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# Molecular structures of unstable isolated-pentagon-rule fullerenes $C_{72}-C_{86}$

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Published data on fullerenes $C_{72}$ to $C_{86}$ which obey the isolated pentagon rule (IPR) are generalized. Analysis of unstable isolated-pentagon-rule fullerenes is carried out and the instability criteria are formulated. Two main reasons for the instability of IPR fullerene molecules are identified: their radical nature and/or local overstrain. The classification of fullerenes and a revised isolated pentagon rule are presented.
The bibliography includes 119 references.

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## I. Introduction

The stability of higher fullerenes is still a serious problem of modern physical chemistry. The present review deals with prirstine fullerenes $C_n$, *i.e.*, hollow molecules consisting of $n$ atoms assembled into closed carbon polyhedra. They include 12 pentagons and $[(n/2)-10]$ hexagons. The most striking feature of fullerenes $C_n$ ($n = 20, 24, 26, 28$, *etc.*) is that, according to the spiral algorithm,[1] the structural topology of any isomer of any fullerene is *a priori* known, *i.e.*, the relative positions of pentagons and hexagons in the molecule are completely defined. One more important distinctive feature of fullerenes is the total absence of information about the stability of a particular fullerene, *i.e.*, it is unknown whether it would be possible to synthesize and isolate it and to characterize the stability of its molecule. It is evident that the possibility of diverse arrangements of pentagons and hexagons in the fullerene cage implies the probable existence of very large numbers of isomers. Indeed, for fullerene $C_{60}$ consisting of 12 pentagons and 20 hexagons, 1812 topological isomers are known.[1]

In terms of stability, all fullerenes were classified into two types: fullerenes that do and that do not meet the empirical isolated pentagon rule (IPR), which states that fullerenes that have no fused pentagons are most stable, while structures in which pentagons share an edge, like in pentalene, are unstable.[2–4] Indeed, the structures of the pristine fullerenes synthesized and isolated to date meet this rule. However, for most of higher fullerenes starting from $C_{78}$, the number of isolated pentagon rule (IPR) isomers markedly exceeds the number of synthesized molecules. Indeed, of the 24 isomers of fullerene $C_{84}$ that satisfy this rule, only 11 isomers have been obtained, while for fullerene $C_{90}$, only three isomers out of the 46 possible ones have been obtained.

The possibility of synthesizing a fullerene in a pure state is determined by its stability (thermodynamic and kinetic). Since the notion 'stability of a fullerene' is somewhat arbitrary, we will call a fullerene stable if it can be synthesized, isolated and identified in the neutral ground state (thermodynamic stability) and if its reactivity is such that its properties can remain unchanged under normal conditions, at least, to allow full characterization of its molecular structure (kinetic stability). From this, we can derive the meaning of the terms 'instability' and 'unstable fullerene', by which is meant that a fullerene cannot be obtained by existing synthetic methods because of structural features of its molecule. Here, it should be specified that the term 'stability' has two aspects (time and energy), and the temporal factor expressed as stability is more general.[5]

Previously, we analyzed the molecular structures of stable fullerenes, *i.e.*, those that have been synthesized,

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isolated and characterized (identified), and surveyed the structural regularities of their molecules.[6] The results of experimental studies and theoretical calculations published to date clearly indicate the existence of a correlation: the experimentally obtained † fullerenes are energetically most favourable among all possible isomers of this fullerene series. In order to make clear which fullerenes are stable and which are not, quantum chemical calculations are used most often. The stability of fullerene molecules is affected by the arrangement of pentagons, the presence of clusters of fused hexagons (for example, the coronene substructure), the presence of radical moieties and electronic effects. All these factors determine the total energy of a fullerene molecule and either stability or instability.[6]

The criteria for fullerene stability can be conventionally divided into two groups: those related to electronic structure and those related to molecular geometry. The first group includes, for example, the energy-related aromaticity criteria, which estimate the energy advantage and, as a consequence, stabilization upon ring delocalization. This is, for example, resonance stabilization, which has been related to electronic effects;[7] the Hückel theory of molecular orbitals and resonance theory have also been used to identify the stable structures.[8] Diner and Alford[9] proposed that fullerenes should be divided into two classes, one including fullerenes that have a large energy gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO), in particular, fullerenes $C_{60}$ and $C_{70}$, and the other class composed of fullerenes that have either small HOMO–LUMO gap or have a radical structure with unpaired electrons.[9] The radical character of the molecules of fullerenes $C_{60}$ and $C_{70}$ was considered theoretically and found to be associated with 'effectively unpaired' electrons.[10]

The second group of criteria was proposed to be related to the geometric or steric factor, which considers the number of hexagons adjoining any arbitrarily chosen hexagon in a fullerene (neighbour index).[7] The stability of all carbon clusters is affected by the number of closest neighbours, the curvature of the molecular surface and the number of adjacent pentagons.[11] Calculations were carried out for all 1812 isomers possible for fullerene $C_{60}$, including non-IPR ones, and it was found that three adjacent hexagons considerably increase the total energy of the molecule.[12] The authors attributed this fact to the appearance of local planarity, which induces high strain. This obvious point about the effect of local strain on the fullerene stability is consistent with the data of other authors; in particular, Haddon[13] asserted that the local strain is an important factor for the fullerene stability and reactivity. This is in line with the studies evaluating the role of local curvature of fullerene molecules in the radical and 1,3-dipolar addition reactions.[14,15] Note that the fullerene $C_{60}$ molecule is most strained among the IPR fullerenes. As the number of carbon atoms increases, the strain of sphere-like molecules decreases, which contributes also to the thermodynamic stability: indeed, it was shown experimentally that fullerene $C_{70}$, although more difficult to synthesize, is still thermodynamically more stable than $C_{60}$.[16]

† In this review, the expression 'experimentally obtained (synthesized)' means that the substance has been prepared, isolated and identified.

Unfortunately, these criteria do not always adequately explain why some fullerenes cannot be prepared, which markedly complicates their use for discussion and/or prediction of experimental results. For example, for estimating the kinetic stability of fullerenes, Aihara[17] proposed correlating the HOMO–LUMO energy gap with the number of carbon atoms $n$ in fullerene $C_n$ and using a number of other parameters, in particular, the bond resonance energy, which represents the contribution of a given π-bond of the molecule to the resonance energy determined by the molecular topology.[17] Assuming that these parameters measure the stability of a molecule, Aihara showed that some fullerenes are expected to be stable. However, fullerene $C_{72}$ ($D_{6d}$ symmetry) and isomers 1 ($D_2$) and 20 ($T_d$) of fullerene $C_{84}$, which meet the proposed stability criteria, have not yet been obtained experimentally.[17]

The absence of a substantiated theoretical base for the *a priori* estimation of the fullerene stability often leads to faulty results in both theoretical and experimental studies. An example is attempted synthesis of isomer 20 ($T_d$) of fullerene $C_{84}$.[18] It was shown that the synthesis of this isomer cannot be successful because of its instability caused by substantial local strain in the molecule.[19–21] Therefore, general analysis of the structures of unstable fullerenes may presumably help to formulate the instability criteria and to identify general structural features, in particular, substructures, that can be destabilizing.

Quite a few review papers on fullerenes (see, *e.g.*, Refs 3, 22–26), which summarize the key data on fullerene structures, functionalization, application prospects and so on, have been published to date. For example, detailed topological analysis of their molecular structures is documented.[25] An interesting approach to evaluation of the possibility of fullerene synthesis from the informational entropy standpoint has been reported.[27] The most important models of the fullerene formation mechanisms have been considered and their relationship with the fullerene stability has been studied.[28] The results of investigation of the structures of halide and perfluoroalkyl derivatives of higher fullerenes from $C_{76}$ to $C_{96}$ are given; this substantially extends the information about the structure and reactivity of higher fullerene isomers.[29] However, all known studies, including those dealing with thermodynamic stability of fullerenes, consider an averaged molecule without analyzing the stability of substructures, the combination of which forms the fullerene molecule. Apparently, this exactly is the drawback of existing approaches to investigation of the fullerene stability.

An alternative approach gives the complete structural formula of a fullerene with distribution of all types of bonds; a fullerene molecule is considered to contain a number of substructures incorporated in the fullerene shell and resembling aromatic analogues such as *sym*-indacene, pyrene, perylene, corannulene, coronene, phenalenyl radical, *etc.*[6] Distribution of the types of bonds is performed by the following rules: double bonds are present only in hexagons; the double and single bonds alternate; if required by the symmetry of the molecule, hexagons with delocalized π-bonds can exist; the arrangement of bonds should not reduce the molecular symmetry; the corannulene and indacene substructures typical of the most stable fullerenes $C_{60}$ and $C_{70}$ are preferred; and the rule of characteristic nature of substructures holds. The information thus obtained clarifies the reasons for stability (instability) of one or

another fullerene molecule before quantum chemical calculations. The present review surveys the results of investigations of a series of higher IPR fullerenes $C_{72}-C_{86}$, isomers of which have not yet been prepared or characterized, as Schlegel diagrams with distribution of all bond types, together with the results of quantum chemical calculations. Also, along with these data, there are data on their (endohedral and exohedral) derivatives obtained to date, demonstrating the possibility of stabilization of some of them. As shown below, analysis of this information made it possible to classify fullerenes in terms of the type of their instability and to revise the known isolated pentagon rule.[2–4]

## II. Unstable higher isolated pentagon rule fullerenes $C_{72}-C_{86}$: molecular structure analysis according to theoretical quantum chemical data

### II.1. Fullerenes $C_{72}$ and $C_{74}$ as characteristic representatives of two types of fullerene instability

The most vivid examples of unstable fullerenes are $C_{72}$ and $C_{74}$ molecules, which have one IPR isomer, but are unstable and, hence, have not yet been isolated. It should be noted that the mass spectra of reactive fullerene soot exhibit peaks corresponding to fullerenes $C_{72}$ and $C_{74}$.[30,31] These two fullerenes are typical representatives of two types of instability.

Back in 1993, Raghavachari[32] showed that the non-spherical geometry of $C_{72}$ attests to unequal strain distribution in its structure and may be responsible for the instability of this fullerene. However, the use of the π-Orbital Axis Vector (POAV) method did not result in appropriate conclusions: the σ–π interorbital angles for fullerene $C_{72}$ were 96.5–102.4° and barely differed from those for $C_{60}$ (101.6°) and $C_{70}$ (98–102°), which are the most stable fullerene molecules.[32]

According to earlier theoretical investigations, the instability of the fullerene $C_{74}$ molecule is caused by the small energy gap between the HOMO and the LUMO.[24] This was well illustrated by Boltalina *et al.*:[33] the relatively high ionization energy (IE) for fullerene $C_{60}$ (7.57 eV) and low IE for $C_{74}$ (7.13 eV) represent the peak deviations, while generally these values decrease from 7.36 eV for $C_{70}$ to 6.92 eV for $C_{106}$; the observed electron affinity (EA) curve for various fullerenes proved to be the mirror image of the ionization energy curve, which demonstrates a large IE–EA difference (*i.e.*, HOMO–LUMO) and high stability for $C_{60}$ as well as low stability for $C_{74}$ with a rather small gap between the frontier orbitals.[33] Some kinetically unstable higher fullerenes, including $C_{74}$, have been considered as either free radicals or having a small HOMO–LUMO gap.[9] The detection of fullerene $C_{74}$ in the mass spectrum of the reaction mixture[30,31] and the lack of solubility of $C_{74}$ in organic solvents[9,34] are in line with the reported[35] synthesis of fullerene $C_{74}$ and are apparently attributable to its stabilization in the polymer form, which has been already discussed previously.[9,36]

