Topology and stability of conjugated hidrocarbons. The dependence of total π-electron energy on molecular topology

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Abstract: In spite of the fact that research on the mathematical properties of the total π-electron energy E (as computed by means of the Hückel molecular orbital approximation) started already in the 1940s, many results in this area have been obtained also in the newest times. In 1978 this author published in this journal a review on E. The present article is another review on E, summarizing the progress in the theory of E, achieved since then.

Keywords: total π-electron energy, chemical graph theory, Hückel molecular orbital theory, HMO theory.

CONTENTS

1. INTRODUCTION

The total π-electron energy is one of the most useful quantum-chemical characteristics of a conjugated molecule that can be obtained by means of the Hückel molecular-orbital (HMO) theory. It is computed as[1−3]

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$$E_\pi = \alpha\, n_e + \beta \sum_{i=1}^{n} g_i \lambda_i = \alpha n_e + \beta E$$

where α and β are the standard HMO parameters, n_e is the number of π-electrons, g_i is the occupation number of the i-th molecular orbital, whereas λ_i, $i = 1,2,...,n$, are the eigenvalues of the respective molecular graph.[1,4,5] The non-trivial part of the above expression is E. For non-charged conjugated systems in their ground electronic state E assumes the form

$$E = \begin{cases} 2\sum_{i=1}^{n/2} \lambda_i & \text{if } n \text{ is even} \\ 2\sum_{i=1}^{(n-1)/2} \lambda_i + \lambda_{(n+1)/2} & \text{if } n \text{ is odd} \end{cases} \tag{1}$$

with the graph eigenvalues being labeled in a non-decreasing manner. For the vast majority of conjugated molecules Eq. (1) can be transformed into

$$E = \sum_{i=1}^{n} |\lambda_i| \tag{2}$$

In the absence of large steric strain in the carbon-atom skeleton, by means of E_π one can calculate remarkably accurate values for the thermodynamic functions of conjugated hydrocarbons such as enthalpy of formation, enthalpy of combustion and similar. This success of E_π is based on the fact, first demonstrted by Schaad and Hess,[6] that not only the π-, but also the σ-electron energy is proportional to E. For more details see pp. 151 − 154 in the book,[4] where also other chemical and physico-chemical applications of E are outlined.

Research on mathematical properties of E started already in the 1940s. In 1940 Coulson published his seminal paper,[7] in which he established the connection between E and the characteristic polynomial of the molecular graph. The present author started his studies of E in the early 1970s.[8–13] In 1978 he was invited to write a review article on E for this journal[14] (which then was called *Bulletin de la Societe Chemique Beograd* and *Glasnik Hemijskog društva Beograd*). Since then the progress in the theory of total π-electron energy was so great that nowadays the review[14] could have only some historic value. Now, a quarter of century later, is became possible to produce another survey on E. Its title is deliberately chosen to be identical with that of the previous review.[14] In it we briefly outline the main directions of research on E done in the last 10−15 years, and mention the main results achieved.

Some standard and much studied themes, that are closely related to the theory of HMO total π-electron energy, but are not parts of this theory, are not discussed in the present article. These are the works concerned with various types of resonance

energies,[15,16] with energy-effects of cycles in polycyclic conjugated hydrocarbons,[17−19] with the energy-aspects of the Hückel $(4n + 2)$-rule,[19−23] with the usage of E for the calculation of thermochemical data,[4,6,15,24] and in QSPR studies,[25] and similar. Parts of the theory of HMO total π-electron energy, in which there was no significant progress in the previous years, are also left out, in particular works concerned with Coulson-type integral formulas for E and their applications[4,5,20,26,27] and with application of Sachs theorem for the elucidation of the dependence of E on molecular structure,[14,20,21] Results that do not belong to the main directions of current research on E are mentioned without going into details. As explained below, among mathematicians there is a rapidly growing interest towards E. This resulted in a number of recently published results on E that are of solely mathematical interest. We quote these papers without outlining their contents.

