Synthesis and investigation of electrochemical properties of novel fluorine derivatives of C_{60}

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After discovery of fullerenes there were offered a wide variety of ways of their practical use. Nowadays a lot of patents in the field of fullerene chemistry concern use of fullerenes and nanotubes in semiconductor and nanoeletronic devices, e.g. photodiodes, transistors, sun batteries[1]. Due to high electronegativity, fullerene C_{60} can easily form charge-transfer complexes in which it acts as acceptor of electrons. Light irradiation of fullerene-based dyads (consisting of an electron-acceptor fullerene cage covalently bonded with photoactive donor part) results in intermolecular and supramolecular photoinduced electron transfer processes. High efficiency of light absorption and charge separation lies in a basis of the working principle of photovoltaic cells. Accordingly, research on fullerene derivatives with enhanced electronegativity is an important task.

Due to high electronegativity of fluorine atom, its addition to fullerenes leads to increase in their electron-acceptor properties. Therefore research on fluorine-containing fullerene derivatives is a matter of great interest. In this work there were carried out synthesis, isolation and investigation of electrochemical properties of two simplest representatives of the new class of fullerene fluorides: $C_{60}(CF_2)$ and $C_{60}(CF_2)_2$.

It was shown that addition of CF_2-bridge to fullerene leads to a considerable shift of reduction potential: [6,6]-open $C_{60}(CF_2)$ and *cis*-2-$C_{60}(CF_2)_2$ undergo reversible reduction at potentials, 150 and 145 mV more positive than that of C_{60}. Structure, electron shell structure and lifetimes of anion-radicals obtained by reduction were determined by means of EPR and DFT calculations. It was shown that monoanions of compounds in question preserve the methylene bridge.

Protonation of monoanion-radical of $C_{60}(CF_2)$ in *o*-DCB with strong H-acid leads to formation of 1,9-dihydro-(1a,1a-difluoro-1a*H*-1(9)a-homo(C_{60}-I_h)fullerene, $C_{60}(CF_2H_2)$. This compound is the first characterized derivative of [6,6]-open $C_{60}(CF_2)$. According to UV-vis spectroscopic, MALDI mass-spectroscopic and ^1H и ^{19}F-NMR data, it has [6,6]-open structure.

Functionalization of fullerenes by CF_2-groups is yet another approach to enhancing their electronegativity, together with fluorination, trifluoromethylation etc. However, in contrast to other acceptor addends, CF_2-groups preserve sp^2-hybrid state of atoms to which they are bonded and, as shown in this work, enhance electronegativity of fullerene cage. Solution to the problem of synthesis of these compounds extends the known classes of fullerene derivatives and opens a new synthetic direction in chemistry of fullerenes.

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Unprecedented ring expansion of C_{60}: difluoromethylene[60]fullerenes and their hydrides

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Fullerene derivatives that exceed pristine fullerenes in electronwithdrawing capabilities are well known nowadays. Among them are various types of fullerene derivatives with electron withdrawing addends. Their prospective importance is due to potential applicability of such molecules as constituents of energy-harvesting complexes and energy conversion systems.

Recently we reported synthesis and isolation of the two difluoromethylenated fullerenes, $C_{60}(CF_2)$ and *cis*-2-$C_{60}(CF_2)_2$ [1]. Having an unusual [6,6]-open structure, these compounds are unparalleled among the fullerene molecules functionalized by divalent addends and retain all 60 carbon atoms in the sp^2 state.

In this work we report the hydrogenated $C_{60}(CF_2)H_2$ compound where the hydrogen atoms share the same sites with the CF_2 addend, which has been obtained by 2 steps: chemically reduce of $C_{60}(CF_2)$ by zinc-copper couple and then protonation of the $C_{60}(CF_2)^-$

The MALDI mass spectrum of this sample was found to feature an additional peak corresponding to $C_{60}CF_2H_2$. HPLC separation has afforded this compound as an isolated peak with retention time before C_{60} and $C_{60}(CF_2)$. ^1H and ^{19}F NMR spectra of $C_{60}CF_2H_2$ indicating magnetic equivalence of the two F atoms and of the two H atoms, as well as rather close location of the H atoms to CF_2. These data are consistent only with hydrogenation of the CF_2- linked positions. Quantum chemical calculations at the DFT level of theory have been employed to assist understanding of our observations. Thus, the experimentally obtained isomer appears to be the most energetically favorable as well, following only the kinetically inaccessible structures with CF_2 bridge cleaved into a CF_2H group.

It is worth noting that hydrogenation results in further increase of the distance between the CF_2-linked atoms to 2.59 A due to conformational effects of their sp^3 coordination.

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Polymerization of hydrogenated fullerene

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Hydrogenated fullerenes have attracted a great interest within the last decade. In this work, we present a combined experimental and theoretical study of $C_{60}H_x$ solid solution with $x \leq 1$. To synthesize $C_{60}H_x$ material with the $C_{60}H$ molecules, we used the treatment of C_{60} thin films with low-temperature and low-pressure d.c. H plasma discharge. The samples of oxygen-free crystalline fullerene films on silicon substrates were prepared by quasiequlibrium vacuum method. This treatment creates conditions for the formation of weakly hydrogenated C_{60}:H film, containing mainly C_{60}, $C_{60}H$, as well as some $C_{60}H_2$ molecules. In order to identify the phase resulted from the plasma treatment of the C_{60} film, we have performed the Raman spectroscopy measurements. We detected the acceleration of the photopolymerization process in weekly hydrogenated C_{60} film on exposure to the red light of 633 nm at the low laser intensity.