As can be seen from the Schlegel diagram, the structure of fullerene $C_{72}$ (Fig. 1 *a*) contains two coronene substructures (seven symmetrically fused hexagons), which lie on a sixfold axis. The low-molecular-mass analogues of fused hexagons (naphthalene, coronene and so on) have a planar structure. In fullerene molecules with a cage curvature, these substructures bring about local overstrain, and, hence, these compounds cannot be synthesized. Therefore, presumably, the instability of $C_{72}$ is caused by high local overstrain, that is, too many fused hexagons for such a small molecule.[37]

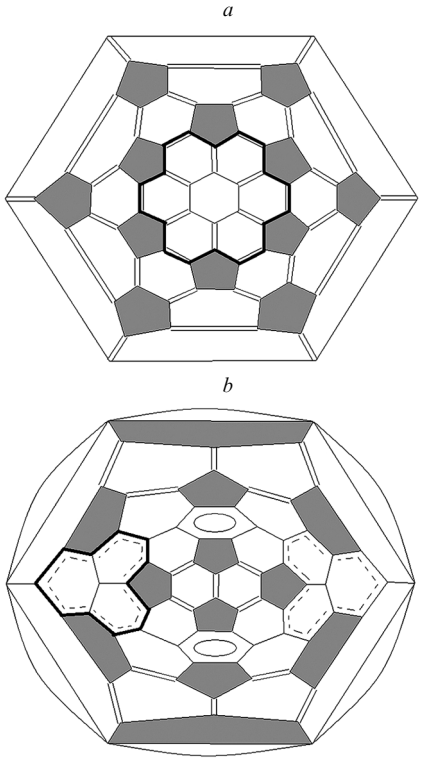



**Figure 1.** Schlegel diagrams of fullerenes $C_{72}$ ($D_{6d}$) (*a*) and $C_{74}$ ($D_{3h}$) (*b*).[37,38]
The coronene and phenalenyl radical substructures are marked.

In the molecule of fullerene $C_{74}$, one can distinguish two phenalenyl radical substructures (see Fig. 1 *b*) on the $C_3$ axis; therefore, the instability of fullerene $C_{74}$ is apparently caused by its biradical structure.[37,38] This moiety has a classical aromatic analogue, which is itself a free radical but can be stabilized as dimers of various derivatives, *e.g.*, 2,5,8-tris(*tert*-butyl)phenalenyl radical dimer,[39] or as the perchlorophenalenyl derivative.[40]

Indeed, according to calculations,[32,37] fullerene $C_{72}$ ($D_{6d}$) has a closed electron shell and, according to energy parameters, in particular, the energy gap, it is expected to be kinetically stable (Table 1). Therefore, the fact that this fullerene has not yet been obtained suggests that the reason is particularly in the molecular geometry.

According to energy parameters,[37,38] in the case of $C_{74}$, the triplet state with two unpaired electrons is lower in energy than the closed-shell singlet state, which implies that the former is energetically more favourable and agrees with the greater HOMO–LUMO energy gap (see Table 1); this confirms the assumed biradical structure of fullerene $C_{74}$.

More evident differences between stable and unstable fullerenes were found upon analysis of the dihedral angles in the rings (hexagons and pentagons) of these fullerenes. This analysis was first systematically performed for fullerene $C_{70}$.[41] It was shown that, unlike $C_{60}$ in which all hexagons and pentagons are planar, in fullerene $C_{70}$ some hexagons and pentagons are non-planar, the most pronounced deviations being observed for five hexagons with delocalized

**Table 1**. Relative total energies ($\Delta E$) and energy differences between the frontier orbitals for fullerenes $C_{72}$ ($D_{6d}$) and $C_{74}$ ($D_{3h}$) determined by DFT B3LYP calculations with different basis sets.[37,38]

| Fullerene | $\Delta E$/kcal mol$^{-1}$ | | HOMO–LUMO/eV | |
|---|---|---|---|---|
| | 6-31G | 6-31G* | 6-31G | 6-31G* |
| $C_{72}$ | – | – | 2.59 | 2.50 |
| $C_{74}$ | | | | |
| singlet | 3.89 | 15.72 | 0.71 | 0.68 |
| triplet | 0.0 | 0.0 | 0.99 | 0.99 |

π-bonds of the equatorial aromatic belt of the molecule (Table 2). It should be emphasized that distortions of these hexagons with delocalized π-bonds lead to fullerene stabilization: non-planar rings are inherent in the spatial reorganization of the molecule which decreases the pyramidality of the equatorial atoms and reduces the strain energy. Conversely, the bond-alternation distortion of hexagons reflects local overstrain in this area of the molecular surface.

**Table 2**. Maximum dihedral angles (deg)[a] in the rings of fullerenes $C_{60}$ ($I_h$), $C_{70}$ ($D_{5h}$), $C_{72}$ ($D_{6d}$) and $C_{74}$ ($D_{3h}$).[37,38]

| Fullerene | In hexagons | | In pentagons |
|---|---|---|---|
| | with alternating bonds | with delocalized π-bonds | |
| $C_{60}$ ($I_h$) | 0.00 (20) | | 0.00 (12) |
| $C_{70}$ ($D_{5h}$) | 4.39 (10) | 12.59 (5) | 1.01 (10) |
| $C_{72}$ ($D_{6d}$) | 9.60 (12) | | 8.45 (12) |
| $C_{74}$ ($D_{3h}$) | 3.85 (12) | 11.82 (3) | 3.31 (6) |

[a] Here and in Tables 4, 6, 8, 10, 12 and 14, the number of equivalent rings according to the symmetry is given in parentheses.

In fullerenes $C_{72}$ and $C_{74}$, ring distortion was also detected. The degree of distortion is measured by the dihedral angles of the appropriate hexagons and pentagons (see Table 2).[37] A comparison of the maximum dihedral angles demonstrated that they are twice as large in hexagons with alternating bonds of fullerene $C_{72}$ as in stable fullerene $C_{70}$; the distortions in pentagons are more than 8 times higher. The most pronounced distortions are observed in hexagons at the periphery of two coronene substructures; this supports the above assumption about high local overstrain in this part of the molecule.

In fullerene $C_{74}$, the most pronounced distortions are observed exactly in hexagons with delocalized π-bonds, which, like in stable fullerene $C_{70}$, do not destabilize the molecule (see Table 2); the distortions of hexagons with alternating bonds in fullerene $C_{74}$ are insignificant. All this indicates that the geometry of fullerene $C_{74}$ does not affect the stability of its molecule.

Thus, it can be stated that instability of fullerene $C_{72}$ is associated with the high local strains caused by the presence of a large number of fused hexagons in two coronene substructures, while the instability of fullerene $C_{74}$ is attributable to its biradical electronic structure. Meanwhile, only one of them, fullerene $C_{74}$ ($D_{3h}$), can be stabilized in the form of derivatives [both endohedral, *e.g.*, Ba@$C_{74}$ and La@$C_{74}$,[42,43] and exohedral ones, *e.g.*, $C_{74}(CF_3)_{12}$],[34,44] whereas the absence of any known derivatives of fullerene $C_{72}$ ($D_{6d}$) indicates apparently that it cannot be stabilized.

### II.2. Fullerene $C_{76}$

In the case of fullerene $C_{76}$, only two isomers, 1 ($D_2$) and 2 ($T_d$), meet the isolated pentagon rule, and only the former one has been prepared and isolated.[45] Earlier theoretical calculations predicted this isomer to be stable, as it is most energetically favourable.[46–53]

The unstable isomer 2 ($T_d$) of $C_{76}$ contains four phenalenyl-radical substructures (Fig. 2); as in the case of $C_{74}$, each of them is supposed to have an unpaired electron; that is, this isomer cannot be synthesized in a pure state because of its radical nature. Note that the isolation of this substance as a polymer is possible, as in the case of radical fullerene $C_{74}$.[35] Indeed, spin unrestricted Kohn–Sham quantum chemical calculations carried out for this isomer in the triplet configuration confirmed the open-shell electronic structure for this species (Table 3).[54]

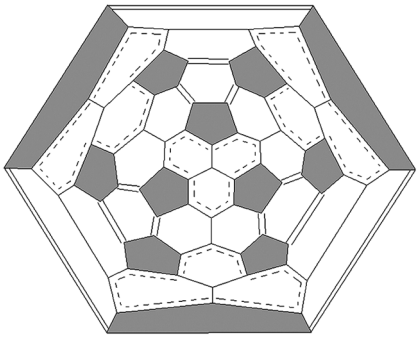


**Figure 2.** Schlegel diagram of isomer 2 ($T_d$) of fullerene $C_{76}$.[54]

Attention is attracted by the reduction of symmetry of isomer 2 ($T_d$) to $D_{2d}$ and $C_{3v}$ for the singlet and triplet configurations, respectively. This is in line with early publications[46–48,51] describing this isomer as an open-shell fullerene with approximately zero HOMO–LUMO energy gap, resulting in the corresponding distortions and reduction of symmetry. It was noted that these distortions can be caused by either general energy-related reasons[55] or by Jahn–Teller effects,[46–48,51] which can, however, be minor and barely determinable for large fullerenes.[25]

As in the case of fullerenes $C_{70}$ and $C_{74}$, the greatest distortions in isomer 2 ($T_d$) occur for exactly the hexagons with delocalized π-bonds, which do not destabilize the molecule (Table 4). Comparison of the dihedral angles in the alternating-bond hexagons shows that they are even smaller in unstable isomer 2 ($T_d$) than in the synthesized stable isomer 1 ($D_2$) (see Table 4).[54] Therefore, presumably, the instability of isomer 2 ($T_d$) is dictated by only its radical nature and is not related to the local strain in the molecule. Meanwhile, there are published data about stabilization of this isomer as an endohedral metallofullerene $Lu_2$@$C_{76}$ (see Ref. 56) and the exohedral derivative $C_{76}(CF_3)_{12}$.[34]

### II.3. Fullerene $C_{78}$

In the case of fullerene $C_{78}$, five isomers meet the IPR; of these, three isomers were synthesized: 1 ($D_3$), 2 ($C_{2v}$) and

**Table 3**. Relative total energies and energy differences between the frontier orbitals for fullerene $C_{76}$.[54]

| $C_{76}$ isomer | $\Delta E$ /kcal mol$^{-1}$ | | | | HOMO–LUMO /eV | | | |
|---|---|---|---|---|---|---|---|---|
| | 6-31G | 6-31G* | 6-31+G* | 6-311+G* | 6-31G | 6-31G* | 6-31+G* | 6-311+G* |
| 1 ($D_2$) singlet | 0.00 | 0.00 | 0.00 | 0.00 | 1.99 | 1.97 | 1.95 | 1.95 |
| 2 ($T_d$) | | | | | | | | |
| singlet ($D_{2d}$) | 16.77 | 18.31 | 16.94 | 16.73 | 0.83 | 0.83 | 0.81 | 0.82 |
| triplet ($C_{3v}$) | 14.48 | 14.48 | 16.24 | 14.64 | 0.94 | 0.96 | 0.96 | 0.94 |

**Table 4**. Maximum dihedral angles (deg) in the rings of two isomers of $C_{76}$.[54]

| $C_{76}$ isomer | In hexagons | | In pentagons |
|---|---|---|---|
| | with alternating bonds | with delocalized π-bonds | |
| 1 ($D_2$) | 12.63 (4) | 17.26 (4) | 6.89 (4) |
| 2 ($T_d$) | 1.59 (12) | 11.43 (12) | 3.36 (12) |

3 ($C_{2v}$).[57–59] Quantum chemical calculations demonstrated that they are energetically most favourable.[7, 22, 24, 50–52, 60–63] Slanina *et al.*[60, 61] calculated the dependence of relative concentrations of these isomers on the temperature of synthesis. At high temperatures, isomer 3 ($C_{2v}$) is formed in the highest concentration. As the temperature decreases ($C_{78}$ leaves the reaction zone), the concentrations of other isomers of $C_{78}$ drops down to zero and the concentration of isomer 3 ($C_{2v}$) reaches 100%. The content of isomer 4 ($D_{3h}$) remains minor over the whole temperature range from 500 to 5000 K.

