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Regularities in the molecular structures of stable fullerenes

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Abstract. The literature data on the stability of fullerenes from C_{60} to C_{84} are generalised. The distribution of the π bonds in the isolated and characterised fullerenes is analysed. General regularities in the molecular structures of fullerenes are considered. It is concluded that closed electronic shells and a uniform distribution of pentagons over the molecule are characteristic of stable fullerenes. The bibliography includes 96 references.

I. Introduction

The first suggestion on the probable existence and relative stability of fullerenes was made in 1970 by Osawa,[1] who described the C_{60} molecule and substantiated its stability. This problem was also addressed in a classical study by Bochvar and Gal'pern[2] and, more recently, by many other authors, both experimentalists and theoreticians within various approximations.[3–18] Fullerenes with the number of atoms in a molecule $\geqslant 60$ can have thousands of isomers, but only those isomers that comply with the isolated pentagon rule (IPR), which is the most important condition for the stability of fullerenes, have actually been isolated and characterised. According to this rule, each of twelve pentagons of a fullerene molecule have to be surrounded by five hexagons. Nevertheless, several fullerenes with the structures violating the IPR are known, *i.e.*, obtained, isolated and characterised. These include, for instance, endohedral metallofullerenes based on C_{66} and C_{68}, which are unusual complexes containing a metal atom inside the fullerene cage.[19–23] These complexes are rather scarce but they are a subject of intense investigations.

The meanings of the terms 'obtained', 'extracted', 'isolated' and 'characterised' (identified) have to be explained in more detail. A fullerene is considered as obtained if a signal (peak) of a certain fullerene molecule was detected in a mass spectrum of a carbon soot sample. A fullerene is called extracted if it was successfully transferred to a solution with some solvents. A fullerene is considered as isolated when a specific isomer was separated from a mixture of isomers and obtained in the individual from. Then this fullerene isomer can be characterised or identified by some experimental techniques (*e.g.*, ^{13}C NMR, X-ray crystallography, *etc.*). Sometimes, only a minute quantity of a compound sufficient exclusively for its identification is available. In other cases, a larger amount of a fullerene isomer can be isolated for a further use.

The total number of fullerenes with the IPR structures is 51 for fullerenes from C_{60} and C_{70} to C_{84} and increases to 300 if the series is extended to C_{94} (Ref. 9). Meanwhile, the number of the obtained fullerenes does not exceed thirty. The extension of the range of the obtained fullerenes is a result of extremely laborious and resource-consuming studies conducted during the last two decades (starting from the discovery of fullerenes in 1985). Nevertheless, according to our estimates, the number of the obtaind isomers of fullerenes from C_{60} to C_{94} is less than 10% of the total number of possible IPR isomers (for a series of fullerenes from C_{60} to C_{84}, this fraction is slightly smaller than 30%).

Presently, only C_{60} and C_{70} are produced on a large scale (hundreds kilograms), whereas the vast majority of higher fullerenes (with more than 70 carbon atoms) complying with the IPR are available only in milligram quantities.

The possibility of the isolation of a fullerene in the individual form is governed by its stability (both thermodynamic and kinetic). Taking into account that the term 'fullerene stability' is not obvious, its definition has to be given. For the further discussion, we shall refer those fullerenes that can be synthesised (the thermodynamic stability) and that possess reactivities allowing them remain unchanged for a long time under normal conditions, *i.e.*, in air at room temperature, (the kinetic stability) to as stable fullerenes. The fullerenes that are detected by mass spectra, but cannot be isolated will be considered unstable.

The fullerenes C_{60} and C_{70} meet the stability conditions most comprehensively. Their properties and reactivities have been thoroughly studied, since they are the most accessible compounds among all fullerenes. In particular, C_{60} remains unchanged under normal conditions for years, whereas some of higher fullerenes undergo decomposition within hours, minutes or even seconds. Still, we shall refer all fullerenes that have successfully been isolated and characterised to as stable ones leaving their finer classification for the future. Other IPR fullerenes can be subdivided into two groups. The first group includes those fullerenes that can be obtained in principle, but have not been isolated so far. The second group includes the fullerenes that cannot be obtained due to their intrinsic instability related to the specific molecular structures.[24] It is apparent that the first group will extend as a result of the research efforts. However, it is important to know, which fullerenes belong to these two groups and why.

A fullerene can be unstable due to an unfavourable electronic structure (an open electronic shell or the presence of one or several unpaired electrons in the molecule) or topology-related strained geometry for the closed electronic shell. In the former case, the

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radical species can be stabilised by converting them into endohedral metallofullerenes.[10, 12, 24] The discussion below is devoted to structural features of stability of proper (or 'empty') fullerenes containing no guest atoms inside the fullerene cage.

To date, a number of reviews[3–9, 14, 15, 18, 25, 26] summarising the literature data on structural studues, functionalisation, prospective applications, *etc*. have been published. The structures and properties of most stable endohedral metallofullerenes have been analysed and surveyed by several authors.[10–13, 16, 17, 24] Nevertheless, no general analysis of the structures of the obtained (isolated and characterised) fullerenes within the context of the search for regularities in their molecular structures has been performed so far. This review represents an attempt to accomplish such an analysis.

