The numbers of isomers in icosahedral fullerene \( C_{60} \) and \( C_{g0} \) series have been enumerated by applying Polya's theorem and analysing symmetries of their molecular frameworks. Cycle indices have been deduced for chiral and achiral derivatives. Program operating with polydigital numbers have been applied to calculate numbers of isomeric derivatives up to \( C_{540} \).

Buckminsterfullerene (Buckyball) \( C_{60} \) made a stir in the XX century. It was called "the most beautiful molecule" [1] and is worthy of this name. It has a nearly spherical molecule of the icosahedral point group \( k \) with 120 symmetry operations.

Buckyball has a lot of relatives that form the fullerene family. This term is assigned to carbon molecules \( C_n \) with so-called isolated pentagon cycles arranged between hexagons on the cage surface, which means that any couple of pentagons is separated by at least one hexagon. Buckminsterfullerene is the simplest fullerene.

Enumeration of isomers arising by addition to, or substitution in, a basic framework is a mathematical problem with many practical applications in chemistry. Therefore, it is no wonder that such a problem as applied to carbon clusters interests both chemists and mathematicians. One of the most convenient methods for solving this problem is based on Polya's and related theorems [2—10]. Thus, Balasubramanian [8—10] has enumerated the isomers of polysubstituted fullerene cages by using the cycle index of the rotational subgroup of the point group of the fullerene cage under consideration.
Other methods of isomer counting of carbon clusters have also been used. Brocas [11] has presented a systematic enumeration of dodecahedrane derivatives, which is based on double cosets and framework groups. Hfsslebarth [12] has reported an alternative method that is based on tables of marks. Mead [13] has presented an alternative method and compared above methods by using common problems.

Fujita [14,15] has reported a systematic enumeration of chemical structures derived from dodecahedrane and soccerane skeletons (7/0) in terms of unit subduced cycle indices.

The classification of the simplest fullerenes based on symmetry of their molecules and isomer counting has been described for some simplest cases in [16]; the structures were confined by C_84 and the pencil-and-paper counting method was applied. There is no doubt automatized calculations give the results quicker and more reliable. Isomer counting in all the series presented in this paper is practically impossible without computers.

I. Vertex substitution of fullerenes
1. Some general principles of structural (position) isomers calculation.

If we consider the most symmetrical structural isomers of fullerenes with icosahedral symmetry of the group Ih (IIF) we cannot avoid the yet unknown but highly possible molecule C_{20} with the dodecahedron skeleton on a purely formal basis. It has to be considered as the simplest carbon structure of h symmetry. In fact it is starting the first series of IIF’s of the common formula C_{106}ρ, where ρ = 1, 2, 3, C_{20}, C_{80}, C_{180}, C_{320}, C_{500}, etc.

The main structural feature of the first series lies in the fact that each couple of the nearest pentagon cycles is separated by p-1 hexagon cycles combined in the linearly annelated ensembles:

\[
Z_2(C_{20p}) = \frac{1}{120} \left( f_2^{20p^2} + 15 f_1^{4p} f_2^{10p^2-2p} + 16 f_2^{10p^2} + 20 f_3^{2p} + 24 f_5^{4p} + 20 f_6^{8p^2} + 24 f_7^{10p^2} \right) \tag{1}
\]

If ρ is not divisible by 3 (type Z_3: C_{15}, C_{30}, C_{225}, C_{555}, C_{995} etc.), the cycle index has the form (2):

\[
Z_2(C_{20p}) = \frac{1}{120} \left( f_2^{20p^2} + 15 f_1^{4p} f_2^{10p^2-2p} + 16 f_2^{10p^2} + 20 f_3^{2p} + 24 f_5^{4p} + 20 f_6^{8p^2} + 24 f_7^{10p^2} \right) \tag{2}
\]

