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# Changing symmetry during the growth of fullerenes originated from the nuclei of six-fold symmetry

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## ABSTRACT

The possible ways of generation and growing the fullerenes having at first six-fold symmetry has been studied. Beginning with a hexagonal prism (elementary fullerene  $C_{12}$ ), six-cornered barrel-shaped fullerene  $C_{24}$  and high six-cornered barrel-shaped fullerene  $C_{36}$ , we obtained their direct descendants through the use of Endo-Kroto's mechanism known as embedding carbon dimers. We have calculated the energies of the possible fullerenes and discussed possible reasons of their dependence on a fullerene size and shape.

## KEYWORDS

carbon • center of curvature concentration • energy • fullerene • fusion reaction • graph representation periodic system • single and double bonds • symmetry

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## Introduction

A fullerene is a molecule of carbon in the form of a hollow sphere, ellipsoid, tube, and many other shapes. The suffix “-ene” indicates that each carbon atom is covalently bonded to three others instead of the maximum of four. Fullerenes were conjectured more than fifty years ago independently in 1970 and 1973 [1–3]. They were discovered by mass spectrometry in 1985 [4], through laser evaporation of graphite in 1992 [5]. The discovery of fullerenes greatly expanded the number of known allotropes of carbon, which had previously been limited to graphite, diamond and amorphous carbon. From that time on the fullerenes have been the subjects of intense research, both for their chemistry and for their technological applications, especially in materials science, electronic, and nanotechnology. Nanostructure carbon, having many isomers, offers a great number of applications [6]. However, up to this point there is no clear and unique theory of fullerene growth, and therefore there is no standard way of obtaining desirable fullerene structures. The studies of fullerenes, in particular fullerene isomers, reflect only partial ways of their formation and have little in common; they are non universal [7–25].

The appearance of the periodic table of fullerenes [26] has changed the strategy of investigation: phenomenological approach to fullerenes was replaced by task-oriented activity. The periodic system of fullerenes gives a base for rigorous fullerene classification. It consists of horizontal series and vertical columns; they include fullerenes from  $C_{14}$  to  $C_{108}$ . The horizontal series form the  $\Delta n$  periodicities, where the fullerene structure changes from three-fold symmetry to six-fold through four and five ones. The

vertical columns (groups) include the fullerenes of one and the same symmetry, the mass difference  $\Delta m$  for each column being equal to a double degree of symmetry.

On the base of periodic system, we have systemized possible ways of fullerene growth. It turned out that there are three the most natural types of growth mechanism [27]:

1. Endo-Kroto: embedding carbon dimers into the hexagons of initial fullerenes;
2. Melker-Vorobyeva: fusion of the carbon cupolas having the same symmetry;
3. Melker-Krupina: fusion of fullerenes having compatible symmetry.

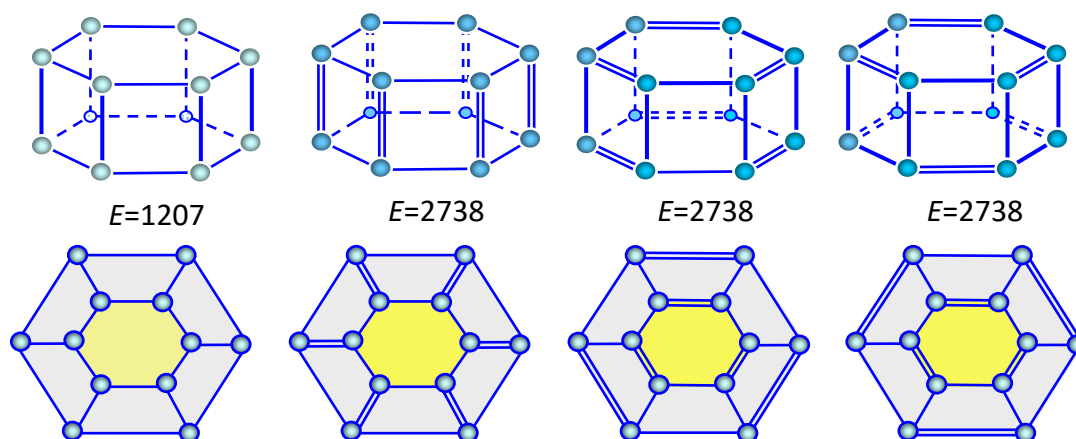
The first mechanism creates both perfect and imperfect fullerenes; the second and third mechanisms do only perfect fullerenes.

Up to now we have considered so called “vertical growth” of fullerenes when a growing object conserves its symmetry, ordinary or topological. It resembles the growth of coniferous trees. Contrary to them deciduous trees grow sometimes in such manner that one of side branches begin to prevail over the main one. We have assumed that such situation was also possible for some fullerenes. In doing so, a fullerene is changing its symmetry, e.g., fullerene  $C_{44}$  having two-fold symmetry has transformed into fullerene  $C_{60}$  of six-fold symmetry.

To gain a better understanding of that phenomenon, we have decided to study it from the very beginning.

### Elementary fullerene $C_{12}$

As was shown earlier [26–31], folding a plain cluster  $C_6C_6$  produces a hexagonal prism of six-fold symmetry which may be thought over as an elementary fullerene  $C_{12}$ . Several electronic configurations are presented in Fig. 1. Here and below, we use area-colored graphs because they gain a better understanding of the structures. In our case, six areas of the prisms are tetragons, and they are grey painted, two areas are hexagons; they are yellow painted.



**Fig. 1.** Hexagonal prisms formed from clusters: structure and graphs;  $E$  is energy, kJ/mol

## Mechanism of growth

The process of changing symmetry was obtained [32] through the use of the mechanism known as “embedding carbon dimers,” which was suggested by M. Endo and the Nobel Prize winner H.W. Kroto in 1992 [33]. According to it, a carbon dimer, colored goldish, embeds into a hexagon of an initial fullerene. This leads to stretching and breaking the covalent bonds which are normal to the dimer and to creating new bonds with the dimer. As a result, there arises a new atomic configuration and there is a mass increase of two carbon atoms (Fig. 2).

