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SUMANENE AND FULLERENE C_{60}

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Abstract. In this contribution we have considered fusion reaction of carbon clusters obtained from the natural blocks of sumanene. We obtained four natural isomers of fullerene C_{60}. Together with the fifth natural isomer found elsewhere through the use of the Endo-Kroto mechanism (dimer embedding model), now we have the structure of all the experimentally observed isomers of fullerene C_{60}. One isomer is a perfect, the other are imperfect and differ in the number of pairs of two adjacent pentagons.

Keywords: fullerene, fusion reaction, graph, natural isomer, sumanene

1. Introduction

Since the discovery of fullerenes more than 30 years ago, there has been considerable activity from the experimental and theoretical side [1, and 277 references therein; 2, and 350 references therein] to gain a detailed understanding of fullerene formation. "However, the formation mechanism, and especially high yield of C_{60}–I_h and C_{70}–D_{5h}, remains elusive and somewhat controversial" [2]. In 2002 we have suggested and confirmed, through the use of molecular dynamics calculations, the fusion reaction mechanism of joining two hemispheres C_{30} for obtaining fullerene C_{60} [3]. This approach has succeeded further development only 15 years later [4-6], at last leading to designing the periodic system of basic perfect fullerenes [5]. According to this system, fullerene C_{60} belongs to the $\Delta n=12$ series, the five-fold symmetry column, and has the lower formation energy than any of its nearest neighbors.

It should be emphasized that the structure of hemisphere C_{30}, both in Ref. [3] and in Ref. [5], was postulated. The question arises: Are there in nature similar molecules, from which it is possible to obtain the hemispheres? To our mind corannulene $C_{20}H_{10}$ with C_{5v} symmetry and sumanene $C_{21}H_{12}$, which possesses C_{3v} symmetry, could be such molecules. We have calculated their optimized structures and energy through the use of Avogadro package [7]; they are shown in Fig. 1. It should be emphasized that we developed a modified geometric color graphics because the package graphics is incomprehensible.

These molecules are usually considered as key fullerene fragments [8,9]. Being π-conjugated compounds, they are bowl-shaped or cupola-shaped species; it depends on a point of view (Fig. 1). The bowl of sumanene (1.15 Å) is anticipated to be deeper than that of corannulene (0.89 Å). According to Ref. 8, deeper π-bowls are more interesting because they may have properties more similar to those of fullerenes. However the mechanism of fullerene assembly from such fragments is not known.

In this contribution we are trying to clarify this problem.

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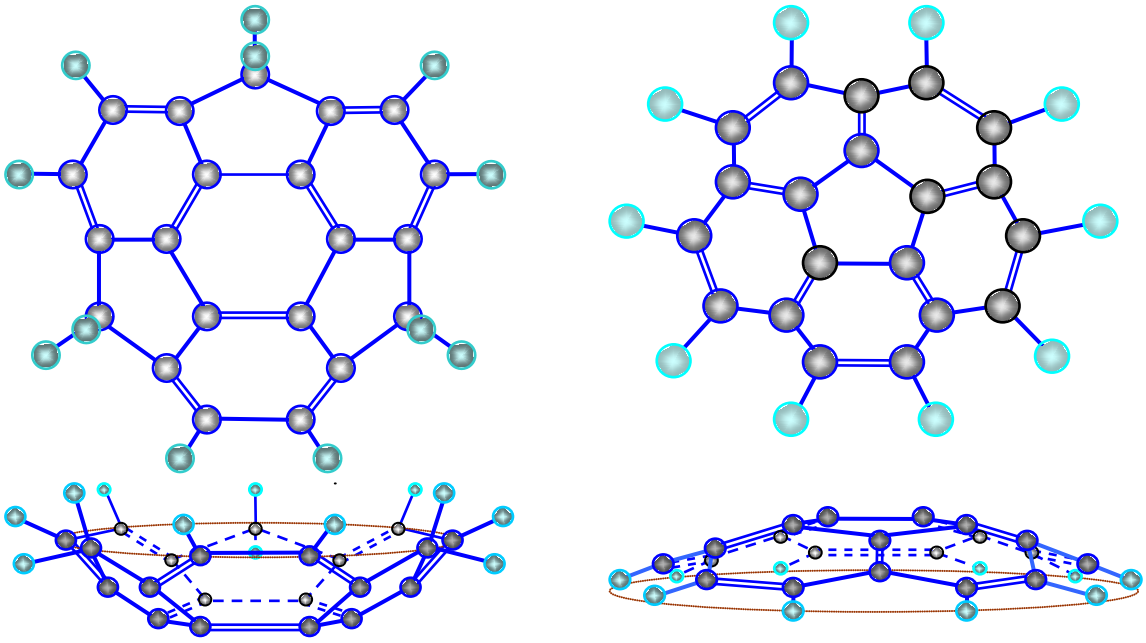


