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# TETRAHEDRAL MINI- AND MIDI-FULLERENES

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**Abstract.** We have considered possible ways of forming the simplest tetrahedral fullerenes, namely elementary tetrahedron $C_4$, truncated tetrahedron $C_{12}$, half-truncated cube $C_{16}$, fullerenes $C_{28}$ and $C_{36}$. By analogy with ionic crystals, we introduced "mathematical" compounds, which form a topological cube of two tetrahedra inserted into each other, and construct graphs for them. Combined with the graph analysis, this approach allows obtain a clear knowledge of the tetrahedral fullerene structure. We extended our model to other tetrahedral fullerenes, in particular, tetrahedral fullerenes $C_{64}$ and $C_{76}$.

**Keywords:** energy, fusion reaction, graph representation, growth, mathematical compound, periodic system, tetrahedral fullerene, topological cube

## 1. Introduction

The periodic system of fullerenes, based on symmetry principles, consists of horizontal series and vertical columns. The horizontal series form the $\Delta n$ periodicities, where the fullerene structure changes from threefold symmetry to sevenfold through four, five and sixfold ones. The system leaves room for the following series: $\Delta n$= 2, 4, 6, 8, 10, 12, 14, 16, 18, 20 and may incorporate into it carbon clusters, nanotubes and fullerenes from $C_2$ to $C_{140}$. However, it is known that there are fullerenes with tetrahedral structure [1 and references therein]. To complete the system, it is necessary to add these fullerenes to the periodic system.

The question arises how to do it. We only know some separate tetrahedral fullerenes which are not connected with each other. We do not know whether the connection laws, established for the fullerenes incorporated into the periodic system, are valid for such fullerenes. In other words, we know almost nothing. For this reason, we will follow the action plan outlined in Ref. [2], namely, "the next step in our investigation is obtaining the structure and energy of missing fullerenes with the purpose to incorporate the missing known and unknown fullerenes into the periodic system". What kind of missing fullerenes it necessary to design, first of all? To our mind, it is essential to begin with the simplest ones and to develop, similar to Ref. [3], the algorithm of the fullerene growth for the fullerenes conserving the tetrahedral symmetry. Then the fullerenes obtained should be arranged to give a successive growing array. What is wanted is the law which connects the nearest neighbors.

In the periodic system of fullerenes 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. In this contribution we have tried to construct a similar column for the tetrahedral fullerenes and to define its $\Delta m$ index.

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## 2. The simplest known tetrahedral fullerenes

**Folding and growth by adding dimers.** We begin with cluster $CC_3$ as one of the germs of future carbon structures. The possible ways of its formation are considered in Ref. [4]. If the further growth is suppressed, the cluster is compelled to fold creating a tetrahedron, the energy being depended on its electronic structure (Fig. 1). If the growth is possible, there are different ways of growing. In particular, the cluster can transform into a cupola adding carbon dimers (Fig. 2). In a similar manner, one may imagine the growth of cluster $C_3$. The process is shown in Fig. 3. Here we have threefold cluster and threefold cupola $C_{12}$, and tetrahedral fullerene $C_{12}$.

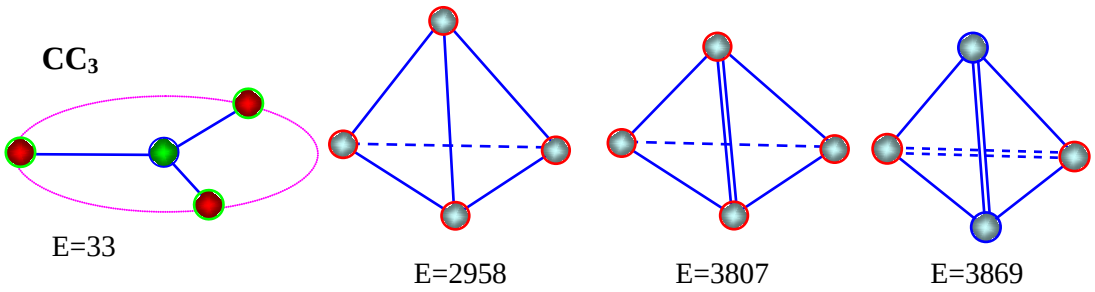


**Fig. 1.** Folding $CC_3$ cluster into tetrahedra; energy in kJ/mol.
Dark-red balls are reacting atoms; other color atoms are neutral ones

