

NATURAL ISOMERS OF FULLERENES FROM C₂₀ TO C₂₈

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Abstract. We have systematized possible ways of forming the isomers of midi-fullerenes, namely C₂₂, C₂₄, C₂₆ and C₂₈. 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 C₂₀ to C₂₈ 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 (tetra-hexa)₃-penta₆ 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.

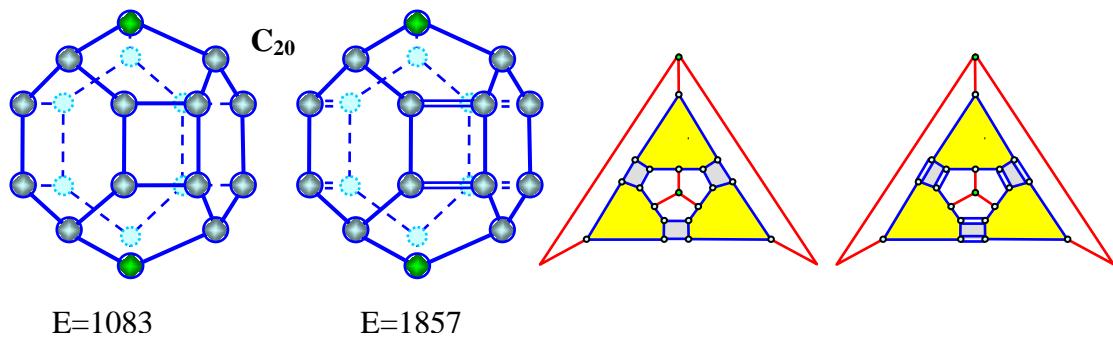


Fig. 1. (Tetra-hexa)₃-penta₆ dodecahedron C₂₀ and its graphs; energy in kJ/mol

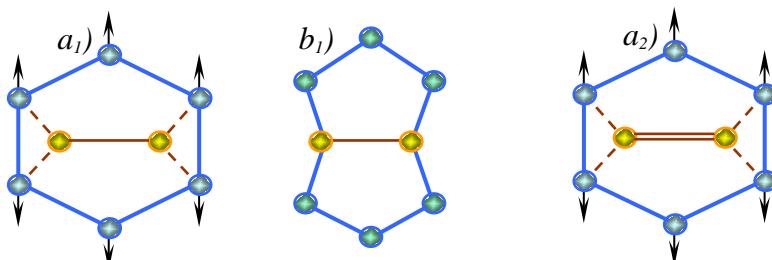


Fig. 2. Carbon dimer embedding into a hexagon (a) and forming two adjacent pentagons (b)

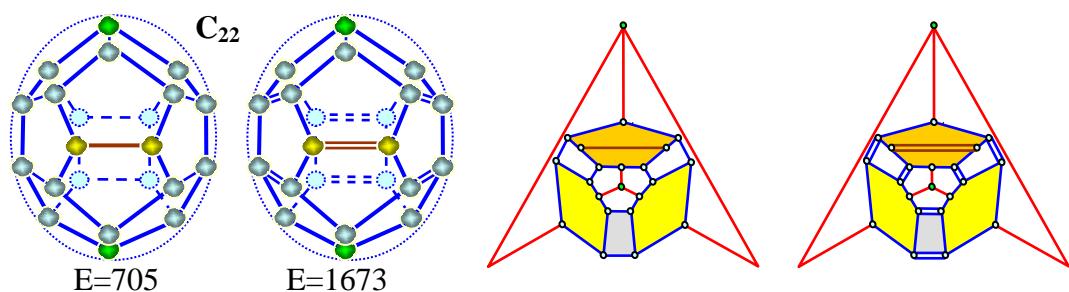


Fig. 3. Fullerene C₂₂ obtained by embedding a dimer into a hexagon of (tetra-hexa)₃-penta₆ dodecahedral fullerene C₂₀: structure and graphs; energy in kJ/mol

The embedding transforms fullerene C₂₀ into fullerene C₂₂. 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 C₂₂ 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).