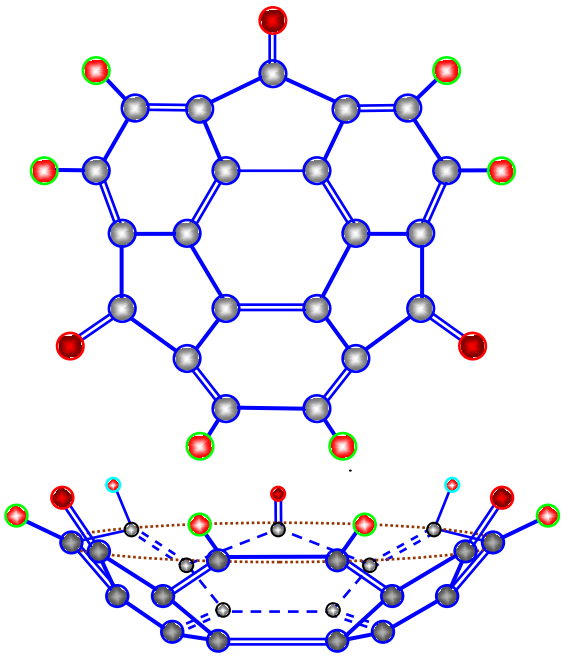
Sumanene $C_{21}H_{12}$ E=294 Corannulene $C_{20}H_{10}$ E=245

Fig. 1. Sumanene as a bowl and corannulene as a cupola (energy, kJ/mol)

2. Sumanene as an origin of fullerene

Carbon clusters. Suppose that we have removed twelve hydrogen atoms from sumanene and added nine carbon atoms instead. In doing so we obtain bowl-shaped carbon cluster C_{30} with two types of carbon atoms (Fig. 2). The carbon atoms of sumanene remain in the initial electronic state; they are considered, as is customary, being sp^2 hybridized atoms. The new added ones are reactive carbon atoms, which are connected with the initial carbon atoms by single or double bonds, they being ionized to a different degree.

Cluster reactions. Two such clusters, combining with each other, are able to create fullerene C_{60}. The atomic configurations, corresponding to reaction between two clusters C_{30}, $C_{30} + C_{30} \rightarrow (C_{30}C_{30}) \rightarrow C_{60}$, are shown in Fig. 3. At first two molecules C_{30} are moving towards each other. Then the atoms, marked with red-grey, react with each other producing a compound. During this process new covalent bonds (red lines) are formed.



Bowl C_{30} E=493 kJ/mol

Fig. 2. Carbon cluster obtained from sumanene by replacing hydrogen atoms with carbon ones

It should be emphasized that there are possible four types of the reaction, namely: perfect reaction (Fig. 3a); one-fault reaction (Fig. 3b); two-fault reaction (Fig. 3c); and three-

fault reaction (Fig. 3d). To gain a better understanding of the reaction structures, their main features are given in the form of scheme (Fig. 4).