The molecule of isomer 4 ($D_{3h}$), which has not been observed experimentally, comprises three coronene substructures, which are likely to introduce considerable local strain (Fig. 3 *a*). In the structure of isomer 5 (see Fig. 3 *b*), three perylene substructures can be distinguished; their presence in the synthesized isomer 3 indicates that this substructure is not destabilizing and may imply the possibility of preparing isomer 5.[64]

Indeed, according to the results of quantum chemical calculations,[63] isomer 5 ($D_{3h}$) is the second most stable one (Table 5). In view of the foregoing, the uniform distribution of pentagons over the sphere, bond distribution similar to that in stable fullerenes, low relative energy and closed-shell electronic structure suggest that this isomer could be syn-

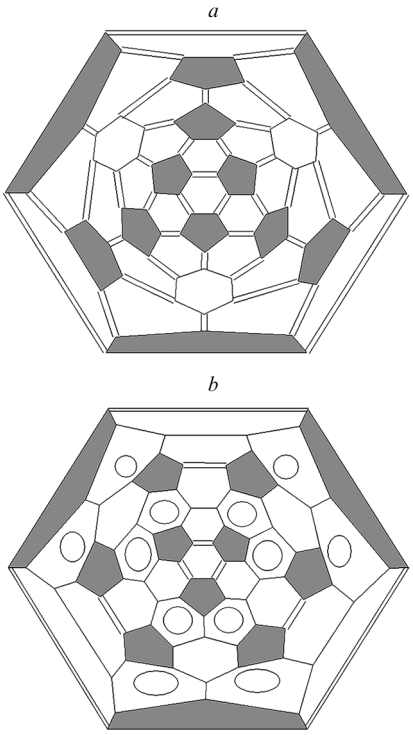



**Figure 3.** Schlegel diagrams of fullerene $C_{78}$ isomers: 4 ($D_{3h}$) (*a*) and 5 ($D_{3h}$) (*b*).[64]

**Table 5**. Relative total energies and energy differences between the frontier orbitals for isomers of fullerene $C_{78}$.[64]

| $C_{78}$ isomer | $\Delta E$ /kcal mol$^{-1}$ | | | HOMO–LUMO /eV | | |
|---|---|---|---|---|---|---|
| | 6-31G | 6-31G* | 6-31+G* | 6-31G | 6-31G* | 6-31+G* |
| *Isomers synthesized* | | | | | | |
| 1 ($D_3$) | 9.37 | 9.93 | 8.69 | 1.66 | 1.62 | 1.60 |
| 2 ($C_{2v}$) | 6.35 | 6.59 | 6.55 | 2.05 | 2.02 | 2.00 |
| 3 ($C_{2v}$) | | | | | | |
| singlet | 0.00 | 0.00 | 0.00 | 1.64 | 1.64 | 1.62 |
| triplet | 15.30 | 16.06 | 14.58 | 0.34 | 0.35 | 0.29 |
| *Isomers not synthesized* | | | | | | |
| 4 ($D_{3h}$) | 24.22 | 23.90 | 23.68 | 2.47 | 2.47 | 2.44 |
| 5 ($D_{3h}$) | | | | | | |
| singlet | 4.93 | 4.55 | 3.62 | 1.51 | 1.52 | 1.50 |
| triplet | 18.48 | 14.68 | 19.45 | 0.37 | 0.37 | 0.35 |

**Table 6**. Maximum dihedral angles (deg) in the rings of five isomers of $C_{78}$.[64]

| $C_{78}$ isomer | In hexagons | | In pentagons |
|---|---|---|---|
| | with alternating bonds | with delocalized π-bonds | |
| | *Isomers synthesized* | | |
| 1 ($D_3$) | 14.74 (6) | 18.49 (3) | 8.39 (6) |
| 2 ($C_{2v}$) | 13.99 (2) | 12.46 (4) | 13.30 (4) |
| 3 ($C_{2v}$) | 11.37 (2) | 12.46 (4) | 11.20 (2) |
| | *Isomers not synthesized* | | |
| 4 ($D_{3h}$) | 15.23 (6) | | 14.36 (6) |
| 5 ($D_{3h}$) | 2.17 (3) | 10.78 (12) | 3.31 (6) |

thesized. Isomer 4 is energetically most unfavourable out of the five $C_{78}$ isomers (see Table 5).

Analysis of the hexagon and pentagon distortions in the synthesized isomers 1 ($D_3$), 2 ($C_{2v}$) and 3 ($C_{2v}$) and in isomer 5 ($D_{3h}$) demonstrated that the degree of distortion in alternating-bond hexagons is comparable with that in hexagons with delocalized π-bonds, which attests to the absence of local overstrain. Furthermore, the distortions in isomer 5 ($D_{3h}$) are even less pronounced than in the other isomers of $C_{78}$; this confirms the assumption of the possible synthesis of this isomer (Table 6). The highest distortions are observed for isomer 4 ($D_{3h}$), which points to substantial local strain.[64]

According to published data, isomer 5 ($D_{3h}$) was isolated as both endohedral metallofullerenes (for example, $Sc_3N@C_{78}$)[65] and exohedral derivatives [for example, $C_{78}(CF_3)_{12}$].[34,44] Isomer 4 ($D_{3h}$), which is unstable because of the local overstrain, has not been obtained as either exohedral or endohedral derivatives, like fullerene $C_{72}$ ($D_{6d}$) with a similar reason for instability.

## II.4. Fullerene $C_{80}$

Out of the seven IPR isomers of fullerene $C_{80}$, only two isomers — 1 ($D_{5d}$) and 2 ($D_2$) — were isolated and characterized.[66–68] Numerous quantum chemical calculations carried out earlier demonstrated that these isomers are energetically most favourable.[22,51–53,68–72]

The structures of isomers that have not been obtained experimentally contain different numbers of radical substructures, which apparently prevent their synthesis (Fig. 4). The number of radical substructures increases in the series of isomers 3–7; finally, in isomer 7, all hexagons are delocalized to form an unusual radical structure (see Fig. 4*e*), no analogues of which have yet been found. Undoubtedly, the greater the number of unpaired electrons in a fullerene, the less stable this structure; this is confirmed by relative energy calculations (Table 7).[73]

Previously, it was believed that apart from already available isomers 1 ($D_{5d}$) and 2 ($D_2$), isomer 3 ($C_{2v}$) could also be obtained;[71] however, according to calculations,[55,73] this isomer and all other isomers have a triplet ground state, *i.e.*, a radical nature, which prevents them from being synthesized.

According to calculations,[71,73,74] isomers 6 and 7 have lower symmetry: the symmetry of isomer 6 ($D_{5h}$) decreases to $C_s$ in the case of the singlet state (the symmetry of the triplet configuration remains the same); in isomer 7 ($I_h$), the symmetry is reduced in both cases, down to $D_{2h}$ in the singlet and to $C_{2h}$ in the triplet configuration. The decrease in the initial symmetry, as noted previously,[52,69,74] is due to the open-shell electronic configuration of these isomers caused by the possible Jahn–Teller effects.

A comparison of the dihedral angles in the synthesized isomers and open-shell isomers showed that distortions of hexagons are even more pronounced in stable isomers than in isomers 3–7 not obtained experimentally.[73] Thus, it can be stated that the instability of open-shell isomers is caused only by their radical nature (Table 8). Meanwhile, according to published data, four isomers were stabilized as

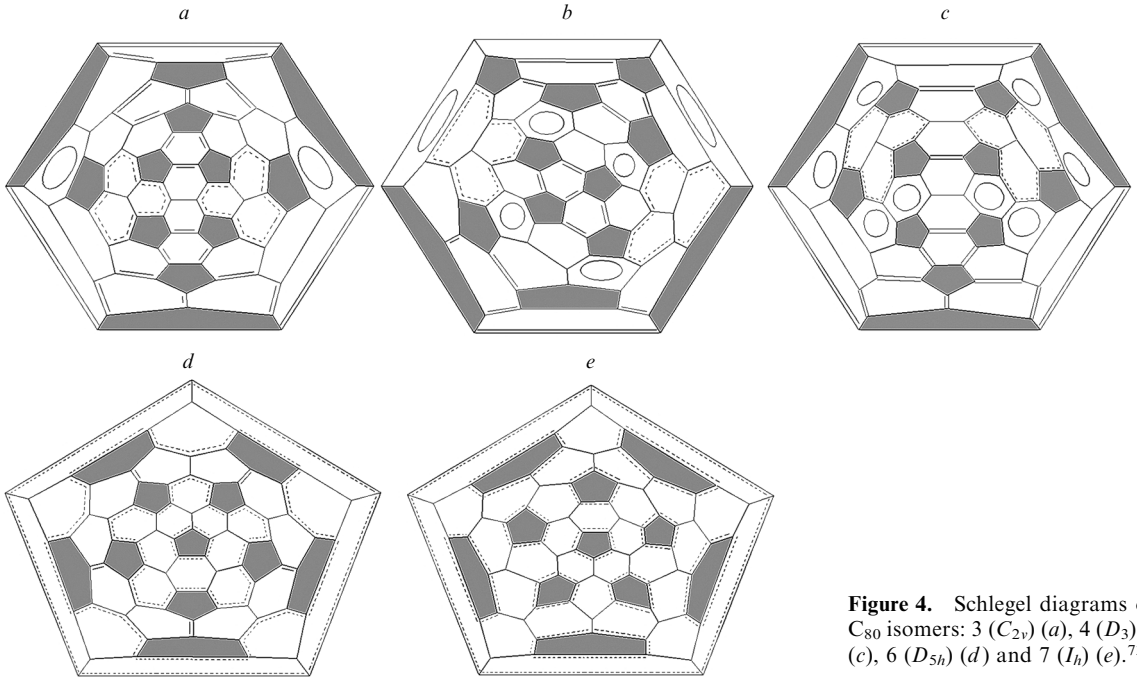



**Figure 4.** Schlegel diagrams of fullerene $C_{80}$ isomers: 3 ($C_{2v}$) (*a*), 4 ($D_3$) (*b*), 5 ($C_{2v}$) (*c*), 6 ($D_{5h}$) (*d*) and 7 ($I_h$) (*e*).[73]

**Table 7**. Relative total energies and energy differences between the frontier orbitals for fullerene $C_{80}$.[73]

| $C_{80}$ isomer | $\Delta E$/kcal mol$^{-1}$ | | | HOMO–LUMO /eV | | |
|---|---|---|---|---|---|---|
| | 6-31G | 6-31G* | 6-31+G* | 6-31G | 6-31G* | 6-31+G* |
| | | | *Isomers synthesized* | | | |
| 1 ($D_{5d}$) | 1.83 | 4.25 | 2.83 | 1.05 | 0.99 | 0.97 |
| 2 ($D_2$) | 0.00 | 0.00 | 0.00 | 1.39 | 1.35 | 1.33 |
| | | | *Isomers not synthesized* | | | |
| 3 ($C_{2v}$) | | | | | | |
| singlet | 7.12 | 7.60 | 9.39 | 0.81 | 0.78 | 0.67 |
| triplet | 3.24 | 2.88 | 4.71 | 0.96 | 0.93 | 0.94 |
| 4 ($D_3$) | | | | | | |
| singlet | 9.54 | 10.49 | 9.45 | 0.78 | 0.75 | 0.73 |
| triplet | 7.85 | 7.68 | 7.04 | 0.92 | 0.94 | 0.94 |
| 5 ($C_{2v}$) | | | | | | |
| singlet | 9.02 | 9.43 | 10.73 | 0.67 | 0.65 | 0.63 |
| triplet | 4.64 | 4.21 | 6.11 | 0.95 | 0.97 | 0.95 |
| 6 ($D_{5h}$) | | | | | | |
| singlet ($C_s$) | 11.85 | 11.60 | 12.51 | 0.65 | 0.63 | 0.63 |
| triplet | 11.88 | 9.18 | 11.97 | 0.64 | 0.63 | 0.64 |
| 7 ($I_h$) | | | | | | |
| singlet ($D_{2h}$) | 29.67 | 27.88 | 27.45 | 0.76 | 0.77 | 0.76 |
| triplet ($C_{2h}$) | 30.11 | 27.71 | 28.56 | 0.73 | 0.74 | 0.73 |

