Comparing the Energy of Two Unicyclic Molecular Graphs

Xiaoxin Xu, a Fuyi Wei, a,* Ivan Gutman b

a Department of Applied Mathematics, College of Science, South China Agricultural University, 510640, Guangzhou, China
e-mail: weifuyi@126.com
b Faculty of Science, University of Kragujevac, P. O. Box 60, 34000 Kragujevac, Serbia
e-mail: gutman@kg.ac.rs

(Received March 14, 2011)

Abstract. The energy \( E(G) \) of a graph \( G \) is the sum of the absolute values of the eigenvalues of \( G \). In 2001 Yaoping Hou et al. proved that among \( n \)-vertex unicyclic bipartite graphs, either \( P^6_n \) or \( C_n \) has maximal energy, where \( P^6_n \) is the graph obtained by attaching a hexagon to a terminal vertex of the \((n-6)\)-vertex path graph, and \( C_n \) is the \( n \)-vertex cycle. In this note we examine the relations between \( E(P^6_n) \) and \( E(C_n) \) and confirm that \( E(C_n) > E(P^6_n) \) holds for \( n = 7, 9, 10, 11, 13, 15 \) whereas \( E(P^6_n) > E(C_n) \) holds for \( n = 8, 12, 14 \) and \( n \geq 16 \). In the limit \( n \to \infty \), the difference \( E(P^6_n) - E(C_n) \) assumes a value between 0.08 and 0.20.

Introduction

The experimental heats of formation of conjugated hydrocarbons are closely related to, and can be reliably calculated from, the total \( \pi \)-electron energy [1–3]. In what follows, the total \( \pi \)-electron energy, calculated within the framework of the
HMO approximation, will be denoted by $E(G)$, where $G$ is the molecular graph [2] of the underlying conjugated hydrocarbon. For the mathematical analysis $E(G)$ (for details see [2,4,5]), the the Coulson integral formula proved to be especially suitable:

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

where $a_0, a_1, a_2, \ldots, a_n$ are the coefficients of the characteristic polynomial of the molecular graph $G$. In the case of bipartite graphs, formula (1) is significantly simplified as:

$$E(G) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{1}{x^2} \ln \left( \sum_{j \geq 0} b_j x^{2j} \right) dx \quad (2)$$

where $b_j = (-1)^j a_{2j}$ and where $b_j \geq 0$ holds for all values of $j$. From Eq. (2) an important consequence follows [6]:

**Theorem 1.** If $G_1$ and $G_2$ are two bipartite graphs, such that $b_j(G_1) \geq b_j(G_2)$ holds for all values of $j$, then $E(G_1) \geq E(G_2)$. If, in addition, $b_j(G_1) > b_j(G_2)$ holds for at least one $j$, then $E(G_1) > E(G_2)$.

By means of Theorem 1, numerous relations between the energies of various (molecular) graphs have been established, and in many cases the graph having extremal (maximal or minimal) value of $E(G)$ could be determined (for details see [5]). One such result was established by Yaoping Hou et al. [7,8].

Let $P_n^6$ be the graph obtained by attaching a hexagon to a terminal vertex of the $(n - 6)$-vertex path graph, and let $C_n$ be the $n$-vertex cycle, see Fig. 1.

![Fig. 1](image_url) The two graphs mentioned in Theorem 2. Note that for $n = 6$, the graphs $P_n^6$ and $C_n$ coincide.
**Theorem 2.** [7, 8] Among all \( n \)-vertex unicyclic bipartite graphs, \( n \geq 6 \), the graph with maximal energy is either \( P_n^6 \) or \( C_n \).

If \( n \) is odd, then the cycle \( C_n \) is not bipartite. Therefore, Theorem 2 has the following immediate consequence:

**Corollary 2.1.** If \( n \) is odd, \( n \geq 7 \), then among all \( n \)-vertex unicyclic bipartite graphs the graph with maximal energy is \( P_n^6 \).

