On the sextet polynomial of fullerenes

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Abstract

We show that the sextet pattern count of every fullerene is strictly smaller than the Kekulé structure count. This proves a conjecture of Zhang and He [J. Math. Chem. 38(3):2005, p. 315–324].

1 Introduction

Fullerenes are cage polyhedral carbon molecules such that all faces are pentagons and hexagons. The icosahedral C_{60}, known as the *buckminsterfullerene*, was predicted by Osawa [13], and discovered by Kroto *et al.* [9]. A fullerene with no adjacent pentagons is said to satisfy the *isolated pentagon rule* (IPR), and is called an *IPR fullerene*. The buckminsterfullerene is the smallest IPR fullerene, and all the most stable fullerenes are IPR fullerenes. Since the discovery of the first fullerene molecule, fullerenes have been studied by scientists across many disciplines.

Various properties of fullerene molecules can be studied using mathematical tools and results. Thus, *fullerene graphs* were defined as 3-connected cubic plane graphs with all faces of size five or six; see e.g. the graph I_h in Figure 1. Such graphs are suitable models for fullerene molecules: carbon atoms are represented by vertices of the graph, whereas the edges represent bonds between adjacent atoms. It is known that there exists a fullerene graph on n vertices for every even $n \geq 20$, $n \neq 22$. See the monograph of Fowler and Manolopoulos [3] for more information on fullerenes.

Since carbon atoms in stable molecules are tetravalent, one of the three σ-bonds of every atom in a fullerene molecule should be augmented by

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a π-bond to create a carbon-carbon double bond. A Lewis structure that localizes the σ- and π-bonds to at most two atoms per bond is called a *Kekulé structure*. It corresponds to the notion of perfect matchings in fullerene graphs: a *perfect matching* in a graph G is a set M of edges of G such that every vertex of G is incident with precisely one edge of M. We let $\mathrm{pm}(G)$ be the number of perfect matchings of G; this corresponds to the number of Kekulé structures in a fullerene, also known as the *Kekulé count* K. The Kekulé count is an important parameter in theoretical chemistry of benzenoid hydrocarbons, for it is an empirically established fact that the total π-electron energy of benzenoid hydrocarbons is a linear function of the Kekulé count (see e.g. the book by Gutman and Cyvin [5]).

Let M be a perfect matching in a fullerene graph G. A hexagonal face is *resonant* (with respect to M) if it is incident with precisely three edges in M. A (possibly empty) set of pairwise vertex-disjoint resonant hexagons is a *sextet pattern* (or *resonant pattern*), and the maximum size of a sextet pattern in G is the *Clar number* of G. The concept of sextet pattern originates from Clar's aromatic theory [2]. The *sextet polynomial* $B_G(x)$ of a benzenoid system G is defined [7, 12] as

$$B_G(x) := \sum_{k=0}^{m} r(G,k)x^k ,$$

where $r(G,k)$ is the number of sextet patterns of G of size k, and m is the Clar number of G. We define $\mathscr{R}(G)$ to be the set of resonant patterns of G. Note that $B_G(1) = |\mathscr{R}(G)|$.

It has been shown [4, 6, 19] that the inequality

$$B_G(1) \leq \mathrm{pm}(G) \tag{1}$$

holds for all benzenoid systems, with equality for catacondensed benzenoid systems [7, 12]. The inequality (1) was subsequently extended to all planar bipartite graphs [8, 16], and eventually to all planar graphs [20]. However, the Kekulé count is a poor indicator of π-electronic stability for fullerenes: although experiments show that the buckminsterfullerene is the most stable isomer of C_{60}, it was shown by Austin *et al.* [1] that there are 20 isomers of C_{60} with a higher Kekulé count than the buckminsterfullerene.

This led Zhang and He [20] to conjecture that no fullerene graph achieves equality in (1).

Conjecture 1 (Zhang and He). *For every fullerene graph G,*

$$B_G(1) < \mathrm{pm}(G)\,.$$

Zhang and He [20] verified Conjecture 1 for fullerene graphs containing at least one pair of adjacent pentagons, i.e. for fullerene graphs violating the IPR. The purpose of this paper is to prove the conjecture for all fullerenes, including the most stable ones. Namely, we prove the following result.

Theorem 2. *For every fullerene graph G,*

$$B_G(1) < \mathrm{pm}(G)\,.$$

2 Notation

Given a graph G, we let $V(G)$ and $E(G)$ be its vertex set and edge set, respectively. For $H \subseteq V(G) \cup E(G)$, we let $G - H$ be the graph obtained from G by removing the elements in H. Let $X \subset V(G)$. We define $G[X]$ to be the subgraph of G induced by the vertices in X. We let $\delta(X)$ be the set of edges of G with exactly one end-vertex in G.

