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Fullerenes with the maximum Clar number☆

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ABSTRACT

The Clar number of a fullerene is the maximum number of mutually resonant disjoint hexagons in the fullerene. It is known that the Clar number of a fullerene with n vertices is bounded above by $\lfloor n/6 \rfloor - 2$, where $\lfloor x \rfloor$ represents the largest integer not greater than x. We show that there are no fullerenes with $n \equiv 2 \pmod 6$ vertices attaining this bound. In other words, the Clar number for a fullerene with $n \equiv 2 \pmod 6$ vertices is bounded above by $\lfloor n/6 \rfloor - 3$. Moreover, we show that two experimentally produced fullerenes C_{80}:1(D_{5d}) and C_{80}:2(D_2) attain the bound $\lfloor n/6 \rfloor - 3$. Finally, we present a graph-theoretical characterization for fullerenes, whose order n is congruent to 2 (respectively, 4) modulo 6, achieving the maximum Clar number $\lfloor n/6 \rfloor - 3$ (respectively, $\lfloor n/6 \rfloor - 2$).

1. Introduction

Clar number is a stability predictor of the benzenoid hydrocarbon isomers. The concept of Clar number originates from Clar's sextet theory [3] and Randić's conjugated circuit model [26]. For any two isomeric benzenoid hydrocarbons, the one with larger Clar number is more stable [3,20]. Hansen and Zheng [15] reduced the Clar number problem of benzenoid hydrocarbons to an integer linear programming. Based on abundant computation, the same authors conjectured the linear programming relaxing is sufficient. The conjecture was confirmed by Abeledo and Atkinson [1].

A *fullerene* (graph) is a 3-connected plane trivalent graph consisting solely of pentagons and hexagons as faces. The molecular graph of a spherical carbon fullerene is a fullerene graph. Grünbaum and Motzkin [14] showed that a fullerene with n vertices exists for $n = 20$ and for all even $n > 22$. To analyze the performance of the Clar number as a stability predictor of the fullerene isomers, we need good upper bounds on the Clar number of fullerenes. Fortunately, Zhang and Ye [34] established an upper bound of the Clar number of fullerenes. An alternative proof was given by Hartung [16].

Theorem 1.1 ([34]). *Let F be a fullerene with n vertices. Then* $c(F) \le \lfloor n/6 \rfloor - 2$.

There are seven experimentally produced fullerenes attaining the bound in Theorem 1.1, namely, C_{60}:1(I_h) [21], C_{70}:1(D_{5h}) [28], C_{76}:1(D_2) [6,29], C_{78}:1(D_3) [4,19,29], C_{82}:3(C_2) [19], C_{84}:22(D_2) [22,29] and C_{84}:23(D_{2d}) [22,29], where $C_n : m$ is the m-th isolated-pentagon fullerene isomer with n atoms generated by the spiral algorithm [10], and the point group of the isomer is presented inside parenthesis. Ye and Zhang [33] gave a graph-theoretical characterization of fullerenes with at least 60 vertices attaining the maximum Clar number $n/6 - 2$, and constructed all 18 fullerenes attaining the maximum value 8 among all 1812 fullerene isomers of C_{60}. Later, Zhang et al. [35] proposed a combination of the Clar number and Kekulé count to predict the stability of fullerenes, which distinguishes uniquely the buckminsterfullerene C_{60} from its

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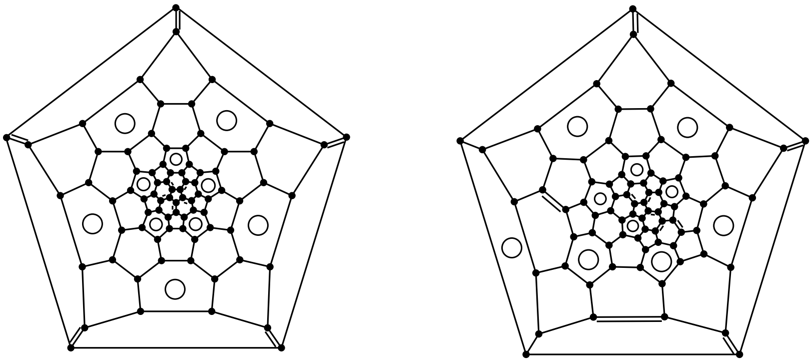

Fig. 1. Two experimentally produced extremal fullerenes (a) C_{80}:1 (D_{5d}), (b) C_{80}:2 (D_2). (These two graphs are generated by a software package [27] for constructing and analyzing structures of fullerenes before further processing.)

all 1812 fullerene isomers. Recently, Hartung [16] gave another graph-theoretical characterization of fullerenes, whose Clar numbers are $n/6 - 2$, by establishing a connection between fullerenes and (4, 6)-fullerenes, where a (4, 6)-*fullerene* is a trivalent plane graph consisting solely of quadrilaterals and hexagons as faces and is the molecular graph of some possible boron–nitrogen fullerene [9].