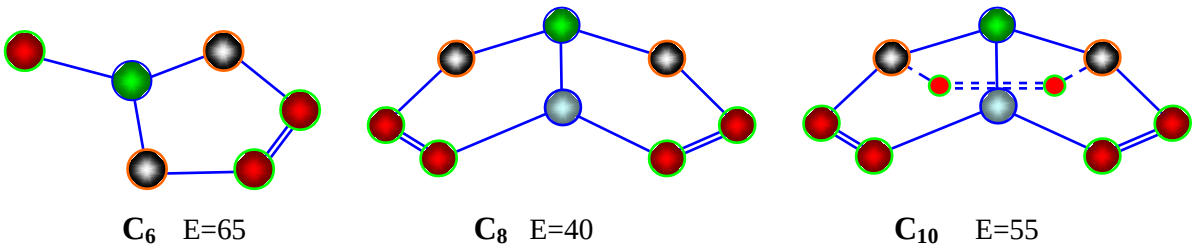


**Fig. 2.** Growth of cluster $CC_3$ and formation of a cupola; energy in kJ/mol

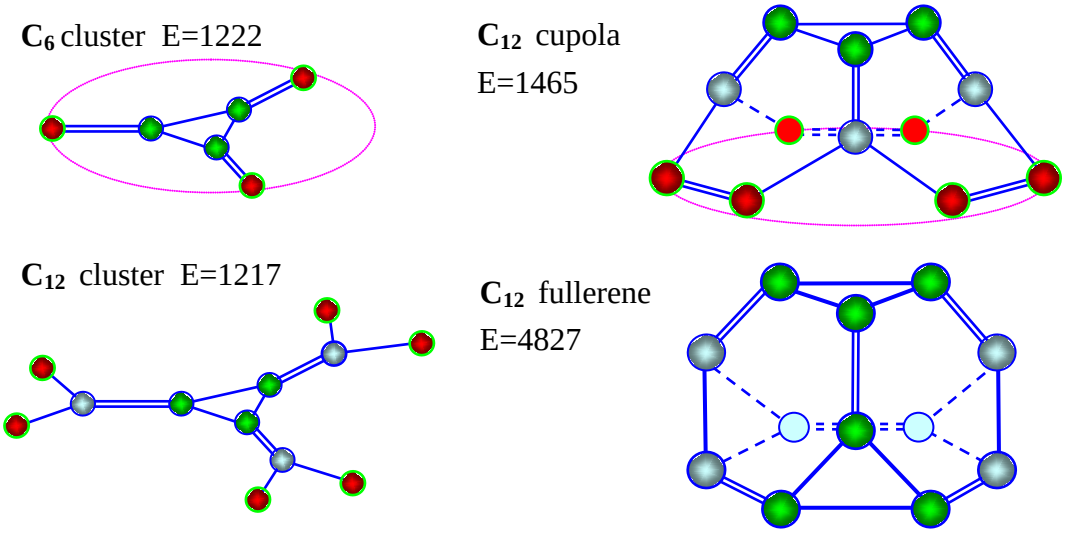


**Fig. 3.** Growth of cluster $C_3$ and formation of a cupola and a fullerene: some triangle atoms showing three-hold and tetrahedral symmetry are marked with green; energy in kJ/mol

**Fusion reactions.** The structure of tetrahedral fullerene $C_{16}$ was designed elsewhere [5]. It is a half-truncated cube and can be obtained by adding cluster $C_4$ to cupola $C_{12}$ (Fig. 4).

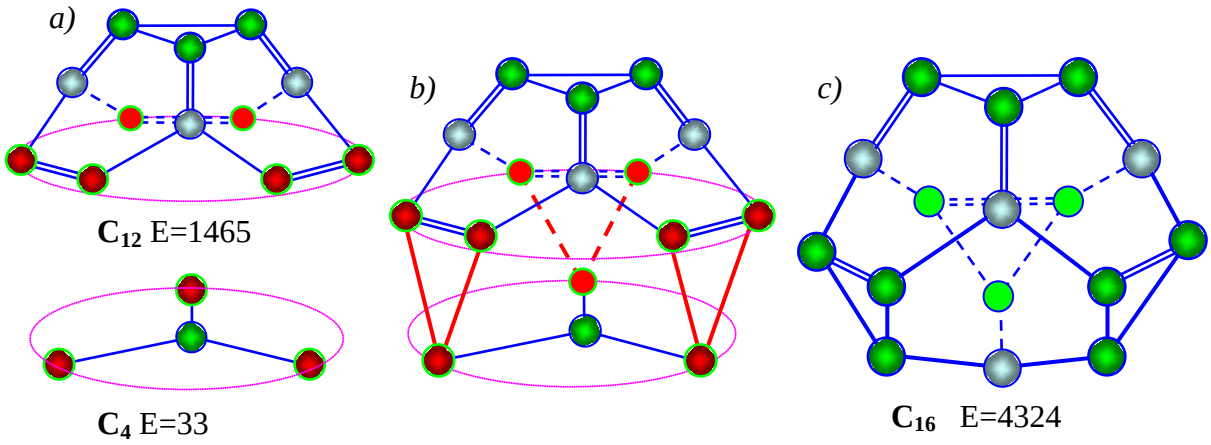


**Fig. 4.** Fusion of cluster $C_4$ with cupola $C_{12}$: (*a*) Separate species; (*b*) Intermediate compound; (*c*) Fullerene $C_{16}$ after relaxation. Red and blue balls are reacting and neutral atoms, respectively; blue solid and dashed lines are old covalent bonds; red solid and dashed lines are new ones; atoms showing tetrahedral symmetry are marked with green; energy in kJ/mol

The next and last known tetrahedral mini-fullerene is $C_{28}$. Its structure was suggested in Ref. [6]. The possible way of the realization is shown in Fig. 5. It is a fusion reaction of cupola $C_{10}$ and bowl $C_{18}$, which can be written in the form $C_{10} + C_{18} \rightarrow (C_{10}C_{18}) \rightarrow C_{28}$.

