

## PHYSICS OF MOLECULES

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### THE WAYS TO FORM MIDI-FULLERENS STRUCTURE EXEMPLIFIED BY $C_{22}$ , $C_{24}$ AND $C_{26}$ ISOMERS

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**Abstract.** In this paper, the possible ways of forming the midi-fullerene isomers, namely  $C_{22}$ ,  $C_{24}$  and  $C_{26}$ , have been systematized. Three simplest mechanisms for their synthesizing are known. They are the fusion of carbon cupolas having the same symmetry; the fusion of fullerenes having compatible symmetry; embedding carbon dimers into initial fullerenes. The structures with minimal energy were formed through the use of the third mechanism retaining the topological three-fold symmetry. The symmetry order of studied fullerenes changed from the third to the sixth. The geometric modeling carried out in conjunction with the analysis of structures' formation energies gives researchers a clear idea of the structure of the resulting fullerenes.

**Keywords:** isomer, periodic system, fusion reaction, growth, fullerene, energy

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### СПОСОБЫ ФОРМИРОВАНИЯ СТРУКТУРЫ МИДИ-ФУЛЛЕРЕНОВ НА ПРИМЕРЕ ИЗОМЕРОВ $C_{22}$ , $C_{24}$ И $C_{26}$

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**Аннотация.** В работе систематизированы возможные способы образования изомеров миди-фуллеренов, а именно  $C_{22}$ ,  $C_{24}$  и  $C_{26}$ . Известны три наиболее простых механизма их получения: слияние углеродных куполов, имеющих одинаковую симметрию; слияние фуллеренов, имеющих совместимую симметрию; встраивание углеродных димеров в исходные фуллерены. Структуры с минимальной энергией образуются по третьему механизму и сохраняют топологическую симметрию третьего порядка. Порядок симметрии рассматриваемых фуллеренов изменяется от третьего к шестому. Проведенное геометрическое моделирование в совокупности с анализом энергий образования структур дает исследователям ясное представление о структурных характеристиках сформированных фуллеренов.

**Ключевые слова:** изомер, периодическая система, реакция синтеза, рост, фуллерен, энергия

**Ссылка для цитирования:** Матвиенко А. Н. Способы формирования структуры миди-фуллеренов на примере изомеров  $C_{22}$ ,  $C_{24}$  и  $C_{26}$ . // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 1. С. 125–131. DOI: <https://doi.org/10.18721/JPM.16110>

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## Introduction

The periodic system of the main fullerenes based on the principles of symmetry is presented in [1]. The idea of such a system relies on the concept of spatial isomerism of molecules, a phenomenon that consists in the existence of molecules with the same molecular weight and composition but different positions of atoms in space, and, consequently, with different chemical and physical properties [2, 3].

The following simplest mechanisms are adopted for obtaining new fullerenes, in particular isomers that distinguish them from potential others:

- fusion of carbon domes with the same symmetry [4];
- fusion of fullerenes with compatible symmetry [5];
- embedding of carbon dimers in the initial fullerenes [6].

This paper presents the structures and energies of three such fullerenes and their isomers:  $C_{22}$ ,  $C_{24}$  and  $C_{26}$ , obtained using these mechanisms.

The goal of our study is to demonstrate the application of methods for obtaining fullerenes, used to find fullerenes that differ in the spatial arrangement of their atoms.

However, there are other isomers that have the same position of atoms but differ in the number and position of single and double bonds. As a result, they also have different energies and can be called electronic isomers.

We considered the structures of fullerenes of two extreme electronic configurations:

- with single bonds only,
- with single and double bonds (provided that the maximum number of potential double bonds are arranged symmetrically).

### Formation of $C_{22}$ fullerene isomers (topological symmetry)

Consider two simple approaches to obtaining new fullerenes formed by embedding carbon dimers in the initial fullerenes.

**I. Embedding of a dimer into a hexagon.** The initial configuration is the  $C_{20}$  fullerene. It consists of three squares, three hexagons and six pentagons and has third-order symmetry [4]. To analyze the growth of fullerenes, it is most effective to apply the mechanism proposed by Endo and Kroto in 1992 [7], where the carbon dimer is embedded into one of the hexagons of the initial fullerene (fullerene  $C_{20}$ ). This procedure leads to stretching and breaking of covalent bonds in the  $C_{20}$  compound, which are parallel to the resulting tensile forces. Consequently, a new atomic configuration emerges and the mass of two carbon atoms increases. Strictly speaking, the Endo–Kroto mechanism refers to a dimer with a single bond. It was concluded based on previous studies, that it is reasonable to consider a double-bond dimer as well in many cases.