2. BOUNDS FOR TOTAL π-ELECTRON ENERGY

An important step forward in the understanding of the structure-dependency of E on molecular structure was done in 1971 when McClelland obtained the first upper and lower bounds for E in terms of simple graph invariants.[28] These are:

$$\sqrt{2m + n(n-1)|\det \mathbf{A}|^{2/n}} \leq E \leq \sqrt{2mn} \tag{3}$$

where n and m denote the number of vertices and edges of the molecular graph,[1,4,5] and $\mathbf{A}$ is its adjacency matrix. (Recall that in the case of molecular graphs representing conjugated hydrocarbons, n is equal to the number of carbon atoms and m to the number of carbon−carbon bonds. In many, but not all, chemically relevant cases $|\det \mathbf{A}|$ is equal to the square of the number of Kekulé structures. On the other hand, the validity of the inequalities (3), as well as of the majority of below stated results for E, is not restricted to molecular graphs). The expression $E_{\mathrm{MC}} = \sqrt{2m\,n}$, usually referred to as the McClelland upper bound, played eventually a significant role in the theory of total π-electron energy.

In the meantime numerous other bounds for E were deduced. We first mention the simple lower and upper bounds for E, depending only on the number of edges of the molecular graph:[29]

$$2\sqrt{m} \leq E \leq 2m \tag{4}$$

and a lower bound, depending only on the number of vertices:[29]

$$E \geq 2\sqrt{n-1} \tag{5}$$

The bound (5) applies to graphs without isolated vertices.

The bounds (4) and (5) are the best possible of their kind, which means that there exist graphs with m edges whose E-values are equal to $2\sqrt{m}$ or $2m$, and n-vertex graphs, possessing no isolated vertices, whose E-values are equal to $2\sqrt{n-1}$. As explained later, the best possible upper bound for E in terms of n is not yet known.

The McClelland upper bound attracted much attention, because it was shown[28] that the total π-electron energy of conjugated hydrocarbons can be reasonably well approximated by means of the simple formula

$$E \approx a\sqrt{2\,m\,n} \qquad (6)$$

with $a \approx 0.9$

It was long time not understood why an upper bound for E should be correlated at all with E. The solution of the problem was found only in 1990, when it was shown[30] that there is a lower bound for E of the form

$$g\sqrt{2\,m\,n}$$

with g being some constant. Initially,[30] it was found that $g = \sqrt{16/27} \approx 0.77$ holds for benzenoid hydrocarbons. This result was later improved. First, Türker[31] proposed $g = 1/2$, but his calculations were shown to be erroneous.[32] Soon bounds better than Türker's were found.[33] $g = \sqrt{4/15} \approx 0.52$ if $n \geq 2$, $g = \sqrt{3/10} \approx 0.55$ if $n \geq 3$, $g = \sqrt{8/25} \approx 0.57$ if $n \geq 4$, and $g = \sqrt{1/3} \approx 0.58$ if $n \geq 5$. These g-values hold provided the number of triangles plus twice the number of quadrangles is less than the number of vertices, a condition satisfied by all molecular graphs. Further improvements are: $g = \sqrt{32/81} \approx 0.63$, valid for all conjugated molecules[34] and $g = \sqrt{32/49} \approx 0.70$, valid for quadrangle-free graphs without isolted vertices, with maximal vertex degree equal to 3 (conditions satisfied by almost all molecular graphs).[35]

In 1984 Türker[36] improved the McClelland upper bound in another way, by showing that E_T,

$$E_T = 2\left[m + \sqrt{n(n-2)a_4/2}\right]^{1/2}$$

is also an upper bound for E, where a_4 is the fourth coefficient of the characteristic polynomial. Türker's upper bound applies to bipartite graphs. It is worth noting that for benzenoid systems, $a_4 = (m^2 - 9m + 6n)/2$, in which case E_T depends only on the parameters n and m. The work[36] triggered the discovery of a series of other upper bounds for E. Some of these are:

$$E_{GTD} = 2\left[3mE_T/2 + \sqrt{3n(n-2)(n-4)a_6/4} - \sqrt{8m^3/n}\right]^{1/3}$$

where a_6 is the sixth coefficient of the characteristic polynomial (taken with positive sign),[37]

$$E_C(1) = 2\left[2m/n + R\sqrt{n/2-1}\right]^{1/2} + (n-2)\left[2m/n - R\sqrt{n/2-1}\right]^{1/2}$$

where $R = (1/n)\sqrt{18m\,n - 12n^2 - 4m^2}$, which holds for benzenoid hydrocarbons,[38] and[39]

$$E_C(2) = 4\left[2m/n + R\sqrt{n/4-1}\right]^{1/2} + (n-4)\left[2m/n - R\sqrt{n/4-1}\right]^{1/2}.$$