II. Stable higher fullerenes: the analysis of their structures according to the experimental and theoretical quantum-chemical data

1. Isolated and characterised isomers of higher fullerenes $C_{72}-C_{84}$

As has been mentioned above, only some of possible isomers of higher fullerenes have been detected and isolated so far. For instance, the first representatives of higher fullerenes, which are also named lost, C_{72} and C_{74}, are still missing[27–32] (their signals were revealed only in mass spectra of soot extracts[27–29]). Meanwhile, their different endohedral derivatives have been characterised, such as $Ca@C_{72}$, $La@C_{72}$, $La_2@C_{72}$, $Ca@C_{74}$, $Sc@C_{74}$, $Sc_2@C_{74}$, *etc*.[10, 19, 28, 33–38] Furthermore, the existence of fullerenes C_{72} and C_{74} in reduced forms was suggested, which can be explained by the fact that both the C_{72}^{2-} and C_{74}^{2-} dianions are characterised by significant energy gaps between their frontier orbitals.[30, 31, 33]

Only one of two isomers of the fullerene C_{76} has been isolated.[40–42] This is characterised by a chiral structure belonging to the point symmetry group D_2.[43] Meanwhile, both isomers have been isolated as endohedral metallofullerenes.[35, 37, 38, 42, 44]

Three of five isomers † of the fullerene C_{78} (Ref. 39) have been isolated, *viz*., 1 (D_3), 2 (C_{2v}) and 3 (C_{2v}).[40, 45] According to the first report,[46] a mixture of two isomers with symmetries C_{2v} and D_3 in a 5 : 1 ratio was detected experimentally. However, the presence of three isomers, C_{2v}, C_{2v} and D_3, in a 5 : 2 : 2 ratio was proven later.[47] Taylor *et al*.[48] also observed the C_{2v}, D_3 and C_{2v} isomers in a ratio 5.2 : 3 : 1.8. The earlier results were qualitatively supported[49] by an analysis of the ^{3}He NMR spectra of the endohedral fullerene $He@C_{78}$. Only one isomer, *viz*., 5 (D_{3h}), has been isolated as the endohedral metallofullerene $Sc_3N@C_{78}$.[50]

The fullerene C_{80} attracts special attention, since this is the first higher fullerene after C_{60} that has an isomer with the highest symmetry of a truncated icosahedron (I_h) as that of C_{60}. In contrast to the best studied buckminsterfullerene C_{60}, this isomer of C_{80} has not been isolated as the 'empty' molecule so far. In total, the fullerene C_{80} has seven IPR isomers:[39] 1 (D_{5d}), 2 (D_2), 3 (C_{2v}), 4 (D_3), 5 (C_{2v}), 6 (D_{5h}) and 7 (I_h). Up to date, two isomers have been obtained.[50, 51] First, the isomer 2 (D_2)[52] and then the isomer 1 (D_{5d})[53] have been isolated and characterised. The isomers 6 (D_{5h}) and 7 (I_h) could be isolated as endohedral metallofullerenes.[50, 54–60]

Dozens of fullerene C_{82} derivatives with different numbers of metal atoms inside the cage are known (*i.e*., have been isolated and studied). Among them, four isomers were identified, *viz*., 5 (C_2),[61, 62] 6 (C_s),[63] 8 (C_{3v})[64] and 9 (C_{2v}).[10, 65, 66] Meanwhile, only one out of nine possible isomers, *viz*., 3 (C_2), has been isolated as the empty molecule.[15, 67–69]

† Hereinafter, the enumeration of fullerene isomers, which uniquely define their molecular symmetry and bonding topology, is given according to Ref. 39.

The fullerene C_{84} takes the third place after C_{60} and C_{70} as regards its occurrence and abundance in fullerene-containing soots. Two of its major isomers, 23 (D_{2d}) and 22 (D_2), out of twenty-four possible isomers complying with the IPR[39] were identified as a 2 : 1 mixture by ^{13}C NMR spectroscopy.[47, 70] An analysis of the ^{3}He NMR spectra of $He@C_{84}$ revealed the presence of eight isomers.[71] The first attempt at their identification was performed by Taylor and co-workers.[72] Following the separation of the isomer mixture, two less accessible high-symmetry isomers, 24 (D_{6h}) and 19 (D_{3d}), were identified.[73] Five isomers were then separated by multistage HPLC:[74] two isomers with the C_s symmetry and isomers with the C_2, D_{2d} and D_2 symmetries, which were ascribed to the isomers 4 (D_{2d}), 5 (D_2), 11 (C_2) and 16 (C_s), respectively. One of isomers with the C_s symmetry was not unequivocally identified (there are five possible isomers with this symmetry). Thus, only ten out of twenty-four isomers of C_{84} have been isolated so far,[15, 47, 70–78] including two unidentified isomers with the C_2 and C_s symmetries. Additionally, isomers 7 (C_{2v}), 10 (C_s) and 23 (D_{2d}) have been isolated as endohedral metallofullerenes.[19, 36, 56, 79, 80]

Table 1. Experimental studies on the IPR isomers of higher fullerenes.

TP	Ref. (EM)	Ref. (EMF)	TP	Ref. (EM)	Ref. (EMF)
Fullerene C_{72} (1)			Fullerene C_{82} (9)		
1(D_{6d})	–	19, 28, 34, 44	8 (C_{3v})	–	64
			9 (C_{2v})	–	10, 65, 66
Fullerene C_{74} (1)			Fullerene C_{84} (24)		
1(D_{3h})	–	10, 28, 33–38	1 (D_2)	–	–
			2 (C_2)	–	–
Fullerene C_{76} (2)			3 (C_s)	–	–
1 (D_2)	40–42	35, 37, 42, 44	4 (D_{2d})	15, 74–76	–
			5 (D_2)	15, 74–76	–
2 (T_d)	–	38	6 (C_{2v})	–	–
Fullerene C_{78} (5)			7 (C_{2v})	–	36, 79
1 (D_3)	40, 45	–	8 (C_2)	–	–
2 (C_{2v})	40, 45	–	9 (C_2)	–	–
3 (C_{2v})	40, 45	–	10 (C_s)	–	36, 79, 80
4 (D_{3h})	–	–	11 (C_2)	75–78	–
5 (D_{3h})	–	50	12 (C_1)	–	–
Fullerene C_{80} (7)			13 (C_2)	75 (?), 78	–
1 (D_{5d})	50, 51	–	14 (C_s)	–	–
2 (D_2)	50, 51	–	15 (C_s)	75 (?), 78	–
3 (C_{2v})	–	–	16 (C_s)	75–78	–
4 (D_3)	–	–	17 (C_{2v})	–	–
5 (C_{2v})	–	–	18 (C_{2v})	–	–
6 (D_{5h})	–	50, 54–60	19 (D_{3d})	15, 73, 75, 76	–
7 (I_h)	–	50, 54–60			
Fullerene C_{82} (9)			20 (T_d)	–	–
1 (C_2)	–	–	21 (D_2)	–	–
2 (C_s)	–	–	22 (D_2)	15, 47, 70, 75, 76	19, 36, 56, 79–80
3 (C_2)	15, 67–69	–	23 (D_{2d})	15, 47, 70, 75, 76	–
4 (C_s)	–	–			
5 (C_2)	–	61, 62	24 (D_{6h})	15, 73, 75, 76	–
6 (C_s)	–	63			
7 (C_{3v})	–	–			

