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Computing the Characteristic Polynomial of a Conjugated System Using the Sachs Theorem*[a]

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> »But to those who could understand, it has always been clear that mathematics was struggling to lay bare the hidden structure of things.«
>
> *C. A. Coulson, »The Spirit of Applied Mathematics,« Inaugural lecture, October 28, 1952, Oxford*

Graph theoretical rules, based on the Sachs theorem, for computing the characteristic polynomials of conjugated systems are given. Conjugated systems considered are conjugated hydrocarbons, heterocycles and Möbius structures. Graph theoretical rules for constructing acyclic polynomials for reference structures, which are essential to the topological theory of aromaticity, are also given. The application of these rules is described in detail and is illustrated by numerous examples.

INTRODUCTION

A simple molecular orbital theory,[1] named after its originator Hückel theory,[2] has been shown to be still very useful, on a qualitative level, in organic chemistry,[3] especially for predicting the stability of unsaturated organic molecules.[4–8]

The standard procedure in applying Hückel theory[1–3, 9–12] (or the graph spectral theory)[13#] to an arbitrarily labelled π-network of a given conjugated system consists of the following steps:

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* Dedicated to Professor Božo Težak, the teacher and the friend, on the happy occasion of his seventieth birthday.

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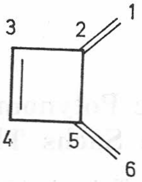
\# The equivalence between the Hückel theory and the graph spectral theory of conjugated systems has been discussed in detail by a number of researchers.[14–17] It is assumed that the reader is familiar with the classical Hückel molecular orbital (HMO) theory.

(*i*) The setting up of the appropriate (vertex) *adjacency*[18,19] (topological)[14] *mitrix*, **A*** by inserting 1 (if two π-centers are connected), or 0 (otherwise). For example, the adjacency matrix of 3,4-dimethylenecyclobutene (I) is given below:



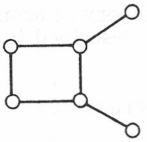
(I)

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

(*ii*) The direct expansion of **A** in the form of *secular determinant* to give the *characteristic polynomial* $P\,(G; x)$ of a conjugated system:

$$P\,(G; x) \equiv det\,|\,x\,\mathbf{1} - \mathbf{A}\,| \tag{2}$$

where **1** is the unit matrix. Thus, when we refer to the characteristic polynomial of a conjugated molecule, we really mean the characteristic polynomial of the adjacency matrix of a conjugated molecule. The symbol G stands for a graph corresponding to a given conjugated system.[20]# For example, graph G_1 corresponds to 3,4-dimethylenecyclobutene (I).**



G_1

The polynomial $P\,(G; x)$ corresponding to a molecule (graph) with N atoms (vertices) has the following form:

$$P\,(G; x) = \sum_{n=0}^{N} a_n\, x^{N-n} \tag{3}$$

where a_n are coefficients.

(*iii*) The evaluation of eigenvalues (Hückel energy levels) and eigenvectors (Hückel molecular orbitals).

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* See the extensive discussion about the use of the topological matrix in quantum chemical studies by D. H. Rouvray in: A. T. Balaban (Ed.), *Chemical Applications of Graph Theory*, Academic Press, London 1976, pp. 175—221.

\# In the present article we will use the formalism of *graph theory*[18,19] because the rules for computing the characteristic polynomial of a conjugated molecule may be formulated more conveniently in terms of graph-theoretical concepts. The basic concepts of graph theory will be introduced during the discussion when necessary.

** There is *one-to-one* correspondence between the π-network of a given conjugated system and the corresponding molecular graph. The hydrogen atoms in such a graph-theoretical representation of a conjugated molecule are neglected. These kinds of molecular graphs are named *Hückel graphs*.[13,17]

The roots of the characteristic polynomial are denoted by x_i ($i = 1, 2, \ldots, N$) and represent the spectrum of eigenvalues of a given graph (molecule):

$$x_i = \frac{-\alpha + E_i}{\beta} \tag{4}$$

where α and β are the Hückel parameters[1-3, 9-12] and E_i ($i = 1, 2, \ldots, N$) are the π-energies of individual HMO's:

$$E_i = \alpha + x_i \beta \tag{5}$$

If α is used as the zero-energy reference point ($\alpha = 0$) and β as the energy unit ($\beta = 1$), then

$$E_i = x_i \tag{6}$$

Eigenvectors $\mathbf{C}_i = (C_{i1}, C_{i2}, \ldots, C_{iN})$ represent solutions of secular equations:

$$\mathbf{C}_i\,(x\,\mathbf{1} - \mathbf{A}) = 0 \tag{7}$$

The outlined procedure is convenient for direct calculations, but it gives no information about the relation between the structure of a conjugated molecule and the coefficients a_n of $P(G; x)$. Such relation may be of certain practical use. For example, the structure-reactivity relation with the polynomial coefficients have been established[21,22].# Therefore, in order to learn some details about the relation between the molecular structure and the coefficients of a characteristic polynomial, it is of prime interest to have a method for constructing $P(G; x)$ without going through the procedure of solving the secular determinant, but solely from the topology of a conjugated system.*

This is a fundamental problem in graph theory and chemistry, and a lot of effort by various researchers from both sides has been devoted to it. However, Coulson[24] was the first (in 1950) to suggest a graph-theoretical method for constructing $P(G; x)$. A very elegant formulation of such a procedure was given by Sachs[25] (in 1964). Our subsequent discussion will be based on this result of Sachs, which we refer to as the *Sachs formula.* The Sachs formula will be reviewed in the next section. There were also other graph-theoretical procedures suggested,[26-34] but it can be shown that most of these are equivalent to the Sachs method.[33,34]**

The value of the coefficient a_N is a good criterion for discriminating annulenes: [$4m + 2$]-annulenes have a non-vanishing value of a_N, while [$4m$]-annulenes have $a_N = 0$ (see discussion later).

* The quantities considered as the basic topological parameters of a conjugated molecule are the following: the number of atoms (vertices) within the π-network of a molecule, N; the number of connections (bonds) between the π-centres, ν; the number of rings of various sizes, n_i ($i = 3, 4, 5 \ldots$); the branching of the molecular skeleton, D, and the algebraic structure count, ASC $= |K^+ - K^-|$. K^+ and K^- are the numbers of Kekulé structures of even (+) and odd (—) parity,[23] respectively.

** A very interesting procedure is that by Hosoya[31]. He has introduced a topological index Z, defined as follows

$$Z = \sum_{k=0}^{m} p(G, k)$$

where $p(G, k)$ is the number of ways in which disjoint k bonds are chosen from graph. G. For example, $Z(\text{benzene}) = p(G, 0) + p(G, 1) + p(G, 2) + p(G, 3) = 1 + 6 + 9 + 2 = 18$. This index is related to the characteristic polynomial of a molecule by the relation

$$P(G; x) = \sum_{k=0}^{m} (-1)^k p(G, k)\, x^{N-2k}$$

Before concluding this section, we wish to mention three important points concerning the characteristic polynomial of a molecule. First, we point out that the structure of $P(G; x)$ is related to the number of bonding (N_+), non-bonding (N_0) and antibonding (N_-) orbitals of a given conjugated system. (Note that $N_+ + N_0 + N_- = N$). These quantities are available directly from the characteristic polynomial of the molecule in the following way:[35,36]

$$a_N = a_{N-1} = \ldots\ldots = a_{N-N_0+1} = 0 \tag{8}$$

$$a_{N-N_0} \neq 0 \tag{9}$$

$$\mathrm{Ch}\,(a_N, a_{N-1}, \ldots, a_1, a_0) = N_+ \tag{10}$$

where Ch denotes the number of sign changes in the corresponding sequence of coefficients. Eq 10 is known as the *Decartes theorem.*[37]

It is of importance for the chemistry of conjugated compounds to know the numbers N_+, N_0 and N_-.[35,38] The presence of N_0 ($x = 0$ in the spectrum of the graph)[20] is suggestive of a reactive compound.[39–42] Similarly, if $N_+ > N_-$, there are unoccupied bonding molecular orbitals and the corresponding systems may be classified as electron-deficient molecules which can form stable anions relatively easily, because they tend to accept electrons from a suitable donor in their empty MO bonding levels.[43] In addition, if $N_+ < N_-$, there are occupied antibonding (or non-bonding) molecular orbitals and such systems may be classified as electron-excessive molecules, because they show a tendency to generate cations.[43] As an illustration, let us compute N_+, N_0 and N_- of 3,4-dimethylenecyclobutene. Its characteristic polynomial (see discussion later) is $P(G_1; x) = x^6 - 6x^4 + 5x^2 - 1$. Then $\mathrm{Ch}(-1, +5, -6, +1) = 3 = N_+$. Since $N = 6$ and $a_N \neq 0$ ($N_0 = 0$), $N_- = 3$. 3,4-dimethylenecyclobutene, thus, belongs to the class[44] $N_+ = N_-$ ($N_0 = 0$), the members of which should be less reactive than those in the classes $N_+ > N_-$, $N_+ < N_-$ and $N_+ = N_-$, $N_0 \neq 0$. This molecule is indeed prepared[45,46] and isolated, though aromaticity indices (REPE, TREPE) predicted it to be an antiaromatic species.[47,48#]

The second point is rather interesting: *the characteristic polynomial does not uniquely determine the topology of a (conjugated) molecule.* It has been found[20,27,49–53] that two or more graphs which are topologically non-equivalent (non-isomorphic) may have the same characteristic polynomial and therefore the common spectrum of eigenvalues. Conjugated systems exhibiting this property are named *isospectral molecules.*[20] (In mathematical literature, two non-isomorphic graphs are called cospectral[18] if they have common eigenvalues.) Therefore, for complete characterization of a molecule, a set of additional rules is needed besides the characteristic polynomial.[54].

The third and, perhaps, most important point concerns our recent work on topological resonance energy, TRE.[48,55–57] TRE is a non-parametric variant

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[#] 3,4-dimethylenecyclobutene is stable for long periods at room temperature when stored under nitrogen,[45] but readily polymerizes in the presence of air. This is, therefore, a case of an antiaromatic molecule which is an isolable compound, because it apparently has no easy conversion routes available in the Diels-Alder sense.

of Dewar resonance energy,[58] DRE,[59] and is directly related to the connectivity (topology) of a given molecular π-network. TRE is defined as follows:

$$\text{TRE} = E_\pi \text{ (conjugated molecule)} - E_\pi \text{ (reference structure)} \tag{11}$$

where E_π (reference structure) in the TRE model contains exactly all acyclic and exactly *no* cyclic contributions to E_π (conjugated molecule). The explicit form of TRE, derived[48] using the Coulson integral formula[60] for E_π (conjugated molecule) and the Sachs theorem,[25] is given by:

$$\text{TRE} = \sum_{j=1}^{N} g_j \left(x_j - x_j^{ac}\right) \tag{12}$$

where q_j is the occupancy number of the j^{th} MO, x_j $(j = 1, 2, \ldots, N)$ are the roots of the characteristic polynomial of a conjugated molecule in question, while x_j^{ac} $(j = 1, 2, \ldots, N)$ represent the roots of the *acyclic polynomial* which is the characteristic polynomial for the corresponding reference structure. A similar approach has also been recently proposed by Aihara;[61] he uses the term *reference polynomial* instead of acyclic polynomial. Both approaches for calculating TRE are identical, although they followed different paths in their development.

The construction of an acyclic polynomial may be best carried out using the graph-theoretical approach.* Therefore, we undertook a task to give graphical rules for constructing the characteristic polynomials of conjugated molecules and acyclic polynomials for the reference structures, which are *essential* to the *topological theory of aromaticity.*# The topological theory of aromaticity embraces all kinds of conjugated and heteroconjugated structures, including ions and radicals.[48,62] Furthermore, TRE may be used for studying the aromatic properties[63] of excited states.[64] Other aromaticity indices proposed are handicapped in these cases.

SACHS FORMULA

The Sachs formula[25] relates the structure of a graph, G, and the coefficients a_n of its characteristic polynomial $P(G; x)$. In order to simplify the use of the Sachs formula, we have introduced the notion *Sachs graph.*[21]** We call graph s a Sachs graph if every component of it is either a complete graph K_2 or a

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* We should realize that graph theory does not introduce any new concept in quantum theory, but it does introduce a new powerful mathematical technique which should be expected to be of the best use where the combinatorial nature of the system plays an important role (in parallel to the application of group theory to problems where the symmetry is an important feature of the system).

