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MODELING FULLERENE GROWTH BY FUSION REACTIONS OF CUPOLA HALF-FULLERENES: Δn=16 SERIES

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Abstract. Fusion reactions of cupola half-fullerenes C_{22}, C_{24}, C_{32}, C_{40} and C_{48} 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. The final structure of fullerenes is obtained with the help of geometric modeling and is optimized through the use of Avogadro package. In general, the fullerenes which tend to take the appearance of a perfect spheroid have lesser formation energy. The energy of nanotubes and fullerenes C_{44}, C_{48}, C_{64}, C_{80} and C_{96} obtained is calculated.

Keywords: cluster, cupola, energy, fullerene, fusion, modeling

1. Introduction

Up to now mechanism of fullerene formation is a controversial point (see [1] and references therein). In the majority of cases there suggests that fullerene assemblage originates of separate atoms and C_2 – dimers, and probably of very small clusters. In Ref. [2-4] we have investigated these mechanisms of growing fullerenes. The fullerene growth of separate carbon atoms is conceptually identical with the usual diffusional growth of vacancy clusters in irradiated metals [5]. The growth through the use of dimer embedding into fullerenes was suggested by M. Endo and H.W. Kroto in 1992 [6]. 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 parallel to arising tensile forces (Fig. 1). As a result, there arises a new atomic configuration and there is mass increase of two carbon atoms.

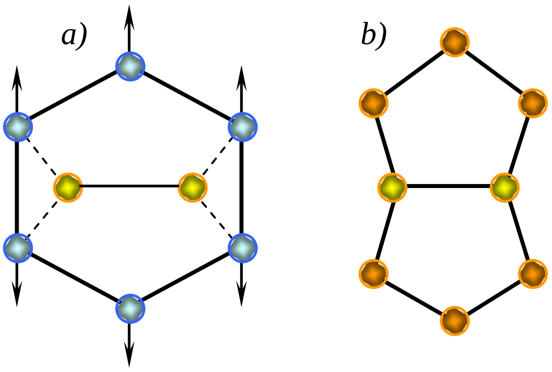

Fig. 1. Carbon dimer embedding into a hexagon (*a*) and its consequence (*b*)

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This mechanism resembles in some respects evolution of an interstitial atom embedded into an octahedral hole of a bcc lattice of alpha-iron, the process being modeled with the help of molecular dynamics by J.M. Beeler, Jr. in 1966 [5]. The result is shown in Fig. 2. We exhaustively studied Endo-Kroto mechanism in Ref. [3,7]. On the basis of these investigations we suggested the periodic system for embedded fullerenes. However this mechanism does not allow obtain pentagon-isolated fullerenes.

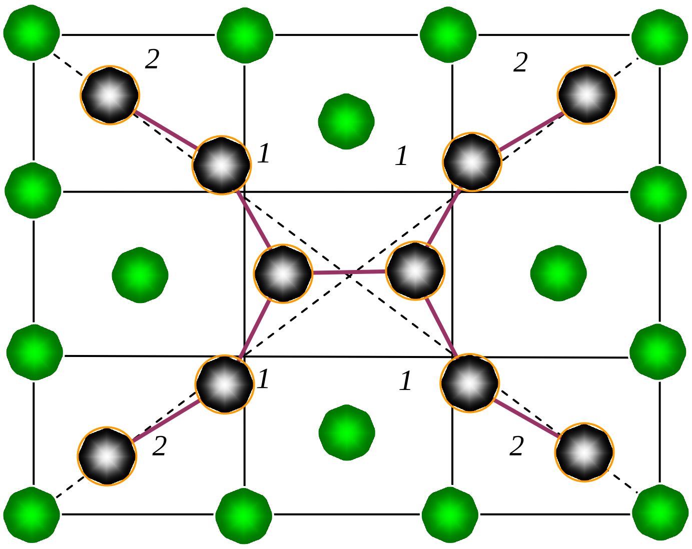

Fig. 2. Plane complex of the most displaced ten atoms forming a bow tie lying in a (110) plane with wings along <111> directions. Atoms 1 are displaced by 17%, atoms 2 by 7%

