CROATICA CHEMICA ACTA CCACAA 52 (3) 233—248 (1979)

CCA-1159

YU ISSN 0011-1643
539.19:516
Original Scientific Paper

On the Reference Structure for the Resonance Energy of Aromatic Hydrocarbons

L. J. Schaad[a], *B. Andes Hess, Jr.*[a], *J. B. Nation,*[b]* *and N. Trinajstić*[c]
with an Appendix by

I. Gutman[d]

[a]*Department of Chemistry, Vanderbilt University, Nashville, Tenn. 37235, USA*
[b]*Department of Mathematics, Vanderbilt University, Nashville, Tenn. 37235, USA*
[c]*»Ruđer Bošković« Institute, P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia, and*
[d]*Faculty of Sciences, University of Kragujevac, P.O.B. 60, 34000 Kragujevac, Serbia, Yugoslavia*

Received July 17, 1978

To use the Zagreb Group and Aihara definition of resonance energy, it is necessary that the roots of the reference polynomial all be real. A partial proof that they are has been obtained in three ways. Direct solution of the reference polynomial for annulenes shows all roots real in this case. Application of Sturm sequences promises the complete proof in principle, but requires the proof of inequalities which we have so far resolved only for molecules with four or fewer atoms. A graph theoretical approach succeeds for all conjugated hydrocarbons in which no edge is shared by two rings. It is also suggested that the reference polynomial may be used for discriminating planar isospectral molecules.

INTRODUCTION

In 1969 Dewar and deLlano[1] made a crucial advance in the theory of aromaticity when they proposed that the resonance energy of a conjugated hydrocarbon be computed as the difference between the π energy of the molecule and that obtained by summing formal single and double bond energy terms. For acyclic polyenes the two energies are nearly equal, and thus such compounds are computed to be nonaromatic. For cyclic molecules the difference may be positive, zero, or negative corresponding to aromatic, nonaromatic, or antiaromatic systems. Although the Dewar and deLlano work was done using the Pariser-Parr-Pople computational method, Hess and Schaad[2–9] have shown that the simple Hückel method used with the Dewar-deLlano reference structure gives results that are at least as accurate.

At the same time as this work on aromaticity was being carried out, the Zagreb Group[10–18] reexamined Hückel theory with the aid of a powerful graph theoretical formula by Sachs[19] which enables one to write down the Hückel characteristic polynomial for a conjugated molecule simply by counting certain

---

* The work of this author was supported in part by NSF Grant MSC 76-06447

subgraphs of the molecular graph. If the characteristic polynomial of the Hückel matrix **H** is written

$$f(x) = (-1)^k \,|\, \mathrm{H} - xI \,| = x^k + a_1 x^{k-1} + \ldots + a_k \tag{1}$$

(note that x here is of opposite sign to that usual in Hückel calculations), then Sachs proved that

$$a_i = \sum_{s \in S_i} (-1)^{c(s)}\, 2^{r(s)} \tag{2}$$

where s is a member of the set S_i of all Sachs graphs[10] (called »Grundfiguren« by Sachs) with i vertices, $c(s)$ is the number of components and $r(s)$ the number of rings in s.

Gutman, Milun and Trinajstić and independently Aihara[20,21] have used Sachs' result to provide an alternative to the Dewar-deLlano reference structure. The Dewar-deLlano reference structure might be described loosely as a hypothetical molecule which has the properties (specifically, the energy additivity) that the actual molecule would have had, had it behaved like an acyclic. Suppose then that all Sachs graphs in eq 2 containing cyclic components are discarded. The resulting coefficients will give a polynomial belonging to a hypothetical molecule that is like the original exept that it behaves as though it were acyclic (but in a somewhat different sense than above). Gutman, Milun and Trinajstić, and Aihara, then compute the energy of the n-electron reference structure as twice the sum of the $n/2$ lowest roots of this reference polynomial[22]. Resonance energies computed in this way closely parallel those of Hess and Schaad though they are not identical with them[17,24]. A strong advantage of the graph theoretical reference is that it is easy to generalize to radicals and ions[25].

I. THE ROOTS OF THE REFERENCE POLYNOMIAL

A Sachs graph is defined as a subgraph of the original molecular graph containing only disjoint rings (= the »Kreise« of Sachs) and single edges (= the »Strecken« of Sachs = the »Γ« of ref 10). In computing the coefficients of the reference polynomial, all Sachs graphs with cyclic components are dropped leaving only those consisting entirely of disjoint single edges. Each edge joins two vertices, hence only Sachs graphs with even numbers of vertices contribute to the reference polynomial. Hence $a_i = 0$ for all odd i in the reference polynomial, and

$$a_{2j} = (-1)^j \sum_{s \in T_j} 1 \tag{3}$$

where T_j is the collection of all subgraph consisting of j disjoint edges of the graph. It follows immediately that if x_0 is the root of the reference polynomial, so is $-x_0$; and in this pairing of energy levels the hypothetical reference molecule is again like a real acyclic.

In order to use the Zagreb Group — Aihara reference, its energy, and hence all its filled orbital energies must be real. In an uncharged hydrocarbon, the lower half of the roots of the reference polynomial will correspond to filled orbitals. Since each of these is paired with an empty orbital of opposite sign, it follows that all roots of the reference polynomial must be real. In the several hundred examples so far calculated[7,17,20,21,24–26] all roots of the reference polynomial have been found to be real.

The work by Heilman and Lieb[27] and by Godsil and Gutman[28,29] (see Appendix) confirms this conjecture that the reference polynomial of a given graph (structure) has real roots. However, the proof these authors give are obtained using the reasoning of mathematical induction. Therefore, roughly speaking, we know that the reference polynomials of all graphs have real roots, but not »why« this theorem holds and which are the graph-theoretical »reasons« for its validity. From the combinatorial point of view, the reference polynomial is only one among many other possible polynomials of analogous structure. But only the reference polynomial possesses the distinguished property that all its zeros are real.

