

ISOMERS OF FULLERENE C₆₀

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Abstract. In this paper we analyzed chromatograms and mass spectra of buckminsterfullerene and its isomers. We have calculated possible structures and formation energies of those isomers. We suppose that the most stable isomer which stability is comparable with that of C₇₀ has the form close to a sphere. It has the symmetry axis of third order that passes through the centers of two hexagons, each of which being surrounded with three pentagons and three hexagons.

1. Experimental

Liquid chromatography combined with mass spectroscopy is the most effective method for analysis of organic complex structures, including fullerenes [1]. With the help of liquid chromatography five isomers of C₆₀ generated in microwave plasma of chloroform were discovered [2]. It should be emphasized that the isomers had a lesser retention time in comparison with buckminsterfullerene. They were stable at room temperature but disintegrated at 250 °C. (Fig. 1)

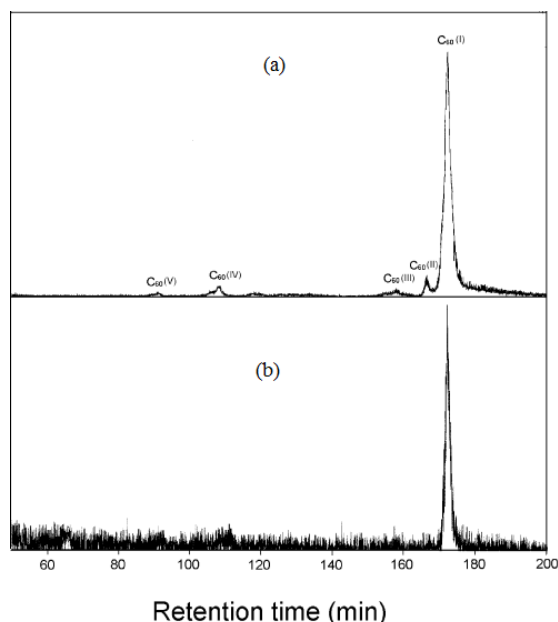


Fig. 1. Chromatograms of fullerene isomers at room temperature (a) and after heating (b) [2].

In 2008 we have synthesized another fullerene isomer (purity 97.3 %) having the retention time larger than that of buckminsterfullerene, 11.8-11.9 and 7.55-7.58 min, respectively. For four years, the part of this fullerene decreased from 97.3 to 91.2 %; for

comparison, the part of buckminsterfullerene decreased from 99.4 to 89.4 % at the same conditions. It means that the stability of isomer obtained is no less than that of buckminsterfullerene.

To gain greater insight into the problem of fullerene isomers, we have synthesized fullerenes C_{60} having retention times which differ from that of buckminsterfullerene (Fig. 2).

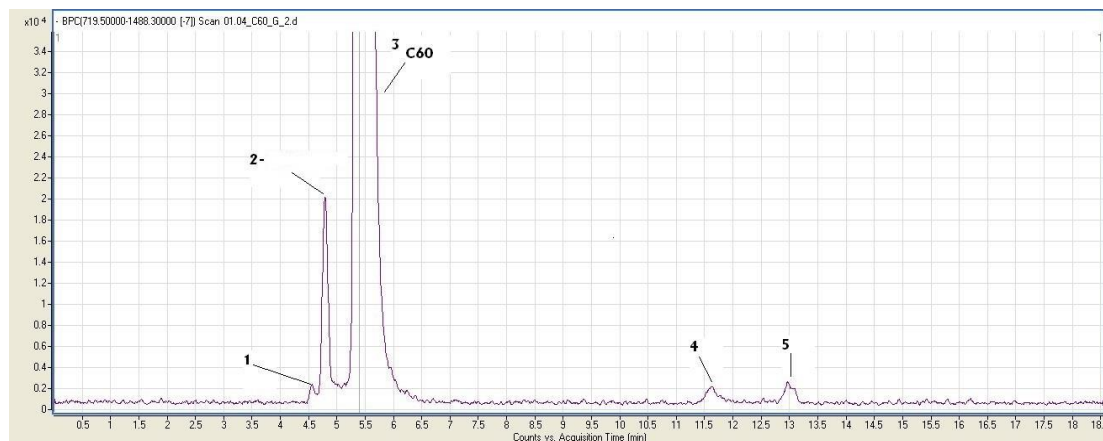


Fig. 2. Chromatogram of a synthesized substance.

