Structure and Energy of the $\Delta n = 14$ Series Fullerenes

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Abstract

Fusion reactions of cupola half-fullerenes $C_{16} + C_{22}$, $C_{18} + C_{24}$, $C_{24} + C_{32}$, $C_{30} + C_{40}$, $C_{36} + C_{48}$ 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. The fullerenes obtained, C_{38} , C_{42} , C_{56} , C_{70} and C_{84} , tend to take the appearance of a perfect spheroid with lesser formation energy. The graphs corresponding to the fusion reaction are given and the energy of fullerenes is calculated.

Keywords

Cupola, Energy, Fullerene, Fusion reaction, Graph, Modeling

Introduction

In Ref. [1,2] we have suggested the periodic system of fullerenes. It consists of horizontal series and vertical columns (groups). The horizontal series form the Δn periodicities having one and the same main characteristic feature; the fullerene structure changes from threefold symmetry to sixfold through four and fivefold ones. The vertical columns include the fullerenes of one and the same symmetry, the mass difference Δm for each column being equal to a double degree of symmetry. We suppose that these features can be taken as a basis for rigorous fullerene classification. The Δn periodicities studied consist of the following series: $\Delta n = 6, 8, 10, 12, 14, 16$ and 18 , fullerenes from C_{14} to C_{108} being incorporated. For the most of series, their structure, energy and formation are discussed elsewhere. We suppose that the fullerenes of one and the same group have similar properties. The fullerene structure for the series $\Delta n = 14$ was also obtained through the use of geometric modeling, but the results were not published. In this contribution we present the structure, energy and graphs of the $\Delta n = 14$ series

fullerenes. Knowing these characteristics allows one to activate the fullerene for farther investigations.

Fusion Reactions of Cupola Half Fullerenes

In Ref. [3] 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} and C_{22}

In Figure 1 the atomic configurations corresponding to reaction $C_{16} + C_{22} \rightarrow (C_{16}C_{22}) \rightarrow C_{38}$ are shown. At first two molecules are moving towards each other (Figure 1a). Then the atoms, marked in dark-red, interact with each other producing a compound (Figure 1b). During this process new covalent bonds (heavy red lines) are being formed. As a result, a distorted polyhedron is formed which relaxes into a perfect polyhedron (Figure 1c). Its atomic configuration consists of nine hexagons and twelve pentagons, so it can be named a $penta_{12}hexa_9$ -polyhedron.

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Figure 1: Joining two half-fullerenes C_{16} and C_{22} and fullerene C_{38} obtained; a) Separate carbon cupolas; b) Intermediate compound; c) Penta₁₂hexa₉-polyhedron C_{38} after relaxation. Dark-red and light-blue balls are reacting and neutral atoms, respectively; light-blue solid and dashed lines are stable covalent bonds; heavy dark-red solid and dashed lines are new covalent bonds.

Figure 2: Joining two half-fullerenes C_{18} and C_{24} and fullerene C_{42} obtained; notations are the same as before.

Figure 3: Joining two half-fullerenes C_{24} and C_{32} and fullerene C_{48} obtained.

Reaction between two cupolas C_{18} and C_{24}

Similar to the previous reasoning, one can consider the atomic configurations corresponding to reaction $C_{18} + C_{24} \rightarrow (C_{18}C_{24}) \rightarrow C_{42}$. As before, at first two molecules are moving towards each other (Figure 2a). Then the boundary atoms interact with each other producing a distorted polyhedron (Figure 2b), which relaxes into a

perfect polyhedron (Figure 2c). Its atomic configuration consists of two triangles, six pentagons and fifteen hexagons and so it was named a tri₂penta₆hexa₁₅-polyhedron.

Reaction between two cupolas C_{24} and C_{32}

The procedure for visualization of reaction $C_{24} + C_{32} \rightarrow (C_{24}C_{32}) \rightarrow C_{56}$ is the same as before. The

atomic configuration of the perfect polyhedron (Figure 3) consists of two squares, eight isolated pentagons and twenty-two hexagons, so it could be named a tetra₂-penta₈-hexa₂₂-polyhedron.

