УДК 620.3:546.26
doi: 10.18323/2782-4039-2022-2-37-53

Nucleation and growth of fullerenes and nanotubes having three-fold T-symmetry

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Received 14.07.2021 *Accepted 14.06.2022*

Abstract: According to the periodic system of fullerenes, all the fullerenes can be classified into the groups having different symmetry. It is supposed that the fullerenes of one and the same symmetry have similar properties. Before the appearance of the periodic system in 2017 the fullerenes were chosen for study at a random way that instead of ordering the results only increased information entropy. We have studied possible ways of generation and growing the fullerenes, which refer to the group having three-fold T-symmetry. Beginning with cyclopropane C_3H_6 producing clusters C_6, we have obtained elementary fullerenes C_6 as well as mini-fullerenes C_{12}, which in their turn have produced the fullerenes from C_{18} to C_{48}, perfect and imperfect, as well as nanotubes. The basic perfect fullerenes C_{18}, C_{24}, C_{30}, C_{36}, C_{42} and C_{48} have the ordinary three-fold symmetry, the intermediate ones having no such symmetry. Their imperfection is connected with extra 'interstitial' or carbon dimers, the dimers playing the role of defects. One can define the imperfect fullerenes with defects as the fullerenes having topological three-fold symmetry. We have calculated their shape and energies using Avogadro package and discussed possible reasons of their dependence on a fullerene size and shape. We have found that the fullerenes can be divided into two groups, alive that can grow, and dead which are impotent. Taking into account the results obtained early, allows us to make predictions that the dead fullerenes C_{24R}, C_{32R}, C_{40R} and C_{48R} of three-, four-, five- and six-fold symmetry have the most chance to be found experimentally with comparison of their isomers.

Keywords: carbon; embedding; energy; fullerene; fusion reaction; graph representation; growth; nanotube; periodic system; single and double bond; topological symmetry.

Acknowledgments: The paper was written on the reports of the participants of the X International School of Physical Materials Science (SPM-2021), Togliatti, September 13–17, 2021.

For citation: Melker A.I., Krupina M.A., Matvienko A.N. Nucleation and growth of fullerenes and nanotubes having three-fold T-symmetry. *Frontier Materials & Technologies*, 2022, no. 2, pp. 37–53. DOI: 10.18323/2782-4039-2022-2-37-53.

INTRODUCTION

Periodic system of fullerenes

The system was formulated at first implicitly as the prediction of the fullerenes conserving symmetry during their growth in Ref [1] and in the final form in Refs [2; 3]. The system consists of horizontal series and vertical columns (groups); they include basic perfect fullerenes from C_{14} to C_{96}. The horizontal series form the Δn periodicities, where the fullerene structure changes from three-fold symmetry to six-fold through four and five ones. The vertical columns have different symmetry. Each column includes the fullerenes of one and the same symmetry, the mass difference Δm for each column being equal to a double degree of symmetry. Two groups of three-fold symmetry differ by the structure of their apices. The three-fold S-symmetry column has two sharp apices; the third-order axis is going through them. The three-fold T-symmetry group has two truncated apices; the third-order axis is going through the centers of their equilateral triangles. Since the vertical columns incorporate the fullerenes of one and the same symmetry, we suppose that the fullerenes of one and the same symmetry have similar properties. The system leaves room for incorporating into it other fullerene families having quite different symmetries than above-mentioned ones. It should be emphasized that the system can be taken as a basis for rigorous fullerene classification.

Ordinary and topological symmetry

At first it has been desirable to work entirely with the Δn series in order to discover general features of the transition from one symmetry to another [3–7]. After we have found the corresponding regularity, we need to focus upon particulars of one and the same column (group). According to the periodic system, in each column there are two main types of fullerenes; the basic perfect ones and intermediate imperfect ones. The basic perfect fullerenes have ideal structure and ordinary symmetry. The intermediate imperfect fullerenes have extra carbon dimers. By analogy with crystal physics, we have assumed [2] that these extra dimers play the role of defects which violate the local symmetry and create imperfections. However, in crystals with defects the long-range-order is observed experimentally. In order to underline this peculiarity, such long-range order is referred to as the topological long-range one [8]. Using analogous terminology, we have defined

the imperfect fullerenes, which conserve the main axis of symmetry, as having topological symmetry.

The previous investigations were done for the fullerenes of three-fold S-symmetry [9], four-fold [10] and tetrahedral one [11; 12]. In this contribution we have studied the nucleation and growth of fullerenes referring to the column of three-fold T-symmetry. In the periodic table of fullerenes there are two columns of three-fold symmetry which differ by the structure of their apices. The 3-fold symmetry group S has two sharp apices, the third-order axis going through them. The 3-fold symmetry group T has two truncated apices, the third-order axis going through the centers of triangles. In our case of three-fold T-symmetry, there are perfect fullerenes C_{12}, C_{18}, C_{24}, C_{30}, C_{36}, C_{42} and C_{48} of ordinary symmetry and imperfect fullerenes C_{20}, C_{22}, C_{26}, C_{28}, C_{32}, C_{34}, C_{38}, C_{40}, C_{44} and C_{46} of topological symmetry.

Aim of study

According to Aristotle (384-322 BC), all essential originates and consists of two principia: *matter and form*; the form being the leading principle. The matter in itself is the passive principle of nature; it is the possibility for appearance of a real thing. In order the thing became the reality; it must receive the form, which transforms the possibility into the reality. The periodic system of fullerenes was suggested for ordering different forms of fullerenes on the base of symmetry [1–3]. As a first approximation, this gives a tolerably correct classification of fullerene "form". It is not enough for comprehensive knowledge of the "form", especially taking into account the fact that since the discovery of fullerenes, carbon nanotubes and graphene, carbon occupies a strategic position in materials science and technology. The purpose of this work is to gain a complete understanding of how fullerenes can be effectively used through providing their abstract "form" with the shape, structure, energy, etc., using the example of fullerenes with triple T-symmetry.

RESULTS

1. Generation of basic fullerenes and nanotubes

1.1. Cyclic carbon molecule and carbon clusters. We assume that the embryo of fullerenes of three-fold symmetry is a cluster having just the same symmetry. The question arises: Are there in nature similar molecules, from which it is possible to obtain such cluster? To our mind cyclopropane C_3H_6 with D_{3h} symmetry [13] could be such a molecule.

Suppose that we have removed six hydrogen atoms and added three carbon atoms instead. In doing so we obtain carbon cluster C_3C_3 with several types of carbon atoms. They are shown, together with cyclopropane C_3H_6, in Fig. 1. We have calculated their optimized structures and energy through the use of Avogadro package [14]. The carbon atoms of cyclopropane remain in the initial electronic state; they are considered, as is customary, being sp^2 hybridized atoms. The new added ones are reactive carbon atoms, which are connected with the initial carbon atoms by single or double bonds, being ionized to a different degree. One way of looking at the gradual evolution of the clusters shown is folding the clusters and fusion the structures obtained with the following growth. Consider this way.

1.2. Cluster folding. The elementary fullerene of three-fold symmetry is a triangular prism. It can be obtained as result of folding the carbon clusters shown above. Two extreme electronic structures are presented in Fig. 2. It refers to the Δn=2 series. It should be emphasized that at first the periodic system of fullerenes was formulated for the series which had begun with Δn=6. Later, in order to close the gap between the clusters and fullerenes, there added two series: Δn=2 and Δn=4 [15; 16].

1.3. Fusion of prisms. The elementary fullerenes can grow, conserving its symmetry, by the mechanism known as "fusion of fullerenes having compatible symmetry" [17]. The final configuration produced by the fusion of two prisms is shown in Fig. 3. The shape of the fullerene resembles a triangular barrel; it was named previously a mini-fullerene. In its turn this fullerene can continue the growth conserving the symmetry, through the use of the above mentioned mechanism, i.e. joining another prism (Fig. 4). The reaction is possible since the both reacting structures have three-fold symmetry and therefore they are compatible with each other.

One can consider the structure obtained both as a fullerene and as an embryo of nanotube. Really, if to continue the fusion of prisms, there appears the ultra narrow nanotube of three-fold symmetry (Fig. 5). It is

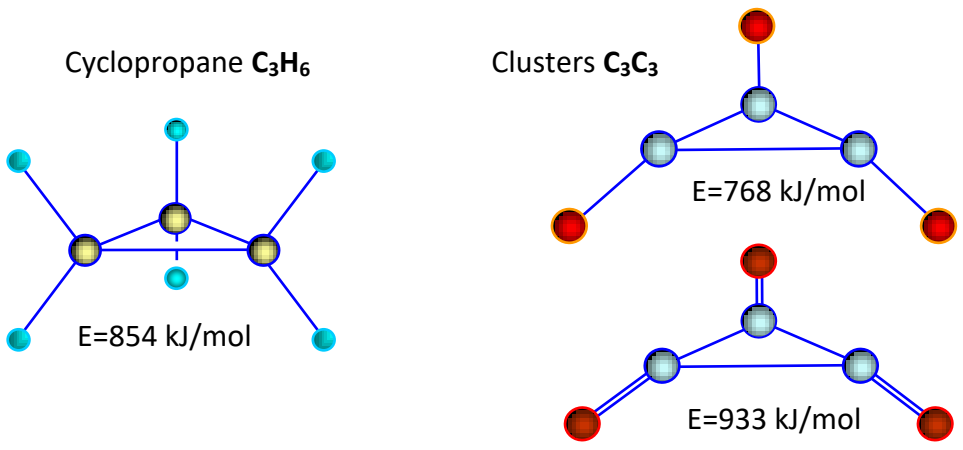


Fig. 1. *Cyclopropane and two six-atom carbon clusters of three-fold symmetry*
Рис. 1. *Циклопропан и два шестиатомных углеродных кластера симметрии третьего порядка*

