**NATURAL ISOMERS OF FULLERENES FROM C\textsubscript{20} TO C\textsubscript{28}**

Alexander I. Melker\textsuperscript{1} and Aleksandra N. Matvienko\textsuperscript{2*}

\textsuperscript{1}St. Petersburg Academy of Sciences on Strength Problems, Peter the Great St. Petersburg Polytechnic University, Polytekhnicheskaya 29, 195251, St. Petersburg, Russian Federation

\textsuperscript{2}Department of Mechanics and Control Processes, Peter the Great St. Petersburg Polytechnic University, Polytekhnicheskaya 29, 195251, St. Petersburg, Russian Federation

*e-mail: matvienko_an@spbstu.ru

**Abstract.** We have systematized possible ways of forming the isomers of midi-fullerenes, namely C\textsubscript{22}, C\textsubscript{24}, C\textsubscript{26} and C\textsubscript{28}. There are three the most natural mechanisms of their obtaining: embedding carbon dimers into initial fullerenes; fusion of carbon cupolas having the same symmetry; fusion of fullerenes having compatible symmetry. The minimum energy fullerenes are obtained through the use of the first mechanism. It is worth noting that these fullerenes conserve the topological three-fold symmetry. At the same time the graph representation shows the change of symmetry from three-fold symmetry to six-fold one. Combined with the graph analysis, this geometric modeling allows obtain a clear knowledge of the structure of the fullerenes formed.

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

**1. Introduction**

The periodic system for basic fullerenes, which is grounded on symmetry principles, is presented in Refs. [1,2]. Once it is done, we need to complete it adding fullerene isomers. 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].

It is our opinion that the most natural mechanisms of obtaining new fullerenes, in particular isomers, which set off them from other possible ones, are:

- Embedding carbon dimers into initial fullerenes [4];
- Fusion of carbon cupolas having the same symmetry [5];
- Fusion of fullerenes having compatible symmetry [6].

In this contribution we present the structure and energy of fullerenes and their isomers in the range from C\textsubscript{20} to C\textsubscript{28} obtained through the use of these mechanisms. 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. However, there are also other isomers, which have identical position of the atoms in space, but differ from each other in a number and a position of the single and double bonds. As a result, they also have different energies and could be named the electronic isomers. Since we are interested in space isomerism, we will not carefully study the electronic isomers. 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.
2. Isomers of fullerene C22

a) Dimer embedding into a \((\text{tetra-hexa})_3\)-penta\(_6\) dodecahedron. The initial configuration is shown in Fig. 1. It consists of three squares, three hexagons and six pentagons and has three-fold symmetry [5]. For studying fullerene growth, it is reasonable to apply the mechanism suggested by M. Endo and H.W. Kroto in 1992 [7]. According to it, a carbon dimer embeds into one of hexagons of an initial fullerene (Fig. 2, left side). This leads to stretching and breaking the covalent bonds which are parallel to arising tensile forces. As a result, there arises a new atomic configuration and there is mass increase of two carbon atoms. Strictly speaking, the Endo-Kroto's mechanism refers to a single-bond dimer. On the basis of our previous research, we came to conclusion that in many cases it is reasonable to consider also a double-bond dimer. Both situations are shown in Fig. 2.

![Fig. 1. (Tetra-hexa)\(_3\)-penta\(_6\) dodecahedron C\(_{20}\) and its graphs; energy in kJ/mol](image1)

![Fig. 2. Carbon dimer embedding into a hexagon (a) and forming two adjacent pentagons (b)](image2)

![Fig. 3. Fullerene C\(_{22}\) obtained by embedding a dimer into a hexagon of (tetra-hexa)\(_3\)-penta\(_6\) dodecahedral fullerene C\(_{20}\); structure and graphs; energy in kJ/mol](image3)

The embedding transforms fullerene C\(_{20}\) into fullerene C\(_{22}\). It influences deeply only on one of hexagons and two its square neighbors. The hexagon transforms into two adjacent pentagons and its square neighbors become pentagons. As a result, one obtains a cluster of four pentagons. By analogy with Ref. [1], we consider the dimer as an 'interstitial' defect and assume that the fullerene C\(_{22}\) has topological three-fold symmetry. The fullerene obtained...
contains one square, ten pentagons and two hexagons and therefore can be named tetra-penta₁₀-hexa₂ triacaidecahedron C₂₂.

