} \right) \left. \right] - \\
 & - h^3 \left[ D \left( \text{Diagram 12} \right) + D \left( \text{Diagram 13} \right) + D \left( \text{Diagram 14} \right) + \right. \\
 & + D \left( \text{Diagram 15} \right) \left. \right] + h^4 D \left( \text{Diagram 16} \right)
 \end{aligned}$$

Chart 2

Then the earlier developed algorithms for the calculation of  $D$  (in particular eqs. (7) and (9)) can be applied and we have finally

$$D(G_3) = -9 + 6h^2$$

As another application we present the following theorem.

Theorem 8. Let  $G(h)$  and  $G$  be the molecular graphs of a heteroconjugated system with one heteroatom and its parent hydrocarbon, respectively. If  $G$  is bipartite,

$$D(G(h)) = D(G) \tag{14}$$

or in other words:  $D(G(h))$  is completely insensitive to the kind and position of the heteroatom.

In order to deduce (14) from (8), one has to remember that since  $n$  is even,  $G-v$  is a bipartite graph with odd number of vertices and therefore<sup>7</sup>,  $D(G-v) = 0$ .

One consequence of Theorem 8 is that the concept of parity of Kekulé structures holds not only in alternant hydrocarbons, but also in alternant heteroconjugated systems.

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