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Unicyclic Hückel molecular graphs with minimal energy

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The minimal energy of unicyclic Hückel molecular graphs with Kekulé structures, i.e., unicyclic graphs with perfect matchings, of which all vertices have degrees less than four in graph theory, is investigated. The set of these graphs is denoted by $\mathcal{H}_n^l$ such that for any graph in $\mathcal{H}_n^l$, n is the number of vertices of the graph and l the number of vertices of the cycle contained in the graph. For a given $n (n \geqslant 6)$, the graphs with minimal energy of $\mathcal{H}_n^l$ have been discussed.

KEY WORDS: Hückel molecular graphs, perfect matching, Kekulé structure, capped graph, energy

MSC 2000: 05C17, 05C35

1. Introduction

The investigation on the graphs with extremal energies is of practical importance and theoretical interest in the subject of chemical graph theory. The results for the extremal energy of acyclic conjugated molecules, unicyclic and bicyclic molecular graphs, catacondensed hexagonal systems have been widely investigated [1–9]. Conjugated molecules in chemistry may be classified into two groups: *Kekuléan* and *non-Kekuléan* molecules, depending on whether or not they possess Kekulé structures, i.e., perfect matchings in graph theory. As well

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known, conjugated hydrocarbon molecules considered in the Hückel molecule orbit theory are usually represented by the carbon-atom skeleton graphs, of which all vertices have degrees less than four. We call such molecular graphs Hückel molecular graphs. In graph theory, the unicyclic Hückel molecular graphs with Kekulé structures are unicyclic graphs with perfect matchings, of which the largest degree of vertices does not exceed three. The set of these graphs is denoted by $\mathcal{H}_n^l$. For any graph in $\mathcal{H}_n^l, n$ is the number of vertices of the graph and l the number of vertices of the cycle contained in the graph. We denote the cycle by C_l. The minimal energy of $\mathcal{H}_n^l$, however, has not been considered fully, which is the objective of this paper.

Let G be a graph with n vertices and $A(G)$ its adjacent matrix. The characteristic polynomial of G is

$$\phi(G, x) = \det[xI - A(G)] = \sum_{i=0}^{n} a_i x^{n-i}, \tag{1}$$

where I is the unit matrix of order n and $a_0, a_1, \ldots, a_n$ are the coefficients of the characteristic polynomial of G. The n roots of $\phi(G, x) = 0$ are denoted by $\lambda_1, \ldots, \lambda_n$, which are the eigenvalues of the corresponding graph G. It is known that the experimental heats due to the formation of conjugated hydrocarbons are closely related to the total π-electron energy. The total energy of all π-electrons in conjugated hydrocarbons, within the framework of HMO approximation [10,11], can be reduced to

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

$E(G)$ can also be expressed as the Coulson integral formula [4]

$$E(G) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{1}{x^2} \ln \left[\left(\sum_{j=0}^{[n/2]} b_{2j} x^{2j} \right)^2 + \left(\sum_{j=0}^{[n/2]} b_{2j+1} x^{2j+1} \right)^2 \right] \mathrm{d}x, \tag{3}$$

where $b_i(G) = |a_i(G)|$. It can be seen from (3) that $E(G)$ is a strictly monotonously increasing function of $b_i(G), i \geqslant 0$. Consequently, if

$$b_i(G_1) \geqslant b_i(G_2) \tag{4}$$

holds for all $i \geqslant 0$, where G_1 and G_2 are unicyclic graphs, then

$$E(G_1) \geqslant E(G_2) \tag{5}$$

and the equality in (5) is attained only if relation (4) is an equality for all $i \geqslant 0$ [7].

Next, formulae (4) and (5) will be employed to study the minimal energy of $\mathcal{H}_n^l$.

