communications in mathematical
match
and in computer chemistry

no. 38, October 1998

ISSN 0340-6253

MATCDY (38) 7-17 (1998)

New Non-spiral Fullerenes from Old: Generalised Truncations of Isolated-pentagon-triple Carbon Cages

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Abstract

348 new unspiralable fullerenes of chiral point-group symmetries are found by a generalised truncation of isolated-pentagon-triple parents of D_2 point-group symmetry. By this truncation, up to 26 fullerenes without a spiral may be produced from one unspiralable parent. Double leapfrog and quadrupling transformations of any known unspiralable fullerene on less than 1000 vertices lead to distinct fullerenes (with vertex counts larger by factors of 9 and 4, respectively) that have the same symmetry as the parent and are also unspiralable.

1991 Mathematics Subject Classification: 05C30, 05C38, 05C75, 05C90

Introduction

Mathematically, a fullerene is a cubic (i.e. trivalent) polyhedron made up entirely of pentagonal and hexagonal faces. Chemically, it is realised as a carbon cage C_n for certain values of n such as 60, 70, 84, ... The *spiral conjecture* is that the surface of every fullerene polyhedron may be unwound in at least one way as a continuous spiral strip of edge-sharing faces. [1] Straightforwardly implemented as a computer algorithm, [1,2] useful in systematic nomenclature, [3] enumeration and construction of isomers [2] of these polyhedral molecules, the conjecture is nonetheless known to fail sporadically at sufficiently high vertex counts. [4–7] Other formally complete and more efficient counting algorithms are now available, [8] as are counting and generation schemes for fullerenes within specific symmetries. [5,6,9] It is known [8] that all fullerenes with $n \leq 176$ vertices have at least one spiral, but that some unspiralable fullerenes exist for $n \geq 380$, [4] though the minimality of the counterexample at $n = 380$ is unproven. From the point of view of chemical synthesis and characterisation, both 176 and 380 are still far out of reach, and the spiral conjecture is an effective tool for present applications, but the question of principle about its range remains intriguing.

For *general* cubic polyhedra the analogous conjecture breaks down much earlier, at only 18 vertices. [10] The smallest counterexample is constructed by truncation of all vertices of the trigonal prism. In fact, omni-truncation of *any* cubic polyhedron other than the tetrahedron leads to an unspiralable polyhedron. [11] Another clue that disparity in face sizes may contribute to spiral breakdown is the increase from $n_s = 36$ for triangle+hexagon to $n_s = 304$ for square+hexagon cubic polyhedra, where n_s denotes the smallest unspiralable member of the series. [11] In this respect, fullerenes seem particularly well suited to a spiral description, having the least possible dispersion in face sizes for cubic polyhedra with $n > 20$.

Amongst the billions of possible fullerene isomers with $n \leq 1000$, 436 examples without spirals have been published. [4–7] Closure of the gap between $n = 176$ and the $n = 380$ counterexample is one target of current investigations, and another is the identification of structural factors associated with spirality/non-spirality. Here we show that a truncation operation on isolated-pentagon-triple (IPT) fullerenes, [5] previously used for tetrahedral parents only, [7] generalises to parents of lower (D_2) symmetry and generates many more counterexamples, sometimes as many as 26 from one unspiralable parent. The extended set of fullerenes without spirals is used to give further evidence for an empirical relationship [11] observed between the leapfrog transformation [12] and fullerene non-spirality.

Previously described counterexamples

As noted earlier, the smallest fullerene polyhedron without a spiral found so far has 380 vertices. It is of chiral T tetrahedral symmetry and has its twelve pentagons arranged in four well separated motifs of fully fused pentagon triples. [4] Systematic searches along various directions in isomer space have revealed, in the range $20 \leq n \leq 1000$, a total of 28 tetrahedral counterexamples of T symmetry [4] (all but three having four IPT motifs), a further 289 of D_2 symmetry (all IPT), [5] 61 belonging to various subclasses of D_3 symmetry [6], and 58 of symmetries C_3 or C_2 derived by a generalised truncation procedure applied to the tetrahedral counterexamples. [7] The smallest known unspiralable fullerene with isolated pentagonal faces has 672 vertices. [6]

Two factors stand out as associated with non-spirality, one steric, the other symmetric. The first could be described loosely as 'pentagon crowding' and comes from the observation that the counterexamples all have fused triples or quadruples of pentagons, or are closely related to fullerenes with these features. To a greater or lesser extent, all are sharp-cornered, pentagon-crowded cages far from the energetic ideal of pentagon isolation and uniform surface curvature. The failure of the spiral for the small counterexamples can be traced to 'traps' at the sharp corners, [4] which function in the same way as the triangular faces of truncated polyhedra [11] in limiting the number of ways that any putatively successful spiral could terminate.