\# The topological theory of aromaticity indicates that the resonance energy is a topological quantity.

** In mathematical literature, (e. g.: A. J. Schwenk, *Ph. D. Thesis,* University of Michigan, Ann Arbor 1973), this kind of subgraphs are called *mutation graphs.* However, there is another proposal in chemical literature by Randić to call them *characteristic graphs.*

cycle C_m.[#**] Let $c(s)$ and $r(s)$ denote, respectively, the total number of components and the total number of cycles (rings) in s. Note, in particular, that the empty graph is a Sachs graph with no components. In addition, let S_n be a set of all Sachs graphs (with exactly n vertices) in a given graph G. In this notation, the Sachs formula may be expressed as

$$a_n = \sum_{s \in S_n} (-1)^{c(s)} 2^{r(s)}; \; 0 \leqslant n \leqslant N \qquad (13)$$

The summation is over all Sachs graphs (with n vertices). a_n is, of course, a particular coefficient of $P(G; x)$ which is being computed. For the case $n = 0$, $a_0 = 1$.

The characteristic polynomial may now be expressed in a different form by substituting eq 13 into eq 3:

$$P(G; x) = \sum_{n=0}^{N} \sum_{s \in S_n} (-1)^{c(s)} 2^{r(s)} x^{N-n} \qquad (14)$$

This form of $P(G; x)$ directly reflects the topology of a given structure.

Sachs graphs are related to permutations of non-zero elements, A_{kl}, in the secular determinant. Taking into account K_2 components corresponds to considering only products A_{kl}, A_{lk}, which are related to edges in G.[#] Counting C_m components corresponds to taking into account only products such as A_{kl}, A_{lm},

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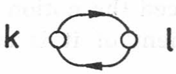
[#**] K_2 is a *complete graph* of valence one. A graph is a complete graph of valence one if it consists of just two vertices joined by an edge, i. e., isolated bond. If all vertices of a connected graph are of valence two, the graph is a *cycle*, i. e., ring. The smallest cycle is a *loop*, i. e., one-cycle. The one-cycle (loop) is an edge joining a vertex to itself. A graph G is *connected* if given any pair of vertices k, l of G there is a path from k to l. Molecular graphs are all connected graphs. If there is no path between two vertices, they belong to different *components* of a graph. Hückel graphs are undirected, planar and connected graphs with the maximal valency 3.

[#] In the case of oriented graphs,[18] the product $A_{kl} A_{lk}$ would really mean a cycle between two vertices,

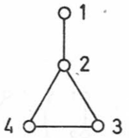


Since we are concerned here with only unoriented graphs, the product $A_{kl} A_{lk}$ represents only a K_2 subgraph of a graph G,

A subgraph of a graph G may be obtained either by removing a vertex v (or vertices) from G or by removing an edge e (or edges) from G. A Sachs graph is, thus, also a subgraph of G which contains only K_2 and/or C_m components. More formally, if $V_1(G_1)$ is a subset of $V(G)$ and $E_1(G_1)$ a subset of $E(G)$, then the graph $G_1 = (V_1 E_1)$ is a subgraph of the graph $G = (V, E)$. $V(G)$ represent a set of vertices and $E(G)$ a set of edges in G. Note: a graph may be its own subgraph.

$A_{mn}, \ldots, A_{zk}$ and $A_{lk}, A_{ml}, A_{nm}, \ldots, A_{kz}$, which are products of matrix elements related to the cycles in G.*

Let us, for example, consider the graph G_2.



G_2

We first construct the corresponding adjacency matrix (only non-vanishing entries, $A_{kl} = 1$, are included),

$$\mathbf{A}(G_2) = \begin{bmatrix} 0 & A_{12} & 0 & 0 \\ A_{21} & 0 & A_{23} & A_{24} \\ 0 & A_{32} & 0 & A_{34} \\ 0 & A_{42} & A_{43} & 0 \end{bmatrix} \tag{15}$$

Then we set up the corresponding secular determinant:

$$\begin{bmatrix} x & -A_{12} & 0 & 0 \\ -A_{21} & x & -A_{23} & -A_{24} \\ 0 & -A_{32} & x & -A_{34} \\ 0 & -A_{42} & -A_{43} & x \end{bmatrix} \tag{16}$$

The expansion of the secular determinant (16) gives the characteristic polynomial:[29,30]

$$\begin{aligned} P(G_2; x) = x^4 &- x^2 (A_{12} A_{21} + A_{23} A_{32} + A_{24} A_{42} + A_{34} A_{43}) \\ &- x (A_{23} A_{34} A_{42} + A_{32} A_{43} A_{24}) + A_{12} A_{21} A_{34} A_{43} \end{aligned} \tag{17}$$

Let us now investigate the relation between the products of matrix elements and the corresponding Sachs graphs in the light of the preceding discussion:

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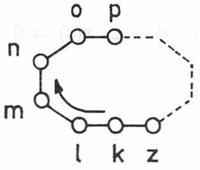
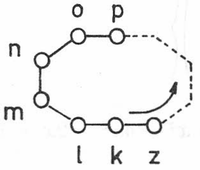
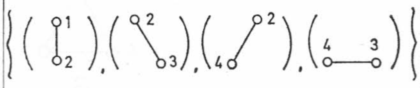
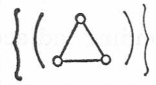
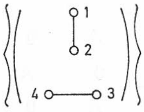
* There are two products because each cycle may be counted in either of two directions





This is the origin of factor 2 in eq 13.

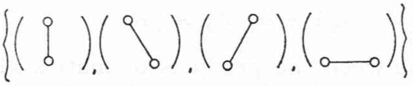
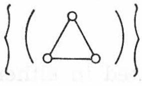
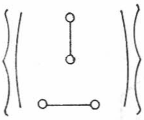
n	Products of Matrix Elements	Sachs Graphs ∅	Numerical Value
0			1
1		∅	0
2	$A_{12}A_{21} + A_{23}A_{32} +$ $+ A_{24}A_{42} + A_{34}A_{43}$		4
3	$A_{23}A_{34}A_{42} + A_{32}A_{43}A_{24}$		2
4	$A_{12}A_{21}A_{34}A_{43}$		1

Substituting the numerical values for products of matrix elements back into (17), the explicit form of the characteristic polynomial $P(G_2; x)$ of G_2 is obtained

$$P(G; x) = x^4 - 4x^2 - 2x + 1$$

with the following graph spectrum:[#] $\{2.17, 0.31, -1.00, -1.48\}$.

The identical result may be reached by *direct* use of the Sachs formula, without going through the expansion of the secular determinant, as shown below for G_2.

n	S_n		a_n
0			1
1	∅		0
2		$c(s) = 1,\ r(s) = 0$	$4(-1)^1 2^0 = -4$
3		$c(s) = 1,\ r(s) = 1$	$(-1)^1 2^1 = -2$
4		$c(s) = 2,\ r(s) = 0$	$(-1)^2 2^0 = 1$

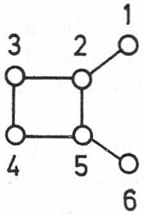
$$P(G_2; x) = x^4 - 4x^2 - 2x + 1$$

[#] The roots of the characteristic polynomial may be obtained by standard computer routines.

APPLICATION OF THE SACHS FORMULA TO CONJUGATED HYDROCARBONS

The application of the Sachs formula to conjugated hydrocarbons[#] will be described in detail for 3,4-dimethylenecyclobutene (**1**). It consists of the following steps:

(*i*) Conjugated hydrocarbon should be depicted by the corresponding labelled molecular graph.



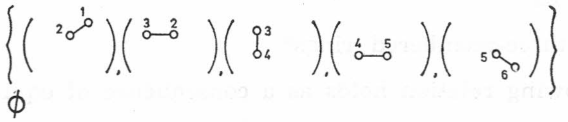
$N = 6$

G_1

(*ii*) Construction of all Sachs graphs belonging to G_1.

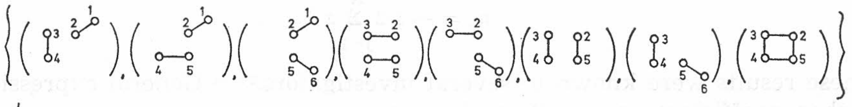
$S_1 = \phi$

$S_2 =$



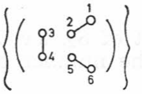
$S_3 = \phi$

$S_4 =$



$S_5 = \phi$

$S_6 =$



(*iii*) Computing the coefficients:

$$a_0 = 1$$

$$a_1 = 0$$

$$a_2 = 6\,(-1)^1\,2^0 = -6$$

$$a_3 = 0$$

$$a_4 = 7\,(-1)^2\,2^1 + (-1)^1\,2^2 = 5$$

$$a_5 = 0$$

$$a_6 = (-1)^3\,2^0 = -1$$

[#] The Sachs formula (13) may be, in the form given, used straightforwardly for conjugated hydrocarbons.[21]

(*iv*) Construction of the characteristic polynomial:

$$P(G_1;\ x) = x^6 - 6x^4 + 5x^2 - 1$$

The roots of this polynomial $\{2.25,\ 0.80,\ 0.56,\ -0.56,\ -0.80,\ -2.25\}$ are, of course, identical with the set of eigenvalues obtained from direct calculations.[65]

An additional example of the application of the Sachs formula to conjugated hydrocarbons is given in Table I.

Some general rules arise from the application of the Sachs formula to conjugated hydrocarbons (in order to see them, the reader should rather carefully inspect the studied examples and perhaps some examples of his own). These are summarized below:

(*a*) There cannot be a Sachs graph of conjugated hydrocarbons with only one vertex. Then $S_1 = \emptyset$ always, and $a_1 = 0$. Therefore,

$$a_1 = \sum_{j=1}^{N} x_j = 0 \tag{18}$$

This means that the sum of the whole spectrum is always zero.

(*b*) It can be seen that

$-a_2$ = number of bonds#

$-a_3/2$ = number of three-membered rings*

In addition, the following relation holds as a consequence of eq 18:

$$a_2 = -1/2 \sum_{j=1}^{N} x_j^2 \qquad (19)^{**}$$

These results were known to several investigators.[24-34] General expressions for higher coefficients are rather clumsy:

\# Any two vertices joined by an edge represent an element of S_2, i. e. K_2 subgraph. Therefore, the number of S_2 Sachs graphs is equal to the number of edges (or K_2 subgraphs) in a graph.

* A Sachs graph with three vertices can only be a C_3 cycle. Since each cycle may be counted in either of two directions, the a_3 coefficient obtain from eq 13 must be divided by two in order to obtain the number of C_3 cycles present in a given graph. However, when we have four or more vertices, then the relations between a_n ($n = 4, 5, 6\ldots$) of $P(G; x)$ and Sachs graphs are, in general, more complicated, because in these situations both K_2 and C_m components may appear simultaneously.

** Relation (19) may be proved in a simple way:

$$a_2 = \sum_{i<j}^{N} x_i x_j = 1/2 \left(\sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j - \sum_{j=1} x_j^2 \right)$$

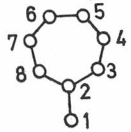
$$= -1/2 \sum_{j=1}^{N} x_j^2 + 1/2 \sum_{i=1}^{N} x_i \sum_{j=1}^{N} x_j$$

$$= -1/2 \sum_{j=1}^{N} x_j^2$$

The first step is known from elementary algebra.

