

- [4] A.I. Melker, M.A. Krupina, Designing mini-fullerenes and their relatives on graph basis, *Materials Physics and Mechanics*, 20(1) (2014) 18-24.
- [5] A.I. Melker, Growth of midi-fullerenes from twenty to sixty, *Proceedings of NDTCS'2015*, 16 (2015) 34-37.
- [6] A.I. Melker, M.A. Krupina, Geometric modeling of midi-fullerenes growth from C_{24} to C_{48} , *St. Petersburg State Polytechnical University Journal. Phys. and Math.* 3(248) (2016) 52-58.
- [7] M.A. Krupina, A.I. Melker, Geometric modeling of midi-fullerene growth from C_{32} to C_{60} , *St. Petersburg State Polytechnical University Journal. Phys. and Math.* 10 (1) (2017) 47-54.
- [8] A.I. Melker, T.V. Vorobyeva, Fusion reactions of cupola half fullerenes, *St. Petersburg State Polytechnical University Journal. Phys. and Math.* 3(248) (2016), 59-67.
- [9] A.I. Melker, *Dynamics of Condensed Matter*, Vol. 3, Noophysics (Science and Scientists), St. Petersburg Academy of Sciences on Strength Problems, 2016, 151 p.
- [10] A.M. Kosevich, *Physical Mechanics of Real Crystals*, Kiev, Naukova Dumka, 1981, 328 p.

STRUCTURE OF THE $\Delta n = 10$ 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 $\Delta n=8$ periodicity for the family of C_n fullerenes originating from the reactions



The structures obtained have threefold, fourfold, fivefold and sixfold symmetry. Earlier we obtained the $\Delta n=4$ periodicity for the family of barrel-shaped mini-fullerenes C_{12} , C_{16} , C_{20} , C_{24} [3] and the $\Delta n=6$ 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 $\Delta n=10$ 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].

Reaction between two cupolas C_{12} and C_{18} . Similar to the previous reasoning, let us consider the atomic configurations corresponding to reaction $C_{12} + C_{18} \rightarrow (C_{12}C_{18}) \rightarrow C_{30}$. As before, at first two molecules are moving towards each other (Figure 1b). Then the boundary atoms interact with each other producing a distorted polyhedron with the new covalent bonds (Figure 1, e; heavy red lines) which relaxes into a perfect polyhedron (Fig. 1, h). It is worth noting that the structure and graph of this fullerene were also obtained by embedding three dimers into a tri2-tetra3-hexa9 fullerene C_{24} [7]. Since its atomic configuration consists of two triangles, three set of adjacent pentagons and nine hexagons; it was named a tri2-penta6hexa9- polyhedron.

Reaction between two cupolas C_{16} and C_{24} . The procedure for visualization of reaction $C_{16} + C_{24} \rightarrow (C_{16}C_{24}) \rightarrow C_{40}$ is the same as before. The atomic configuration corresponding to a perfect polyhedron consists of two squares, eight pentagons and twelve hexagons (Figure 1, i), so it can be named a tetra2-penta8-hexa12 polyhedron. It is worth noting that the structure and graph of this fullerene can be obtained by embedding four dimers into a tetra6-hexa12 polyhedron C_{32} .