A *k-edge-cut* of G is a set Y of k edges of G for which there exists a set $X \subset V(G)$ such that $Y = \delta(X)$. A k-edge-cut Y is *cyclic* if at least two components of $G - Y$ contain a cycle. Given a plane embedding of a graph G, two faces of G are *adjacent* if they share an edge. A cyclic edge-cut Y is *trivial* if one of the connected components of $G - Y$ is a cycle.

Zhang and He [20] extended the notion of resonant patterns to all plane graphs. Let G be a plane graph.The unbounded face of G is the *outer face*, the other faces are the *inner faces*. Given a perfect matching M of G, a face F of G of even size is *resonant* (with respect to M) if exactly half of the edges incident with F belong to M. A *resonant pattern* of G is a (possibly empty) set R of pairwise disjoint inner faces such that there exists a perfect matching M of G with respect to which every face in R is resonant. In particular, every face in R is bounded by a cycle of even order. In case G is a fullerene graph, this definition coincides with the one given in the introduction: it suffices to choose a pentagon as the outer face of G, since a pentagon is never resonant. Similarly as for fullerene graphs, $\mathscr{R}(G)$ is defined as the set of all resonant patterns of the plane graph G.

We end this section by stating Tutte's theorem [11, 18]. A graph (or a connected component of a graph) is *odd* if it has an odd number of vertices. It is *even* otherwise.

Theorem 3. *A graph G has no perfect matching if and only if there exists a set $S \subset V(G)$ such that the number of odd components of $G - S$ is greater than $|S|$.*

3 The proof of Theorem 2

We start with a straightforward observation.

Observation 4. *Let G be a cubic bridgeless graph, and let Y be a k-edge-cut of G with $k \in \{2, 3\}$. Then Y is cyclic if and only if both $|X|$ and $|V \setminus X|$ are greater than 1, where $Y = \delta(X)$.*

Proof. Set $G' := G[X]$. By the symmetry of the roles played by X and $V \setminus X$, it suffices to prove that G' contains a cycle. To see this, note that G' has at most one vertex of degree less than 2, and hence G' cannot be a forest. □

Since Zhang and He [20] proved that Conjecture 1 is true for fullerene graphs containing adjacent pentagons, we focus on fullerene graphs that satisfy the IPR. In particular, such fullerene graphs have no non-trivial cyclic 5-edge-cut. Indeed, fullerene graphs that contain a non-trivial cyclic 5-edge-cut were characterised by Kutnar and Marušič [10], and by Kardoš and Škrekovski [14]: it turns out that those fullerene graphs do contain adjacent pentagons.

We now prove a crucial property of fullerene graphs with no non-trivial cyclic 5-edge-cut.

Proposition 5. *Let G be a fullerene graph with no non-trivial cyclic 5-edge-cut. Suppose that there is an 8-edge-cut that separates an even subgraph $H \subset G$ from $G - H$, and $G - H$ contains at least three pairwise non-adjacent pentagons. Then $G - H$ has a perfect matching.*

Proof. Suppose that $G' := G - H$ does not contain a perfect matching. Then Tutte's theorem ensures the existence of a set S of vertices of G' such that $G' - S$ contains more than $|S|$ odd components. Let $\mathcal{O}$ be the set of odd components of $G' - S$. Since the number of vertices of G is even, $|\mathcal{O}|$ and $|S|$ have the same parity. Thus, since $|\mathcal{O}| > |S|$ we deduce that $|\mathcal{O}| \geq |S| + 2$.

The number $e_G(S, \mathcal{O})$ of edges between $\mathcal{O}$ and S in G is at most $3|S|$. Moreover, the number of edges between H and $\mathcal{O}$ is at most 8. Hence,

$$e_G(S \cup H, \mathcal{O}) \leq 3|S| + 8 \leq 3|\mathcal{O}| + 2\,. \tag{2}$$

Let $O \in \mathcal{O}$. Notice that the number of edges e_O between O and $S \cup H$ is odd, for otherwise the subgraph of G induced by O would have an odd number of vertices of odd degrees. Moreover, $e_O > 1$ because G is bridgeless. Hence, $e_O \geq 3$ for each odd component $O \in \mathcal{O}$. In particular,

$$e_G(S \cup H, \mathcal{O}) \geq 3|\mathcal{O}|\,. \tag{3}$$

So (2) and (3) imply that $|\mathcal{O}| = |S| + 2$.

We now prove that $G' - S$ has no even components. To see this, suppose on the contrary that C is an even component of $G' - S$. By Observation 4, there are at least 4 edges between C and $S \cup H$. Then, $e_G(S \cup H, \mathcal{O}) \leq 3|S| + 8 - 4 < 3|\mathcal{O}|$; a contradiction.