2. Preliminaries

Specially, let G be a connected unicyclic graph on n vertices with perfect matchings. It is evident that n is an even. Let $m(G, k)$ be the number of k-matchings in G, where k is a positive integer and $0 \leqslant k \leqslant n/2$. Obviously, $m(G, 1) = n$. In addition, it is consistent to define $m(G, 0) = 1$. Let $Q(G) = L(G) - M(G)$, where $L(G)$ is the edge set of G and $M(G)$ the perfect matching of G. It is clear that $|M(G)| = |Q(G)| = n/2$, where $|M(G)|$ and $|Q(G)|$ are the numbers of edges in $M(G)$ and $Q(G)$ respectively. Let $\widehat{G}$ be the graph induced by $Q(G)$, that is, $\widehat{G} = G - M(G) - S_0$, where S_0 is the set of singletons in $G - M(G)$. We call $\widehat{G}$ the capped graph of G and G the original graph of $\widehat{G}$. Each k-matching Ω of G can be partitioned into two parts: $\Omega = \Phi \cup \Psi$, where Φ is a matching in $\widehat{G}$ and $\Psi \subset M(G)$. On the other hand, any i-matching Φ of $\widehat{G}$ and $k-i$ edges Ψ of $M(G)$ that are not adjacent to Φ form a k-matching Ω of G with partition $\Omega = \Phi \bigcup \Psi$. Thus, we have [1]

$$m(G, k) = \sum_{i=0}^{n/2} m(\widehat{G}, i) \cdot \binom{n/2 - j}{k - i}, \tag{6}$$

where j is the number of edges in $M(G)$ which are adjacent to i-matching Φ.

There is a relationship between $b_i(G)$ and $m(G, k)$: [7]

$$b_{2k}(G) = m(G, k) + 2(-1)^{r+1} m(G - C_l, k - r) \text{ and } b_{2k+1}(G) = 0 \text{ when } l = 2r$$

while $b_{2k}(G) = m(G, k)$ and

$$b_{2k+1}(G) = \begin{cases} 0, & 2k+1 < l \\ 2m(G - C_l, k - r), & 2k+1 \geqslant l \end{cases}$$

when $l = 2r + 1$, where r is a positive integer.

3. Results

Let $S_n^{n/2}$ be a graph obtained by attaching a pendant edge to each vertex of $C_{n/2}$. For instance, S_8^4 and $\widehat{S}_8^4$ are shown in figure 1. In chemistry, $S_n^{n/2}$ is called radialene graph, i.e., the molecular graph of $n/2$ radialene. The theoretical studies on radialenes can be found in Refs. [12–15]. In particular, Gutman [12] made some statements about the energy of $S_n^{n/2}$. Gutman [13] examined three graphic polynomials of annulenes and radialenes. By using of generalized total π-electron energy indices, Aihara [14] elucidated two major features of radialene, i.e., specific stability and enhanced diamagnetism.

We denote the largest degree of vertices of G and the path with n vertices by $\Delta(G)$ and P_n, respectively. Let $G \in \mathcal{H}_n^l$ hereinafter. Obviously, $\Delta(G) \leqslant 3$.

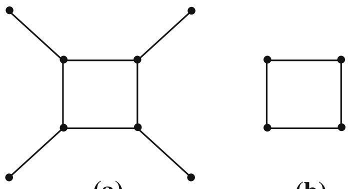

Figure 1. (a) S_8^4, (b) $\widehat{S}_8^4$.

Lemma 1. [10] Let $e = uv$ be an edge of G. Then

$$m(G,k) = m(G-e,k) + m(G-u-v,k-1) \text{ for } k \geqslant 1.$$

From lemma 1, we have lemma 2 as follows.

Lemma 2. For a given n ($n \geqslant 6$), we have $m(G,k) \geqslant m\left(S_n^{n/2},k\right)$ with equality for all values of k if and only if $G = S_n^{n/2}$.

Proof. Because every vertex of G is incident with an edge in $M(G)$ and $\Delta(G) \leqslant 3$, we have $\Delta(\widehat{G}) \leqslant 2$. Thus, $\widehat{G}$ is C_l, the union of C_l and path(s), $P_{n/2+1}$, or the union of disjoint paths whose total length is $n/2$. Three cases will be considered for $\widehat{G}$ as follows.

