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FULLERENES OF THE ΔN=10 SERIES

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Abstract. Fusion reactions of cupola half-fullerenes C_{10}, C_{12}, C_{16}, C_{18}, C_{20}, C_{24}, C_{30} and C_{36} 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. However, in some case self-organization of unshared electron pairs prevails. The energy of fullerenes C_{26}, C_{30}, C_{40}, C_{50} and C_{60} obtained is calculated and is explained in the context of strain-related stability as well as in the framework of interaction of electron valence pairs.

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

1. Introduction

The formation mechanism of fullerenes is still disputable and unresolved question. Many different models have been proposed to explain their arising. The known mechanisms can be categorized into two major groups: bottom-up and top-down models [1]. In the first case, fullerene cages and nanotubes are considered to be formed from carbon atoms and small carbon clusters. In the second case, fullerenes and nanotubes are thought as direct transformation of graphene into fullerenes and nanotubes. However the fullerenes can be also imagined to grow by reacting with each other, similar to bubbles in a soap solution. In Ref. [2] we considered this possibility using geometrical modeling. As a result, we have found the Δn=8 periodicity for the family of C_n fullerenes originating from the reactions:

$C_{12}+C_{12} \rightarrow C_{24}$, $C_{16}+C_{16} \rightarrow C_{32}$, $C_{20}+C_{20} \rightarrow C_{40}$, $C_{24}+C_{24} \rightarrow C_{48}$.

The structures obtained have threefold, fourfold, fivefold and sixfold symmetry. Earlier we obtained the Δn=4 periodicity for the family of barrel-shaped mini-fullerenes C_{12}, C_{16}, C_{20}, C_{24} [3] and the Δn=6 periodicity for both the family of truncated bipyramids and the family beginning with a bi-shamrock (bi-trefoil); both families consisting of fullerenes C_{14}, C_{18}, C_{24}, C_{30}, C_{36} [4]. All these periodicities have one and the same main characteristic feature; the fullerene structure changes from threefold symmetry to sixfold through four and fivefold ones. For this reason, it seems reasonable to take this feature as a basis for fullerene classification. The question arises of whether there are other periodicities having the same symmetry character.

To answer this question, in this contribution we consider the growth of fullerenes through a series of joining reactions of cupola half-fullerenes C_{10}, C_{12}, C_{16}, C_{18}, C_{20}, C_{24}, C_{30}, and C_{36}. It will be shown that there appears the Δn=10 periodicity that allows extend the range of Δn periodicities.

2. Fusion reactions of cupola half fullerenes

In 1889 Svante August Arrhenius postulated that a chemical reaction goes in the following way. 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 follows $A + B \to (AB) \to C$. In Ref. [2] 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=10 series.

Reaction between two cupolas C_{10} and C_{16}. In Figure 1 the atomic configurations corresponding to reaction $C_{10} + C_{16} \to (C_{10}C_{16}) \to C_{26}$ between two cupola-half-fullerenes are shown. At first two molecules are moving towards each other (Fig. 1, *a*). Then the boundary atoms, marked in dark-red, interact with each other producing a compound (Fig. 1, *b*). During this process new covalent bonds (heavy red lines) are generated. As a result, a distorted polyhedron is created which relaxes into a perfect polyhedron (Fig. 1, *c*). Its atomic configuration consists of three hexagons and twelve pentagons, so it can be named a hexa$_3$-penta$_{12}$ polyhedron. It is worth noting that the structure of this fullerene was also obtained by embedding dimer C_2 into fullerene C_{24} [5]; the dimer-embedding model being suggested by Endo and Kroto for the first time in 1992 [6].