TABLE I

The Computation of the Characteristic Polynomial of Heptafulvene



$N = 6$

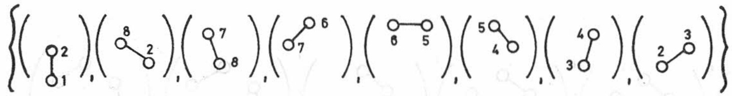
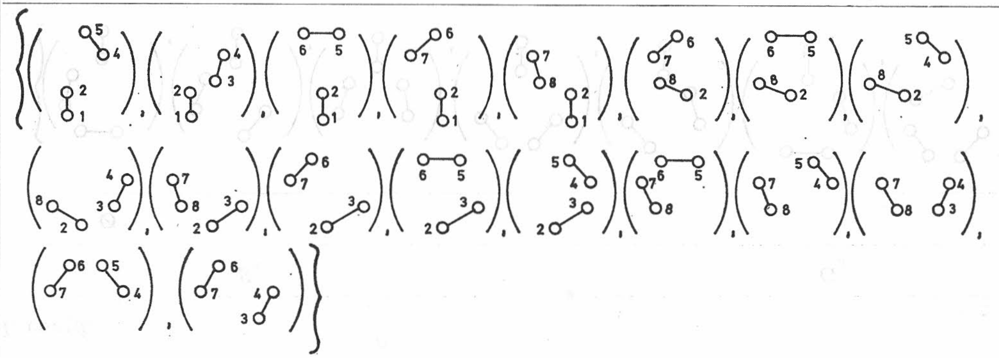
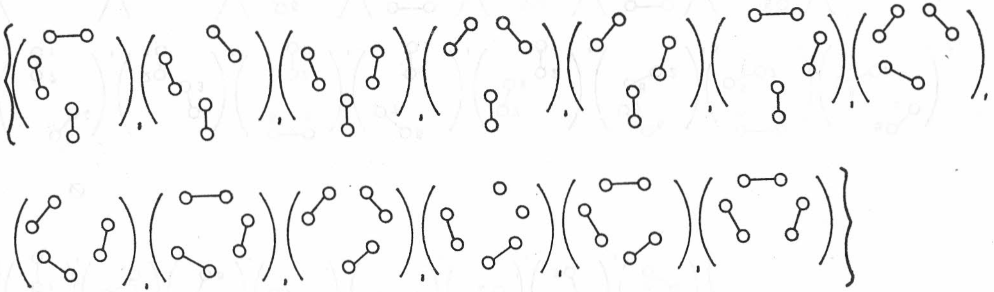
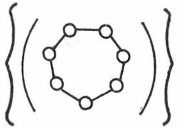
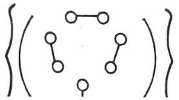
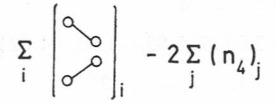
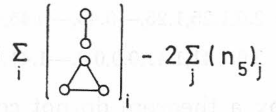
n	S_n G_3	a_n
0		1
1	Ø	0
2		$8\,(-1)^1\,2^0 = -8$
3	Ø	0
4		$19\,(-1)^2\,2^0 = 19$

Table I. contd.

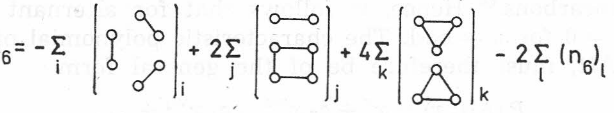
n	S_n	G_3	a_n
5	∅		0
6			$13\,(-1)^3\,2^0 = -13$
7			$(-1)^1\,2^1 = -2$
8			$(-1)^4\,2^0 = 1$



(20)



(21)



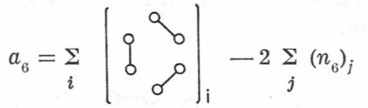
(22)

etc.

The symbols have their previous meaning. n_i ($i = 3, 4, 5, \ldots$) stands for cycles of various sizes. Each combination within the parentheses contributes one to the numerical value of the coefficient concerned.

Eqs 21 and 22 may be simplified for the special case: Hückel monocylic graphs (annulenes):

$$a_5 = -2 \sum_j (n_5)_j \tag{23}$$



(24)

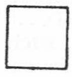
In addition, general formulae for the a_{even} and a_{odd} coefficients of $P(G; x)$, valid only for monocycles,are the following:

$$a_{\text{even}} = \pm \sum_i [(K_2)_n;\ n = 1, 2, 3, \ldots]_i - 2 \sum_j (C_m;\ m = \text{even})_j \tag{25}$$

$$a_{\text{odd}} = -2 \sum_j (C_m;\ m = \text{odd})_j \tag{26}$$

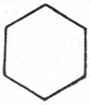
The first summation in (25) is positive if n = even, otherwise negative.

Let us now evaluate using formulae 25 and 26 the characteristic polynomials of C_4(cyclobutadiene), C_5(cyclopentadienyl), C_6(benzene), C_7(cycloheptatrienyl) and C_8 (cyclooctatetraene) ring systems, because we need them late on in our discussion.

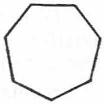


C_4

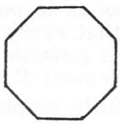
C_5



C_6



C_7



C_8

$$P(C_4; x) = x^4 - 4x^2; \qquad \{x = 2,0,0,-2\} \tag{27}$$

$$P(C_5; x) = x^5 - 5x^3 + 5x - 2; \qquad \{x = 2.0,0.62,0.62,-1.62,-1.62\} \tag{28}$$

$$P(C_6; x) = x^6 - 6x^4 + 9x^2 - 4; \qquad \{x = 2,1,1,-1,-1,-2\} \tag{29}$$

$$P(C_7; x) = x^7 - 7x^5 + 14x^3 - 7x - 2; \qquad \{x = 2.0,1.25,1.25,-0.45,-0.45,-1.80,-1.80\} \tag{30}$$

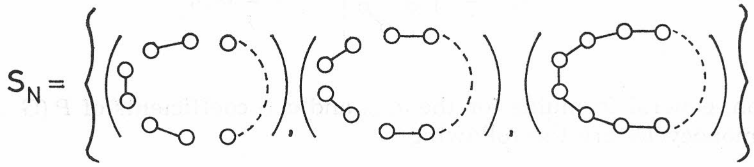
$$P(C_8; x) = x^8 - 8x^6 + 20x^4 - 16x^2; \qquad \{x = 2.0,1.41,1.41,0.0,0.0,-1.41,-1.41,-2.0\} \tag{31}$$

(*c*) *Bipartite (bicolorable)* graphs[#] by a theorem do not contain odd-membered cycles.[*] Conjugated hydrocarbons depicted by bipartite graphs are called *alternant* hydrocarbons.[68] Hence, it follows that for alternant hydrocarbons $S_n = \emptyset$ and $a_n = 0$ for $n =$ odd. The characteristic polynomial of an alternant hydrocarbon, AH, must therefore be of the general form

$$P(\mathrm{AH}; x) = x^N + a_2 x^{N-2} + a_4 x^{N-4} + \ldots \tag{32}$$

This means that the graph's spectrum of AH *must be* symmetrically arranged with respect to $x = 0$, because if x is a root of $P(\mathrm{AH}; x)$, then $-x$ must also be a root. This is, therefore still another demonstration of the *pairing theorem* of Coulson and Rushbrooke.[69]

(*d*) Analysis of the a_N coefficient of [N]annulenes (monocyclic rings of the general formula C_NH_N) may be used for rationalizing the Hückel rule[70], according to which [$4m + 2$]-annulenes are thermodynamically more stable than [$4m$]-annulenes (with the restriction, found later,[71] that this difference disappears at m sufficiently large; the critical value of m being 6).[72] *A* cycle (representing [N]annulene) with N vertices ($N =$ even) has *three* Sachs graphs with N vertices. These are shown below:



(33)

Then

$$a_N = 2\,(-1)^{N/2}\, 2^0 + (-1)^1\, 2^1 = \begin{cases} 0 & \text{for } N = 4m \\ -4 & \text{for } N = 4m + 2 \end{cases} \tag{34}$$

Therefore, [$4m + 2$]-annulenes have closed-shell ground states and *no* zero elements in their spectra [see eqs 6—8], while [$4m$]-annulenes have open-shell ground states and zero elements in their eigenvalue spectra. [$4m$]-annulenes have doubly degenerate zero eigenvalues in their spectra and this result follows

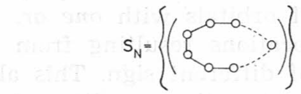
---

[#] Graphs that may be coloured in two colours are called bicolourable graphs. This corresponds to partitioning of the vertex set $V(G)$ into two subsets $V_1(G)$ and $V_2(G)$ such that every edge in G joint V_1 with V_2. Therefore, a graph G is *n-partite* ($n \geqslant 2$) if it is possible to partition $V(G)$ into n subsets $V_1(G)$, $V_2(G)$, ... $V_n(G)$ such that every element $E(G)$ joins a vertex of $V_i(G)$, $i \neq j$. For $n = 2$, such graphs are called bipartitite graphs (or *bigraphs*).[18,66]

[*] A graph is bipartite (bicolourable) if and only if all its cycles are even-membered.[67]

from the pairing theorem, because [4*m*]-annulenes belong to even AH's[#] and their eigenvalues always appear in pairs.

A cycle representing [*N*]-annulene with N = odd ([$4m+1$]- and [$4m+3$]-annulenes) have only *one* Sachs graph with N vertices:

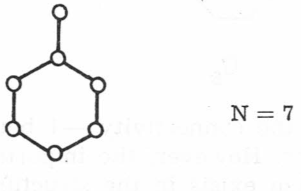
$S_N =$  (35)

Then,

$$a_N = (-1)^1\,2^1 = -2 \text{ for } \begin{cases} N = 4m+1 \\ \text{or} \\ N = 4m+3 \end{cases} \tag{36}$$

These compounds are less stable than [$4m+2$]- but more stable than [$4m$]-annulenes.[73] Their stabilization or destabilization may be attained by adding or subtracting π-electrons. [$4m + 1$]-annulenes (for m small) become quite *stable* species by accepting one π-electron and producing mono-anions, i. e. systems with $(4m+2)\pi$-electrons, and quite *unstable* by giving away a π-electron and producing mono-cations, i. e. cyclic systems with $(4m)\pi$-electrons.[74,75] [$4m + 3$]-annulenes (for m small) behave in the opposite way. They stabilize by giving away a π-electron and producing monocations (i. e. $(4m+2)$ π-electron systems) and destabilize by accepting one π-electron in their half-empty MO's and thus producing mono-annions [i. e. monocyclic systems with $(4m)$ π-electrons].[74,75]

As an example, let us evaluate the characteristic polynomial of benzyl (G_4), an example of odd AH, following rules (*a*)—(*d*):



G_4

This can be done now without any difficulty:

$$P(G_4; x) = x^7 - 7x^5 + 13x^2 - 7x \tag{37}$$

Examination of the characteristic polynomial [see eqs 8—10] leads to the results: $N_+ = 3$, $N_- = 3$ and $N_0 = 1$. The roots of $P(G_4; x)$ $\{x = 2.1,\ 1.26,\ 1.0,\ 0.0,\ -1.0,\ -1.26,\ -2.1\}$ are in accord with the above result.

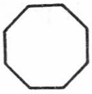
To summarize this section, we state that the greatest advantage of the Sachs theorem over other methods proposed lies in the simplicity of its algebraic formulation. However, eq 14 gives one a very difficult task of computing the characteristic polynomial of a large molecular system. This difficulty can be resolved by using the recursion formulae (see discussion later) as explained by Hosoya.[31]

[#] The spectrum of the odd-membered AH always contains at least *one* zero. This is the consequence of the pairing theorem, because in order to preserve the symmetry of the spectrum, the odd eigenvalue must be zero.

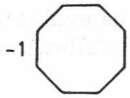
EXTENSION OF THE SACHS FORMULA TO MÖBIUS SYSTEMS

In recent years, the use of the Hückel-Möbius concept[3,76-78] has become increasingly popular[79-85] for studying molecules and transition states for certain pericyclic reactions (i. e. electrocyclic closures of polyenes). *Möbius systems* are defined[86] as cyclic arrays of orbitals with *one* or, more generally, with and *odd* number of phase dislocations resulting from the negative overlap between the adjacent orbitals of different sign. This allows a more general definition of *Hückel cyclic systems* as those cyclic systems in which there is *no* phase dislocation or in which there is an *even* number of sign inversions among the adjacent $2p_z$-atomic orbitals. Such systems obey the Hückel rule. For Möbius systems it is predicted[82,86] that those with ($4m$) π-electrons should exhibit aromatic stability, whereas those with ($4m+2$) π-electrons should be antiaromatic species. Therefore, Möbius-like structures should follow the anti-Hückel rule.[3]

In order to extend the Sachs formula to Möbius systems, we need to define a new type of graphs which we call *Möbius graphs*.[87,88#,*] The weight of edges in these graphs is either $+1$ or $—1$, depending on whether two $2p_z$-atomic orbitals in a Möbius system are in the positive-positive ($+1$) or positive-negative ($—1$) overlap relationships, respectively. As an example, below we give graphs which correspond to the Hückel (G_5) and Möbius (G_6) cyclooctatetraenes, respectively.