**Table 8**. Maximum dihedral angles (deg) in the rings of seven isomers of fullerene $C_{80}$.[73]

| $C_{80}$ isomer | In hexagons | | In pentagons |
|---|---|---|---|
| | with alternating bonds | with delocalized π-bonds | |
| | *Isomers synthesized* | | |
| 1 ($D_{5d}$) | 17.63 (10) | | 0.22 (10) |
| 2 ($D_2$) | 17.89 (4) | 17.52 (2) | 8.23 (4) |
| | *Open-shell isomers* | | |
| 3 ($C_{2v}$) | 5.21 (4) | 11.99 (2) | 11.33 (2) |
| 4 ($D_3$) | 8.70 (6) | 17.49 (6) | 6.13 (6) |
| 5 ($C_{2v}$) | 10.48 (2) | 12.07 (4) | 10.57 (2) |
| 6 ($D_{5h}$) | 1.94 (10) | 8.24 (10) | 2.32 (10) |
| 7 ($I_h$) | | 5.14 (30) | 0.57 (12) |

endohedral metallofullerenes, in particular, 3 ($C_{2v}$) (*e.g.*, Yb@$C_{80}$),[75] 5 ($C_{2v}$) ($Sc_2C_2$@$C_{80}$),[76] 6 ($D_{5h}$) (*e.g.*, $Sc_3N$@$C_{80}$)[77] and 7 ($I_h$) (*e.g.*, $La_2$@$C_{80}$);[78] and only isomer 5 ($C_{2v}$) was stabilized as exohedral $C_{80}(CF_3)_{12}$.[34]

## II.5. Fullerene $C_{82}$

Currently, out of the nine IPR isomers of fullerene $C_{82}$, only isomer 3 ($C_2$) has been isolated.[79] It was noted[58] that fullerene $C_{82}$ is formed as the mixture of three major isomers of $C_2$, $C_{2v}$ and $C_{3v}$ symmetry in a 8 : 1 : 1 ratio plus at least three minor isomers; however, no other experimental data about the preparation of these isomers were reported. The stability of isomer 3 ($C_2$) of fullerene $C_{82}$ was confirmed theoretically by molecular dynamics,[80] semiempirical calculations[51,79,80] and density functional theory methods.[22,24,51,79–81]

Analysis of the structures of $C_{82}$ isomers that have not been obtained experimentally indicates that isomers 1, 2, 4, 5 and 6 have not only indacene but also coronene (isomer 2) and perylene substructures (Fig. 5). Therefore, presumably, these isomers, which are structurally similar to stable isomer 3 ($C_2$), can also be isolated as pristine fullerenes.[37,82] Considering similar values for the total energy, the HOMO–LUMO energy gaps and calculated $^3$He@$C_{82}$ chemical shifts, which were close to the values measured experimentally for isomer 3 ($C_2$),[83] the possibility to prepare isomers 1 ($C_2$), 2 ($C_s$) and 4 ($C_s$) was indicated.[24,79]

Isomers 7, 8 and 9 contain substructures that, like phenalenyl, can be of a radical nature (see Fig. 5*f*–*h*) and for this reason, they can be unstable. Indeed, according to calculations,[37,82] isomers 1–6 of fullerene $C_{82}$ have closed electron shells (Table 9). The energy characteristics of isomers 7, 8 and 9 indicate that they exist preferably in triplet forms and, hence, they are radical species (see Table 9).

Also, according to calculation data, the molecular symmetry of the singlet forms of isomers 7 ($C_{3v}$) and 8 ($C_{3v}$) decreases to $C_s$ upon optimization, while the triplet forms retain $C_{3v}$ symmetry. This type of symmetry reduction for isomers 7, 8 and 9 has been noted at different theoretical levels for neutral open-shell fullerenes.[79–81]

For all isomers of fullerene $C_{82}$, distortion of hexagons and pentagons was found, not exceeding that for isomer 3 obtained experimentally ($C_2$) (Table 10).[82] Therefore, the favourable energy and geometric parameters of isomers 1, 2 and 4–6 suggest that these isomers could be isolated as pristine fullerene molecules.

As in the case of fullerene $C_{70}$, in open-shell isomers the greatest distortions are inherent in hexagons with delocalized π-bonds (see Table 10), which do not destabilize the molecule. Thus, the absence of significant differences between the dihedral angles of the experimentally obtained

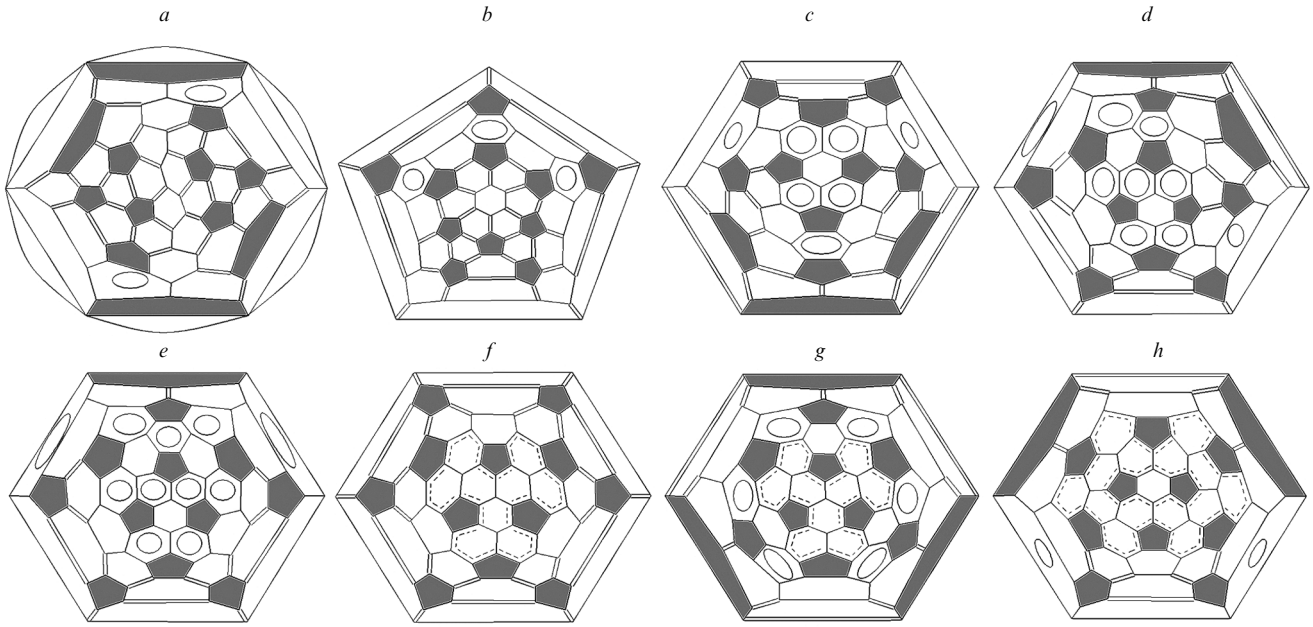



**Figure 5.** Schlegel diagrams of fullerene $C_{82}$ isomers: 1 ($C_2$) (*a* ), 2 ($C_s$) (*b*), 4 ($C_s$) (*c*), 5 ($C_2$) (*d*), 6 ($C_s$) (*e*), 7 ($C_{3v}$) (*f*), 8 ($C_{3v}$) (*g*) and 9 ($C_{2v}$) (*h*).[37, 82]

**Table 9**. Relative total energies and energy differences between the frontier orbitals for fullerene $C_{82}$.[37, 82]

| $C_{82}$ isomer | $\Delta E$ /kcal mol$^{-1}$ | | | HOMO – LUMO /eV | | |
|---|---|---|---|---|---|---|
| | 6-31G | 6-31G* | 6-31 + G* | 6-31G | 6-31G* | 6-31 + G* |
| | | | *Isomer synthesized* | | | |
| 3 ($C_2$) singlet | 0.00 | 0.00 | 0.00 | 1.67 | 1.63 | 1.61 |
| | | | *Isomers not synthesized* | | | |
| 1 ($C_2$) singlet | 7.40 | 6.67 | 7.31 | 1.31 | 1.26 | 1.24 |
| 2 ($C_s$) singlet | 6.70 | 7.98 | 7.23 | 1.71 | 1.65 | 1.63 |
| 4 ($C_s$) | | | | | | |
| singlet | 4.20 | 1.14 | 3.16 | 1.58 | 1.55 | 1.54 |
| triplet | 17.63 | 15.81 | 21.64 | 0.41 | 0.43 | 0.42 |
| 5 ($C_2$) | | | | | | |
| singlet | 8.73 | 2.99 | 7.37 | 1.29 | 1.28 | 1.27 |
| triplet | 15.29 | 7.32 | 14.57 | 0.72 | 0.73 | 1.12 |
| 6 ($C_s$) | | | | | | |
| singlet | 12.97 | 10.80 | 11.40 | 1.10 | 1.10 | 1.09 |
| triplet | 15.48 | 17.81 | 15.08 | 0.89 | 0.90 | 0.89 |
| 7 ($C_{3v}$) | | | | | | |
| singlet ($C_s$) | 26.59 | 26.19 | 26.08 | 0.85 | 0.85 | 0.83 |
| triplet | 22.54 | 21.93 | 22.20 | 1.14 | 1.16 | 1.27 |
| 8 ($C_{3v}$) | | | | | | |
| singlet ($C_s$) | 28.36 | 30.70 | 32.17 | 0.72 | 0.74 | 0.73 |
| triplet | 28.44 | 25.42 | 27.61 | 0.95 | 0.95 | 0.95 |
| 9 ($C_{2v}$) | | | | | | |
| singlet | 19.24 | 17.65 | 18.14 | 0.73 | 0.73 | 0.73 |
| triplet | 17.69 | 12.05 | 16.72 | 0.86 | 0.87 | 0.86 |

isomer 3 ($C_2$) and open-shell isomers implies that the instability of open-shell isomers is related only to their radical nature.

