Periodic system of fullerenes: the column of six-fold symmetry

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ABSTRACT
The possible ways of generation and growing the fullerenes having six-fold symmetry have been studied. Beginning with cyclohexane C_6H_{12}, benzol C_6H_6 and clusters C_6C_6, we obtained elementary fullerenes C_{12} and mini-fullerenes C_{24}, which produce the fullerenes from C_{24} to C_{84}; perfect (basic), as well as nanotubes. The basic fullerenes C_{24}, C_{36}, C_{48}, C_{60}, C_{72} and C_{84} have the ordinary six-fold symmetry. We have calculated their energies and discussed possible reasons for their dependence on a fullerene size and shape in the framework of the periodic system of fullerenes.
KEYWORDS
carbon • energy • fullerene • fusion   reaction • graph   representation • nanotube • periodic   system single and double bonds • symmetry

Introduction

Up to now an origin and growth of fullerenes and nanotubes is hotly debated [1–34]. The appearance of the periodic table of fullerenes [35,36] allowed change the strategy of investigation: phenomenological approach to fullerenes was replaced by task-oriented activity. The periodic table of fullerenes consists of horizontal series and vertical columns; they include fullerenes from C_{14} to C_{108}. The horizontal series form the Δn periodicities, Δn=2, 4, 6, 8, 10, 12, 14, 16, 18, where the fullerene structure changes from three-fold symmetry to six-fold through four and five 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, i.e. Δm=6, 8, 10, 12. We declare that the periodic system must be taken as a base for rigorous fullerene classification.

At first we have studied isomers of fullerenes from C_4 to C_{60} [37–41]. In parallel we have investigated nucleation and growth of the fullerenes referring to the columns of three-fold [42], four-fold [43] and five-fold symmetry [44]. In this contribution we present the results obtained for the fullerenes referring to the column of six-fold symmetry.

Nucleation and growth of embryos

We assume that the embryos of fullerenes of six-fold symmetry are similar to cyclic hydrocarbons of the same symmetry: cyclohexane (C_6H_{12}) or benzol (C_6H_6).

Cyclohexane

At first, cyclohexane was depicted as a molecule having a plane carbon ring. Later it was established that it has highly symmetric 'chair' configuration which belongs to the symmetry group D_{3d} (Fig. 1(a)). Here [45] four carbon atoms lie in one plane, two others are disposed bilaterally along the plane, all the valence angles CCC are tetrahedral, and all the C-H bonds of neighboring methylene groups are disposed in chess order with respect to each other. From twelve C-H bonds, six bonds are axial and parallel to the symmetry axis of the third order; other six bonds are equatorial. Geometric parameters of the molecule are as follows: r(C-C)=1.54 Å, r(C-H) = 1.09 Å. The chair is a stable conformation of cyclohexane. Another conformation is a boat (a bath) which belongs to the symmetry group C_{2v} and is shown in Fig. 1(b). It is unstable and at room temperature only one molecule from a thousand has a boat conformation. Chemical and physical methods are unable to fix each conformation separately; they see only an average picture. We have calculated their frozen structures and energy through the use of Avogadro package [46].

(a)   (b)

E=55.5 E=854
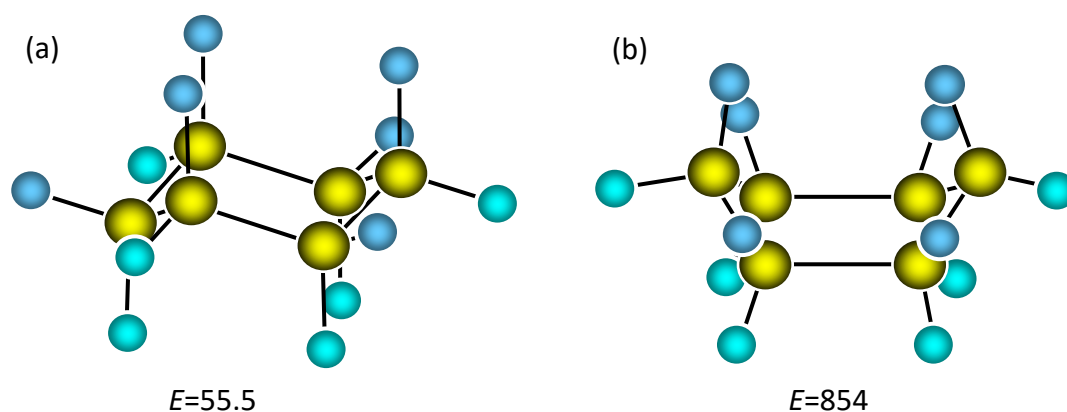
Fig. 1. Structure of a cyclohexane molecule: (a) chair conformation, (b) boat conformation. Large spheres are carbon atoms, small spheres are hydrogen atoms: E is energy, kJ/mol

Benzol

Another embryo of fullerenes of six-fold symmetry is similar to benzol (C_6H_6). For benzol it is customary to assume that the benzol molecule is a regular hexagon with D_{6h} symmetry [45,47] and not a system of alternating long and short bonds. It is believed that in this case there appear delocalized electrons which create bonds. This question is beyond the scope of our study. Nevertheless, it should be mentioned the following. As noted above, chemical and physical methods are unable to fix each electronic conformation separately; they see only an average picture. However, an electronic conformation can be fixed if the system is frozen. Such situation takes place in fullerenes, where the benzol hexagon is rigidly incorporated into a fullerene molecule. Here for fullerene C_{60} atomic force microscopy picture of one of the symmetry equivalent hexagons clearly shows the two different types of bonds [48]. The measured bond lengths are r_{hh} = 1.38 Å and r_{hp} = 1.4654 Å. For this reason, we take in consideration the bond-order discrimination in our study. We have calculated the frozen structure and energy of benzol through the use of Avogadro package [46]. The result is shown in Fig. 2.
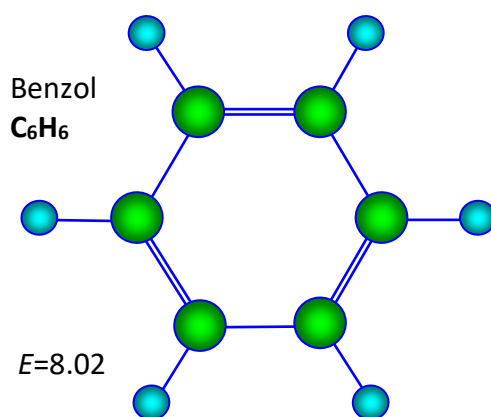
Fig. 2. Benzol: carbon ring and six hydrogen atoms on its periphery, *E* is energy, kJ/mol

Clusters

Suppose that we have removed hydrogen atoms from cyclohexane and added carbon atoms instead. In doing so we obtain clusters C_6C_6 with several types of carbon atoms. The carbon atoms of cyclohexane remain in the initial electronic state. The new added ones are reactive carbon atoms; they are connected with the initial carbon atoms by single or double bonds, being ionized to a different degree. Similar to cyclohexane, we can remove hydrogen atoms from benzol and add carbon atoms instead. In doing so we obtain also cluster C_6C_6 with several types of carbon atoms. We have calculated the optimized structures and energy of these compounds through the use of Avogadro package [46]. The results are presented in Fig. 3.
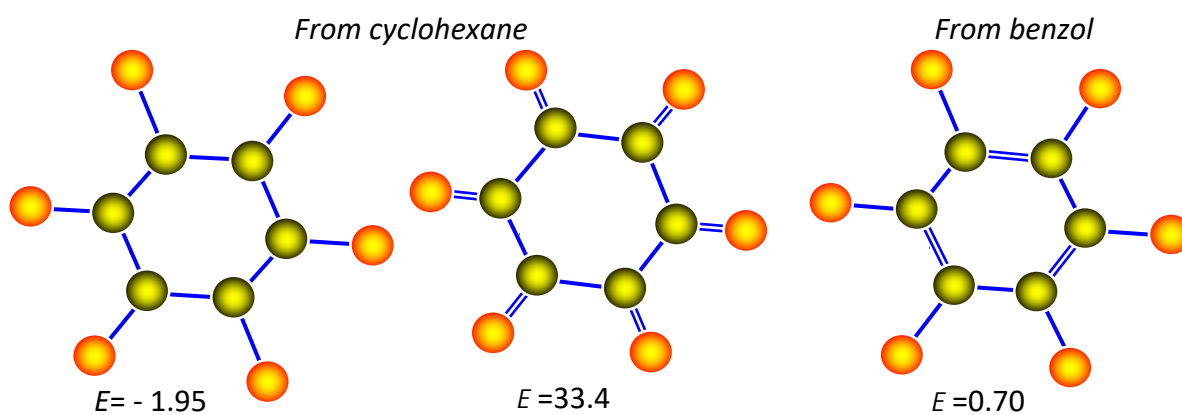

Fig. 3. Carbon clusters C_6C_6 obtained from cyclohexane and benzol, *E* is energy, kJ/mol

Folding and elementary fullerenes

One of the ways of further cluster evolution is folding and forming a hexa-angular prism (Fig. 4). 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.

Consider cluster folding more closely. The folding produces a hexagonal prism of six-fold symmetry which may be thought over as an elementary fullerene. Several electronic configurations are presented in Fig. 4.