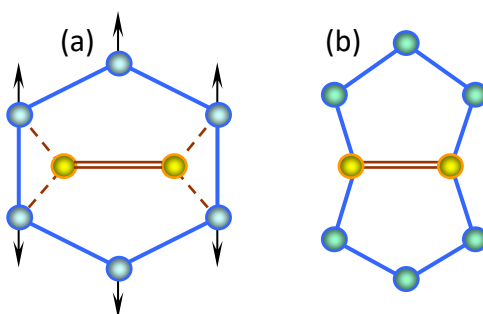


Fig. 2. Carbon dimer embedding into a hexagon (a) and forming two adjacent pentagons (b)

## Growth of elementary fullerene $C_{12}$

The fullerenes produced during the growth of initial fullerene  $C_{12}$  through the use of the Endo-Kroto mechanism are illustrated in Figs. 3–7. Here the dimer embedding is made at the “frigid zone” near the axis of symmetry.

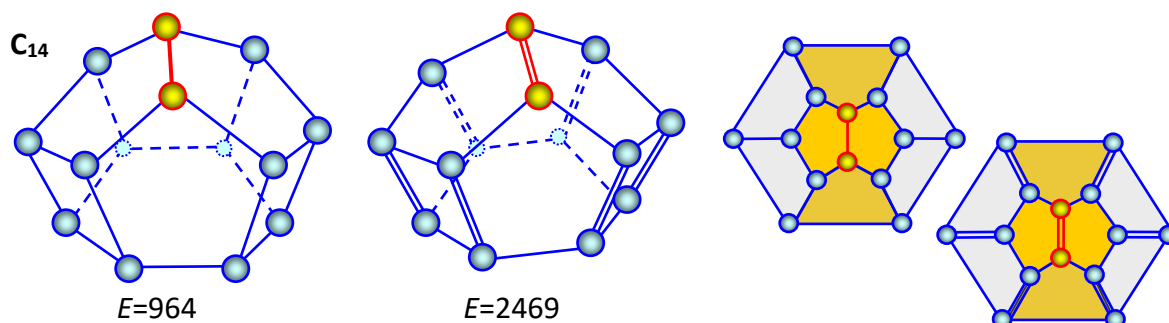


Fig. 3. Fullerene  $C_{14}$  as a result of a dimer embedding into a hexagonal prism; its graphs and energy  $E$  (kJ/mol)

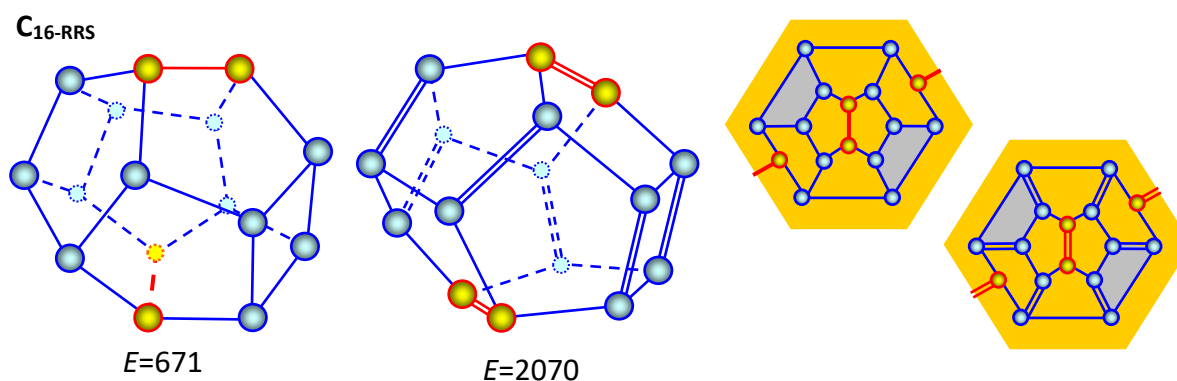
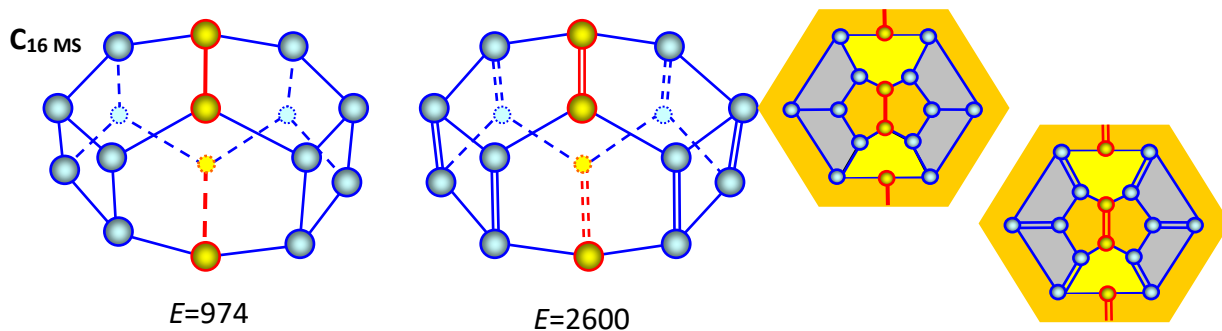
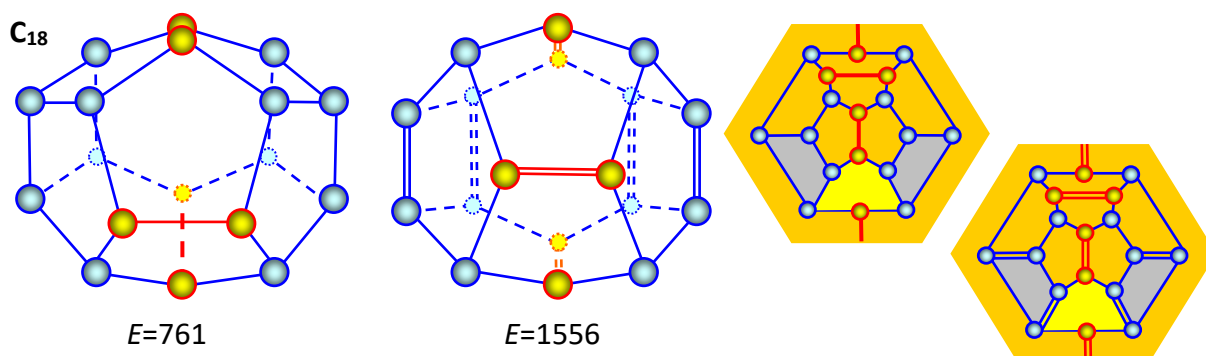