Reaction between two cupolas C_{12} and C_{18}. Similar to the previous reasoning, let us consider the atomic configurations corresponding to reaction $C_{12} + C_{18} \to (C_{12}C_{18}) \to C_{30}$. As before, at first two molecules are moving towards each other (Fig. 1, *d*). Then the boundary atoms interact with each other producing a distorted polyhedron with the new covalent bonds (Fig. 1, *e*; heavy red lines) which relaxes into a perfect polyhedron (Fig. 1, *f*). It is worth noting that the structure and graph of this fullerene were also obtained by embedding three dimers into a tri$_2$-tetra$_3$-hexa$_9$ fullerene C_{24} [7]. Since its atomic configuration consists of two triangles, three set of adjacent pentagons and nine hexagons; it was named a tri$_2$-penta$_6$hexa$_9$- polyhedron.

Reaction between two cupolas C_{16} and C_{24}. The procedure for visualization of reaction $C_{16} + C_{24} \to (C_{16}C_{24}) \to C_{40}$ is the same as before. The atomic configuration corresponding to a perfect polyhedron consists of two squares, eight pentagons and twelve hexagons (Fig. 1, *i*), so it can be named a tetra$_2$-penta$_8$-hexa$_{12}$ polyhedron. It is worth noting that the structure and graph of this fullerene can be obtained by embedding four dimers into a tetra$_6$-hexa$_{12}$ polyhedron C_{32}.

Reaction between two cupolas C_{20} and C_{30} can be written as $C_{20} + C_{30} \to (C_{20}C_{30}) \to C_{50}$. The atomic structure corresponding to a perfect polyhedron (Fig. 1, *i*) consists of two isolated pentagons, five sets of adjacent pentagons and fifteen hexagons, so it can be named a penta$_{12}$-hexa$_{15}$ polyhedron. It is worth noting that the structure and graph of this fullerene can be also obtained by embedding five carbon dimers into a tetra$_5$-penta$_2$-hexa$_{15}$ polyhedron C_{40}.

Reaction between two graphene fragment C_{24} and cupola C_{36}. The procedure for visualization of reaction $C_{24} + C_{36} \to (C_{24}C_{36}) \to C_{60}$ is the same as before. The atomic structure corresponding to a perfect polyhedron (Fig. 1, *o*) consists of six sets of adjacent pentagons and twenty hexagons, so it can be named a penta$_{12}$-hexa$_{20}$ polyhedron. It is worth noting that the similar structure and graph of this fullerene can be also obtained using Endo-Kroto model by embedding six carbon dimers into a tetra$_6$-hexa$_{20}$ polyhedron C_{48}.