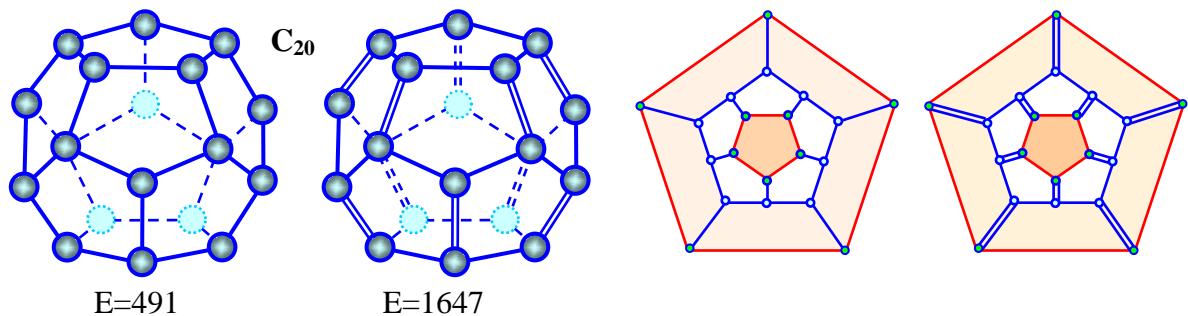


Fig. 4. Dodecahedron C₂₀ and its graphs; energy in kJ/mol

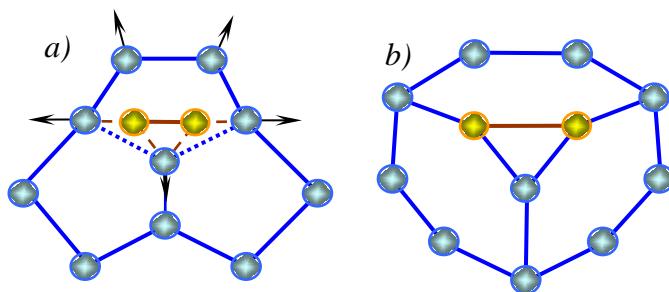


Fig. 5. Carbon dimer embedding into a pentagon (a) and forming three adjacent hexagons (b)

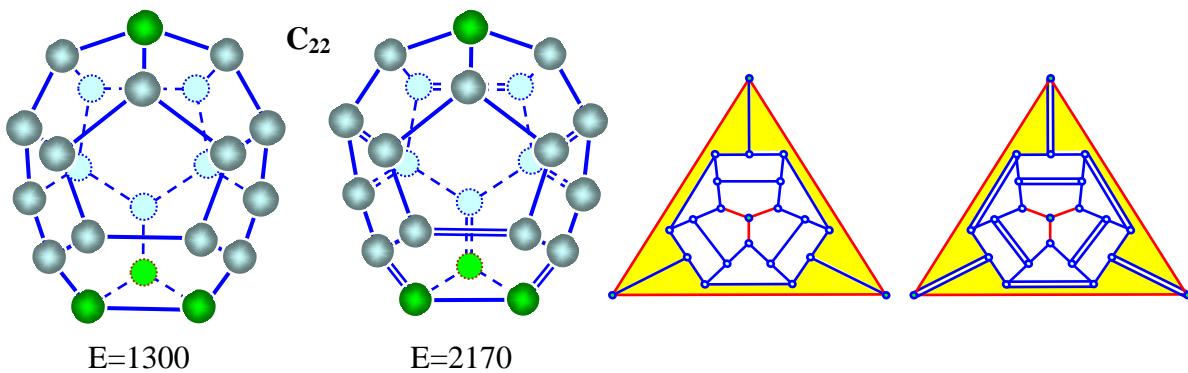


Fig. 6. Fullerene C₂₂ obtained by embedding a dimer into a pentagon of perfect dodecahedral fullerene C₂₀: structure and graphs; energy in kJ/mol

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-penta₆ 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.

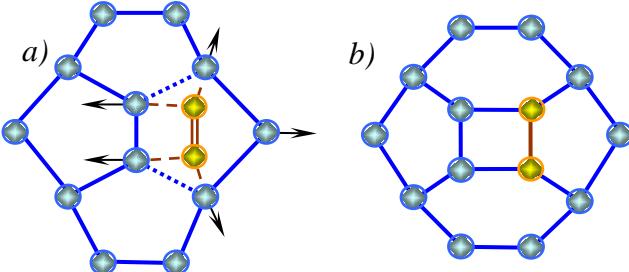


Fig. 7. Carbon dimer embedding into a pentagon (*a*) and forming a square (*b*)