Case (i) $\widehat{G}$ is C_l.

Since every vertex of C_l is saturated, obviously, $G = S_n^{n/2}$. Thus, lemma 2 holds.

Case (ii) $\widehat{G}$ is the union of C_l and path(s).

Let $e = uv$ be an edge both of C_l contained in $\widehat{G}$ and of $C_{n/2}$ contained in $\widehat{S}_n^{n/2}$. By lemma 1, we have

$$m(\widehat{G},k) = m(\widehat{G}-e,k) + m(\widehat{G}-u-v,k-1), \tag{7}$$

$$m\left(\widehat{S}_n^{n/2},k\right) = m\left(\widehat{S}_n^{n/2}-e,k\right) + m\left(\widehat{S}_n^{n/2}-u-v,k-1\right). \tag{8}$$

Since $\widehat{G}-e$ is the union of disjoint paths whose total length is $n/2-1$ and $\widehat{S}_n^{n/2}-e$ is $P_{n/2}$, we have

$$m(\widehat{G}-e,k) \geqslant m\left(\widehat{S}_n^{n/2}-e,k\right). \tag{9}$$

The equality in (9) does not hold for all values of k since $\widehat{G}-e$ has sharply more 2-matchings than $\widehat{S}_n^{n/2}-e$. Since $\widehat{G}-u-v$ is the union of disjoint paths whose total length is $n/2-3$ or $P_{n/2-2}$ and $\widehat{S}_n^{n/2}-u-v$ is $P_{n/2-2}$, we have

$$m(\widehat{G}-u-v,k-1) \geqslant m\left(\widehat{S}_n^{n/2}-u-v,k-1\right). \tag{10}$$

Substitution of (9) and (10) into (7) and (8) yields $m(\widehat{G},k) \geqslant m(\widehat{S}_n^{n/2},k)$ with the equality that does not hold for all values of k.

Case (iii) $\widehat{G}$ is $P_{n/2+1}$ or the union of disjoint paths whose total length is $n/2$.

By the approach similar to Case (ii), we can get $m(\widehat{G},k) \geqslant m(\widehat{S}_n^{n/2},k)$ with the equality that does not hold for all values of k since $\widehat{G}$ has sharply more 2-matchings than $\widehat{S}_n^{n/2}$.

Combining Cases (i), (ii) and (iii), we have $m(\widehat{G},k) \geqslant m\left(\widehat{S}_n^{n/2},k\right)$ with equality for all values of k if and only if $G = S_n^{n/2}$. Furthermore, noting that any i-matching of $\widehat{S}_n^{n/2}$ is adjacent to $2i$ edges of $M\left(S_n^{n/2}\right)$ while any i-matching of $\widehat{G}$ to at most $2i$ edges of $M(G)$, we have

$$m(G,k) = \sum_{i=0}^{n/2} m(\widehat{G},i) \cdot \binom{n/2-j}{k-i} \geqslant \sum_{i=0}^{n/2} m\left(\widehat{S}_n^{n/2},i\right) \cdot \binom{n/2-2i}{k-i} = m\left(S_n^{n/2},k\right). \tag{11}$$

The equality in (11) holds for all values of k if and only if $G = S_n^{n/2}$. Lemma 2 has been proved.

It should be noted that h, r and j hereinafter denote positive integers. From lemma 3, we have theorem 1 as follows.

Theorem 1. For a given n ($n \geqslant 6$), we consider four cases as follows: (i) $n/2 = 2h + 1$ and $l = 2r + 1 \leqslant n/2$; (ii) $n/2 = 4h$ and $l = 2r + 1$; (iii) $n/2 = 4h$ and $l = 4j + 2$; (iv) $n/2 = 4h + 2$ and $l = 4j + 2 \leqslant n/2$. If any of the four cases holds, then $E(G) \geqslant E(S_n^{n/2})$ with equality if and only if $G = S_n^{n/2}$.

Proof. *Case (i)* $n/2 = 2h + 1$ and $l = 2r + 1 \leqslant n/2$.