Ab initio computer modelling of $C_{60}H$, $C_{60}H_2$ and $(C_{60}H)_2$ molecules has been performed within the density functional theory (DFT) with B3LYP hybrid functional using MO LCAO SCF method. The energetics of a formation of the both [2+2] cyclo-adduct and singly bonded dimers $(C_{60}H)_2$ from a $(C_{60}H)_2$ molecule bonded by the van der Waals forces was examined. Both ground and excited states were considered. It was found that (i) Hydrogenation gives rise to a decrease of the energetic barrier between doubly bonded dimer state and van der Waals state; (ii) A doubly bonded $(C_{60}H)_2$ isomers predominate for the most part of hydrogen atom locations on the fullerene molecules surfaces. A singly bonded isomer is favourable only if both hydrogen atoms are located symmetrically at special positions on the fullerene molecules. Thus, theory predicts that hydrogenation reduces the depolimerization temperature at small x. Frequencies of vibrational modes with their Raman and IR intensities have been calculated for $C_{60}H$ and $C_{60}H_2$ molecules. A good agreement has been obtained between the results of modelling and the results of the Raman spectroscopic experiments on $C_{60}H_x$ films. The work is supported by Russian Foundation for Basic Research (Grant № 09-02-01008).

Aggregation in hydroxylated endohedral fullerene solutions

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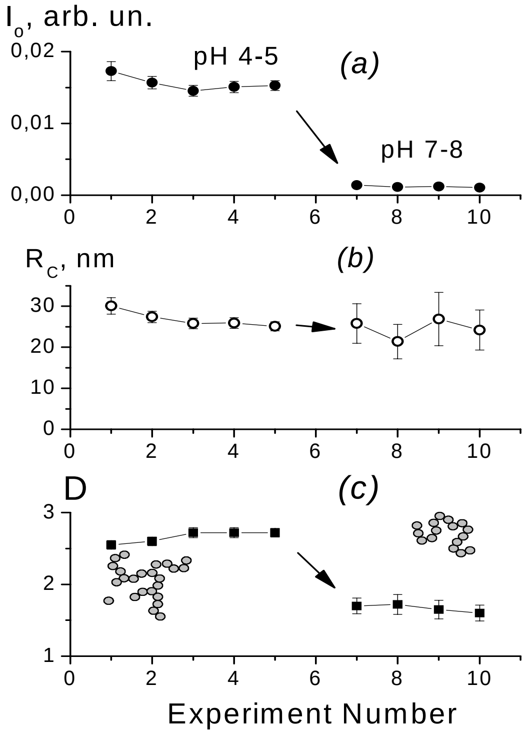
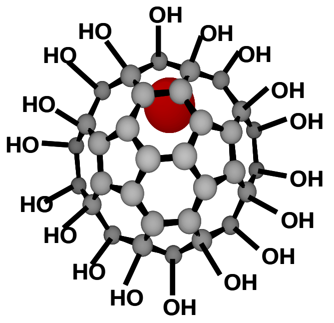
Mechanisms of supramolecular ordering in solutions of hydroxylated endohedral fullerenes Gd@$C_{82}(OH)_{18}$ have been studied by small-angle neutron scattering regarding to their application to improve the contrast in NMR-tomography. It was established that in H_2O fullerene molecules exist in cluster form and these formations are characterized by correlation radius R_C~20-30 nm and fractal dimension D~1.5-2.5 both found from the data described by scattering law

$$I(q) = I_o/[1+ (qR_C)^2]^{D/2}$$

where q~0.03-1 nm^{-1} is momentum transfer and I_o is forward scattering intensity. Structural analysis has shown a domination of chain-like structures in solution and the variation of pH do substantial changes in geometry of these formations (figure). It was observed the transition from ***branched structures*** (D ~ 2.5) to rare ***coil-like objects*** (D~1.5) as a result of increase of pH from 4-5 to 7-8 (fig. c). Despite of such a transition in geometry the cluster size still remains at the same level R_C ~ 25 nm (fig. b).

The work is supported by the Program of Presidium of Russian Academy of Sciences “Quantum Physics of Solid State”.





Gd @ C82(OH)18

Long-range self-assembly in solutions of star-shaped polymers with fullerene C_{60} multifunctional centers

