Materials Physics and Mechanics 34 (2017) 18-28 Received: October 3, 2017

MODELING GROWTH OF MIDI-FULLERENES FROM C_{20} TO C_{60}

Alexander I. Melker[1*] and Maria A. Krupina[2]

[1] Department of Mechanics and Control Processes,

[2] Department of Experimental Physics,

Peter the Great St. Petersburg Polytechnic University, Polytekhnicheskaya 29,

195251, St. Petersburg, Russia

*e-mail: newton@imop.spbstu.ru

Abstract. Axonometric projections together with corresponding graphs for the first branch of the family of tetra-hexa-cell equator fullerenes including some isomers are constructed in the range from 20 to 60. Some of graphs were obtained earlier but the majority is given for the first time. A unified approach for drawing axonometric projections of these fullerenes is used; namely, it is the dimetric representation which symmetry coincides with that of a corresponding graph. The growth of fullerenes is studied on the basis of two mechanisms, according to which a carbon dimer embeds either in a hexagon or a pentagon of an initial fullerene. This leads to stretching and breaking the covalent bonds which are parallel to arising tensile forces. In both cases there arises a new atomic configuration and there is mass increase of two carbon atoms. We considered direct descendents of the first branch of the tetra-hexa-cell equator family beginning with C_{20}; namely C_{22}, C_{24}, C_{26}, C_{28}, C_{30}, C_{32}, C_{34}, C_{36}, C_{38}, C_{40}, C_{42}, C_{44}, C_{46}, C_{48}, C_{50}, C_{52}, C_{54}, C_{56}, C_{58}, and C_{60}.

Keywords: carbon dimer, fullerene, graph, structure.

1. Introduction

In Ref. [1] we considered the following problem; namely; how to design new fullerenes and their graphs, if one knows a basic elementary graph of a mini-fullerene playing the role of progenitor. We have developed a way of designing different families of fullerenes using this approach. As a result, we have found the family of cupola half-fullerenes: C_{10}, C_{12}, C_{16}, C_{20}, C_{24}; the family of bi-polyfoils: C_{14}, C_{18}, C_{24}, C_{30}, C_{36}; the family of truncated bipyramids: C_{14}, C_{18}, C_{24} C_{30}, C_{36}; and the family of tetra-hexa-cell equator fullerenes: C_{20}, C_{24}, C_{32}, C_{40}, and C_{48}. All the families contain five members and have a layer structure. Our classification gives not only fullerene symmetry, and so determines the fullerene uniquely, but also connects it with its relatives.

In addition to the graphs, we have given axonometric views of the first members of each family. Similar to many researchers, at that time we used different axonometric projections for presenting fullerene structure. It is justified for small fullerenes, which structure is rather simple, but if one tries to find common structural elements of large fullerenes, one needs use a unified approach. Drawing an axonometric view of any fullerene is a rather tedious procedure, and at that moment the story was not complete.

In Ref. [2] we have suggested a unified approach for drawing axonometric projections of both small and large fullerenes, and we have constructed the axonometric projections and corresponding graphs for the fullerenes in the range from 20 to 36 together with some their isomers. In the long run we came to conclusion that the best way is dimetric axonometry, more properly the dimetric representation which symmetry coincides with that of a corresponding graph. It should be emphasized that the axonometric projections and graphs were constructed not only for the members of the families of bi-polyfoils and truncated bipyramids mentioned above, but also for 'intermediate' members, namely for C_{22}, C_{26}, C_{28}, C_{32}, C_{34}. In doing so, we have exhaustively investigated a dimer mechanism of growing fullerenes. According to it, a carbon dimer embeds either into a hexagon or a pentagon of an initial fullerene. This leads to stretching and breaking the covalent bonds which are parallel to arising tensile forces. In the first case instead of the hexagon adjoining two pentagons, when the dimer embeds in this hexagon, one obtains two adjacent pentagons adjoining two hexagons. In the second case, when the dimer embeds in the pentagon, one obtains two pentagons separated by a rectangle. In both cases there arises a new atomic configuration and there is mass increase of two carbon atoms. This process can continue until a new stable configuration is reached.

In this contribution we consider direct descendents of the first branch of the family of tetra-hexa-cell equator fullerenes beginning with C_{20}; namely C_{22}, C_{24}, C_{26}, C_{28}, C_{30}, C_{32}, C_{34}, C_{36}, C_{38}, C_{40}, C_{42}, C_{44}, C_{46}, C_{48}, C_{50}, C_{52}, C_{54}, C_{56}, C_{58}, and C_{60}. Our aim is to model their growth obtaining at first their graphs, what is simpler, and then constructing their structure on the basis of the graphs obtained.

2. (Tetra-hexa)$_3$-penta$_6$ polyhedral fullerene C_{20}

Its atomic configuration consists of three squares, three hexagons and six pentagons (Fig. 1) so it was named a (tetra-hexa)$_3$-penta$_6$ polyhedron [3]. This structure together with its consistent electronic structure was obtained in Ref. [3] on the basis of a new mathematic concept of fullerenes. According to the concept a fullerene is any shape composed of atoms, each atom having three nearest neighbors, which can be inscribed into a spherical, ellipsoidal, or similar surface. But what is more important, it was supposed that not only atoms but also shared electron pairs, forming covalent bonds, were located on one and the same sphere, ellipsoid or similar surface, Thereafter we used two rules formulated by Sidgwick and Powell [4] for simple molecules:

- all the electron pairs of a molecule arrange themselves into a such configuration which ensures their maximal removing from each other;
- geometry of a molecule is dictated by the arrangement of the electron pairs.

Incorporating these rules into our concept, we have developed method for calculating electronic and atomic structure of fullerenes of a broad sense [3]. The most interesting result obtained is discovering structural isomers of some fullerenes.

(Tetra-hexa)$_3$-penta$_6$ polyhedral fullerene being a structural isomer of a widely known dodecahedral fullerene is the progenitor of the of tetra-hexa-cell equator family of fullerenes. A possible way of generating this fullerene is suggested in Ref. [5].

