

POSSIBLE WAYS OF FORMING MINI-FULLERENES AND THEIR GRAPHS

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Abstract. The diagrams, describing the process of forming mini-fullerenes of single carbon atoms and carbon dimers, are suggested. The diagrams have much in common for different fullerenes. Forming fullerenes incorporates several stages. In the first stage an initial reaction-active single atom adds another atom and activates it. In its turn the second atom adds two other atoms creating a chain reaction whereupon mutual turning of the covalent bonds generated leads to folding and to giving rise further covalent bonds that results in fullerene formation. Another way consists in the following. Here a reaction-active carbon dimer adds at once two atoms which create two covalent pairs connected with the dimer. Thereafter the chain reaction is going in two opposite directions similar to the previous case. In both cases the process consists of several stages which differ, but the final configuration, due to folding, is one and the same fullerene. We have constructed graphs for all the mini-fullerenes considered. This approach simplify the analysis both the ways of fullerene forming and its structure.

1. Introduction

It is customary to assume that fullerenes are the carbon molecules having a shape close to a spherical surface which can be composed of regular pentagons combined with regular hexagons. From this it follows that the least fullerene has twenty atoms forming twelve pentagons. We have supposed that this restriction is unnecessary [1]. In other words, we have taken the term “*fullerene*” in a broad sense as any convex shape inscribed into a spherical surface which can be composed of atoms, each atom having *three nearest neighbors*, as in usual fullerenes, whenever discussing hollow carbon clusters. This geometrical approach allowed us to obtain possible forms of such broad-sense fullerenes. To gain a more penetrating insight into their nature, we have also taken into consideration, along with the atomic structure of these spherical molecules, their electronic structure [2]. For this purpose we have developed an enlarged version of the theory by Sidgwick and Powell whose theory, created in 1940, allowed explaining and predicting stereochemical properties of many simple molecules having a central atom (more than 1500 [3]). According to the theory:

- Geometry of a molecule is dictated by the arrangement of electron pairs in the valence shell of atoms;
- Each shared electron pair, forming a covalent bond, can be considered as a point charge;
- All the electron pairs of a molecule arrange themselves into such configuration which ensures their equal and maximal removing from each other.

In the twenty-first century, this theory was extended and applied to cyclic molecules

such as cyclohexane [4] and usual fullerenes [5], which have no a central atom. The all-important result of such extension consists in the following:

The hidden symmetry of special electronic pattern does not coincide with that of atomic one, but it is precisely the electronic pattern that defines the atomic structure.

The modified approach developed in [4] was applied to the broad-sense fullerenes [1]. However, contrary to the previous approaches [3, 4], where atoms and electron pairs were located on their own spheres, the main innovation in [1] is the crucial postulate:

- *Atoms and shared electron pairs, forming covalent bonds, are located on one and the same sphere.*

It follows herefrom that geometry of both the electronic structure as well as of the atomic structure of fullerenes can be most conveniently constructed and studied with the help of *spherical geometry*.

Up to now mechanism of fullerene formation is unclear. The irrefutable fact is as follows. If to take one electrode of ${}_6C^{I3}$ – graphite and another of ordinary ${}_6C^{I2}$ – graphite, the fullerene, formed in an electric arc, has ${}_6C^{I3}$ – and ${}_6C^{I2}$ – atoms arranged on a fullerene surface in a random way. It follows herefrom that fullerene assemblage originates of separate atoms and C_2 – dimers (or maybe of very small clusters).

In this contribution we used this fact and the approach developed in [1] as the basis for predicting possible ways of broad-sense fullerenes formation. Besides, as in [6], we have used graph theory [7] to represent formation of carbon clusters, their transformation from a cluster to a fullerene, and their final configurations. The short-cut description is given in [8].

2. Tetrahedral fullerene C_4 as an explanation of the main idea

Let us start with a reaction-active single carbon atom. At first the initial reaction-active single atom adds another atom and activates it, both atoms creating a covalent bond. In its turn the second atom adds two other atoms, producing two additional covalent bonds (Fig. 1a). Here the large circles represent carbon atoms; the small ones refer to unshared electron pairs. In other words, we have a cluster with three covalent bonds; the tail atoms having unshared electron pairs. According to our postulate, each carbon atom can have, as in usual fullerenes, three neighbors which are located with the nucleus atom on one and the same sphere. The unshared electron pairs also lie on some sphere.

If the growth of this cluster is suppressed, the unshared electron pairs begin to attract to each other. As a result, they create three new covalent bonds between the tail atoms (Fig. 1b). It should be emphasized that in the qualitative theory by Sidgwick and Powell any electron pairs, shared or unshared, can only repel, but not attract. This is a consequence of their assumption that the electron pairs can be considered as point static electric negative charges. More careful quantitative analysis on the basis of dynamics reveals that it is necessary to take into account eigenvibrations of electron pairs considering them as dynamic variables [2].

With this in mind, we have shown that each pair plays the role of an external field with respect to other pair, thus polarizing it. Therefore the electron pair is rather a dynamic electric dipole than a point static electric charge. Such dipole represents itself to be an oscillator, i.e. the system of two opposite point charges which are equal in absolute value; the distance between them is changing in consequence of quick vibrations near a stable equilibrium position. As a result, there appears intramolecular van der Waals interaction between the electron pairs. It follows herefrom an essential difference between static charges and dynamic dipoles. The firsts produce only Coulomb repulsion whereas the seconds both repulsion and van der Waals attraction. It is just this attraction which leads at first to mutual turning of the covalent bonds (folding), and then to producing a tetrahedral fullerene (Fig. 1c).

Briefly the way of fullerene formation considered incorporates four stages. In the first stage an initial reaction-active single atom adds another atom and activates it. In its turn the

second atom adds two other atoms, forming a simple branching (second stage), whereupon mutual turning of the covalent bonds generated leads to folding (third stage) and to giving rise further covalent bonds that results in tetrahedron formation (final stage).