Although it is clear that the third peak refers to buckminsterfullerene, there is no evidence of existing C_{60} in other peaks, so we investigated these peaks with the help of mass spectrometry (Figs. 3-5). From these data it follows that the second, third, fourth, and fifth peaks contain isomers of C_{60} , but we can say nothing about their structure.

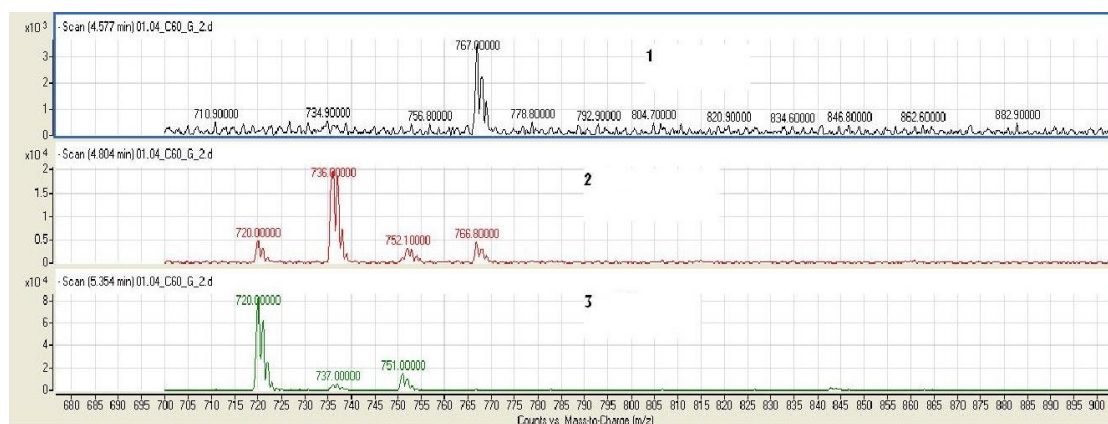


Fig. 3. Mass spectra of the first three peaks.

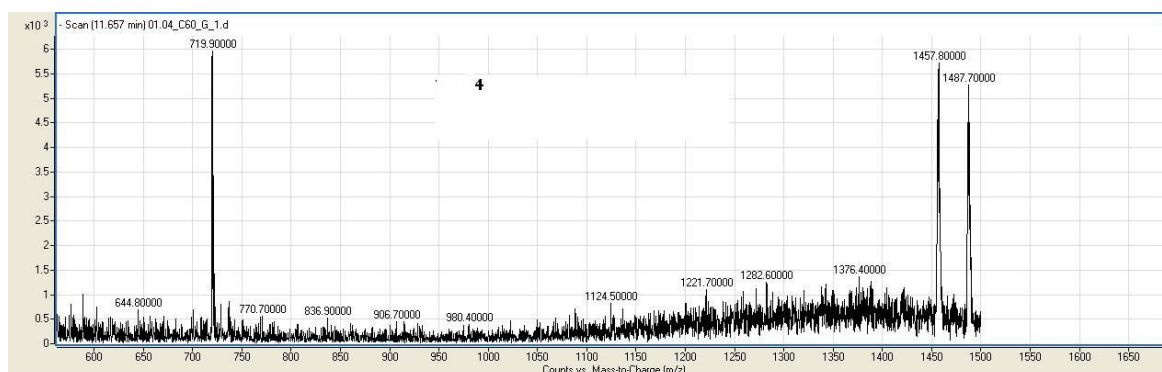


Fig. 4. Mass spectrum of the fourth peak.

