Fully-angular polyhex chains with minimal total $\pi$-electron energy

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Abstract

By Hückel molecular orbital (HMO) theory, the calculation of the total energy of all $\pi$-electrons in conjugated hydrocarbons can be reduced to that of $E(G) = |\lambda_1| + |\lambda_2| + \cdots + |\lambda_n|$, where $\lambda_i$ are the eigenvalues of the corresponding graph $G$. Denote by $\Psi_n$ the set of all fully-angular polyhex chains with $n$ hexagons. In this paper, we show that $H_n$ has the minimum total $\pi$-electron energy among chains in $\Psi_n$, where $H_n$ is the helicene chain.

Keywords: Fully-angular polyhex chain; Helicene chain; Energy of graph

1. Introduction

In chemistry, the experimental heats from the formation of conjugated hydrocarbons are closely related to the total $\pi$-electron energy (a theoretically calculated quantity). In fact, it is often repeated claim that the HMO (Hückel Molecular Orbital) $\pi$-electron energies are in good agreement with experimental enthalpies of the respective conjugated compounds [11]. The general theory of the HMO total $\pi$-electron energy as well as its chemical applications are outlined in full detail in the book [12]. The calculation of the total energy of all $\pi$-electrons in conjugated hydrocarbons can be reduced to (within the framework of HMO approximation) that of...
Fig. 1. The smallest helicenic chain—the helicene chain.

\[ E(G) = |\lambda_1| + |\lambda_2| + \cdots + |\lambda_n|, \]
where \( \lambda_i \) are the eigenvalues of the corresponding graph \( G \).

From a chemical point of view, it is of interest to find the extremal values of \( E \) for significant classes of molecular graphs. For recent results on this topic, one can refer to [13–20].

A hexagonal system is a 2-connected plane graph whose every interior face is bounded by a regular hexagon of unit length 1. Hexagonal systems are of great importance for theoretical chemistry because they are the natural graph representation of benzenoid hydrocarbons [9–11]. A hexagonal system is said to be catacondensed if it has no three hexagons share a common vertex. A hexagon \( C \) of a catacondensed hexagonal system has either one, two or three neighboring hexagons. If \( C \) has one neighboring hexagon, then it is said to be terminal; and if it has three neighboring hexagons, to be branched. A catacondensed hexagonal system possessing at least one branched hexagon is said to be a branched catacondensed hexagonal system. A catacondensed hexagonal system without branched hexagons is called a hexagonal chain [11].

More generally, a polyhex chain is a 2-connected geometrical system of congruent regular hexagons in which each hexagon has either one or two neighboring hexagons. The polyhex chains are divided into (geometrically planar) hexagonal chains and (geometrically non-planar) helicenic chains. Clearly, a helicenic chain is a polyhex chain with overlapping edges if drawn in a plane. The other concepts concerning hexagonal chains can be defined for polyhex chains similarly. Helicenic chains correspond a type of hydrocarbons. These chemical compounds have attracted much attention among chemists. M.S. Newman, W.B. Lutz and D. Lednicer synthesized first such hydrocarbon \( C_{26}H_{16} \) as shown in Fig. 1 [1,2]. Then many helicenic chains have been synthesized, actually, up to helicenic chain with fourteen hexagons [3]. The enumeration of polyhex chains, in addition, has been studied extensively by mathematical chemists, such as Balaban, Brunvoll, Cyvin and Harrary [4–7]. Now we attempt to consider the extremal problem of polyhex chains with regard to the total \( \pi \)-electron energy. Examining the proof in [19,20] we can see that the main results in [19,20] are still valid for the polyhex chain. Namely, we have the following theorems.

**Theorem A.** Let \( B_n \) be a polyhex chain with \( n \) hexagons, if \( B_n \neq L_n \) then \( E(B_n) > E(L_n) \), where \( L_n \) denotes the linear hexagonal chain.

**Theorem B.** For any polyhex chain \( B_n \neq Z_n \) with \( n \) hexagons, \( E(B_n) < E(Z_n) \), where \( Z_n \) denotes the zig-zag hexagonal chain.

