Facts and Conjectures about Fullerene Graphs: Leapfrog, Cylinder and Ramanujan Fullerenes

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Abstract

The definition of a fullerene as a cubic polyhedron made up entirely of pentagons and hexagons is compatible with a huge variety of isomeric forms for structures of chemically achievable size ($n \sim 100$ or fewer vertices $\equiv$ carbon atoms). Generation of complete sets of structures in this size range allows evaluation of conjectures, both chemical and mathematical, on energetics and graph-theoretical properties of this class of molecular graphs. Counterexamples to conjectures of GRAFFITI, including some on fullerenes that are Ramanujan graphs (ramafullerenes) are provided. Graph-theoretical indicators for closure of π shells and low overall energy of fullerenes are also briefly discussed.

Résumé

La définition d'un fullerène comme un polyèdre cubique composé entièrement de pentagones et d'hexagones est compatible avec une large variété de formes isomères pour des structures de taille chimiquement réalisable ($n \sim 100$ sommets ou atome de carbone au plus). La génération complète d'ensembles de structures de cette taille permet l'évaluation de conjectures, tant chimiques que mathématiques, sur l'énergétique et les propriétés graphiques de cette classe de graphes moléculaires. On présente des contre-exemples pour des conjectures de GRAFFITI, y compris certaines sur des fullerènes qui sont des graphes de Ramanujan (ramafullerènes). Des indicateurs graphiques pour la complétude des couches π-électroniques et pour l'énergie totale des fullerènes sont aussi brièvement discutés.

1 Introduction

With the discovery of the fullerenes and related novel forms of carbon, the chemistry, physics and materials science of this central element have undergone a revolution in the past 15 years [1]. The new forms of carbon give new opportunities for collaboration between mathematicians and chemists, as they are examples of discrete mathematical structures where graph theory, combinatorics and symmetry may help to generate qualitative chemical understanding [2]. The fullerenes themselves, the subjects of the present article, are mathematically well defined objects, being pseudospherical polyhedral shells of carbon atoms in which each carbon atom (vertex) is linked by a bond (edge) to three nearest neighbours, and all rings (faces) are either pentagonal or hexagonal. Simple reasoning based on the Euler equation shows that such a cage with n vertices, C_n, will have twelve pentagonal and $h = (n/2 - 10)$ hexagonal faces, and it is known that at least one fullerene can be realised for any even value of $n \geq 20$, with the exception of $n = 22$ for which the number of hexagons would have to be one [3]. Once past the first few small cases, the series C_n with $n = (20 + 2h)$ displays the usual combinatorial explosion of such objects, and $\#(n)$, the number of conceivable structural isomers grows as a high power of n (e.g. $\#(20) = 1$, $\#(40) = 40$, $\#(60) = 1,812$, $\#(80) = 31,924$, $\#(100) = 285,913, \ldots$). However, very few of the mathematically possible isomers are found in experiment. Confirmed characterisations of about a dozen isomers of the higher fullerenes, with $n \geq 60$ and all twelve pentagons disjoint, have been reported in the chemical literature, and one pressing task of theory is to identify the factors that determine this selection of a small subset from the millions of possibilities.

Construction of isomer sets and elucidation of structure–stability rules of thumb are central to this task and these topics will be treated briefly here. Two methods for fullerene isomer construction have been used in the Exeter group. One is based on the early work of Goldberg on medial polyhedra [4] and uses the equivalence between fullerene tessellations of the sphere and construction of nets from their dual triangulations on the equilateral triangular planar lattice. Within any accessible symmetry group, isomers are found by solving bilinear equations for integer parameters that describe the net; this is an easy task for high symmetries but impractical for low symmetries and especially for the C_1 group to which the majority of fullerene isomers belong [5]. A second method, which is independent of molecular symmetry, is the spiral construction first proposed by Manolopoulos and coworkers [6]. Here a fullerene isomer is 'peeled' to yield a continuous spiral strip of faces; reversing the procedure, such sequences of faces yield fullerene isomers when wrapped back onto the sphere. Construction and testing of spirals is easily automated. The method has the disadvantage that it misses some isomers at large n ($n \geq 380$) [2, 7, 8], but as these appear to be a tiny proportion of the total set, beyond the present and foreseeable size range of chemical synthesis, and energetically disfavoured by their crowded arrangement of pentagons, this seems to be more a technicality than a significant problem. The spiral construction gives a compact code for each fullerene that it can represent, as an $(n/2+2)$-digit number, twelve of whose digits are 5 and $n/2-10$ are 6, or simply as the set of twelve pentagon positions in this sequence. Lexicographic spiral codes have been adopted in

IUPAC recommendations for the nomenclature of fullerenes [9], and can be supplemented to deal with the exceptional 'unspirallable' fullerenes, should the need arise [10].