Further investigations are therefore necessary in order to elucidate the relations between the combinatorial, i. e. graph-theoretical nature of the reference polynomial and its algebraic properties. In the present work we attempt to give a partial proof of the reality of the zeros of the reference polynomial using the graph-theoretical arguments. We hope that our initial step may be a stimulus for a future work in this area.

A) *Explicit Solution of the Reference Polynomial*

In the case of [*n*] annulenes the Hückel characteristic equation is easily obtained in terms of Tschebysheff polynomials using the method of Goodwin and Vand[30] as

$$H_n(x) = T_n(x) - T_{n-2}(x) - 2 \tag{4}$$

With the transformation $x = 2\cos\Theta$ the Tschebysheff polynomials for even n can be written

$$T_n = 2\,[\cos n\,\Theta + \cos(n-2)\,\Theta + \ldots + 1/2] \tag{5}$$

Substituting eq 5 into 4 gives

$$H_n(x) = 2\cos n\,\Theta - 2 \tag{6}$$

Using Sachs' theorem, it is apparent that the only cyclic contribution to H_n occurs in the constant term and that the reference polynomial for an [*n*] annulene is

$$R_n(x) = H_n(x) + 2 = 2\cos n\,\Theta \tag{7}$$

the roots of which are

$$x = 2\cos\frac{m\,\pi}{2\,n}\,;\ m = 1, 3, \ldots, 2\,n-1 \tag{8}$$

Hence for an [*n*] annulene the roots of the reference polynomial are shown explicitly all to be real.[31]

Certain other cases, especially those like the radialenes[2,27] and the polyacenes whose secular equations can be solved by the method of finite differences,[33] might be treated in the same way; but instead of pursuing this approach we have searched for a more general solution.

B) *Use of Sturm Sequences*

The problem of determining the number of real roots of a polynomial in a given interval is an old one to which Descartes' early rule, »The number of positive roots equals the number of variations in signs of the coefficients, or this decreased by an even number.«, gives only a partial solution.

The reference polynomial $R(x)$ contains only even terms and hence is a polynomial $P(y)$ in $y = x^2$. Since the roots of $R(x)$ must all be real, those of $P(y)$ must all be real and nonnegative. From Descartes' rule it then follows that the coefficients of $P(y)$ must alternate in sign. Sachs' theorem easily shows that this necessary but not sufficient condition on the realness of the roots of $R(x)$ does hold since each Sachs graph contributing to the coefficient of y^{i+1} contains one more edge (and hence one more component) than those giving the coefficient of y^i. Thus the coefficients in $P(y)$ do alternate in sign.

In 1829 Sturm showed[34,35] that the number of real roots of the n^{th} degree polynomial equation, $f(x) = 0$, lying between x_0 and x_1 equals the diferrence between the number of sign changes in the sequence, $f_0(x_0), f_1(x_0) \ldots f_n(x_0)$ and in the sequence, $f_0(x_1), f_1(x_1) \ldots f_n(x_1)$. The first two members of the Sturm sequence are $f_0 = f(x)$ and $f = \frac{\mathrm{d}}{\mathrm{d}x} f(x)$. For $i \geq 2$, f_i is the negative of the remainder obtained on dividing f_{i-2} by f_{i-1}.

Let the Sturm sequence for the reference polynomial of a hydrocarbon with $2n$ carbon atoms be

$$
\begin{aligned}
f_0 &= P(y) = c_{00}\, y^n + c_{01}\, y^{n-1} + \ldots + c_{0,\,n-1}\, y + c_{0n} \\
f_1 &= \frac{\mathrm{d}P}{\mathrm{d}y} = c_{11}\, y^{n-1} + \ldots + c_{1,\,n-1}\, y + c_{1n} \\
&\cdots\cdot \qquad \cdots\cdot \\
f_i &= c_{ii}\, y^{n-i} + \ldots + c_{i,\,n-1}\, y + c_{in} \\
&\cdots\cdot \qquad \cdots\cdot \\
f_{n-1} &= c_{n-1,\,n-1}\, y + c_{n-1,\,n} \\
f_n &= c_{nn}
\end{aligned}
\tag{9}
$$

Since only the leading and constant terms respectively will be important at $y = \infty$ and $y = 0$, application of Sturm's theorem is simplified and the number of real positive roots will be the number of sign changes in the sequence

$$c_{0n},\ c_{1n},\ c_{2n},\ \ldots,\ c_{nn} \tag{10}$$

minus the number in

$$c_{00},\ c_{11},\ c_{22},\ \ldots,\ c_{nn} \tag{11}$$

In order that all roots be real and positive, it then follows that the sequence (10) must alternate in sign and (9) be of constant sign.

Eqs 9 to 11 are written for the case in which all roots of f_0 are distinct. The Sturm method counts multiple roots only once rather than multiply, but this requires only minor modification in the above. If f_0 has multiple roots, then f_1 and f_0 will have common factors; and the process in (9) will terminate before reaching f_n. In this case sequences (10) and (11) will terminate short of c_{nn}; nevertheless such terms as are in (10) must still alternate in sign and those in (11) be of the same sign.

Since Sachs' theorem gives all the coefficients of f_0 in terms of subgraphs of the original molecular graph, and since the coefficients in the other f_i's are obtained simply from those of f_0, in principle the necessary conditions on the coefficients in (10) and (11) can be expressed as inequalities in the numbers of various Sachs graphs. It should then be possible to show that these inequalities do in fact hold.

From (1), $c_{00} = 1$; and then, since $f_1 = \frac{df_0}{dy}$, $c_{11} = nc_{00} = n$, so that the first two members of (11) are of the same sign as required. Further, $c_{1n} = c_{0,n-1}$ which, as shown above, is of opposite sign to c_{0n}. Hence the first two members of (11) do alternate in sign as required.

