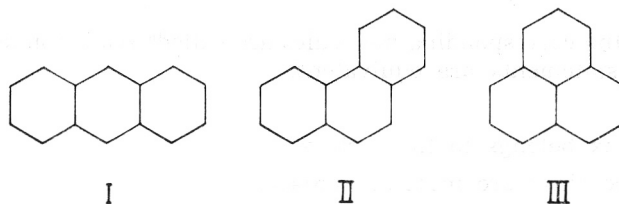# Some Topological Properties of Benzenoid Systems

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INTRODUCTION

In recent years conjugated molecules have been intensely studied by means of graph theory[1] and a number of their chemical and physical properties could be described and/or predicted. The aim of the present note is to analyze a special class of molecular graphs[2] which are of doubtless importance for chemistry since they represent benzenoid hydrocarbons.

In fact, there is no uniquely adopted agreement as to which conjugated systems are benzenoid, but it seems that most organic chemists call benzenoid those molecules which are built entirely from (regular) hexagons. The network obtained by any combination of regular hexagons in a plane such that two hexagons have either exactly one common edge or are disjoint will be called a *»benzenoid graph«*. It is assumed that the considered graphs are connected[2], that is, have only one component. For example, I—III are the only possible benzenoid graphs with three rings. Of course, they represent anthracene, phenanthrene and phenalenyl, respectively.

I   II   III

In graph-theoretical literature only the problem of enumeration of benzenoid graphs (*i. e.* the problem how many different arrangements of a given number of hexagons is possible) is studied[4]. The nomenclature of benzenoid graphs is discussed in Ref. 5. For theoretical studies of conjugated molecules the graph spectrum[2] is of utmost importance[3]. However, the spectral properties of benzenoid graphs seem to be almost completely unknown. In fact, *only one exact result is known*, namely the relation[6,7]

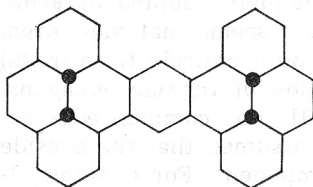$$\prod_{j=1}^{N} x_j = (-1)^{N/2} K^2 \tag{1}$$

where the set of numbers $\{x_1, x_2, \ldots x_N\}$ is the graph spectrum, N is the number of vertices, and K is the number of Kekulé structures. Of course, all

relations which hold for bipartite graphs[2] hold for benzenoid graphs as well. Recently, Hall has analyzed[8] these relations and was able to derive a set of *approximate* formulae for resonance energy, bond orders *etc.* of benzenoid systems. Additional approximate formulae of this kind can be found in Ref. 9.

SOME ELEMENTARY PROPERTIES OF BENZENOID GRAPHS

The number of rings (R) is one of the most obvious structural details of benzenoid graphs. Since the number of vertices (N) and edges (M) is not uniquely determined by R, as it can be seen when graphs I—III are compared, the notion of *internal vertex* is introduced.

A benzenoid graph divides the plane in one infinite and R finite regions (*i. e.* rings). All vertices and edges which lie on the boundary of the infinite region form the *perimeter* of the graph. The vertices which do not belong to the perimeter are internal. Their number is N_i. It is easily seen that all internal vertices are of degree[2] three, that is to say that they have three adjacent vertices. Therefore the internal vertices belong to three rings. Every internal vertex lies in the interior of a 12-membered cycle. N_i can be any non-negative integer. In example IV the internal vertices are labelled by ●.

IV

If $N_i = 0$, the corresponding molecules are called[5] »cata-condensed«. Hence, the following statements are equivalent:
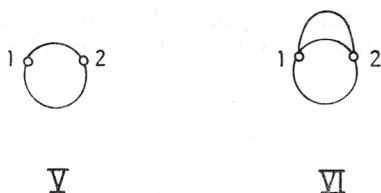
— $N_i = 0$,

— no vertex belongs to three rings,

— no three rings are mutually adjacent,

— all vertices belong to the perimeter,

— all cycles contained in the graph are of the length $4m + 2$ ($m = $ = natural number)[7],

— the dual graph of the molecular graph contains no triangles[10], and any of them can be used as a definition of cata-condensed systems.

