CCA-896

Graph Spectral Theory of Conjugated Molecules*

*I. Gutman and N. Trinajstić***

The Rugjer Bošković Institute, 41001 Zagreb, Croatia, Yugoslavia

The graph spectral theory of conjugated molecules is presented. It is shown that the number of bonding, non-bonding, and antibonding Hückel molecular orbitals may be obtained directly from the topological features of a conjugated molecule. Similarly, it is also shown that the total Hückel π-electron energy and the π-resonance energy may be approximated rather accurately by the corresponding topological expressions. The estimation of the π-electron energy of infinite conjugated systems is also given. A graphical classification of conjugated hydrocarbons is proposed and the restricted extension of the Coulson-Rushbrooke pairing theorem to certain heteroconjugated molecules is discussed.

INTRODUCTION

The earliest application of graph theory in chemistry*** (more precisely in organic chemistry) goes back to 1857, when Cayley[1] enumerated the isomers of saturated hydrocarbons C_nH_{2n+2} (with a given n of carbon atoms) using for this purpose a class of graphs called *trees*[2]. This may be surprising in a way because graph theory has been relatively recently founded as a branch of pure mathematics[3], though it has been discovered the first time[4] by Euler in 1736. However, there seems to be hardly any concept in natural sciences which is closer to the notion of a graph than the structural formulae of chemical compounds. In fact, there is no essential difference between a graph and a structural formula. A graph is, simply said, a mathematical structure which may be used to represent the topology of a given molecule. Therefore, chemists can easily grasp the concepts of graph theory. Moreover, chemists actually know and use a number of graph-theoretical theorems without being aware of this fact in many cases. A classic example is provided by the concept of *alternant hydrocarbons* introduced by Coulson and Rushbroke[5], which is for graph-theorists the *two-colour problem*[2]. However, the language of graph theory is very different from that of chemistry. Therefore, a short, glossary is offered

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* Reported in part at the Micro-symposium »Graph Theory in Chemistry« held in Mülheim a. d. Ruhr on May 26—28, 1975.

** Also at the Chemistry Department, Faculty of Science and Mathematics, University of Zagreb, 41000 Zagreb, Croatia, Yugoslavia.

*** Dr. D. H. Rouvray (Johannesburg) has pointed out to us that the first application of graph theory to chemistry actually appears to be two papers by Kopp published in 1842 (H. K o p p, *Ann. Chem.* **41** (1842) 79, 169) in which the author has studied the additive properties of molecular species. We thank Dr. Rouvray for this information.

in Table I, which should help the reader to follow more easily the text, because we will freely use and interchange the mathematical and chemical terminologies throughout this work.

TABLE I

The correspondence between the graph-theoretical and chemical terminology

Graph-theoretical terminology	Chemical terminology
Molecular (chemical) graph	Structural formula
Vertex	Atom
Rooted vertex	Atom of a specified element
Edge	Covalent chemical bond
Degree of a vertex	Valency of an atom
Tree	Acyclic hidrocarbon
Cycle	Ring
Chain	Linear polyene
Bipartite (bichromatic) graph	Alternant hydrocarbon
Non-bipartite graph	Non-alternant hydrocarbon
Adjacency matrix **A**	Topological (structural) matrix
Eigenvector of **A**	Topological MO
Eigenvalue of **A**	MO energy level
Characteristic polynomial	Secular equation

The advantage of using the graph theory in chemical studies lies in the possibility to apply *directly* its mathematical apparatus and proof techniques. Besides, one may consider a given problem on a higher level of abstraction which enables a relatively simple insight into the structural features of the molecule. Finally, a graph-theoretical language is much more precise and contains numerous terms which have no equivalent in chemistry.

Every molecule may be understood as a geometric object; similarly, chemical reactions may be considered as movements and rearrangements of geometric objects. This point of view is inherent in the static and dynamic conformational theory. Although the prime importance of conformational geometric data for understanding and predicting chemical facts cannot be denied, useful conclusions could be drawn also in a number of cases and predictions made without the actual knowledge of molecular geometry. The idea that one may sometimes neglect *metric* characteristics (that is to say, bond lengths and bond angles) in chemical studies became gradually more and more popular in 1960's. The term *molecular topology* is appropriately used to describe the *non-metric* molecular properties. It should be noted that topology, a branch of mathematics, investigates the **non-metric** relationships of geometric (and more abstract) structures. *We define molecular topology as the totality of information contained in the molecular graph.* Perhaps here is a good point to indicate for the chemical community at large, in order to avoid possible misunderstanding of the use and potential of graph theory, that graph-theore-

tical methods should be expected primarily to be of use as a complementary approach where the topology and the combinatorial nature play an important role, in parallel to the application of the group theory to problems where symmetry is an important feature of the system.

Concepts of topology (and graph theory, though not always recognized as such) are nowadays analyzed and applied to a variety of branches of chemical science: photochemistry[6], stereochemistry[7], transition metals chemistry[8], boron hydride chemistry[9], saturated[10] and unsaturated[11] hydrocarbon chemistry, chemical documentation[12] and classification[13], isomer enumeration[14], n. m. r.[15], stoichiometry[16], etc, ... etc, ... Furthermore, basic concepts of chemistry such as configuration, isomerism, valency, etc. are shown to have a topological basis[17]. Finally, it is worthy to be noted that the Woodward-Hoffmann approach to the study of concerted reactions[18] is also based on the topological properties of reactants and products[19].

In the present article we wish to review mainly the results of our investigations of the topological properties of conjugated molecules using the *graph spectral theory*. A question could, of course, be asked immediately: why go through all this trouble to develop and use the graph spectral theory when it does not give any information which is not already available from Hückel MO calculations? We feel that there are several good points in favour of developing the graph spectral theory of conjugated systems:

(*i*) A number of results could be obtained without the use of computers just by using pencil and paper. This is of importance for experimental chemists who are sometimes kept away from using current computational theories because of the necessity to carry them out on computers, using specialized programs.

(*ii*) Sometimes a purely numerical computerized examination hides away the importance of a particular structural feature of a molecule which may account for some properties of the molecule.

(*iii*) The obtained graphical results have a general validity and may be formulated as theorems and/or rules which can be then applied to any similar group of molecules without any further numerical or conceptual work.

(*iv*) Finally, it is not our intention to compete with standard HMO calculations, but rather to develop a symbolism that permits chemists to think graphically, *i. e.* to learn as much as possible about the possible chemical behaviour of the molecule by examining the properties of its graph.

But, before we proceed to discuss the graph spectral theory, a brief survey of the basic concepts and definitions[2,20] of graph theory will be given for the benefit of those readers who are not very familiar with the apparatus of graph theory. This will be presented in the next section.

BASIC DEFINITIONS AND CONCEPTS OF GRAPH THEORY

In this section a condensed survey of the language and formalism of graph theory is given. For more detailed and rigorous expositions see[2,20].

