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Symmetric decomposition of buckminsterfullerene

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Abstract

Possible ways for decomposition of buckminsterfullerene into identical monomer units, in a completely symmetric way, are systematically searched for. Under the requirement that each monomer atom is treated as different from others, it was found that symmetric decomposition is possible into monomers with 30, 20, 15, 12, 10 and 6 atoms. All possible ways are enumerated and some particularly interesting are depicted. Possible application of these results is in the synthesis design of buckminsterfullerene.

1 Introduction

Insight into the mechanism of spontaneous formation of buckminsterfullerene and other fullerenes is among the most tempting questions of fullerene physics and chemistry. Understanding of this process should enable better control and lead to higher yields in the production of fullerenes. However, this molecule is also a great challenge for synthetic chemists, and its synthesis will be important achievement in organic chemistry [1-3].

Much of an interest in buckminsterfullerene stems from its symmetry. It also makes the molecule of buckminsterfullerene a prospective candidate for synthesis by polymerization from appropriately designed monomers. Some specific ideas for synthesis or spontaneous formation of buckminsterfullerene have been mentioned in [4-9]. For reasons of simplicity and elegance it would be desirable that polymerization involves only a single type of monomer. If that were possible, the structure of the target molecule should allow decomposition into identical fragments. Even more, it would be good if decomposition could be achieved in a symmetric way, because then the monomers could close into the target molecule by uniform linking between themselves. In principle, carbon skeleton obtained by the decomposition, could be a basis for functionalization with specific and complementary reactive groups, so that side reactions between centers not intended to interact would be minimized.

This leads to a question of possible decompositions of the target molecule into identical monomer units, in a completely symmetric way, yet so that each monomer atom can be assumed as specifically functionalized. In a formal language, the problem is formulated as symmetric decomposition of buckminsterfullerene graph into connected subgraphs in which vertices are differently coloured. Possible realizations of this goal are subject of the present paper.

2 Method

Symmetrical relationship, required to exist between monomers, on one side, and additional nonequivalence of any two vertices in a given monomer, pose strict conditions on decomposition procedure. Graph in which vertices are coloured according to these conditions, must possess symmetry operation(s) which shift(s) vertices of one monomer onto corresponding vertices of another. All present symmetry operations should make all monomers equivalent, and should not interchange any two vertices of the same monomer. Furthermore, the vertices belonging to the same monomer must be connected.

If the pertaining symmetry group would be identical to the symmetry group of the buckminsterfullerene, I_h, the result would be trivial: monomer would consist from a single atom/vertex. All other possibilities are realized with some subgroup of I_h. In order to reduce consideration of all subgroups of I_h (and their various realization in buckminsterfullerene), one should note that symmetry planes are not allowed in any relevant subgroup. Each symmetry plane passes through 4 vertices, after decomposition these vertices can be connected only among themselves (otherwise not all vertices in the monomer would be different). This would imply that monomer is an isolated edge between six-membered rings. However, each symmetry plane passes also accross two edges between six-membered rings, thus making the terminating vertices equivalent. As a consequence, no symmetry subgroup, relevant for the present consideration, can include a symmetry plane.

As the allowed elements there remain: 5-fold, 3-fold and 2-fold axis (C_5, C_3, and C_2, respectively), inversion center, and all their products. The subgroups with these elements are: C_i, C_2, D_2, C_3, $C_{3i} \equiv S_6$, D_3, C_5, C_{5i} and D_5. Their realizations in buckminsterfullerene are unique, up to different but equivalent possibilities in choosing a specific subgroup of elements.

Systematic search for possible decompositions begins with identifying vertex orbits for a chosen subgroup. After that, each connected combination of vertices such that each one belongs to a different orbit, represents a fragment into which symmetric decomposition may be achieved. In order to find all possibilities, systematic generation of all combinations should be performed. For each generated combination, operations of the given symmetry subgroup will produce all of its copies in the graph. Algorithm for realization of this task is fairly simple, but includes one additional problem. In order to differentiate between vertices in different orbits they are somehow labeled. However, in this way an additional difference between vertices is introduced which results in generating equal monomers more than once. If one wishes to systematically generate (or only enumerate)

all **different** combinations, the monomers produced by the generator have to be checked for this type of equivalence. Thence, each new fragment is submitted to symmetry operations of the buckminsterfullerene, and if any of them produces a replica of some kept fragment, the present one is abandoned. Otherwise, it is added to the set of fragments being kept. More efficient algorithm is possible, but the simple one is sufficient for the present purpose.

