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FUSION REACTIONS OF CUPOLA HALF FULLERENES

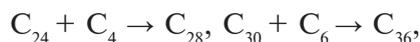
Reactions of cupola half fullerenes C_{10} , C_{12} , C_{16} , C_{20} and C_{24} with each other are considered on the basis of Arrhenius's postulate. It means that at first there forms an intermediate compound and only afterwards a usual chemical reaction is going on. We supposed that during the reactions new covalent bonds are formed and some old covalent bonds between the reacting atoms are destroyed. The final structure of a fullerene is obtained through the use of geometric modeling. As applied to fullerenes, geometric modeling supposes that a forming fullerene tends to take the appearance of a perfect spheroid with equal covalent bonds. The graphs describing the process are constructed.

CUPOLA HALF FULLERENE, FUSION REACTION, GRAPH, MODELING.

1. Introduction

Up to now the fullerene-formation mechanism is a controversial point. Research suggests that fullerene assemblage originates of individual atoms and C_2 dimers, and, probably, of very small clusters. In Ref. [1, 2], we have exhaustively investigated a dimer mechanism of fullerene growing. 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 both cases there arises a new atomic configuration and there is a mass increase of two carbon atoms. However, the above-stated mechanisms of fullerene growth are not unique. Fullerenes can be imagined to grow by reacting with each other, similar to a bubble growth in the soap solution.

This possibility was demonstrated by the example of such reactions as



and



through the use of a new molecular dynamics that takes into consideration both atomic and electronic degrees of freedom simultaneously, especially the excited electronic states created by electronic transitions [4 – 7]. Fullerenes and nanotubes are formed at high temperatures and

the new molecular dynamics, termed ‘charged-bond’ molecular dynamics, accounts for this factor properly. At first this molecular dynamics was developed as a rather sophisticated design, but later it obtained a strict theoretical basis [8].

Any molecular dynamics needs input data. For mini-fullerenes (up to C_{20}) the number of possible configurations is not very large, but as one passes to midi-fullerenes ($C_{20} - C_{60}$) one obtains a monstrous size of isomers. It is clear that there is no big sense in studying all of them, so it is desirable to restrict their number to the most stable. In this respect, it makes sense to use geometric modeling as a first step of a computer simulation and further theoretical analysis [9]. We suppose that the geometric modeling will allow us to envision a possible way of growing carbon clusters from the very beginning and thereby to decrease the number of configurations being worthy of further study.

In this contribution, we treat the growth of fullerenes as a series of joining reactions of cupola half fullerenes C_{10} , C_{12} , C_{16} , C_{20} , and C_{24} [5] through the use of the geometrical modeling.