E=1207 E=2738 E=2738 E=2738
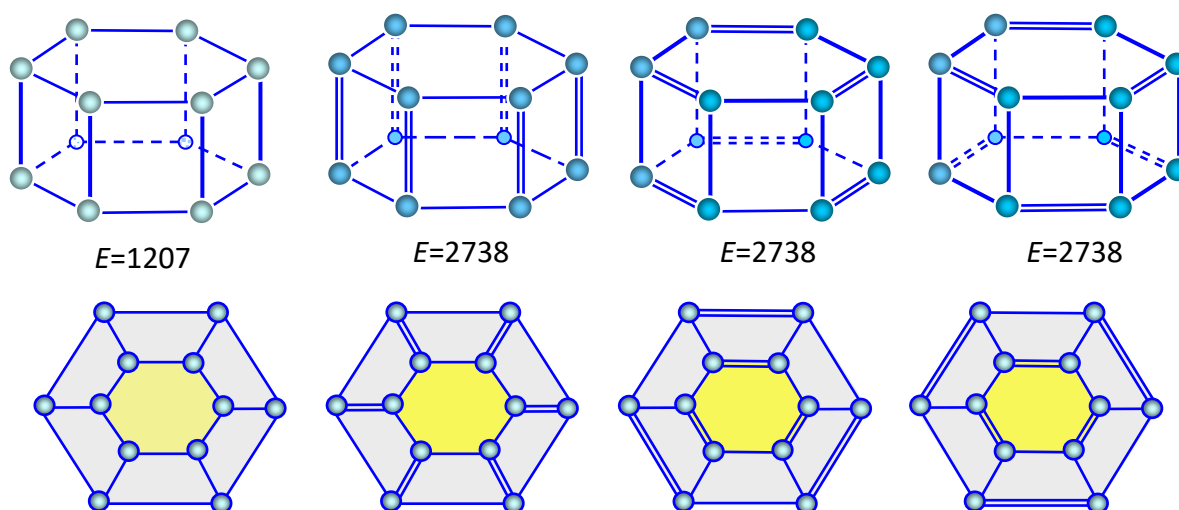
Fig. 4. Folding clusters into hexagonal prisms: structure and graphs; E is energy, kJ/mol

Fusion of prisms

From this point we will consider the prisms as elementary fullerenes. The 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. 5. To gain a better understanding of the fullerene structure, the graph areas are also painted in different colors: pentagons in goldish and hexagons in yellow as before.

E=697 E=1778 E=1478
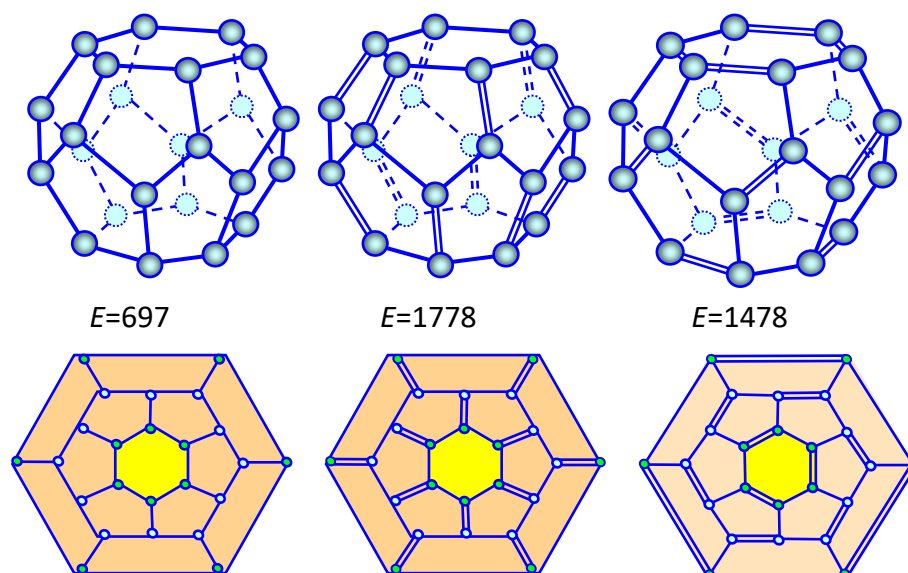
Fig. 5. Six-cornered barrel-shaped fullerene C_{24} as a result of prisms fusion; its graphs and energy E, kJ/mol

In its turn this barrel-shaped fullerene can continue the symmetry-conserving growth through the use of the above mentioned mechanism, i.e. joining with another hexagonal prism according to reaction $C_{24}+C_{12}$ (Fig. 6). The reaction is possible since the reacting structures have six-fold symmetry and therefore they are compatible with each

other. The subsequent-fusion growth of the fullerene, $C_{36}+C_{12}$ or $C_{24}+C_{24}$, is presented in Fig. 7. However further fusions create nanotubes.
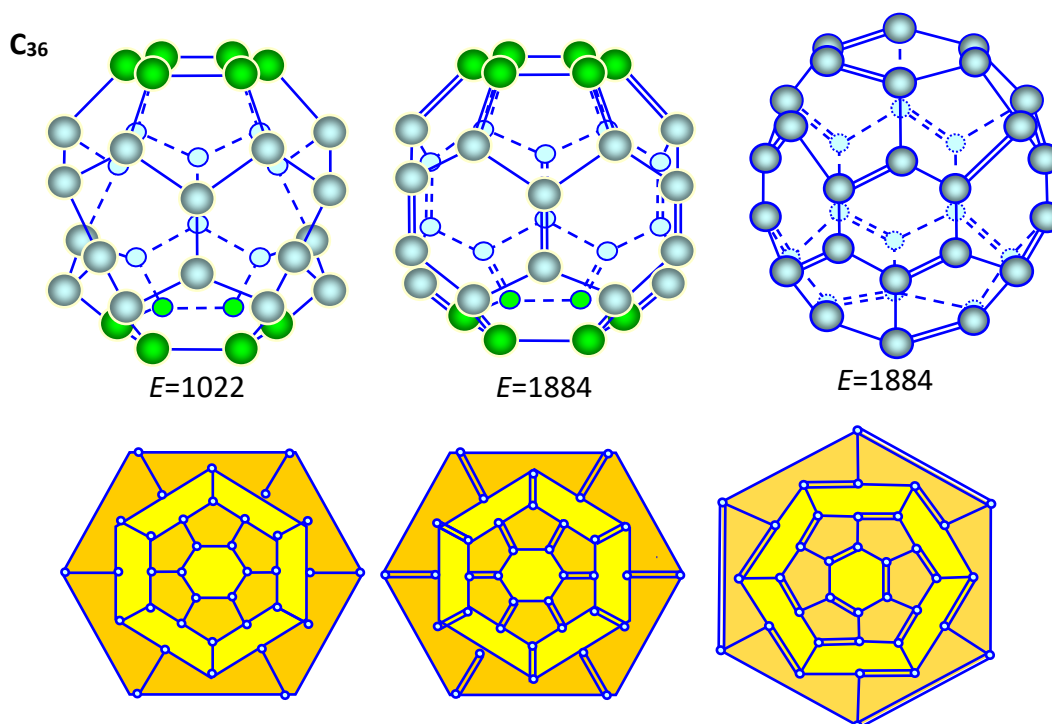

Fig. 6. Joining barrel-shaped fullerene C_{24} with prism C_{12}; structure, graphs; *E* is energy, kJ/mol
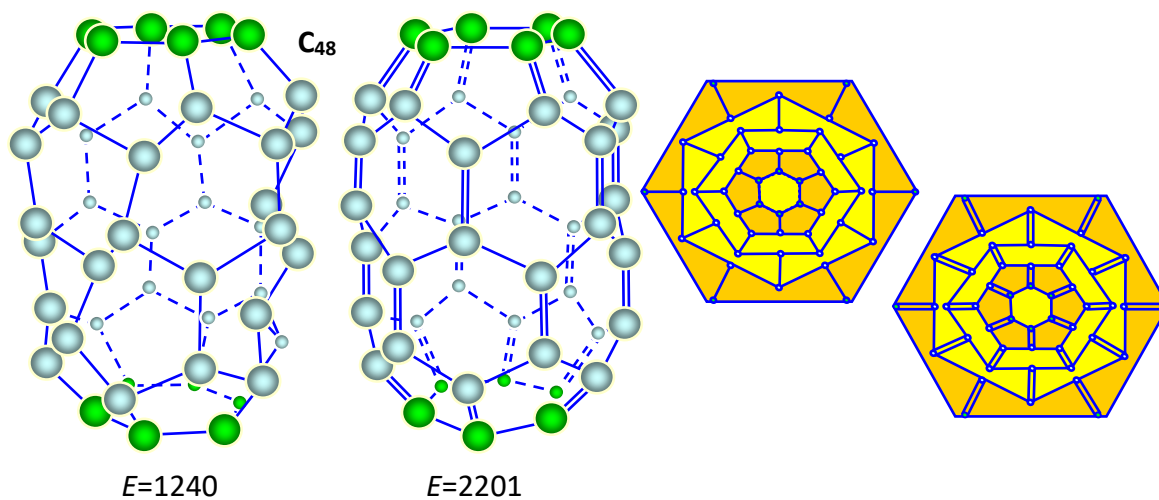

Fig. 7. Nanotube as joining two fullerenes C_{24}; structure and graphs; *E* is energy, kJ/mol

Cluster growth

Another way of looking at the gradual evolution of the clusters is the growth of initial clusters by joining single carbon atoms or carbon dimers. The complexes formed then transform into half-fullerenes (cupolas) conserving the symmetry of clusters [36].