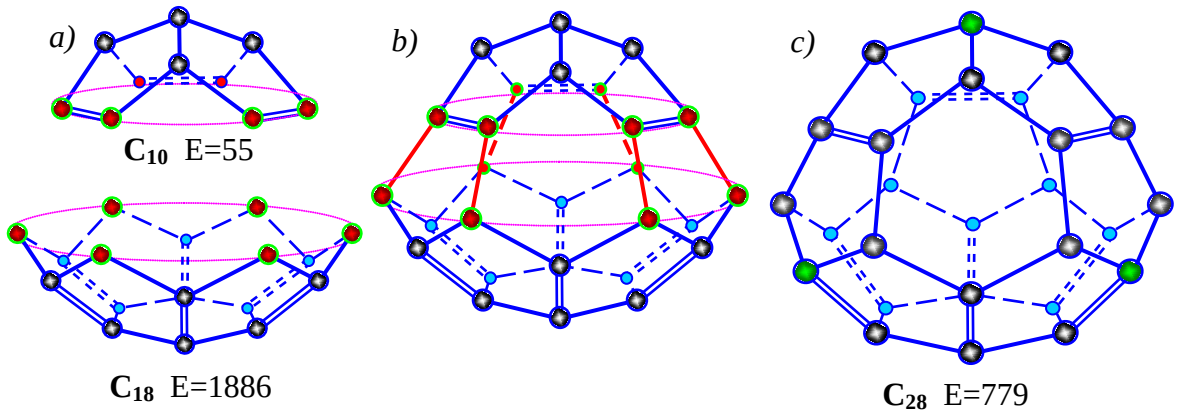


**Fig. 5.** Fusion of cupola $C_{10}$ with bowl $C_{18}$ and formation of fullerene $C_{28}$; all notations are the same as before; energy in kJ/mol

### 3. A new tetrahedral midi-fullerene

For completeness sake, it is desirable to add to the simplest fullerenes one more fullerene $C_{36}$. It can be imagined as a truncated fullerene $C_{28}$. The situation is similar to that of a tetrahedron and a truncated tetrahedron, $C_4$ and $C_{12}$. But how the truncated tetrahedral fullerene $C_{36}$ can be obtained naturally?

Let us consider the structure of fullerene $C_{28}$. It is seen from Fig. 5 that this fullerene consists of two parts: the bottom part, or bowl $C_{18}$, having six-fold symmetry and the upper part, or cupola $C_{10}$, with three-fold symmetry. By analogy, it seems reasonable to take bowl $C_{24}$ and truncated cupola $C_{12}$ as constituents for producing the tetrahedral fullerene $C_{36}$. The corresponding reaction $C_{12} + C_{24} \rightarrow (C_{12}C_{24}) \rightarrow C_{36}$ is illustrated in Fig. 6. To gain a better understanding of the tetrahedral symmetry, the triangle atoms are specially marked with green.

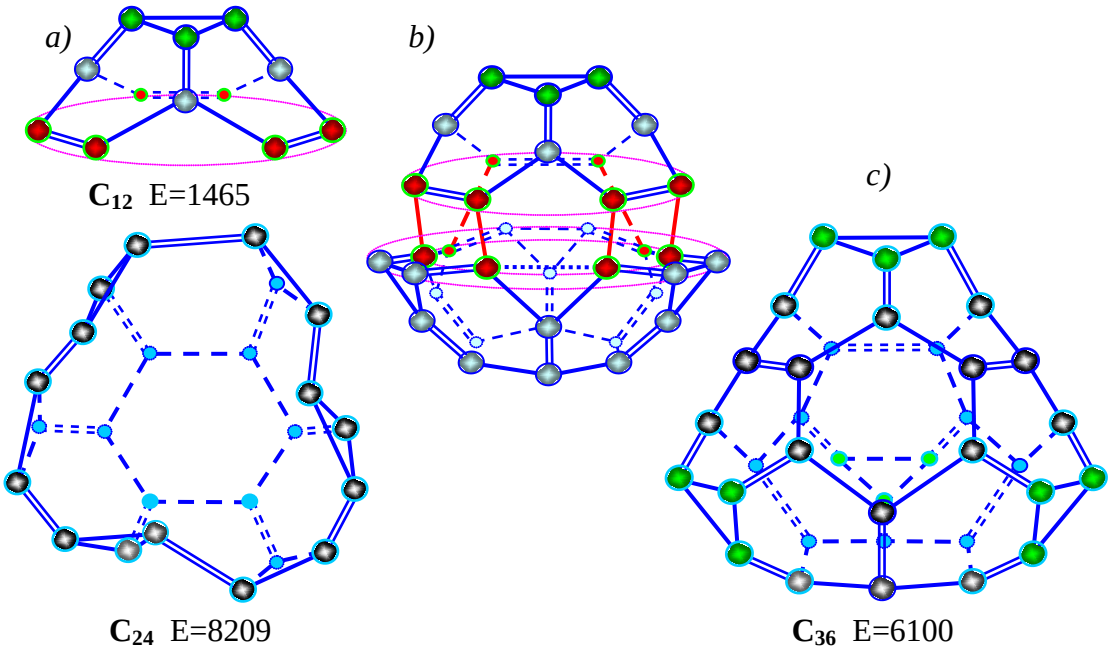


**Fig. 6.** Fusion of cupola $C_{12}$ with bowl $C_{24}$: separate species (*a*); intermediate compound (*b*); fullerene $C_{36}$ after relaxation (*c*); old covalent bonds to be destroyed are blew dotted lines, other notations are the same as before