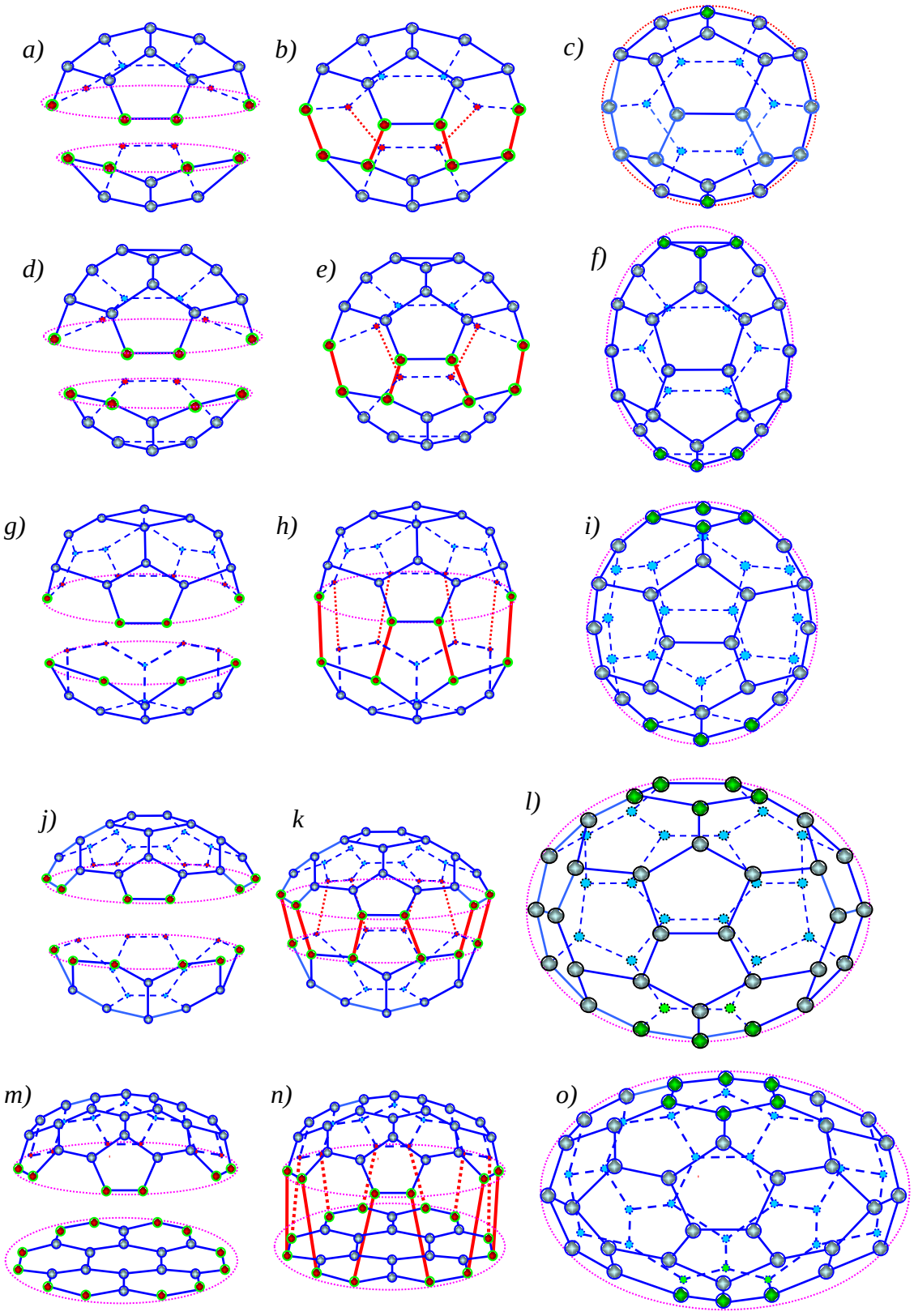

Fig. 1. Joining of cupolas C_{10}, C_{12}, C_{16}, C_{18}, C_{20}, graphene fragment C_{24}, cupola C_{30}, and cupola C_{36}; separate carbon cupolas (*a*, *d*, *g*, *j*, *m*); intermediate compounds (*b*, *e*, *h. k*, *m*); polyhedrons after relaxation (*c*, *f*, *i*, *l*, *o*, *m*). Dark-red and light-blue balls are reacting and neutral atoms, respectively; thin light-blue solid and dashed lines are covalent bonds; heavy dark-red solid and dashed lines are new covalent bonds.

3. Single and double bonds, energy

Atomic force microscopy clearly showed [8] the two different types of bonds for symmetry equivalent hexagons in fullerene C_{60}. The measured bond lengths are $r_{hh}=1.38\,(2)$ Å and $r_{hp}=1.454\,(12)$ Å. The short bonds are attributed to double bonds. Knowing this fact, it is not difficult to incorporate the double bonds into the structure of fullerene C_{60} [9, 10]. But how it can be done in the case of other fullerenes and cupolas?

We assume that the symmetry of double bonds location about the major axis of cupolas and fullerenes coincides with that of fullerene C_{60}. Using this postulate, we have all the necessary input data for the optimization of the fullerene and cupola structures designed by means of geometric modeling and for subsequent calculation of their properties. As it was described above, the cupolas having one and the symmetry can react with each other producing fullerenes C_{30}, C_{40}, C_{50}, and C_{60} with single and double covalent bonds and, in the case of fullerene C_{26}, with partially delocalized bonds too. The optimized structures of these fullerenes obtained through the use of Avogadro package [11] are shown in Figure 2. It should be emphasized that we developed a modified geometric graphics because the package graphics is incomprehensible.

