

FULLERENES OF THE $\Delta n=12$ SERIES

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Abstract. Fusion reactions of cupola half-fullerenes C_{16} , C_{18} , 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. The energy of fullerenes C_{32} , C_{36} , C_{48} , C_{60} and C_{72} obtained is calculated. The periodic system of basic perfect fullerenes is suggested.

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

1. Introduction

Fullerenes can grow by reacting with each other, similar to bubbles in a soap solution. This possibility was demonstrated by the example of such reaction as $C_{24}+C_4 \rightarrow C_{28}$, $C_{30}+C_30 \rightarrow C_{60}$ through the use of a new molecular dynamics that takes into account simultaneously both atomic and electronic degrees of freedom [1, 2]. In spite of these encouraging results we came to conclusion that the problem of fullerene growth must be split into two: geometry and calculations. The reasons are as follows.

In 1984 it has been found that the time-of-flight mass spectrometry (TOF-MS) distribution of laser-evaporated graphite soot had a bimodal character [3], the low-mass distribution having peaks for C_{11} , C_{15} , C_{19} and C_{23} species with $\Delta n = 4$ periodicity. Little later fullerenes C_{60} and C_{70} were synthesized and a set of simple, empirical chemical and geodesic rules was presented by H.W. Kroto to explain the remarkable stability observed for the C_{60} molecule [4]. The rules yield cluster magic numbers consistent with observation. The authors of the large review having 277 references [5] state: "Today we interpret the TOF-MS distribution as linear carbon chains in the region $1 < n < 10$, macrocyclic rings $10 < n < 30$, and fullerenes $n > 36$ with a forbidden zone between $n=30$ and 36 ".

We can't agree with this interpretation for many reasons, two of the most serious are:

- The interpretation does not explain $\Delta n = 4$ periodicity.
- It was shown through the use of molecular dynamics [6] as well as analytically [7]

that linear chains with free ends and with periodic boundary conditions (rings) are unstable with respect to vibrations; they transform at first into zigzag chains, helices, and then folds into compact structures. The reason is that small longitudinal vibrations transfer their energy to large transversal vibrations. This phenomenon was named as parametric resonance.

In Ref. [8, 9] using the analogy with polymer physics and radiation solid state physics we unexpectedly obtained the $\Delta n = 4$ periodicity for caged carbon molecules C_{12} , C_{16} , C_{20} , C_{24} . The structures have threefold, fourfold, fivefold and sixfold symmetry. Clearly the following reasoning was: if there exists the $\Delta n = 4$ periodicity, provably there are other periodicities.

Really, we have found the $\Delta n=8$ periodicity [10] for the family of C_n fullerenes originating from the reactions of cupolas $C_{10}+C_{10} \rightarrow C_{20}$, $C_{12}+C_{12} \rightarrow C_{24}$, $C_{16}+C_{16} \rightarrow C_{32}$, $C_{20}+C_{20} \rightarrow C_{40}$, $C_{24}+C_{24} \rightarrow C_{48}$, where the structures had also the same symmetry. Since all these periodicities have one and the same main feature, namely, the transition from threefold symmetry to sixfold, it seems reasonable, to take this feature as a basis for fullerene classification and to search other periodicities. It should be noted that calculations performed for small fullerenes are unable to be such a basis on default of any other adequate explanation. For example, for C_{20} the most stable isomer can have a ring, a bowl or a fullerene structure, depending on the computational method employed [11].

In this contribution we consider the growth of fullerenes through a series of joining reactions of cupola half-fullerenes C_{16} , C_{18} , C_{24} , C_{30} , and C_{36} . It will be shown that there appears the $\Delta n=12$ periodicity having the same symmetry transition.

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 $A + B \rightarrow (AB) \rightarrow C$. In Ref. [10] 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.