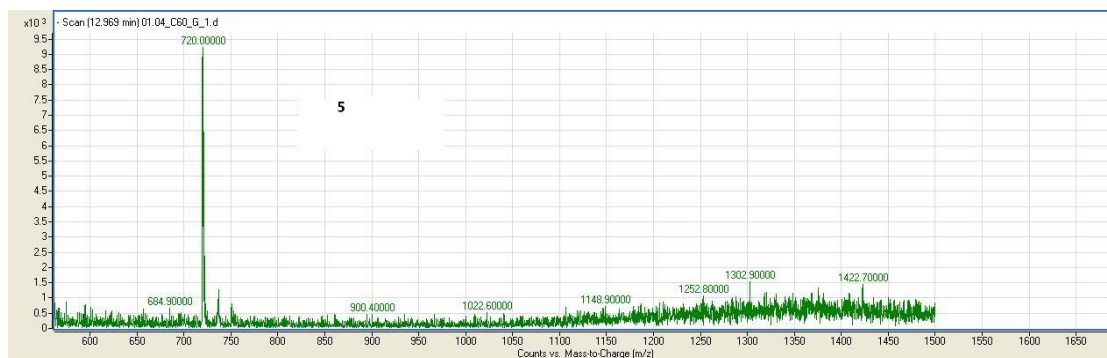


Fig. 5. Mass spectrum of the fifth peak.

For this reason, the following study was decided to do in favour of computer simulations, choosing the most probable isomers of C₆₀ fullerene for investigation.

2. Structures of isomers

Selection of C₆₀ isomers was limited by the number of paired pentagons, because it was supposed that they cause local strains decreasing formation probability of such structures and their stability. So we have confined structures with four contact pentagons. The simulation was performed with Avogadro visualization package. The resulting structures were optimized in Gaussian 09 W by the RHF method with a basis 3-21 G.

a) Three pairs of two adjacent pentagons on an equator at angle 45° (Fig. 6). The axis *z* passes through the centers of two hexagons, each of which being surrounded with three pentagons and three hexagons.

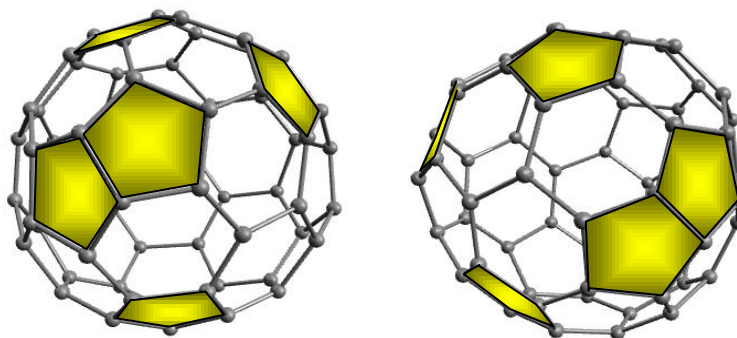


Fig. 6. Three pairs of pentagons on an equator at angle 45° (C_{60m3}).

The bond lengths range from 1.342 Å to 1.482 Å (Fig. 7), unlike buckminsterfullerene, whose bond lengths range from 1.373 Å to 1.449 Å.

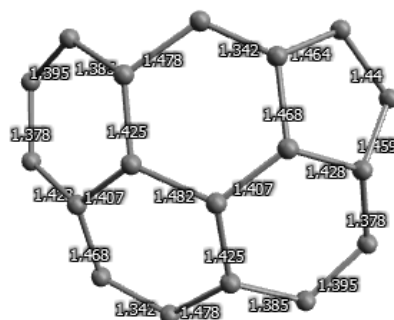


Fig. 7. Part of the structure with the largest value of a bond length.

b) Four pairs of two adjacent pentagons on an equator. Here the axis z passes through the central bond of each of two pyracylene units. A pyracylene unit contains two adjacent hexagons and two disjoint pentagons. (Fig. 8).

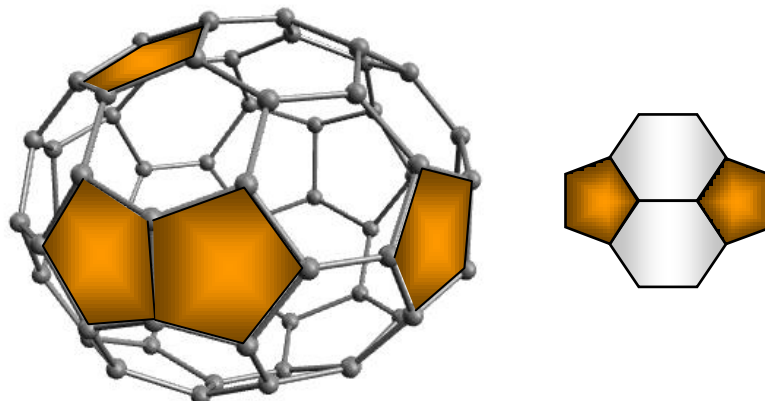


Fig. 8. Four pairs of adjacent pentagons on an equator (C_{60m1}). A pyracylene unit is shown on the right, each of two units being located around its pole.

