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Quantum-Chemical Study of Endohedral Fullerenes

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Abstract—State-of-the-art in quantum-chemical research on endohedral fullerenes is considered. Separate chapters are devoted to complexes with noble gases, main group elements, and methals and their nitrides. The structures and the mechanisms of formation and decomposition of these compounds are highlighted. Applicability of various quantum-chemical methods for endohedral fullerene complexes is discussed. Problems associated with the use of the ROHF and UHF methods are revealed. The DFT method with hybrid functionals and effective core potentials for heavy atoms is shown to hold the greatest promise.

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INTRODUCTION

The discovery by Kroto et al. in 1985 [1] of the carbon cluster C_{60} in the mass spectra of graphite vapor, formed under laser irradiation, has initiated research into fullerenes—allotropic crystalline modifications of carbon, formed of hollow spheroidal molecules C_n. It however should be mentioned that such structures had been even earlier predicted by theoreticians. Thus Osawa [2] first alone in 1970 and then together with Yoshida [3] in 1971 discussed the possibility of existence of three-dimensional icosahedral carbon structures. They suggested a graphic image of the structure of fullerene C_{60} as a football ball. Bochvar and Gal'pern [4] were the first theoretical structural study of C_{60} by the Huckel method. The results of this and further works were summarized by the review of Stankevich et al. [5]. In 1980 Davidson [6] published a paper in which he made use of the graph theory to find a simplified algebraic solution for calculation of molecular orbitals of C_{60} and suggested that this molecule and its homologs possess three-dimensional aromaticity. The same conclusion was drawn by Haymet [7].

An interesting feature of fullerenes is that they can enclose various atoms and small molecules in their inner sphere. There are two types of endohedral fullerenes (Fig. 1). In the first case, the guest atom resides in the center of the carbon cavity, and the stabilizing factor here are electrostatic interactions; in the second case, stable endohedral fullerenes are formed due to covalent bonding of the guest atom with the carbon carcass. Of the greatest interest are complexes of the first type, since their enclosed atoms and molecules not infrequently exhibit unusual properties.

Experimental observation of endohedral fullerenes were first reported already 1985, i.e. in the same year as the discovery of fullerene had occurred. Kroto and co-workers [8] revealed the ability of the fullerene molecule to trap lanthanum atoms and detected in the mass spectra signals of the endohedral complexes La@C_{60} and La_2@C_{60}.

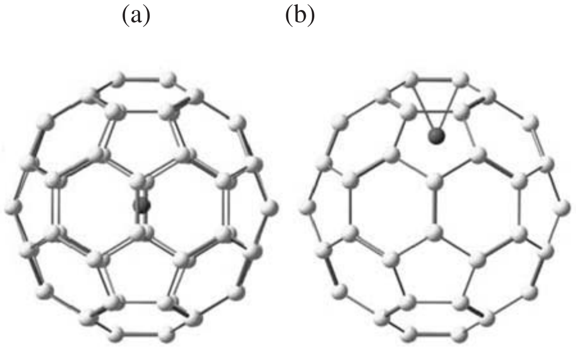


Fig. 1. Types of endohedral fullerenes: (a) with a cetrosymmetric guest atom and (b) with bonds between the guest atom and carbon cage.

Fullerenes and endofullerenes are quite difficult to prepare, and they can generally be isolated in less than milligram amounts; therefore, theoretical studies on this class compounds are quite urgent. This especially important for predicting properties of endohedral compounds whose experimental study is hindered by their high reactivity.

At present a great body of experimental and theoretical information on the structure and properties of fullerenes and their derivatives is available. These data are summarized in the monographs [9–12] and reviews [13–19]. Most of these works focus primarily on fullerene complexes with heavy metals. In the present review, aimed at systematizing theoretical results for endohedral fullerenes, we dwelt on quantum-chemical studies of the structure and properties of unsubstituted fullerenes with entrapped atoms and molecules. The state-of-the-art of quantum-chemical research on endohedral fullerenes which are of great interest in terms of design of materials for molecular electronics, hydrogen storage, etc., was described. The structures and the mechanisms of formation and decomposition of these compounds were discussed. It was shown that calculation results sometimes initiated preparation of new structures.

Complexes with Noble Gases

The mass spectral observation of endohedral fullerene with entrapped noble gases was first reported in 1991 [20–22].

Saunders et al. in 1994 prepared the complex He@C_{60} in trace amounts sufficient for NMR studies [23]. It should be noted that theoretical research on endohedral fullerenes doped with noble gases was initiated before their experimental detection [24–26]. The possibility of stabilization of noble gases inside the carbon cage was studied by ab initio calculations with the 4-31G basis set. According to the calculations, the guest atom in the Ne@C_{60} complex resides in the center of the carbon cage, and the complex is slightly destabilized (by 0.4 kcal mol^{-1}) with respect to its isolated components. Slight interaction of neon with the carbon frame was predicted. Vibration frequencies were calculated, which further allowed assignment of experimental IR spectra. Bug et al. [27] performed a molecular dynamics study of vibrations of the neon atom in Ne@C_{60}; therewith, for C–Ne and C–C interactions a series of empirical potentials were introduced. Nonlinear vibrations of the neon atom inside the cage with a frequency of about 90 cm^{-1} were revealed.

A molecular dynamics study of nonbonded intermolecular interactions in endohedral complexes of C_{60} and C_{70} with He, Ne, Ar, Kr, and X was reported by Pang and Brisse [28]. The formation energies of the endohedral complexes, determined by the Lennard–Jones model, were correlated by the packing densities of noble gases in the fullerene cage. The calculations showed that He and Ne can reside inside the C_{60} and C_{70} cages, whereas the complexes with larger atoms, such as Ar, Kr, and Xe, are less stable in view of the strong overlap of their van der Waals surfaces of the fullerene cage.

The formation energy and equilibrium constant of He@C_{60} were calculated by Patchkovskii and co-workers [29, 30]. It was found that the DFT method incorrectly predicts the stabilization energy of He@C_{60}, whereas ab initio calculations (with inclusion of electron correlation at the second-order Moeller–Plesset perturbation theory level with extended basis sets and inclusion of basis set superposition error (BSSE), results in a reasonable value of 2 kcal mol^{-1}. The calculated equilibrium yield of the complex at 900 K and 3000 atm is about 10%, whereas the experimental yield is much lower (0.1%). The referees concluded that the yield of the complex can be much improved by the use of suitable catalysts.

Shimshi et al. [31] suggested that the most probable mechanism of entrapment of atoms in the cage involves reversible cleavage of one or several carbon–carbon bonds to form a window through which guest atoms enter the fullerene cage (Figs. 2a and 2b). To check this suggestions, semiempirical (MNDO), ab initio (HF/3-21G), and DFT (BLYP/3-21G, BP86/3-21G) calculations were performed. The resulting energy characteristics of the entrance of helium through the window in the carbon cage proved to be close to each other (of about 220 kcal mol^{-1}). Calculations for a model complex HeC_6H_6 gave evidence showing that helium can enter through the center of the six-membered ring (Fig. 2c). It is surprising that the barriers to the reaction by this mechanism compare with each other and equal 240 kcal mol^{-1}. This circumstance with account for the fairly low level of calculations allowed no unambiguous conclusions in favor of one or another mechanism.

Sanville and BelBruno [32] resorted to the more sophisticated DFT calculations at the B3LYP/6-31G (d,p) level of theory to study the mechanism of entrance of noble gases in the fullerene cage. The objects for study were complexes X@C_{60}, where X = H, He, N, NO, P, and As. Like in the previous work, two ways of entrance of guest atoms in the fullerene cage were considered: direct entrance and via window formation. As found by calculations with partial geometry optimization, the energy barriers to entrance through the six-membered ring are 75, 253, 372, 552, 698, and 724 kcal mol^{-1} for H, He, N, P, As, and NO, respectively. Thus, the direct entrance mechanism is only possible with H, He, and N. The entrance via opening a window in the carbon frame was explored by semiempirical calculations at the PM3 level of theory. The resulting data point to the possibility of this mechanism with H and N.

Molecular mechanics was used to study the mechanism of interaction between fullerene C_{70} and noble gas atoms [33]. All exohedral X@C_{70} complexes (X = He, Ne, Ar, Kr, Xe) with the noble gas atom residing over six-membered rings are more stable that isomers with the noble gas atom over five-membered rings. At the same time, all endohedral complexes are preferred over the corresponding exohedral derivatives. According to calculations, the most stable is endofullerene Kr@C_{70}. The calculation results were compared with those in [28].

The stabilization energies of the complexes H_2@C_{60}, Ne@C_{60}, and N_2@C_{60}, obtained by DFT calculations with the MPWB1K and B3LYP functional, as well as ab initio MP2 calculations with varied basis sets [34] proved to diverge considerably (for Ne@C_{60}, 0.22–7.20 kcal mol^{-1}).