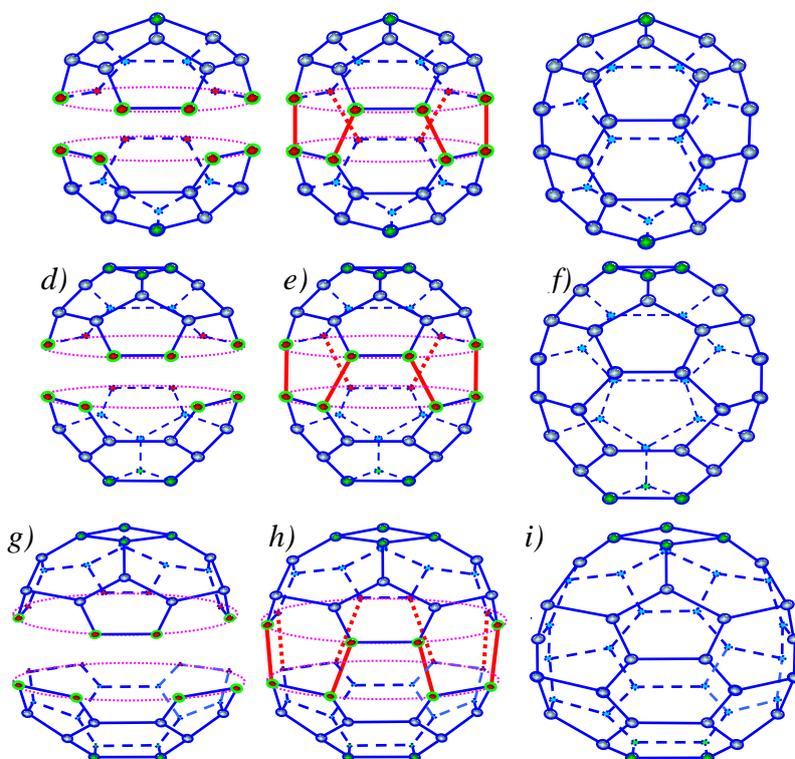
Reaction between two cupolas $C_{16} + C_{16} \rightarrow (C_{16}C_{16}) \rightarrow C_{32}$ is shown in Figure 1 a, b, c.

Reaction between two cupolas $C_{18} + C_{18} \rightarrow (C_{18}C_{18}) \rightarrow C_{36}$ is presented in Figure 1 d, e, f.

Reaction between two cupolas $C_{24} + C_{24} \rightarrow (C_{24}C_{24}) \rightarrow C_{48}$ is displayed in Figure 1 g, h, i.

Reaction between two cupolas $C_{30} + C_{30} \rightarrow (C_{30}C_{30}) \rightarrow C_{60}$ is exhibited in Figure 1 j, k, l.

Reaction between two cupolas $C_{36} + C_{36} \rightarrow (C_{36}C_{36}) \rightarrow C_{72}$ is shown in Figure 1 m, n, o.



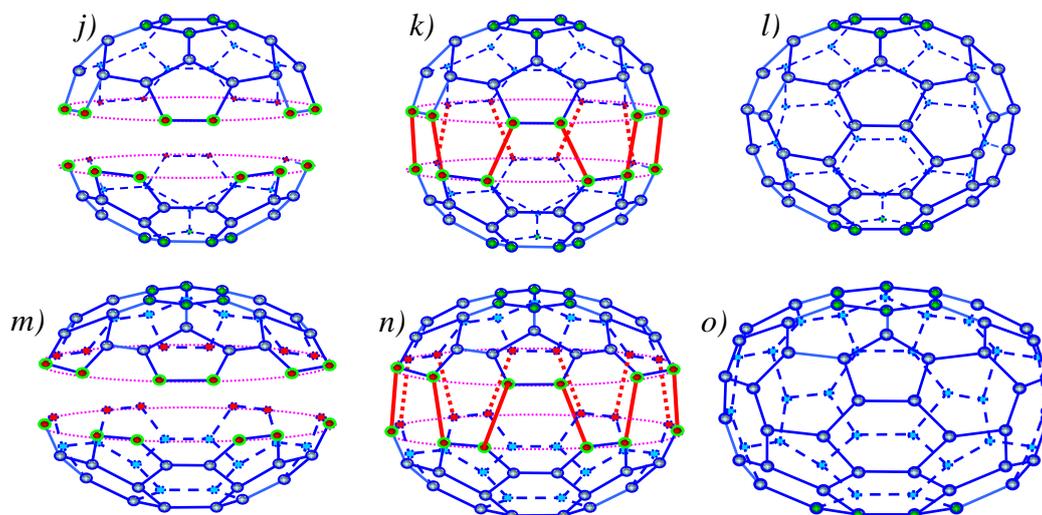


Fig. 1. Joining of two half-fullerenes C_{16} , C_{18} , C_{24} , C_{30} and C_{36} ; separate carbon cupolas (*a*, *d*, *g*, *j*, *m*); intermediate compounds (*b*, *e*, *h*, *k*, *m*); polyhedrons after relaxation (*c*, *f*, *i*, *l*, *o*, *m*). Dark-red and light-blue balls are reacting and neutral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

