Face-spiral codes in cubic polyhedral graphs with face sizes no larger than 6

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Abstract

According to the face-spiral conjecture, first made in connection with enumeration of fullerenes, a cubic polyhedron can be reconstructed from a face sequence starting from the first face and adding faces sequentially in spiral fashion. This conjecture is known to be false, both for general cubic polyhedra and within the

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specific class of fullerenes. Here we report counterexamples to the spiral conjecture within the 19 classes of cubic polyhedra with positive curvature, i.e., with no face size larger than six. The classes are defined by triples $\{p_3, p_4, p_5\}$ where p_3, p_4 and p_5 are the respective numbers of triangular, tetragonal and pentagonal faces. In this notation, fullerenes are the class $\{0, 0, 12\}$. For 11 classes, the reported examples have minimum vertex number, but for the remaining 8 classes the examples are not guaranteed to be minimal. For cubic graphs that also allow faces of size larger than 6, counterexamples are common and occur early; we conjecture that every infinite class of cubic polyhedra described by allowed and forbidden face sizes contains non-spiral elements.

MSC Codes: 05C30; 05C85; 52B99; 92E10

1 Introduction

Cubic polyhedral structures built from carbon and other atoms are of current interest in chemistry, physics and materials science for many reasons. They are exemplified by the fullerenes,[1–3] and also occur as skeletons of the polyhedral hydrocarbons[4–7] known collectively as 'spheroalkanes'.[8] They are studied as models for electron-precise clusters involving other elements (e.g., clusters with pairwise replacement of carbon atoms by BN).[9] They occur as motifs in supramolecular frameworks,[10] and act as finite models for many of the forms of carbon that have emerged since the discovery of the fullerenes[11–17] and for chemically plausible 'spheroarene'[18] generalisations of the fullerene class.[19–23]

One aspect of the systematic study and nomenclature of chemically relevant polyhedra is treated here. It involves the applicability and limitations of the face-spiral conjecture and associated algorithms. The face-spiral conjecture for fullerenes[3,24] was that the surface of a fullerene polyhedron may be unwound in a continuous spiral of edge-sharing pentagons and hexagons such that each new face in the spiral after the second shares an edge with both (a) its immediate predecessor in the spiral and (b) the first face in the preceding spiral that has an open edge. In other words, it was conjectured that any fullerene (cubic polyhedral graph with faces of size five and six only) could be constructed by a spiral algorithm in which faces were added in a given sequence starting from an initial face and winding around in spiral fashion until the structure closed. The list of

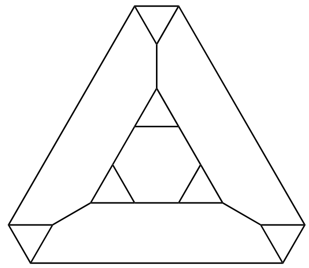

Figure 1: The smallest cubic polyhedron without a face spiral.[36]

positions of the pentagons in the spiral sequence gives a compact representation of any fullerene that can be constructed in this way, one from which the graph, point group symmetry, approximate structure and various useful properties can be reconstructed.[3] The conjecture was the basis of the first successful attempt to enumerate fullerene isomers of mderate size,[3] although a more efficient method was soon devised,.[25,26] The spiral approach is enshrined in IUPAC proposals for naming fullerenes.[27,28] A stronger version of the conjecture replaces 'fullerene' with 'cubic polyhedron' everywhere in the statement. However, it has been known for some time that the conjecture is false even in its weak fullerene form,[3,29] although the known fullerene counterexamples were all large, likely to be chemically unstable, and still seem well beyond the reach of present-day techniques for directed synthesis of these molecules. Fullerene graphs exist for all even vertex numbers $n \geq 20$, with the exception of 22,[30] and the smallest unspirallable fullerenes found by construction occur at $n = 380$,[29] and $n = 384$.[31] Various studies have investigated symmetries and pentagon arrangements in possible counterexamples and generated hundreds of further fullerene examples at higher vertex counts.[32–34] Recent work on the efficient generation of fullerene graphs[35] has completed the story, by confirming that the cases with 380 and 384 vertices are the smallest counterexamples to the spiral conjecture and that there are no other counterexamples with $n \leq 400$.

