АТОМНАЯ ФИЗИКА, ФИЗИКА КЛАСТЕРОВ И НАНОСТРУКТУР

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GEOMETRIC MODELING OF MIDI-FULLERENE GROWTH FROM C$_{32}$ TO C$_{60}$

Axonometric projections together with the corresponding graphs for fullerenes are constructed in the range from 32 to 60. The growth of fullerenes is studied on the basis of a mechanism according to which a carbon dimer embeds in a hexagon of an initial fullerene. This leads to stretching and breaking the covalent bonds which are parallel to arising tensile forces. In this case, instead of a hexagon adjoining two pentagons, two adjacent pentagons adjoining two hexagons are obtained. As a result, there arises a new atomic configuration and there is a mass increase of two carbon atoms. We considered the direct descendants of fullerene C$_{32}$; namely, C$_{2n}$ where $n = 17 - 30$.

FULLERENE, MODELING, GROWTH, CARBON DIMER, GRAPH, STRUCTURE.

Introduction

Since the discovery of fullerenes [1, 2] and carbon nanotubes [3], carbon occupies a strategic position in materials science and technology as one of the most versatile and far-reaching materials [4, 5]. Obtaining fullerenes smaller than C$_{60}$, e.g., C$_{36}$ [6] and C$_{20}$ [7], has attracted considerable attention, since smaller fullerenes are highly strained due to the presence of fused five-membered rings. Caged molecules with low mass in the fullerene family are especially interesting because of their high curvature and increased strain energy that give rise to high reactivity.

Current studies on fullerenes and their compounds mainly focus on large-size fullerenes. Experimental researches and practical applications of small-size fullerenes are still limited by their low yield and poor stability. The comprehensive experimental study on small or medium-size fullerenes revealed the following [8]. In the mass spectra of products of benzene pyrolysis, the authors found out the ions of all kinds of carbon molecules including

(*i*) Small carbon molecules (C$_3$ − C$_{20}$);

(*ii*) Quasi-fullerenes C$_{21}$, C$_{23}$, C$_{33}$, C$_{48}$, C$_{52}$, C$_{54}$, C$_{56}$ and C$_{58}$;

(*iii*) Hydrides of small carbon molecules, such as C$_5$H$_2$, C$_{10}$H$_4$, C$_{14}$H$_4$, C$_{16}$H$_8$ and C$_{18}$H$_2$;

(*iv*) Hydrides of quasi-fullerenes, such as C$_{25}$H$_2$, C$_{27}$H$_2$, C$_{31}$H$_4$, C$_{37}$H$_6$, C$_{39}$H$_6$, C$_{43}$H$_8$, C$_{47}$H$_{10}$ and C$_{49}$H$_{10}$.

(We preserve here the terminology employed by the authors).

However the structures of these molecules are not known; therefore theoretical methods are helpful in this field to identify some potential compounds with good properties.

It must be emphasized that most investigations of fullerenes have centered on either obtaining these materials experimentally or studying properties of these materials whose structure was previously postulated. To our mind, the crucial questions for advanced applications of these materials are the following:

How the materials are originated,

And what structure they obtain.

The answer to these questions gives the possibility to develop nanotechnology on a scientific basis.

Various ingenious schemes have been proposed for the mechanism of fullerene formation [e.g., Refs. 9 − 11]. They can be categorized into two major groups: bottom-up and top-down models. In the first case, fullerene cages and nanotubes are considered to be formed from carbon atoms and small carbon clusters [9, 10]. In the second case, fullerenes and nanotubes are thought as direct transformation of graphene into fullerenes [11]. We will follow one of the first-group mechanisms suggested for the first time in Ref. [12] because, to our mind, it has better justification [10]. Briefly, it consists in the following. A carbon dimer embeds into a hexagon of an initial fullerene. This leads to stretching and breaking the covalent bonds which are parallel to the arising tensile forces. As a consequence, instead of the hexagon adjoining two pentagons, when the dimer embeds into this hexagon, one obtains two adjacent pentagons adjoining two hexagons. It means that there arises a new atomic configuration and there is a mass increase of two carbon atoms.