A mathematically more satisfactory solution of the isomer problem, which is both efficient and complete, is the PentHex puzzle algorithm of Brinkmann and Dress [11]. This represents the state-of-the-art in fullerene enumeration and it is to this method that we owe the certainty that the spiral algorithm is 'safe' up to 176 vertices. In view of the exact equivalence in the range, and the convenience of the spiral codes for generating adjacency matrices, the spiral algorithm will be used here for our search for isomers C_n ($n \leq 100$).

Quite apart from their chemical utility, lists of structures allow testing of the many mathematical conjectures that have been put forward for fullerenes. The GRAFFITI program [12] is a fertile source of these conjectures, and one such, that all fullerene graphs have at least $n/2$ non-negative eigenvalues, has already been disproved by a counterexample from the list of tetrahedrally symmetric fullerenes generated by the extended Goldberg method [13]. The present article will include further 'experimental mathematics' investigations of GRAFFITI conjectures, but first reviews some known facts and chemical rules of thumb for fullerenes.

2 Fullerene Energetics

The molecular graph of a fullerene is that of a cubic polyhedron, which in chemical terms implies an unsaturated molecule with a system of π electrons delocalised (at least to some extent) over the surface of the spherical framework of σ bonds defining the edges of the polyhedron. Approximations to the energy levels of the π system are to be found by diagonalisation of the adjacency matrix of the polyhedron according to the usual prescription of Hückel theory [14]. Once the eigenvalues $\{\lambda_i\}$ are found and ordered as $+3 = \lambda_1 > \lambda_2 \geq \lambda_3 \geq \ldots \geq \lambda_n > -3$, the π-electronic configuration is determined by filling the orbitals with the n π electrons according to the three chemical rules: the Aufbau principle (fill the stack of eigenvalues in decreasing order of λ_i), the Pauli principle (put no more than two electrons in any level λ_i) and Hund's rule of maximum multiplicity (when a multiple eigenvalue is reached, place up to one electron in each before adding a second to any member of the set).

The possible configurations for neutral C_n (n π electrons) are: properly closed ($\lambda_{n/2} \neq \lambda_{n/2+1},\ \lambda_{n/2} > 0,\ \lambda_{n/2+1} \leq 0$); pseudo-closed ($\lambda_{n/2} \neq \lambda_{n/2+1},\ \lambda_{n/2+1} > 0$); meta-closed ($\lambda_{n/2} \neq \lambda_{n/2+1},\ \lambda_{n/2} \leq 0$); open ($\lambda_{n/2} = \lambda_{n/2+1}$). The properly closed π shell is in a sense an ideal one for the π electrons: all electrons are in bonding levels, and no bonding capacity is 'wasted' in unfilled but potentially bonding levels. Open shells, on the other hand, are particularly undesirable as they will correspond to species that are highly reactive (and probably of high energy). Chemical intuition suggests that pseudo-closed shells will be common, as pentagons are electron-deficient (mathematically, a C_5 ring has three positive eigenvalues and hence the capacity for six electrons). This expectation turns out to be well founded. Overwhelmingly most fullerenes have the pseudo-closed π configuration. The three cases where ideal properly closed π shells are found are reviewed below.

(i) Leapfrogs. All *leapfrog* fullerenes have closed π shells [15]. A leapfrog is obtained by omnicapping and then dualising a parent fullerene, giving a new fullerene of the same symmetry, with a larger separation of its pentagons (in particular, they are all disjoint) and with $3n$ atoms [15]. Leapfrog fullerenes therefore occur at $n = 60 + 6k$ ($k \neq 1$) with the number of leapfrogs at n equal to the total number of fullerene isomers at $n/3$. The split nature of the eigenvalue spectrum of leapfrog fullerenes can be proved by detailed arguments [16] but is readily rationalised once it is realised that each edge of the parent has a descendant that carries a double bond in a fully symmetric Kekulé structure in the leapfrog [17]. The result for leapfrog fullerenes is part of a full classification for leapfrogs of cubic maps. Analogues of leapfrog fullerenes on the torus, Klein-bottle and elliptic plane, for example, have four, two and zero non-bonding (zero) eigenvalues, respectively, and leapfrog toroidal and Klein-bottle fullerenes have open shells if considered as neutral chemical species [18].

