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Vertex Spirals in Fullerenes and Their Implications for Nomenclature of Fullerene Derivatives

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Abstract: The IUPAC nomenclature of fullerene derivatives is based on the vertex spiral, but not all fullerenes possess one. There are 1495 isomers with ≤ 20 vertices (66 isolated-pentagon isomers with ≤ 150 vertices) that are vertex-aspiral, but only four for which all vertex spiral starts succeed. Vertex-aspiral trivalent polyhedra are common (40190 with ≤ 24 vertices); infinite series include truncates of all trivalents larger than the tetrahedron. An alternative and readily automated breadth-first-search numbering scheme is proposed to deal with all trivalent polyhedra including fullerenes and incidentally to give robust, efficient determination of the automorphism/point group. For fullerenes, the new scheme has two clear advantages over the vertex spiral nomenclature: it is exception-free, removing the need for complex prescriptions to deal with exceptional cases, and it is mathematically simpler in that the numbering can be found in linear rather than quadratic time (as all canonical numberings for a fullerene begin on a pentagon).

Keywords: chemical graph theory · face spiral · fullerenes · nomenclature · vertex spiral

Introduction

The emergence of a rich chemistry of functionalised fullerenes[1–4] has brought with it the need for systematic nomenclature to distinguish between the many closely similar isomeric forms derived by addition to a common underlying cage structure. The IUPAC recipe for naming exohedral fullerene derivatives[5,6] is based on vertex spirals and, as with cookery recipes, the first problem is to find the ingredients. Even if Mrs. Beeton never wrote the phrase, folklore has it that her recipe for jugged hare starts with "First catch your hare". Here the problem would be "First find your vertex spiral".

The preamble to the IUPAC recipe for numbering the carbon atoms of the cage states "The identification of a well-defined and preferably contiguous helical numbering pathway is the cornerstone of fullerene numbering".[6] Rules are given for choosing between alternative contiguous helical numbering pathways (in our terms, vertex spirals). It is recognised that such pathways do not always exist: complex rules are given for dealing with fullerenes having a non-trivial rotational axis but no vertex spiral, and applied to a number of fullerenes and other trivalent polyhedra. No recommendations are given for C_s, C_i and C_1 fullerenes without contiguous numbering, on the grounds that since "these fullerenes have a large number of possible numbering pathways, it seems rather unlikely that a contiguous numbering cannot be found for most of these structures" (§3.4.4).[6]

For easy use of the IUPAC recipe, the first requirement is a vertex spiral, but it is known that a fullerene may have no vertex spiral at all. An example[7] is the icosahedral isomer of C_{80}. Investigation of the essentially graph-theoretical question of existence of a vertex spiral seems timely in the light of these nomenclature recommendations. Will it be necessary to invoke arcane rules for discontiguous numbering for a large number of fullerenes, or is I_h C_{80} a special case? Is there a better solution, without exceptions?

Fullerenes are usually defined in chemistry as trivalent polyhedral carbon cages composed entirely of pentagonal and hexagonal faces, but in some contexts,[8] the class of fullerenes is taken to include all trivalent polyhedra above some minimal size. Apparently the vertex-spiral properties of this larger class have not been discussed. Existence of *face* spirals for trivalent polyhedra and in particular for fullerenes has been discussed extensively, as the face spiral is used in the earliest systematic method for fullerene enumeration and construction;[9] all fullerenes on up to at least 176

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vertices[10] are known to have at least one face spiral, but some large fullerenes ($n \geq 380$) have no face spiral,[11–16] and the smallest trivalent polyhedron without a face spiral has only 18 vertices.[10] Within the range of present synthetic chemical interest, the face-spiral approach is "safe" for fullerenes, but the indications are that a vertex-spiral approach is not.

In the present study, we check the existence of a vertex spiral for chemically accessible fullerenes and other trivalent polyhedra, and prove some results on infinite classes of vertex unspirallable and vertex omnispiral polyhedra. It will be seen that lack of a vertex spiral is not unusual for trivalent polyhedra and is a feature of a significant minority of fullerenes in the chemical size range, both general and isolated-pentagon. There are many conceivable fullerene derivatives that are not nameable under IUPAC rules without recourse to complex back-up procedures for discontiguous spirals. We therefore take the opportunity to suggest an alternative, robust method based on breadth-first-search[17] that is capable of naming all exohedral derivatives and is easily automated.

Definitions

We deal with trivalent (known in mathematics as "cubic") polyhedral graphs in which by definition each vertex is connected by edges to three neighbours, and for which there is a unique embedding of the graph as a polyhedral framework on the surface of the sphere, without holes or handles. Such polyhedra have an even number of vertices, n. They have $3n/2$ edges and $n/2 + 2$ faces.

The IUPAC description of the "helical pathway" is as follows:[6] "The construction of the pathway starts with the numbering of a whole elementary ring of the fullerene. Then, the numbering proceeds to cover all of the other atoms keeping the pitch of the helix as small as possible (keeping the movement "as tight as possible") and maintaining its clockwise or counterclockwise directionality." The vertex spiral is our interpretation of this description in terms of an algorithm that works with the molecular graph.

We can imagine walking through the graph on the sphere, going from vertex to vertex following edges according to a "tight-winding" rule. The clockwise version of the walk is: begin at a vertex and walk along edges, visiting no vertex more than once, and taking at each vertex the path along the rightmost unused edge. The counterclockwise version takes the leftmost available edge at every step. The walk stops at the first vertex that has no unused edge. If either procedure, starting from some vertex, succeeds, that is, allows us to visit all vertices of the polyhedron exactly once, then the polyhedron has a *vertex spiral*. The procedure may be started from any vertex, move initially along any one of its three incident edges and keep to the right or the left, so there are $6n$ possible vertex-spiral starts for an n-vertex trivalent polyhedron. This is the same as the number of possible face-spiral starts, as both are equal to the number of flags (triples comprising a mutually adjacent vertex, edge midpoint and face-centre) covering the polyhedron.

Each successful spiral and each spiral start can be seen as a directed corkscrew-like curve on the polyhedral surface. Only the identity operation leaves a given spiral in place; all other operations of $\mathcal{G}$, the point group (automorphism group) of the polyhedron, shift the spiral, and so the site symmetry of each spiral start is C_1, the trivial group. Thus each vertex-spiral start occurs in $|\mathcal{G}|$ isomorphic copies.

