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A combination of Clar number and Kekulé count as an indicator of relative stability of fullerene isomers of C_{60}

Heping Zhang · Dong Ye · Yunrui Liu

Abstract   Kekulé count is not as useful in predicting the thermodynamic stability of fullerenes as it is for benzenoid hydrocarbons. For example, the Kekulé count of the icosahedral C_{60}, the most stable fullerene molecule, is surpassed by its 20 fullerene isomers (Austin et al. in Chem Phys Lett 228:478–484, 1994). This article investigates the role of Clar number in predicting the stability of fullerenes from Clar's ideas in benzenoids. We find that the experimentally characterized fullerenes attain the maximum Clar numbers among their fullerene isomers. Our computations show that among the 18 fullerene isomers of C_{60} achieving the maximum Clar number (8), the icosahedral C_{60} has the largest Kekulé count. Hence, for fullerene isomers of C_{60}, a combination of Clar number and Kekulé count predicts the most stable isomer.

Keywords   Fullerene · C_{60} · Kekulé structure · Clar number · Stability

1 Introduction

Icosahedral C_{60} (buckminsterfullerene, carbon football, or 60:1812), a spherical carbon cage consisting of 60 carbon atoms, was first synthesized by the method of evaporation of graphite by Kroto et al. [1] in 1985 and further confirmed by later experiments [2,3]. A fullerene is a spherical carbon cage with n carbon atoms arranged on 12

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pentagonal rings and $\frac{1}{2}n - 10$ hexagonal rings. There are total 1,812 fullerene isomers with 60 carbon atoms [4] among which the icosahedral isomer C_{60} is the only one with firmly experimental characterization, and is believed to be the most thermodynamically stable isomer.

Fullerene chemistry has inspired many scientists to investigate connections between structural properties (or topological indices) and fullerene stability. In 1980s Schmalz et al. [5,6] and Kroto [7] proposed the "Isolated Pentagon Rule" (IPR) which says that the most stable fullerenes do not contain abutting pentagons. The IPR for fullerene stability is compatible with both steric strain arguments and the Hückel $4n + 2$ rule which implies that the most stable fullerene isomers avoid destabilizing 8-length conjugated circuits. The IPR was generalized by Liu et al. [8] to the rule, that the most stable fullerene isomers minimize the number of pentagon adjacencies (i.e., the number of pairs of pentagons with a common edge). These rules can distinguish uniquely $C_{60}(I_h)$ and $C_{70}(D_{5h})$ from their fullerene isomers, but is less selective for these with larger numbers of atoms. For instance, C_{84} and C_{100} have 24 and 450 fullerene isomers that obey the IPR, respectively [4]. Electronic structure arguments [9] show that the favorable fullerenes have closed π shell structures and large HOMO–LUMO gaps. Isolated-pentagonal C_{60} and C_{70} have such electronic properties among their fullerene isomers. The HOMO–LUMO gap of C_{60} is $\Delta = 0.7566$. But this rule also cannot uniquely characterize the most stable fullerenes. For example, C_{84} has two fullerene isomers with the same maximum HOMO–LUMO gap [10], but these are not the favorable experimental isomers [11]. Motivated by Graffiti's Conjecture 899 [12], independence numbers [13] and bipartivity indices of fullerenes [14] have also been considered as possible stability predictors. Fajtlowicz and Larson [13] found that the stable isomers of C_{60}, C_{70} and C_{76} uniquely minimize independence number among their fullerene isomers. However, it has been illustrated [15] by more detailed comparisons that the minimum independence number is not an overall good predictor for fullerene stability.