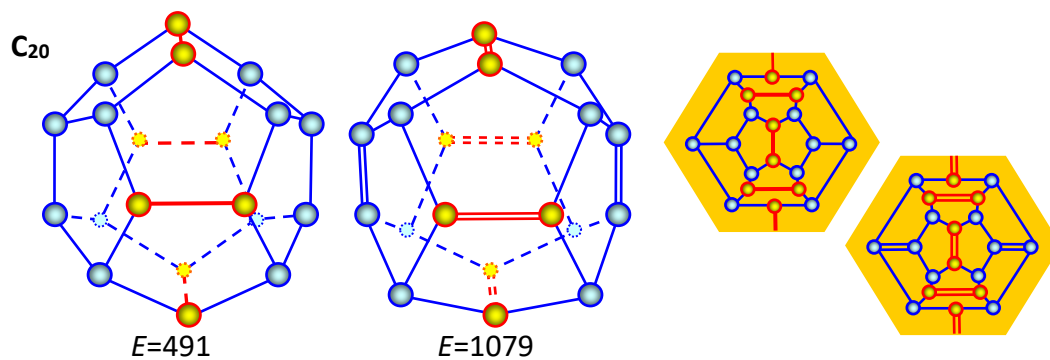
Fig. 4. Fullerene  $C_{16}$  produced by rotation-reflection-symmetry embedding two dimers into a hexagonal prism; its graphs and energy  $E$  (kJ/mol)



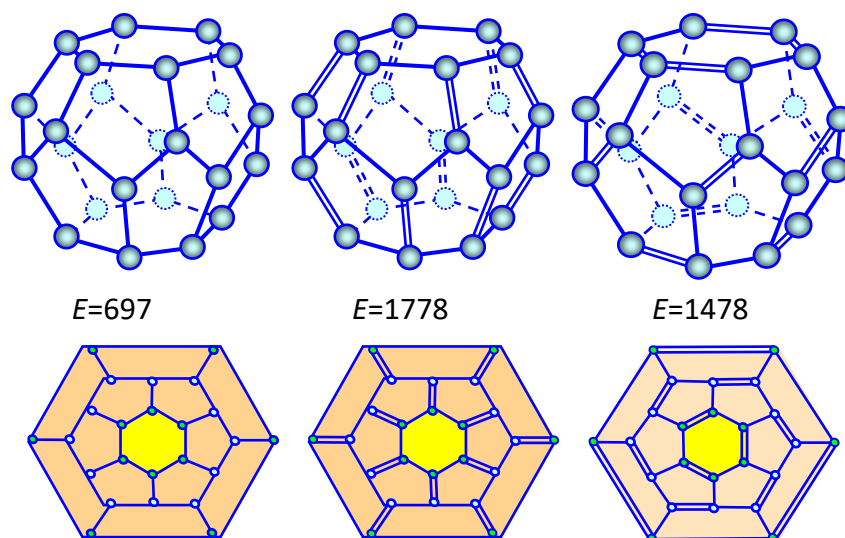
**Fig. 5.** Fullerene  $C_{16}$  produced by mirror-symmetry embedding two dimers into a hexagonal prism; its graphs and energy  $E$  (kJ/mol)



**Fig. 6.** Fullerene  $C_{18}$  as a result of three-dimers embedding into a hexagonal prism; its graphs and  $E$  (kJ/mol)



**Fig. 7.** Fullerene  $C_{20}$  as a result of four-dimers embedding into a hexagonal prism; its graphs and energy  $E$  (kJ/mol)



**Fig. 8.** Six-cornered barrel-shaped fullerene  $C_{24}$  as a result of prisms fusion; its graphs and energy  $E$  (kJ/mol)

### Six-cornered barrel-shaped fullerene $C_{24}$

As was shown earlier [26], fusion of two prisms with conserving their symmetry produces a fullerene which shape resembles a six-cornered barrel. The structure of several electronic isomers is shown in Fig. 8; the structure and graph areas are painted as before in different colors.

### Growth of six-cornered barrel-shaped fullerene $C_{24}$

The fullerenes  $C_{26}$  –  $C_{36}$  produced from the initial fullerene  $C_{24}$  through the use of the Endo-Kroto mechanism are illustrated in Fig. 9.