Hexagons being adjacent to exactly two other hexagons are classified as angularly or linearly connected. A hexagon \( C \) being adjacent to exactly two other hexagons possesses two vertices of degree 2. If these two vertices are adjacent, then the hexagon \( C \) is angularly connected. If these two vertices are not adjacent, then the hexagon \( C \) is linearly connected. In this paper, we will consider a subset of polyhex chains—fully-angular polyhex chains in which all the hexagons are
angularly connected except two terminal hexagons. From theorem $B$ we see that the fully-angular polyhex chains with the maximum total $\pi$-energy are zigzag chains. In the further, we will determine the fully-angular polyhex chains with minimum total $\pi$-electron energy. We show that, for any fully-angular polyhex chain $B_n$, $E(B_n) \geq E(H_n)$, where $H_n$ is the helicene chain. Moreover, equality holds only if $B_n = H_n$. Note that the extremal fully-angular polyhex chains with respect to Hosoya’s index, Merrifield–Simmons index and the largest eigenvalue were determined by [21,22].

2. Notations and auxiliary results

The degree of any vertex of a polyhex chain $B_n$ is either 2 or 3. Denote $V_3 = V_3(B_n)$ the set of the vertices in $B_n$ with degree 3. The subgraph of $B_n$ induced by $V_3$ is denoted by $B_n[V_3]$. A polyhex chain $B_n$ is fully angular if and only if $B_n[V_3]$ is a tree. A polyhex chain $B_n$ is a zig-zag or helicene if and only if $B_n[V_3]$ is a path or a comb, respectively. If $B_n[V_3]$ consists of parallel edges then $B_n$ is said to be linear. Put $\Phi_n = \{B_n: B_n$ is a polyhex chain with $n$ hexagons$\}$. We write $B_n = C_1C_2 \cdots C_n$ if $C_1, C_2, \ldots, C_n$ are the $n$ hexagons of $B_n$, where $C_i$ and $C_{i+1}$ are adjacent for $i = 1, 2, \ldots, n - 1$. Any polyhex chain $B_n$, where $n \geq 3$, can be obtained from an appropriate chosen graph $B_{n-1} \in \Phi_{n-1}$ by attaching to it a new hexagon when we oriented the common edge of $C_{n-1}$ and $C_{n-2}$ to be vertical. There are three possible types of attachment: $\alpha$-type, $\beta$-type and $\gamma$-type, see Fig. 2.

Let $B$ is a polyhex chain. We denote by $[B]_\theta$ the polyhex chain obtained from $B$ by $\theta$-type attaching to it a new hexagon, where $\theta \in \{\alpha, \beta, \gamma\}$. Obvious, each $B_n$ with $n \geq 2$ can be written as $\cdots [[[[[L_2]_{\theta_2}]_{\theta_3}] \cdots]_{\theta_{n-1}}$, where $\theta_j \in \{\alpha, \beta, \gamma\}$. We set $B_n = \beta\theta_2\theta_3 \cdots \theta_{n-1}$ in short. For each $j$, if $\theta_j = \beta$, then $B_n = L_n$; if $\theta_j \in \{\alpha, \gamma\}$ and $\theta_j \neq \theta_{j+1}$, then $B_n = Z_n$; and if $\theta_j = \alpha$ (or $\gamma$) then $B_n = H_n$, see Fig. 3. Clearly, $B_1 = \{L_1 = Z_1 = H_1\}$, $B_2 = \{L_2 = Z_2 = H_2\}$ and $B_3 = \{L_3, Z_3 = H_3\}$.
Set 
\[
\tilde{\theta} = \begin{cases} 
\gamma & \text{if } \theta = \alpha, \\
\beta & \text{if } \theta = \beta, \\
\alpha & \text{if } \theta = \gamma. 
\end{cases}
\]

It follows that \( B_n = \beta \theta_2 \theta_3 \cdots \theta_{n-1} \) is isomorphic to \( \overline{B_n} = \beta \tilde{\theta}_2 \tilde{\theta}_3 \cdots \tilde{\theta}_{n-1} \). A polyhex chain \( B_n \) is fully angular if each mode of attachment of the hexagons is realized with either \( \alpha \) type or \( \gamma \) type. Denote by \( \Psi_n \) the set of all fully-angular polyhex chains with \( n \) hexagons. Note that for \( n = 1 \) or 2, \( \Phi_n = \Psi_n \), and both sets contain exactly one element. So, we always suppose that \( n \geq 3 \) in the following.

