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BIPARTITE UNICYCLIC GRAPHS WITH GREATEST ENERGY

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Abstract

If $\lambda_1, \lambda_2, \ldots, \lambda_n$ are the eigenvalues of a graph G, then the energy of this graphs is defined as $E(G) = |\lambda_1| + |\lambda_2| + \cdots + |\lambda_n|$. For $n \geq 7$, let P_n^6 be the graph obtained by joining a pendant vertex of the path P_{n-6} with a vertex of the circuit C_6. Let $\mathcal{U}_b(n)$ be the set of all bipartite unicyclic graphs on n vertices. We show that for all values of n, $n \geq 7$, if $G \in \mathcal{U}_b(n) \setminus \{C_n\}$ then $E(G) \leq E(P_n^6)$. In addition to this, we claim that for all $n \geq 12$, the energy of P_n^6 exceeds also the energy of C_n, but we can support this inequality only by numerical calculations. Hence, P_n^6 is the unicyclic bipartite graph with greatest energy.

INTRODUCTION. PART 1

An important quantum-chemical characteristic of a conjugated molecule is its total π-electron energy. Within the Hückel molecular-orbital (HMO) theory this quantity is computed as

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

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 , $i = 1, 2, \ldots, n$ are the eigenvalues of the respective molecular graph; for details see [1–3]. For non-charged conjugated systems in their ground electronic state the non-trivial part of the above expression is of the form

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

where it is assumed that $\lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_n$. For the vast majority of conjugated molecules Eq. (1) can be transformed into

$$E = E(G) = \sum_{i=1}^{n} |\lambda_i| \, . \tag{2}$$

A CHEMICAL INTERLUDE

The total π-electron energy is one of the chemically most useful quantities that can be obtained from the HMO theory. In the absence of large steric strain in the carbon-atom skeleton (e. g., absence of three-membered rings), by means of E_π one can calculate remarkably accurate values for the thermodynamic functions of conjugated hydrocarbons. This especially applies to enthalpies (heats of atomization, heats of formation, heats of combustion, heats of hydrogenation). The success of E_π in reproducing the thermochemical constants of conjugated molecules is based on the noteworthy fact, first demonstrated by Schaad and Hess [4], that not only the π–, but also the σ-electron energy of the carbon–carbon bonds is proportional to E . In particular, the heat of atomization of a polycyclic (non-strained) conjugated hydrocarbon with n_{CH} carbon–hydrogen and n_{CC} carbon–carbon bonds is calculated by means of

$$\Delta H_a = -[n_{CH} \, E_{CH} + n_{CC} \, E^\circ_{CC} + \beta \, E]$$

with $E_{CH} = -411.09 \, kJ/mol$, $E^\circ_{CC} = -325.18 \, kJ/mol$ and $\beta = -137.00 \, kJ/mol$. For more details see pp. 151–154 in the book [5] and the references cited therein.

In the case of benzenoid hydrocarbons, the enthalpies calculated by using HMO total π-electron energy turned out to be significantly closer to the experimental values than the results of the highly parameterized semiempirical molecular-mechanics and molecular-orbital (MNDO) models; for details see [6].

At this point it is worth noting that the HMO total π-electron energy was shown to be related to the total SCF energy [7], in particular to the kinetic energy in the Hartree–Fock MO approach [8].

Numerous "*resonance energies*" and other related quantities, aimed at measuring the aromaticity of polycyclic conjugated molecules, are based on the total π-electron energy, especially on the HMO total π-electron energy, Eq. (1). These are always obtained by subtracting from E a term E^{ref}, interpreted as the total π-electron energy of some "*reference structure*"; E^{ref} is often chosen to be an additive function of carbon–carbon bond contributions. Conjugated systems for which $E - E^{ref} > 0$ are classified as "*aromatic*", those for which $E - E^{ref} < 0$ as "*antiaromatic*", whereas those for which $E - E^{ref} \approx 0$ as "*non-aromatic*". The most important (i. e., the most frequently applied) resonance energies are those of Hückel (often referred to as "*classical*") [9], Dewar [10, 11], Hess and Schaad [12], Jiang, Tang and Hoffmann [13], as well as the "*topological*" resonance energy of Aihara [14] and Gutman et al. [15, 16]. Scores of papers exist in the chemical literature on various applications of resonance energies; for details and further references see pp. 151–154 of the book [5]; for most recent works along these lines see [17].