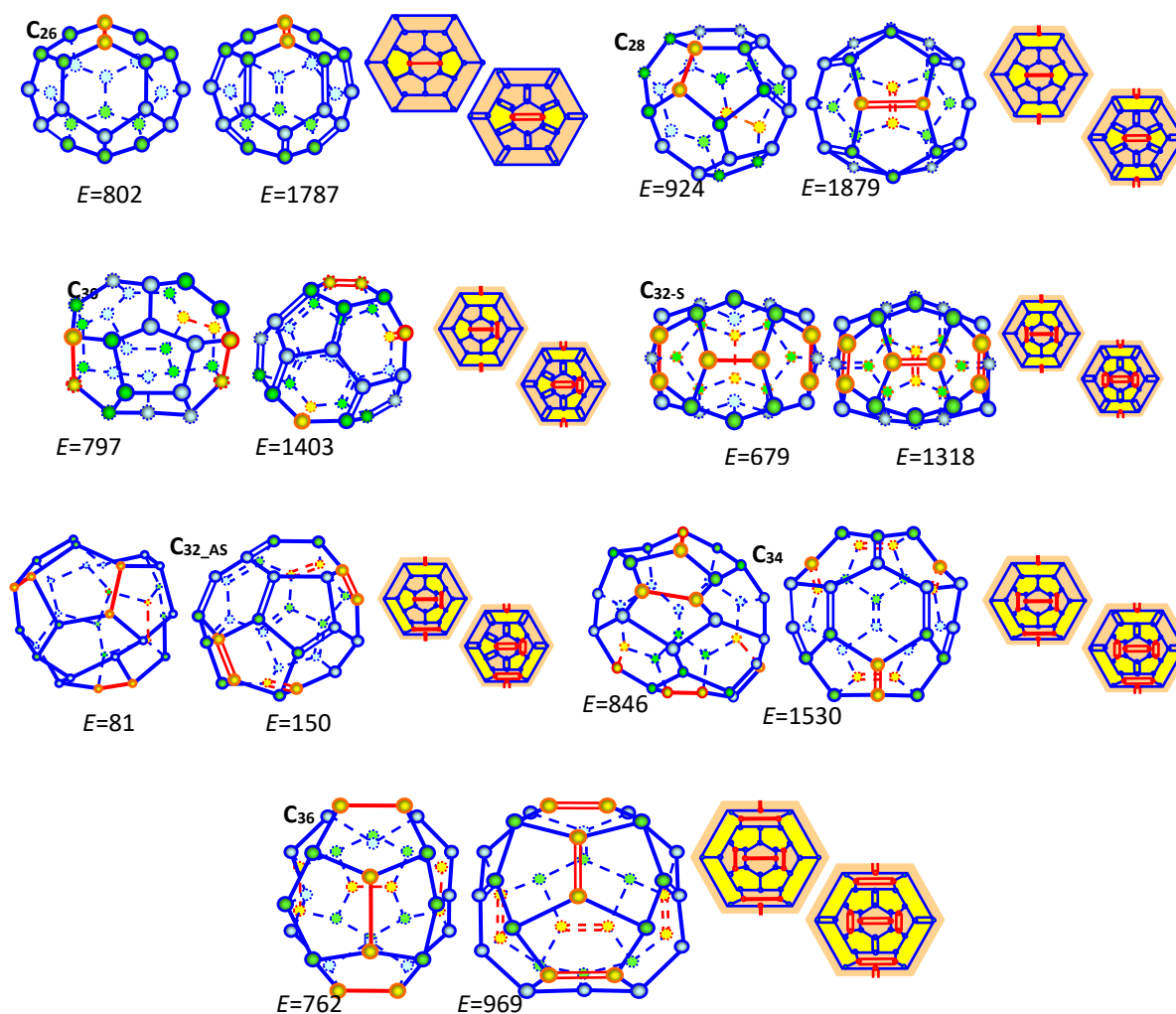
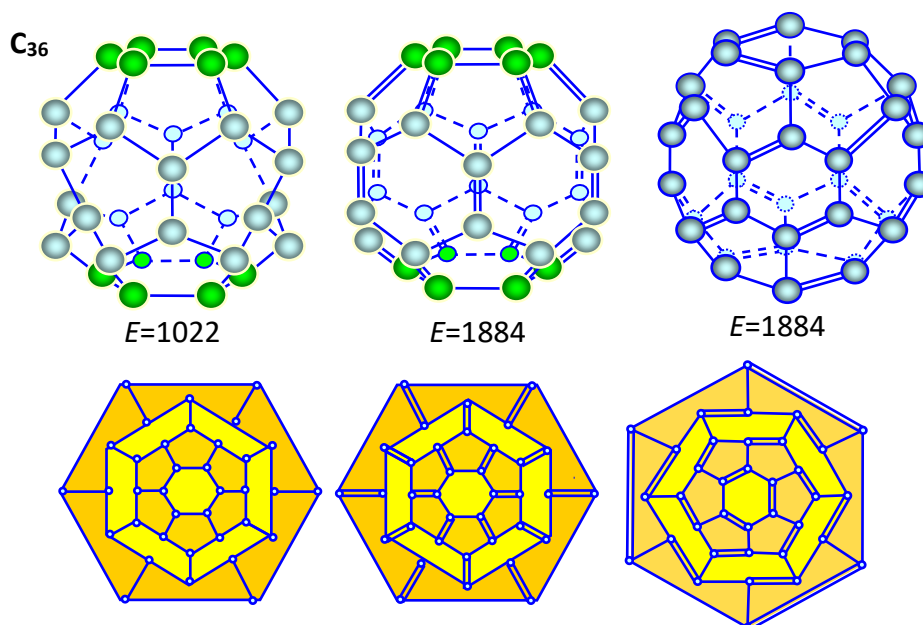


Fig. 9. Dimer embedding into fullerene  $C_{24}$ ; graphs and energy in kJ/mol of  $C_{26}$