(ii) Carbon Cylinders. Carbon cylinder fullerenes have closed π shells with a positive eigenvalue $\lambda_{n/2}$ and $\lambda_{n/2+1} = 0$ [19]. The carbon cylinders are formed by tubular extension along the high-symmetry axis of the truncated icosahedron, or of the unique C_{72} leapfrog structure. Analysis in terms of standing waves on a cylinder shows that closed shells of this type occur for every third member of the series, at the vertex numbers $n = 70 + 30k$ ($k = 0, 1, 2, \dots$) and $n = 84 + 36k$ ($k = 0, 1, 2, \dots$).

(iii) 'Sporadic' Closed Shells. These extra closed-shell isomers occur outside series (i) and (ii) for large enough values of n [2]. If their number is $n(\#s)$ at n vertices, the pairs for $n \leq 140$ are 112(1), 116(1), 120(1), 122(1), 124(3), 128(3), 130(3), 132(4), 134(7), 136(9), 138(4), 140(12). All members of this set have very small first negative eigenvalues (typically $\sim -10^{-3}$) and in the absence of apparent distinguishing features it is thought that they are 'numerical accidents', unlikely to be different in chemical properties from the pseudo-closed fullerenes with similar gaps between occupied (HOMO) and unoccupied (LUMO) levels.

Series (i) and (ii) are chemically satisfactory in that both of the two most easily produced fullerenes, C_{60} and C_{70}, appear as parents of infinite families of isolated-pentagon isomers. Leapfrog fullerenes have non-zero HOMO–LUMO gaps, $\lambda_{n/2} - \lambda_{n/2+1}$. As the size of the fullerene increases, the typical gap is expected on physical grounds to decrease, as graphite itself has a zero gap; numerical evidence confirms this general expectation but gives no detailed picture of the asymptotics. One chemically plausible conjecture is:

Conjecture 1 *For numbers n at which a leapfrog fullerene is possible, i.e. $n = 60 + 6k$ ($k \neq 1$), the greatest HOMO–LUMO gap $\lambda_{n/2} - \lambda_{n/2+1}$ will belong to a leapfrog isomer.*

For C_n ($n < 100$) the maximum gaps (Δ) over all fullerene isomers are indeed found for leapfrogs: (n:m:m', Δ) = (60:1812:1, 0.75660), (72:11190:1, 0.70229), (78:24108:4, 0.63331), (84:51588:20, 0.69620), (90:99888:16, 0.64994), (96:191788:136, 0.64184), where the isomer on n vertices is mth in the spiral sequence for general fullerenes and m'th in

the sequence of isolated-pentagon fullerenes. Beyond $n = 100$ a leapfrog is known to have the largest gap amongst isolated-pentagon fullerenes in all cases tested, for example, C_{120} where the winning candidate is 120:10666, the leapfrog of 40:39 [2].

Thus the systematics of the π energies of fullerenes is broadly understood. Unfortunately, the π system accounts for only a quarter of the valence electrons of a fullerene, and for only part of the total energy. In addition, direct calculation of the relative energies of fullerene isomers, for which many quantum-chemical methods give very similar orderings, shows a poor correlation with π energy. The experimental structures of, for example, C_{84} are not the π-ideal leapfrog or cylinder isomers, but are those with lowest calculated energies. What determines this energy ordering?