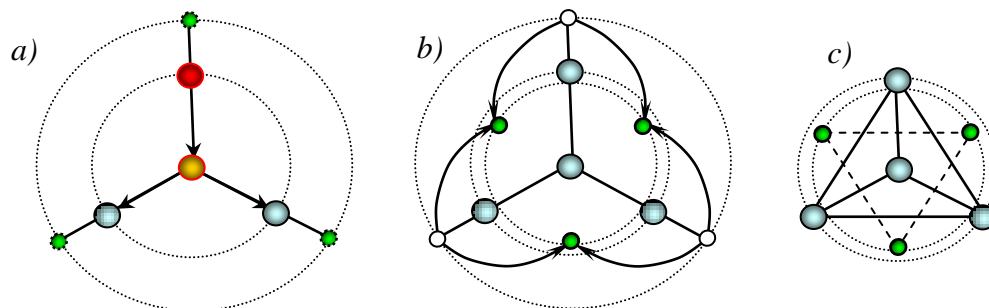


Fig. 1. Top view: (a) cluster of four carbon atoms, each tail atom having an unshared electron pair; (b) formation of new covalent bonds gives rise to a tetrahedron (c). Atomic and electronic parallels are shown by dotted circles. The edge length of the tetrahedron is a ; the radius of the atomic parallel is $a/\sqrt{3}$; the radius of the electronic parallel is $a/2$.

One can envision another way of forming a cluster of four carbon atoms. Here a reaction-active carbon dimer adds at once two atoms which create two covalent pairs connected with the dimer (first stage). Thereafter mutual turning of the covalent bonds existed occurs (second stage, folding) leading to generating further covalent bonds and to fashioning a tetrahedron (final stage).

In both cases the process consists of several stages which differ, but the final configuration, due to folding, is one and the same tetrahedron. It can be represented with two diagrams (Figs. 2a, 2b) and with two isomorphic graphs having four vertices (Figs. 2c, 2d). Remember some notions of the graph theory [7]. Edges having a common vertex are named adjacent. Graphs having one-to one correspondence and conserving the adjacency are isomorphic.

It should be emphasized that the first diagram shown in Fig. 2a is identical with one of the diagrams illustrating a formation of an athermal tetravacancy under irradiation (simple branching) [6].

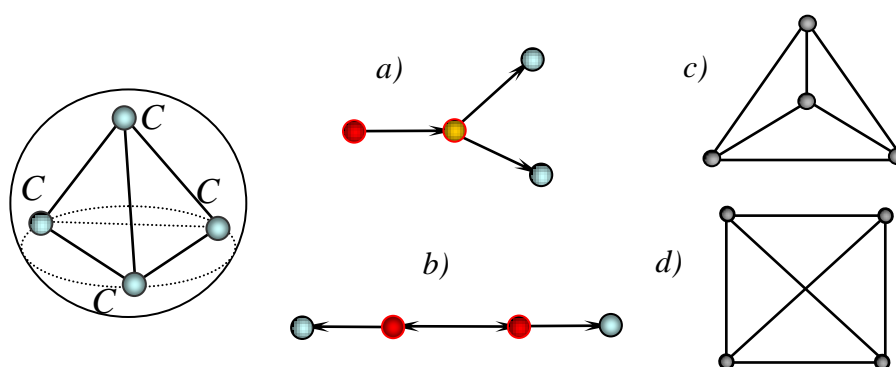


Fig. 2. Carbon tetrahedron inscribed into a sphere (on the left); here any three atoms lie on one and the same parallel. Possible ways of forming a cluster of four carbon atoms (a, b) and the isomorphic graphs (c, d) representing a tetrahedral fullerene.

3. Mini-fullerenes from C_6 to C_{10}

This family of fullerenes will be named the elementary fullerenes. It contains together with a base-truncated tetrahedron four members.

a) Triangular prism C_6 . Similar to the previous procedure for a tetrahedral fullerene, we can envision different ways of forming at first a cluster of six carbon atoms (Figs. 3a, 3b) and then its transform into a triangular-prism fullerene. The final configuration can be represented as two isomorphic graphs having six vertices (Figs. 3c, 3d). From a mathematical standpoint, diagram (a) is identical with one of the diagrams (double branching) illustrating formation process of an athermal hexavacancy at irradiation [6].

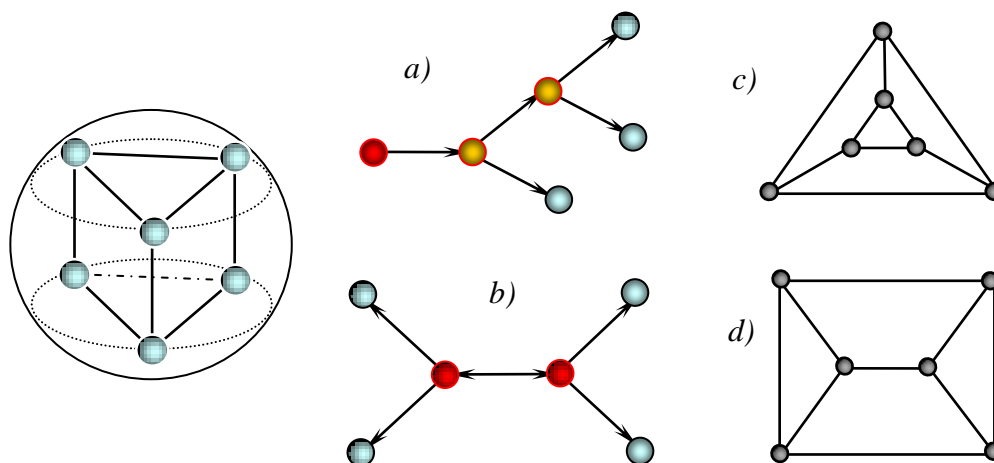


Fig. 3. Carbon triangular prism inscribed into a sphere (on the left); here three atoms of two bases lie on one and the same parallel. Possible ways of forming a cluster of six carbon atoms (a, b) and the isomorphic graphs (c, d) representing a triangular-prism fullerene.

b) Cube C_8 . The next in size carbon cluster, each atom of it having three nearest neighbors, which can be inscribed into a sphere, is a cube. In Fig. 4, different ways of forming a cluster of eight atoms and the graph representation of a cubic fullerene are shown.

