SOME GRAPH-THEORETICAL RESULTS OF THE ZAGREB GROUP IN 1975

(received: January 1976)

We give here short summaries of the graph theo-
retical papers completed in 1975 in the Theoretical Chemis-
try Group of the Rugjer Bošković Institute, Zagreb, Croatia,
Yugoslavia.

The following notation is used throughout this
paper. G denotes the molecular graph which has N vertices
and ν edges. The characteristic polynomial of G is $P(G, x)$

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

1. On molecules with identical topological spectra

T. Živković, N.Trinajstić and M.Randić, Mol.Phys. 30 (1975)
517; M.Randić, N.Trinajstić and T.Živković, J.C.S.Faraday
11, in press; T.Živković, N.Trinajstić and M.Randić, in
preparation.

Properties of molecular graphs having identical
topological spectra (so called isospectral graphs or cospec-
tral graphs) are investigated in some detail. The theoreti-
cal foundation for the construction of isospectral graphs
rests on the factorization of the eigenvalue problem of
the adjacency matrix associated with molecular graphs. The
above procedure is analogous to a fragmentation of a secu-

lär determinant of a Hückel MO problem as outlined some time ago by Heilbronner (Helv.Chim.Acta 36 (1953) 170). Procedure for construction of larger isospectral systems is devised. Discussions of some interesting features of isospectral systems reflected in special properties of topological eigenfunctions is also included.

2. An algorithm for the enumeration of bonding and anti-bonding MO´s in conjugated hydrocarbons

I.Gutman, Chem.Phys.Letters 26 (1974) 85; ibid., in press.

Let N_+, N_O and N_- $(N_+ + N_O + N_- = N)$ denote the number of bonding, non-bonding and antibonding MO´s and Ch be the number of changes of the sign in a sequence of numbers.

It has been proved that, assuming the conditions

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

are fulfilled, the following relations hold

$$N_- = Ch(D_O, D_1, \ldots, D_{N-1}, D_N) \tag{2}$$

$$N_+ = Ch(D_O, -D_1, \ldots, (-1)^{N-1}D_{N-1}, (-1)^N D_N) \tag{3}$$

By definition $D_O=1$ and D_j is the determinant of the adjacency matrix of the graph Gj. The graph Gj is obtained by the deletion of a vertex from the graph G_{j+1} (j=N-1,...,1,0) and $G_N=G$ is the molecular graph. Hence for the calculation of N_- and N_+ it is necessary to find a sequence of graphs $G_N, G_{N-1}, \ldots, G_1, G_O$ for which the conditions (1) are valid

and to calculate D_j. This latter presents no difficulty because of a number of known graph-theoretical techniques for the evaluation of the determinant of a graph.

The following algorithm provides a sequence of graphs with required properties.

Start with j=N.

Step 1. Calculate D_j. If $D_j=0$, go to step 2. If $D_j \neq 0$ go to step 3.

Step 2. Construct the non-bonding MO of the graph G_j. Then G_{j-1} can be obtained by deleting from G_j any of the vertices with non-zero NBMO coefficients. Go to step 1.
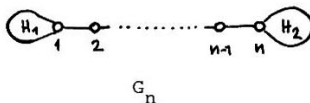
Step 3. G_{j-1} can be obtained by deleting of an arbitrary vertex from G_j. Go to step 1.

Finish with j=0.

3. Theoretical studies on conjugated systems containing a linear polyene fragment

I.Gutman, Croat.Chem.Acta, submitted for publication

Conjugated molecules of the general form G_n are studied.

G_n

The index n denotes the length of the linear polyene fragment (L_n) contained in G_n. All graphs G_n form the class $\mathscr{L}_n$. There exist several relations for the characteristic polynomials of graphs from $\mathscr{L}_n$.

$$P(G_n, x) = x \, P(G_{n-1}, x) - P(G_{n-2}, x)$$

$$P(G_n, x) = P(G_1, x) \frac{\sin nt}{\sin t} - P(G_0, x) \frac{\sin(n-1)t}{\sin t}$$

$$P(G_n, x) = P(G_1\ x)\ P(L_{n-1}, x) - P(G_0, x)\ P(L_{n-2}, x)$$

where $2 \cos t = x$.

Analytical formulae for the spectra of 10 graphs for $\mathcal{L}_n$ have been deduced as well as analytical expressions for the total Pi-electron energy and HOMO-LUMO separation.