Fortunately the above-stated mechanisms of fullerene growth are not unique. One may imagine that fullerenes can grow reacting with each other, similar to bubbles in a soap solution. This possibility was demonstrated by the example of such reactions as $C_{24}+C_4 \rightarrow C_{28}$, $C_{30}+C_6 \rightarrow C_{36}$, and $C_{30}+C_{30} \rightarrow C_{60}$, 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 [8-10]. Fullerenes and nanotubes are formed at high temperatures and the new molecular dynamics, named charged-bond molecular dynamics, accounts for this factor properly. At first, this molecular dynamic was developed as a rather sophisticated design, but later it obtained a strict theoretical basis [11].

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 (C_{20} – C_{60}) and maxi-fullerenes (> 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 which are usually symmetric. In this respect it is very useful using geometric modeling as a first step of a computer simulation for further theoretical analysis [5]. We suppose that the geometric modeling allow us to imagine from the very beginning a possible way of growing carbon clusters and thereby to decrease the number of configurations being worth for studying. Using the geometrical modeling, we have considered the growth of fullerenes through a series of joining reactions of cupola half-fullerenes [12]. We have obtained the most symmetric isomers of fullerenes in the range from C_8 to C_{72}, calculated their energy and constructed their graphs. Moreover, on the basis of these investigations we suggested the periodic system for basic perfect fullerenes [13, and references therein].

For the purpose of enlarging the periodic system discovered, in this contribution we present the structure and energy of the Δn=16 series fullerenes, C_{44}, C_{48}, C_{64}, C_{80} and C_{96}, obtained by fusion reactions of cupola half-fullerenes C_{22}, C_{24}, C_{32}, C_{40}, and C_{48}.

2. Reaction between two cupolas C_{22}

In 1889 Svante August Arrhenius postulated that a chemical reaction goes in the following way [14]. At first there forms some intermediate compound and only afterwards a usual chemical reaction is going on. For fullerenes this postulate can be written as

$A + B \leftrightarrow (AB) \rightarrow C$.

In Ref. [12] we have developed an algorithm that has proved itself in predicting the growth of perfect fullerenes conserving an initial symmetry, so called the fusion reaction algorithm. Consider now the reaction for fullerenes of the Δn=16 series.

The atomic configurations corresponding to reaction $C_{22} + C_{22} \rightarrow (C_{22}C_{22}) \rightarrow C_{44}$ between two cupolas C_{22} are shown in Fig. 3. At first two molecules C_{22} are moving towards each other (Fig. 3a). Then the atoms, marked with red, interact with each other producing a compound (Fig. 3b). During this process new covalent bonds (thick red lines) are formed. As a result, a distorted polyhedron is formed that relaxes into a perfect polyhedron (Fig. 3c). It should be emphasized that the symmetry of double bond location about the major axis of cupolas coincides with that of fullerene C_{60}.

To make clear the symmetry of the fullerene obtained one needs to turn to its graph. It is shown in Fig. 4 together with the graph of the initial cupolas. The atomic configuration of initial cupolas consists of six pentagons and three hexagons; due to the fusion there appear six new hexagons and so we have twelve pentagons and twelve hexagons forming a polyhedron.