Let s be the number of edges of $G[S]$, and $e_G(H, S)$ the number of edges with an end-vertex in H and the other in S. We observe that $s + e_G(H, S) \leq 1$. Indeed, $e_G(S \cup H, \mathcal{O}) \leq 3|S| + 8 - 2(s + e_G(H, S)) \leq 3|\mathcal{O}| + 2 - 2(s + e_G(H, S))$. Hence, $s + e_G(H, S) \leq 1$ by (3).

Since $G' - S$ has no even components, this last remark implies that $e_G(S \cup H, \mathcal{O}) \neq 3|\mathcal{O}| + 1 = 3|S| + 7$.

Now observe that each odd component $O \in \mathcal{O}$ such that $e_O = 3$ is an isolated vertex of $G' - S$. Indeed, if O contains a cycle, then $e_O \geq 5$ since G is cyclically 5-edge-connected. Further, if O is a tree then e_O is at least twice the number of leaves of O. Hence O is a tree with one leaf, i.e. a single vertex.

We consider two cases regarding the value of $e_G(S \cup H, \mathcal{O})$.

$e_G(S \cup H, \mathcal{O}) = 3|\mathcal{O}|$. Then $e_O = 3$ for each $O \in \mathcal{O}$. Consequently, each odd component is an isolated vertex of $G' - S$.

Recall that $G[S]$ has at most one edge and $G' - S$ has no even components. Thus, S is not a stable set of G, for otherwise $G - H$ would be bipartite. Consequently, $G[S]$ contains exactly one edge e, and $G - H - e$ is bipartite. But since $G - H$ contains at least three pentagons, $G - H - e$ contains a pentagon; a contradiction.

$e_G(S \cup H, \mathcal{O}) = 3|\mathcal{O}| + 2$. Then S is an independent set. Since e_O is an odd number greater than 2 for every odd component $O \in \mathcal{O}$, let O' be the unique odd component such that $e_{O'} = 5$. Hence, every odd component other than O' is an isolated vertex of $G' - S$.

Let us now consider O'. If O' contains a cycle, then since G has no non-trivial cyclic 5-edge-cut, we deduce that O' is a pentagon of G

(note that $G-O'$ cannot be a cycle: $|\mathcal{O}|>1$ since $G-H$ is even, and hence $G-O'$ contains vertices of degree 3). If O' is acyclic, then it is a tree with at most (and hence exactly) two leaves (for otherwise $e_{O'}$ would be at least 6). Consequently, $e_{O'}=5$ implies that O' is a path or order 3.

In both cases $G-H-O'$ is bipartite; this is a contradiction since $G-H$ contains at least three pairwise non-adjacent pentagons.

□

Let L be the 'lollipop graph' in Figure 1. Proposition 5 immediately implies the following.

Corollary 6. *Let G be an IPR fullerene graph, and suppose that $H\subset G$ is a subgraph isomorphic to L. Then every perfect matching of H can be extended to a perfect matching of G.*

Let us point out that Proposition 5 also implies that every perfect matching of a pair of adjacent hexagons of an IPR fullerene can be extended to the whole graph.

The following lemma was proved by Zhang and He [20, Lemma 3.3].

Lemma 7 (Zhang and He). *Let G be a connected plane graph with a perfect matching, uv an edge incident with the outer face of G and another face C. Then*

$$\mathscr{R}(G)\subseteq\mathscr{R}(G-uv)\cup\mathscr{R}(G-u-v)\cup\{R\cup\{C\}:R\in\mathscr{R}(G-uv)\cap\mathscr{R}(G-u-v)\}\,. \tag{4}$$

Notice that in the last term of the right-hand side of (4), we may require that R be vertex-disjoint from C, for otherwise $R\cup\{C\}\notin\mathscr{R}(G)$. Consequently, under the same hypothesis as in Lemma 7, we can write

$$\begin{aligned}|\mathscr{R}(G)|\leq&|\mathscr{R}(G-uv)\cup\mathscr{R}(G-u-v)|\\&+|\{R:R\in\mathscr{R}(G-uv)\cap\mathscr{R}(G-u-v)\text{ and }V(R)\cap V(C)=\emptyset\}\,.\end{aligned} \tag{5}$$

We shall also use the following theorem of Zhang and He [20, Theorem 2.3] in the proof of Theorem 2.