### High-six-cornered barrel-shaped fullerene $C_{36}$

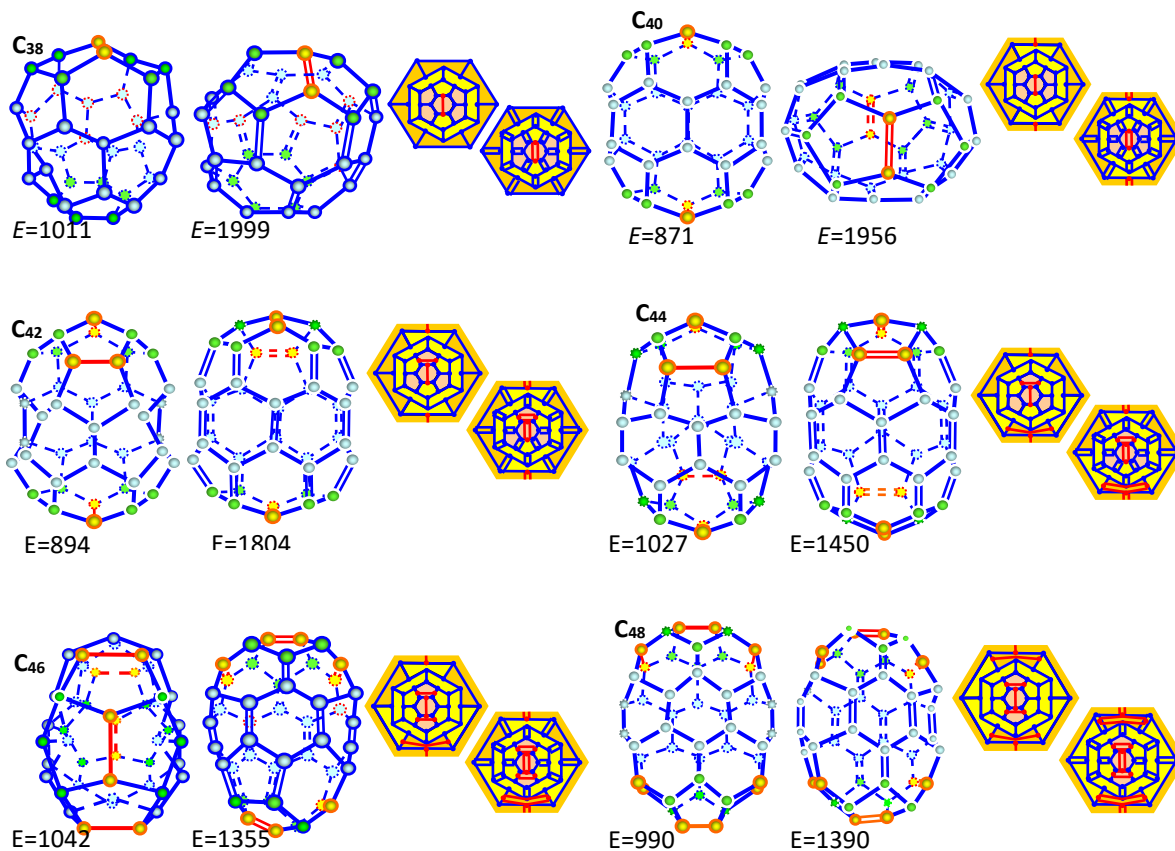
As was shown earlier [26], fusion of two prisms with conserving their symmetry produces a fullerene which shape resembles a six-cornered barrel. The structure of several electronic isomers is shown in Fig. 10; the structure and graph areas are painted as before in different colors.



**Fig. 10.** Joining fullerene  $C_{24}$  with prism  $C_{12}$ ; structure, graphs and energy  $E$  (kJ/mol)

### Growth of high-six-cornered barrel-shaped fullerene $C_{36}$

The fullerenes produced during the growth of initial fullerene  $C_{36}$  through the use of the Endo-Kroto mechanism are illustrated in Fig. 11.



**Fig. 11.** Fullerenes produced by embedding carbon dimers into a fullerene  $C_{28}$ ; their graphs and energy  $E$  (kJ/mol)



## Summary

We have studied possible ways of generation and growing the fullerenes having at first six-fold symmetry. Beginning with a hexagonal prism (elementary fullerene  $C_{12}$ ), six-cornered barrel-shaped fullerene  $C_{24}$  and high six-cornered barrel-shaped fullerene  $C_{36}$ , we obtained their direct descendants through the use of Endo-Kroto's mechanism known as embedding carbon dimers. We have calculated the structure and energy of the possible fullerenes.

In Tables 1, the calculated energies of fullerenes are presented, for fullerenes with single bonds only and single and double bonds.

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

Fullerenes	Single	Single+double
$C_{12}$	1207	2738
$C_{14}$	964	2469
$C_{16}$ rrs	671	2070
$C_{16}$ ms	(974)	(2600)
$C_{18}$	761	1556
$C_{20}$	491	1079
$C_{24}$	697	1778
$C_{26}$	802	1787
$C_{28}$	924	1879
$C_{30}$	787	1403
$C_{32}$ s	679	1318
$C_{32}$ as	817	1507
$C_{34}$	841	1530
$C_{36}$	762	969
$C_{36}$	1022	1884
$C_{38}$	1011	1999
$C_{40}$	871	1956
$C_{42}$	894	1804
$C_{44}$	1027	1450
$C_{46}$	1042	1355
$C_{48}$	990	1390

## Continuity and discontinuity. Curvature of fullerenes

These notions are connected with the Ionic and Pythagorean schools of philosophy (VI-IV century B.C.) [34]. Plato of Athens (Πλατων, 427 B.C.) has tried to combine both notions, putting five forms of matter (fire, air, earth, water, ether) into consistency to five regular polyhedra (tetrahedron, octahedron, cube, icosahedron, dodecahedron). According to Aristotle every thing is the unity of matter and form (*η ύλη και τό είδος*); the form being an active element produces movement [34].

In mathematics, there are such notions as curvature, tensor of curvature [35]. The curvature is defined as the quantity which characterizes a deviation of a surface from a plane at a given point. The latter is defined in the following manner. Through the normal at a given point of surface all the possible planes are drawn. The sections of the surface by these planes are called normal sections, the curvatures of normal sections being normal curvatures of the surface at a given point. Maximum and minimum curvatures are

called principal curvatures. Their combinations give Gauss and average curvatures which are used for analysis of the surface curvature.

We will follow to Aristotle trying finding such parts of fullerene's shape, which define surface curvature of a fullerene. In other words, we will search first of all "space fragments of curvature", but not a curvature value. Further we will use the following notions: curvature as a continuity property and curvature fragments as discontinuity. Analysis of the fullerene structures shown before allows us to separate the following curvature fragments (Fig. 12). It should be emphasized that an isolated fragment CF-6 does not create curvature; it becomes a curvature fragment under the influence of surroundings. Different curvature fragments have their own symmetry. We name their center of symmetry "curvature concentration center" (CCC).