Three special cases are when a trivalent polyhedron turns out to have no successful vertex-spiral start, only one successful vertex spiral start up to isomorphism, or a successful spiral from every one of the $6n$ spiral starts. These cases will be called (vertex) *aspiral* (or *unspirallable*), *unispiral* and *omnispiral*, respectively.

Method

To survey the vertex spiral characteristics of chemical graphs, a search was made of three sample sets of graphs: i) fullerene polyhedra on up to 120 vertices, ii) isolated-pentagon fullerenes on up to 150 vertices, iii) general trivalent polyhedra on up to 24 vertices. Sets (i) and (ii) may be generated by the fully general pent-hex puzzle algorithm[18,19] with the fullgen program (see http://cs.anu.edu.au/~bdm/index.html) or by the face-spiral algorithm,[7,9] which is known to be complete in this range. For convenience, in what follows, the fullerene isomers C_n will be labelled *n:p* by their vertex number and place in the list of lexicographically minimum face spirals (either the list of spirals of all fullerenes or the list of spirals of the isolated-pentagon fullerenes, depending on the context). Set (iii) is generated using the plantri program[20] (see http://cs.anu.edu.au/~bdm/plantri). General trivalent polyhedra will be labelled *n:p*, by vertex number and place in the plantri generation order. Given an adjacency list and a consistent rotation scheme (i.e., a list of the three neighbours of each vertex, ordered clockwise seen from outside the sphere) for each graph in sets (i) to (iii), a computer program checks all $3n$ clockwise and $3n$ counterclockwise vertex spiral starts.

Results

Fullerenes: Tables 1–3 report the results of the computer search on the two sets of fullerenes. One immediate observation is that *omnispiral* fullerenes are rare: there are only four found amongst the over ten million fullerenes with $n \leq 120$ (Table 1) and none amongst the set of isolated-pentagon fullerenes with $120 \leq n \leq 150$ (Table 2). These four are the unique fullerene isomers of C_{20} and C_{24} and the unique isolated-pentagon fullerene isomers of C_{60} and C_{72}. The molecular symmetries are I_h (C_{20} and C_{60}, 120 symmetry operations) and D_{6d} (C_{24} and C_{72}, 24 operations).

Unispiral fullerenes are found with $n \geq 50$ vertices. At small n, roughly half the isomers have only the trivial C_1

Table 1. Vertex spiral characteristics of the general fullerenes C_n on up to 120 vertices.[a]

n	N_{all}	N_{omni}	$N_{uni}(N_1)$	$N_{aspiral}$	n	N_{all}	N_{omni}	$N_{uni}(N_1)$	$N_{aspiral}$
20	1	1	1(0)	0	72	11190	1	3(0)	0
24	0	1	0	0	74	14246	0	0	0
26	1	0	0	0	76	19151	0	0	1
28	2	0	0	0	78	24109	0	0	0
30	3	0	0	0	80	31924	0	0	1
32	6	0	0	0	82	39718	0	0	0
34	6	0	0	0	84	51592	0	0	3
36	15	0	0	0	86	63761	0	2(1)	4
38	17	0	0	0	88	81738	0	2(0)	9
40	40	0	0	0	90	99918	0	1(1)	2
42	45	0	0	0	92	126409	0	2(1)	15
44	89	0	0	0	94	153493	0	8(3)	11
46	116	0	0	0	96	191839	0	14(7)	14
48	199	0	0	0	98	231017	0	11(7)	9
50	271	0	1(0)	0	100	285914	0	17(8)	28
52	437	0	0	0	102	341658	0	36(19)	12
54	580	0	0	0	104	419013	0	67(29)	51
56	924	0	1(0)	1	106	497529	0	77(49)	29
58	1205	0	0	0	108	604217	0	116(59)	55
60	1812	1	2(0)	1	110	713319	0	143(85)	70
62	2385	0	0	0	112	860161	0	209(152)	124
64	3465	0	1(0)	0	114	1008444	0	242(190)	130
66	4478	0	0	0	116	1207119	0	362(250)	236
68	6332	0	1(0)	1	118	1408553	0	427(363)	233
70	8149	0	1(0)	0	120	1674171	0	641(490)	455

[a] N_{all}, N_{omni}, N_{uni} and $N_{aspiral}$ are the numbers of all, omnispiral, unispiral and aspiral isomers, respectively. N_1 is the number of isomers with exactly one successful spiral, that is, the unispiral isomers of C_1 symmetry.

Table 2. Vertex spiral characteristics of the isolated-pentagon fullerenes C_n on up to 150 vertices.[a]

n	N_{ipr}	N_{omni}	N_{uni}	$N_{aspiral}$	n	N_{ipr}	N_{omni}	N_{uni}	$N_{aspiral}$
60	1	1	0	0	110	2355	0	0	0
70	1	0	0	0	112	3342	0	0	1
72	1	1	0	0	114	4468	0	0	0
74	1	0	0	0	116	6063	0	0	0
76	2	0	0	0	118	8148	0	0	0
78	5	0	0	0	120	10774	0	1	2
80	7	0	0	1	122	13977	0	0	0
82	9	0	0	0	124	18769	0	1	1
84	24	0	0	0	126	23589	0	0	0
86	19	0	0	0	128	30683	0	1	2
88	35	0	0	0	130	39393	0	0	0
90	46	0	0	0	132	49878	0	1	20
92	86	0	0	0	134	62372	0	2	2
94	134	0	0	0	136	79362	0	2	1
96	187	0	0	0	138	98541	0	1	3
98	259	0	0	0	140	121354	0	3	8
100	450	0	0	0	142	151201	0	2	0
102	616	0	0	0	144	186611	0	7	8
104	823	0	0	0	146	225245	0	3	7
106	1233	1	0	0	148	277930	0	4	8
108	1799	0	0	0	150	335569	0	7	2

[a] N_{ipr}, N_{omni}, N_{uni} and $N_{aspiral}$ are the numbers of all, omnispiral, unispiral and aspiral isomers, in the class, respectively. Of the 35 unispiral isomers, one at $n = 142$ and three at 148 have trivial C_1 symmetry.

symmetry and so have literally only one successful vertex spiral, and this proportion increases as n increases (see Table 1 and Table 2). An indication that there might be an infinite series of unispiral fullerenes comes from inspection of the unispiral isomers at $n = 50, 60, 70, \cdots 120$. At each of these vertex counts, isomer n:1 in the face spiral ordering has one vertex spiral; this isomer is the long thin cylindrical fullerene with two hemidodecahedral caps and, in each case, there are 20 symmetry-equivalent spirals starting on one vertex of the central pentagon of the cap, running clockwise or counterclockwise around that face and then spiralling down the cylinder to the other cap. The smaller cylinders, at $n = 30$ and $n = 40$ have additional successful vertex spiral starts, but from $n = 50$ onwards all those others fail.