It was shown[39] that fot benzenoid hydrocarbons with 3 or more hexagons,

$$E < E_C(2) < E_C(1) < E_{GTD} < E_T < E_{MC}.$$

A few more bounds of the same kind were communicated.[40–43]

A new breakthrough in this direction happened in 2001 when Koolen and Moulton (both mathematicians) discovered the first generally valid (n, m)-type upper bound for E, better than McClelland's.[44–46] Their result reads:

$$E \leq 2m/n + \sqrt{(n-1)(2m - 4m^2 / n^2)} \tag{7}$$

valid for any (n, m)-graph,[44] and

$$E \leq 4m/n + \sqrt{(n-2)(2m - 8m^2 / n^2)} \tag{8}$$

valid for any bipartite (n, m)-graph.[45] From (7) follows

$$E \leq \frac{n}{2}(\sqrt{n} + 1). \tag{9}$$

Formula (9) is nowadays the best known upper bound for E in terms of the number of vertices. However, as explained in a subsequent section, in contrast with the lower bound (5), except for $n = 64, 256, 1024, 4096, \ldots$ it is not the best possible.

Many other bounds for E were communicated, both of (n, m)-type[47–50] and depending on some other graph invariants.[51–56] Bounds whose applicability is limited to polymers[57] acyclic polyenes,[58] and phenylenes[59,60] where also established.

3. (n, m)-TYPE APPROXIMATIONS FOR TOTAL π-ELECTRON ENERGY

Under (n, m)-type approximate formulas for E we understand expressions in which the only variables are the number of vertices (n) and the number of edgs (m) of the underlying moleculr graph.[4,5] The conjugated hydrocarbon corresponding to such a graph has the formula C_nH_{3n-2m}. Therefore (n, m)-type approximations predict equal values for E for all isomers. In view of this, one sometimes speaks of isomer-undistinguishing approximate formulas for E.

The first (n, m)-type expression for E was McClelland's formula[28] (6). As already explained, the reason for the success of this formula is that there are both (reasonably narrow) lower and upper bounds for E, proportional to $E_{MC} = \sqrt{2mn}$.

From McClelland's original considerations[28] it is evident that the equality $E = E_{MC}$ would hold only if all bonding π-electron energy levels would be mutually equal, which, of course, if physically impossible. As a kind of surprise, it was shown[61] that by assuming a uniform (that is, equidistant) distribution of the energy levels, one obtains

$$E \approx F(n)\, E_{MC}$$

where

$$F(n) = \frac{n}{2}\sqrt{3 / (n^2 - 1)}$$

is a function which for chemically relevant values of n assumes values close to its limit $\sqrt{3/4} = 0.87$. This is remarkably close to the empirically determined value for the multipler a in Eq. (6), revealing that the McClelland approximation (6) is based on that tacit assumption of the uniformity of the energy level distribution. This conclusion was eventually corroborated by applying probability theory and considering more general types of energy level distributions.[62,63]

In spite of its isomer-undistinguishing nature, the McClelland formula (6) is capable of reproducing the E-values of conjugated hydrocarbons with an error less than 1 %. The existence of a simple proportionality between a bound for E and E itself naturally raised the question if other, perhaps more accurate, relations of this kind could be found. As outlined in the preceding section, a large number of lower and upper bounds for E of (n, m)-type are known. Each of them could, potentially, provide an approximate expression for E. In addition to these, many other (n, m)-type approximations for E were put forward.[64–78] Of them we mention only Türker's remarkably accurate expression.[42]

$$E \approx 2\, m\, n/(m + n)/2)$$

in which there is no fitting parameter.