Graphite

One additional comment is necessary for the six-fold-symmetry clusters. "Carbon atoms in graphite are arranged in plane paralleled layers which are slightly connected with each other. In each layer each carbon atom is bounded with three others by one double and two single bonds. A plane configuration of these bonds defines a plane structure of the entire layer. In reality all the three bonds are equivalent and valent angles are equal to $120°$, since a double bond can occupy any of three possible positions around a carbon atom. This leads to indefinitely high number of different resonant structures of the layer (Fig. 8). Such description is equivalent to another, when an electron pair of each double bond displaces into a delocalized orbital enveloping the entire layer [49]. However, this does not influence on the geometry of a molecule which is dictated by the plane arrangement of three localized single bonds; the bonds being around each carbon atom". We assume that this phenomenon is referred to fullerenes too. In the following, we will use this fact in producing input data for calculations.
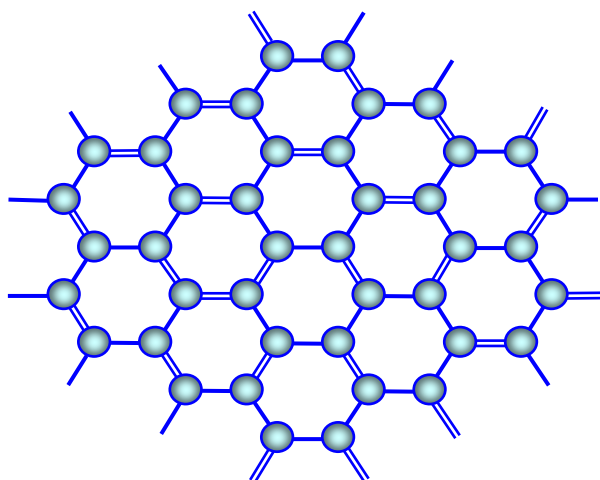
Fig. 8. One of possible resonant structures for a carbon-layer fragment in graphite. Based on [49]

Gaudi cupolas

They can be obtained by joining single carbon atoms to clusters C_6C_6 shown in Fig. 3. The result is presented in Fig. 9. From the figure it is seen that the cupolas have one and the same base of six atoms; they can combine with each other creating a new fullerene of six-fold symmetry. Reaction $C_{18}+C_{18}$ is equivalent to reaction $C_{24}+C_{12}$ considered above and has just the same result. The fullerene obtained is shown in Fig. 6.
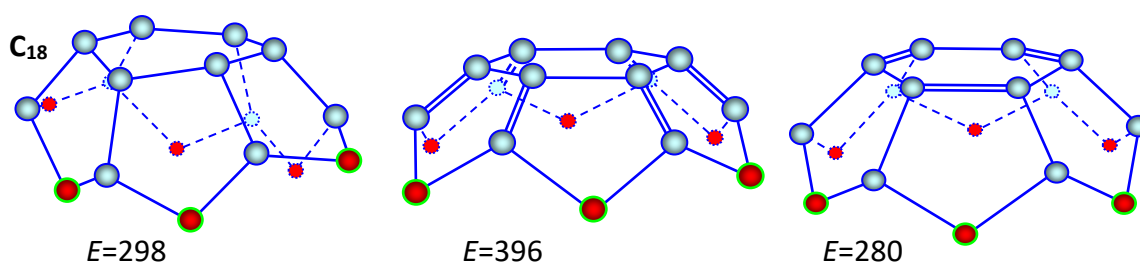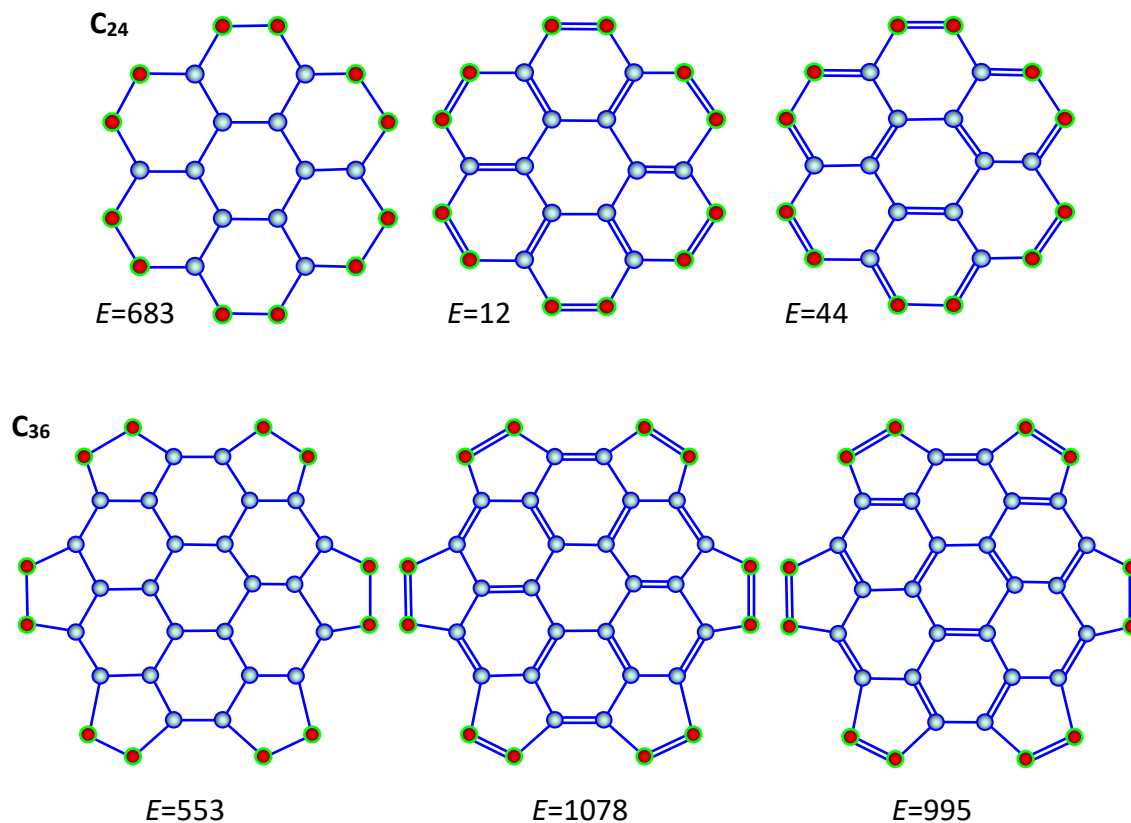
C_{18}

$E=298$ $E=396$ $E=280$

Fig. 9. Gaudi cupolas of six-fold symmetry: structure, E is energy, kJ/mol

Graphene fragments

Another way of looking at gradual evolution of the clusters C_6C_6 is the growth of initial clusters by joining carbon dimers, with producing graphene fragments conserving six-fold symmetry (Fig. 10).

Fig. 10. Graphene fragments of six-fold symmetry: structure, *E* is energy, kJ/mol
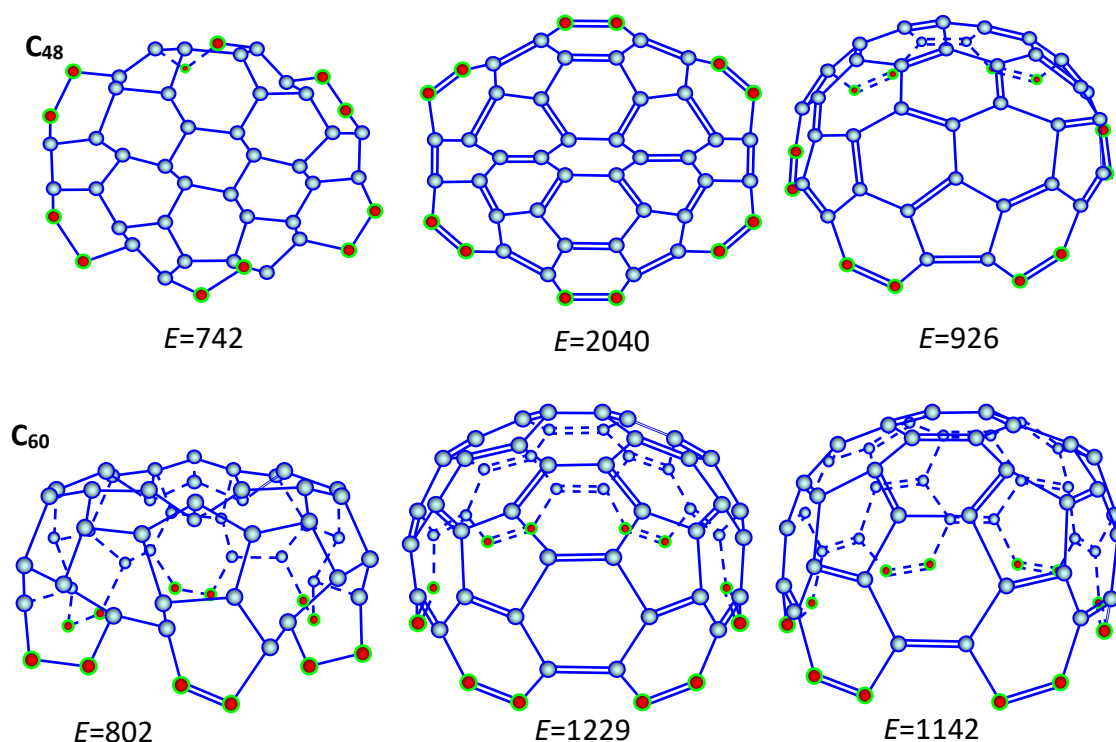
Fuller cupolas

Beginning with C_{36} the graphene fragments contain pentagons. As a result of further growth transforms the plane surface into a curved one and the graphene fragments begin to grow as Fuller cupola (Fig. 11). From the figure it is seen that all the cupolas have one and the same base of twelve atoms; therefore, they can combine with each other creating new fullerenes.

Basic perfect and intermediate imperfect fullerenes

According to the periodic system of fullerenes [35,36], there are two main types of fullerenes; the basic perfect ones and intermediate imperfect ones. The basic perfect fullerenes have ideal structure and common symmetry. The intermediate imperfect fullerenes have extra carbon dimers. By analogy with crystal physics, we have assumed that these extra dimers play the role of defects which violate the common symmetry and create local imperfections. However, for defect crystals the long-range-order is observed experimentally. In order to underline this peculiarity, such long-range order is referred to

as the topological long-range one [50]. Using analogous terminology, we have defined the imperfect fullerenes, which conserve the main axis of common symmetry, as having topological symmetry.

C₄₈

E=742   *E*=2040   *E*=926

C₆₀

E=802   *E*=1229   *E*=1142

Fig. 11. Fuller cupolas of six-fold symmetry: structure, *E* is energy, kJ/mol

Perfect fullerenes

According to the first issue of periodic system of fullerenes in 2017 [36] there are the following basic perfect fullerenes and nanotubes of six-fold common symmetry: C_{36}, C_{48}, C_{60}, C_{72}, C_{84}, C_{96} and C_{108}. In 2018, we enlarged the system from above adding series $\Delta n=2$ and 4 [36]. Series $\Delta n=2$ contains the elementary fullerenes of similar shape (prisms) but having different symmetries. Series $\Delta n=4$ contains the barrel-shape fullerenes of different symmetries. As a result, the column of six-fold-symmetry fullerenes incorporated two new perfect fullerenes, C_{12} and C_{24}. Consider all these fullerenes in more detail.