We will consider a finite non-empty set of some elements ϑ and a binary (symmetric and antireflexive) relation **R** defined on the set ϑ. *An ordered pair* $(\vartheta, \mathbf{R}) = G$ *is called a graph.* Elements of the set ϑ are called *vertices* and their number is denoted by N. It is customary to depict a graph by means of a diagram in which the vertices are drawn as circles (o) and two vertices

are connected by a line if they belong to relation **R**. These lines are called *edges* and their number is denoted by ν. Thus, for example, a graph:

$$G = (\{1,2,3,4\}, \ \{(1,2), (2,1), (2,3), (3,2), (3,4), (4,3), (4,1), (1,4)\}) \tag{1}$$

can be drawn as follows:

G
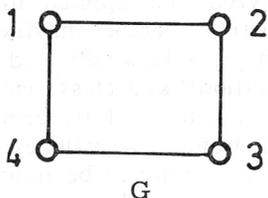
We call this graph a *molecular graph,* but we also give it a more specific name: *Hückel graph*[21], because it represents a π-electron network of cyclobutadiene. Note that edges in G do not cross. Such a graph is called a *planar* graph. It can be easily seen that all graphs related to conjugated molecules must be planar. Therefore, *planarity* will be a property of all graphs considered in this article.

Any arbitrary graph G appropriately labelled may be represented by a matrix. There are several ways of assigning a matrix to a graph but for our purpose only the *(vertex) adjacency matrix* of a graph **A** (G) is important. The adjacency matrix **A** of a labelled graph with N vertices is the N × N matrix defined as follows:

$$A_{pq} = \begin{cases} 1 \text{ if, and only if, } (p, q) \in \mathbf{R} \\ 0 \text{ if, and only if, } (p, q) \ non \in \mathbf{R} \end{cases} \tag{2}$$

As an example, the adjacency matrix of the cyclobutadiene graph G (see (1) and the corresponding figure) is given below:

$$\mathbf{A} (G) = \begin{bmatrix} 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{bmatrix} \tag{3}$$

Clearly, this matrix reflects the topology of cyclobutadiene, and therefore, all molecular properties which may be obtained by mathematical handling of such a matrix must be topology-dependent.

If $\vartheta_i \subset \vartheta$ and $\mathbf{R}_i \subset \mathbf{R}$, and if $\mathbf{R}_i$ is a binary relation defined on a set ϑ_i, then the graph G_i

$$G_i = (\vartheta_i, \mathbf{R}_i) \tag{4}$$

is called a *subgraph* of graph G. Graphs G′, and G″ are subgraphs of the cyclobutadiene graph G:

G′   G″

A *spanning subgraph* is a subgraph containing all vertices of a graph. G''' is a spanning subgraph of cyclobutadiene graph G.

G'''

A *path* in a graph G is an ordered set of edges $(e_1, e_2, \ldots, e_n)$ with a property; the edge e_j $(1 < j \leqslant n)$ starts from the edge where e_{j-1} ends. The length of such a path is n. The adjacency matrix is related to the number of paths in a graph in the following way:

$$(\mathbf{A}^n)_{pq} = \text{number of paths of length } n \text{ between the vertices } p \text{ and } q \qquad (5)$$

When graph theory is used in chemical problems, the relation **R** has to be *symmetric* and *antireflexive, i. e.*:

$$(p, q) \in \mathbf{R} \Rightarrow (q, p) \in \mathbf{R} \qquad (6)$$

$$(p, q) \in \mathbf{R} \Rightarrow p \neq q \qquad (7)$$

Because of (2), (6), and (7), the adjacency matrix is *symmetric* and has *zero diagonal elements*:

$$\mathbf{A}^+ = \mathbf{A} \qquad (8)$$

$$A_{pp} = 0; \; p = 1, 2, \ldots., N \qquad (9)$$

If there is no path between two vertices, they belong to different *components* of a graph. The number of graph components is denoted as $c(G)$. Thus, *connected* graphs all have $c(G) = 1$. All molecular graphs necessarily have only *one* component.

The shortest path between two vertices p and q is called the *distance* between two vertices and is denoted by $d(p, q)$. Several important properties of the distance function are summarized below:

$$d(p, q) = 0 \text{ if, and only if, } p = q \qquad (10)$$

$$d(p, q) = d(q, p) \qquad (11)$$

$$d(p, q) + d(q, r) \geqslant d(p, r) \qquad (12)$$

$$d(p, q) = 1 \text{ if, and only if, } (p, q) \in \mathbf{R} \qquad (13)$$

All the vertices among which the distance is unity are called the *first neighbours*. Second $d(p, q) = 2$, third $d(p, q) = 3$, *etc.*, neighours are defined in a completely analogous way. The number of first neighbours of a given vertex is called the *degree (valency)* of this vertex, $D_1^{(p)}$. The sum of degrees of all vertices in a graph is related to the number of edges in a graph:

$$\sum_{p=1}^{N} D_1^{(p)} = 2\nu \qquad (14)$$

Only vertices of degree 1, 2, and 3 can appear in graphs belonging to conjugated hydrocarbons.

A graph in which every vertex has the same degree is called a *regular* graph. A connected graph which is *regular* of degree two is called a *cycle*. The cyclobutadiene graph is a regular graph and a cycle. If the distance between all vertices is unity, the graph is *complete*. The degree of all vertices in such a graph is given by

$$D_1^{(p)} = N - 1 \tag{15}$$

and is called the complete graph of degree $D_1^{(p)}$. Graph G' is a complete graph of degree 1. These definitions will be necessary later for the introduction of the notion of a Sachs graph.

Graphs, the vertices of which can be coloured in two colours in such a way that two vertices of the same colour are *never* in the relation **R**, are called *bipartite (bi-colourable)* graphs. A characterization of a bipartite graph is given by a following theorem: *a graph is bicolourable if, and only if, it has no odd--membered cycles.* Conjugated hydrocarbons which may be depicted by bipartite graphs are called alternant hydrocarbons (AH)[22]. Hydrocarbons which can be represented by non-bipartite graphs are called *non-alternant hydrocarbons* (NAH).

Since the rows and columns of the adjacency matrix correspond to an arbitrary labelling of the vertices of the graph, it is clear that we shall be interested primarily in those properties of the adjacency matrix which are invariant under the permutations of the rows and columns. Foremost among such properties are the spectral properties of **A**. The *spectrum* of a graph (the *graph spectrum*) is the set of numbers which are eigenvalues of **A**, *i. e.* the set of all solutions of a polynomial:

$$P(x) = \det |x\mathbf{1} - \mathbf{A}| \tag{16}$$

where **1** is the unity matrix. Polynomial $P(x) = P(G; x)$ is called the *characteristic polynomial* of a graph and has the following form:

$$P(G; x) = \sum_{n=0}^{N} a_n x^{N-n} \tag{17}$$

where a_n are the *coefficients* of $P(G; x)$. $P(G; x)$ is of degree N. The solutions of $P(G; x)$ are denoted as x_i ($i = 1, 2, \ldots, N$). x_i represent *eigenvalues* of the adjacency matrix:

$$\mathbf{C}_i \mathbf{A} = x_i \mathbf{C}_i; \; i = 1, 2, \ldots, N \tag{18}$$

where $\mathbf{C}_i$ are the *eigenvectors* of **A**:

$$\mathbf{C}_i = (C_{i_1}, C_{i_2}, \ldots, C_{iN}) \tag{19}$$

Eq. (18) may be also given in a matrix notation:

$$\mathbf{C} \mathbf{A} = \mathbf{X} \mathbf{C} \tag{20}$$

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$$\sum_{p=1}^{N} D_1^{(p)} = 2\,\nu \qquad (14)$$

where

$$\mathbf{C} = \begin{bmatrix} \mathbf{C}_1 \\ \mathbf{C}_2 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \mathbf{C}_N \end{bmatrix} \tag{21}$$

and

$$\mathbf{X} = \begin{bmatrix} x_1 & & & & \\ & x_2 & & \mathbf{O} & \\ & & \cdot & & \\ & & & \cdot & \\ \mathbf{O} & & & \cdot & \\ & & & & x_N \end{bmatrix} \tag{22}$$