Aspiral fullerenes are also apparently initially rare. All fullerene isomers with $n \leq 54$ vertices have at least one spiral. The first vertex nonspirallable fullerene is the T_d isomer 56:622 which has four fused triples of pentagonal faces (Figure 1). The vertices fall into orbits (equivalent sets) of 4, 4, 12, 12 and 24, with site symmetries C_{3v}, C_{3v}, C_s, C_s, C_1 and hence there are $1+1+3+3+6=14$ non-isomorphic spiral starts. It is not difficult to verify from Figure 2 that all 14 fail, each ending prematurely in a cul-de-sac where the last added vertex has no free edge along which to continue the spiral.

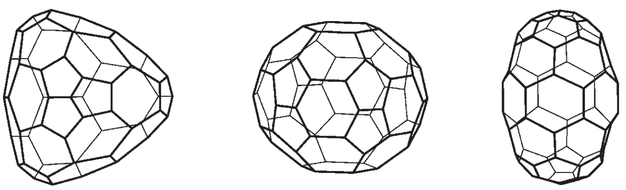

Figure 1. The smallest vertex unspirallable fullerenes, 56:622, 60:1784 and 68:677 shown as projections of the 3D structures.

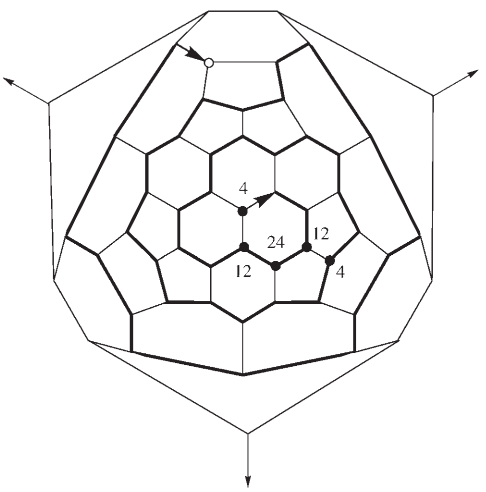

Figure 2. A Schlegel-like representation (with one vertex at infinity) of 56:622 illustrating examples of the five symmetry distinct vertex types and their multiplicities (black circles). An example of a failed spiral start is marked on the diagram: it starts from the vertex in the C_{3v} site at the fusion of three hexagons, and terminates at the vertex marked with the open circle.

Beyond $n=56$, the examples of vertex unspirallable fullerenes occur at first at multiples of 4 and then for all fullerene values of n. Figure 1 shows the first three vertex aspiral fullerenes. From $n=84$ onwards, at least one unspirallable isomer is found for every fullerene number in the range investigated. Exactly 100 unspirallable fullerenes have $n \leq 100$; 1495 have $n \leq 120$. Unspirallable fullerenes are not confined to high symmetry groups. As Table 3 shows, 19 of the 28 possible fullerene point groups are already represented in the first 100 examples, and in particular the trivial group C_1 occurs 18 times and the reflection group C_s seven times, so that the IUPAC recipe would need to be augmented by rules for discontiguous spirals also for the groups of low order.

Only one isolated-pentagon fullerene without a vertex spiral occurs for $n \leq 100$: the isomer 80:31 924 in the se-

Table 3. Vertex unspirallable fullerene isomers C_n on up to 100 vertices.[a]

n	$P(\mathcal{G})$				
56	622 (T_d)				
60	1784(D_{6h})				
68	677(D_{3h})				
76	8226(T)				
80	**31 924**(I_h)				
84	32 744(C_2)	32 745(D_2)	32 830(D_2)		
86	17 265(D_3)	19 855(C_{3v})	22 424(C_{2v})	27 096(C_2)	
88	3656(C_2)	14 798(D_2)	23 665(D_{2d})	23 667(D_2)	**23 668**(D_{2h})
	61 421(D_2)	**62 952**(C_3)	62 981(D_2)	63 969(D_{2d})	
90	3948(C_1)	98 692(D_{3h})			
92	4851(D_{3d})	4865(C_s)	33 532(C_2)	33 544(C_2)	38 532(D_2)
	39 302(C_3)	39 303(T_d)	47 684(C_2)	47 782(C_2)	96 995(D_{2d})
	113 067(C_2)	113 071(C_2)	124 265(C_{2v})	124 600(C_2)	**124 604**(D_{2h})
94	1655(C_{2v})	1660(C_2)	5267(C_s)	8650(C_1)	44 925(C_s)
	78 698(C_1)	79 908(C_1)	94 734(C_1)	94 754(C_1)	105 111(C_1)
	150 732(C_{2v})				
96	368(D_{2h})	10 289(C_1)	43 912(C_2)	**54 836**(D_2)	56 114(C_s)
	966 379(D_{6d})	111 555(C_1)	113 579(C_2)	113 705(C_2)	130 774(C_1)
	131 127(C_1)	132 509(C_1)	164 170(C_2)	**191 202**(D_{6h})	
98	6879(C_1)	7364(C_1)	10 936(C_2)	26 753(C_2)	48 572(C_2)
	52 063(C_s)	157 559(C_2)	157 879(C_2)	167 534(C_s)	
100	2991(D_2)	10 050(C_2)	**57 850**(C_2)	**64 542**(C_2)	72 989(C_2)
	89 519(C_1)	90 830(C_1)	121 316(C_2)	**124 136**(C_{2h})	124 137(D_2)
	132 483(C_1)	173 461(C_2)	181 481(C_2)	188 369(C_2)	188 370(C_2)
	192 261(C_3)	**200 253**(C_{2h})	200 482(D_2)	200 989(C_2)	246 033(C_2)
	263 917(S_4)	263 918(D_2)	272 117(C_2)	275 093(C_{2v})	275 192(C_1)
	275 576(C_2)	275 802(C_s)	285 136(C_{3v})		

[a] Isomers are listed as n:p where p is the place in the lexicographic face-spiral order of the full set of fullerene isomers on n vertices. The point group symmetry $\mathcal{G}$, is also given for each isomer. The eleven isomers marked in bold are those that have unspirallable leapfrogs.

quence of general fullerenes, which is 80:7 in the isolated-pentagon sequence. This is the icosahedral isomer already noted. It has two symmetry-distinct vertices, in sites of C_{3v} and C_s symmetry, respectively, and hence $1+3$ distinct spiral starts, all of which terminate early. Beyond $n=112$, examples of vertex unspirallable isolated-pentagon fullerenes occur sporadically (Table 2).

