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COMPARING THE ENERGY OF TWO UNICYCLIC MOLECULAR GRAPHS[1]

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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_n^6 or C_n has maximal energy, where P_n^6 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 $E(P_n^6)$ and $E(C_n)$ and confirm that $E(C_n) > E(P_n^6)$ holds for $n = 7, 9, 10, 11, 13, 15$ whereas $E(P_n^6) > E(C_n)$ holds for $n = 8, 12, 14$ and $n \geq 16$. In the limit $n \to \infty$, the difference $E(P_n^6) - E(C_n)$ 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 π-electron energy [1–3]. In what follows, the total π-electron energy, calculated within the framework of the

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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:

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

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:

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

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.

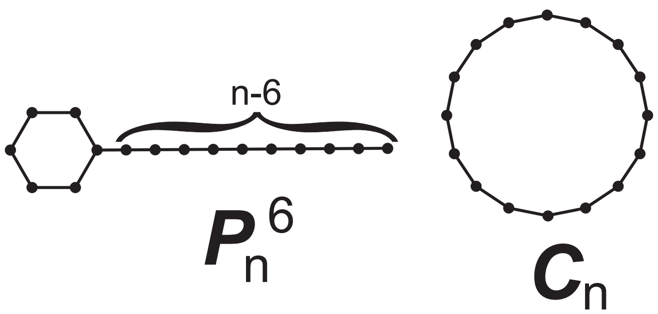

Fig. 1. The two graphs mentioned in Theorem 2. Note that for $n = 6$, the graphs P_n^6 and C_n coincide.

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 $n = 12$:

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

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 $P_n^6 \cong C_n$.

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

NUMERICAL WORK

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

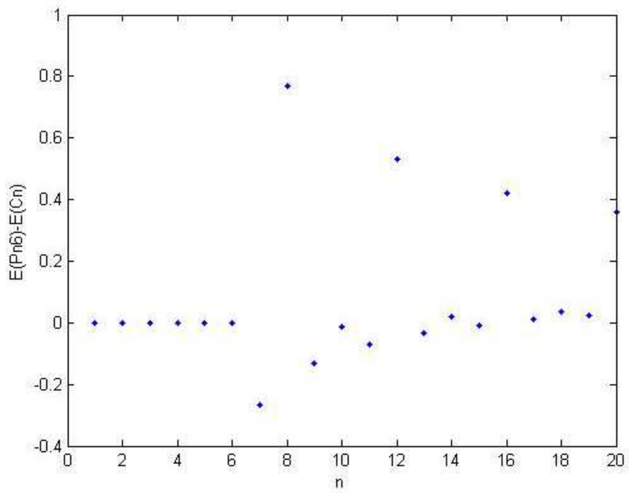

Fig. 2a. Dependence of the difference $E(P_n^6) - E(C_n)$ on the first few values of the number of vertices n.

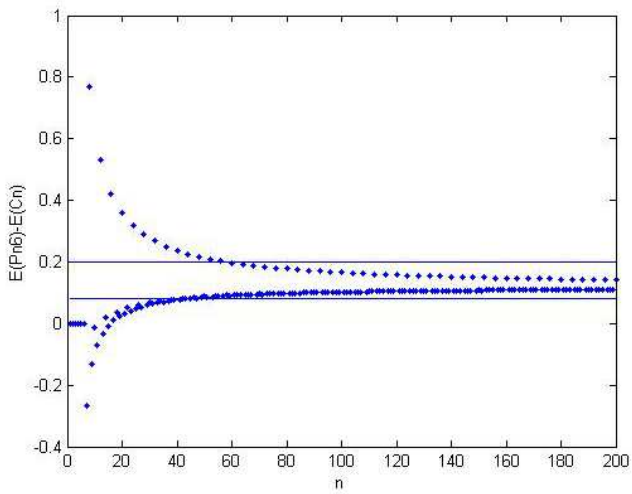

Fig. 2b. Dependence of the difference $E(P_n^6) - E(C_n)$ on larger values of the number of vertices n ($n \leq 200$).

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].

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