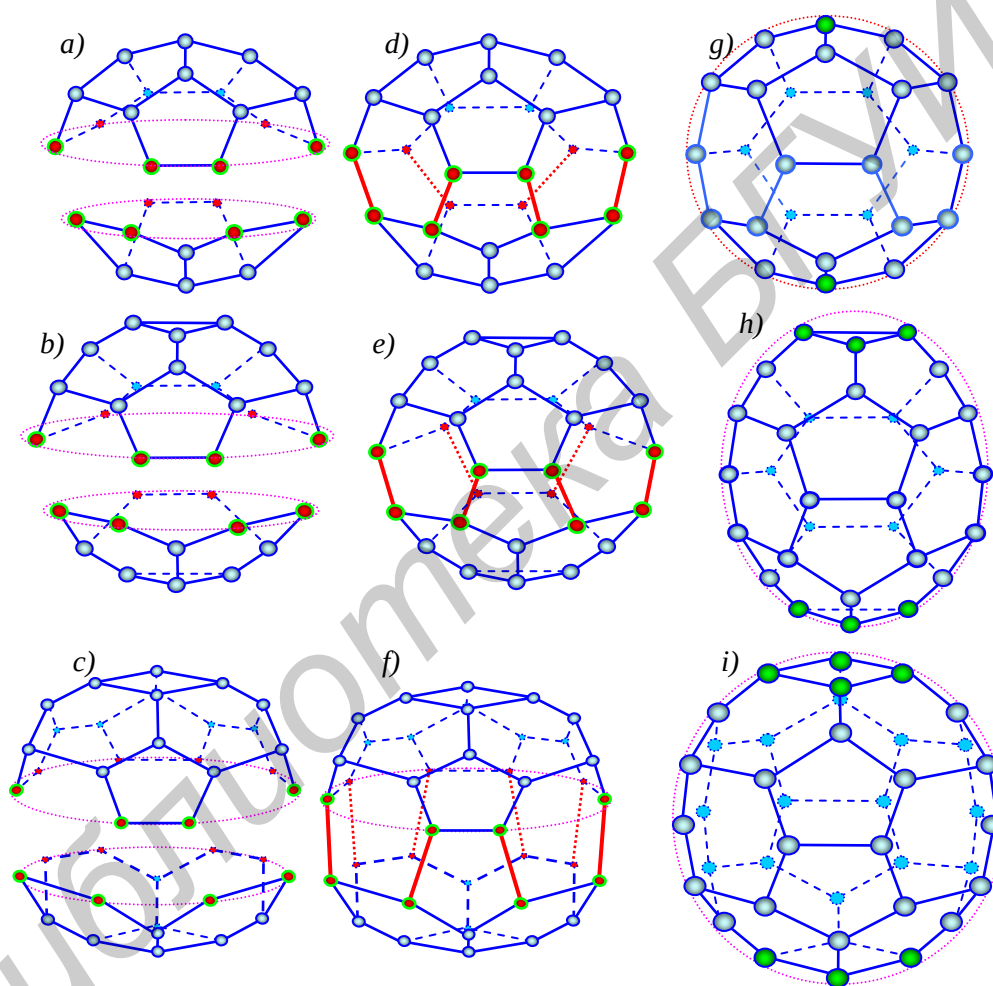


Figure 1 – Joining of two half-fullerenes: C_{10} and C_{16} ; C_{12} and C_{18} ; C_{16} and C_{24} ;
 a, b, c) Separate carbon cupolas; d, e, f) Intermediate compounds; g, h, i) Polyhedrons after relaxation.
 Dark-red and light-blue balls are reacting and neutral atoms, respectively; thin light-blue solid and dashed lines are covalent bonds; heavy dark-red solid and dashed lines are new covalent bonds

Reaction between two cupolas C_{20} and C_{30} can be written as $C_{20} + C_{30} \rightarrow (C_{20}C_{30}) \rightarrow C_{50}$. The atomic structure corresponding to a perfect polyhedron (Figure 2e) consists of two isolated pentagons, five sets of adjacent pentagons and fifteen hexagons, so it can be named a penta12-hexa15 polyhedron. It is worth noting that the structure and graph of this fullerene can be also obtained by embedding five carbon dimers into a tetra5-penta2-hexa15 polyhedron C_{40} .

Reaction between two cupolas C_{24} and C_{36} . The procedure for visualization of reaction $C_{24} + C_{36} \rightarrow (C_{24}C_{36}) \rightarrow C_{60}$ is the same as before. The atomic structure corresponding to a perfect polyhedron (Figure 2f) consists of six sets of adjacent pentagons and twenty hexagons, so it can be named a

penta12-hexa20 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 tetra6-hexa20 polyhedron C_{48} .