In doing so, we geometrically modeled growth of the second branch of the family of tetra-hexa-cell equator fullerenes beginning with C_{24} [13] in the range from 24 to 48. We have constructed the axonometric projections and the corresponding graphs for these fullerenes. The structure of the initial fullerene C_{24} was suggested in Ref. [14] on the basis of one of the types of graph presentation developed for

scanning cyclohexane electronic structure [15]. Later it was obtained as a mirror-symmetry fusion reaction of two half fullerenes C_{12} [16]. The main characteristic feature of the initial fullerene C_{24} is that it is perfect and has a three-fold symmetry (D_{3h} symmetry). It was found that during the growth, along with imperfect fullerenes, the perfect fullerenes C_{30}, C_{36}, and C_{48} were formed. The first two conserve three-fold symmetry, the third one changes it to D_{6d} symmetry. According to Ref. [2], perfect fullerenes should have enhanced stability relative to near neighbors.

In this contribution we consider the geometric modelling of middle-size fullerenes growth beginning with C_{32}; namely 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}. We have studied their growth at first obtaining their graphs, what is simpler, and then designing their structure on the basis of the graphs obtained. The aim of the study is to find perfect fullerenes.

Branch of tetra$_6$-hexa$_{12}$ polyhedral fullerene C_{32}

The initial perfect fullerene C_{32} consists of six squares and twelve hexagons (Fig. 1) so it was named a tetra$_6$-hexa$_{12}$ polyhedron. It has D_{4h} symmetry. The fullerene was predicted together with its graph in Ref. [14], but the structure was not given.

First stage. Starting with this fullerene, it is possible to obtain its direct descendants with the help of the mechanism of dimer embedding into a hexagon. We have emphasized in our
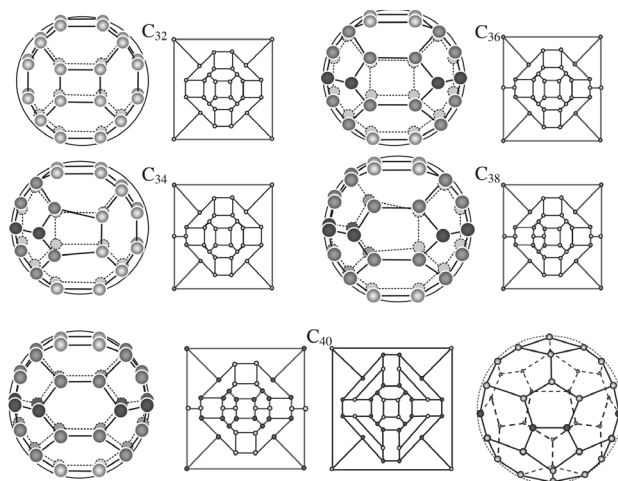

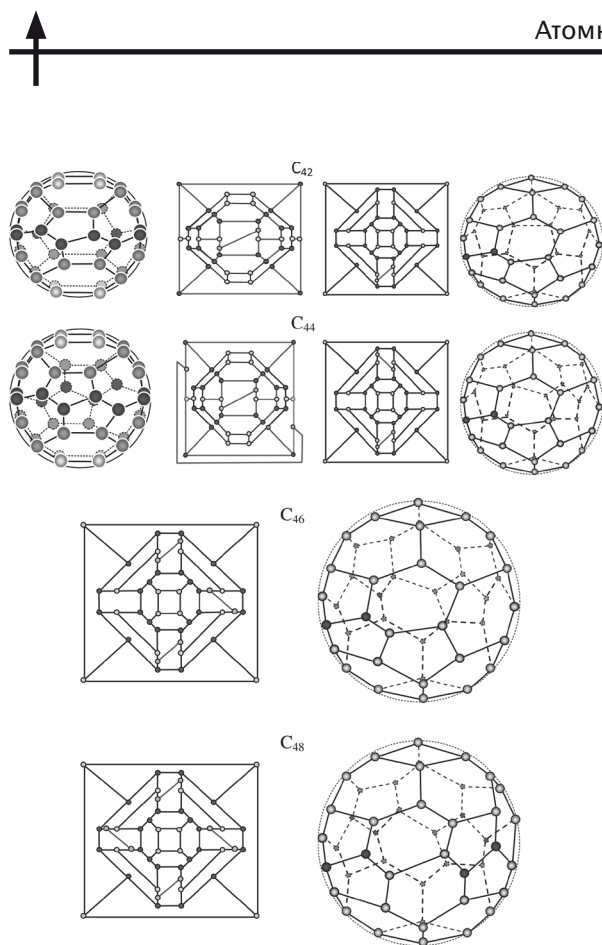Fig. 1. Atomic structure and graphs of fullerenes C_{32}, C_{34}, C_{36}, , C_{38}, and C_{40}