A graph spectrum is an important graph invariant and is a topic of intensive studies in mathematics[23]. An important property of a graph spectrum is given below:

$$- D_{max} \leqslant x_i \leqslant + D_{max} \tag{23}$$

where D_{max} is the maximal degree of a vertex in a graph. Therefore, the whole spectrum of the Hückel graphs lies in the interval[24] —3 to +3. However, it is interesting to note that only *six* Hückel graphs have integral spectra[25] (the so called integral graphs[26]), *i. e.* the whole spectrum consisting of integers (see Fig. 1)

$$\{1, -1\} \qquad \{2, -1, -1\} \qquad \{2, 0, 0, -2\}$$

$$\{2, 1, 1, -1, -1, -2\} \qquad \{2, 1, 0, 0, -1, -2\} \qquad \{2, 1, 1, 0, -1, -1, -2\}$$

Fig. 1 — Hückel graphs with integral spectra

The coefficients of the characteristic polynomial of a graph may be obtained[27] from the Sachs' formula[28]:

$$a_n = \Sigma \, (-)^{c(s)} \, 2^{r(s)}; \quad 0 \leqslant n \leqslant N \tag{24}$$
$$s \, \epsilon \, S_n$$

where the symbols have the following meaning: s denotes a Sachs graph[27], S_n is a set of all Sachs graphs (with n vertices) of a graph G, $c(s)$ is the total number of components of a Sachs graph s, and, finally, $r(s)$ is the number of cyclic components of a Sachs graph s. The summation in (24) is over all elements of the set S_n. A *Sachs graph*[27] s is a subgraph of a graph G with only components complete graphs of degree one and cycles. Below we list all Sachs graphs of the cyclobutadiene graph:

$$S_1 = \varnothing$$

$$S_2 = \left\{ \left({}^1_4 \right), \left(\overset{1\;\;2}{\circ{-}\circ} \right), \left({}^2_3 \right), \left(\underset{4\;\;3}{\circ{-}\circ} \right) \right\}$$

$$S_3 = \varnothing$$

$$S_4 = \left\{ \left(\right), \left(\right), \left(\right) \right\}$$

Now, using the Sachs' formula, one may obtain directly a characteristic polynomial associated with the cyclobutadiene graph:

$$P(G; x) = x^4 - 4x^2 \tag{25}$$

with a graph spectrum: $\{2, 0, 0, -2\}$.

It should be noted here that Coulson[24] first, and later Spialter[12], Hosoya[10a, b, 29] have independently developed graphical methods for the enumeration of a_n; however, it can be shown that these are fully equivalent to the method of Sachs[30].

EQUIVALENCE BETWEEN THE HÜCKEL THEORY AND THE GRAPH SPECTRAL THEORY

The Hamiltonian matrix (**H**) in Hückel's theory[31,32] is given by

$$\mathbf{H} = \alpha\,\mathbf{1} + \beta\,\mathbf{A} \tag{26}$$

where **1** is the unity matrix, **A** an adjacency (topological) matrix of a Hückel graph, α and β are the Coulomb (27) and resonance (28) integrals, respectively, of some effective one-electron Hamiltonian operator (H_{eff}).

$$< i\,|\,H_{eff}\,|\,i > = \alpha \tag{27}$$

$$< i\,|\,H_{eff}\,|\,j > = \begin{cases} \beta \text{ if atoms } i \text{ and } j \text{ are bonded} \\ 0 \text{ otherwise} \end{cases} \tag{28}$$

The secular equation of Hückel's theory is expressed as follows (since the basis functions $|\,i >$ are orthonormal):

$$\det |\,\mathbf{H} - E_i\,\mathbf{1}\,| = 0; \quad i = 1, 2, \ldots, N \tag{29}$$

Introducing Eq. (26) in (29) one obtains:

$$\det \left|\, \left(\frac{E_i - \alpha}{\beta} \right) \mathbf{1} - \mathbf{A} \,\right| = 0 \tag{30}$$

If we compare the above equation with Eq. (16) it is seen that the numbers

$\dfrac{E_i - \alpha}{\beta}$ are actually making up the spectrum of a Hückel graph, *i. e.:*

$$E_i = \alpha + x_i\,\beta;\ i = 1,\, 2,\, \ldots.,\ N \tag{31}$$

Using β as an energy unit and α as the zero-energy point, we have

$$E_i = x_i \tag{32}$$

or, in other words, *the eigenvalues of the adjacency matrix are identical with Hückel orbital energy levels.* From Eq. (26) it is seen that **H** and **A** commute and have, therefore, the same eigenvectors. Since (compare with Eq. (18)):

$$\mathbf{C}_i\,\mathbf{H} = E_i\,\mathbf{C}_i;\ i = 1,\, 2,\, \ldots.,\ N \tag{33}$$

and because of the LCAO form of

$$\Psi_i = \sum_j \mathbf{C}_{ij}\,|\,j> \tag{34}$$

or

$$\Psi_i = (C_{i_1},\ C_{i_2},\ \ldots.,\ C_{iN}) \tag{35}$$

and from the comparison with Eq. (19) it follows:

$$\Psi_i = \mathbf{C}_i \tag{36}$$

or, *the eigenvectors of the adjacency matrix are identical with the Hückel molecular orbitals.*

Therefore, it is clear that the spectrum of the graph is rather important in Hückel-type calculations. The Hückel theory is in fact fully equivalent to the graph spectral problem. This was first emphasized by Günthard and Primas[33] and later by Schmidtke[8].

Hückel orbitals corresponding to $x > 0$, $x = 0$, and $x < 0$ are called *bonding, non-bonding,* and *antibonding,* respectively. Note that the number of linearly independent non-bonding molecular orbitals (NBMO) is equal to the multiplicity of the number zero in the graph spectrum[34]. The number of bonding, non-bonding, and antibonding MO's is denoted by N_+, N_o, and N_-, respectively. They are related to the total number of atoms in a conjugated molecule (N):

$$N_+ + N_o + N_- = N \tag{37}$$

The total Hückel π-electron energy of a conjugated molecule in the ground state is given by:

$$E_\pi = \sum_{i=1}^{N} g_i\,E_i \tag{38}$$

or, using Eq. (32):

$$E_\pi = \sum_{i=1}^{N} g_i\,x_i \tag{39}$$

g_i is the orbital occupancy number. In the majority of conjugated systems the occupancy number fulfills the equation:

$$g_i = \begin{cases} 2 & \text{for } x_i > 0 \\ 1 & \text{for } x_i = 0 \\ 0 & \text{for } x_i < 0 \end{cases} \tag{40}$$

Utilizing Eq. (40) we can now put down the working formulae for E_π calculations:

$$E_\pi = 2 \sum_{i=1}^{N/2} x_i; \quad N = \text{even} \tag{41}$$

$$E_\pi = x_{(N+1)/2} + 2 \sum_{i=1}^{(N-1)/2} x_i; \quad N = \text{odd} \tag{42}$$

