Investigation of the structure and properties of several endohedral clusters and generalization of the concept of molecular topological form

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The problem of structural characterization of nanoparticles and endohedral clusters is discussed. The concept of molecular topological form introduced earlier for the description and classification of stereochemical configurations of organic molecules is generalized. The proposed definition is illustrated taking the $Cr(CO)_3(C_6H_6)$ complex and onion carbon clusters as examples. Topological and geometric characteristics of several multilayer fullerenes are discussed. A basis of invariants for molecular graphs of the icosahedral onion $C_{60}@C_{240}@C_{540}$ cluster was found. This type of basis can be used for estimations of physicochemical properties of multilayer fullerenes in the topological approximation and for calculations of different topological indices. The results of MNDO/PM3 simulation of molecular and electronic structure of a hypothetical endohedral $C_{20}@C_{60}$ cluster are reported.

Key words: carbon clusters, fullerenes, endohedral complexes, molecular topological form; molecular graphs, quantum-chemical calculations, MNDO/PM3 method.

The discovery of new allotropic modifications of carbon consisting of polyhedral molecules, fullerenes,[1,2] followed by studies of properties of various carbon materials showed that there are spheroidal particles built of encapsulated fullerene molecules with different numbers of atoms.[3–6] The structure of such clusters is similar to that of the Russian "matryoshka" dolls or onions; for this reason, they are called onion (or multilayer) fullerenes.[4] It was established that multilayer fullerenes can be formed under different conditions: upon combustion of graphite rods in carbon arc,[3] upon irradiation of graphite by electron beam,[4] upon combustion of hydrocarbons,[5] and upon annelation of ultradisperse diamond.[6] Onion-like carbon particles were found in meteorites.[7] It is also assumed that they can exist in the interstellar dust.[8]

The structure of onion fullerenes is not known with certainty. However, the distance between neighboring encapsulated molecules in such particles must be close to interlayer separation in graphite (~3.35 Å).[9] This imposes restrictions on the size of fullerenes that can be encapsulated. For instance, icosahedral C_n fullerenes built only of five- and six-membered rings can form an onion cluster of composition $C_{60}@C_{240}@C_{540}@C_{960}$ (1) (the symbol @ in expressions of the $M@C_n$ type denotes that an M species is inside the C_n polyhedral cluster).

It should be noted that the space between encapsulated C_n molecules as well as the C_n cages can be filled with impurity atoms or ions. For instance, the first endohedral complex of C_{60} obtained experimentally was a $La@C_{60}$ complex,[10] in which a lanthanum atom was inside the carbon framework. Currently, various endohedral complexes of higher fullerenes have been synthesized, *e.g.*, $Ca@C_n$ (n = 72, 74, 76), $Sc_2@C_{84}$, $Cd@C_{82}$, *etc.*[11] In principle, onion systems in which individual layers are built of polyhedral clusters of other elements can also exist. For instance, a double-layer $(SiC)_{60}$ cluster was calculated by the MNDO/PM3 method.[12] Sixty silicon atoms constitute the outer layer of this cluster and are chemically bonded to carbon atoms of fullerene C_{60} constituting the inner layer.

The properties of onion carbon nanoparticles and endohedral complexes of the type $M@C_n$ are dependent on both the structure of outer carbon cages and the nature of species inside the cages. However, it is difficult to predict the properties of onion fullerenes using quantum-chemical methods because of the large number of atoms constituting this type of systems (a total of 1800 atoms in cluster 1!). In this connection the approaches using topological indices take on great significance in attacking the "structure—property" problem for endohedral clusters. One should keep in mind that nanoparticles similar to complex 1 have a non-classical structure, which cannot be described in the topological approximation in terms of the only Schlegel diagram. An

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analogous problem concerned with pictorial description of structure also arises in the case of highly branched molecules, *e.g.*, dendrimers. Because of this, the problem of correct structural characterization of this type of particles becomes topical.