Fig. 2. Atomic structure and graphs
of fullerenes C_{40}, C_{42}, C_{44}, C_{46}, and C_{48}

previous papers that drawing the axonometric projections of fullerenes is a rather tedious procedure, but it allows avoiding many mistakes in subsequent reasoning. Constructing the graphs of fullerenes is easier than drawing the axonometric projections. Taking the structure as a basis and the graph of fullerene C_{32}, we have obtained the fullerenes from C_{32} to C_{44} (Figs. 1 and 2). To gain a better understanding of the mechanism of dimer embedding, its main features are given in the form of schematic representation (Fig. 3).

Let us analyze these figures. From the configurations shown it follows that the first embedding, which transforms fullerene C_{32} into fullerene C_{34}, influences deeply only one of the hexagons and two of its square neighbours. This hexagon transforms into two adjacent pentagons and its square neighbors become pentagons; the fullerene C_{34} loses four-fold symmetry. It becomes an imperfect fullerene with C_1 symmetry. At that, a cell which contains four pentagons appears in the fullerene.

The second imbedding transforms fullerene C_{34} into fullerene C_{36}. Similar to the previous case, one of two remaining hexagons transforms into two adjacent pentagons, its square neighbour into a pentagon, and its pentagon neighbour into a hexagon. As a result, the more symmetric fullerene C_{36} with two-fold symmetry is obtained. The fullerene is semi-perfect with two cells of three adjacent pentagons and belongs to C_2 symmetry. The third embedding leads to the transition from fullerene C_{36} to fullerene C_{38}. It eliminates one more hexagon and two its neighbours, a pentagon and a square, but in return creates an adjacent hexagon of another local orientation and a new pentagon. Again the fullerene becomes less symmetric. As fullerene
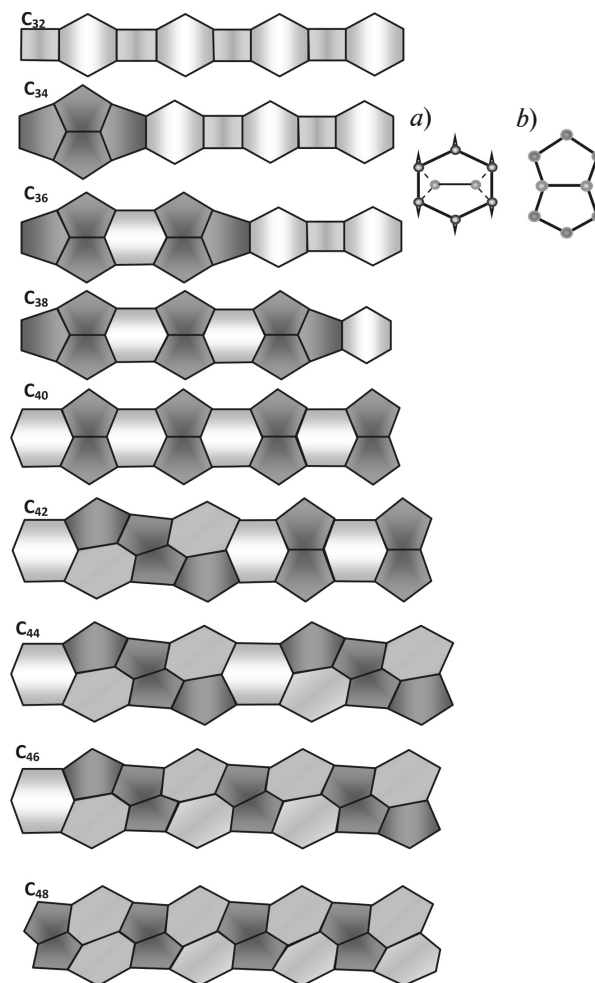

Fig. 3. Scheme reflecting the main structural changes during the growth of fullerene C_{32}. Dimer embedding into a hexagon (*a*) transforms it into two adjacent pentagons (*b*)

C_{34}, fullerene C_{38} belongs to C_1 symmetry. At last the fourth embedding restores D_{4h} symmetry. The perfect fullerene C_{40} obtained could be named a tetra$_2$-penta$_8$-hexa$_{12}$ polyhedron where every two adjacent pentagons have the form of a bow tie.