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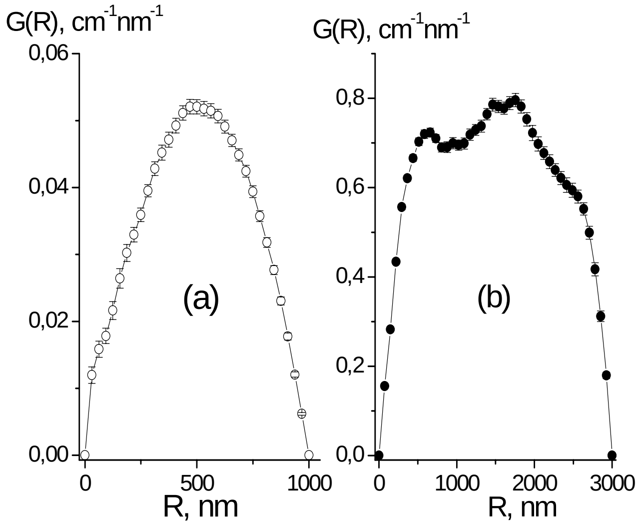
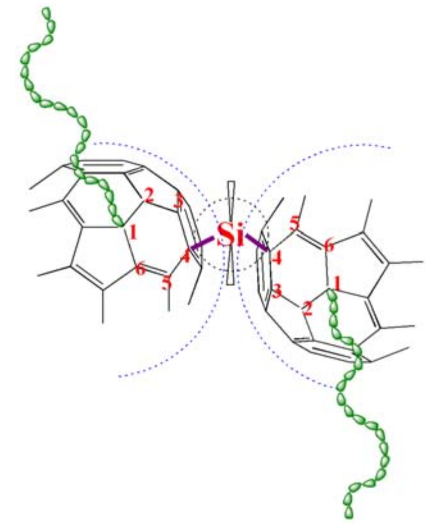
A review of recent neutron scattering studies of self-organization phenomena in solutions of star-shaped polystyrenes (PS) with different kinds of centres (single C_{60} [1] or 2 fullerenes linked by bridge, scheme below) is presented. The supramolecular ordering in ensembles of "stars" $(PS)_6C_{60}$ and $(PS)_6C_{60}$-$C_{60}(PS)_6$ in toluene in the range R~1-3000 nm is discussed regarding to the mechanisms of fullerene influence on conformations and interaction of arms that induces the formation of macromolecular domains. Their correlation radius is of $R_C \sim 80$ nm for single-centre "stars" while the double-centre "stars" create very large entities, $R_C^* \sim 300$ nm. A strongly pronounced trend to self-assembly gives rise the formation of multilevel structures (hierarchy) of macromolecules $(PS)_6C_{60}$-$C_{60}(PS)_6$ shown in figure where correlation functions (a,b) of $(PS)_6C_{60}$ and $(PS)_6C_{60}$-$C_{60}(PS)_6$ in deuterated toluene (polymer content 6 and 4 g/dl respectively) are displayed as dependent on correlation radius R.

The work is supported by RAS Presidium Program N 27.





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Structure and electronic properties of fullerene derivative: quantum chemical calculations

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In recent years fullerene-based materials have brought up steadily increasing attention both in academic and industrial researches. It is of great interest to use fullerenes and fullerite not only by itself but also as modified derivatives, that enhance the properties of fullerenes and extend the application possibility. In present work we report results of computer simulation of crystalline and electronic structure of the molecular complexes – fullerene C_{60} and Leuco Crystal Violet (LCV), C_{60} and Bz_4BTPE (tetrabenzo(1,2-bis [4H-thiopyran-4-ylidene]ethene)), C_{60} and LMG (Leucomalachite Green).

Optimization of geometry of complexes was determined used a method of molecular mechanics UFF and two semi-empirical methods PM3 and AM1 with various parameterization. Results of calculation of cluster structure obtained by various methods do not contradict each other.

Quantum chemical calculations regard to 3D cluster built of up to three layers comprising nine C_{60}-donor molecules each. The steady state of molecular complex LCV·C_{60} (a=0.99 nm, b=1.16 nm, c=0.97 nm, α=85°, β=79°, γ=89°; crystal system - triclinic; space group - $P\bar{1}$) and LMG·C_{60} (a=1.29 nm, b=1.37 nm, c=1.55 nm, α=78°, β=68°, γ=72°; crystal system - triclinic; space group - $P\bar{1}$). It is revealed molecular complexes have layered structure. The determined center distances of the fullerene spheres in neighboring layers of the crystal have following values L~1.29 nm (LMG·C_{60}), L~1.16 nm (LCV·C_{60}) and L~0.97 nm (Bz4BTPE·C_{60}). For an example the AFM dada have values L_{AFM}=0.94±0.04 nm (real Bz_4BTPE·C_{60}) and L_{AFM}=1.07±0.09 nm (real LCV·C_{60}).

Optimization of geometry of molecular complexes has allowed to estimate energy of charge transfer excitons (CT-excitons characterized by the localization of an electron and a hole on the acceptor and the donor molecules correspondingly) as 1.32 eV (LMG·C_{60}), 1.25 eV (Bz4BTPE·C_{60}) and 1.34 eV (LCV·C_{60}). Quantum chemical calculations (PM3) of molecular structures has allowed to construct dependence of width of HOMO-LUMO gap (E) on the number of C_{60} – donor pairs in molecular clusters LMG·C_{60} and LCV·C_{60}. Value E decreases from 2.9 eV for one isolated pair LCV-C_{60} to 2.2 eV for nanocluster , consisting of several layers and tens pairs LCV-C_{60}. For LMG·C_{60} similar dependence is observed, E decreases from 3.0 eV for isolated pair LMG-C_{60} to 2.3 eV for nanocluster, consisting of three layers and tens pairs LMG-C_{60}. The same dependence of HOMO-LUMO gap is observed and for fullerene C_{60} at transition from the isolated molecules to a solid-state status.

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Isomers of fullerene C_{60}

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Fullerene soot was obtained in the electric arc between two graphite rods in the atmosphere of helium. The method is similar to [1]. Then the fullerenes were extracted by xylene and the resulting solution was subjected to chromatographic separation procedure. The original mixture of fullerenes in solution, as well as separated products (mainly C_{60} and C_{70}) were analyzed in Schimadzu LC-20AD chromatograph by HPLC method, in Schimadzu UV-1700 spectrophotometer and in MX-1320 mass-spectrometer, using the principle of spatial separation of ionized particles under investigation in the transverse magnetic field. The ion formation occurred using electron impact technique. Scanning of mass spectrum was carried out by continuous change of magnetic field at the constant accelerating voltage and energy analyzer voltage.