The bond lengths range from 1.345 Å to 1.502 Å, the largest bond value being between adjacent pentagons (Fig. 9).

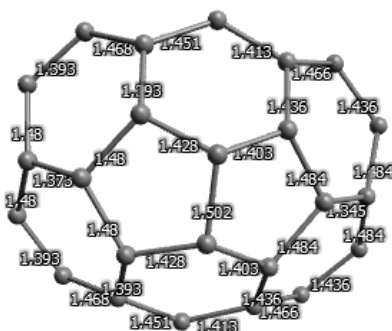


Fig. 9. Part of the structure with the largest value of a bond length.

c) Two pairs of adjacent pentagons on a meridian and two pairs on an equator. The structure is shown in Fig. 10.

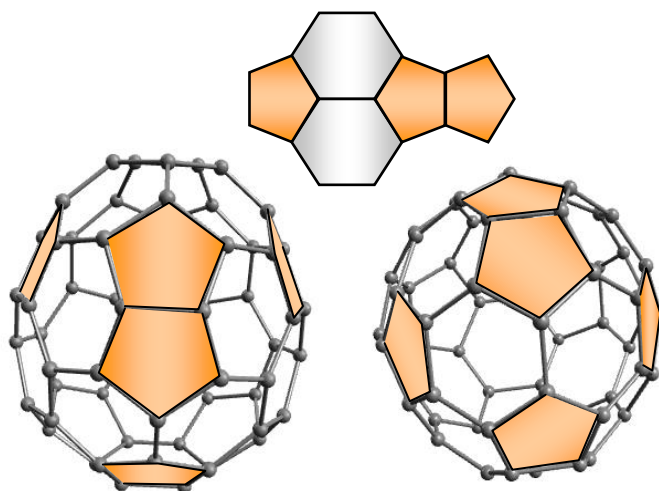


Fig. 10. Two pairs of pentagons on an equator and two pairs on a meridian (C_{60m2}). A pyracylene unit is shown on the top, each of two units being located around its pole.

Here the axis z passes through the central bond of each of two pyracylene units. Contrary to the previous case, one of the unit pentagons has an adjacent pentagon which is shown on the right side of the unit (Fig. 10, on the top).

The bond lengths range from 1.33 Å to 1.481 Å (Fig. 11).

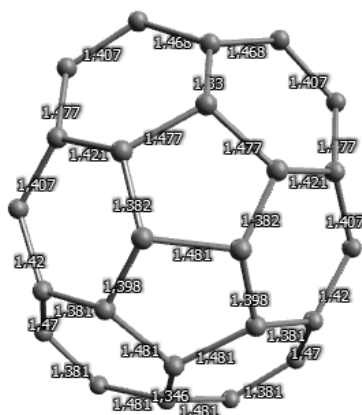


Fig. 11. Part of the structure with the largest value of a bond length.

d) Two chains of four adjacent pentagons normal to each other (Fig. 12). Here the bond lengths range from 1.331 Å to 1.511 Å (Fig. 13).

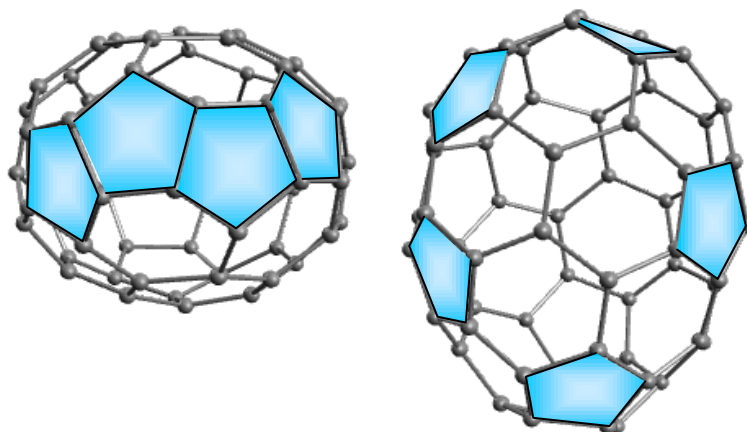


Fig. 12. Two chains of four adjacent pentagons (C_{60m6}).