The following equation

$$N + N_i = 4 R + 2 \qquad (2)$$

can be simply proved by induction. For $F = 1, 2, 3$ eq. (2) is fulfilled. Now, let V have R rings and eq. (2) becomes:

$$N (V) + N_i (V) = 4 R + 2 \qquad (3a)$$

$$\underline{\text{V}} \qquad\qquad \underline{\text{VI}}$$

Let there be A vertices on the perimeter of V between the vertices 1 and 2. If one generates a new ring in VI by joining a chain of B vertices to 1 and 2, it is obvious that

$$N_i \, (\text{VI}) = N_i \, (\text{V}) + A \tag{3b}$$

$$N \, (\text{VI}) = N \, (\text{V}) + B \tag{3c}$$

But since VI is benzenoid,

$$A + B + 2 = 6 \tag{3d}$$

Substituting eqs. (3b)—(3d) back into (3a) one obtains

$$N \, (\text{VI}) + N_i \, (\text{VI}) = 4 \, (R + 1) + 2 \tag{3e}$$

which completes the proof of eq. (2). Similarly it can be shown that

$$M + N_i = 5 \, R + 1 \tag{4}$$

Note that eqs. (2) and (4) are a generalization of the Euler formula $M - N = R - 1$.

By inspection of graphs V and VI, the equation

$$T = 2 \, (R - 1) \tag{5}$$

follows immediately, where T is the number of vertices of degree three. Actually, the vertices 1 and 2 are of degree two in V and of degree three in VI, while the degree of other vertices is not changed. If S is the number of vertices of degree two and D_p the degree of the vertex p,
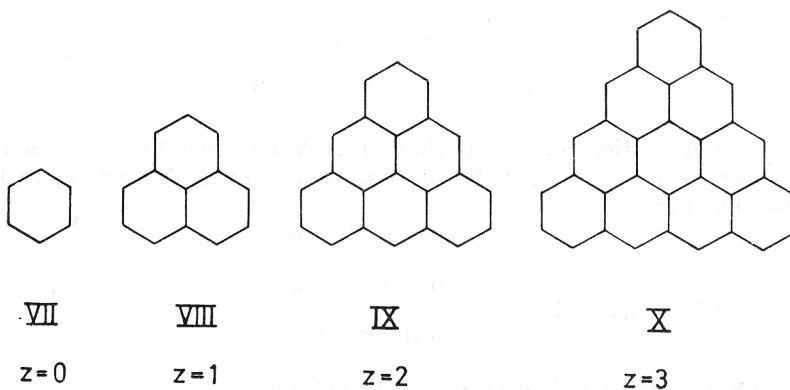
$$S = 2 \, R - N_i + 4 \tag{6}$$

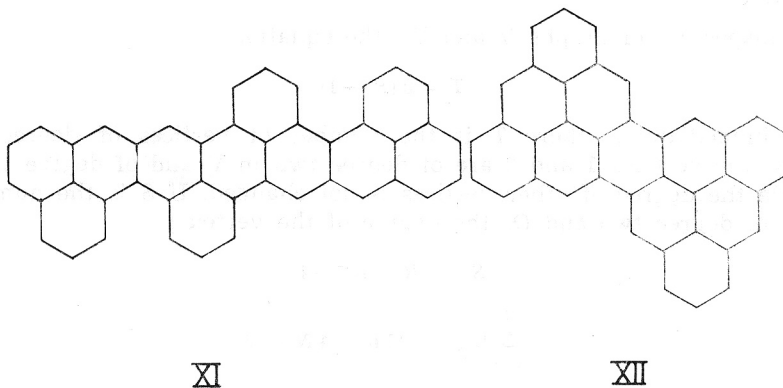$$\sum_{p=1}^{N} D_p^2 = 26 \, R - 4 \, N_i - 2 \tag{7}$$

Because of eq. (1) Kekulé structures play an important role in the graph spectral studies of conjugated systems[6,7]. Hall has demonstrated[8] that the total π-electron energy in a series of isomeric benzenoid hydrocarbons is a linear function of K. It can be shown that if a benzenoid graph has at least one Kekulé structure, $K \geqslant 4$ (except for $R = 1$ and $R = 2$). However, it is not simple to find in the general case the conditions for $K > 0$.

Benzenoid graphs are bipartite, that is their vertices can be separated in a unique manner into two groups — »starred« and »unstarred« — such that starred vertices are adjacent to the unstarred and *vice versa*. Let X and Y denote the number of starred and unstarred vertices, respectively and $Z = |X - Y|$.