*Elementary fullerene C_{12}.* It is a hexahedral right–angle prism (Fig. 4). Its generation was discussed above.

Barrel-shaped fullerene C_{24}. It is a barrel-shaped fullerene (Fig. 5). Other features are considered above,

Fullerene C_{36}. The fullerene was obtained by fusion barrel-shaped fullerene C_{24} with prism C_{12} (Fig. 6). There are other ways of producing this fullerene (Fig. 12), e.g. fusion of two cupolas C_{18}, or fusion of two graphene fragments C_{12} and C_{24}.

At first two molecules C_{18}, or C_{12} and C_{24}, are moving towards each other (Fig. 12(a,d)). Then the boundary atoms (dark-red) interact with each other producing a compound (Fig. 12(b,e)). During this process new covalent bonds (heavy red lines) are

generated, distorted polyhedrons are formed; they relaxing into perfect polyhedrons (Figs. 12(c,f)).
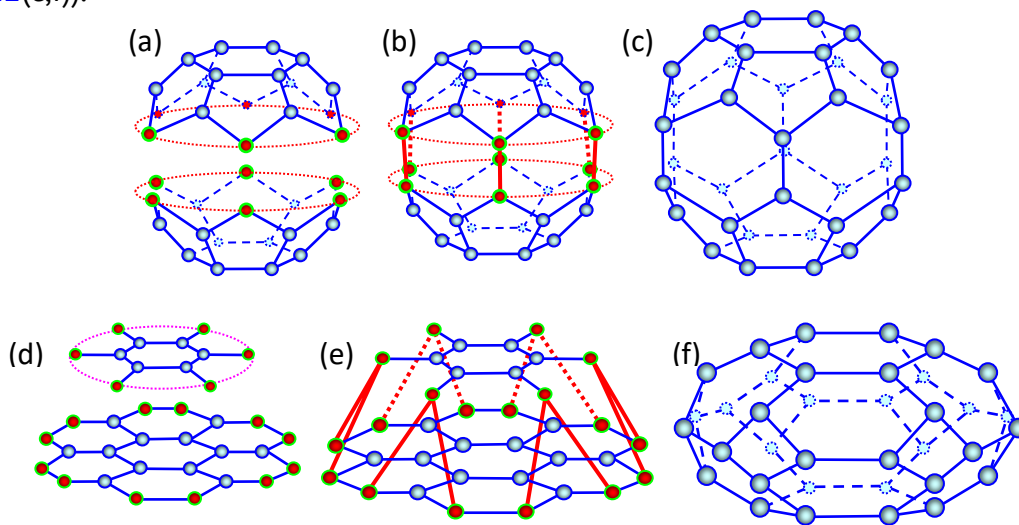

Fig. 12. C_{36} as joining two cupolas C_{18} (a,d) and two graphene fragments C_{12} (b,e) and C_{24} (c,f)

In the first case one obtains just the same fullerene as is shown in Fig. 6, having the same energy. In the second case we have an isomer of this fullerene (Fig. 13). The isomer obtained consists of six tetragons and fourteen hexagons; it contains twenty four faces. One may name this perfect isomer, having six-fold symmetry, a truncated six-angular bipyramid.
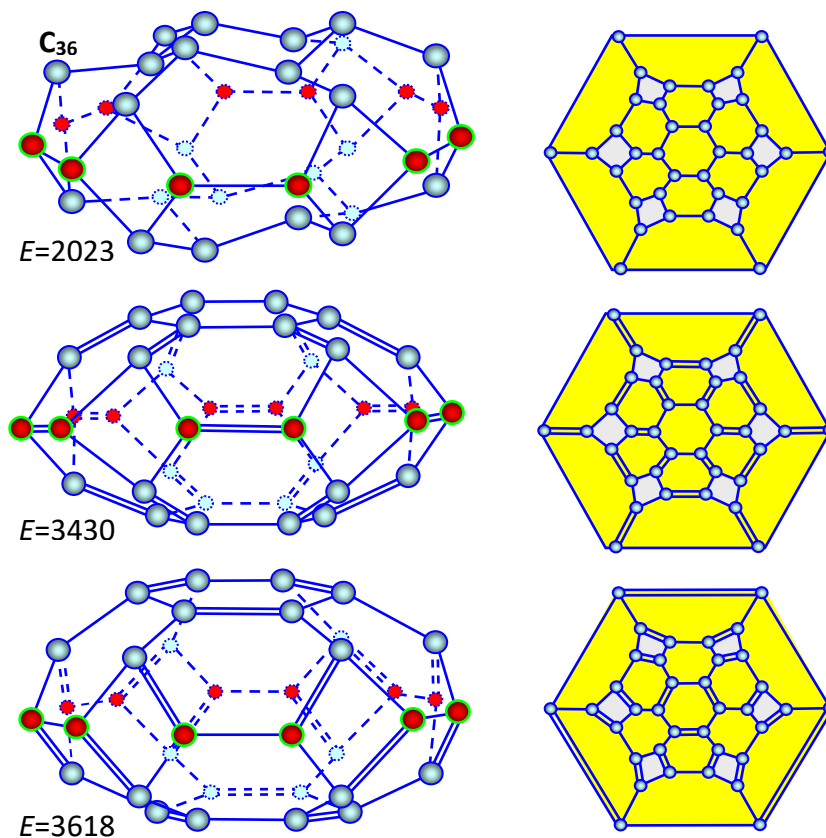
Fig. 13. Truncated six-angular bipyramid C_{36} and its graphs; E is energy, kJ/mol
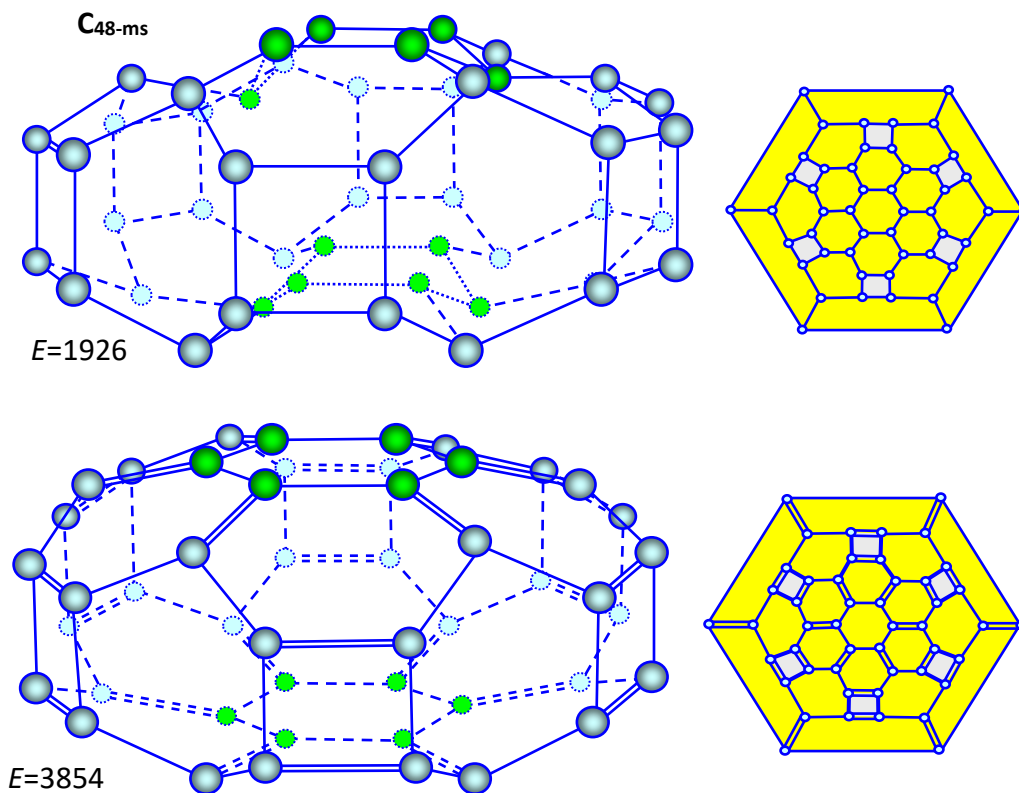
Fig. 14. Fullerene C_{48} as a result of joining two cupolas C_{24} of six-fold symmetry: the mirror symmetry fusion, structure and graphs; E is energy, kJ/mol
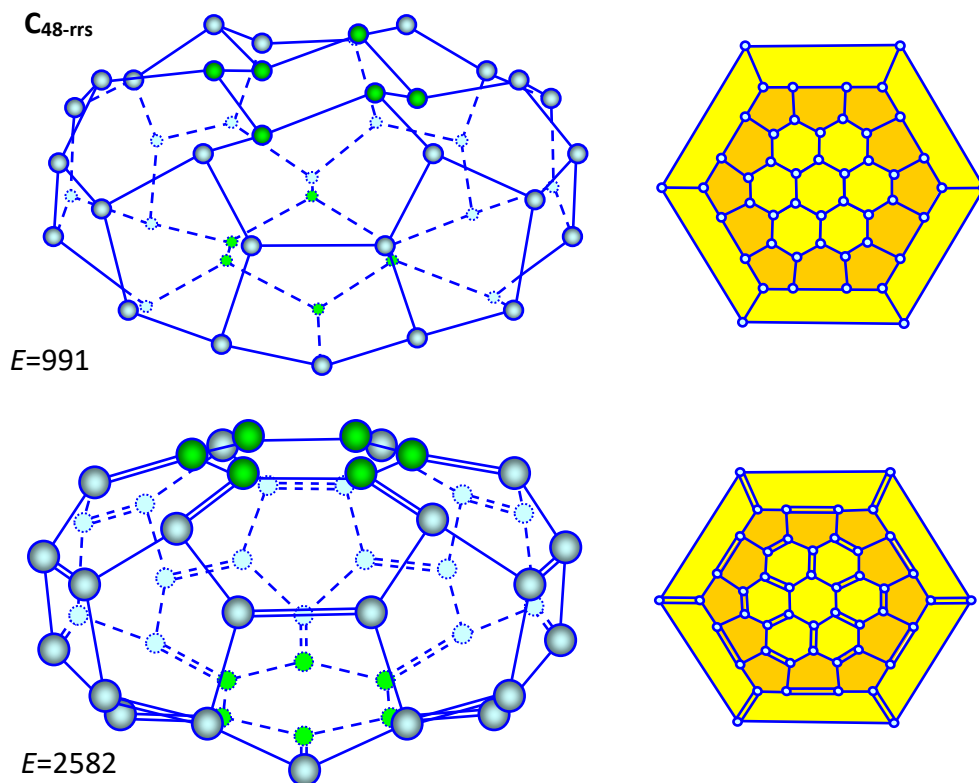