The analysis of chromatograms and mass spectra has revealed that the results do not coincide with each other. Thus, the chromatographic analysis of some samples showed only the presence of fullerene C_{70}. However, the mass spectrum of the same samples in addition to C_{70} indicated a large amount of C_{60} (60%). It could not be a classic C_{60} (icosahedron) that was allocated first at chromatographic separation, and its absence in these samples was argued chromatographically. Therefore, it was assumed the existence of isomer (isomers) of C_{60} the structure of which allows pentagon–pentagon ring fusion.

In order to characterize the main structural and electronic properties four isomers C_{60} with one, two and three pairs of fused pentagon rings have been studied by DFT calculations. All calculations were performed at B3LYP/6-31g(d) level with full geometry optimization for the I_h-, C_{2v}-, C_s-, C_2- and D_{2h}-symmetric C_{60} cages. It turned out that the calculated isomers C_{60} have the form similar to an ellipsoid of revolution like C_{70}. The dimensions and dipole moments of the C_{2v}- and C_s-symmetric C_{60} isomers are close to those of C_{70}. To confirm the existence of isomers C_{60} the absorption spectra (in region 300-800 nm) and the luminescence excitation spectra (in region 580-850 nm) for C_{60} and iso-C_{60} in toluene were obtained; these spectra showed distinctly that these were different compounds .

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Thiophene derivatives of methanofullerene and pyrrolidinofullerenes

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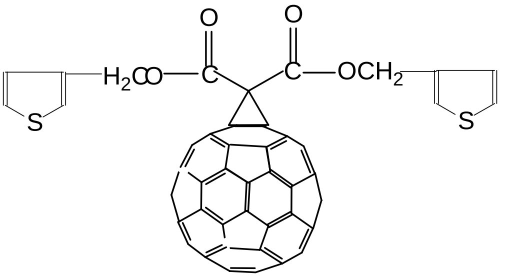
Polythiophenes are used in compositions with fullerenes for creating solar cells. The polymers containing thiophene and fullerenes may exhibit optical properties. Herewith we report our results on new thiophene containing fullerenes and their ability to give polymers upon electrochemical oxydation.



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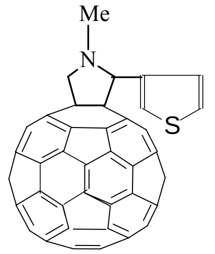

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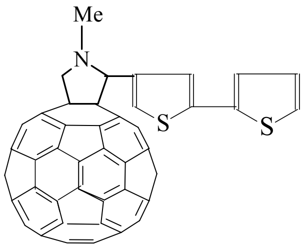

3

It has been shown, that obtaining fullerene containing polythiophenes upon oxydation of 1 and 2 is difficult, because the fullerene core is oxydized easier than thiophene fragments. The CVA data have proved to be true in a course of the film formation. The fullerene containing films are easier obtained by electrochemical oxidation if one uses bithiophenes and terthiophenes.

The electrochemical oxidation of 3 in presence of bithiophene results in formation of electrode polymeric films, containing methanofullerene 3. The presence of methanofullerene 3 in a film is proved by EPR and Raman spectroscopy.

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Functionalization of C_s-$C_{70}(CF_3)_8$: the Bingel reaction

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Earlier we reported first successful example of further functionalization of trifluoromethylated fullerene – the Bingel reaction with p^7mp-$C_{70}(CF_3)_{10}$ [1]. It was found that cyclopropanation in the case of p^7mp-$C_{70}(CF_3)_{10}$ leads to selective formation of isomeric pure monoadduct $C_{70}(CF_3)_{10}[C(CO_2Et)_2]$ what was proofed by single crystal X-ray diffraction study and theoretical calculations. Here we report results of the Bingel reaction with 1,4,11,19,31,41,51,64-$C_{70}(CF_3)_8$ (one of the known isomers with C_s symmetry [2]).

The mixture of higher trifluoromethylated fullerene derivatives ($C_{70}(CF_3)_n$, n=10-18) was prepared by reaction of C_{70} with CF_3I in ampoule at 420°C by technique described in [3]. Reaction of C_{70} and obtained mixture gave the mixture of lower trifluoromethylfullerenes with n=2-10. Isolation of the individual C_s-$C_{70}(CF_3)_8$ was carried out by means of HPLC.

The Bingel reaction performed with C_s-$C_{70}(CF_3)_8$ leads to the formation of two monoadducts, $C_{70}(CF_3)_8[C(CO_2Et)_2]$, approximately in the equal ratio and also one bisadduct, $C_{70}(CF_3)_8[C(CO_2Et)_2]$, according to MALDI mass spectra and HPLC analysis. The HPLC separation of the crude reaction mixture resulted in the main products – two fractions containing different isomers of $C_{70}(CF_3)_8[C(CO_2Et)_2]$ and one fraction with bisadduct $C_{70}(CF_3)_8[C(CO_2Et)_2]_2$. All of the isolated compounds were characterized by ^1H and ^{19}F NMR spectrometry. Slow evaporation of *o*-dichlorobenzene solution of $C_{70}(CF_3)_8[C(CO_2Et)_2]$ (one isomer) gave crystalline material suitable for X-ray crystallographic study. Single crystal X-ray diffraction study using synchrotron radiation showed the formation of monoadduct dimer $\{C_{70}(CF_3)_8[C(CO_2Et)_2]\}_2$.

Theoretical calculations showed that experimental isomers are the most preferable from both energetic and kinetic viewpoints.