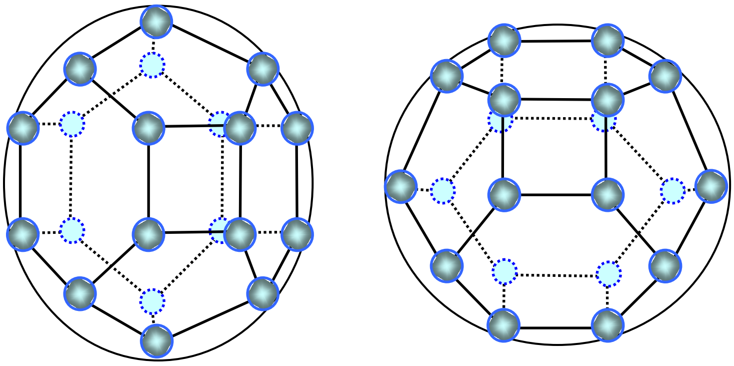

Fig. 1. Atomic structure of a (tetra-hexa)$_3$-penta$_6$ polyhedron fullerene, D_{3h} symmetry.

3. Branch of (tetra-hexa)$_3$-penta$_6$ polyhedral fullerene C_{20}

First stage. Starting with this fullerene, one can obtain its direct descendants with the help of mechanism of dimer embedding into a hexagon. Drawing the axonometric projections of the fullerenes C_{22}, C_{24} and C_{26} is a rather tedious procedure, but it allows avoiding many mistakes in subsequent reasoning. Constructing the graphs of these fullerenes is easier than drawing the axonometric projections. Taking as a basis the structure and graph of fullerene C_{20}, we have obtained the following pictures (Fig. 2). Here fullerenes C_{20} and C_{26} are perfect (D_{3h} symmetry), and fullerenes C_{22} and C_{24} are imperfect (C_1 symmetry).To gain a better understanding of the mechanism of dimer embedding, its main features are given in the form of schematic representation (Fig. 3).

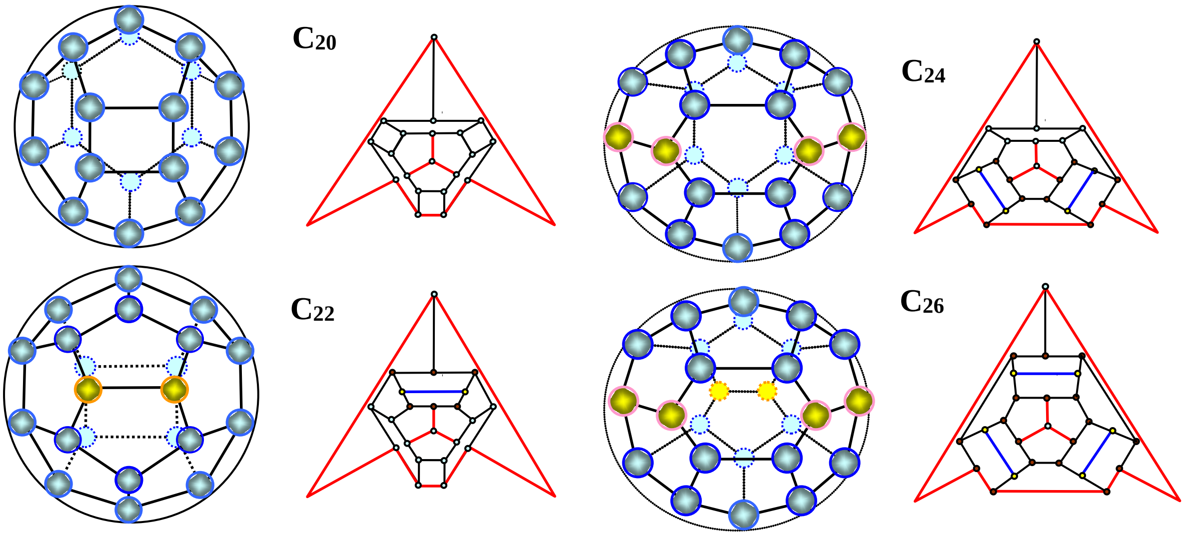

Fig. 2. Atomic structure and graphs of fullerenes C_{20}, C_{22}, C_{24} and C_{26}.

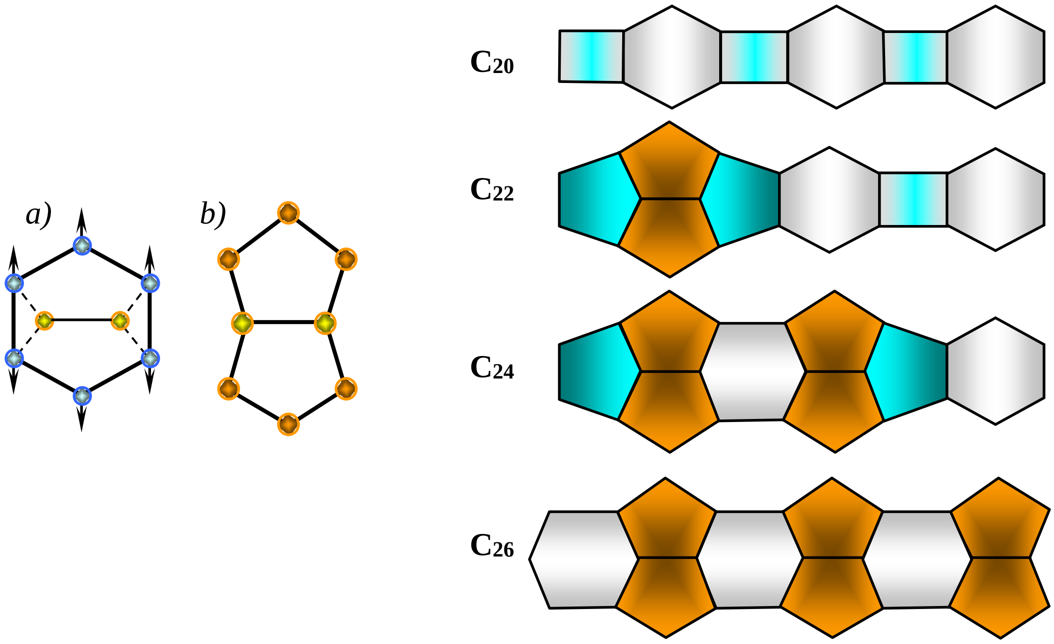

Fig. 3. Scheme reflecting the main local changes during the growth of fullerene C_{20}. Embedding dimer into a hexagon (*a*) and its transform into two adjacent pentagons (*b*).