INTRODUCTION. PART 2

The right-hand side of Eq. (2) is used as the *definition* of the so-called *energy of the graph G*. Needless to say that it can be applied to all graphs, irrespective whether they represent conjugated molecules or not. For details on the graph-energy concept and a survey of its mathematical theory see [5, 18, 19].

In what follows we use usual graph-theoretic notation and terminology. The *degree* of a vertex is the number of its first neighbors. A vertex of degree one is said to be *pendant*. A vertex of degree zero is said to be *isolated*. The *path* P_n is the n-vertex

tree (= connected and acyclic graph) possessing exactly two pendant vertices. The *circuit* C_n is the connected n-vertex graph in which all vertices are of degree two. The graph obtained by joining a pendant vertex of P_{n-6} with a vertex of C_6 is denoted by P_n^6.

A graph is *bipartite* if it does not contain, as subgraph, odd-membered circuits. A graph is *unicyclic* if it contains, as subgraph, exactly one circuit.

Bipartite unicyclic graphs are thus graphs containing exactly one circuit, which must be of even size. Such graphs need not be connected. The set of all n-vertex unicyclic graphs is denoted by $\mathcal{U}_b(n)$. This set is non-empty for any $n \geq 4$. Recall that $C_n \in \mathcal{U}_b(n)$ if, and only if, n is even (and, of course, if $n \geq 4$). Obviously, $P_n^6 \in \mathcal{U}_b(n)$ for every $n \geq 7$.

* * * * *

The fact that P_n has the greatest energy among all n-vertex trees was established long time ago [20]. The analogous problem for unicyclic graphs was recently considered by Caporossi et al. [21], who used a computer–aided search method. They formulated the following:

Conjecture [21]. *Among unicyclic graphs on n vertices, C_n has maximal energy if $n \leq 7$ and $n = 9, 10, 11, 13$ and 15. For all other values of n, the unicyclic graph with maximal energy is P_n^6.*

In this paper we provide a partial proof of Caporossi's conjecture. We namely demonstrate the validity of:

Theorem 1a. *For all values of n, $n \geq 7$, among bipartite unicyclic graphs on n vertices, different from the circuit C_n, the graph with maximal energy is P_n^6.*

Another, more formal but equivalent, way of stating the same result is:

Theorem 1b. *For all values of n, $n \geq 7$, if $G \in \mathcal{U}_b(n) \setminus \{C_n\}$, then $E(G) \leq E(P_n^6)$.*

In order to prove Theorem 1 we need some preparations.

AN APPLICATION OF THE COULSON INTEGRAL FORMULA

One of the oldest theoretical results on HMO total π-electron energy (and, *mutatis mutandis*, on the energy of a graph) is the Coulson integral formula [22] (see also in [5, 18, 19]):

$$E(G) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \left[n - \frac{ix\,\phi'(G, ix)}{\phi(G, ix)} \right] dx \tag{3}$$

where $\phi(G, \lambda)$ stands for the characteristic polynomial of the (molecular) graph G and $i = \sqrt{-1}$. If we write the characteristic polynomial as

$$\phi(G, \lambda) = \sum_{k=0}^{n} a_k(G)\, \lambda^{n-k} \tag{4}$$

then Eq. (3) can be rewritten as [18, 20]

$$E(G) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{dx}{x^2} \ln \left[\left(\sum_{k \geq 0} (-1)^k\, a_{2k}(G)\, x^{2k} \right)^2 + \left(\sum_{k \geq 0} (-1)^k\, a_{2k+1}(G)\, x^{2k+1} \right)^2 \right] . \tag{5}$$

Bipartite graphs have the properties $a_{2k+1}(G) = 0$ and $(-1)^k\, a_{2k}(G) > 0$, and these relations hold for all values of k , $k = 0, 1, 2, \ldots$ [5, 23]. Therefore, if G is a bipartite graph, then instead of Eq. (4) we have

$$\phi(G, \lambda) = \sum_{k=0}^{\lfloor n/2 \rfloor} (-1)^k\, b(G, k)\, \lambda^{n-2k} \tag{6}$$

whereas Eq. (5) is simplified as:

$$E(G) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{dx}{x^2} \ln \left(\sum_{k \geq 0} b(G, k)\, x^{2k} \right) \tag{7}$$

where, for convenience, $(-1)^k\, a_{2k}(G)$ is denoted by $b(G, k)$. Recall that all the parameters $b(G, k)$ are either positive-valued or are equal to zero. In particular, $b(G, 0) = 1$ and $b(G, 1)$ is the number of edges of G. If G is acyclic, then $b(G, k) = m(G, k)$ where $m(G, k)$ is the number of k-matchings of G; for details see [5, 23].