## 4. Graph representation

Consider the graphs which characterize the formation of the tetrahedral mini-fullerenes. We have five fullerenes: $C_4$, $C_{12}$, $C_{16}$, $C_{28}$, and $C_{36}$. Their graphs are shown in Figs. 7 and 8.

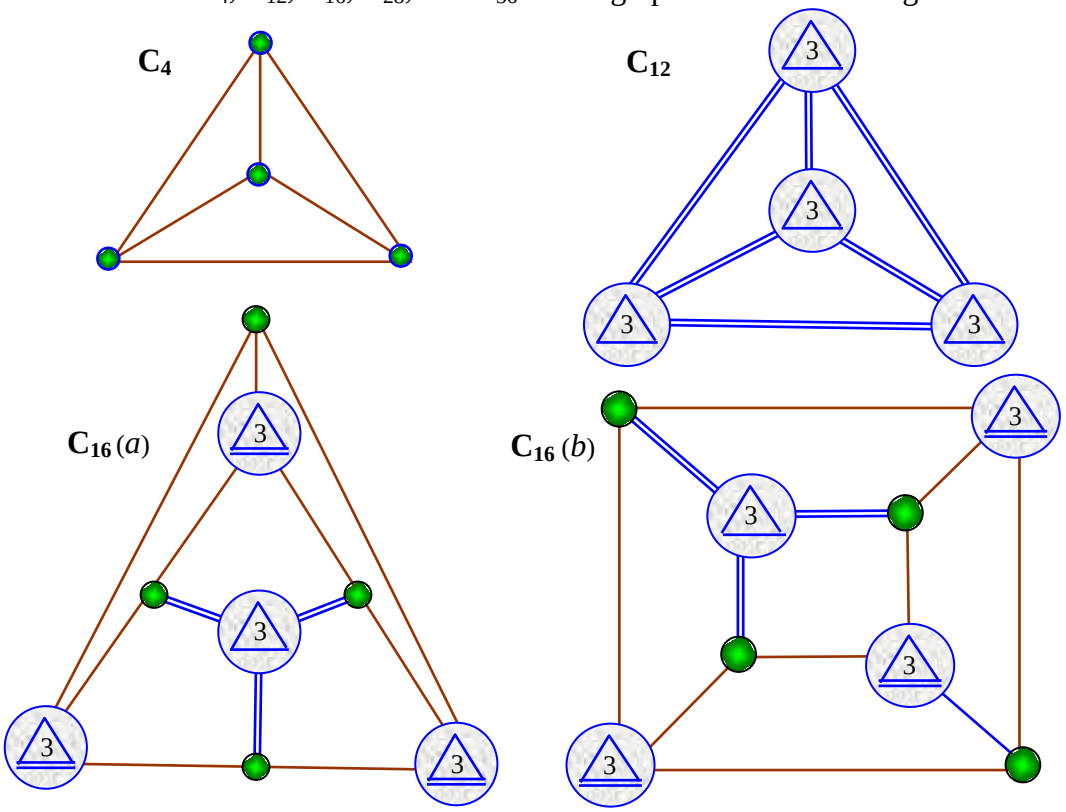


**Fig. 7.** Graphs of mini-fullerenes $C_4$, $C_{12}$ and $C_{16}$: light-turquoise ball are simple vertices (one-atomic); grey circles are big-size vertices (atom clusters); symbols and numbers inside the circles indicate the number of atoms in a cluster as well as the number of single (brown color) and double (blue color) bonds