Kekulé count is an effective predictor for the stability of benzenoid hydrocarbons. However, Schmalz et al. [5,6] and Liu [9] found that some fullerene isomers of C_{60} have larger Kekulé count than the Kekulé count 12,500 [4] of icosahedral C_{60}. Further, Austin et al. [16] constructed all such 20 distinct fullerene isomers of C_{60} whose Kekulé counts surpass that of icosahedral C_{60}. So, the maximality of Kekulé counts of fullerene isomers may not be coincident with their stabilities. In Clar's aromatic sextet theory, Clar number, the maximum number of disjoint benzenoid hexagons (alternating in single bonds and double bonds for a given Kekulé structure), is another effective stability predictor for benzenoid hydrocarbons. A benzenoid hydrocarbon isomer is more stable if it has larger Clar number [17]. Clar's ideas can be viewed to be intimately embodied in conjugated circuit theory [18]. Fries ideas were explicitly introduced by Liu et al. [19]. In this article, we investigate a connection between Clar numbers of fullerenes and their stabilities. We find that the experimentally characterized C_{60}, C_{70}, C_{76}, $C_{84} : 22D_2(\text{IV})$ and $C_{84} : 23D_{2d}(\text{II})$ attain the maximum Clar number among their fullerene isomers. Furthermore, a combination of Clar number and Kekulé count as a stability predictor distinguishes uniquely the icosahedral C_{60} from its all 1,812 fullerene isomers.

2 Combination of Clar number and Kekulé count

A Kekulé structure (perfect matching in graph theory) of a fullerene graph F is a set of independent edges covering all vertices. The edges in a Kekulé structure are illustrated by double bonds. A set S of disjoint hexagons of F is called a *sextet pattern* if F has a Kekulé structure such that every hexagon in S contains three double bonds (or equivalently if the deletion of the hexagons in S together with their incident edges results in a subgraph of F with a Kekulé structure). A sextet pattern of F with the maximum number of hexagons is called a *Clar formula* or *Clar structure*. The number of hexagons in any Clar formula is called the *Clar number* of a fullerene F. In Clar's model [17], a sextet pattern S is designated by depicting circles within hexagons of S (see Fig. 1).

Flocke et al. [20] found that the Kekulé structures of a fullerene do not contribute equally to its molecule resonance energy. By the Heisenberg model (or equivalently the Pauling-Wheland valence-bond model), among all 12,500 Kekulé structures of icosahedral C_{60}, 5,828 of them give 99.82% of the ground-state molecular energy of the full set of Kekulé structures. By a more effective model, Wu et al. [21] improve this proportion to 99.96%. Every Kekulé structure M of these 5,828 Kekulé structures defines a different sextet pattern S such that every hexagon in S contains three double bonds of M. This gives an one-to-one correspondence between these 5,828 Kekulé structures and all sextet patterns of C_{60}. In fact, the sextet polynomial of icosahedral C_{60} for counting the sextet patterns was computed in [22], which is

$$B_{C_{60}}(x) = 5x^8 + 320x^7 + 1240x^6 + 1912x^5 + 1510x^4 \\ + 660x^3 + 160x^2 + 20x + 1.$$

The sextet pattern count of C_{60} is $B_{C_{60}}(1) = 5828$. This indicates that the aromatic sextets still play an important role even in this non-alternant system.

In Clar's aromatic sextet theory [17], Clar found that various electronic properties of benzenoid hydrocarbons can be roughly measured by their sextet patterns from a purely empirical standpoint. When the Clar number increases within all isomeric benzenoid hydrocarbons, the stability increases correspondingly. Aihara [23] found that the Clar number of a benzenoid hydrocarbon gives a rough estimate of its Dewar-type resonance energy. Clar's idea was refined by Randić [24,25], Herndon [26] and their
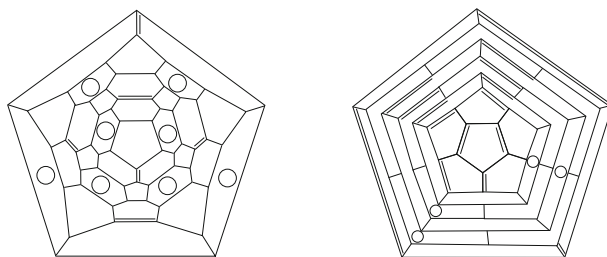