Such embedding transforms fullerene  $C_{20}$  (initial configuration) into fullerene  $C_{22}$ . This strongly affects only one hexagon and two adjacent squares. A hexagon turns into two pentagons, and adjacent squares become pentagons. The result is a cluster of four pentagons. Similarly to [1], we consider the dimer as an intermediate defect and assume that the fullerene  $C_{22}$  has a third-order topological symmetry. The resulting fullerene contains one square, ten pentagons and two hexagons (Fig. 1, *a*). It can be called a tri-hexa<sub>3</sub>-penta<sub>9</sub>tricaideahedron  $C_{22}$ .

**II. Embedding of a dimer into a pentagon.** The initial atomic configuration is a regular polyhedron. It consists of twelve pentagons and is known as one of 5 Platonic solids [4]. Another type of embedding can be suggested, similar to the Endo–Kroto embedding, when a carbon dimer is usually embedded into the opposite sides of a hexagon. Here the carbon dimer is embedded into a pentagon parallel to one of its sides. As a result, the new polyhedron  $C_{22}$  retains only one axis of symmetry consisting of three parts (Fig. 1, *b*).

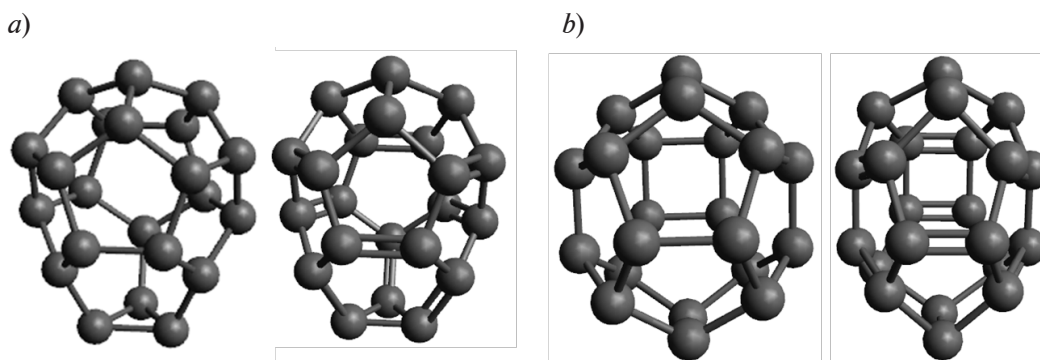
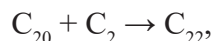


Fig. 1. Structures of  $C_{22}$  fullerene obtained by methods I (a) and II (b).  
The energies of isomer formation are given in Table

### Formation of $C_{24}$ fullerene isomers (topological symmetry)

Consider six methods for obtaining new fullerenes by embedding carbon dimers into the initial fullerenes.

**III. Embedding of a dimer in a fullerene  $C_{22}$ .** The initial fullerene consists of two hexagons, ten pentagons and one square. Embedding a dimer into one of the two hexagons transforms the fullerene  $C_{22}$  into the fullerene  $C_{24}$ . Similar to the reaction



one of the two hexagons transforms into two adjacent pentagons, its adjacent square transforms into a pentagon, and its adjacent pentagon transforms into a hexagon. The result is an isomer with a sixth-order rotation/reflection symmetry. However, to preserve the relationship with the initial fullerene, the resulting fullerene can be assumed to have a third-order topological symmetry. The configuration can include another dimer, which returns the fullerene  $C_{26}$  to the third-order symmetry group of the periodic system of main fullerenes.

Thus, the missing dimer can be regarded as a «vacancy» defect. Therefore, we can assume that fullerene  $C_{22}$  has a third-order topological symmetry. The resulting fullerene contains twelve pentagons and two hexagons. It can be called a penta<sub>12</sub>-hexa<sub>2</sub>tetradecaedron  $C_{24}$ .

**IV. Fusion of two domes  $C_{12}$  with third-order symmetry.** It was established in [2] for the reaction



that two types of bond are possible: mirror symmetry and rotation/reflection symmetry. In the first case (Fig. 2,a), the lower dome is a mirror reflection of the upper one. The resulting fullerene contains two triangles, three squares and nine hexagons. In the second case (Fig. 2,b), the lower dome is formed as a rotating reflection of the upper one.