4. Coulson integral formulae for total Pi-electron energy

A.Graovac, I.Gutman, N.Trinajstić, Chem.Phys.Letters 35 (1975) 555; ibid.,in press; I.Gutman and N.Trinajstić, J.Chem.Phys, in press.

Let us use the abbreviate notation

$$\left\langle F(x) \right\rangle \equiv \frac{1}{\pi} \int_{-\infty}^{+\infty} F(x)\ dx$$

Then the well known Coulson integral formula (Proc.Cambridge Phil.Soc.36 (1940) 201) for total Pi-electron energy E reads

$$E_{\pi} = \left\langle N - ix\ P'(G, ix)/P(G, ix) \right\rangle \tag{1}$$

An elementary derivation of eq. (1) is proposed, which is not based on contour integration as that of Coulson.

If we write $P(G, x) = x^{N_0}\ \tilde{P}(G, x)$, with N_0 being the number of zero roots of $P(G, x)$, the following more

or less straightforward consequences of eq. (1) are valid

$$E_\pi = \left\langle \tilde{N} - ix\, \tilde{P}'(G,\, ix)/\tilde{P}(G,\, ix) \right\rangle$$

$$E_\pi = \left\langle \tilde{N} - x\, \frac{d}{dx}\, \ln \left| \tilde{P}(G,\, ix) \right| \right\rangle$$

$$E_\pi = \left\langle W(x) \right\rangle \qquad \text{for } W(x) = x^{-2}\, \ln\, x^{\tilde{N}}\, \left| \tilde{P}(G,\, -i/x) \right|$$

where $\tilde{N} = N - N_0$. Further, for $\tilde{N}_1 = \tilde{N}_2$,

$$E_\pi(G_1) - E_\pi(G_2) = \left\langle \ln \left| \tilde{P}(G_1,\, ix)/\tilde{P}(G_2,\, ix) \right| \right\rangle$$

and as two special cases,

$$E_\pi = \tilde{N} + \left\langle \ln \left\{ \left| \tilde{P}(G_1,\, ix) \right|\ (x^2 + 1)^{-\tilde{N}/2} \right\} \right\rangle$$

$$E_\pi = \sqrt{2\, \tilde{N} \nu} + \left\langle \ln \left\{ \left| \tilde{P}(G_1,\, ix) \right| (x^2 + 2\nu/\tilde{N})^{-\tilde{N}/2} \right\} \right\rangle$$

For alternant hydrocarbons,

$$W(x) = x^{-2}\, \ln \sum_{j=0}^{\tilde{N}/2} \left| a_{2j} \right| x^{2j}$$

and

$$E_\pi = \sum_{j=1}^{\tilde{N}/2} 2j\, \left| a_{2j} \right| \left\langle \partial W(x)/\, \partial \left| a_{2j} \right| \right\rangle$$

Since the integrals $\left\langle \partial W(x)/\partial \left| a_{2j} \right| \right\rangle$ are not very sensitive to small changes in $\left| a_{2j} \right|$'s, one can use an approximation

$$\left\langle \partial W(x)/\partial \left| a_{2j} \right| \right\rangle = x^{2j-2}\ (1 + \theta^2 x^2)^{-\tilde{N}/2}$$

with Θ being a suitably chosen parameter. This approxima-
tion results in a linear relationship

$$E_\pi \doteq \sum_{j=1}^{N/2} B_j \, |a_{2j}|$$

with $B_j = 2j \; \Theta^{1-2j} \left\langle x^{2j-2}(1 + x^2)^{-\widetilde{N}/2} \right\rangle$. The optimal
value for the parameter Θ has been determined and the
numbers B_j are tabulated for a chemically relevant range
of $\widetilde{N}$.

5. The proof of the Hückel rule for an arbitrary conjugated molecule and its extension to non-alternant hydrocarbons

I.Gutman and N.Trinajstić, J.Chem.Phys., in press;I.
Gutman and N.Trinajstić, in preparation.

The reason for the analysis of the Coulson-type
integral formulae for E_π lies in a possibility to get
insight into the structural factors which determine E_π.
The present topological analysis goes via the knowledge
of the dependence of the coefficients a_j on the molecular
structure. This latter dependence is nowadays completely
elucidated (Hosoya, Theoret.Chim.Acta 25 (1972) 215; Graovac
et al, ibid., 26 (1972) 67).

