NATURAL ISOMERS OF FULLERENES FROM C_4 TO C_{20}

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Abstract. We have systematized possible ways of forming the isomers of mini-fullerenes, namely elementary fullerenes: tetrahedron C_4, triangular prism C_6, cube C_8, pentagonal prism C_{10}, hexagonal prism C_{12}, as well as their derivatives, which were obtained by joining elementary fullerenes. Combined with the graph analysis, this approach allows obtain a clear knowledge of their structure. Among them there are barrel-shaped fullerenes: C_{12}, C_{16}, C_{20}; tetrahedral ones C_{12} and C_{16}; bi-shamrocks C_{14} and C_{18}, bipyramids C_{14} and C_{18}; regular and irregular dodecahedrons C_{20} as well as intermediate compounds. The three simplest elementary fullerenes, C_4, C_6, C_8; have only electronic isomers and no space atomic isomers at all. After a cube, the next in size carbon fullerene C_{10} is a pentagonal prism. We have designed an isomer of it by fusion of a tetrahedron and a triangular prism. For the pentagonal prism shape fullerene the energy lies in the range from 974 to 2464 kJ/mol, for the hybrid of a tetrahedron and a triangular prism does in the range from 1396 to 2433 kJ/mol; it depends both on the number of single and double bonds as well as on their position in space. Fullerene of twelve carbon atoms C_{12} produces four isomers: a hexagonal prism, a barrel-shape fullerene, a truncated tetrahedron and a tetra-penta octahedron. They have different energies depending on the number of single and double bonds and their position in space. In a like manner other fullerenes studied, C_{14}, C_{16}, C_{18} and C_{20}, have two or three isomers with different energies.

Keywords: atomic isomer, electronic isomer, energy, fullerene, fusion reaction, graph representation, growth, periodic system

1. Introduction

The crucial questions for fullerenes are: how they are originated and what structure they obtain naturally, but the most important and most difficult question for any science is classification. Modeling the growth of fullerenes of different symmetries, we have found that from time to time there appeared perfect fullerenes conserving the initial symmetry. On the basis of those investigations, the periodic system for perfect fullerenes was submitted [1]. The periodic system, grounded on symmetry principles, 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 sevenfold through four, five and sixfold 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 assume that the fullerenes of identical groups have similar properties.

In addition to the classification, the crucial point which should be given more attention to is space isomerism of the fullerene molecules. Knowledge of the relative positions in space of the atoms in a molecule is of great importance since the heat of activation is largely the
energy required to bring the atoms into their proper position for reaction [2]. "Space isomerism of molecules is the phenomenon which consists in the existence of molecules having an equal molecular mass and composition but different positions of the atoms in space, and therefore having different chemical and physical properties" [3].

In this contribution we present the structure and energy of fullerenes and their isomers in the range from C₄ to C₂₀.

2. Graph representation
In Ref. [4] it has been suggested designing fullerenes taking as a basis their graphs. Such approach allows distinguish different families of fullerenes if one knows their graphs. The simplest family of fullerenes contains five members: a tetrahedron and five prisms of different symmetry. They form the family of elementary fullerenes and can be classified as the Δn=2 series of the periodic system of fullerenes. Their structure is shown in Figure 1 together with their graphs.

![Figure 1. Fullerenes of the Δn=2 series with single bonds and their graphs; energy in kJ/mol](image)

The question arises as to whether there are their isomers. It seems that a tetrahedron, a triangular prism and a cube have no space isomers at all. However, they have such isomers which differ in a number and a position of the single and double bonds. As a result, they can have different energy and could be named the **electronic isomers**. Some of them are presented in Fig. 2.
At this moment we have only a philosophical explanation of the fact that the three elementary fullerenes have no space atomic isomers. Their faces are regular triangles and squares. Plato (427-347 BC) accepted them for the letters of entity language [5]. Probably they are too short for producing more complex words.

![Some electronic isomers of a tetrahedron, a triangular prism and a cube, energy in kJ/mol](image)

**Fig. 2.** Some electronic isomers of a tetrahedron, a triangular prism and a cube, energy in kJ/mol

### 3. Isomers of fullerene C\textsubscript{10}

As stated above, we are interested in space isomerism of fullerenes, i.e. our aim is to find fullerenes which have different positions of their atoms in space. For this reason we will not further discuss the electronic isomers and restrict ourselves with space isomerism. Nevertheless we will give the structure of fullerenes of two extreme electronic configurations: with single bonds only and with single and double ones, the maximum number of possible double bonds being positioned symmetrically.