According to literature data, the isomers stabilized as endohedral metallofullerenes include 5 ($C_2$) (*e.g.*, $Ca@C_{82}$),[84] 6 ($C_s$) (*e.g.*, $Er_2@C_{82}$),[85] 7 ($C_{3v}$) ($La@C_{82}$),[86] 8 ($C_{3v}$) (*e.g.*, $Sc_2C_2@C_{82}$)[87] and 9 ($C_{2v}$) (*e.g.*, $Sc@C_{82}$).[88] Among isomers that have not been synthesized, only isomer 5 ($C_2$) was stabilized as an exohedral derivative, namely, $C_{82}(CF_3)_{12}$.[37, 89]

**Table 10**. Maximum dihedral angles (deg) in the rings of isomers of $C_{82}$.[82]

| $C_{82}$ isomer | In hexagons | | In pentagons |
|---|---|---|---|
| | with alternating bonds | with delocalized π-bonds | |
| | *Closed-shell isomers* | | |
| 1 ($C_2$) | 17.28 (2) | 14.77 (2) | 9.91 (2) |
| 2 ($C_s$) | 16.39 (2) | 12.52 (2) | 12.74 (2) |
| **3 ($C_2$)** | **16.47 (2)** | **13.66 (2)** | **10.68 (2)** |
| 4 ($C_s$) | 15.09 (2) | 12.86 (2) | 11.04 (2) |
| 5 ($C_2$) | 13.77 (2) | 12.94 (2) | 10.09 (2) |
| 6 ($C_s$) | 11.07 (2) | 12.81 (2) | 9.27 (2) |
| | *Open-shell isomers* | | |
| 7 ($C_{3v}$) | 11.94 (3) | 12.27 (6) | 11.55 (6) |
| 8 ($C_{3v}$) | 10.39 (6) | 10.63 (6) | 8.59 (3) |
| 9 ($C_{2v}$) | 7.83 (4) | 10.38 (4) | 6.88 (4) |

**Note**. Data for the isomer prepared experimentally are typed in bold.

## II.6. Fullerene $C_{84}$

Fullerene $C_{84}$ is the third, after $C_{60}$ and $C_{70}$, most often encountered and abundant in fullerene soot. Out of the 24 IPR isomers, eleven isomers of this fullerene have now been obtained, namely, 4 ($D_{2d}$), 5 ($D_2$), 11 ($C_2$), 13 ($C_2$), 14 ($C_s$), 15 ($C_s$), 16 ($C_s$), 19 ($D_{3d}$), 22 ($D_2$), 23 ($D_{2d}$) and 24 ($D_{6h}$).[24, 58, 90–96] Early theoretical calculations of fullerene $C_{84}$ and more recent *ab initio* calculations were both aimed, first of all, at determination of the relative energies and simulation of NMR spectra of various isomers at different approximation levels; according to the results, the synthesized isomers are most favourable in energy.[22, 24, 51, 95, 97–105]

Upon analysis of the structures of the 13 fullerene $C_{84}$ isomers that have not been synthesized, these species can be divided into three groups. One group includes isomers with closed-shell electronic configurations and with the same substructures as contained in the most stable isomers (Fig. 6). This suggests the prospects for the subsequent practical synthesis of isomers 6 ($C_{2v}$), 7 ($C_{2v}$), 12 ($C_1$), 17 ($C_{2v}$), 18 ($C_{2v}$) and 21 ($D_2$). According to quantum chemical calculations, the total energies of these six isomers differ insignificantly from those for the already prepared isomers (Table 11).[20, 21] The predictive value of the elaborated approach has been practically confirmed. Indeed, the synthesis of isomer 14 predicted in 2006 to be stable (see Ref. 6) was actually accomplished in 2008.[94]

The second group consisting of not yet synthesized isomers of fullerene $C_{84}$ is composed of four open-shell isomers, *i.e.*, those containing radical groups (Fig. 7); this, apparently, prevents them from being synthesized and isolated. Indeed, these isomers possess increased relative total energies, and their open-shell electronic configuration is confirmed by considerable energetic favourability of their triplet or singlet biradical states and great HOMO–LUMO energy gaps (see Table 11).[20, 21]

The third group includes isomers 1 ($D_2$), 2 ($C_2$) and 20 ($T_d$), which possess closed-shell configurations but contain substructures composed of large numbers of fused hexagons (Fig. 8). Indeed, the molecule of isomer 1 ($D_2$) has two substructures, each consisting of 12 fused hexagons. Isomer 2 ($C_2$) comprises 2 substructures composed of 10 fused hexagons, and isomer 20 ($T_d$) contains 4 coronene substructures (7 fused hexagons each), which is probably also a reason for their instability. The closed-shell configuration of isomer 20 ($T_d$) has also been noted before.[53] According to quantum chemical calculations, these isomers with overstrained molecules have the highest relative total energies (see Table 11).[19–21]

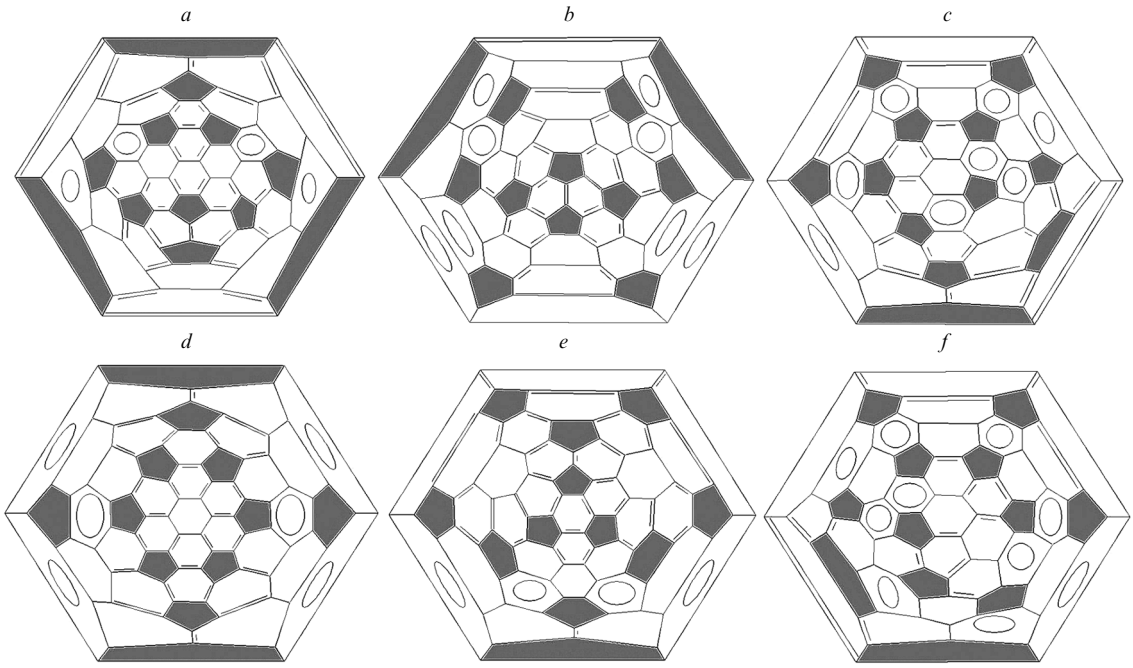



**Figure 6.** Schlegel diagrams of fullerene $C_{84}$ isomers: 6 ($C_{2v}$) (*a*), 7 ($C_{2v}$) (*b*), 12 ($C_1$) (*c*), 17 ($C_{2v}$) (*d*), 18 ($C_{2v}$) (*e*) and 21 ($D_2$) (*f*).[20, 21]

**Table 11**. Relative total energies and energy differences between the frontier orbitals for fullerene $C_{84}$.[19–21]

| $C_{84}$ isomer | $\Delta E$/kcal mol$^{-1}$ | | | HOMO–LUMO/eV | | |
|---|---|---|---|---|---|---|
| | 6-31G | 6-31G* | 6-31+G* | 6-31G | 6-31G* | 6-31+G* |
| | | | *Isomer synthesized* | | | |
| 4 ($D_{2d}$) | 16.21 | 15.82 | 16.82 | 2.12 | 1.88 | 2.10 |
| 5 ($D_2$) | 17.65 | 17.02 | 15.46 | 1.88 | 1.88 | 1.87 |
| 11 ($C_2$) | 8.38 | 8.46 | 8.37 | 1.68 | 1.64 | 1.63 |
| 13 ($C_2$) | 25.47 | 30.77 | 25.11 | 1.17 | 1.16 | 1.14 |
| 14 ($C_s$) | 15.38 | 20.66 | 15.13 | 1.96 | 1.91 | 1.89 |
| 15 ($C_s$) | 11.75 | 11.18 | 11.42 | 1.56 | 1.54 | 1.53 |
| 16 ($C_s$) | 8.07 | 7.78 | 9.49 | 1.83 | 1.78 | 1.76 |
| 19 ($D_{3d}$) | 10.04 | 10.64 | 10.21 | 1.44 | 1.38 | 1.37 |
| 22 ($D_2$) | 0.26 | 0.25 | 0.06 | 2.02 | 1.98 | 1.96 |
| 23 ($D_{2d}$) | 0.00 | 0.00 | 0.00 | 2.08 | 2.05 | 2.03 |
| 24 ($D_{6h}$) | 7.32 | 2.43 | 7.19 | 2.40 | 2.34 | 2.32 |
| | | | *Closed-shell isomers* | | | |
| 6 ($C_{2v}$) singlet | 17.29 | 17.99 | 17.71 | 1.41 | 1.36 | 1.35 |
| 7 ($C_{2v}$) | | | | | | |
| singlet | 25.08 | 25.43 | 24.89 | 1.34 | 1.30 | 1.28 |
| triplet | 34.92 | 29.55 | 33.54 | 0.49 | 0.54 | 0.52 |
| 12 ($C_1$) | | | | | | |
| singlet | 12.56 | 8.43 | 13.66 | 1.48 | 1.46 | 1.44 |
| triplet | 24.22 | 22.87 | 24.77 | 0.49 | 0.51 | 0.54 |
| 17 ($C_{2v}$) | | | | | | |
| singlet | 21.92 | 28.74 | 22.90 | 1.40 | 1.37 | 1.34 |
| triplet | 31.32 | 18.69 | 37.51 | 0.61 | 0.64 | 0.66 |
| 18 ($C_{2v}$) singlet | 15.94 | 17.26 | 15.74 | 1.99 | 1.95 | 1.94 |
| 21 ($D_2$) | | | | | | |
| singlet | 16.83 | 17.01 | 16.10 | 1.36 | 1.34 | 1.33 |
| triplet | 29.53 | 29.71 | 28.28 | 0.25 | 0.27 | 0.25 |
| | | | *Open-shell isomers* | | | |
| 3 ($C_s$) | | | | | | |
| singlet | 32.89 | 28.01 | 41.58 | 0.79 | 0.77 | 0.76 |
| triplet | 29.21 | 30.41 | 37.59 | 0.89 | 0.91 | 0.87 |
| singlet biradical | 27.64 | 46.79 | 26.58 | 1.07 | 1.05 | 1.02 |
| 8 ($C_2$) | | | | | | |
| singlet | 22.72 | 32.87 | 21.65 | 0.99 | 0.98 | 0.98 |
| triplet | 25.61 | 25.88 | 24.35 | 0.73 | 0.74 | 0.73 |
| singlet biradical | 22.58 | 30.26 | 21.56 | 1.06 | 1.05 | 1.04 |
| 9 ($C_2$) | | | | | | |
| singlet | 26.98 | 26.38 | 26.31 | 0.82 | 0.81 | 0.79 |
| triplet | 25.00 | 34.00 | 24.12 | 0.97 | 0.99 | 0.98 |
| singlet biradical | 24.91 | 31.36 | 24.22 | 1.05 | 1.04 | 1.02 |
| 10 ($C_s$) | | | | | | |
| singlet | 29.97 | 29.61 | 29.71 | 0.61 | 0.64 | 0.64 |
| triplet | 27.11 | 25.65 | 27.51 | 0.85 | 0.85 | 0.84 |
| | | | *Overstrained isomers* | | | |
| 1 ($D_2$) singlet | 53.11 | 58.26 | 50.81 | 2.45 | 2.37 | 2.34 |
| 2 ($C_2$) singlet | 34.79 | 35.57 | 32.47 | 1.99 | 1.95 | 1.93 |
| 20 ($T_d$) singlet | 31.18 | 30.12 | 30.13 | 2.73 | 2.66 | 2.63 |

In the overstrained isomer molecules, hexagons with alternating single and double bonds are most distorted, unlike the experimentally synthesized isomers and the closed-shell isomers that presumably could be prepared (Table 12).[19–21] Comparison of the maximum dihedral angles in the rings of overstrained isomers with these parameters for stable fullerenes clearly shows a boundary between them, as they reach higher values for overstrained molecules (see Table 12). It is noteworthy that the number of distorted hexagons is also important for destabilization of the molecule: indeed, the dihedral angles in alternating-bond hexagons of isomers 1 ($D_2$) and 2 ($C_2$) reach 20.8 and 19.6°, respectively (see Table 12); this is much greater than the distortions of hexagons in isomer 20 ($T_d$) (12.6°).