Graph-theoretical arguments, though no longer those of Hückel theory, are useful here too. The key observation is that pentagon crowding, presumed to be energetically unfavourable, is measured by N_p, the number of pentagon fusions. The quantum-mechanically calculated energies show a tendency to rise with N_p: if ΔE (energy relative to the best isomer at the same vertex count) is plotted against ΔN_p (difference of N_p from the minimal achievable value at the same vertex count) for several thousand isomers (C_n, $n \leq 50$ and all $1,812$ for $n = 60$), a convincing universal linear correlation emerges [20]. Physically, this is equivalent to determining an effective energy penalty per pentagon adjacency (~ 0.7 to 1.5 eV depending on method [20, 21]). The dependence is not expected to be strictly linear, as N_p may still conceal significant variation in geometry, but it implies that a major determinant of energy has been found. Minimisation of N_p is therefore a driving force to low energy for lower fullerenes ($n < 60$). A direct consequence for higher fullerenes of this approximate relation is the isolated-pentagon rule (IPR):

Conjecture 2 *Where fullerene isomers with disjoint pentagons are possible ($n = 60$, $n \geq 70$), one of them will be the isomer of lowest total energy.*

Distinction *between* IPR isomers can also be made on graph-theoretical grounds. A rule in which the topological invariant to be minimised is the second moment of the hexagon-neighbour signature, $H = \sum_k k^2 h_k$, where h_k is the number of hexagons with exactly k hexagonal neighbours, appears to be highly selective in the range $60 \leq n \leq 140$. Minimisation of H is a way of satisfying Raghavachari's criterion of maximum similarity between environments of hexagonal rings [2, 22, 23]. Again, strong correlations between H and energy are found in calculations suggesting H as a useful invariant for distinguishing IPR structures within the range $60 \leq n \leq 140$. Beyond $n = 140$, nearly all IPR structures have minimal H and invariants sensitive to the longer-range ordering of the pentagons will be required.

3 Some Conjectures on Fullerenes

The GRAFFITI and MINUTEMAN programs [12] have produced several conjectures about relationships between mathematical properties of fullerene graphs (such as their second eigenvalues), and the stability (in a chemical sense) of the associated carbon frameworks. The present section reports some new calculations of fullerene eigenvalue spectra and other

invariants which furnish counterexamples to some of the conjectures and in turn suggest new generalisations.

Some terms and definitions are required (see [12, 24]). As before, the n adjacency eigenvalues of the fullerene graph, arranged in non-increasing order are $+3 = \lambda_1 > \lambda_2 \geq \lambda_3 \geq \ldots \geq \lambda_n > -3$. A *Ramanujan* graph is a finite regular graph of degree k for which all eigenvalues (other than $\pm k$) have modulus at most $2\sqrt{k-1}$. Ramanujan fullerenes (*ramafullerenes*, for short) are therefore those with one eigenvalue $\lambda_1 = +3$, and for all others $|\lambda_i| \leq 2\sqrt{2}$. We call here *positive* ramafullerenes those that fail to meet the Ramanujan criterion only at the end of the ordered eigenvalue spectrum, i.e. those for which $\lambda_2 \leq 2\sqrt{2}$ but $\lambda_n < -2\sqrt{2}$. Likewise, *negative* ramafullerenes fail at the beginning of the spectrum, with $\lambda_n \geq -2\sqrt{2}$ but $\lambda_2 > 2\sqrt{2}$.

The *separator*, $s(G)$, of the adjacency matrix of a graph G is the difference between its largest and second largest eigenvalues, i.e. $s(G) = \lambda_1 - \lambda_2$. The *radius*, $r(G)$, of a graph G is the minimum *eccentricity*, where the eccentricity of a vertex is the maximum number of edges required to reach *any* other vertex by the shortest path from the chosen vertex. The *diameter*, $d(G)$, of a graph is the maximum eccentricity taken over all vertices. $\overline{l(G)}$ is the *average distance* of the graph, taken over all pairs of vertices; this is related to the *Wiener index*, $W(G)$, by $\overline{l(G)} = 2W(G)/(n(n-1))$. The set of vertices of minimum eccentricity is called the *centre* of the graph; any vertex can be reached in $r(G)$ or fewer steps from some central vertex. Another subset of vertices, which may be called the *perimeter*, consists of those vertices with the largest eccentricity; vertices in this set are called *extreme*. $E(G)$ will denote the number of extreme vertices of a graph G. The *independence number*, $I(G)$, of a graph G is defined by a colouring of the vertices: colour vertices black or white, such that no two black vertices are adjacent; $I(G)$ is then the size of the largest possible set of black vertices.