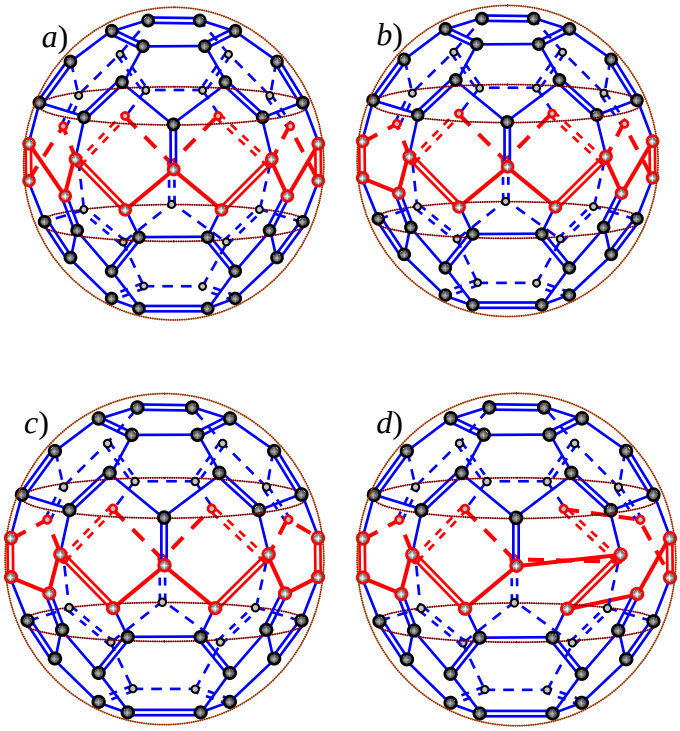


Fig. 3. Joining two hydrogen-replaced-by-carbon sumanene compounds: a) perfect reaction, b) one-fault reaction, c) two-fault reaction, d) three-fault reaction

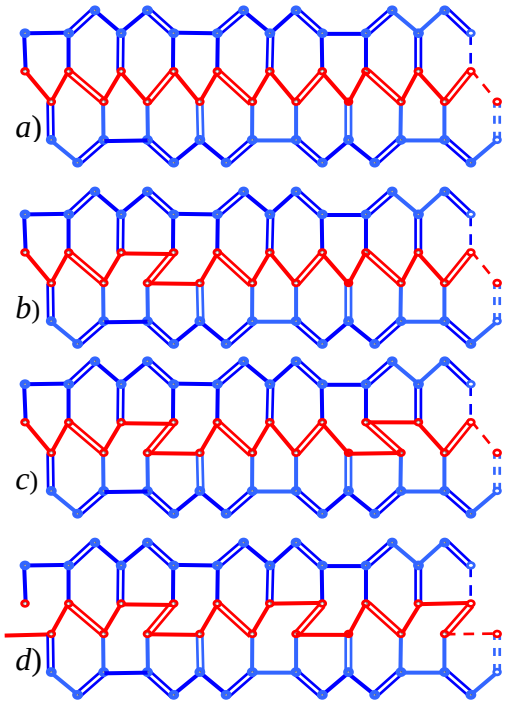


Fig. 4. Scheme reflecting the main structural changes during the fusion of two compounds

Graph representation of perfect reaction. To make clear the structure of the fullerenes obtained, one needs to turn to their graphs. They are shown in Fig. 5 for the initial bowl and the polyhedron obtained. The atomic configuration of the initial bowl consists of three pentagons, four hexagons and nine excited atoms; due to the fusion there appear six new pentagons and twelve hexagons. Therefore we have twelve pentagons and twenty hexagons forming polyhedrons. It should be emphasized that all pentagons are isolated from each other, creating perfect fullerene C_{60}.