TOTAL π-ELECTRON ENERGY

The total π-electron energy (E_π) is a very important property of conjugated molecules and it can be in a proper way related to their measurable thermodynamic properties[35]. Here we wish to show how F_π can be estimated by considering the topological characteristcs of a conjugated molecule. Several authors were engaged in such a research[36]. The following analysis about the relation between E_π and topological properties of conjugated molecules can be simply carried out[37,38]. The total π-electron energy (in β units) is given by

$$E_\pi = 2 \sum_{i=1}^{N/2} x_i \tag{43}$$

For alternant and a greater part of non-alternants the following formula is assumed to hold:

$$E_\pi = \sum_{i=1}^{N} |x_i| \tag{44}$$

The coefficients a_n of the characteristic polynomial of the graph G corresponding to the conjugated molecule may be evaluated by inspection of the molecular topology using the Sachs formula (24). Let S_n be defined as

$$S_n = \sum_{i=1}^{N} x_i^n \tag{45}$$

It is known from the work of Günthard and Primas[33] and others[39] that

$$a_1 = -S_1 \tag{46}$$

$$a_2 = -\tfrac{1}{2} S_2 \tag{47}$$

$$a_3 = -\tfrac{1}{3} S_3 \tag{48}$$

Assuming that $S_1 = 0$, which is true in the case of hydrocarbons[27] (though in the case of heteroconjugated systems it might be $S_1 \neq 0$)[40,41], the following relation holds (detailed proof see ref. 38).

$$n a_n + \sum_{i=1}^{n} a_{n-i} S_i = 0 \tag{49}$$

$|x|$ can be expanded in a Taylor series and, hence, using Eq. (44), the following expression is obtained:

$$E_\pi = g \sum_{n=0}^{\infty} \sum_{i=1}^{N} \binom{1/2}{n} \left[\left(\frac{x_i}{g} \right)^2 - 1 \right]^n \tag{50}$$

where g is an arbitrary number, and the condition $g \geqslant 3/\sqrt{2}$ is sufficient for the convergence of the infinite summation. Of course, Eq. (50) is independent of g. The k-th approximation for E_π

$$E_\pi^{(k)} = g \sum_{n=0}^{k} \sum_{i=1}^{N} \binom{1/2}{n} \left[\left(\frac{x_i}{g} \right)^2 - 1 \right]^n \tag{51}$$

can be now written in terms of S_n. For $2k \leqslant N$, $E_\pi^{(k)}$ is a function of N, a_2, a_4, ..., a_{2k}. E_π can be calculated with reasonable accuracy by applying the Sachs formula, assuming N being large enough. A tedious, but not complicated calculation using the Sachs formula gives

$$E_\pi^{(1)} = g \left[\frac{N}{2} + \frac{\nu}{g^2} \right] \tag{52}$$

$$E_\pi^{(2)} = g \left[\frac{3N}{8} + \left(\frac{3}{2\,g^2} + \frac{1}{4\,g^4} \right) \nu - \frac{n_4}{g^4} - \frac{1}{4\,g^4} \Sigma D_1^2 \right] \tag{53}$$

$$E_\pi^{(3)} = g \left[\frac{5N}{15} + \left(\frac{15}{8\,g^2} + \frac{5}{8\,g^4} - \frac{1}{8\,g^6} \right) \nu - \left(\frac{5}{2\,g^4} + \frac{3}{g^6} \right) n_4 + \right.$$

$$\frac{3}{4\,g^6} \Sigma D_1 \, \square + \frac{3\,n_6}{4\,g^6} - \frac{5}{8\,g^4} \Sigma D_1^2 + \frac{1}{16\,g^6} \Sigma D_1^3 +$$

$$\left. \frac{3}{8\,g^6} \Sigma D_1 D_2 - \frac{3}{8\,g^6} \Sigma D_2 - \frac{3}{16\,g^6} \Sigma D_3 \right] \tag{54}$$

where n_4 and n_6 denote the number of 4- and 6-membered rings and D_1, D_2, D_3 are the number of first, second, third, neighbours of a vertex (these values really represent the branching of a carbon skeleton)[42]. Summation in Eqs. (52)—(54) are going over all vertices of the graph. Σ indicates the summation
$$\square$$
only over vertices belonging to a 4-membered ring. These formulae are rather clumsy to work with, but we learn from them several important points concerning the topological origin of the total π-electron energy of a conjugated molecule:

(1) the major part of E_π comes from the number of atoms and bonds present in a molecule. Thus, the McClelland formula[36f] is given by Eq. (52), and Hall formula [36b] by Eq. (53).

(2) the presence of 4- and 6-membered rings decreases and increases the value of E_π, respectively; the effect of 4-membered ring being stronger then that of a 6-membered one (this may be easily generalized for all $[4m]$- and $[4m + 2]$-membered ring systems[43,44]).

(3) the branching of the carbon skeleton, that is the increase of the number of vertices with $D_1 = 3$ will decrease E_π. Particularly, a closed-shell linear polyene is always more stable than a branched one[42] (almost all conjugated polyenes occuring in nature, e. g. carotenoids, are linear[45]). However, the branching of a 4-membered ring will give a small energy gain. This is in good accord with experience in cyclobutadiene chemistry[46-49].

The above results have stimulated the search for the semiempirical relationships between the total π-electron energy and the topological parameters that characterize the adjacency matrix. The following parametric relationship has been found[50]:

$$E_\pi = C_1 N + C_2 \nu + C_3 (4 n_4 + \Sigma D_1{}^2) + C_4 \ln (\text{ASC}) \qquad (55)$$

where the symbols have the same meaning as before and ASC is the algebraic structure count[51] which is equal to the difference of the Kekulé structures when their parity[52] is taken into account:

$$\text{ASC} = | K^+ - K^- | \qquad (56)$$

The precision of the four-parameter expression (55) for E_π is good, with an average error of about $2^0/_0$ in E_π. Similarly, the topological formula to approximate the π-resonance energy, for example in the Hess-Schaad approach[53], is derived[54,55]. A similar but rather qualitative attempt has been made earlier by Knop et al.[56].

Here we also mention briefly our efforts to estimate the π-electron energies of infinite conjugated systems[57] in order to indicate where the power of the topological method really is displayed. An infinite graph G_∞ will be understood as the limes of a sequence of graphs $G_0, G_1, G_2, \ldots.$, where G_n may be obtained from G_{n-1} according to a given formula. Symbolically,

$$G_\infty = \lim G_n \qquad (57)$$

For example,

$$G_0 \qquad G_1 \qquad G_2 \qquad G_n$$
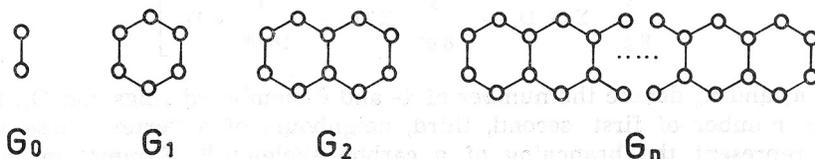
For infinite graphs E_π is infinite, and besides

$$\lim N_n = \lim \nu_n = \infty \qquad (58)$$

but

$$<D>_\infty = \lim <D>_n \leqslant 3 \qquad (59)$$

$<D>$ is the mean vertex degree. It may be shown[36f,58] that the following inequality is valid for (finite) molecular graphs:

$$2 [2 \nu - N(\det \mathbf{A})^{2/N}] \leqslant 2 N\nu - E_\pi{}^2 \leqslant (N-2) [2 \nu - N(\det \mathbf{A})^{2/N}] \qquad (60)$$

This expression may be transformed by use of Eq. (14) into

$$(2/N) [<D> - (\det A)^{2/N}] \leqslant <D> - e \leqslant [(N-2)/N] [<D> - (\det A)^{2/N}] \qquad (61)$$

where $e = E_\pi/N$ is the total π-electron energy per electron. e Has also a finite value for infinite conjugated systems. Therefore, $\lim(\det \mathbf{A})^{2/N} = \mathbf{D}$ must be finite, and hence,

$$\lim \{(2/N) [<D> - (\det \mathbf{A})^{2/N}]\} = 0 \qquad (62)$$

Finally,

$$\mathbf{D}^{1/2} \leqslant e_\infty \leqslant (<D>_\infty)^{1/2} \qquad (63)$$

and

$$e_\infty \approx {}^1\!/_2 \, (\mathbf{D}^{1/2} + <D>_\infty^{1/2}) \tag{64}$$

The applicability of the approximate equation (64) is illustrated for several infinite conjugated systems in Table II.