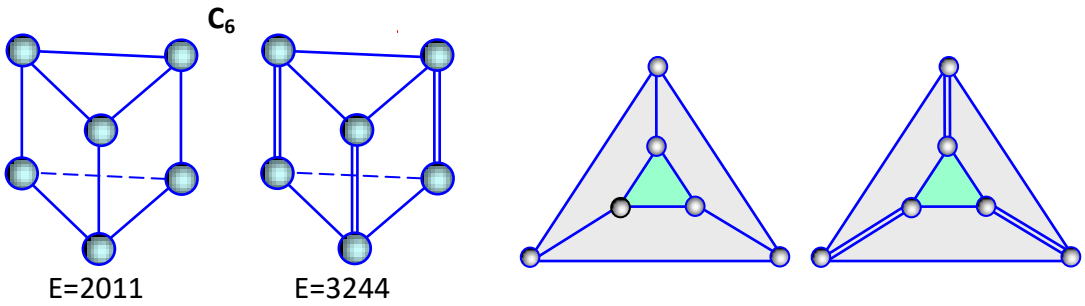


Fig. 2. *Two electronic isomers of a carbon triangular prism; energy in kJ/mol*
Рис. 2. *Два электронных изомера углеродной треугольной призмы; энергия в кДж/моль*

worth noting that at first extremely narrow nanotubes were considered only as a new type of nanotubes being of academic interest [18; 19]. Recently it has been discovered that small diameter single-walled carbon nanotubes were mimics of ion channels found in natural systems [20]. These properties make them a promising material for developing membrane separation technologies [21].

1.4. Cupolas and their fusion. There is the second way for the generation of fullerenes having the three-fold symmetry [17]. It consists in the growth of initial clusters which then transform into half-fullerenes (cupolas) conserving the three-fold symmetry (Fig. 6). From the figure it is seen that all the cupolas have one and the same base of six atoms; therefore they can combine with each other creating new fullerenes as well as nanotubes. Let us investigate this process in detail.

1.5. Fusion of cluster C_6 with cupola C_{12}. The fullerene obtained contains two triangles, three squares and six hexagons (Fig. 7). It is a tri_2-$tetra_3$-$hexa_6$ polyhedron. Its shape is a truncated triangular bipyramid having three-fold symmetry. The fullerene is an isomer of the bifurcation fullerene C_{18} shown in Fig. 4.

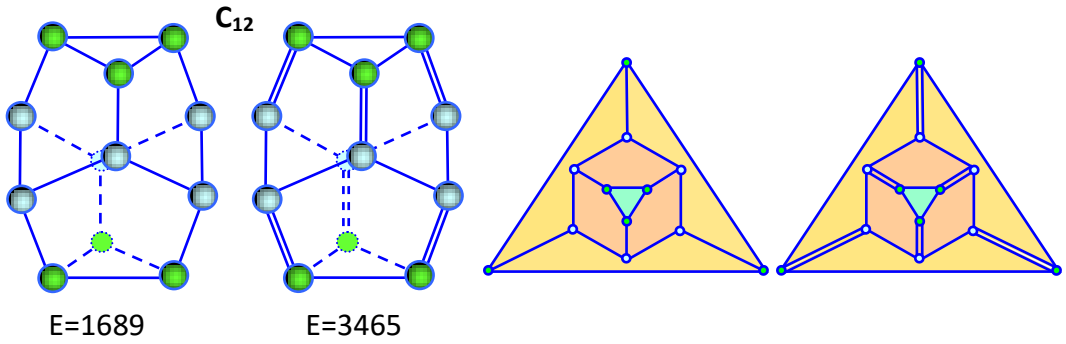


Fig. 3. *Triangle-barrel-shaped mini-fullerene C_{12} and its graphs; energy in kJ/mol*
Рис. 3. *Треугольный бочкообразный мини-фуллерен C_{12} и его графические изображения; энергия в кДж/моль*

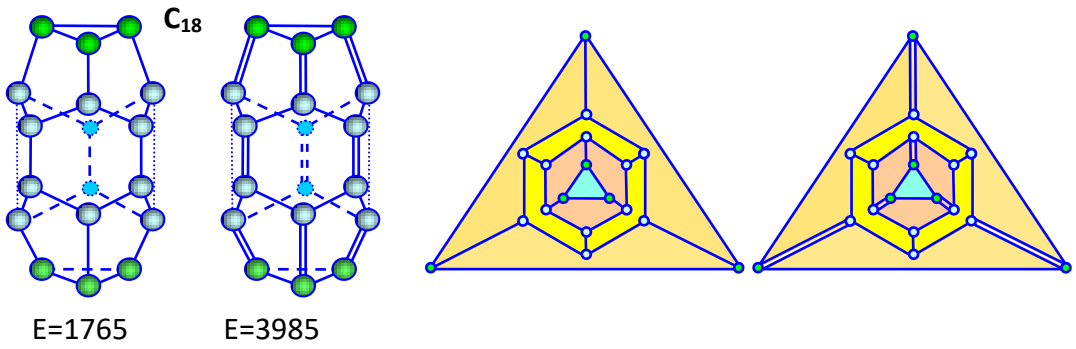


Fig. 4. *Fusion of two fullerenes C_6 and C_{12}: structure and graphs; energy in kJ/mol*
Рис. 4. *Слияние двух фуллеренов C_6 и C_{12}: структура и графические изображения; энергия в кДж/моль*

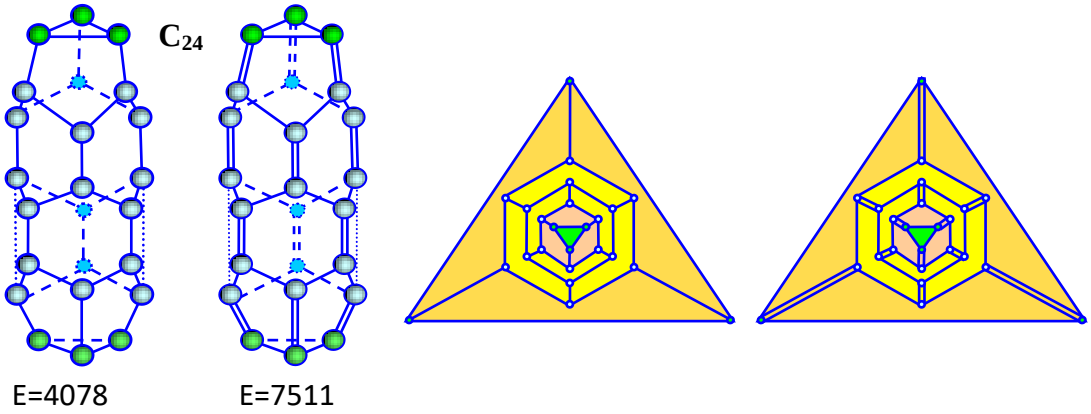


Fig. 5. *Joining two mini-fullerenes C_{16} through the use of the rotation-reflection symmetry: structure and graphs; energy in kJ/mol*
Рис. 5. *Соединение двух мини-фуллеренов C_{16} с использованием зеркально-поворотной симметрии: структура и графические изображения; энергия в кДж/моль*

1.6. Fusion of two cupolas C_{12}. There are two ways of joining the cupolas: mirror symmetry and rotation-reflection one. In the first case (Fig. 8) the lower cupola is a mirror copy of the upper one. The fullerene obtained contains two triangles, three squares and nine hexagons forming a tri_2-$tetra_3$-$hexa_9$ polyhedron. In the second case (Fig. 9) the lower cupola is a rotatory reflection of the upper one. The fullerene contains two triangles, six pentagons and six hexagons. It is a truncated dodecahedron with the energy less than the first fullerene.

1.7. Fusion of two cupolas: C_{12} and C_{18} (Fig. 10). The fullerene obtained contains two triangles, three pairs of adjacent pentagons and nine hexagons. It is a tri_2-$(penta_2)_3$-$hexa_9$ polyhedron.

1.8. Fusion of two cupolas C_{18}. The fullerene formed is shown in Fig. 11. It consists of two triangles, six pentagons and twelve hexagons, so it is a tri_2-$penta_6$-$hexa_{12}$ polyhedron. We see that the growth is ensured by adding three hexagons. The number of pentagons is the same as before and equal to six.

1.9. Fusion of two cupolas: C_{18} and C_{24} (Fig. 12). The fullerene contains two triangles, six pentagons and fifteen hexagons. It is a tri_2-$penta_6$-$hexa_{15}$ polyhedron.