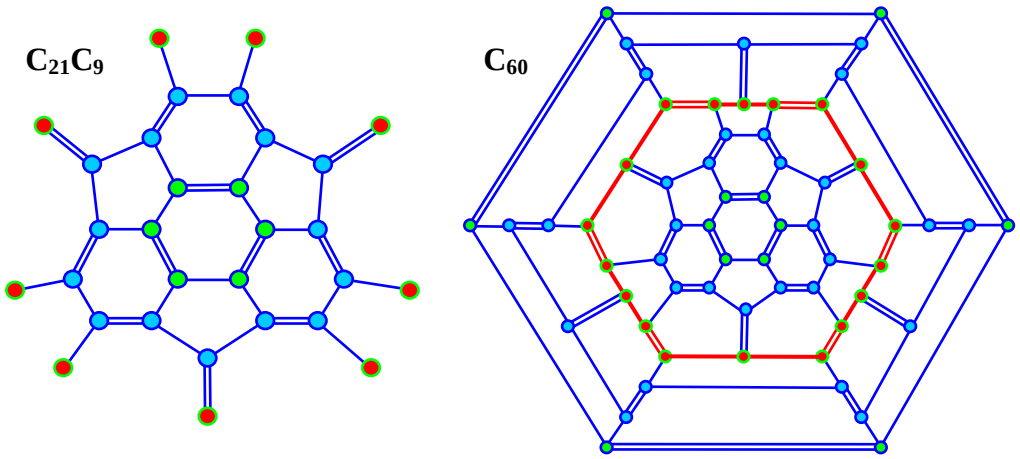


Fig. 5. Graphs of bowl C_{30} and fullerene C_{60}; new covalent bonds are heavy red lines

Structure of fullerenes obtained. Consider the fusion reactions in detail. As a result of the reactions, at first the distorted polyhedrons are fashioned, and then they relax into a perfect polyhedron (Fig. 6a) or faulted structure polyhedrons (Fig. 6b, c, and d). The perfect fullerene C_{60} is shown in Fig. 6a. It can be imagined as composed of pyracylene units. A pyracylene unit contains two pentagons and two hexagons and a central reactive double bond [10]. One of the units is shaded in Fig. 6a; the atoms of the central bond are marked in green. The faulted fullerene, presented in Fig. 6b, contains the same unit; its boundary atoms are connected by brown lines. It looks, as if its shaded pyracylene unit had undergone the Stone-Wales transformation [11, 12]. The latter corresponds to the rotation of the central bond by 90 degrees, resulting in the creation of two adjacent pentagon-pentagon pairs; their atoms marked in turquoise (Fig. 6b′). In a similar way one can think over other faulted fullerenes. They differ in the number of pairs, namely, four (Fig. 6c) and six ones (Fig. 6d).

Graph representation of fullerene structures. Here again, to make clear the structure of the fullerenes obtained, one needs to turn to their graphs. They are shown in Figs. 7 and 8. In Fig. 7 the boundaries of pyracylene units are brown-colored and the atoms of the rotating central bonds are marked in green. In Fig. 8 the isolated pentagons and adjacent pentagon-pentagon pairs are marked in brown.