Chen et al. [35] performed a DFT (B3LYP/6-31G(d)) study of the structures of a series of small fullerenes (C_{20}, C_{24}, C_{28}, C_{32}, C_{36}, C_{40}, and C_{50}) and their helium complexes. To assess the degree of spherical electron delocalization, nucleus-independent chemical shifts (NICS) in the center of the carbon cage were calculated.

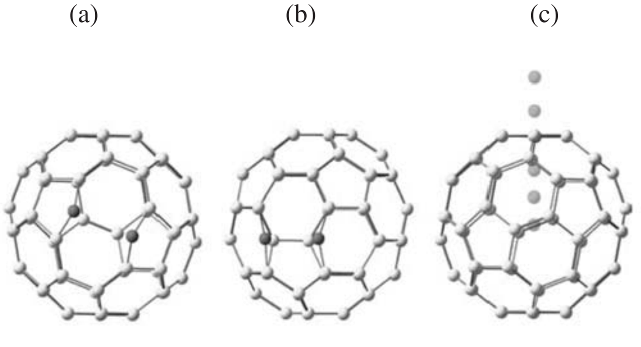


Fig. 2. Mechanisms of entrance of endo atoms into the fullerene cage: (a) window formation with 6.6 bond cleavage; (b) window formation with 5.6 bond cleavage; and (c) entrance of guest atom through the hexahedron center.

In [36] we studied the possibility of stabilization of endohedral complexes of the small fullerenes C_{20}, C_{24}, C_{30}, C_{32}, C_{40}, C_{50}, and C_{60} with the noble gases He, Ne, and Ar. The stabilization energies of various fullerene isomers and their complexes with noble gases were calculated by the DFT method with the 6-31G(d) and 6-311G(d) basis sets. It was shown that the geometry of helium endohedral complexes only slightly differs from the original geometry of the carbon cage, whereas replacement of the central atom (helium) by Ne and Ar increases the mean C–C bond length proportionally to the radii of these atoms to 0.05 Å in Ne@C_{20} and 0,12 Å in Ar@C_{20}. The calculated geometries of the fullerenes and their endohedral compexes were used to estimate the pressure exerted by guest atoms to the carbon shell. This parameter correlates with the general tendency of the complexes to stabilize with increasing size of the carbon polyhedron. A conclusion was thus drawn that endoherals He@C_n ($n \geq 20$), as well as Ne@C_n ($n \geq 30$) and Ar@C_n ($n \geq 40$) can be synthesized.

The simplest version of the Tomas–Fermi method and the DFT method in the B3LYP/6-311G(d) approximation were used to estimate [37] the excess energy (compared with the energy of a free X atom) of the endo atom in complexes X@C_n (X = He, Ne, Ar; n = 20–50). The energy capacity of these systems is primarily defined by the energy contribution by the compressed electron system of the encapsulated atom,

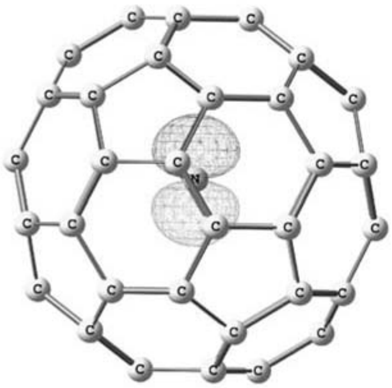


Fig. 3. View of one of the degenerate nitrogen 2*p* orbitals in N@C_{60}.

which is much higher than the energy contribution of the deformed fullerene carbon cage.

Complexes with Nonmetals

A characteristic feature of endohedral complexes of fullerene C_{60} with nonmetals is the chemical inertness of the encapsulated atom with respect to the fullerene shell. As known, the lifetimes of N@C_{60} and P@C_{60} are several hours, and the spin states of endo atoms are identical to those of the free atoms [38]. Therewith, the chemical stability in the inner surface of the fullerene sphere contrasts sharply with the high chemical activity of its outer surface which is readily modified in radical and molecular reactions.

Of particular interest are endohedral fullerene complexes with nitrogen. Their characteristic feature is that the nitrogen atom excapsulated in the carbon cage preserves its quartet spin state. Such complexes are paramagnetic and, according to experimental results [39], can be used as spin cubits in memory cells of quantum computers.

An interesting result was obtained by Dietel et al. [40] for endohedral complexes of nitrogen with modified fullerenes (exohedral modification of the carbon frame via nucleophilic cyclopropanation of 6,6 double bonds with malonates in the presence of a base). It was shown that even in a substantially modified carbon frame nitrogen preserves its atomic nature, i,e. its spin state**.**

Here we would like to mention a discussion concerning the relative position of nitrogen 2*p* orbitals in the N@C_{60} complex of I_h symmetry (Fig. 3). Greer [41] who explored the atomic nature of the endohedral nitrogen by means of Hartree–Fock calculations came to a conclusion that complex formation decreases the energy of nitrogen 2*p* orbitals and that Koopmans' theorem overestimates the ionization potential of this system. Plakhutin et al. [42] reported the results of ROHF, UHF, and DFT calculations for neutral and charged endohedral N@C_{60} complexes. It was shown that the one-electron MO energies in N@C_{60}, obtained by ROHF/6-31G(d) calculations using different quantum-chemical programs (Gamess, GAUSSIAN 98, Monster-gauss, and Turbomole), vary over a wide range. The ionization potentials were calculated by the ΔSCF method and Koopmans' theorem and compared with previous results. In the most recent work on this subject [43], a new canonical Hamiltonian of the Hartree–Fock equation, whose eigenvalues satisfy Koompans' theorem, was proposed.

In the framework of research on the possibility of synthesis of endohedral complexes of small fullerenes with a nitrogen atom [44], we performed a systematic structural study of N@C_n (n = 20, 24, 30, 32, 40, 50) by means of DFT B3LYP/6-31G(d) calculations with full geometry optimization and force constant calculations. As shown, the optimized geometric parameters of fullerene C_n and endofullerene N@C_n are close to each other for n = 32, 40, 50, and 60, and, therewith, the C–C bond length vary within 0.01 Å. Unlike this, the encapsulated nitrogen atom affects considerably the geometry of the C_{20}, C_{24}, and C_{30} fullerene frame.

Figure 4 depicts the potential energy profiles along the trajectories of motion of the nitrogen atom from the center to a wall of the carbon cage in endofullerenes N@C_{40} and N@C_{50}, calculated at the B3LYP/3-21G level. As the guest molecule moves farther way from the cage center, its energy steadily increases to reach a maximum when the guest has turned out to be in the center in a five- or six-membered edge of the fullerene polyhedron and then decreases on further motion along the trajectory beyond the fullerene cage. Vibrational analysis shows that structures with a centrosymmetric position of the nitrogen atom are only possible for N@C_{32}, N@C_{40}, and N@C_{50}. However, the formation energy of N@C_{32} is fairly high (52.9 kcal mol^{-1}), and, therefore, this complex is hardly synthesizable. The spin densities on the central N atom in N@C_{32}, N@C_{40}, and N@C_{50} are 2.78, 2.87, and 2.93, respectively (cf.. 2.97 for N@C_{60}), which implies a quartet spin state of these molecules and lack of essential interactions of nitrogen with the carbon frame.