We have calculated formation energies of the fullerenes (Fig. 2). The energy change for fullerenes C_{30}, C_{40}, C_{50} and C_{60} can be easily explained in the context of the second from “five basic empirical arguments” formulated by Harold Kroto who shared the 1996 Nobel Prize for chemistry for his co-discovery of fullerenes [12].

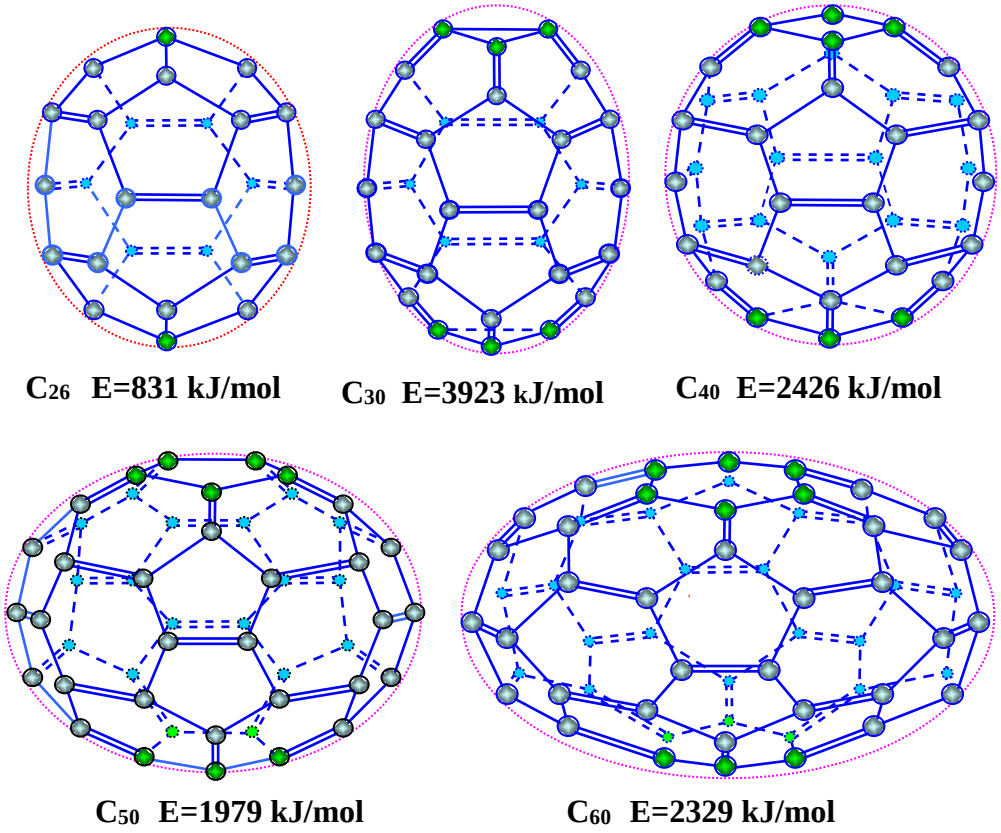

Fig. 2. Structure and energy of the Δn=10 series fullerenes with single and double bonds.

Polyaromatic hydrocarbons with five- and six-membered rings are abundant, but three- and four-membered rings are very unstable and seven-membered ones are rare. This suggests that only 5/6–ring networks are likely to occur readily. The cages must contain 12 pentagonal rings, but the number of hexagonal ones is not directly restricted.

Really, this is reflected in the structure and energy of fullerenes mentioned above, but this argument cannot explain why fullerene C_{26} has the least energy which drastically differs from that of fullerene C_{50}; both fullerenes have a similar structure formed from pentagons and hexagons only. We assume that the reason of discrepancy lies in ignoring an electron structure of fullerenes.