The second feature of known unspiralable fullerenes, even more clearly indicated by the empirical evidence, is an apparent connection between their chirality and lack of a spiral. Every known fullerene without a spiral belongs to a chiral point group. Of the 28 point groups possible for fullerene structures, [13] 9 are chiral (I, D_6, D_5, T, D_3, D_2, C_3, C_2 and C_1). For the first three, non-spiral fullerenes are impossible, ruled out by a proof that any fullerene with a five- or six-fold rotational axis has at least one spiral. [13] All the other chiral fullerene groups contain at least one known counterexample. Amongst the achiral groups, I_h, D_{5h}, D_{5d}, D_{6h} and D_{6d} are ruled out by the same proof, and T_h, T_d, D_{3h} and D_{3d} have been searched exhaustively in the range and show no counterexamples.

No rationale for an overall chirality limitation on non-spiral fullerenes has been suggested, and indeed the example of the truncated trigonal prism [10] shows that achiral general cubic polyhedra without spirals are possible. Both features described here may yet turn out to be accidents of restricted search procedures, but they are at least helpful in pointing out directions for further investigation.

Generalised truncation of fullerenes

Given the wide application of the spiral algorithm in the chemical literature to fullerenes, their names, properties and structures, there is some interest in finding constructions that might produce smaller non-spiral cages from larger, with the ultimate target of putting pressure on the $n = 380$ bound. One such construction has been described.[7] This is the generalised truncation.

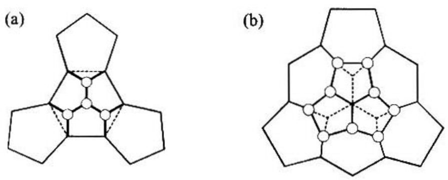

Figure 1: Generalised truncations of a fused pentagon-triple in a fullerene to give C_{60}- and C_{80}-like corner patch within a fixed perimeter. Open circles and bold lines represent atoms and bonds to be removed, dotted lines to be extended in the formal truncation process.

In this procedure, a fused pentagon-triple is replaced by a locally isolated-pentagon fragment of the type found in icosahedral C_{60} or C_{80}, thus 'blunting' a sharp corner of the parent IPT structure (Figure 1). Truncations of the C_{60} type are called a, and those of C_{80}-type are called b in what follows. Each a operation removes 4, each b operation 6 vertices from the original. Perhaps counter-intuitively, given that curvature is being averaged out, the result of these procedures is often a fullerene without a spiral.

In a search of all those fullerenes with ($n \leq 1000$) that could be produced by sequential truncation from IPT tetrahedral parents, a number of regularities were noticed.[7]

(i) Truncation can produce unspiralable fullerenes, but only for *some* truncates of *some* unspiralable parents.

(ii) The spiral behaviour of sequential truncates $a^x b^y$ is systematic: appearance of an unspiralable fullerene at some order $x + y$ implies lack of a spiral for *all* truncates of lower order.

(iii) A consequence of (i), given that all T_+ IPT unspiralable fullerenes in the range are in fact of T symmetry, is that all unspiralable truncates are themselves chiral. Truncation of an IPT fullerene of T symmetry leads to symmetries C_3 (a, b), C_2

(*aa*, *bb*), C_1 (*ab*), C_3 (*aaa*, *bbb*), C_1 (*aab*, *abb*), T (*aaaa*, *bbbb*), C_3 (*aaab*, *abbb*), C_2 (*aabb*).

(iv) A refinement on (ii) is that the spiral counts for C_{60}- and C_{80}-like truncations are similar, so that with one exception in the range (a parent at $n = 980$), truncates $a^x b^y$ of the same parent with $x + y$ =constant are either all spiralable or all unspiralable.