It is also known that the strong face-spiral conjecture fails much earlier than for fullerenes, and that the numbers of unspirallable cubic polyhedra grow rapidly with n.[36] The smallest cubic polyhedron without a face spiral has only 18 vertices (See Figure 1),[36] and is derived from the trigonal prism by truncation at all vertices (*omnitruncation*). Omnitruncation of any cubic polyhedral parent, apart from the tetrahedron, leads to an unspirallable cubic polyhedron.[37] This can be understood in terms of the small faces (or regions of high curvature) acting as 'traps' for putative face spirals.

The size of the gap between onset of unspirallable cubic polyhedra and the onset of unspirallable fullerenes suggests a natural question: What is the smallest non-spirallable cubic polyhedron for any given face recipe? Where would chemical nomenclature of the type used for fullerenes first break down for the more general cubic polyhedra described in the opening paragraph of the Introduction? Here we consider the subset of cubic polyhedra with no faces of size greater than six, i.e., those cubic polyhedra with positive curvature.

2 Spirals and classes of cubic polyhedra

Face Signature	Order	Figure	Point Group
$\{4, 0, 0\}$	36	Figure 2g	T_d
$\{3, 1, 1\}$	304	Figure 2a	C_s
$\{3, 0, 3\}$	80	Figure 2h	C_{3h}
$\{2, 3, 0\}$	2170	Figure 3	C_1
$\{2, 2, 2\}$	96	Figure 2i	C_{2v}
$\{2, 1, 4\}$	98	Figure 2e	C_{2v}
$\{2, 0, 6\}$	96	Figure 2j	C_{2v}
$\{1, 4, 1\}$	304	Figure 2b	C_1
$\{0, 6, 0\}$	306	Figure 2c	D_3
$\{0, 5, 2\}$	304	Figure 2d	C_2
$\{0, 0, 12\}$	380	Figure 2f	T

Table 1: Minimal counterexamples found by exhaustive generation. In each case, there is a unique counterexample with the given vertex number within the class.

If the maximum face size is restricted to six, and $p_2 = 0$ for graphs without multiple edges, simple counting with Euler's theorem for polyhedra gives 19 distinct face signatures $\{p_3, p_4, p_5\}$, where p_3, p_4 and p_5 are the respective numbers of triangular, tetragonal and pentagonal faces. All are realisable with some numbers of hexagonal faces.[38,39] Realisable point-group symmetries for the 19 classes have been listed.[40] In the following, we explore each face-signature class and attempt to provide a minimal unspirallable example, or at least to place bounds on the size of the smallest unspirallable polyhedron in the class. The initially plausible suggestion that fullerenes may be the 'best' cubic polyhedra for the spiral conjecture proves to be incorrect with respect to vertex numbers: while the smallest non-spiral fullerene has 380 vertices, the smallest non-spiral polyhedron in the class $\{2, 3, 0\}$ has as many as 2170 vertices. If, instead, we consider the number of structures in the class that are smaller than the minimal counterexample, fullerenes can, however, still be claimed to be best suited for spiral coding.

Two methods are used here for finding counterexamples. The first method is exhaustive generation of each family, at each vertex number, followed by a check of the results for spirals. The counterexamples resulting from this approach are presented in Table 1. We used the program *CGF* by Thomas Harmuth[41,42] which can be obtained as part of the package *CaGe*.[43] The non-spiral examples were all tested independently by the two programs used elsewhere[35] to check fullerenes without spirals, and, for the case of fullerenes only, the generation step itself was also checked with an independent program.

