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On the Partially Random Generation of Fullerenes

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In this brief review a few available methods for generating various mixed-ring-size fullerenes, especially toroidal fullerenes, and especially with a view to random processes are discussed.

Key words: fullerene, toroidal, torusene, random generation, polyhex, benzenoid.

INTRODUCTION

The study of random graphs in general is an active area of research,[1–18] and some of these studies have included fullerene graphs.[11] Reasons for interest in fullerenes generated at random include their being (*i*) a serendipitous aid to considering arbitrary network variations without prejudice, and, (*ii*) conceivably, a way of modeling the behavior of high temperature carbon vapor as it condenses into graphitic and fullerene-like clusters by inter-atomic bonding.

Truly random graph generation by computer is impossible, because a computer algorithm can only approach, never arrive at, a genuinely random sequence of numbers. Nevertheless, many very good algorithms exist,[19] and the output of an appropriately seeded random-function in a modern high-level language is certainly very near to being random for all practical purposes. Much more important is the problem of how to limit the field for selection without excluding some desirable candidates. The set of all arbitrary graphs is vast, and even the much smaller subset of cubic graphs (where every vertex is of degree-3) increases in size very rapidly with the number of vertices or atoms.[20] Restricting the consideration even further, even the class of conventional fullerenes – topologically planar cubic graphs having hexagons and twelve pentagons – is quite populous. With only sixty carbon atoms, buckminsterfullerene is already one of 1812 isomers for example.[21,22]

Contributing to this intractability is the difficulty of recognising what is produced. Efficient algorithms exist for determining whether a given graph is planar or not, but beyond this, how can one determine whether a cubic graph has genus 1, 2, or higher? We know of no methods that are both precise, and quick and simple to apply.

Here, therefore, the interest is in being able to generate graphs known to fall within a certain class of interest by some constraining process, but then to generate graphs within this class as randomly as possible, *i.e.* so that every graph within the class has an equal chance of appearing. In this way, instead of generating the very large set of graphs that one is interested in (often an impossibly long task) and then from it making a random selection, one could directly generate a representative sample. The main difficulty here is to ensure that the constraining mechanism of the generator, designed to exclude non-members of the full set, is not biased in its construction of examples within the set. It is therefore important to understand and be aware of any bias that does operate (which itself may not be easy), in case it renders the sample invalid for its intended purpose.

We consider these problems with a view to obtaining non planar and toroidal fullerenes in particular.

DISCUSSION

There are many theoretical sequences or bond rearrangements by which closed 3-valent networks may be derived, which can classified as, firstly, a stepwise synthetic approach, which is relevant in the contexts of both theoretical and practical chemistry. Here the desired structure is built up from smaller graphs or molecules, in general using operations that are systematically applied. Random steps are not particularly appropriate, and we do not consider this group further here. Secondly there are rearrangements of an existing structure, such as, for example, the conversion of a purely polyhex structure embedded on some surface to a network on the same surface containing rings other than hexagons. Operations to effect this may leave the number of vertices unchanged, or they may involve addition or subtraction of vertices. These methods may be applied on either a systematic or a random basis. A third category starts from a set of empty (degree 0) vertices, analogous to a cloud of dissociated atoms, and builds up structures by forming edges between pairs that are within some pre-specified distance apart. This method is the one most appropriate to the random approach, but is the one that involves the most difficulty in defining a useful generator algorithm. The various strategies for this will be discussed in a future paper. We therefore concentrate on reviewing class 2 above. The possibilities are all, of course, constrained by and deducible from the simple requirements of the well known generalized Euler relationship between vertices (n), edges (m), faces (f) and genus (g): $n - m + f = 2 - 2g$.

REARRANGEMENTS WHERE THE NUMBER OF VERTICES REMAINS CONSTANT

A simple 'safety first' approach is to start with the form we want, say a toroidal fullerene, and change the size of some or all the faces by uncoupling connections and then re-coupling in a different way. This produces new isomers, but maintains the same number of vertices and edges, and the same overall topology. However, a little paper and pencil experimentation soon shows that this is not a simple matter without a systematic approach; one all to easily obtains an intermediate that cannot be fully recoupled without crossing edges.