The list of aspiral fullerenes in the tables can be compared with the examples of fullerenes in the same size range without contiguous numbering quoted in the IUPAC document.[6] The examples are: a D_{6h} isomer of C_{60} (§3.2.5), a C_{2v} isomer of C_{70} (§3.2.6), an I_h isomer of C_{80} (§3.2.7), a C_{3v} isomer of C_{82} (§3.2.8), a D_{2d} isomer of C_{84} (§3.2.9), and a T_d isomer of C_{112} (§3.2.10). The first two have their pentagons arranged in six pentalene-type fused pairs; the remainder have isolated pentagons. The six examples can be identified as 60:1784, 70:7720 in the general fullerene list, and 80:7, 82:8, 84:23, 112:3342 in the isolated-pentagon list. The C_{60} and C_{80} cases are confirmed by our calculations as vertex unspirallable, as is the isomer of C_{112} (icosahedral C_{80} and this tetrahedral isomer of C_{112} are the first two isolated-pentagon vertex aspiral fullerenes). However, three of the examples that are listed as aspiral[6] do in fact have vertex spirals—70:7720, 82:8 and 84:23 have 44, 66 and 144 (11, 11 and 18 symmetry-distinct) vertex spirals, respectively. The discontiguous vertex numbering proposed in reference [6] can be avoided for these three fullerenes. The search used there to detect vertex spirals apparently missed out some of the possibilities by concentrating only on spiral starts on or near to a rotational axis, leading to incorrect assignments in these cases.

It is also natural to inquire whether the occurrence of vertex unspirallable fullerenes will continue beyond the range of n of immediate chemical interest. Direct testing of all isomers soon becomes prohibitively expensive, but some systematic soundings can be taken. For example, all *icosahedral* fullerenes are available by the Goldberg construction.[7,21,22] Icosahedrally symmetric fullerenes occur at

$$n = 20\ (i^2 + ij + j^2),$$

where the integers (i, j) obey $i \geq j \geq 0$, $i + j > 0$. Testing of the 21 icosahedral isomers with $n<1000$ yields mainly vertex aspiral fullerenes. The unique icosahedral isomers at $n=20$, 60, 140 and 380 have 1, 3, 6 and 1 symmetry-distinct vertex spirals, respectively. All other icosahedral fullerenes in the range, including electronically closed-shell isomers whenever n is divisible by 3, are vertex aspiral. In contrast, all icosahedral fullerenes have *face* spirals.[23]

The smallest known fullerene graph without a face spiral has 380 vertices.[11] It has no vertex spiral, and nor have any of the other 27 examples of tetrahedrally symmetric fullerenes without a face spiral that are presented in the same paper.

Various expansion techniques for fullerenes and other trivalent polyhedra are based on generalisations of the Goldberg construction. The leapfrog transformation,[7,24] $\mathscr{L}$, is significant in electronic-structure theory as, starting from *any* fullerene isomer C_n, it yields a fullerene C_{3n} with a properly closed shell;[25] geometrically, the leapfrog of a fullerene can be found by truncating all vertices of the dual, or by capping all faces and taking the dual, and it retains all faces of the parent, rotated and separated from one another by new hexagons.

Another operation, quadrupling, $\mathscr{Q}$, also possesses a simple geometrical interpretation, as it arises by chamfering all edges, and hence preserves all original faces as unrotated inset facets surrounded by hexagons.[26] Both operations stay within the class of fullerenes when applied to a fullerene parent. For example, the unique vertex unspirallable isomer of C_{80} is the quadruple of C_{20}. The operation $\mathscr{Q}$ in particular seems to show a tendency to increase the number of aspirals: for example, at $n=40$, the 40 C_{40} isomers include no aspiral cases and nor do their leapfrogs, but the set of quadruples includes 7; at $n=60$, the 1812 C_{60} include 1 aspiral case, and their leapfrogs only 5, but the set of 1812 quadruples includes 219. When $\mathscr{L}$ and $\mathscr{Q}$ are applied to the set of all fullerene isomers with $20 \leq n \leq 100$, we find 24018 vertex unspirallable fullerenes and 389488 vertex unspirallable fullerenes (from 1456598 parent fullerenes of which only 100 were themselves unspirallable). Note that, by construction, all of these have isolated pentagons, and all the leapfrogs have ideal closed-shell π-electron configurations. Leapfrogging of the 100 unspirallable fullerenes with $n \leq 100$ produces only 11 fullerenes that are themselves vertex unspirallable whereas, intriguingly, all 100 unspirallable fullerenes with $n \leq 100$ are found to have unspirallable quadruples. In the range, at least, quadrupling one unspirallable fullerene produces another unspirallable fullerene.

Trivalent polyhedra: Results of vertex-spiral testing for the general trivalent polyhedra on $n=4$ to 24 vertices are shown in Table 4. Figure 3 shows some of the smallest unspirallable trivalent polyhedra in Schlegel representation. Vertex spiralling fails very early in the series, and the unspirallable polyhedra are numerous. For $n \leq 24$, there are 40190 aspiral cases out of a total of 398438 polyhedra, that is, more than 10% have no vertex spiral, in a range where only about 0.75% are without face spirals.

The smallest example, 16:209, has T_d symmetry and is the quadruple of the tetrahedron itself, with the same relation to the smallest trivalent polyhedron as the first isolated-pentagon vertex unspirallable fullerene, C_{80}, to the smallest fullerene, C_{20}. The four distinct spiral starts are all easily seen to fail (Figure 4). Amongst the seven 18-vertex trivalent polyhedra without vertex spirals, 18:489 is of particular interest. It is derived by truncation of all vertices of the trigonal prism and is the smallest trivalent polyhedron without a *face* spiral.[10] Hypothetical C_{18} and derivatives $C_{18}X_q$ based on this cage would be doubly un-nameable under the basic versions of the face- and vertex-spiral nomenclature rules. There are many more examples of trivalent polyhedra that have neither face nor vertex spirals, as Table 4 shows. For $n \leq 28$, over one half of the trivalent polyhedra that have no