The second series of IIF’s starts with the C_60-buckminsterfullerene and has the common formula C_{106}A where m = 1, 2, 3, ..., (C_{60}, C_{240}, C_{360} etc.). In this series each couple of the nearest pentagon cycles is separated by p-1 hexagon cycles combined in the para-phenylene-like ensembles:

This kind of IIF’s structural isomers has the cycle index (3):

\[
Z_3(C_{60m}) = \frac{1}{120} \left( f_1^{60m^2} + 15 f_1^{4m} f_2^{30m^2-2m} + 16 f_2^{10m^2} + 20 f_3^{20m^2} + 24 f_4^{6m^2} + 24 f_5^{10m^2} \right) \tag{3}
\]

The numbers of isomers formed by adding one or more couples of hydrogens or other atoms to the fullerene skeleton (for example, C_{60}H_2 or C_{60}Cl_4), substituting heteroatoms for carbons (for example, C_{79}Si or C_{78}N_22+) or substituting other atoms or groups for hydrogens in fully hydrogenated fullerenes (for example, C_{60}H_{58}Cl_2), can be calculated by the standard substitution of \((1+x^m)^n\) for \(f_2\) into the formulae (If-3), which gives the generating functions. Here is the beginning of the generating functions for C_{60} and C_{80}:

\[
P(C_{60}) = \sum a_{ij}x^i = 1 + x + 23x^2 + 303x^3 + 4190x^4 + 45718x^5 + 418470x^6 + 3220218x^7 + ...
\]

\[
P(C_{80}) = \sum a_{ij}x^i = 1 + 2x + 40x^2 + 732x^3 + 13506x^4 + 201230x^5 + 2508958x^6 + 26484548x^7 + ...
\]

The coefficients \(a_{ij}\) of above generating functions correspond to the numbers of structural isomers of fullerene addition-products or their heteroanalogues. For example, there may be 2 theoretically possible structural isomers of C_{60}Si, 40 dications C_{25}N_21+, 732 trications C_{28}N_32+, 23 structural isomers of C_{30}H_{24}Cl, 4190 isomers of C_{60}Cl, or 303 isomers of C_{60}H_{58}Cl_2. The coefficients \(a_{ij}\) were calculated with the help of a special
program operating with large polydigital numbers. It is obvious that the pencil-and-paper method would not work here.

If we need to calculate the numbers of isomers for the cases of different substituents or different heteroatoms we have to substitute \((1 + x^m + y^m + \ldots)^n\) for \(f_n\) in the cycle indices formulae (1) — (5). It is not so simple a procedure as to use the pencil-and-paper method but the computer program works here too.

2. Stereoisomerism of fullerenes.

Until now we had not taken into account the stereoisomerism of fullerenes. Actually, some of structural isomers are chiral, others are not. The total number \(S_n\) of stereoisomers includes \(Q_n\) couples of chiral and \(R_n\) achiral structures, i.e. \(S_n = Q_n + R_n\), while the number of structural isomers that do not take into account the IF’s stereoisomerism, is \(P_0\). Thus, \(Q_n = S_n - P_n\). It may be shown that chirality is the reflection of the corresponding molecular polygon symmetry. The IF’s stereoisomers produce a symmetry group of rotations \(I\) that has half as many symmetry operations (60) as the IF’s structural isomers with their group \(I_h\) (120 symmetry operations). The corresponding cycle indices are the following:

\[
Z_4(C_n) = \frac{1}{60} \left( f_n + 15 f_3^2 + 20 f_5^3 + 24 f_7^3 \right),
\]

if \(n\) is divisible by 3, and

\[
Z_5(C_n) = \frac{1}{60} \left( f_n + 15 f_3^2 + 20 f_5^3 + 24 f_7^3 \right),
\]

if \(n\) is not divisible by 3.