Let us analyze this figure. From the configurations shown it follows that the first embedding which transforms fullerene C_{20} into fullerene C_{22}, influences deeply only on one of hexagons and two its square neighbors. The hexagon transforms into two adjacent pentagons and its square neighbors become pentagons. As a result, one obtains a cluster which contains four pentagons. The fullerene C_{22} as a whole is identical to the fullerene obtained from a dodecahedron by imbedding a dimer into a pentagon (Fig. 11 in Ref. [2]). The second imbedding transforms fullerene C_{22} into fullerene C_{24}. Similar to the previous case, one of two remaining hexagons transforms into two adjacent pentagons, its square neighbor into a pentagon, and its pentagon neighbor into a hexagon. As a result, one obtains one more isomer in addition to four considered in Ref. [2]. At last, the third embedding which leads from fullerene C_{24} to fullerene C_{26}, eliminates a last remaining hexagon and two its neighboring pentagons, but in return creates two adjacent pentagons and two hexagons of another local orientation. The fullerene obtained is an isomer of the fullerene considered in Ref. [2]. It is named a hexa-octa-cell equator fullerene where every two adjacent pentagons have the form of a bow tie.

Second stage. It should be emphasized that fullerene C_{24} can grow not only by the way shown in Figures 2 and 3. If a carbon dimer embeds into the newly formed hexagon instead of the remaining one, one obtains a new isomer of fullerene C_{26} presented in Figure 4. Thereafter both isomers grow in an equal way. As before, to gain a better understanding of the mechanism of dimer embedding, its main features are given in the form of schematic representation (Fig. 5). During the further growth each hexagon transforms into a bow tie, so the hexa-octa-cell equator fullerene finally becomes a bow-tie-cell equator fullerene C_{32} (Fig. 4), each bow tie having two bow-tie neighbors normal to it.

At the same time, in the pole areas there appear clusters composed of three adjacent hexagons, each hexagon having two adjacent pentagons. To gain a better understanding of this structure, coloring of the fullerene structure is changed in such a way that the pole areas atoms are specially marked in Figure 4. At first glance it might appear that such structure can grow as before embedding carbon dimmers. However the first embedding into one of three adjacent hexagons in any pole area does two residuary adjacent hexagons impotent, so there is the possibility of embedding only one dimmer into each pole area. As a result, one obtains four imperfect fullerenes C_{28}, C_{30}, C_{34} and C_{36} having C_1 symmetry, and one perfect C_{32} with D_{3h} symmetry (Fig. 4).

One can consider fullerenes C_{20}, C_{26} (the isomer shown in Fig. 2), and C_{32} as perfect fullerenes having a threefold axis of symmetry. The symmetry can be easily discovered looking at their graphs. Other fullerenes, C_{22}, C_{24}, C_{26} (the isomer shown in Fig. 3), C_{28}, C_{30}, and C_{34}, are imperfect. By analogy with crystal physics it can be said that that the reason of imperfection is connected with the fact that the fullerenes have extra ‘interstitial’ dimmers or ‘vacant’ dimmers.

At first glance fullerene C_{36} having two extra interstitial dimmers is imperfect in comparison with fullerene C_{32}. It would be expected also from its graph (Fig. 4). However it must be emphasized that applying graph approach for analysis of fullerene structure, it is necessary not only to use plane graphs but do such plane graphs which show the best correlation with the symmetry of a corresponding polyhedron [6]. Any fullerene atomic structure given in Figures 1–4 is in essence a modified cartographic projection which in addition to a front projection shows also a back projection of the fullerene ellipsoid. Here the main symmetry axis of a fullerene must be in the center of the corresponding fullerene graph normal to its plane. The graph of fullerene C_{36} shown in Figure 4 was constructed as a simple geometrical continuation of the graph of fullerene C_{32}. From Figure 4, it also follows that in contrast to fullerene C_{32}, fullerene C_{36} lost rotation symmetry having a three-fold axis, and it made its graph clumsy.