Table 4. Vertex spiral characteristics of the trivalent polyhedra on up to 24 vertices.[a]

n	N_{all}	N_{omni}	N_{aspiral}	N_{face} (N_{fv})	N_{bip}	$N_{\mathrm{bip\text{-}a}}$	N_{tf}	$N_{\mathrm{tf\text{-}a}}$
4	1	1	0	0	0	0	0	0
6	1	1	0	0	0	0	0	0
8	2	1	0	0	1	0	1	0
10	5	1	0	0	0	0	1	0
12	14	1	0	0	1	0	2	0
14	50	1	0	0	1	0	5	0
16	233	1	1	0	2	0	12	0
18	1249	1	7	1(1)	2	0	34	0
20	7595	2	126	11(6)	8	0	130	0
22	49566	1	2529	184(97)	8	0	525	1
24	339722	2	37527	2800(1690)	32	2	2472	2

[a] N_{all}, N_{omni}, N_{uni} and N_{aspiral} are the numbers of all, omnispiral, unispiral and aspiral isomers, respectively. An entry in parentheses in the unispiral column indicates the number of unispiral isomers that have the trivial C_1 symmetry. N_{face} is the number of *face* aspiral trivalent polyhedra,[10] of which N_{fv} are both face and vertex aspiral. N_{bip} is the number of bipartite trivalent polyhedra and $N_{\mathrm{bip\text{-}a}}$ is the number of these without vertex spirals. N_{tf} is the number of triangle-free trivalent polyhedra and $N_{\mathrm{tf\text{-}a}}$ is the number of these without vertex spirals. For $n=26$ and 28, the numbers N_{face} (N_{fv}) are 41763 (28490) and 612755 (452485), respectively.

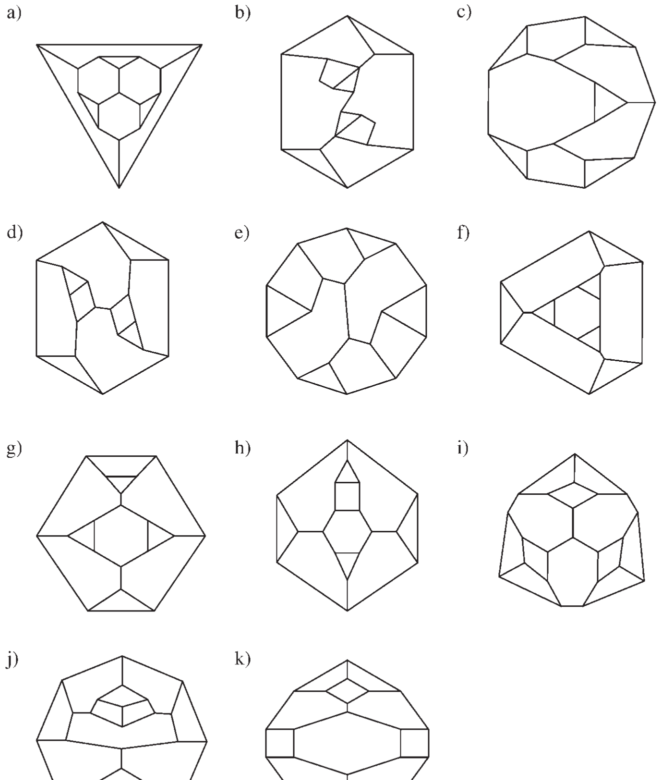

Figure 3. Small vertex unspirallable trivalent polyhedra, represented in Schlegel-diagram form: a) 16:209 (T_d), the smallest vertex aspiral trivalent polyhedron, b) 18:128 (C_2), c) 18:176 (C_s), d) 18:296 (C_2), e) 18:387 (C_2), f) 18:489 (D_{3h}), the smallest face aspiral trivalent polyhedron, g) 18:1015 (C_s), h) 18:1098 (C_s), i) 22:28723 (C_{3v}), the smallest triangle-free aspiral trivalent polyhedron, j) 24:40542 (C_{2v}), and k) 24:40954 (C_{2h}), the smallest aspiral bipartite trivalent polyhedra.

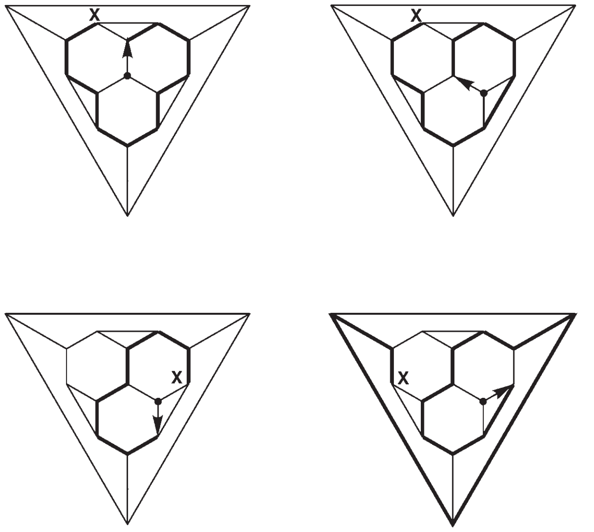

Figure 4. Illustration of the vertex unspirallable character of the trivalent polyhedron 16:209. All four distinct spiral starts terminate early on a vertex of one of the four triangular faces. A black circle denotes the initial vertex, and a black cross the final vertex in each case.

face spiral,[10] have no vertex spiral either. All four combinations of vertex and face spirallable/unspirallable occur for the small trivalent polyhedra. Several examples of larger trivalent polyhedra with face sizes four and six that have no contiguous helical vertex numbering under the IUPAC scheme are known.[6]

Triangular faces act as "traps" for vertex (and face) spirals in that, if a spiral passes through two vertices of a triangular face and does not immediately take in the third vertex, then it must either return later to terminate on that vertex, or must miss it out altogether. Informally speaking, a trivalent polyhedron cannot "afford" too many triangular faces if it is to have successful spirals. The importance of triangles for the small aspiral trivalent polyhedra can be seen by comparing the counts of general, triangle-free and bipartite aspiral isomers (see Table 4). When triangles are excluded, the number of aspiral trivalents in the range $4 \leq n \leq 24$ drops from 40190 to three, of which two are bipartite. The three are illustrated in Figure 3i–k. The trivalent polyhedra that maximise the number of triangular faces at each n are the tetrahedron and the omnitruncates (those polyhedra obtained by truncation of a trivalent polyhedron on all vertices). As will be seen below, apart from the tetrahedron and its omnitruncate, these maximum-triangle trivalent polyhedra are all both vertex and face unspirallable.