3. Single and double bonds

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_{36} , C_{48} , C_{60} , and C_{72} with single and double covalent bonds and, in the case of fullerene C_{32} , with partially delocalized bonds too. The optimized structures of the fullerenes obtained through the use of Avogadro package [12] are shown in Figure 2.

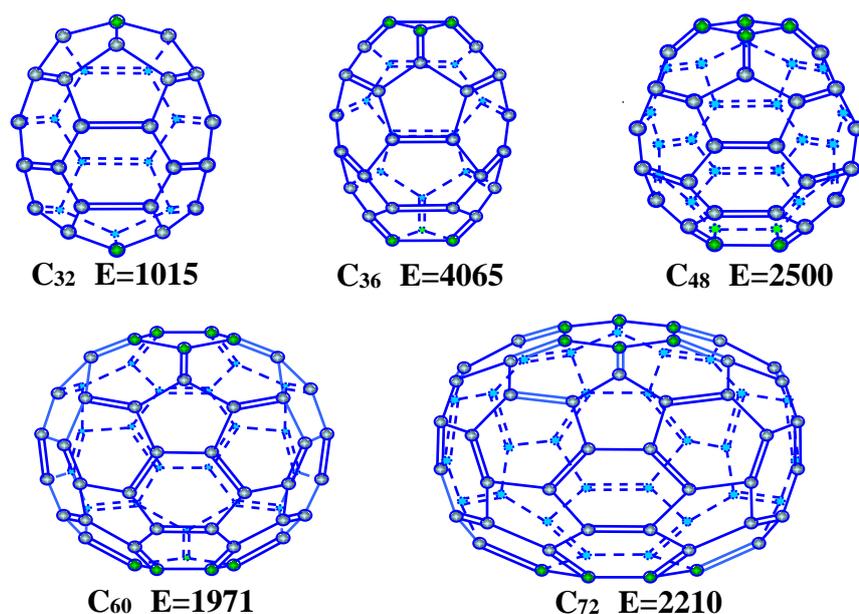


Fig. 2. Structure and energy (in kJ/mol) of the $\Delta n=12$ series fullerenes.

4. Symmetry and energy of perfect fullerenes

Modeling the growth of fullerenes from C_{24} (D_{3h} symmetry) to C_{48} , we have obtained the perfect fullerenes C_{30} and C_{36} conserving three-fold symmetry [13]. Modeling the growth of fullerenes from C_{32} (D_{4h} symmetry) to C_{60} , we found perfect fullerenes C_{40} and C_{48} conserving four-fold symmetry [14]. The mass difference between successive fullerenes in the first case is $\Delta m=6$, in the second case $\Delta m=8$. It should be emphasized that in both cases the mass difference is equal to a double degree of symmetry.

It is intriguing to combine periodicities, Δm and Δn , in order to gain a better understanding of the energy results obtained. With this in mind, we designed the fullerenes of the neighbor periodicities $\Delta n=6, 8, 10, 14$ and 16 using geometrical modeling, optimized their structures through the use of Avogadro package, and calculated their energies (in kJ/mol). The results are given in the Table where 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. For the $\Delta n=6$ series fullerenes, there are two energy values because this series has two families [15].