In this work, we propose a method of attacking this problem, based on generalization of the concept of molecular topological form (MTF) introduced[13] in order to describe stereochemical configurations of organic molecules. We illustrate its descriptive potentialities taking a tricarbonyl(benzene)chromium complex and a $C_{60}@C_{240}@C_{540}$ onion cluster as examples. We studied the topological properties of the latter and estimated selected geometric characteristics of its constituent fullerenes (their diameters, surface areas, and volumes). In addition, we report geometric and energy characteristics of a model endohedral $C_{20}@C_{60}$ cluster calculated by the MNDO/PM3 method[14] using the GAMESS program[15] on a DEC 3000 Alpha AXP-400X workstation.

Results and Discussion

Generalization of the concept of molecular topological form (MTF). According to the MTF definition,[13] a molecule was considered as a point set $\mathfrak{N}$ in the three-dimensional space, and the coordinates of the points of this set corresponded to the coordinates of the nuclei of the atoms constituting the molecule at a given instant. Then, a convex hull $\aleph$ of the set $\mathfrak{N}$ was constructed, which was called the molecular topological form generated by the set of the nuclei of the atoms constituting the molecule under study. In the general case, an MTF is a convex polyhedron (CPH). If all points of the set $\mathfrak{N}$ lie in the same plane or on the same straight line, then the MTF is respectively a convex polygon (CPG) or a line segment. Two MTFs are considered to be equivalent if they are homeomorphic in the topological sense, *i.e.*, if they contain the same number of vertices between which a one-to-one correspondence with retention of the adjacency relation can be established.

Let us assume that, according to the above definition, an MTF $\aleph = \aleph_0$ is constructed for the molecular system (MS) under study. Then the nuclei of all atoms constituting the molecule can be divided into two groups. The first group comprises the atomic nuclei arranged on the faces of the MTF $\aleph_0$ (the positions of certain of these points can coincide with none of the vertices of the $\aleph_0$ polyhedron). The second group comprises the nuclei of all atoms that are inner atoms with respect to the MTF $\aleph_0$. Let us denote by $\aleph_1$ a convex hull of the set of the points corresponding to the nuclei of the inner atoms. It was mentioned above that, in the general case, such a convex hull is a CPH or a CPG. Using the procedure described above, let us subdivide the points of the set $\aleph_1$ into two groups comprising respectively the points arranged on the faces of $\aleph_1$ and the inner points. This makes it possible to construct yet another CPH, $\aleph_2$. By repeating this procedure we get a finite sequence of embedded convex sets:

$$\aleph_0 \supset \aleph_1 \supset \aleph_2 \supset \ldots \aleph_{k-1} \supset \aleph_k. \qquad (1)$$

If $k \geq 1$, then $\aleph_k$ either contains no points of the set $\mathfrak{N}$ within or degenerates into a line segment (possibly, into a point). We call the MTFs $\aleph_k$ and $\aleph_0$ the central and the outer convex polyhedra, respectively. It should be noted that each convex polyhedron $\aleph_i$ ($i = 0, 1, \ldots, k$) can be chiral or achiral. The total number of chemical bonds between the atoms arranged on the surfaces of convex polyhedra $\aleph_i$ and $\aleph_{i+1}$ is called connectedness of two adjacent convex polyhedra. Therefore, the sequence (1) can be associated with a connectivity graph, which is a linear multigraph with $k + 1$ vertices. Each vertex v_i corresponds to one of the convex polyhedra $\aleph_i$. We say that two vertices, v_i and v_{i+1}, are connected by an edge if the corresponding convex polyhedra are adjacent. The (v_i, v_{i+1}) edge multiplicity reflects the connectednesses of the two convex polyhedra. Each element $\aleph_i$ of the sequence (1) can be characterized by its topological characteristics, *e.g.*, the topological dimension and the number of vertices and faces.