Second stage. Now the fullerene C_{40} is up against the problem that it can grow only at an angle to its main axis of symmetry, for example, by the way shown in Figs. 2 and 3. It is connected with the fact that embedding can be realized only normal to a direction along which a hexagon has two neighbouring mutually antithetic pentagons. During further growth fullerenes C_{42}, C_{44}, C_{46}, and C_{48} (Figs. 2 and 3) are obtained. Similar to the first stage, the fullerenes with an odd number of embedded dimers are imperfect (C_{42} and C_{48}, C_1 symmetry), fullerene C_{44} having two embedded dimers is semi-perfect (C_2 symmetry) and fullerene C_{48} having four embedded dimers is perfect (four-fold D_4 symmetry). It should be emphasized that in this case the number of embedded dimers is equal to the degree of symmetry.

The structure of all the fullerenes obtained at the first and the second stages has one common feature. For visualization of this feature 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 squares. It is easy to verify that each square surrounded with four hexagons forms a cluster. The clusters are separated by other atoms creating an equator. It is worth to note that all the equator atoms are former dimer atoms.

Bifurcation. In principle, any hexagon having two neighboring mutually antithetic pentagons is capable of embedding a dimer. However, it can embed a hexagon having not only two neighbouring mutually antithetic pentagons, but one pentagon and a mutually antithetic square. Such a possibility appears for all fullerenes formed at the second stage and leads to branching. The reason is connected with the well-known fact: the less is the fullerene surface (or the curvature), the less is its distortion energy. In its turn the local curvature is defined by the sum of adjacent angles having a common vertex. The larger is the sum, the less is the curvature, and there-

fore the less is the local stress concentration. We consider this possibility by the example of fullerene C_{44}.

The fullerene C_{44} of configuration shown in Fig. 2 has eight hexagons, each of them having two vertices where the angle sum is

$$90 + 2 \cdot 120 = 330°.$$

Even a first embedding of a dimer into one of these hexagons increases the sum to

$$2 \cdot 108 + 120 = 336°,$$

and so decreases the curvature.

Therefore the configuration can be more stable. Growing fullerene C_{46} is shown in Fig. 4. It continues until fullerene C_{52} is obtained. For visualization study of the growth it is convenient to use the same system of coordinates as before, where the axis z is the main axis of symmetry.

The structure of fullerene C_{52} is unusual. It is formed of eight hexagons along a meridian which divides the fullerene into two hemispheres, each of them containing two chains of three adjacent pentagons and two crosses of four hexagons. To gain a better understanding of this structure, the pentagon chains are specially marked in Fig. 4. During the following growth (Fig. 5) the end pentagons of chains transform into hexagons and the middle pentagons become isolated. At the same time there appear pairs of two adjacent pentagons. The final result is fullerene C_{60}. It contains four isolated pentagons and four pairs of two adjacent pentagons. Again to gain a better understanding of its structure, the isolated pentagons and pentagon pairs are specially marked in Fig. 5.

