

Graph-Theoretic Independence as a Predictor of Fullerene Stability

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Abstract

The independence number of the graph of a fullerene, the size of the largest set of vertices such that no two are adjacent (corresponding to the largest set of atoms of the molecule, no pair of which are bonded), appears to be a useful selector in identifying stable fullerene isomers. The experimentally characterized isomers with 60, 70 and 76 atoms uniquely minimize this number among the classes of possible structures with, respectively, 60, 70 and 76 atoms. Other experimentally characterized isomers also rank extremely low with respect to this invariant. These findings were initiated by a conjecture of the computer program Graffiti.

Key words: fullerenes, independence, stability, separator, Graffiti, rational synthesis

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1 Introduction

A conjecture of the conjecture-making program Graffiti [3,4,12] and a feature of that program for identifying *stability sorting patterns* led to the observation that, for the very limited (less than fifty) number of examples of stable and presumed unstable fullerenes known to the program, the stable isomers had smaller independence numbers than the unstable ones. It was originally Graffiti's Conjecture 899 in [7], that the independence number on an n -atom fullerene is no more than $\frac{n}{2} - 2$, and its associated stability pattern that led the first author to make this conjecture. Graffiti can, in principle, make conjectures about invariants of any objects that can be represented by a computer. The conjectures are of the form of inequalities between functions of invariants. For fullerenes, the difference between the sides of an inequality (itself an invariant) can be sorted by smallest or largest values. When the known stable fullerenes appear at the top (or bottom) of this list, this difference suggests itself for investigation [5–7].

Upon announcing the above conjecture at a conference in the Fall of 2001, Patrick Fowler, while initially very skeptical, later that same day confirmed that icosahedral C_{60} is the unique model minimizing its independence number in the class of mathematically possible classical fullerenes with 60 atoms, and that $C_{70}(D_{5h})$ is the unique model minimizing this number in the class of 70-atom isomers [5]. The second author has since computed that stable C_{76} also minimizes its independence number in the class of 76-atom isomers and that the known stable isomers of C_{78} and C_{84} also rank very low with respect to this invariant—that is, those eight stable, best-characterized (according to [9]) fullerenes rank very low with respect to their independence numbers. We are not aware of any physical or chemical justifications that would explain these exceptional statistics.

We will compare this topological invariant with other predictors of fullerene stability, including the isolated pentagon criteria, the uniformity of hexagonal environments, and the second moment of the hexagon neighbor signature.

Determining the criteria which distinguish the most stable fullerenes have been given new impetus by the recent rational synthesis of stable C_{60} by Scott and his colleagues [17]. It may one day be possible to synthesize heretofore unseen fullerenes based on blueprints of isomers predicted to be stable.

2 Predictors of Fullerene Stability

Fullerenes with a wide range of numbers of carbon atoms have been produced in experiment. Isomers with 60, 70, 76, 78, and 84 atoms have been produced in sufficient quantity to be characterized by NMR spectroscopy. The term “stable” is ambiguous, is used to refer alternately to thermodynamic and kinetic stability and, less formally, it is applied to those fullerenes that have actually been observed. These uses of the term are presumably related. For the purposes of this paper we will refer to those fullerenes that have been produced in bulk quantity as “stable fullerenes.” These include at least $C_{60}(I_h)$, $C_{70}(D_{5h})$, $C_{76}(D_2)$, $C_{78}(D_3)$, $C_{78}(C_{2v})$ (2 kinds), $C_{84}(D_2)$ and $C_{84}(D_{2d})$ [9]. (In the numbering scheme of [9] these are $C_{60}:1$, $C_{70}:1$, $C_{76}:1$, $C_{78}:1$, $C_{78}:2$, $C_{78}:3$, $C_{84}:22$ and $C_{84}:23$.) One problem chemists face is characterizing the stable fullerenes that appear in experiment from the sometimes enormous numbers of possible isomers. Suppose, for instance, that a certain n -atom fullerene is produced. Can it be predicted ahead of time what it will be? What rules are there that can limit the space of possibilities? Another interesting question, not addressed here, is predicting from which atom classes the stable fullerenes will come from. Is it likely that there will be stable 100-atom fullerenes? There has been speculation on how fullerenes “grow”—but the final story has not yet been told. It will surely relate to this question.