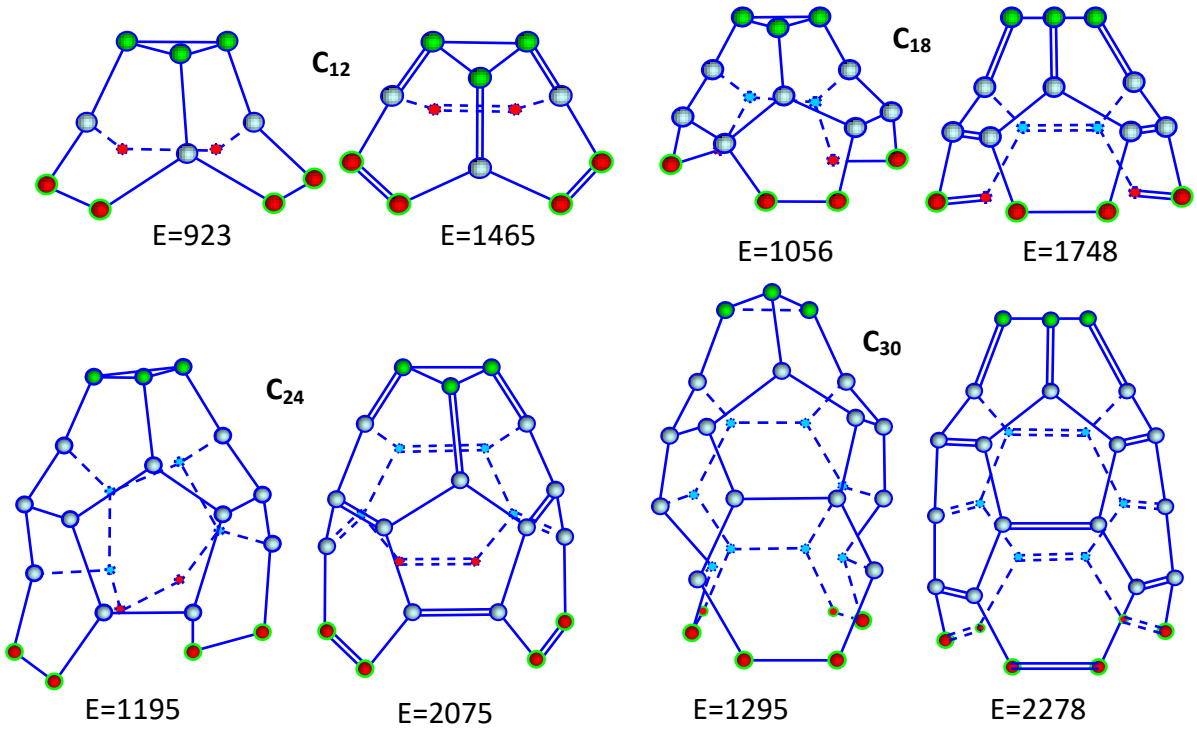


Fig. 6. *Growth of cupolas of three-fold symmetry: structure and graphs; energy in kJ/mol*
Рис. 6. *Рост куполов симметрии третьего порядка: структура и графические изображения; энергия в кДж/моль*

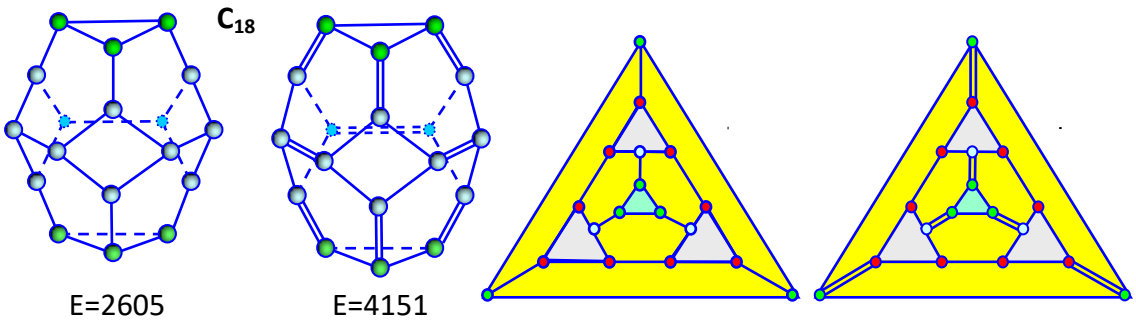


Fig. 7. *Truncated-triangular-bipyramid fullerene C_{18} and its graphs; energy in kJ/mol*
Рис. 7. *Фуллерен C_{18} в виде усеченной треугольной бипирамиды и его графические изображения; энергия в кДж/моль*

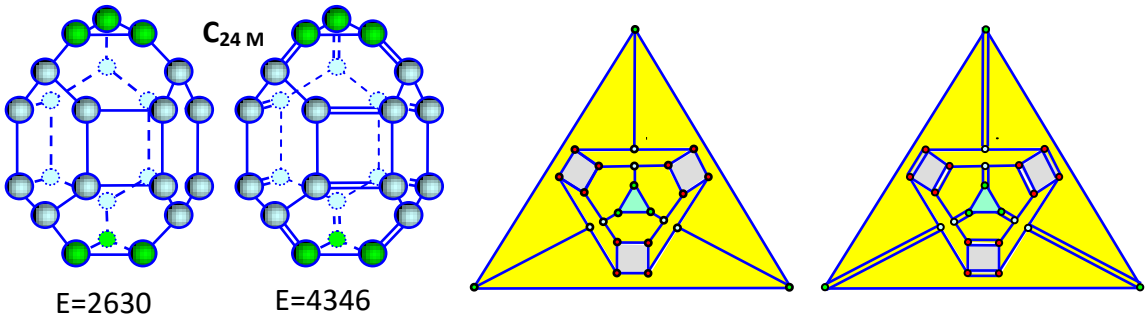


Fig. 8. *Mirror symmetry joining two half fullerenes C_{12} of three-fold symmetry: structure and graphs; energy in kJ/mol*
Рис. 8. *Зеркальная симметрия, соединяющая два половинчатых фуллерена C_{12} симметрии третьего порядка: структура и графические изображения; энергия в кДж/моль*

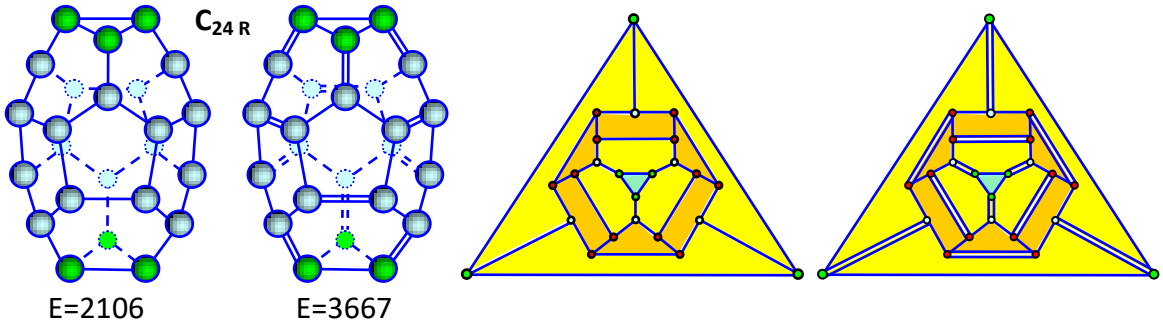


Fig. 9. *Rotation-reflection symmetry fusion of two half fullerenes C_{12} of three-fold symmetry: structure and graphs; energy in kJ/mol*
Рис. 9. *Слияние двух половинчатых фуллеренов C_{12} симметрии третьего порядка с помощью зеркально-поворотной симметрии: структура и графические изображения; энергия в кДж/моль*

1.10. Fusion of two cupolas C_{24} (Fig. 13). The polyhedron obtained contains two triangles, six pentagons and eighteen hexagons. Formally it is a tri_2-$penta_6$-$hexa_{18}$ polyhedron. However we admit that it is a nanotube. The reason for such conclusion is discussed below.

1.11. Fusion of two cupolas: C_{24} and C_{30} (Fig. 14). The polyhedron consists of two triangles, six pentagons and twenty-one hexagons. It is a tri_2-$penta_6$-$hexa_{21}$ nanotube.

1.12. Fusion of two cupolas C_{30} (Fig. 15). The polyhedron contains two triangles, six pentagons and twenty-four hexagons. It is a tri_2-$penta_6$-$hexa_{24}$ nanotube.

1.13. A fullerene or a nanotube? Let's analyze Fig. 7–15. We have obtained all the basic fullerenes having three-fold T-symmetry predicted earlier [2; 3]. However the question arises: They are fullerenes or nanotubes? As indicated above, one can consider the structure C_{18} shown in Fig. 4 as a fullerene and as an embryo of nanotube. This is a bifurcation structure. The situation is not uncommon in nature. For example, in radiation solid state physics it is well known that one and the same small vacancy cluster (embryo) during its growth can transform either into a void (volume configuration) or into a dislocation loop (plane configuration)

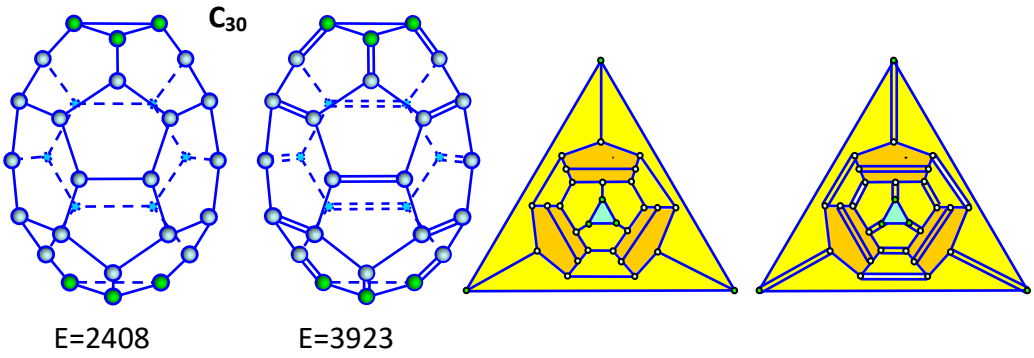


Fig. 10. *Mirror symmetry fusion of two cupolas (half-fullerenes) C_{12} and C_{18} having three-fold symmetry: structure and graphs; energy in kJ/mol*