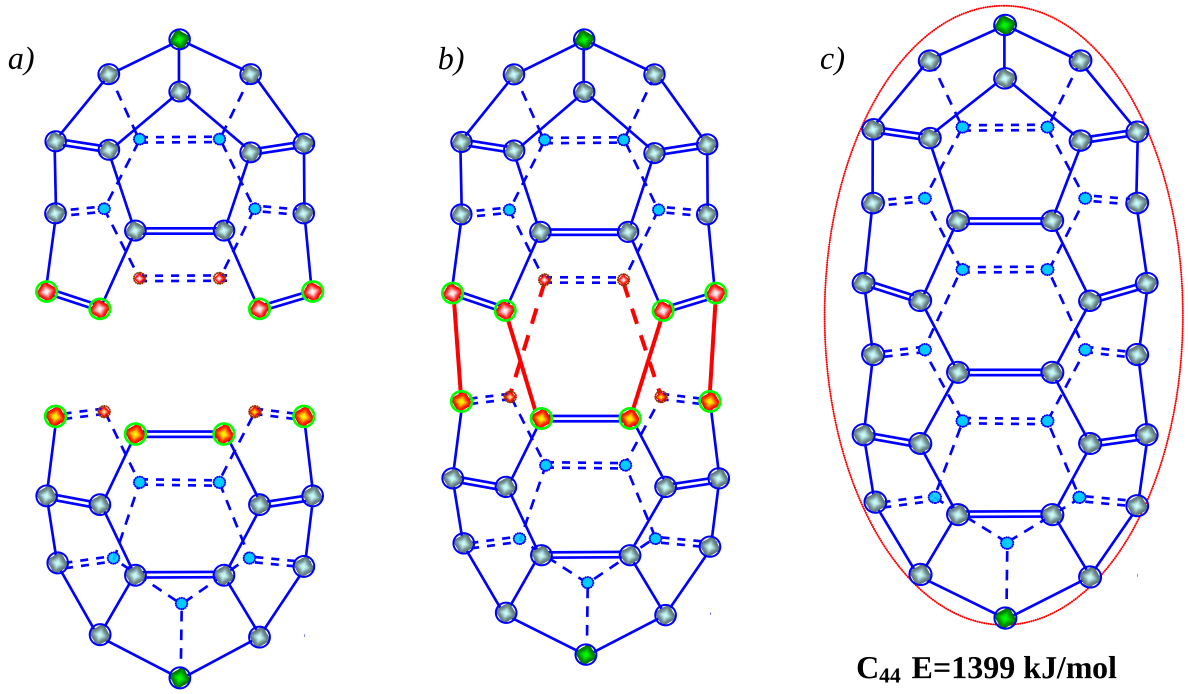

Fig. 3. Joining two cupolas C_{22}: *a*) separate cupolas C_{22}; *b*) intermediate compound; covalent bonds (blue lines), neutral atoms (blue spheres); reacting atoms (red spheres), new covalent bonds (heavy red lines), *c*) nanotube C_{44} after relaxation

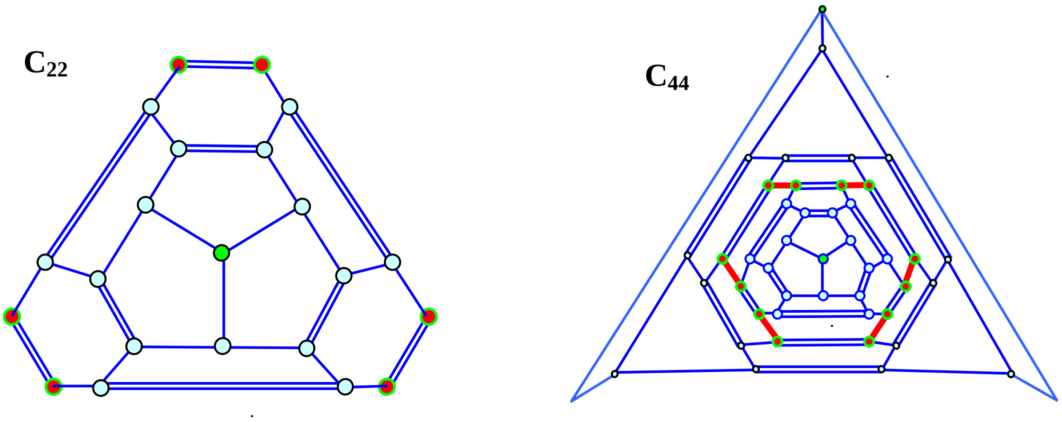

Fig. 4. Graphs of cupola C_{22} and nanotube C_{44}; new covalent bonds are heavy red lines

3. Reaction between two cupolas C_{24}

Similar to the previous reasoning one may consider the atomic configurations corresponding to reaction $C_{24} + C_{24} \rightarrow (C_{24}C_{24}) \rightarrow C_{48}$ between two cupolas C_{24}. As before, we have rotation-reflection-symmetry joining (Fig. 5). The graphs of reacting molecules and polyhedron obtained are shown in Figure 6; they enable us to gain a better insight into the symmetry of the process. The atomic configuration of initial cupola consists of one trigon, three pentagons and six hexagons; due to the fusion there appear six new hexagons and so we have two trigons, six pentagons and eighteen deformed hexagons forming a polyhedron.