2. Reaction between two base-truncated triangular pyramids

The atomic configurations corresponding to reaction



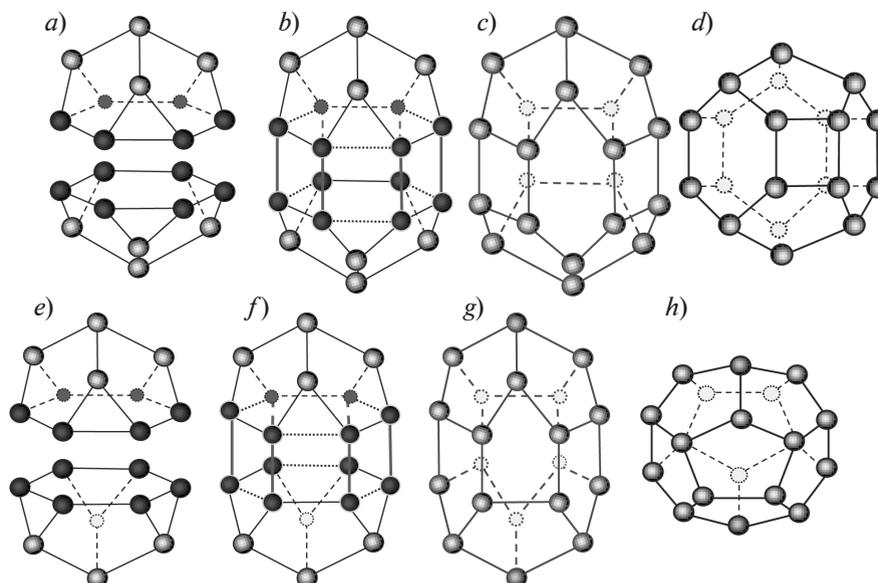


Fig. 1. Joining of two half fullerenes C_{10} with the mirror symmetry ($a - d$) and the rotation-reflection symmetry ($e - h$):

(a, e) Separate carbon cupolas C_{10} ; (b, f) Intermediate compound; (c, g) Distorted polyhedron formed; (d) (Tetra-hexa)₃-penta₆ polyhedron C_{20} ; (h) Dodecahedron C_{20} after relaxation; Black and light-grey balls are reacting and neutral atoms, respectively; thin black solid and dashed lines are covalent bonds; light-grey dashed lines are old covalent bonds to be destroyed; heavy-black solid lines are new covalent bonds

between two base-truncated triangular pyramids C_{10} are presented in Fig. 1. At first two molecules C_{10} are moving towards each other (Fig. 1, a). Then the atoms, marked in black, interact with each other producing a compound (Fig. 1, b). New covalent bonds (heavy-black solid lines) have formed in this process, whereas the old covalent bonds between the reacting atoms (light-grey dashed lines) have splitted. As a result, a distorted polyhedron has formed (Fig. 1, c), then it relaxes into a perfect polyhedron (Fig. 1, d). The surface of its atomic configuration consists of three squares, three hexagons and six pentagons so it has been termed a (tetra-hexa)₃-penta₆ polyhedron

[1]. This structure together with its consistent electronic one was obtained in Ref. [1] on a basis of a new mathematic concept of fullerenes. According to this concept, a fullerene has any shape composed of atoms, each atom having three nearest neighbors, which can be inscribed into a spherical, ellipsoidal, or similar surface.

We have examined the case when the lower cupola is a mirror copy of the upper one. However, there is another case when the lower cupola is a rotary reflection of the upper one (Fig. 1, $e - h$). Here the reacting atoms and the broken covalent bonds are the same (Fig. 1, a, b, e, f), but due to changing the sym-

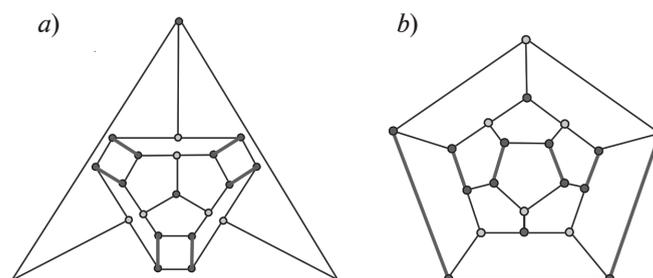


Fig. 2. Graphs of two isomers of fullerene C_{20} : (tetra-hexa)₃-penta₆ polyhedron (a) and dodecahedron (b); heavy-black lines are new covalent bonds