Systematic comparative studies of all the known (n, m)-type approximate formulas for E were undertaken on several occasions.[24,79,80] A standard basis, consisting of 106 benzenoid hydrocarbons was used for this purpose. Whereas in the first such study[79] (in 1983) less than five (n, m)-type formulas had to be examined, in the second[24] (1992) their number was 24, and in the last study[80] (2001) already 44. After the work[80] was published, hundreds of novel (n, m)-type formulas were designed,[77,78] making further comparative analysis unfeasible. The conclusion of the studies[24,79,80] was always the same: of the numerous (n, m)-type approximate formulas for E, some of which have rather complicated algebraic form, the simple McClelland relation (6) is the best. More precisely, a few formulas having same accuracy as (6) were found,[80] but because of its simplicity, preference should be given to (6).

Türker proposed[70] to approximate E by means of a linear combination of a lower and an upper bound for E. This approach gave very good results,[40,70] but was nevertheless not further pursued.

Some other approaches to approximate the total π-electron energy of polymers,[57,81] linear polyacenes,[58] benzenoid hydrocarbons,[82–84] and phenylenes[60,85,86] deserve to be mentioned.

4. THE GRAPH ENERGY CONCEPT

The form of Eq. (1) is so awkward that it hardly would capture the attention of a single mathematician. Fortunately, the right-hand side of (1) can often be simplified. Namely, in majority of cases of interest in chemistry, all bonding π-electron

energy levels are occupied and all antibonding levels are empty. This, for instance, happens in the case of all alternant hydrocarbons (including benzenoids and phenylenes), but also for the vast majority of non-alternant hydrocarbons. If so, then the righ-hand side of (1) becomes equal to twice the sum of the positive-valued eigenvalues of the molecular graph. Because the sum of all graph eigenvalues is equal to zero, we arrive at (2).

Expression (2) was known[87] to Hall in 1955, and was explicitly stated[88] by Ruedenberg in 1961. It could well be that Coulson knew it[7] already in 1940.

Until the end of the 1970s, numerous mathematical results were obtained in the theory of HMO total π-electron energy. Without a single exception, in all these results it was assumed (either explicitly or tacitly) that Eq. (2) is applicable. Bearing this in mind, and realizing that (2) would be much more attractive to mathematically thinking people than (1), this author launched the concept of *graph energy*:[89]

Definition 1. Let G be a graph on n vertices, and let $\lambda_1, \lambda_2, ... \lambda_n$ be its eigenvalues. The *energy* of the graph G, denoted by $E(G)$, is the sum of the absolute vlaues of the eigenvalues of G, *i.e.,*

$$E(G) = \sum_{i=1}^{n} |\lambda_j|. \tag{10}$$

At the first glance there is no difference between (2) and (10). However, whereas the right-hand side of (2) was viewed as chemically meaningful only if the underlying graph belongs to the restricted class of "Hückel molecular graphs",[1,4,5] the right-hand side of (10) is (by definition) applicable to all graphs. Without the restriction to molecular graphs it is often much easier to envisage certain general regularities, and to verify them. Therefore, the introduction of the graph energy concept resulted in the discovery of numerous novel results, some of which of undeniable chemical relevance. Definition 1 was aimed to make E interesting to mathematicaians. This indeed happened, but with a significant delay.

Paper,[89] in which Definition 1 was proposed for the first time, is hard to find in science libraries. However, the concept of graph energy was elaborated in due detail also in the book[4] and elsewhere.[58,90]

In the twenty-years period 1978–1997 there was practically no mathematical research on graph energy. In 1983 the Chinese mathematician Zhang published two papers[91,92] concerned with $E(G)$. In the 1980s Fajtlowicz, by means of his computer-aided conjecture-generator *Grafitti* arrived at a few conjectures involving the sum of the positive eigenvalues of graphs,[93,94] of which some were eventually verified by a group of French mathematicians.[95]

Near the end of the 20th century a dramatic change occurred. In addition to mathematical works coauthored by the present author,[29,96–98] a number of other mathematicians entered the field;[44,45,99–108] the list of references quoted here is far from being complete.