Dividing f_0 by f_1 and changing the sign of the remainder gives

$$c_{22} = \left(\frac{n-1}{n^2} c_{01}{}^2 - \frac{2}{n} c_{02} \right); \quad c_{2n} = \left(\frac{c_{01}\, c_{0,\,n-1}}{n^2} - c_{0n} \right) \tag{12}$$

The coefficient c_{2n} must be of the same sign as c_{0n}. $c_{0,n-1}$ has opposite sign to c_{0n}, and c_{01} is negative; therefore $c_{01}\, c_{0,n-1}$ and c_{0n} have the same sign. Thus c_{2n} and c_{0n} will be of the same sign if

$$\left| \frac{c_{01}\, c_{0,\,n-1}}{n^2} \right| > | c_{0n} | \tag{13}$$

The Sachs graphs contributing to c_{0n} correspond to the Kekulé structures of the molecule; $| c_{0n} |$ equals the number of Kekulé structures, and n equals the number of formal double bonds in each.[10] Since $| c_{01} |$ equals the total number of π bonds (edges) in the molecule, it is clear that

$$\frac{c_{01}}{n} > 1 \tag{14}$$

except in the case of ethylene (which is of no interest, being acyclic and having identical reference and Hückel polynomials) where $c_{01} = n = 1$. Dropping an edge from any Sachs graph s_{2n} contributing to c_{0n} will generate a contributor s_{2n-2} to $c_{0,n-1}$. Each of the n edges in a given s_{2n} will give a distinct s_{2n-2}. Two distinct s_{2n}'s cannot give identical s_{n2-2}'s unless two Kekulé structures could differ in only one double bond, and this is impossible. Hence

$$| c_{0,\,n-1} | \geq n \, | c_{0n} | \tag{15}$$

Combining (14) and (15) gives (11), and shows that the sequence c_{0n}, c_{1n}, c_{2n} does alternate in sign.

Our proof that c_{22} is positive is more tedious. Let $m = | c_{01} |$ = the number of π bonds and $N = 2n$ = the number of carbon atoms in the molecule. Because of the sign alternation in f_0, c_{02} is positive and therefore from (12) it is seen that

$$c_{02} < m^2 \left({}^1\!/_2 - \frac{1}{N} \right) \tag{16}$$

must hold if c_{22} is to be positive. In a conjugated hydrocarbon each carbon atom must be bonded to 1, 2 or 3 other carbon atoms. If α_2 equals the number of carbon atoms bonded to 2 and α_3 the number bonded to 3 other carbon atoms, then

$$c_{02} = {}^1/_2\, m\, (m - 1) - \alpha_2 - 3\, \alpha_3 \tag{17}$$

Substituting (17) into (16) and simplifying yields

$$m^2 < \frac{m\, N}{2} + N\, \alpha_2 + 3\, N\, \alpha_3 \tag{18}$$

as the equation we wish to establish. We may assume that our molecule contains at least one ring; otherwise the reference polynomial is identical with the characteristic polynomial and the problem is solved. For graphs with at least one ring, $m \geq N$; and therefore it will suffice to show that

$$m^2 < \frac{N^2}{2} + N\, \alpha_2 + 3\, N\, \alpha_3 \tag{19}$$

At this point we recall Euler's Theorem for planar graphs[36]

$$F - E + V = 2 \tag{20}$$

where F is the number of faces of the graph (the outside region is counted as a face), E the number of edges, and V the number of vertices. In our case $V = N$, $E = m$ and the inequality $F \leq 2 + {}^1/_2\, \alpha_3$ is easily established (notice that $F = 2$ for a single ring, and each additional face requires that two vertices of degree 2 be raised to degree 3). Combining this with (20) gives

$$m \leq N + {}^1/_2\, \alpha_3 \tag{21}$$

and therefore

$$m^2 \leq N^2 + N\, \alpha_3 + {}^1/_4\, \alpha_3{}^2 \leq N^2 + \frac{5}{4} N\, \alpha_3 \tag{22}$$

since $\alpha_3 \leq N$. Substituting the right-hand side of (22) for the left-hand side of (18) and simplifying, using $m \geq N$, yields

$$N < 2\, \alpha_2 + \frac{7}{2}\, \alpha_3 \tag{23}$$

as our objective. This is easily shown to be true however, for we may write $N = \alpha_1 + \alpha_2 + \alpha_3$ (where α_1 equals the number of carbon atoms bonded to precisely one other carbon atom) and observe that $\alpha_1 \leq \alpha_2 + 2\alpha_3$, whence

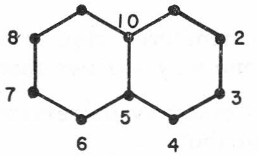
$$N \leq 2\, \alpha_2 + 3\, \alpha_3 \tag{24}$$

is true. Therefore (23), and consequently (16), hold if $\alpha_3 > 0$. On the other hand, the only graphs with $\alpha_3 = 0$ are the linear polyenes and the annulenes; and in both these cases we have already established independently the desired result.

Constructing f_3 gives expressions for c_{33} and c_{3n} that have so far proved intractable. Thus our Sturm sequence proof that the roots of the reference polynomial are real is complete only for systems with 4 or fewer atoms. However, a computer program using Sturm sequence written by Rebecca Polk at Vanderbilt has been used to verify that the roots of the reference polynomial are real for all systems with six or eight atoms. Many more systems with 10 to 16 atoms have been checked using this program, but because of the large amounts of computing time involved these cases were not exhausted.

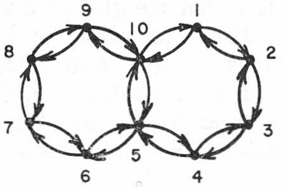
C) *A Graph-Theoretical Proof*

The Hückel polynomial is known to have all real roots since it is the characteristic polynomial of a Hermitian matrix. If it is possible to construct a Hermitian matrix whose characteristic polynomial is the reference polynomial, then the roots of the reference polynomial would be immediately proved real. Sachs' proof of (2) suggests a way to do this in a number of important cases.