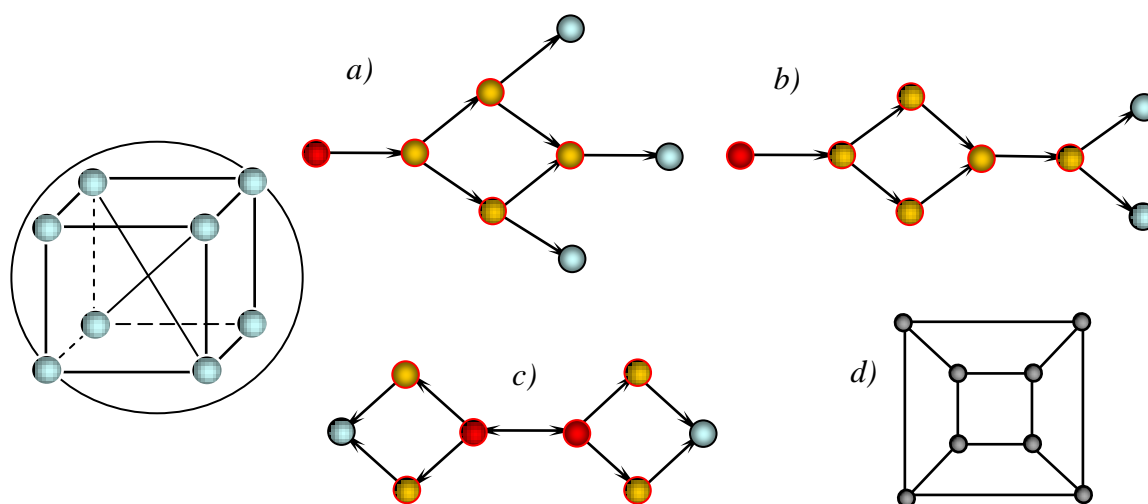


Fig. 4. Carbon cube inscribed into a sphere (on the left). Possible ways of forming a cluster of eight carbon atoms (a, b, c), and a cubic-fullerene graph (d) are shown.

c) Pentagonal prism C_{10} . The next in size carbon cluster, each atom of it having three nearest neighbors, which can be inscribed into a sphere, is a pentagonal prism. The ways of forming this cluster and the graph representation of a fullerene obtained are shown in Fig. 5. It should be noted that all three graphs are isomorphic. At this, two first graphs reflect better the diagrams of generating the prism. The third graph has no such property, but it has an advantage for an analysis being symmetric.

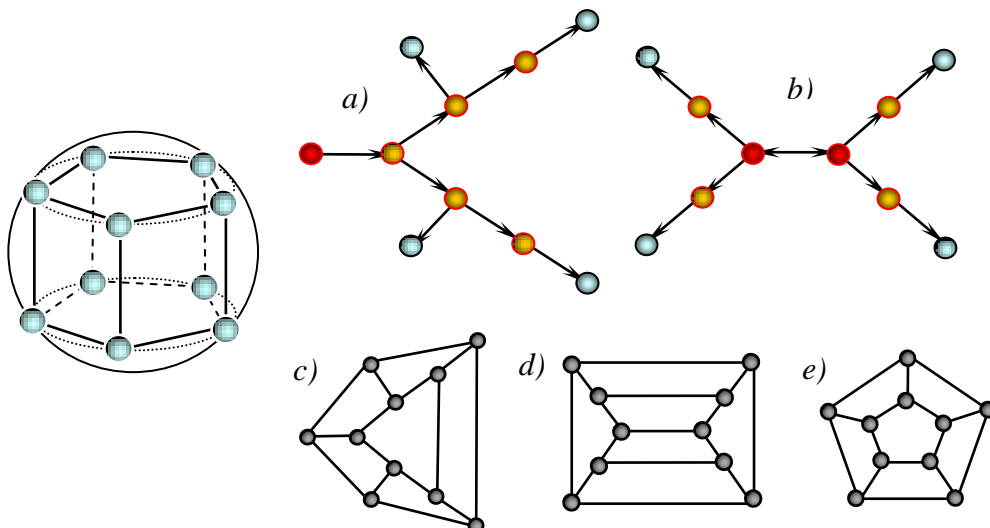


Fig. 5. Carbon pentagon prism inscribed into a sphere (on the left). Possible ways of forming a cluster of ten carbon atoms (*a, b*), and fullerene graphs obtained (*c, d, e*) are shown.

d) Base-truncated triangular pyramid C_{10} (Fig. 6). It should be noted that in the previous paper [1] we have not catch sight of this mini-fullerene structure.