G_5



G_6

The location of the connectivity $—1$ between two vertices in the Möbius graph G_6 is arbitrary. However, the important information is given that one (odd) phase dislocation exists in the structure called Möbius cyclooctatetrane. This should also be reflected in the corresponding very particular »adjacency« matrix, sometimes called the *switch matrix***, because it contains 1, 0 or $—1$ elements. The switch (»adjacency«) matrix, **S**, corresponding to Möbius cyclooctatetraene may be constructed rather simply:

There should be no confusion with the *Möbius ladder graphs*.[89] The Möbius ladder, G_n, is a *trivalent* graph with $2n$ vertices ($n \geqslant 3$). It is constructed from circuit graphs C_{2n} by adding new edges joining each pair of opposite vertices. The eigenvalues of G_n are the numbers:

$$x_j = 2 \cos \frac{\pi j}{n} + (-1)^{\cdot} \quad (0 \leqslant j \leqslant 2n - 1)$$

* This type of graphs are used in other fields, for example, in anthropology (e. g.: P. Hage, *Anthropological Forum* **3** (1973—1974) 280) under the name *signed graphs*. I am indebted to Dr. Per Hage (The University of Utah, Department of Anthropology, Salt Lake City, Utah 84112, U.S.A.) for discussions on the properties of signed graphs and their use in humanities.

** I thank Professor K. Horvatić (Zagreb) for helpful discussions concerning the properties of switch matrices.

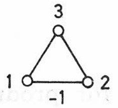
$$\mathbf{S}(G_6) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \tag{38}$$

Möbius graphs are a special case of more general graphs with an arbitrary number of —1 edges which we call *switch graphs.*## In the case of switch graphs, there are two distinctive binary relations,* R^+ and R^-, but of the opposite meaning, between the pairs of vertices of a Möbius system. Therefore, a Möbius graph, $G_{\text{Mö}}$, is in general defined as:

$$G_{\text{Mö}} = (V, R^+, R^-) \tag{39}$$

The meaning of this is that the two vertices either belong to R^+ (if there is a $+1$ connectivity between the two vertices) or to R^- (if there is a -1 connectivity between the two vertices), or they do not belong to either of these binary relations (if there is no connectivity of any kind between the two vertices). A Möbius graph is fully defined when the binary relations between all pairs of vertices are defined.**

Now we wish to demonstrate how the structure of a Möbius graph is related to the coefficients of the characteristic polynomial. Let us, for example, consider graph G_7:



G_7

The corresponding switch matrix is given by:

$$\mathbf{S}(G_7) = \begin{bmatrix} 0 & -A_{12} & A_{13} \\ -A_{21} & 0 & A_{23} \\ A_{31} & A_{32} & 0 \end{bmatrix} \tag{40}$$

This is an analogy with switch matrices. There are some other proposals to label these graphs differently such a *generalized* graphs[87] or *extended* graphs.[90] However, these proposals are not quite acceptable, inasmuch as there are various kinds of graphs which are suited much more for the above labels.[89,91]

* Ordinarily when dealing with the Hückel graphs, we consider a finite non-empty set of vertices $V(G)$ and a binary (symmetric and antireflexive) relation R defined on the set $V(G)$. An ordered pair $G = (V, R)$ is called a graph.[18]

** Professor Milan Randić (Ames) has discussed the reaction matrices in this connection in his unpublished work. I thank him for helpful correspondence.

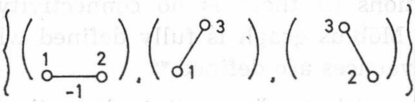
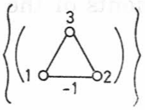
The expansion of the related secular determinant:

$$\begin{vmatrix} x & A_{12} & -A_{13} \\ A_{21} & x & -A_{23} \\ -A_{31} & -A_{32} & x \end{vmatrix} = 0 \tag{41}$$

gives the following characteristic polynomial:

$$P(G_7; x) = x^3 - x(A_{12}A_{21} + A_{23}A_{32} + A_{31}A_{13}) + (A_{12}A_{23}A_{31} + A_{21}A_{32}A_{13}) \tag{42}$$

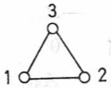
The relationship between the products of the matrix elements and the corresponding Sachs graphs are given below:

n	Products of Matrix Elements	Sachs Graphs	Numerical Values
0			1
1		$\emptyset$	0
2	$A_{12}A_{21} + A_{23}A_{32} + A_{21}A_{13}$		3
3	$A_{12}A_{23}A_{31} + A_{21}A_{32}A_{13}$		2

Substitution of numerical values for products of matrix elements into (42) leads to the polynomial:

$$P(G_7; x) = x^3 - 3x + 2; \quad \{x = 1, 1, -2\} \tag{43}$$

Let us compare the polynomial (43) with $P(G_8; x)$, where G_8 is the three membered Hückel cycle. $P(G_8; x)$ may be constructed very easily:



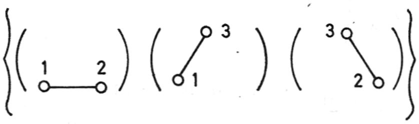
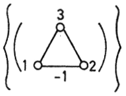
G_8

$$P(G_8; x) = x^3 - 3x - 2; \quad \{x = 2, -1, -1\} \tag{44}$$

The difference between these two polynomials is only in the sign of the last coefficient to the construction of which the contribution comes from the C_m component. This result indicates that the extented Sachs formula should differ from the original one only in one factor which should take care of the number of —1 edges in the C_m components. This also means that Sachs graphs, s, corresponding to Möbius graphs, $G_{Mö}$, should consist of only K_2 subgraphs and Möbius cycles, C_m. Hence the extended Sachs formula may be easily given

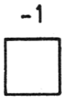
$$a_n = \sum_{s \in S_n} (-1)^{c(s)+P_{r(s)}} \, 2^{r(s)} \tag{45}$$

where $P_{r(s)}$ is the number of —1 connectivities in the rings of a Sachs graph s. Other symbols have their previous meaning. Using this formula, we can directly evaluate the characteristic polynomial of Möbius cyclopropenyl (G_7).

n	S_n	a_n
0		1
1	Ø	0
2	 $c(s) = 1,\ P_{r(s)} = 0$ $r(s) = 0$	$3\,(-1)^{1+0}\,2^0 = -3$
3	 $c(s) = 1,\ P_{r(s)} = 1,\ r(s) = 1$	$(-1)^{1+1}\,2^1 = 2$

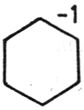
$P(G;x) = x^3 - 3x + 2$

Since in the previous section we gave the characteristic polynomials of Hückel C_4, C_5, C_6, C_7 and C_8 rings, let us now evaluate $P(G_{Mö}; x)$ of Möbius systems corresponding to these cycles.

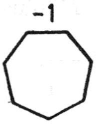


$C_4^{Mö}$

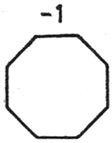
$C_5^{Mö}$



$C_6^{Mö}$



$C_7^{Mö}$



$C_8^{Mö}$

$$P(C_4^{Mö}; x) = x^4 - 4x^2 + 4; \qquad \{x = \sqrt{2}, \sqrt{2}, -\sqrt{2}, -\sqrt{2}\} \tag{45}$$

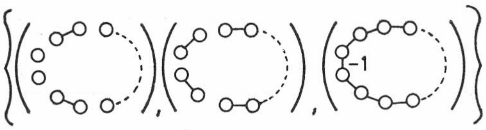
$$P(C_5^{Mö}; x) = x^5 - 5x^3 + 5x + 2; \qquad \{x = 1.62, 1.62, -0.62, -0.62, -2.0\} \tag{46}$$

$$P(C_6^{Mö}; x) = x^6 - 6x^4 + 9x^2; \qquad \{x = \sqrt{3}, \sqrt{3}, 0, 0, -\sqrt{3}, -\sqrt{3}\} \tag{47}$$

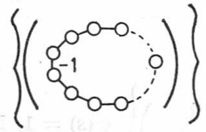
$$P(C_7^{Mö}; x) = x^7 - 7x^5 + 14x^3 - 7x + 2;$$
$$\{x = 1.80, 1.80, 0.45, 0.45, -1.25, -1.25, -2.0\} \tag{48}$$

$$P(C_8^{Mö}; x) = x^8 - 8x^6 + 20x^4 - 16x^2 + 4;$$
$$\{x = 1.85, 1.85, 0.77, 0.77, -0.77, -0.77, -1.85, -1.85\} \tag{49}$$

These results indicate that the alternant Hückel and Möbius annulenes differ only in the *value* of the a_N coefficient, while the non-alternant systems differ only in the *sign* of the a_N coefficient. This observation is not surprising, inasmuch as monocyclic systems contain cycles only in the S_N set of Sachs graphs. Let us construct Sachs graphs with N vertices for Möbius annulenes.

S_N (N=even) =


(50)

S_N (N=odd) =


(51)

Then

$$a_N\,(N = \text{even}) = 2\,(-1)^{N/2+0}\,2^0 + (-1)^{1+1}\,2^1 = \begin{cases} 4 \text{ for } N = 4m \\ 0 \text{ for } N = 4m+2 \end{cases} \tag{52}$$

$$a_N\,(N = \text{odd}) = (-1)^{1+1}\,2^1 = 2 \text{ for} \begin{cases} N = 4m+1 \\ \text{or} \\ N = 4m+3 \end{cases} \tag{53}$$

The above results should be compared with those reported for Hückel annulenes, eqs 34 and 36. This comparison leads to the conclusion that the a_N coefficient may be used for establishing a simple classification scheme of all generalized monocyclic systems:

$$a_N = 0 \begin{cases} \text{Hückel } [4m]\text{-annulenes} \\ \text{Möbius } [4m+2]\text{-annulenes} \end{cases} \tag{54}$$

$$a_N\,(N = \text{even}) \neq 0 \begin{cases} -4; & \text{Hückel } [4m+2]\text{-annulenes} \\ 4; & \text{Möbius } [4m]\text{-annulenes} \end{cases} \tag{55}$$

$$a_N\,(N = \text{odd}) \neq 0 \begin{cases} -2; & \text{Hückel } [4m+1]\text{- and} \\ & [4m+3]\text{-annulenes} \\ 2; & \text{Möbius } [4m+1]\text{- and} \\ & [4m+3]\text{-annulenes} \end{cases} \tag{56}$$

This scheme is a graph-theoretical justification of the general Hückel rule which embraces Hückel and Möbius annulenes and according to which Hückel $[4m+2]$- and Möbius $[4m]$- annulenes should exhibit closed-shell stability and aromaticity, while Hückel $[4m]$- and Möbius $[4m+2]$-annulenes exhibit open-shell reactivity and antiaromaticity.[82,86] Möbius $[4m+1]$- and $[4m+3]$-annulenes are in between the Möbius $[4m]$- and $[4m+2]$-systems. Stabilization of Möbius $[4m+1]$-annulenes may be achieved by giving away a π-electron and producing mono-cations, i. e. systems with $(4m)$ π-electrons. Destabilization of such a system is obtained by adding one π-electron and thus producing a mono-anion, i. e. a Möbius system with $(4m+2)$ π-electrons. A Möbius $[4m+3]$-system stabilizes by receiving a π-electron and producing a mono-anion [i. e. a system with $(4m)$ π-electrons] and destabilizes by giving away one π-electron and producing a mono-cation [i. e. a system with $(4m+2)$ π-electrons]. All these systems may be conveniently tabulated including the earlier discussion concerning the Hückel systems (see Table II).

TABLE II

General Hückel Rule which Embraces Hückel and Möbius Ring Systems[a]

Monocyclic system	Rings					
	Even-membered		Odd-membered			
			$4m + 1$		$4m + 3$	
	$4m$	$4m + 2$	Cations	Anions	Cations	Anions
Hückel	—	+	—	+	+	—
Möbius	+	—	+	—	—	+

[a] (+) denotes stable, aromatic; (—) denotes unstable antiaromatic species.