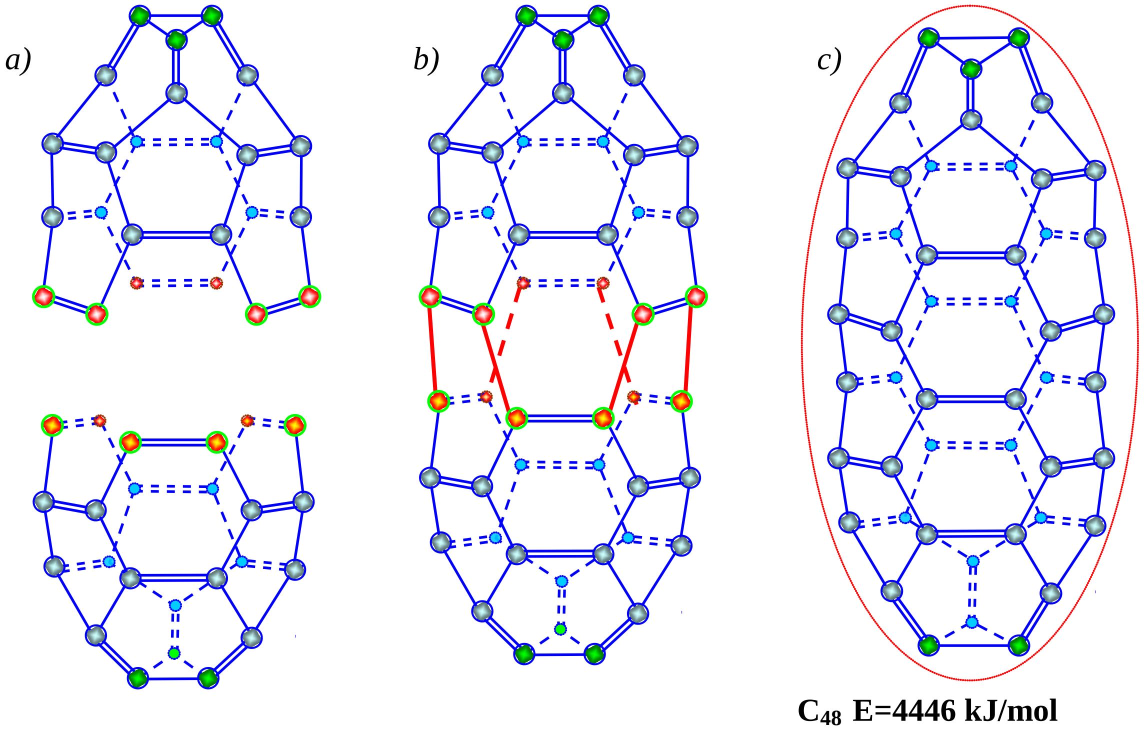

Fig. 5. Joining two cupolas C_{24}: *a*) separate cupolas C_{24}; *b*) intermediate compound; covalent bonds (blue lines), neutral atoms (blue spheres); reacting atoms (red spheres), new covalent bonds (heavy red lines), *c*) nanotube C_{48} after relaxation

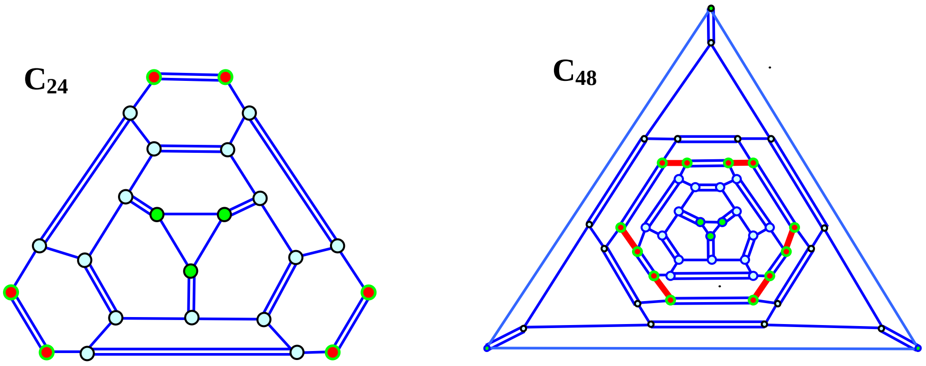

Fig. 6. Graphs of cupola C_{24} and nanotube C_{48}; new covalent bonds are heavy red lines

