IV. CONCLUSION

Referring to results obtained, we may conclude that $Ag(PMe_3)_2$ and $(Ag(PMe_3)_4$ satisfying the main requirements of the stability and toxicity could be used as precursors for FEBID. $Ag(PMe_3)_3$ could not be used as precursor because of low chemical stability

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GEOMETRIC MODELING OF MIDI-FULLERENE GROWTH FROM C_{40} TO C_{68}

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I. INTRODUCTION

Most investigations of fullerenes have centered on either obtaining these materials experimentally or studying properties of the materials which structure was known before. Are there fullerenes smaller than C_{60} and other than known ones which are stable enough to be discovered? The comprehensive experimental study on small or middle-size fullerenes revealed the following [1]. In the mass spectra of products of benzene pyrolysis, the authors found out the ions of all kinds of carbon molecules including small carbon molecules (C_3-C_{20}) and "quasi-fullerenes" C_{21}, C_{23}, C_{33}, C_{48}, C_{52}, C_{54}, C_{56} and C_{58}. (We conserve here the terminology by the authors). However, up to now the structure of these molecules is unknown. To our mind, the crucial questions for advanced applications of these materials are: how the materials are originated, what structure they obtain during growth, and how to classify them. Answer to these questions gives the possibility to develop nanotechnology on a scientific basis.

Numerous theoretical calculations have been performed for smaller fullerenes which structure was postulated by the founding fathers, mainly by H.W. Kroto [2]. However, it should be realized that "Man proposes, God disposes", so even the postulates by famous scientists do not give a guarantee of predicting all the possible structures. We claim that the geometric modeling in combination with the graph theory [3-5] allows not only to postulate a possible way of forming and growing carbon clusters (Man proposes), but to receive their structure automatically. It should be emphasized that the final structure obtained is unknown beforehand and mostly is unexpected for a researcher (God disposes).

Using such approach and taking as a basis different mini-fullerenes, we have designed various families of midi-fullerenes [4] and have carefully studied Endo-Kroto mechanism of growing fullerenes [5-7], according to which a carbon dimer embeds into a hexagon of an initial fullerene. In this case there arises a new atomic configuration and there is mass increase of two carbon atoms. Modeling the growth of fullerenes originating from fullerene C_{24} (D_{3h} symmetry), we have obtained the perfect fullerenes C_{30} and C_{36}

conserving three-fold symmetry. Modeling the growth of fullerenes originating from fullerene C_{32} (D_{4h} symmetry), we have obtained the perfect fullerenes C_{40} and C_{48} conserving four-fold symmetry. The mass difference between successive fullerenes in the first case is Δm = 6, in the second case Δm = 8. It should be emphasized that in both cases the mass difference is equal to a double degree of symmetry. We have supposed that this empirical rule is valid for fullerenes having other symmetries. If it is so, then during the growth of fullerenes originating from fullerene C_{40} (D_{5h} symmetry), it is possible to obtain perfect fullerenes C_{50} and C_{60}, conserving five-fold symmetry; here Δm = 10.

The aim of this contribution is to verify the hypothesis. For this purpose we have studied the growth of the fullerene family which begins with C_{40} through the use of the dimer embedding mechanism. In doing so, we designed the graphs of direct descendents of fullerene C_{40}, namely C_{42}, C_{44}, C_{46}, C_{48}, C_{50}, C_{52}, C_{54}, C_{56}, C_{58}, C_{60}, C_{62}, C_{64}, C_{66}, C_{68}, and C_{68}, and then constructed their structure. On the basis of this investigation we are able to submit a periodic system for embedded fullerenes.

II. FIRST STAGE

The initial perfect fullerene consists of five squares, two pentagons and fifteen hexagons (Figure 1) so it was named a tetra5-penta2-hexa15 polyhedron. Its graph was designed in Ref. [4], the structure being obtained in Ref. [8] as the mirror-symmetry fusion reaction of two half fullerenes C_{20}. Starting with this fullerene, one can obtain its direct descendants with the help of mechanism of dimer embedding into a hexagon. Designing the graphs of these fullerenes is easier than drawing axonometric projections. Taking as a basis the structure and graph of fullerene C40, we have obtained the picture shown in Figure 1, where fullerenes C_{40} and C_{50} are perfect (D_{5h} symmetry), fullerenes C_{42}, C_{44}, C_{46} and C_{48} are imperfect (C_1 symmetry).