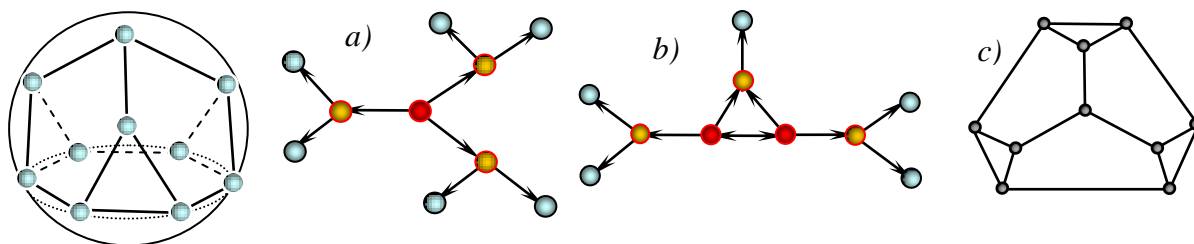


Fig. 6. Base-truncated triangular pyramid inscribed into a sphere (on the left). Possible ways of forming a cluster of ten carbon atoms (*a, b*) and a fullerene graph obtained (*c*).

4. Fullerene of twelve carbon atoms C_{12}

Here we confront with a new phenomenon, namely, different forms of carbon hollow molecules. Earlier we have shown that there are four structural isomers of this fullerene [1].

a) Hexagonal prism. It is the simplest form that can be thought of. The atomic structure, the ways of forming this cluster and the graph representation of a fullerene obtained are shown in Fig. 7.

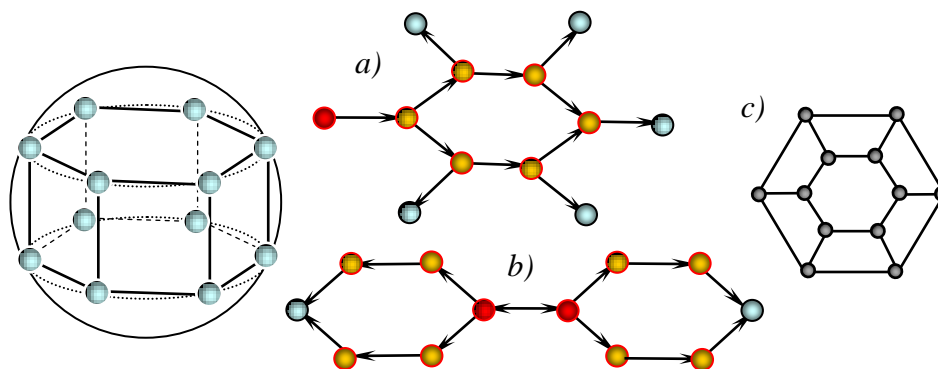


Fig. 7. Hexagonal prism inscribed into a sphere (on the left). Possible ways of forming a cluster of twelve carbon atoms (*a, b*), and a symmetric fullerene graph obtained (*c*).

b) Twisted hexagonal prism. It is a rather exotic shape that can be thought of. The atomic structure, a possible way of forming this cluster and graph representation of a fullerene is shown in Fig. 8.

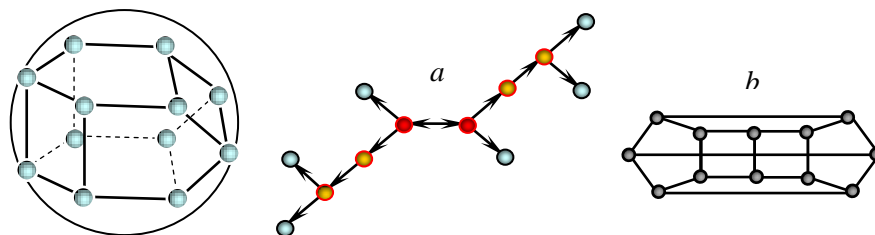


Fig. 8. Twisted hexagonal prism inscribed into a sphere (on the left). One of the possible ways of forming a cluster of twelve carbon atoms (*a*) and a fullerene graph obtained (*b*).

c) Truncated tetrahedron. The atomic structure, possible ways of forming the cluster and the graph representation of the fullerene are shown in Fig. 9.

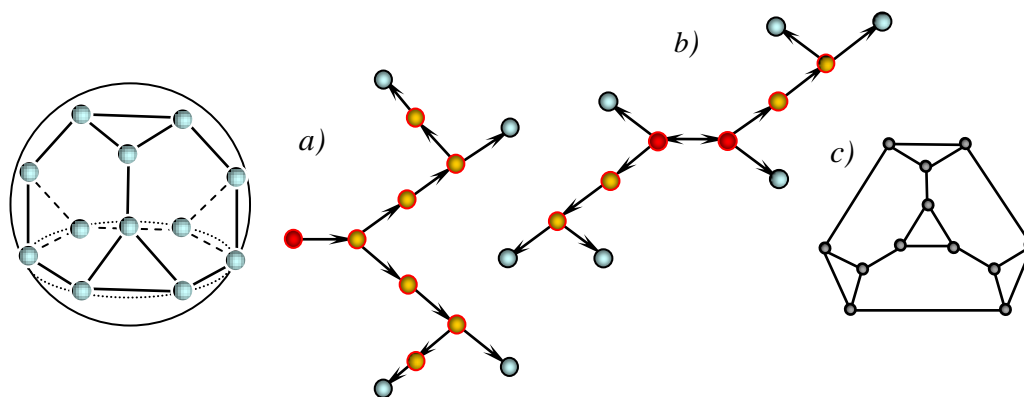


Fig. 9. Truncated tetrahedron inscribed into a sphere (on the left). Possible ways of forming a cluster of twelve carbon atoms (*a*, *b*) and a fullerene graph obtained (*c*).

d) Triangular barrel (double tri-penta₃ polyhedron). The atomic structure of this fullerene resembling a triangular barrel or a rugby ball is shown in Fig. 10. The possible ways of forming this cluster of twelve carbon atoms and the graph representation of a fullerene obtained are also shown in Fig. 10. It should be noted that the diagrams shown are identical with the diagrams illustrating formation of a zigzag polymer during polymerization.