The problem that Curl, Kroto and Smalley faced when they found 60-atom carbon clusters in their experiments was to identify the structure of these molecules. They initially proposed a soccer ball structure for the C_{60} molecules they had produced, but this is only one of 1812 isomers (up to chirality) consistent with the fullerene hypothesis. Their proposed model has isolated pentagonal faces, while none of the others do.

Schmalz *et al.* predicted that structures with isolated pentagons would be more favorable than ones with abutting pentagons, which could contain “destabilizing conjugated 8-circuits” [16, p. 206]. Kroto’s name became associated with this criterion when, shortly thereafter, he proposed his Isolated Pentagon Rule (IPR), that stable fullerenes will have isolated pentagons [11]. No fullerene with fewer than 60 atoms can satisfy this criterion. Of the stable fullerenes, all those with 60 or more atoms have isolated pentagons.

This rule does suffice to characterize both the 60 and 70-atom isomers that were found—as there are unique isomers in the classes with 60 and 70 atoms that have isolated pentagons. This rule does not suffice to uniquely characterize the fullerenes with 76, 78 or 84 atoms—as there are two 76 atom isomers with isolated pentagons, five among the 78-atom isomers and 24 among the 84-atom isomers. The rule does, though, greatly reduce the number of possible structures that must be considered: from 19151 to 2 in the case of 76-atom

isomers, from 24109 to 5 for 78-atom isomers and from 51592 to 24 for 84 atom isomers. As the number of atoms n increases, the number of n -atom fullerene isomers increases rapidly—as does the number of isomers with isolated pentagons. If a 100-atom fullerene were to appear in experiment, for instance, there are 285,914 structures consistent with the fullerene hypothesis—450 of which have isolated pentagons. If a 120-atom fullerene were to appear in experiment, there are 1,674,171 possible 120-atom isomers, 10,744 of which have isolated pentagons.

As the isolated pentagon criterion cannot be used to characterize the lower fullerenes (those with fewer than 60 atoms) and suffices to uniquely identify candidate structures for only a handful of the higher fullerene classes, chemists have looked for other rules of thumb to help limit the search in characterizing those fullerenes that appear in experiment.

Besides steric criteria for stability (the IPR rule), electronic criteria were also quickly proposed: in particular, that closed shell structures would be more favorable than open shelled structures (which have a 0.0 HOMO-LUMO gap) and that structures with larger HOMO-LUMO gaps would be favorable to those with smaller ones [14]. $C_{60}(I_h)$, for instance, has the largest gap among 60-atom isomers. $C_{70}(D_{5h})$ also has the largest gap in the class of 70-atom isomers. For other classes, the fullerenes that have been produced often rank high with respect to this measure (see Table 1), but this criterion is not enough to uniquely characterize these fullerenes.

Atoms	Isomer	Number of Isomers	HOMO-LUMO	Rank	Max	Min
60	$C_{60}:1 (I_h)$	1812	0.7566	1	0.7566	0.0 (5)
70	$C_{70}:1 (D_{5h})$	8149	0.5293	1	0.5293	0.0 (8)
76	$C_{76}:1 (D_2)$	19151	0.3436	11	0.3993	0.0 (16)
78	$C_{78}:1 (D_3)$	24109	0.2532	241	0.6333	0.0 (2)
	$C_{78}:3 (C_{2v})$		0.1802	2120		
	$C_{78}:2 (C_{2v})$		0.3481	13		
84	$C_{84}:22 (D_2)$	51592	0.3449	24 (2)	0.6962	0.0 (11)
	$C_{84}:23 (D_{2d})$		0.3449	24 (2)		

Table 1

HOMO-LUMO data for experimentally produced fullerenes. *Rank* is by largest value of HOMO-LUMO. *Max* and *Min* are the largest and smallest values within the corresponding class. The numbers in parentheses record the number of isomers that share the corresponding rank or value.