**b) Dimer embedding I into a perfect dodecahedron.** The initial atomic configuration is a regular polyhedron (Fig. 4). It consists of twelve pentagons [5] and is known as one of five regular Plato’s bodies. By analogy with the Endo-Kroto’s embedding, when a carbon dimer is incorporated normally to hexagon opposite sides, one can imagine another type of embedding shown in Fig. 5. Here a carbon dimer is embedded into a pentagon parallel to one of its sides. As a result, the new polyhedron, tri-hexa₃-penta₉ triacaidecahedron C₂₂ conserves only one three-fold symmetry axis (Fig. 6).

![Fig. 4. Dodecahedron C₂₀ and its graphs; energy in kJ/mol](image1)

**Fig. 5. Carbon dimer embedding into a pentagon (a) and forming three adjacent hexagons (b)**

![Fig. 6. Fullerene C₂₂ obtained by embedding a dimer into a pentagon of perfect dodecahedral fullerene C₂₀: structure and graphs; energy in kJ/mol](image2)

**c) Dimer embedding II into a perfect dodecahedron.** The fullerene C₂₂ as a tetra-hexa₂-penta₁₀ triacaidecahedron can be also obtained by embedding a dimer into a perfect dodecahedron in a manner shown in Fig. 7. At first glance it is a new configuration (Fig. 8). However, this fullerene C₂₂ as a whole is identical to the fullerene constructed from a (tetra-hexa)₃-penta₀ dodecahedron C₂₀ by embedding a dimer into a hexagon (Fig. 3). It should be
emphasized that any graph is a projection, which helps to understanding, but it reflects only a specific side of symmetry which is of interest at that moment. In our case, it is two-fold symmetry.

![Fig. 7. Carbon dimer embedding into a pentagon (a) and forming a square (b)](image)

**Fig. 7.** Carbon dimer embedding into a pentagon (a) and forming a square (b)

![Fig. 8. Tetra-hexa$_2$-penta$_{10}$ triacaidecahedron C$_{22}$ and its graphs; energy in kJ/mol](image)

**Fig. 8.** Tetra-hexa$_2$-penta$_{10}$ triacaidecahedron C$_{22}$ and its graphs; energy in kJ/mol

3. **Isomers of fullerene C$_{24}$**

a) **Dimer embedding into tetra-hexa$_2$-penta$_{10}$ triacaidecahedron C$_{22}$.** The initial fullerene is shown in Figure 3. Embedding a dimer into one of the two hexagons transforms fullerene C$_{22}$ into fullerene C$_{24}$. Similar to reaction C$_{20}$ + C$_2 \rightarrow$ C$_{22}$, one of two hexagons transforms into two adjacent pentagons, its square neighbor into a pentagon, and its pentagon neighbor into a hexagon. As a result, one obtains an isomer having six-fold rotation-reflection symmetry. However, in order not to lose touch with the initial fullerene, we may consider the fullerene obtained as the one having topological three-fold symmetry. The reason for such labeling is as follows. The configuration is able to incorporate one more dimer what returns fullerene C$_{26}$ to the three-fold symmetry group of the periodic system of basic fullerenes. So we may consider the absent dimer as a ‘vacancy’ defect. And therefore we also may assume that the fullerene C$_{22}$ has topological three-fold symmetry. The fullerene obtained contains twelve pentagons and two hexagons and therefore can be named penta$_{12}$-hexa$_2$ tetraacaidecahedron C$_{24}$. It presented in Fig. 9 together with the graphs illustrating the topological three-fold symmetry.

b) **Fusion of two cupolas C$_{12}$ having three-fold symmetry.** This reaction C$_{12}$ + C$_{12}$ → C$_{24}$ was studied in Ref. [5], but the energy and its dependence on the electronic structure was not calculated. Now we correct this drawback. As it was shown in Ref. [5], there are two ways of joining: mirror symmetry and rotation-reflection-symmetry one. In the first case (Fig. 10, above) the lower cupola is a mirror copy of the upper one. The fullerene obtained contains two triangles, three squares and nine hexagons and therefore was named a tri$_2$-tetra$_3$-hexa$_9$ polyhedron. In the second case (Fig. 10, below) the lower cupola is a rotary reflection of the upper one. The fullerene contains two triangles, six pentagons and six hexagons. It was named a truncated dodecahedron. Its energy is less than that of the first fullerene.
c) Fusion of two cupolas \( C_{12} \) having four-fold symmetry. Although this reaction was also studied elsewhere [8], the energy dependence on the electronic structure was not investigated. Now we fill it up. The final atomic configuration is presented in Fig. 11. It consists of two squares, eight pentagons and four hexagons, the hexagons having a boat conformation. It is a tetra-penta-hexa polyhedron.