Early similar isomers, containing four isolated pentagons and four pairs of two adjacent pentagons, were carefully studied with the help of the Avogadro visualization package [17]. The authors calculated the formation energies of the isomers and have found that the less are their surfaces, the less are their Gibbs free energies. The energy of a fullerene with four pairs of two adjacent pentagons on an equator (Fig. 6,*a*) differs from the energy of a fullerene with two pairs of adjacent pentagons on an equator and two pairs on a meridian (in limits of errors).
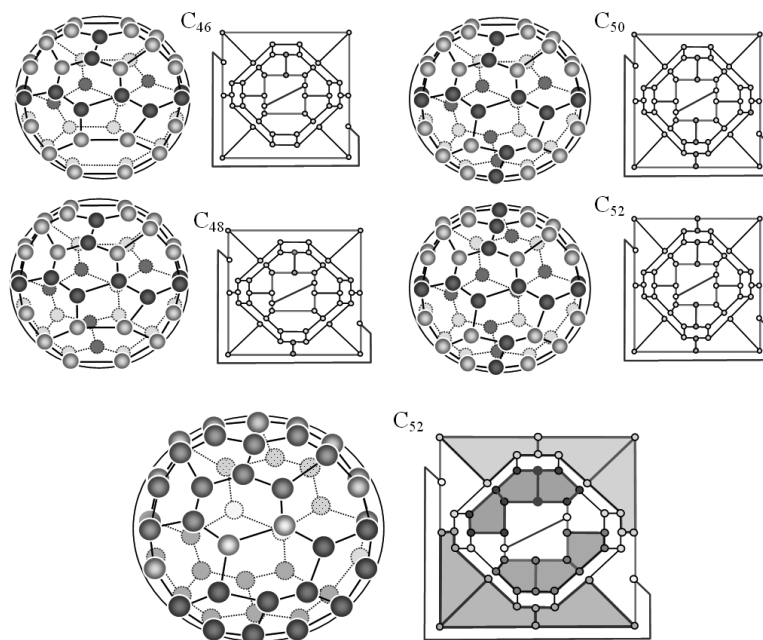
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Fig. 4. Atomic structure and graphs of fullerenes C_{46}, C_{48}, C_{50} and C_{52}. Four chains of three adjacent pentagons in fullerene C_{52} are presented below
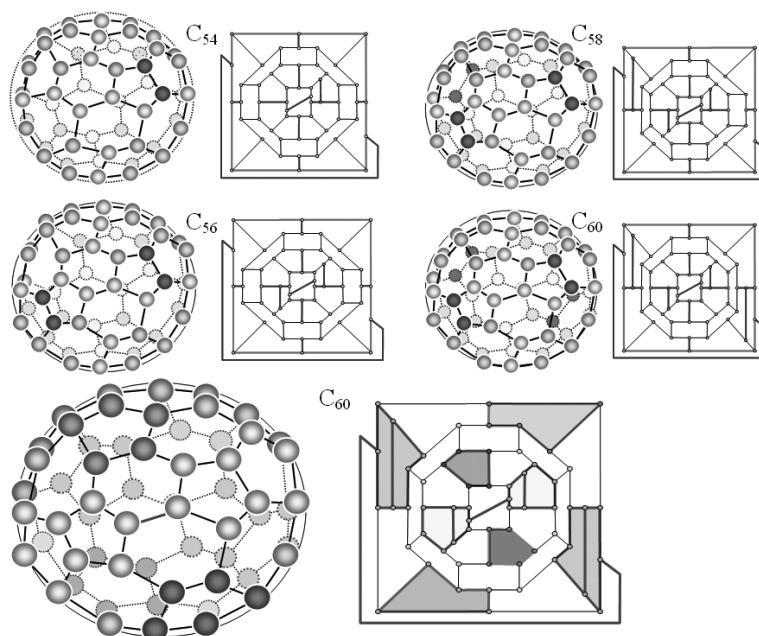

Fig. 5. Atomic structure and graphs of fullerenes C_{54}, C_{56}, C_{58} and C_{60}. Four isolated pentagons and four pairs of two adjacent pentagons in fullerene C_{60} are shown below

They were the least energies that exceed a little the energy of fullerene C_{70}. In our case two pairs of adjacent pentagons form a zigzag (Fig. 6, b). It is worth to note that each two pairs are connected by means of either one bond or a pair of two bonds. This fullerene is one of four possible isomers containing four isolated pentagons and four pairs of two adjacent pentagons. The volume models of these isomers were constructed in Ref. [17]; all of them can
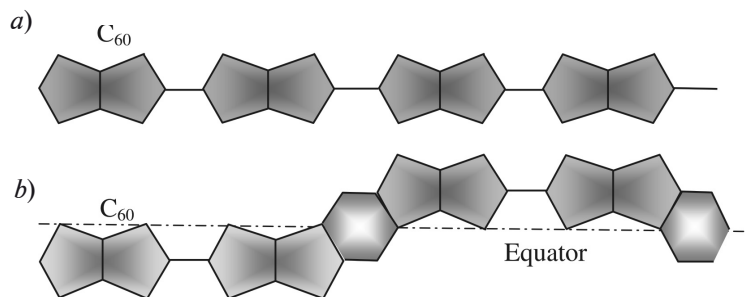
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Fig. 6. Arrangement of two pairs of adjacent pentagons:
postulated (*a*) and modeled (*b*)

be imagined as being composed of one and the same pairs of clusters having different orientation. For this reason, we suppose that all four isomers, including the isomer obtained with the help of embedding modeling, have free energies being close enough.