Liu *et al.* proposed that fullerenes that minimized their number p of pentag-

onal adjacencies (that is, the number of pairs of abutting pentagonal faces) would be favorable [13]. This criterion is clearly a generalization of the isolated pentagon rule, since, for a fullerene with isolated pentagons, the number of pentagonal adjacencies is zero. For the lower fullerenes and those few other classes of isomers without isolated pentagons, this criterion applies while the isolated pentagon rule does not.

Raghavachari argued that steric strain would be minimized if the environments of the hexagons were as “uniform” as possible [15]. For instance, the hexagonal faces of $C_{60}(I_h)$ all have three neighbors which are hexagons. Using this criteria, he was able to identify the two 84-atom fullerene isomers which had been produced in experiment.

This criterion though will be of less utility as the size of the considered fullerenes increases. In this case there will be large numbers of isomers with 60 hexagons having exactly 5 neighboring faces which are hexagons and $\frac{n}{2} - 70$ hexagons where all the neighboring faces are hexagons.

Fowler also proposed a quantitative version of Raghavachari’s criterion. He considered the second moment of the hexagon neighbor signature, $H = \sum k^2 h_k$, where h_k is the number of hexagons with k hexagonal neighbors. Fowler’s criterion is that fullerenes which minimize H are more likely to be stable than those that do not [9]. This index is highly selective for those fullerenes that have been produced in bulk (see Table 2). This index will be minimized by any fullerene in which no hexagon is adjacent to two pentagons (those where 60 different hexagons have a single pentagonal neighbor). For larger fullerenes, the number of fullerenes with the minimum hexagon signature will grow very large. (For 100-atom fullerenes, 38 models—all IPRs—minimize this index).

3 Graph Theoretic Independence and the Separator

The *independence number* (sometimes called the *stability number*) of a graph is the size of the largest set of vertices (or nodes) such that no two are adjacent (corresponding to the largest set of atoms of the molecule, no pair of which are bonded). For instance, the independence number of a 5-ring is 2, that of a 6-ring is 3, and that of the truncated icosahedron is 24 (as every vertex belongs to one of the twelve pentagonal faces and, as each of these faces is contains no more than 2 members of a largest independent set, the independence number can be no more than 24 see Fig. 1).

Minimization of this index is often highly selective: it uniquely selects the stable 60, 70 and 76-atom isomers from their respective classes—and all those fullerenes that have been produced in bulk rank first or second within their

Atoms	Isomer	Number of Isomers	H	Rank	Max	Min
60	$C_{60}:1 (I_h)$	1812	180	1	520	180
70	$C_{70}:1 (D_{5h})$	8149	330	1	700	330
76	$C_{76}:1 (D_2)$	19151	428	2	776	420
78	$C_{78}:1 (D_3)$	24109	462	4	780	450
	$C_{78}:3 (C_{2v})$		454	2		
	$C_{78}:2 (C_{2v})$		460	3		
84	$C_{84}:22 (D_2)$	51592	548	1 (3)	920	548
	$C_{84}:23 (D_{2d})$		548	1 (3)		

Table 2

Second Moment of the Hexagon Signature H for experimentally produced fullerenes. *Rank* is by largest value of this index. *Max* and *Min* are the largest and smallest values within the corresponding class. The numbers in parentheses record the number of isomers that share the corresponding rank or value.