I

In his proof[19] Sachs replaced the undirected molecular graph by a graph in which a pair of oppositely directed edges replaces each edge of the original. For example, the molecular graph of naphthalene is replaced by the directed graph



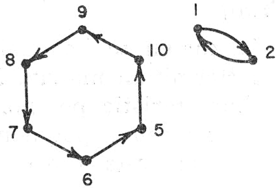
II

Since the element a_{ij} of the adjacency matrix of an undirected graph is defined as 1 if there is an edge between vertices i and j and 0 otherwise, while for the directed graph $a_{ij} = 1$ if there is a directed edge *from i to j*, the graphs I and II have the same adjacency matrices.

In terms of the directed graph Sachs' Theorem (2) can be rewritten[19]

$$a_i = \sum_{\vec{L}_i \in \vec{G}} (-1)^{n(\vec{L}_i)} \tag{25}$$

where $\vec{G}$ is the directed graph corresponding to the original molecular graph. $\vec{L}_i$ is a linear subgraph of $\vec{G}$ with i vertices, and $n(\vec{L}_i)$ is the number of components (disjoint parts) of $\vec{L}_i$. A linear graph is one in which one and only one directed edge arises from, and one and only one directed edge ends on each vertex. A linear graph thus consists only of disjoint directed cycles, including perhaps the two-membered cycles corresponding to the single edges of the molecular graph. For example III is one $\vec{L}_8$ of the $\vec{G}$ shown in II. There



III

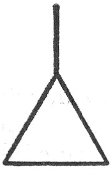
is another in which the six-membered ring is clockwise instead of counterclockwise, but there is only one way the two-membered ring can be drawn so that there is not another $\vec{L}_8$ formed by its reversal.

The linear graph III contributes

$$(-1)^2 (a_{12}\, a_{21})\, (a_{10,9}\, a_{9,8}\, a_{8,7}\, a_{7,6}\, a_{6,5}\, a_{5,10}) \tag{26}$$

to the coefficient of x^2 in the Hückel polynomial with the first two a_{ij}'s coming from the two-membered cycle and the others from the six-membered cycle. This term reduces to $(-1)^2$ since all these nonvanishing adjacency matrix elements equal 1. The matrix element a_{ij} can equivalently be thought of as the weight assigned to the directed edge $i \rightarrow j$.

Suppose the edge $i \rightarrow j$ is given weight $e^{i\alpha}$ and the edge $j \rightarrow i$ weight $e^{-i\alpha}$. Then the adjacency matrix will be Hermitian and all 2-membered cycles (corresponding to the single edges of the undirected graph) will have weight $(e^{i\alpha})\,(e^{-i\alpha}) = 1$ for all values of α. Consider a conjugated molecule consisting of a single n-membered ring ($n \geq 3$) plus any number of side chains. Methylene-cyclopropene, whose molecular (undirected) graph is shown in IV, is



IV

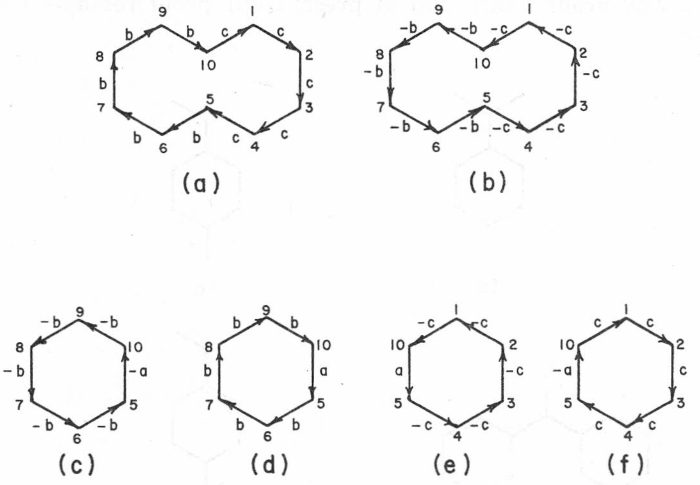
one such system. If $\alpha = \pi/2n$ for the clockwise edges of the n-membered ring in the corresponding directed graph, then the clockwise cycle will have weight $(e^{\frac{\pi i}{2\pi}})^n = i$ and the counterclockwise cycle will have weight $(e^{-\frac{\pi i}{2n}})^n = -i$. Hence all Sachs graphs containing these cycles will cancel in pairs and the characteristic polynomial of the adjacency matrix constructed with these weights will be just that of the reference polynomial. Edges involved only in two-membered cycles in the directed graph (i. e. side-chain edges of the original molecular graph) may be assigned weight $e^{\frac{\pi i}{4}}$ consistent with this recipe, but weight = 1 will serve as well since there are not pairs of two-membered rings to be cancelled. Thus the determinant

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & a & a^* \\ 0 & a^* & x & a \\ 0 & a & a^* & x \end{vmatrix} = x^4 - 4x^2 + 1 \qquad (27)$$

where $a = \exp(\pi i/6)$ gives the reference polynomial of IV.

This result generalizes at once to any conjugated hydrocarbon with any number of rings of any size plus any number of side chains, *as long as no rings share a common edge.* Thus the reference polynomial for all such systems is the characteristic polynomial of a Hermitian matrix, and hence all roots are real.

Unfortunately we do not see a way to include the important case of molecules with shared edges. Consider naphthalene whose directed graph II contains the cycles



(a) (b)

(c) (d) (e) (f)

V

It is required

$$e^{(5b + 5c)\, i\pi} = e^{i\pi(2n + 1)/2} \qquad (28)$$

which implies that

$$5b + 5c = (1/2)\ (2n + 1) \qquad (29)$$

leading to

$$10b + 10c = 2n + 1 \qquad (30)$$

where n is an integer.