4. Reaction between two cupolas C_{32}

The procedure for visualization of reaction $C_{32}+C_{32}\rightarrow(C_{32}C_{32})\rightarrow C_{64}$ is the same as before (Figs. 7 and 8). The atomic configuration of initial cupola consists of one square, four pentagons and eight hexagons; due to the fusion there appear eight new hexagons and so we have two squares, eight pentagons and twenty-four hexagons forming a polyhedron.

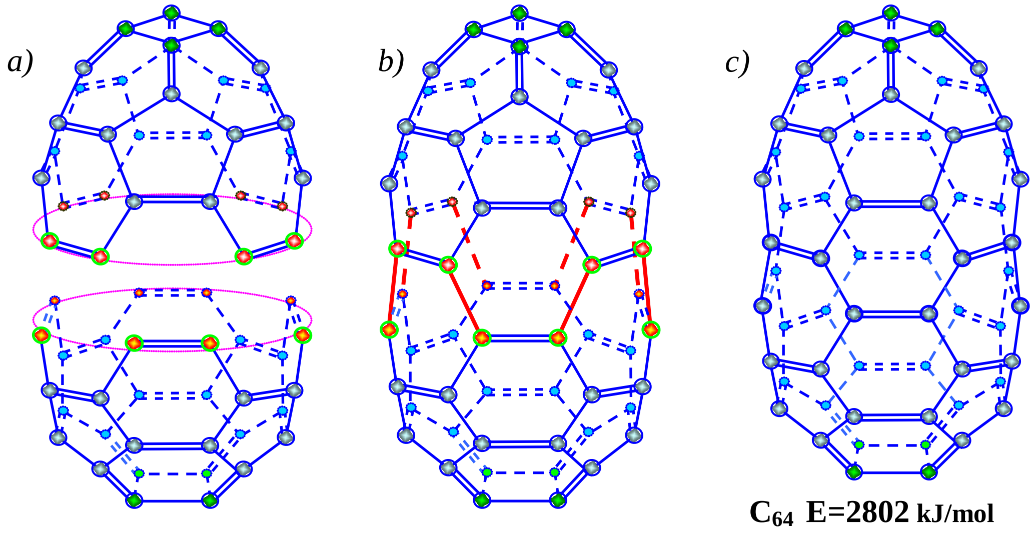

Fig. 7. Rotation-reflection-symmetry joining of two half-fullerenes C_{32}: *a*) separate cupolas C_{32}; *b*) intermediate compound; covalent bonds (blue lines), neutral atoms (blue spheres), reacting atoms (red spheres), new covalent bonds (heavy red lines); *c*) fullerene C_{64} after relaxation

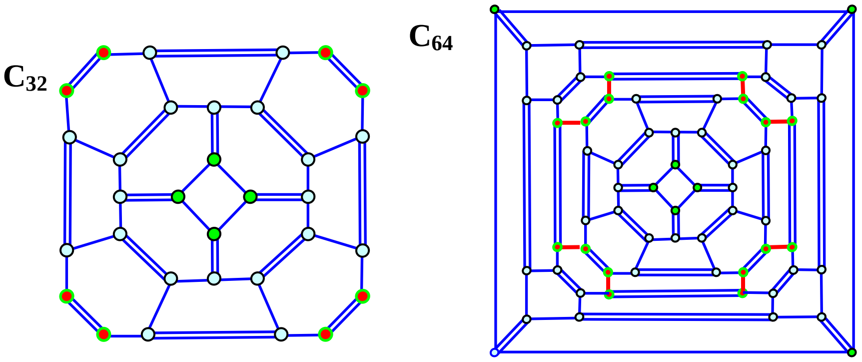

Fig. 8. Graphs of cupola C_{32} and fullerene C_{64}; new covalent bonds are heavy red lines

5. Reaction between two cupolas C_{40}

The procedure for visualization of reaction $C_{40} + C_{40} \rightarrow (C_{40}C_{40}) \rightarrow C_{80}$ is the same as before (Figs. 9 and 10). The atomic configuration of initial cupola consists of six pentagons and ten hexagons; due to the fusion there appear ten new hexagons and so we have twelve pentagons and thirty hexagons forming a polyhedron.