Fig. 15. Fullerene C_{48} as a result of fusion of two cupolas C_{24} having six-fold symmetry: rotation-reflection symmetry joining: structure, graphs, E is energy, kJ/mol

Fullerene C_{48}. One can design two isomers of six-fold-symmetry fullerene by two different ways of joining two cupolas C_{24}. It should be emphasized that there are two modes of cupola joining: mirror symmetry and rotation-reflection one. In the first case the lower cupola is a mirror copy of the upper one. The fullerene obtained consists of six tetragons and twenty hexagons (Fig. 14); it has twenty-six faces. It is a tetra$_6$-hexa$_{20}$ polyhedron. In the second case the lower cupola is a rotatory reflection of the upper one. The fullerene obtained contains twelve pentagons and ten hexagons, the number of faces being the same (Fig. 15). It is a penta$_{12}$-hexa$_{14}$ polyhedron. Its energy is less than that of the first fullerene.

Fullerene C_{60}. We have designed this fullerene of six-fold symmetry by fusion of a graphene fragment C_{24} and a cupola C_{36} (Fig. 16). The fullerene obtained contains six pairs of two adjacent pentagons and twenty hexagons (Fig. 17). It is a penta$_{12}$-hexa$_{20}$ polyhedron of six-fold symmetry.
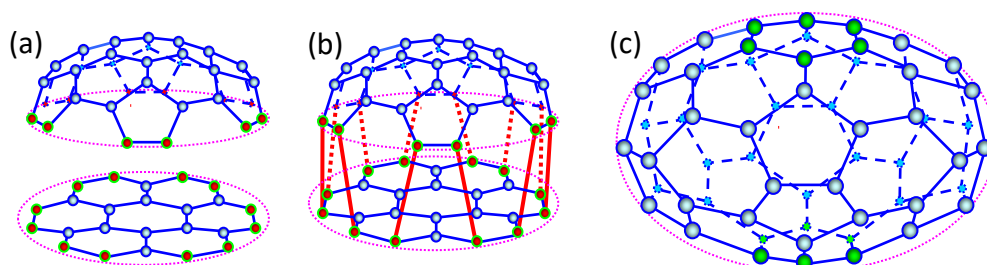

Fig. 16. Scheme of joining graphene fragment C_{24} and cupola C_{36}: (a) separate carbon components; (b) intermediate compounds; (c) polyhedron obtained
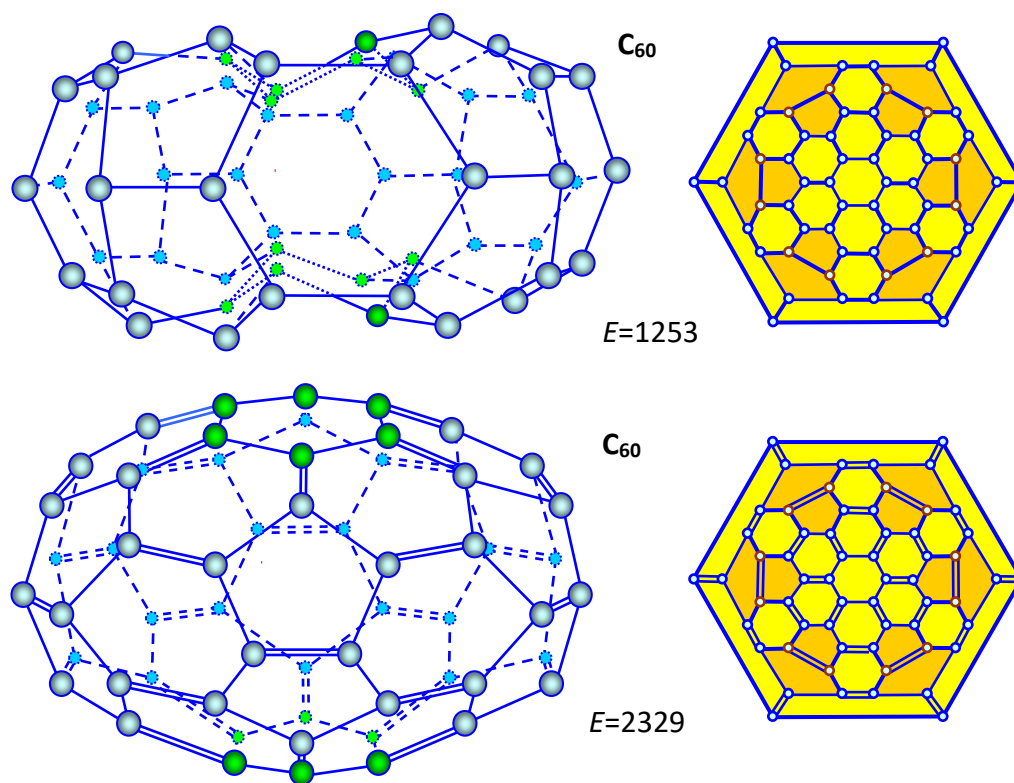

Fig. 17. Structure, energy and graphs of fullerene C_{60} with single and double bonds
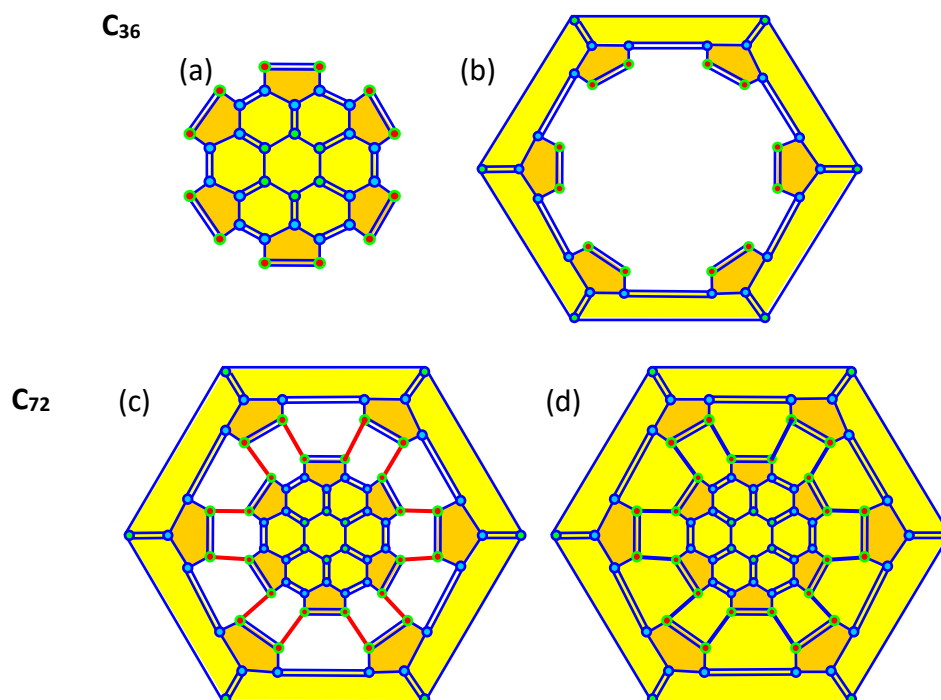
Fullerene C₇₂. One can design this fullerene of six-fold symmetry by fusion of two cupolas C₃₆ what is shown in Figs. 18–20. It should be emphasized that one of the graphs is reverse.
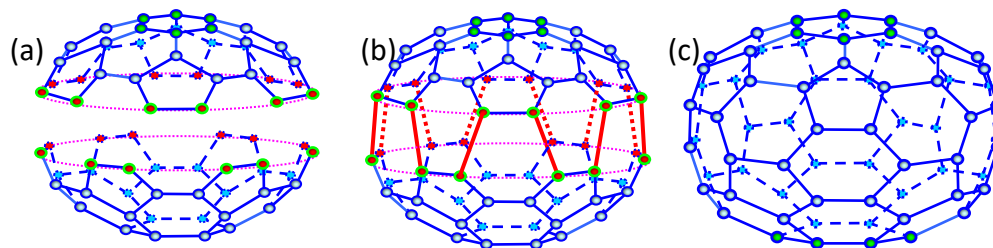
Fig. 18. Scheme of joining two half-fullerenes C₃₆:
(a) separate carbon cupolas; (b) intermediate compound; (c) polyhedron C₇₂ obtained
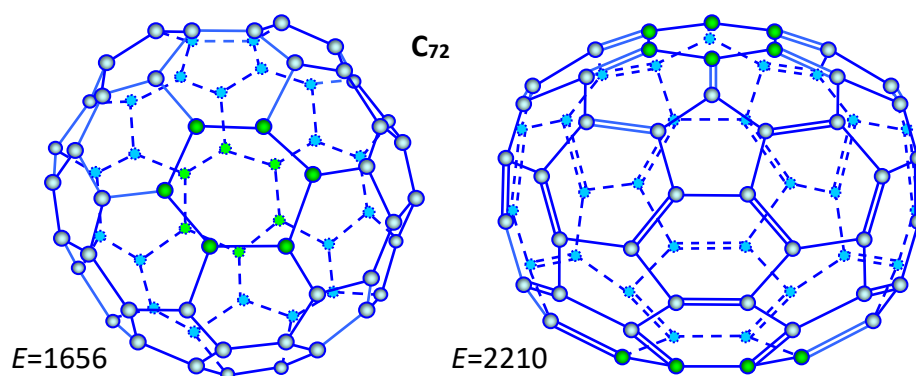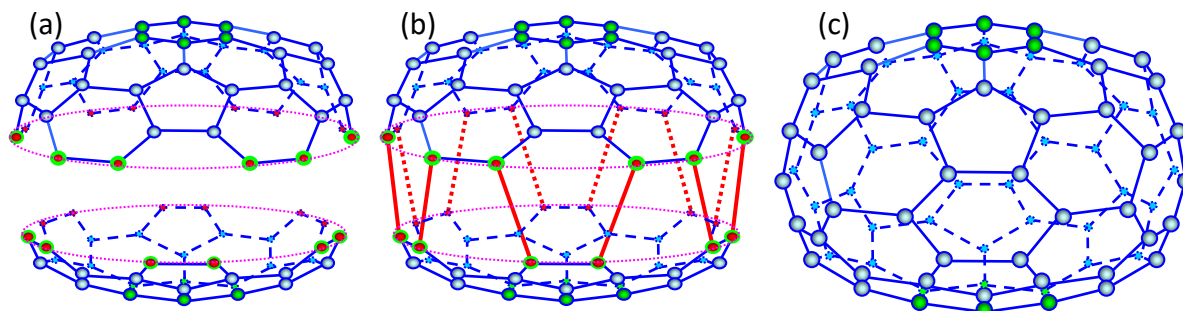