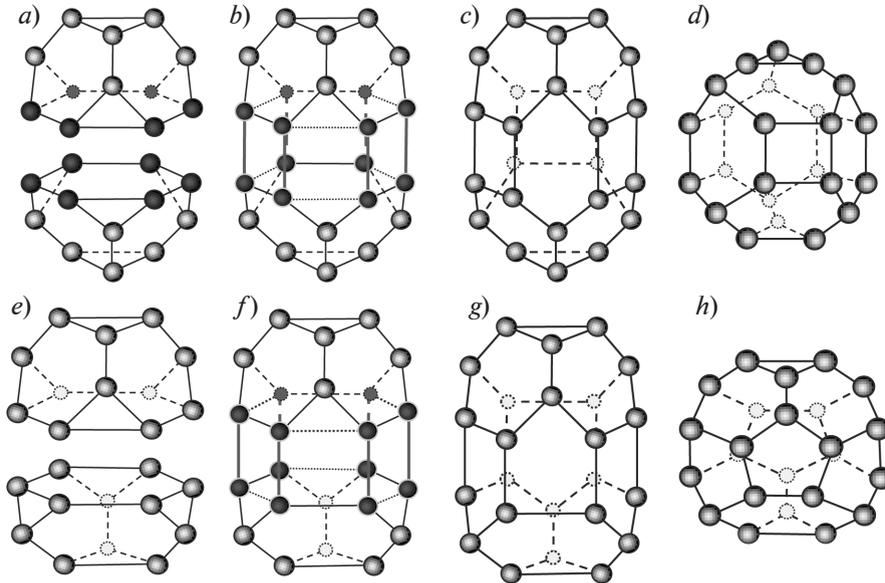


Fig. 3. Joining of two half fullerenes C_{12} . This caption is almost identical to that of Fig. 1, with the following differences: (a, e) Separate carbon cupolas C_{12} ; (d) Tri_2 - $tetra_3$ - $hexa_9$ polyhedron C_{24} ; (h) Truncated dodecahedron C_{24} after relaxation

metry at first a distorted dodecahedron is formed (Fig. 1, g). Then it relaxes into a perfect dodecahedron (Fig. 1, h).

To make clear the symmetry of the obtained fullerenes it is necessary to turn to their graphs (Fig. 2). It can be assumed that the most stable fullerenes will have the form close to a spherical one. It is apparent that the dodecahedron is more stable than the $(tetra-hexa)_3$ - $penta_6$ polyhedron. However, the latter can become more spherical if it is modified by embedding three dimers into its three hexagons [7]. In doing so it transforms into a C_{26} fullerene.

Reaction between two truncated triangular pyramids

Similar to the previous reasoning, let us consider the atomic configurations

corresponding to the reaction



between two truncated triangular pyramids C_{12} . As before, we have two joinings, mirror-symmetry and rotation-reflection-symmetry ones (Fig. 3).

The first case (see Fig. 3, d) results in the atomic configuration corresponding to a perfect polyhedron that consists of three equilateral triangles, three squares, and nine hexagons, so it could be named a tri_2 - $tetra_3$ - $hexa_9$ polyhedron. This structure was constructed in Ref. [5] on the basis of the graph theory. In the second case (see Fig. 3, h) an isomer of fullerene C_{24} considered in Ref. [6] is obtained; it is a truncated dodecahedron.

The symmetry of both polyhedrons is shown

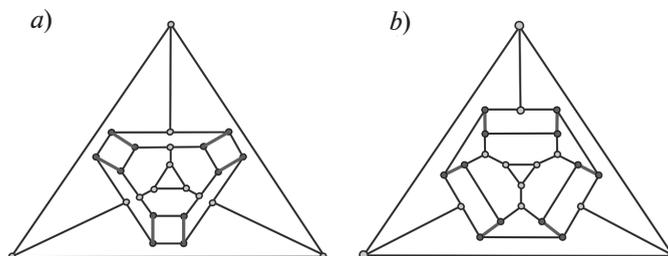


Fig. 4. Graphs of two isomers of fullerene C_{24} : Tri_2 - $tetra_3$ - $hexa_9$ polyhedron (a) and fullerene obtained by truncating two opposite vertices of a dodecahedron (b) [6]