Notes. (1) The following notations for fullerenes are adopted: TP is theoretically possible, EM is isolated experimentally as 'empty' molecules, EMF is isolated experimentally as endohedral metallofullerenes. (2) The numbers in parentheses are the numbers of theoretically possible IPR isomers of the fullerene. (3) The numbering and symmetries of fullerene isomers are given according to Ref. 39. (4) The symbol '?' marks those isomers of the fullerene C_{84} that have presumable been isolated (taking into account their symmetries, structural and energy parameters) but not unequivocally identified.[75, 78]

The literature data on fullerene isomers isolated to date as 'empty' molecules and endohedral metallofullerenes are summarised in Table. 1. As can be seen, the isomers that preferably occur as endohedral metallofullerenes differ, as a rule, from those that occur as 'empty' molecules.[24]

2. The results of quantum-chemical calculations of stable fullerenes

Quantum-chemical calculations is the primary tool used to establish the stability of a specific fullerene. An analysis of the literature and our own results [24, 30, 31] demonstrates that the order of the relative stabilities of isomers is reproduced in the majority of cases, irrespective of differences in the accuracy and predictive power of semiempirical and *ab initio* methods (performed either in minimum or extended basis sets, with account for the electron correlation or neglecting it). A comparative analysis of the relative total energies of m isomers of a fullerene C_n complying with the IPR makes it possible only to estimate probability of the isolation of a particular isomer. The total energy of the fullerene molecule and, respectively, its stability or instability depend on the mutual arrangement of pentagons, which defines the surface curvature of the molecule, the presence of fused hexagons and electronic effects. According to correlation of the calculated total energies for fullerene isomers the isolated fullerenes possess the minimum total energies among the IPR isomers of the fullerene in question. This is a reliable test for stability. Meanwhile, for fullerenes with only one IPR isomer, nothing but total energy value can be stated.

However, the total energies alone are insufficient for the prediction of probability of the synthesis of IPR isomers. In particular, 8 isomers of the fullerene C_{84} have been isolated and characterised. On the scale of relative energies, they all are located from 0 to 18 kcal mol^{-1} with respect to the energetically most favourable isomer, 23 (D_{2d}).[75] The number of stable fullerenes from C_{70} to C_{84} estimated by taking this energy range as the stability criterion and extending it to other higher fullerenes should be significantly larger. And it remains unclear whether the missing isomers can be synthesised at all.

Unfortunately, there are currently no satisfactory criteria for the evaluation of the stability and possibility of the synthesis of fullerenes. Diener and Alford suggested [33] to subdivide all fullerenes into two groups: fullerenes with a large energy gap between the highest occupied and the lowest unoccupied molecular orbitals (HOMO – LUMO) (these include fullerenes C_{60} and C_{70}) and fullerenes with either a small HOMO – LUMO energy gap or even a radical structure (*i.e.*, with one or more unpaired electrons). A similar classification was proposed by Stevenson and co-workers [81] based on electrochemical studies of fullerenes. In other words, the HOMO – LUMO energy gap was suggested as a simple criterion for the stability of fullerenes. Indeed, a large gap between the frontier orbitals implies a high stability and low reactivity of the molecule. However it was found that this criterion, the HOMO – LUMO energy gap, alone is not always sufficient for the prediction of the stability of fullerenes. To provide a more unambiguous estimate for the kinetic stability of fullerenes, the HOMO – LUMO energy gap should be correlated to the number n of conjugated carbon atoms in the fullerene molecule C_n and supplemented with other parameters,[82] such as the bond resonance energy (which represents the contribution of a given π bond of the molecule to the total topological resonance energy [83]) or the localisation energy (which characterises the heat of protonation of the respective fullerene [76]). Using such a scheme, Aihara [83] concluded that fullerenes with the bond resonance energies smaller than $-0.100\,|\beta|$ and with small or zero HOMO – LUMO energy gap multiplied by the number of carbon atoms in the fullerene molecule are unstable. Nevertheless, the values of these parameter for some higher fullerenes that have not been isolated so far are nearly the same as those for C_{60}. In particular, this scheme fails to explain the impossibility of isolation of fullerenes C_{72} and C_{74} or isomers 1 (D_2) and 20 (T_d) of the fullerene C_{84}, despite these molecules meet the above criteria.

Thus, the conventional quantum-chemical calculations and the stability criteria considered above fail to fully explain the instability of some fullerenes. This may be due to the lack of analysis of the local stability, *i.e.*, the stability of substructures that constitute the fullerene molecule. Such substructures were ignored in the earlier theoretical calculations predominantly focused on the molecules as a whole.[84] It might be hoped that the analysis of the electronic structures of stable (*i.e.*, isolated) fullerenes from this viewpoint will help revealing common regularities in their molecular structures.