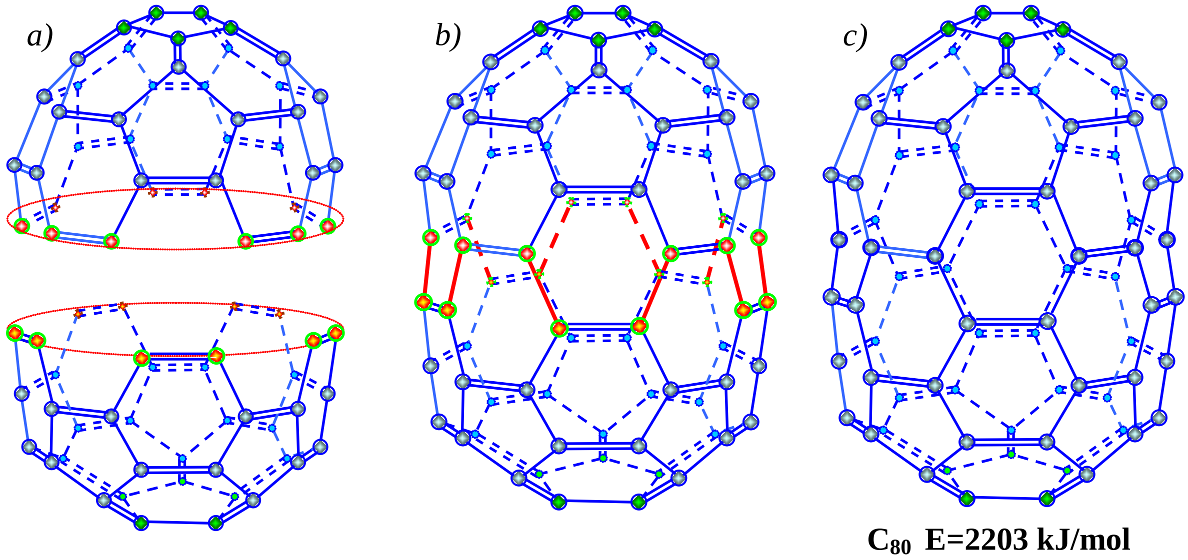

Fig. 9. Rotation-reflection-symmetry joining of two cupolas C_{40}: *a*) separate cupolas C_{40}; *b*) intermediate compound; covalent bonds (blue lines), neutral atoms (blue spheres), reacting atoms (red spheres), new covalent bonds (heavy red lines); *c*) fullerene C_{80} after relaxation

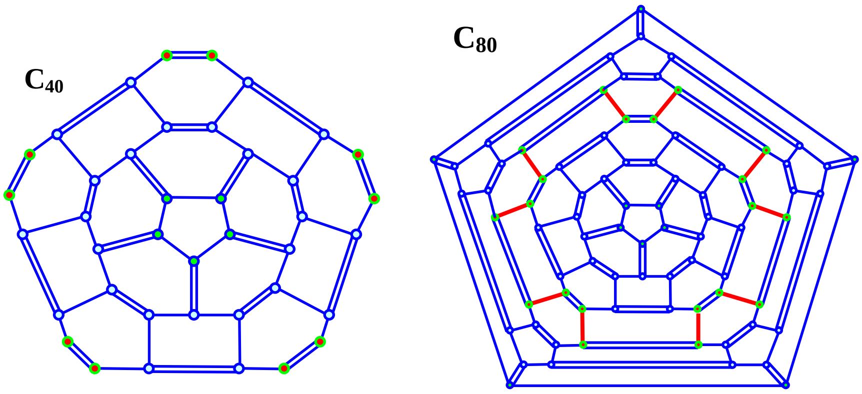

Fig. 10. Graphs of cupola C_{40} and fullerene C_{80}; new covalent bonds are heavy red lines