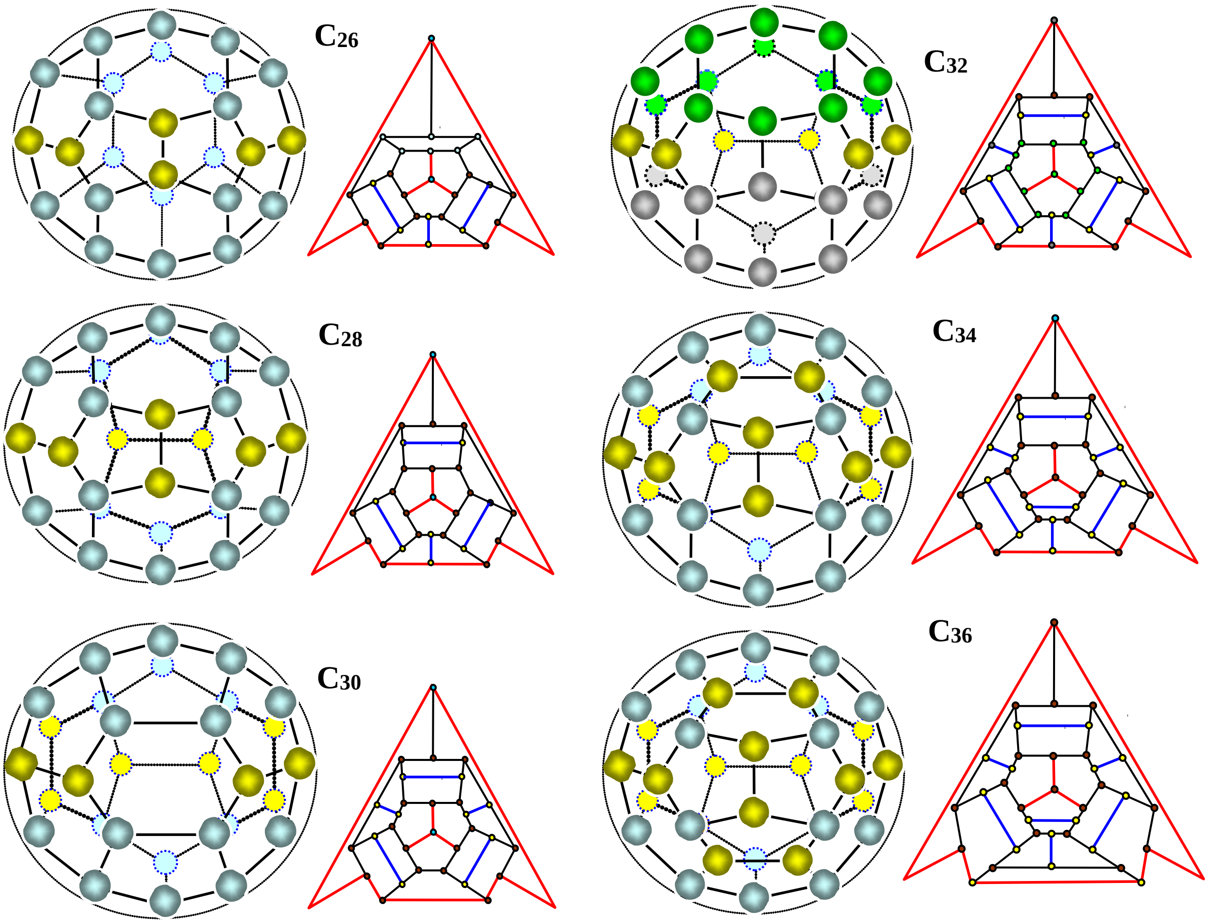

Fig. 4. Atomic structure and graphs of fullerenes C_{26}, C_{28} C_{30}, C_{32}, C_{34}, and C_{36}.

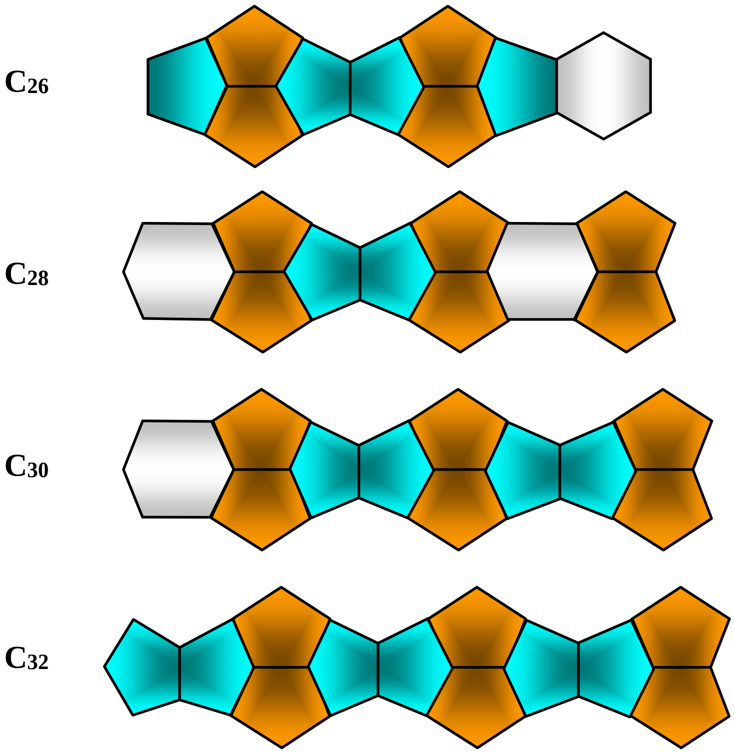

Fig. 5. Scheme reflecting the main structural changes during the growth of fullerene C_{24}.

4. Changing symmetry

The structure of fullerene C_{36} is rather interesting. It is a dodecahedron which is formed of twelve pentagons and eight hexagons. For study of this fullerene it is convenient to use a new system of coordinates where the axis *z*, or the main axis of symmetry, passes through the centers of two clusters formed of four pentagons; here nearest three of which being adjacent. In doing so, we have the polar-axis change of 90 degrees conserving the symmetry. The clusters are separated by a zigzag ring of twelve atoms. To gain a better understanding of this structure, the clusters are specially marked in Figure 6. Here one confronts with a quite unexpected phenomenon; the fullerene is changing its symmetry during growth. The graph taking into account a new symmetry of fullerene C_{36} looks nice (Fig. 6). From this figure it follows that the new symmetry is rotation-reflection symmetry D_{4d} having a fourfold axis. The fullerene is perfect, and we have the group of perfect fullerenes including C_{20}, C_{26}, C_{32}, and C_{36}.