3 Results

In TABLE I are listed, for each relevant symmetry subgroup, the numbers of all generated combinations and the numbers obtained after removing those equivalent. As one could expect, the number of possible ways rapidly decreases with the number of different orbits (which equals to the fragment size). It is interesting to note that although the total numbers of generated combinations for C_i and C_2 are comparable, the numbers of different combinations differ by an order of magnitude. This is because vertices in some orbits obtained under the action of C_2 are close to each other (e.g. vertices terminating the edges through which C_2 passes). As mentioned in the Section 2, equivalent combinations are recognized as those for which exists a symmetry operation in I_h which interconverts them. Alternatively, one could examine how many 'different' combinations can be obtained from a given one by performing the symmetry operations from I_h. This number shows how many times the particular combination will be generated again. Many symmetry operations from I_h do not preserve different colouring of vertices by acting on fragments obtained from C_2 subgroup due to those close vertices with the same colour, and thus a relatively small number (typically 4) of equivalent replicas for each monomer can be obtained. In C_i case, vertices in each orbit are at the greatest possible distance, and many I_h operations preserve the different colouring of vertices in acting on a given fragment (typically 60).

TABLE 1: Numbers of symmetric decompositions of buckminsterfullerene

Symmetry subgroup	Monomer size	All generated combinations	Different combinations	Combinations without terminal vertices
C_i	30	439680	7397	8
C_2	30	381604	95453	37
D_2	15	1448	244	2
C_3	20	8648	2187	15
C_{3i}	10	294	134	2
D_3	10	148	70	1
C_5	12	98	28	0
C_{5i}	6	15	8	0
D_5	6	7	4	0

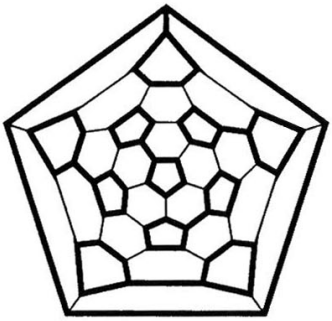

FIGURE 1: Decomposition obtained under action of D_3

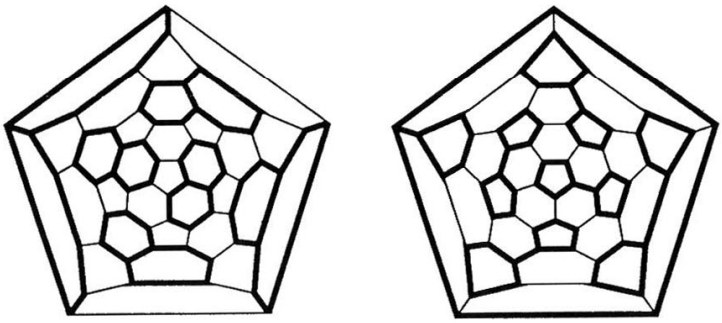

FIGURE 2: Decompositions obtained under action of C_{3i}.

Monomer combinations without terminal vertices could be more significant for practical synthesis because each new bond is formed between unique two centers, and thus each center could be specifically activated for interaction with the complementary center. Such monomers are separately counted. Those with 10 atoms are also drawn in FIGURE 1 (the two conforming to C_{3i}) and FIGURE 2 (the only one from D_3). Note that the two decompositions depicted in FIGS. 1 and 2, with the bicyclopentadiene-like fragment, look like very similar, but are not identical. The difference is easy to see as one complying to C_{3i} has a plane of symmetry (not relevant for decomposition purposes), which is absent in that one obtained from D_3. Note also that decomposition into naphthalene-like fragments (FIGURE 2) is a symmetrical one.