The relevant conjectures made by the GRAFFITI program are:

895: If G is a fullerene, then $s(G) \leq 1$;

896: The separator of a fullerene with n atoms is at most $1 - 3/n$;

898: If the second largest eigenvalue of a fullerene G is $\lambda_2 \leq 2\sqrt{2}$, then G is a ramafullerene, i.e. in our terms, no positive ramafullerenes exist;

902: If G is a ramafullerene, then $r(G)/s(G) \leq 2I(G)$ [this conjecture also appears as **910**: For every ramafullerene, $I(G)/r(G) \geq (2s(G))^{-1}$];

903: If G is a ramafullerene, and $S_+(G)$ is the sum of the positive eigenvalues, then $r(G)/s(G) \leq 2S_+(G)$;

905: If G is a fullerene, $d(G)s(G) \leq E(G) + 1$;

907: If G is a fullerene, $I(G)/(d(G)s(G)) \leq 1 + \lambda_n + \overline{l(G)}/s(G)$;

908: If G is a fullerene, $I(G)/r(G) \leq r(G)$;

909: If G is a fullerene, $I(G)/r(G) \leq \overline{l(G)}$;

911: For every fullerene, $I(G)/r(G) \geq \log(n/2 - 1)$;

912: For every fullerene, $I(G) \geq 2(d(G) - 1))$.

A hypothesis in Written on the Wall [12], which is not given as a conjecture in the formal sense, is that the (physical) stability of fullerenes (for a given number of atoms) may be an increasing function of their separators. This hypothesis and the conjectures were tested by explicit computation of the invariants for the full set of fullerene graphs on up to 100 vertices, and our observations are now reported. Tables 1 and 2 show the distribution of Ramanujan graphs within the test set.

Table 1: Ramafullerene statistics for general fullerenes on $20 \leq n \leq 100$ vertices. N is the total number of distinct fullerene isomers (counting each enantiomer pair as a single isomer), N_r is the number of ramafullerenes, N_+ and N_- are the numbers of positive and negative ramafullerenes. s is the value of the largest separator at the given n, marked with an asterisk when achieved by an isolated-pentagon fullerene. At 74 and 84 vertices, the maximum separator is shared by two isomers; both are IPR for $n = 84$ but for $n = 74$, one has pentagon adjacencies.

n	N	N_r	N_+	N_-	s		n	N	N_r	N_+	N_-	s	
20	1	1	0	0	0.7639		62	2,385	1,772	5	549	0.2263	
24	1	1	0	0	0.5691		64	3,465	2,180	25	1,098	0.2219	
26	1	1	0	0	0.4859		66	4,478	2,276	8	1,863	0.2128	
28	2	2	0	0	0.5272		68	6,332	2,527	27	3,018	0.2128	
30	3	3	0	0	0.4558		70	8,149	2,292	25	4,592	0.2031	
32	6	6	0	0	0.4012		72	11,190	1,723	28	6,958	0.1991	
34	6	6	0	0	0.3870		74	14,246	1,300	11	8,823	0.1923	*
36	15	15	0	0	0.3916		76	19,151	745	19	11,202	0.1913	*
38	17	17	0	0	0.3768		78	24,109	156	4	13,041	0.1845	
40	40	40	0	0	0.3614		80	31,924	25	3	14,265	0.1819	*
42	45	45	0	0	0.3289		82	39,718	7	1	14,508	0.1743	
44	89	89	0	0	0.3261		84	51,592	2	0	14,577	0.1721	*
46	116	116	0	0	0.3014		86	63,761	0	0	14,229	0.1672	
48	199	197	0	1	0.2934		88	81,738	0	0	13,657	0.1643	*
50	271	268	0	1	0.2845		90	99,918	0	0	12,433	0.1593	
52	437	424	0	11	0.2799		92	126,409	0	0	11,100	0.1576	*
54	580	554	1	22	0.2579		94	153,493	0	0	9,688	0.1519	
56	924	853	1	60	0.2527		96	191,839	0	0	8,349	0.1470	
58	1,205	1,076	0	113	0.2451		98	231,017	0	0	6,721	0.1477	*
60	1,812	1,456	3	313	0.2434	*	100	285,913	0	0	5,615	0.1446	

A trivial first observation is that the number of ramafullerenes is finite. From Table 1, all fullerenes on $n \leq 46$ vertices are ramafullerenes, but from then on the proportion as a percentage of all fullerenes on n vertices starts to fall, reaching zero at $n = 86$. The fact that the class of ramafullerenes is finite follows from the result [25] that the class of planar, cubic Ramanujan graphs is finite (SF thanks Noga Alon for discussion on this point). The tapering to zero of the counts for $n \geq 86$ suggests to us that we have found all of the ramafullerenes.