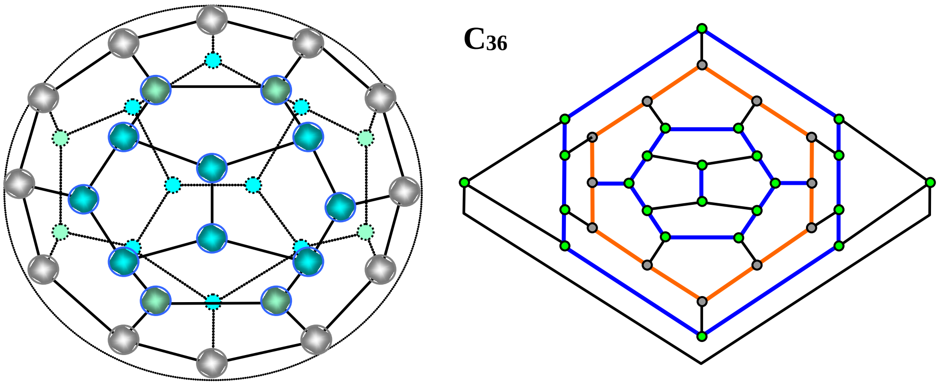

Fig. 6. Two clusters of twelve atoms in fullerene C_{36}; each cluster containing four pentagons, and symmetric graph of its fullerene.

5. Growth in new symmetry

The obtained fullerene C_{36} is able to grow further. It is felt that the process is going conserving the new symmetry. Moreover, we believe that the dimer embedding takes place in regions of the largest curvature attempting to do the fullerene surface looking like a sphere. The two cells of twelve atoms, each cell having four pentagons, the nearest three of which being adjacent, have the largest curvature. Therefore it is reasonable to suggest that dimer embedding will occur inside these cells. The mechanism of carbon dimer embedding into a pentagon was suggested in Ref. [2]. In our case it looks like it is shown in Figure 7. As a consequence one obtains fullerene C_{38} which receives the possibility for growing further with the help of Endo-Kroto mechanism, i.e. by embedding carbon dimmers in hexagons having two adjacent pentagons or, as in our case, two adjacent polygons, one of which is a pentagon and the other is a rectangle. The process creates fullerenes C_{40}, C_{42}, C_{44}, C_{46}, and C_{48}. (Fig. 8).

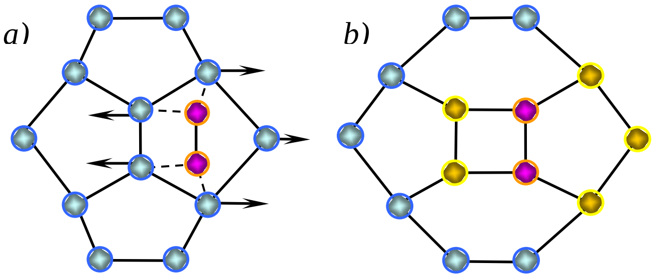

Fig. 7. Carbon dimer embedding into a pentagon (*a*) and local structural changing (*b*).

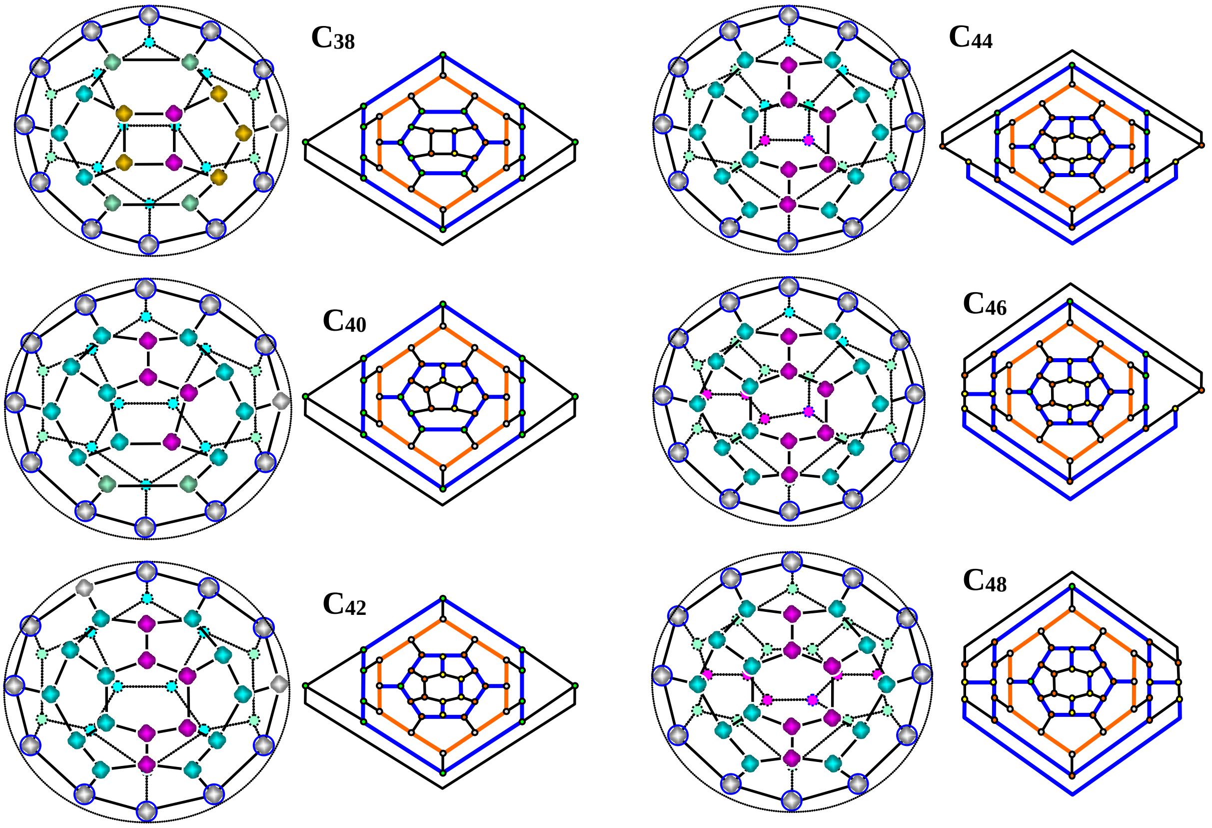

Fig. 8. Atomic structure and graphs of fullerenes C_{38}, C_{40}, C_{42}. C_{44}, C_{46}, and C_{48}.