Now, for alternant hydrocarbons

$$E_\pi = \left\langle x^{-2} \ln \sum_{j=0}^{\widetilde{N}/2} |a_{2j}| \; x^{2j} \right\rangle$$

and one can see that E_π is a monotonously increasing func-

tion of every $|a_{2j}|$. It is proved that

$$|a_{2j}| = \sum_{s \in S_{2j}} (-1)^{n_0(s)} \tag{1}$$

where $n_0(s)$ is the total number of $(4m)$-membered cycles
in the graph s. The summation in eq. (1) goes over the
set S_{2j} of all directed Sachs graphs (of the molecular
graph) with 2j vertices. Eq. (1) is, in fact, an algebraic
expression of the Hückel 4m+2 rule, namely that every $(4m)$-
-cycle gives a negative and every $(4m+2)$-cycle a positive
contribution to E_π . Therefore a general proof of the
Hückel rule is now completed.

The extension of the Hückel rule to non-alternants
is straightforward. However, also odd-membered cycles give
non-negligible contributions to E_π . It is proved that

$$E_\pi = \frac{1}{2} \langle x^{-2} \ln \left\{ \left[\sum_{S_{2j}} (-1)^{n_0 + (n_3 - n_1)/2} \right]^2 + \left[\sum_{S_{2j+1}} (-1)^{n_0 + (n_3 - n_1 + 1)/2} \right]^2 \right\} \tag{2}$$

where $n_3(s)$ and $n_1(s)$ are the total number of $(4m+3)$- and
$(4m+1)$-membered cycles in the graph s. The following rules
have been deduced from eq. (2).

Rule 1. If there is only one odd-cycle in the molecule,
there will be a small stabilization effect arising from its
presence.

Rule 2. Similarly, in the polycyclic case there exist
also positive contributions to E_π arising from all cycles
being of the same modulo 4 type as the smallest odd-cycle
of the molecule.

Rule 3. A pair of odd-cycles causes stabilization if the cycles are of the opposite modulo 4 type and destabilization if they are of the same modulo 4 type.

Rule 4. A non-alternant system is relatively stable (aromatic) only if the number of (4m+1)-cycles is equal to the number of (4m+3)-cycles.

6. A class of approximate topological formulae for total Pi-electron energy

I.Gutman, in preparation

The following method is proposed for generating a class of approximate formulae for E_π starting from Coulson-type integral expressions. Let $E_\pi = \langle f(x) \rangle$. One can conclude relatively easily about the behaviour of $f(x)$ near x=0 and $x \to \infty$. Now, let us construct a function $\bar{f}(x)$ which is as simple as possible and has equal behaviour as $f(x)$ near x=0 and $x \to \infty$. Then $\langle \bar{f}(x) \rangle$ results in an approximate formula for E_π . From different variants of the Coulson formula, the following approximations have been obtained.

$$E_\pi \doteq \sqrt{2\, \tilde{N}\, \nu} \tag{1}$$

$$E_\pi \doteq T\nu + \tilde{N}\, \frac{\ln(1 + T)}{T} \tag{2}$$

$$E_\pi \doteq N + \sqrt{2(\nu - N/2)\, \ln(ASC)} \tag{3}$$

$$E_\pi \doteq \sqrt{2\, N\nu} - (1/2) \sqrt[4]{A\, B^3} \tag{4}$$

with

$$A = (N/2) \ln(2 \, \nu /N) - 2 \ln(ASC)$$

$$B = (1/2) \sum_{p=1}^{N} (d_p)^2 + 2n_4 - \nu^2/N - \nu/2$$

where ASC is the algebraic structure count, n_4 is the number of 4-membered cycles and d_p is the degree of the vertes p. In eq. (2) T is a positive parameter which can arbitrarily depend on the topology of the molecule. The choice

$$T = \sqrt{\frac{2 \, \nu - \widetilde{N} \ln 2}{2 \, \nu - 2 \ln z}} \quad , \quad z = \sum_{j=0}^{\widetilde{N}/2} |a_{2j}|$$

is especially convenient.

The obtained formulae contribute towards the understanding of the main structural factors which determine E_π . In particular, it has been shown that N and determine the gross part of E_π ; the presence of NBMO´s decrease E_π because then $\widetilde{N}$ ($\widetilde{N} < N$) is to be taken into account instead of N. The influence of the ring sizes can be seen explicitly from the Z-dependence of eq. (2) or implicitly from the ASC-dependence of eqs. (3) and (4). E_π is a monotonously increasing function of $\ln(ASC)$. Eq.(4) reproduces also the fact that branching is a destabilizing factor in conjugated molecules.