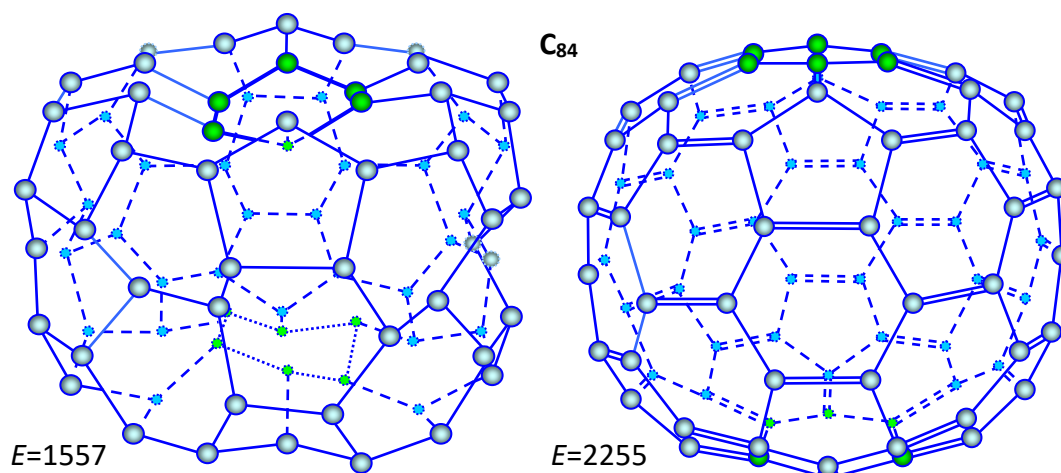**Fig. 19.** Structure and energy *E* (kJ/mol) of fullerene C₇₂

Fig. 20. Fusion reactions of cupolas C₃₆ as graph embedding: (a) graph of cupola C₃₆; (b) reciprocal graph of cupola C₃₆; (c) graph embedding; (d) graph of fullerene C₇₂

Fullerene C_{84}. In a similar manner it is possible to construct this fullerene of six-fold symmetry by fusion of cupolas C_{36} and C_{48} what is shown in Figs. 21–23.

Fig. 21. Joining two half-fullerenes C_{36} and C_{48}, and fullerene C_{84} obtained: (a) separate carbon cupolas; (b) intermediate compound; (c) polyhedron after relaxation

E=1557 E=2255

Fig. 22. Structure and energy E (kJ/mol) of fullerene C_{84}

Fig. 23. Fusion reactions of cupolas C_{36} and C_{48} as graph embedding: (a) graph of cupola C_{48}; (b) reciprocal graph of cupola C_{36}; (c) graph embedding; (d) graph of fullerene C_{84}
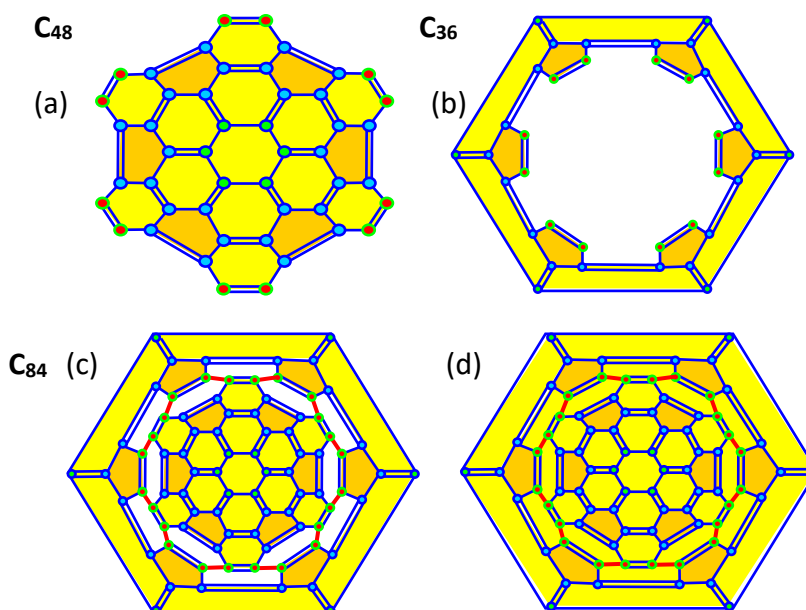
Nanotube C96. The next perfect fullerene is a nanotube. One can design this nanotube of six-fold symmetry by fusion of two cupolas C_{48} what is shown in Figs. 24–26. Let's analyze these figures. The question arises: what we have obtained, fullerenes or nanotubes? Where is the boundary between fullerenes and nanotubes? An intuitive idea says that a fullerene is a spheroid, whereas a nanotube with open ends is a cylinder and a nanotube with closed ends is a cylinder with two hemispheres. Each spheroid can be divided into three parts; two hemispheres. If the height of cylinder is less than the height of two hemispheres, we assume that it is a fullerene. On the contrary we have a nanotube. In its turn the cylinder height is defined by the number of adjacent hexagons. To form a cylinder one needs to have along its height at least one hexagon which is not connected with pentagons. Referring to the graphs shown, we admit that the nanotubes begin with the structure C_{96}.