Periodic System of Basic Perfect Fullerenes

Series (horizontal) Groups (vertical)	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 $\Delta m=12$
$\Delta n=6$	C₁₄ 1657 1367	C₁₈ 3985 4060	C₂₄ 3985 3046	C₃₀ 1907 3059	C₃₆ 1884 2443
$\Delta n=8$	C₂₀ 1647	C₂₄ 3667	C₃₂ 2291	C₄₀ 2007	C₄₈ 2562
$\Delta n=10$	C₂₆ 831	C₃₀ 3923	C₄₀ 2426	C₅₀ 1979	C₆₀ 2329
$\Delta n=12$	C₃₂ 1015	C₃₆ 4065	C₄₈ 2500	C₆₀ 1970	C₇₂ 2210
$\Delta n=14$	C₃₈ 1206	C₄₂ 4253	C₅₆ 2643	C₇₀ 2069	C₈₄ 2255
$\Delta n=16$	C₄₄ 1399	C₄₈ 4446	C₆₄ 2802	C₈₀ 2203	C₉₆ 2365
$\Delta n=18$	C₅₀	C₅₄	C₇₂	C₉₀	C₁₀₈

The energy minimum for the fullerenes of 3-fold-symmetry group S refer to fullerene C_{26} , for the fullerenes of 3-fold-symmetry group T corresponds to fullerene C_{24} , for the fullerenes of 4-fold-symmetry to fullerene C_{32} , for the fullerenes of 5-fold-symmetry matches to well-known fullerene C_{60} and for the fullerenes of 6-fold-symmetry to fullerene C_{72} . These results need further consideration.

References

- [1] A.I. Melker, S.N. Romanov, D.A. Kornilov, Computer simulation of formation of carbon fullerenes // *Materials Physics and Mechanics* **2(1)** (2000) 42-50.

- [2] D.A. Kornilov, A.I. Melker, S.N. Romanov, Conformation transitions in fullerenes at non-zero temperatures // *Proceedings of SPIE* **5127** (2003) 81-85.
- [3] E.A. Rohlfing, D.M. Cox, A. Kaldor, Production and characterization of supersonic carbon cluster beams // *J. Chem. Phys.* **81(7)** (1984) 3322-3330.
- [4] H.W. Kroto, The stability of the fullerenes C_n , with $n=24, 28, 32, 36, 60, 60$ and 70 // *Nature* **329** (1987) 529-531.
- [5] S. Irle, A.J. Page, B. Saha, Y. Wang, K.R.S. Chandrakumar, Y. Nishimoto, H-J. Qian, K. Morokuma, Atomistic mechanisms of carbon nanostructure self-assembly as predicted by nonequilibrium QM/MD simulations, In: *Practical Aspects of Computational Chemistry II: An Overview of the Last Two Decades and Current Trends*, Ed. by J. Leszczynski and M. K. Shukla (Springer-European Academy of Sciences, 2012) 59 p.
- [6] A.I. Melker, T.V. Vorobyeva, Polymer crystallization as the self-organization of chain macromolecules // *Zeitschrift für Naturforschung* **49a(11)** (1994) 1045-1052.
- [7] A.I. Melker, T.V. Vorobyeva, Parametric resonance of the transverse waves in polymer macro-molecules: a reason for folding // *Nanobiology* **4** (1996) 71-82.
- [8] A.I. Melker, Possible ways of forming mini-fullerenes and their graphs // *Materials Physics and Mechanics* **20(1)** (2014) 1-11.
- [9] 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.
- [10] A.I. Melker, T.V. Vorobyeva, Fusion reactions of cupola half-fullerenes // *St. Petersburg State Polytechnical University Journal. Physics and Mathematics* **3(248)** (2016) 59-67.
- [11] Z. Chen, H. Jiao, M. Bühl, A. Hirsch, W. Thiel, Theoretical investigation into structures and magnetic properties of smaller fullerenes and their heteroanalogues // *Theoretical Chemistry Accounts* **106** (2001) 352-363.
- [12] 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/>
- [13] A.I. Melker, M.A. Krupina, Geometric modeling of midi-fullerenes growth from C_{24} to C_{48} // *St. Petersburg State Polytechnical University Journal. Physics and Mathematics* **3(248)** (2016) 52-58.
- [14] A.I. Melker, M.A. Krupina, Geometric modeling of midi-fullerenes growth from C_{32} to C_{60} // *St. Petersburg State Polytechnical University. Physics and Mathematics* **10(1)** (2017) 47-54.
- [15] A.I. Melker, M.A. Krupina, Designing mini-fullerenes and their relatives on graph basis // *Materials Physics and Mechanics* **20(1)** (2014) 18-24.