**a) Pentagonal prism (basic fullerene).** After a cube, the next in size carbon fullerene, each atom having three nearest neighbors, which can be inscribed into a sphere, is a pentagonal prism. Here the five atoms of each base can be laid on one and the same plane (Fig. 3). The minimum and maximum energy of their configurations are given in the figure.

![Carbon pentagonal prisms inscribed into a sphere (a) and their graphs (b)](image)

**Fig. 3.** Carbon pentagonal prisms inscribed into a sphere (a) and their graphs (b)
b) Hybrid of a tetrahedron and a triangular prism. In addition to this basic fullerene considered, we have designed an isomer of it using fullerene reaction \( C_4 + C_6 \rightarrow (C_4C_6) \rightarrow C_{10} \).

![Fig. 4](image)

Fig. 4. Fullerenes obtained by joining together a tetrahedron and a triangular prism and their graphs

4. Isomers of fullerene \( C_{12} \)

Following the approach developed in Ref. [6], we are able not only to design the basic fullerene \( C_{12} \), but to obtain its isomers also. It will be recalled that the approach consists in obtaining new more complex fullerenes by means of reaction between already existing ones. From a geometric standpoint, there are three possible compatible reactions between triangular prisms leading to the isomers.

a) Hexagonal prism. It is the simplest isomer that can be thought of. Here six atoms of each base are laid on one and the same plane. This basic fullerene belonging to the family of prisms can be obtained by the method shown in Fig. 5.

![Fig. 5](image)

Fig. 5. Joining together two parallel triangular prisms:
(a) Separated objects; (b) Intermediate compound; (c) Hexagonal prisms.
Grey and blue balls are reacting and neutral atoms, respectively; red solid and dash lines are new forming covalent bonds; blue solid and dash lines are old and new covalent bonds; blue dot lines are covalent bonds to be destroyed
b) Joining of two triangular prisms lying along one and the same axis. This fullerene, resembling a triangular barrel or a rugby ball, is presented in Fig. 6.

![Diagrams of fullerenes obtained by joining together two triangular prisms and their graphs](image)

**Fig. 6.** Fullerenes obtained by joining together two triangular prisms and their graphs

![Diagrams of joining together two crossed triangular prisms](image)

**Fig. 7.** Joining together two crossed triangular prisms:
(a) Prisms; (b, c) Intermediate compounds

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c) Two crossed triangular prisms combined. Up to now this way of joining was not discussed, so examine it in detail. There are two extremal paths of fusion, both being depended on the electronic state of combining prisms (Fig. 7). As a result, there appear two
different fullerene configurations: a truncated tetrahedron and a tetra-penta octahedron (Fig. 8). It should be emphasized that the fullerene having the shape of tetra-penta octahedron is obtained for the first time. This fullerene is remarkable for having the least energy among all other configurations.

![Fig. 8. Joining together two crossed triangular prisms: (d) Truncated tetrahedron; (e) Tetra-penta octahedron and their graphs. All notations are the same as in Fig. 5](image)

5. Isomers of fullerene \( C_{14} \)

a) Bi-shamrock nonahedron. It can be obtained by different ways: namely, through the use of fullerene reaction \( C_4 + C_{10} \rightarrow (C_4C_{10}) \rightarrow C_{14} \) [6] and by joining two cupolas \( C_7 \). The fullerene is shown in Fig. 9.

![Fig. 9. Bi-shamrock (or bi-trefoil) fullerene \( C_{14} \) and its graphs; energy in kJ/mol](image)

b) Based-truncated triangular bipyramid. Similar to the previous case, the fullerene can be also designed by different ways. The fullerene obtained is presented in Fig. 10.
6. Isomers of fullerene $C_{16}$

a) Barrel-shaped square fullerene. Different ways of constructing this fullerene are discussed in Ref. [6]. The final configuration is shown in Fig. 11. The shape of the fullerene resembles a square barrel.

b) Tetrahedral fullerene $C_{16}$. It can be also obtained by different ways. The atomic configuration, presented in Fig. 12, has much in common with that of a truncated tetrahedron. Both fullerenes refer to the tetrahedral group of the periodic system of fullerenes [7]. In our case the tetrahedral fullerene can be imagined as a mathematical compound, which forms a topological cube (half-truncated cube) of two tetrahedra inserted into each other [7]. The cube is shown in Fig. 12a, its graph is given in Fig. 12b.