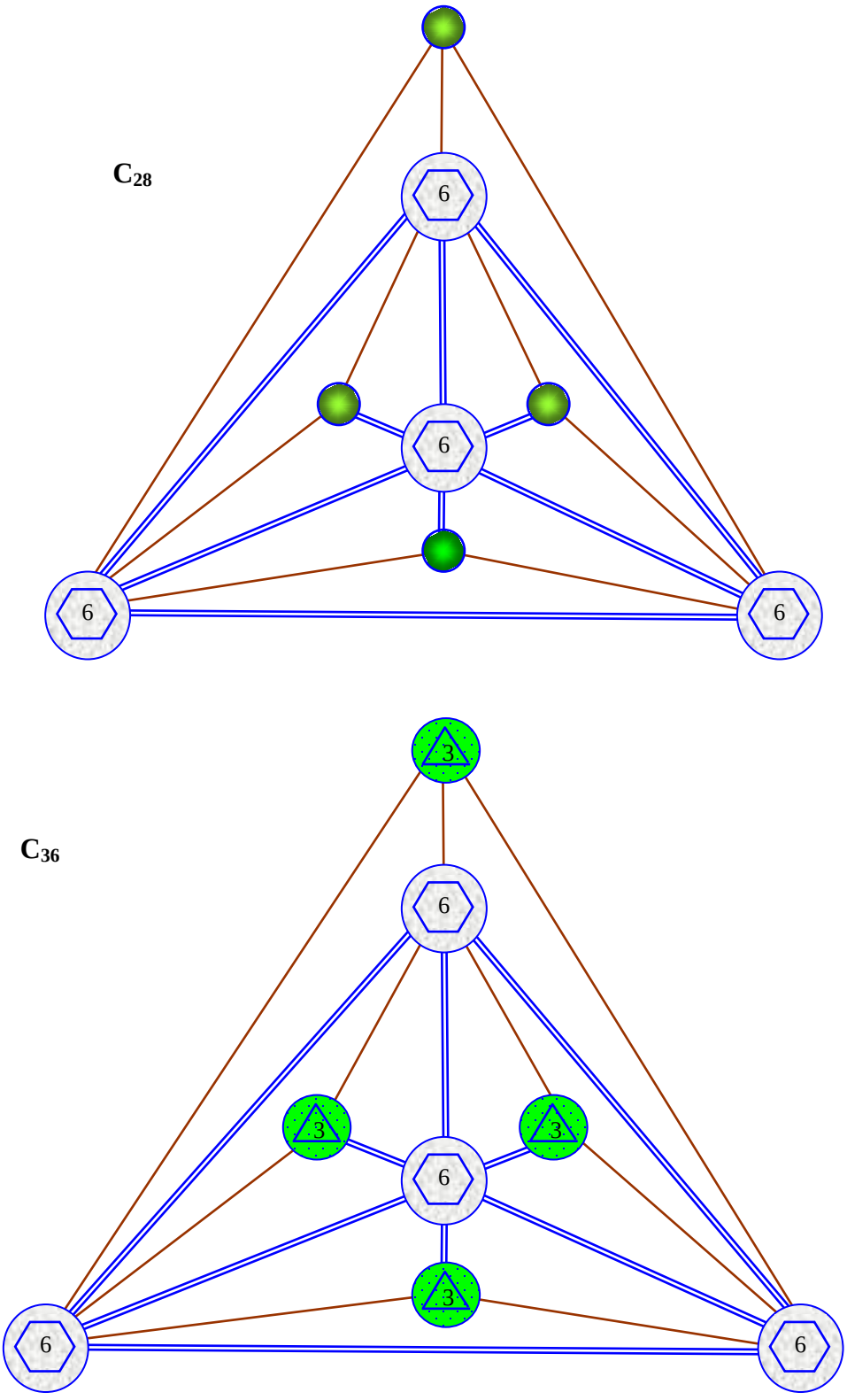


**Fig. 8.** Graphs of mini-fullerene $C_{28}$ and midi-fullerene $C_{36}$: light-turquoise ball are simple vertices (one-atomic); grey and green circles are big-size vertices (atom clusters); other notations are the same as before

Here different presentations of the fullerenes are given. The reason is as follows. It would endeavor natural to illustrate the structure of a graph considered with the help of lesser–size graphs having more simple structure. Hence, for tetrahedron $C_4$ it is a routine

graph, each vertex (zero-size point) corresponding to one carbon atom. For truncated tetrahedron $C_{12}$ we used the innovation to the graph theory developed in Ref. [4]. Here each vertex (big-size point) agrees to a cluster of three atoms. In this case we obtain a graph, which is identical to the graph of a simple tetrahedron. It is worth noting that such approach allows do some operations with such graph in the same manner as with a usual graph that simplifies an analysis.

It should be emphasized that in Ref. [4], where the innovation was first presented, a distinction is not made between single and double bonds, so all the edges were identical. Here we use two kinds of edges, single and double, so the graphs presented reflect not only geometry (atomic structure), but also electronic one. It allows gain a more penetrating insight into the fullerene structure, and therefore to study them more elaborately.

For truncated cube $C_{16}$, we utilize both kinds of vertices, one-atomic and atom-cluster, as well as both kinds of edges, single and double bonds. The left-hand graph coincides with a tetrahedral symmetry; it shows that the structure is composed of two tetrahedra inserted into each other. The right-hand graph reflects a cubic symmetry.

In a similar manner, the graphs are designed for fullerenes $C_{28}$ and $C_{36}$. From the graphs it follows that their structure is also composed of two tetrahedra inserted into each other.

## 5. Summary and discussion

We have considered possible ways of forming the simplest tetrahedral fullerenes, namely elementary tetrahedron $C_4$, truncated tetrahedron $C_{12}$, half-truncated cube $C_{16}$, fullerenes $C_{28}$ and $C_{36}$. We assume that tetrahedron $C_4$ could be produced by folding cluster $CC_3$ under high pressure similar to diamond. It has three different electronic isomers, which differ in number of single and double bonds, and therefore in energy.