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Structure of thin fullerene C_{60} polymer and composite C_{60}-PTFE and C_{60}-PANi layers

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Thin fullerene C_{60} films can be polymerized using different techniques such as excitation by photons, excitation by electrons, in plasma discharge, using different chemical means. Usually previously prepared fullerene film is subjected to polymerization process. The product of polymerization differs significantly depending on the method used. Previously proposed by us novel method of thin C_{60} polymer based films deposition – vacuum electron-beam dispersion (EBD) [1] – allows simultaneously deposit from the active gas phase and polymerize thin fullerene films as well as deposit composite coatings such as fullerene-organic polymer or even triple systems fullerene-fullerene polymer-organic polymer which to best of our knowledge were never studied before.

Vacuum EBD of fullerite targets leads to thin C_{60}-polymer containing films deposition on the substrates at room temperature. Formation of polymerized phase occurs due to irradiation of the growing layer by reflected primary and true secondary electrons from the material of the target and crucible. It is showed using Raman, FT-IR spectroscopy, AFM and SEM that by deposition process parameters adjustment it is possible to deposit films from only C_{60} monomer containing to fully polymerized. At certain deposition parameters formation of different types of C_{60}-polymer crystals was revealed. The role of charged and excited C_{60} molecules in the formation of different fullerene polymer structures is discussed.

It is showed that in composite coatings deposited by EBD of C_{60}-PANi mixture formation of areas with donor-acceptor charge transfer occurs. In the case of PANi with average molecular weight of 5 000 000 the structure of the coating was homogeneous. At the same time in the case of PANi with average molecular weight of 5 000 the structure was heterogeneous with easily distinguished areas of fullerene structures and supramolecular structures of PANi.

For composite coatings deposited from the C_{60}-PTFE mixture heterogeneous structure was revealed as well. The size of typical polymer PTFE and fullerene phases were about 1 μm. Possibility of interaction between C_{60} and PTFE as well as formation of orthorhombic C_{60}-polymer structure is discussed.

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Chemical evaluation of anti-oxidative property of the aminofullerene C_{60} derivative mixtures

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Since 1990, several physical and chemical properties of fullerene C_{60} such as the ability to accept and release electrons [1], free-radical trapping [2], the reaction with peroxy radicals [3], photoactivity [4], biocompatibility and relatively high chemical reactivity allowing structural modification [5] have been studied extensively.

Furthermore, oxidation of cumene in the presence of AIBN as initiator is a well-known example of chain oxidation of hydrocarbons which has been reported previously [6]. In this reaction an antioxidant would be capable to inhibit chain reaction by scavenging the radicals and consequently decreases oxygen consumption.

Our previous observations showed that C_{60} and its aliphatic amine derivative (octadecylaminofullerene) act as efficient inhibitors in the auto-oxidation reaction of cumene in the presence of AIBN [7]. Since the aminofullerene are formed as mixtures of fullerene derivatives having different numbers of substitutions [8], in this work we plan to compare the anti-oxidative property of aliphatic amine derivative of C_{60} in their mixtures. The radical chain oxidation reaction of cumene was applied to explore whether this property originates from the fullerene or its aliphatic amine moiety.

It was found that although there was no significant difference in the anti-oxidative properties of free amines, but their relative C_{60} derivatives showed remarkable differences in this reaction. Further experiments showed that as the chain length of the lipophilic aminofullerene increases, there would be left more active sites on C_{60} backbone during the derivatization reaction as a result of steric hindrance of the alkyl group. This is assumed to make them more eligible for participating in chain retardation reactions than C_{60} and conclusively affects on its anti-oxidative property. To probe into the role of C_{60}, the octadecyaminofullerene derivative was reacted with excess amount of nonylamine to capture the remained C_{60} active sites. It was shown that the new mixed-amine C_{60} derivative renders rather less anti-oxidative properties than to its parent aminofullerene.

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The thermodynamic properties of the derivatives of C_{60} fullerene with elementorganic ligands $R_{12}C_{60}$ (R= t-Bu, Me_3Si)

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The discovery of the method for producing C_{60} fullerenes in macroquantities has led to a new field of research. Because of extremely good prospects of the practical application of fullerenes and their functional derivatives the intensity of studies of these materials is continuously increasing.

Firstly, the temperature dependences of heat capacities $C_p^o = f(T)$ of C_{60} derivatives – $(t\text{-}Bu)_{12}C_{60}$ and $(Me_3Si)_{12}C_{60}$ – in the range from 6 to 350K by adiabatic vacuum calorimetry and in the range from 330 to 420K by differential scanning calorimetry were measured.

The low-temperature ($T \leq 50$K) dependences of the heat capacity were analyzed based on the heat capacity theory of solids of Debye's and the multifractal variant and, as a results, a chain-layer structure topology of their was estimated.

The experimental data were used for calculating the standard thermodynamic functions $C_p^o(T)$, $H^o(\Phi) - H^o(0)$, $S^o(\Phi)$ and $G^o(\Phi) - H^o(0)$ in the range from $T \to 0$ to 350 (420)K. The values of standard entropy of formation of the complexes from simple substances at $T = 298.15$K as entropy of some hypothetical reactions with their involving were determined.

The standard thermodynamic properties of the studied derivatives C_{60} fullerene and initial C_{60} fullerite were comprised and discussed. It was indicated, that an orientation phase transformation and glass-like transition of the *G*-type which are seen for the initial fullerite C_{60} over the range from $T = (185$ to $275)$K and $T = (81.0$ to $88.5)$K are absent in the $C_p^o = f(T)$ plot of the tested fullerene complexes.

On the based of our thermodynamic data, information about the structure and the composition of their and the respective data for C_{60} fullerite the some conclusions about the bound nature between fullerene fragment and ligands in the complexes were made.

The work was performed with the financial support of the Russian Foundation of Basic Research (project № 08-03-00214a).