(v) The threshold for non-spirality in the tetrahedral IPT series is $n = 380$, but in the truncated series it is higher: at $n = 612$ (a), 610 (b), 712 (aa), 710 (ab), 708 (bb), 812 (aaa), 810 (aab), 808 ($aaaa$), 806 ($aaab$), 804 ($aabb$), 802 ($abbb$), 800 ($bbbb$). These correspond to T parents at 616 ($x + y = 1$), 716 ($x + y = 2$), 816 ($x + y = 3$ or 4).

Truncation of non-tetrahedral IPT fullerenes

We rely on a net construction for IPT fullerene polyhedra [5] which follows earlier work on symmetrical cages. [9,14,15] Each IPT fullerene can be considered to be derived from a triangle+hexagon cubic polyhedron in which each triangular face has been contracted to a point. The underlying polyhedra are represented as nets defined each by a signature of four integer parameters (i, j, k, l). These parameters specify the defining vectors of a scalene triangle that joins lattice points of the equilateral triangular tessellation of the plane. Assembly of four such (congruent) scalene faces gives a decorated master tetrahedron of the most general possible symmetry. Dualisation gives the triangle+hexagon polyhedron, and compression of the four triangles, if they are sufficiently well separated, yields the fullerene which is therefore represented by the same set of parameters.

A canonical choice of parameters can be defined, and IPT fullerenes to arbitrarily high values of n generated. [5] The derived fullerene has $n = 4|il - jk| - 8$ vertices and, as the tessellation construction shows, belongs to one of only five point groups D_2, D_{2h}, D_{2d}, T, T_d ($\equiv D_{2+}$). In the range $20 \leq n \leq 1000$ there are 8373 distinct structural isomers of IPT fullerenes (counting each enantiomeric pair as one isomer), which break down by symmetry group as 7667 (D_2), 281 (D_{2h}), 341 (D_{2d}), 64 (T), and 20 (T_d). Of these, 289 D_2 and 23 T isomers are without spirals. [4,7]

A given D_2 IPT fullerene generates up to 26 distinct truncates $a^x b^y$, with $n - 4$ to $n - 24$ vertices. Each vertex of the master tetrahedron is a site of C_1 symmetry and each of the three symmetry-distinct edge midpoints is a site of C_2 symmetry, so that the truncate symmetries are C_1 (*a*, *b*, *ab*, *aaa*, *aab*, *abb*, *bbb*, *aaab*, *abbb*), C_2 (*aa*, *bb*, *aabb*), or D_2 (*aaaa*, *bbbb*). Similar considerations apply to D_{2h} and D_{2d} parents but need not be described here as it turns out that all non-spiral truncated fullerenes in the range are descended from parents of D_2 symmetry. Most $a^x b^y$ truncations of a D_2 parent give just one enantiomeric pair of structures but *aa*, *ab*, *bb*, *aabb* give up to three distinct pairs, the maximum being reached only when all three distinct edge lengths of the master tetrahedron are large enough. Anisotropic D_{2+} structures with two or more very short edges can occur at any value of n, whereas in the tetrahedral subset all edges grow as $\sqrt{n}$.

The computational procedure adopted was as follows. A list of signatures (i, j, k, l) was generated by the procedures of ref. [5] and for each case corresponding to an IPT fullerene, the net was 'wrapped up' by a computer program to define a connection list for a fullerene. Adjacency matrices for truncates a, b, ... *bbbb* were constructed by a second program. Finally, each was tested for the existence of a face spiral using the

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Table: Non-spiral fullerenes produced by truncation of sub-tetrahedral IPT fullerenes. n_p is the number of vertices of the parent and (i, j, k, l) the signature of the net.[5] $O(t)$ is the highest order of truncation yielding an unspiralable result. n_t is the list of vertex counts in non-spiral truncates in the order *a*, *b*, *aa*, *ab*, *bb*, *aaa*, *aab*, *abb*, *bbb*, *aaaa*, *aaab*, *aabb*, *abbb*, *bbbb*. Where needed, a number in brackets after an entry counts distinct unspiralable truncates. Ambiguity for 924 and 992 cages is avoided by noting the gaps between eigenvalues $n/2$ and $n/2 + 1$ for the anomalous *aa*, *ab*, *bb* trios: at 916, 914, and 912 vertices, these are 0.0431, 0.0464 and 0.0135 (non-spirals) and at 984, 982 and 980 0.0599, 0.0063 and 0.0409 (*spirals*).