4. Graph representation and electronic structure

Today there is no clear and unique theory of fullerene growth. "The problem is not the lack of imagination, because quite numerous models have been proposed. What is rather lacking is a model using quantities that might be evaluated and measured. Moreover, a theoretical model, in order to deserve its name, should lead to numerical predictions. In order to represent something more than a set of circular arguments, a model should predict more numerical values, parameters or functional relations than the number of input parameters" [13].

At this time there are a lot of papers on fullerene properties [14, and 277 references therein]. 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. To our mind, the absence of appreciable progress in understanding fullerene nature is determined by the domination of numerical calculations on the known structures. However, such 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 [10, and 350 references therein]. "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" [10]. 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".

Earlier we have used 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 [16]. Such geometrical approach allowed obtaining possible forms of mini-fullerenes from C_4 and C_{20}. At that, we have constructed graphs for all thee mini-fullerenes [3, 17]. The graph analysis simplifies an understanding of both the ways of fullerene growth and their structures obtained.

Consider the graphs which characterize the formation of the fullerenes of the $\Delta n=10$ series (Fig. 3). From the graph representation it follows that the main difference of fullerene C_{26} from others is the absence of double bonds in the graph center. Therefore the electronic structure in this area of fullerene C_{26} differs from that of other fullerenes. In other words, fullerene C_{26} does not refer to classical fullerenes defined in Ref. [10]. Let us take up the situation in more detail.

In 1940 Sidgwick and Powell supposed that the geometry of a forming molecule is dictated by repulsion of valence electron pairs [18, 19]. They formulated the following rule: electron pairs arrange themselves inside the valence shell of an atom into such configuration which ensures their maximal removing from each other. In other words, the electrons pairs behave themselves as if were repelling each other similar to point charges. The assumption is in a good agreement with experimental data for more than 1500 molecules.