DFT modeling of the complexes of osmium with fullerene C_{70}

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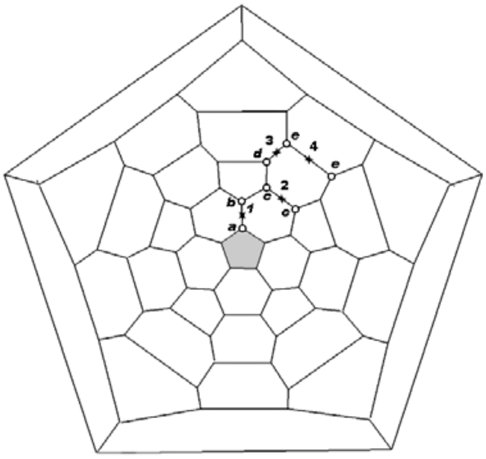
For the C_{60} fullerene, much transition metal complexes are known, whereas those for higher fullerenes are limited to a few metals. Recently in the work [1] the formation of complex (з^{2}-C_{70})$Os(CO)(t\text{-}BuNC)(PPh_3)_2$ was reported as a result of reaction of C_{70} with cis-$OsH_2(CO)(PPh_3)_2$ in the presence of *t*-BuNC. Detailed investigation allowed the authors [1] to recognize two isomers obtained in the mixture.

All this stimulated our interest in the theoretical investigation of complex (з^{2}-C_{70})$Os(CO)(t\text{-}BuNC)(PPh_3)_2$. By means of quantum chemical methods we have calculated systematically isomers **a-b**, **b-c**, **d-e**, **e-e** of з^{2}-complex (з^{2}-C_{70})$Os(CO)(CNCH_3)(PPh_3)_2$ in DFT/PBE approach.

For all isomers, optimized geometries, affinity to electron and other characteristics such as charges and electron densities were obtained. The analysis of the ground state energies gave that two most stable isomers found experimentally. We were also investigated the reaction of splitting up the complex (з^{2}-C_{70})$Os(CO)(CNCH_3)(PPh_3)_2$ to the fullerene C_{70} and group $Os(CO)(CNCH_3)(PPh_3)_2$.



The most stable isomers related to these channels of decomposition were found. The results pointed to the same isomers which were obtained.

This work was supported by the grant of Presidium of the RAS P27 "Origins of fundamental studies nanotechnology and nanomaterials".

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Trifluormethylation of sodium fullerides

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Trifluoromethylation, a synthetic approach widely applied for fullerenes was used for modification of a novel object, namely, sodium fulleride. The experiments were carried out in evacuated glass ampoules as in [1]. The previously obtained samples of fullerides Na_xC_{60}, x=1,3,6,10 [2] were the initial materials.

Experiments were performed at 300 – 420 °C. Since the heating of ampoules was conducted in an oven with a temperature gradient, the major part of reaction products vaporized and condensed at cold zones of the ampoules, where the temperature was usually 100 degrees lower than the reaction temperature. Black powder residues insoluble in hexane and toluene were obtained in the reaction zone.

Complex mixtures trifluormethylfullerenes ($C_{60}(CF_3)_n$, $n = 10 – 18$) were found in these residues. According to the MALDI mass spectral data, the content of higher trifluormethylfullerenes in the mixtures increased corresponding to the increment of quantity of sodium in the initial fullerides. On the other hand, MALDI mass spectra of the products evaporated to cold part of the reaction ampoule showed the $C_{60}(CF_3)_n$ distribution similar to that observed upon trifluormethylation of C_{60} under the same conditions.

The MALDI mass spectra of a yellow product skimmed from walls of the reaction ampoule after trifluormethylation of fulleride $Na_{10}C_{60}$ at 300 °C showed low intensity peaks which were assigned to double-cage cycloadducts of trifluormethyl fullerene. These earlier unknown compounds had 12 – 16 CF_3-groups attached to each fullerene cage and even number (2, 4) of CF_2-groups. Presumably, these carbene fragments connect two spheres to form a stable hexagonal ring between them involving C-C bonds of the fullerene cages.

This work was supported by the Russian Foundation for Basic Research, project no. 08-03-00880.

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New CF_3 derivatives of [60]fullerene

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Trifluoromethylated fullerenes represent a promising class of fullerene derivatives due to their high thermal stability, good solubility in organic solvents and strong electron acceptor properties [1]. To date, trifluoromethylated derivatives have been isolated for a variety of fullerenes: C_{74}, C_{76}, C_{78}, C_{80}, C_{82}, C_{84}, C_{90}. Though structural data for many isomers of $C_{60}(CF_3)_n$ and $C_{70}(CF_3)_n$ (n=2-18) are available, some other isomers are awaiting structural characterization.

Reactions of C_{60} with CF_3I vapor at 350-400 °C in glass ampoules usually result in complex mixtures of $C_{60}(CF_3)_n$ (n=8-18) [2]. The use of a sublimate from fullerene soot (instead of pure [60]fullerene) as a starting material has provided preparation and isolation of several new $C_{60}(CF_3)_n$ isomers. The trifluormethylation reaction of “sublimate” carried out at 410 ºC has produced two types of products. The first one originated from the cold zone of reaction ampoule and consisted of a mixture of $C_{60}(CF_3)_n$ with n = 10-16 and $C_{70}(CF_3)_m$ with m = 12-16 according to MALDI MS analysis. The second type of products from a hot zone of reaction ampoule was a mixture of trifluoromethylated derivatives of C_{60}, C_{70}, C_{74}, C_{78} and C_{82}. The first mixture was further separated by means of HPLC using hexane as an eluent. In a number of cases slow evaporation of solvent from the obtained fractions yielded crystals. Crystal structures of the new isomers of $C_{60}(CF_3)_{12}$ and $C_{60}(CF_3)_{14}$ were determined by X-ray crystallography using laboratory equipment or synchrotron radiation. Besides in some cases important structural information was extracted from 1D and 2D NMR data, namely, NMR spectra let deduce addition pattern of CF_3-groups [3].