Now we introduce the following definition: we call the sequence (1) a *generalized molecular topological form* (GMTF) generated by the MS under study. In general, the GMTF structure is dependent on the conformation of the molecular system. Two conformations are called equivalent if they can be transformed into each other using a transformation considered as a continuous change of the coordinates of the atomic nuclei such that it occurs with retention of the topological equivalence and the connectednesses of all convex polyhedra $\aleph_i$. The set of equivalent conformations of the MS is called the *generalized configuration* of the MS. In other words, the generalized configuration of the MS is an invariant of its GMTF.

The convex polyhedra $\aleph_i$ corresponding to fixed positions of the nuclei can be described using different geometric characteristics, *e.g.*, the volume, the surface area, the surface areas of individual faces, and the distances between the faces. One can evaluate the linear size of the molecular system using the distance $r_{\max}$ between the most distant vertices of the $\aleph_0$ CPH.

Let us assume that an *i*th component of the GMTF is a CPH and that a segment connecting the most distant vertices of the CPH is inside this polyhedron. Let us construct a sphere of radius $r_{\max}/2$ with the center at the midpoint of this segment. We denote by r_s the longest distance between the points of the CPH and the sphere; then the degree of asphericity of the CPH can be evaluated using the parameter $(r_{\max} - 2r_s)/r_{\max}$.

If the structure of an MS under study is described by a molecular graph, the size of the MS can be characterized in topological terms using the definition of the distance between the vertices of a graph.

Each CPH $\aleph_i$ naturally generates a graph G_i whose vertices and edges correspond respectively to those of the CPH $\aleph_i$. The graph G_i can be considered as a weighted molecular graph. The weighting factor of a vertex can be assigned a specific meaning, *e.g.*, the effective volume of the corresponding atom or its effective charge.

Basis of topological invariants for GMTF. A basis of invariants can be found for the set of graphs $\{G_i\}$ (i = 0, ..., k) generated by the GMTF (1). The values of any topological indices of graphs G_i can be represented as linear combinations of these invariants. Such a basis can be constructed as follows.

Let us choose a subgraph H_i for each graph G_i. Let G be an arbitrary graph, $g_i(G)$ be an invariant of G equal to the occurrence number of the subgraph H_i in G, and **B** be a square $(k+1)\times(k+1)$ matrix with elements $b_{ij} = g_j(G_i)$. It can easily be shown that one can always choose subgraphs H_i such that det**B** $\neq 0$.[16] Then any invariant f on graphs $\{G_i\}$ is uniquely represented in the form

$$f(G_i) = \Sigma a_j(f) g_j(G_i), \qquad (2)$$

where the coefficients $a_j(f)$ are dependent on the invariant f only. For instance, the graphs shown in Fig. 1 can be chosen as subgraphs H_i in the case of the $C_{60}@C_{240}@C_{540}$ onion cluster consisting of fullerene molecules with I_h symmetry and built only of five- and six-membered rings. In this case, the matrix **B** is a nondegenerate triangular matrix and each of its diagonal elements is equal to 12. This number coincides with the number of pentagons in the polyhedral structure of fullerenes built only of pentagons and hexagons. The approach described above can be used for improving the method of topological indices[17] used in finding the "structure—property" correlations for onion clusters and molecules of a rather complex structure.

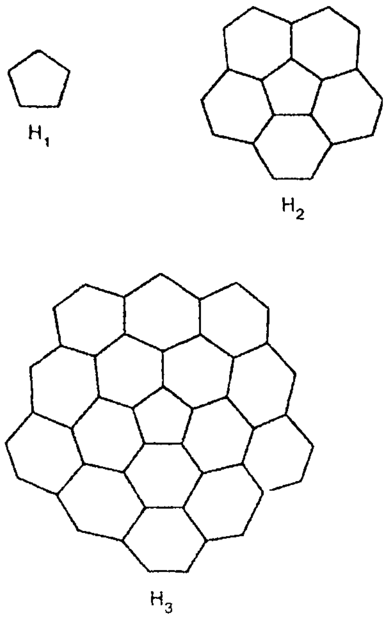

Fig. 1. Subgraphs H_i (i = 1, 2, 3) of graphs generated by C_{60}, C_{240}, and C_{540} clusters.