The simplest reliable operation of this type is the well known Stone-Wales transformation[21,22] illustrated in Figure 1. Although, chemically, such a transformation is likely to be more subtle, for graph-theoretical generation purposes it is convenient to regard it as a rotation, or cyclic permutation, of the inner 2,3-dimethylbutane subgraph about the centre of its central bond/edge. It converts a group of four rings of size p, q, r and s to have sizes p–1, q+1, r–1 and s+1 (Figures 1 and 2). This rotation can be applied to any edge, or to a sequence of edges in iterative fashion to generate a graph whose overall size and topology is unchanged, but which may be a non isomorphic variation of the network, *i.e.* a new isomer.[11]

However, this rotation process can itself be generalized,[23–28] and applied to any suitable subgraph of the network that has does not have complete rotational symmetry; see Figure 3.

Figure 1. The Stone-Wales transformation; (a) in generalized form, and (b) applied to the pyrene graph. It can be viewed as a rotation of the inner tree.

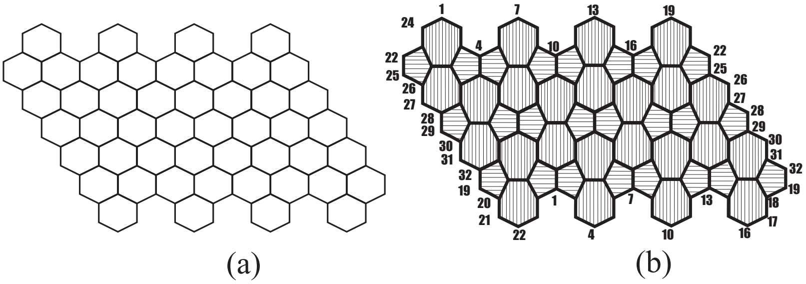


Figure 2. (a) A 48-hexagon or 12-pyrene polyhex, and (b) the 24-pentagon, 24-heptagon polycyclic system resulting from a Stone-Wales transformation applied to each pyrene tile of (a). The numbers show a possible labelling for the graph (b) to represent a 48-face (96 vertex) toroidal fullerene having only 5- and 7-membered rings.

Reverting to the simplest Stone-Wales transformation of pyrene (Figures 1b and 2), in a larger system, pyrene itself can be taken as the rotation subgraph (Figure 4), and this yields the same range of non-hexagon ring sizes, but with a different spatial arrangement. These rotation processes, especially of fairly small subgraphs, have the attraction that they are fairly easy to incorporate into an algorithm. The location of the chosen subgraph is identified, either at random or on the basis of some pattern, and the appropriate set of connections is permuted. For larger subgraphs (which, therefore, have many connections) the *angle of rotation* also, may be chosen on either a random or systematic basis.

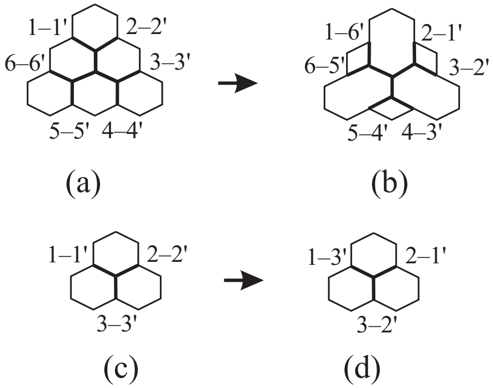


Figure 3. Each pair of numbers *i–i′* represents a label of the periphery and of the inner tree, respectively. Rotation of the inner tree of triangulene (a) converts six hexagons into three 4-rings plus three 8-rings (b), whereas a rotation of the more symmetrical isopropyl subgraph within phenalene (c) to (d) is degenerate and causes no such change.