3. Analysis of molecular structures of stable fullerenes

According to an approach developed by Kovalenko and Semyashova,[85, 86] the distribution of π bonds over the fullerene molecules in the series from C_{60} to C_{84} can be represented as the Schlegel diagrams. These diagrams show the positions of localised double and delocalised π bonds. A number of characteristic substructures with distinct electronic structures (as in their aromatic analogues: naphthalene, indacene, pyrene, perylene, corannulene, coronene, *etc*.) can be identified by analysing the local symmetry in the distribution of single, double and π bonds delocalised over the hexagons of the fullerene molecules. These substructures retain their electronic properties irrespective of the fullerene molecule they belong to.

Two types of bonds occur in the C_{60} molecule (Fig. 1 *a*): the five-membered rings are composed of single bonds, whereas single and double bonds alternate in the six-membered rings.[87] The C_{60} molecule (I_h) comprises exclusively corannulene substructures (Fig. 2 *a*) and is characterised by a uniform distribution of the pentagons over the molecule. The C_{70} molecule (Fig. 1 *b*) can be regarded as two poles with the same pattern of the bond distribution as in C_{60} and an equatorial belt composed of five hexagons with the delocalised π bonds [10, 88] forming five indacene substructures (Fig. 2 *b*). Thus, only two substructures, *viz*., corannulene and indacene, occur in these two fullerenes. It would be reasonable to suggest that these substructures constituting the stable fullerenes C_{60} and C_{70} are characterised by the highest stability.[88]

As has been mentioned above (see Table 1), two next fullerenes, C_{72} (D_{6d}) and C_{74} (D_{3h}), have not been isolated so far as 'empty' molecules.[27–32] In the case of C_{72}, this can be explained by the presence of two coronene substructures in the molecule (Fig. 2 *c*), which induce large sterical strains: these substructures are planar, whereas the fullerene cage tends to be spherical.[24, 31] The instability of C_{74} can be explained by its biradical structure due to the presence of two phenalenyl radical substructures (Fig. 3).[24, 30, 32]

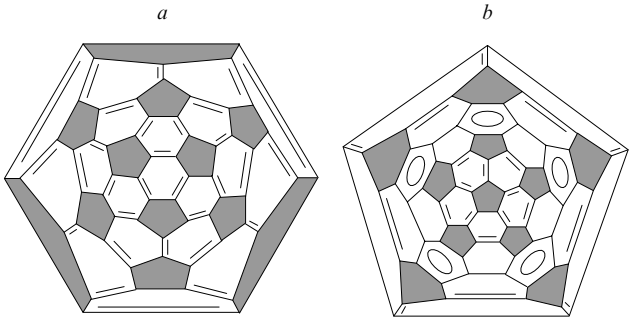


Figure 1. The Schlegel diagrams of the fullerenes C_{60} (*a*) and C_{70} (*b*). Hereinafter, all pentagons are marked grey; single and double bonds are marked with single and double lines, respectively. The hexagons with the delocalised π bonds are marked with circles.

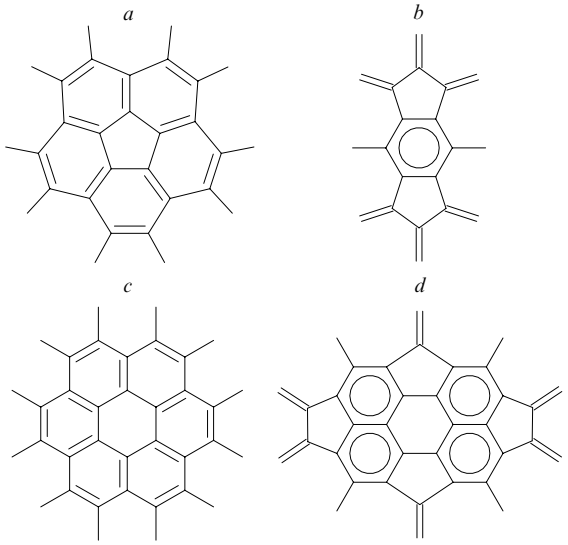


Figure 2. Characteristic substructures of stable fullerenes: corannulene (*a*), indacene (*b*), coronene (*c*) and perylene (*d*).

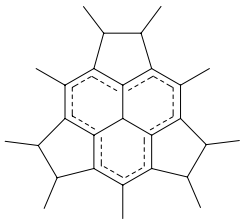


Figure 3. The phenalenyl radical substructure.

According to quantum-chemical calculations,[89] the difference in the total energies of two possible isomers of fullerene C_{76} (see Table 1) exceeds 12 kcal mol^{-1}. An analysis of the molecular structure of the energetically most favourable isomer 1 (D_2) (Fig. 4), which has been obtained experimentally, demonstrates that the distribution of the π bonds therein is similar to that in the C_{70} molecule: it includes four corannulene (see Fig. 2 *a*) and four indacene (see Fig. 2 *b*) substructures. The presence of four phenalenyl radical substructures (see Fig. 3) is a possible reason for the instability of the second isomer, 2 (T_d), which has not been obtained.

According to theoretical calculations reported in the literature [9, 18, 40, 45, 90, 91] and our own data [24, 30, 31] (Fig. 5),‡ five possible isomers [39] of fullerene C_{78} can be arranged in the following series of decreasing stability: 3 (C_{2v}), 2 (C_{2v}), 1 (D_3), 5 (D_{3h}) and 4 (D_{3h}). Up to date, three most stable isomers of the above series (see Table 1) have actually been obtained and isolated experimentally.[40, 45–49] The distribution pattern of the π bonds in the isomer 1 (D_3) (Fig. 6 *a*) is similar to that in C_{70}. Meanwhile, one coronene substructure occurs in the isomer 2 (C_{2v}) (Fig. 6 *b*) in addition to four indacene substructures (see Fig. 2 *c*). The isomer 3 (C_{2v}) (Fig. 6 *c*) contains one perylene substructure (see Fig. 2 *d*).