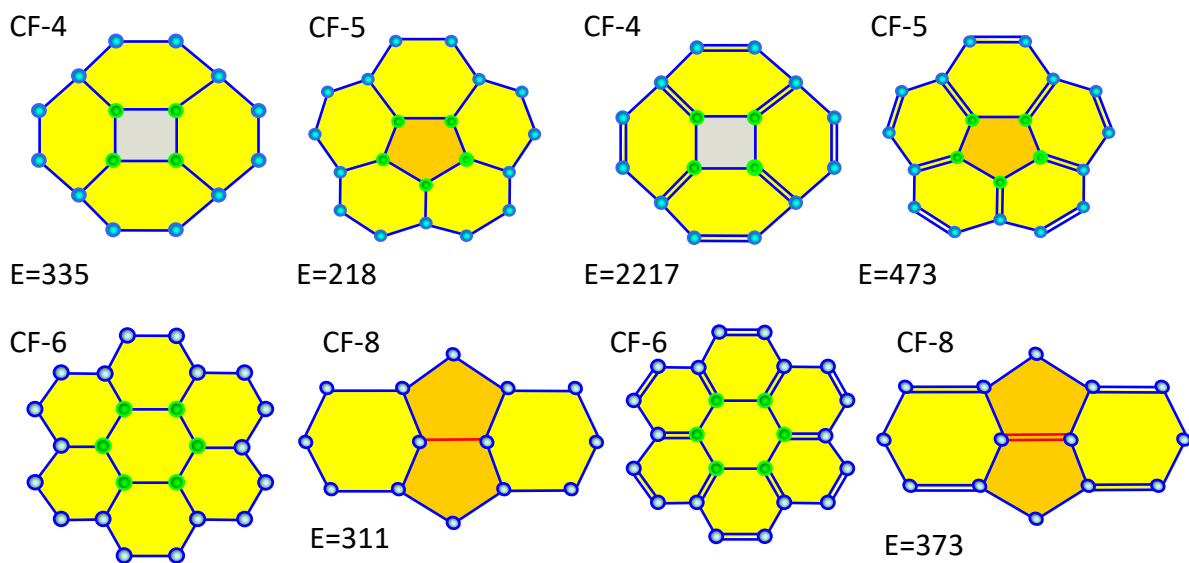


Fig. 12. Curvature fragments of fullerenes

In mathematics [35], surface is introduced as a bit of plane subjected to continuous deformations (tension, compression, bending). In its turn, curvature is defined as the quantity which characterizes a deviation of a surface from a plane at a given point. In mechanics [36] for characteristics of deformation one introduces tensor of strain, which diagonal elements characterize volume change; non-diagonal elements show the change of a form. If stress is a function of strain in each point of continuum, such continuum is said to be an elastic body. In a simple case, the function which connects strain and stress is Hooke's law.

We assume that in fullerenes the curvature concentration centers are strain centers and since strain is connected with stress, they are centers of stress concentration. Therefore the energy of a fullerene consists of two parts: chemical energy of formation and strain energy of construction.

Now we are able to understand and explain the dependence of fullerene energy on size and shape (Fig. 13). The study of the CCC arrangement for the family of fullerene  $C_{12}$  has given the following picture (Figs. 14,15). Fullerenes with single bonds relax through the transformation of plane hexagons into chair or boat conformation and so their energy



has incorporated only a small part of strain energy. Fullerenes with single and double bonds are more rigid constructions, and here the contribution of strain energy is high.

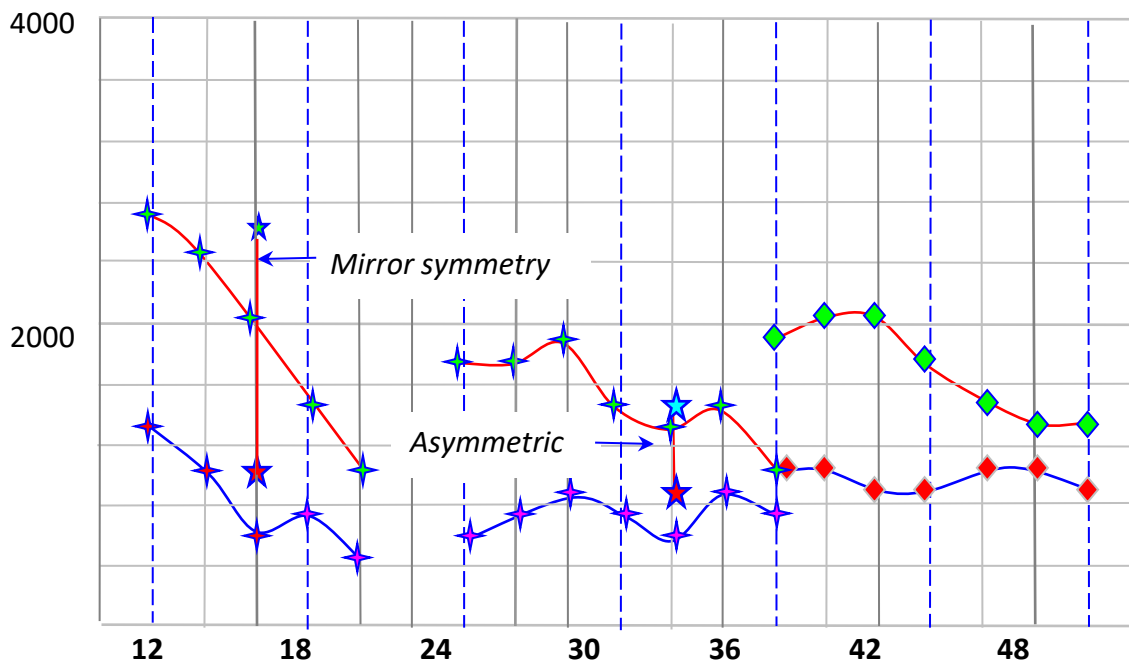


Fig. 13. Energy of fullerenes in kJ/mol as a function of fullerene size and shape

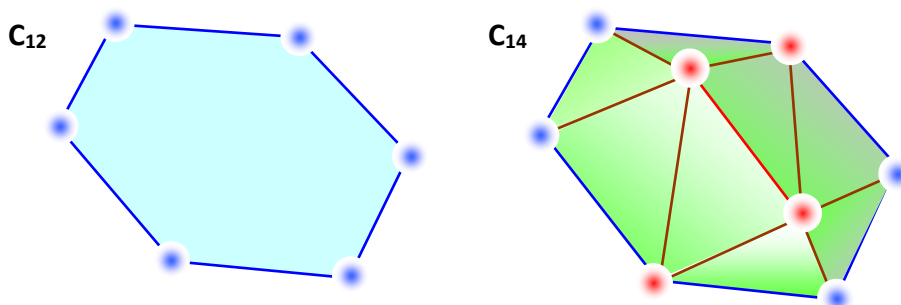


Fig. 14. Frames of CCC (curvature concentration centers) of fullerenes  $C_{12}$  and  $C_{14}$

