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A Graphical Study of Heteroconjugated Molecules

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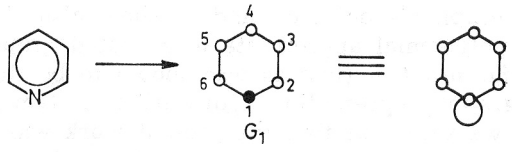
A graphical (graph-theoretical) approach, which has previously been applied systematically only to conjugated hydrocarbon systems, extended to include consideration of the (rooted) graphs representing certain conjugated molecules which contain a restricted class of heteroatoms. The use of the modified Sachs formula for rooted graphs is discussed.

Recent extensive investigations[1–9] have fully confirmed earlier proposals[10–13] that conjugated hydrocarbons may conveniently be studied by means of a *graphical* (that is to say, a graph-theoretical)[14,15] formalism. In the present communication, we attempt to go some way towards extending this approach to a consideration of conjugated systems containing hetero-atoms. It is first necessary to define graphs which correspond to such »hetero-conjugated« molecules. Conjugated systems containing hetero-atoms may be depicted graphically by use of what is known as a *rooted graphs representation*[16,17]. A rooted graph is a graph which has one (or more) of its vertices distinguished in some way from the others, such a vertex which has been thus singled out being called a »*root*«[16,17]. Hence, in the molecular graphs which we use here to represent hetero-conjugated molecules, we shall indicate carbon atoms in the usual way (○)[18], whereas hetero-atoms will be distinguished by means of different »kinds« of vertices (●)[19]. We shall find it convenient, later, to represent this difference by means of the addition of a *self-loop with weight* h[15,18,20] to the vertex (or vertices) in question. Examples of such graphs are given below. The molecular graphs G_1 and G_2 representing the pyridine and trivinylamine molecules are described[16], respectively, as a *rooted cycle* (since the graph G_1 has circuit rank $\geqslant 1$)[21] and a *rooted tree* (since G_2 is of circuit rank zero)[21].



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G_2

Just as the graph representing a conjugated hydrocarbon system can be described by its associated *vertex adjacency matrix*[18,22], so here the rooted graphs appropriate to hetero-conjugated molecules may also be represented by »adjacency matrices« (**A** (G)), but of a particular type[22–24]. For example, the following matrices, assigned to the rooted graphs G_1 and G_2, can be considered as »adjacency matrices« of such graphs:

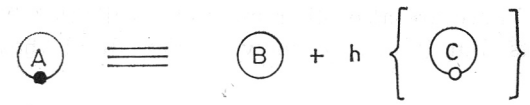
$$\mathbf{A}(G_2) = \begin{pmatrix} h & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \tag{1}$$

$$\mathbf{A}(G_1) = \begin{pmatrix} h & 1 & 0 & 0 & 1 & 1 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \tag{2}$$

It should be noted that, in the above adjacency matrices, the symbol h is inserted in a position corresponding to a »root« (that is to say, a self-loop with weight h) in the given graph, with vertices labelled as in G_1 and G_2.

The matrices, **A** (G_1) and **A** (G_2) are, of course, none other than what we conventionally identify[10] as the Hamiltonian matrices occuring in the Hückel molecular orbital (HMO) theory,[25,26] when an adjustment for heteroatoms[26,27] (to the Coulomb integrals only — see below)has been accommodated.

We now wish to show how the structure of a rooted graph is related to the various coefficients appearing in the characteristic polynomial ($P(G, x) = \sum_{n=o}^{N} a_n x^{N-n}$, where N is the number of vertices in G) of the vertex adjacency matrix of such a graph (as defined), and to show also that construction of the characteristic polynomial appropriate to a rooted graph is, once more, a *purely combinatorial problem* (just as was shown to be the case earlier[3,18,23], when non-rooted graphs, representing hydrocarbon systems, were considered). Before doing this, we point out that the present work was largely stimulated by previous studies[28] on a very practical computational problem; earlier workers[28] in the field of HMO theory made attempts to derive general formulae for calculating the secular equations describing conjugated systems containing a single hetero-atom, from those appropriate to the corresponding hydrocarbon analogue. Their results may be presented graphically as follows:



where the symbols have the following meaning:

(A) is the characteristic polynomial of a *singly*-rooted graph $\mathscr{A}$, corresponding to a given conjugated system containing a single heteroatom, the root vertex representing this heteroatom being denoted by ●

$\equiv$ (identically equal) emphasises that the equality is valid for every value of the variable x

(B) is the characteristic polynomial of the non-rooted graph $\mathscr{B}$ which has the same set of vertices (but all of them now of the same »type« — *i. e.* none singled out for special treatment) and the same set of edges as the *singly*-rooted graph $\mathscr{A}$

(C) is the characteristic polynomial of the subgraph $\mathscr{C}$ of the *singly*-rooted graph $\mathscr{A}$ obtained after the »root« vertex, and all the edges joining it to other vertices in $\mathscr{A}$, have been removed

h is identified with the usual Hückel parameter[25,26] featuring in the expression

$$\alpha_X = \alpha_C + h\,\beta_{CC}$$

h therefore reflects the difference (in units of β_{CC}, the »standard« carbon-carbon resonance integral[25]) 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 hetero-atom, X. It is important to note at this stage that, in the present study, variation of resonance integrals from the »standard« (benzene) value is *not* considered, and neither is a graph-theoretical interpretation of this aspect of simple HMO theory attempted here; the formulae we propose below do not, therefore, at present, have the flexibility to encompass this particular variant.

Evaluation of the coefficients of (B) and (C) may be carried out by application of the formula due to Sachs[29], in the way, for example, described

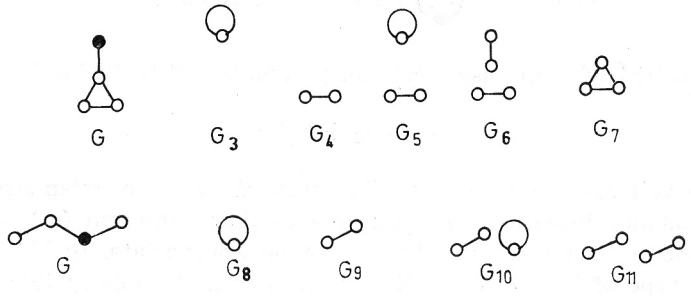
by Graovac *et al.*[3] There are also other methods available[21,25–34] for evaluation of the a_n coeffients, but it can be shown[35] that all of these are related to Sachs' formula.

We now propose an alternative way in which we wish to show the use of the Sachs formula for rooted graphs and thus to show the coefficients a_n, in the characteristic polynomial of a rooted graph, depend *directly* on its structure.

The original Sachs formula[3,29] is as follows:

$$a_n = \sum_{s \in S_n} (-)^{c(s)} 2^{r(s)} \tag{4}$$

in which **s** is a Sachs graph[3] and S_n is the set of Sachs graphs of a graph G. The total number of components of a Sachs graph **s** is denoted by c(**s**) and the number of cyclic components is denoted by r (**s**). N is the number of vertices in the graph G. The reader may note that $a_0 = 1$, from the definition[29]. 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)[3]; such subgraphs we shall call *rooted Sachs graphs.* We define a rooted Sachs graph as such a subgraph of a rooted graph which has no components other than complete graphs of degree one (o—o), cycles, or self-loops ( ), or some combinations of these. It is also immediately evident that a rooted graph may contain both types of Sachs graphs — that is to say, non-rooted and rooted ones. We give below some examples of Sachs graphs, both non-rooted (G_4, G_6, G_7, G_9, and G_{11}) as well as rooted (G_3, G_5, G_8, and G_{10}) of a given rooted graph G:



The modified Sachs formula* for evaluation of the coefficients of a rooted graph is given below:

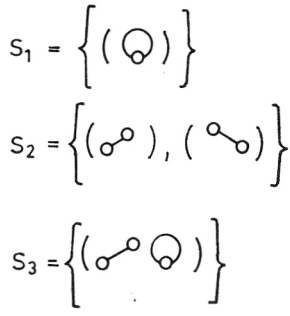
$$a_n = \sum_{s \in S_n} (-)^{c(s)} 2^{r(s)} h^{l(s)} \tag{5}$$