When $l = n/2$, we have $G = S_n^{n/2}$ since G has n vertices and every vertex of C_l is saturated. Thus, $E(G) = E\left(S_n^{n/2}\right)$. Next, we consider $l < n/2$.

Since $b_{2k}\left(S_n^{n/2}\right) = m\left(S_n^{n/2},k\right)$ and $b_{2k}(G) = m(G,k)$, from lemma 2, we have

$$b_{2k}(G) \geqslant b_{2k}\left(S_n^{n/2}\right). \tag{12}$$

The equality in (12) does not hold for all values of k since $G \neq S_n^{n/2}$. Since

$$b_{2k+1}\left(S_n^{n/2}\right) = \begin{cases} 0, & 2k+1 < n/2 \\ 2m\left(S_n^{n/2} - C_{n/2}, k-h\right), & 2k+1 \geqslant n/2 \end{cases}$$

and $S_n^{n/2} - C_{n/2}$ is $n/2$ isolated vertices, we have

$$b_{2k+1}\left(S_n^{n/2}\right) = \begin{cases} 2, & k = h \\ 0, & k \neq h \end{cases}. \tag{13}$$

Since

$$b_{2k+1}(G) = \begin{cases} 0, & 2k+1 < l \\ 2m(G - C_l, k - r), & 2k+1 \geqslant l \end{cases}, \tag{14}$$

we consider the case of $k = h$. Because every vertex of C_l is saturated, the vertices of C_l are incident with at most l edges of $M(G)$. It is noted that $|M(G)| = n/2$. So at least $n/2 - l$ independent edges of $M(G)$ are contained in $G - C_l$ as its subgraph. We have $m(G - C_l, n/2 - l) \geqslant 1$. Furthermore, since $l < n/2$, we have $(n/2 - l) - (h - r) = \frac{1}{2}(n/2 - l) > 0$. Therefore, $m(G - C_l, h - r) \geqslant m(G - C_l, n/2 - l)$. Obviously, $m(G - C_l, h - r) \geqslant 1$. Thus, we get

$$b_{2k+1}(G) \geqslant \begin{cases} 2, & k = h \\ 0, & k \neq h \end{cases}. \tag{15}$$

By comparing (13) and (15), we have

$$b_{2k+1}(G) \geqslant b_{2k+1}\left(S_n^{n/2}\right). \tag{16}$$

It follows from (12) and (16) that $E(G) > E\left(S_n^{n/2}\right)$. Finally, we have $E(G) \geqslant E\left(S_n^{n/2}\right)$ with equality if and only if $G = S_n^{n/2}$.

Case (ii) $n/2 = 4h$ and $l = 2r + 1$.

Since $b_{2k}\left(S_n^{n/2}\right) = m\left(S_n^{n/2}, k\right) - 2m\left(S_n^{n/2} - C_{n/2}, k - 2h\right)$ and $S_n^{n/2} - C_{n/2}$ is $n/2$ isolated vertices, we have

$$b_{2k}(S_n^{n/2}) = \begin{cases} m\left(S_n^{n/2}, k\right) - 2, & k = 2h \\ \\ m\left(S_n^{n/2}, k\right), & k \neq 2h \end{cases}. \tag{17}$$

From $b_{2k}(G) = m(G, k)$ and lemma 2, we readily arrive at

$$b_{2k}(G) \geqslant b_{2k}\left(S_n^{n/2}\right). \tag{18}$$

The equality in (18) does not hold for all values of k. For example, $b_{4h}(G) > b_{4h}\left(S_n^{n/2}\right)$. It is noted that

$$b_{2k+1}(G) = 2m(G - C_l, k - r) > 0 = b_{2k+1}\left(S_n^{n/2}\right). \tag{19}$$

The equality in (19) does not hold for all values of k. For example, $b_{2r+1}(G) > b_{2r+1}\left(S_n^{n/2}\right)$. It follows from (18) and (19) that $E(G) > \left(S_n^{n/2}\right)$.

Case (iii) $n/2 = 4h$ and $l = 4j + 2$.