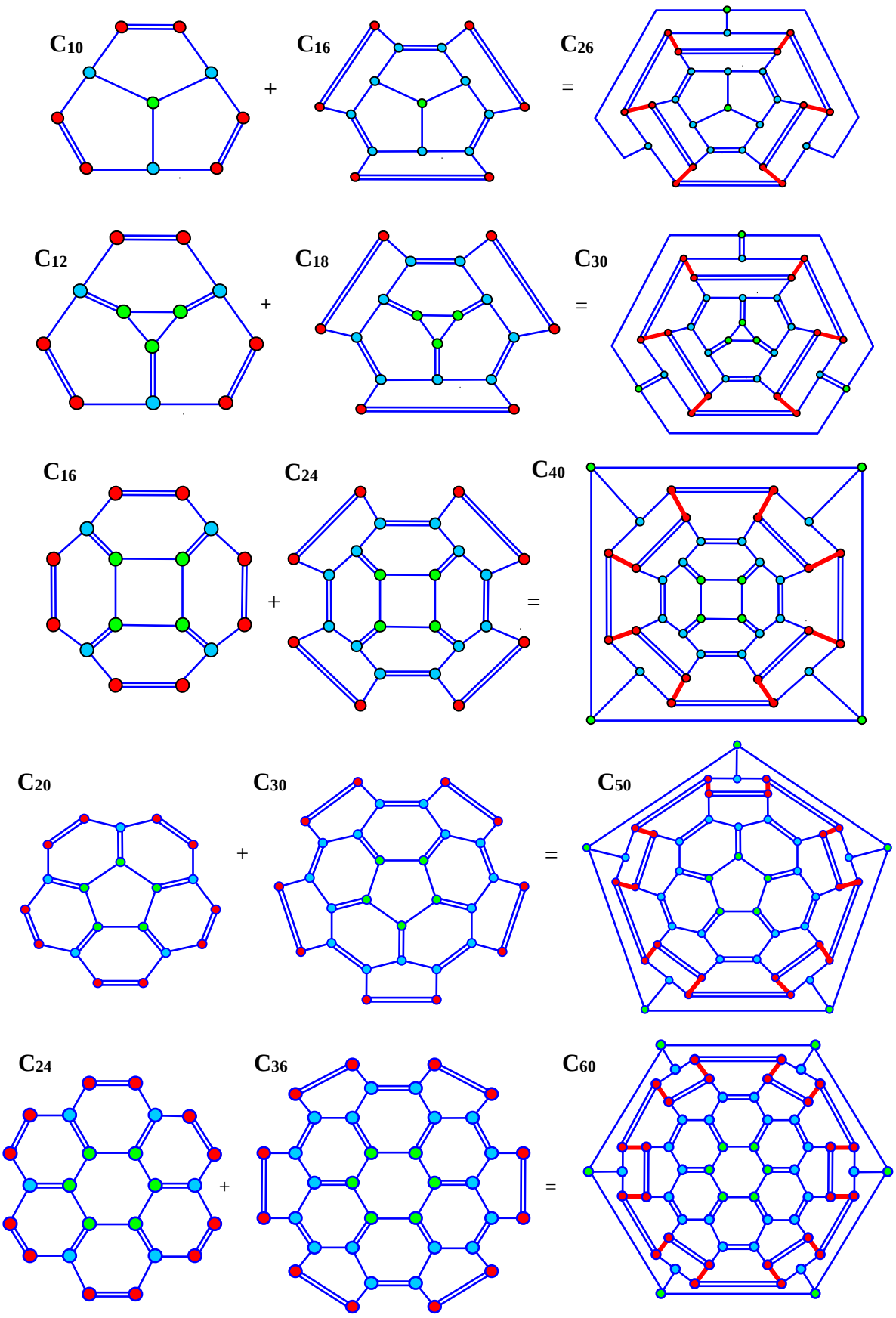

Fig. 3. Fusion reactions of cupolas as connection of two graphs; all notations are the same as before.

If each electron pair present as a point and to connect the points by direct lines, one obtains the electronic configuration of chemical bonds [19, 20]. Each configuration at a given number of electron pairs can create several space molecular structures. It depends on the number of binding and unshared pairs.

Denote a central atom of a molecule by letter *A* and a noncentral atom by *B*. Let a molecule AB_4 has no multiple bonds. For four binding electron pairs, the configuration is a tetrahedron, and we have a tetrahedral molecule, for example, methane (Fig. 4). Here the atomic configuration repeats the electronic. For a molecule AB_3 the valence shell of which contains three binding pairs and one unshared, the situation is radically different. Here the unshared electron pair is on a line which connects the central atom with one of tetrahedron apices. As a result, the molecule has the form of pyramid, for example, a molecule of ammonia (Fig. 4). In this case the electronic and atomic configurations do not coincide and we have so called *hidden symmetry* [21].

We studied the growth of fullerene C_{26} from methane through isobutene and carbon hydrides, conserving three-fold symmetry, to its final form and have come to conclusion that C_{26} has the electronic structure shown in Figure 4.