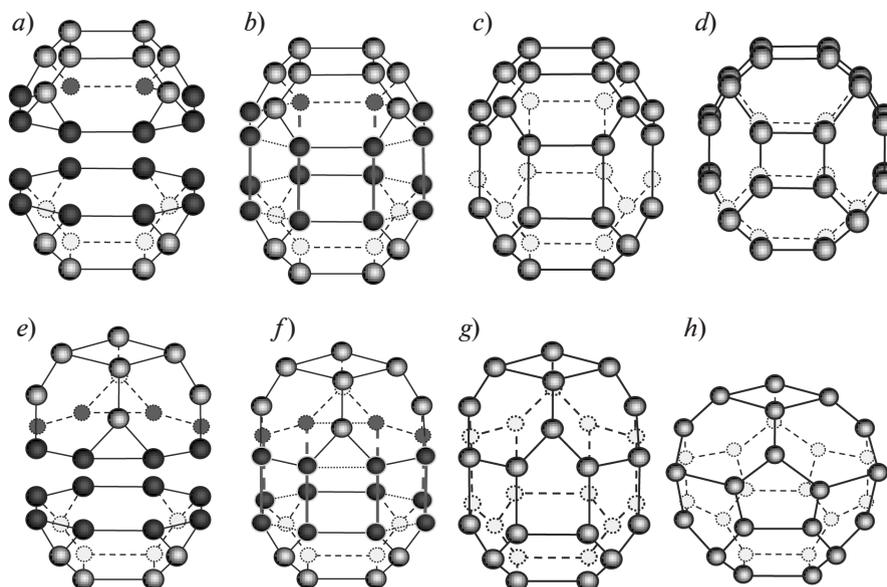


Fig. 5. Mirror-symmetry joining of two half fullerenes C_{16} . This caption is almost identical to those of Figs. 1, 3 with the following differences:
 (a, e) Separate carbon cupolas C_{16} ; (d) Tetra₆-hexa₁₂ polyhedron C_{32} and (h) Tetra₂-(penta-hexa)₈ polyhedron C_{32} after relaxation

in Fig. 4. It is apparent that the truncated dodecahedron is more stable than the tri₂-tetra₃-hexa₉ polyhedron. However, the latter can become more spherical if it is modified by embedding three dimers into its three hexagons. As a result, C_{30} fullerene is obtained.

Reaction between two truncated tetra-angular pyramids

The procedure for visualization of reaction



is the same as before. In the case of mirror-symmetry joining (Fig. 5), the atomic configuration corresponding to a perfect polyhedron (see

Fig. 5, d) consists of six squares and twelve hexagons, so it could be termed a tetra₆-hexa₁₂ polyhedron. This structure was constructed in Ref. [5] on the basis of the graph theory. In the case of rotation-reflection-symmetry joining an isomer of fullerene C_{32} is obtained (Fig. 5, h); it is composed of two squares, eight pentagons and eight hexagons, so it could be termed a tetra₂-(penta-hexa)₈ polyhedron. In both cases their structure and symmetry can be described by application of their graphs. The graphs of both polyhedrons are shown in Fig. 6; they enable us to gain some insight into the symmetry of these polyhedrons. The tetra₆-hexa₁₂ polyhedron can become more spherical if it is modified by

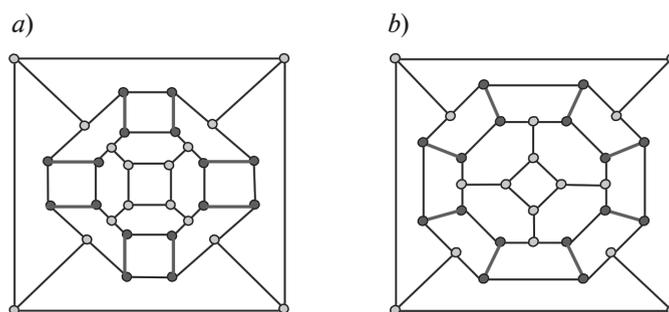


Fig. 6. Graphs of two isomers of fullerene C_{32} : Tetra₆-hexa₁₂ polyhedron (a) and Tetra₂-(penta-hexa)₈ polyhedron (b)

embedding four dimers into its four hexagons lying along an equator or a meridian. This leads to the formation of C_{40} fullerene.

