Geometric Families of Giant Fullerenes

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A number of examples of a novel class of carbon allotropes, the polyhedral fullerenes, C_n, with n in the range 60–94, have now been isolated, and their structures have been either proved or postulated.[1] Even larger "giant" fullerenes have been suggested as components of soot and interstellar matter.[2] The epidemic spread of this research area[3] has led to the proposal of a wide variety of methods of generating the possible polyhedral cages. These methods include the leapfrog construction,[4] the ring-spiral algorithm,[5] the lattice-projection method,[6] and several randomization-annealing techniques.[1h,7] This circumstance in turn has resulted in a chaotic proliferation of model structures; this communication is intended as a first step in developing a taxonomy for this "fullerene zoo",[8] especially in the light of suggestions that it might be possible to form similar boron–nitrogen networks[9] or giant *closo*-borane structures based on the polyhedral duals of the fullerenes.[10]

The fact is these polyhedral cage molecules have introduced new possibilities into the analysis of isomer counting in chemistry. A previous paper[11] considered one specific series, the icosahedral fullerenes C_{20m}, from the point of view of using crystallographic enumeration techniques to determine the precise number and symmetry of such Goldberg[12] polyhedra, which also form the basis of geodesic domes and many virus particles.[13] The same crystallographic approach will now be combined with the lattice projection method[6] of constructing fullerene cages to provide a comprehensive classification scheme for fullerene cages capable of predicting many potential structures of giant fullerenes.

There are several equivalent approaches[6,11,14] to the construction of an icosahedral fullerene by selecting hexagons on a two-dimensional derivative lattice[15] of the graphene sheet, to become the 12 pentagons of the final polyhedron. If the same 12 pentagons are chosen in an irregular manner, rather than on the array of equilateral triangles, a more general fullerene may result. In fact, as has been asserted,[6] it is possible to project any fullerene onto a hexagonal net in such a fashion; a proof of this will be presented elsewhere.[16] In turn this approach to the construction of the cage immediately gives rise to a remarkable and very useful theorem; all fullerenes whose constructions conform to the normal rules may be arranged in infinite families, such that the number of isomeric cage structures C_{xm} within any family conforms to the same rules as does the icosahedral family C_{20m} of Goldberg polyhedra. This result arises in the following way.

The general shape of the polyhedron produced will be determined by the arrangement of pentagons; in fact we can define a "frame polyhedron" as that described by the centroids of the 12 pentagons once the graphene sheet has been folded into the fullerene cage. These frame polyhedra will be geometrically similar provided the original planar arrangements are. However, whichever set of hexagons are chosen to become pentagons, they must lie on a hexagonal derivative lattice of index at most m, where m nmust conform to the usual hexagonal quadratic form:

$$m = h^2 + hk + k^2 \quad (h, k \text{ integers})$$

Here we define the derivative lattice by the index in hexagonal coordinates of its closest lattice point in the sextant $h > 0$, $k \geq 0$. Where $m = 1$, we shall describe the resultant polyhedron as a parent, since any polyhedron with $m = k > 1$ can be derived from one with $m = 1$ by a uniform expansion by $k^{1/2}$ and appropriate rotation[17] of the defining set of points. This leads us to the conclusion that all the possible fullerenes may be arranged in infinite families, each related to some parent through the geometrical similarity of their frame polyhedra. The family members each correspond to a distinct hexagonal derivative lattice which and are therefore enumerated by the Dirichlet generating functions[18] derived previously[19] for this purpose and which are used elsewhere[11] to discuss the icosahedral family. For such Dirichlet functions the arithmetic function, which is the coefficient of n^{-s} in the series expansion, gives the number of distinct lattices or isomers for that value of n. They frequently have the additional advantage of discriminating among the various possible symmetry groups for the objects enumerated. For example, in this particular case, we have

$$F(p6) = \zeta(s)\, L[s,\chi(3)] = 1 + 3^{-s} + 4^{-s} + 2.7^{-s} + 9^{-s} + 12^{-s} + 2.13^{-s} + \ldots$$

in the unrestricted case, and

$$F(p6mm) = (1 - 3^{-2s})\zeta(2s)/(1 - 3^{-s}) = 1 + 3^{-s} + 4^{-s} + 9^{-s} + 12^{-s} + 16^{-s} + \ldots$$

where the symmetry requires that a mirror plane present in the original lattice is retained in the polyhedron. The relevant

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(17) This rotation is through an angle (2/3) arctan(k/h) in terms of the graphene sheet; this becomes a rotation of the pentagons by (4/5) arctan(k/h) in the resulting fullerene.