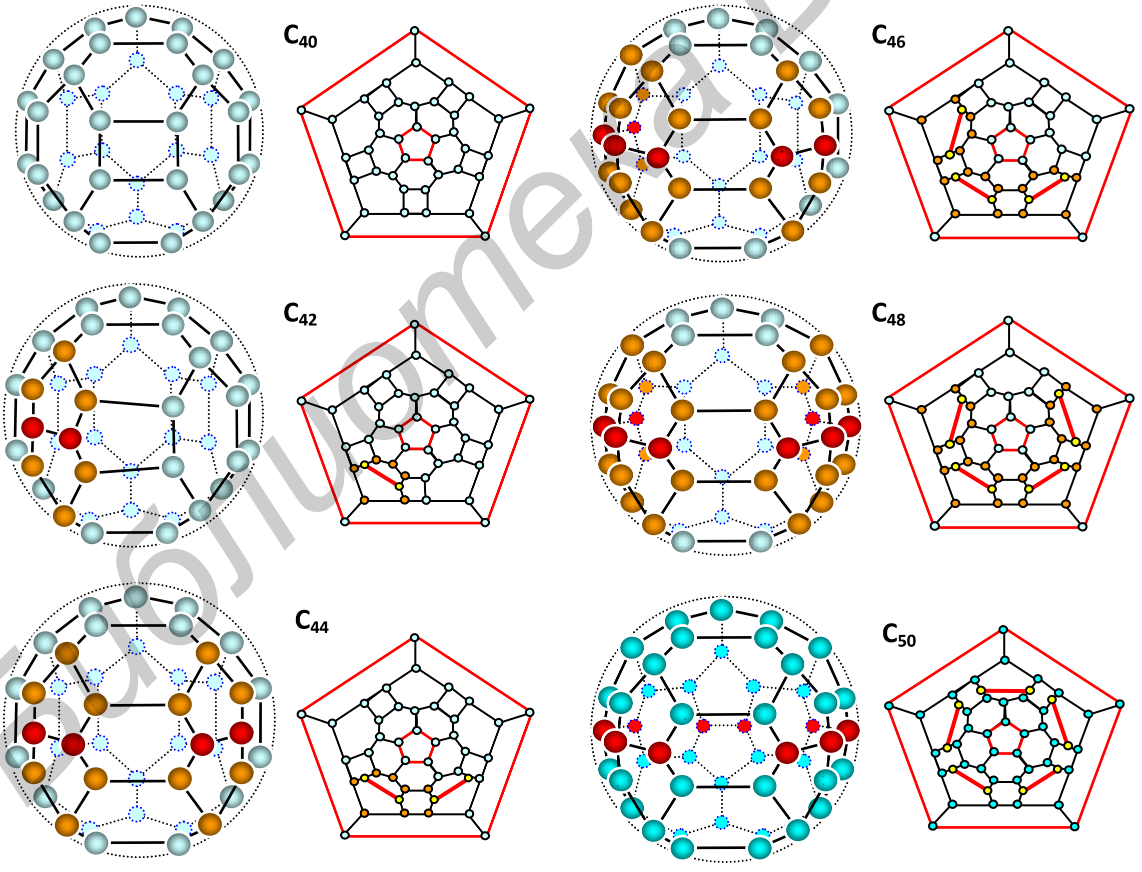

Figure 1 – Atomic structure and graphs of fullerenes C40, C42, C44, C46, C48, and C50

Let us analyze these figures. From the configurations shown it follows that the first embedding, which transforms fullerene C_{40} into fullerene C_{42}, influences deeply only on one of hexagons and two its square neighbors. The hexagon transforms into two adjacent pentagons and its square neighbors become pentagons; the whole fullerene losing five-fold symmetry. The second embedding transforms fullerene C_{42} into fullerene C_{44}. Here one hexagon transforms into two adjacent pentagons, its square neighbor into a pentagon, and its pentagon neighbor into a hexagon. The third embedding (transition from C_{44} to C_{46})

eliminates one more hexagon and two its neighbors, a pentagon and a square; in return it creates an adjacent hexagon of another local orientation and a new pentagon. The fourth imbedding transforms fullerene C_{46} into fullerene C_{48}. At last the fifth embedding which leads to fullerene C_{50} restores the five-fold symmetry.

III. SECOND STAGE

Now the fullerene C_{50} is up against the same problem as the fullerene C_{40} of the four-fold symmetry [7]; it can grow only at an angle to its axes of symmetry. It is connected with the fact that any embedding can be realized only opposite to a direction along which a hexagon has two neighboring mutually antithetic pentagons. During its growth by means of dimer embedding one obtains imperfect fullerenes C_{52}, C_{54}, C_{56}, C_{58} having C_1 symmetry, and one perfect C_{60} with D_{5h} symmetry (Figure 2). The structure of fullerene C_{60} is rather interesting. It is formed of five pairs of two adjacent pentagons along an equator separated with five pairs of two adjacent hexagons. Here the pentagon pairs are specially marked. It should be emphasized that the total number of pentagons during the second stage does not change and is equal to 12.