Reaction between two truncated penta-angular pyramids

The procedure for visualization of reaction



is the same as before. In the case of mirror-symmetry joining (Fig. 7), the atomic configuration corresponding to a perfect polyhedron (see Fig. 7, *d*) consists of five squares, two pentagons and ten hexagons, so it could be termed a tetra₅-penta₂-hexa₁₅ polyhedron. This structure was constructed

in Ref. [5] on the basis of the graph theory. In the case of rotation-reflection-symmetry joining (Fig. 11) one obtains an isomer of fullerene C_{40} (Fig. 7, *h*) composed of twelve pentagons and ten hexagons, so it could be termed a penta₁₂-hexa₁₀ polyhedron. In both cases their structure and symmetry can be described with the help of their graphs. The graphs of both polyhedrons are shown in Fig. 8; they enable us to gain some insight into the symmetry of these polyhedrons. The tetra₅-penta₂-hexa₁₀ polyhedron can become more spherical if it is modified by embedding five dimers into its five hexagons lying along an equator, and so transforming into an isomer of fullerene C_{50} .

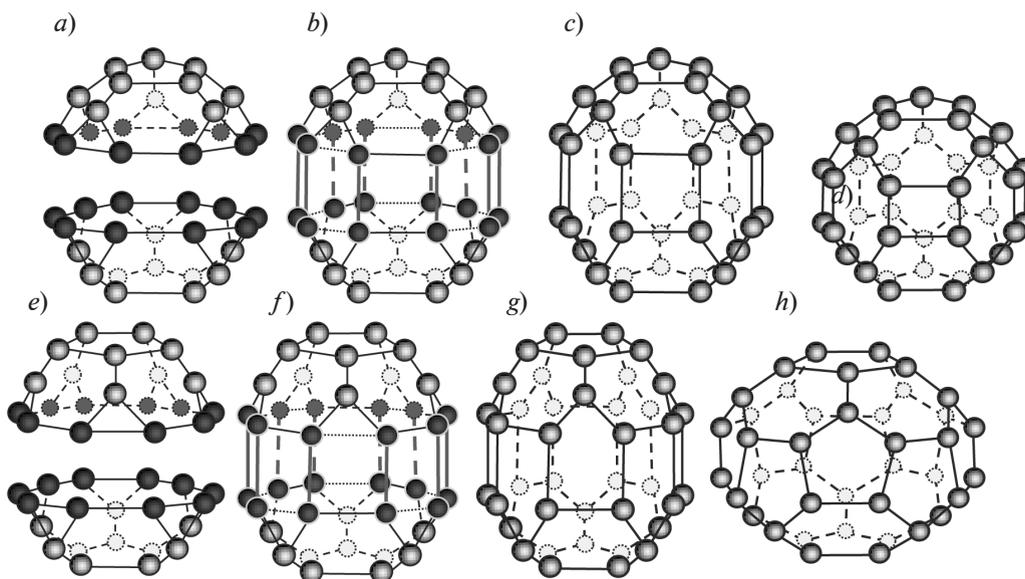


Fig. 7. Joining of two half fullerenes C_{20} . This caption is almost identical to those of Figs. 1, 3, 5 with the following difference:
 (*a, e*) Separate carbon cupolas C_{20} ; (*d*) Tetra₅-penta₂-hexa₁₅ polyhedron C_{40} and (*h*) Penta₁₂-hexa₁₀ polyhedron C_{40} after relaxation

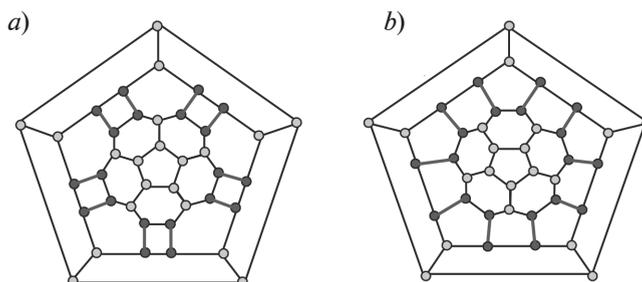


Fig. 8. The graphs of two C_{40} fullerene isomers: tetra₅-penta₂-hexa₁₅ polyhedron (*a*) and penta₁₂-hexa₁₀ polyhedron (*b*)