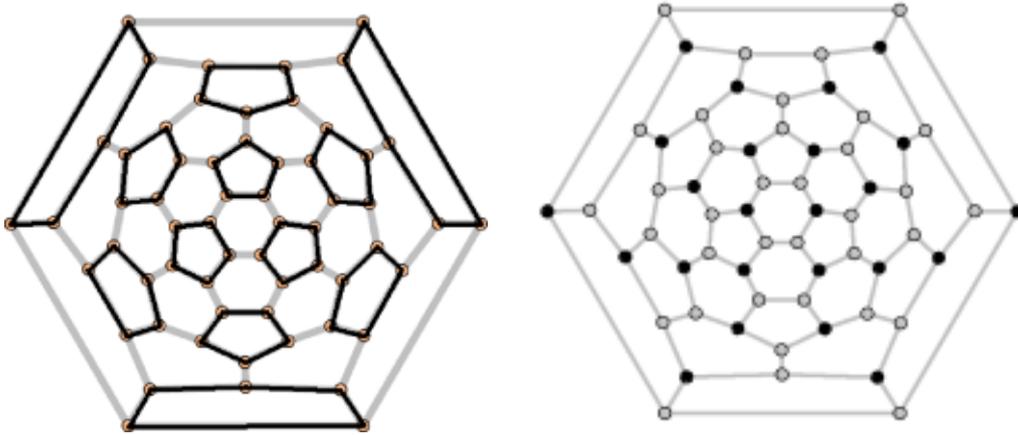


Fig. 1. (a) The truncated icosahedron with pentagons highlighted and (b) with a 24-vertex maximum independent set highlighted.

respective atom classes (see Table 3). That stable fullerenes tend to minimize their independence numbers is, at present, simply a statistical observation—no physical or chemical justification has been proposed. Furthermore, this predictor, used alone, will fail to predict the stability of sufficiently large capped nanotubes (which are fullerenes), as the independence numbers of these fullerenes will be larger than that of other isomers having the same number of atoms.

Buckminsterfullerene, it is worth noting, has many 24-element independent sets, but the one displayed in Fig. 1 plays a special role in the chemistry of fullerenes and in the non-standard representation of icosahedral C_{60} [8,2]. This

Atoms	Isomer	Number of Isomers	Independence Number	Rank	Max	Min
60	$C_{60}:1 (I_h)$	1812	24	1	28	24
70	$C_{70}:1 (D_{5h})$	8149	29	1	33	29
76	$C_{76}:1 (D_2)$	19151	32	1	36	32
78	$C_{78}:1 (D_3)$	24109	33	1 (3)	37	33
	$C_{78}:3 (C_{2v})$		34	2		
	$C_{78}:2 (C_{2v})$		33	1 (3)		
84	$C_{84}:22 (D_2)$	51592	36	1 (17)	40	36
	$C_{84}:23 (D_{2d})$		36	1 (17)		

Table 3

Independence Number data for experimentally produced fullerenes. *Rank* is by smallest value of Independence Number. *Max* and *Min* are the largest and smallest values within the corresponding class. The numbers in parentheses record the number of isomers that share the corresponding rank or value.

24-element independent set, in fact, is the unique one (up to isomorphism) in which every vertex not in the independent set shares an edge with two vertices in the independent set and, the first author has proved, is the only fullerene with 60 or more atoms that contains such an independent set [2]. This fact may relate to the exceptional stability of icosahedral C_{60} .

As far as we know, the possible chemical significance of graph-theoretical independence appears first implicitly in the findings of Taylor, who discovered that the bromine decoration in $C_{60}Br_{24}$ determines a maximum independent set in C_{60} [18, pp. 126-7], and then explicitly in the conjectures of Graffiti. The first author's presentation on Graffiti's conjectures at the 1998 DIMACS Workshop on Discrete Mathematical Chemistry led shortly to [8].