II. Edge substitution of fullerenes

As it has been above shown (see 1.1) there are two series of structural isomers of IF’s with the common formulae \(C_{20}P_2\) and \(C_{60}m_2\). Their cycle indices of edge substitution are following:

\[
Z_6(C_{20p_2}) = \frac{1}{120} \left( f_{10p_2}^2 + f_{20p_2}^3 + 15 f_3^{10p_2} + 15 f_4^{10p_2} + 15 f_5^{10p_2} + 15 f_6^{10p_2} + 15 f_7^{10p_2} + 15 f_8^{10p_2} + 15 f_9^{10p_2} + 15 f_10^{10p_2} \right),
\]

and

\[
Z_7(C_{60m_2}) = \frac{1}{120} \left( f_{30m_2}^2 + f_{45m_2}^3 + 15 f_3^{30m_2} + 15 f_4^{30m_2} + 15 f_5^{30m_2} + 15 f_6^{30m_2} + 15 f_7^{30m_2} + 15 f_8^{30m_2} + 15 f_9^{30m_2} + 15 f_{10}^{30m_2} \right),
\]

The cycle indices for stereoisomers of IF’s take the form:

\[
Z_8(C_n) = \frac{1}{60} \left( f_e^2 + 15 f_3^2 + f_5^2 + 20 f_7^3 + 24 f_9^3 \right),
\]

where \(e\) is the number of edges in the fullerene.

Edge substitution of fullerenes takes place when oxygen or methylene group bridges an edge, or in hypothetical expanded cages where a fullerene -C—C edge becomes -C=C=C—C linkage [17] etc. Addition reactions of fullerenes, for example, the reduction through hydrogenation can also be considered as edge substitution as by the reaction double bonds transform into single ones. As attachment occurs only at formal double bonds of fullerenes, the corresponding modified cycle indices of IF structural isomers assume the form:

\[
Z_6'(C_{20p_2}) = \frac{1}{120} \left( f_{10p_2}^2 + f_{20p_2}^3 + 15 f_3^{10p_2} - 4 f_2^{10p_2} - 2p_2^2 + 15 f_4^{10p_2} f_2^{10p_2} - 2p_2^2 + 15 f_5^{10p_2} f_2^{10p_2} - 1 + 15 f_6^{10p_2} f_2^{10p_2} + 24 f_3^{10p_2} + 24 f_5^{10p_2} + 24 f_7^{10p_2} + 24 f_9^{10p_2} \right),
\]

if \(\rho\) is divisible by 3;

\[
Z_7'(C_{60m_2}) = \frac{1}{120} \left( f_{30m_2}^2 + f_{45m_2}^3 + 15 f_3^{30m_2} + 15 f_4^{30m_2} + 15 f_5^{30m_2} + 15 f_6^{30m_2} + 15 f_7^{30m_2} + 15 f_8^{30m_2} + 15 f_9^{30m_2} + 24 f_4^{30m_2} + 24 f_5^{30m_2} + 24 f_6^{30m_2} + 24 f_7^{30m_2} + 24 f_8^{30m_2} + 24 f_9^{30m_2} + 24 f_{10}^{30m_2} \right),
\]

If only double bonds are taken into account, the cycle indices for stereoisomers of IF’s depend on \(\rho\) value (here \(d\) is the number of double bonds):

\[
Z_8'(C_n) = \frac{1}{60} \left( f_e^2 + 15 f_3^2 + f_5^2 + 20 f_7^3 + 24 f_9^3 \right),
\]

when \(\rho\) is divisible by 3.

In case \(C_{20p_2}\) of fullerenes where \(\rho\) is not divisible by 3 introduction of formal double bonds reduces the symmetry of structures, and their cycle indices of edge substitution for double bonds will not be here considered.

III. The action of a group of symmetries \(I_h\) and a group of rotations \(I\) on a set of fullerene vertices

The \(I_h\) symmetry group is a symmetry group of fullerenes \(C_n\) (\(n\) is the number of carbon atoms) at the uniform distribution of 5-faces on the fullerene surface. This is the case when \(\eta = 60m^2\) or \(\eta = 20p^2\), where \(m, p\) are natural numbers. The \(h\) group has the icosahedral subgroup of rotations of order 60.