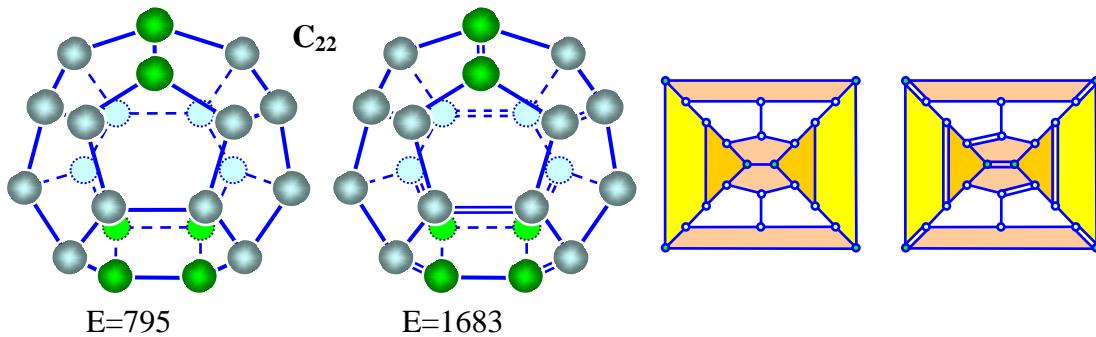


Fig. 8. Tetra-hexa₂-penta₁₀ tricahedron C₂₂ and its graphs; energy in kJ/mol

3. Isomers of fullerene C₂₄

a) Dimer embedding into tetra-hexa₂-penta₁₀ triacaiidecahedron C₂₂. The initial fullerene is shown in Figure 3. Embedding a dimer into one of the two hexagons transforms fullerene C₂₂ into fullerene C₂₄. 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 C₂₆ 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 C₂₂ has topological three-fold symmetry. The fullerene obtained contains twelve pentagons and two hexagons and therefore can be named penta₁₂-hexa₂ tettarecaidecahedron C₂₄. It presented in Fig. 9 together with the graphs illustrating the topological three-fold symmetry.

b) Fusion of two cupolas C₁₂ having three-fold symmetry. This reaction $C_{12} + C_{12} \rightarrow C_{24}$ 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 tri₂-tetra₃-hexa₉ 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.

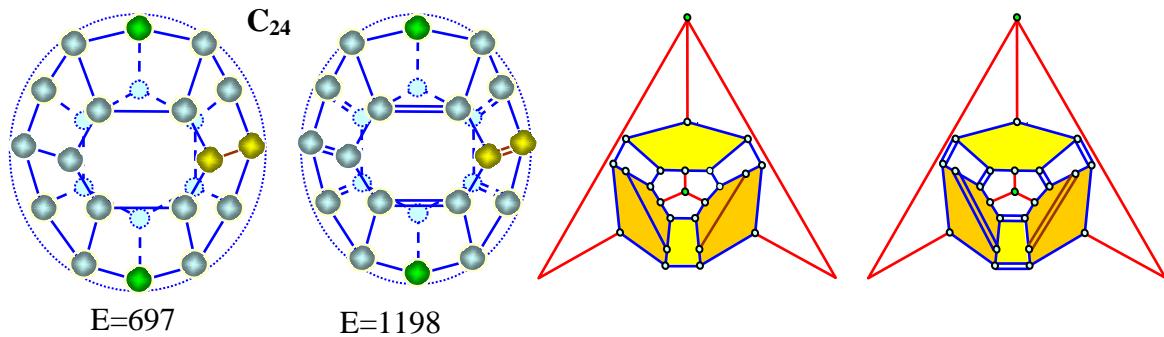


Fig. 9. Fullerene C₂₄ obtained by embedding a dimer into penta₁₂-hexa₂ polyhedral fullerene C₂₂: structure and graphs; energy in kJ/mol