In this paper, we will show that there are no fullerenes with $n \equiv 2 \pmod 6$ vertices attaining this bound. Thus Theorem 1.1 is refined as the following theorem.

Theorem 1.2. *Let F be a fullerene with n vertices. Then*

$$c(F) \le \begin{cases} \lfloor n/6 \rfloor - 3, & \text{if } n \equiv 2 \pmod 6, \\ \lfloor n/6 \rfloor - 2, & \text{otherwise}. \end{cases}$$

We say a fullerene *extremal* if the Clar number of the fullerene attains the bound in Theorem 1.2. In addition to the seven experimentally produced extremal fullerenes mentioned before, there are two experimentally produced extremal fullerenes C_{80}:1(D_{5d}) [17,30], C_{80}:2(D_2) [17] (see Fig. 1). Moreover, the minimum fullerene C_{20} is also an extremal fullerene.

Furthermore, we give a graph-theoretical characterization of fullerenes, whose order n is congruent to 2 (respectively, 4) modulo 6, attaining the maximum Clar number $\lfloor n/6 \rfloor - 3$ (respectively, $\lfloor n/6 \rfloor - 2$).

2. Preliminaries

This section presents some concepts and results to be used later. For the concepts and notations of graphs not defined, we refer to [31].

Let F be a fullerene. A *perfect matching* (or *Kekulé structure*) M of F is a set of edges such that each vertex is incident with exactly one edge in M. A face with exactly half of their bounding edges in a perfect matching M of F is called an *alternating face* with respect to M. A *resonant pattern* of F is a set of disjoint alternating faces (hexagons) with respect to some perfect matching. The *Clar number* $c(F)$ of F is the maximum size of all resonant patterns of F. A *Clar set* is a resonant pattern of size $c(F)$. If $\mathcal{H}$ is a resonant pattern of F and M_0 is a perfect matching of $F - \mathcal{H}$, then we say $(\mathcal{H}, M_0)$ is a *Clar cover* [37] of F. We say a Clar cover $(\mathcal{H}, M_0)$ is a *Clar structure* if $\mathcal{H}$ is a Clar set of F. In a Clar cover $(\mathcal{H}, M_0)$ of F, a hexagon of $\mathcal{H}$ is indicated by drawing a circle in its interior and an edge in M_0 by a pair of double lines in a diagram; for example, see Fig. 1.

Leapfrog transformation for a 2-connected plane graph G is defined as the truncation of the dual of G [13,24]. The *leapfrog graph* $\mathcal{L}(G)$ is obtained from G by performing the leapfrog transformation. The *dual* of a plane graph is built as follows: Place a point in the inner of each face and join two such points if their corresponding faces share a common edge [24]. The *truncation* of a 2-connected plane graph G can be obtained by replacing each vertex v of degree k with k new vertices, one for each edge incident to v. Pairs of vertices corresponding to the edges of G are adjacent, and k new vertices corresponding to a single vertex of G are joined in the cyclic order given by the embedding to form a face of size k [13]. Fig. 2 illustrates the generation procedure of a fullerene with 78 vertices from another fullerene with 26 vertices by leapfrog transformation. Leapfrog transformation is defined equivalently as the dual of the omnicapping [12]. Leapfrog fullerenes have their own chemical importance. Firstly, they obey the isolated-pentagon rule [10]. Secondly, they are known to be one of the two constructions that always have properly closed-shell configurations [11]. Finally, they attain the maximum Fries number $n/3$ and thus are maximally stable in a localized valence bond picture [7].

Let F be a fullerene and $(\mathcal{H}, M)$ a Clar cover of F. For a face f of F, we say that an edge e in M *exits* f if e shares exactly one vertex with f. The following lemma is essentially due to Hartung [16].

Lemma 2.1. *Let F be a fullerene and $(\mathcal{H}, M)$ a Clar cover of F. Then there are an even number of edges in M (possibly* 0*) exiting any hexagon and an odd number of edges in M exiting any pentagon.*