TABLE II

Approximate π-electron energies of infinite conjugated systems

Molecule[a]	$<D>_\infty$	$\mathbf{D}$	e_∞ Eq. (64)	e_∞ Literature
(1)	2	1	1.207	1.273[c]
(2)	2	1	1.207	1.216[d]
(3)	14/6	1.260	1.394	—
(4)	10/4	1	1.291	1.403[e]
(5)	10/4	1.272[b]	1.427	1.437[e]
(6)	26/10	1.246	1.429	1.461[e]
Graphite	3	1.297	1.515	1.576[e]

[a] Presented in Fig. 2.
[b] Since $K_n = (1/\sqrt{5}) \{[(1 + \sqrt{5})/2]^{n+2} - [(1 - \sqrt{5})/2]^{n+2}\}$, it is $\mathbf{D} = \sqrt{(1 + \sqrt{5})/2}$ (note that $|\det \mathbf{A}| = K^2$).
[c] O. E. Polansky, *Monat. Chem.* **91** (1960) 916.
[d] I. Gutman, N. Trinajstić, and T. Živković, *Croat. Chem. Acta* **44** (1972) 501.
[e] C. A. Coulson and G. S. Rushbrooke, *Proc. Roy. Soc. (Edinburgh)* **A62** (1948) 350.

(1)

(2)

(3)

(4)

(5)

(6)
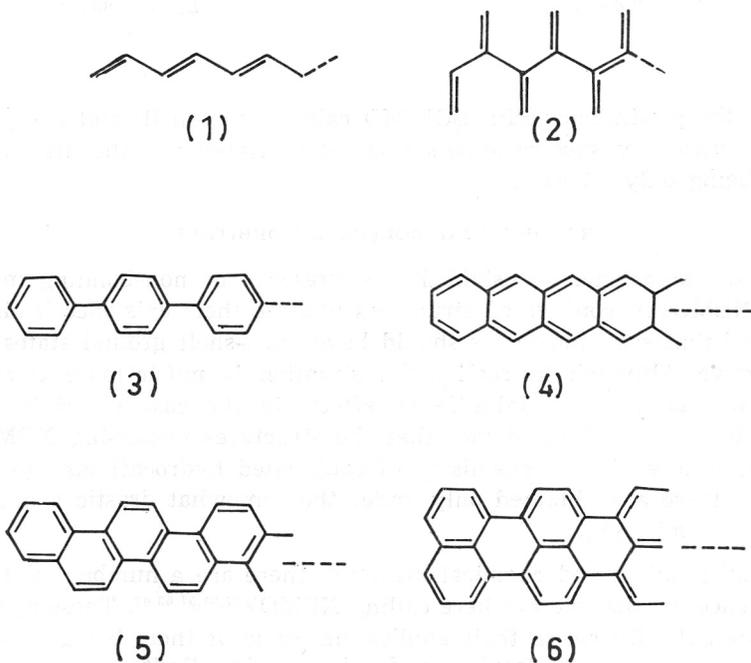
Fig. 2 — Some infinite conjugated systems

Finally, we wish to mention briefly that there are possible non-identical graphs with the same total π-electron energy. However, this is not an accidental identity. The inspection of their spectra shows that these are identical. Such molecules are called *isospectral* molecules[39] (in the mathematical literature[2] two non-isomorphic graphs are called *cospectral* if they have the same eigenvalues). Recently several reports were published[59,60] on the properties of isospectral molecules. An isospectral pair of molecules is, for example, 1,4-divinyl--benzene (I) and 2-phenyl-butadiene (II):

(I)

{2.214,   1.675,   1.0,   1.0,   0.539,
— 0.539, — 1.0, — 1.0, — 1.657, — 2.214}[61]
$$E_\pi = 12.857\ \beta$$

(II)
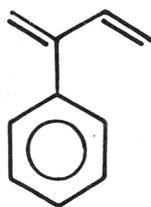
{2.214,   1.675,   1.0,   1.0,   0.539,
— 0.539, — 1.0, — 1.0, — 1.675, — 2.214}[61]
$$E_\pi = 12.857\ \beta$$

Note that the preliminary PPP SCF MO calculations on (I) and (II) predicted their theoretical u. v. spectra to be similar; the difference in the first transition energies being only 0.1 eV[62].

NON-BONDING MOLECULAR ORBITALS

It is of importance to establish the presence of non-bonding molecular orbitals (NBMO) in conjugated structures because their existence leads to the prediction[63] that such molecules should have open-shell ground states and be very reactive Although in reality the situation is much more complicated (for example because of, Jahn-Teller effects in the case of triplet ground states [64]) it is an established fact that the structures possessing NBMO's are rarely encountered in the chemistry of conjugated hydrocarbons[65] (or, at the very least, these are obtained only under the somewhat drastic conditions of rigid-glass chemistry[66]).

In mathematical and chemical literature there are a number of studies of the occurence of what we are here calling NBMO's[27,34,51,63,67]. These approaches are considerably diverse in their application, some of them being particularly impractical for larger molecules, and others being limited to one class of molecules only. Here we will outline a simple method for the determination of

NBMO's. Since we know that the number of NBMO's is identical with the number of zeros in the graph spectrum, and since

$$\det \mathbf{A} = \prod_{j=1}^{N} x_j \tag{65}$$

the determinant of $\mathbf{A}$ *will be zero if, and only if, there exists at least one zero in the graph spectrum.* Hence, the problem of determining the number of zeros in the graph spectrum is closely related to the problem of evaluating the determinant of the adjacency matrix of the graph in question.