This is also a basis of generalized rules for predicting, for example, the electrocyclic closures of polyenes by considering the topology of the corresponding transition states.[76,77,92]

CHARACTERISTIC POLYNOMIAL OF HETEROCONJUGATED MOLECULES

In this section, we present a graphical approach to computing the characteristic polynomial of heteroconjugated systems. It is necessary first to define graphs corresponding to heteroconjugated molecules. Heteroconjugated molecules may be represented by *vertex-* and *edge-weighted graphs*.[93][#] A vertex- and edge-weighted graph, G_{VEW}, is a graph which has one or more of its vertices and edges distinguished in some way from other vertices and edges. These vertices and edges of different »type« are weighted and their weights are identified with Hückel parameters[9][*] h (weighted vertices) and k (weighted edges) for heteroatoms and heterobonds, respectively. This is reflected on some diagonal and off-diagonal elements of the »adjacency« matrix.[16,98] In order to avoid any confusion, we call this type[93] of the »adjacency« matrix the *weight matrix*, **W**.

[#] Originally, these graphs were named »rooted« graphs,[94-96] a name which is not quite appropriately used there, because this type of graph belongs to *trees*.[18,97]

[*] The Hückel parameters used in heteroconjugated systems are given as follows:

$$\alpha_x = \alpha_c + h\beta_{cc}$$

$$\beta_{cx} = k\beta_{cc}$$

where α_c and β_{cc} represent the »standard« carbon Coulomb integrals and carbon--carbon resonance integrals, respectively. Thus h reflects the difference between the Coulomb integral of a carbon atom (α_c) and that (α_x) thought to be appropriate, in Hückel theory, for a given type of heteroatom X. Similarly, k ($\neq 1$) signifies the difference between the carbon-carbon resonance integral (β_{cc}) and the resonance integral of a C—X bond (β_{cx}), respectively.

In the case when only ordinary vertices are present, the diagonal elements of the adjacency matrix **A** of a graph G are all zero, that is:

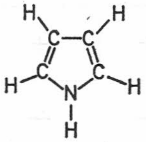
$$\mathrm{Tr}\,\mathbf{A}\,(G) = 0 \tag{57}$$

However, in the case of vertex- and edge-weighted graphs,

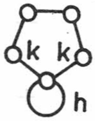
$$\mathrm{Tr}\,\mathbf{W}\,(G_{\mathrm{VEW}}) = \sum_{i} h_i \tag{58}$$

where the summation is over all weighted vertices in G_{VEW}.

Let us, for example, represent pyrrole by the corresponding vertex- and edge-weighted graph G_{VEW} (**9**). Note the weighted vertex (indicating the presence of the nitrogen atom in pyrrole) will be denoted by one-cycle with weight h.[94]



pyrrole



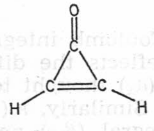
G_{VEW} (**9**)

The weighted matrix, assigned to the pyrrole graph, is given below:

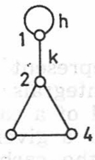
$$\mathbf{W}\,[G_{\mathrm{VEW}}\,(9)] = \begin{bmatrix} h & k & 0 & 0 & k \\ k & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 1 \\ k & 0 & 0 & 1 & 0 \end{bmatrix} \tag{59}$$

h is inserted in a position corresponding to the weighted vertex (nitrogen), while k indicates that the connectivity between the nitrogen atom and the adjacent carbon atoms is altered in comparison with the corresponding purely carbon skeleton.

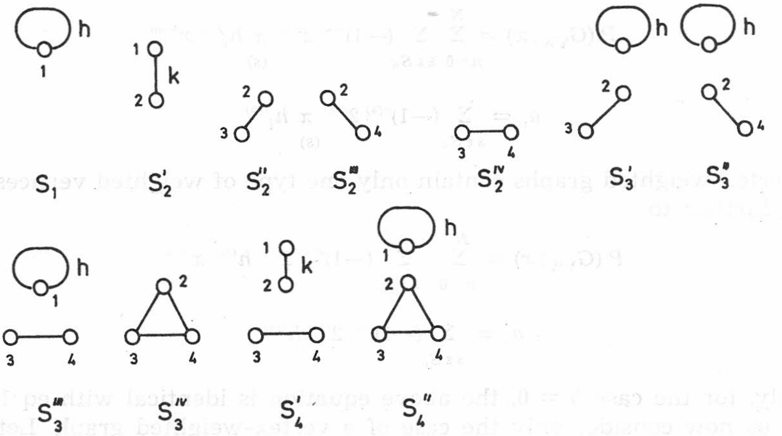
Now we wish to demonstrate how the structure of a vertex- and edge-weighted graph is related to the corresponding characteristic polynomial $P\,(G_{\mathrm{VEW}};\,x)$. Before doing this we need to introduce a new type of Sachs graph containing weighted vertices and/or weighted edges. It is also immediately evident that a graph G_{VEW} may contain both types of Sachs graphs, that is to say, non-weighted and weighted ones. We define a *vertex-* or *edge-weighted Sachs graph* as such a subgraph of a G_{VEW} which has no other components than one-cycles and/or (weighted) K_2 and/or (weighted) C_m subgraphs. A complete set of Sachs graphs of a given vertex- and edge-weighted graph G_{VEW} (**10**), corresponding to cyclopropenone, is given below:



Cyclopropenone



G_{VEW} (**10**)



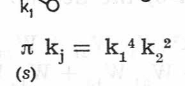
Sachs graphs s_2^{II}, s_2^{III}, s_2^{IV}, and s_3^{IV} are non-weighted, whereas all others (i. e. s_1, s_2^{I}, s_3^{I}, s_3^{II}, s_3^{III}, s_4^{I}, and s_4^{II}) are weighted Sachs graphs. s_1, s_3^{I}, s_3^{II}, s_3^{III} and s_4^{II} are vertex-weighted, and s_2^{I} and s_4^{I} are edge-weighted Sachs graphs. The characteristic polynomial $P(G_{\mathrm{VEW}}; x)$ of a vertex- and edge-weighted graph G_{VEW} is given by:

$$P(G_{\mathrm{VEW}}; x) = \sum_{n=0}^{N} \sum_{s \varepsilon S_n} (-1)^{c(s)} 2^{r(s)} \underset{(s)}{\pi} h_i^{l(s)} \underset{(s)}{\pi} k_j x^{N-m} \qquad (60)$$

where

$$a_n = \sum_{s \varepsilon S_n} (-1)^{c(s)} 2^{r(s)} \underset{(s)}{\pi} h_i^{l(s)} \underset{(s)}{\pi} k_j \qquad (61)$$

In the above equations, $l(s)$ is the number of loops in any particular vertex-weighted Sachs graph. Other symbols in (60) have their previous meaning. $\underset{(s)}{\pi} h_i^{l(s)}$ gives the contribution from the weighted vertices with weight h in the vertex-weighted Sachs graph s (the index i signifies the number of different heteroatoms in a conjugated molecule). In the case when there is only *one* type of weighted vertices, with weight h, present in the G_{VEW} graph, the product $\underset{(s)}{\pi} h_i^{l(s)}$ reduces to $h^{l(s)}$. The product $\underset{(s)}{\pi} k_j$ (index j signifies the number of different heterobonds in a conjugated structure), which reflects the presence of an edge-weighted Sachs graph s, is obtained by multiplication of k's in the following way. For a weighted K_2 component of a Sachs graph s, k's are squared; while for an edge-weighted C_m component of s, k's are multiplied »around« the ring. As an example, consider the product $\underset{(s)}{\pi} k_j$ for the following edge-weighted Sachs graph s:



$$\underset{(s)}{\pi} k_j = k_1^4 k_2^2$$

In the case when we consider only the vertex-weighted graphs, G_{VW}, the product $\pi k_j = 1$ and eq 60 reduces to

$$P(G_{\mathrm{VW}}; x) = \sum_{n=0}^{N} \sum_{s \varepsilon S_n} (-1)^{c(s)}\, 2^{r(s)}\, \pi_{(s)}\, h_i^{\,l(s)}\, x^{N-m} \qquad (62)$$

with

$$a_n = \sum_{s \varepsilon S_n} (-1)^{c(s)}\, 2^{r(s)}\, \pi_{(s)}\, h_i^{\,l(s)} \qquad (63)$$

If the vertex-weighted graphs contain only one type of weighted vertices, eq 62 reduces further to:

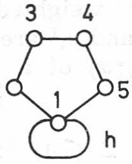
$$P(G_{\mathrm{VW}}; x) = \sum_{n=0}^{N} \sum_{s \varepsilon S_n} (-1)^{c(s)}\, 2^{r(s)}\, h^{l(s)}\, x^{N-n} \qquad (64)$$

with

$$a_n = \sum_{s \varepsilon S_n} (-1)^{c(s)}\, 2^{r(s)}\, h^{l(s)} \qquad (65)$$

Obviously, for the case $h = 0$, the above equation is identical with eq 14.

Let us now consider only the case of a vertex-weighted graph. Let graph G_{VW} **(11)** represent a thiophene-like system.



G_{VW} **(11)**

We will first derive the characteristic polynomial of G_{VW} **(11)**, $P(G_{VW}\,\mathbf{(11)}; x)$ in the conventional way, i. e. by expanding the secular determinant. This procedure can be carried out through several steps:

(a) The Setting up of the Weighted Matrix Corresponding to G_{VW} **(11)**;

$$\mathbf{W}\,[G_{\mathrm{VW}}\,\mathbf{(11)}] = \begin{bmatrix} h & W_{12} & 0 & 0 & W_{15} \\ W_{21} & 0 & W_{23} & 0 & 0 \\ 0 & W_{32} & 0 & W_{34} & 0 \\ 0 & 0 & W_{43} & 0 & W_{45} \\ W_{51} & 0 & 0 & W_{54} & 0 \end{bmatrix} \qquad (66)$$

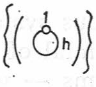
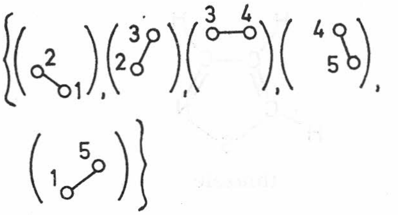
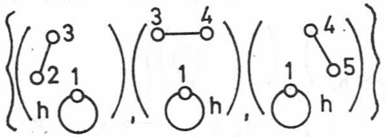
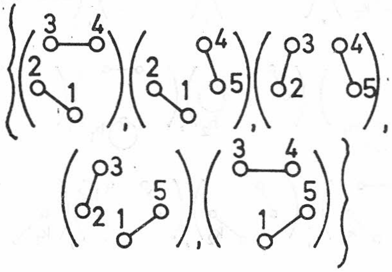
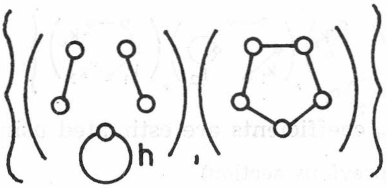
(b) Construction of the Secular Determinat:

$$\begin{vmatrix} x-h & -W_{12} & 0 & 0 & -W_{15} \\ -W_{21} & x & -W_{23} & 0 & 0 \\ 0 & -W_{32} & x & -W_{34} & 0 \\ 0 & 0 & -W_{43} & x & -W_{45} \\ -W_{51} & 0 & 0 & -W_{54} & x \end{vmatrix} = 0 \qquad (67)$$

(c) Expansion of the Secular Determinat:

$$\begin{aligned} P(G_{\mathrm{VW}}\,\mathbf{(11)}; x) = {} & x^5 - x^4 h - x^3 (W_{12} W_{21} + W_{23} W_{32} + W_{34} W_{43} + W_{45} W_{54} + \\ & + W_{51} W_{15}) + x^2 h (W_{23} W_{32} + W_{34} W_{43} + W_{45} W_{54}) + x (W_{12} W_{21} W_{34} W_{43} + \\ & + W_{12} W_{21} W_{45} W_{54} + W_{23} W_{32} W_{45} W_{54} + W_{23} W_{32} W_{51} W_{15} + W_{34} W_{43} W_{51} W_{15}) - \\ & - h (W_{23} W_{32} W_{45} W_{54}) - (W_{12} W_{23} W_{34} W_{45} W_{51} + W_{21} W_{32} W_{43} W_{54} W_{15}) \qquad (68) \end{aligned}$$

(d) Interpretation of Products of Matrix Elements in Terms of Sachs Graphs:

n	Products of Matrix Elements	Sachs Graphs	Numerical value#
1	h		h
2	$W_{12}W_{21} + W_{23}W_{32} +$ $+ W_{34}W_{43} + W_{45}W_{54} +$ $+ W_{51}W_{15}$		5
3	$h(W_{23}W_{32} + W_{34}W_{43} +$ $+ W_{45}W_{54})$		3h
4	$W_{12}W_{21}W_{34}W_{43} +$ $+ W_{12}W_{21}W_{45}W_{54} +$ $+ W_{23}W_{32}W_{45}W_{54} +$ $+ W_{23}W_{32}W_{51}W_{15} +$ $+ W_{34}W_{43}W_{51}W_{15}$		5
5	$hW_{23}W_{32}W_{45}W_{54} +$ $+ W_{12}W_{23}W_{34}W_{45}W_{51} +$ $+ W_{21}W_{32}W_{43}W_{54}W_{15}$		h+2

The selection of actual numerical value for h in any specific HMO calculation (and the reasoning by which such a value is thought to be appropriate in any given case) is not relevant to our present purpose. However, there is such a selection of Hückel parameters given in the book by Streitwieser.[9] In our work, we use, the HMO parameter set of Hess and Schaad.[99-101]

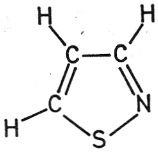
(e) Computing the Characteristic Polynomial:

$$P\,(G_{\mathrm{VW}}\,(\mathbf{11});x) = x^5 - x^4\,h - 5x^3 + 3x^2\,h + 5x - (h+2) \tag{69}$$

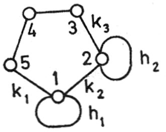
The same result can be obtained directly by using formula 64. This is given in Table III.