Table 2: Ramafullerene statistics for isolated-pentagon fullerenes on $60 \leq n \leq 100$ vertices. Symbols are as in Table 1, but apply to the IPR subset of fullerenes.

n	N	N_r	N_+	N_-	s	n	N	N_r	N_+	N_-	s
60	1	1	0	0	0.2434	86	19	0	0	19	0.1651
70	1	1	0	0	0.1864	88	35	0	0	35	0.1643
72	1	1	0	0	0.1852	90	46	0	0	45	0.1546
74	1	1	0	0	0.1923	92	86	0	0	85	0.1576
76	2	1	0	1	0.1913	94	134	0	0	134	0.1483
78	5	2	0	3	0.1794	96	187	0	0	179	0.1462
80	7	3	0	4	0.1819	98	259	0	0	252	0.1477
82	9	2	0	7	0.1741	100	450	0	0	419	0.1442
84	24	2	0	22	0.1721						

Figure 1 identifies the first few non-ramafullerenes, i.e. the exceptional cases at 48 and 50 vertices, and Fig. 2 gives what we conjecture to be the complete list of 14 IPR ramafullerenes.

Conjecture 3 *All ramafullerenes have* 84 *or fewer vertices. There are* 20,175 *general ramafullerenes, of which all but* 14 *have pentagon adjacencies.*

The statistics in Table 1 allow an immediate comment on Conjectures **895** and **896**. All fullerenes within the test set easily obey the relation $s(G) \leq 1 - 3/n$. In fact, all would obey a stronger rule such as $s(G) \leq 3 - \sqrt{5}$, as the dodecahedron appears to have the largest separator of any fullerene. A plot of extrema of $s(G)$ against n (Fig. 3) settles down, after initial undulations, to a set of more-or-less monotonically decreasing curves. At $n = 68$ for general fullerenes, there is a small rise in maximum $s(G)$ (of only 5×10^{-5}). Some bumps in the curves are due to cases with high symmetries where $\lambda_2 = \lambda_3 = \lambda_4$ (tetrahedral or icosahedral) or $\lambda_2 = \lambda_3$ (dihedral groups) where the separator is larger than when all three eigenvalues are distinct.

The data in Table 1 provide an immediate refutation of Conjecture **898**: positive ramafullerenes exist and each is a counterexample to the conjecture. Positive ramafullerenes are comparatively rare, appearing first at $n = 54$ with a D_{3h} isomer containing three

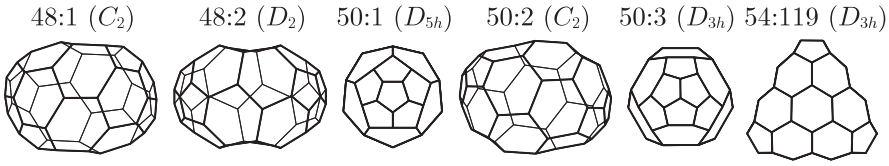

Figure 1: The five smallest non-ramafullerenes and the smallest positive ramafullerene (54:119) labelled n:m (G), where n is the number of vertices, m the isomer position in the list of lexicographically ordered spirals and G the maximal point group [2]