From $b_{2k}(G) = m(G,k) + 2m(G - C_l, k - 2j - 1)$, (17) and lemma 2, we have

$$b_{2k}(G) \geqslant b_{2k}\left(S_n^{n/2}\right). \tag{20}$$

The equality in (20) does not hold for all values of k. For example, $b_{4j+2}(G) > b_{4j+2}\left(S_n^{n/2}\right)$. It is noted that

$$b_{2k+1}(G) = b_{2k+1}\left(S_n^{n/2}\right) = 0. \tag{21}$$

It follows from (20) and (21) that $E(G) > E\left(S_n^{n/2}\right)$.

Case (iv) $n/2 = 4h + 2$ and $l = 4j + 2 \leqslant n/2$.

When $l = n/2$, from Case (i), we have $E(G) = E\left(S_n^{n/2}\right)$. Next, we consider $l < n/2$.

Since $b_{2k}\left(S_n^{n/2}\right) = m(S_n^{n/2}, k) + 2m(S_n^{n/2} - C_{n/2}, k - 2h - 1)$ and $S_n^{n/2} - C_{n/2}$ is $n/2$ isolated vertices, it follows that

$$b_{2k}\left(S_n^{n/2}\right) = \begin{cases} m(S_n^{n/2}, k) + 2, & k = 2h + 1 \\ m(S_n^{n/2}, k), & k \neq 2h + 1 \end{cases}. \tag{22}$$

Since $b_{2k}(G) = m(G,k) + 2m(G - C_l, k - 2j - 1)$, we consider the case of $k = 2h + 1$. From Case (i), we have $m(G - C_l, n/2 - l) \geqslant 1$. Furthermore, since $l < n/2$, we have $(n/2 - l) - [(2h + 1) - (2j + 1)] = \frac{1}{2}(n/2 - l) > 0$. Therefore, $m(G - C_l, (2h + 1) - (2j + 1)) \geqslant m(G - C_l, n/2 - l)$. Obviously, $m(G - C_l, (2h + 1) - (2j + 1)) \geqslant 1$. Thus, we have

$$b_{2k}(G) \geqslant \begin{cases} m(G,k) + 2, & k = 2h + 1 \\ m(G,k), & k \neq 2h + 1 \end{cases}. \tag{23}$$

By comparing (22) and (23) and from lemma 2, we have

$$b_{2k}(G) \geqslant b_{2k}\left(S_n^{n/2}\right). \tag{24}$$

The equality in (24) does not hold for all values of k since $G \neq S_n^{n/2}$. It is noted that

$$b_{2k+1}(G) = b_{2k+1}\left(S_n^{n/2}\right) = 0. \tag{25}$$

It follows from (24) and (25) that $E(G) > E\left(S_n^{n/2}\right)$. Finally, we have $E(G) \geqslant E\left(S_n^{n/2}\right)$ with equality if and only if $G = S_n^{n/2}$.

By combining the aforementioned results, theorem 1 is proved.

Theorem 1 shows partial results for $l > n/2$. Next, a further discussion will be conducted.

Lemma 3. For a given n $(n \geqslant 6)$, when $l > n/2$, $\widehat{G}$ is $P_{n/2+1}$ or the union of disjoint paths whose total length is $n/2$ and there are two edges e_1 and e_2 of C_l which are adjacent to 3 edges in $M(G)$ and to at most 2 edges in $Q(G)$.

Proof. By contradiction. If all the vertices of C_l were attached by at least one edge, we would have $n \geqslant 2l$. If only one vertex of C_l were attached by no edge, we would have $n \geqslant (l-1) + l = 2l - 1$. However, $l > n/2$ is the prerequisite for lemma 3. Therefore, it can be concluded that at least two vertices of C_l, denoted by x and y, are attached by no edge. Next, we prove that x and y should be adjacent. If x were not adjacent to y, x and its adjacent vertex z would be matched since $G \in \mathcal{H}_n^l$. z would be attached by a path of length 2 at least. The analysis on y is the same as that for x. So we would get $n \geqslant 2l$, a contradition. Thus, x and y are matched and $xy \in M(G)$. Because $\Delta(\widehat{G}) \leqslant 2$, $\widehat{G}$ is $P_{n/2+1}$ or the union of disjoint paths whose total length is $n/2$. Denote by e_1 and e_2 the two edges of C_l which are adjacent to xy. It is clear that e_1 and e_2 satisfy lemma 3. Lemma 3 has been proved.