Conclusion, discussion and prediction

Axonometric projections together with the corresponding graphs for tetra-hexa-cell-equator fullerenes are constructed in the range from 32 to 60. Growth of fullerenes is studied on the basis of graph theory using the mechanism according to which a carbon dimer embeds in a hexagon of an initial fullerene. It leads to stretching and breaking the covalent bonds which are parallel to arising tensile forces. In this case, instead of the hexagon adjoining two pentagons, two adjacent pentagons adjoining two hexagons are obtained. As a result, there arises a new atomic configuration and there is a mass increase of two carbon atoms.

We obtained direct descendants of the tetra-hexa-cell-equator family beginning with C_{32}; namely 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}. Among them we can set off perfect symmetric fullerenes C_{32}, C_{40}, and C_{48}. The symmetry can be easily discovered looking at their graphs.

As pointed out in the Introduction, there is no clear and unique theory of fullerene growth. "The problem here is not the lack of imagination, because quite numerous models have been proposed. What is rather lacking is a model using quantities that might be evaluated and measured. Moreover, a theoretical model,

in order to deserve its name, should lead to numerical predictions. In order to represent something more than a set of circular arguments, a model should predict more numerical values, parameters or functional relations than the number of input parameters" [18].

Let us consider to what degree our model developed on the basis of combination of graph theory and group theory meets these requirements.

Predictions. Modeling the growth of fullerenes originating from fullerene C_{24} (D_{3h} symmetry), we have obtained the perfect fullerenes C_{30} and C_{36} conserving three-fold symmetry. In the present study the found perfect fullerenes originating from fullerene C_{32} (D_{4h} symmetry) and conserving four-fold symmetry are C_{40} and C_{48}. The mass difference between successive fullerenes in the first case is $\Delta m = 6$, in the second case $\Delta m = 8$. It should be emphasized that in both cases the mass difference is equal to a double degree of symmetry.

Suppose that this empirical rule is valid for fullerenes of other symmetries. We consider this possibility by the example of fullerenes C_{40} and C_{48} designed in Ref. [14]. In the first case perfect fullerenes C_{50} and C_{60}, the fullerenes conserving five-fold symmetry, can be obtained during the growth of fullerenes originating from fullerene C_{40} (D_{5h} symmetry). In a similar way, during the growth of fullerenes originating from fullerene C_{48} (D_{6h} symmetry) perfect fullerenes C_{60} and C_{72} conserving six-fold symmetry can be formed. Preliminary studies confirmed these predictions.

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Мелькер А.И., Крупина М.А. ГЕОМЕТРИЧЕСКОЕ МОДЕЛИРОВАНИЕ РОСТА МИДИ-ФУЛЛУРЕНОВ ОТ C_{32} ДО C_{60}.

Аксонометрические проекции вместе с соответствующими графами для фуллеренов сконструированы в диапазоне от 32 до 60. Рост фуллеренов изучался на основе механизма, согласно которому углеродный димер внедряется в шестиугольник исходного фуллерена. Это приводит к растяжению и разрыву ковалентных связей, которые параллельны возникающим растягивающим силам. В этом случае вместо шестиугольника, смежного к двум пятиугольникам, возникают два соседних пятиугольника, смежные к двум шестиугольникам. В результате возникает новая конфигурация, и масса фуллерена увеличивается на два атома. Мы рассмотрели потомки фуллерена C_{32}, а именно C_{2n}, где $n = 17 − 30$.

ФУЛЛЕРЕН, МОДЕЛИРОВАНИЕ, РОСТ, УГЛЕРОДНЫЙ ДИМЕР, ГРАФ, СТРУКТУРА.

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СВЕДЕНИЯ ОБ АВТОРАХ

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