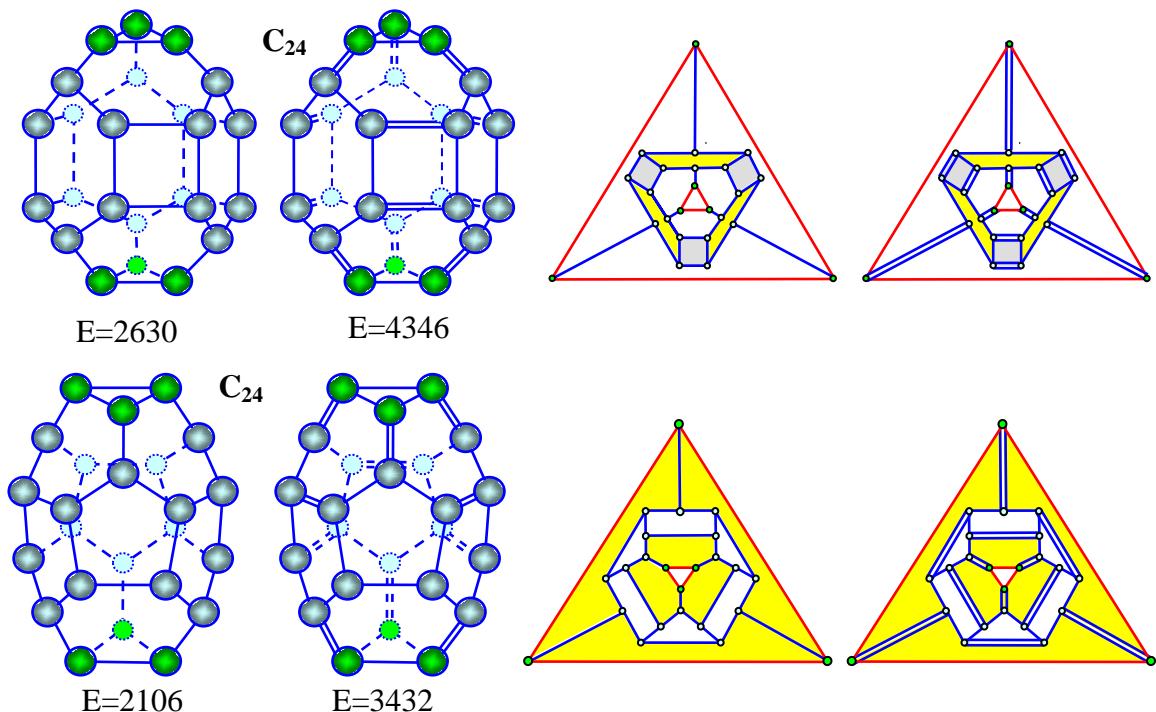


Fig. 10. Joining two half fullerenes C₁₂ of three-fold symmetry: the mirror symmetry fusion (above) and the rotation-reflection symmetry (below); structure and graphs; energy in kJ/mol

c) Fusion of two cupolas C₁₂ 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 tetra₂-penta₈-hexa₄ polyhedron.

d) Fusion of two mini-fullerenes C₈ and C₁₆. This reaction of cube C₈ with square barrel C₁₆ 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 C₂₄ as a whole is identical to the fullerene constructed by means of the fusion of two cupolas C₁₂ having four-fold symmetry (Fig. 11). Therefore we have only another way of producing this fullerene.

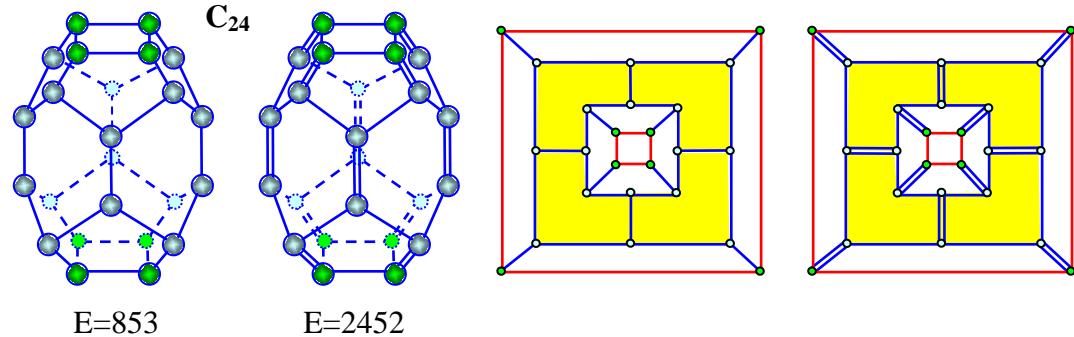


Fig. 11. Joining two half fullerenes C_{12} of four-fold symmetry: the mirror symmetry fusion; structure and graphs; energy in kJ/mol

e) Fusion of plane cluster C_8 with cupola C_{16} . 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.

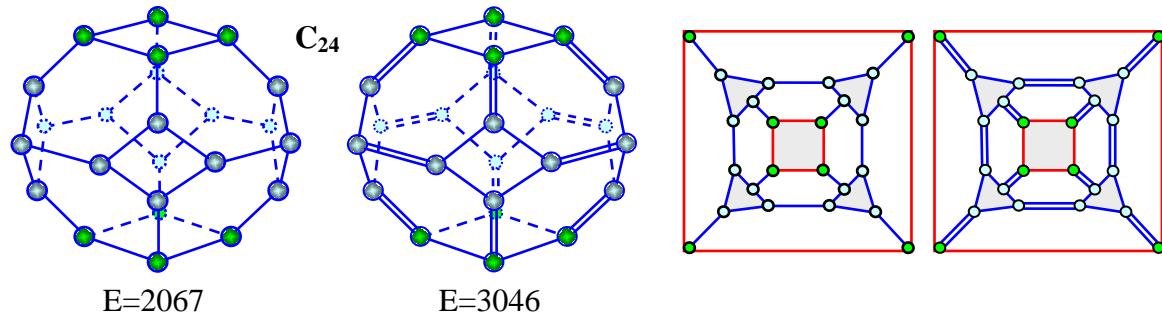


Fig. 12. Joining plane cluster C_8 with cupola C_{16} : structure and graphs; energy in kJ/mol