Рис. 10. *Слияние двух куполов (полуфуллеренов) C_{12} и C_{18} с симметрией третьего порядка с помощью зеркальной симметрии: структура и графические изображения; энергия в кДж/моль*

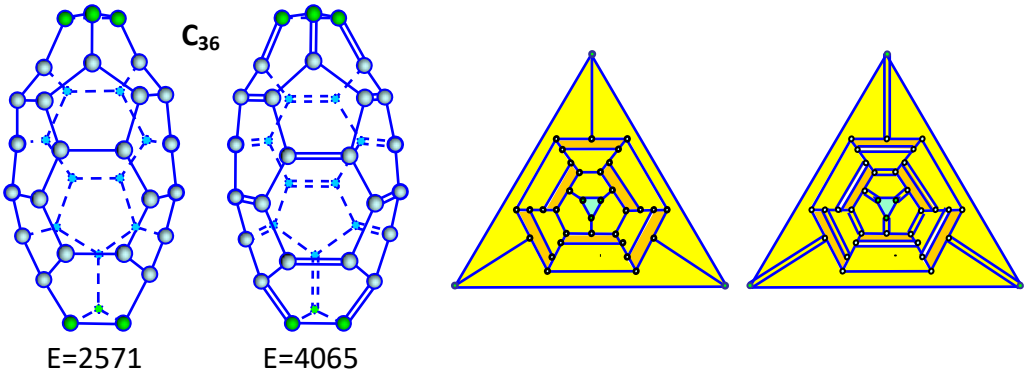


Fig. 11. *Rotation-reflection symmetry fusion of two cupolas (half-fullerenes) C_{18} having three-fold symmetry: structure and graphs; energy in kJ/mol*

Рис. 11. *Слияние двух куполов (полуфуллеренов) C_{18} с симметрией третьего порядка с помощью зеркально-поворотной симметрии: структура и графические изображения; энергия в кДж/моль*

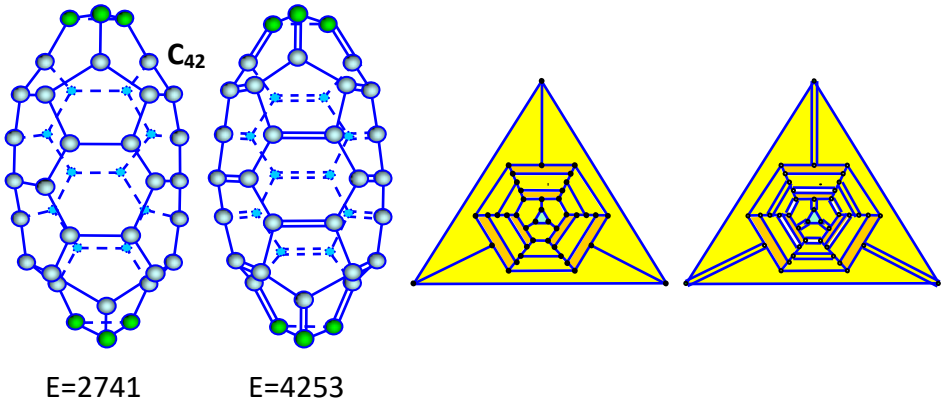


Fig. 12. *Mirror symmetry fusion of two cupolas (half-fullerenes) C_{18} and C_{24} having three-fold symmetry; structure and graphs; energy in kJ/mol*

Рис. 12. *Слияние двух куполов (полуфуллеренов) C_{18} и C_{24} с симметрией третьего порядка с помощью зеркальной симметрии: структура и графические изображения; энергия в кДж/моль*

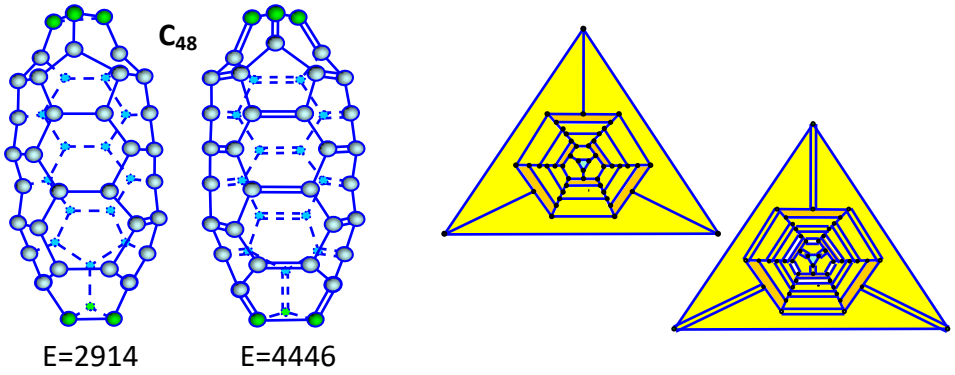


Fig. 13. *Rotation-reflection symmetry fusion of two cupolas (half-fullerenes) C_{24} having three-fold symmetry: structure and graphs; energy in kJ/mol*
Рис. 13. *Слияние двух куполов (полуфуллеренов) C_{24} с симметрией третьего порядка с помощью зеркально-поворотной симметрии: структура и графические изображения; энергия в кДж/моль*

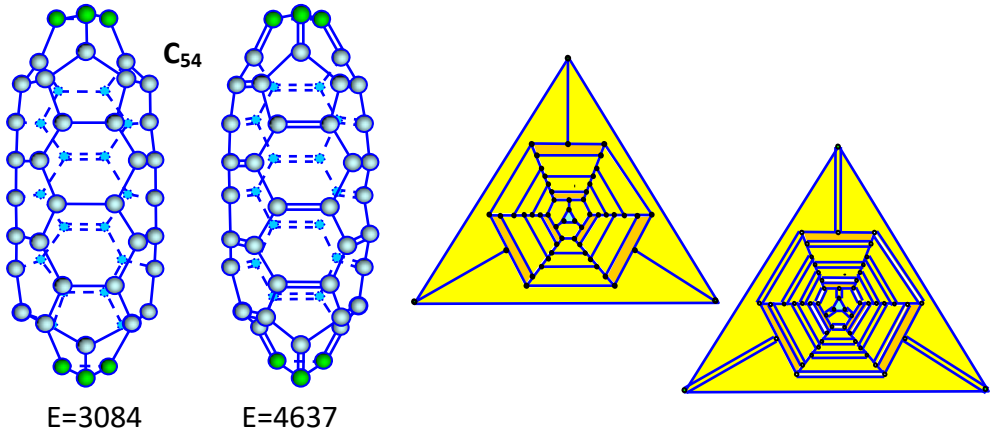


Fig. 14. *Mirror symmetry fusion of two cupolas (half-fullerenes) C_{24} and C_{32} having three-fold symmetry: structure and graphs; energy in kJ/mol*
Рис. 14. *Слияние двух куполов (полуфуллеренов) C_{24} и C_{32} с симметрией третьего порядка с помощью зеркальной симметрии: структура и графические изображения; энергия в кДж/моль*

[22]. In our case this brings up the question: Where is the boundary between fullerenes and nanotubes? An intuitive idea says that a fullerene is a spheroid, whereas a nanotube with open ends is a cylinder and a nanotube with closed ends is a cylinder with two hemispheres. However we need an exact quantitative criterion. Under these circumstances we should look at the electron theory for clues.

Buckminsterfullerene C_{60}–I_h is a truncated icosahedron [23]. This fullerene is considered as an ideal one, having only equal isolated pentagons and forming a perfect sphere; each hexagon has three single and three double bonds. The measured bond lengths are r_{hh} = 1.38 Å and r_{hp} = 1.4654 Å. The larger bonds are singular, the lesser bonds are double ones. In contrast to this, in an ideal nanotube with open ends there are only hexagons with four single and two double bonds. Each spheroid can be divided into three parts; two hemispheres with hexagons having three single and three double bonds and one cylinder with hexagons of four single and two double bonds. If the height of cylinder is less than the height of two hemispheres, we assume that it is a fullerene. On the contrary we have a nanotube. In its turn the cylinder height is defined by the number of adjacent hexagons with four single and two double bonds. To form a cylinder one needs to have along its height at least one such hexagon which is not connected with pentagons. Referring to the graphs shown, we admit that the nanotubes begin with the structure C_{48}.

It is worth noting that all of them have one and the same number of pentagons, namely six, being equal to a double degree of symmetry.

2. Alive and dead fullerenes

The tri_2-$penta_6$-$hexa_3$ polyhedron shown in Fig. 4 can be thought over as a primary fullerene having the possibility to use for growing the mechanism known as “embedding carbon dimers.” It was suggested by M. Endo and the Nobel Prize winner H.W. Kroto in 1992 [24]. According to it, a carbon dimer embeds into a hexagon of an initial fullerene. This leads to stretching and breaking the covalent bonds which are normal to the dimer and to creating new bonds with the dimer (Fig. 16, at the left). As a result, there arises a new atomic configuration and there is mass increase of two carbon atoms.