The graphs \( P_n^6 \) and \( C_n \) cannot be compared by means of Theorem 1. As illustrative examples of this incomparability, we list here their characteristic polynomials for \( n = 10 \) and \( n = 12 \):

\[
\begin{align*}
\phi(P_{10}^6, \lambda) &= \lambda^{10} - 10 \lambda^8 + 34 \lambda^6 - 48 \lambda^4 + 27 \lambda^2 - 4 \\
\phi(C_{10}, \lambda) &= \lambda^{10} - 10 \lambda^8 + 35 \lambda^6 - 50 \lambda^4 + 25 \lambda^2 - 4 \\
\phi(P_{12}^6, \lambda) &= \lambda^{12} - 12 \lambda^{10} + 53 \lambda^8 - 105 \lambda^6 + 104 \lambda^4 - 42 \lambda^2 + 4 \\
\phi(C_{12}, \lambda) &= \lambda^{12} - 12 \lambda^{10} + 55 \lambda^8 - 112 \lambda^6 + 105 \lambda^4 - 36 \lambda^2 .
\end{align*}
\]

Because of this difficulty, the problem of characterizing the unicyclic bipartite graph with maximal energy was long time not completely resolved. Numerical calculations [7, 9, 10] indicated that the maximal energy graph is \( P_n^6 \), except in the case \( n = 10 \), when the maximal energy graph is the cycle \( C_n \). These calculations were restricted for the first few (even) values of \( n \). Only quite recently it has been proven [11–13] that for sufficiently large \( n \), the difference \( E(P_n^6) - E(C_n) \) is positive–valued, which provided a complete solution of the problem.

Caporossi et al. [9] conjectured that Theorem 2 can be extended to all (both bipartite and non-bipartite) unicyclic graphs as follows:

**Conjecture 3.** If \( n = 7, 9, 10, 11, 13, \) and \( 15 \), then among all \( n \)-vertex unicyclic graphs, the graph with maximal energy is \( C_n \). If \( n = 8, 12, 14 \), and \( n \geq 16 \), then among all \( n \)-vertex unicyclic graphs, the graph with maximal energy is \( P_n^6 \). If \( n = 6 \), then the maximal–energy graph is \( P_n^6 \simeq C_n \).

The correctness of this conjecture was recently verified [14].
NUMERICAL WORK

In this note we offer some further numerical results on the comparison of $E(P^6_n)$ and $E(C_n)$, embracing both the case of even and odd $n$ and corroborating Conjecture 3. Our findings show that the inequality $E(P^6_n) > E(C_n)$ holds for all values of $n$, except for $n = 7, 9, 10, 11, 13, \text{ and } 15$. In order to achieve this result, appropriate computer–based investigations of the energies of $P^6_n$ and $C_n$, were undertaken. Let $\Delta(n) = E(P^6_n) - E(C_n)$. The dependence of $\Delta(n)$ on $n$ is shown in Figs. 2a and 2b.

Fig. 2a. Dependence of the difference $E(P^6_n) - E(C_n)$ on the first few values of the number of vertices $n$.

Fig. 2b. Dependence of the difference $E(P^6_n) - E(C_n)$ on larger values of the number of vertices $n$ ($n \leq 200$).
From the data shown in Fig. 2a we see that $\Delta(n) < 0$ exactly for $n = 7, 9, 10, 11, 13, 15$, in full agreement with Conjecture 3. From Fig. 2b we see that for all values of $n$, greater than 15, $\Delta(n) > 0$. In the limit case $n \to \infty$, $\Delta(n)$ tends to a finite value that lies between 0.08 and 0.20. This finding is remarkable (but not surprising), in view of the fact that for $n \to \infty$, both $E(P_n^6)$ and $E(C_n)$ tend to infinity.

CONCLUDING REMARKS

The numerical results reported in this note support the conclusion that for $n = 7, 9, 10, 11, 13, 15$, the unicyclic $n$-vertex graph with maximal energy is $C_n$ whereas $P_n^6$ has the second-maximal energy. For other values of $n$, $n > 6$, the opposite is the case: the unicyclic $n$-vertex graph with maximal energy is $P_n^6$ whereas $C_n$ has the second-maximal energy. However, these numerical results must not be considered as mathematically satisfactory proofs. Such proofs have recently been offered by Huo et al. [14].

Acknowledgement. The first two authors thank the South China Agriculture University (SCAU), and the College of Science for support. The third author thanks the Serbian Ministry of Science, for support through Grant no. 174033.

REFERENCES