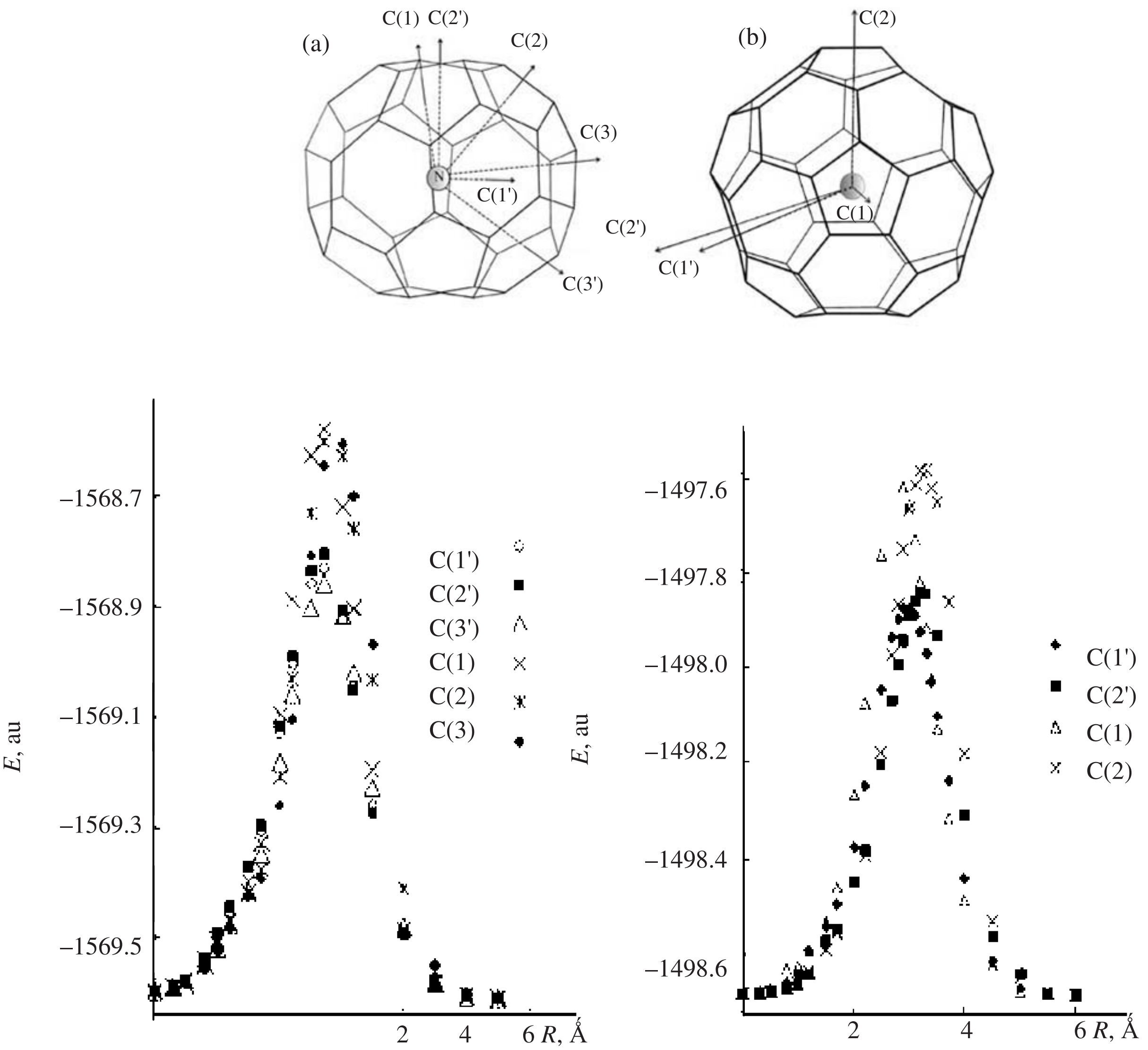


Fig. 4. B3LYP/3-21G potential energy profiles along linear trajectories of motion of the nitrogen atom from the center of fullerene C_n for n = (a) 40 and (b) 50 to a wall of the carbon cage. Shown are trajectories passing through the centers of nonequivalent pentahedral [C(1), C(2), C(3)] and hexahedral [C(1′), C(2′), C(3′)] facets of the fullerene polyhedron.

Thus, the DFT calculations gave evidence for the possible existence of small fullerenes $N@C_{40}$ and $N@C_{50}$ (Fig. 5) with a quartet nitrogen atom in the center of the carbon cluster. According to Dietel et al. [44], such molecules can be synthesized provided appropriate conditions are found.

In one of the most recent works concerning nitrogen-doped endofullerenes [45], the DFT method (B3LYP/6-31G(d)) was used to calculate an experimentally known charged the complex $N@C_{60}^{+}$, as well as $N@C_{20}^{+}$ whose formation and structure have still not been reported; characteristics of these complexes were compared with those of their neutral analogs $N@C_{60}$ and $N@C_{20}$. The calculation results for structures having nitrogen in the center of the carbon cage revealed on the potential energy surfaces (PES) of these complexes (Fig. 4) several stationary points with close geometries and energies.

The minima correspond to a C_{5v} structure (Fig. 6b) in which the nitrogen atom is displaced with respect to the center of the fullerene frame by 0,2 Å, as well as to a centrosymmetric (C_I) structure with a slightly deformed carbon frame (Fig. 6). The I_h structure (Fig. 6a) has three imaginary frequencies and, as a consequence, does not correspond to a minimum on the PES. The energy gap between the stationary point

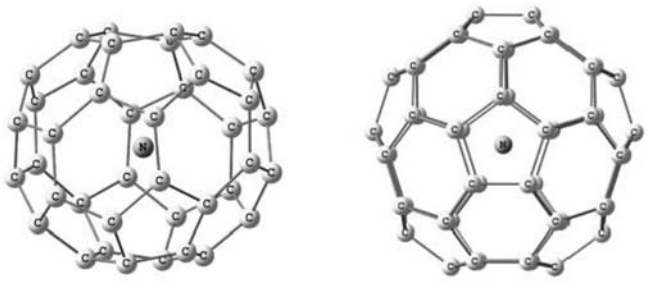
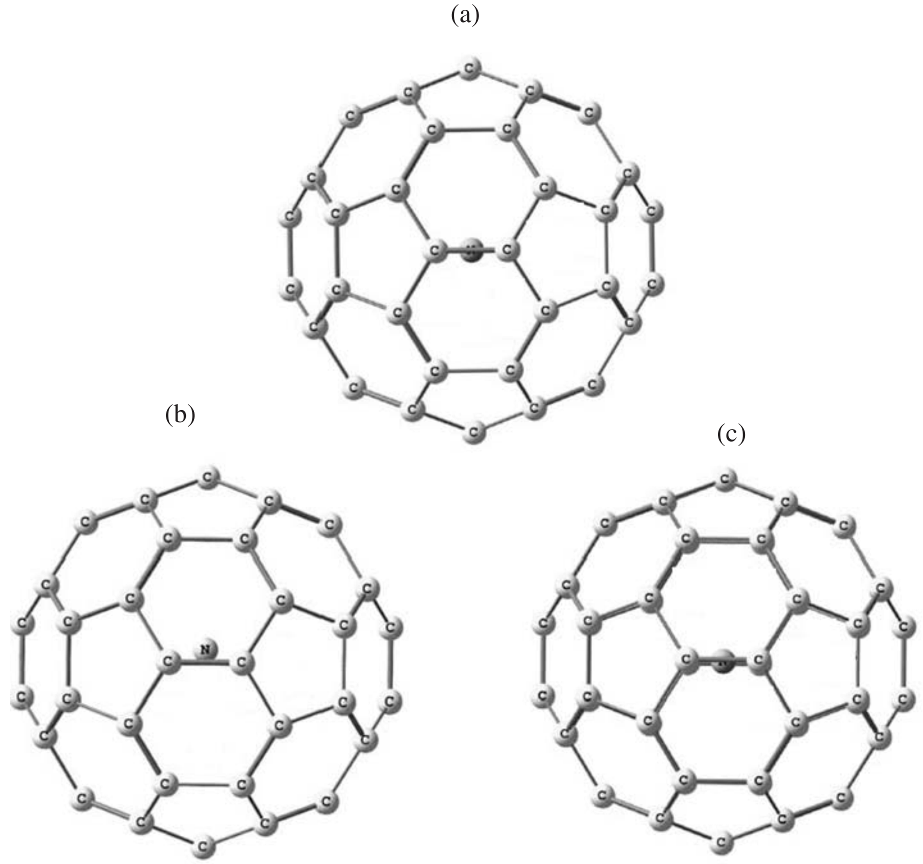


Fig. 5. Endofullerenes N@C_{40} and N@C_{50}.

is small (0.5 kcal mol^{-1}). However, correction for zero-point vibration energy results in that the I_h structure becomes more preferred. This result suggests that the entrapment of a nitrogen atom into the fullerene carbon cage results in disordering of the system, associated with that, first, nitrogen is displaced with respect to the molecular center, and, second, the carbon cage is deformed. The same picture is observed in the charged complex N@C_{60}^{+} with the only difference that the deformation of the carbon frame in the structure of C_I symmetry is much stronger than in the neutral complex. The C–C bond lengths in the charged complex are altered by up to 0.01 Å. These results are nicely consistent with experimental vibration data [46] for nitrogen in the fullerene C_{60} cavity. As follows from the calculation results, there is no charge on the nitrogen atom both in the neutral and charged complex. Analysis of the NBO charges in N@C_{60}^{+} reveals charge redistribution: The nitrogen cation "withdraws" one electron, and the positive charge is redistributed between carbon atoms. Complex formation also affects the spin density on the entrapped nitrogen cation; according to calculations, it is now 2.97 e. Thus, the positively charged complex N@C_{60}^{+} should be considered as a charged carbon frame with an electroneutral nitrogen atom N[C_{60}^{+}]. This result is fully consistent with the results of an experimental mass spectral study of the escape of the nitrogen atom from the fullerene cage [47]. As shown, metal- and noble gas–containing endohedral fullerenes, the ions N@C_{60}^{+} and N@C_{70}^{+} do not lose C^2 groups unimolecularly but lose the nitrogen atom instead.