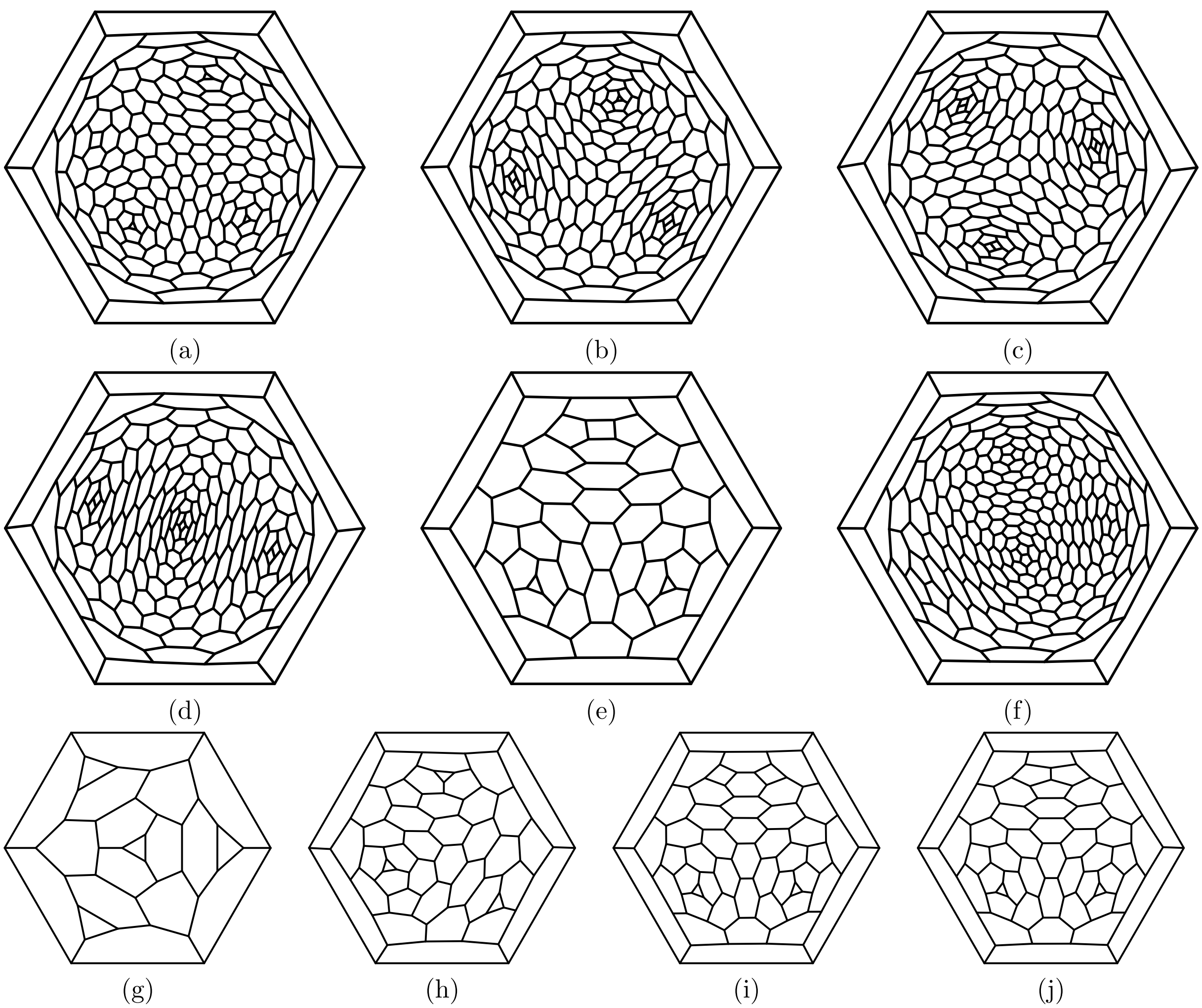

Figure 2: Minimal counterexamples

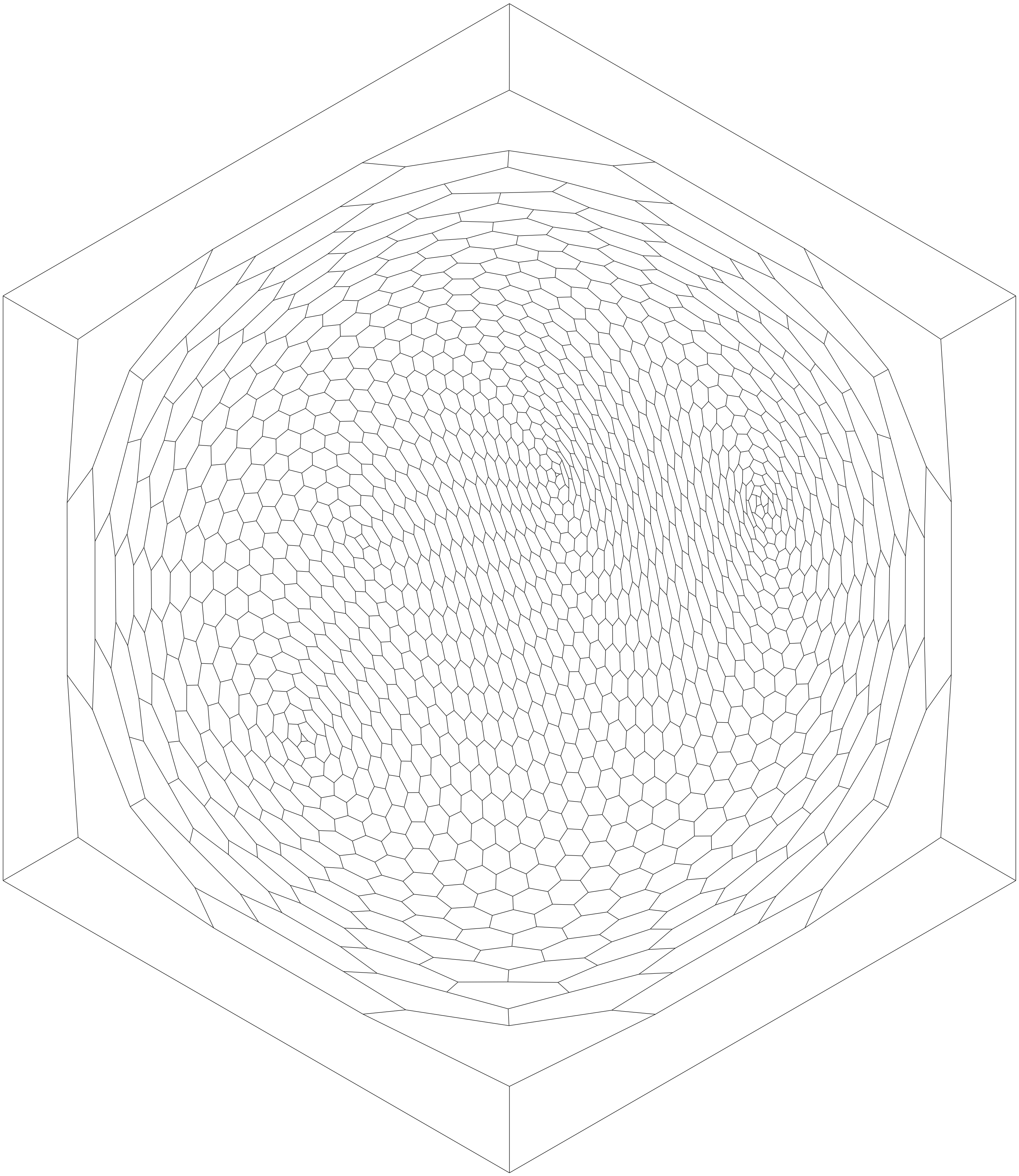

Figure 3: Minimal counterexample for sequence $\{2, 3, 0\}$ (33444)

In cases where, within reasonable time limits, no counterexamples could be found by exhaustive generation, we modified existing counterexamples from other classes. We used the four operations shown in Figure 4 to make new counterexamples. The numbers in the figure represent face sizes in the motif used for the operation. The list of graphs generated in this way is presented in Table 2.