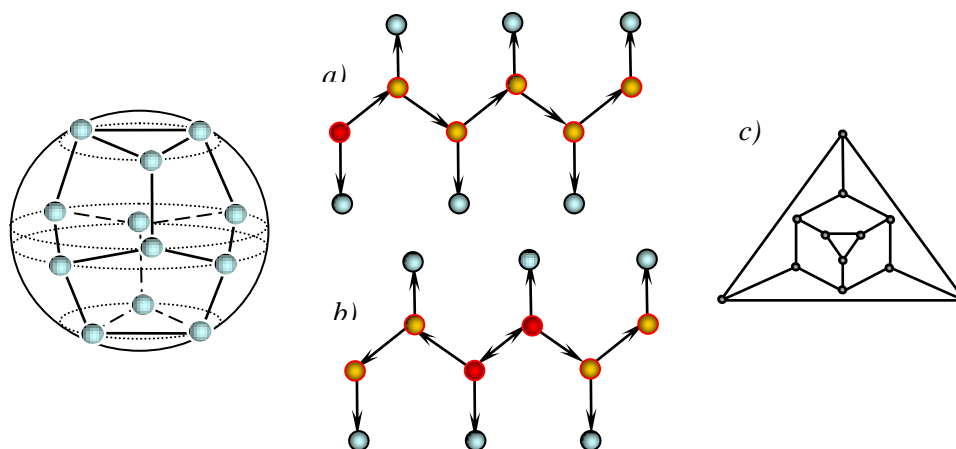


Fig. 10. Triangular-barrel fullerene inscribed into a sphere (on the left). Possible ways of forming a cluster of twelve carbon atoms (*a*, *b*) and a fullerene graph obtained (*c*).

5. Fullerene of fourteen carbon atoms C_{14}

We have shown elsewhere that there are two structural isomers of this fullerene [1].

a) Bi-shamrock (tetragonal trefoil-pair polyhedron). The atomic structure is given in Fig. 11. The possible ways of forming this cluster and the graph representation of the fullerene are also shown in Fig. 11.

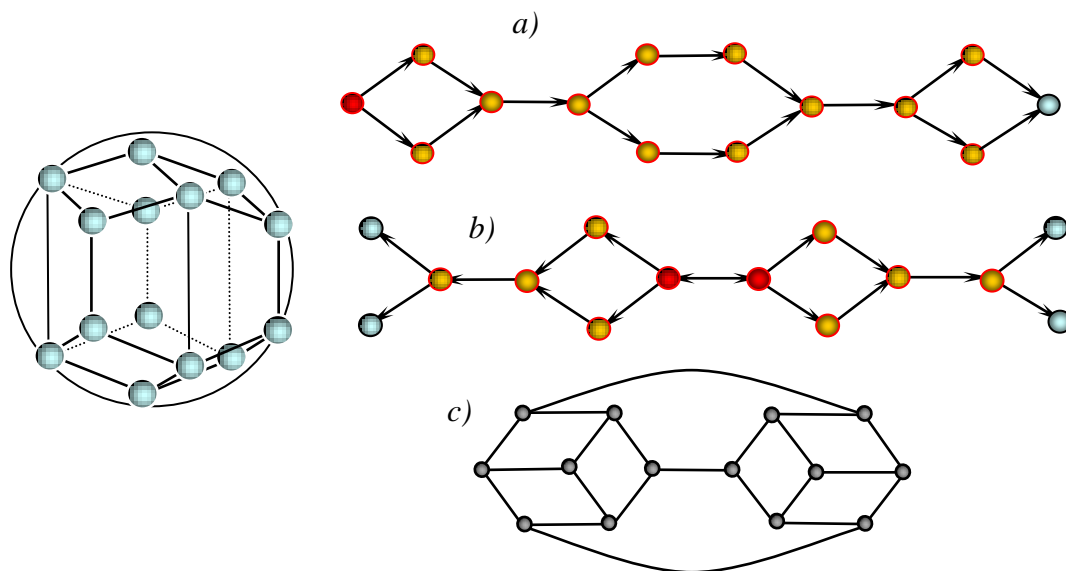


Fig. 11. Bi-shamrock polyhedron inscribed into a sphere (on the left). Possible ways of forming a cluster of fourteen carbon atoms (*a*, *b*) and a fullerene graph obtained (*c*).

b) Base-truncated triangular bipyramid. The atomic structure is given in Fig. 12. The possible ways of forming this cluster and two isomorphic graphs of the fullerene obtained are also shown in Fig. 12. Notice that graph (*c*) better corresponds to diagram (*a*) that reflects a carbon cluster nucleation initiated by a single atom whereas graph (*d*) concerns more closely the nucleation started by a dimer.