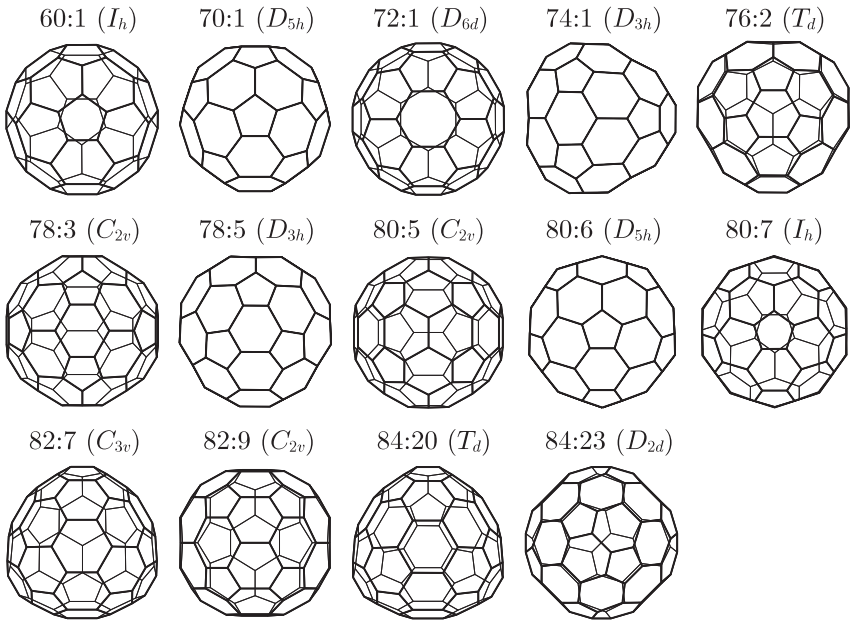

Figure 2: The complete list of 14 isolated-pentagon ramafullerenes

fused quadruples of pentagons (Fig. 1), and apparently disappearing for $n > 82$. It seems likely that the 161 cases found are the only positive ramafullerenes. All the positive ramafullerenes found in the search have pentagon adjacencies, and so a weaker version of Conjecture **898** is consistent with the facts:

898′: If the second largest eigenvalue of an isolated-pentagon fullerene G is $\lambda_2 \leq 2\sqrt{2}$, then G is a ramafullerene.

Negative ramafullerenes are encountered much more frequently, rising to 62% of all fullerenes on 72 vertices, but falling as a proportion, and eventually in absolute terms, as n continues to increase. It seems reasonable to suppose that this class too is finite. The negative ramafullerenes include many isolated-pentagon cases (Table 2). The fact that negative ramafullerenes are more common than positive is consistent with the chemical observation that fullerenes tend to be electron-deficient, i.e. having a spectrum with (usually) more positive than negative eigenvalues [26].

It is perhaps worth noting that no case is found of an 'exact' ramafullerene, i.e. a ramafullerene with $|\lambda_2| = 2\sqrt{2}$ or $|\lambda_n| = -2\sqrt{2}$. Dias [27] has remarked that examples of chemical graphs of maximum degree three having an eigenvalue $|\lambda| = \sqrt{l}$ are known for all integer values $1 \leq l \leq 9$ except for $l = 8$. The present search has not changed that position.

The computations of separator values also show that the correlation suggested in [12] between maximum separator and maximum stability at a given n is not generally true. It is known that the fullerene isomers of lowest total energy at a given value of n have the

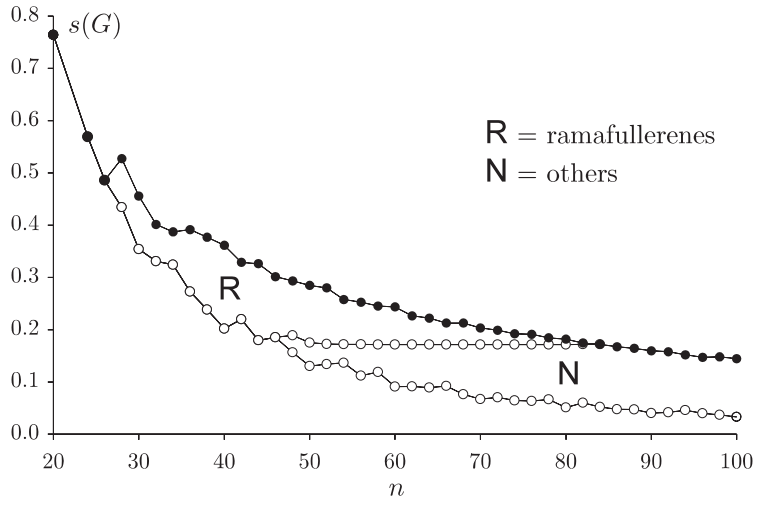

Figure 3: Maximum (•) and minimum (○) values of the separator $s(G)$ for fullerenes