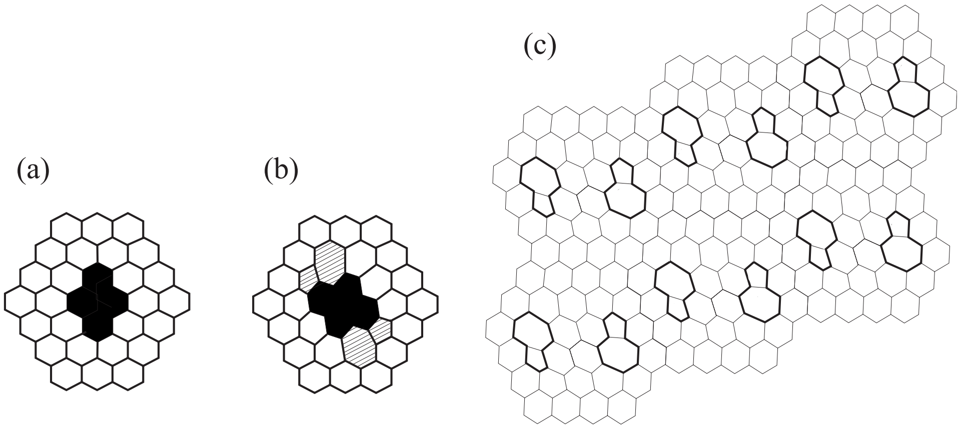


Figure 4. (a) A transformation using rotation of the pyrene subgraph. (b) Rotation at this angle gives the same two pentagon-heptagon pairs (azulenes) as does rotation of the inner tree (Figure 1b), but separates them. (c) A wider pattern of dispersed azulene units induced by rotation of pyrene at regular intervals.

REARRANGEMENTS OF A STRUCTURE WITH ADDITION OF VERTICES

This possibility is more limited in scope. Vertices can be inserted into existing edges, but must be added to the system in pairs, each to a different edge, because a cubic graph, and therefore any fullerene, must have an even number of vertices. A new edge must join the two new vertices, because all vertices must be of degree 3, and one extra face will be formed. Furthermore, in order to avoid creating crossings (and therefore changing the graph's topology), it is possible to insert a pair of vertices only into edges that are part of one facial ring. It is generally more helpful to view this as one operation, the insertion of a K_2 graph. So, for a hexagonal face there are three possibilities, and edges 1–2, 1–3 and 1–4 can be connected in this way

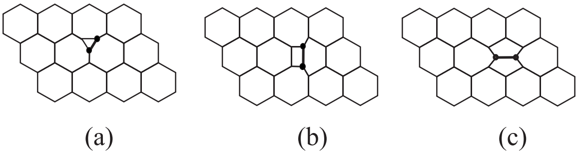


Figure 5. Modes of insertion of one edge into a polyhex to give non hexagonal faces, including one extra face: (a) 1–2 insertion to give one 3-ring plus three 7-rings; (b) 1–3 insertion to give one 4-ring plus two 7-rings, and (c) 1–4 insertion to give two 5-rings plus two 7-rings.

(Figure 5). The process can of course be iterated or, alternatively and equivalently, a larger tree may be inserted (*e.g.* Figure 6). Any planar graph with no degree 2 vertices, and terminal vertices that can all be accommodated among the edges of a single face of the existing network can be inserted this way without changing the topology, although it may change what is a plausible geometry.

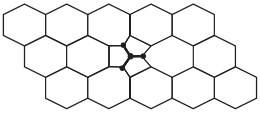
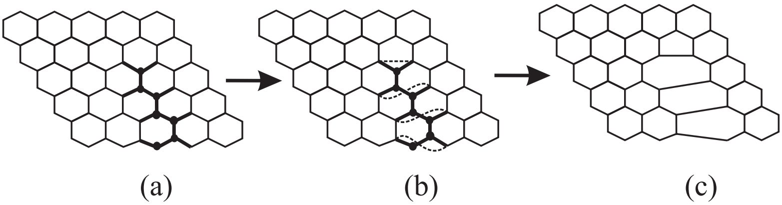


Figure 6. Insertion of the isopropyl graph into a hexagonal face to give two extra faces, and to form three incident azulene units.

REARRANGEMENTS OF A STRUCTURE WITH SUBTRACTION OF VERTICES

More care is needed here, because it is easy to create a non local peturbation; *i.e.* one where a change is not be terminated locally, but instead propagates through the network (see Figure 7). On the other hand this can sometimes be useful. Borštnik and Lukman,[29] for example, used the creation of azulenes by vertex deletion to narrow and ease the bending of toroidal fullerene tubes in their molecular mechanics study. Even more disturbance is caused by formation of 4- and 8-ring pairs; see Figure 8.