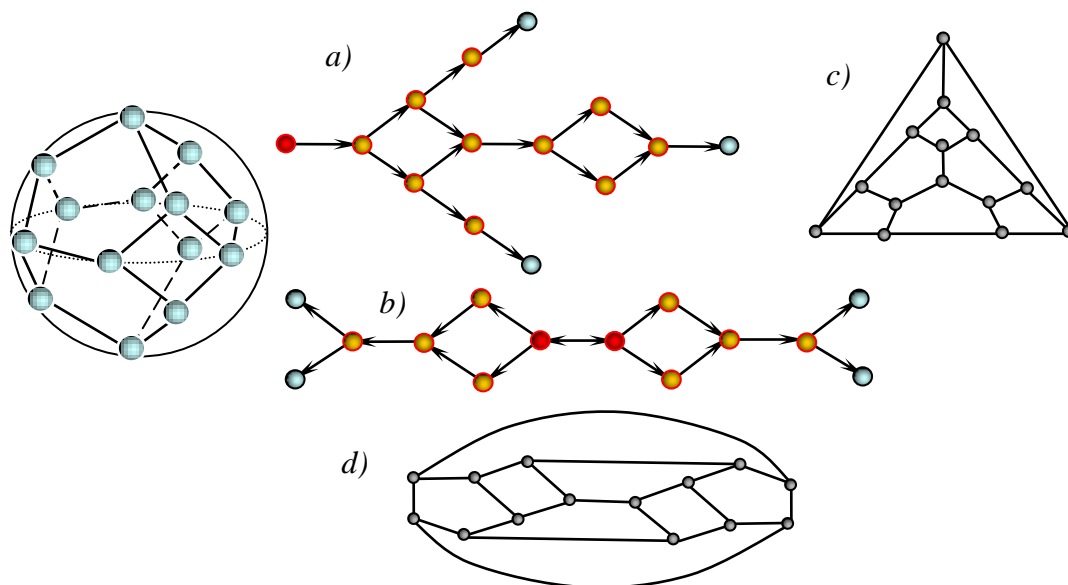


Fig. 12. Base-truncated triangular bipyramid inscribed into a sphere (on the left). Possible ways of forming a cluster of fourteen carbon atoms (*a*, *b*) and fullerene graphs obtained (*c*, *d*) are shown.

6. Fullerene of sixteen carbon atoms C_{16}

There are two structural isomers of this fullerene [1].

a) Half-truncated cube. The atomic configuration has much in common with that of a truncated tetrahedron fullerene. It consists of triangles and hexagons (Fig. 13). The possible ways of forming this cluster and the graph representation of a fullerene are shown in Fig. 13.

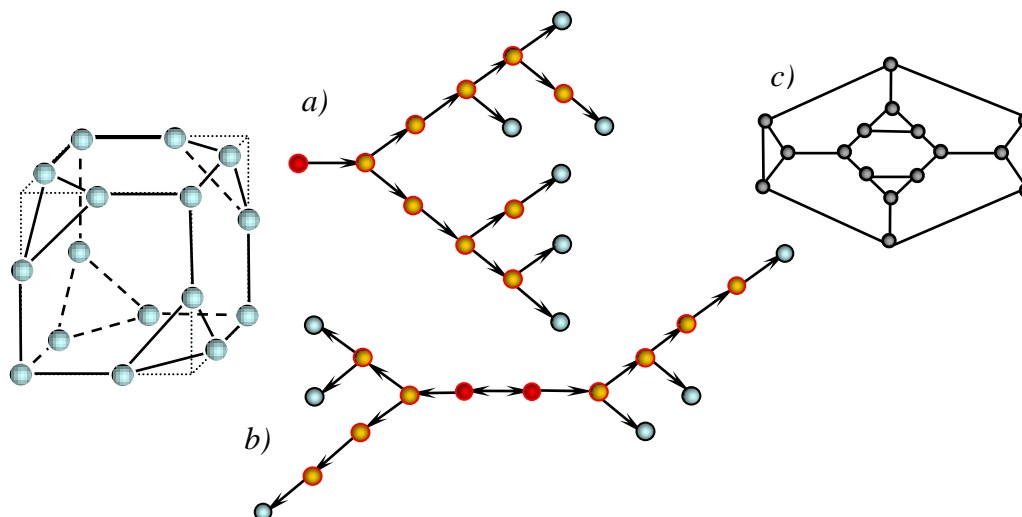


Fig. 13. Half-truncated cube (on the left). Possible ways of forming a cluster of sixteen carbon atoms (*a*, *b*) and a fullerene graph obtained (*c*).

b) Square barrel (double tetra-penta₄ polyhedron). The atomic configuration is formed from two squares and eight pentagons (Fig. 14). The possible ways of forming this cluster of sixteen carbon atoms and the graph representation of a fullerene obtained are also shown in Fig. 14. As in the case of a triangular barrel, the diagrams shown are identical with the diagrams illustrating formation of a zigzag polymer during polymerization. The only difference is a length of a chain.

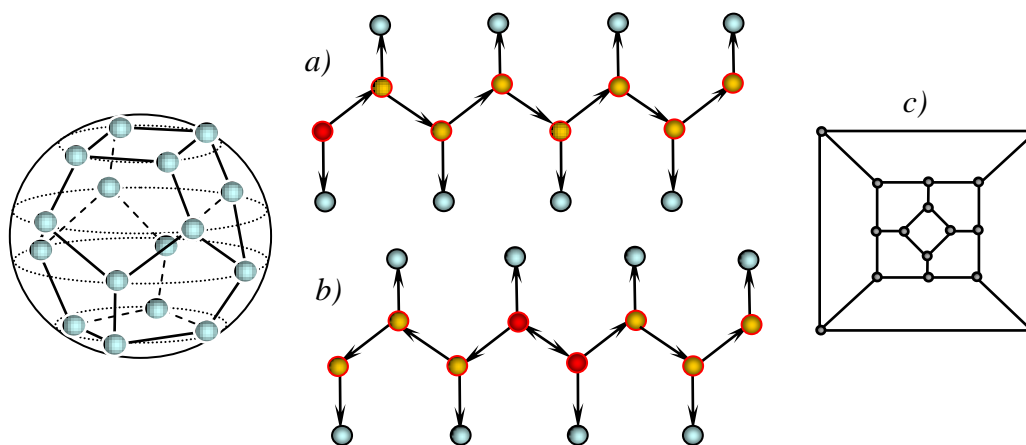


Fig. 14. Square-barrel fullerene inscribed into a sphere (on the left). Possible ways of forming a cluster of sixteen carbon atoms (*a*, *b*) and a fullerene graph obtained (*c*).

7. Fullerene of eighteen carbon atoms C_{18}

There are two structural isomers of this fullerene [1].

a) Truncated triangular bipyramid. The atomic structure is given in Fig. 15. It has much in common with that of a base-truncated triangular bipyramid. Possible symmetric ways of forming this cluster and a graph of the fullerene obtained are also shown in Fig. 15.