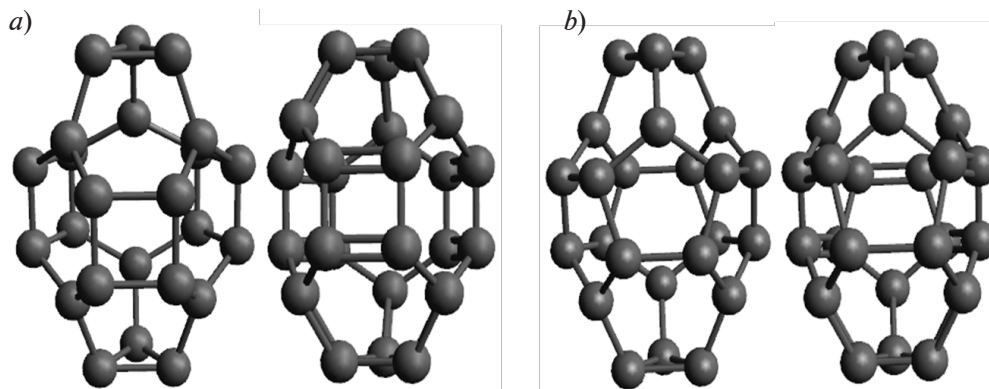


Fig. 2. Structures of fullerene  $C_{24}$  obtained by fusion of carbon domes with the same symmetry (method IV); two types of compounds are shown: mirror symmetry (a) and rotation/reflection symmetry (b).  
The energies of isomer formation are given in Table

The structures shown in Fig. 2, *a* and *b* were called the tri<sub>2</sub>-tetra<sub>3</sub>-hexa<sub>9</sub>polyhedron and the truncated dodecahedron, respectively.

**V. Fusion of two C<sub>12</sub> domes with fourth-order symmetry.** This model was also studied in [8]. The final atomic configuration consists of two squares, eight pentagons and four hexagons, with the hexagons having the shape of a boat. This is a tetra<sub>2</sub>-penta<sub>8</sub>-hexa<sub>4</sub> polyhedron.

**VI. Fusion of two mini-fullerenes: C<sub>8</sub> and C<sub>16</sub>.** Such a configuration of the C<sub>8</sub> cube with a square C<sub>16</sub> barrel was considered in [5] based on graph theory. The reaction is possible because both configurations have fourth-order symmetry and are therefore compatible with each other. However, this fullerene C<sub>24</sub> is generally identical to the fullerene obtained by fusion of two C<sub>12</sub> domes with fourth-order symmetry. Therefore, there is only another way to obtain this fullerene.

**VII. Fusion of a flat cluster C<sub>8</sub> with a C<sub>16</sub> dome.** Here, both configurations have fourth-order symmetry. The results are shown in Fig. 3, *a*. The fullerene contains six squares and eight hexagons. This isomer is a truncated octahedron (cuboctahedron) with fourth-order symmetry.

**VIII. Fusion of two mini-fullerenes C<sub>12</sub>.** Here, both configurations have sixth-order symmetry. At first glance, it seems that this is a new configuration (Fig. 3, *b*). However, as before, this fullerene C<sub>24</sub> is generally identical to a fullerene constructed from a polyhedron C<sub>22</sub> by embedding a dimer into a hexagon. In our case, it is a polyhedron with sixth-order symmetry. This is a hexa<sub>2</sub>-penta<sub>12</sub> polyhedron.

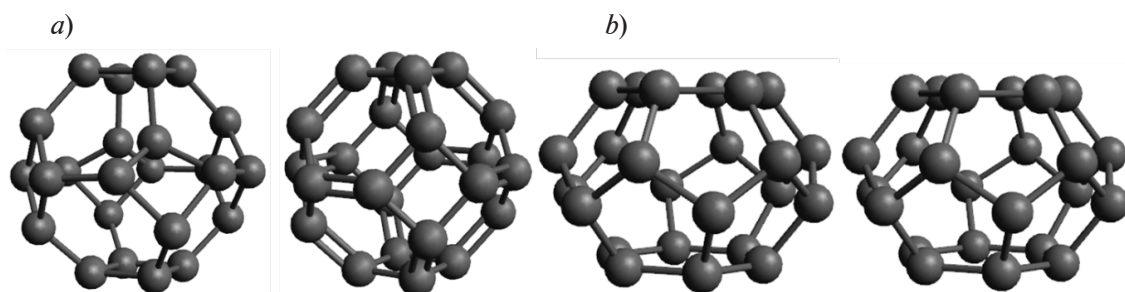


Fig. 3. Structures of fullerene C<sub>24</sub> obtained by methods VII (*a*) and VIII (*b*), namely, by fusion of fullerenes with compatible symmetry  
The energies of isomer formation are given in Table

#### Formation of C<sub>26</sub> fullerene isomers

Consider the case of a fullerene with ordinary symmetry.

**IX. Fullerene with third-order symmetry.** The initial fullerene consists of twelve pentagons and two hexagons. Embedding a dimer into a hexagon in the background transforms a fullerene C<sub>24</sub> into a fullerene C<sub>26</sub>. It is an ideal fullerene with third-order symmetry. The resulting fullerene contains twelve pentagons and three hexagons (Fig. 4, *a*) [9]. It can be called a C<sub>26</sub> penta<sub>12</sub>-hexa<sub>3</sub> pentacaideahedron.

Let us now return to the mechanism forming a fullerene with topological symmetry.