(a)

(b)

(c)

Fig. 6. B3LYP/6-31G(d) geometries of endofullerenes N@C60. Here and in the other figure legends, bond lengths are in Å.

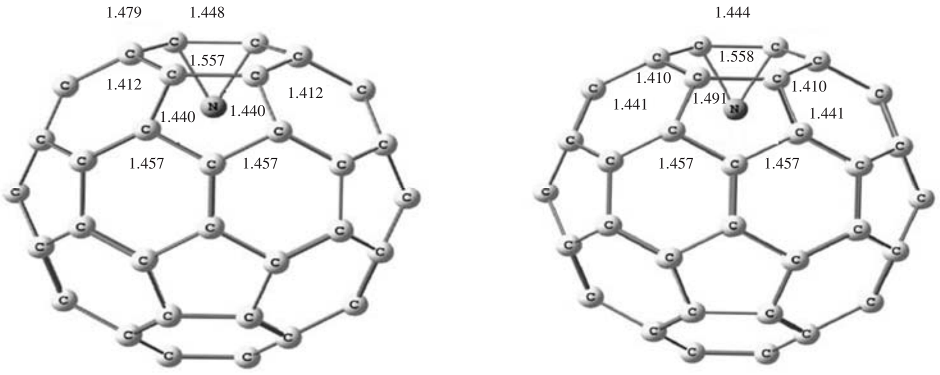


Fig. 7. B3LYP/6-31G(d) geometries of endofullerenes N@C60 and N@C$_{60}^{+}$, containing C–N bonds.

To assess the stabilization energies of centrosymmetric endohedral complexes with respect to structures involving covalent bonds between nitrogen and the carbon frame, a C_{2v} σ-complex with the nitrogen atom coordinated by the fullerene 6.6 bond was calculated (Fig. 7). The stabilization energy of this complex was lower by 56 kcal mol^{-1} than a centrosymmetric structures. Analogous results were obtained for the charged complex N@C$_{60}^{+}$: Its total energy is higher by 17 kcal mol^{-1} than the energy of an endofullerene having nitrogen in the cage center. Thus, endohedral fullerenes N@C$_{60}$ with a central nitrogen atom are energetically preferred over σ-bonded ones. Structures like those in Fig. 7 can serve as intermediated in the process of nitrogen escape from the fullerene cage [48].

Thermodynamic stability of the endohedrals N@C$_{60}^{+}$ and N@C$_{60}$ relative to the isolated fullerene molecules and, consequently, nitrogen cation and atom was studied. The calculations showed that the total energy of N@C$_{60}^{+}$ is lower by 173 kcal mol^{-1} than the sum of the energies of the isolated molecules, i.e. the complex is favored by energy. By contrast, the neutral complex N@C$_{60}$ is destabilized by 0,8 kcal mol^{-1} with respect to atomic nitrogen and the fullerene.

According to structural studies, N@C$_{20}$ (Fig. 8a) with the nitrogen atom in the center of the carbon cage corresponds to a third-order stationary point on the PES [44]. Motion along the internal coordinates leads to a structures corresponding to minima on the PES. The structure in Fig. 8c corresponds to an intermediate on the way of nitrogen escape from the fullerene cage. This conclusion follows from the fact that the C–C bonds in the five-membered ring bound to nitrogen are much elongated and equal 1.60–1.62 Å (Fig. 8).

The structure in Fig. 8b corresponds to a global energy minimum of the endohedral complex N@C$_{20}$. In view of the fact that the nitrogen atom in this complex is bound to the carbon cage, the structure ^{2}N@C$_{20}$ (doublet spin state) was calculated to find that it has a lower total energy. A conclusion thus could be drawn that nitrogen changes multiplicity when enters the fullerene C$_{20}$ cage.

Calculations of the ^{3}N@C$_{20}^{+}$ complex with nitrogen in the center of the carbon cage, too, predict three imaginary frequencies. Minima on the PES correspond to structures containing bonds between nitrogen and fullerene C$_{20}$ carbons. Like with the neutral complex, lower multiplicity structures are energetically more preferred. The stabilization energies are 69 and 127 kcal mol^{-1} for ^{3}N@C$_{20}^{+}$ and ^{1}N@C$_{20}^{+}$, respectively.

Of certain interest is the question whether atoms experience contraction when enter the fullerene cage. Buchachenko [49] considered the effect of atom contraction inside the fullerene cage and showed that in the case of nitrogen it is fairly strong.

The nature of interactions of paramagnetic atoms A = ^{4}N, ^{4}P, ^{3}O, and ^{3}S (subscripts relate to multiplicity) with π systems and C$_{60}$ in complexes $A\cdots C_6H_6$ and A@C$_{60}$ [50]. The calculated geometric parameters show that paramagnetic N and P lie on the C_6 axis of the benzene ring in complex A...C$_6$H$_6$ and in the center of the carbon cage in A@C$_{60}$, whereas O and S are slightly displaced to the benzene C–C bond in complex $A^{\cdot\cdot}C_6H_6$. As to the formation energies of paramagnetic benzene and fullerene complexes with a noble gas, specifically He...C$_6$H$_6$ and He@C$_{60}$, the former have a much higher formation energy. The energy barrier to O

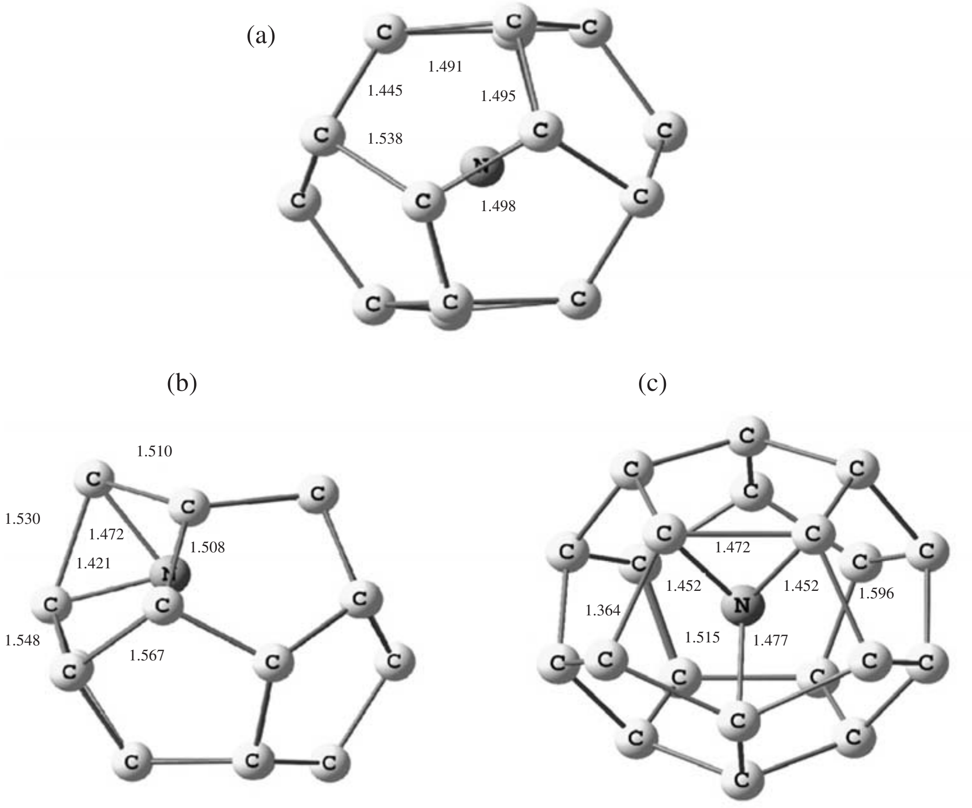


Fig. 8. B3LYP/6-31G(d) geometries of endofullerenes N@C20.

entrapment through the 6,6 bond is lower that that for helium and higher than that for nitrogen.

Plakhutin et al. [51] reported abnormally high S^2 values obtained by UHF/6-31G(d) calculations for a series of structures, including N@C_{20} (4.26 and 13.14 before and after annihilation, respectively). Single-step annihilation failed to improve the wave function. It was shown that the wave function is contributed by at least for multiplets $S' = S$, $S + 1$, $S + 2$, and $S + 3$.

Interesting results were reported by Mauser et al. [52]. They showed by quantum-chemical calculations that the endohedral nitrogen atom escapes the carbon cage by forming bonds with the latter or via aza bridges (a process like this can be seen in Fig. 4: As nitrogen moves from the center of the fullerene cage, it should approach, earlier or later, cage walls, which should inevitably entail formation of any bonds that then will break to let nitrogen escape the cage).