Although two coronene substructures make the fullerene C_{72} unstable,[31, 92] their presence becomes less critical for larger fullerenes, which can remain stable. Nevertheless, the occurrence of three or more coronene substructures in one molecule dramatically destabilise it due to the development of substantial strain. Thus the calculations the isomer 4 (D_{3h}) of the fullerene C_{78}, which includes three coronene substructures, is the least stable. High kinetic instability of the isomer 5 (D_{3h}) of the fullerene C_{78} is probably [90] the rationale for the fact that it cannot be obtained.

In the case of the fullerene C_{80}, the isomers 1 (D_{5d}) and 2 (D_2) (Fig. 7) are characterised by the lowest total energies according to calculations.[9, 18, 51, 93–95] It is these two isomers (out of seven

‡ Hereinafter, all calculations were performed using the DFT/B3LYP method with the full geometry optimisation in the 6-31G basis set; the total energies were recalculated for the optimised geometries in the 6-31G* basis set.

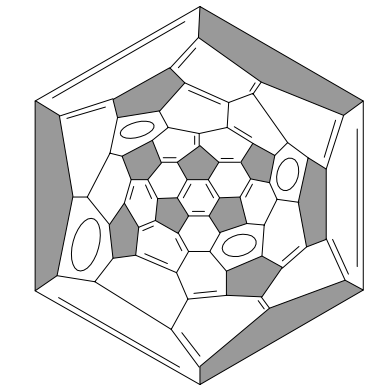


Figure 4. The Schlegel diagram of the fullerene C_{76} [the isomer 1 (D_2)].

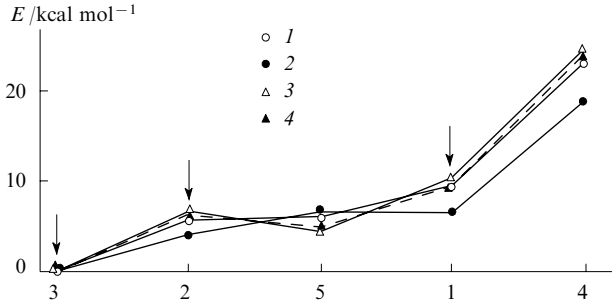


Figure 5. Relative energies of IPR isomers of the fullerene C_{78} calculated at the following theory levels: B3LYP/STO-3G (*1*), B3LYP/3-21G (*2*), B3LYP/6-31G* (*3*), B3LYP/6-31G (*4*);
(*1*–*3*) from Ref. 40, (*4*) the present authors' data. Hereinafter, the arrows point to the obtained isomers.

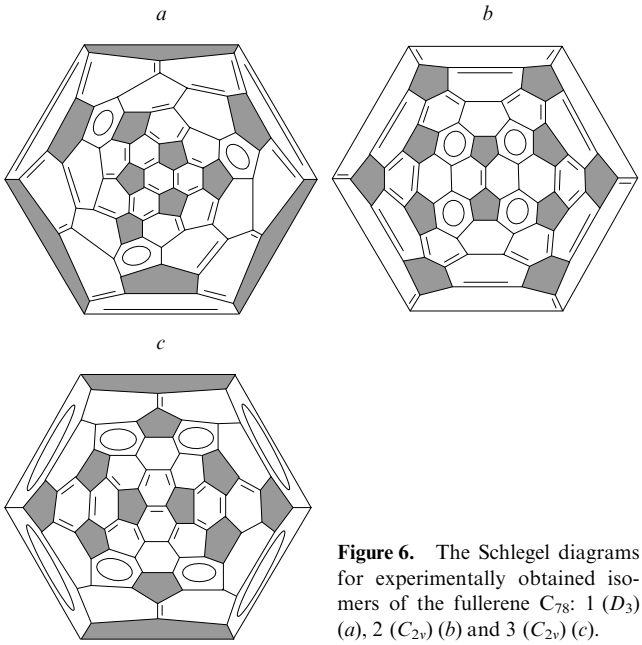


Figure 6. The Schlegel diagrams for experimentally obtained isomers of the fullerene C_{78}: 1 (D_3) (*a*), 2 (C_{2v}) (*b*) and 3 (C_{2v}) (*c*).

In the case of the fullerene C_{80}, the isomers 1 (D_{5d}) and 2 (D_2) (Fig. 7) are characterised by the lowest total energies according to calculations.[9, 18, 51, 93–95] It is these two isomers (out of seven

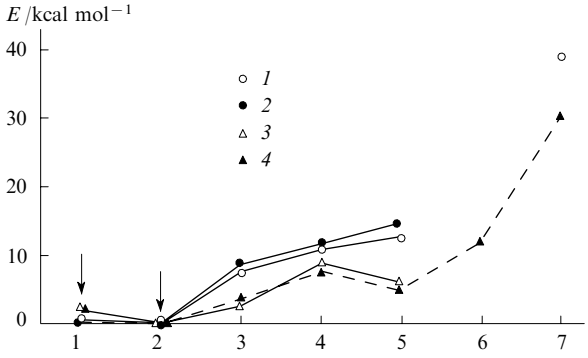


Figure 7. Relative energies of IPR isomers of the fullerene C_{80} calculated at the following theory levels: B3LYP/STO-3G (*1*), B3LYP/3-21G (*2*), B3LYP/6-31G* (*3*), B3LYP/6-31G (*4*);
(*1*–*3*) from Ref. 93, (*4*) the present authors' data.

possible ones[39]) that have actually been isolated and identified[50–53] (see Table 1). The energy of the isomer 3 (C_{2v}), which has not been synthesised so far, is higher by $\sim$5 kcal mol^{-1} than those of the isolated isomers 1 (D_{5d}) and 2 (D_2). This is rather surprising taking into account that the respective energy difference between the most stable isomer and other experimentally obtained isomers for other fullerenes, *e.g.*, for C_{84}, by far exceeds this value.