Fig. 10. Based-truncated triangular bipyramid $C_{14}$ and its graphs; energy in kJ/mol

Fig. 11. Barrel-shaped square fullerene $C_{16}$ and its graphs; energy in kJ/mol

Fig. 12. Tetrahedral fullerene $C_{16}$ and its graphs: (a) Half-truncated cube and (b) Its block graph; energy in kJ/mol
7. Isomers of fullerene C\textsubscript{18}

a) Truncated bi-shamrock polyhedron is presented in Fig. 13. It can be designed by two different manners: by fullerene reaction \( C_6 + C_{12} \rightarrow (C_6C_{12}) \rightarrow C_{18} \)\[6\] and joining two cupolas C\textsubscript{9}.

Fig. 13. Truncated bi-shamrock (or bi-trefoil) fullerene C\textsubscript{18} and its graphs; energy in kJ/mol

b) Truncated triangular bipyramid. It can be constructed by combining plane cluster C\textsubscript{6} with cupola C\textsubscript{12}, the configuration obtained being presented in Fig. 14.

Fig. 14. Truncated triangular bipyramid C\textsubscript{18} and its graphs; energy in kJ/mol

8. Isomers of fullerene C\textsubscript{20}

There are three space isomers of this fullerene.

a) Dodecahedron. The atomic configuration is a regular polyhedron (Fig. 15). It consists of twelve pentagons and is known as one of five regular Plato's bodies. It can be obtained by different ways \[6\], the most interesting is fusion of two pentagonal prisms lying along one and the same axis.

Fig. 15. Dodecahedron C\textsubscript{20} and its graphs; energy in kJ/mol

b) \((\text{Tetra-hexa})_3\)-pentagon dodecahedron. The configuration is shown in Fig. 16. It consists of three squares, three hexagons and six pentagons and has three-fold symmetry.
9. Conclusion and discussion

We have systematized possible ways of forming the isomers of mini-fullerenes, namely elementary fullerenes: tetrahedron C₄, triangular prism C₆, cube C₈, pentagonal prism C₁₀, hexagonal prism C₁₂, as well as their derivatives, which were obtained by joining elementary fullerenes. Combined with the graph analysis, this approach allows obtain a clear knowledge of their structure. Among them there are barrel-shaped fullerenes: C₁₂, C₁₆, C₂₀; tetrahedral ones C₁₂ and C₁₆; bi-shamrocks C₁₄ and C₁₈, bipyramids C₁₄ and C₁₈; regular and irregular dodecahedrons C₂₀ as well as intermediate compounds. For completeness sake, we recalculated some configurations removing double bonds or redistributing them in order to obtain more symmetric their positions.

The three simplest elementary fullerenes, C₄, C₆, C₈; have only electronic isomers and no space atomic isomers at all. After a cube, the next in size carbon fullerene C₁₀ is a pentagonal prism. We have designed an isomer of it by fusion of a tetrahedron and a triangular prism. For the pentagonal-prism-shape fullerene the energy lies in the range from 974 to 2464 kJ/mol, for the hybrid of a tetrahedron and a triangular prism does in the range from 1396 to 2433 kJ/mol; it depends both on the number of single and double bonds as well as on their position in space. Fullerene of twelve carbon atoms C₁₂ produces four isomers: a hexagonal prism, a barrel-shape fullerene, a truncated tetrahedron and a tetra-penta octahedron. Similar to the previous fullerene, they have different energies depending on the number of single and double bonds and their position in space. In a like manner other fullerenes studied, C₁₄, C₁₆, C₁₈ and C₂₀, have two or three isomers with different energies.

In Table 1 the calculated energies of fullerenes are presented, for different isomers the minimum energies being designated with bold figures. They are also shown in Fig. 18. It is
interesting to note that the energies decrease almost linearly with the growing fullerene size and decreasing number of cubes incorporated into the structure.

Table 1. Energy of fullerenes in kJ/mol as a function of fullerene size and shape

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Fig. 20. Minimum energy of smallest fullerenes in kJ/mol

It must be emphasized that the smallest classical fullerene C_{20} discovered [8] consists only of pentagons. It has the minimum energy 491 kJ/mol. The smallest nonclassical fullerenes C_{10}, C_{12}, C_{14} and C_{16}, which contain not only pentagons and hexagons, but also squares, are waiting for their discoverers.

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References