In this connection a very interesting and important relation between the elementary MO theory and resonance theory arises: the determinant $\mathbf{A}$ may be evaluated from the knowledge of the number of Kekulé structures associated with the graph having adjacency matrix $\mathbf{A}$. We denote, in accordance with Dewar and Longuet-Higgins[67a], the number of Kekulé structures as K and consequently the number of Kekulé structures of *even* and *odd* parity as K^+ and K^-, respectively. There is some difficulty in determinig the parity of Kekulé structures by use of the Dewar-Longuet-Higgins method. Wilcox[51] tried to overcome this difficulty by giving a set of rules which, however, cover only special types of molecules. Accordingly we have endeavoured to establish simple rules for determining the mutual parity of two Kekulé structures[68]. For an arbitrary conjugated system (subjected to the limitation[68] that it should not contain only odd-membered rings if it is a three-or many-cyclic system) the following rule is appropriate for determining the parity of two Kekulé structures: *if the Sachs graph obtained by superposition of two Kekulé graphs contains an even (odd) number of [4m]-membered rings, the Kekulé structures in question have the same (opposite) parity.* Kekulé graphs correspond to Kekulé structures[69]. K^+ and K^- are related to the adjacency matrix in the following way[70]:

$$\det \mathbf{A} = (-)^{N/2} (K^+ - K^-)^2 + (-)^N \sum_{s \in S_n^{00}} (-)^{c(s)} 2^{r(s)} \tag{66}$$

where S_n^{00} is the set of Sachs graphs which are simultaneously spanning subgraphs of a graph and which contain at least one odd cycle. For AH's which do not contain odd-membered rings ($S_\pi^{00} = \emptyset$), the above equation reduces to the Dewar-Longuet-Higgins formula:

$$\det \mathbf{A} = (-)^{N/2} (K^+ - K^-)^2 \tag{67}$$

Furthermore, for AH's when $K = 0$, because $K^+ = K^- = 0$, Eq. (67) gives

$$\det \mathbf{A} = 0 \tag{68}$$

This result, which represents one of the most important cases of the congruency between the resonance theory and molecular orbital theory, has also been verified experimentally; all systematic attempts to prepare stable AH's with no single Kekulé structure have so far failed[65].

Formulae (66) and (67), together with the rule for enumeration of K^+ and K^-, give the organic chemists a very simple, but powerful method for evaluating det $\mathbf{A}$. This is illustrated for pyracyclene (III).
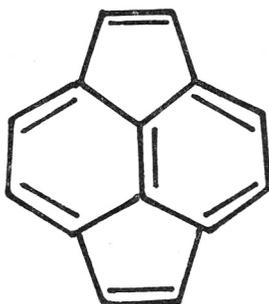
(III)

We first give all Kekulé structures of pyracyclene:

K_1 K_2 K_3 K_4
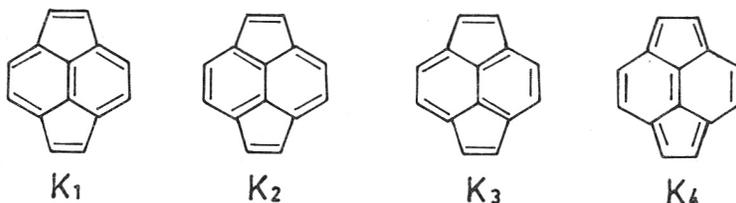
The reader may easily verify that K_1, K_2, and K_3 are Kekulé structures of even parity ($K^+ = 3$) and K_4 is a Kekulé structure of odd parity ($K^- = 1$). Since pyracyclene belongs to the class of NAH's, we must also determine S_n^{00}, which is in this case given below:

S_{10}^{00}
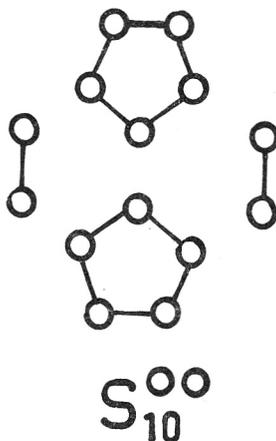
Putting all this into formula (66), we finally obtain det $\mathbf{A} = 0$ for pyracyclene. Therefore, pyracyclene must have at least one NBMO in its spectrum. The chemistry of pyracyclene appears to be in accord with this graphical prediction; pyracyclene is a very unstable molecule and it could not be isolated from solution[71,72]. Some other theoretical studies (based on the PPP SCF MO formalism)[73] also indicated a low stability of pyracyclene[74].

Therefore, the problem whether a conjugated molecule has or has not NBMO's can be solved; another problem, however, is how to enumerate graphically NBMO's.

The number of zeros in the graph spectrum may be obtained in the following way. If $\mathbf{C} = (C_1, C_2, \ldots, C_N)$ is a NBMO (not necessarily normalized), the following equation holds:

$$\mathbf{C A} = 0 \qquad (69)$$

This equation may be also given in scalar form:

$$\sum_{p \to q} C_p = 0; \quad q = 1, 2, \ldots, N \qquad (70)$$

The summation is over all vertices p joined to the vertex q. This equation has been first used by Longuet-Higgins[63]. The number of NBMO's is denoted by η. It should be also noted[67e] that the number of independent parameters in unnormalised NBMO is equal to η. Thus, the elucidation of η is reduced to a determination of the number of independent parameters which satisfy the requirements (70). Application of this method is illustrated for pyracyclene below:
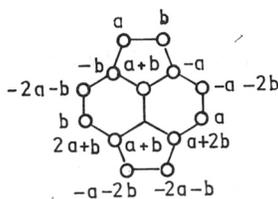
In order that Eq. (70) be fulfilled for the last (unmarked) vertex of pyracyclene, the following relation must hold: $a + b = 0$. Thus, only *one* parameter ($b = -a$) is independent, and consequently, η (III) = 1. The NBMO of III therefore looks like
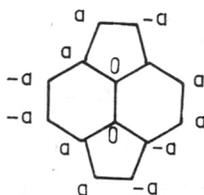
with $a = 0.29$.

The whole procedure may, in fact, be simplified by applying some graph transformations under which the value of η does not change, but which make this graphical approach much easier to apply. These transformations are detailed in[67f,75,76].

ANTIBONDING MOLECULAR ORBITALS

We have already emphasized several times the importance of knowing the number of bonding (N_+), non-bonding (N_0), and antibonding (N_-) MO's. For instance, when $N_- > N_+$, the corresponding molecule is electron-excessive and forms relatively stable cations[75,77-79]. Since N_+, N_0, and N_- are just

numbers of positive, zero, and negative elements in the spectrum of the molecular graph (see discussion earlier), their determination is a pure graph-theoretical problem. In this section we wish to show how the number of antibonding MO's can be determined.

We will use the following symbolism: ϑ_1, ϑ_2, ..., ϑ_N are the vertices of G. G-ϑ denotes a graph obtained after the deletion of the vertex ϑ (and the edges incident to it) from G. $\mathbf{D} = \mathbf{D}_N$ is a sequence of graphs: G_N, G_{N-1}, ..., G_1, G_0, where $G_{N-1} = G_N - \vartheta_N$, $G_{N-2} = G_{N-1} - \vartheta_{N-1}$, ..., $G_1 = G_2 - \vartheta_2 =$ the vertex ϑ_1, $G_0 = G_1 - \vartheta_1 =$ the empty graph. It is evident that G_n has exactly n vertices. The numbers of positive, zero, and negative elements in the spectrum of G_n will be denoted by $N_+(n)$, $N_0(n)$, and $N_-(n)$, respectively. We call $\mathbf{D}$ »the decomposition« of the graph G. In this way the sequence $\mathbf{D}_n = (G_n, G_{n-1}, ..., G_1, G_0)$ is the decomposition of G_n ($n = 1, 2, ..., N$). The adjacency matrix of G_n is denoted by $\mathbf{A}_n$ and det $\mathbf{A}_n = D_n$ ($n = 1, 2, ...,$ N). Besides, by definition, $D_0 = 1$. The sequence of numbers (D_n, D_{n-1}, ..., D_1, D_0) will be written $[\mathbf{D}_n]$.

In Ref.[80] the following three statements have been proved,

Lemma 1

$$D_N = D_{N-1} = \ldots = D_{N-N_0+1} = 0 \tag{71}$$

for all $\mathbf{D}$.