As for the distribution pattern of the π bonds in the isomers under discussion, the molecular structure of the isomer 1 (D_{5d}) (Fig. 8 *a*) is similar to that of C_{60} since it contains only corannulene substructures (see Fig. 2 *a*). The molecular structure of the isomer 2 (D_2) (Fig. 8 *b*) is analogous to that of C_{70}: it contains two indacene substructures in addition to the corannulene structures (see Fig. 2 *b*). Molecules of all other isomers contain different number of phenalenyl radical substructures[24, 30] (see Fig. 3). The isomer 7 (I_h) probably represents an unusual radical structure with the π bonds delocalised over all fused hexagons; this has no analogues. Undoubtedly, the number of unpaired electrons in a fullerene molecule affects its kinetic stability.

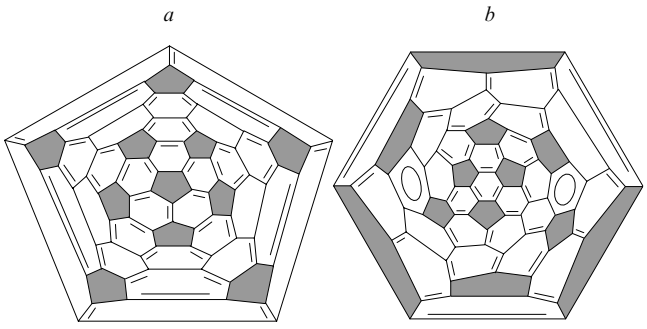


Figure 8. The Schlegel diagrams of the experimentally obtained isomers of the fullerene C_{80}: 1 (D_{5d}) (*a*) and 2 (D_2) (*b*).

According to numerous calculations,[9, 15, 18, 67–69] the isomer 3 (C_2) of the fullerene C_{82} is characterised by the minimum total energy among its nine IPR isomers[39] (Fig. 9 *a*). Accordingly, it is the only isomer that has been obtained to date[15, 67–69] (see Table 1). Its molecular structure (Fig. 9 *b*) features a combination of four corannulene (see Fig. 2 *a*) and four indacene (see Fig. 2 *b*) substructures. Despite the isomers 1 (C_2), 2 (C_s) and 4 (C_s) possess similar structures (in addition to the corannulene substructures, they include two, three and two indacene substructures, respectively[24]), they have not been obtained so far. Other five isomers[24] are described by the molecular structures with

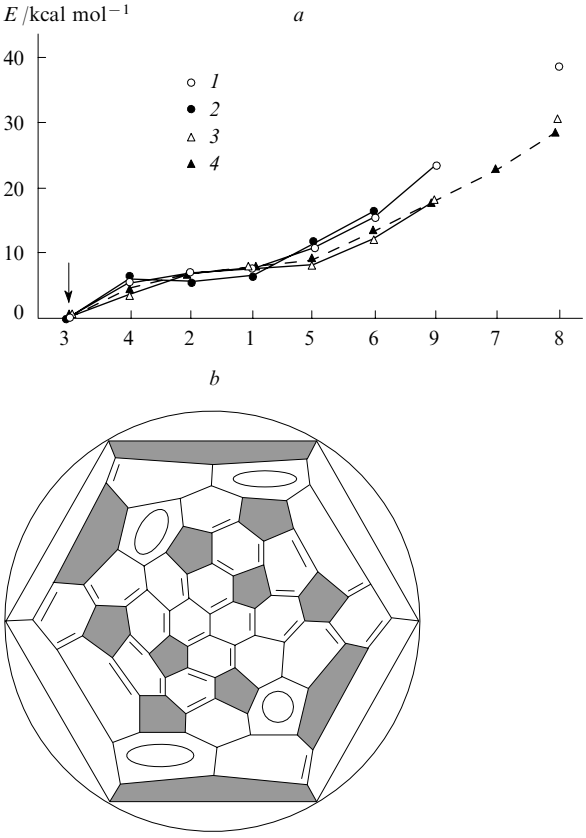


Figure 9. Relative energies of IPR isomers of the fullerene C_{82} (*a*) and the Schlegel diagram of the experimentally obtained isomer 3 (C_2) (*b*).
The calculations at the following theory levels: (*1*) B3LYP/STO-3G, (*2*) B3LYP/3-21G, (*3*) B3LYP/6-31G*, (*4*) B3LYP/6-31G;
(*1*–*3*) from Ref. 67, (*4*) the present authors' data.

phenalenyl radical substructures (see Fig. 3), which are responsible for their instability.

The results of quantum-chemical calculations for 24 isomers of the fullerene C_{84} are depicted in Fig. 10. Only 10 of them have been isolated. The isomers 4 (D_{2d}), 5 (D_2), 11 (C_2), 16 (C_s), 19 (D_{3d}), 22 (D_2), 23 (D_{2d}) and 24 (D_{6h}) have been reliably identified, whereas only point symmetry groups, *viz.*, C_2 and C_s, have been determined for the remaining two isolated isomers[15, 47, 70–78] (see Table 1). Indeed, according to calculations,[9, 15, 18, 75, 76, 89] the

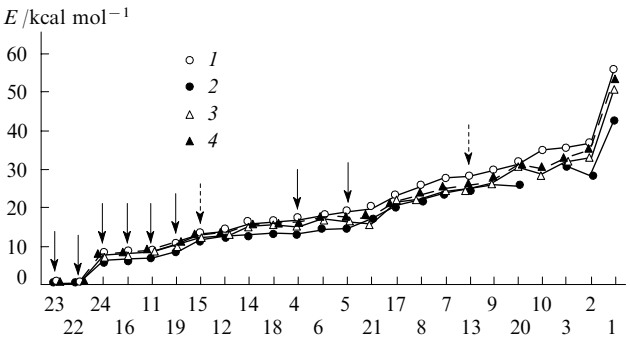


Figure 10. Relative energies of IPR isomers of fullerene C_{84} calculated at the following theory levels: (*1*) B3LYP/STO-3G, (*2*) B3LYP/3-21G, (*3*) B3LYP/6-31G*, (*4*) B3LYP/6-31G;
(*1*–*3*) from Ref. 75, (*4*) the present authors' data. Dashed arrows indicate the most probable candidates for the isolated, but not identified isomers.[75, 78]