Similarly,

$$e^{(a + 5b)\, i\pi} = e^{i\pi(2p + 1)/2} \qquad (31)$$

leading to

$$2a + 10b = 2p + 1 \tag{32}$$

where p is an integer also.

Finally,

$$e^{(a - 5c)\, i\, \pi} = e^{i\, \pi\, (2q + 1)/2} \tag{33}$$

leads to

$$2a - 10c = 2q + 1 \tag{34}$$

where q is an integer.

Eqs 30, 32 and 34 in which n, p, and q are arbitrary integers, require that

$$2p + 1 = 2\,(n + q + 1) \tag{35}$$

of which the left-hand-side is odd, and the right-hand-side even. Hence, here is the contradiction showing that it is not possible to construct a Hermitian matrix in this way to give the reference polynomial of naphthalene. We do not see a way around this, and at present our proof remains restricted as stated above.

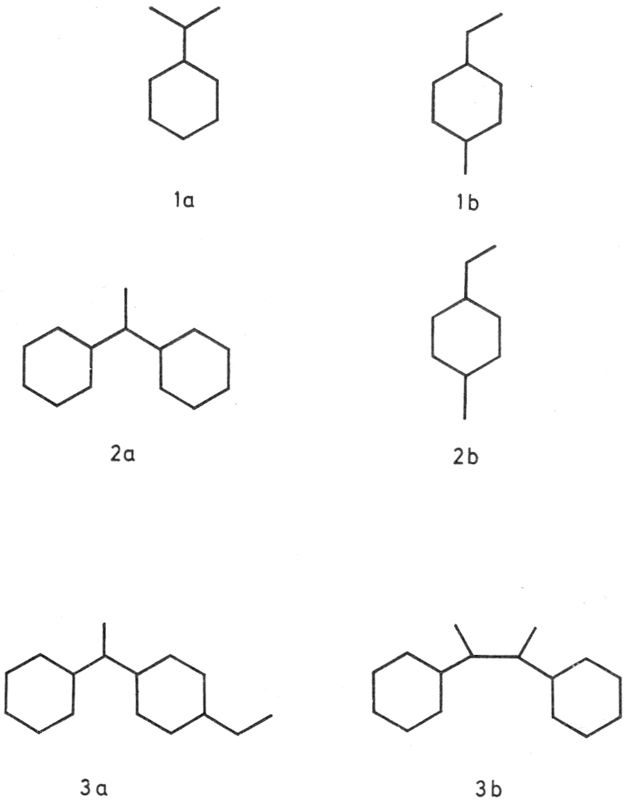
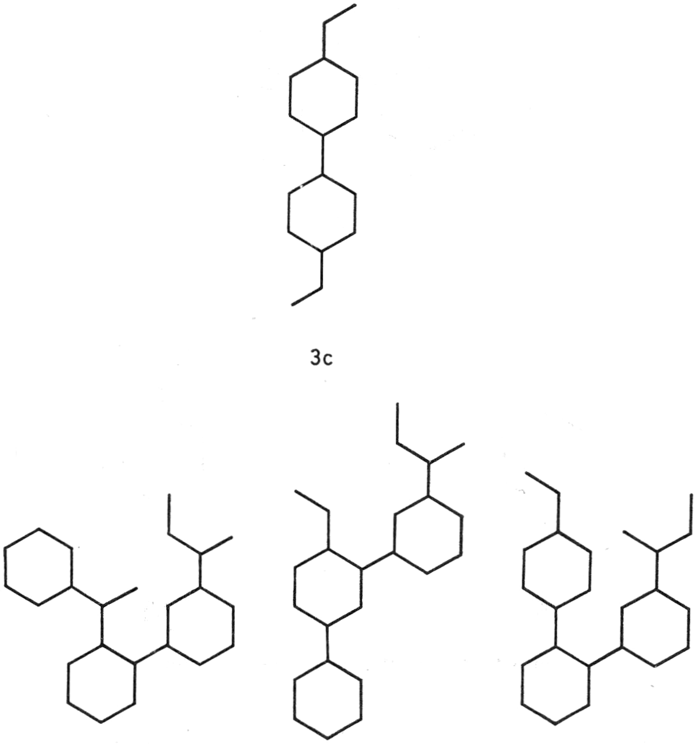


Figure 1. (1a — 3b) Some isospectral systems

II. REFERENCE POLYNOMIAL OF PLANAR ISOSPECTRAL MOLECULES

Planar isospectral molecules are conjugated hydrocarbons having identical Hückel orbital energies.[37–40] Molecules of that kind can be represented by isospectral (cospectral)[41] Hückel graphs[18] which are non-isomorphic planar graphs* whose nonidentical adjacency matrices give identical characteristic polynomials and consequently identical graph spectra. A classical example of such molecular systems is the 1,4-divinylbenzene(**6a**) and 2-(1′,3′-butadienyl)-benzene(**6b**) isospectral pair. Their common characteristic polynomial is $f(x) = x^{10} - 10x^8 + 33x^6 - 43x^4 + 23x^2 - 4$ with a spectrum: ± 2.21, ± 1.67, ± 1.00, ± 1.00, ± 0.54.