A peculiarity of the present class of approximate expressions is that they contain no fitting parameters.

7. Analysis of the Coulson integral formula for Pi-electron charge distribution

I.Gutman and N.Trinajstić, <u>Croat</u>.<u>Chem</u>.<u>Acta</u>, in press.

Let G-r be the graph obtained by deletion of the vertex r from the graph G.

Then the Pi-electron charge density Q_r on the atom r is

$$Q_r = 1 + \left\langle \frac{UV_r - VU_r}{x \ (U^2+V^2)} \right\rangle \qquad \qquad (1)$$

where

$$U = U(x) = \sum_j (-1)^j \ a_{2j} \ x^{2j}$$

$$V = V(x) = \sum_j (-1)^j \ a_{2j+1} \ x^{2j+1}$$

and U_r and V_r are defined analogously by means of the coefficients of P(G-r, x).

The main topological properties of eq. (1) are discussed. Alternant systems have always $a_{2j+1}=0$, and therefore $V=V_r=0$. This simply gives $Q_r=1$. The following rule is proved. In a conjugated hydrocarbon containing only one odd-cycle, all atoms belonging to this cycle are negatively charged ($Q_r > 1$) if the size of this cycle is 4m+1 and positively charged ($Q_r < 1$) if the size of this cycle is 4m+3. The result is independent of any other detail in the molecular structure.

8. An approximate expression for the self-polarizability

I.Gutman and N.Trinajstić, J.Chem.Phys., in press.

Let K and K_{pq} denote the number of Kekulé structures of the molecular graph G and of G-pq. The graph G-pq is obtained by deleting the vertices p and q from G. Let the super-scripts + and - denote even and odd Kekulé structures, respectively (as defined by Dewar and Longuet-Higgins, Proc.Roy.Soc.A 214 (1952) 482).

In resonance theory it is usual to correlate the reactivity of a site p with the index $\varrho_p = \sum_q K_{pq}$. Starting from the integral formula for self-polarizability π_{pp} of an atom p,

$$\pi_{pp} = \left\langle \left[\frac{P(G-r,\ ix)}{P(G,\ ix)} \right]^2 \right\rangle$$

one have derived an approximate expression

$$\pi_{pp} \doteq \frac{1}{2(K^+ - K^-)} \sqrt{\sum_q (K_{pq}^+ - K_{pq}^-)^2} \tag{1}$$

In cata-fused benzenoid hydrocarbons eq. (1) becomes

$$\pi_{pp} \doteq (1/2K) \sqrt{\sum_q K_{pq}^2} \tag{2}$$

Relation (2) is in fact valid for all benzenoid molecules, and only for them. Hence,

$$\pi_{pp} / \pi_{rr} \doteq \rho_p / \rho_r \qquad (3)$$

indicating that the concepts of resonance theory are applicable only for benzenoids. Besides, instead of the index ρ , a slightly different index $\bar{\rho}$ should be used.

$$\bar{\rho} = \sum_q K_{pq}^2$$

Eq. (3) presents a novel case of congruity between Hückel MO theory and resonance theory.

9. Möbius structures and graphs

A.Graovac and N.Trinajstić, Croat.Chem.Acta 47 (1975) 95; J.Mol.Struct., in press.

Möbius structures are characterized by the appearance of one sign inversion resulting from the negative overlaps between the adjacent orbitals of different sign. These systems appear as transition states, for example in the conrotatory closure of butadiene and disrotatory closure of hexatriene. Graphs associated with Möbius structures are named Möbius graphs and the weight of an edge associated with the sign inversion is -1. The structure of a Möbius graph may be related to the coefficients of P(G, x) through the extended Sachs formula:

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

where the symbols have the following meaning: s denotes
a Sachs graph, S_n is the set of all Sachs graphs with n
vertices, $c(s)$ is the total number of components of
s, $r(s)$ is the number of rings of s and $p(s)$ is the number
of -1 edges in the ring components of s. The summation is
over all elements of the set S_n. The properties of various
Möbius structures and corresponding graphs are discussed
including the generalized Hückel rule to cover Hückel and
Möbius annulenes.