Lemma 2

There exists such a $\mathbf{D}$ that

$$D_{N-N_0} \neq 0 \tag{72}$$

Theorem

The equation

$$\text{Ch} (D_N, D_{N-1}, \ldots, D_1, D_0) = N_- \tag{73}$$

(Ch denotes the number of sign changes in the corresponding sequence of numbers), or in another notation,

$$\text{Ch} [\mathbf{D}] = N_- \tag{74}$$

holds for every $\mathbf{D}$ which fulfills the conditions (72) and (75):

$$(D_{j-1})^2 + (D_j)^2 \neq 0 \quad j = 1, 2, \ldots, N-N_0 \tag{75}$$

There is an obvious analogy between Eqs. (71)—(73) and the folloving relations between N_0, N_+, and $P(G; x)$[77]:

$$a_N = a_{N-1} = \ldots = a_{N-N_0+1} = 0 \tag{76}$$

$$a_{N-N_0} \neq 0 \tag{77}$$

$$\text{Ch} (a_N, a_{N-1}, \ldots, a_1, a_0) = N_+ \tag{78}$$

From the practical point of view, however, Eqs. (71)—(73) are much more convenient since the values of D_n may be determined relatively easily by the graph-theoretical techniques developed for the calculation of the determinant of a graph adjacency matrix.

The application of the above procedure will be illustrated on pentalene (IV).
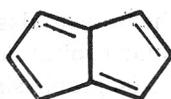
(IV)

We consider the following decomposition of the pentalene molecular graph G_n $(n = 8)$:
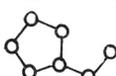
G_8 G_7 G_6 G_5

G_4 G_3 G_2 G_1

G_0 = EMPTY GRAPH

$[\mathbf{D}] = (0, -2, -1, 2, 1, 0, -1, 0, 1)$ and $N_- = \text{Ch} [\mathbf{D}] = 3$. Therefore, $N_0 = 1$ and $N_+ = 4$. Since $N_+ - N_- > 0$, pentalene should be a reactive electron-deficient molecule; this prediction agrees with experimental findings[72]. In addition, the pentalene dianion is relatively stable[81].

Fortunately, a complete calculation of the above type is hardly ever necessary. Because of the identity

$$\text{Ch} (D_N, \ldots, D_n, D_{n-1}, \ldots, D_0) = \text{Ch} (D_N, \ldots, D_n) + \text{Ch} (D_n, D_{n-1}, \ldots, D_0) \quad (79)$$

one obtains from (74):

$$N_- = \text{Ch} (D_N, \ldots, D_n) + N_- (n) \quad (80)$$

If we know $N_- (n)$, it is sufficient to calculate $(D_N, \ldots, D_n)$. Moreover, if $D_n \neq 0$ and G_n is a bipartite graph $N_- (n) = n/2$, as a consequence of the pairing theorem. The application of this consideration to the pentalene graph gives
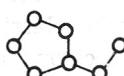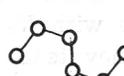
G_8 G_7 G_6

$(D_8, D_7, D_6) = (0, -2, -1)$ and $N_- = \text{Ch} (0, -2, -1) + N_-(6) = 0 + 6/2 = 3$.

A GRAPH-THEORETICAL CLASSIFICATION OF CONJUGATED HYDROCARBONS BASED ON THEIR SPECTRAL CHARACTERISTICS

This proposal for the graph-theoretical classification of conjugated hydrocarbons is based on their π-molecular orbital energy level distribution and the relationship between the $N_+ - N_-$ (a graph signature) and N_o. We define[82] a vector $\vec{n}$ as

$$\vec{n} \equiv \vec{n}(G) = (N_+ - N_-, N_o) \tag{81}$$

which determines a point with integer coordinates in the upper half-plane of a two-dimensional coordinate system. The set of all $\vec{n}(G)$ generate a network shown in Fig. 3.
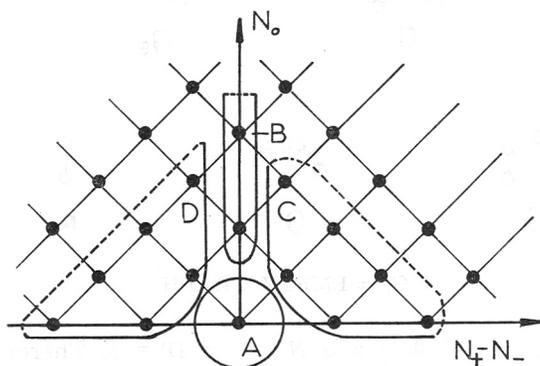
Fig. 3

Note that

$$\vec{n} = \vec{0} \tag{82}$$

is a necessary condition for a π-electron system to be stable. There are also other reasons for chemical stability, hence Eq. (82) alone is not a sufficient condition for a π-electron system to be stable. Similarly, all conclusions are valid only if the planarity of the studied molecules is assumed.

If Eq. (82) holds, then $N_+ = N_- = N/2$ and all bonding MO's are doubly occupied in the ground state, which implies a singlet π-electron configuration and chemical stability. In the case of $N_+ > N_-$, there are unoccupied bonding MO's, while for $N_+ < N_-$ there are occupied antibonding (or non-bonding) MO's, both causing high reactivity and/or instability of the π-electron system[77]. Besides, systems with $N_+ > N_-$ may be classified as electron-deficient molecules because they tend to accept electrons from a suitable donor in their empty MO bonding levels[72]. Systems with $N_+ < N_-$ are electron-excessive molecules and show a tendency to generate cations[72]. Finally, if $N_+ = N_-$ and $N_o > 0$, a polyradical ground state is expected[63] and such structures are extremely reactive. Therefore, conjugated molecules having $|\vec{n}| > 0$ are of very

low chemical stability. The overwhelming majority of chemically relevant graphs have $|\vec{n}| \leqslant 2$, although some exceptions are known[83].

This discussion enables us to propose a graph-theoretical classification of conjugated hydrocarbons according to $\vec{n}$. Thus, *four* classes of conjugated molecules are possible: (A) *stable*, (B) *polyradical*, (C), *electron-deficient* and (D) *electron-excessive* molecules as indicated on Fig. 3 by areas A, B, C, and D, respectively.

Because of the pairing theorem, bipartite graphs belong either to classes A or B. The existence of a $(4m-1)$-membered ring in the molecular graph is a necessary topological condition for a corresponding molecule to belong to the class C and similarly, $(4m+1)$-membered rings are required for class D.

EXTENSIONS TO HETEROCONJUGATED SYSTEMS

In the previous sections of this article we have seen that conjugated hydrocarbons may conveniently be studied by means of a graphical formalism. In the present section, we attempt to go some way towards extending this approach to a consideration of conjugated systems containing heteroatoms. However, it is first of all necessary to define graphs which correspond to such heteroconjugated molecules. Conjugated systems containing heteroatoms may be depicted graphically by use of what is known as a *rooted* graph representation[84,85]. A rooted graph* is a graph which has one (or more) of its vertices distinguished in some way from the others; such a vertex (or vertices) which has been thus singled out being called a »root«. Hence, in the molecular graphs which we use to represent heteroconjugated molecules, we shall indicate carbon atoms in the usual way (O), whereas heteroatoms will be distinguish by means of different »kinds« of vertices (●)[86]. We shall find convenient to represent this difference by means of the addition of a *loop* with weight h to the vertex (or vertices) in question. An example of such a graph is given below:
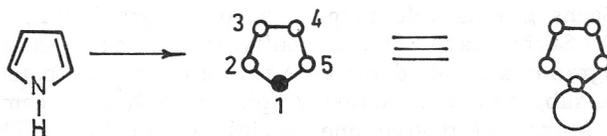
The molecular graph representing pyrrole is described as a *rooted cycle* (since this graph has circuit rank $\geqslant 1$)[2].