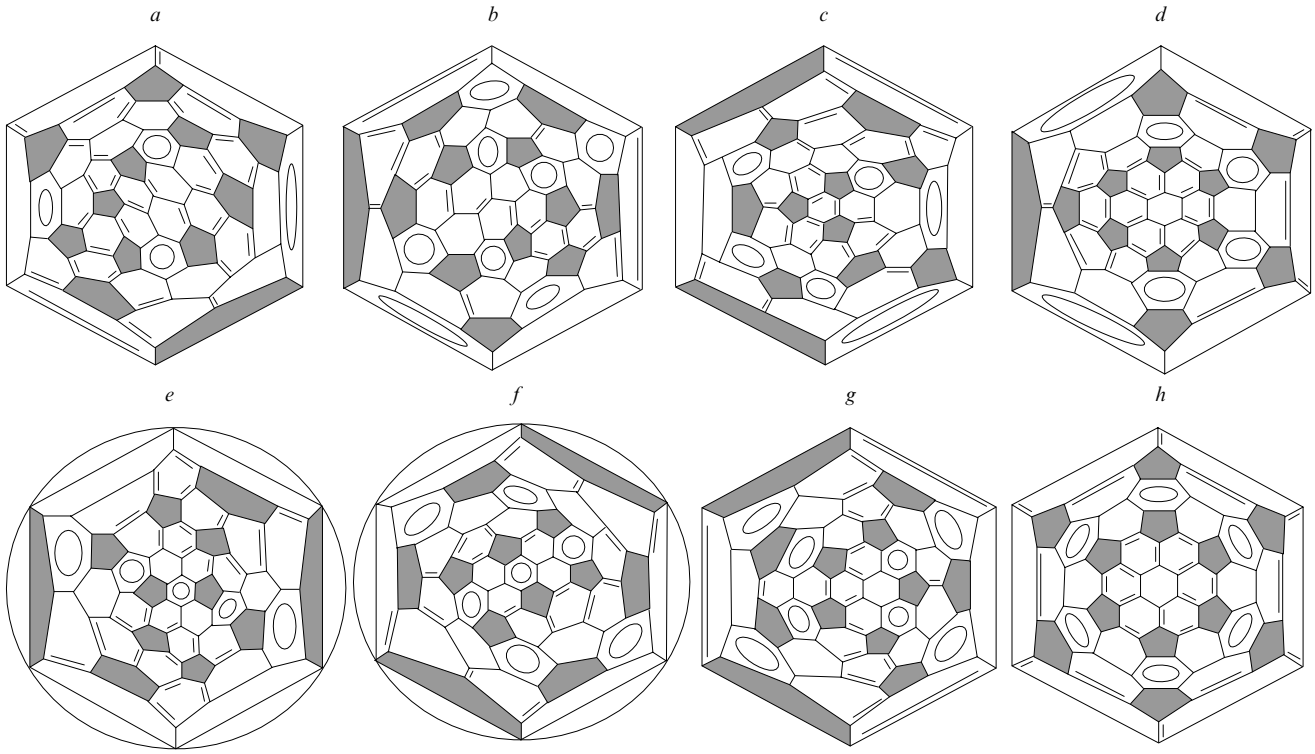


Figure 11. The Schlegel diagrams of the experimentally obtained isomers of the fullerene C_{84}: 4 (D_{2d}) (*a*), 5 (D_2) (*b*), 11 (C_2) (*c*), 16 (C_s) (*d*), 19 (D_{3d}) (*e*), 22 (D_2) (*f*), 23 (D_{2d}) (*g*) and 24 (D_{6h}) (*h*).

isomers 11, 16, 19, 22, 23 and 24 are the most energetically stable. Meanwhile, the total energies of other two isolated isomers, 4 and 5, are comparable to that of the isomer 15 (C_s). Presumably, the latter is the unidentified isolated isomer with the C_s symmetry. The second unidentified C_2 isomer can then by interpreted as the isomer 13, which is the most stable one among molecules with this symmetry containing no radical substructures [in contrast to the isomer 8 (C_2), which is characterised by a somewhat lower total energy]. The energy difference between the most stable isomer and other isomers obtained for this fullerene lies in the range [75] of 10–15 kcal mol^{-1}, which by far exceeds the aforementioned value of $\sim$5 kcal mol^{-1} for C_{80}.[93]

The molecular structures of eight identified isomers are shown in Fig. 11. It is apparent that only corannulene (see Fig. 2 *a*) and indacene (see Fig. 2 *b*) substructures occur in the isomers 4, 5, 11, 19, 22 and 23. In the isomer 16, one coronene substructure (see Fig. 2 *c*) appears, and the isomer 24 contains two such substructures, which supports the suggestion that the destabilising influence of the coronene substructure attenuates with an increase in the fullerene size. Taking into account the results of computation discussed above, a fullerene appears unstable if it includes radical substructures (*i.e.*, it has one or more unpaired electrons) or planar substructures with a large number of fused hexagons (*e.g.*, coronene, ovalene, *etc.*).