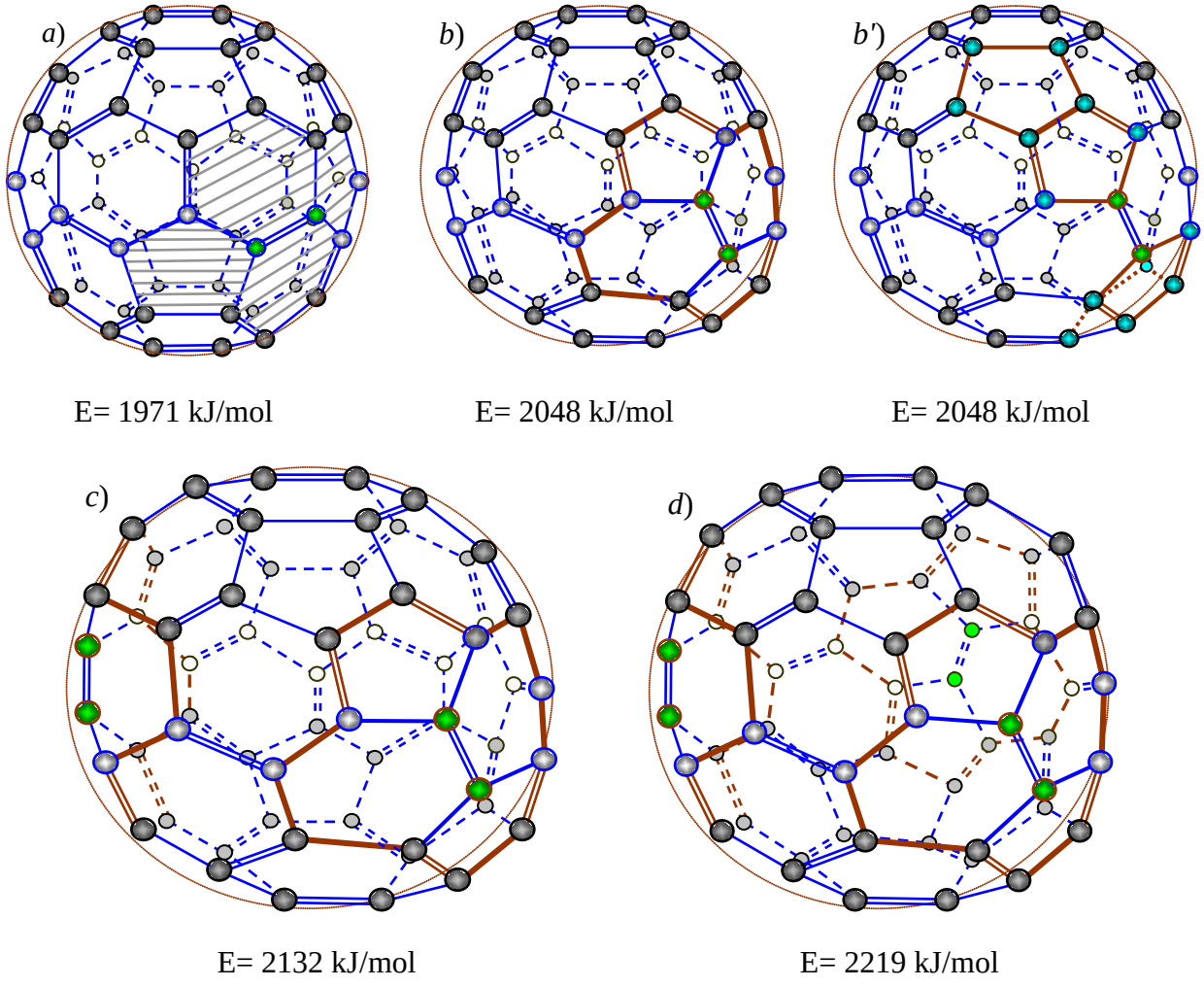


Fig. 6. Fullerenes obtained from sumanene-like carbon compounds after relaxation: a) perfect reaction, b) one-fault reaction, c) two-fault reaction, d) three-fault reaction