It is not our aim to review the current mathematical research on graph energy. In brief: lower and upper bounds for $E(G)$ are established; for a variety of classes of graphs, the species having external (minimal and maximal) energy are characterized; the existence, structure, and construction of hyperenergetic graphs are examined; pairs and families of equienergetic graphs are discovered.

5. HYPERENERGETIC GRAPHS

According to the McClelland formula (6), as well as the numerous other (n,m)-type approximate formulas for total π-electron energy, E is a monotonically increasing function of both parameters n and m. If this regularity would hold for all graphs, then the n-vertex graph with maximal energy would be the complete graph K_n, for which $m = n(n-1)/2$. It is easy to show that $E(K_n) = 2(n-1)$. In view of this, in 1978 the present author conjectured[89] that $E \leq 2(n-1)$ holds for all n-vertex graphs.

This conjecture is false.

The first counterexample was found[109] in 1986 by using Cvetković's computer system *Graph*. In 1998, by means of a Monte Carlo construction of graphs with n vertices and $1,2,...,n(n-1)/2$ edges,[110–112] it became clear that among graphs with large number of edges there are numerous species whose energies are greater than $2(n-1)$. Almost in the same time the Indian mathematician Walikar with coworkers[101] communicated the first systematic construction of such graphs. Eventually more results of the same kind followed.[96,113]

These observational led[114] to the concept of "*hyperenergetic graphs*", namely graphs whose energy exceeds $2(n-1)$. It was shown[114] that hyperenergetic n-vertex graphs exist for all values of $n \geq 8$.

From the Koolen–Moulton bound (7) it follows that the energy of an n-vertex graph cannot be greter than $n^{3/2}$. It was possible[115] to construct graphs whose energy is (approximately) equal to $0.5n^{3/2}$. These, of course, are hyperenergetic.

Graphs that are usually encountered in chemical considertions cannot be hyperenergetic.[116] A stronger result was also found,[97] namely that graphs for which $m \leq 2n-2$ cannot be hyperenergetic. (Recall that in molecular graphs representing conjugated hydrocarbons, $m < 1.5n$.)

6. DEPENDENCE OF TOTAL π-ELECTRON ENERGY ON THE NUMBER OF KEKULÉ STRUCTURES

The problem of how the total π-electron energy of a conjugated hydrocarbon depends on structural features other than the number of carbon atoms and carbon-carbon bonds (*i.e.*, other than n and m) has long intrigued the theoretical chemists. It is not easy to guess which of the numerous structural features would be the third-important one. This third-important parameter would, however, be the most significant structural detail responsible for the energy-differences between isomers.

In the case of benzenoid hydrocarbons it is more-or-less generally agreed (although not based on some convincing theoretical argument) that the third-important parameter, influencing the value of E, is the number of Kekulé structures K. (For details on Kekulé structures in benzenoid hydrocarbons see the books.[117,118] Recently the importance of K for determining the stability of benzenoid hydrocarbons was criticized.[119]

Based on an early empirical observation,[120] Hall formulated[121] a simple regularity nowadays referred to[118,122] as the *Hall rule:* Within groups of isomeric benzenoid hydrocarbons, E is a linear funciton of K. More specifically,

$$E \approx Ah + B + C\,K\,e^{-Dh} \tag{11}$$

where h is the number of hexagons and *A, B, C, D* are positive-valued constants. Somewhat later, not knowing Hall's works,[120,121] the present author arrived[123] at an approximate formula identical with (11).

In an attempt to prove the Hall rule it was shown[123,124] that a necessary condition for its validity is that the highest and second-highest occupied molecular orbital energy levels are sufficiently separated from each other. In large benzenoid systems this condition cannot be satisfied, causing violations from the Hall rule.

Because of the Cioslowski formula, which postulates a different K-dependence of E (see below), extensive numerical testings of the Hall rule were undertaken.[125,126] These corroborated its validity. However, these testings included only sets of benzenoid isomers with not more than 8 hexagons.