6. Second changing symmetry and growth in the second new symmetry

Similar to fullerene C_{36} the structure of fullerene C_{48} is also rather interesting. The fullerene contains two clusters of eighteen atoms, each cluster having six pentagons forming a ring around a hexagon in the center. The clusters are separated by a zigzag ring of twelve atoms. To gain a better understanding of this structure, the clusters are specially marked in Figure 9. Here one confronts again with a quite unexpected phenomenon; the fullerene has changed its symmetry again during the growth. From Figure 9 it follows that the new symmetry is rotation-reflection symmetry D_{6d} having a sixfold axis. The fullerene is perfect, and one has the group of perfect fullerenes including C_{20}, C_{26}, C_{32}, C_{36}, and C_{48}, each fullerene having its own symmetry.

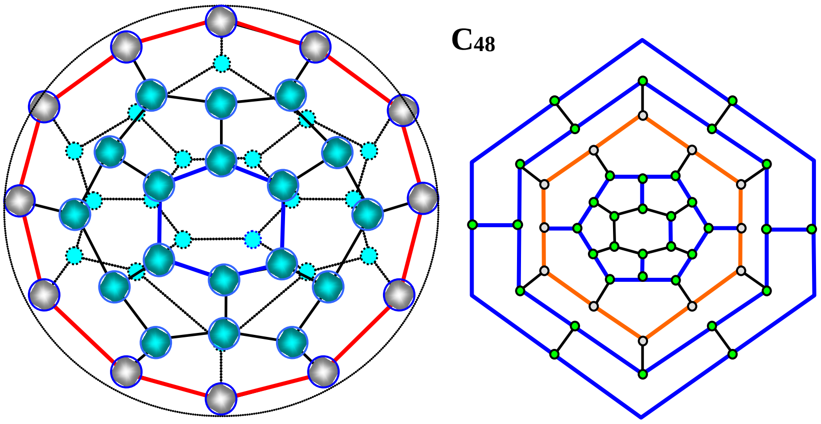

Fig. 9. Two clusters of eighteen atoms in fullerene C_{48}; each cluster containing six pentagons, and symmetric graph of its fullerene.

Embedding a dimer into a hexagon of any polar area of fullerene C_{48} gives fullerene C_{50} which is a bifurcation point. Thereafter fullerene C_{50} can grow, following various paths. They are shown in Figure 10. In the first case one obtains asymmetric fullerene C_{52} and symmetric fullerene C_{54}; in the second case symmetric fullerene C_{52} and asymmetric fullerene C_{54}. We suppose that symmetric fullerenes are more stable than asymmetric ones because the latter have a larger curvature. Fullerene C_{56} can be obtained either from symmetric or from asymmetric fullerene C_{54}. In both case the structure is just the same. Further growing creates fullerenes C_{58} and C_{60} (Fig. 11).

It is interesting to compare the structures of fullerenes C_{36} and C_{60} (Fig. 12). Both fullerenes have similar polar areas formed of four pentagons, nearest three of which being adjacent. These clusters are separated by one zigzag ring of twelve atoms in the case of fullerene C_{36}. For fullerene C_{60} there are two such rings; in addition between these rings there is one more zigzag ring of twelve atoms. By analogy with geography we can say that for fullerene C_{36} one has two frigid zones formed of four pentagons and two temperate zones formed of two pentagons and four hexagons. For fullerene C_{60} in addition to those zones there appear two torrid zones formed of six hexagons.