Complexes with Ions

Cioslowski [53, 54] considered the possibility of formation of complexes of C_{60} with F^-, Na^+, Mg^{2+}, and Al^{3+} ions. It was found that the entrapment of an anion (F^-) into the fullerene cage leads to cage contraction, while entrapped metal cations induce expansion of the cage. According to calculations, structures with centrosymmetrically located ions correspond to local energy maxima, and minima correspond to complexes with the ion displaced from the centrum. Thus, the minimum-energy structure of the complex $Na^+@C_{60}$ is that in which the sodium ion is displaced by 0,66 Å. The electronic structure of such complexes is suggested to be considered as a result of interaction of a polarizable two-layer C_{60} frame with positively charged nuclei inside the cage and a negatively charged outer electron cloud, and the electrostatic potential generated by the guest atom.

De Proft et al. [55] performed a systematic ab initio study of C_{60}, Si_{60}, and Ge_{60} complexes with the alkali metal cations Li^+, Na^+, K^+, and Rb^+ and the halide ions F^-,Cl^-, Br^-, and I^- . The calculations were performed by the Hartree–Fock method with the 3-21G basis using the multiplicative integral approximation (MIA) [56] and self-consistent field method [57]. It was shown the stabilization energy of ions in the fullerene cage depends on the endohedral electrostatic potential, ioninduced dipole interaction of the central ion with the polarized carbon cage, and electrostatic repulsion between the ion and the electron cloud of the cage. The stabilization energies were explained in terms of the hard–soft acid–base (HSAB) theory. The stability of the complexes increases in the cation order $Rb^+ < K^+ < Na^+ < Li^+$ and anion order $I^- < Br^- < Cl^- < F^-$, in parallel with the harness order of the ions. It should be noted that De Proft et al. [55] did not observe the correlation of cage size with ion nature, described by Cioslowski [53].

Guo et al. [58] showed in their theoretical study on endohedral complexes of C_{28} with various cations that electronegativity is a qualitatively reliable criterion for metal entrapment into the C_{28} cage and that the possibility of formation of endohedral complexes with small fullerenes depends on the radius of the metal ion.

At present there has been little theoretical work on endohedral complexes of ions with the smallest fullerene C_{20} sinthesized as late as 2000 [59]. At the same time, its hydrogen-containing derivative, viz. dodecahedrane, was known much earlier [60], and theoretical studies into endohedral derivatives of fullerene C_{20} were initiated well before its discovery (Fig. 9). As early as 1978 Schulman and Disch [61] published a work in which they employed the INDO, CNDO, and MINDO/3 methods to calculate the formation energies of endohedral complexes of H, H^+, H^-, Li, $L^{+,}$ Be, Na^+, and H_2. It was shown that among the endohedral complexes studied only those with H^+, Li^+ , and Be are stabilized.

Later fullerene complexes with H^+, He, Li^+, Be^+, Be^{2+}, and Mg^{2+} were calculated at a higher level of theory (HF/6-311G(d,p) и MP2/6-311G(d,p)) with full geometry optimization and calculation of force constants [62]. Main emphasis was put on the complex $H^+@C_{20}H_{20}$, since the above-cited work and some other works [63, 64] mentioned the possibility of existence of an H^+ complex whose stabilization energy is 130 (INDO), 42.4 (STO-3G), 19,1 (PRDDO) kcal mol^{-1}. However, the force constant calculations at the HF/6-311G(d,p) level showed that the I_h structure has three imaginary frequencies, while symmetry-unconstrained calculations with geometry optimization place hydrogen outside the carbon cage. These results rule out formation of an endohedral complex of H^+ with dodecahedrane, in contradiction to previous conclusions. The endohedral complex with Li^+, too, is unlikely to exist. According to MP2/6-311G(d,p) calculations, this is about 7 kcal mol^{-1} less stable that the isolated dodecahedrane and Li^+, but, unlike the H^+ complex, this structure corresponds to a minimum on the PES. A high stabilization energy is predicted only for endohedral complexes with Be^{2+} and Mg^{2+} (224 and 102 kcal mol^{-1}, respectively).

Moran et al. [65] considered the structure, stability, and ionization potentials of endohedral complexes of dodecahedrane with H, He, Ne, Ar, Li, Li^+, Be, Be^+, Be^{2+}, Na, Na^+, Mg, Mg^+, and Mg^{2+}. Energy optimization and force constant calculations were performed by the DFT method at the B3LYP/6-311+G(d,p) level for I_h structures. Except for $Be@C_{20}H_{20}$, $Be^+@C_{20}H_{20}$, and $Be^{2+}@C_{20}H_{20}$, all high-symmetry structures fall in minima on the corresponding PESs. The central atom in beryllium complexes are displaced, which reduces the symmetry of the resulting structures to C_{5v}.

Chen et al. [66] reported one more B3LYP/6-31G(d,p) study of endo- and exohedral complexes of dodecahedrane with H^+, H, N, P, C^-, Si^-, O^+, and S^+. It was found that the endohedral complex with H^+ cannot form, in agreement with the semiempirical calculations in [62]. Except for O^+, the other guest atoms all reside in the center of the fullerene cage. The endohedral complexes are less favored by energy than exohedral. A change in the multiplicity of P and Si on their complex formation with dodecahedrane was predicted.

Minyaev et al. [67] performed a B3LYP/6-311G (d,p) study of the endohedral complex $C@C_{20}H_{20}^{4-}$ and its salt $C@C_{20}H_{20}Li_4$. The complex $C@C_{20}H_{20}^{4-}$ has a spherical symmetry (I_h), and it is an isoelectronic analog of the complex $Ne@C_{20}H_{20}$ whose stability had been predicted previously by quantum-chemical calculations [65]. The interatomic distances between the central atom and cage atoms in the complex are fairly large (2.191 Å), but, nevertheless, Bader's topological analysis [68] revealed twenty bond paths linking the central atom with peripheral (Fig. 10). A conclusion can thus be drawn that this complex contains a supercoordinate carbon atom.

As follows from the calculation results, the entrapment of a carbon atom into dodecahedrane results in a considerable extension of the C_{20} cage, and, therewith, C–C bond lengths vary no more than 0.01 Å. The research in [67] was continued in [69], where B3LYP calculations with the 6-311G(d,p), 6-311+G(d,p), and 6-311G(df,p) basis sets were used to study endohedral complexes of dodecahedrane with C^{4-}, N^{3-}, O^{2-}, and F^-. With all the complexes, structures of I_h symmetry correspond to minima on the

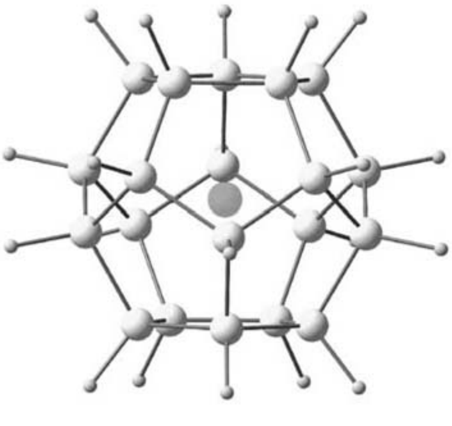


Fig. 9. General view of the structure of endofullerenes $X@C_{20}H_{20}$ (X is ion).

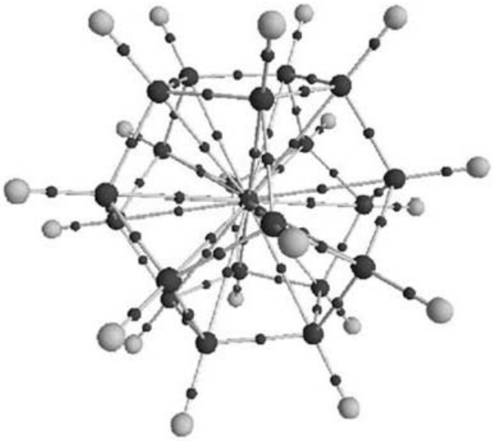


Fig. 10. Bader's molecular graph for the endohedral complex $C@C20H_{20}^{4-}$.

PESs. The calculated Mulliken charges on the central atoms were 0,19, –0,60, –0,79, and –0,62 e for the endohedral complexes with C^{4-}, N^{3-}, O^{2-}, and F^{-}, respectively. These results suggest a strong guest-to-cage charge transfer. Addition of lithium counterions forms neutral complexes, but the coordination properties of the parent anionic structures are therewith preserved (Fig. 11).

Complexes with Metals

Endohedral complexes of fullerenes with metals form one of the most interesting fields of research of carbon-containing compounds due to their unusual properties. Their electronic structure much differs from the structure of "pure" fullerenes. In some cases, especially if the encaged metals possess magnetic and radioactive properties, these complexes can be considered as promising candidates for nanotechnologies and biomedicine.