Curiously, violations from the Hall rule were first recognized in a study of the total π-electron energy of long-chain phenylenes.[127] After recognizing that violations have to be expected in the case of large h, new testings of the rule were done.[128–130] This time it could be shown that when the number of hexagons h exceeds 9, the relation between E and K becomes curvilinear. The cause of this curvilinearity is not known and no mathemticial model for it has been proposed so far.[122] This, in turn, means that at the present moment the form of the dependence of the total π-electron energy of benzenoid hydrocarbons on the number of Kekulé structures is an open problem, awaiting to be solved in the future.

In 1986 Cioslowski put forward[131] a model for the π-electron properties of benzenoid hydrocarbons, based on the assumption that the HMO energy levels of all such hydrocarbons have the same distribution pattern. This "*universal distribution approach*" was then further elaborated.[132–138]

According to Cioslowski's approach,

$$E \approx \Gamma(x)\,\sqrt{2mn} \tag{12}$$

where

$$x = K^{2/n}\,\sqrt{\frac{n}{2m}}$$

and where $\Gamma(x)$ is a universal function (that is, same for all benzenoids), whose exact analytical form was not determined. Cioslowski's formula (12) should be compared with McClelland's (6). We see that (6) is a special case of (12) if $\Gamma(x)$ is assumed to be constant.

Whatever is the form of the function $\Gamma(x)$, formula (12) predicts a K-dependence of E that significantly differs from that claimed by Hall. After an early attempt[139] to reconcile the two contradicting formulas for total π-electron energy, extensive numerical comparisons thereof were done.[125,126] These doubtlessly showed that the Hall formula is better than Cioslowski's, at least for benzenoid molecules of usual size. Consequently, one had to conclude that the universal distribution approach, in spite of its algebraic elegance, disagrees with empirical facts and thus has to be abandoned.

7. DEPENDENCE OF TOTAL π-ELECTRON ENERGY ON THE NUMBER OF NON-BONDING MOLECULAR ORBITALS

Denote by n_0 be the number of non-bonding molecular orbitals (NBMOs), as computed by the HMO model. Numerical examples clearly indicate that within classes of isomeric and structurally similar conjugated molecules, E is a decreasing function of n_0. The effect of HBMOs on E was considered[140] already in the 1970s. In that time this problem was believed to be solved in the following manner (see, for instance, pp. 54, 57, 75 in the book[1]).

Rule A. If for $n_0 = 0$ there is an expression for E in which one variable is n, then the same expression is applicable also in the case $n_0 > 0$, provided n is replaced by $n - n_0$.

In particular, because (6) holds as a good approximation in the case $n_0 = 0$, according to Rule A, if $n_0 > 0$, then

$$E \approx a \sqrt{2m(n - n_0)}$$

would be an equally satisfactory approximate formula.[53]

It was belived that Rule A has resolved the problem of the effect of NBMOs on total π-electron energy, and in the next 25 years this matter was not further investigated. Only quite recently,[141] examining the relation between E and the Hosoya topolgical index Z, it was recognized that the reasoning leading to Rule A might have been erroneous. This motivated us to revisit Rule A and to check its validity on pertinently chosen examples.[142]

In the attempts to assess the effect of NBMOs on E the following difficulty is encountered. The actual value of E depends on numerous (simultaneously present) structural features of the underlying molecular graph G. The structure-dependence of E has been, until now, only partially resolved.[21] Anyway, it is known[58,140] that in acyclic systems, in addition to the size-dependent parameters n and $m = n - 1$, the extent of branching and n_0 seem to be the factors determining the gross part of E. In cyclic systems the situation is far more complicated: here also the number, size,

and mutual arrangement of cycles, as well as the Kekulé structure count significantly influence the value of E. In order to "extract" the effect of NBMOs on total π-electron energy, we must compare the E-values of systems that differ in n_0, but in which all other relevant structural parameters are either equal of differ as little as possible. In the work[142] a class of acyclic molecular graphs was designed, satisfying the above requirements. What could be established is a remarkably simple and remarkably accurate regularity:[142,143]

Rule B. Provided other effects are kept constant, the effect of non-bonding molecular orbitals on total π-electron energy is linearly proportional to the number of NBMOs.