If \( uv \) is an edge of \( G \) we write \( G - uv \) for the graph obtained from \( G \) by deleting \( uv \). For \( v \in V(G) \), \( G - v \) denotes the graph obtained from \( G \) by deleting the vertex \( v \) and all edges incident with \( v \). Denote by \( N(x) \) the set \( \{ y \in V(G) : xy \in E(G) \} \). Let \( S \) be a subset of \( V(G) \). The subgraph of \( G \) induced by \( S \) is denoted by \( G[S] \), and \( G[V \setminus S] \) is denoted by \( G - S \). If \( G \) is a bipartite graph then the characteristic polynomial of it can be written as [8,9]

\[
\phi(G) = \sum_{k=0}^{\lfloor n/2 \rfloor} (-1)^k b(G,k)x^{n-2k},
\]

where \( n \) is the number of vertices of \( G \), \( b(G,0) = 1 \) and \( b(G,k) \geq 0 \) for all \( 0 \leq k \leq \lfloor n/2 \rfloor \). For the other \( k \), we assume \( b(G,k) = 0 \) for convenience. In [13], Gutman define a quasi-order relation “\( \succeq \)” (i.e., a reflexive and transitive relation) over the set of all bipartite graphs in the study of the total \( \pi \)-electron energy of graphs, i.e., if \( G_1 \) and \( G_2 \) are bipartite graphs whose characteristic polynomials are in the form (1) then

\[
G_1 \succeq G_2 \iff b(G_1,k) \geq b(G_2,k) \quad \text{for all } k \geq 0.
\]

In particular, if \( G_1 \succeq G_2 \) and there exists \( k \) such that \( b(G_1,k) > b(G_2,k) \) then we write \( G_1 \succ G_2 \). It is well known that for two bipartite graphs \( G_1 \) and \( G_2 \), if \( G_1 \succeq G_2 \) then \( E(G_1) \geq E(G_2) \); if \( G_1 \succ G_2 \) then \( E(G_1) > E(G_2) \) [12,20].

The following lemmas will be used in the sequel (see [8,9]).

**Lemma 1.** Let \( G \) be composed by two components \( G_1 \) and \( G_2 \), then the characteristic polynomial of \( G \) is \( \phi(G) = \phi(G_1)\phi(G_2) \).

**Lemma 2.** Let \( G \) be a graph and \( uv \) an edge of \( G \), then the characteristic polynomial

\[
\phi(G) = \phi(G - uv) - \phi(G - u - v) - 2 \sum_{C_j \in C_{uv}} \phi(G - C_j),
\]

where \( C_{uv} \) is the set of cycles of \( G \) containing the edge \( uv \).

**Lemma 3.** Let \( G \) be a graph and \( u \) a vertex of \( G \), then the characteristic polynomial

\[
\phi(G) = x\phi(G - u) - \sum_{w \in N(u)} \phi(G - u - w) - 2 \sum_{C_j \in C_u} \phi(G - C_j),
\]

where \( C_u \) denotes the set of cycles of \( G \) containing the vertex \( u \).
Lemma 4. Let \( u \) and \( v \) be adjacent vertices in a graph \( G \). Then
\[
\phi(G) = \phi(G - uv) - \phi(G - u - v)
\]
\[
- 2\sqrt{\phi(G - u)\phi(G - v) - \phi(G - uv)\phi(G - u - v)},
\]
where the square root is interpreted as a polynomial with a positive coefficient in the highest term.

Lemma 5. Let \( u \) and \( v \) be adjacent vertices in a graph \( G \). Then
\[
4(\phi(G - u)\phi(G - v) - \phi(G)\phi(G - u - v)) = (\phi(G) - \phi(G - uv) - \phi(G - u - v))^2.
\]

Lemma 6. [19] Let \( G \) and \( G' \) be two bipartite graphs of order \( n \) with the characteristic polynomials \( \phi(G) = \sum_{i=0}^{\lfloor n/2 \rfloor} b_i x^{n-2i} \) and \( \phi(G') = \sum_{i=0}^{\lfloor n/2 \rfloor} b'_i x^{n-2i} \), respectively, then \( G \succeq G' \) iff \( b_0 - b'_0 = 0 \) and \((-1)^i (b_i - b'_i) \geq 0 \) for \( i = 1, 2, \ldots, \lfloor n/2 \rfloor \); \( G \succ G' \) iff \( G \succeq G' \) and there is an \( i \in \{1, 2, \ldots, \lfloor n/2 \rfloor \} \) such that \((-1)^i (b_i - b'_i) > 0 \).