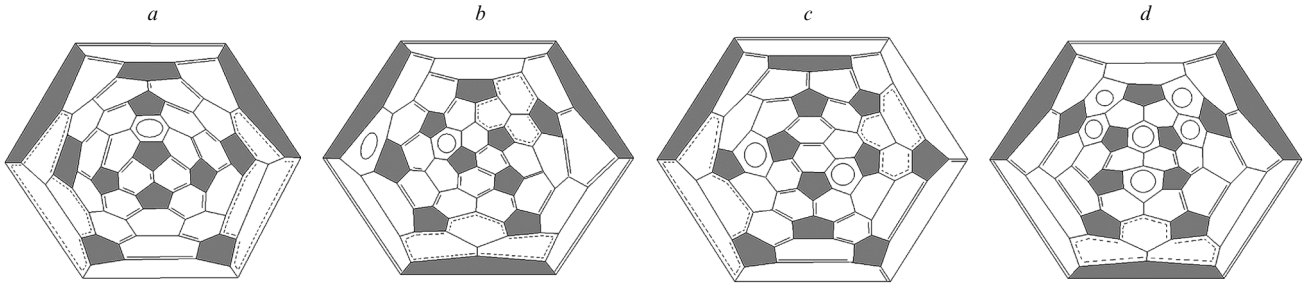



**Figure 7.** Schlegel diagrams of open-shell isomers of fullerene $C_{84}$: 3 ($C_s$) (*a*), 8 ($C_2$) (*b*), 9 ($C_2$) (*c*) and 10 ($C_s$) (*d*).[20,21]

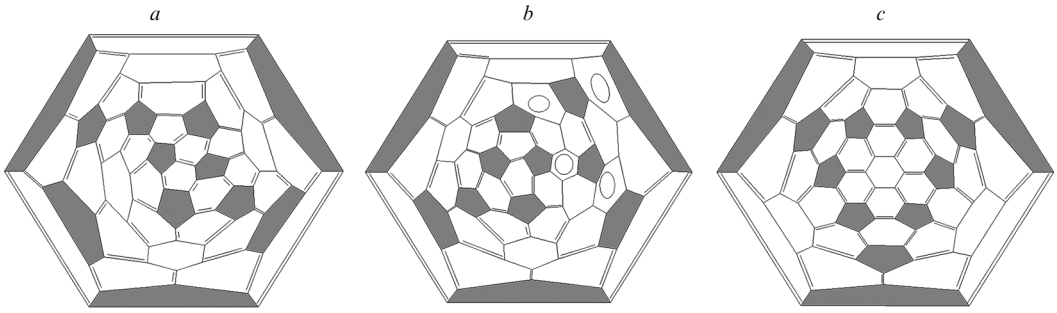



**Figure 8.** Schlegel diagrams of overstrained isomers of fullerene $C_{84}$: 1 ($D_2$) (*a*), 2 ($C_2$) (*b*) and 20 ($T_d$) (*c*).[19–21]

**Table 12**. Maximum dihedral angles (deg) in the rings of 24 isomers of fullerene $C_{84}$.[19–21]

| $C_{84}$ isomer | In hexagons | | In pentagons | $C_{84}$ isomer | In hexagons | | In pentagons |
|---|---|---|---|---|---|---|---|
| | with alternating bonds | with delocalized π-bonds | | | with alternating bonds | with delocalized π-bonds | |
| | | | *Isomer synthesized* | | | | |
| 4 ($D_{2d}$) | 9.6 (8)* | 13.2 (4) | 10.6 (4) | 16 ($C_s$) | 12.4 (2) | 11.9 (2) | 10.9 (2) |
| 5 ($D_2$) | 8.9 (4) | 16.2 (4) | 4.8 (4) | 19 ($D_{3d}$) | 10.9 (6) | 11.4 (3) | 8.3 (6) |
| 11 ($C_2$) | 12.9 (2) | 11.6 (2) | 9.1 (2) | 22 ($D_2$) | 9.3 (4) | 12.3 (2) | 7.7 (4) |
| 13 ($C_2$) | 12.7 (2) | 17.2 (1) | 9.6 (2) | 23 ($D_{2d}$) | 8.7 (8) | 10.2 (8) | 7.2 (8) |
| 14 ($C_s$) | 14.4 (2) | 14.4 (2) | 11.4 (2) | 24 ($D_{6h}$) | 8.6 (12) | 5.9 (6) | 8.4 (12) |
| 15 ($C_s$) | 13.8 (2) | 12.9 (2) | 9.9 (1) | | | | |
| | | | *Closed-shell isomers* | | | | |
| 6 ($C_{2v}$) | 14.2 (4) | 14.2 (4) | 9.9 (2) | 17 ($C_{2v}$) | 11.5 (4) | 9.1 (4) | 10.6 (4) |
| 7 ($C_{2v}$) | 15.1 (4) | 10.3 (4) | 10.7 (2) | 18 ($C_{2v}$) | 11.8 (4) | 9.7 (4) | 12.5 (2) |
| 12 ($C_1$) | 11.7 (1) | 14.4 (1) | 9.4 (1) | 21 ($D_2$) | 10.9 (4) | 11.2 (4) | 6.7 (4) |
| | | | *Open-shell isomers* | | | | |
| 3 ($C_s$) | 15.6 (2) | 13.9 (2) | 11.2 (2) | 9 ($C_2$) | 11.9 (2) | 13.9 (2) | 9.5 (2) |
| 8 ($C_2$) | 14.7 (2) | 13.2 (2) | 9.6 (2) | 10 ($C_s$) | 12.2 (2) | 14.2 (2) | 9.1 (2) |
| | | | *Overstrained isomers* | | | | |
| 1 ($D_2$) | 20.8 (4) | | 17.8 (4) | 20 ($T_d$) | 12.6 (12) | | 11.9 (12) |
| 2 ($C_2$) | 19.6 (2) | 17.4 (2) | 17.4 (2) | | | | |

However, the number of these distorted hexagons (12) in isomer 20 ($T_d$) is much greater than that in the other two isomers.

According to published data, out of the isomers of fullerene $C_{84}$ not yet synthesized, three isomers were obtained as endohedral metallofullerenes. Two of them, 7 ($C_{2v}$) and 12 ($C_1$), are presumably stable [obtained, *e.g.*, as $Sc_2@C_{84}$ (see Ref. 106) and $Yb@C_{84}$ (see Refs 75 and 107), respectively] and one open-shell isomer, 10 ($C_s$), can be stabilized as $Sc_2@C_{84}$.[106] Only isomer 18 ($C_{2v}$) was isolated

as an exohedral derivative $[C_{84}(C_2F_5)_{12}]$;[108] according to our data, this isomer could be stable.

### II.7. Fullerene $C_{86}$

Fullerene $C_{86}$ has 19 IPR isomers, of which only two have been experimentally obtained and isolated, namely, 16 ($C_s$) and 17 ($C_2$).[109–111] Their stability is confirmed by quantum chemical calculations.[22, 24, 51, 108–112]

The other 17 out of the possible 19 isomers of fullerene $C_{86}$ can be subdivided into two groups. One group covers all isomers that have not been prepared except for isomer 2 ($C_2$). The key distinction of these isomers from stable isomers 16 ($C_s$) and 17 ($C_2$) is the open-shell electronic configuration, *i.e.*, the presence of unpaired electrons, which is probably responsible for their instability (Figs 9 and 10). The radical nature of these isomers is confirmed by quantum chemical calculations: either triplet or singlet biradical state is energetically more favourable than the closed-shell singlet state (Table 13),[113] while the HOMO–LUMO energy gaps are rather small for all configurations, indicating that they are kinetically unstable.

The second group consists of only one isomer 2 ($C_2$), the molecule of which has two substructures each consisting of nine fused hexagons (Fig. 11). It is clear that these planar substructures would introduce considerable local strain into the fullerene molecule, which tends to a spherical shape; this is confirmed by quantum chemical calculations,[110, 113] which demonstrate that isomer 2 ($C_2$) is one of the most unstable species (Table 13).

In open-shell isomers, as in stable isomers, hexagons with delocalized π-bonds, which do not destabilize the molecule, are most distorted (Table 14). This implies that the instability of these isomers is caused by their radical nature.[113] It can also be seen that distortions in isomer 2 ($C_2$) are much higher than those in other isomers, which confirms the assumption that its instability is caused by local overstrain. According to published data, only isomer 19 ($D_3$) was isolated as endohedral derivatives (*e.g.*, $Tb_3N@C_{86}$),[111] while stable isomers 16 ($C_s$) and 17 ($C_2$) were obtained as exohedral derivatives [*e.g.* , chloro derivatives $C_{86}(16)Cl_{16}$, $C_{86}(17)Cl_{18}$, $C_{86}(17)Cl_{20}$ and $C_{86}(17)Cl_{22}$ ].[114]

## III. Isolated pentagon rule and classification of fullerenes

The whole set of above data on what isomers of various fullerenes have been isolated as hollow $C_n$ molecules or as