Infinite classes of aspiral and omnispiral trivalent polyhedra: The result that the 18-vertex truncated prism, 18:489, is unspirallable is part of a general pattern. It has been shown that, with the sole exception of the truncated tetrahedron, all those trivalent polyhedra produced by truncation of all vertices ("omnitruncation") of a trivalent parent are without *face* spirals.[15] It is easy to see that the omnitruncates of trivalent polyhedra, with the same exception of the truncated tetrahedron, are also without *vertex* spirals. A sketch pictorial proof is given in Figure 5, where it is seen that all spiral starts from a typical vertex terminate on a face that has an edge in common with the triangle containing the initial vertex. Only for the truncated triangle is one of the types of spiral start consistent with exhaustion of all vertices. Thus we have the result that truncation on all vertices of any trivalent polyhedron with $n>4$ yields a trivalent polyhedron that has neither a face spiral nor a vertex spiral.

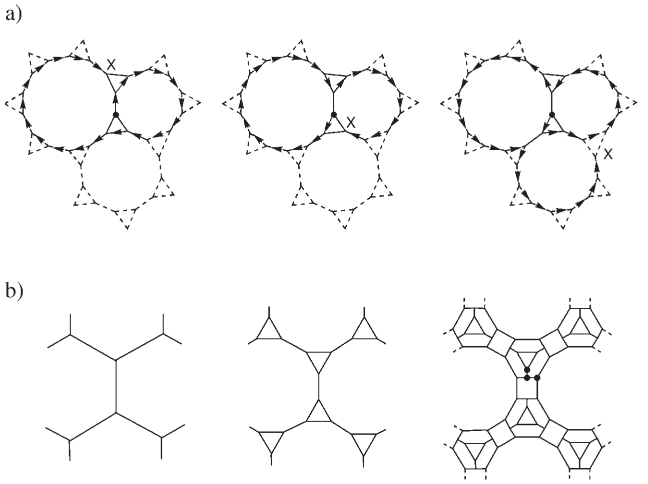

Figure 5. Two series of vertex aspiral polyhedra. a) Scheme of pictorial proof that omnitruncation of trivalent polyhedra larger than the tetrahedron leads to polyhedra without vertex spirals. For the typical vertex (black circle) all spiral starts terminate at X on a nearby face (only clockwise starts are shown). The truncated tetrahedron is small enough for all vertices to be covered by the termination of the spiral start of the third type; otherwise all spiral starts of all types fail. b) Construction of an aspiral trivalent polyhedron from a parent, by truncation on all vertices (centre) and quadrupling (right). The three typical vertex types are indicated as black dots. If the parent is any trivalent polyhedron except the tetrahedron, all spiral starts fail.

Another question, motivated by the observation on quadrupling of the first 100 aspiral fullerenes, is whether the quadrupling operation always preserves unspirallable character. A more limited result is easily proved, again pictorially (Figure 5b). When an aspiral truncated trivalent polyhedra is quadrupled, the resulting trivalent polyhedron is itself aspiral. The proof depends on inspection of nine cases of spiral starts in the generic configuration and is not given here. The result is: truncation on all vertices of any trivalent polyhedron with $n>4$, followed by quadrupling, $\mathcal{Q}$, yields a trivalent polyhedron that has no vertex spiral.

As quadrupling and omnitruncation ($\mathcal{Q}$ and $\mathcal{T}$, respectively) do not commute, the two previous observations imply the existence of at least two distinct aspiral trivalent polyhedra on $24n$ vertices (n even, $n > 4$) for every n-vertex trivalent polyhedron P, one $[=\mathcal{Q}(\mathcal{T}(\mathrm{P}))]$ with n and one $[=\mathcal{T}(\mathcal{Q}(\mathrm{P}))]$ with $4n$ triangular faces.

The survey of the small trivalent polyhedra also reveals some patterns for the vertex omnispiral property. In the range $4 \leq n \leq 24$ there is one omnispiral isomer at each vertex number except at $n=20$ and 24, where there are two. One isomer at 20 and one at 24 are accounted for by the fullerenes—these are the dodecahedral C_{20} and the sixfold-symmetric barrel-shaped C_{24} fullerenes. The omnispiral polyhedron with $n=4$ is the tetrahedron. All the remaining cases turn out to be $n/2$-gonal prisms. The typical member of the series has $D_{(n/2)h}$ symmetry, with all vertices equivalent, and a total of three distinct spiral starts (the exception is for $n=8$, the cube, where the symmetry is O_h and all spiral starts are equivalent). It is easy to show (Figure 6 gives a sketch proof) that the q-gonal prism is vertex omnispiral for all q.

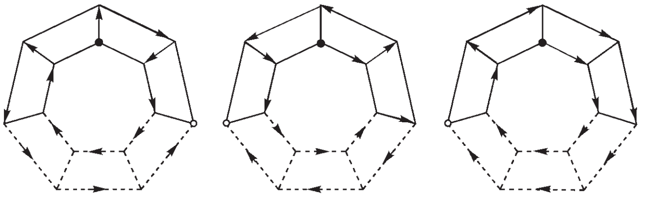

Figure 6. Scheme of pictorial proof that prisms are vertex omnispiral. The vertices are all equivalent and occupy sites of C_s symmetry, with three distinct spiral starts, all of which succeed for all sizes of polar polygon.

The two fullerene examples in the omnispiral list suggest the definition of a *barrel* graph: the [$4n$]-barrel is the trivalent polyhedron constructed by taking an n-gon and circumscribing it successively with two rings of n pentagons. The fullerenes C_{20} and C_{24} are barrels with $n=5$ and 6, respectively. The typical member of the series has $D_{(4n)d}$ symmetry, with vertices falling into two sets of size $2n$, and a total of six distinct spiral starts (the exception is for $n=5$, where the symmetry is I_h and all vertices are equivalent). As Figure 7 shows, all six spirals complete successfully if the polar polygon is large enough; for $n=3$ and $n=4$, some spiral starts terminate early, so that although [12]- and [16]-barrels have vertex spirals, they are not omnispiral. We can conclude that the [$4n$]-barrel with $n>4$ is vertex omnispiral. In this connection it is interesting to note that the only vertex omnispiral fullerenes of which we are aware are the two [$4n$]-barrel fullerenes and their leapfrogs.