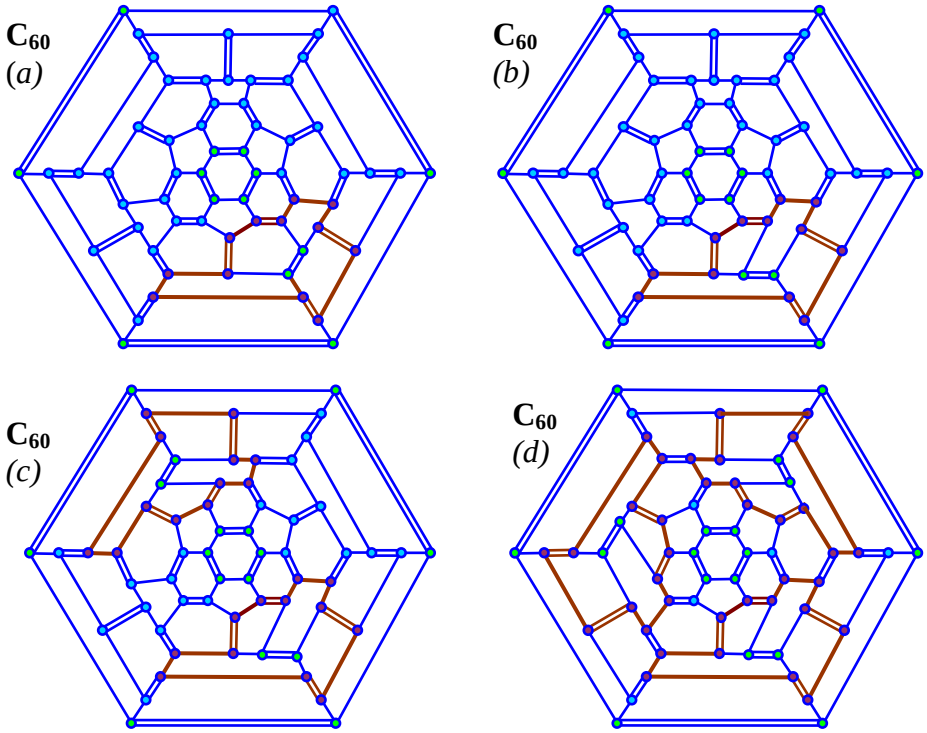


Fig. 7. Graphs of fullerenes C_{60}; the boundaries of pyracylene units are brown-colored and the atoms of the rotating central bonds are marked in green: a) perfect reaction, b) one-fault reaction, c) two-fault reaction, d) three-fault reaction

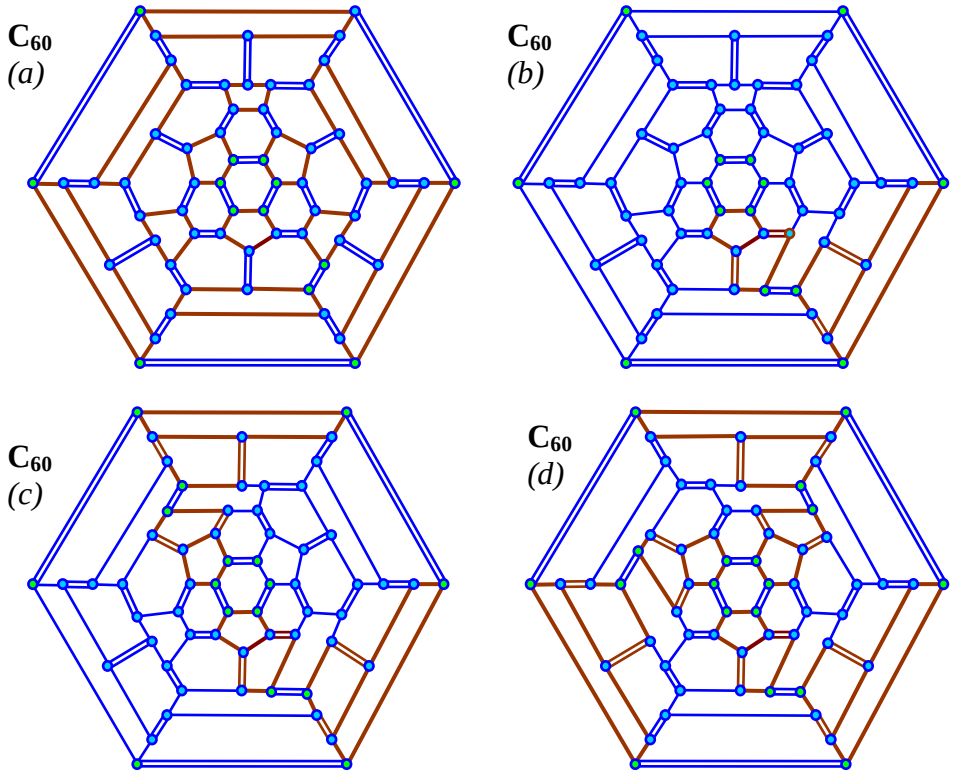


Fig. 8. Graphs of fullerenes C_{60}; the isolated pentagons and adjacent pentagon-pentagon pairs are marked in brown: a) perfect reaction, b) one-fault reaction, c) two-fault reaction, d) three-fault reaction

From the Figs. 6, 7, and 8, it follows that the most drastic changes occur inside the pyracylene units. Here the rotation of the central double bonds by 90 degrees leads to displacement of their four nearest-neighbor atoms; the other parts of fullerenes remaining stable.