It was show[144] that Rule B is applicable until extremely large values of n_0, in particular, for $n_0 \leq 20$.

8. GRAPHS AND MOLECULAR GRAPHS WITH EXTREMAL ENERGY

One frequently encountered question in the theory of total π-electron energy is which species (from a given class) have the greatest and which the smallest E-value. The first result along these lines was obtained in 1977, when it was shown that the n-vertex trees with maximal and minimal a energy are the path and the star, respectively.[145] Since then the graphs with extremal (maximal or minimal) E values were determined in many cases.

The two most important problems in this are are the following:

1° Find the graph with n vertices, having minimal E.

2° Find the graph with n vertices, having maximal E.

The solution of problem 1° is trivial: this is the graph without edges, whose energy is zero. If one requires that the graph be connected, then the star has minimal energy,[29] equal to $2\sqrt{n-1}$.

Problem 2° is practically open, in spite of several attempts to find its solution.[29,109] Koolen and Moulton not only deduced the upper bound (9), but for some values of n were able[44,115] to construct the graph for which

$$E = \frac{n}{2}(\sqrt{n} + 1)$$

Unfortunately, the above equality holds only for $n = 64,256, 1024,4096,...$ For other values of n (greater than 10) the structure of the maximal-energy graphs is not known.

<center>* * * * *</center>

In what follows we mention a few more results having direct chemical interest.

Several recent researches were concerned with the characterization of the acyclic molecular graphs having minimal[100,105,146,147] and maximal[102] E-values.

Finding of the monocyclic graphs with minimal energy was a relatively easy task.[148] The search[29] for the monocyclic graph with maximal energy suggested that

the cycle C_n has maximal energy for $n \leq 7$ and $n = 9, 10, 11, 13, 15$. For other values of n the graph with maximal energy is $P_n{}^6$, obtained by attaching an $(n-6)$-vertex path to the hexagon C_6. Only a partial proof of this conjecture was offered.[98,149]

A Monte Carlo search[150,151] resulted in the characterization of bicyclic, triciclic, and tetracyclic molecular graphs with maximal energy. These are the α,ω-diphenyl-, α,α',ω-triphenyl, and $\alpha,\alpha', \omega,\omega'$-tetraphenyl polyenes, respectively.

Among unbranched catacondensed benzenoid hydrocarbon, the linear polyenes have minimal,[152] whereas the zig-zig fibonacenes maximal[153] total π-electron energy. There exists a generalization of this result to systems possessing cycles other than hexagons.[106]

9. MISCELLANEOUS

Because of space limitation, in this review we cannot discuss the recent research on various other topics in the theory of total π-electron energy and graph energy. Limiting ourselves only to papers published in this century,[154–164] these topics are the following:

1° (n, m)-type mathematical relations for E, obtained as a consequence of the Koolen–Moulton bounds (7) and (8);[154,155]

2° the Coulson function;[141,156,157]

3° the Türker angle;[158–163]

4° equienergetic molecular graphs.[164]

ИЗВОД

ТОПОЛОГИЈА И СТАБИЛНОСТ КОНЈУГОВАНИХ УГЉОВОДОНИКА, ЗАВИСНОСТ УКУПНЕ π-ЕЛЕКТРОНСКЕ ЕНЕРГИЈЕ ОД МОЛЕКУЛСКЕ ТОПОЛОГИЈЕ

ИВАН ГУТМАН

Природно-математички факултет у Крагујевцу

Без обзира на то што су истраживања математичких особина укупне π-електронске енергије E (рачунате помоћу Хикелове молекулско-орбиталне апроксимације) започела још у четрдесетим годинама 20. века, на том подручју је добивено много резултата и у новије време. Године 1978. овај аутор је објавио у овом часопису један прегледни чланак о E. Садашњи чланак је нови преглед теорије укупне π-електронске енергије, који приказује напредак у тој области, постигнут од тада.

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