The independence number is, in general, difficult to compute. For those isomer classes for which we have data, the range of values for this index is very small—for these classes the difference between the largest and smallest values of the independence number is never more than five. Nevertheless, the percentage of models that minimize their independence number is often surprisingly small. In the case of 100-atom isomers, for instance, there are 450 fullerene IPRs, only one of which minimizes its independence number ($C_{100}:321(T)$, Fig. 2). There are exceptions, though, 355 of 14246 74-atom isomers that minimize their independence number. We do not know for which isomer classes this invariant will be highly selective.

Another conjecture of Graffiti led the first author to predict that the separator of a fullerene, the difference between the largest and next largest eigenvalue

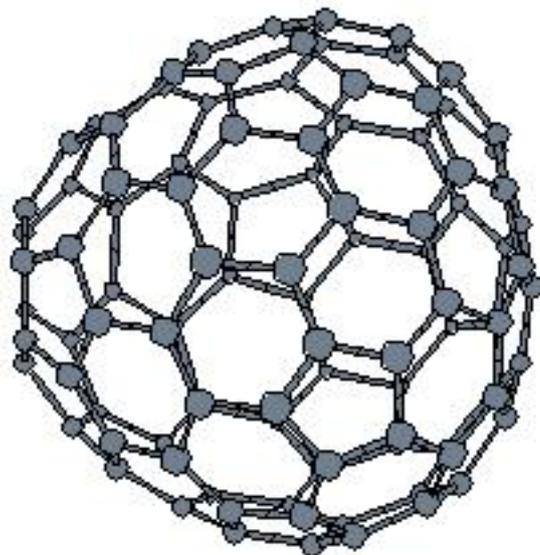


Fig. 2. The unique 100-atom IPR isomer with minimum independence number.

of the associated graph (corresponding to the difference in the energy levels of the two lowest energy π -orbitals in the Hückel theory) is a selector of fullerene stability [10].

On its own the separator is not a particularly strong selector—but it is effective in combination with other selectors (See Table 4). When restricted to the class of fullerenes with isolated pentagons, for instance, those fullerenes which have been produced in bulk rank very high.

Fowler has written that there is no known physical or chemical reason that the separator would be useful in predicting fullerene stability [10, p. 143]. These orbitals contribute negligibly to the molecules total π -energy. This may be. Nevertheless, the fact that there is no known existing reason for the satisfaction of some criterion to be of predictive value does not mean that it is not. It is just such anomalies that have led to theoretical advances in the past. In fact, one of the virtues of an automated conjecture-making program is that it may find simple, interesting conjectures totally overlooked by humans—as Grafitti already has found such conjectures.

We are indebted to Gunnar Brinkmann's Fullgen program for producing complete lists of all the mathematically possible fullerenes in each atom class [1]. The second author is responsible for all the computations in this paper. A longer version of this paper, originally submitted and subsequently shortened due to length restrictions, discussed the correctness of the computations.

Atoms	Isomer	Number of Isomers	Separator	Rank	IPR Rank	Max	Min
60	$C_{60}:1 (I_h)$	1812	0.2434	1	1	0.2434	0.0907
70	$C_{70}:1 (D_{5h})$	8149	0.1864	269	1	0.2031	0.0668
76	$C_{76}:1 (D_2)$	19151	0.1690	1183	2	0.1913	0.0633
78	$C_{78}:1 (D_3)$	24109	0.1588	3714	5	0.1845	0.0664
	$C_{78}:3 (C_{2v})$		0.1721	134	2		
	$C_{78}:2 (C_{2v})$		0.1652	1399	3		
84	$C_{84}:22 (D_2)$	51592	0.1666	20	5	0.1721	0.0519
	$C_{84}:23 (D_{2d})$		0.1721	1 (2)	1 (2)		

Table 4

Separator data for experimentally produced fullerenes. *Rank* is by largest value of separator. *IPR Rank* is rank by largest separator among the IPR fullerenes. *Max* and *Min* are the largest and smallest values within the corresponding class. The numbers in parentheses record the number of isomers that share the corresponding rank or value.

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