It is worth noting that both fullerenes and a nanotube have one and the same number of pentagons, namely twelve, being equal to a double degree of symmetry.
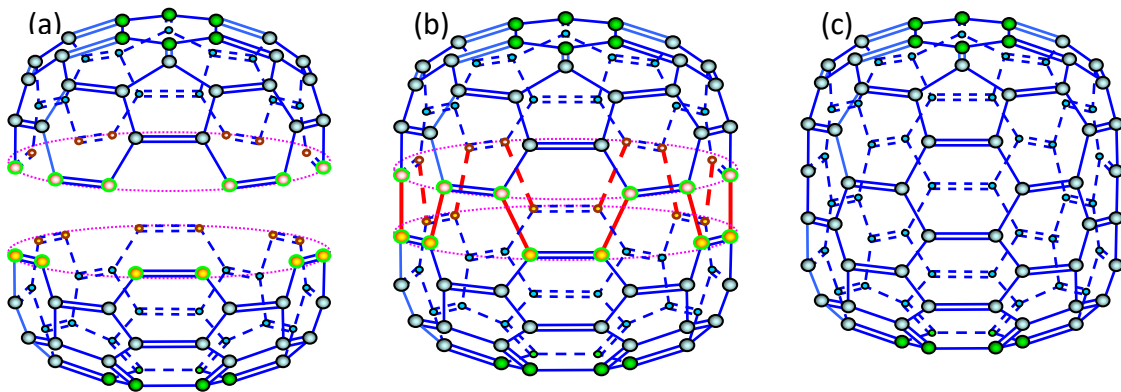
Fig. 24. Rotation-reflection-symmetry joining of two cupolas C_{48}: (a) separate cupolas C_{48}; (b) intermediate compound; (c) nanotube C_{96} obtained
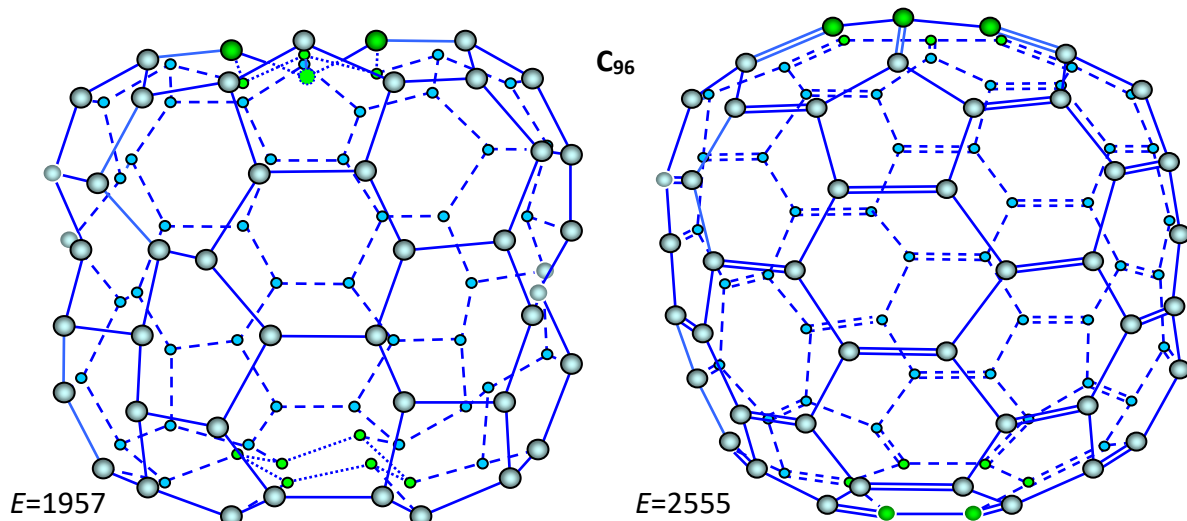
Fig. 25. Structure and energy *E* (kJ/mol) of nanotube C_{96}
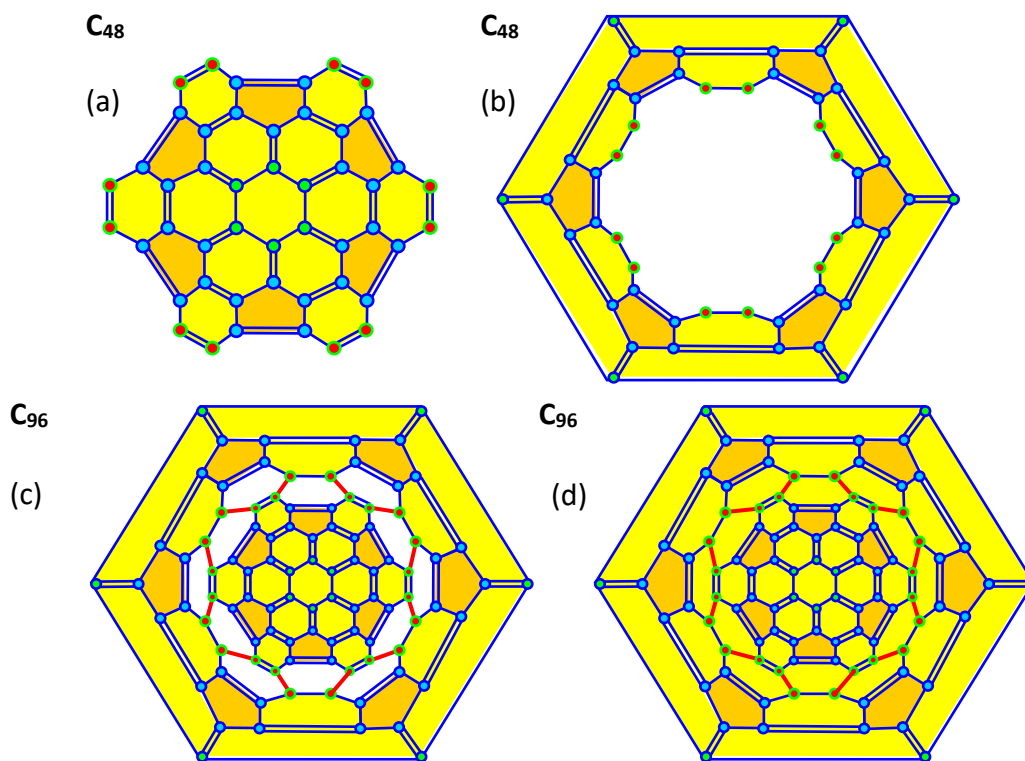
Fig. 26. Fusion reactions of cupolas C_{48} as graph embedding: (a) graph of cupola C_{48};
(b) reciprocal graph of cupola C_{48}; (c) graph embedding; (d) graph of nanotube C_{96}

Summary and Discussion

We have studied possible ways of generation and growing the fullerenes having six-fold symmetry. Beginning with cyclohexane C_6H_{12}, benzol C_6H_6 and clusters C_6C_6, we obtained at first elementary fullerenes C_{12} and mini-fullerenes C_{24}, and then the fullerenes from C_{36} to C_{96}, including a nanotube. We have calculated the energies of the possible fullerenes.
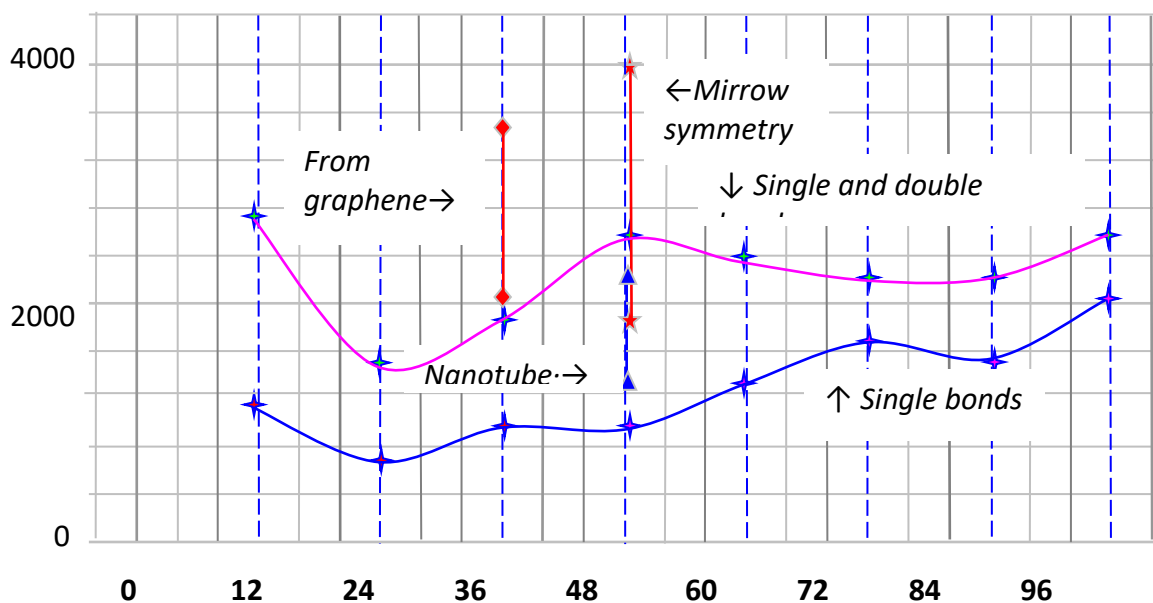
Fig. 27. Energy *E* of fullerenes in kJ/mol as a function of fullerene size and shape

In Table 1, the energies of fullerenes are presented, for fullerenes with single bonds only (above) and single and double bonds (below). The energies are also shown in Fig. 27.

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

| C_{12}	C_{24}	C_{36}	$C_{36graph}$	$C_{48\,rrs}$	$C_{48\,ms}$	C_{48tube}	C_{60}	C_{72}	C_{84}	C_{96tube}
1207	697	1022	(2023)	991	(1926)	(1240)	1253	1656	1557	1957
2738	1478	1844	(3430)	2582	(3854)	(2201)	2329	2210	2255	2555

Continuity and discontinuity

These notions are connected with the Ionic and Pythagorean schools of philosophy (VI–IV century B.C.) [51]. 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 ϋλη καί τό είδος*); the form being an active element produces movement [51].

In mathematics there are such notions as curvature, tensor of curvature [52]. 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 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.
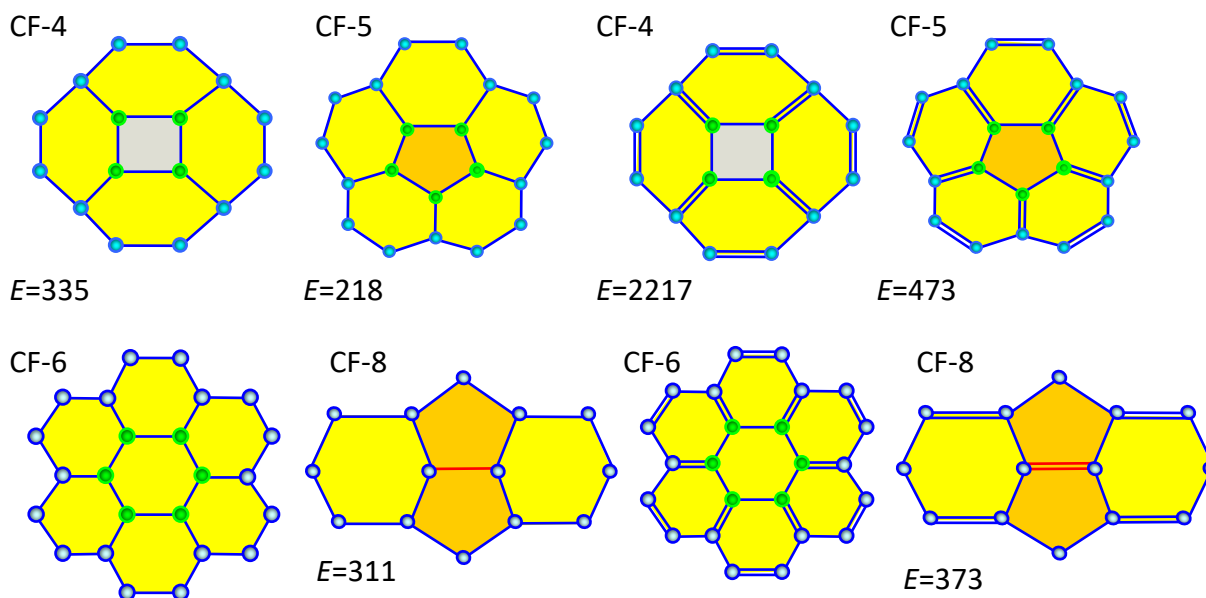
Fig. 28. Curvature fragments of fullerenes

Curvature of fullerenes

We will follow to Aristotle trying finding the forms of fullerenes, which define its surface curvature. In other words, we will search first of all "fragments of curvature", but not a curvature value. Further we will use the following notions: curvature as continuity

property and curvature fragments as discontinuity. Analysis of the fullerene structures shown before allows us to separate the following curvature fragments (Fig. 28). It should be emphasized that an isolated fragment CF-6 does not creates curvature; it becomes a curvature fragment under the influence of surroundings.