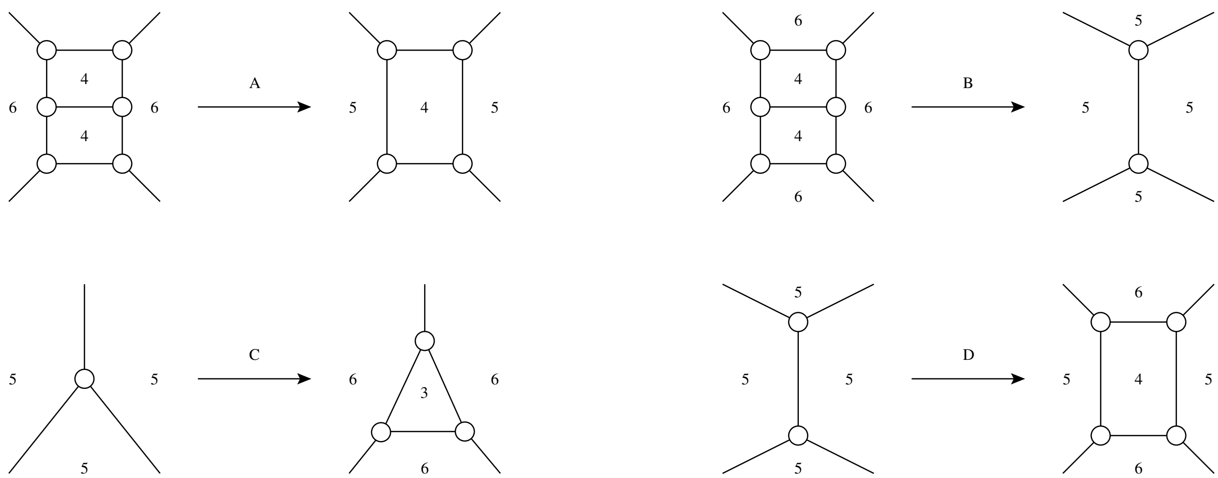

Figure 4: Operations used for converting graphs between face signature classes

Parent			Counterexample		
Signature	Order	Operation	Signature	Order	Point Group
$\{1,4,1\}$	$304^{\#}$	A	$\{1,3,3\}$	302	C_1
		A^2	$\{1,2,5\}$	300	C_1
$\{0,5,2\}$	$304^{\#}$	A	$\{0,4,4\}$	302	C_2
		A^2	$\{0,3,6\}$	300	D_3
$\{0,0,12\}$	$384^{\star}$	D	$\{0,1,10\}$	386	C_2
		D^2	$\{0,2,8\}$	388	C_2
$\{0,0,12\}$	$380^{\#}$	C	$\{0,1,9\}$	382	C_3
$\{1,3,3\}$	$330^{\dagger}$	B	$\{1,1,7\}$	326	C_1

Table 2: Counterexamples generated by modification. The parents marked with # are unique minimal counterexamples within their own family. The parent marked with $\star$ is the unique second smallest counterexample within the fullerene family,[31,35] which has D_3 symmetry. The parent marked with † is a non-minimal counterexample for $\{1,3,3\}$ which is shown in Figure 5.

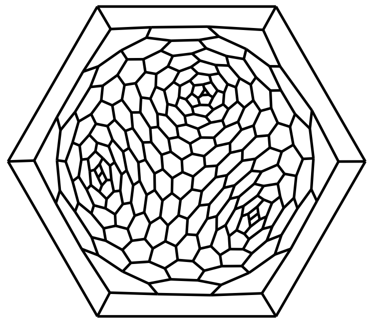

Figure 5: Parent of the counterexample for the class $\{1, 1, 7\}$ (345555555)