Our starting point is the observation [20], immediately seen from formula (7), that in the case of bipartite graphs $E(G)$ is a monotonically increasing function of

the parameters $b(G,k)$, $k = 1,2,\ldots,\lfloor n/2 \rfloor$. Consequently, if G_1 and G_2 are bipartite graphs for which

$$b(G_1,k) \leq b(G_2,k) \tag{8}$$

holds for all $k \geq 0$, then

$$E(G_1) \leq E(G_2) \ . \tag{9}$$

Equality in (9) is attained only if relation (8) is an equality for all $k \geq 0$.

If relations (8) hold for all k , then we write $G_1 \prec G_2$. If relation (8) holds for some k , but not for all k , then we write $G_1 \not\prec G_2$. Using this notation, we re-state the above conclusion as:

Lemma 1. *Let G_1 and G_2 be bipartite graphs (not necessarily with equal number of vertices). Then $G_1 \prec G_2$ implies $E(G_1) \leq E(G_2)$.*

PROOF OF THEOREM 1

Instead of Theorem 1 we prove a somewhat stronger statement, namely:

Theorem 2. *For all values of n , $n \geq 7$, if $G \in \mathcal{U}_b(n) \setminus \{C_n\}$, then $G \prec P_n^6$.*

By means of Lemma 1, Theorem 1 is an immediate consequence of Theorem 2.

In our proof we use the following well known [5, 23] or previously proven [20, 24, 25] results:

Lemma 2. *Let G be a graph possessing a pendant vertex v . Let u be the (unique) first neighbor of v . Then $\phi(G,\lambda) = \lambda\,\phi(G-v,\lambda) - \phi(G-u-v,\lambda)$. If G is bipartite, then in view of Eq. (6),*

$$b(G\,,\,k) = b(G-v\,,\,k) + b(G-u-v\,,\,k-1) \ . \tag{10}$$

Lemma 3. *Let G be a graph possessing an isolated vertex v . Then $\phi(G,\lambda) = \lambda\,\varphi(G-v,\lambda)$. If G is bipartite, then in view of Eq. (6),*

$$b(G\,,\,k) = b(G-v\,,\,k) \ . \tag{11}$$

Lemma 4. *For any subgraph H of a graph G and for all $k \geq 1$.*

$$m(H, k) \leq m(G, k) \ . \tag{12}$$

Lemma 5 [20]. *If G is an n-vertex acyclic graph (either connected or disconnected), then*

$$m(G, k) \leq m(P_n \ , \ k) \ . \tag{13}$$

Lemma 6. [24, 25]. *If $G \in \mathcal{U}_b(n)$ and if the (unique) circuit Z of G is of the size 2ℓ , then*

$$b(G, k) = m(G, k) - (-1)^{\ell} \, 2 \, m(G - Z \ , k - \ell) \ . \tag{14}$$

Proof of Theorem 2. We use induction on the number n of vertices, starting with $n = 7$.

First, the validity of the statement

$$G \in \mathcal{U}_b(n) \setminus \{C_n\} \Longrightarrow G \prec P_n^6 \tag{15}$$

needs to be checked for $n = 7$ and $n = 8$. This is done directly, by computing the characteristic polynomials of all members of $\mathcal{U}_b(7)$ and $\mathcal{U}_b(8)$, except of C_8 , and by checking that the relations

$$b(G, k) \leq b(P_n^6 \ , \ k) \tag{16}$$

are always obeyed.

$\mathcal{U}_b(7)$ has 20 elements, 10 connected and 10 disconnected. $\mathcal{U}_b(8)$ has 58+1 elements, 32+1 connected and 26 disconnected. The respective $b(G, k)$-values are easily obtained by means of a suitable computation technique [26, 27].

Suppose now that $r \geq 9$ and that the statement (15) holds for $n = r - 2$ and $n = r - 1$. We have to demonstrate that then (15) holds also for $n = r$.

For $r \geq 9$, application of (10) to the (unique) pendent vertex of P_r^6 yields

$$b(P_r^6 \ , \ k) = b(P_{r-1}^6 \ , \ k) + b(P_{r-2}^6 \ , \ k - 1) \ . \tag{17}$$

For any $r > 8$, all elements of $\mathcal{U}_b(r) \setminus \{C_r\}$ contain either a pendant or an isolated vertex.

Case 1: $G \in \mathcal{U}_b(r) \setminus \{C_r\}$ contains a pendant vertex.