Let us now derive the characteristic polynomial of a vertex- and edge-weighted graph G_{VEW} (**9**) representing pyrrole-like systems. This is reported in Table IV.

Eq 60 may be applied to various systems without any difficulty. We will construct the characteristic polynomial of 1,2-thiazole-like systems — systems containing two different heteroatoms — which may be represented by graph G_{VEW} (**12**).

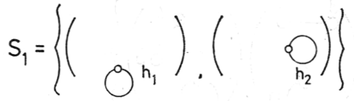


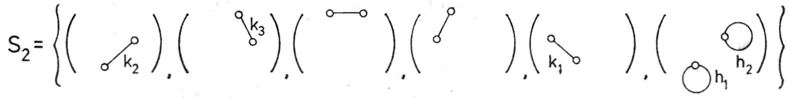
thiazole

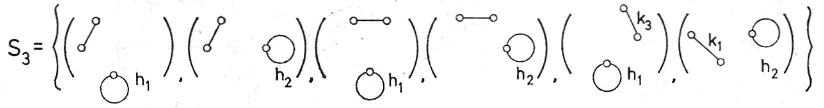


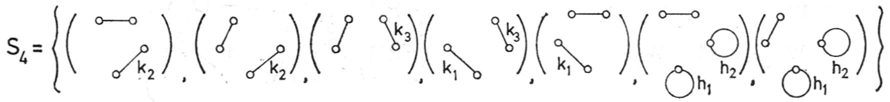
G_{VEW} (**12**)

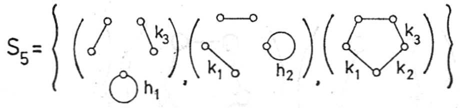
We first give all Sachs graphs of G_{VEW} (**12**):











Then the a_n coefficients are estimated using eq 61,

$a_0 = 1$ (see previous section)

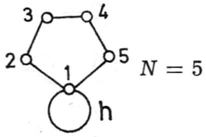
$$a_1 = (-1)^1\,2^0 h_1{}^1 + (-1)^1\,2^0\,h_2{}^1 = -(h_1 + h_2)$$

$$\begin{aligned} a_2 &= (-1)^1\,2^0\,k_1{}^2 + (-1)^1\,2^0\,k_2{}^2 + (-1)^1\,2^0\,k_2{}^2 + 2\,(-1)^1\,2^0 + (-1)^2\,2^0\,h_1{}^1\,h_2{}^1 = \\ &= -\,(k_1{}^2 + k_2{}^2 + k_3{}^2) - 2 + h_1\,h_2 \end{aligned}$$

$$\begin{aligned} a_3 &= 2\,(-1)^2\,2^0\,h_1{}^1 + (-1)^2\,2^0 h_1{}^1\,k_3{}^2 + (-1)^2\,2^0\,h_2{}^1\,k_1{}^2 + 2\,(-1)^2\,2^0 h_2{}^1 = \\ &= 2\,h_1 + h_1\,k_3{}^2 + h_2\,k_1{}^1 + 2\,h_2 \end{aligned}$$

TABLE III

The Computation of the Characteristic Polynomial of a Vertex-Weighted Graph G_{VW} **(11)** *Representing Thiophene-Like Systems*



G_{VW} **(11)**

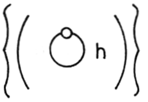
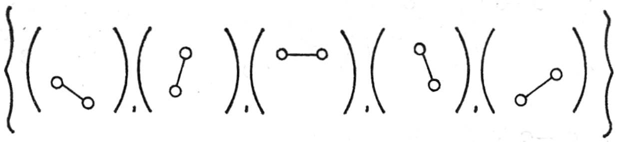
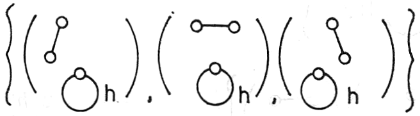
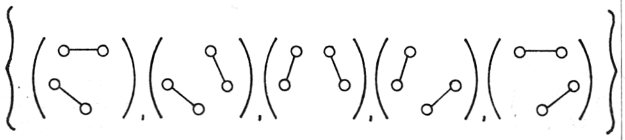
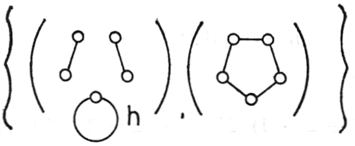
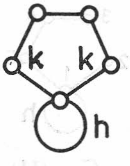
n	S_n	a_n
0		1
1		$(-1)^1 2^0 h^1 = -h$
2		$5(-1)^1 2^0 h^0 = -5$
3		$3(-1)^2 2^0 h^1 = 3h$
4		$5(-1)^2 2^0 h^0 = 5$
5		$(-1)^3 2^0 h^1 +$ $+ (-1)^1 2^1 h^0 =$ $= -(h + 2)$
	$P(G_{VW}\,(\mathbf{11}); x) = x^5 - hx^4 - 5x^3 + 3hx^2 + 5x - (h + 2)$	

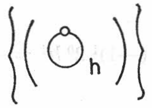
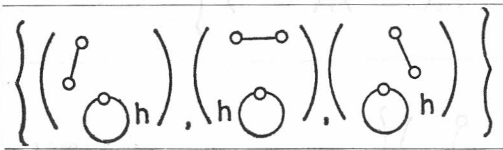
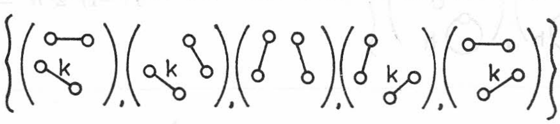
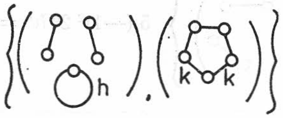
TABLE IV

The Computation of the Characteristic Polynomial of a Vertex-Weighted and Edge-Weighted Graph G_{VEW} **(9)** *Representing Pyrrole-Like Systems*



$N = 5$

G_{VEW} (9)

n	S_n	a_n
0	Ø	1
1		$(-1)^1\, 2^0\, h^1\, k^0 = -h$
2		$2\,(-1)^1\, 2^0\, h^0\, k^2 +$ $+\, 3\,(-1)^1\, 2^0\, h^0\, k^0 =$ $= -2k^2 - 3$
3		$3\,(-1)^2\, 2^0\, h^1\, k^0 =$ $= +\, 3h$
4		$4\,(-1)^2\, 2^0\, h^0\, k^2 +$ $+\, (-1)^2\, 2^0\, h^0\, k^0 =$ $= 4k^2 + 1$
5		$(-1)^3\, 2^0\, h^1\, k^0 +$ $+\, (-1)^1\, 2^1\, h^0\, k =$ $= -h - 2k^2$

$$P\,(G_{VEW}\,\mathbf{(9)};\, x) = x^5 - hx^4 - (2k^2 + 3)\, x^3 + 3hx^2 + (4k^2 + 1)\, x - (h + 2k^2)$$

$$a_4 = (-1)^2\, 2^0\, k_1{}^2 + (-1)^2\, 2^0\, k_1{}^2\, k_2{}^2 + (-1)^2\, 2^0\, k_3{}^2 + 2\,(-1)^2\, 2^0\, k_2{}^2 + 2\,(-1)^3\, 2^0\, h_1{}^1\, h_2{}^1 =$$
$$= k_1{}^2 + k_1{}^2\, k_2{}^2 + k_3{}^2 + 2k_2{}^2 - 2h_1\, h_2$$

$$a_5 = (-1)^3\, 2^0\, h_1{}^1\, k_3{}^2 + (-1)^3\, 2^0\, h_2\, k_1{}^2 + (-1)^1\, 2^1\, k_1\, k_2\, k_3 =$$
$$= -\, h_1\, k_3{}^2 - h_2\, k_1{}^2 - 2k_1\, k_2\, k_3$$

Finally, the characteristic polynomial is constructed:

$$P(G_{\mathrm{VEW}}(\mathbf{12}); x) = x^5 - (h_1 + h_2)\,x^4 - (2 - h_1 h_2 + k_1^2 + k_2^2 + k_3^2)\,x^3 + \\ + [2(h_1 + h_2) + h_1 k_3^2 + h_2 k_1^2]\,x^2 + (k_1^2 + 2k_2^2 + k_3^2 + k_1^2 k_2^2 - 2h_1 h_2)\,x - \\ - (h_1 k_3^2 + h_2 k_1^2 - 2k_1 k_2 k_3) \qquad (69)$$

In the molecular graph $G_{\mathrm{VEW}}(\mathbf{12})$ there are three different types of vertices. Vertices corresponding to sulphur and nitrogen atoms are weighted differently (h_1 and h_2) than those related to carbon atoms ($h_c = 0$). Similarly, edges corresponding to bonds C—S, C—N and N—S are indicated with weights k_1, k_2 and k_3, respectively. The C—C bonds, of course, have a weight of unity. The polynomial $P(G_{\mathrm{VEW}}(\mathbf{12}); x)$ for $h_2 = 0$, $k_3 = 1$ and $k_1 = k_2 = k$ reduces to the polynomial corresponding to thiophene-like systems:

$$P(G_{\mathrm{VEW}}; x)' = x^5 - h_1 x^4 - (3 + 2k^2)\,x^3 + 3h_1 x^2 + (1 + 4k^2)\,x - (h_1 + 2k^2) \qquad (70)$$

If we further assume that $k_1 = k_2 = 1$, the above polynomial reduces even further to:

$$P(G_{\mathrm{VEW}}, x)'' = x^5 - h_1 x^4 - 5x^3 + 3h_1 x^2 + 5x - (h_1 + 2) \qquad (71)$$

This polynomial corresponds to that representing thiophene-like systems $P(G_{\mathrm{VW}}(\mathbf{11}); x)$. Finally, for $h_2 = 0$, it reduces, of course, to the polynomial $P(C_5, x)$ representing cyclopentadienyl. An additional example is given in Table V.

A rather limited set of general rules arises from the application of formulae (60) and (61) to heteroconjugated systems:

(*a*) In the case of heteroconjugated systems there are Sachs graphs with *one* weighted vertex, i. e. loops. Therefore:

$$a = -\sum_{j=1}^{N} x_j = -\sum_j h_j \qquad (72)$$

This means that the sum of the whole spectrum of the vertex- and edge-weighted graph is equal to the selected weight of the one-cycles.

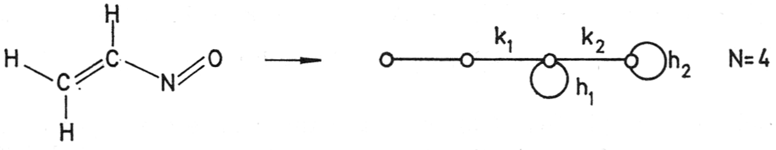
(*b*) It is easily seen that the a_2 coefficient is still equal to (minus) the number of (weighted) bonds in a weighted graph.

(*c*) The building of all other polynomial coefficients (a_n, $n \geqslant 2$) cannot be expressed by simple expressions, because the appearance of loops in Sachs graphs allows various combinations which, in the case of conjugated hydrocarbons, were not possible.