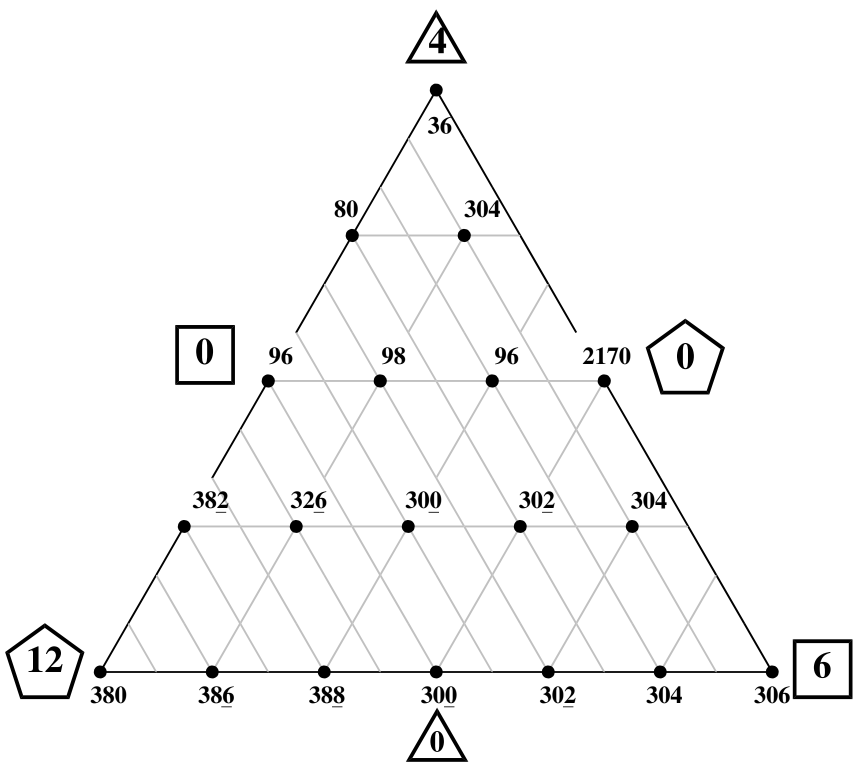

Figure 6: The landscape of spiral counterexamples. In the triangular coordinate system, the vertices of the master triangle represent 'pure' types $\{4, 0, 0\}$, $\{0, 6, 0\}$ and $\{0, 0, 12\}$, and in general the values p_3, p_4, and p_5 are proportional to the lengths of perpendiculars to the triangle sides. Each black dot represents a counterexample with the number of vertices indicated; minimal counterexamples are labelled in bold face; those numbers marked with an underline are not claimed to be minimal.

3 Conclusions

One obvious comment on the results presented here is that non-spiral cases are found reasonably early for all but one of the 19 classes, with one set of classes having non-spiral counterexamples of order 100 or less, and another having counterexamples in the range 300 to 400. The outstanding exception is the class $\{2, 3, 0\}$ which requires about five times as many vertices as the smallest fullerene counterexample. This example is an egregious exception (Figure 6). It is natural to wonder why it needs so many vertices. Although

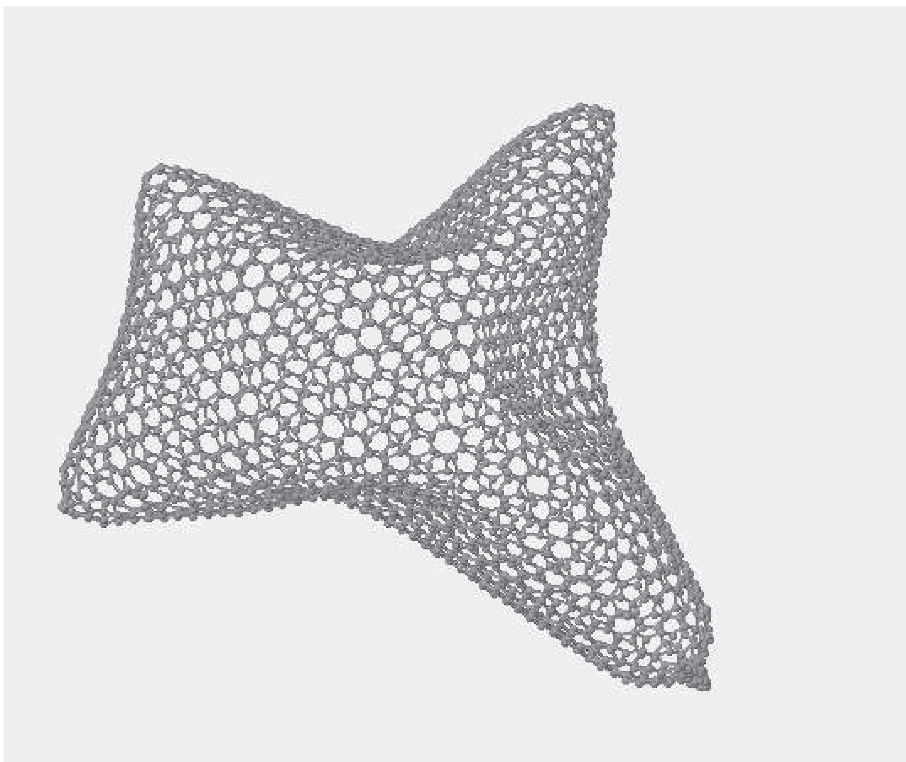

Figure 7: A 3D embedding of the minimal counterexample from the class $\{2, 3, 0\}$ (33444)

this is perhaps not the most precisely defined of questions, we can at least note that all the other counterexamples have one of two rough shapes: either a characteristic roughly tetrahedral cluster of defects, or a trigonal-sandwich structure. The class 33444 does not allow either of these groupings. For polyhedra in this class, the total defect of 12 is made up of contributions 3, 3, 2, 2, 2. A triangular shape would require distribution of these defects in 3 groups of defect 4 each (not possible) Similarly, a tetrahedral shape would require 4 groups of defect 4 each (again not possible) The eventual first counterexample in 33444 includes four groups of defect 3, 2, 3 and 4, respectively, and spring embedding[43] suggests a starfish-like shape, with four arms (Figure 7).