f) Fusion of two mini-fullerenes C_{12} . 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 C_{24} as a whole is identical to the fullerene constructed from tetra-hexa₂-penta₁₀ polyhedron C_{22} by embedding a dimer into a hexagon (Fig. 9). It should be emphasized again that any graph is a projection, which helps to understand, but it reflects 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.

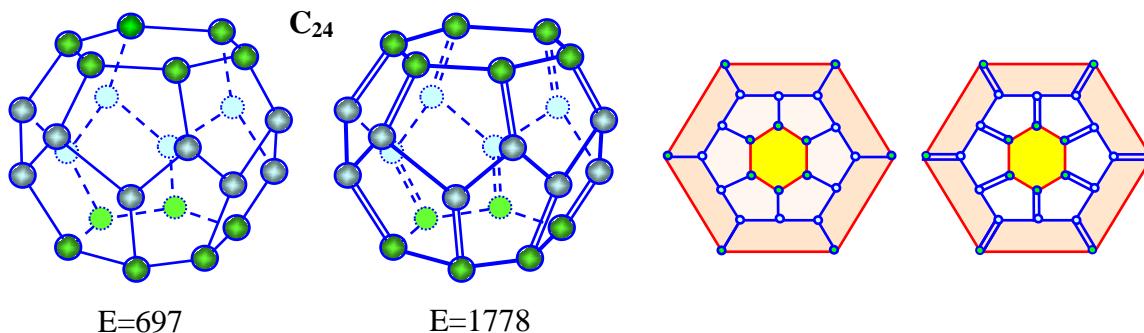


Fig. 13. Joining two fullerenes C_{12} of six-fold symmetry: the rotation-reflection symmetry fusion; structure and graphs; energy in kJ/mol

4. Isomers of fullerene C₂₆

a) Dimer embedding into penta₁₂-hexa₂ polyhedron C₂₄. The starting fullerene is shown in Fig. 9. Embedding a dimer into the hexagon in the background transforms fullerene C₂₄ into fullerene C₂₆. 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 penta₁₂-hexa₃ pentecaidecahedron C₂₆.

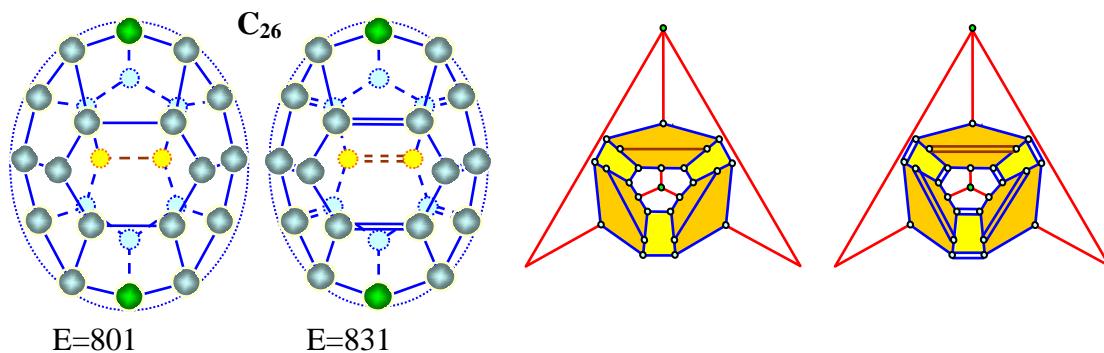


Fig. 14. Fullerene C₂₆ obtained by embedding a dimer into penta₁₂-hexa₂ polyhedral fullerene C₂₄ shown in Figure 9: structure and graphs; energy in kJ/mol

b) Dimer embedding into tri₂-tetra₃-hexa₉ polyhedron C₂₄. The initial perfect fullerene is shown in Fig. 10 above. Embedding a dimer into the hexagon in the background transforms fullerene C₂₄ into fullerene C₂₆. 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 tri₂-tetra₄-penta₄-hexa₈ pentecaidecahedron C₂₆.