At present a great number of endohedral fullerenes with transition and rare-earth metals, specifically of Hf, Ti, U, U_2, and Zr with C_{28}; U with C_{36}; K, La, U with C_{44}; Cs with C_{48}; U with C_{50}; U_2 with C_{58}; Ca, Co, Cs, Fe, K, La, La_2, Ne, Rb, U, U_2, and Y_2 c C_{60}; La and U with C_{70}; U with C_{72}; La, Sc, and Sc_2 with C_{74}; La and La_2 with C_{76}; La_2 with C_{80}; La, La_2, Sc, Sc_2, Sc_3, Y, and Y_2 with C_{82}; and La, La_2, Sc_2 , and Sc_3 with C_{84} [70]. The structures of some of them were extablished by means of X-ray diffraction analysis [18].

One of the first theoretical studies of endohedralых fullerene complexes with metals [71] was a local density approximation study of the structure of the complex $La@C_{60}$. Its ionization potential and proton affinity were compared with those of fullerene C_{60}. The calculated ionization potential of the complex was 6.9 eV, which is consistent with the experimental value (6.4 eV).

The electronic structures and properties of metal endofullerenes were considered in the monograph [11] and a more recent review [72]. Therefore, here we will consider works not covered in the cited publications.

The structure and properties of $La_2@C_{78}$ (Fig. 12) were studied both theoretically and experimentally [73]. The calculated formation energy of this complex of D_{3h} symmetry is 277 kcal mol^{-1}, which implies a considerable stabilization of the two lanthanum atoms inside the carbon cage. There is a strong charge transfer in the complex, which reveals itself in that siz electrons of the entrapped lanthanum atoms are distributed over carbon atoms. Thus, this complex can be written down as $(La^{3+})_2C_{7\,8}^{6-}$. The calculations showed the energy gap between the HOMO and LUMO are mach smaller than in $Sc_3N@C_{78}$ [74] and equals 0.81 eV.

The above work has something in common with the research of Wu and Lu [75] with dimetallic fullerene complexes $U_2@C_{60}$ [75]. It was established by DFT calculations that the most stable is a structure of a highly symmetric (I_h) carbon frame, while the U_2 groups resides between two six-membered rings; therewith, the complex has a D_{3d} structure. According to the calculations, the uranium atoms bear a large positive charge. These findings allow the complex to be represented as $[U_2]^{6+}@C_{60}^{6-}$ (Fig. 13). The interaction between U_2 and C_{60} is not purely ionic, since the covalent contribution is fairly large.

The structural unit $[U_2]^{6+}$ involves a unique one-electron two-center U–U bond. This is the first observation of a multiple metal–metal bond inside the fullerene cage. The results of the cited work are at the interface of the chemistry of polynuclear complexes and the chemistry of fullerenes, which may initiate development of a new line of research in this field.

One more theoretical study of the electronic and steric structures of dimetallic fullerene complexes dealt with two $Ti_2@C_{80}$ complexes of D_{5h} and D_{5d} symmetry. It was shown that these complexes are much differ from each other both in geometry and in energy. As follows from experimental data [77], a D_{5h} complex is favored by energy. The calculated charges on each Ti atom are +1,9 e, i.e. we deal here with noninteracting ions. The calculated charge distribution maps point to covalent bonding between Ti and the carbon cage. Such interaction and Ti–cage charge transfer are factors that, according to the cited work, ensure a greater stability of the D_{5h} изомера.

Escape of Gd^{3+} and Ca^{2+} from the complexes $Gd@C_{82}$ and $Ca@C_{82}$ containing defects in the C_{82} carbon cage of C_{2v} symmetry was studied by B3LYP DFT calculations [78]. Ion migration is initiated by the presence of defects in the carbon cage, which gives rise to formation of coordinately unsaturated carbon atoms (Fig. 14). As a result, antibonding orbitals are formed between two carbon atoms. Sine antibonding orbitals can interact with vacant *d* orbitals of Gd^{3+}, and attractive interactions allow the latter to embed into a defect in the carbon cage. As a result, the metal ion passes through the defect.

As to the Ca^{2+} complex, vacant *s* orbitals of Ca^{2+} are unable to such interaction. As a result, when calcium approaches a defect, the C–C bond is reformed and this prevents Ca^{2+} escape from the C_{82} cage. The resulting data point to the importance of allowance for orbital interactions in studying the mechanism of migration of endo atoms through defects in the fullerene frame. Probably, analogous processes underlie escape of atoms from nanotubes. Further research in this field is quite important for the design of "atomic sieves" on the basis of nanomaterials.

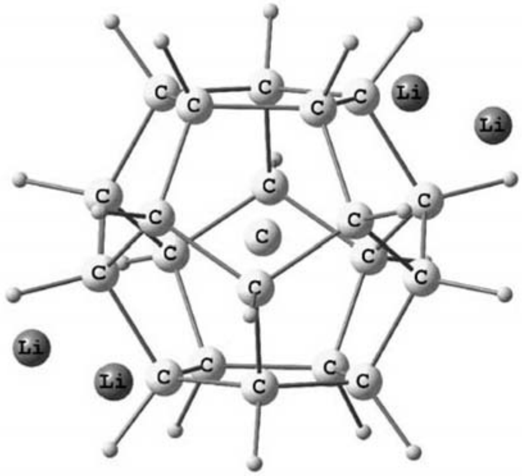


Fig. 11. Neutral endohedral complex $C@C_{20}H_{20}\cdot Li_4$.

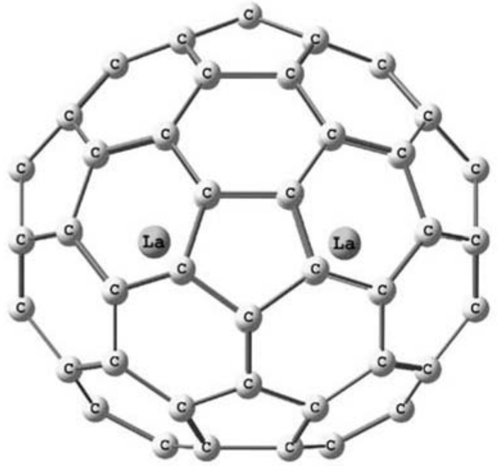


Fig. 12. Endohedral complex $La_2@C_{78}$.

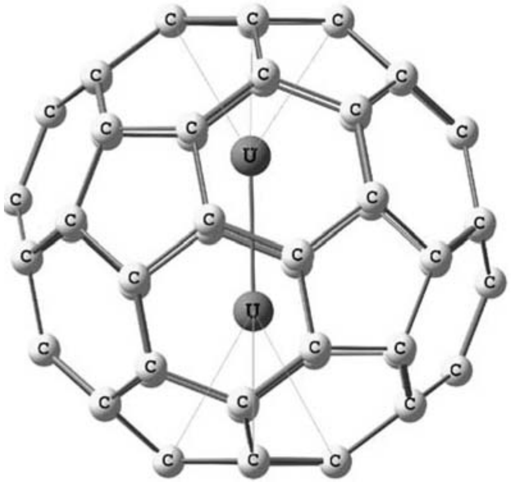


Fig. 13. Endohedral complex $U_2@C_{60}$.

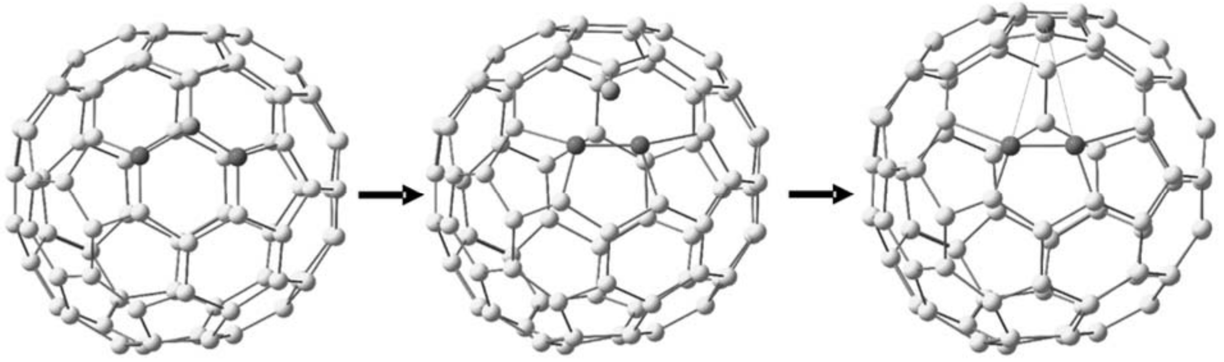


Fig. 14. Scheme of defect formation in C_{82} fullerene.

Exohedral complexes $C_{53}Rh$ and $C_{54}M$ (M = Rh, Y) were calculated by the DFT method at the B3LYP/STO-3G and B3LYP/3-21G levels [79]. It was shown that yttrium tends to form endohedral structures, whereas rhodium can form exohedral complexes, as well as fullerides. A possibility is discussed that such complexes are formed by a window opening mechanism.