However, it is necessary to take into account the nearest circumference of a hexagon. From the figures, of special

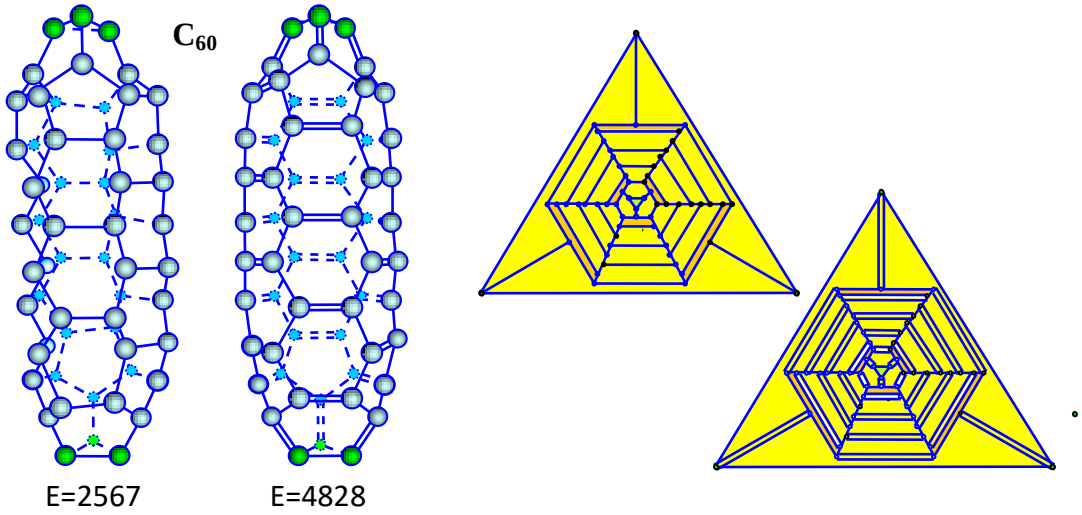


Fig. 15. *Rotation-reflection symmetry fusion of two cupolas (half-fullerenes) C_{40} having four-fold symmetry: structure and graphs; energy in kJ/mol*
Рис. 15. *Слияние двух куполов (полуфуллеренов) C_{40} с симметрией четвертого порядка с помощью зеркально-поворотной симметрии: структура и графические изображения; энергия в кДж/моль*

note are the graphs, it follows that there are two ways of joining the cupolas: mirror symmetry fusion and rotation-reflection one. In the first case we notice on the fullerene equator the three mutually penetrating cells consisting of a central hexagon with two pairs of adjacent pentagons (fullerene C_{30}, Figs. 10, 16) or the three separated cells of a hexagon with two neighboring pentagons above and below the equator (fullerene C_{42}, Figs. 12, 16). In the second case there are the six mutually penetrating cells of a central hexagon with radially sited three pentagons and three hexagons (fullerene C_{36}, Figs. 11, 16) or the six separated cells of a central hexagon with radially sited one pentagons and five hexagons such ones. The fullerenes of the first subgroup, C_{30} and C_{42}, can grow further by using the Endo-Kroto's mechanism and producing new fullerenes; they are alive. Therefore, together with the above mentioned fullerenes C_{18} and C_{24}, we have four basic perfect fullerenes of three-fold symmetry, which are alive, namely:

– tri_2-$penta_6$-$hexa_3$ polyhedron C_{18}
– tri_2-$tetra_3$-$hexa_9$ polyhedron C_{24}
– tri_2-$(penta_2)_3$-$hexa_9$ polyhedron C_{30}
– tri_2-$penta_6$-$hexa_{15}$ polyhedron C_{42}

The fullerenes of the second subgroup, C_{36} and C_{48}, are the dead-end ones; the first has no diametrically opposite pentagons, the second has only one adjacent pentagon. Truncated triangular bipyramid C_{18} or tri_2-$tetra_3$-$hexa_6$ polyhedron (Fig. 7) refers also to the subgroup of dead-end fullerenes.

3. Intermediate fullerenes

3.1. Growth of fullerene C_{18}. The fullerenes designed through the use of the Endo-Kroto's mechanism are illustrated in Fig. 17. From the figures, of special note are the graphs, we notice that only the initial C_{18} and final C_{24} fullerenes have ordinary three-fold symmetry. However, the three-fold symmetry of these fullerenes is different, namely C_{18}–D_{3h} and C_{24}–D_3. They are perfect fullerenes, but only fullerene C_{18}–D_{3h} is basic. Moreover fullerene C_{24}–D_3 is a dead-end one; it follows from its graph. The intermediate fullerenes C_{20} and C_{22} have topological three-fold symmetry.

3.2. Growth of fullerene C_{24}. The fullerenes designed through the use of the Endo-Kroto mechanism are illustrated in Fig. 18. Taking as a base the structure and graph of fullerene C_{24} (Fig. 8), we have obtained the fullerenes

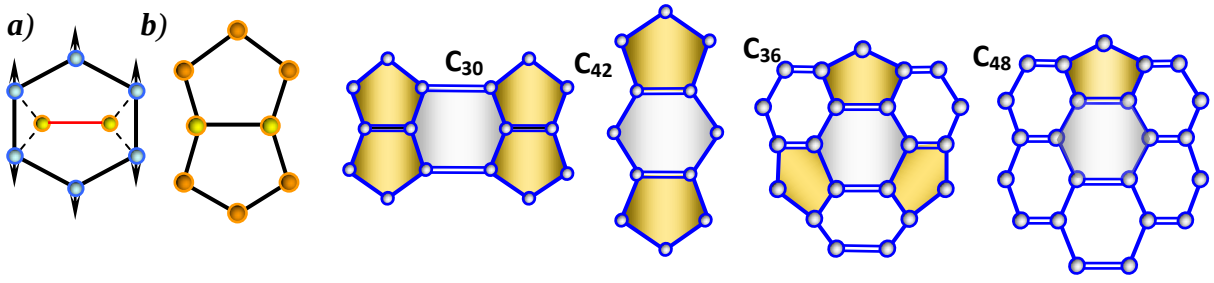


Fig. 16. *Dimer embedding into a hexagon (**a**) transforms it into two adjacent pentagons (**b**). Nearest circumference of a hexagon in different fullerenes*
Рис. 16. *Внедрение димера в шестиугольник (**a**), трансформирующее его в два прилегающих пятиугольника (**b**). Ближайшая окружность шестиугольника в различных фуллеренах*

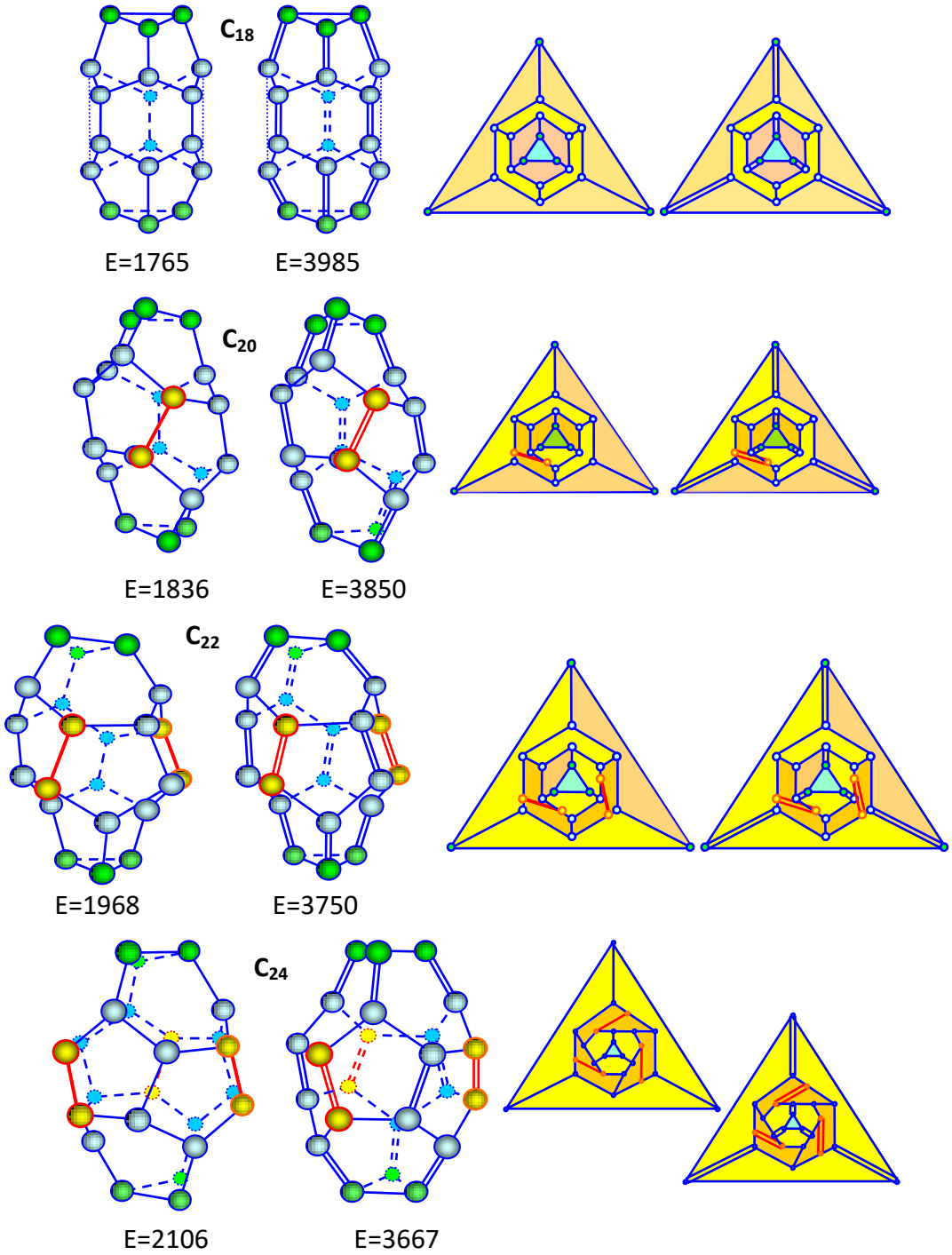


Fig. 17. *Fullerenes C_{20}, C_{22}, C_{24} obtained by one-after-another embedding a carbon dimer (yellow atoms) into fullerene C_{18}: structure and graphs; energy in kJ/mol*