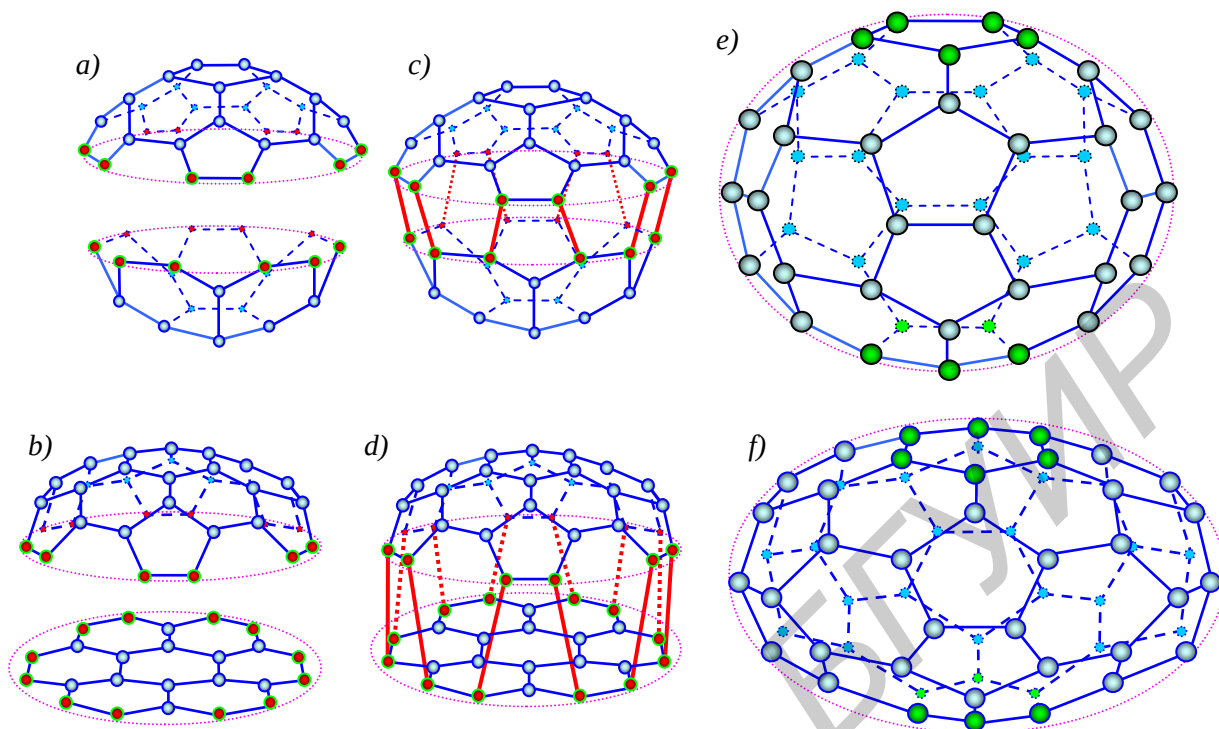


Figure 2 – Joining of two half-fullerenes: C_{20} and C_{30} ; C_{24} and C_{36} ; a, b) Separate carbon cupolas; c, d) Intermediate compounds; e) Polyhedrons after relaxation. Dark-red and light-blue balls are reacting and neutral atoms, respectively; thin light-blue solid and dashed lines are covalent bonds; heavy dark-red solid and dashed lines are new covalent bonds

III. 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 other 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 3. 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 (Figure 3). The energy change for fullerenes C_{30} , C_{40} , C_{50} and C_{60} can be easily explained in the context of strain-related instability [7, 12], however, the least energy obtained unexpectedly for fullerene C_{26} contradicts to this concept and needs more careful investigation. At this point we have a semi-quantitative explanation in the framework of electronic theory of molecule vibrations.