Theorem 8. *For every plane graph G,*

$$|\mathscr{R}(G)|\leq\mathrm{pm}(G)\,.$$

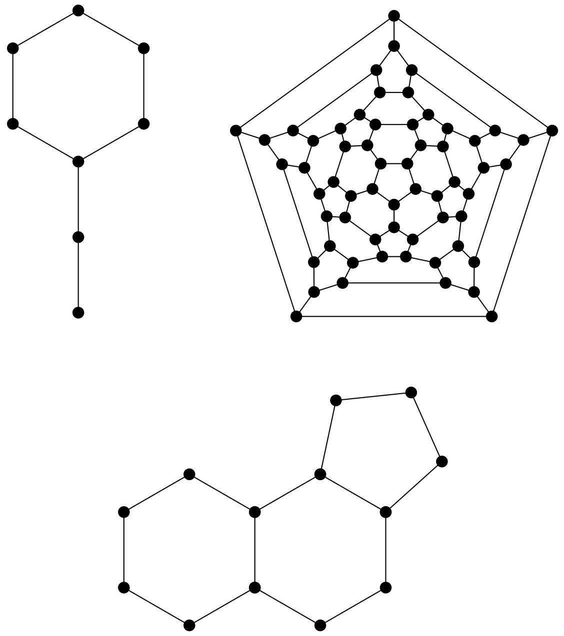

Figure 1: The lollipop graph L, the truncated icosahedron I_h, and the graph F in Lemma 10.

We formalise the following well-known (and straightforward) fact as an observation.

Observation 9. *For every graph G and every edge uv of G,*

$$\mathrm{pm}(G) = \mathrm{pm}(G - uv) + \mathrm{pm}(G - u - v)\,.$$

Let I_h be the graph of the truncated icosahedron, and let F be the graph in Figure 1 consisting of one pentagon and two hexagons.

Lemma 10. *Every IPR fullerene graph other than I_h contains a subgraph isomorphic to F.*

Proof. If G is a fullerene graph that satisfies the IPR and does not contain a subgraph isomorphic to F, then every hexagon of G is adjacent to zero or three pentagons. First, let us show that every hexagon of G is adjacent to three pentagons. If not, then there exists a hexagon H_0 adjacent to zero pentagons and to a hexagon H_1 that is adjacent to three pentagons (because G is connected and contains pentagons). This would imply that G violates the IPR; a contradiction.

Let n, e, f, and f_d be the number of vertices, edges, faces and faces of size d of G, respectively. Since G is cubic, $3n = 2e$. Substituting into Euler's formula ($n - e + f = 2$), we obtain $n = 2f - 4$. Since every hexagon is adjacent to three pentagons, and there are twelve pentagons altogether, $3f_6 = 5f_5 = 60$, so $f = f_5 + f_6 = 32$, and hence $n = 60$. This implies that G is the truncated icosahedron I_h, and the proof is complete. □

We are now ready to prove Theorem 2.

Proof of Theorem 2. If G violates the IPR, then Zhang and He [20] proved that $B_G(1) < \mathrm{pm}(G)$. Now, suppose that G is an IPR fullerene graph not containing F as a subgraph. Lemma 10 implies that G is the truncated icosahedron I_h. Shiu et al. [17] calculated the sextet polynomial of I_h, and found that $B_{I_h}(1) = 5,828$; whereas Schmalz et al. [15] showed that $\mathrm{pm}(I_h) = 12,500$. In particular $B_{I_h}(1) < \mathrm{pm}(I_h)$, as required.

So we may suppose that G is an IPR fullerene containing a subgraph isomorphic to the graph F of Figure 1. The graph G can be embedded in the plane so that the outer face is bounded by the pentagon C_1. By Corollary 6, there is a perfect matching M_1 of G such that C_3 is resonant and $uv \notin M_1$, and a perfect matching M_2 of G such that C_3 is resonant and $uv \in M_2$. In particular, C_3 is resonant in both $G - uv$ and $G - u - v$. Hence,

$$|\{R \in \mathscr{R}(G-uv) \cap \mathscr{R}(G-u-v) : V(R) \cap V(C_3) = \emptyset\}| < |\mathscr{R}(G-uv) \cap \mathscr{R}(G-u-v)|\,.$$

Therefore, applying (5) to uv and using Theorem 8 and Observation 9 gives

$$\begin{aligned} B_G(1) =& |\mathscr{R}(G)| \\ <& |\mathscr{R}(G-uv) \cup \mathscr{R}(G-u-v)| + |\mathscr{R}(G-uv) \cap \mathscr{R}(G-u-v)| \\ =& |\mathscr{R}(G-uv)| + |\mathscr{R}(G-u-v)| \\ \le& \,\mathrm{pm}(G-uv) + \mathrm{pm}(G-u-v) \\ =& \,\mathrm{pm}(G)\,, \end{aligned}$$

as required. This completes the proof of Theorem 2. □

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