d) Fusion of two mini-fullerenes \( C_{8} \) and \( C_{16} \). This reaction of cube \( C_{8} \) with square barrel \( C_{16} \) was considered in Ref. [6] on the basis of graph theory. The reaction is possible since the both configurations have four-fold symmetry and therefore they are compatible with each other. However, this fullerene \( C_{24} \) as a whole is identical to the fullerene constructed by means of the fusion of two cupolas \( C_{12} \) having four-fold symmetry (Fig. 11). Therefore we have only another way of producing this fullerene.
Fig. 11. Joining two half fullerenes C₁₂ of four-fold symmetry: the mirror symmetry fusion; structure and graphs; energy in kJ/mol

e) Fusion of plane cluster C₈ with cupola C₁₆. Here both configurations have four-fold symmetry. This reaction was also studied elsewhere [8], but the energy dependence on the electronic structure was not calculated. Now we fill it up again. The results are shown in Fig. 12. The fullerene contains six squares and eight hexagons. This isomer is a truncated octahedron (cuboctahedron) having four-fold symmetry.

Fig. 12. Joining plane cluster C₈ with cupola C₁₆: structure and graphs; energy in kJ/mol

f) Fusion of two mini-fullerenes C₁₂. Here both configurations have six-fold symmetry. This reaction was also studied elsewhere [6], but the energy and its dependence on the electronic structure was not calculated. Now we fill it up again. At first glance we have a new configuration (Fig. 13). However, as before, this fullerene C₂₄ as a whole is identical to the fullerene constructed from tetra-hexa₂-penta₁₀ polyhedron C₂₂ by embedding a dimer into a hexagon (Fig. 9). It should be emphasized again that any graph is a projection, which helps to understanding, but it reflect only a specific side of symmetry which is of interest at that moment. In our case, it is a hexa₂-penta₁₂ polyhedron having six-fold symmetry.

Fig. 13. Joining two fullerenes C₁₂ of six-fold symmetry: the rotation-reflection symmetry fusion; structure and graphs; energy in kJ/mol
4. Isomers of fullerene $C_{26}$

a) Dimer embedding into penta$_{12}$-hexa$_2$ polyhedron $C_{24}$. The starting fullerene is shown in Fig. 9. Embedding a dimer into the hexagon in the background transforms fullerene $C_{24}$ into fullerene $C_{26}$. It is a perfect fullerene having a three-fold axis of symmetry. The symmetry can be easily discovered by looking at its graph. The fullerene obtained contains twelve pentagons and three hexagons and therefore can be named penta$_{12}$-hexa$_3$ pentecaidecahedron $C_{26}$.

![Fig. 14. Fullerene $C_{26}$ obtained by embedding a dimer into penta$_{12}$-hexa$_2$ polyhedral fullerene $C_{24}$ shown in Figure 9: structure and graphs; energy in kJ/mol]

b) Dimer embedding into tri$_2$-tetra$_3$-hexa$_9$ polyhedron $C_{24}$. The initial perfect fullerene is shown in Fig. 10 above. Embedding a dimer into the hexagon in the background transforms fullerene $C_{24}$ into fullerene $C_{26}$. Since it contains an extra interstitial, it is an imperfect fullerene having topological three-fold symmetry. The symmetry can also be discovered by looking at its graph. The fullerene obtained contains two triangles, one square, four pentagons and eight hexagons and therefore can be named tri$_2$-tetra$_3$-hexa$_8$ pentecaidecahedron $C_{26}$.

![Fig. 15. Fullerene $C_{26}$ obtained by embedding a dimer into tri$_2$-tetra$_3$-hexa$_9$ polyhedral fullerene $C_{24}$ shown in Fig. 10: structure and graphs; energy in kJ/mol]

5. Isomers of fullerene $C_{28}$

a) Dimer embedding 1 into penta$_{12}$-hexa$_3$ polyhedron $C_{26}$. The starting perfect fullerene is shown in Fig. 14. Embedding a dimer into the hexagon in front, parallel to the three-fold axis, transforms fullerene $C_{26}$ into fullerene $C_{28}$. It is a perfect fullerene having rotation-reflection two-fold symmetry. The symmetry can be easily discovered by looking at its graph. The fullerene obtained contains twelve pentagons and four hexagons and therefore can be named penta$_{12}$-hexa$_4$ eccaidecahedron (90) $C_{28}$.
**Fig. 16.** Fullerene $C_{28}$ obtained by embedding a dimer into penta$_{12}$-hexa$_3$ polyhedral fullerene $C_{26}$ shown in Fig. 14: structure and graphs; energy in kJ/mol

**b) Dimer embedding II into penta$_{12}$-hexa$_3$ polyhedron $C_{26}$** The initial perfect fullerene is the same as before. However, here embedding is done at an angle of 60° to the three-fold axis of symmetry of the initial fullerene. As a result, we have also a perfect fullerene but having rotation-reflection two-fold symmetry. Contrary to the previous case, where the initial fullerene half is needed to be rotated through 90 degrees to get a mirror image, here the rotation is done only through 30 ones. The symmetry can be easily discovered by looking at its graph. The fullerene obtained also contains twelve pentagons and four hexagons and therefore can be named penta$_{12}$-hexa$_4$ eccaidecahedron (30) $C_{28}$.