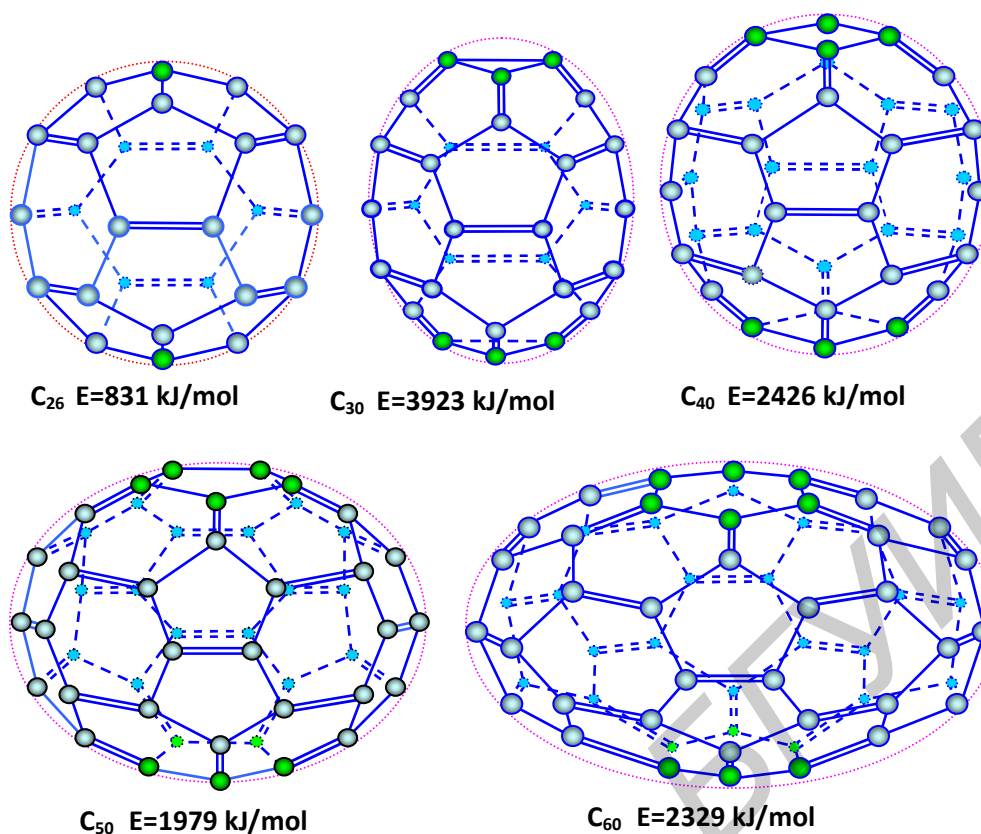


Figure 3 – Structure and energy of the $\Delta n=10$ series fullerenes with single and double bonds

REFERENCES

- [1] A.I. Melker, M.A. Krupina, Geometric modeling of midi-fullerenes growth from C32 to C60, St. Petersburg State Polytechnical University Journal. Phys. and Math. 10 (1) (2017) 47-54.
- [2] A.I. Melker, T.V. Vorobyeva, Fusion reactions of cupola half-fullerenes, St. Petersburg State Polytechnical University Journal. Phys. and Math. 3 (248) (2016) 59-67.
- [3] A.I. Melker, S.A. Starovoitov, T.V. Vorobyeva, Classification of mini-fullerenes on graph basis, Materials Physics and Mechanics, 20 (1) (2014) 12-17.
- [4] A.I. Melker, M.A. Krupina, Designing mini-fullerenes and their relatives on graph basis, Materials Physics and Mechanics, 20 (1) (2014) 18-24.
- [5] M.A. Krupina, A.I. Melker, S.A. Starovoitov, T.V. Vorobyeva, Structure and graphs of midi-fullerenes, Proceedings of NDTCS' 2015. 16 (2015) 23-26.
- [6] M. Endo, H.W. Kroto, Formation of carbon nanofibers, J. Phys. Chem. 96 (1992) 6941-6944.
- [7] A.I. Melker, M.A. Krupina, Geometric modeling of midi-fullerenes growth from C24 to C48, St. Petersburg State Polytechnical University Journal. Phys. and Math. 3 (248) (2016) 52-58.
- [8] L. Gross, F. Mohn, N. Moll, B. Schuler, A. Criado, E. Guitián, D. Peña, A. Gourdon, G. Meyer, Bond-order discrimination by atomic force microscopy, Science 337 (2012) 1326-1329..
- [9] S.V. Kozyrev, V.V. Rotkin, Fullerene. Composition, dynamics of crystal lattice, electronic structure and properties, Fiz. Tverd. Tela 27 (9) (1993) 1409-1434.
- [10] P. Schwerdtfeger, L.N. Wirz, J. Avery, The topology of fullerenes, WIREs Comput. Mol. Sci. 5 (2015) 96-145.
- [11] M.D. Hanwell, D.E. Curtis, D.C. Lonie, T. Vandermeersch, E. Zurek, G.R. Hutchison, Avogadro: an advanced semantic chemical editor, visualization, and analysis platform, Journal of Cheminformatics 4 (17) (2012); Avogadro: an open-source molecular builder and visualization tool. Version 1.XX. <http://avogadro.cc/>
- [12] H.W. Kroto, The stability of the fullerenes C_n, with n= 24, 32, 36, 50, 60 and 70, Nature 329 (1987) 529-531.