Lemma 7. [20] Let \( G \) be a bipartite graph with \( n \) vertices and \( uv \) is an edge of \( G \). Suppose \( u \) does not belong to any cycle of size 4s. We define \( f(x) = \sum_{i=0}^{\lfloor n/2 \rfloor} f_i x^{n-2i} = \phi(G) - x\phi(G - u) + \phi(G - v) \), where \( \phi(G) \) is the characteristic polynomial of \( G \). Then \( f_0 = 0 \) and \((-1)^i f_i \geq 0 \) for \( i = 1, 2, \ldots, \lfloor n/2 \rfloor \). Furthermore, if \( v \) is not the only neighbor then \( f_1 < 0 \).

3. Main results

Lemma 8. If \( B_n \in \Psi_n \ (n \geq 2) \) is obtained from \( B_{n-1} \in \Psi_{n-1} \) by attaching to it a new hexagon which is labelled as in Fig. 4(a), then

(i) [20] \( \phi(B_n - e - d) < \phi(B_n - c - d) \) and \( \phi(B_n - e - d) < \phi(B_n - e - f) \);
(ii) \( \phi(B_n - e) < \phi(B_n - f) \);
(iii) \( \phi(B_n - d) < \phi(B_n - c) \).

![Fig. 4.](image-url)

(a) \( B_n \)  
(b) \( B_n^{(n-2)} \)  
(c) \( B_n^{(n-2)} \)

(d) \( B_n^{(n-3)} \)
(e) \( B_n^{(n-3)} \)
Proof. Let $B_n = C_1C_2\cdots C_n$ and let $B_{n-k} = C_{k+1}C_{k+2}\cdots C_n$ be a sub-chain of $B_n$. If $C_k$ is attached to $B_{n-k}$ by $\gamma$-type then we denote $B_n$ by $B_n^{k\gamma}$, and if $C_k$ is attached to $B_{n-k}$ by $\alpha$-type then we denote $B_n$ by $B_n^{k\alpha}$ (as shown in Fig. 4(b) and (c), respectively). Note that (iii) is equivalent to (ii). We only need prove (ii) by induction on $n$.

When $n = 2, 3$, by simple computing, from Lemmas 1–2 we know that
\[
\phi(B_2 - e) = x^9 - 9x^7 + 25x^5 - 26x^3 + 8x,
\]
\[
\phi(B_2 - f) = x^9 - 9x^7 + 26x^5 - 29x^3 + 11x,
\]
\[
\phi(B_3^{1\gamma} - f) = 26x - 129x^3 + 224x^5 - 181x^7 + 73x^9 - 14x^{11} + x^{13},
\]
\[
\phi(B_3^{1\alpha} - e) = 24x - 116x^3 + 208x^5 - 174x^7 + 72x^9 - 14x^{11} + x^{13},
\]
\[
\phi(B_3^{1\gamma} - f) = 29x - 135x^3 + 228x^5 - 182x^7 + 73x^9 - 14x^{11} + x^{13}
\]
and
\[
\phi(B_3^{1\gamma} - e) = 21x - 113x^3 + 207x^5 - 174x^7 + 72x^9 - 14x^{11} + x^{13}.
\]
Clearly, (ii) holds.