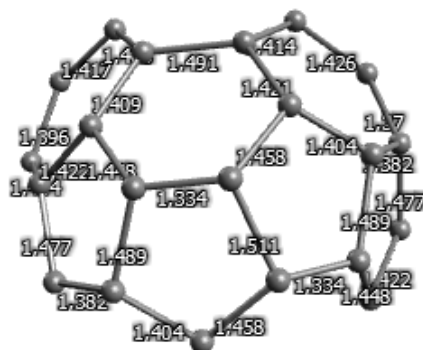


Fig. 13. Part of the structure with the largest value of a bond length.

e) Four triple adjacent pentagons (Fig. 14). Here the bond lengths range from 1.359 Å to 1.502 Å (Fig. 15).

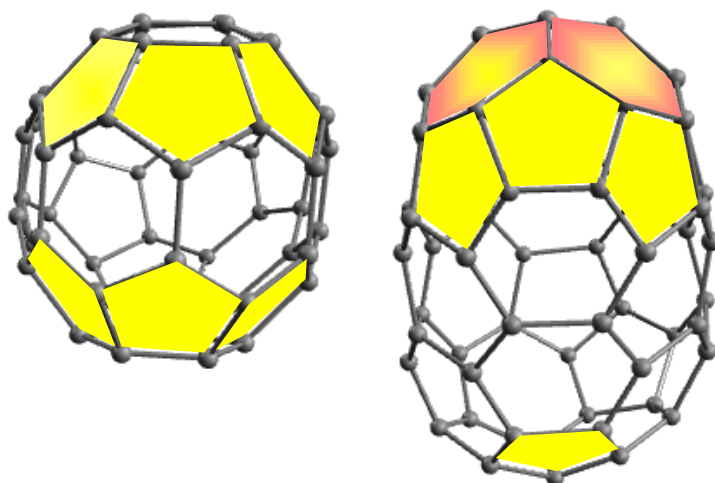


Fig. 14. Four triple adjacent pentagons (C_{60m5}).



Fig. 15. Part of the structure with the largest value of a bond length.

f) Two pairs of three adjacent pentagons of two types (Fig. 16). One type is a chain of pentagons, another is a compact cluster. Here the bond lengths range from 1.353 to 1.511 Å for the first type and from 1.321 to 1.511 Å for the second type (Fig. 17).

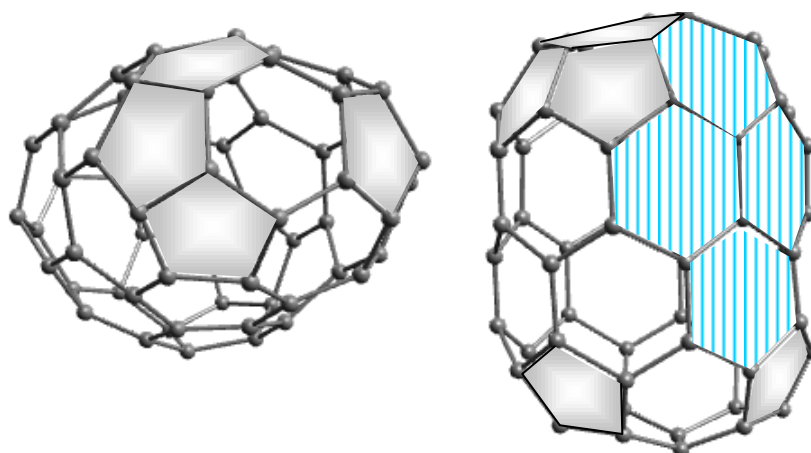


Fig. 16. Two pairs of three adjacent pentagons of two types (C_{60m4}).