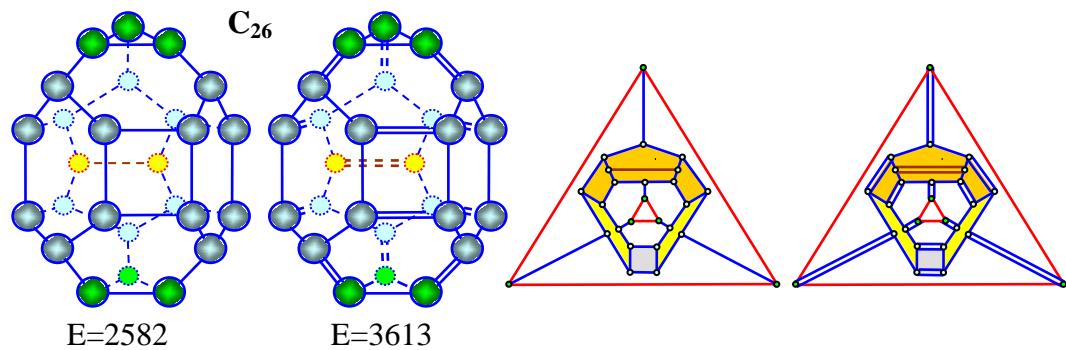


Fig. 15. Fullerene C₂₆ obtained by embedding a dimer into tri₂-tetra₃-hexa₉ polyhedral fullerene C₂₄ shown in Fig. 10: structure and graphs; energy in kJ/mol

5. Isomers of fullerene C₂₈

a) Dimer embedding I into penta₁₂-hexa₃ polyhedron C₂₆. 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 C₂₆ into fullerene C₂₈. 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 penta₁₂-hexa₄ eccaidecahedron (90) C₂₈.

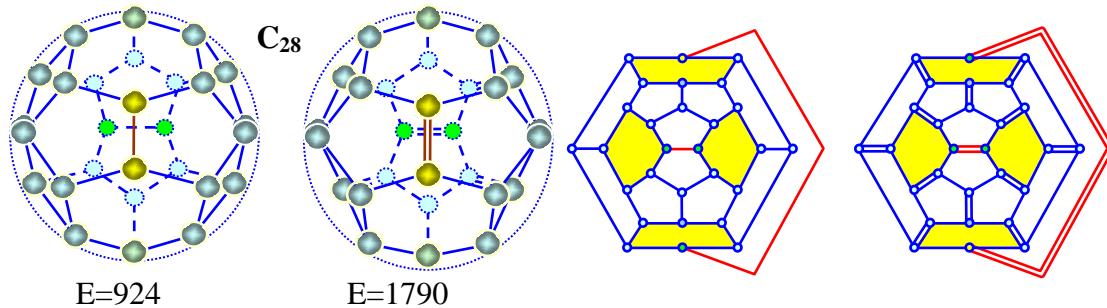


Fig. 16. Fullerene C_{28} obtained by embedding a dimer into penta₁₂-hexa₃ polyhedral fullerene C_{26} shown in Fig. 14: structure and graphs; energy in kJ/mol

b) Dimer embedding II into penta₁₂-hexa₃ 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 penta₁₂-hexa₄ eccaidecahedron (30) C_{28} .

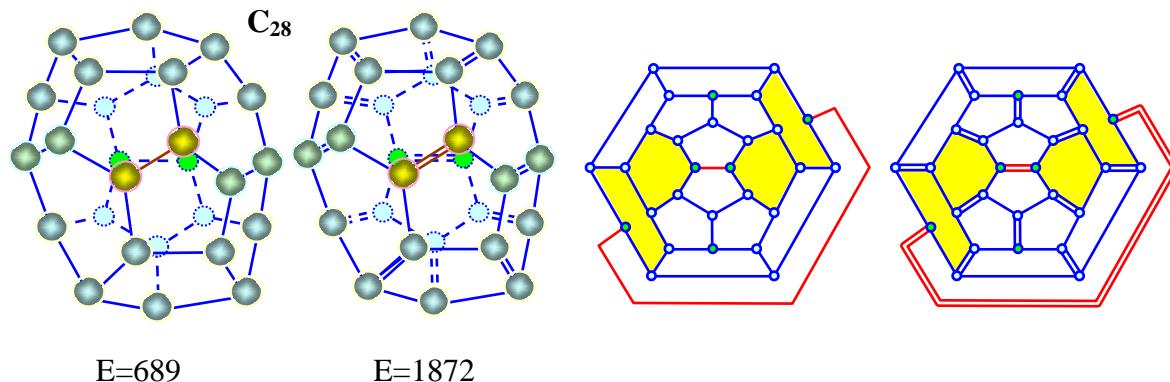


Fig. 17. Fullerene C_{28} obtained by embedding a dimer into penta₁₂-hexa₃ polyhedral fullerene C_{26} : structure and graphs; energy in kJ/mol

c) Dimer embedding into tri₂-tetra-penta₄-hexa₈ 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 tri₂-penta₆-hexa₈ 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 $C_{10} + C_{18} \rightarrow C_{28}$.