An alternative: BFS numbering: Given that atom numbering using a single vertex spiral is not possible for all ful-

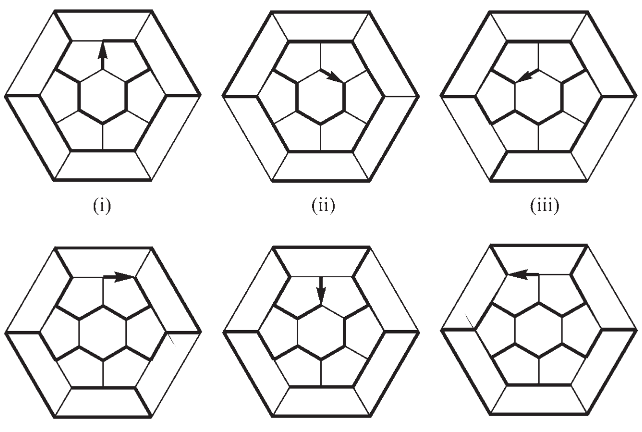

Figure 7. Scheme of pictorial proof that members of an infinite class of trivalent polyhedra are vertex omnispiral. In generic [n]-barrels there are distinct polar and equatorial vertices in sites of C_s symmetry, implying six distinct starts. Types (iii), (v) and (vi) terminate early for $n=3$, and types (iv) and (v) terminate early for $n=4$, but all six lead to vertex spirals for all larger central polygons.

lerenes, even on the strictest definition of a fullerene, various approaches are possible. As with face spirals[27] it is possible to devise a backtracking approach to restart the spiral at some well defined nearest point after a dead-end. The IUPAC rules include procedures for choosing these discontiguous spirals in certain cases. If the special simplicity of the vertex-spiral approach is to be lost, then it seems better, as the authors of reference [28] argue, to use a more firmly based and computer-codable algorithm. The particular numbering method they proposed[28] is to take the smallest possible binary molecular code obtained from the adjacency matrix when its rows are read from left to right and from top to bottom, but this has a very poor complexity (it belongs to the class of problems known as #P-complete[29]) and will rapidly become very expensive for large fullerenes. There are no known polynomial-time algorithms for finding such an adjacency matrix and, since the problem is #P-complete, it is unlikely that one exists.

A much simpler idea is to use a canonical breadth-first-search labelling. Two common ways of traversing a graph are Depth First Search (DFS) and Breadth First Search (BFS).[17] The aim in both is to visit each vertex of a graph exactly once: in DFS, a path is followed as far as possible before backing up; in BFS, all neighbours of the current node are visited before backing up. A special form of BFS will be used here.

Given an embedding of a graph, a *rotation system* is an adjacency list where the neighbours of each vertex are listed in clockwise order. The neighbour lists are considered to be cyclic and so it is traditional when a well-defined representation is required to select the starting point of the list so that the neighbour lists are lexicographically minimised. A *clockwise breadth first search* is a special type of breadth first search[17] which is applied to a rotation system. It starts with a specified root vertex r, and first child u.

The neighbours of a vertex are always traversed in clockwise order starting with vertex u for vertex r and the BFS-parent for the other vertices. The vertices are renumbered by the order in which they are visited by this BFS and this results in a relabelled rotation system.

It is well-known that any 3-connected planar graph has a unique planar embedding[30] (considering that reversal of the sense of clockwise gives the same embedding). To obtain a canonical form for any 3-connected planar graph, apply a clockwise-BFS to the embedding and also its *flip* (the embedding obtained by reversing the sense of clockwise). Each re-labelled rotation systems is then converted to a sequence of integers as follows:

1) Write down n.
2) For each vertex v_i, $i=1, 2, 3, .., n$, write down the degree of v_i followed by the list of neighbours as labelled by the clockwise-BFS in clockwise order, starting with the smallest neighbour.

The smallest such sequence lexicographically is defined to be the canonical form for the graph.

It is easy to argue that for a fullerene, the canonical form must result from a clockwise-BFS where vertices 1, 2 and 4 lie on a pentagon. This is because the canonical form (see Figure 8) starts with

```
n
3 2 3 4
3 1 5 6
3 1 7 8
3 1 9 10
3 2 x y
```

and x is 10 if F_1 in Figure 8 is a pentagon, but otherwise x is equal to 11. Similarly, it is better to have both faces F_1 and

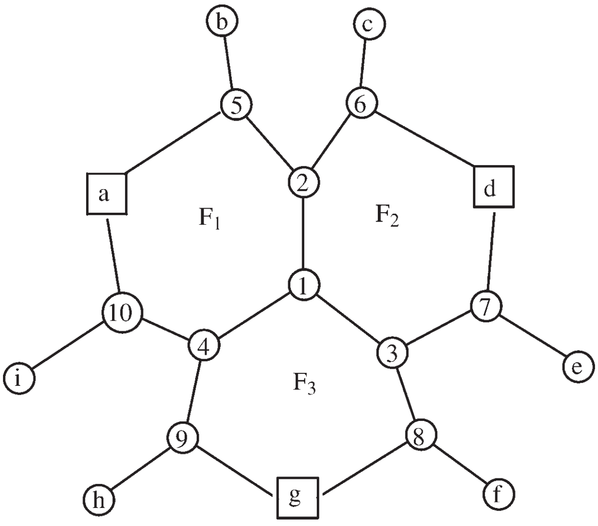

Figure 8. Clockwise BFS canonical form for a fullerene. Starting the BFS search for a fullerene: F_1, F_2 and F_3 are faces of the fullerene: each may be a hexagon, in which case the squared vertex is present, or a pentagon consisting of the circled vertices only.

F_2 as pentagons, and the best possible situation is when F_1, F_2 and F_3 are all pentagons.

This requirement means that for any fullerene there are at most 120 potential starting locations which could lead to a minimum sequence and that the dodecahedron and the isolated-pentagon fullerenes are the only fullerenes that require potentially 120 iterations of the clockwise-BFS to find the canonical form. Note that the algorithm finds all the automorphisms of the graph (these correspond to the clockwise BFS labellings that give rotation systems equal to the canonical system) on the way to determining the canonical form, and the maximum number of these for a fullerene is also 120. BFS-clockwise canonical form thus gives an efficient and completely robust way to determine the point group, in addition to the labelling.

An algorithm runs in $O(n)$ time if there is some constant c such that the number of machine operations taken by the algorithm is at most $c \times n$ on any reasonable machine. Since an individual clockwise-BFS takes $O(n)$ time, and canonical form for a fullerene can be computed with a constant number of clockwise-BFS (120), it takes at most $O(n)$ total time in the worst case to compute the canonical form for a fullerene. It is not possible to have a better worst-case time complexity given a rotation system of the fullerene as input, since it requires at least this amount of time to examine the input.

Figure 9 shows the canonical clockwise-BFS numberings for the smallest vertex-aspiral fullerene, 56:622, and for the two main experimental fullerenes, isolated-pentagon C_{60} and C_{70}. The procedure delivers a numbering Scheme for any 3-connected planar graph.