Рис. 17. *Фуллерены C_{20}, C_{22}, C_{24}, полученные путем последовательного внедрения углеродного димера (желтые атомы) в фуллерен C_{18}: структура и графические изображения; энергия в кДж/моль*

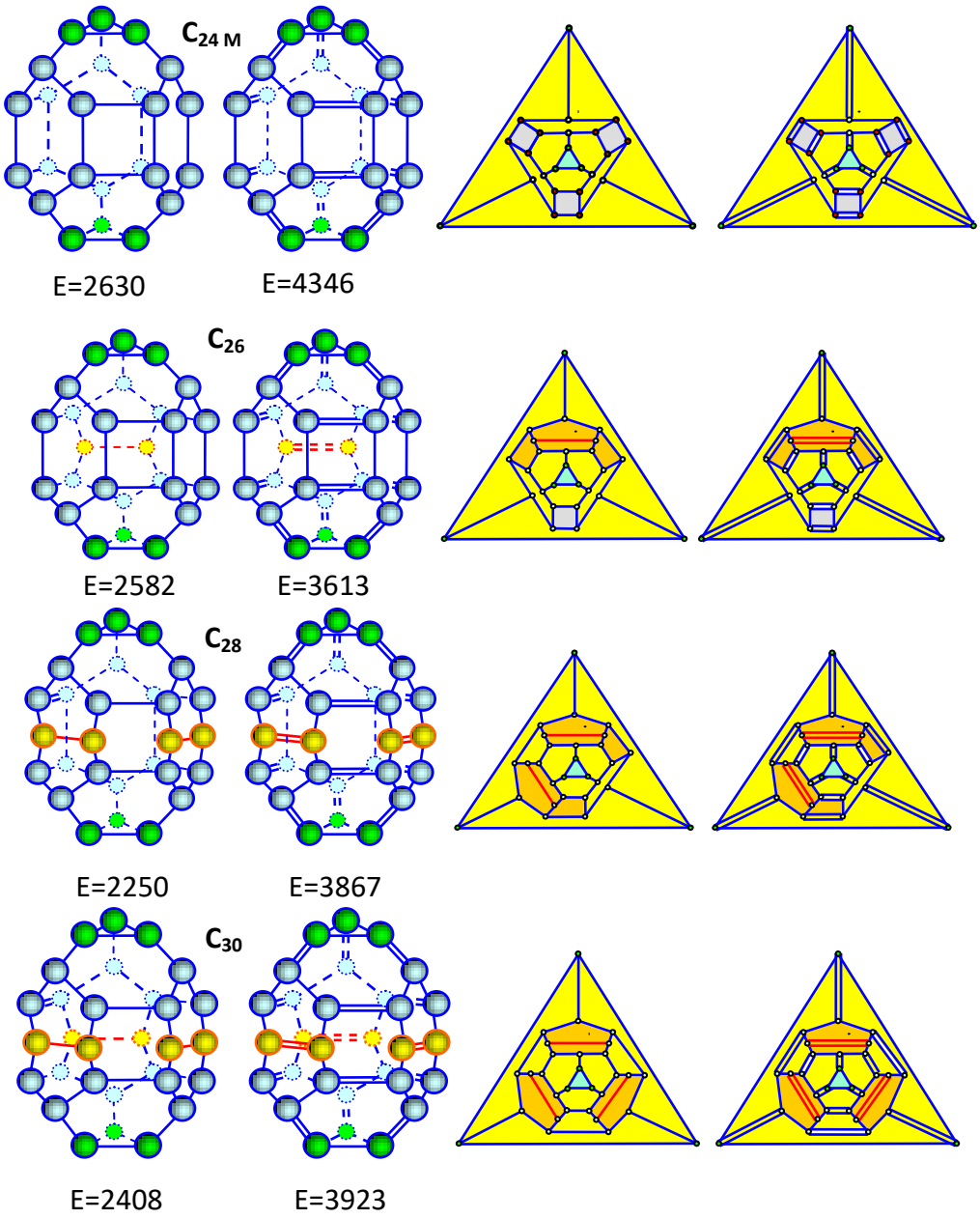


Fig. 18. *Fullerenes C_{26}, C_{28} and C_{30} as a result of one-after-another embedding a carbon dimer into fullerene C_{24}: structure and graphs; energy in kJ/mol*

Рис. 18. *Фуллерены C_{26}, C_{28}, C_{30} как результат последовательного внедрения углеродного димера в фуллерен C_{24}: структура и графические изображения; энергия в кДж/моль*

from C_{24} to C_{30}. From the figures it follows that only the initial and final fullerenes, C_{24} and C_{30}, have ordinary three-fold symmetry. They are basic perfect fullerenes. The intermediate fullerenes C_{26} and C_{28} have topological three-fold symmetry. To gain a better understanding of the mechanism of dimer embedding, its main features are given in the form of schematic representation (Fig. 19).

We see that the first embedding, which transforms fullerene C_{24} into fullerene C_{26}, influences deeply only on one of hexagons and two its square neighbours. This hexagon transforms into two adjacent pentagons and its square neighbors become pentagons; the fullerene C_{26} losing three-fold symmetry. It becomes an imperfect fullerene with ordinary D_1 symmetry, however conserving topological three-fold symmetry. At that in the fullerene, there appears a cell which contains four pentagons. The second imbedding transforms fullerene C_{26} into fullerene C_{28}. The third embedding leads to transition from fullerene C_{28} to fullerene C_{30}. It transforms one more hexagon and two its neighbors into two adjacent pentagons with abut hexagons of another local orientation. The embedding restores D_{3h} symmetry. The perfect fullerene C_{30} obtained is a tri_2-$penta_6$-$hexa_9$ polyhedron where every two adjacent pentagons have the form of a bow tie. Its structure coincides with that of the fullerene formed by the fusion of two cupolas C_{12} and C_{18} (Fig. 10).

3.3. Growth of fullerene C_{30}. The growth can continue producing imperfect fullerenes C_{32}, C_{34} and perfect fullerene C_{36} (Fig. 20). To gain a better understanding of the process, its main features are given in the form of schematic representation (Fig. 21).

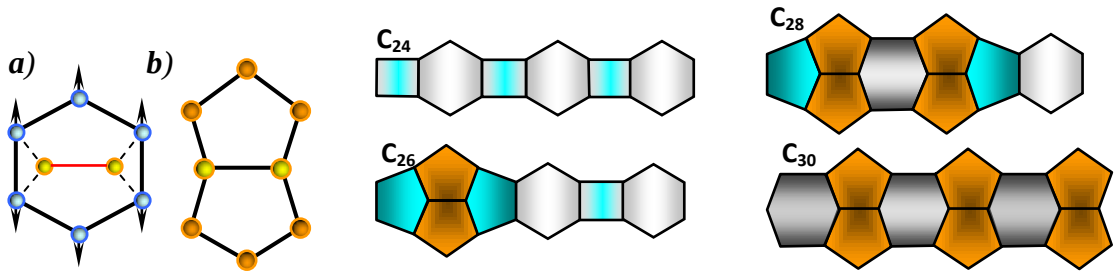


Fig. 19. *Scheme of the main structural changes during the growth of fullerene C_{24}.*
*Dimer embedding into a hexagon (**a**) transforms it into two adjacent pentagons (**b**)*
Рис. 19. *Схема основных структурных изменений во время роста фуллерена C_{24}.*
*Внедрение димера в шестиугольник (**a**), трансформирующее его в два прилегающих пятиугольника (**b**)*