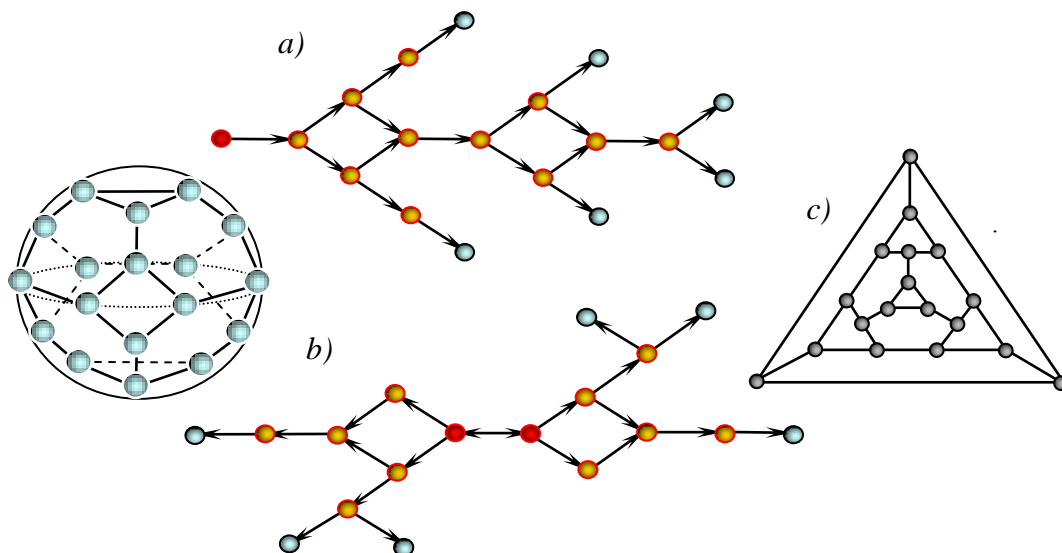


Fig. 15. Truncated triangular bipyramid inscribed into a sphere (on the left). Possible ways of forming a cluster of eighteen carbon atoms (*a*, *b*), and a fullerene graph obtained (*c*).

b) Truncated bi-shamrock ((tri-penta₃)₂-hexa₃ polyhedron). It should be emphasized that contrary to all the previous shapes of fullerenes this configuration can be inscribed only into an ellipsoid of revolution (Fig. 16). Some possible ways of forming this cluster and a graph of the fullerene obtained are also shown in Fig. 16.

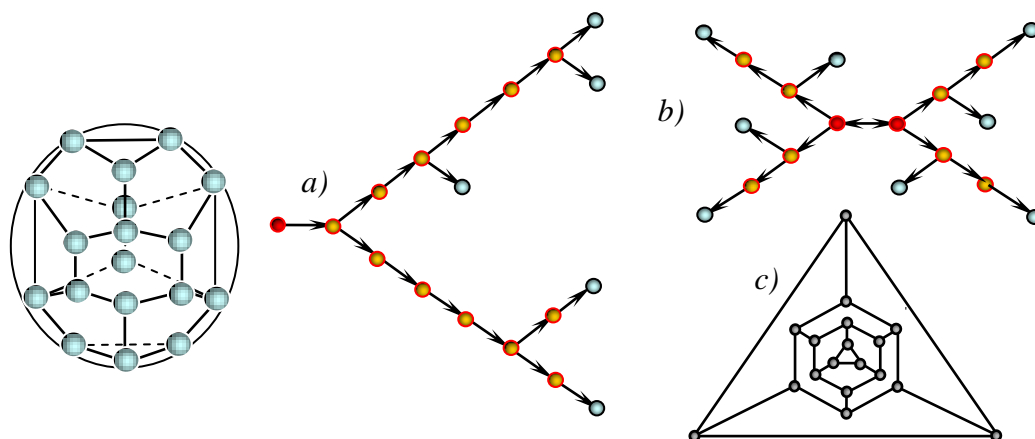


Fig. 16. Truncated bi-shamrock inscribed into a sphere (on the left). Possible ways of forming a cluster of eighteen carbon atoms (*a*, *b*), and a fullerene graph obtained (*c*).

8. Fullerene of twenty carbon atoms C₂₀

There are three structural isomers of this fullerene [1].

a) Dodecahedron (five-cornered barrel). The atomic configuration is a regular polyhedron (Fig. 17). It consists of twelve pentagons and is well known. The possible ways of forming this cluster of twenty carbon atoms and the graph representation of a fullerene obtained is also shown in Fig. 17. As for triangular and square barrels, the diagrams shown are identical with the diagrams illustrating formation of a zigzag polymer during polymerization. The only difference is a length of a chain.

It is interesting to note that Sir William Hamilton pioneered in applying such graph in 1859 for the game “Around the World” thought out by him [7]. In it each vertex is associated with one of the famous cities. A player, traveling around the world, must find such a way going along edges which passes through each vertex only one time.