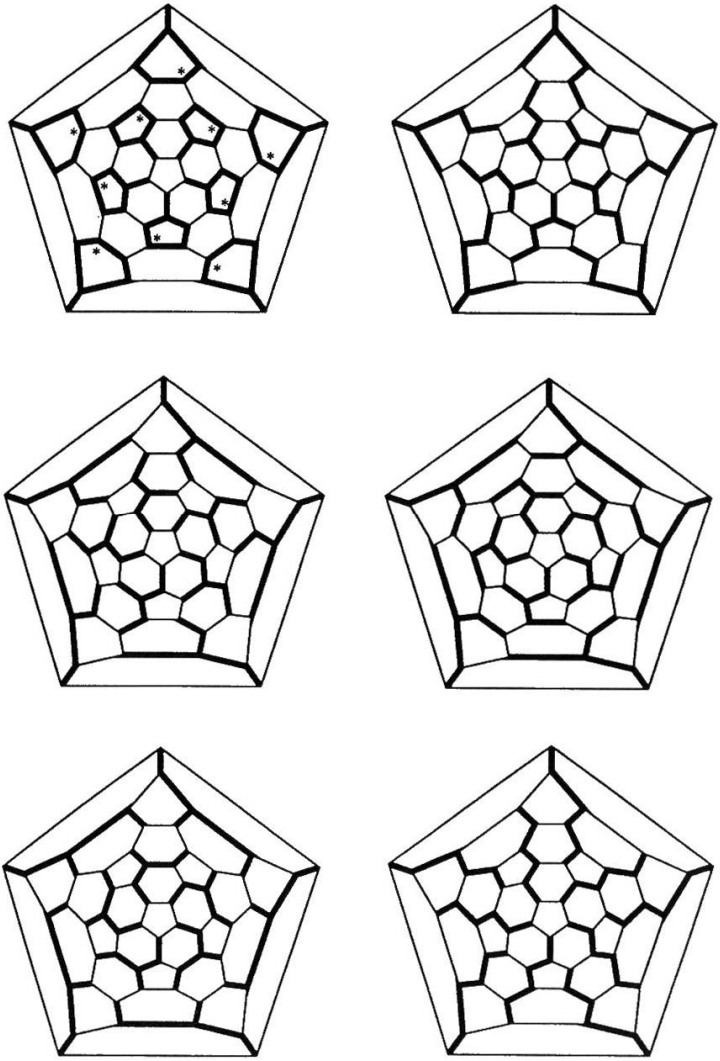

FIGURE 3: (contd.)

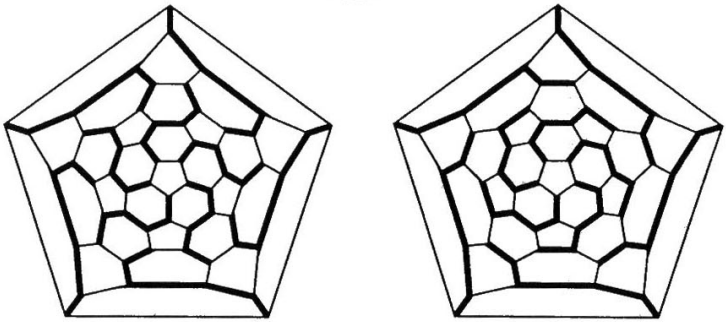

FIGURE 3: Decompositions obtained under the action of C_{5i}.

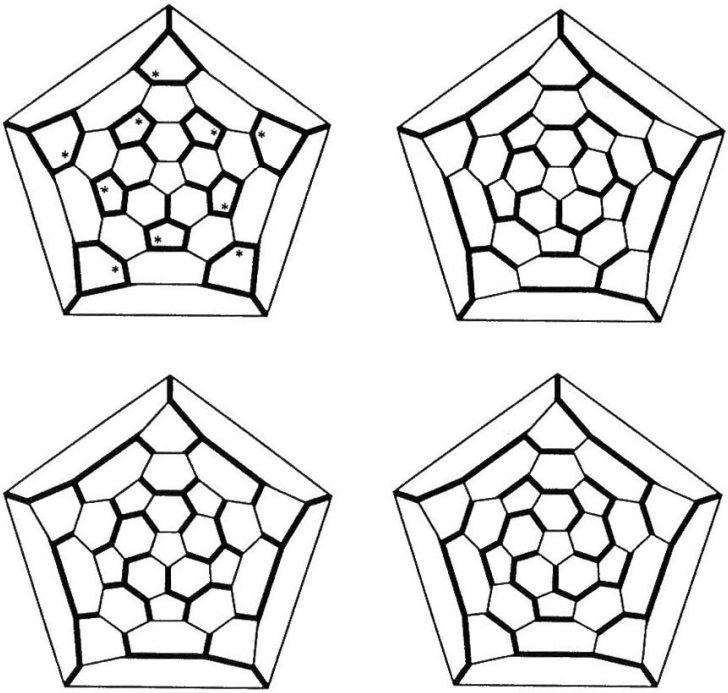

FIGURE 4: Decompositions obtained under action of D_5.

FIGURES 3 and 4 shows decompositions into smallest possible monomers, having 6 atoms. They are considered as interesting due to its smallness and availability. FIGURE 3 shows decomposition obtained under the action of C_{5i} and in FIGURE 4 are those obtained from D_5. The equivalence of the two decompositions in FIGS. 3 and 4 into the cyclic fragments, is only apparent. A distinct vertex in each monomer is starred in both decompositions in order to show the difference: note that in FIG. 3 the starred vertices are linked, and are not linked in FIG 4.

List of all other possible decompositions can be obtained upon request from the authors [10].

There are no monomers with two and five vertices, because there is no proper symmetry subgroup (without symmetry planes) which produces orbits of the cardinality less than 10. One could wonder about the fact that symmetric decomposition into monomers with five and two vertices are obviously possible: these are mutually complementary decompositions into pentagon rings, and into dimers corresponding to edges between hexagons. However, the vertices in these monomers can not be differently coloured keeping the symmetric relationship towards other monomers.

4 Conclusions

The method for symmetric decomposition of buckminsterfullerene has been outlined, and the results of enumeration of all possible ways are tabulated. Monomers without terminating vertices are separately counted as they could be more significant for eventual practical realization of the synthesis through a polymerization or a similar reaction. Decompositions into such monomers with 10 vertices are depicted in full detail. More importance has been attributed also to the smallest possible monomers, with 6 vertices, due to their availability, and all possible decompositions into fragments of this size are also drawn.

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