For cubic graphs that also allow faces of size larger than 6, counterexamples occur early, and are abundant.[36] These results suggest the conjecture that every infinite class of cubic polyhedra described by allowed and forbidden face sizes contains non-spiral elements.

References

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, C_{60}: Buckminsterfullerene, *Nature* **318** (1985), 162–163.

[2] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. Huffman, Solid C_{60}: a new form of carbon, *Nature* **347** (1990), 354–358.

[3] P. W. Fowler, D. E. Manolopoulos, *An Atlas of Fullerenes*, Oxford University Press: Oxford 1995, Dover Publications Inc.: New York 2006.

[4] P. E. Eaton T. W. Cole, Cubane, *J. Am. Chem. Soc.* **86** (1964), 3157–3158.

[5] T. J. Katz, N. Acton, Synthesis of prismane, *J. Am. Chem. Soc.* **95** (1973), 2738–2739.

[6] L. Cassar, P. E. Eaton, J. Halpern, Silver(I)- and palladium(II)-catalyzed isomerizations of cubane. Synthesis and characterization of cuneane, *J. Am. Chem. Soc.* **92** (1970), 6366–6368.

[7] R. J. Ternansky, D. W. Balogh, L. A. Paquette, Dodecahedrane, *J. Am. Chem. Soc.* **104** (1982), 4503–4504.

[8] A. Rassat, G. Scalmani, D. Seroussi, G. Berthier, Structure and stability of spheroalkanes $(CH)_{10}$, *Journal of molecular structure. Theochem* **338** (1995), 31–41.

[9] O. Stéphan, Y. Bando, A. Loiseau, F. Willaime, N. Shramchenko, T. Tamiya, T. Sato, Formation of small single-layer and nested BN cages under electron irradiation of nanotubes and bulk material, *Applied Physics A Materials Science & Processing* **67** (1998), 107–111.

[10] A. Stephenson, M. D. Ward, An octanuclear coordination cage with a 'cuneane' core - a topological isomer of a cubic cage, *Dalton Trans.* **40** (2011), 7824–7826.

[11] S. Iijima, Helical microtubules of carbon, *Nature* **354** (1991), 56–58.

[12] D. Ugarte, Curling and closure of graphitic networks under electron-beam irradiation, *Nature* **359** (1992), 707–709.

[13] B. W. Smith, M. Monthioux, D. E. Luzzi, Encapsulated C_{60} in carbon nanotubes, *Nature* **396** (1998), 323–324.

[14] J. Liu, H. Dai, J. H. Hafner, D. T. Colbert, R. E. Smalley, Fullerene 'crop circles', *Nature* **385** (1997), 780–781.

[15] A. Krishnan, E. Dujardin, M. M. J. Treacy, J. Hugdahl, S. Lynum, T. W. Ebbesen, Graphitic cones and the nucleation of curved carbon surfaces, *Nature* **388** (1997), 451–454.

[16] S. Iijima, M. Yudasaka, R. Yamada, S. Bandow, K. Suenaga, F. Kokai, K. Takahashi, Nano-aggregates of single-walled graphitic carbon nanohorns, *Chem. Phys. Lett.* **309** (1999), 165–170.

[17] K. S. Novoselov A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Electric field effects in atomically thin carbon films, *Science* **306** (2004), 666–669.

[18] A. Rassat, Chirality and symmetry aspects of spheroarenes, including fullerenes, *Chirality* **13** (2001), 395-402.

[19] P.W. Fowler, T. Heine, D.E. Manolopoulos, D. Mitchell, G. Orlandi, R. Schmidt, G. Seifert, F. Zerbetto, Energetics of fullerenes with four-membered rings, *J. Phys. Chem.* **100** (1996), 6984–6991.

[20] A. Ayuela, P.W. Fowler, D. Mitchell, R. Schmidt, G. Seifert, F. Zerbetto, C_{62}: theoretical evidence for a non-classical fullerene with a heptagonal ring, *J. Phys. Chem.* **100** (1996), 15634–15636.