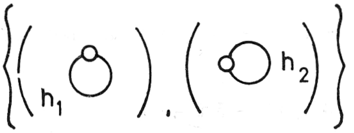
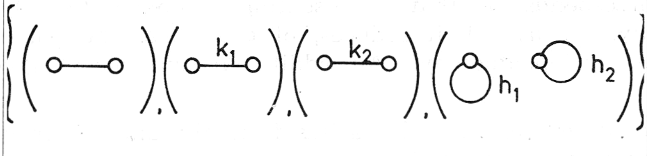
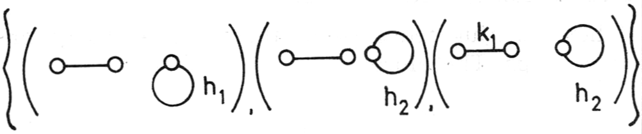
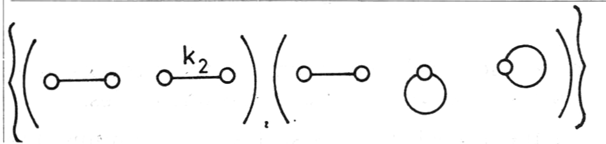
We emphasize once more that our aim here has been to show how the topological structure of a heteroconjugated molecule is related to the form of the characteristic polynomial of a vertex- and edge-weighted graph which represents it, and not to concern ourselves at all with the relative virtues of particular numerical values of Hückel parameters. We may also note, in passing, that our expressions (60) and (61) embrace the results of Bochvar and Stankevich[102,103] when they are applied to borazines. In addition, many other individual

TABLE V

The Characteristic Polynomial of a Vertex- and Edge-Weighted Molecular Graph



G_{VEW} **(13)**

n	S_n	a_n
0	Ø	1
1		$(-1)^1\, 2^0\, h_1{}^1 +$ $+ (-1)^1\, 2^0\, h_2{}^2 =$ $= -h_1 - h_2$
2		$(-1)^1\, 2^0 +$ $+ (-1)^1\, 2^0\, k_1{}^2 +$ $+ (-1)^1\, 2^0\, k_2{}^2 +$ $+ (-1)^2\, 2^0\, h_1\, h_2 =$ $= -1 - k_1{}^2 -$ $- k_2{}^2 + h_1\, h_2$
3		$(-1)^2\, 2^0\, h_1 +$ $+ (-1)^2\, 2^0\, h_2 +$ $+ (-1)^2\, 2^0\, h_2\, k_1{}^2 =$ $= h_1 + h_2 + h_2\, k_1{}^2$
4		$(-1)^2\, 2^0\, k_2{}^2 +$ $+ (-1)^3\, 2^0\, h_1\, h_2 =$ $= k_2{}^2 - h_1\, h_2$

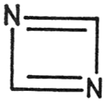
$$P\,(G_{\text{VEW}}\,(\mathbf{12});\,x) = x^5 - (h_1 + h_2)\,x^4 - (1 + k_1{}^2 + k_2{}^2 - h_1\,h_2)\,x^3 + (h_1 + h_2 + h_2\,k_1{}^2)\,x - (h_1\,h_2 - k_2{}^2)$$

results obtained for heteroconjugated systems may now be generalized with our approach. Here we single out only one example and this concerns the restricted extension of the pairing theorem to heteroconjugated molecules.[96] The restricted extension of the Coulson-Rushbrooke pairing theorem can be formulated as follows:

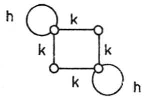
If G is a bipartite graph with the same number of vertices in each set, and exactly those vertices in the first set are weighted, then:

$$x_i + x_{n+1-i} = h \qquad \text{for } 1 \leqslant i \leqslant n$$

In order to illustrate this, let us consider 1,3-diazacyclobutadiene# which is represented by the vertex- and edge-weighted graph G_{VW} **(14)**.



1,3-diazacyclobutadiene

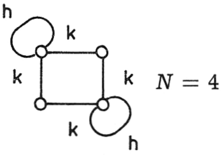


G_{VEW} **(14)**

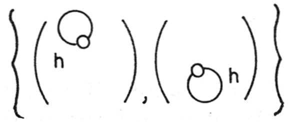
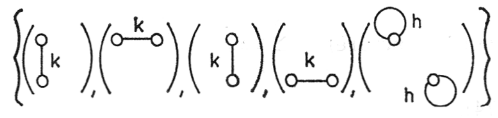
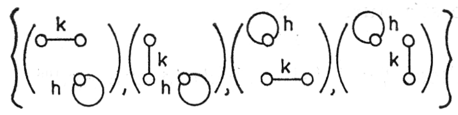
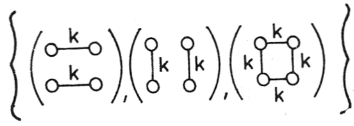
We first construct its characteristic polynomial by means of eq 60. This is reported in Table VI.

TABLE VI

Computing the Characteristic Polynomial of 1,3-Diazabutadiene.



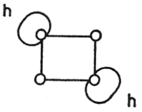
G_{VEW} **(14)**

n	S_n	a_n
0	Ø	1
1		$2\,(-1)^1\,2^0\,h^1 = -2\,h$
2		$4\,(-1)^1\,2^0\,k^2 +$ $+\,(-1)^2\,2^0\,h^2 =$ $= -4\,k^2 + h^2$
3		$4\,(-1)^2\,2^0\,hk^2 = 4\,hk^2$
4		$2\,(-1)^2\,2^0\,k^4 +$ $+\,(-1)^1\,2^1\,k^4 = 0$

$$P\,(G_{VEW}\,\mathbf{(14)};\,x) = x^4 - 2\,hx^3 - (4\,k^2 - h^2)\,x^2 + 4\,hk^2\,x$$

1,3-diazacyclobutadiene should be a more stable compound than cyclobutadiene itself;[104] the stabilizing effect is attributed to the quantity h.[105]

To simplify the discussion, we select $k = 1$. This gives $P(G_{VEW}$ **(14)**$; x)$ in the form of polynomial belonging to the vertex-weighted graph G_{VW} **(15)**:



G_{VEW} **(15)**

$$P(G_{VW}\,\mathbf{(15)}; x) = x^4 - 2hx^3 - (4 - h^2)x^2 + 4hx$$

Solutions of this polynomial are:

$$x_1 = \frac{h + (h^2 + 16)^{1/2}}{2}$$

$$x_2 = h$$

$$x_3 = 0$$

$$x_4 = \frac{h - (h^2 + 16)^{1/2}}{2}$$

and are paired about $\frac{h}{2}$, as asserted.

CONSTRUCTION OF THE ACYCLIC POLYNOMIAL

The acyclic polynomial for a given graph (conjugated structure) G is defined[55] as follows:

$$P^{ac}(G; x) = \sum_{n=0}^{N} a_n^{ac} x^{N-n} \tag{73}$$

Let the roots of $P^{ac}(G; x)$ be $x_1^{ac}, x_2^{ac}, \ldots, x_N^{ac}$ ($x_i^{ac} \geqslant x_j^{ac}$ if $i < j$). They form the »acyclic spectrum« of graph G. The »energy« of the reference structure is then given by:

$$E_\pi\ (\text{reference structure}) = \sum_{j=1}^{N} \left| x_j^{ac} \right| \tag{74}$$

In the general case, instead of (74),

$$E_\pi\ (\text{reference structure}) = \sum_{j=1}^{N} g_j x_j^{ac} \tag{75}$$

These equations are analogous to those for total π-electron energy,[106]

$$E_\pi\ (\text{conjugated molecule}) = \sum_{j=1}^{N} \left| x_j \right| \tag{76}$$

or

$$E_\pi\ (\text{conjugated molecule}) = \sum_{j=1}^{N} g_j x_j \tag{77}$$

By substituting (75) and (77) into (71), one obtains the expression for TRE (12).

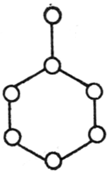
The coefficients of the acyclic polynomial, which is of *utmost importance* for the topological theory of aromaticity, may be obtained using the adapted

Sachs formula for this case. Since the acyclic polynomial does not contain any cyclic contributions, the original Sachs formula (13) for $r(s) = 0$ reduces to

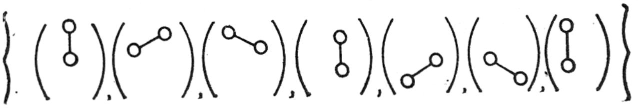
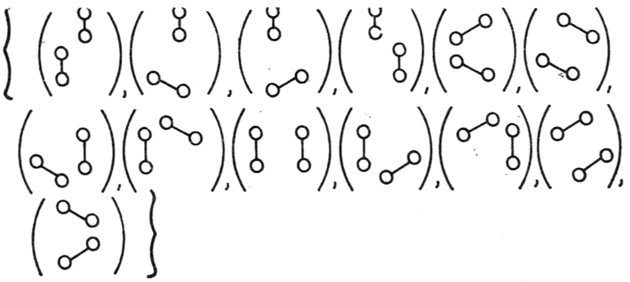
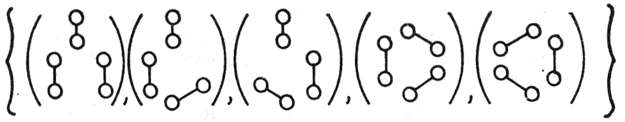
$$a_n^{ac} = \sum_{s \in S_n^{ac}} (-1)^{c(s)} \qquad (78)$$

The acyclic Sachs graphs, S_n^{ac}, are composed entirely from K_2 graphs.

Let us, as an example, evaluate the acyclic polynomial of benzyl represented by graph G_4.



G_4

n	S_n^{ac}	a_n^{ac}
0	Ø	1
2		$7(-1)^1 = -7$
4		$13(-1)^2 = 13$
6		$5(-1)^3 = -5$

$P(G_{16}; x) = x^7 - 7x^5 + 13x^3 - 5x$

The procedure for evaluating $P^{ac}(G; x)$ may be simplified using the recurrence relation:

$$P^{ac}(G; x) = P^{ac}(G - e; x) - P^{ac}(G - (e); x) \qquad (79)$$

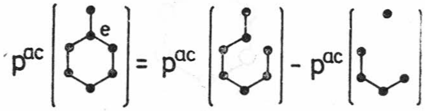
which represents a generalization of the Heilbronner formula:[107]

$$P(G; x) = P(G - e; x) - P(G - (e); x) \tag{80}$$

which was valid only for polyenes. Recently, eq 80 has been independently derived by Lovász and Pelikán.[108] Eq 79 has been obtained by Hosoya in a different but equivalent form.[109]

In the above relations, G-e and G-(e) denote the subgraphs of graph G obtained by deletion of the edge and by deletion of the edge e and incident vertices, respectively, from G.

Let us now, for example, derive the acyclic polynomial for benzyl using (79):



$$= L_7 - L_1 L_4 = x^7 - 7x^5 + 13x^3 - 5x \tag{81}$$

For brevity we denote the characteristic polynomial of a linear graph by L_N. The following relation

$$L_N = xL_{N-1} - L_{N-2} \tag{82}$$

enables one to calculate L_N's starting with $L_0 = 1$ and $L_1 = x$. In Table VII we tabulate these polynomials up to $N = 20$.