The most energetically stable isomer C_{3v}-$C_{60}(CF_3)_{18}$ has been isolated from a complex $C_{60}(CF_3)_n$ isomer mixture by two different methods: thermal impact and product chlorination. This isomer was characterized by means of ^{19}F NMR spectroscopy and single crystal X-ray crystallography.

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Substitutional fluorination in liquid phase - new way to fluorofullerenes

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Fluorofullerenes are one of the most plentiful classes of fullerene derivatives at the present moment. For instance, more than two dozens fluoroderivatives of C_{60} are known. However only few of them may be obtained selectively [1-4].

Most known fluorofullerenes are minor products of solid-state reactions of fullerenes with binary and complex fluorides of transitional metals. Varying fluorinating agent, increased yield of particular substances may be achieved. However their content is few percent at most and the major products are still unwanted ones (like $C_{60}F_{18}$ or $C_{60}F_{36}$ for C_{60}).

In this work new way to fluorofullerenes has been suggested – substitutional fluorination of halogenofullerenes in liquid phase.

As a starting material chlorofullerenes $C_{60}Cl_6$ and $C_{70}Cl_{10}$ were used (these substances are rather simple to obtain [5-7] and can be considered as a good initial point of synthetic method). Most interesting results were obtained for reaction with silver (I) fluoride. In case of $C_{60}Cl_6$ products are fluorofullerenes $C_{60}F_2$, $C_{60}F_4$, $C_{60}F_6$ and mixed fluorochloroderivatives $C_{60}F_nCl_{6-n}$. The latter were not obtained in an individual state previously. Fluorination of $C_{70}Cl_{10}$ gives a series of fluorofullerenes like $C_{70}F_{2n}$, where $n = 1$-5.

Products of these reactions may be separated by HPLC method into individual substances and the method may be used as a new way of preparative synthesis of lower (less than 18 F atoms per fullerene core) fluorofullerenes.

It is also significant that lower fluoroderivatives of fullerenes C_{70} and higher were not obtained previously.

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Non-linear effects at the non-equilibrium fullerene aggregation

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Neutral molecules of the fullerenes are being considered as primary model elements for designing nanosystems with predetermined properties. The influence of the creation methods on the fullerite structure using optical, scanning electron and atomic force microscopes, IK-spectroscopy has been investigated. The “Mimicry” effect of the fullerite structure resulting from the influence of the substrate orientation has been discovered during fullerene deposition from Knudsen shell on the substrate from the monocrystalline graphite. Growing fullerite film repeats the graphite structure. Fullerite crystals are deposited in the form of longitude structures 0.71nm wide (diameter of the fullerene C_{60} molecule). Thereby self-similarity of the oriented films of the fullerite is being observed. Hierarchy of aggregated structures has been discovered when investigating the kinetic of the non-equilibrium fullerene’s aggregation at the evaporation from the toluene. Along with the crystal fullerite a fractal aggregation (DLA) is being observed. Studying of non-equilibrium forms with creation of non-periodical structures at the hydrodynamic non-equilibricity of a solution arising under solvent evaporation is of special interest. The hydrodynamic non-equilibricity in a solution leads to formation of selforganized fullerene’s structures which presents circle layers generated near the aggregation centre. Three types of self-organized structures of fullerenes which are classified according to the aggregation centre position: central, with shifting centre, edging have been discovered. Regularities for all types of the macrostructures: non-linear dependence of the layer radius on the layer number (mainly exponential) and periodical character of the dependence of the layer width on the layer number have been revealed. Layers consist of micro- and nanoscopic self-organized cluster systems. Structure forming elements of layers of fullerites are clusters with non-equilibrium forms – Makkey structures, hexagons.

Complexes $Pd_n(C_{60})_m$. Computer modeling of structure and prediction of electron properties

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It is known that complexes M_nC_{60} (M=Ru, Pd, Pt) catalyze reactions with participation of molecular hydrogen: hydrogenation of olefins, acetylenes, fullerenes and similar compounds. Complexes of Pd with fullerene C_{60} are the most investigated among metallocomplexes. It is proposed that these molecular systems have polymeric structures consisting of alternating atoms Pd and fullerenes which chemically linked by η^2-bonds. Three-dimensional nets can be produced at increase of Pd portion. In the case of Pd_3C_{60}, complex has the regular structure of body-centered type with lattice parameter a=11.3 Å [1]. Each molecule C_{60} disposes in the center of the Pd atom octahedron. Each Pd atom is linked to two fullerenes. Distance from Pd to the nearest carbon atom is equal to 2.27 Å. (Bond length Pd-Pd in dimer Pd_2 is equal to 2.57 Å). Besides Pd_3C_{60} structure, compounds Pd_xC_{60} were described where $1.44<x<6.3$ [2]. Therefore problem emerges about the nature and structure of complexes that can be formed in the system $\{Pd_x + [C_{60}]_y\}$.