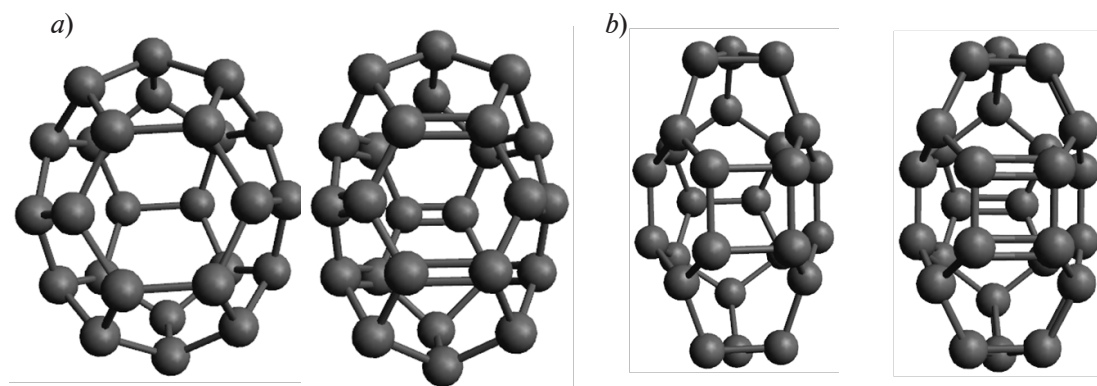


Fig. 4. Embedding of a carbon dimer into the initial perfect fullerene; cases with ordinary (*a*) and topological (*b*) symmetry are shown.  
The energies of isomer formation are given in Table

**X. Embedding of a dimer into a  $C_{24}$  polyhedron.** The initial ideal fullerene is shown in Fig. 2,*a*. Embedding a dimer into a hexagon in the background transforms a fullerene  $C_{24}$  into a fullerene  $C_{26}$ . Since it contains an additional intermediate unit, it is an imperfect fullerene with third-order topological symmetry. The resulting fullerene contains two triangles, one square, four pentagons and eight hexagons (Fig. 4,*b*) [10]. It can be called a tri<sub>2</sub>-tetra-penta<sub>4</sub>-hexa<sub>8</sub> pentecaideahedron  $C_{26}$ .

#### Formation energies of the obtained isomers

The formation energies of various isomers considered in this paper were determined using the Avogadro software (see Table). The energy  $E_{\min}$  is calculated for fullerenes with single chemical bonds,  $E_{\max}$  for fullerenes with double bonds.

Fullerene  $C_{20}$ , with  $E_{\min} = 1083$  kJ/mol [9], serves here as the initial structure for constructing structures consisting of a larger number of carbon atoms. This fullerene, together with the compound  $C_{26}$ , whose  $E_{\min} = 801$  kJ/mol, can be regarded as perfect fullerenes with third-order symmetry. Their formation energies are minimal. In other words, perfect fullerenes are not produced when a structure with even lower energy is constructed. The only possible mechanism to form such fullerenes is the third one, namely, embedding of carbon dimers into the initial fullerenes. Notably, in addition to such fullerenes, the minimal formation energy is characteristic of fullerenes with topological symmetry of the third and fourth orders (Methods II, III, VI and VIII, see Table). They are formed by the mechanisms outlined in this paper.

Table

Calculated formation energies of fullerene isomers

Chemical formula	Number number $E_{\max}$	Energy, kJ/mol		
		$E_{\min}$		
$C_{22}$	I	2170	1300	
	II	1673	<b>795</b>	
$C_{24}$	III	1198	<b>697</b>	
	IV	<i>a</i>	4346	2630
		<i>b</i>	3432	2106
	VI	2452	<b>853</b>	
	VII	3046	2067	
	VIII	1778	<b>697</b>	
$C_{26}$	IX	831	<b>801</b>	
	X	3613	2582	

Note. Method IV includes mirror symmetry (a) and rotation/reflection symmetry (b).

#### Conclusion

The study systematizes different methods for forming midi-fullerene isomers, namely  $C_{22}$ ,  $C_{24}$  and  $C_{26}$ . As mentioned in the introduction, there are three most natural mechanisms for constructing these fullerenes. Analyzing the results, we conclude that ideal fullerenes with minimal energy are obtained by the third mechanism, namely, by embedding carbon dimers in the initial fullerenes. Fullerenes with topological symmetry also have minimal energy. We should emphasize that the presented fullerenes preserve the topological symmetry of the third order, and changes in the order of symmetry from the third to the sixth are also observed. Recall that topological symmetry implies an imperfection in the form of an intermediate or free dimer.

Thus, geometric modeling provides a clear understanding of the structure of the resulting fullerenes.

The results obtained in the study should prove useful for researchers both in the field of chemical technologies and in practical applications for developing a variety of devices based on fullerenes.



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