When $n \geq 4$, we suppose that (ii) is true for $n - 1$. Using Lemmas 1 and 2 to $B_n - f$ and $B_n - e$, respectively, we get
\[
\phi(B_n - f) = (x^3 - 2x)\phi(B_{n-1}) - (x^2 - 1)\phi(B_{n-1} - s_{n-1})
\]
and
\[
\phi(B_n - e) = (x^3 - x)\phi(B_{n-1}) - (x^2 - 1)\phi(B_{n-1} - r_{n-1}) - x^2\phi(B_{n-1} - s_{n-1})
\]
\[+ x\phi(B_{n-1} - r_{n-1} - s_{n-1}),
\]
which imply that
\[
\phi(B_n - f) - \phi(B_n - e) = -x\left[\phi(B_{n-1}) - x\phi(B_{n-1} - r_{n-1}) + \phi(B_{n-1} - r_{n-1} - s_{n-1})\right]
\]
\[+ \left[\phi(B_{n-1} - s_{n-1}) - \phi(B_{n-1} - r_{n-1})\right]. \quad (2)
\]
Thus, there are two cases which need to be considered (see Fig. 4(b) and (c)). For Fig. 4(b), since $\phi(B_{n-1} - s_{n-1}) > \phi(B_{n-1} - r_{n-1})$ by the inductive hypotheses, then checking the highest order of each term of the both sides of (2), we know that (ii) holds by Lemmas 6 and 7. And for Fig. 4(c), it follows that $\phi(B_{n-1} - s_{n-1}) < \phi(B_{n-1} - r_{n-1})$ by the inductive hypotheses. So, we continue to consider the subcases of Fig. 4(c), i.e., Fig. 4(d) and (e).

From (2) and Lemmas 1–3 we deduce that
\[
\phi(B_n - f) - \phi(B_n - e)
\]
\[= x\phi(B_{n-1} - r_{n-1} - s_{n-2})
\]
\[+ 2x \sum_{c_j \in C_{r_{n-1}}} \phi(B_{n-1} - c_j) + \phi(B_{n-1} - s_{n-1}) - \phi(B_{n-1} - r_{n-1})
\]
\[= x\phi(B_{n-2}) + (x^4 - 3x^2 + 1)\phi(B_{n-2} - s_{n-2}) + (-x^3 + 2x)\phi(B_{n-2} - r_{n-2} - s_{n-2})
\]
\[+ \phi(B_{n-2} - r_{n-2}) + 2x \sum_{c_j \in C_{r_{n-1}}} \phi(B_{n-1} - c_j). \quad (3)
\]
And, by Lemmas 4 and 5,
\[2 \sum_{c_j \in C_{r_{n-1}}} \phi(B_{n-1} - c_j) = \phi(B_{n-2} - r_{n-2}s_{n-2}) + \phi(B_{n-2} - r_{n-2} - s_{n-2}) - \phi(B_{n-2}).
\]
Note that, for Fig. 4(d), we have
\[ \phi(B_{n-2} - r_{n-2}s_{n-2}) = x\phi(B_{n-2} - r_{n-2}) - \phi(B_{n-2} - r_{n-2} - t_{n-2}) \]
by Lemmas 1–2 and
\[ \phi(B_{n-2} - r_{n-2} - s_{n-2}) > \phi(B_{n-2} - r_{n-2} - t_{n-2}) \]
by (i); and for Fig. 4(e), we have
\[ \phi(B_{n-2} - r_{n-2}sg_{n-2}) = x\phi(B_{n-2} - s_{n-2}) - \phi(B_{n-2} - s_{n-2} - t_{n-2}) \]
by Lemmas 1–2 and
\[ \phi(B_{n-2} - r_{n-2} - s_{n-2}) > \phi(B_{n-2} - s_{n-2} - t_{n-2}) \]
by (i). So, substituting the expressions of \( 2 \sum c_j \in C_{r_{n-1}} \), \( \phi(B_{n-1} - c_j) \) and \( \phi(B_{n-2} - r_{n-2}s_{n-2}) \)
into (3), and checking the highest order of each term of the right side of (3) we deduce that
\[
\phi(B_n - f) - \phi(B_n - e) = f^{(1)}_{4n-3}(x) + (x^2 - 1) \\
\times \left[ (x^2 - 1)(\phi(B_{n-2} - s_{n-2}) - \phi(B_{n-2} - r_{n-2})) - x\phi(B_{n-2} - r_{n-2} - s_{n-2}) \right],
\]
where \( f^{(1)}_{4n-3}(x) \) has the form (1) with order \( 4n - 3 \).

Since, for Fig. 4(d), \( \phi(B_{n-2} - s_{n-2}) > \phi(B_{n-2} - r_{n-2}) \) by the inductive hypotheses. Then, from (4) and Lemma 6 it follows that (ii) is true. And for Fig. 4(e), we know that \( \phi(B_{n-2} - s_{n-2}) < \phi(B_{n-2} - r_{n-2}) \) by the inductive hypotheses. Thus, we need to consider the subcases of Fig. 4(e), namely, \( B^{(n-4)}_{a} \) and \( B^{(n-4)}_{n} \).