Let $R_n^{n/2+1}$ be a graph in which only two adjacent vertices in $C_{n/2+1}$ are attached by no edges and each of the others by a pendant edge. Obviously, $R_n^{n/2+1}$ satisfies lemma 3. For instance, R_6^4, $\widehat{R}_6^4$, x, y, e_1 and e_2 are shown in figure 2.

Lemma 4. For a given n $(n \geqslant 6)$, when $l > n/2$, we have $m(G,k) \geqslant m\left(R_n^{n/2+1}, k\right)$ with equality for all values of k if and only if $G = R_n^{n/2+1}$.

Proof. It is noted that

$$m(G,k) = \sum_{i=0}^{n/2} m(\widehat{G}, i) \cdot \binom{n/2 - j}{k-i}$$
$$= \binom{n/2}{k} + \frac{n}{2} \cdot \binom{n/2-2}{k-1} + \sum_{i=2}^{n/2} m(\widehat{G}, i) \cdot \binom{n/2-j}{k-i}. \qquad (26)$$

For any $G \in \mathcal{H}_n^l$, the first and second term of the expansion in (26) are fixed. Next, we consider $m(G,k)$ for $2 \leqslant i \leqslant n/2$.

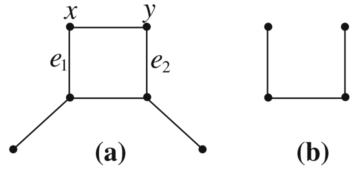

Figure 2. (a) R_6^4, (b) $\widehat{R}_6^4$.

As stated in lemma 3, e_1 and e_2 are adjacent to 3 edges in $M(G)$ and to at most 2 edges in $Q(G)$. So we divide all the i-matchings of $\widehat{G}$ into two groups: one containing e_1 and e_2 and the other not containing e_1 or e_2. The numbers of i-matchings of $\widehat{G}$ in the first and second group are denoted by $m_1(\widehat{G}, i)$ and $m_2(\widehat{G}, i)$, respectively. Obviously, $m_1(\widehat{G}, i) + m_2(\widehat{G}, i) = m(\widehat{G}, i)$. From lemma 3, $\widehat{G}$ is $P_{n/2+1}$ or the union of disjoint paths whose total length is $n/2$. Therefore, $m_1(\widehat{G}, i)$ is the numbers of $(i-2)$-matchings in $P_{n/2-3}$ or of the union of disjoint paths whose total length is at least $n/2-4$. Thus, $m_1(\widehat{G}, i)$ reaches its minimum when $G = R_n^{n/2+1}$. Since e_1 and e_2 are adjacent to 3 edges in $M(G)$ and the other $(i-2)$-matchings of $\widehat{G}$ to at most $2i-4$ edges in $M(G)$, we have $j \leqslant 2i-1$. When $G = R_n^{n/2+1}$, we have $j = 2i-1$ since e_1 and e_2 are adjacent to 3 edges in $M\left(R_n^{n/2+1}\right)$ and the other $(i-2)$-matchings of $\widehat{R}_n^{n/2+1}$ to exactly $2i-4$ edges in $M\left(R_n^{n/2+1}\right)$. For the second group, using the approach similar to that for $m_1(\widehat{G}, i)$, we get that $m_2(\widehat{G}, i)$ reaches its minimum when $G = R_n^{n/2+1}$. Since any i-matching of $\widehat{G}$ is adjacent to at most $2i$ edges in $M(G)$, we have $j \leqslant 2i$. When $G = R_n^{n/2+1}$, we have $j = 2i$ since any i-matching of $\widehat{R}_n^{n/2+1}$ is adjacent to exactly $2i$ edges in $M(R_n^{n/2+1})$. Thus, we have