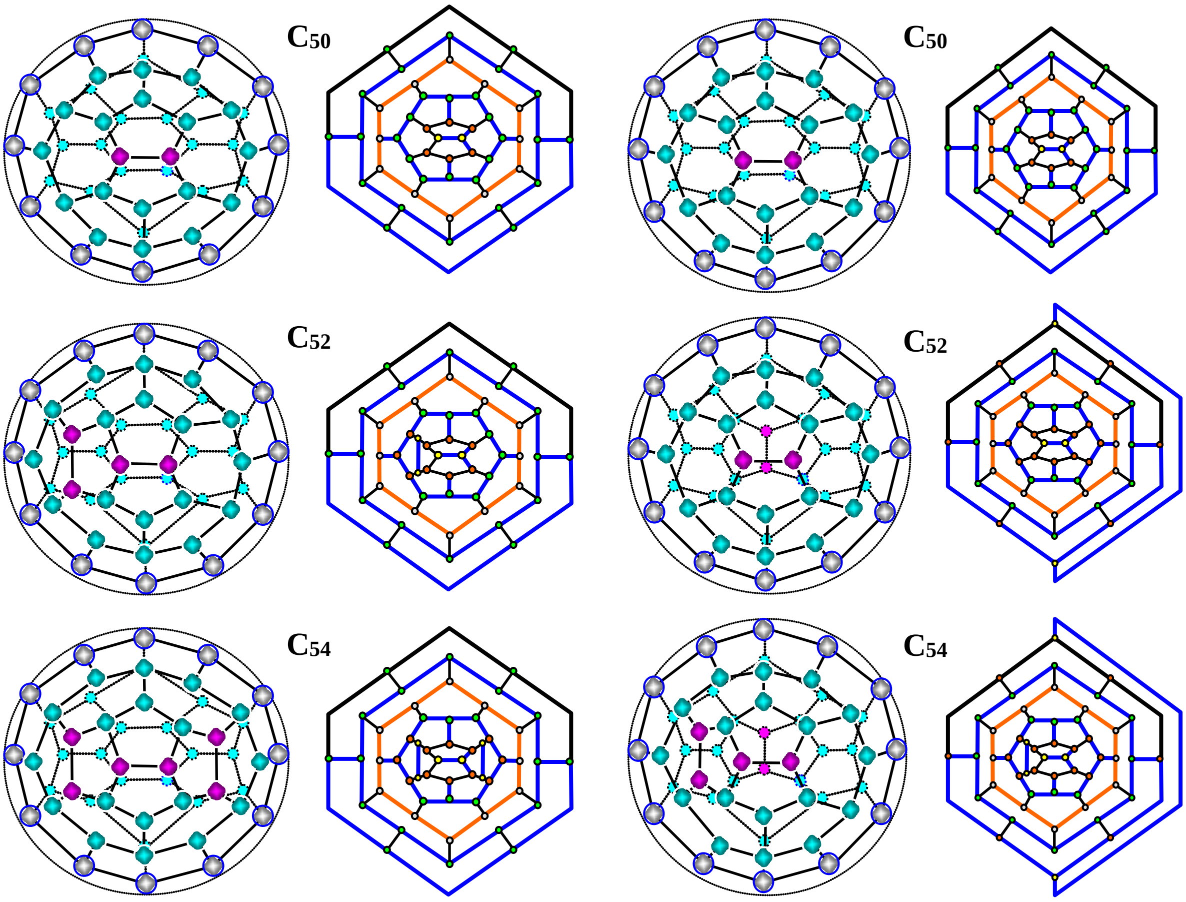

Fig. 10. Atomic structure and graphs of fullerenes C_{50}, C_{52}, and C_{54}; the first way of growing is on the left, the second way is on the right.

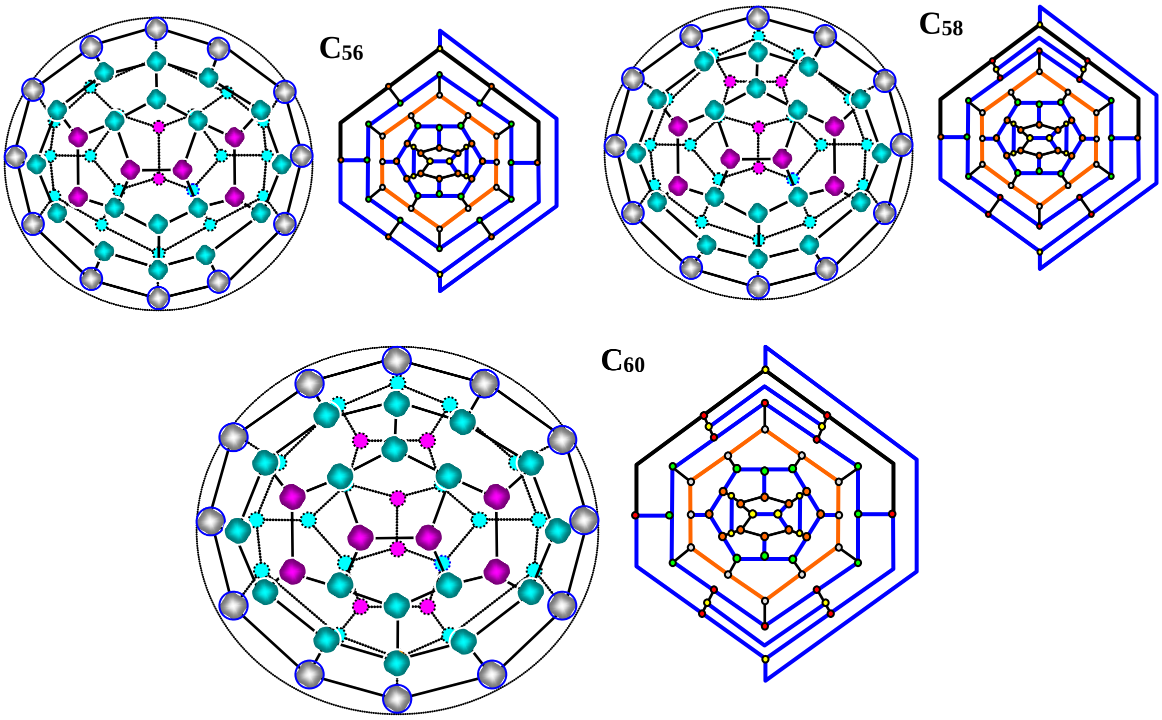

Fig. 11. Atomic structure and graphs of fullerenes C_{56}, C_{58}, and C_{60}.

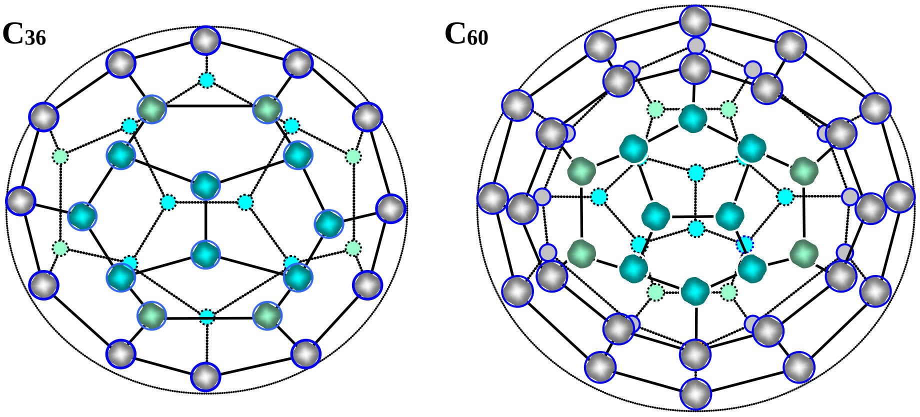

Fig. 12. Collation of atomic structure of fullerenes C_{36} and C_{60}.

7. Conclusion and discussion

Axonometric projections together with corresponding graphs for the first branch of the family of tetra-hexa-cell equator fullerenes including some isomers are constructed in the range from 20 to 60. A unified approach for drawing axonometric projections of these fullerenes is suggested; namely, it is the dimetric representation which symmetry coincides with that of a corresponding graph. The growth of fullerenes is studied on the basis of two mechanisms, according to which a carbon dimer embeds either in a hexagon or a pentagon of an initial fullerene. This leads to stretching and breaking the covalent bonds which are parallel to arising tensile forces. In both cases there arises a new atomic configuration and there is mass increase of two carbon atoms. We considered direct descendents of the first branch of tetra-hexa-cell equator family beginning with C_{20}; namely C_{22}, C_{24}, C_{26}, C_{28}, C_{30}, C_{32}, C_{34}, C_{36}, C_{38}, C_{40}, C_{42}, C_{44}, C_{46}, C_{48}, C_{50}, C_{52}, C_{54}, C_{56}, C_{58}, and C_{60}.