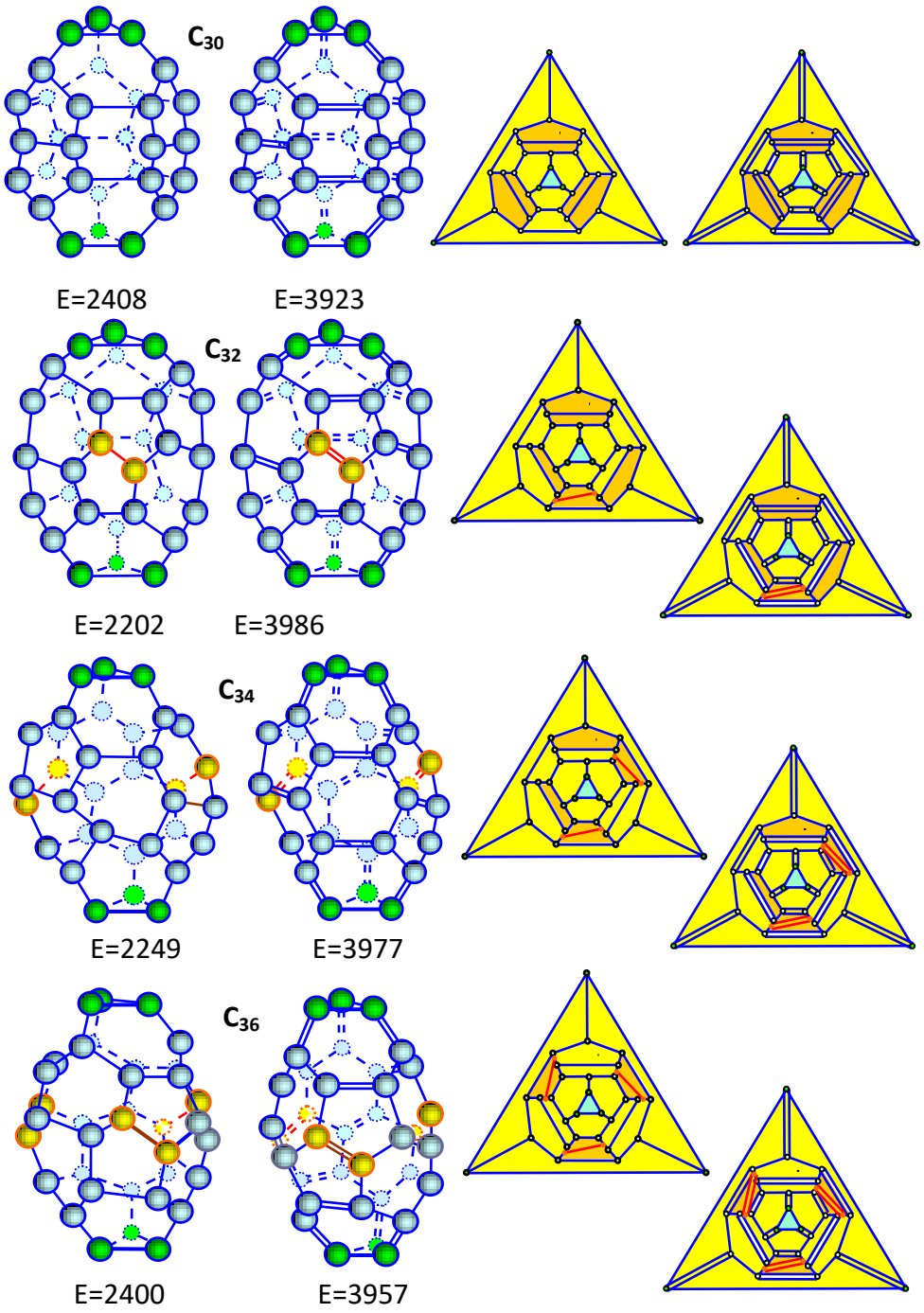


Fig. 20. *Fullerenes C_{32}, C_{34} and C_{36} as a result of embedding one after another carbon dimer into fullerene C_{30}: structure and graphs; energy in kJ/mol*
Рис. 20. *Фуллерены C_{32}, C_{34}, C_{36} как результат последовательного внедрения углеродного димера в фуллерен C_{30}:*

структура и графические изображения; энергия в кДж/моль

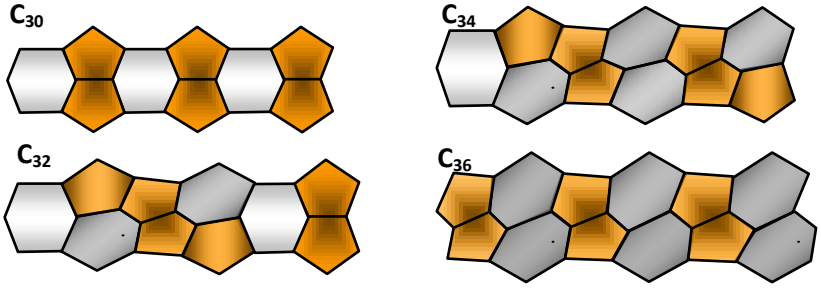
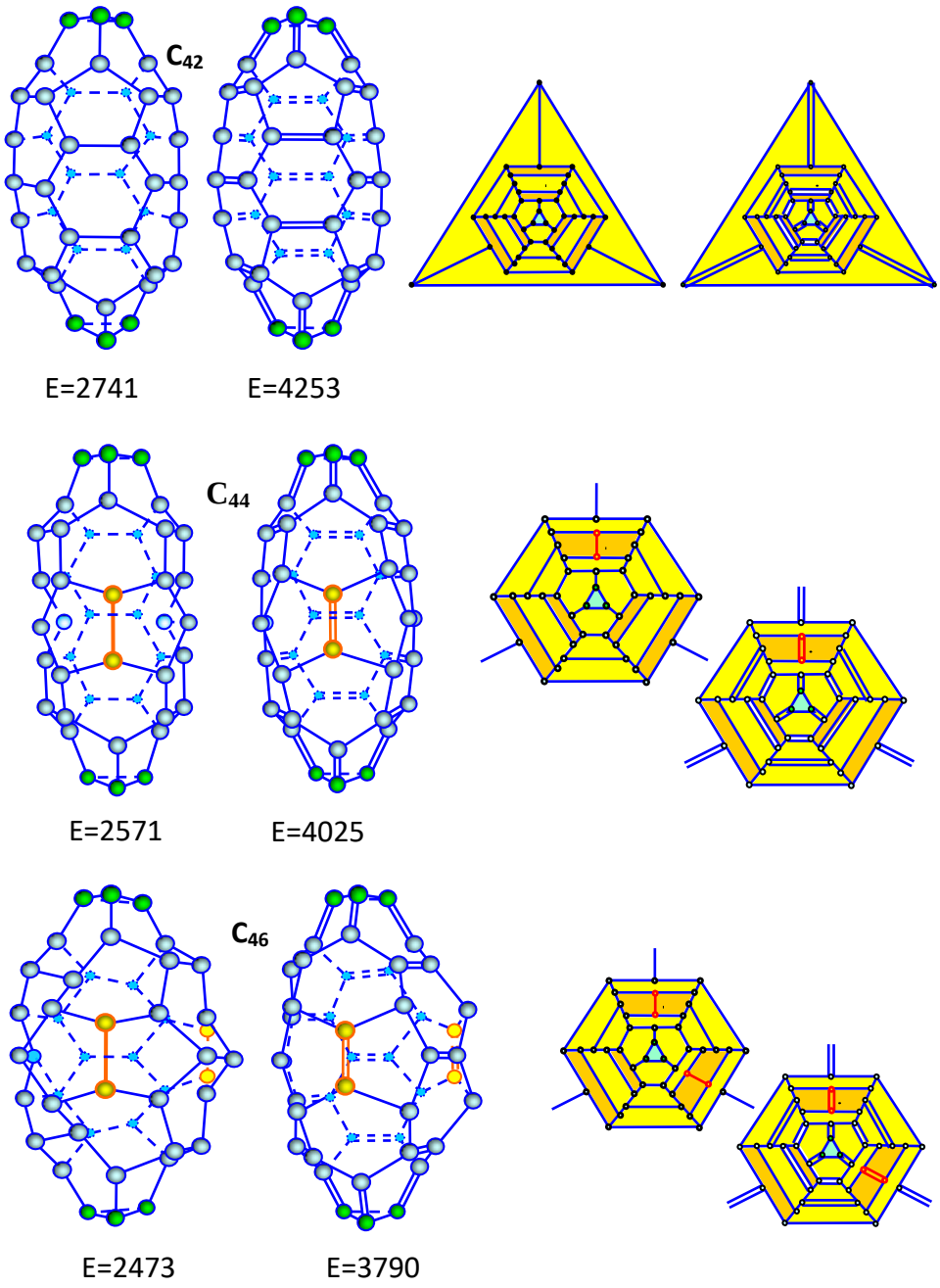


Fig. 21. *Scheme of the main structural changes during the growth of fullerene C_{30}*
Рис. 21. *Схема основных структурных изменений во время роста фуллерена C_{30}*



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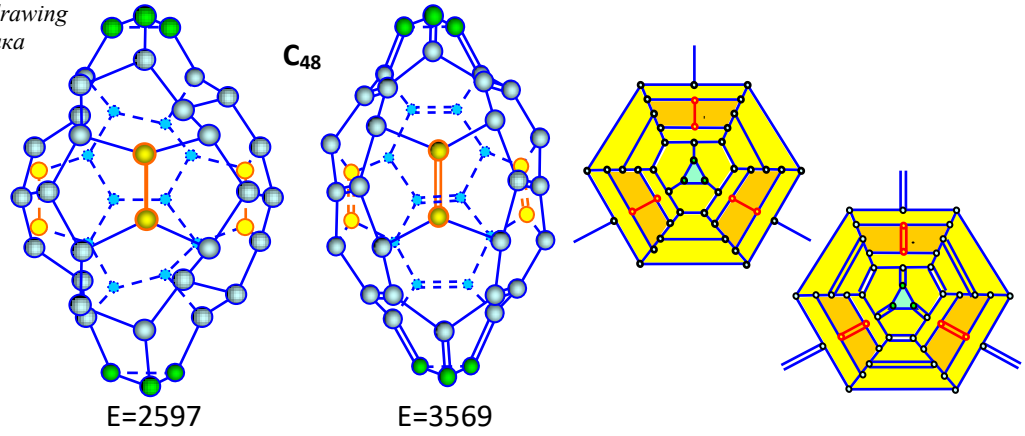

Fig. 22. *Fullerenes C_{44}, C_{46} and C_{48} as a result of embedding one after another carbon dimer into fullerene C_{42}: structure and graphs; energy in kJ/mol*
Рис. 22. *Фуллерены C_{44}, C_{46}, C_{48} как результат последовательного внедрения углеродного димера в фуллерен C_{42}: структура и графические изображения; энергия в кДж/моль*

We see that fullerene C_{30} can grow by embedding the dimers only at an angle to its main axis of symmetry; it follows from Fig. 20 and 21. The phenomenon is connected with the fact that embedding can be realized only normal to a direction along which a hexagon has two neighboring mutually antithetic pentagons. During the further growth one obtains fullerenes C_{32}, C_{34} and C_{36}. The intermediate fullerenes are imperfect (C_{32} and C_{34}) having topological three-fold symmetry, but fullerene C_{36}–D_3 with three imbedded dimers is perfect. It should be emphasized that in this case the number of imbedded dimers is equal to the degree of symmetry. However it is a dead-end fullerene; as can be seen from its graph.