The growth of truncated tetrahedron $C_{12}$ is a more complex process. It can be envisaged as a successive increase of cluster $CC_3$ through appearance of intermediate clusters $C_6$, $C_8$ and $C_{10}$; and by folding the final cluster $C_{12}$. Another way is the appearance of cupola $C_{12}$ and folding it. Since the energies of the cluster and cupola are close to each other, both ways seem probable.

The formation of fullerene $C_{16}$ is designed as the fusion of cluster $C_4$ with cupola $C_{12}$. From the graph of this fullerene it follows that its structure is composed of two tetrahedra inserted into each other. It is worth noting that in this case two species, entering into the reaction, conserve its own electronic structure. As a result, we obtain the fullerene, in which electronic and atomic configurations do not coincide, and we have so called hidden symmetry. This situation is thoroughly analyzed in Ref. [2].

Fullerene $C_{28}$ was suggested by Nobel Prize winner H.W. Kroto [6] as one of fullerenes having magic number of enhanced stability. He is also thoroughly discussed its possible electronic structure. To his mind, "the stability depends on the ability of spare electrons on the four carbon atoms at the centers of the four ten-atom configurations of adjoined pentagons to stabilize by configuration". These four electrons are the nearest neighbors of an atom marked with green in Fig. 5. We have obtained fullerene $C_{28}$ using the fusion reaction $C_{10} + C_{18} \rightarrow (C_{10}C_{18}) \rightarrow C_{28}$. It has the energy 749 kJ/mol. It is not the only one way of generation. In other study, where we modeled the formation of fullerene $C_{28}$ similar to the growth and folding of cupola $C_{12}$, the electronic structure of some of such four carbon atoms was changed. As a result, we have obtained 1399 kJ/mol and a less distorted structure, more close to a sphere.

Fullerene $C_{36}$ is a truncated fullerene $C_{28}$. It was imagined at first by analogy with truncated-tetrahedron fullerene $C_{12}$ and only afterwards a possible fusion reaction was found.

**Analogy with ionic crystals.** From the geometry standpoint, fullerenes $C_4$ and $C_{12}$ are simple tetrahedra. Beginning with fullerene $C_{16}$, they are composed of two tetrahedra inserted

into each other. In nature there are alkali-haloid compounds (ionic crystals $A_1B_7$), which crystallize in f.c.c. structure, which is called the structure of NaCl type. However, in this structure it is possible to isolate a primitive cube of two tetrahedra inserted into each other, each tetrahedron having the atoms of only one kind (Fig. 9). The plane graph of such cube is shown in Fig. 10.