Using Lemmas 1 and 2 to the right side of (4) we get
\[
\phi(B_n - f) - \phi(B_n - e) = f^{(2)}_{4n-3}(x) - (x^2 - 1)^2 \\
\times \left[ (x^2 - 1)(\phi(B_{n-3} - s_{n-3}) - \phi(B_{n-3} - r_{n-3})) - x\phi(B_{n-3} - r_{n-3} - s_{n-3}) \right],
\]
where \( f^{(2)}_{4n-3}(x) \) has the form (1) with order \( 4n - 3 \).

Similarly, for \( B^{(n-4)}_{n} \), we know that (ii) holds by induction, Lemma 6 and (5); and for \( B^{(n-4)}_{a} \), we need to consider its subcases. Again using Lemmas 1–2 to the right side of (5) we get the form
\[
\phi(B_n - f) - \phi(B_n - e) = f^{(m)}_{4n-3}(x) + (-1)^{m-1}(x^2 - 1)^m \\
\times \left[ (x^2 - 1)(\phi(B_{n-(m+1)} - s_{n-(m+1)}) - \phi(B_{n-(m+1)} - r_{n-(m+1)})) \\
- x\phi(B_{n-(m+1)} - r_{n-(m+1)} - s_{n-(m+1)}) \right],
\]
where \( f^{(m)}_{4n-3}(x) \) has the form (1) with order \( 4n - 3 \) and \( m = 3 \).

So, this partition method will continue until \( m = n - 2 \). In this case, by \( \phi(B_1 - s_1) = \phi(B_1 - r_1) \) we have \( \phi(B_n - f) - \phi(B_n - e) = f^{(n-1)}_{4n-3}(x) \), where \( f^{(n-1)}_{4n-3}(x) \) has the form (1) with order \( 4n - 3 \). Hence (ii) is true by Lemma 6. The proof of Lemma 8 is complete. □
Lemma 9. Let $A_1$ and $B_1$ be two fully-angular polyhex chains with $j$ and $n - j$ hexagons, respectively. Denote by $A$ the polyhex chain induced by the former $j - 1$ hexagons of $A_1$. If $G_{\theta}$, where $\theta = \alpha$ (or $\gamma$), is obtained from $A_1$ (or $B_1$) by identifying the vertices $e, f$ with $u, v$ (or $q, p$), respectively (as shown in Fig. 5), then

$$
\sum_{C \in C_{uv}(G_\gamma)} \phi(G_\gamma - C) = \sum_{C' \in C_{pq}(G_\alpha)} \phi(G_\alpha - C').
$$

Proof. It is easy to see that, for each $C \in C_{uv}(G_\gamma)$ there is $C' \in C_{pq}(G_\alpha)$ and bijection $\eta : C_{uv}(G_\gamma) \rightarrow C_{pq}(G_\alpha)$ such that $\phi(G_\gamma - C) = \phi(G_\alpha - C')$. In fact, if $C$ is a cycle in $C_{uv}(G_\gamma)$, then $C'$ is defined to be the cycle of $G_\alpha$ which contains the same hexagons in $A$ and $B_1$ as $C$. Thus, Lemma 9 is proved. \qed

Theorem 10. For any $n \geq 1$ and any $B_n \in \Psi_n$, we have $E(H_n) \leq E(B_n)$ with relevant equality holding only if $B_n = H_n$.