(a) (b) (c)

Figure 7. The excision of vertices from a polyhex to give a polyhex with one embedded azulene unit: (a) identifies (in bold) the vertices and edges to be excised; (b) shows (dotted) the new connections to be formed, and (c) the result. Note, however, that although we might expect that only four vertices need be removed, this operation creates a defect that continues to the bottom and necessitates, in this case, the removal of seven, so the width at the bottom of the strip has been reduced by one hexagon. Were this strip converted to a cylinder by gluing side to side, it would be conical in shape; in order to glue top to bottom, another azulene must be created, with an opposing alignment.

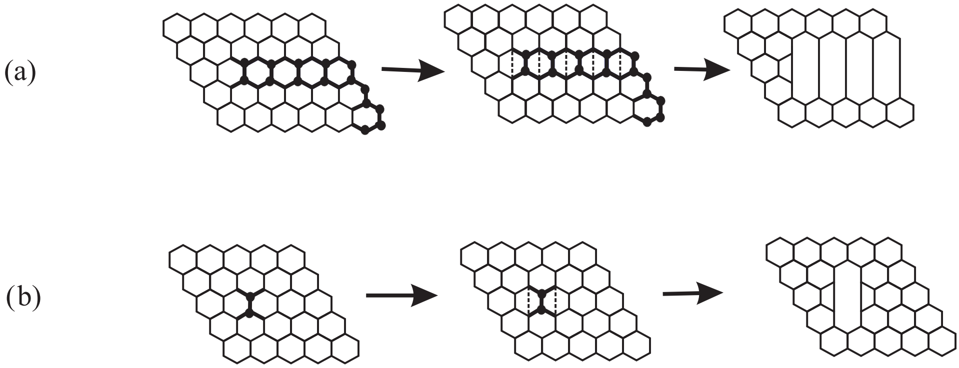


Figure 8. Attempted creation (*c.f.* Figure 7) of a 4,8-ring pair (a) propagates a disturbance in two directions throughout a polyhex network, so that neither pair of opposite sides of the resultant quadrilateral can be matched. On the other hand, formation of a 4,10,4-ring triplet (b) is simple, and the result is self contained.

A TOTAL CONSTRUCTION APPROACH: ADDITION OF NEW EDGES TO VERTICES THAT ARE LESS THAN 3-VALENT

This is the nearest approach to a fully random construction considered, and is the subject of a current project whereby, in the main step, a suitably bounded planar surface is populated by empty (degree 0) vertices, and the random graph generator instals edges among pairs of neighbouring vertices

HOW CAN THESE NETWORK-CHANGING OPERATIONS BE USED IN AN ALGORITHM?

We may express the operations already discussed in somewhat more formal and mathematical language as a possible basis for a useful computer implemented algorithm:

Let G be a cubic graph embedded in any surface, and select a closed curve C that cuts the edges of this graph (and no vertices) and has the property that it cuts the surface into two pieces, G1 and G2, the first of which is planar, and both of which have pending half-edges. Let k be the number of pending edges of either piece. Now attach G1 to the curve C (seen as a cycle of length k) to give a cubic graph P1, embedded in the plane in such a way that the perimeter is an induced k-gon. Similarly, if G2 is attached to a copy of C, this gives a cubic graph P2 embedded in the same surface as G, with one face a k-gon.

Now P1 (which is planar) may be rotated or reflected, and in general there will be $2k$ ways of doing this. Alternatively we may replace P1 with some other planar graph Q1 having the same k-gon as its perimeter. Then P1 and P2, or Q1 and P2, are glued together along the induced k-gons. Deletion of the resulting k-gon generates G', which will be embedded in the same surface as the original graph G.

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SAŽETAK

O djelomično slučajnom generiranju fullerena

Edward C. Kirby

Dan je kratki prikaz nekih metoda za generiranje fullerena s prstenovima različitih veličina, s posebnim osvrtom na torusne fullerene i ulogu slučajnih procesa pri njihovu nastajanju.