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mathematical properties of the corresponding generating functions have been presented in detail elsewhere.[11]

However, it is important to note that in the latter series the coefficient is unity, where in the former series it is odd, and is zero where the previous series coefficient was even. This governs the distribution of point symmetries[20] within any given family, for child polyhedra will not necessarily have the same symmetry as their parent and frame. If the frame polyhedron belongs to a point group which does not contain a mirror plane, the individual fullerenes will normally[21] belong to the same point group as the frame. However, if the frame belongs to a point group containing a mirror plane, the distribution of isomers follows the pattern indicated by the two series above, i.e. the second series selects

$$n = 1, 3, 4, 9, 12, 16, ...$$

isomers which conserve the full symmetry of the parent[6a] and which normally have the same point symmetry as the frame, while the remainder by termwise subtraction

$$n = 7, 13, 19, 21, 28, ...$$

occur as pairs of the corresponding lower point symmetry. By contrast, these latter pairs are actually structural isomers in the case of a chiral frame, since their enantiomers along to the distinct family of the enantiomorphous frame.

We may use the stable C_{70} isomer as the exemplary parent. Here the frame has symmetry D_{5h}, and its vertices lie on a slightly prolate spheroid. There are then isomers of formulae C_{210} and C_{280} with geometrically similar frames and belonging to the same point group, but for C_{490} we find a chiral pair of point symmetry D_5. The orientation of their patterns on the graphene sheet is shown in Figure 1.

The further intention of this work is to use the lattice projection method to search for enumerating formulas for fullerene isomers of specific idealized point symmetries and, hence, a convenient way to break down the total number of isomers for a given mass according to their symmetry. Unfortunately, although appropriate lattice projections exist for some symmetries,[6] these are not available in general. Some work has already been done in regard to generating parent fullerenes of specific point symmetries, for example, the C_{70+30n} series of Fowler,[23] with symmetries D_{5h} and D_{5d}. This series is also derived from C_{70} but is not to be confused with its children above, although some may have common masses. D_{5d}-C_{280} in Fowler's parent series is a cylindrical tubule with C_{60}-like hemispherical caps, while D_{5h}-C_{280} has the same "rugby ball" proportions as its parent C_{70}.

Another aspect to be considered is the degree of separation of the individual pentagons in the cage. The isolated-pentagon rule[23] has been recognized as an important guide to the stability of fullerenes, and some of the constructions mentioned[4,5] are specifically designed to yield such isomers. Examination of the transformation used above to generate a family from its parent shows that only the parent may have adjacent pentagonal faces, as these move to the (1,1) vertex-facing (VF) position in the $m = 3$ child, this being equivalent to the leapfrog procedure, to the (2,0) side-facing (SF) position in the $m = 4$ child, and even farther away for higher values of m. In fact buckminsterfullerene, C_{60}, the smallest fullerene conforming to the isolated-pentagon rule, is the $m = 3$ child of the smallest conceivable fullerene, C_{20}, which has no hexagons at all. The smallest actual parent with isolated pentagons is the D_{5h} isomer of C_{70}; however, such parents rapidly become numerous beyond that point.[24]

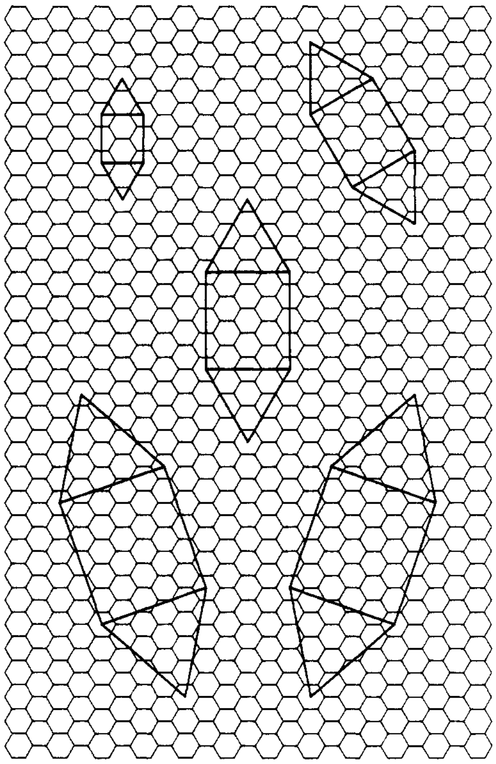

Figure 1. Frame patterns of the first five members of the family of D_{5h}-C_{70}, arranged on the graphene sheet. Only one-fifth of each complete pattern is shown.

These same considerations will also apply, mutatis mutandis, to related non-carbon cages.[9,10]

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[20] For the restrictions determining possible fullerene point symmetries, see ref 6a and: Fowler, P. W.; Manolopoulos, D. E.; Redmond, D. B.; Ryan, R. P. *Chem. Phys. Lett.*, in press.

[21] Reference 20 distinguishes eight point groups which admit frame polyhedra but not fullerenes.

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