minimal number of pentagon adjacencies, and that this minimum-adjacency rule lies behind the isolated-pentagon rule (IPR) for fullerenes (Conjecture 2). Thus, of $1,812$ isomers of C_{60}, the I_h IPR isomer 60:1812 is significantly lower in energy than its nearest (and as yet unobserved) rival with two pentagon adjacencies. For C_{70}, the low-energy isomer is the experimentally characterised D_{5h} IPR isomer 70:8149. However, whilst 60:1812 has the largest separator of all 60-vertex fullerenes, 70:8149 has only the 269th largest separator of all fullerenes on 70 vertices. Again at $n = 84$, the two fullerenes with largest separator are 84:20 and 84:23, of which 84:23 is in fact a low-energy cage, but is isoenergetic with 84:22 which has only 5th largest separator of the 24 IPR isomers. Table 1 shows that the fullerene of largest separator is often one with adjacent pentagons, even in the IPR range. Amongst the lower fullerenes there are also many cases where $s(G)$ fails to predict the low-energy isomer; for example, at C_{40} the T_d isomer 40:40 has the largest separator $s = 0.3614$ and 12 pentagon adjacencies, whereas isomer 40:38, favoured by all quantum-mechanical methods [21], has only 10 pentagon adjacencies and a smaller separator of $s = 0.3362$.

From the chemical point of view, there is no particular reason to expect a correlation of s with either total energy or reactivity, as the reactivity is determined by the frontier π orbitals (i.e. those around the middle of the eigenvalue spectrum) and the total energy is heavily influenced by strain in the σ framework. A chemically more plausible correlation would be between stability and the range of the positive part of the eigenvalue spectrum; in this respect, C_{70} is an interesting case where the most stable isomer has the smallest range, although this correlation does not hold generally.

Conjectures **902** and **903** refer to ramafullerenes only. Direct calculation of the 'balance functions' $b_{902}(G) = 2I(G) - r(G)/s(G)$ and $b_{903}(G) = 2S_+(G) - r(G)/s(G)$ shows that both are positive for all ramafullerenes. The first function is always at least ~ 3.690 (isomer 52:6), and $b_{903}(G)$ at least $(49 + 19\sqrt{5})/4 \approx 22.871$ [$= b_{903}(C_{20})$]. If Conjecture 3, that all

ramafullerenes have $n \leq 84$ vertices is correct, then both **902** and **903** have been verified by exhaustion, and **903** could be trivially strengthened by subtraction of the dodecahedral balance term. Conjectures **902** and **903** are not fully independent, however, as a simple argument based on uniform distribution of eigenvalues would predict $S_+(G)/I(G) \geq 1.5$ for fullerenes; in fact this ratio lies between ~ 2.001 and ~ 1.625 for all fullerenes with $n \leq 100$ vertices.

Neither conjecture extends to general fullerenes, as the term with $s(G)$ in the denominator can take very large values. Amongst the general fullerenes, $b_{902}(G)$ first becomes negative at $n = 50$ and $b_{903}(G)$ at $n = 70$. Only a small number of isomers would fail the general-fullerene version of **903**: there are $1, 1, 1, 1, 0, 4, 1, 3, 3, 8, 11, 19, 19, 30, 48$ and 52 failures for $n = 70, 72, \ldots, 100$. Fullerenes with $n \leq 100$ would obey a version of **903** where 'ramafullerene' is replaced by 'isolated-pentagon fullerene', but the falling balance in the range indicates a probable breakdown at large n for IPR fullerenes.

The remaining six conjectures are not restricted to ramafullerenes. No counterexamples to any of them were found in the range. Conjecture **905** comes close to failure for isomer 26:1, where the balance $b_{905}(G) = E(G) + 1 - d(G)s(G)$ is only 0.085. It is interesting to note that the simpler inequality $d(G)s(G) \leq 3$, the truth of which would imply Conjecture **905**, fails for just two fullerenes with $n \leq 100$ – dodecahedral 20:1 and tetrahedral 28:2. The inequality in Conjecture **912** is sharp for 20:1.

In summary, this search has disproved one conjecture of GRAFFITI, given a number of directions for future exploration of others and provided what we believe is the complete list of the family of ramafullerenes, showing that fullerene enumeration can have mathematical as well as chemical interest.

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