The question 'why the number of isolated isomers of certain fullerenes is larger than that for some others, despite a larger scatter in the total energies in the former case?' has no clear answer up to now. Nevertheless, some comparisons can be made based on the available data. Let us consider the general correlation between the stability of a fullerene and its total energy. The total energies and standard enthalpies of formation per carbon atom (*i.e.*, TE/n and $\Delta H_f/n$, respectively) are useful for such a comparative analysis. Trends in TE/n and $\Delta H_f/n$ as a function of n have been analysed by Khamatgalimov and Kovalenko [96] based on the literature data [9, 15, 18] and own computation results (Fig. 12). This graph reveals a specific 'beam' of stability. Its top border is defined by the minimum total energies and enthalpies of formation (TE/n and $\Delta H_f/n$, respectively) typical of the most stable fullerenes, including C_{60}, C_{70}, C_{84} [the isomers 23 (D_{2d}) and 22 (D_2)] and the isomer 133 (C_2) of fullerene C_{94}. The bottom border of the 'beam' is defined by the maximum total energies and enthalpies of formation for all known stable isomers of fullerenes C_n. The instability region lies just below this border.

The prominent trend towards a decrease in the energy with an increase in the number of carbon atoms (*i.e.*, in the fullerene size) is of particular note. Apparently, this trend reflects a progressive relieve of strains in spherical molecules on going from C_{60} to larger

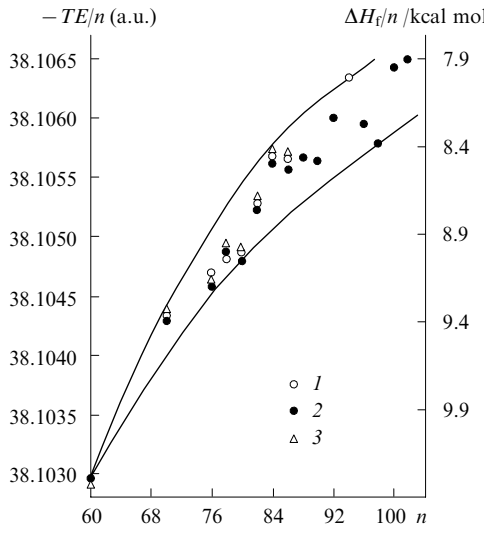


Figure 12. Changes in the total energies (*1*, *3*) and standard enthalpies of formation (*2*) per carbon atom for the synthesised, isolated and characterised stable fullerenes C_n as a function of n;
(*1*) from Ref. 96; (*2*) from Refs 9, 18; (*3*) from Ref. 15.

higher fullerenes. We emphasise that it is the C_{60} and C_{70} molecules that are the most strained and, at the same time, the most stable in the series. Probably, a rather uniform distribution of the local strains over the entire molecule is realised therein due to a respective uniform distribution of the pentagons. For other fullerene molecules, despite their larger sizes, steric strains can be localised in specific regions of the sphere thus destabilising the entire molecule. Yet another important feature of the plot shown in Fig. 12 is that the 'beam' of stability encompasses all known stable fullerenes complying with the isolated pentagon rule.

Based on this 'beam' of stability, a simple scheme for the prediction of the number of stable isomers for any fullerene can be suggested. If the most energetically favourable isomer of a fullerene C_n is located at the upper border of the 'beam', the isolation of other stable isomers of this fullerene might be expected with total energies falling in the interval between the upper and the lower points of the 'beam'. For instance, for C_{84}, this interval amounts to 25 kcal mol^{-1} (and 10 isomers of this fullerene with a total energy gap of 20 kcal mol^{-1} have been obtained and characterised). It might be assumed that within the range of 25 kcal mol^{-1}, several other isomers of this fullerene might be isolated in future, including 6 (C_{2v}), 15 (C_s), 12 (C_1), 14 (C_s), 17 (C_{2v}), 7 (C_{2v}), 13 (C_2) and 21 (D_2) with closed electronic shells. At the same time, only two isomers of the fullerene C_{80} with a total energy difference of only 5 kcal mol^{-1} have been obtained, although their calculated total energies are located near the bottom border of the 'beam' of stability. Under these circumstances, the isolation of any other isomers is hardly possible. And to the contrary, the probability of the isolation of new isomers is high for the fullerenes with the most energetically favourable isomer lying near the upper border of the 'beam' of stability (as in the aforementioned case of C_{84}). Despite the evident predictive power of this scheme, this is based on the use of the integral molecular parameters, *viz*., their total energies, which prevents the analysis of reasons underlying the stability or instability of certain isomers.

The energies, geometric and electronic structures of fullerene molecules can be calculated irrespective of whether they have experimentally been obtained. However, analysis of the total energies (or enthalpies of formation) cannot confidently predict the possibility of the isolation of a specific fullerene isomer. The newly suggested approach summarised in Fig. 12 enables such a prediction. A fullerene may be unstable due to a number of factors related to its geometric and electronic structures. The 'beam' of stability reflects the net result of all these effects, thus making it possible to estimate the possibility of isolation (*i.e*., the stability) of a target isomer based solely on its energy characteristics. In particular, this plot that also includes the data for the most stable fullerene isomers from C_{86} to C_{102} predicts stability of isomers of the fullerenes C_{86}, C_{88}, C_{92}, C_{94} and C_{100} and instability of C_{98}. Supplementation of this plot with new points for the fullerenes discussed already and its extension to larger fullerenes C_n with $n > 84$ will allow prediction of the stability of particular isomers.

III. Conclusion

Owing to the detailed analysis of the electronic structures of stable (isolated) fullerenes, common regularities of their molecular structures have been revealed. In particular, all stable fullerenes

(1) represent molecules with closed electronic shells, which are characterised by a relatively uniform distribution of pentagons over the sphere;

(2) comprise corannulene and indacene substructures typical of the most stable fullerenes C_{60} and C_{70}. The presence of perylene and coronene substructures is also possible. The latter substructures substantially destabilise the molecules of the first members of higher fullerenes, but their destabilising effect attenuates with an increase in the number of carbon atoms in the molecule.

It has been shown that the possibility of the synthesis and isolation of an isomer of a higher fullerene is governed by the location of the energetically most favourable isomer of this fullerene in the suggested 'beam' of stability that has been constructed by correlating the theoretical and experimental data on stable of fullerenes with closed electronic shells.

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