Reaction between two truncated hexa-angular pyramids

The procedure for visualization of reaction



is the same as before. In the case of mirror-symmetry joining (Fig. 9), the atomic configuration corresponding to a perfect polyhedron (Fig. 9, *d*) consists of six squares and twenty hexagons, so it could be termed a tetra₆-hexa₂₀ polyhedron. This structure was constructed in Ref. [5] on the basis of the graph theory. In the case of rotation-reflection-symmetry joining (Fig. 9) one obtains an isomer of fullerene C₄₈ (see Fig. 9, *h*) composed of twelve pentagons and ten hexagons, so it could

be termed a penta₁₂-hexa₁₄ polyhedron. In both cases their structure and symmetry can be described using their graphs. The graphs of both polyhedrons are shown in Fig. 10; they enable us to gain some insight into the symmetry of these polyhedrons.

The tetra₅-penta₂-hexa₁₀ polyhedron can become more spherical by embedding six dimers into its six hexagons lying along an equator [21]. This leads to transforming an isomer of fullerene C₄₈ into an isomer of fullerene C₆₀.

Summary

The growth of fullerenes through a series of joining reactions of cupola half fullerenes C₁₀, C₁₂, C₁₆, C₂₀, and C₂₄ has been considered. We

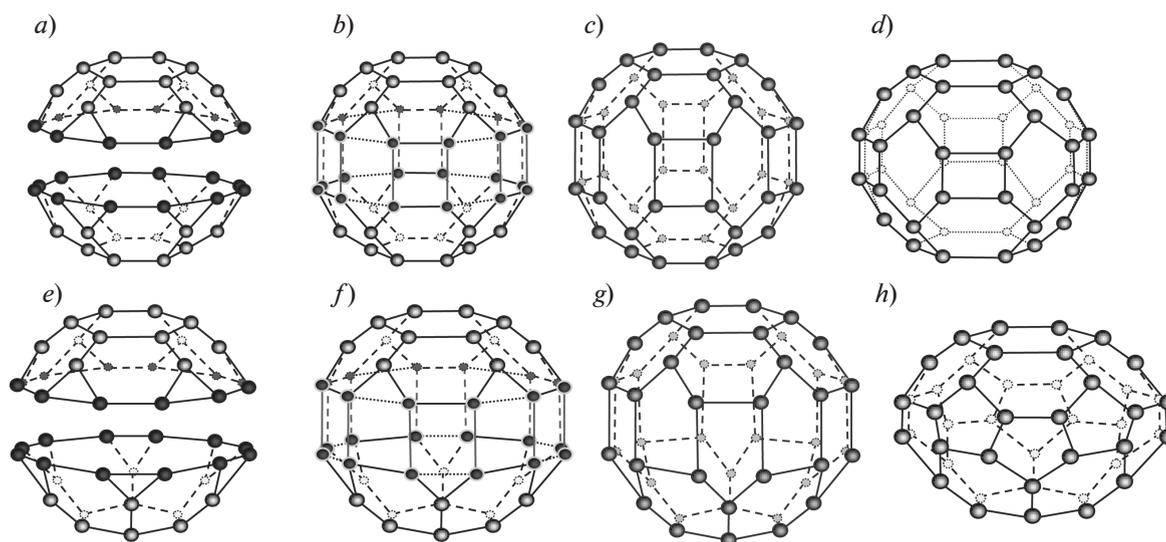


Fig. 9. Joining of two half fullerenes C₂₄. This caption is almost identical to those of Figs. 1, 3, 5, 7 with the following differences:
 (*a, e*) Separate carbon cupolas C₂₄; (*d*) Tetra₆-hexa₂₀ polyhedron C₄₈ and (*h*) Penta₁₂-hexa₁₄ polyhedron C₄₈ after relaxation