$$\begin{aligned}
&\sum_{i=2}^{n/2} m(\widehat{G}, i) \cdot \binom{n/2-j}{k-i} \\
&\geqslant \sum_{i=2}^{n/2} \left\{ m_1\left(\widehat{G}, i\right) \cdot \binom{n/2-2i+1}{k-i} + m_2(\widehat{G}, i) \cdot \binom{n/2-2i}{k-i} \right\} \\
&\geqslant \sum_{i=2}^{n/2} \left\{ m_1\left(\widehat{R}_n^{n/2+1}, i\right) \cdot \binom{n/2-2i+1}{k-i} + m_2\left(\widehat{R}_n^{n/2+1}, i\right) \cdot \binom{n/2-2i}{k-i} \right\}
\end{aligned} \tag{27}$$

with equalities if and only if $G = R_n^{n/2+1}$.

From (26) and (27), it follows that for all values of k,

$$m(G, k) \geqslant m(R_n^{n/2+1}, k) \tag{28}$$

with equality if and only if $G = R_n^{n/2+1}$. Lemma 4 has been proved.

From lemma 4, we have theorem 2 as follows.

Theorem 2. For a given n $(n \geqslant 6)$, when $n/2 + 1 = 4h$ and $l = 2r + 1 > n/2$ or $l = 4j + 2 > n/2$, we have $E(G) > E(R_n^{n/2+1})$.

Proof. *Case (i)* $n/2 + 1 = 4h$ and $l = 2r + 1 > n/2$.

Since $b_{2k}\left(R_n^{n/2+1}\right) = m\left(R_n^{n/2+1}, k\right) - 2m\left(R_n^{n/2+1} - C_{n/2+1}, k-2h\right)$ and $R_n^{n/2+1} - C_{n/2+1}$ is $n/2-1$ isolated vertices, we have

$$b_{2k}(R_n^{n/2+1}) = \begin{cases} m(R_n^{n/2+1}, k) - 2, & k = 2h \\ m(R_n^{n/2+1}, k), & k \neq 2h \end{cases}. \tag{29}$$

From $b_{2k}(G) = m(G, k)$ and lemma 4, it follows that

$$b_{2k}(G) \geqslant b_{2k}(R_n^{n/2+1}). \tag{30}$$

The equality in (30) does not hold for all values of k. For example, $b_{4h}(G) > b_{4h}(R_n^{n/2+1})$. It is noted that

$$b_{2k+1}(G) = 2m(G - C_l, k - r) \geqslant 0 = b_{2k+1}\left(R_n^{n/2+1}\right). \tag{31}$$

The equality in (31) does not hold for all values of k. For example, $b_{2r+1}(G) > b_{2r+1}(R_n^{n/2+1})$. It follows from (30) and (31) that $E(G) > E(R_n^{n/2+1})$.

Case (ii) $n/2 + 1 = 4h$ and $l = 4j + 2 > n/2$.

Since $b_{2k}(G) = m(G, k) + 2m(G - C_l, k - 2j - 1)$, by lemma 4, (29) and the approach similar to Case (i), we have

$$b_{2k}(G) \geqslant b_{2k}\left(R_n^{n/2+1}\right). \tag{32}$$

The equality in (32) does not hold for all values of k. For example, $b_{4j+2}(G) > b_{4j+2}(R_n^{n/2+1})$. It is noted that

$$b_{2k+1}(G) = b_{2k+1}\left(R_n^{n/2+1}\right) = 0. \tag{33}$$

It follows from (32) and (33) that $E(G) > E\left(R_n^{n/2+1}\right)$.

By combining Cases (i) and (ii), theorem 2 is proved.

4. Conclusion

By comparing the absolute values of the coefficients of the characteristic polynomials of graphs, the unicyclic Hückel molecular graph possessing Kekulé structures with the minimal energy has been obtained for six cases which are given in theorems 1 and 2. The other unsolved cases remain a mathematical task for the future.

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