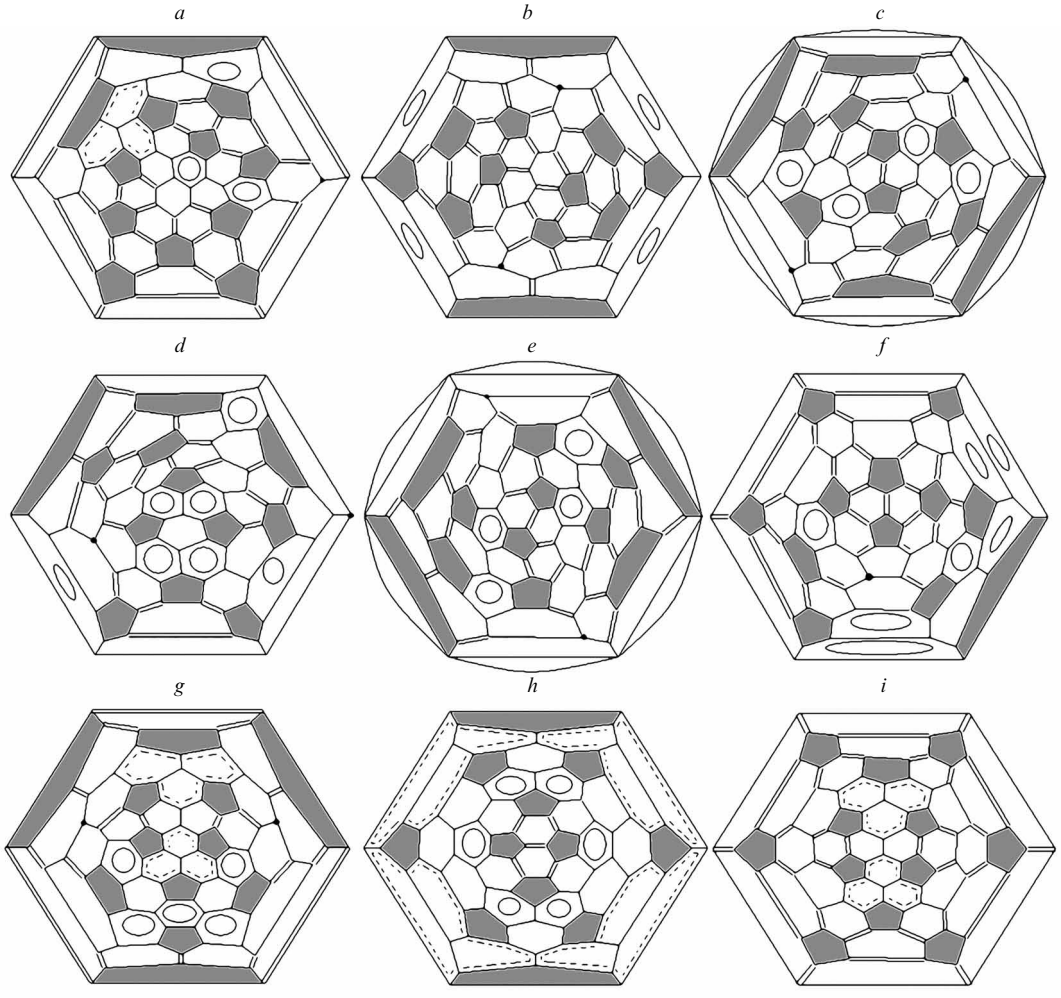



**Figure 9.** Schlegel diagrams of open-shell isomers of fullerene $C_{86}$: 1 ($C_1$) (*a*), 3 ($C_2$) (*b*), 4 ($C_2$) (*c*), 5 ($C_2$) (*d*), 6 ($C_2$) (*e*), 7 ($C_1$) (*f* ), 8 ($C_s$) (*g*), 9 ($C_{2v}$) (*h*) and 10 ($C_{2v}$) (*i*).[113]

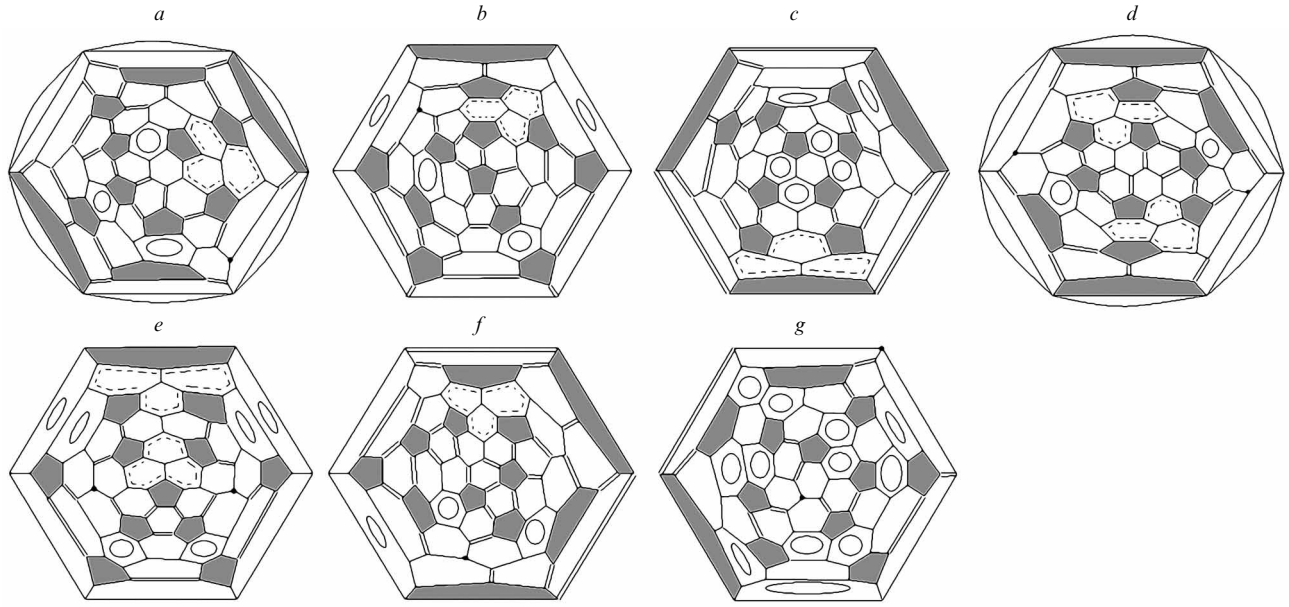



**Figure 10.** Schlegel diagrams of open-shell isomers of fullerene $C_{86}$: 11 ($C_1$) (*a*), 12 ($C_1$) (*b*), 13 ($C_1$) (*c*), 14 ($C_2$) (*d*), 15 ($C_s$) (*e*), 18 ($C_3$) (*f*) and 19 ($D_3$) (*g*).[113]

**Table 13**. Relative total energies and energy differences between the frontier orbitals for fullerene $C_{86}$.[113]

| $C_{86}$ isomer | $\Delta E$/kcal mol$^{-1}$ | | | HOMO – LUMO /eV | | |
|---|---|---|---|---|---|---|
| | 6-31G | 6-31G* | 6-31 + G* | 6-31G | 6-31G* | 6-31 + G* |
| | | | *Isomers synthesized* | | | |
| 16 ($C_s$) singlet | 6.52 | 3.26 | 7.49 | 1.91 | 1.88 | 1.85 |
| 17 ($C_2$) singlet | 0.00 | 0.00 | 0.00 | 1.56 | 1.53 | 1.50 |
| | | | *Open-shell isomers* | | | |
| 1 ($C_1$) | | | | | | |
| singlet | 28.52 | 24.29 | 26.90 | 1.10 | 1.12 | 1.11 |
| triplet | 32.47 | 29.90 | 31.75 | 0.75 | 0.75 | 0.72 |
| singlet biradical | 28.52 | 24.73 | 27.05 | 1.10 | 1.15 | 1.14 |
| 3 ($C_2$) | | | | | | |
| singlet | 20.85 | 17.01 | 17.49 | 1.12 | 1.14 | 1.13 |
| triplet | 26.83 | 23.47 | 24.42 | 0.60 | 0.58 | 0.57 |
| singlet biradical | 20.85 | 12.12 | 16.95 | 1.12 | 1.15 | 1.14 |
| 4 ($C_2$) | | | | | | |
| singlet | 22.01 | 20.51 | 20.54 | 0.90 | 0.87 | 0.88 |
| triplet | 22.05 | 18.23 | 20.14 | 0.89 | 0.91 | 0.89 |
| 5 ($C_1$) | | | | | | |
| singlet | 21.38 | 15.82 | 33.81 | 1.02 | 1.00 | 1.00 |
| triplet | 25.06 | 21.24 | 24.55 | 0.67 | 0.68 | 0.67 |
| 6 ($C_2$) | | | | | | |
| singlet | 15.87 | 19.42 | 14.76 | 0.99 | 0.97 | 0.96 |
| triplet | 18.91 | 18.50 | 17.31 | 0.72 | 0.79 | 0.74 |
| singlet biradical | 15.81 | 12.99 | 14.76 | 1.03 | 1.02 | 1.01 |
| 7 ($C_1$) | | | | | | |
| singlet | 24.94 | 22.20 | 24.19 | 0.88 | 0.87 | 0.86 |
| triplet | 23.79 | 14.67 | 22.80 | 0.95 | 0.97 | 0.95 |
| 8 ($C_s$) | | | | | | |
| singlet | 36.67 | 33.33 | 38.21 | 0.82 | 0.82 | 0.82 |
| triplet | 36.92 | 31.12 | 39.78 | 0.84 | 0.82 | 0.77 |
| 9 ($C_{2v}$) | | | | | | |
| singlet | 43.17 | 36.61 | 40.49 | 0.78 | 0.79 | 0.78 |
| triplet | 42.91 | 44.39 | 40.78 | 0.87 | 0.81 | 0.83 |
| singlet biradical | 42.67 | 38.74 | 40.29 | 0.87 | 0.81 | 0.81 |

**Table 13** (continued).

| $C_{86}$ isomer | $\Delta E$/kcal mol$^{-1}$ | | | HOMO – LUMO /eV | | |
|---|---|---|---|---|---|---|
| | 6-31G | 6-31G* | 6-31 + G* | 6-31G | 6-31G* | 6-31 + G* |
| | | | *Open-shell isomers* | | | |
| 10 ($C_{2v}$) | | | | | | |
| singlet | 18.82 | 21.36 | 17.22 | 1.06 | 1.06 | 1.06 |
| triplet | 21.77 | 20.35 | 20.49 | 0.82 | 0.82 | 0.83 |
| singlet biradical | 18.75 | 17.18 | 17.28 | 1.10 | 1.10 | 1.09 |
| 11 ($C_1$) | | | | | | |
| singlet | 10.81 | 16.76 | 11.23 | 1.17 | 1.15 | 1.14 |
| triplet | 16.53 | 7.13 | 15.64 | 0.65 | 0.67 | 0.67 |
| singlet biradical | 10.81 | 5.95 | 9.37 | 1.17 | 1.13 | 1.12 |
| 12 ($C_1$) | | | | | | |
| singlet | 10.79 | 7.95 | 11.27 | 1.20 | 1.18 | 1.17 |
| triplet | 16.77 | 7.79 | 15.99 | 0.68 | 0.69 | 0.69 |
| singlet biradical | 10.79 | 7.93 | 11.46 | 1.20 | 1.20 | 1.19 |
| 13 ($C_1$) | | | | | | |
| singlet | 14.88 | 14.90 | 16.30 | 1.22 | 1.19 | 1.19 |
| triplet | 20.98 | 21.43 | 22.02 | 0.67 | 0.69 | 0.69 |
| singlet biradical | 14.88 | 17.88 | 16.31 | 1.22 | 1.21 | 1.19 |
| 14 ($C_2$) | | | | | | |
| singlet | 22.29 | 21.03 | 20.89 | 0.97 | 0.97 | 0.95 |
| triplet | 25.83 | 11.91 | 27.75 | 0.69 | 0.69 | 0.68 |
| singlet biradical | 22.29 | 21.19 | 20.17 | 0.97 | 1.00 | 1.00 |
| 15 ($C_s$) | | | | | | |
| singlet | 22.67 | 23.02 | 21.25 | 1.07 | 1.05 | 1.04 |
| triplet | 31.11 | 28.02 | 29.32 | 0.55 | 0.57 | 0.56 |
| singlet biradical | 22.67 | 20.03 | 21.28 | 1.07 | 1.03 | 1.02 |
| 18 ($C_3$) | | | | | | |
| singlet | 11.87 | 6.71 | 12.06 | 1.14 | 1.13 | 1.13 |
| triplet | 19.41 | 18.89 | 19.61 | 0.48 | 0.54 | 0.49 |
| singlet biradical | 11.87 | 9.29 | 12.16 | 1.14 | 1.13 | 1.12 |
| 19 ($D_3$) | | | | | | |
| singlet | 24.25 | 23.22 | 23.16 | 1.02 | 0.99 | 0.99 |
| triplet | 29.28 | 22.83 | 27.55 | 0.59 | 0.62 | 0.61 |
| singlet biradical | 24.29 | 21.51 | 22.37 | 1.09 | 1.06 | 1.08 |
| | | | *Closed-shell isomers* | | | |
| 2 ($C_2$) | | | | | | |
| singlet | 29.23 | 26.26 | 26.58 | 2.10 | 2.10 | 2.09 |
| triplet | 57.65 | 56.21 | 56.21 | 0.28 | 0.25 | 0.27 |

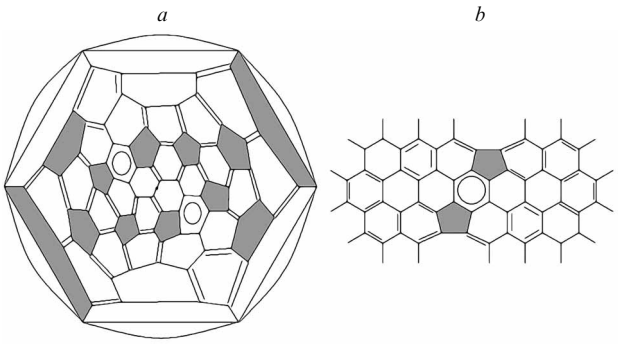



**Figure 11.** Schlegel diagram of overstrained isomer 2 ($C_2$) of fullerene $C_{86}$ (*a*) and a substructure composed of 17 fused hexagons (*b*).[113]

endo- and exohedral derivatives are summarized in Table 15.