Fig. 1 Clar formulas of icosahedral C_{60} (*left*) and tubular isomer of C_{60} (*right*)

co-authors to the conjugated circuit model. In the conjugated circuit model, benzenoid hexagons contribute the most to resonance energy, among all $(4n + 2)$-length conjugated circuits. For icosahedral C_{60}, Klein et al. [18] found that the count of conjugated hexagons and 10-length circuits can offer a quantitative estimation to its resonance energy. There is a more computationally effective scheme available to estimate fullerene stabilities [27].

Can the Clar number predict the stability of fullerenes? By an enumerative approach, El-Basil [28] showed that the Clar number of icosahedral C_{60} is equal to 8 and it has five Clar formulae, one of which is shown in Fig. 1 (left). For a fullerene F_n with n atoms, Zhang and Ye [29] obtained an upper bound for the Clar number $c(F_n)$, i.e. $c(F_n) \leq \frac{n-12}{6}$. By this bound, we can easily see that icosahedral C_{60} has the maximum Clar number 8 among all its fullerene isomers. Another remarkable fact is that the tubular isomer (see Fig. 1, right) of C_{60} has the smallest Clar number 4, even though its Kekulé count achieves the maximum 16,501 over all fullerene isomers of C_{60} [16]. The tubular isomer also has the minimum HOMO–LUMO gap $\Delta = 0$ and maximizes the number of pentagon adjacencies. These facts imply that the tubular isomer should be less stable, which is consistent with its small Clar number. The implication is that Clar number is more efficient than Kekué count as a predictor of stability for fullerenes.

However, Clar number has a small range of values and is typically highly degenerate for fullerenes. Among the 1,812 fullerene isomers of C_{60}, Clar number alone does not uniquely pick out the experimental C_{60}. The first two authors of this article have rigorously proved that exactly 18 fullerenes with 60 atoms (including icosahedral C_{60}) achieve the maximum Clar number 8 by a graph-theoretic method, and all such fullerene isomers of C_{60} are illustrated in Fig. 2; the detailed mathematical proof was given in [30]. A comparison shows that none of these 18 fullerenes belongs to the collection of the 20 fullerene isomers with Kekulé counts surpassing 12,500 in [16]. That is, the Clar numbers of these 20 fullerene isomers are less than 8. On the other hand, using the method based on Pfaffian orientation of planar graphs that was devised for an application in physics by Kasteleyn [31], we have computed the Kekulé counts of these 18 extremal fullerene isomers as listed in Table 1, which shows that of these 18 fullerene isomers, the icosahedral C_{60} has the maximum Kekulé count (isomer No. 18 in Table 1).