* Here, we simply quote equation (5) without proof. Readers interested in the mathematical details of its derivation are referred to our article in the forthcoming publication arising from the Second Czechoslovak Symposium on Graph Theory, Prague, June, 1974.

where all the symbols mentioned previously have their usual meaning, h can be thought of as the weight of the self-loop in question and l is the number of self-loops in a particular Sachs graph **s**. Self-loops do not contribute to r, but they are permitted to be components of a Sachs graph.

We shall illustrate use of the generalized Sachs formula presented here by means of the several examples outlined below. Sachs graphs **s** are drawn within small brackets, and the set of all Sachs graphs, S_n, is denoted in braces.

(1) *Vinyl-chloride-like systems*



Therefore, $a_0 = 1$

$$a_1 = (-)^1\, 2^0\, h^1 = -h$$

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

$$a_3 = (-)^1\, 2^0\, h^1 = h$$

and

$$P_G(x) = x^3 - h\,x^2 - 2x + h$$

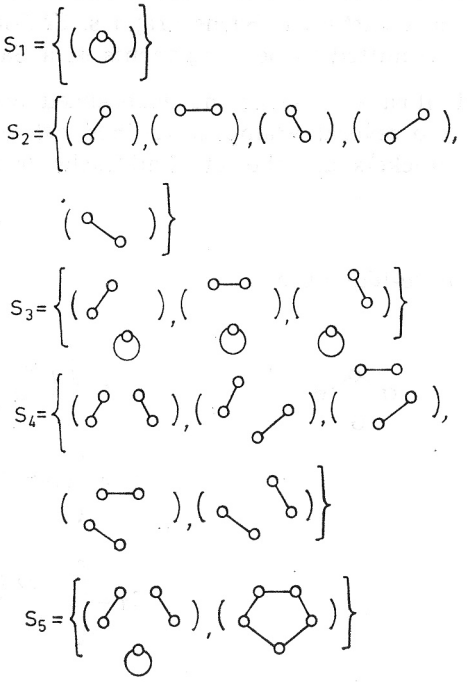
The actual value selected for h in any specific HMO calculation (and the reasoning by which such a value is thought to be appropriate in any given case) is not relevant for our present purpose; if, however, as a check, we choose arbitrarily the value[26,36] $h = 1.00$, then the following *graph spectrum*[15,18] (the set of all eigenvalues — that is to say, the roots of the characteristic polynomial) is readily obtained:

$$\{+1.80194, \quad +0.44504, \quad -1.24698\}$$

and these numbers are identical with those obtained from the direct calculations[36].