The discovery of isospectral structures has an inference that the graphic quantities based on the adjacency matrix cannot be used for the identification of individual molecules in the set of isospectral systems.[42–44] However, application of the topological resonance energy, TRE, approach to various iso-



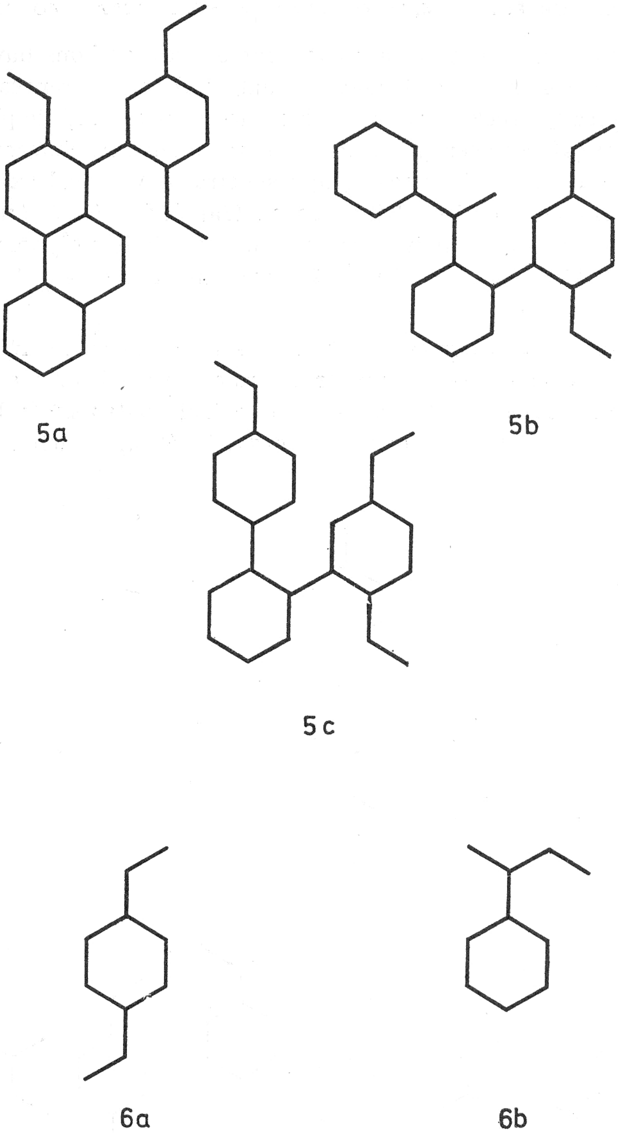
3c

4a 4b 4c

Figure 1. (3c—4c) Some isospectral systems

---

* A graph is planar if it can be drawn in the plane in such a way that no two edges intersect.[18,36]



5a 5b

5c

6a 6b

Figure 1. (5a—6b) Some isospectral systems.

spectral molecules leads to the result, contrary to expectations[39], that the TRE indices differentiate isospectral cyclic π-systems. This result is indicative of the possibility that the reference polynomial may be used to label uniquely each individual member of the isospectral set belonging to Hückel graphs.

In Figure 1 we show several isospectral Hückel systems whose corresponding reference polynomials are listed in Table.

TABLE

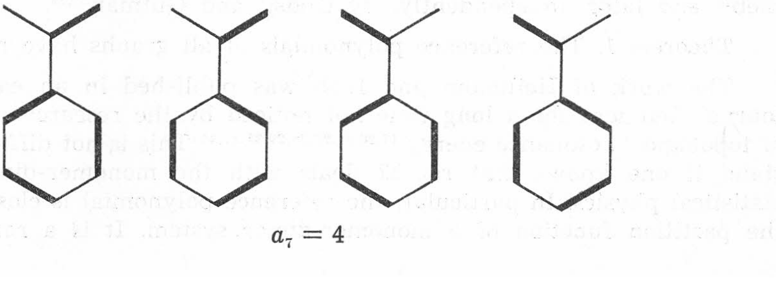
Reference Polynomials of Isospectral Molecules Given in Figure

Molecule	Reference polynomial
1a	$x^9 - 9x^7 + 25x^5 - 23x^3 + 4x$
1b	$x^9 - 9x^7 + 25x^5 - 23x^3 + 6x$
2a	$x^{14} - 15x^{12} + 86x^{10} - 238x^8 + 329x^6 - 211x^4 + 52x^2 - 4$
2b	$x^{14} - 15x^{12} + 86x^{10} - 238x^8 + 331x^6 - 219x^4 + 58x^2 - 4$
3a	$x^{16} - 17x^{14} + 114x^{12} - 386x^{10} + 703x^8 - 681x^6 + 326x^4 - 64x^2 + 4$
3b	$x^{16} - 17x^{14} + 114x^{12} - 386x^{10} + 701x^8 - 669x^6 + 308x^4 - 60x^2 + 4$
3c	$x^{16} - 17x^{14} + 114x^{12} - 386x^{10} + 705x^8 - 693x^6 + 344x^4 - 72x^2 + 4$
4a	$x^{24} - 26x^{22} + 290x^{20} - 1821x^{18} + 7103x^{16} - 17920x^{14} + 29540x^{12} - 31458x^{10} +$ $+ 20991x^8 - 8349x^6 + 1841x^4 - 200x^2 + 8$
4b	$x^{24} - 26x^{22} + 290x^{20} - 1821x^{18} + 7103x^{16} - 17948x^{14} + 29692x^{12} - 31866x^{10} +$ $+ 21561x^8 - 8749x^6 + 1965x^4 - 212x^2 + 8$
4c	$x^{24} - 26x^{22} + 290x^{20} - 1821x^{18} + 7105x^{16} - 17950x^{14} + 29714x^{12} - 31954x^{10} +$ $+ 21721x^8 - 8883x^6 + 2013x^4 - 218x^2 + 8$
5a	$x^{24} - 26x^{22} + 290x^{20} - 1822x^{18} + 7122x^{16} - 18068x^{14} + 30145x^{12} - 32839x^{10} +$ $+ 22730x^8 - 9475x^6 + 2162x^4 - 228x^2 + 8$
5b	$x^{24} - 26x^{22} + 290x^{20} - 1822x^{18} + 7122x^{16} - 18040x^{14} + 29993x^{12} - 32431x^{10} +$ $+ 22156x^8 - 9059x^6 + 2026x^4 - 216x^2 + 8$
5c	$x^{24} - 26x^{22} + 290x^{20} - 1822x^{18} + 7122x^{16} - 18070x^{14} + 30167x^{12} - 32929x^{10} +$ $+ 22900x^8 - 9625x^6 + 2220x^4 - 236x^2 + 8$
6a	$x^{10} - 10x^8 + 33x^6 - 42x^4 + 20x^2 - 2$
6b	$x^{10} - 10x^8 + 33x^6 - 42x^4 + 18x^2 - 2$