**Fig. 17.** Fullerene $C_{28}$ obtained by embedding a dimer into penta$_{12}$-hexa$_3$ polyhedral fullerene $C_{26}$: structure and graphs; energy in kJ/mol

**c) Dimer embedding into tri$_2$-tetra-penta$_4$-hexa$_8$ polyhedron $C_{26}$** The starting fullerene is shown in Fig. 15. Embedding a dimer into the hexagon in the background transforms fullerene $C_{24}$ into fullerene $C_{26}$. Since it contains two extra interstitials, it is an imperfect fullerene having topological three-fold symmetry. The symmetry can also be discovered by looking at its graph. The fullerene obtained contains two triangles, six pentagons and eight hexagons and therefore can be named a tri$_2$-penta$_4$-hexa$_8$ eccaidecahedron.

**d) Fusion of two different cupolas having compatible symmetry.** The structure of tetrahedral mini-fullerene $C_{28}$ was suggested by H.W. Kroto [9]. One of the possible ways of the realization is a fusion reaction of cupola $C_{10}$ and bowl $C_{18}$, which can be written in the form $C_{10} + C_{18} \rightarrow C_{28}$. 
9. Conclusion and discussion

We have systematized possible ways of forming the isomers of midi-fullerenes, namely $C_{22}$, $C_{24}$, $C_{26}$ and $C_{28}$. There are three the most natural mechanisms of their obtaining:

1) Embedding carbon dimers into initial fullerenes;
2) Fusion of carbon cupolas having the same symmetry;
3) Fusion of fullerenes having compatible symmetry.
In Table 1 the calculated energies of fullerenes are presented, for different isomers the minimum energies being designated with bold figures. The isomers having the minimum energies are shown in Fig. 21 together with their graphs.

<table>
<thead>
<tr>
<th></th>
<th>C_{20} (a, b)</th>
<th>C_{22} (a, b)</th>
<th>C_{24} (a, b1, b2, c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E max</td>
<td>1857</td>
<td>1647</td>
<td>1198</td>
</tr>
<tr>
<td>E min</td>
<td>1083</td>
<td><strong>491</strong></td>
<td><strong>697</strong></td>
</tr>
<tr>
<td>ΔE</td>
<td>774</td>
<td>1156</td>
<td>1716</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>C_{24} (c, f)</th>
<th>C_{26} (a, b)</th>
<th>C_{28} (a, b, c, d, e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E max</td>
<td>3046</td>
<td>1178</td>
<td>1790</td>
</tr>
<tr>
<td>E min</td>
<td>2067</td>
<td><strong>697</strong></td>
<td>924</td>
</tr>
<tr>
<td>ΔE</td>
<td>979</td>
<td>481</td>
<td>866</td>
</tr>
</tbody>
</table>

From the Figures it follows that the minimum-energy fullerenes are obtained through the use of the first mechanism. It should be emphasized that instead of the perfect dodecahedron having the smallest energy of 491 kJ/mol, we inset into the figure the (tetra-hexa)_{3}-penta_{6} dodecahedron having a larger energy of 1083 kJ/mol. It is connected with the fact that the perfect dodecahedron does not produces afterwards fullerenes of minimum energy whereas the (tetra-hexa)_{3}-penta_{6} dodecahedron does it. It is worth noting that the fullerenes shown conserve the topological three-fold symmetry. The corresponding axis goes through the atoms marked in green. At the same time the graphs shown better reflect the real symmetry changes induced by embedding carbon dimers. As we said before, any graph is a projection, giving a better insight into the mechanism of fullerene formation, but it reflects only a specific side of symmetry which is of interest at that moment. In our case, it shows the change of symmetry from three-fold symmetry to seven-fold one. The graph representation is most convenient to use for studying it. Thus combined with the graph analysis, this geometric modeling allows obtain a clear knowledge of the structure of the fullerenes formed.

**Fig. 21.** Fullerene isomers of minimum energy, their graphs and energies in kJ/mol

**Acknowledgements.** No external funding was received for this study.
References