(2) *Pyrrole-like systems*

G



Therefore, $a_0 = 1$

$a_1 = (-)^1\, 2^0\, h^1 = -h$

$a_2 = (-)^1\, 2^0\, h^0\, 5 = -5$

$a_3 = (-)^2\, 2^0\, h^1\, 3 = 3h$

$a_4 = (-)^2\, 2^0\, h^0\, 5 = 5$

$a_5 = (-)^3\, 2^0\, h^1 + (-)^1\, 2^1\, h^0 = -h - 2$

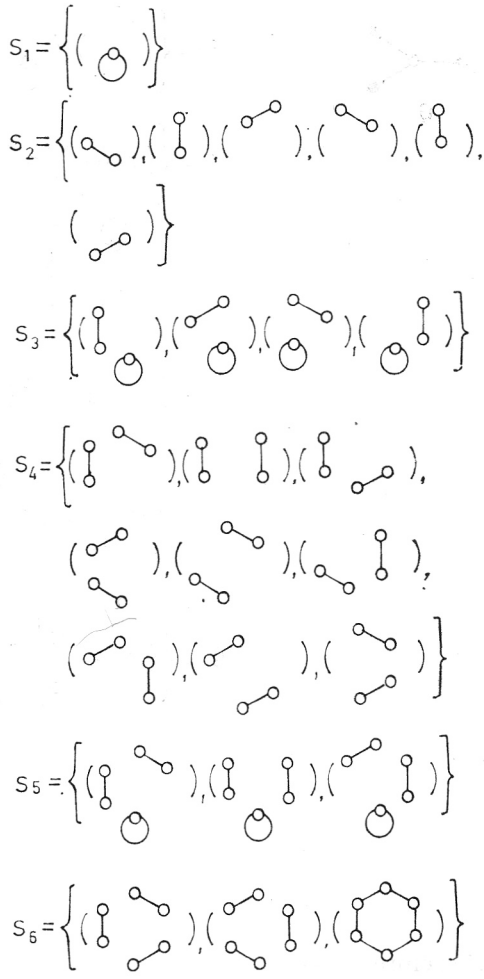
and

$$P_G(x) = x^5 - hx^4 - 5x^3 + 3hx^2 + 5x - h - 2$$

If we arbitrarily select $h = 1.0$, the following graph spectrum is obtained

$$\{+2.30278,\quad +1.00000,\quad +0.61803,\quad -1.30278,\quad -1.161803\}$$

(3) *Pyridine-like systems*



Therefore, $a_0 = 1$
$a_1 = (-)^1\, 2^0\, h^1 = -h$
$a_2 = (-)^1\, 2^0\, h^0\, 6 = -6$
$a_3 = (-)^2\, 2^0\, h^1\, 4 = 4h$
$a_4 = (-)^2\, 2^0\, h^0\, 9 = 9$
$a_5 = (-)^3\, 2^0\, h^1\, 3 = -3h$
$a_6 = (-)^3\, 2^0\, h^0\, 2 + (-)^1\, 2^1\, h^0 = -4$

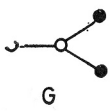
and

$$P_G(x) = x^6 - hx^5 - 6x^4 + 4hx^3 + 9x^2 - 3hx - 4$$

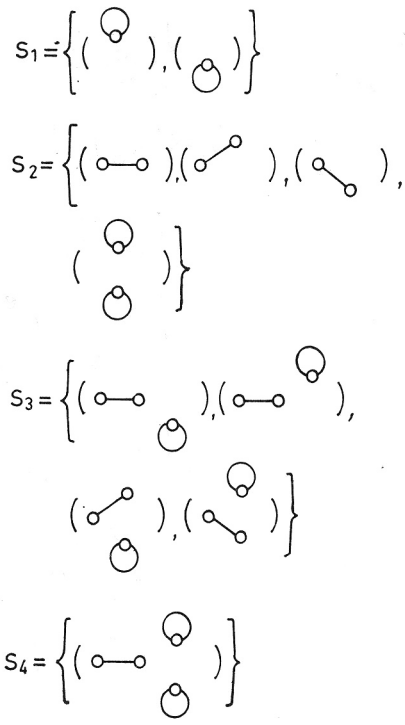
If we now select, for example, $h = 0.5$, the following graph spectrum is obtained:

$$\{+2.10745,\quad +1.16719,\quad +1.00000,\quad -0.84096,\quad -1.00000,\quad -1.93368\}$$