3. Discussion and conclusion

Five isomers of fullerene C_{60} were generated in microwave plasma of chloroform [13]. They were stable at room temperature but four of them disintegrated at 250°C. The authors have suggested possible structures and calculated the formation energies of these isomers. However, a thought pattern of final configuration does not guarantee that the postulated configurations coincide with the structures obtained experimentally. It seems more reasonable to study the final configurations obtained by one of well-known mechanism of fullerene formation, which demonstrated its validity in many cases. This raises the question how to choose the best mechanism. To our mind, the best mechanism must satisfy the principle of least action. As a rule, this principle is tightly connected with symmetry and conservation laws.

Consider the analogy with house-building. It is clear that more cheaply and easier to build a house from blocks than from bricks. In the case of fullerenes, the nature gives us the ready blocks in the form of sumanene and corannulene. Replacing hydrogen atoms with carbon ones, we obtain cement for binding together the blocks.

In this contribution we have considered fusion reaction of carbon clusters obtained from the natural blocks of sumanene. Now we have four natural isomers of fullerene C_{60}. For completeness sake it is necessary to add the fifth, probably also natural, isomer. It was obtained earlier [14] by another way, through the use of the Endo-Kroto mechanism (dimer embedding model), i.e. from natural bricks (dimers C_2). The structure and graph of this isomer are shown in Fig. 9. It contains four isolated pentagons and four pairs of two adjacent pentagons, its energy being equal to 5747 kJ/mol. To gain a better understanding of its structure, the isolated pentagons and pentagons pairs are specially marked.

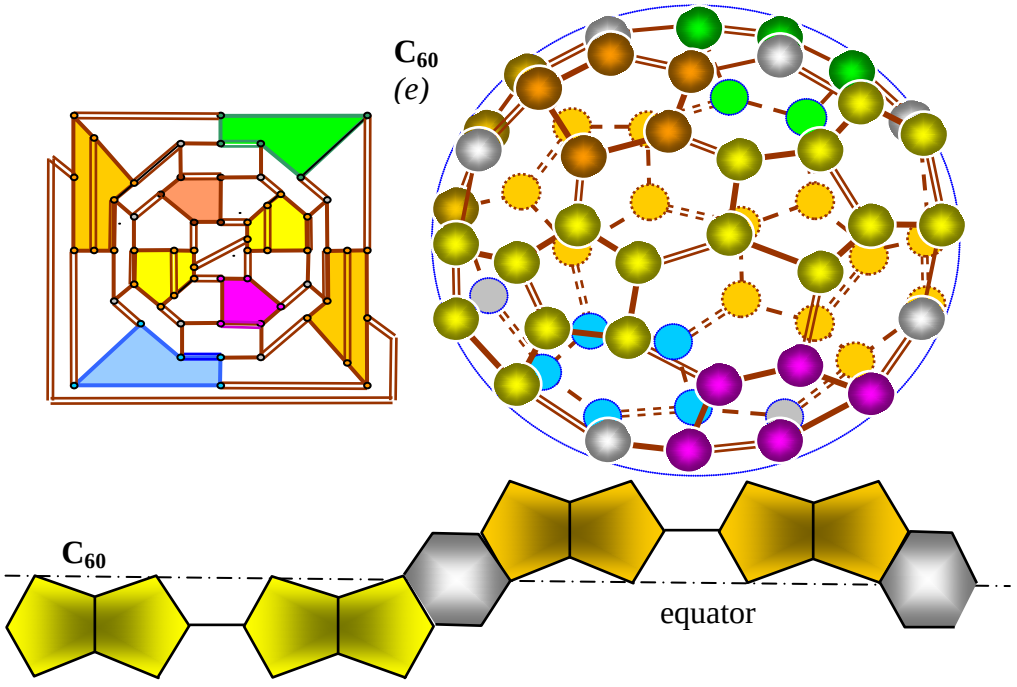


Fig. 9. Single and double bonds of fullerene C_{60} with four isolated and four pairs of two adjacent pentagons (top); arrangement of two pairs of adjacent pentagons (bottom)

Thus we have the structure of all the experimentally observed isomers of fullerene C_{60}. The isomer (a) is a perfect, the other are imperfect and differ in the number of pairs of two adjacent pentagons. It should be emphasized that the imperfect isomers possess topological symmetry.

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