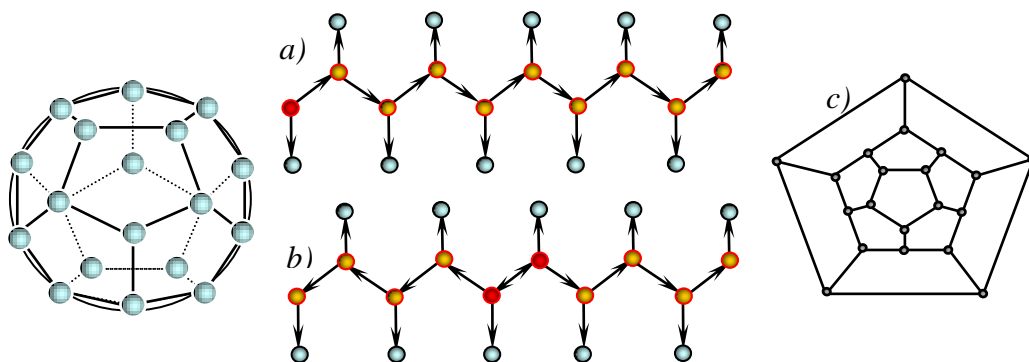


Fig. 17. Dodecahedron inscribed into a sphere (on the left). Possible ways of forming a cluster of twenty carbon atoms (*a*, *b*), and a dodecahedron graph obtained (*c*).

b) (Tetra-hexa)₃-penta₆ polyhedron. The atomic configuration consists of three squares, three hexagons and six pentagons (Fig. 18). It should be noted that the diagrams shown are identical with the diagrams illustrating formation of a zigzag polymer during polymerization (Figs. 18a, b). Contrary to the previous structure which is composed only of antisymmetric zigzags giving a regular chain, one can see also two symmetric zigzags. According to [10] the sections with symmetric zigzags can be regarded as structural defects.

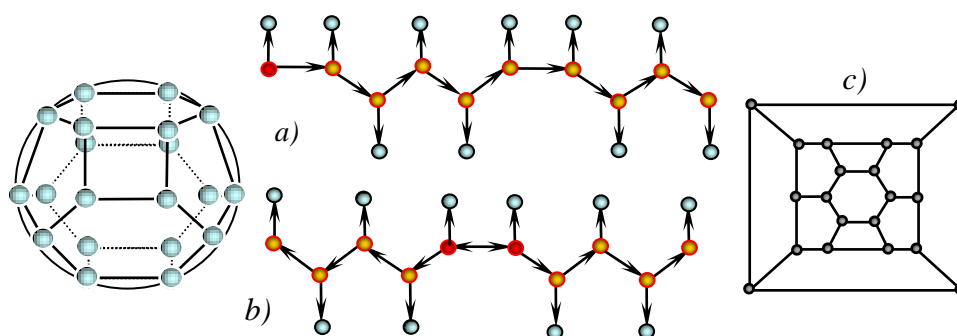


Fig. 18. (Tetra-hexa)₃-penta₆ polyhedron inscribed into a sphere (on the left). Possible ways of forming a cluster of twenty carbon atoms (*a*, *b*), and a fullerene graph obtained (*c*).

c) (Tetra-penta-hexa)₄ polyhedron. The atomic configuration consists of four rhombs, four pentagons and four hexagons (Fig. 19).

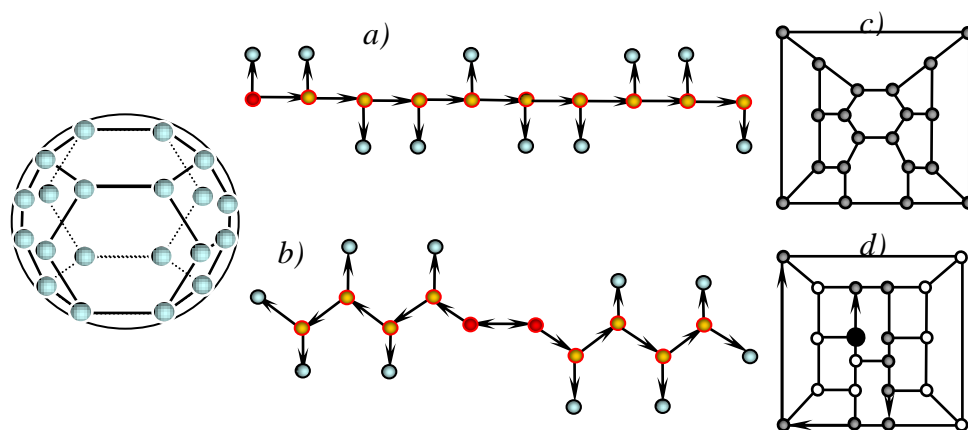


Fig. 19. (Tetra-penta-hexa)₄ polyhedron inscribed into a sphere (on the left). Possible ways of forming a cluster of twenty carbon atoms (*a*, *b*) and two isomorphic graphs of a fullerene obtained (*c*, *d*). Dark circles of graph (*d*) correspond to atoms of a main chain, light circles to those of side chains; big black circle denotes a start atom.

Here one can also discover the similarity between forming this fullerene and a zigzag polymer during polymerization (Figs. 19a, b). However, the way finding is rather tiresome if one uses a volume structure, but it can be simpler if one uses a graph diagram (Fig. 19c), especially in a more abstract form (Fig. 19d).

9. Conclusion

We have suggested diagrams describing the process of forming mini-fullerenes of single carbon atoms and carbon dimers. The diagrams have much in common for different fullerenes. Here we took the term fullerene in a broad sense to mean any hollow shape inscribed into a spherical surface which can be composed of carbon atoms, each atom having three nearest neighbors.

Briefly forming fullerenes incorporates several stages. In the first stage an initial reaction-active single atom adds another atom and activates it. In its turn the second atom adds two other atoms creating a chain reaction whereupon mutual turning of the covalent bonds generated leads to folding and to giving rise further covalent bonds that results in fullerene formation. Another way of forming fullerenes consists in the following. Here a reaction-active carbon dimer adds at once two atoms which create two covalent pairs connected with the dimer. Thereafter the chain reaction is going in two opposite directions similar to the previous case. Although in both cases the process consists of several stages which differ, the final configuration, due to folding, is one and the same fullerene.

We have constructed graphs for all the mini-fullerenes considered. This approach simplify the analysis both the ways of fullerene forming and its structure. The graphs similar to the formation diagrams have much in common for different fullerenes. More careful analysis is given elsewhere [11].

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