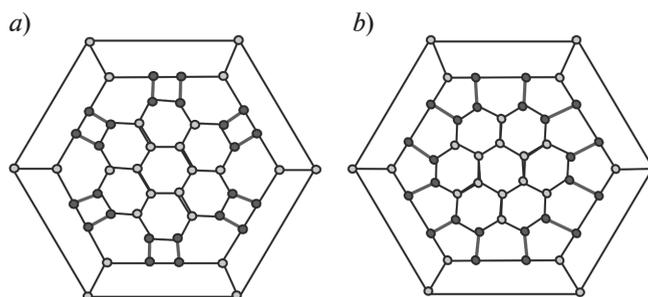


Fig. 10. Graphs of two isomers of fullerenes C₄₈: tetra₆-hexa₂₀ polyhedron (*a*) and penta₁₂-hexa₁₄ polyhedron (*b*)

supposed that during the reactions new covalent bonds are formed and some old covalent bonds between the reacting atoms are splitted. The final structure of fullerenes was obtained through the use of geometric modeling. The fullerene symmetry was shown by means of graphs constructed. As to fullerenes, the geometric modeling was based on the principle “the minimum surface at the maximum volume”. In other words, a forming fullerene tends to take the form of a perfect spheroid with equal covalent bonds.

The geometric modeling has shown its efficiency as a first step of a computer simulation, usually of molecular dynamics, and further theoretical analysis. The reason is that any molecular dynamics needs input data. For mini-fullerenes (up to C_{20}) the number of possible configurations is not very large, but by passing to half fullerenes ($C_{20} - C_{60}$), one obtains a monstrous size of isomers. It is clear that there is no big sense in studying all of them, so it is desirable to restrict their number to the most stable configuration. In this respect, the geometric modeling allows one to imagine a possible way of growing carbon clusters from the very beginning and thereby to decrease the number of configurations worth for studying.

Using geometrical modeling we obtained two families of fullerenes, each being composed of C_{20} , C_{24} , C_{32} , C_{40} , and C_{48} fullerenes. Both families have a layer structure. By analogy with geography, one can distinguish an equator zone, two temperate zones and two polar circles. The first family, designed in Ref. [5] on the graph basis, was termed the family of 4 – 6 equator fullerenes.

The second family was constructed for the first time. Its progenitor C_{20} is a pentagonal dodecahedron, the next fullerene C_{24} can be realized as a twice truncated dodecahedron along one of three-fold symmetry axis. With the exception of the dodecahedron, the other fullerenes of this family can be considered similar to the previous case. Their equator zone consists of adjacent pentagons creating a zigzag; the temperate zones are formed by hexagons; each polar circle consists of an equilateral triangle, a square, a pentagon or a hexagon, these figures defining symmetry of the related fullerene. The family progenitor C_{20} is an exception; it has six five-fold symmetry axes, ten three-fold symmetry axes and fifteen two-fold symmetry ones. For this reason its graph is given in the form reflecting its highest symmetry.

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Мелькер А.И., Воробьева Т.В. РЕАКЦИИ СИНТЕЗА КУПОЛООБРАЗНЫХ ПОЛУ-ФУЛЛЕРЕНОВ.

На основе постулата Аррениуса рассмотрены реакции синтеза куполообразных полуфуллеренов C_{10} , C_{12} , C_{16} , C_{20} и C_{24} друг с другом. Согласно постулату, вначале образуется промежуточное соединение, а затем проходит обычная химическая реакция. Предполагается, что во время реакции возникают новые ковалентные связи, а старые ковалентные связи между атомами, вступающими в реакцию, разрушаются. Конечная структура фуллерена получена с помощью геометрического моделирования. В случае фуллеренов геометрическое моделирование предполагает, что образующийся фуллерен стремится принять форму совершенного сфероида с равными ковалентными связями. Построены графы, отражающие этот процесс.

КУПОЛООБРАЗНЫЙ ПОЛУФУЛЛЕРЕН, РЕАКЦИЯ СИНТЕЗА, ГРАФ, МОДЕЛИРОВАНИЕ.

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