The canonical form we are computing could also be used as an efficient test for checking whether or not a polyhedral molecule is chiral. The two enantiomers of a chiral fullerene receive the same canonical labelling under the present scheme, as the procedure tries out both the embedding of the graph and the inverted embedding with the rotation scheme reversed on all vertices, and takes the overall lexicographically minimal labelling. To check chirality, we would carry out three steps:

1) Find G_1, the minimum BFS labelling considering only the $3n$ possible starts of G.
2) Find G_2, the minimum BFS labelling considering only the $3n$ possible starts of the flip of G.
3) If G_1 is the same labelled graph as G_2 then the molecule is achiral, otherwise the molecule is chiral.

If two enantiomers are to have the same canonical form, we use the minimum from the pair $\{G_1, G_2\}$ as the canonical form (as the code does now). This means that in some cases the canonical "clockwise BFS" labelling will correspond to the flip of the embedding. We could assign a different labelling to each enantiomer by simply taking G_1, and not checking G_2.

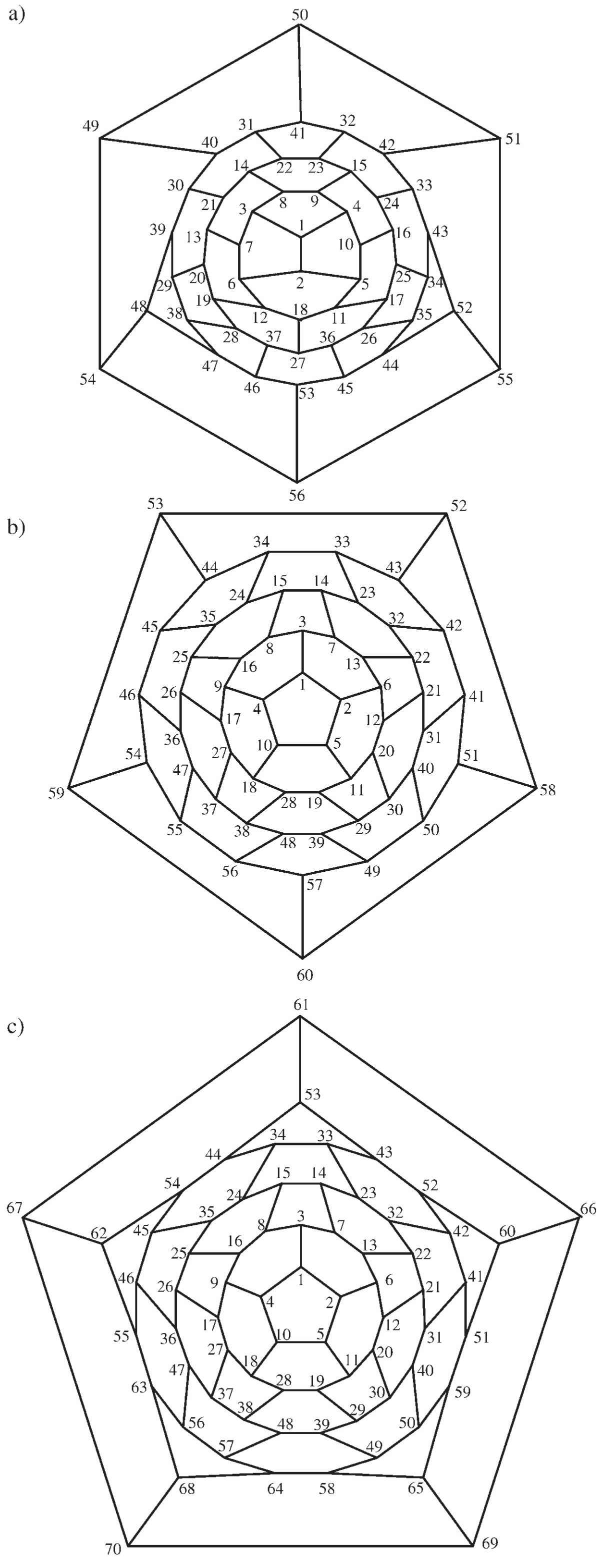

Figure 9. Clockwise BFS canonical form numberings of a) the smallest vertex-aspiral fullerene 56:622, b) [60]-fullerene, c) [70]-fullerene.

Various extensions of the BFS scheme can be envisaged for different applications. For example, a heterofullerene could be treated by labelling the vertices additionally with an atom type; then the embedding would be ordered according to (vertex number, atom type) rather than number alone; likewise, bonds of different type could be distinguished in the neighbour lists as (neighbour number, bond type). This would allow labellings that were specific to Kekulé structures. Addends could be incorporated into the vertex labels, and the strings compared as before to find canonical forms when it was required to obtain a realisation of the symmetry group of a particular fullerene derivative.

Conclusion

This paper set out to explore some aspects of the vertex spiral, the basis of the proposed IUPAC nomenclature for fullerene derivatives. From the calculations on the fullerene graphs, it was found that there are 100 vertex-unspirallable isomers with at most 100 vertices, 1495 with at most 120 vertices and 66 isolated-pentagon vertex-unspirallable isomers with at most 150 vertices. As a percentage, these constitute a minute fraction of the total number of mathematically possible isomers, and some of them have energetically unfavourable pentagon fusions, but the set does include many chemically plausible isolated-pentagon isomers. In the wider class of trivalent polyhedra, many aspiral cases were found and it was shown that an infinite number of vertex-aspiral cases are easily constructed using the operations of truncation and quadrupling. There is a hint that the quadrupling operation may *always* produce an unspirallable polyhedron from an unspirallable parent.

These findings can be read optimistically, as saying that many fullerenes are covered within the vertex-spiral approach, or pessimistically, as pointing out that this approach is ad hoc. One of the advantages of the vertex-spiral approach is said to be its intuitive appeal and the possibility of using it “by hand” but, as we have seen, this process can itself be error-prone.[6] Once the need for computer checking is acknowledged, it seems logical to use the BFS numbering proposal, which is easily coded and covers all cases without exceptions or the need for complex sets of rules and subrules. In fact, the BFS numbering proposal is not only complete, but it is also easier to implement, even “by hand”. To test in a general fullerene for the existence of a vertex spiral, a linear number of spiral starts must be explored. To find the canonical BFS scheme, only a constant number of spiral starts need ever be explored (a canonical scheme starts on a pentagon). It would seem logical to switch to a nomenclature scheme based on clockwise BFS.

Acknowledgements

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