Different curvature fragments have their own symmetry. We name a center of symmetry "curvature concentration center". The study of its arrangement in different fullerenes has given the following picture (Fig. 29). The figures resemble rings (C_{12}, C_{48ms}), zig-zag ring (C_{48rrs}), prisms (C_{60}, C_{84}), Archimedes antiprisms (C_{24}, C_{72}) and a biantiprism (C_{36}).
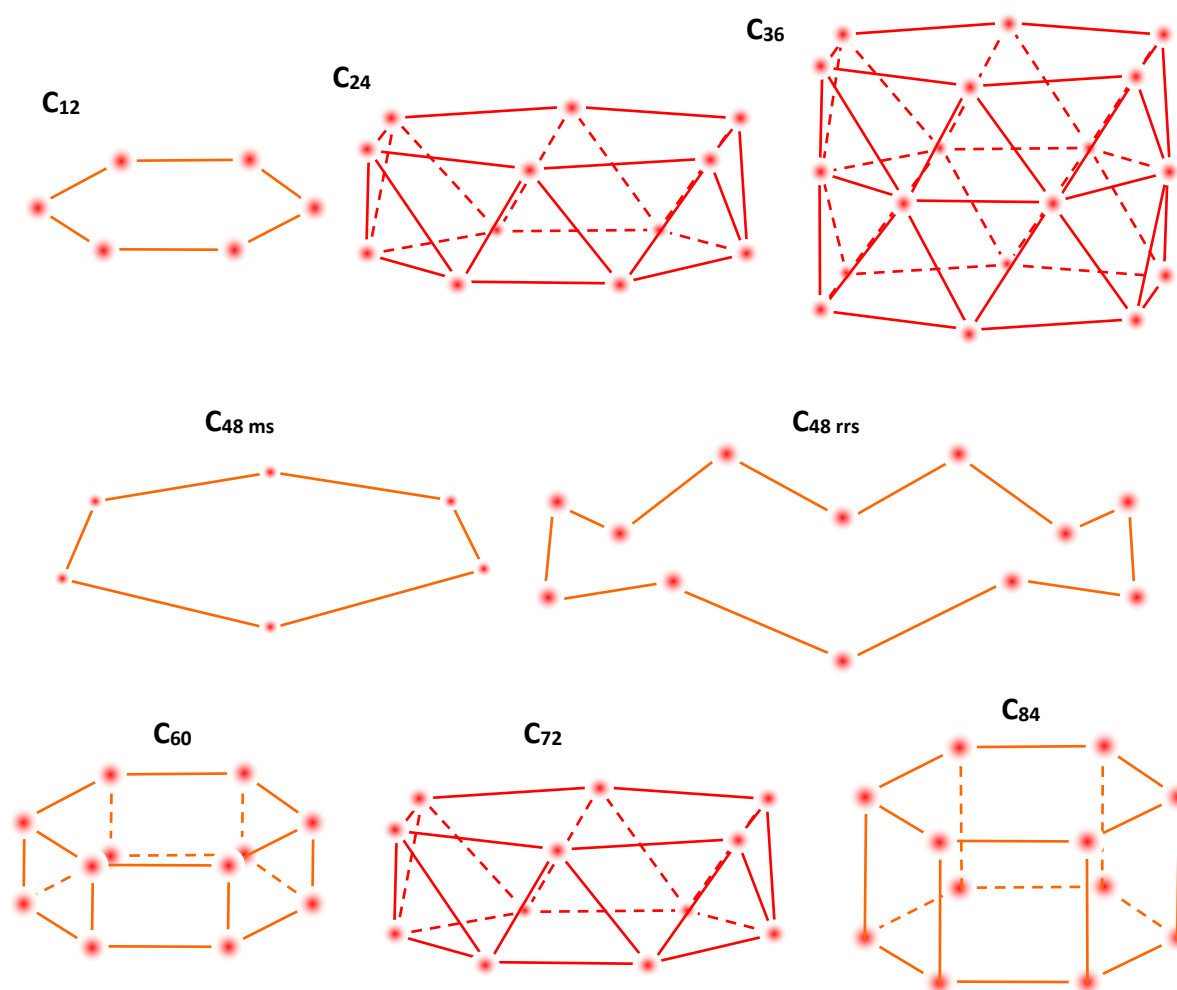
Fig. 29. Geometry of curvature concentration centers (CCC)

Curvature, strain and stress concentration

In mathematics [52], the surface is introduced as a bit of a 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 [53] 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.

In mechanical engineering [54], the problem of weakening stress concentration is very important. Unloading local stress can be obtained through the use of a correct construction, in particular, a construction which consists of frames. Frame bridges were already used by Romans. An advance of the network of railway lines has led to widespread use of frame bridges and, as a consequence, to development of the methods of their designing. The first three farms are shown in Figs. 30–32. The problem was to design a farm in which the stress in farm rods would be minimum when a bridge is in work; the knots of systems being the centers of stress concentration.
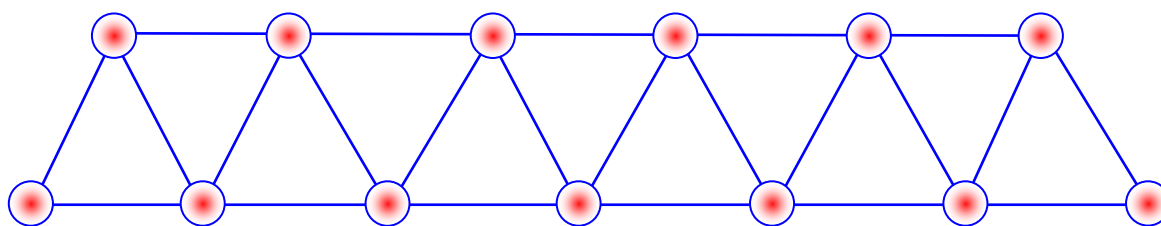
Fig. 30. Triangle lattice of Warren's frame (UK, 1846). Based on [54]
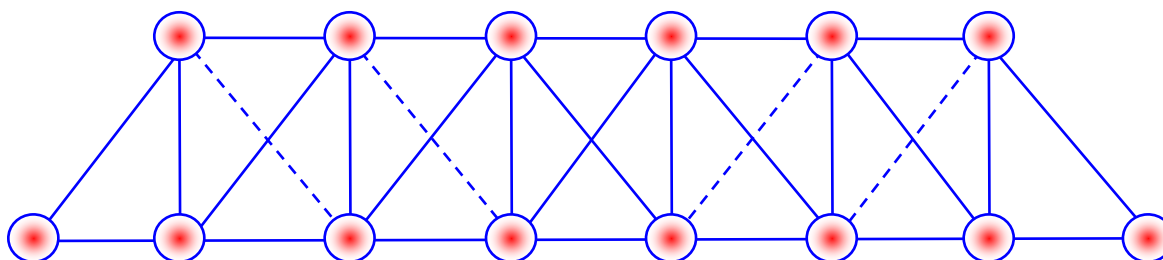
Fig. 31. Whipple's frame (USA, 1852). Based on [54]
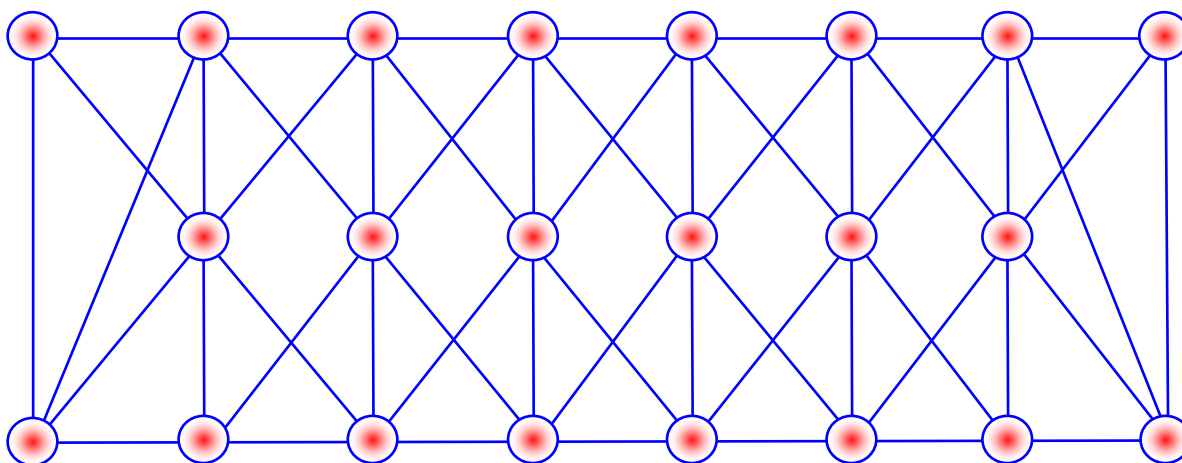
Fig. 32. Zhuravskiy's frame (Russia, 1850). Based on [54]

Studying cyclic molecules [36], we developed a procedure which shows their side view. It can be named the *method of cutting and unrolling*. The procedure allowed us to discover a new phenomenon: hidden symmetry of molecules. It is interesting to note that

if to act in a similar manner, i.e. to cut the prisms shown in Fig. 29 along a vertical line going through one of its curvature concentration points, we obtain the figures resembling farm bridges.

Based on this similarity, 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 form (Fig. 27). Fullerenes with single bonds relax through the transformation of plane hexagons into chair conformation and so their energy has incorporated only a small part of strain energy. As a result, the dependence of fullerene energy on size and shape is almost monotonic. Fullerenes with single and double bonds are rigid constructions, and here the contribution of strain energy is high. The fullerene shape is a result of self-organization and here there are possible several types of curvature. The most stress state is characteristic for fullerenes which curvature concentration centers (CCC) are plane hexagons, the least refers to CCC in the form of antiprisms which highly resemble farm bridges. The other fullerenes have intermediate strain energy.

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 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, 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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