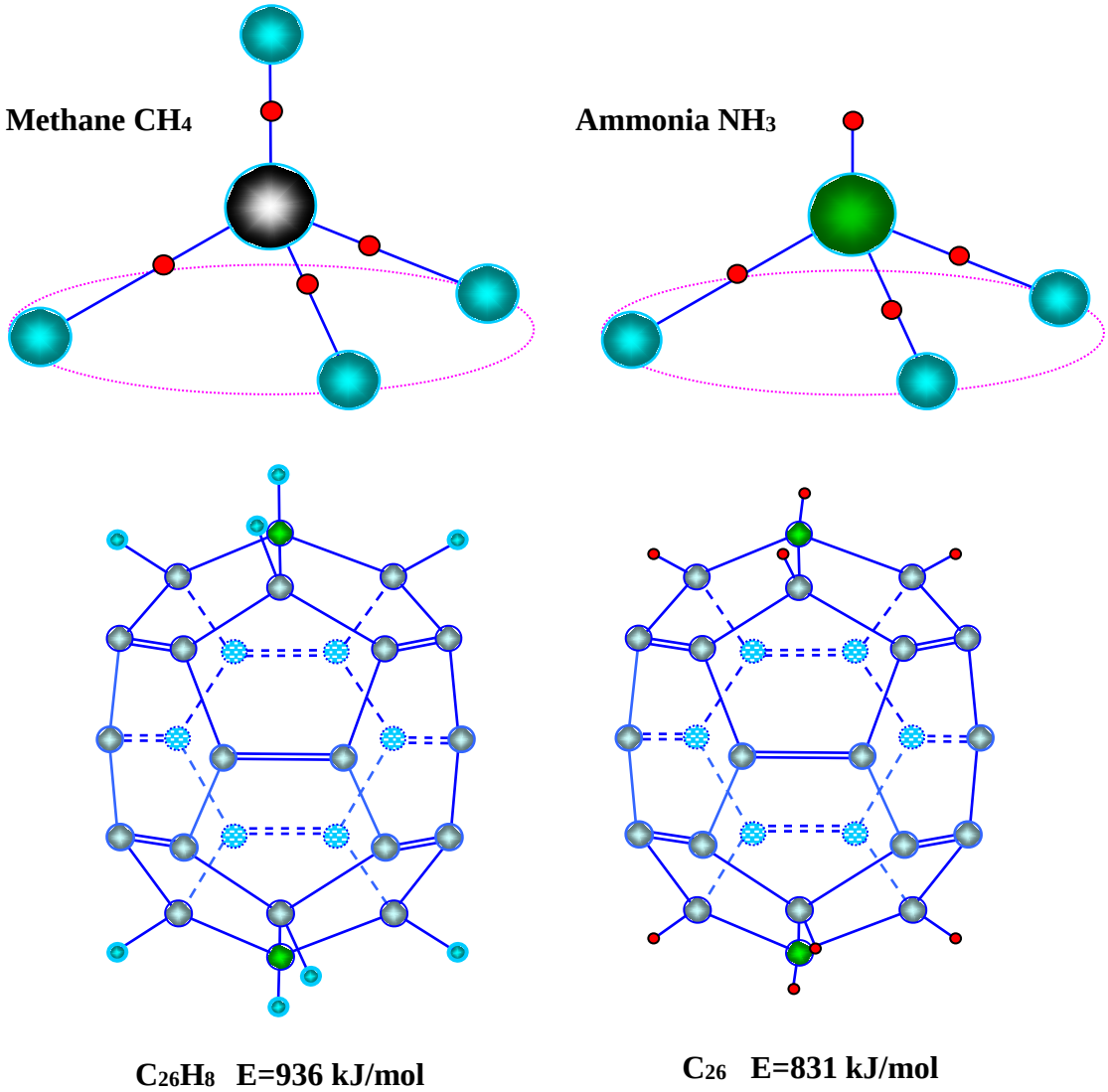

Fig. 4. Methane, ammonia, fullerene hydride $C_{26}H_8$ and fullerene C_{26} having three-fold symmetry; red dots denote electron pairs.

Therefore fullerene C_{26} does not represent a classical fullerene which is defined as "a convex polyhedron with exactly three edges (bonds) joining every vertex occupied by carbon, idealized as sp^2 hybridized atoms". To our mind, fullerene C_{26} consists only of sixteen sp^2 hybridized atoms (as in a classical fullerene) and eight sp^3 hybridized carbon atoms having unshared electron pairs much as nitrogen atom in ammonia.

5. Conclusion

In this contribution fusion reactions of cupola half-fullerenes C_{10}, C_{12}, C_{16}, C_{18}, C_{20}, C_{24}, C_{30} and C_{36} 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. However, in some case self-organization of unshared electron pairs prevails. The energy of fullerenes C_{26}, C_{30}, C_{40}, C_{50} and C_{60} obtained is calculated and is explained in the context of strain-related stability as well as in the framework of interaction of electron valence pairs.

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