Reaction between two cupolas C₃₀ and C₄₀

It is written as $C_{36} + C_{48} \rightarrow (C_{36}C_{48}) \rightarrow C_{84}$. The atomic structure corresponding to a perfect polyhedron (Figure 4) consists of twelve isolated pentagons and twenty-five hexagons, so it could be named a penta₁₂-hexa₂₅ polyhedron.

Reaction between two cupolas C₃₆ and C₄₈

The procedure for visualization of reaction $C_{36} + C_{48} \rightarrow (C_{36}C_{48}) \rightarrow C_{84}$ is the same as before. The atomic structure corresponding to a perfect polyhedron (Figure 5) consists of twelve isolated pentagons and thirty-two hexagons, so it could be named a penta₁₂-hexa₃₂ polyhedron.

Single and Double Bonds, Energy

We assume that the symmetry of double bonds location about the major axis of cupolas and other fullerenes coincides with that of fullerene C₆₀. 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 C₃₈, C₄₂, C₅₆, C₇₀, and C₈₄ with single and double covalent bonds and, in the case of fullerene C₃₈, with partially delocalized bonds too. The optimized

structures of the fullerenes obtained through the use of Avogadro package [4] are shown in Figure 6. The energy change of the fullerenes can be explained in a similar manner as in Ref. [5].

Graph Representation and Electronic Structure

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" [6]. 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 sp² hybridized atoms".

Consider the graphs which characterize the formation of the $\Delta n = 14$ series fullerenes (Figure 7). From the graph representation it follows that the main difference of fullerene C₃₈ from others is the absence of double bonds in the graph center. Therefore the electronic structure in this area of fullerene C₃₈ differs from that of other fullerenes. In other words, fullerene C₃₈ does not refer to classical fullerenes defined in Ref. [6]. 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 [7,8]. They formulated the following rule: Electron pairs arrange themselves inside the valence

Figure 4: Joining two half-fullerenes C₃₀ and C₄₀ and fullerene C₇₀ obtained.

Figure 5: Joining of two half-fullerenes C₃₆ and C₄₈ and fullerene C₈₄ obtained.

Figure 6: Structure of the $\Delta n = 14$ series fullerenes with single and double bonds. Energy in kJ/mol.

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. If each electron pair present as a point and to connect the points by direct lines, one obtains the electronic configuration of chemical bonds [8,9]. 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.

Consider two simple molecules, methane and ammonia. 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, methane (Figure 8). Here the atomic configuration repeats the electronic. In the case of a molecule AB_3 , where the valence shell contains three binding pairs and one unshared, the situation is radically different. 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, and we obtain ammonia (Figure 8). In this case the electronic and atomic configurations do not coincide and we have so called *hidden symmetry* [10].

Discussion

Today there are a lot of papers on fullerene proper-

ties. 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 [11].

As already noted the theoretical approach to fullerenes is based on the topological and graph treatment. However, it was 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" [12]. 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

Figure 7: Fusion reactions of cupolas as connection of two graphs; all notations are the same as before.

mini-fullerenes [13,14]. The graph analysis simplifies an understanding of both the ways of fullerene growth and their structures obtained.

Consequently, the aim of research is not to do calculations for calculations, but at first to develop a system (mathematical model) as a basis for the calculations. The first step of creating any mathematical model is the formulation of the laws that connect the main objects of the

model [15]. In our case the main objects are perfect basic fullerenes; we have also the preliminary law in the form of the periodic system [2] and the fusion algorithm for obtaining perfect basic fullerenes, but we do not know the structure of all the main objects. Besides, not all perfect fullerenes, the structure of which being known, are incorporated in the suggested periodic system. Therefore, the next step in our investigation is obtaining the struc-

Figure 8: Methane and ammonia; red dots denote electron pairs.

ture and energy of missing fullerenes with the purpose to incorporate the missing known and unknown fullerenes in the periodic system. Only afterwards, having a comprehensive picture, it seems reasonable to try to explain why some fullerenes are more stable than others.

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