n_p	i	j	k	l	$O(t)$	n_t
672	10	4	-5	15	1	668 666
728	10	4	-6	16	1	724 722
732	10	5	-15	11	1	728 726
776	11	4	-5	16	2	772 770 768(3) 766(3) 764(3)
784	4	10	-17	7	1	780 778
792	10	5	-16	12	1	788 786
792	11	4	-6	16	1	788 786
836	11	4	-6	17	2	832 830 828(3) 826(3) 824(3)
840	11	5	-16	12	2	836 834 832(3) 830(3) 828(3)
852	10	5	-17	13	1	848 846
852	11	4	-7	17	1	848 846
856	10	6	-16	12	1	852 850
860	11	5	-6	17	1	856 854
888	12	4	-5	17	4	884 882 880(3) 878(3) 876(3)
						876 874(3) 872(3) 870
						872 870 868(3) 866 864
896	4	11	-18	7	2	892 890 888(3) 886(3) 884(3)
904	11	5	-17	13	2	900 898 896(3) 894(3) 892(3)
904	12	4	-6	17	2	900 898 896(3) 894(3) 892(3)
912	11	4	-8	18	1	908 906
920	10	6	-17	13	1	916 914
920	12	4	-7	17	1	916 914
924	3	13	-17	4	2	920 918 916(1) 914(1) 912(1)
924	4	9	-21	11	1	920 918
924	5	11	-18	7	1	920 918
928	11	6	-17	12	1	924 922
940	11	4	-7	19	1	936 934
952	12	4	-6	18	4	948 946 944(3) 942(3) 940(3)
						940 938(3) 936(3) 934
						936 934 932(3) 930 928
956	5	12	-13	17	4	952 950 948(3) 946(3) 944(3)
						944 942(3) 940(3) 938
						940 938 936(3) 934 932
956	11	4	-8	19	1	952 950
968	4	12	-18	7	2	964 962 960(3) 958(3) 956(3)
968	11	5	-18	14	2	964 962 960(3) 958(3) 956(3)
972	6	11	-13	17	2	968 966 964(3) 962(3) 960(3)
972	11	4	-9	19	1	968 966
976	12	5	-6	18	2	972 970 968(3) 966(3) 964(3)
984	4	12	-18	8	1	980 978
988	5	11	-19	8	1	984 982
988	10	7	-17	13	1	984 982
992	4	13	-14	17	2	988 986 984(2) 982(2) 980(2)
996	6	11	-13	18	1	992 990
996	12	5	-7	18	1	992 990
1000	1	13	-19	5	1	996 994
1008	13	4	-5	18	4	1004 1002 1000(3) 998(3) 996(3)
						996 994(3) 992(3) 990
						992 990 988(3) 986 984
1016	12	4	-7	19	3	1012 1010 1008(3) 1006(3) 1004(3)
						1004 1002(3) 1000(3) 998
1024	12	5	-18	14	4	1020 1018 1016(3) 1014(3) 1012(3)
						1012 1010(3) 1008(3) 1006
						1008 1006 1004(3) 1002 1000
1024	13	4	-6	18	4	1020 1018 1016(3) 1014(3) 1012(3)
						1012 1010(3) 1008(3) 1006
						1008 1006 1004(3) 1002 1000

program written for ref. 10. As the aim was to produce *all* unspiralable truncates with $n \leq 1000$, it was necessary to examine IPT parents $n \leq 1024$. Over 150,000 distinct truncated structures were checked. Almost all were found to have a spiral, as might have been expected.

Details of the 348 new unspiralable fullerenes generated in the search are listed in the Table. The smallest of the new set has 666 vertices, and comes from b truncation of a 672-vertex IPT fullerene. The smallest of the new set to have isolated pentagons is the 872-vertex *aaaa* truncate of an 888-vertex IPT fullerene.

Several observations paralleling (i) to (v) can be made on the results in the Table.

(i′) As in the T_+ series, only *some* truncates of *some* unspiralable parents are unspiralable.

(ii′) Again as in the T_+series, existence of an unspiralable truncate $a^x b^y$ implies lack of a spiral for all $a^u b^v$ with $u + v < x + y$.

(iii′) All unspiralable parents here are of D_2 symmetry, and so their unspiralable truncates are all also chiral.