Here is a pel-by-pel description of the elements of above groups (see also Table 1).

1. The neutral element of \(D\) and \(I\) groups does not move any vertex; it is a product of \(\eta\) cycles of length 1.

2. Inversion which is an element of \(I_h\) group reflects each fullerene vertex into its diametrically opposite one. The inversion is a product of \(n/2\) cycles of length 2.

3. Each of 15 rotations by the angle 180° defines the symmetry axis that passes through the middles of the opposite edges; 15 corresponding elements of \(D\) or \(I\) groups are products of \(n/2\) cycles of length 2.
4. Each of 24 rotations by angles divisible by 72° defines in their totality 6 axes of rotations by these angles which pass through centres of the opposite fullerene 5-faces; each of 24 corresponding elements of $D$ or $/\$ groups is a product of $n/5$ cycles of length 5.

5. Each of 20 rotations by the angles divisible by 120° defines in their totality 10 axes of rotations by these angles which pass through a couple of diametrically opposite points — centres of triangles the vertices of which are centres of the nearest fullerene 5-faces; each of 20 corresponding elements of $//, /, /$ groups are products of $n/3$ cycles of length 3 in case $\eta = 60m^2$ or $\eta = 20p^2$, where $p$ is divisible by 3 and is a product of two cycles of length 2 and $(n-2)/3$ cycles of length 6 in case $\eta = 20p^2$, when $p$ is not divisible by 3.

6. Each of 15 symmetry operations relative to the plane reflects each of fullerene vertices into the symmetrical one relative to the plane, each plane passing through 4m fullerene vertices when $\eta = 60m^2$ and through 4p fullerene vertices when $\eta = 20p^2$. Each of 15 corresponding elements of $I$ group is a product of 4m cycles of length 1 and 30m — 2m cycles of length 2 in case $\eta = 60m^2$ or 4p cycles of length 1 and 10p — 2p cycles of length 2 in case $\eta = 20p^2$.

7. Each of 24 mirror rotations by angles divisible by 72° is a consecutive execution of the inversion and rotation described above; elements of $I_s$ group are products of $n/10$ cycles of length 10.

8. Each of 20 mirror rotations by angles divisible by 120° is a consecutive execution of the inversion and rotation described above; each of 20 corresponding elements of $Ih$ group is a product of $n/6$ cycles of length 6 in case $\eta = 60m^2$ or $\eta = 20p^2$, where $\rho$ is divisible by 3 and is a product of two cycles of length 2 and $(n-2)/6$ cycles of length 6 in case $\eta = 20p^2$, when $\rho$ is not divisible by 3.

Summary

The isomer numbers of fullerenes can be calculated on the basis of cycle indices of their molecular frameworks. The cycle indices result from the analysing frameworks symmetries. Cycle indices of vertex and edge substitution for fullerenes of $Ih$ symmetry have been developed and generalized. It has been shown that there are two series of structural isomers of fullerenes with the common formulae $C_{60m^2}$ and $C_{50n2}$ which form icosahedral $I_s$ symmetry group. The stereoisomers of fullerenes belong to icosahedral $I$ subgroup. The standard transformation of the cycle indices into generating functions results in the values of structural isomers or stereoisomers of fullerenes. Chiral and achiral derivatives have been counted separately.

### Table 1. The terms in the cycle indices.

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### Table 2. Buckminsterfullerene $C_{60}$ and its isomers of vertex substitution

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<th>N</th>
<th>stereoisomers (chiral and achiral isomers)</th>
<th>structural (position) isomers</th>
<th>chiral isomers (enantiomer pairs)</th>
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Table 3. $C_{60}$ and its isomers of vertex substitution
(N — the number of substituents).

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