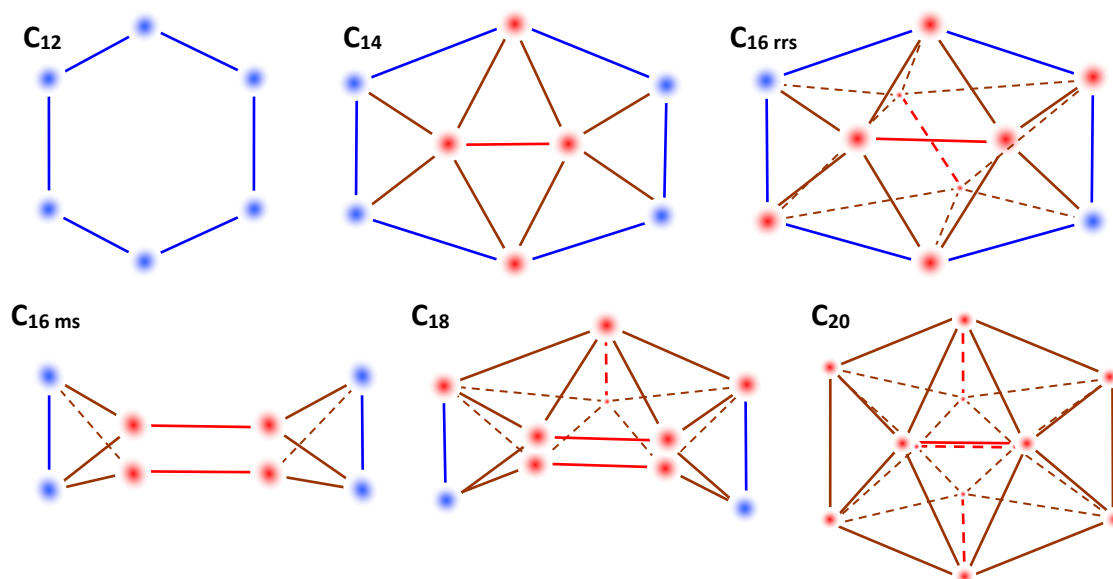


Fig. 15. Graphs of CCC (curvature concentration centers) for family  $C_{12}$

It is worth noting some facts. The most energy (and therefore the most stress state) is characteristic for fullerenes which curvature concentration centers (CCC) compose plane hexagons. The least energy (and therefore the least stress state) refers to those having CCC in the form of an icosahedron. It must be remembered that the fullerene, creating such CCC, is a dodecahedron, an icosahedron and dodecahedron being dual.

Fullerene  $C_{16}$  ms has a larger energy in comparison with fullerene  $C_{16}$  rrs. Probably this phenomenon is associated with the fact that mirror symmetry doesn't create, as rotation reflection symmetry, a compact structure of CCC where the centers of stress concentration are compensated.

In a similar manner it is possible to explain the dependence of fullerene energy on size and shape for families  $C_{24}$  and  $C_{36}$ , if to design the structure of their CCC (Figs. 16–19). The local maxima of energy correspond to loose or asymmetric CCC structures; the local minima refer to compact ones.

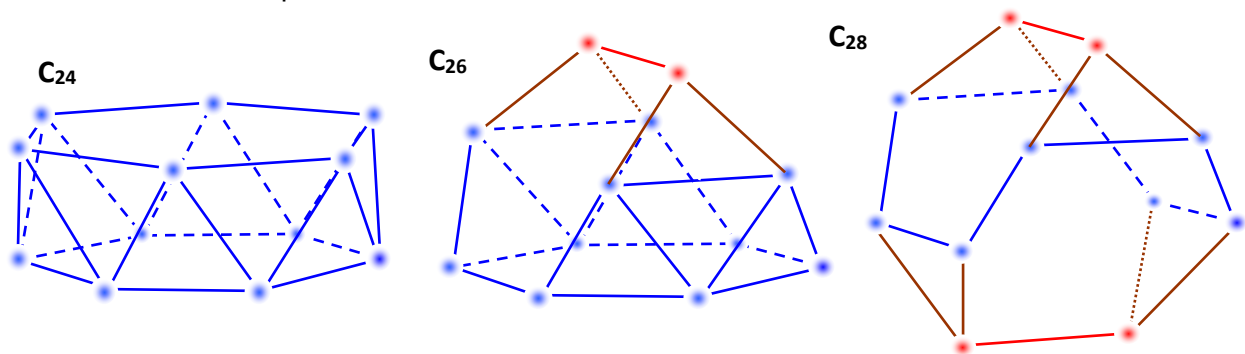


Fig. 16. Frames of CCC (curvature concentration centers) for fullerenes  $C_{24}$ ,  $C_{26}$  and  $C_{28}$