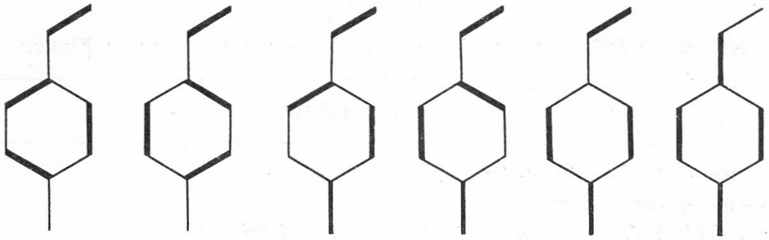
The results presented in Table are rather surprising at first sight, because the reference polynomial is a mathematical structure simpler than the characteristic polynomial. Since the reference polynomial is identical to the characteristic polynomial for acyclic system,[17] the isospectrality of cyclic conjugated molecules must be traced to combinatorial properties of the cyclic Sachs graphs.[10,40]

Let us consider the case of the isospectral pair **1a** and **1b**. The corresponding reference polynomials differ only in last (a_7) coefficients ($N = 7$). This is expected because only these coefficients have cyclic contributions in the related characteristic polynomials of **1a** and **1b**.

In the case of the reference polynomials of structures **1a** and **1b** a_7 coefficients are built from the following acyclic Sachs graphs:

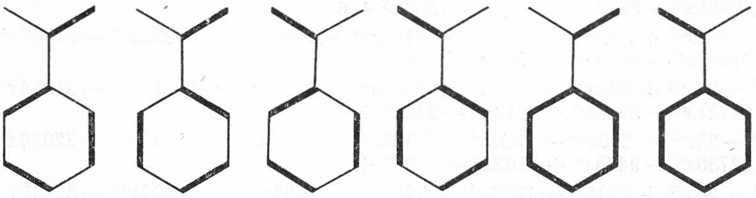


$a_7 = 4$

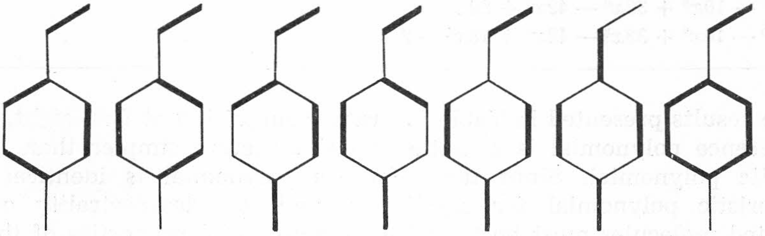


$a_7 = 6$

However, in the characteristic polynomial these coefficients are the resultant of combination of acyclic and cyclic Sachs graphs.



$a_7 = 4$ (acyclic part) + 4 (cyclic + acyclic parts) = 8



$a_7 = 6$ (acyclic part) + 2 (cyclic + acyclic parts) = 8

Appendix

by I. Gutman

There exists a complete solution of the problem considered in the present paper. Namely, the following result was proved in 1972 by Heilmann and Lieb[27] and later, independently, by Godsil and Gutman[28,29].

Theorem 1. The reference polynomials of all graphs have real zeros.

The work of Heilmann and Lieb was published in an easily available journal, but was for a long time not noticed by the researchers in the field of topological resonance energy.[17,20,21,26,28,29,31,32,45] This is not difficult to understand if one knows that ref 27 deals with the monomer-dimer theory in statistical physics. In particular, the reference polynomial is closely related to the partition function of a monomer-dimer system. It is a remarkable fact that the same mathematical object — the reference polynomial — plays an important role in such two diverse fields of science as statistical physics and theory of aromaticity.

In refs 27 and 28 are proved many other properties of the reference polynomial and its zeros. We present here three results which all are generalizations of Theorem 1.

Theorem 2.[27,28] The reference polynomial of a graph with arbitrarily weighted edges has real zeros.

Let $x_j(G)$ $(j = 1, 2, \ldots, n)$ be the zeros of the reference polynomial of the graph G, labeled in a non-increasing order. Let v be an arbitrary vertex of G.

Theorem 3.[27,28] The zeros $x_j(G—v)$ interlace the zeros $x_j(G)$:

$$x_j(G) \geqslant x_j(G-v) \geqslant x_{j+1}(G) \qquad (j = 1, 2, \ldots, n-1) \tag{1}$$

Theorem 4.[27] If the graph G possesses a Hamiltonian path which terminates at the vertex v, then the inequalities 1 are strict:

$$x_j(G) > x_j(G-v) > x_{j+1}(G) \qquad (j = 1, 2, \ldots, n-1)$$

Therefore, if G possesses a Hamiltonian path, then the zeros of its reference polynomial are all mutually distinct.