(4) *1,1-Dichloro-ethylene-like systems*



G



Therefore, $a_0 = 1$

$a_1 = (-)^1\, 2^0\, h^1\, 2 = -2h$

$a_2 = (-)^1\, 2^0\, h^0\, 3 + (-)^2\, 2^0\, h^2 = -3 + h^2$

$a_3 = (-)^2\, 2^0\, h^1\, 4 = 4h$

$a_4 = (-)^3\, 2^0\, h^2 = -h^2$

and

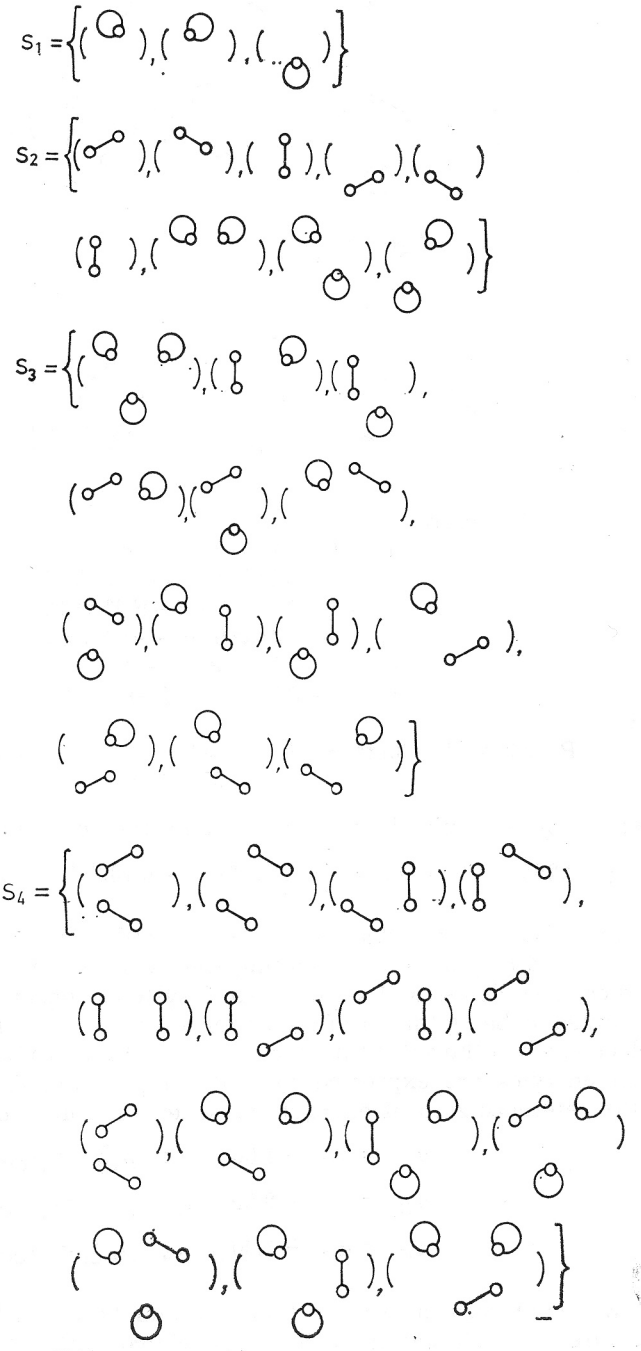
$$P_G(x) = x^4 - 2hx^3 + (h^2 - 3)\, x^2 + 4hx - h^2$$

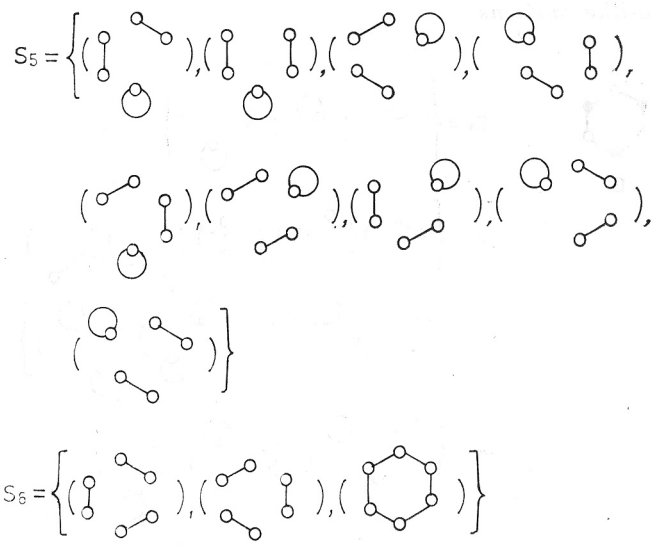
If, for the sake of giving a further example, we arbitrarily select the value $h = 1.00$, the following graph spectrum is obtained:

$$\{+2.17009,\quad +1.00000,\quad +0.31111,\quad -1.48119\}$$

(5) s-*Triazine-like systems*

G





Therefore, $a_0 = 1$

$a_1 = (-)^1\, 2^0\, h^1\, 3 = -3h$

$a_2 = (-)^1\, 2^0\, h^0\, 6 + (-)^2\, 2^0\, h^2\, 3 = -6 + 3h^2$

$a_3 = (-)^3\, 2^0\, h^3 + (-)^2\, 2^0\, h^1\, 12 = -h^3 + 12h$

$a_4 = (-)^2\, 2^0\, h^0\, 9 + (-)^3\, 2^0\, h^2\, 6 = 9 - 6h^2$

$a_5 = (-)^3\, 2^0\, h^1\, 9 = -9h$

$a_6 = (-)^3\, 2^0\, h^0\, 2 + (-)^1\, 2^1\, h^0 = -4$

and

$$P_G(x) = x^6 - 3hx^5 + (3h^2 - 6)x^4 + (-h^3 + 12h)x^3 + (9 - 6h^2)x^2 - 9hx - 4$$

Taking, for example, $h = 0.5$, we obtain the following graph spectrum:

$$\{+2.26556,\ +1.28078,\ +1.28078,\ -0.78078,\ -0.78078,\ -1.76556\}$$

In HMO theory, what we have called the graph spectrum $\{x_i\}$ of each of the rooted graphs representing the vinyl-chloride-, pyrrole-, pyridine-, 1,1-dichloroetylene-, and *s*-triazine-like systems considered above is, of course, intepreted as being the set of π-electron energy levels, $\{E_i\}$ in the corresponding molecule, when the substitution $x_i = (E_i - \alpha_C)/\beta_{CC}$ has been made (that is to say, when energies are expressed in units of β_{CC}, and α_C is taken conveniently as the reference zero of energy) and when the following parameters are used:

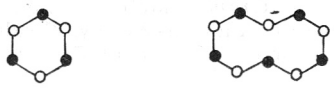
$$\alpha_{\ddot{N}} = \alpha_C + 1.00\,\beta_{CC}\ ;\quad \beta_{C\ddot{N}} = \beta_{CC} \tag{6}$$

$$\alpha_{\dot{N}} = \alpha_C + 0.50\,\beta_{CC}\ ;\quad \beta_{C\dot{N}} = \beta_{CC} \tag{7}$$

$$\alpha_{\ddot{C}l} = \alpha_C + 1.00\,\beta_{CC}\ ;\quad \beta_{C\ddot{C}l} = \beta_{CC} \tag{8}$$

We emphasize once more that our aim here has been to show how the structure of a heterocyclic molecule is related to the form of the characteristic

polynomial of the rooted graph which represents it, and not to concern ourselves at all with the relative virtues, or otherwise, of particular numerical values for Hückel parameters. We may also note, in passing, that our expression (5) embraces the results of Bochvar and Stankevich[37,38], when it is applied to compouds such as those depicted graphically below:



G_{12} G_{13}

(A class of compounds corresponding to the above graphs G_{12} and G_{13} is, for example, the borazines).

Because, in this Journal, we are addressing ourselves primarily to a *chemical* readership, we have chosen particularly to emphasize applications of the theory of rooted graphs to problems in the very simplest of all the MO theories with which most chemists are, by now, very familiar. In concluding, however, we do just draw attention to the fact that the abstract theory of rooted graphs which chemists have been long applying (albeit, in most cases, unknowingly) in the context of the simple HMO theory of conjugated molecules, does have potentially very wide application, not only outside simple HMO theory, but even outside chemistry itself. These applications are, for example, distribution — and »bottle-neck« traffic problems in the field of commerce and operational research.

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SAŽETAK

Studij heterokonjugiranih molekula teorijom grafova

R. B. Mallion, A. J. Schwenk i N. Trinajstić

Teorija grafova, koja je prije bila sustavno primijenjena jedino na konjugirane ugljikovodike, upotrijebljena je za studij nekih klasa heterokonjugiranih molekula. Pokazano je kako se na osnovi strukture grafa, koji odgovara heterokonjugiranoj molekuli, i s pomoću modificirane Sachsove formule može napisati karakteristični polinom takvog grafa.

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Primljeno 1. travnja, 1974.