6. Reaction between two cupolas C_{48}

The procedure for visualization of reaction $C_{48} + C_{48} \rightarrow (C_{48}C_{48}) \rightarrow C_{96}$ is similar to the previous cases and is shown in Figs. 11 and 12. The atomic configuration of initial cupola half-fullerene consists of six pentagons and thirteen hexagons; due to the fusion there appear twelve new hexagons and so we have twelve pentagons and thirty-eight hexagons forming a polyhedron.

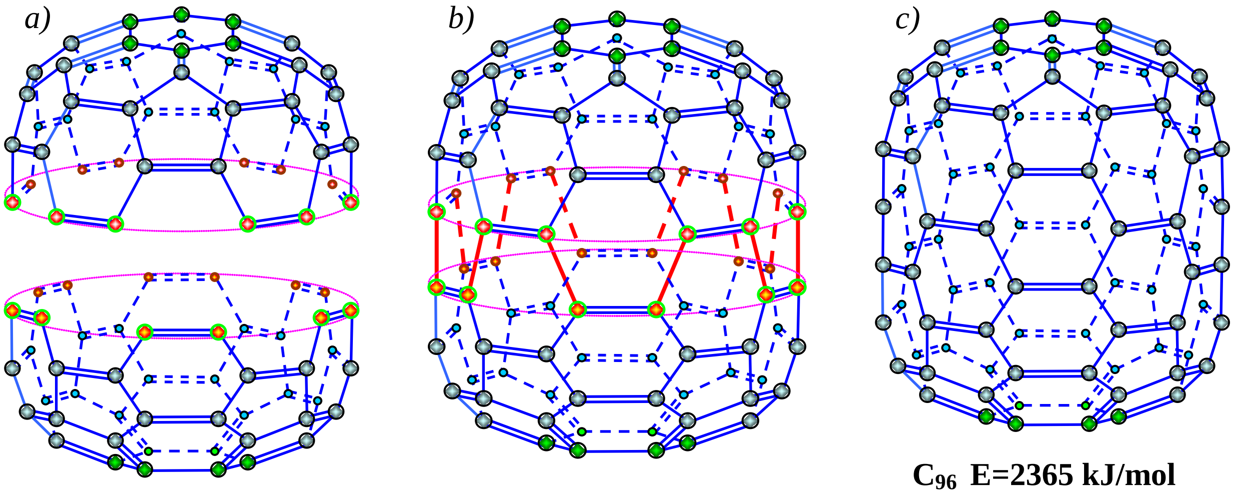

Fig. 11. Rotation-reflection-symmetry joining of two cupolas C_{48}: *a*) separate cupolas C_{48}; *b*) intermediate compound; covalent bonds (blue lines), neutral atoms (blue spheres), reacting atoms (red spheres), new covalent bonds (heavy red lines); *c*) fullerene C_{96} after relaxation

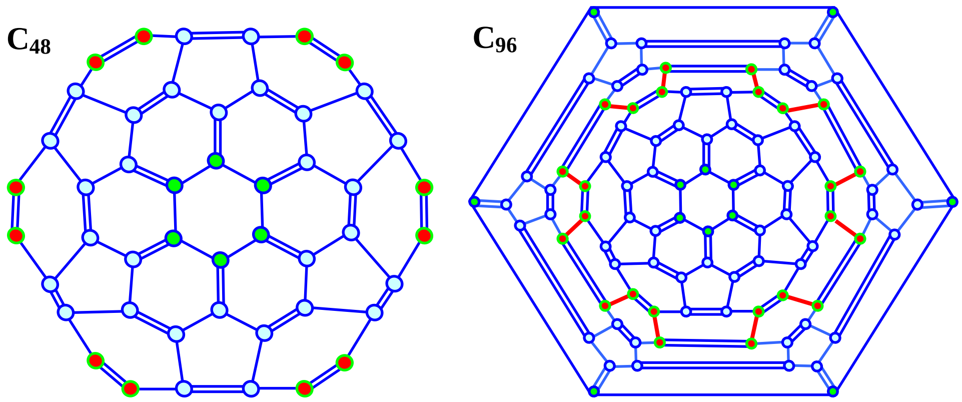

Fig. 12. Graphs of cupola C_{48} and fullerene C_{96}; new covalent bonds are heavy red lines