It is noteworthy that endohedral fullerene derivatives were obtained for isomers other than those isolated as hollow molecules. Yet another conclusion from this statistics is that the overstrained fullerene molecules [fullerene $C_{72}$ ($D_{6d}$), isomer 4 ($D_{3h}$) of fullerene $C_{78}$, isomers 1 ($D_2$), 2 ($C_2$) and 20 ($T_d$) of fullerene $C_{84}$ and isomer 2 ($C_2$) of fullerene $C_{86}$] have not been isolated as any derivatives; this apparently indicates that they cannot be stabilized and the molecular strain cannot be relieved. However, molecules that are unstable because of the radical electronic structure can be stabilized as both endohedral metallofullerenes and exohedral derivatives as well as polymeric forms. Moreover, although some of the radical fullerenes have not yet been obtained as derivatives, the possibility for them to be synthesized in the future can be assumed.

**Table 14**. Maximum dihedral angles (deg) in the rings of 19 isomers of $C_{86}$.[113]

| $C_{86}$ isomer | In hexagons | | In pentagons | $C_{86}$ isomer | In hexagons | | In pentagons |
|---|---|---|---|---|---|---|---|
| | with alternating bonds | with delocalized π-bonds | | | with alternating bonds | with delocalized π-bonds | |
| | | | *Isomers synthesized* | | | | |
| 16 ($C_s$) | 13.46 (2)* | 17.54 (2) | 11.54 (1) | 17 ($C_2$) | 14.12 (2) | 17.27 (1) | 9.29 (1) |
| | | | *Closed-shell isomers* | | | | |
| 2 ($C_2$) | 16.14 (2) | 25.11 (1) | 13.15 (2) | | | | |
| | | | *Open-shell isomers* | | | | |
| 1 ($C_1$) | 17.72 (1) | 23.62 (1) | 14.19 (1) | 10 ($C_{2v}$) | 13.21 (4) | 14.27 (4) | 12.09 (2) |
| 3 ($C_2$) | 20.59 (2) | 17.47 (2) | 9.89 (2) | 11 ($C_1$) | 14.37 (1) | 19.58 (1) | 9.76 (1) |
| 4 ($C_2$) | 14.61 (2) | 22.37 (1) | 11.75 (2) | 12 ($C_1$) | 11.49 (1) | 19.44 (1) | 9.59 (1) |
| 5 ($C_1$) | 16.11 (1) | 21.81 (1) | 11.78 (1) | 13 ($C_1$) | 11.12 (1) | 16.97 (1) | 9.76 (1) |
| 6 ($C_2$) | 16.62 (2) | 23.51 (1) | 8.64 (2) | 14 ($C_2$) | 13.69 (2) | 20.37 (1) | 8.07 (2) |
| 7 ($C_1$) | 15.93 (1) | 20.93 (1) | 11.76 (1) | 15 ($C_s$) | 10.79 (2) | 17.10 (2) | 7.70 (1) |
| 8 ($C_s$) | 15.85 (2) | 18.53 (2) | 12.92 (1) | 18 ($C_3$) | 12.94 (3) | 18.69 (3) | 8.34 (3) |
| 9 ($C_{2v}$) | 10.29 (4) | 17.67 (4) | 9.77 (2) | 19 ($D_3$) | 9.87 (6) | 13.20 (6) | 5.65 (6) |

**Table 15**. Higher fullerene isomers in the series $C_{60}-C_{86}$ experimentally obtained and identified as pristine fullerenes $C_n$, endohedral metallofullerenes $M@C_n$ and exohedral fullerenes $X_mC_n$.

| *n* in $C_n$ | Number of possible isomers | Number of IPR isomers | Obtained and characterized IPR isomers | | |
|---|---|---|---|---|---|
| | | | $C_n$ | $M@C_n$ | $C_nX_m$ |
| 60 | 1812 | 1 | $I_h$ | $I_h$ | $I_h$ |
| 70 | 8149 | 1 | $D_{5h}$ | $D_{5h}$ | $D_{5h}$ |
| 72 | 11190 | 1 | | | |
| 74 | 14246 | 1 | | $D_{3h}$ | $D_{3h}$ |
| 76 | 19151 | 2 | 1 ($D_2$) | 1 ($D_2$), 2 ($T_d$) | 1 ($D_2$), 2 ($T_d$) |
| 78 | 24109 | 5 | 1 ($D_3$), 2 ($C_{2v}$), 3 ($C_{2v}$) | 5 ($D_{3h}$) | 1 ($D_3$), 2 ($C_{2v}$), 3 ($C_{2v}$), 5 ($D_{3h}$) |
| 80 | 31924 | 7 | 1 ($D_{5d}$), 2 ($D_2$) | 1 ($D_{5d}$), 3 ($C_{2v}$), 5 ($C_{2v}$), 6 ($D_{5h}$), 7 ($I_h$) | 2 ($D_2$), 5 ($C_{2v}$) |
| 82 | 39719 | 9 | 3 ($C_2$) | 5 ($C_2$), 6 ($C_s$), 7 ($C_{3v}$), 8 ($C_{3v}$), 9 ($C_{2v}$) | 3 ($C_2$), 5 ($C_2$) |
| 84 | 51592 | 24 | 4 ($D_{2d}$), 5 ($D_2$), 11 ($C_2$), 13 ($C_2$), 14 ($C_s$), 15 ($C_s$), 16 ($C_s$), 19 ($D_{3d}$), 22 ($D_2$), 23 ($D_{2d}$), 24 ($D_{6h}$) | 7 ($C_{2v}$), 10 ($C_s$), 11 ($C_2$), 12 ($C_1$), 13 ($C_2$), 19 ($D_{3d}$), 23 ($D_{2d}$) | 4 ($D_{2d}$), 5 ($D_2$), 11 ($C_2$), 16 ($C_s$), 18 ($C_{2v}$), 22 ($D_2$), 23 ($D_{2d}$) |
| 86 | 63761 | 19 | 16 ($C_s$), 17 ($C_2$) | 19 ($D_3$) | 16 ($C_s$), 17 ($C_2$) |

Thus, as noted above, following the isolated pentagon rule does not indicate the possibility of practical preparation of some fullerene isomer. Obeying this rule is a necessary but not a sufficient condition: not all IPR isomers have been synthesized, as some of them are unstable. In view of this finding, one can formulate the following stability criterion for hollow fullerene molecules: those fullerenes are stable that have a closed-shell electronic configuration, meet the isolated pentagon rule and have no local overstress produced by fused hexagons.

Meanwhile, many unstable fullerene isomers can be stabilized as endohedral or exohedral derivatives (see, for example, Refs 4, 115–119).

The conducted analysis allowed us to propose a fullerene classification based on their structure, meeting the isolated pentagon rule and reasons for stability/instability. All fullerenes can be divided into two major groups (Fig. 12): pristine fullerenes $C_n$, including homofullerenes and heterofullerenes, and their derivatives, either endohedral $M@C_n$ (M is a metal cation, metal cluster, molecule and so on) or exohedral $C_n X_m$ (X is an addend attached to the fullerene cage on the outside). All pristine fullerenes are further classified into two groups:

— fullerenes with $n < 60$ (lower fullerenes, *e.g.*, $C_{20}$, $C_{28}$ and so on); they all do not obey the IPR;

— fullerenes with $n \geqslant 60$ (higher fullerenes). They are, in turn, subdivided into IPR and non-IPR ones.

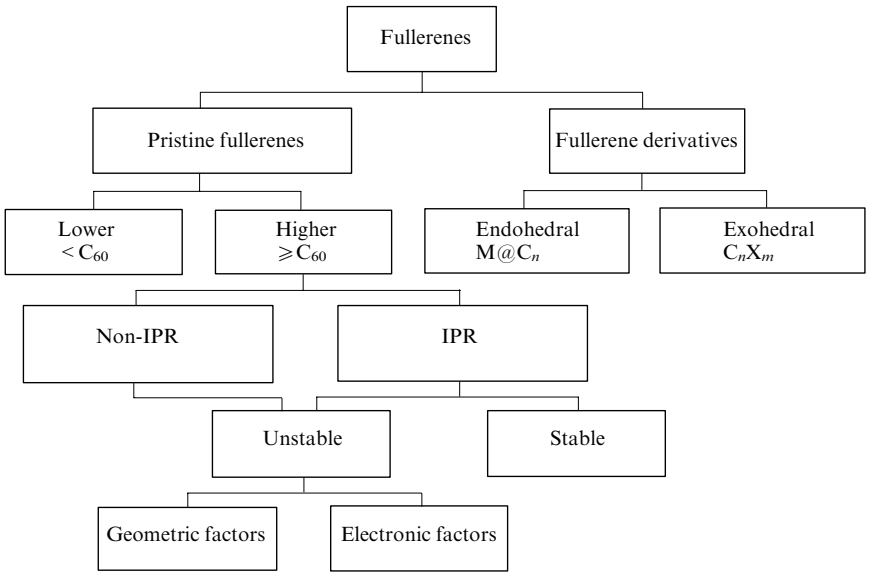



**Figure 12.** Classification of fullerenes.

All IPR fullerenes can be split into two groups: stable (that have already been prepared or can be prepared) and unstable ones, which are subdivided into those unstable because of local overstrain (geometric factors) and radical fullerenes (electronic factors).

* * *

Analysis of the geometric and electronic structures of all unstable, although IPR, isomers of higher fullerenes in the $C_{72}-C_{86}$ series in the neutral ground state under normal conditions made it possible to classify them into two groups. The first group (fullerene $C_{74}$ group) includes fullerenes the instability of which is mainly determined by the electronic structure, namely, by the presence of unpaired electrons in the molecule, *i.e.*, by an open-shell electronic configuration.

The instability of second group fullerene molecules (fullerene $C_{72}$ group) is related to local overstrain caused by geometric factors. These are closed-shell molecules characterized by large substructures consisting only of hexagons and introducing substantial local strain.

The instability of a fullerene may be caused by both factors, as for example, is the case for isomer 7 ($C_{3v}$) of fullerene $C_{82}$ and isomers 1 ($C_1$) and 10 ($C_{2v}$) of fullerene $C_{86}$.

The set of features characteristic of stable fullerenes (the presence of substructures inherent in stable fullerenes, closed-shell electronic configuration, uniform distribution of hexagons and pentagons over the molecular cage and low total energy values) suggest that it is possible, in principle, to experimentally obtain some isomers, for example, isomer 5 ($D_{3h}$) of fullerene $C_{78}$, isomers 1 ($C_2$), 2 ($C_s$), 4 ($C_s$), 5 ($C_2$) and 6 ($C_s$) of fullerene $C_{82}$ and isomers 6 ($C_{2v}$), 7 ($C_{2v}$), 12 ($C_1$), 17 ($C_{2v}$), 18 ($C_{2v}$) and 21 ($D_2$) of fullerene $C_{84}$.

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