A DFT study of La@C_{74} and Ca@C_{74} was reported by Nikawa et al. [80]. The complex La@C_{74} is paramagnetic, and its electronic structure is La^{3+}@C_{74}^{3-}. To find out why this complex exhibits enhanced reactivity, the ionization potentials and proton affinities of the complexes La@C_{74}, Ca@C_{74}, and La@C_{82}(C_{2v}) were calculated. It was found that the ionization potentials of these complexes are close to each other, and, consequently, the reactivity of La@C_{74} is not related to this factor. At the same time, as follows from calculations, the spin density in La@C_{82} is distributed over all cage carbon atoms, where as in La@C_{74} about 50% of the total spin density is localized on carbon atoms of three types. This circumstance allows the enhanced reactivity of La@C_{74} to be explained in terms of the radical nature of fullerene C_{74}.

Gorelik and Plakhutin [81] performed a group-theoretical and quantum-chemical (ROHF, CI) study of the energy spectrum of states in icosahedral fullerene complexes M@C_{60}, where M = Mn, Cr, Fe. It was shown that the C_{60} carbon cage only slightly affects atomic states of encapsulated metals, specifically, the d^N terms are slightly shifted but not split. The same takes place even when the charge on carbon atoms varies considerably. As shown, the d^N terms of encapsulated metals can only be split in the case of a strong contraction of the carbon cage.

The DFT method was used to study two mechanisms of formation of metallofullerene Y@C_{82} [82]. The first suggests cage expansion with subsequent complex formation inside the cage via combination of the Y@C_{80} and C_2 fragments. The second mechanism suggests interaction of an unclosed C_{76} fragment and C_6Y. The second mechanism is energetically preferred.

In one of the most recent theoretical works [83] on the structure of the complex La_2@C_{80}, geometry optimization and vibrational analysis by means of the Am-sterdam density functional (ADF) program were performed. Relativistic effects were included using the zero-order regular approximation (ZORA). It was found that a D_{2h} structure corresponds to a global minimum on the PES, but this structure is as little as 1 kcal mol^{-1} lower by energy than a D_{3d} structure which was earlier predicted as the most stable [84]. A mechanism of the motion of La_2 pairs was proposed, according to which two La ions pass through a saddle point of C_{2h} symmetry, which lies between two equivalent D_{2h} configurations. The calculated low-frequency Raman spectra of La_2@C_{80} agree with available experimental data.

A B3LYP DFT study of the four possible isomers of the complex Ti_2@C_{80} (Fig. 15) was reported by Gan and Wang [85]. Two isomers contain Ti atoms inside the C_{80} cage, and the other two isomers described by the formula Ti_2C_2@C_{78} are Ti_2C_2 clusters encapsulated in the C_{78} cage. Optimization of the Ti_2C_2 cluster revealed two ways in which it can be arranged inside

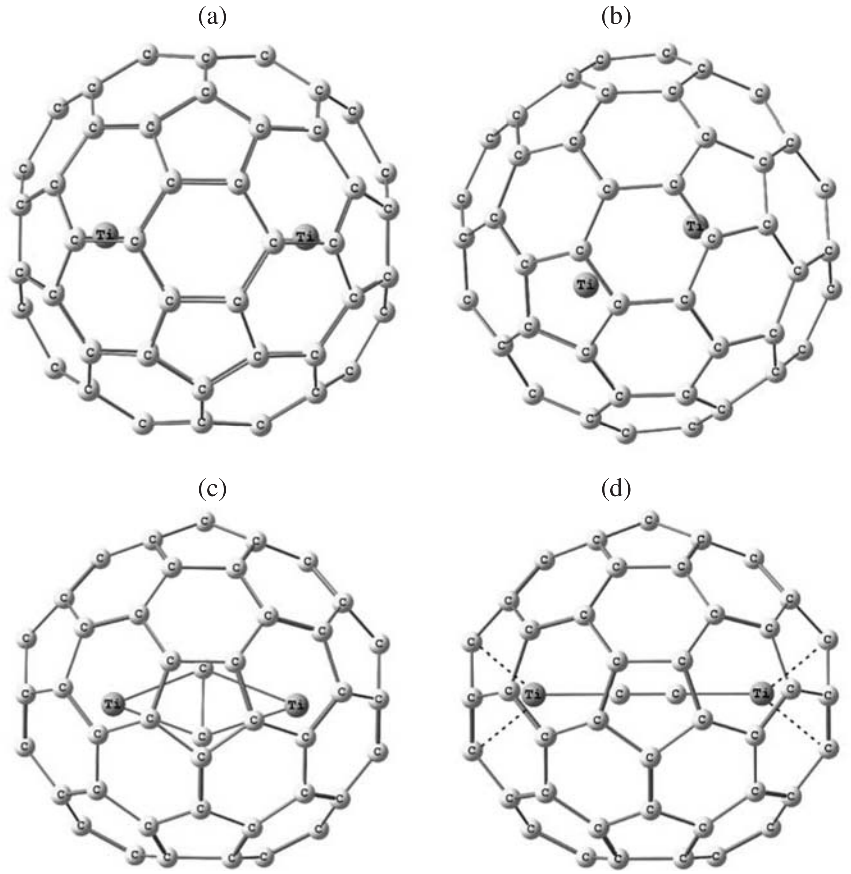


Fig. 15. Isomers of the complexes (a, b) $Ti_2@C_{80}$ and (c, d) $Ti_2C_2@C_{78}$.

the C_{78} cage: as a linear structure Ti-C-C-Ti and as a butterfly (i.e. two Ti atoms and C_2 group are acoplanar). The isomer with a linear Ti_2C_2 group inside C_{78} (Fig. 15d) has the highest stabilization energy of the isomers considered. An important stabilization factor here is orbital interaction between Ti_2C_2 and the carbon frame.

A systematic quantum-chemical research allowed characterization of metallofullerenes $La_2@C_{72}$ and $Sc_2@C_{72}$ [86]. The calculations revealed violation in the hexaanion C_{72}^{6-} of the rule of isolated pentahedra, which consists in that fullerene five-membered rings should not share vertices. The same is true of highly stable complexes $La_2@C_{72}$ and $Sc_2@C_{72}$. The resulting data agree with those in the earlier work of Kobayashi et al. [87] for the complex $Ca@C_{72}$.

Slanina et al. [88] studied six isomers of $Yb@C_{74}$ by the DFT method with B3LYP/3-21G/CEP-4G geometry optimization. Comparison of the relative energies of these isomers made the referees to conclude that the lack of shared five-membered rings in the parent fullerene favors greater stability of the endofullerene.

Complexes with Metal Nitrides

Difficulties in preparation and isolation of large quantities of endohedral metallofullerenes make difficult to study their physical and chemical properties. A breakthrough in this field was achieved when Stevenson at al. [89] synthesized a trimetallic nitride cluster inside a fullerene. Template metal nitride synthesis allowed isolation of macroquantities of $Sc_3N@C_{80}$. The same approach was used to synthesize a large number of endohedral metallofullerenes in quantities large enough for experimental studies. It is important to note that endohedral fullerenes encapsuling metal nitrides are stable in normal conditions, but certain nitrides cannot be prepared beyond the carbon cage.

One of the first theoretical research on endohedral metal nitride fullerenes dealt with interaction of

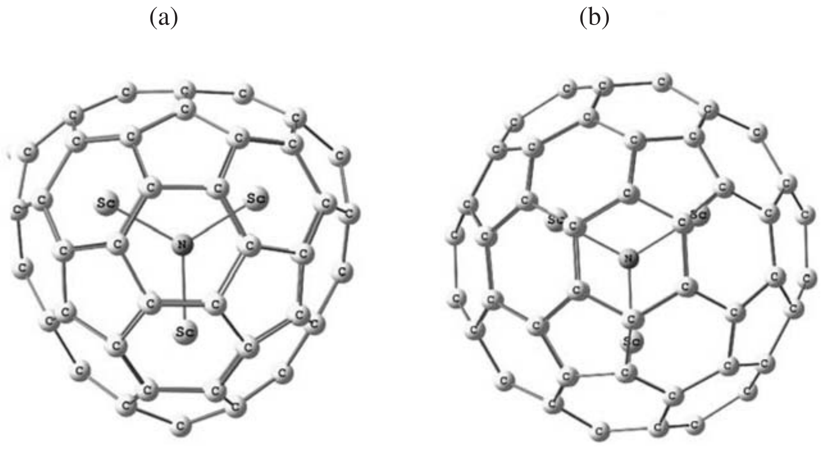


Fig. 16. Endohedral complexes (a) $Sc_3N@C_{78}$ and (b) $Sc_3N@C_{80}$.

scandium atoms and the carbon cage in the complexes $Sc_3N@C_{80}$ and $Sc_3N@C_{78}$ (Fig. 16) [74]. Encapsulation of the Sc_3N cluster is an exothermal process (the stabilization energy of $Sc_3N@C_{78}$ is 224 kcal mol^{-1}) which involves transfer of six electrons from Sc to the carbon cage in both complexes. An isolated Sc_3N molecule is pyramidal, but being encapsulated in the fullerene cage it assumes a planar structure. In $Sc_3N@C_{78}$, the metal ion interacts with three 6.6 carbon–carbon bonds common for two six-membered rings located in the central part of the fullerene cage. Such bonding prevents free rotation of the Sc_3N cluster inside the cage. Geometry optimization shows that the fullerene cage in $Sc_3N@C_{78}$ is stretched to accommodate the Sc_3N group. By contrast, in $Sc_3N@C_{80}$, the Sc_3N unit is not fixed in a certain position in the fullerene cage of I_h symmetry and can freely rotate. Regardless of the fact that Sc_3N electrons are transferred to the carbon cage, both complexes exhibit fairly hing proton affinities and ionization potentials.