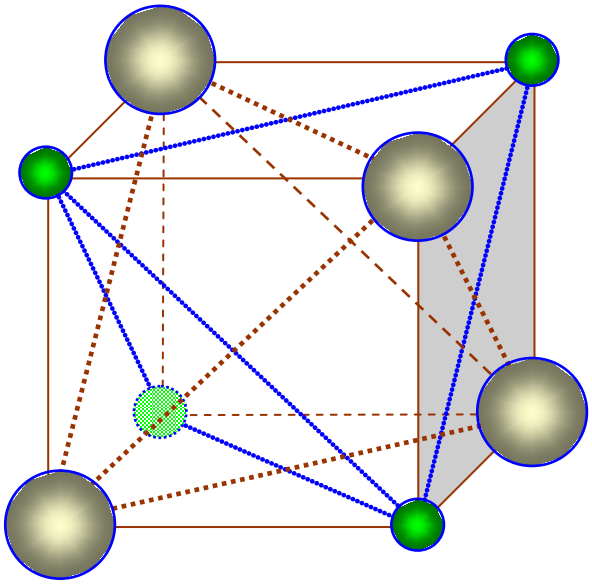

**Fig. 9.** Tetrahedra of NaCl type structure

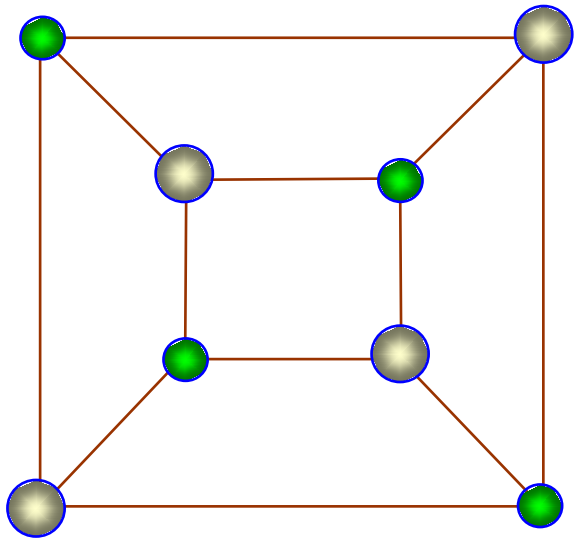

**Fig. 10.** Plane graph of a primitive cube in the NaCl structure

By analogy, we can imagine "mathematical" compound, which forms a topological cube of two tetrahedra inserted into each other, and construct graphs for it. In this case, instead of atoms one has clusters of two kinds. Strictly speaking, we have already considered this possibility for the simplest fullerene $C_{16}$, having two tetrahedra (Fig. 7, $C_{16}$ b). For this fullerene two plane graphs, shown in Fig. 7, are isomorphic. In ionic crystals $A_1B_7$ (alkali-haloid compounds), the inferior index denotes the number of valence electrons, which are able to take part in reactions. By analogy, for our mathematical compound, fullerene $C_{16}$, we can write the 'chemical' formula in the form $A_1B_3$. However, here the inferior index denotes the number of atoms in each tetrahedron interacting with atoms of another tetrahedron. For example, the tetrahedral fullerenes studied in this research, $C_{28}$ and $C_{36}$; have the formulas $A_1B_6$ and $A_3B_6$, respectively. Combined with the graph analysis, one can obtain a clear knowledge of the tetrahedral fullerene structure.

We can extend this model to a broad spectrum of tetrahedral fullerenes. Consider, for example, tetrahedral fullerenes $C_{64}$ and $C_{76}$, their structure being given in Ref. [1]. Fullerene $C_{64}$ contains 12 squares, 10 hexagons and 12 heptagons. Each face of the structure is formed by 3 adjoined heptagons, which are surrounded by 6 squares and 6 hexagons. Fullerene $C_{76}$ contains 24 pentagons, 4 hexagons and 12 heptagons. Each face of the structure is formed by one hexagon, surrounded by 3 pentagons and 3 heptagons. Such description gives detail, but does not allow find correlation between the fullerenes.

We have designed the graphs for these fullerenes by analogy with that of fullerene $C_{36}$. They are presented in Fig. 11. Since we do know the history of fullerene designing, there is no distinction between chemical single and double bonds. This problem is beyond the scope of geometry. It is necessary to do some elucidation of the symbols used. The correspondence between graph symbols and atomic structure is shown in Fig. 12.