Geometric characteristics of convex polyhedra. The effective volume V_i of a CPH $\aleph_i$ corresponding to fixed positions of the nuclei can be defined as the volume of a convex body in the three-dimensional space. Then, V_0 and V_j can be respectively called the volume of the molecular system and the volume of jth CPH. The V_k value is equal to the volume of the central CPH determining the size of the inner cavity of the molecule (if such exists). Using a sequence of convex polyhedra $\aleph_i$ (i = 0, ..., k) analogous to that described above, one can perform a detailed analysis of the topological and geometric structure of rather complex molecular systems. In Fig. 2, the $\aleph_0$ and $\aleph_i$ convex polyhedra generating the GMTF of the $Cr(CO)_3(C_6H_6)$ complex are shown as an example. It should be emphasized that the sequence of embedded convex polyhedra complemented with structural and topological information is best suited to the description of the structure of multilayer (onion-like) fullerenes.

Selected properties of onion structures. The properties of onion carbon clusters can be investigated either in the topological approximation or by considering the geometric characteristics. It is of interest to compare the two approaches taking the simplest systems as an example.

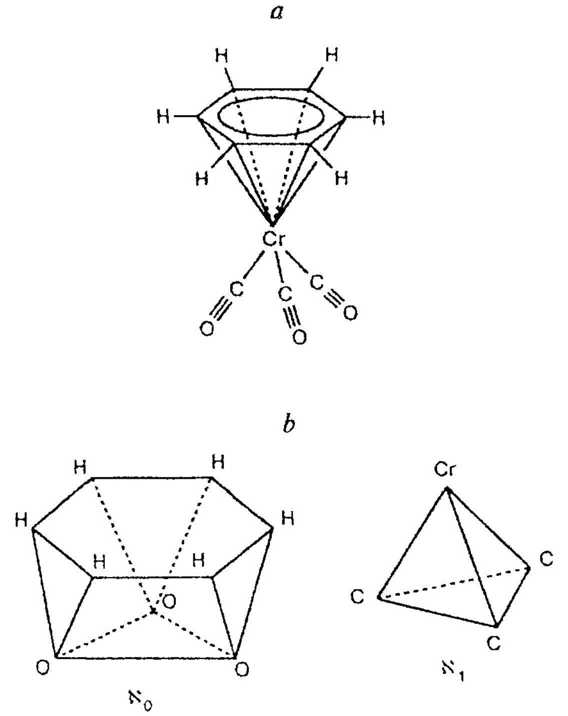

Fig. 2. Structure of tricarbonyl(benzene)chromium (*a*) and its generalized molecular topological forms $\{\aleph_0, \aleph_1\}$ (*b*).

In the topological approximation, the π-electron spectra of multilayer fullerenes are combinations of the π-electron spectra of individual layers. Let $l_{\min}(i)$ and $l_{\max}(i)$ denote respectively the lowest and the highest occupied (in the ground state) π-electron energy level of an ith fullerene onion cluster. Then all occupied π energy levels of the ith fullerene lie on the line segment of length $\sigma(i) = [l_{\min}(i), l_{\max}(i)]$. Since the extension of the π-electron system decreases as i increases, in the regular case the $\sigma(i)$ values should form a decreasing sequence of embedded line segments $\sigma(0) \supset \sigma(1) \supset \sigma(2) \supset \ldots \sigma(k)$. Because of this, in the topological approximation the structure of the upper region of the filled π-band in the spectrum of a multilayer fullerene is determined by the properties of the π-electron spectrum of the outer layer. It should be emphasized that in this approximation the topological indices of onion clusters are calculated separately for each layer. However, taking into account the interaction between different shells may violate the additivity of properties.