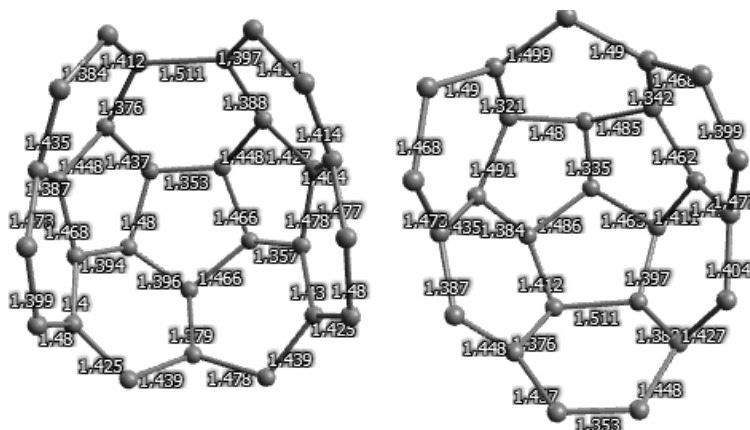


Fig. 17. Bond lengths related to two types of location pentagons.

3. Energies of formation and bond lengths

We have calculated formation energies of isomers. They are given below.

Table 1. Number of adjacent pentagons and formation energies.

Name	2 adjacent pentagons	3 adjacent pentagons	4 adjacent pentagons	Gibbs free energy, kJ/mol
Buckminster fullerene C ₆₀	0	0	0	2573
C ₇₀	0	0	0	2975
C _{60m3}	3	0	0	3039
C _{60m1}	4	0	0	3129
C _{60m2}	4	0	0	3134
C _{60m6}	0	0	2	3436
C _{60m5}	0	4	0	3636
C _{60m4}	0	4	0	3975

A comparison between the energies of isomers and their structures shows that the less is a surface the less is energy. The least surface has a sphere and so the least energy has a buckminsterfullerene. The adjacent pentagons induce declination from a sphere what leads to an energy increase.

We have also compared formation energies of isomers with their bond length (see below).

Table 2. Bond lengths and formation energies.

Name	Bond lengths, Å	Difference, Å	Gibbs free energy, kJ/mol
Buckminster fullerene C ₆₀	1.373 (5-6) ÷ 1.449 (6-6)	0.076	2573
C _{60m3}	1.342 (6-6) ÷ 1.482 (6-6)	0.140	3039
C _{60m1}	1.345 (6-6) ÷ 1.502 (5-5)	0.157	3129
C _{60m2}	1.330 (6-6) ÷ 1.481 (5-6)	0.151	3134
C _{60m6}	1.331 (5-6) ÷ 1.512 (5-5)	0.181	3436
C _{60m5}	1.359 (6-6) ÷ 1.502 (5-6)	0.143	3636
C _{60m4}	1.331 (5-6) ÷ 1.512 (5-5)	0.181	3975

For the first three isomers, which shape is close to a sphere (C_{60m3}) and to an ellipsoid (C_{60m1} and C_{60m2}), it seems that there is a correlation, but for the isomers with a large declination from these shapes a correlation is absent.

Now discuss a possible form of the stable isomer synthesised in 2008. It has the retention time equal to 11.833 min which is close to that of C_{70} , 11.957 min respectively, so we suppose that their formation energies are also close. On the basis of the calculations done, one can concede that the form of this isomer is (C_{60m3}). The energy difference is only 64 kJ/mol.

4. Conclusion

In this paper we analyzed chromatograms and mass spectra of buckminsterfullerene and its isomers. We have calculated possible structures and formation energies of those isomers. A comparison between the energies of isomers and their structures shows that the less is a surface the less is energy. The least surface has a sphere and so the least energy has a buckminsterfullerene. The adjacent pentagons induce declination from a sphere what leads to an energy increase.

We have also compared formation energies of isomers with their bond length. For the isomers, which shape is close either to a sphere or to an ellipsoid, it seems that there is a correlation, but for the isomers with a large declination from these shapes a correlation is absent. We suppose that the most stable isomer which stability is comparable with that of C_{70} has the form close to a sphere. It has the symmetry axis of third order that passes through the centers of two hexagons, each of which being surrounded with three pentagons and three hexagons.

References

- [1] V.I. Gerasimov, M.Y. Matuzenko, O.V. Proskurina // *Materials Physics and Mechanics* **13** (2012) 181.
- [2] S.Y. Xie, S.L. Deng, R.B. Huang, L.J. Yu, L.S. Zheng // *Chemical Physics Letters* **343** (2001) 458.