7. Discussion

Today there are a lot of papers on fullerene properties. Using different computational methods (there are also a lot of programs), the authors calculate the properties of the most popular fullerenes which structure is known. As a result, the numbers obtained contradict to each other and only increase disordered information. The absence of appreciable progress in understanding fullerene nature is determined by the domination of numerical calculations on the known structures. However, any numerical calculations are unable to predict new structures, so the 'numerical progress' results mainly in increasing numerical entropy. It should be emphasized that numerical calculations are not a theory, but a kind of numerical experiment [15].

The theoretical approach to fullerenes is based on the topological and graph treatment. "The fullerene graphs contain all the information we need, and we able to sort through the millions of isomers, finding a few candidates for the most stable, by way of simple, easily computed topological indices for pentagons or hexagons" [16]. At that, the authors define (classical) fullerenes as "cage-like, hollow molecules of pseudospherical symmetry consisting of pentagons and hexagons only, resulting in a trivalent (and in the most ideal case) convex polyhedron with exactly three edges (bonds) joining every vertex occupied by carbon, idealized as sp^2 hybridized atoms".

The theoretical approach to fullerenes, based on the topological and graph treatment, is developed only for classical fullerenes consisting of pentagons and hexagons only. Luckily there is another approach to the fullerenes (classical and non-classical), where "the fullerene is defined 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" [2]. It should be emphasized that there is no restriction on the electronic structure and on the polyhedrons; they can be not only pentagons and hexagons, but also triangles, square and heptagons. Such approach allowed obtaining possible forms of mini-fullerenes from C_4 and C_{20}. At that, we have constructed graphs for all the mini-fullerenes [2, 4] and incorporated them into the family of classical fullerenes.

In Ref. [17] we have considered forming fullerenes and nanotubes in the context of a single graph approach. In this study we have obtained the fullerenes which geometrically resemble in some aspects small nanotubes. The question arises where the boundary between fullerenes and nanotubes is. An intuitive idea says: a fullerene is a spheroid; a nanotube with open ends is a cylinder; a nanotube with closed ends is a cylinder with two hemispheres. However the effort to reduce physical phenomena to mathematics can justify hopes only at the early stage of investigation. We need an exact quantitative criterion. Under these circumstances we should look at the electron theory for clues.

Electronic aspects to structure and stability of fullerenes are briefly considered in Ref. [16]. In C_{60}–I_h there are two different types of bonds according to atomic field microscopy (AFM) image. The measured bond lengths are r_{hh} = 1.38(2) Å and r_{hp} = 1.4654(12) Å. This fullerene is considered as an ideal one, having only equal isolated pentagons and forming a perfect sphere. The larger bonds are singular, the lesser bonds are double ones. Therefore in an ideal fullerene each hexagon has three single and three double bonds. In contrast to this, in an ideal nanotube with open ends there are only has 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 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.

8. Conclusion

The growth of fullerenes through a series of joining reactions of cupola half-fullerenes C_{22}, C_{24}, C_{32}, C_{40}, and C_{48} is considered. We supposed that during the reactions new covalent bonds are formed; the final structure of fullerenes is obtained through the use of geometric modeling. The fullerene symmetry is shown by means of graphs constructed. The geometric modeling is very effective as a first step of a computer simulation. The reason is that any molecular mechanics 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 (C_{20} – C_{60}) and maxi-fullerenes (> 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 the geometric modeling allows one to imagine from the very beginning a possible way of growing carbon clusters and thereby to decrease the number of configurations being worth for studying. Using geometrical modeling we obtained fullerenes C_{44}, C_{48}, C_{64}, C_{80}, and C_{96} fullerenes having the form close to an ellipsoid of revolution. All of them, except fullerene C_{44}, have isolated pentagons. The final structure of the fullerenes is optimized through the use of Avogadro package.

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