Just as the graph representing a conjugated hydrocarbon system may be described by its associated adjacency matrix, so the rooted graphs appropriate to heteroconjugated molecules may be represented by »adjacency matrices«, but of a particular type[8,12]. For example, the following matrix, assigned to the rooted graph corresponding to pyrrole, may be considered as »adjacency matrix« of such a graph:

---

* Professor O. E. Polansky (Mülhiem a. d. Ruhr) has suggested another term for *rooted graph:* the *vertex-weighted graph,* because the adjective *rooted* was originally used only for graphs called *trees,* the so-called *rooted trees*[84] We thank Professor Polansky for helpful discussions concerning the properties of this type of graphs.

$$\begin{bmatrix} h & 1 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 1 & 0 \end{bmatrix} \tag{83}$$

h is identified with the usual Hückel parameter[32] featuring in the expression:

$$\alpha_X = \alpha_C + h\beta_{CC} \tag{84}$$

It should be noted that, in the above adjacency matrix, the symbol h is inserted in a position corresponding to a »root« (that is to say, a loop with weight h) in the given graph, with vertices labelled accordingly. The matrix (83) is, of course, what we conventionally identify as the Hückel Hamiltonian matrix when adjustment for heteroatoms (to the Coulomb integral) has been accomodated. Therefore, h, reflects the difference (in units of β_{CC}, the »standard« carbon-carbon resonance integral) between the Coulomb integral (α_C) of a carbon atom in benzene and that (α_X) thought to be appropriate, in Hückel theory, for a given type of heteroatom X. It is important to note that the variation of resonance integrals from the »standard« (benzene) value is not attempted yet in the graph-theoretical manner, though some work in this direction is in progress[87] resulting thus far in complicated expressions.

The structure of a rooted graph may be related to the various coefficients appearing in the characteristic polynomial of the vertex adjacency matrix of such a graph using the modified Sachs formula[40,41,88]:

$$a_n = \sum_{s \in S_n} (-)^{c(s)} \, 2^{r(s)} \, h^{l(s)} \tag{85}$$

where the symbols have meaning as before and l is the number of loops in a particular Sach graph s. Self-loops do not contribute to r. It is evident that some of the Sachs graphs belonging to a rooted graph will also contain a »root« (since the Sachs graphs are, in reality, subgraphs of the graph in question); such subgraphs are called *rooted Sachs graphs*[40]. A rooted Sachs graph is defined as a subgraph of a rooted graph which has no components other than complete graphs of degree one, cycles, and/or loops. The use of the modified Sachs formula is illustrated for amino-ethylene-like systems on Chart 1.

The actual value chosen for h in any specific case is not relevant for our purpose here; if, however, as a check of the result in Chart 1, we choose arbitrarily the value $h = 1.00$, then the following graph spectrum is obtained: $\{1.80194, 0.44504, -1.24698\}$. These values are, of course, identical with those reported by Coulson and Streitwieser[62], which are obtained from direct Hückel MO calculations. Here we also point out that our expression (85) embraces the results of Bochvar and Stankevich[89], when it is applied to compounds depicted by graphs shown below:

Chart 1

The use of modified Sachs formula for amino-ethylene-like systems
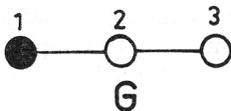
$S_0 = 0$ $a_o = 1$

$S_1 = \left\{ \left(\bigcirc \right) \right\}$ $a_1 = (-)^1 \, 2^0 \, h^1 = -h$

$S_2 = \left\{ \left(\overset{1}{\circ}\!-\!\overset{2}{\circ} \right), \left(\overset{2}{\circ}\!-\!\overset{3}{\circ} \right) \right\}$ $a_2 = 2 \, (-)^1 \, 2^0 \, h^0 = -2$

$S_3 = \left\{ \left(\bigcirc \;\; \overset{2}{\circ}\!-\!\overset{3}{\circ} \right) \right\}$ $a_3 = (-)^2 \, 2^0 \, h^1 = h$

$$P \, (G; x) = x^3 - h \, x^2 - 2 \, x + h$$

A class of compounds corresponding to these graphs is, for example, the class of borazines.

Finally, we wish to present a somewhat restricted extension of the pairing theorem to certain rooted graphs. Let $x_1 \geqslant x_2 \geqslant \ldots \geqslant x_n$ be the n eigenvalues of $P \, (G; x)$. The spectral characterization of bipartite graphs may be then stated as follows: *a graph is a bipartite if, and only if,* $x_i + x_{n+1-i} = 0$ *for* $1 \leqslant i \leqslant n$. This was derived in the context of the present formalism by Sachs, other graph-theoretical discussions of it being due to Collatz and Sinogowitz[90], Cvetković[23], Graovac et al.[27], and Mallion and Rouvray[67d,91]. The characterization was first proved in 1940 in the chemical literature (where it is konwn as the Pairing Theorem); the general proof was due to Coulson and Rushbrooke[5], although the result was observed empirically by Hückel eight years earlier[92].

The derivation of a restricted extension of the Coulson-Rushbrooke Pairing Theorem to rooted graphs proceeds via the use of the modified Sachs formula[40,41] and it can be formulated as follows: *if G is a bipartite graph with the same number of vertices in each set, and exactly those vertices in the first set are rooted, then* $x_i + x_{n+1-i} = h$ *for* $1 \leqslant i \leqslant n$. For example, if G represents 1,3-diazacyclobutadiene (*i. e.* a cycle with alternate vertices rooted):

We apply Eq. (85) to find that $P \, (G; x) = y \, (y - 4)$ with $y = x^2 - hx$, has for $y = 0$ the pair of solutions $x = h$ and $x = 0$ and similarly for $y = 4$ two paired solutions: $x = \{h + (h^2 + 16)^{1/2}\}/2$ and $x = \{h - (h^2 + 16)^{1/2}\}/2$.

CONCLUSIONS

In the present work we have reviewed some results of the *graph spectral theory of conjugated compounds*. This theory belongs to a more general theory called *topological theory of chemistry* which is nowadays a very intensively developing branch of theoretical chemistry. The topological theory of conjugated hydrocarbons is certainly not completed or closed; many new developments are still expected to appear.

However, even at the present stage of its development it has a considerable predictive power and when properly applied it can be a very useful and powerful tool in the hands of an experimental organic chemist.

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SAŽETAK

Spektralna teorija grafova konjugiranih molekula

I. Gutman i N. Trinajstić

Prikazana je spektralna teorija grafova konjugiranih molekula. Pokazano je kako se broj veznih, ne-veznih i antiveznih Hückelovih molekularnih orbitala može dobiti izravno iz topoloških značajki pojedine konjugirane molekule. Također je pokazano kako se totalna π-elektronska energija i π-rezonancijska energija molekule može aproksimirati pomoću pogodnih topoloških izraza. Izveden je izraz za izračunavanje π-elektronskih energija beskonačnih konjugiranih molekula. Konjugirane molekule klasificirane su na temelju topoloških značajki. Također je navedeno i proširenje teorema parova Coulsona i Rushbrooke-a na neke heterocikličke molekule.

INSTITUT »RUĐER BOŠKOVIĆ«,
    P. O. B. 1016, 41001 Zagreb,
        HRVATSKA