TABLE VII

Characteristic Polynomials of Linear Polyenes

$L_0 = 1$

$L_1 = x$

$L_2 = x^2 - 1$

$L_3 = x^3 - 2x$

$L_4 = x^4 - 3x^2 + 1$

$L_5 = x^5 - 4x^3 + 3x$

$L_6 = x^6 - 5x^4 + 6x^2 - 1$

$L_7 = x^7 - 6x^5 + 10x^3 - 4x$

$L_8 = x^8 - 7x^6 + 15x^4 - 10x^2 + 1$

$L_9 = x^9 - 8x^7 + 21x^5 - 20x^3 + 5x$

$L_{10} = x^{10} - 9x^8 + 28x^6 - 35x^4 + 15x^2 - 1$

$L_{11} = x^{11} - 10x^9 + 36x^7 - 56x^5 + 35x^3 - 6x$

$L_{12} = x^{12} - 11x^{10} + 45x^8 - 84x^6 + 70x^4 - 21x^2 + 1$

$L_{13} = x^{13} - 12x^{11} + 55x^9 - 120x^7 + 126x^5 - 56x^3 + 7x$

$L_{14} = x^{14} - 13x^{12} + 66x^{10} - 165x^8 + 210x^6 - 126x^4 + 27x^2 - 1$

$L_{15} = x^{15} - 14x^{13} + 78x^{11} - 220x^9 + 330x^7 - 252x^5 + 83x^3 - 8x$

$L_{16} = x^{16} - 15x^{14} + 91x^{12} - 186x^{10} + 435x^8 - 462x^6 + 209x^4 - 35x^2 + 1$

$L_{17} = x^{17} - 16x^{15} + 105x^{13} - 364x^{11} + 715x^9 - 792x^7 + 461x^5 - 118x^3 + 3x$

$L_{18} = x^{18} - 17x^{16} + 120x^{14} - 455x^{12} + 1001x^{10} - 1287x^8 + 723x^6 - 327x^4 + 44x^2 - 1$

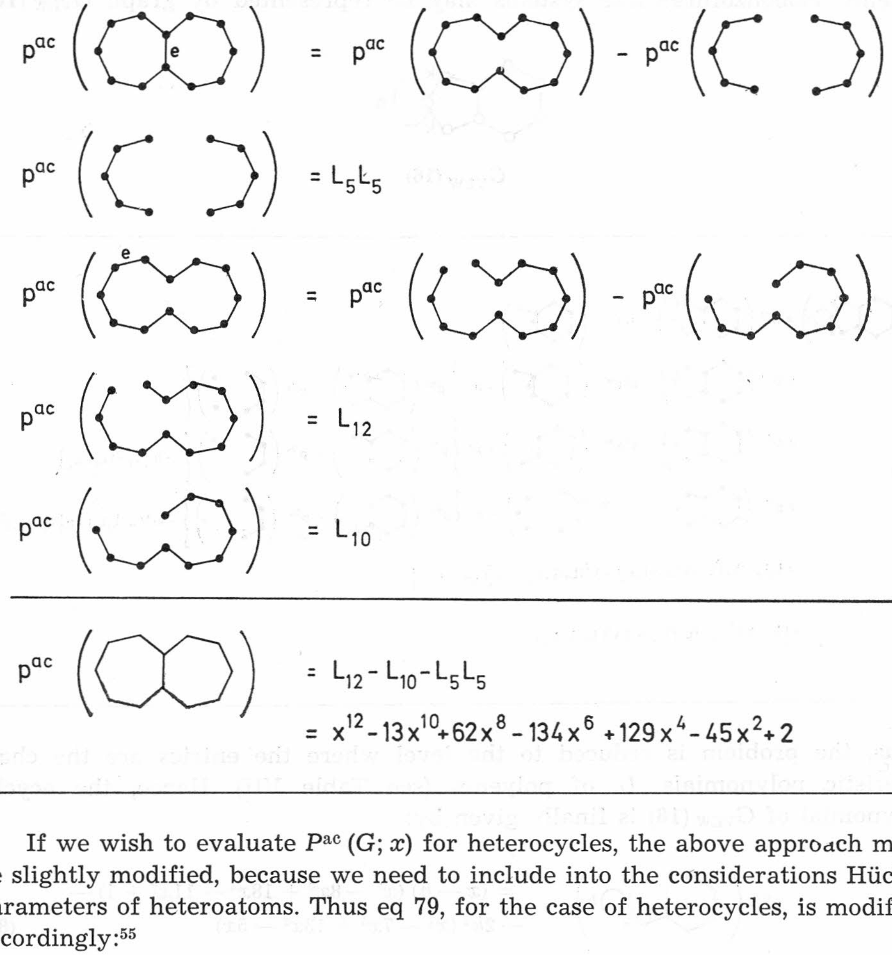
$L_{19} = x^{19} - 18x^{17} + 136x^{15} - 560x^{13} + 1365x^{11} - 2002x^9 + 1715x^7 - 788x^5 + 162x^3 - 10x$

$L_{20} = x^{20} - 19x^{18} + 153x^{16} - 680x^{14} + 1820x^{12} - 3003x^{10} + 3002x^8 - 1711x^6 + 487x^4 - 54x^2 + 1$

A further example of the application of relation (73) is given in Table VIII, where the acyclic polyene of heptalene is evaluated.

TABLE VIII

Calculation of the Acyclic Polynomial for Heptalene



$$= L_{12} - L_{10} - L_5L_5$$

$$= x^{12} - 13x^{10} + 62x^8 - 134x^6 + 129x^4 - 45x^2 + 2$$

If we wish to evaluate $P^{ac}(G; x)$ for heterocycles, the above approach must be slightly modified, because we need to include into the considerations Hückel parameters of heteroatoms. Thus eq 79, for the case of heterocycles, is modified accordingly:[55]

$$P^{ac}(G_{VEW}; x) = P^{ac}(G_{EW}; x) - h\, P^{ac}(G - v; x) \tag{82}$$

$$P^{ac}(G_{EW}; x) = P^{ac}(G - e; x) - k^2\, P^{ac}(G - (e); x) \tag{83}$$

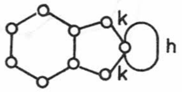
where G_{VEW} is a vertex- and edge-weighted graph with a loop of weight h attached to the vertex v, while G_{EW} is an edge-weighted graph with an edge e of weight k. Graphs G_{EW} and $G - v$ are obtained from G_{VEW} by deleting the loop at the vertex v and by deleting the vertex v and incident edges, respectively. Other symbols have their previous meaning.

Eqs 82 and 83 represent generalizations,[55,110,111] of the following expressions:

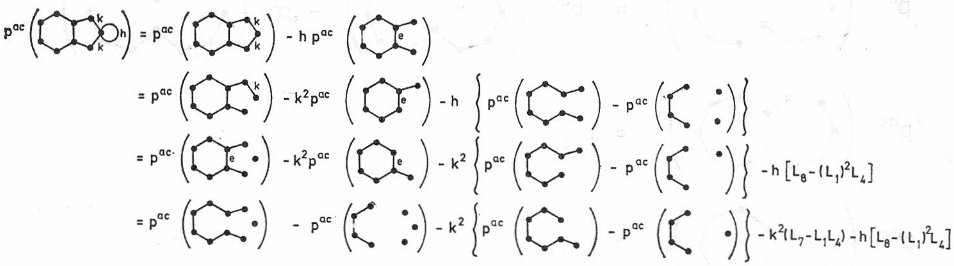
$$P\,(G_{\text{VEW}};x) = P\,(G_{\text{EW}};x) - h\,P\,(G - v;x) \tag{84}$$

$$P\,(G_{\text{EW}};x) = P\,(G - e;x) - k^2\,P\,(G - (e);x) \tag{85}$$

We will illustrate the use of (82) and (83) for the case of isobenzofuran-like systems. Isobenzofuran-like systems may be represented by graph G_{VEW} **(16)**.



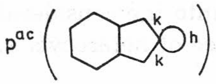
G_{VEW} **(16)**



$$= L_1L_8 - (L_1)^3L_4 - k^2(L_7 - L_1L_4) - k^2(L_7 - L_1L_4) - h\,[L_8 - (L_1)^2L_4]$$

$$= (L_1 - h)\,[L_8 - (L_1)^2L_4] - 2\,k^2(L_7 - L_1L_4)$$

Thus, the problem is reduced to the level where the entries are the characteristic polynomials, L, of polyenes (see Table VII). Hence, the acyclic polynomial of G_{VEW} **(16)** is finally given by:



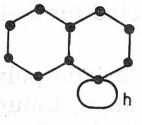
$$= (x - h)\,(x^8 - 8x^6 + 18x^4 - 11x^2 + 1) - \\ - 2k^2\,(x^7 - 7x^5 + 13x^2 - 5x) \tag{87}$$

As an additional example, in Table IX we report the calculation of the acyclic polynomial for α-quinoline-like systems.

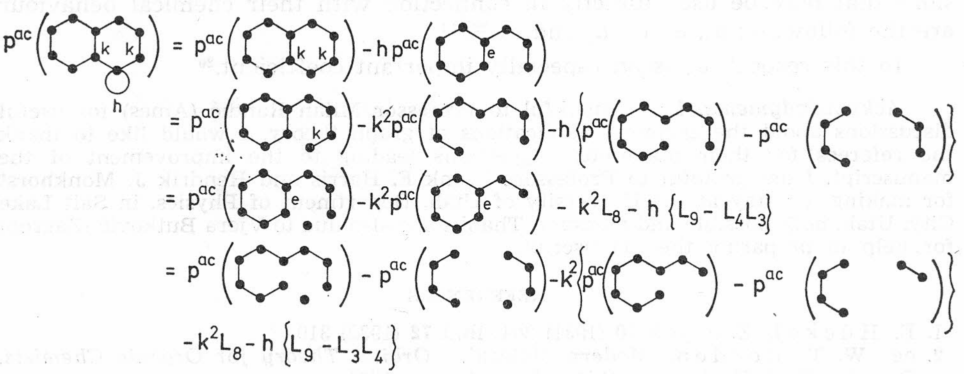
In our work on a TRE model[48] for Hückel parameters, h and k, we used the values suggested by Hess and Schaad in their papers reporting DRE values of heteroconjugated systems.[99-101] These are actually the *only* parameters needed in the topological theory of aromaticity, because this theory is independent of any empirical parameters used for reference structures.[4-6,58]

TABLE IX

Calculation of the Acyclic Polynomial for α-Quinoline-Like Systems Represented by the Graph G_{VEW} **(17)**



G_{VEW} (17)



$$
\begin{aligned}
&- k^2 L_8 - h \{L_9 - L_3 L_4\} = \\
&= L_1 L_9 - L_1 L_3 L_4 - k^2 \{L_8 - L_2 L_4\} - k^2 L_8 - h \{L_9 - L_3 L_4\} = \\
&= L_1 L_9 - L_1 L_3 L_4 - k^2 (2L_8 - L_2 L_4) - h \{L_9 - L_3 L_4\} = \\
&= x^{10} - 9x^8 + 26x^6 - 27x^4 + 7x^2 - k^2 (2x^8 - 15x^6 + 34x^4 - 24x^2 + 3) - \\
&- h (x^9 - 9x^7 + 26x^5 - 27x^3 + 7x)
\end{aligned}
$$

CONCLUDING REMARKS

In the present article, we have presented an approach, based on graph-theoretical concepts and the Sachs formula, for computing the characteristic and acyclic polynomial for a conjugated molecule. In the past this problem attracted both graph-theoretists[25–30,32,33] and theoretical chemists,[21,24,31,34–36] and it is still attracting the attention of various researchers.[112,113]*

Our present efforts may be summarized in the following way:

(*i*) The original Sachs formula may be applied to hydrocarbons directly.

(*ii*) It may be extended to cover Möbius systems.

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*
Note added in proof:

In meantime while this article was reviewed and rewritten in part to meet the references comments and was under print a paper by M. J. Rigby, R. B. Mallion, and A. C. Day appeared in *Chem. Phys. Lett.* **51** (1977) 179 reporting an expression for the general characteristic polynomial of an arbitrarily weighted graph. Their expression is equivalent to that one reported by us for vertex- and edge-weighted graphs. However, these authors have introduced a terminology which differs from ours.

(iii) The vertex and edge-weighted graphs, representing heteroconjugated molecules, are embraced by the modified Sachs formula.

(iv) The acyclic polynomial (which is essential for the topological theory of aromaticity) may be easily constructed for a given conjugated molecule following simple graphical rules.

(v) Coefficients of the characteristic polynomial are related to the topological structure of a conjugated system, though these relations are rather complicated for higher coefficients.

The only coefficients for the evaluation of which there exist simple expressions that may be used directly in connection with their chemical behaviour are the following: a_0, a_1, a_2, a_3 and a_N.[22,114]

In this respect, a_N is an especially important coefficient.[20]

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SAŽETAK

Računananje karakterističnog polinoma konjugiranog sustava pomoću Sachsova teorema

N. Trinajstić

Dana su graf-teorijska pravila koja se temelje na Sachsovu teoremu, za računanje karakterističnog polinoma konjugiranog sustava. Razmatrani su ovi konjugirani sustavi: ciklički ugljikovodici, heterocikli i Möbiusove strukture. Također su dana graf-teorijska pravila za konstruiranje acikličkog polinoma koji odgovara referentnoj strukturi, a bitan je za topološku teoriju aromatičnosti.

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