Krause et al. [90] studied endofullerenes $Tm_3N@C_{80}$, $Er_3N@C_{80}$, $Ho_3N@C_{80}$, $Tb_3N@C_{80}$, $Gd_3N@C_{80}$, and $Y_3N@C_{80}$ by IR and Raman spectroscopy, cyclic voltammetry, and quantum-chemical calculations. The gap between HOMO and LUMO as a function of metal was analyzed. The complexes studied feature a considerable charge transfer, and the metal atoms in them bear the formal charge 3+. In this respect these complexes differ from $Tm@C_{82}$ (2+). Thus, by varying the chemical composition inside the carbon cage one can control the charge on the encapsulated metal atom.

The structure of the endohedral complexes $Dy_3N@C_{78}$ and $Tm_3N@C_{78}$ was studied by IR and Raman spectroscopy and DFT calculations [91]. According to the calculation results, stability of $M_3N@C_{78}$ (M =Sc, Y, Lu, La) isomers depends on the size of the nitride cluster. Whereas Sc_3N is planar, the relatively large trimetal nitrides Y_3N and Lu_3N should undergo pyramidalization inside the carbon cage and thus destabilize the cluster. However, in those isomers of $Y_3N@C_{78}$ and $Lu_3N@C_{78}$, that do not obey the rule of isolated pentagons, Y_3N and Lu_3N are planar, thus ensuring stabilization of such complexes. Detailed analysis of the experimental and calculated IR and Raman spectra showed that that in $Tm_3N@C_{78}$ and $Dy_3N@C_{78}$, too, structures that do not obey the above rule are stabilized.

Complexes with Hydrides

Endohedralые complexes of fullerene C_{60} with hydrides can present interest for hydrogen storage technologies. Erkoc and Turker [92] explored the capacity of the C_{60} cage with respect to ammonia molecules by means of semiempirical at the PM3 level within RHF formalism. It was found that the fullerene can accommodate up to six NH_3 molecules. If one more molecule is included in the calculations, the carbon cage opens to let ammonia to escape.

The electronic and structural properties of a series of C_{60} complexes with the hydrides BH_3, CH_4, NH_3, AlH_3, SiH_4, and PH_5 (Fig. 17) [93]. The PM3 calculation predicts that such structures can exist, but their formation is an endothermic process. It was found that complex formation makes the negative charge to concentrate on guest atoms, whereas in endofullerenes containing aluminum hydrides and phosphorus the gap between the HOMO and LUMO is reduced.

Gagliardi [94] performed a theoretical study of the metal hydride fullerene complexes $ZrH_4@C_{60}$, $ScH_{15}@C_{60}$, and $ZrH_{16}@C_{60}$ (Fig. 18) [94]. It was shown that such complexes can exist, and, therewith, their metal–hydrogen bonds are much shorter than isolated hydride molecules. Thus, for example, the Zr–H bonds in ZrH_4 encapsulated in C_{60} are shortened by 0,15 Å. According to the calculations, metal polyhydrides like ScH_{15} and ZrH_{16} can be formed inside the carbon cage. Such molecules are unknown in the isolated state. It is suggested that hydrides can be synthesized directly in the fullerene cage, but stabilization of such systems requires too much energy. Use of nanotubes instead of fullerenes is suggested as an alternative approach. The possibility of existence of two TiH_{16} clusters inside C114 nanotube capped at both ends. The use of this approach may lead to a new method of synthesis and storage of metal polyhydrides.

CONCLUSION

Analysis of published data covered in the present review shows that endohedral fullerene complexes were most commonly studied by the DFT method with the B3LYP hybrid functional. Calculations at the ROHF and UHF levels of theory sometimes posed certain problems. With complexes containing paramagnetic ions and metals, a reasonable com-

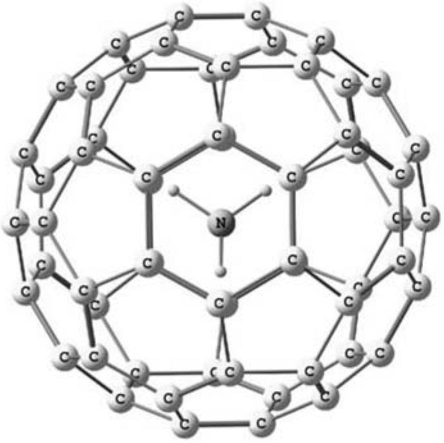


Fig. 17. Endohedral complex $NH_3@C_{60}$.

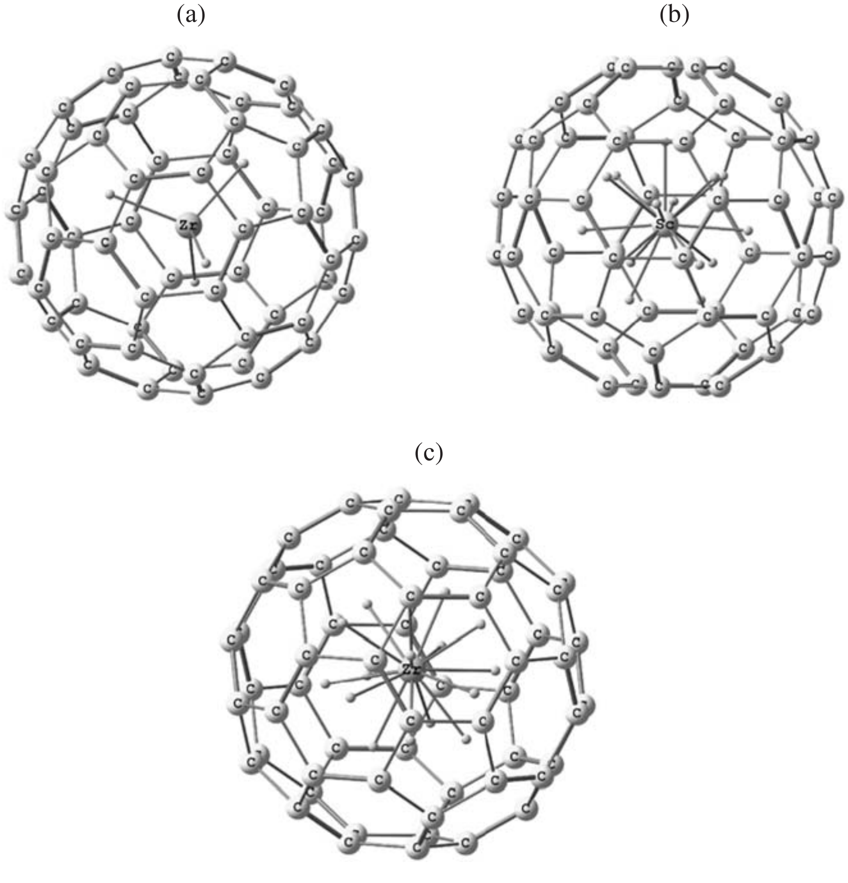


Fig. 18. Endohedral metal hydride complexes (a) $ZrH_4@C_{60}$, (b) $ScH_{15}@C_{60}$, and (c) $ZrH_{16}@C_{60}$.

promise providing the most correct results is the use of 6-31G(d) and higher level basis sets. In the case of complexes containing heavy metals, relativistic effects should be included and, as a consequence, mixed basis sets are needed; therewith, for carbon 6-31G(d) is chosen, whereas for heavy atoms, effective core potentials SBK [95] or SDD [96]. Additional difficulties arise with endohedral derivatives of higher fullerenes, in view of the fact that they have a lot of isomers. Even though theoretical research on endohedral fullerenes is associated with certain problems, high-level quantum-chemical calculations allow one to predict, with a high degree of probability, existence and properties of previously unknown structures.

ACKNOWLEDGMENTS

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