Let this pendant vertex v be adjacent to the vertex u. Then Eq. (10) is satisfied. Because $G - v \in \mathcal{U}_b(r-1) \setminus \{C_r\}$, by the induction hypothesis,

$$b(G - v\,,\, k) \leq b(P^6_{r-1}\,,\, k) \tag{18}$$

holds for all values of k.

The subgraph $G - u - v$ has $r - 2$ vertices. It is either unicyclic or acyclic. If $G - u - v$ is unicyclic then by the induction hypothesis,

$$b(G - u - v\,,\, k-1) \leq b(P^6_{r-2}\,,\, k-1) \tag{19}$$

holds for all values of k. Bearing in mind the inequalities (18) and (19), from Eqs. (10) and (19) follows that the relations (16) are satisfied for $n = r$ and for all k, i. e., that $G \prec P^6_r$.

If $G - u - v$ is acyclic, then

$$\begin{aligned} b(G - u - v\,,\,, k-1) &= m(G - u - v\,,\, k-1) && (20)\\ &\leq m(P_{r-2}\,,\, k-1) && (21)\\ &\leq m(P^6_{r-2}\,,\, k-1) && (22)\\ &\leq b(P^6_{r-2}\,,\, k-1)\,. && (23) \end{aligned}$$

Relation (20) holds because $G - u - v$ is acyclic; inequality (21) holds because of Eq. (13); inequality (22) is a special case of Eq. (12), since P_{r-2} is a subgraph of P^6_{r-2}; inequality (23) holds because of Eq. (14), where $\ell = 3$. In summary, the inequality (19) holds for all values of k, and therefore $G \prec P^6_r$, also if $G - u - v$ is acyclic.

This completes the proof of Theorem 2 in the Case 1.

Case 2: $G \in \mathcal{U}_b(r) \setminus \{C_r\}$ contains an isolated vertex.

If this vertex is v, then Eq. (11) is applicable. By the induction hypothesis, $b(G - v\,,\, k) \leq b(P^6_{r-1}\,,\, k)$. which, in view of Eq. (17), immediately implies (16) for $n = r$. Therefore $G \prec P^6_r$.

Because Cases 1 and 2 cover all elements of $\mathcal{U}_b(r)$, except (if r is even) the circuit C_r, the proof of Theorem 2 is completed.

Corollary 1.1. *If n is odd, then for $n \geq 7$ the element of $\mathcal{U}_b(n)$ with maximal energy is P_n^6.*

Corollary 1.2. *If n is even, then for $n \geq 8$ the element of $\mathcal{U}_b(n)$ with maximal energy is either P_n^6 or C_n.*

BEYOND THEOREM 1

For $n \geq 8$, $C_n \not\in P_n^6$ and therefore $E(P_n^6)$ and $E(C_n)$ cannot be compared by means of Lemma 1. To see this note that the identity

$$\phi(C_n : \lambda) = \phi(P_n^6 ; \lambda) + \phi(C_{n-6} ; \lambda) + (\lambda^3 - \lambda)\,\phi(P_{n-7} ; \lambda) \tag{24}$$

holds for $n \geq 9$. Because expressions for the coefficients of the characteristic polynomials of circuits and paths are well known [5, 23], from (24) we directly obtain that for even n:

$$b_4(C_n , 2) = b_4(P_n^6 , 2) + 1$$

implying $b(C_n , 2) > b(P_n^6 , 2)$, and

$$b(C_n , n/2 - 1) = b(P_n^6 , n/2 - 1) - \frac{1}{4}(n - 6)(n - 8)$$

implying $b(C_n , n/2 - 1) < b(P_n^6 , n/2 - 1)$ for $n \geq 10$.

Thus $C_n \not\in P_n^6$ for $n = 10, 12, 14, \ldots$. To see that the same holds for $n = 8$ note that $b(C_8 , 2) = 20$, $b(P_8^6 , 2) = 19$ whereas $b(C_8 , 4) = 0$, $b(P_8^6 , 4) = 4$.

Numerical calculations clearly indicate that for even n , $n \geq 12$ the energy of P_n^6 is greater than the energy of C_n. This is inferred by the following data, where $\Delta_n = E(P_n^6) - E(C_n)$.

n	Δ_n	n	Δ_n
8	0.7674	10	−0.0122
12	0.5308	14	0.0177
16	0.4225	18	0.0375
20	0.3597	22	0.0510
24	0.3184	26	0.0607
28	0.2892	30	0.0680
32	0.2675	34	0.0736
36	0.2506	38	0.0781
40	0.2372	42	0.0818

We see that the numbers Δ_{4k} , $k = 2, 3, 4, \ldots$ monotonically decrease, whereas Δ_{4k+2} , $k = 2, 3, 4, \ldots$ monotonically increase. It is plausible to expect that

$$\lim_{k\to\infty} \Delta_{4k} = \lim_{k\to\infty} \Delta_{4k+2}$$

which would then imply $\Delta_n > 0$ for all even n , $n \geq 12$. A rigorous mathematical proof of this assertion remains a task for the future.