(iv′) A stronger version of (iv) holds for most cases, in that all accessible truncates of given order, including symmetry variants such as the three *aa* truncates, either all have or all lack spirals. The exceptions in the Table are at 924 (992), where *aa*, *ab* and *bb* truncations each give only 1 (2) non-spirals instead of 3.

(v′) The thresholds are higher than in the tetrahedral series, reflecting the later onset of non-spirality in the D_{2+} parent series (n = 424 *vs.* 380). The thresholds are: n = 668 (a), 666 (b), 768 (aa), 766 (ab), 764 (bb), 876 (aaa), 874 (aab), 872 (abb), 870 (bbb), 872 ($aaaa$), 870 ($aaab$), 868 ($aabb$), 866 ($abbb$), 864 ($bbbb$). These correspond to D_2 parents at 672 ($x+y=1$), 776 ($x+y=2$), 888 ($x+y=3$ or 4).

Creating larger unspiralable fullerenes

One reason for extending the application of the truncation procedure was simply to enlarge the sample set for testing several conjectures about unspiralable fullerenes. The generalised truncation has been shown to give a semi-systematic way of reaching smaller fullerenes from a known counterexample to the spiral conjecture, but there is evidence that such counterexamples can also be inflated to give much larger fullerenes without spirals.

From previous work on the leapfrog transformation it is known that double leapfrogging of a number of examples of fullerenes without spirals, taking them from C_n to C_{9n}, gives

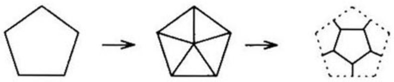

Figure 2: Fate of a typical face of a cubic polyhedron under the two-stage omnicapping + dualisation *leapfrog* transformation.

results that are also unspiralable [11].

The leapfrog transformation is described elsewhere: [12] it produces fullerenes of the same symmetry as the starting cage but with three times as many vertices and with all original faces isolated from one another by intervening new hexagons (Figure 2). One way of carrying out the transformation is first to cap all faces of the original, then to take the dual. This operation may be repeated any number of times, always inflating the fullerene by a further factor of 3. Its chemical interest lies in the fact that it generates fullerenes with adjacency spectra consisting of equal numbers of positive and negative eigenvalues, [16] and hence, at least in simple theories of bonding, with properly closed-shell π electronic configurations.

Application of the double leapfrog transformation to the full set of known counterexamples for $n \leq 1000$, including the new D_2-derived truncates gives a clear result: every one of the 784 unspiralable fullerenes in the range transforms to an unspiralable fullerene with nine times as many vertices. This regularity does not apply to the single leapfrog operation, where the product may or may not gain a spiral in any particular case.

Another transformation that takes non-spiral fullerene to non-spiral fullerene for the whole set of counterexamples with $n \leq 1000$ is the quadrupling operation Q which converts C_n to C_{4n}. [9] This may be carried out in three-stages: first convert the polyhedron to its edge-dual (i.e. its line graph), then cap pentagonal and hexagonal faces, and finally take the dual (Figure 3).

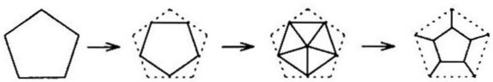

Figure 3: Fate of a typical face of a cubic polyhedron under the three-stage realisation (edge dual, capping of original faces, dualisation) of the *quadrupling* transformation.

This operation again goes from a fullerene to a fullerene without change in point group symmetry and again, in the given range at least, preserves non-spirality.

It is an open question whether these two operations and others like them *always* preserve non-spirality of fullerenes. They do not so in the wider class of trivalent polyhedra, but there the parents and transformed polyhedra are often in different face-signature classes. We note that both double-leapfrogging and quadrupling restore the same mutual orientation of all parent faces, unlike the single leapfrog which rotates parent r-gonal faces by π/r.

Conclusion

Semi-systematic ways of generating both larger and smaller unspiralable fullerenes of low symmetries have been demonstrated. Empirical observations on chirality, leapfrogging and quadrupling of non-spiral fullerenes have all survived the expansion of the database afforded by generalised truncation. Such constructions may prove useful in further exploration of the limits of the intuitively attractive but mathematically incomplete spiral method of describing and generating fullerenes.

Acknowledgment

The authors thank the Japanese Society for the Promotion of Science and EU TMR Network contract FMRX-CT97-0126 'USEFULL' for partial financial support.

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