Proof. Let $B_n \in \Psi_n$ be the polyhex chain with the minimum total $\pi$-energy. Then $B_n$ can be written as $B_n = \beta \theta_2 \theta_3 \cdots \theta_{n-1}$ with $\theta_j \in \{\alpha, \gamma\}, 2 \leq j \leq n - 1$. Assume, without loss of generality, that $\theta_2 = \alpha$ (otherwise, we consider $B_n = \beta \theta_2 \theta_3 \cdots \theta_{n-1}$). Suppose that $B_n \neq H_n$. Since $\Psi_1 = \{H_1\}, \Psi_2 = \{H_2\}$ and $\Psi_3 = \{H_3\}$, thus $n \geq 4$. Let $\theta_j$ be the first element of $\theta_2, \theta_3, \ldots, \theta_{n-1}$ such that $\theta_j = \gamma$. Thus, $J \geq 3$ and $B_n = \beta \alpha \xi \cdots \alpha \gamma \theta_{j+1} \cdots \theta_{n-1}$. Set $G_\gamma = B_n = \beta \alpha \cdots \alpha \gamma \theta_{j+1} \cdots \theta_{n-1}$. Also, we write $G_\gamma = C_1 C_2 \cdots C_n$ if $C_1, C_2, \ldots, C_n$ are $n$ hexagons of $B_n$, where $C_i$ and $C_{i+1}$ are adjacent for $i = 1, 2, \ldots, n - 1$. Let $A = C_1 C_2 \cdots C_{j-1}$ and $B_1 = C_{j+1} C_{j+2} \cdots C_n$ (see Fig. 5). Note that $A = H_{j-1}$. Let $G_\alpha = \beta \alpha \cdots \alpha \alpha \xi \theta_{j+1} \theta_{j+2} \cdots \theta_{n-1}$ (as shown in Fig. 5). Using Lemma 2 to the edge $uv$ of $G_\gamma$, then by Lemmas 1 and 3 we have

$$
\phi(G_\gamma) = (x^2 - 1) \left[ \phi(A) \phi(B_1) - \phi(A - v_{j-1}) \phi(B_1 - e) \right]
- x \left[ \phi(A) \phi(B_1 - f) - \phi(A - v_{j-1}) \phi(B_1 - e - f) \right]
+ \phi(A - u_{j-1}) \phi(B_1) - \phi(A - u_{j-1} - v_{j-1}) \phi(B_1 - e) \right]
+ \left[ \phi(A - u_{j-1}) \phi(B_1 - f) - \phi(A - u_{j-1} - v_{j-1}) \phi(B_1 - e - f) \right]
- 2 \sum_{C \in C_{uv}} \phi(G_\gamma - C).
$$

Similarly, using Lemma 2 to edge $pq$ of $G_\alpha$ and by Lemmas 1 and 3 we get

$$
\phi(G_\alpha) = (x^2 - 1) \left[ \phi(A) \phi(B_1) - \phi(A - u_{j-1}) \phi(B_1 - e) \right]
- x \left[ \phi(A) \phi(B_1 - f) - \phi(A - u_{j-1}) \phi(B_1 - e - f) \right]
+ \phi(A - v_{j-1}) \phi(B_1) - \phi(A - u_{j-1} - v_{j-1}) \phi(B_1 - e) \right]
$$
\[+ \left[ \phi(A - v_{j-1})\phi(B_1 - f) - \phi(A - u_{j-1} - v_{j-1})\phi(B_1 - e - f) \right]\]
\[-2 \sum_{C' \in C_{pq}} \phi(G_\alpha - C').\]

Since \(\sum_{C \in C_{uv}} \phi(G_\gamma - C) = \sum_{C' \in C_{pq}} \phi(G_\alpha - C')\) by Lemma 9, then
\[
\phi(G_\gamma) - \phi(G_\alpha) = \left( \phi(A - u_{j-1}) - \phi(A - v_{j-1}) \right) \times \left[ -x \left( \phi(B_1) - x\phi(B_1 - e) + \phi(B_1 - e - f) \right) + \phi(B_1 - f) - \phi(B_1 - e) \right]
\]

If \(B_2\) is obtained from \(B_1\) by attaching edge \(ef\) to a new hexagon which is labelled as in Fig. 5, then, by Lemmas 1 and 2 we have
\[
\phi(G_\gamma) - \phi(G_\alpha) = \left( \phi(A - u_{j-1}) - \phi(A - v_{j-1}) \right) \left( \phi(B_2 - c) - \phi(B_2 - d) \right).
\]

Since, \(\phi(A - u_{j-1}) > \phi(A - v_{j-1})\) and \(\phi(B_2 - c) > \phi(B_2 - d)\) by Lemma 8, then, checking the highest order of each term of the both sides of the above equality, we have \(\phi(G_\gamma) > \phi(G_\alpha)\) by Lemma 6. It contradicts the minimum of \(G_\gamma\). So, the proof of Theorem 10 is complete. \(\square\)

Finally we would like to point out that the paper is the first one to deal with the extremal problem with regard to the total \(\pi\)-energy for helicenic polyhex.

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**References**