Fullerenes C_{20}, C_{26} (the isomer shown in Fig. 2), C_{32}, and C_{36} are perfect fullerenes having threefold symmetry. The symmetry can be easily discovered looking at their graphs. Fullerenes, C_{22}, C_{24}, C_{26} (the isomer shown in Fig. 4), C_{28}, C_{30}, and C_{34} are imperfect. By analogy with crystal physics it can be said that that the reason of imperfection is connected with the fact that the fullerenes have extra 'interstitial' dimmers or 'vacant' dimmers. The structure of fullerene C_{36} is rather interesting. It is a dodecahedron which is formed of twelve pentagons and eight hexagons. For study of this fullerene it is convenient to use the system of coordinates where the axis *z*, or the main axis of symmetry, passes through the centers of two clusters formed of four pentagons, where nearest three of which being adjacent. In doing so, the polar-axis change is of 90 degrees conserving the symmetry. The clusters are separated by a zigzag ring of twelve atoms (Fig. 6). It must be emphasized that applying graph approach for analysis of fullerene structure, it is necessary not only to use plane graphs but do such plane graphs which show the best correlation with the symmetry of a corresponding polyhedron. A quite unexpected phenomenon was discovered; the fullerene is changing its symmetry during growth. From Figure 6 it follows that the new symmetry is rotation-reflection symmetry having a fourfold axis. The fullerene is perfect, and it must be included in the group of perfect fullerenes. It is notable that among the perfect fullerenes there is one which has a "magic" number 32 [7]. Stability of the magic fullerene C_{32} can be understood by reference to Figure 6 where its structure is shown.

Similar to fullerene C_{36} the structure of fullerene C_{48} is also rather interesting. The fullerene contains two clusters of eighteen atoms, each cluster having six pentagons forming a ring and one hexagon in the center. The clusters are separated by a zigzag ring of twelve atoms. Here one confronts again with a quite unexpected phenomenon; the fullerene is changing its symmetry again during the growth. From Figure 9 it follows that the new symmetry is rotation-reflection symmetry having a sixfold axis. The fullerene is perfect, and therefore the group of perfect fullerenes increases having C_{20}, C_{26}, C_{32}, C_{36}, and C_{48}, each fullerene with its own symmetry. Embedding a dimer into a hexagon of any polar area of fullerene C_{50} gives fullerene C_{50} which is a bifurcation point. Thereafter fullerene C_{50} can grow, following various paths (Fig. 10). In the first case one obtains symmetric fullerene C_{52} and asymmetric fullerene C_{54}, in the second case asymmetric fullerene C_{52} and symmetric fullerene C_{54}. We suppose that symmetric fullerenes are more stable than asymmetric ones because the latter have a larger curvature. Fullerene C_{56} can be obtained either from symmetric or from asymmetric fullerene C_{54}. In both case the structure is just the same. Further growing creates fullerenes C_{58} and C_{60} (Fig. 11).

The structure of fullerenes C_{36} and C_{60} has much in common (Fig. 12). Both fullerenes have similar polar areas formed of four pentagons, nearest three of which being adjacent. These clusters are separated by one zigzag ring of twelve atoms in the case of fullerene C_{36}. For fullerene C_{60} there are two such rings; besides between these rings there is one more zigzag ring of twelve atoms. By analogy with geography one can say that fullerene C_{36} has two frigid zones formed of four pentagons and two temperate zones formed of two pentagons and four hexagons. For fullerene C_{60} in addition to those zones there appear two torrid zones formed of six hexagons.

Hidden symmetry and periodicity. We have collated fullerenes C_{36} and C_{60} (Fig. 12) and have found that they have similar frigid zones formed of four pentagons. Besides these fullerenes belong to the same symmetry which is rotation-reflection symmetry D_{4d} having a four-fold axis. It was not difficult because the fullerenes were presented in the form of identical axonometric projections. However in many cases fullerenes are shown in different forms. In such a situation, graph analysis is useful. In Ref. [6] it is emphasized that on the basis of graph analysis one can distinguish different families of fullerenes and therefore one can do some classification of these unusual carbon structures. However graph analysis is able not only to divide but also to unite.

Consider the structure of fullerene C_{48} obtained in this study and fullerene C_{36} designed through the use of fusion algorithm in Refs. [8, 9]. At first glance they have nothing in common (Fig.13). However, comparing their graphs shows that both fullerenes have the six-fold symmetry. It is worth noting that the mass difference between these fullerenes is $\Delta m=12$ being equal to a double degree is suggested [11].

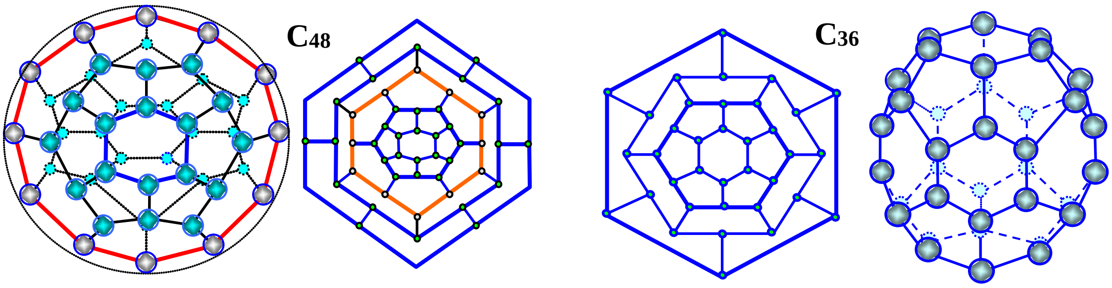

Fig. 13. Collation of atomic structure of fullerenes C_{36} and C_{48}.

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