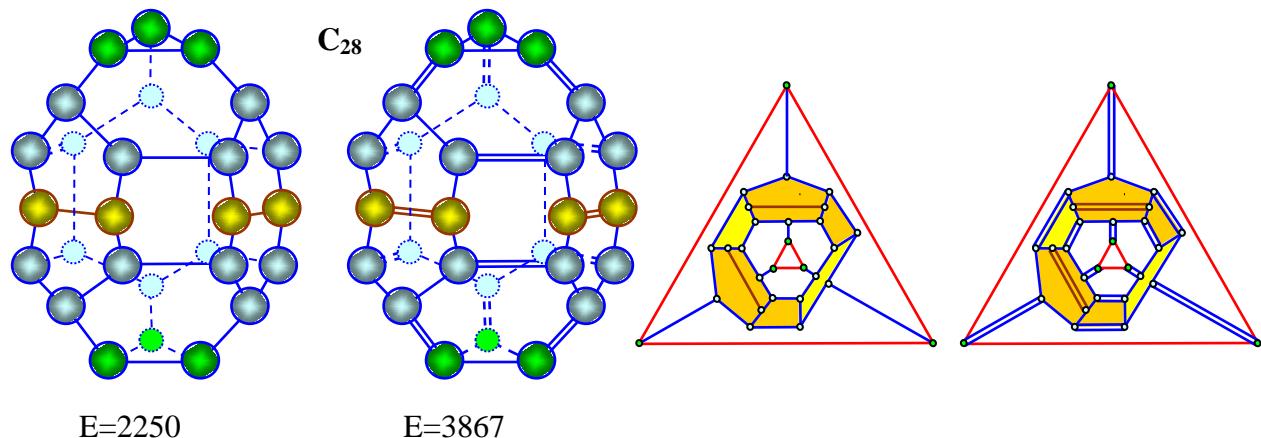


Fig. 18. Fullerene C₂₈ obtained by embedding a dimer into tri₂-tetra₄-penta₄-hexa₈ polyhedral fullerene C₂₆: structure and graphs; energy in kJ/mol

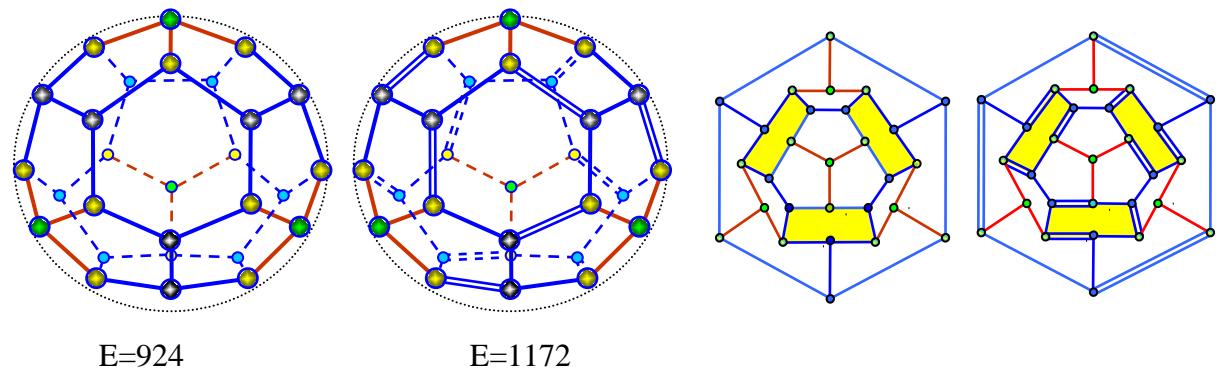


Fig. 19. Fullerene C₂₈ obtained by fusion of different cupolas; energy in kJ/mol

e) Fusion of two heptagonal prisms. Here both initial fullerenes have one and the same seven-fold symmetry. The result of reaction $C_{14} + C_{14} \rightarrow (C_{14}C_{14}) \rightarrow C_{28}$ is presented in Fig. 8 together with the graphs of fullerene C₂₈ obtained.