Anyway, we deem that the above numerical evidence is sufficiently convincing to allow the formulation of the following improvement of Corollary 1.2:

Assertion 1.3. *If n is even, then for $n \geq 12$ the element of $\mathcal{U}_b(n)$ with maximal energy is P_n^6.*

For non-bipartite unicyclic graphs the entire consideration of this paper is not applicable. For such graphs some odd coefficients, a_{2k+1} , of the characteristic polynomial, Eq. (4), are non-zero. Therefore, the characteristic polynomial cannot be written in the form (6) and formula (5) cannot be reduced to (7). Consequently, Lemma 1 is not usable.

The quest for the maximal-energy non-bipartite unicyclic (as well as polycyclic) graphs would require some novel mathematical methods. These, however, still await to be discovered.

References

[1] A. Graovac, I. Gutman and N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules*, Springer Verlag, Berlin, 1977.

[2] C. A. Coulson, B. O'Leary and R. B. Mallion, *Hückel Theory for Organic Chemists*, Academic Press, London, 1978.

[3] J. R. Dias, *Molecular Orbital Calculations Using Chemical Graph Theory*, Springer–Verlag, Berlin, 1993.

[4] L. J. Schaad and B. A. Hess, *J. Am. Chem. Soc.* **94** (1972) 3068.

[5] I. Gutman and O. E. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer–Verlag, Berlin, 1986.

[6] I. Gutman, *Topics Curr. Chem.* **162** (1992) 29.

[7] L. J. Schaad, B. H. Robinson and B. A. Hess, *J. Chem. Phys.* **67** (1977) 4616.

[8] H. Ichikawa and Y. Ebisava, *J. Am. Chem. Soc.* **107** (1985) 1161.

[9] E. Hückel, *Grundzüge der Theorie ungesättigter und aromatischer Verbindungen*, Verlag Chemie, Berlin, 1940.

[10] M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.* **91** (1969) 789.

[11] M. Milun, Ž. Sobotka and N. Trinajstić, *J. Org. Chem.* **37** (1972) 139.

[12] B. A. Hess and L. J. Schaad, *J. Am. Chem. Soc.* **93** (1971) 305.

[13] Y. Jiang, A. Tang and R. Hoffmann, *Theor. Chim. Acta* **65** (1984) 255.

[14] J. Aihara, *J. Am. Chem. Soc.* **98** (1976) 2750.

[15] I. Gutman, M. Milun and N. Trinajstić, *Commun. Math. Chem. (MATCH)* **1** (1975) 171.

[16] I. Gutman, M. Milun and N. Trinajstić, *J. Am. Chem. Soc.* **99** (1977) 1692.

[17] M. U. Frederiksen, R. F. Langler, K. J. Watson, A. Penwell and K. V. Darvesh, *Austral. J. Chem.* **53** (2000) 443.

[18] I. Gutman, *Ber. Math.–Statist. Sekt. Forschungszentrum Graz* **103** (1978) 1.

[19] I. Gutman, in: A. Betten, A. Kohnert, R. Laue and A. Wassermann (Eds.), *Algebraic Combinatorics and Applications*, Springer-Verlag, Berlin, 2001, pp. 000–000 (in press).

[20] I. Gutman, *Theor. Chim. Acta* **45** (1977) 79.

[21] G. Caporossi, D. Cvetković, I. Gutman and P. Hansen, *J. Chem. Inf. Comput. Sci.* **39** (1999) 984.

[22] C. A. Coulson, *Proc. Cambridge Phil. Soc.* **36** (1940) 201.

[23] D. Cvetković, M. Doob and H. Sachs, *Spectra of Graphs – Theory and Application*, Academic Press, New York, 1980.

[24] H. Hosoya, *Theor. Chim. Acta* **25** (1972) 215.

[25] I. Gutman and O. E. Polansky, *Theor. Chim. Acta* **60** (1981) 203.

[26] K. Balasubramanian, *Theor. Chim. Acta* **65** (1984) 49.

[27] T. P. Živković, *J. Comput. Chem.* **11** (1990) 217.