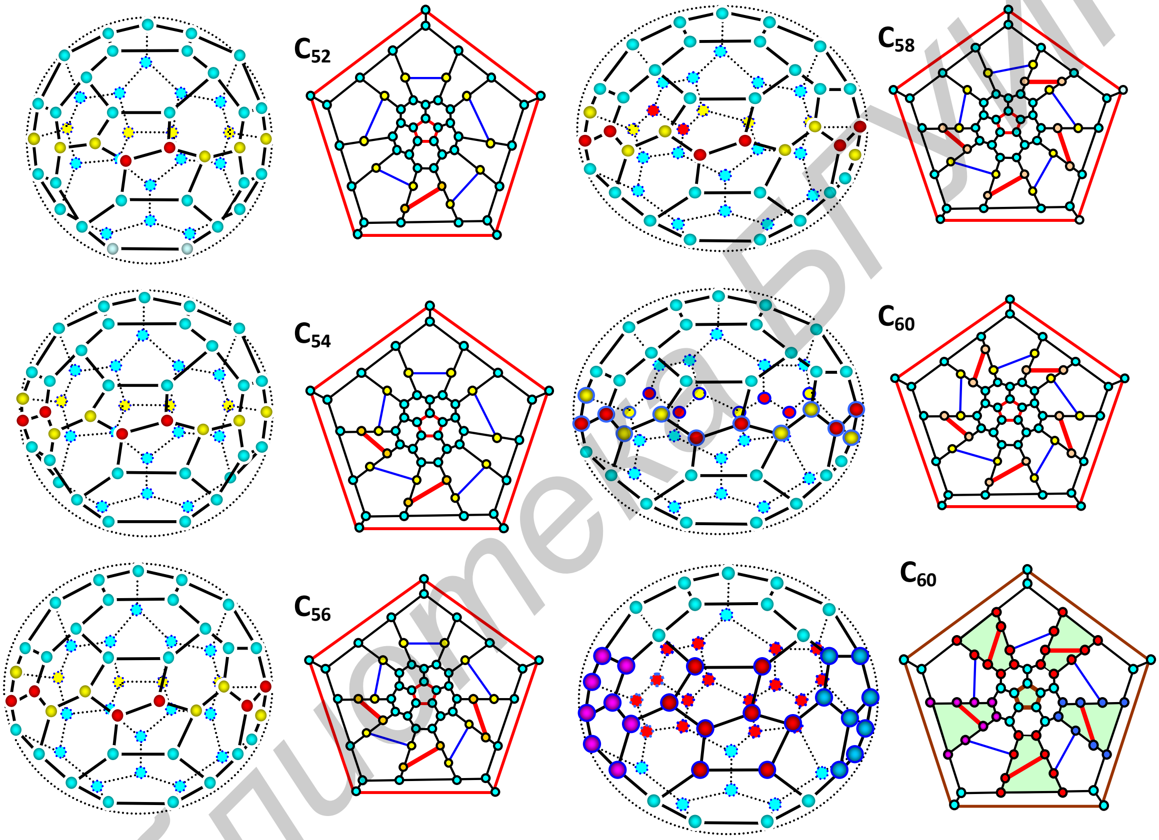

Figure 2 – Atomic structure and graphs of fullerenes C_{52}, C_{54}, C_{56}, C_{58}, and C_{60}

IV. THIRD STAGE: RANDOM GROWTH

The further dimer embedding is shown in Figure 3. The newly formed fullerene C_{62} has three pairs of two adjacent pentagons, one chain of three adjacent pentagons, two former isolated pentagons in the polar zones, and a new formed isolated pentagon in the equatorial zone. After the first embedding, the fullerene can grow in a random way. Some possible isomers are shown in Figure 3. They contain isolated pentagons, adjacent pentagons, and chain of pentagons. However the total number of pentagons during the third stage does not change and is equal to 12.