[21] P.W. Fowler, D. Mitchell, G. Seifert, F. Zerbetto, Energetics of fullerenes with octagonal rings, *Fullerene Sci. Tech.* **5** (1997), 747–768

[22] A. Dress, G. Brinkmann, Phantasmagorical fulleroids, *MATCH Commun. Math. Comput. Chem.* **33** (1996), 87–100.

[23] F. Kardoš, Tetrahedral Fulleroids, *Journal of Mathematical Chemistry* **41** (2006), 101–111.

[24] D. E. Manolopoulos, J. C. May, S. E. Down, Theoretical studies of the fullerenes C_{34} to C_{70}, *Chem. Phys. Lett.* **181**, (1991), 105–111.

[25] G. Brinkmann, A.W.M. Dress, A constructive enumeration of fullerenes, *Journal of Algorithms* **23** (1997), 345–358.

[26] G. Brinkmann, A.W.M. Dress, PentHex puzzles - A reliable and efficient top-down approach to fullerene-structure enumeration, *Advances in Applied Mathematics* **21** (1998), 473–480.

[27] E.W. Godly, R. Taylor, Nomenclature and terminology of fullerenes: A preliminary survey, *Fullerene Science and Technology* **5** (1997), 1667–1708.

[28] Nomenclature and terminology of fullerenes: A preliminary survey, F. Wudl, R.E. Smalley, A.B. Smith, R. Taylor, E. Wasserman, E.W. Godly, *Pure and Applied Chemistry* **69** (1997), 1412–1434.

[29] D. E. Manolopoulos, P.W. Fowler, A fullerene without a spiral, *Chem. Phys. Lett.* **204**, (1993), 1–7.

[30] B. Grünbaum, T. S. Motzkin, The number of hexagons and the simplicity of geodesics on certain polyhedra, *Can. J. Math.* **15** (1963), 744–751.

[31] M. Yoshida, P.W. Fowler, Dihedral fullerenes of threefold symmetry with and without face spirals, *J. Chem. Soc. Faraday Transactions* **93** (1997), 3289–3294.

[32] M. Yoshida, P.W. Fowler, Systematic relationships between fullerenes without spirals, *Chem. Phys. Lett.* **278** (1997), 256-261.

[33] P. W. Fowler, J. E. Cremona, Fullerenes containing fused triples of pentagonal rings, *J. Chem. Soc. Faraday* **93** (1997), 2255–2262

[34] G. Brinkmann, P.W. Fowler, M. Yoshida, New non-spiral fullerenes from old: Generalised truncations of isolated-pentagon-triple carbon cages, *MATCH Commun. Math. Comput. Chem.* **38** (1998), 7–17.

[35] G. Brinkmann, J. Goedgebeur, B. D. McKay, The smallest fullerene without a spiral, *Chem. Phys. Lett.* **522** (2012), 54–55.

[36] G. Brinkmann, Problems and scope of spiral algorithms and spiral codes for polyhedral cages, *Chem. Phys. Lett.* **272** (1997), 193–198.

[37] G. Brinkmann, P. W. Fowler, Spiral Coding of Leapfrog Polyhedra, *J. Chem. Inf. Comput. Sci.* **38** (1998), 463–468.

[38] B. Grünbaum, *Convex Polytopes*, Interscience, 1967.

[39] V. Eberhard, *Zur Morphologie der Polyeder*, Teubner, 1891.

[40] M. Deza, M. Dutour-Sikirić, P. W. Fowler, The symmetries of cubic polyhedral graphs with largest face size 6, *MATCH Commun. Math. Comput. Chem* **61** (2009), 589–602.

[41] T. Harmuth, The Construction of Cubic Maps on Orientable Surfaces, PhD thesis, University of Bielefeld (2000).

[42] G. Brinkmann, O. Heidemeier, T. Harmuth, The Construction of Cubic and Quartic Planar Maps with Prescribed Face Degrees, *Discr. Appl. Math.* **128** (2003) 541–554.

[43] G. Brinkmann, O. Delgado-Friedrichs, S. Lisken, A. Peeters, N. Van Cleemput, CaGe - a Virtual Environment for Studying Some Special Classes of Plane Graphs - an Update, *MATCH Commun. Math. Comput. Chem.* **63** (2010) 533–552.