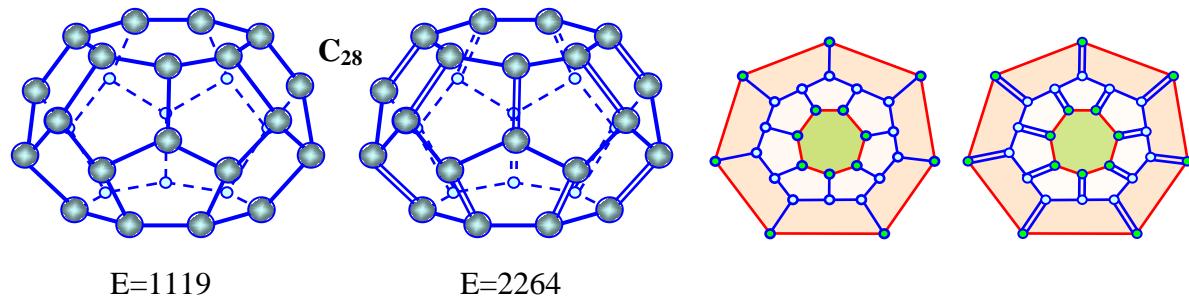


Fig. 20. Joining two fullerenes C₁₄ of seven-fold symmetry: the rotatory-reflection symmetry fusion; structure and graphs; energy in kJ/mol

9. Conclusion and discussion

We have systematized possible ways of forming the isomers of midi-fullerenes, namely C₂₂, C₂₄, C₂₆ and C₂₈. 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 1. Energy of fullerenes in kJ/mol as a function of fullerene size and shape

	C₂₀ (a, b)	C₂₂ (a, b)	C₂₄ (a, b1, b2, c)				
E max	1857	1647	1673	2170	1198	4346	3432
E min	1083	491	795	1300	697	2630	2106
ΔE	774	1156	878	870	501	1716	1326
							1599

	C₂₄ (e, f)	C₂₆ (a, b)	C₂₈ (a, b, c, d, e)					
E max	3046	1178	831	3613	1790	1872	3867	1172
E min	2067	697	801	2582	924	689	2250	924
ΔE	979	481	30	1031	866	1183	1617	248
								1145

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-penta₆ dodecahedron having a larger energy of 1083 kJ/mol. It is connected with the fact that the perfect dodecahedron does not produce afterwards fullerenes of minimum energy whereas the (tetra-hexa)₃-penta₆ 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.

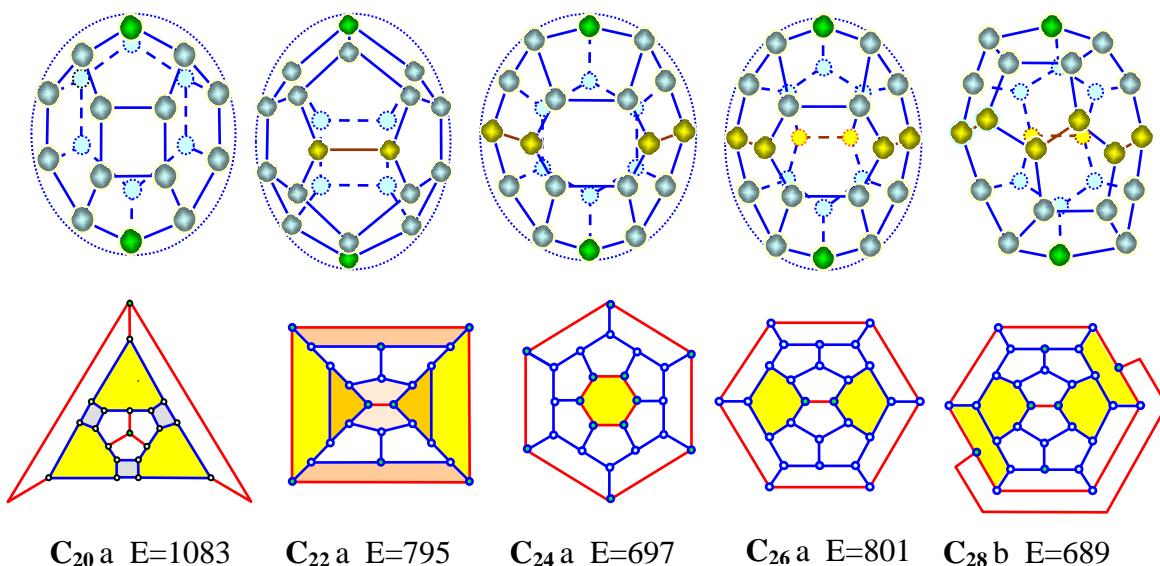


Fig. 21. Fullerene isomers of minimum energy, their graphs and energies in kJ/mol

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