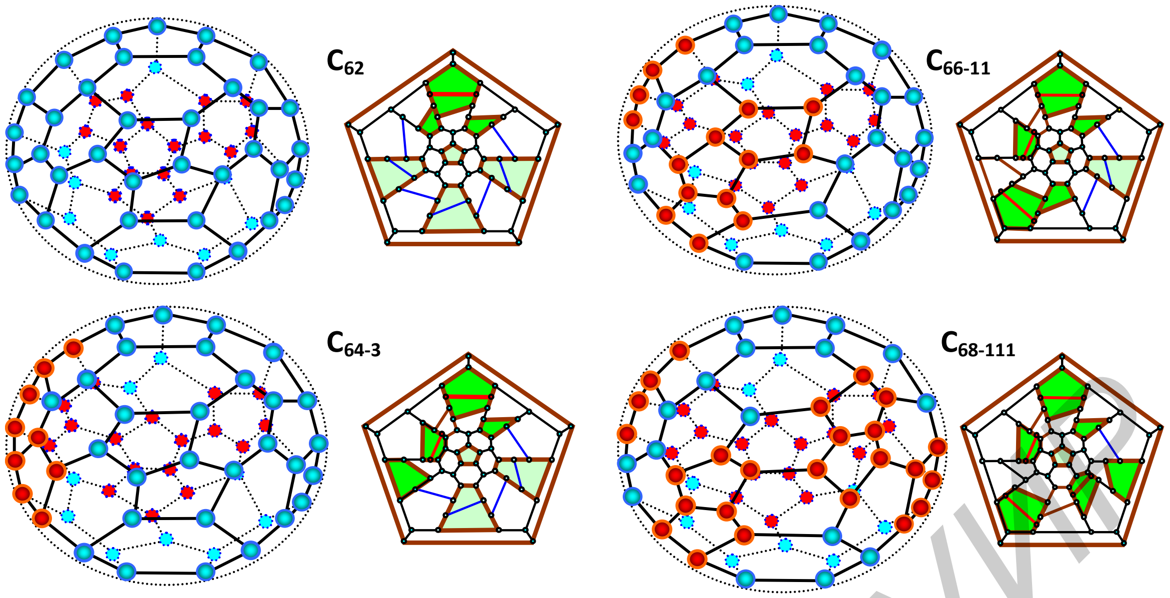

Figure 3 – Atomic structure and graphs of some fullerenes C62, C64, C66, and C68

V. PERIODIC SYSTEM OF EMBEDDED FULLERENES

In the introduction, we have set off for fullerenes the crucial questions from the rest ones; in particular, how the fullerenes are originated and what structure they obtain naturally. However, the most important and most difficult question for any science is classification [9]. On the basis of our investigations we are able to submit the following periodic system for embedded fullerenes.

Periodic table of embedded fullerenes

Symmetry of Fullerenes				
3-fold S $\Delta m=6$	3-fold T $\Delta m=6$	4-fold $\Delta m=8$	5-fold $\Delta m=10$	6-fold $\Delta m=12$
C_{20} C_{22} C_{24}	C_{24} C_{26}, C_{28}	C_{32} C_{34}, C_{36} C_{38}	C_{40} C_{42}, C_{44}, C_{46}, C_{48}	C_{48} C_{50}, C_{52}, C_{54}, C_{56}, C_{58}
C_{26} C_{28}, C_{30}	C_{30} C_{32}, C_{34}	C_{40} C_{42}, C_{44}, C_{46}	C_{50} C_{52}, C_{54}, C_{56}, C_{58}	C_{60} C_{62}, C_{64}, C_{66}, C_{68}, C_{70}
C_{32}	C_{36}	C_{48}	C_{60}	C_{72}

All the fullerenes form five vertical columns (groups), having different symmetry. Two groups of three-fold symmetry 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. We suppose that the fullerenes of one and the same group have similar physical and chemical properties.

Strictly speaking, only the fullerenes denoted by bold symbols have the symmetry of corresponding column. They are ideal (perfect) fullerenes. The others are imperfect or semi-perfect. As noted in Ref. [6] by analogy with crystal physics, the imperfection is connected with extra ‘interstitial’ dimers, playing the role of defects. Let us continue this analogy. In real crystals a long-range order is impossible in the strict sense of the word, because of such defects as dislocations which violate translational symmetry. Nevertheless, the long-range order is observed experimentally, but this order is defined otherwise and is referred to as topological long-range order [10]. Following this example, we define the imperfect fullerenes conserving the main symmetry axis as having topological symmetry.

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STRUCTURE OF THE Δn = 10 SERIES FULLERENES

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I. 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.

II. FUSION REACTIONS OF CUPOLA HALF FULLERENES

In [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 reaction between two cupolas C_{10} and C_{16}. In Fig. 1 the atomic configurations corresponding to reaction $C_{10}+C_{16}\rightarrow(C_{10}C_{16})\rightarrow C_{26}$ between two cupola-half-fullerenes are shown. At first two molecules are moving towards each other (Figure. 1a). Then the boundary atoms, marked in dark-red, interact with each other producing a compound (Figure 1d). 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 (Figure 1g). Its atomic configuration consists of three hexagons and twelve pentagons, so it can be named a hexa3-penta12 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].