3.4. Growth of fullerene C_{42}. The fullerenes designed through the use of the Endo-Kroto mechanism are illustrated in Fig. 22. Taking as a base the structure and graph of fullerene C_{42} (Fig. 12), we have obtained fullerenes C_{44}, C_{46} and C_{48}. From Fig. 22 it follows that only the initial and final fullerenes, C_{42} and C_{48}, have ordinary three-fold symmetry. They are perfect fullerenes. The intermediate fullerenes C_{44} and C_{46} have topological three-fold symmetry.

SUMMARY AND DISCUSSION

The results obtained are summarized and classified in Tables 1–4.

We have studied possible ways of generation and growing the fullerenes having T-three-fold symmetry. Beginning with cyclopropane C_3H_6 and clusters C_3-C_3, we obtained elementary fullerenes C_6 and mini-fullerenes C_{12}, which produce the fullerenes from C_{18} to C_{48}, perfect and imperfect, as well as nanotubes. For the purpose of ordering, the results are divided into four groups. From the tables follows that the energy of clusters, cupolas and nanotubes (produced by folding the clusters and further fusion) enlarge monotonically with increasing the number of carbon atoms. For perfect and intermediate imperfect fullerenes designed by the Endo-Kroto mechanism, there is some deviation induced by fullerene C_{26}, but the difference is small.

The perfect fullerenes C_{18}, C_{24}, C_{30}, C_{36}, C_{42} and C_{48} have the ordinary three-fold symmetry; they were designed by fusion of cupolas and can be named *basic fullerenes*. In addition to the basic fullerenes, there are also so called *intermediate fullerenes* which fill up the gaps between the basic ones. In general, the intermediate ones have no three-fold symmetry. Their imperfection is connected with extra ‘interstitial’ carbon dimers, the dimers playing the role of defects. One can define the imperfect fullerenes with defects as the fullerenes having topological three-fold symmetry.

Among the perfect fullerenes there is fullerene C_{24R} with a minimal energy; it is obtained by rotation-reflection symmetry fusion of two half fullerenes C_{12} of three-fold symmetry. Its structure has an equatorial belt composed of adjacent pentagons of mutually antiparallel directions. It is interesting to note that the same effect takes place for the fullerene group of four-fold symmetry; fullerene C_{32R} [10] In spite of their different symmetry these fullerenes have the resembling equatorial belts. Moreover they belong to one and the same series of the periodic system of fullerenes

Table 1. *Energy of clusters and cupolas in kJ/mol*
Таблица 1. *Энергия кластеров и куполов, кДж/моль*

	C_3H_6	C_3C_3	C_{12}	C_{18}	C_{24}	C_{36}
E_{max}		933	1465	1748	2075	2278
E_{min}	854	768	923	1056	1195	1295
ΔE		165	542	692	880	983

Table 2. *Energy of nanotubes (folding the clusters and further fusion) in kJ/mol*
Таблица 2. *Энергия нанотрубок (уплотнение кластеров и дальнейшее слияние), кДж/моль*

	C_3C_3	C_{12}	C_{18}	C_{24}	C_{36}
E_{max}	933	1465	1748	2075	2278
E_{min}	768	923	1056	1195	1295
ΔE	583	574	1784	44	1707

Table 3. *Energy of perfect and intermediate imperfect fullerenes designed by the Endo-Kroto mechanism in kJ/mol*
Таблица 3. *Энергия совершенных и промежуточных несовершенных фуллеренов, созданных с помощью механизма Эндо-Крото, кДж/моль*

	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30}	C_{32}	C_{34}	C_{36}	C_{44}	C_{46}	C_{48}
E_{max}	3850	3750	3667	**3613**	3867	3923	3986	3977	3957	4025	3790	3569
E_{min}	1836	1968	2106	2582	2250	2408	2202	2249	2400	2571	2573	2597
ΔE	2014	1782	1561	1031	1617	1535	1784	1728	1557	1454	1217	972

Table 4. *Energy of basic perfect fullerenes and nanotubes (fusion of cupolas) in kJ/mol*
Таблица 4. *Энергия основных совершенных фуллеренов и нанотрубок (слияние куполов), кДж/моль*

	C_{18}	$C_{24\,M}$	$C_{24\,R}$	C_{30}	C_{36}	C_{42}	C_{48}	C_{54}	C_{60}
E_{max}	4151	4346	**3667**	3923	4065	4253	4446	4637	4828
E_{min}	2605	2630	**2106**	2408	2571	2741	2914	3084	2567
ΔE	1546	1716	1326	1515	1494	1512	1532	1553	2261

(Δ*n*=8) and can't grow (so called dead fullerenes). Suppose that this effect is valid for the fullerene groups of other symmetry, five- and six-fold. Preliminary studies have shown that for fullerene C_{40R} of five-fold symmetry it really takes place. Then we are able to do some prediction, namely, the dead fullerenes C_{24R}, C_{32R}, C_{40R} and C_{48R} have the most chance to be found experimentally than their isomers, since they can't grow.

In conclusion it is pertinent to add also the words which were said in 2004 by one of the authors of this study [25]. "Computer simulations have in general descriptive character and in this respect they are akin to an ordinary experiment. There comes a point when the accumulated computational data must be redacting into a theory. If it is managed, the following investigations will be more effective". In the case of question, we have used as a basis for study the periodic system of fullerenes formulated in 2017 by two of the authors of this study. As a consequence, for the first time in the world it has become possible not only to describe the properties of fullerenes, but to classify them and even more, to make predictions.

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Образование и рост фуллеренов и нанотрубок, имеющих Т-симметрию третьего порядка

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Поступила в редакцию 14.07.2021 *Принята к публикации 14.06.2022*

Аннотация: В соответствии с периодической системой фуллеренов все фуллерены можно классифицировать по группам, имеющим разную симметрию. Есть основания полагать, что фуллерены с одним и тем же типом симметрии имеют схожие свойства. До возникновения периодической системы в 2017 году фуллерены для изучения выбирались случайным образом, что вместо упорядочения результатов только увеличивало энтропию информации. Мы изучили возможные способы создания и выращивания фуллеренов, относящихся к группе фуллеренов, имеющих Т-симметрию третьего порядка. Начиная с кластеров C_6, образующих циклопропан C_3H_6, мы получили элементарные фуллерены C_6, а также мини-фуллерены C_{12}, которые, в свою очередь, образовали фуллерены от C_{18} до C_{48}, идеальные и неидеальные, а также нанотрубки. Основные идеальные (совершенные) фуллерены C_{18}, C_{24}, C_{30}, C_{36}, C_{42} и C_{48} имели обычную симметрию третьего порядка, промежуточные фуллерены не имели такой симметрии. Их несовершенность связана с дополнительными «внедренными», или углеродными, димерами, играющими роль дефектов. Можно описать неидеальные (несовершенные) фуллерены с дефектами как фуллерены, имеющие топологическую симметрию третьего порядка. Используя редактор Авогадро, мы рассчитали их форму и энергии и обсудили возможные причины их зависимости от размера и формы фуллерена. Установлено, что фуллерены можно разделить на две группы: живые и способные расти и мертвые, неактивные. Учитывая полученные ранее результаты, можно предположить, что мертвые фуллерены C_{24R}, C_{32R}, C_{40R} и C_{48R} с симметриями третьего, четвертого, пятого и шестого порядка имеют больше шансов быть обнаруженными экспериментально по сравнению с их изомерами.

Ключевые слова: углерод; внедрение; энергия; фуллерен; реакция синтеза; графическое представление; рост; нанотрубка; периодическая система; одинарная и двойная связь; топологическая симметрия.

Благодарности: Статья подготовлена по материалам докладов участников X Международной школы «Физическое материаловедение» (ШФМ-2021), Тольятти, 13–17 сентября 2021 года.

Для цитирования: Мелькер А.И., Крупина М.А., Матвиенко А.Н. Образование и рост фуллеренов и нанотрубок, имеющих Т-симметрию третьего порядка // Frontier Materials & Technologies. 2022. № 2. С. 37–53. DOI: 10.18323/2782-4039-2022-2-37-53.