We present the results of our MNDO/PM3 calculations of a hypothetical double-layer $C_{20}@C_{60}$ (D_{5d}) system (Fig. 3) carried out assuming symmetry conservation. A local minimum was found on the corresponding potential energy surface. This minimum is characterized by a rather high specific heat of formation (49.5 kcal mol^{-1} per atom), which is about 30 kcal mol^{-1} higher than the specific heat of formation of noninteracting I_h-C_{60} and D_{5d}-C_{20} clusters. An isolated C_{20} cluster with D_{5d} symmetry has a closed electron shell, $E_{\text{HOMO}} = -9.2$ eV, and $E_{\text{LUMO}} = -4.0$ eV. In the case of cluster C_{60}, these energies are −9.5 and −2.9 eV, respectively. In the endohedral $C_{20}@C_{60}$ cluster the HOMO energy increases by about 2.4 eV, whereas the LUMO energy is close to that of the C_{20} cluster. It should also be noted that the inner C_{20} cluster undergoes compression, which manifests itself in shortening of the C—C bonds down to 1.38—1.39 Å. The volume of the outer fullerene increases: the lengths of several C—C bonds become equal to 1.60 Å. The interlayer separation is ~1.0 Å less than in graphite.

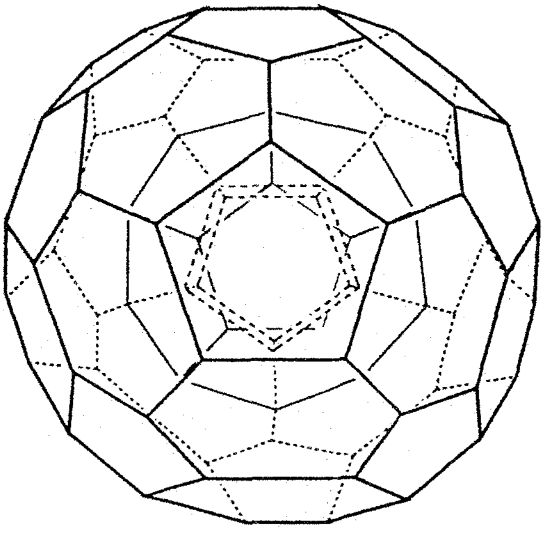

Fig. 3. Structure of the double-layer $C_{20}@C_{60}$ cluster.

In conclusion we present selected topological and geometric characteristics of a three-shell $C_{60}@C_{240}@C_{540}$ icosahedral cluster. The structure of this cluster is described by three convex polyhedra with I_h symmetry generated by σ-skeletons of corresponding fullerenes. The C_{60}, C_{240}, and C_{540} clusters are the first three members of a set of C_n fullerenes ($n = 60(m + 1)^2$, where $m = 0, 1, 2, \ldots$). In the π-electron approximation, these fullerenes have closed electron shells. These clusters each have 12 pentagons and two groups of hexagons, planar hexagons (arranged on the faces of corresponding truncated icosahedra) and curved hexagons (shared by two adjacent faces). The number of planar hexagons is $30m(m + 1) + 20$ and the number of curved hexagons is $30m$. The topological distance between the nearest pentagons is $(1 + 4m)$. Assuming that all C—C bonds are of the same length r, we get the following expressions for calculating the volumes of the fullerenes considered: $V(C_{60}) = 16.035r^3$, $V(C_{240}) = 153.48r^3$, and $V(C_{540}) = 1586.86r^3$. At $r = 1.42$ Å, the radii $R(C_n)$ of the spheres passing through the atoms of pentagons in the C_{60}, C_{240}, and C_{540} molecules are $R(C_{60}) = 3.52$ Å, $R(C_{240}) = 7.65$ Å, and $R(C_{540}) = 12.09$ Å.

Thus, in this work we proposed a method of detailed analysis of structure of nanoparticles of a rather complex structure. Such an approach seems to be the most fruitful for studying the structure and predicting the properties of onion carbon clusters.

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