Z can be any non-negative integer. This statement, which is not necessarily obvious, can be illustrated with the triangulene series VII—X.
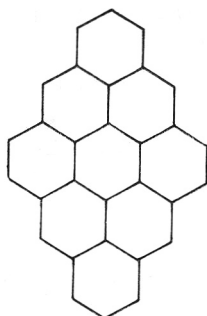

In every Kekulé structure a starred vertex is paired with an unstarred one. Therefore, $Z = 0$ is a necessary condition for the existence of Kekulé structures. However, this condition is not sufficient and one can find benzenoid graphs with $Z = 0$ which do not possess Kekulé structures. A trial and error procedure shows that XI and XII are such graphs with minimum R value ($R = 11$).

A sufficient condition for $K > 0$ is the existence of a Hamiltonian path in the molecular graph. If $N_i = 0$, the perimeter is a Hamiltonian cycle and therefore cata-condensed systems always possess Kekulé structures. Unfortunately, there are benzenoid graphs with $K > 0$ having no Hamiltonian paths. XIII is the smallest example of this kind ($R = 9$).

In concluding this section it is to be emphasized that there is no simple recipe to decide by inspection of the molecular graph whether $K = 0$ or not. In other words, the necessary and sufficient conditions for the existence of Kekulé structures seem to be rather complicated.

XIII

A SPECTRAL PROPERTY OF BENZENOID GRAPHS

The polynomial

$$P(x) = \sum_{j=0}^{N} a_j \, x^{N-j} \tag{8}$$

is called the characteristic polynomial of a graph[2] if

$$P(x) = \prod_{j=1}^{N} (x - x_j) \tag{9}$$

The relations that exist between the structure of the molecular graph and the coefficients a_j of the characteristic polynomial (the Sachs theorem[11]) are extensively discussed elsewhere[3,12]. Thus, it is well known that for all graphs the following simple expressions are valid:

$$a_1 = 0 \quad \text{or} \quad \sum_{j=1}^{N} x_j = 0 \tag{10}$$

$$a_2 = -M \quad \text{or} \quad \sum_{j=1}^{N} x_j^2 = 2\,M \tag{11}$$

This also means that *not only the values of N and M, but also the parameters R, N_i, T and S can be calculated from the graph spectrum*. Here we will be interested in a topological formula for a_4.

For benzenoid graphs which, of course, do not contain three- and four--membered cycles, a_4 is equal to the number of choices of a pair of nonadjacent edges[11,12]. This purely combinatorial problem can be solved using the following reasoning.

Let us consider an edge (p, q) between the vertices p and q. There are $M - D_p - D_q + 1$ edges which are not adjacent with (p, q). Therefore,

$$a_4 = \frac{1}{2} \sum_{(p,q)} (M - D_p - D_q + 1) \tag{12}$$

where the summation goes over all edges. Of course,

$$\sum_{(p,q)} (M + 1) = M (M + 1) \tag{13}$$

Now, every vertex p appears D_p times in the above summation and therefore

$$\sum_{(p,q)} (D_p + D_q) = \sum_{p=1}^{N} D_p^2 \tag{14}$$

This finally gives

$$a_4 = \frac{1}{2} [M (M + 1) - \sum_{p=1}^{N} D_p^2] \tag{15}$$

and since[13]

$$4 a_4 + a_2 \sum_{j=1}^{N} x_j^2 + \sum_{j=1}^{N} x_j^4 = 0 \tag{16}$$

$$\sum_{j=1}^{N} x_j^4 = 2 \sum_{p=1}^{N} D_p^2 - 2 M \tag{17}$$

Using the equations (4) and (7), both relations (15) and (17) can be expressed in terms of the topological parameters N_i and R:

$$a_4 = \frac{1}{2} [(5 R - N_i)^2 - 11 R + N_i + 4] \tag{18}$$

$$\sum_{j=1}^{N} x_j^4 = 6 (7 R - N_i - 1) \tag{19}$$

The fact that the expression (19) is equal to the number of closed walks of length four in the graph, and its consequences on the value of the total π-electron energy is discussed elsewhere[14].

The simple relations which are presented in this note are only the first step in a complex topological study of benzenoid systems. Hope can be expressed that this work will stimulate further investigations in the same direction.

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SAŽETAK

O nekim topološkim svojstvima benzenoidnih sustava

Ivan Gutman

Definirana je klasa grafova koja reprezentira benzenoidne sustave i izvedene su neke elementarne relacije koje važe u toj klasi. Diskutirana je egzistencija Kekuléovih struktura i ukazano na niz teškoća oko rješavanja tog problema. Izvedena je jednadžba koja povezuje spektar benzenoidnih grafova s nizom topoloških parametara tih grafova; ta jednadžba jedina je poznata relacija u toj klasi grafova.