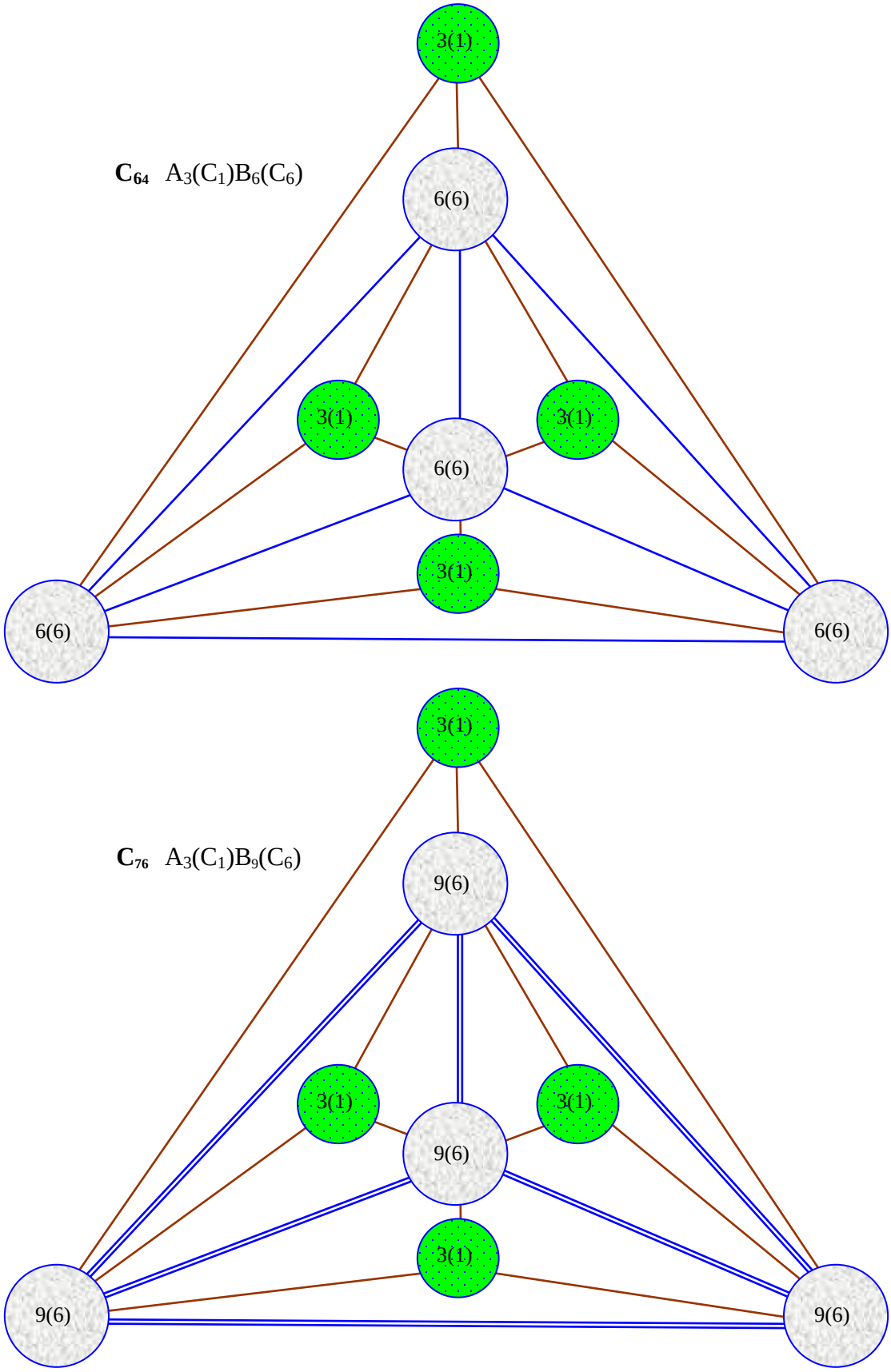


**Fig. 11.** Graphs of midi-fullerenes $C_{64}$ and $C_{76}$

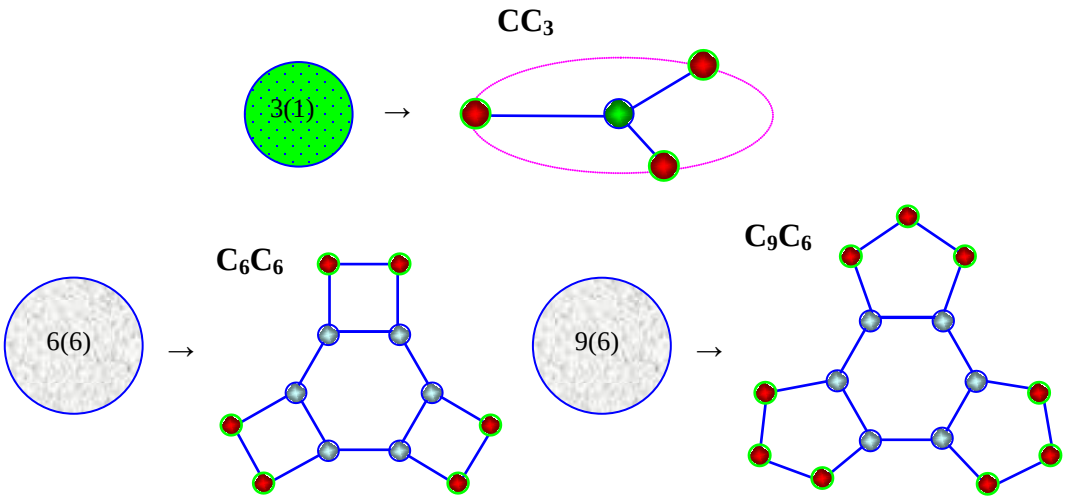


**Fig. 12.** Graph symbols and their relation to atomic structure

From this figure it follows that only outer atoms of atom clusters take part in the interaction with other atom clusters. In other words, the big-size vertices of graphs, characterizing the structure of fullerenes $C_{64}$ and $C_{76}$, are more complex than those of fullerene $C_{36}$. To emphasize this fact, we have changed the chemical formulas of these fullerenes, and write them as $A_3(C_1)B_6(C_6)$ and $A_3(C_1)B_9(C_6)$. Here the additional symbol C refers to inner, passive core atoms. It must be also emphasized that double lines in the graph for fullerene $C_{76}$ do not refer to double chemical bonds. As we mentioned above, we do not know the electronic structure of this fullerene. These lines only show that apices 9(6) are connected between themselves by two edges.

**Search for periodicity.** The aim of our study is to find the mass difference Δm-index for tetrahedral fullerenes with the purpose to incorporate this fullerene group into the periodic system of fullerenes. Now we have the following information:

| Fullerenes | Chemical formula | Number of atoms |
|---|---|---|
| $C_4$ | $A_1$ | 4◦1=4 |
| $C_{12}$ | $B_3$ | 4◦3=12 |
| $C_{16}$ | $A_1B_3$ | 4◦(1+3)=16 |
| $C_{28}$ | $A_1B_6$ | 4◦(1+6)=28 |
| $C_{36}$ | $A_3B_6$ | 4◦(3+6)=36 |
| $C_{64}$ | $A_3(C_1)B_6(C_6)$ | 4◦[(3+1)+(6+6)]=64 |
| $C_{76}$ | $A_3(C_1)B_9(C_6)$ | 4◦[(3+1)+(9+6)]=76 |

This allows do some predictions.

The mass difference for these fullerenes can be written as Δm = 8, 4, 12, 8, 28, 12. It is clear that the gap between fullerenes $C_{36}$ and $C_{64}$ is too large. However it can be decreased by the following way. Let us change in formula $A_3B_6$ for fullerene $C_{36}$ component $A_3$ to component $A_3(C_1)$. Then we obtain fullerene $C_{40}$, in which instead of 12 hexagons there will be 12 heptagons. In a similar way, changing component $A_3(C_1)$ in formula $A_3(C_1)B_6(C_6)$ for fullerene $C_{64}$ with component $A_3$ creates fullerene $C_{60}$. As a result, we have now the following data series: Δm = 8, 4, 12, 8, 4, 20, 4, 12. Although the gap became less, it is nevertheless is again large. Probably it is worth to search after fullerene $C_{48}$ or $C_{52}$, or both.

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