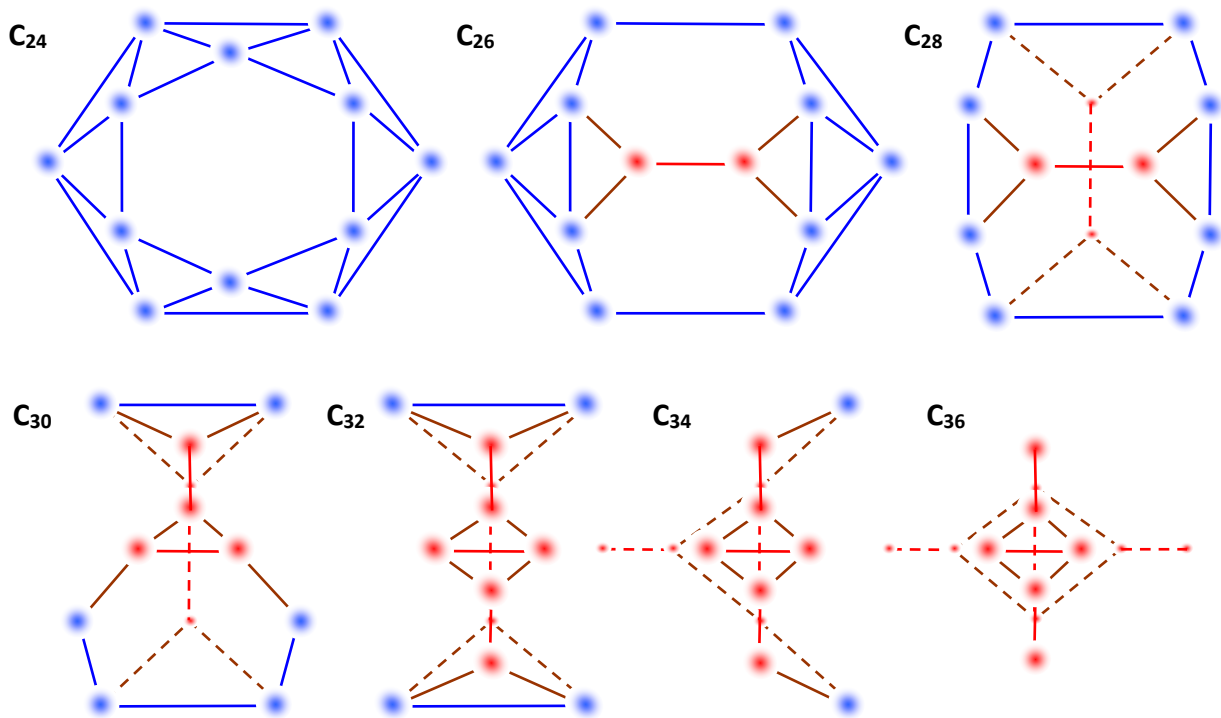
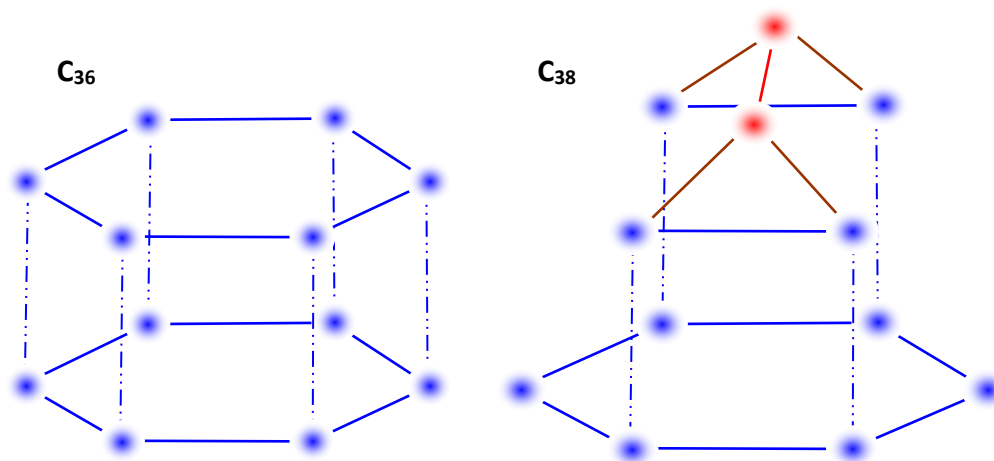
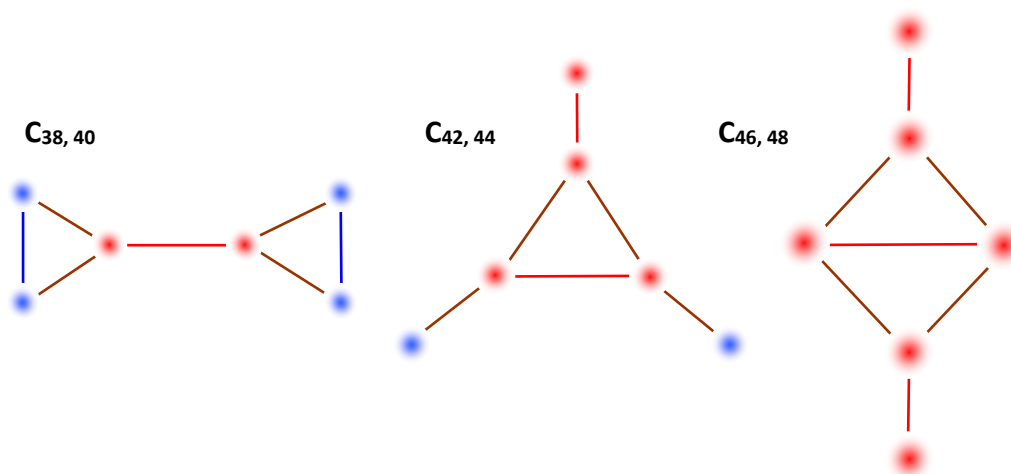


Fig. 17. Graphs of CCC (curvature concentration centers) for family of  $C_{24}$



**Fig. 18.** Frames of CCC (curvature concentration centers) of fullerenes  $C_{36}$  and  $C_{38}$



**Fig. 19.** Graphs of CCC (curvature concentration centers) for family of  $C_{26}$  (only a half is shown; the second half is symmetric)

The fullerene shape is a result of self-organization and here there are possible several types of curvature. During the growth old CCC-s disappear, new CCC-s are generated, but the number of CCC-s remains constant for each family.

## Future investigations

We assume that first of all it is necessary to find the curvature concentration centers. In doing so, we gain the arrangement of stress concentration, can apply the elasticity theory not only to the fullerenes (this task is very cumbersome) but to the polyhedrons of curvature concentration centers (the task is easier). Moreover, the energy of fullerenes can be considered not only as a global quantity, but as a surface distribution. Since the CCC polyhedrons resemble crystals, and the crystals are studied for years [37], we can use this knowledge for understanding such processes as, e.g. sublimation, fracture of fullerenes. As a result, we would be able to gain more profound insight into their nature.

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