The above facts stimulate us to propose a combination of Clar number and Kekulé count of fullerenes as a stability predictor of fullerenes. Let $(c(F), k(F))$ be a bi-index of a fullerene graph F, where $c(F)$ and $k(F)$ denote the Clar number and the Kekulé count of F, respectively. Inspired by a multi-object programming, our idea to maximize the bi-index $(c(F), k(F))$ is proposed as follows: the index $c(F)$ has priority; that is, for two fullerene isomers F_1 and F_2, $(c(F_1), k(F_1)) \succeq (c(F_2), k(F_2))$ if and only if $c(F_1) > c(F_2)$, or $c(F_1) = c(F_2)$ and $k(F_1) \geq k(F_2)$. From this point of view, the icosahedral C_{60} is the unique member with the maximal $(c(F), k(F))$ among 60-atom fullerene isomers. Hence such a combination of Clar number and Kekulé count can determine uniquely the icosahedral C_{60}.
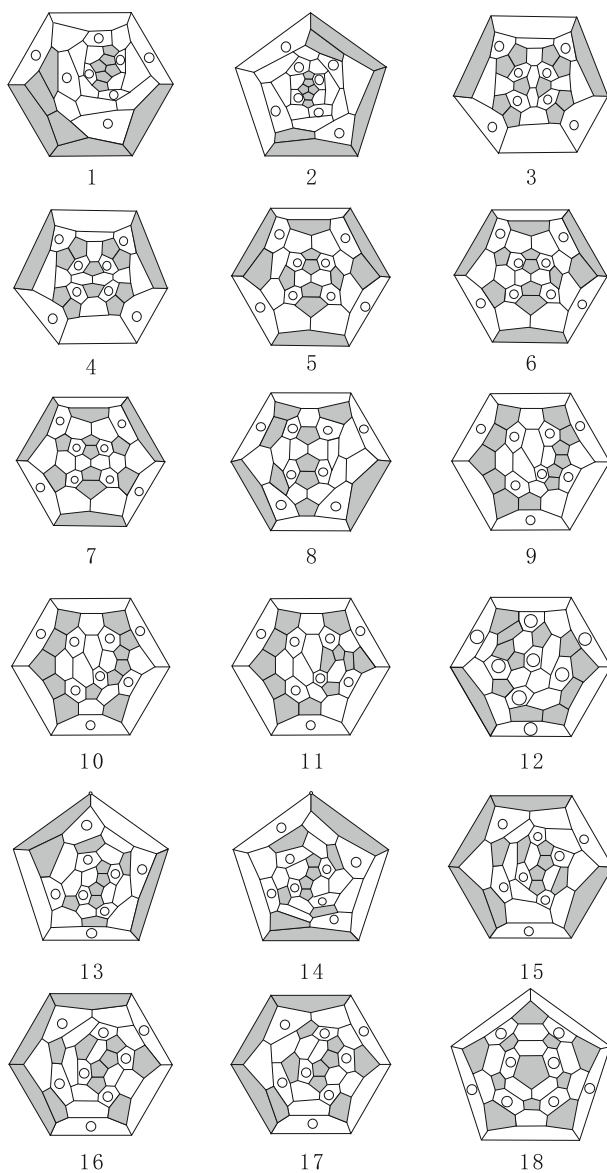
Fig. 2 All fullerene isomers of C_{60} with Clar number 8

3 Discussion

The combination bi-index of Clar number and Kekulé count works well in predicting the stability of icosahedral C_{60}. How does it work for other stable fullerenes?

The synthesized fullerene $C_{70}(D_{5h})$ also maximizes the Clar number 9. This can be verified by a sextet pattern (in fact, a Clar formula) of 9 benzenoid rings shown in

Table 1 Fullerenes isomers of C_{60} with Clar number 8 and their Kekulé counts

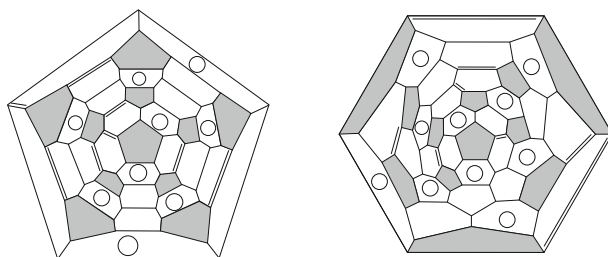| Isomer (no.)	Ring spiral codes	Kekulé count
1	1 2 3 4 7 10 25 28 29 30 31 32	11259
2	1 2 3 4 7 10 23 26 29 30 31 32	11102
3	1 2 9 12 15 17 20 22 24 27 29 31	10760
4	1 2 9 12 14 17 20 22 25 27 30 31	10476
5	1 2 9 12 15 17 20 21 23 24 27 30	10476
6	1 2 9 12 14 17 20 21 23 25 27 30	10536
7	1 2 9 12 15 17 20 22 24 26 28 30	11230
8	1 2 9 12 14 17 20 21 23 25 26 28	10250
9	1 2 4 7 11 15 20 24 25 28 31 32	10538
10	1 2 4 7 11 16 20 23 25 28 31 32	10610
11	1 2 4 7 9 13 20 24 27 30 31 32	10340
12	1 2 4 7 9 12 21 24 27 30 31 32	10356
13	1 2 4 7 12 16 18 22 25 28 31 32	10130
14	1 2 4 7 12 16 19 23 25 28 31 32	10254
15	1 2 4 7 9 13 20 24 26 29 31 32	10386
16	1 2 4 7 9 12 21 24 26 29 31 32	10370
17	1 2 4 7 12 16 18 22 27 30 31 32	10258
18	1 7 9 11 13 15 18 20 22 24 26 32	12500