REFERENCES

1. M. J. S. Dewar and C. DeLlano, *J. Amer. Chem. Soc.* **91** (1969) 789.
2. B. A. Hess, Jr. and L. J. Schaad, *J. Amer. Chem. Soc.* **93** (1971) 305.
3. B. A. Hess, Jr. and L. J. Schaad, *J. Amer. Chem. Soc.* **93** (1971) 2413.
4. B. A. Hess, Jr. and L. J. Schaad, *J. Org. Chem.* **36** (1971) 3418.
5. L. J. Schaad and B. A. Hess, Jr., *J. Amer. Chem. Soc.* **94** (1972) 3068.
6. B. A. Hess, Jr. and L. J. Schaad, *J. Amer. Chem. Soc.* **95** (1973) 3907.
7. B. A. Hess, Jr. and L. J. Schaad, *J. Org. Chem.* **41** (1976) 3058.
8. B. A. Hess, Jr., L. J. Schaad, and M. Nakagawa, *J. Org. Chem.* **42** (1977) 1669.
9. B. A. Hess, Jr. and L. J. Schaad, *J. Chem. Soc. Chem. Commun.* (1977) 243.
10. A. Graovac, I. Gutman, N. Trinajstić, and T. Živković, *Theoret. Chim. Acta* **26** (1972) 67.
11. D. Cvetković, I. Gutman, and N. Trinajstić, *J. Chem. Phys.* **61** (1974) 2700.
12. A. Graovac and N. Trinajstić, *Croat. Chem. Acta* **47** (1975) 95.
13. I. Gutman, B. Ruščić, N. Trinajstić, and C. F. Wilcox, Jr., *J. Chem. Phys.* **62** (1975) 3399.
14. I. Gutman, N. Trinajstić, and C. F. Wilcox, Jr., *Tetrahedron* **31** (1975) 143.
15. I. Gutman, M. Milun, and N. Trinajstić, *MATCH* **1** (1975) 171.
16. I. Gutman and N. Trinajstić, *Croat. Chem. Acta* **47** (1975) 507.
17. I. Gutman, M. Milun, and N. Trinajstić, *J. Amer. Chem. Soc.* **99** (1977) 1692.
18. N. Trinajstić, *Hückel Theory and Topology,* in: *Modern Theoretical Chemistry,* Vol. 7 (G. A. Segal, Ed.) Plenum Press, New York (1977), Chapt. 1.
19. H. Sachs, *Publ. Math. (Debrecen)* **11** (1964) 119.
20. J. Aihara, *J. Amer. Chem. Soc.* **98** (1976) 2750, 6840.
21. J. Aihara, *J. Amer. Chem. Soc.* **99** (1977) 2048.
22. The Zagreb Group uses term »acyclic polynomial« for »reference polynomial«, a name originally proposed by Aihara. In mathematical literature this polynomial is discovered by Farrell[23] and is named »matching polynomial«.
23. E. J. Farrell, *J. Combinatorial Theory B,* in press.
24. B. A. Hess, Jr., L. J. Schaad, and I. Agranat, *J. Amer. Chem. Soc.* **100** (1978) 5268.

25. P. Ilić and N. Trinajstić, work in preparation.
26. M. Milun, Ph. D. Thesis, University of Zagreb, 1976.
27. O. J. Heilmann and E. H. Lieb, *Commun. Math. Phys.* **25** (1972) 190.
28. C. D. Godsil and I. Gutman, *Z. Naturforsch.* **34a** (1979) 776.
29. The results of ref 28 were communicated at the International Colloquium on Algebraic Methods in Graph Theory, Szeged (Hungary) in August 1978.
30. T. H. Goodwin and V. Vand, *J. Chem. Soc.* (1955) 1683.
31. I. Gutman, M. Milun, and N. Trinajstić, *Croat. Chem. Acta* **49** (1977) 441.
32. I. Gutman, *Publ. Inst. Math. (Belgrade)* **22** (1977) 63.
33. T. K. Rebane, in: *Methods of Quantum Chemistry,* M. G. Veselov, Ed., Academic Press, New York, 1965.
34. C. C. MacDuffee, *Theory of Equations,* John Wiley and Sons, New York, 1954, Chapt. 4.
35. W. S. Burnside and A. W. Panton, *The Theory of Equations,* Longmans, Green, and Co., London, 1886, Chapt. IX.
36. F. Harary, *Graph Theory,* Addison-Wesley, Reading, Mass., 1969, Chapt. 11.
37. I. Gutman and N. Trinajstić, *Topics Curr. Chem.* **42** (1973) 49.
38. T. Živković, N. Trinajstić, and M. Randić, *Mol. Phys.* **30** (1975) 517.
39. W. C. Herndon and M. C. Ellzey, Jr., *Tetrahedron* **31** (1975) 99.
40. G. G. Hall, *Mol. Phys.* **33** (1977) 551.
41. L. Collatz and U. Sinogowitz, *Abh. Math. Sem. Univ. Hamburg* — **21** (1963) 63.
42. A. T. Balaban and F. Harary, *J. Chem. Docum.* **11** (1971) 258.
43. W. C. Herndon, *J. Chem. Docum.* **14** (1974) 150.
44. D. M. Cvetković, M. Doob, and H. Sachs, *Spectra of Graphs. A Monograph,* Deutscher Verlag der Wissenschaften, Berlin 1979.
45. I. Gutman and H. Hosoya, *Theort. Chim. Acta* **48** (1978) 279.

SAŽETAK

O referentnoj strukturi rezonancijske energije aromatičkih ugljikovodika

L. J. Schaad, B. A. Hess, Jr., J. B. Nation, N. Trinajstić i I. Gutman (dodatak)

Da bi se rezonancijska energija, definirana na način predložen istovremeno od Zagrebačke grupe i Aihare, mogla upotrijebiti potrebno je da su korijeni referentnog polinoma realni. Djelomični dokaz toga dobijen je na nekoliko načina. Izravno rješenje za referentni polinom anulena pokazuje da su svi korijeni realni u tom slučaju. Graf-teorijski dokaz vrijedi za sve konjugirane ugljikovodike kod kojih nema niti jedne zajedničke veze između prstenova. U radu je također sugerirano da bi se referentni polinom mogao upotrijebiti za razlikovanje planarnih izospektralnih molekula.

ODJEL ZA KEMIJU I ODJEL ZA MATEMATIKU,
SVEUČILIŠTE VANDERBILT, NASHVILLE,
TENNEESSEE, INSTITUT »RUĐER BOŠKOVIĆ«,
41000 ZAGREB, HRVATSKA I ODJEL ZA KEMIJU,
SVEUČILIŠTE U KRAGUJEVCU,
34000 KRAGUJEVAC, SRBIJA

Prispjelo, 17. srpnja 1978.