Fig. 3 Clar formulas of C_{70} (*left*) and C_{76} : 1 (D_2) (*right*)

Fig. 3 (left) and the inequality $c(F_{70}) \leq \frac{70-12}{6} = 9\frac{4}{6}$ since Clar number is always an integer. Similarly, we have that $c(F_{76}) \leq 10$ and $c(F_{84}) \leq 12$. There are two isomers of C_{76} with IPR. Only C_{76} : 1 (D_2) has experimental evidence [32]. It also maximizes the Clar number 10 (see Fig. 3, right). Among the fullerenes with experimental evidence, C_{84} is the third most abundant member after C_{60} and C_{70} [33]. Early ^{13}C NMR studies showed that the synthesized remainder consists of two major isomers with D_2(IV) and D_{2d}(II) symmetry [34,35]. Both C_{84} : $22D_2$(IV) and C_{84} : $23D_{2d}$(II) attain the maximum Clar number 12 since each of them has a Clar formula consisting of 12 hexagons (see Fig. 4).

The priority of Clar number in the bi-index $(c(F), k(F))$ conforms to the experimental evidences. That is, the experimentally characterized fullerenes attain the maximum Clar numbers among their fullerene isomers. In order to test the efficiency of
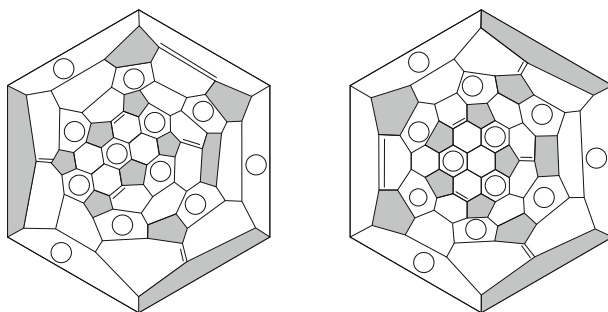
Fig. 4 Clar formulas of $C_{84} : 22$ (D_2 (IV)) (*left*) and $C_{84} : 23$ (D_{2d}(II)) (*right*)

the combination of Clar number and Kekulé count on fullerene stability, we should construct all fullerene isomers with the maximal Clar number and compare their Kekulé counts. But the previous graph-theoretical approach for constructing the extremal fullerene isomers of C_{60} is not suitable for the case that the number of atoms is not divisible by 6. For benzenoids, Hansen and Zheng [36] formulated the Clar problem as an integer program and conjectured that solving the linear programming relaxation always yields integral solutions. Abeledo and Atkinson [37,38] established this conjecture by proving that the constraint matrix of the integer program for the Clar problem is always unimodular. When applying such an integer program to fullerenes, we also obtain the same 18 fullerene isomers of C_{60} with the maximum Clar number 8. Relaxing the integer program to a linear program, however, we often obtain non-integral optimal solutions because of the fact that all fullerenes are non-bipartite. Up to now there is no generally effective way to compute Clar numbers of fullerenes. How to compute Clar numbers of fullerenes is an interesting problem in both mathematics and theoretical chemistry. The combination bi-index of Clar number and Kekulé count has not yet been examined completely for C_{70} and other stable fullerenes. It is worthwhile to seek the combinations of Clar number with other invariants [39] as stability predictors of fullerenes.

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