In the present report, results of the theoretical model of the structures of complexes $Pd(C_{60})_2$, $Pd_2(C_{60})_2$, $Pd_3(C_{60})_2$, $Pd_6(C_{60})_3$ are reported. Geometry of these complexes was calculated by the DFT method in the PBE approach [3-5]. Geometry obtained for $Pd_6(C_{60})_3$. was used for modeling the structure of polymer $[Pd_3(C_{60})]_x$. Electron spectrum of $[Pd_3(C_{60})]_x$ was calculated within the tight-binding scheme based upon the extended Hückel theory (EHT). Band structure calculations show that polymer has the gap which is equal to 0.6 eV.

Possibility is discussed how to use the results obtained for the interpretation of catalytic properties of the system $\{Pd_x + [C_{60})]_y\}$.

This work was supported by the grant of Presidium of the RAS P27 "Origins of fundamental studies nanotechnology and nanomaterials".

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NT-MDT
SOLVER nEXT
RH = 40,0 %
T = 26,4 °C
NT-MDT
SOLVER nEXT

Derivatization and structure elucidation of higher fullerenes

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Since the discovery and characterization of fullerenes C_{60} and C_{70}, isolation and characterization of higher fullerenes remains a continuing task. Due to a low content of higher fullerenes in the fullerene soot, isolation of most of the higher fullerenes requires the use of a multi-step HPLC process. Their characterization proceeds typically through ^{13}C NMR spectroscopy supported by theoretical calculations of relative stabilities. Another method to characterize higher fullerenes is based on the use of their derivatives which, as a rule, are much easier to separate. An additional problem for higher fullerenes arises from the growing number of their cage isomers obeying the Isolated Pentagon Rule (IPR). Derivatization followed by isolation and investigation of derivatives may effectively contribute to structural characterization of higher fullerenes.

Reactions of a higher fullerenes mixture (also containing C_{60} and C_{70}) with CF_3I or C_2F_5I were carried out in ampoules at 200-400°C. Reaction products were separated by HPLC using Cosmosil Buckyprep column and hexane as the eluent. The crystals obtained from hexane fractions were investigated by X-ray diffraction. Structural data obtained for several CF_3 and C_2F_5 derivatives allowed us to establish cage isomers of higher fullerenes from C_{76} to C_{96}. For example, derivatives of C_{84} are represented by six different IPR cage isomers. Addition patterns of 10-18 CF_3 or C_2F_5 groups to higher fullerene cages are discussed in terms of preferable attachment to the sites of PHH junctions.

In other experiments, a mixture of higher fullerenes reacted with inorganic chloride ($SbCl_5$) or a ($TiCl_4$ + Br_2) mixture in ampoules at elevated temperature to produce fullerene chlorides. Single crystal X-ray investigation resulted in structure elucidation for chlorides of higher fullerenes such as $C_{76}Cl_{24}$, $C_{78}Cl_{18}$, and $C_{90}Cl_{32}$. It was shown that addition patterns of fullerene chlorides are very specific for different fullerene cage isomers.

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Selective [2+1]-cycloaddition of diazomethane to [60]fullerene assisted by metal complex catalysts

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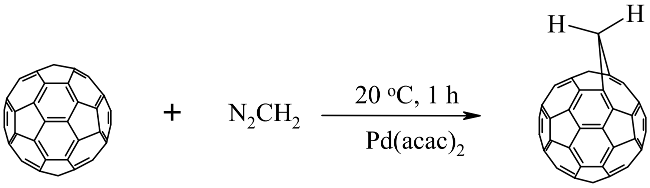
In the report the new approach to the selective synthesis of 5,6-open and 6,6-closed cycloadducts of [60]fullerene by the reaction of C_{60} with diazomethane in the presence of catalysts based on Pd complexes are presented.

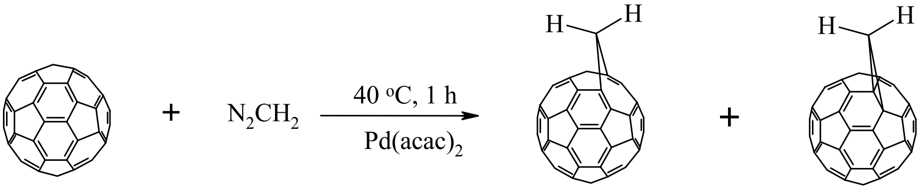
Growing interest to methanofullerene is caused by prospects of application of the last as component of high-energy combustible, and also nanomaterials for synthesis of modern additives for highly loaded mechanisms and machine, initial compounds in the synthesis of medical products.

The reaction of [60]fullerene with ethereal diazomethane in *o*-dichlorobenzene at 20°C for 1 h in the presence 20 mol.% $Pd(acac)_2$ was found to selectively produce 5,6-open fulleroid **1** with ~ 60% yield.



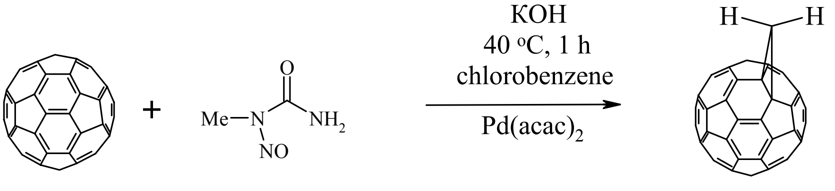
1

The increase of temperature of the reaction up to 40 °C leads to a formation of a mix of 5,6-open **1** and 6,6-closed **2** adducts of fullerene.



1 **2**

Carrying out the reaction of [60]fullerene with diazomethane, generated *in situ* from N-methyl-N-nitrozourea, in conditions 40°C, 1 h, 20 mol.% $Pd(acac)_2$, in chlorobenzene affords individual 6,6-closed methanofullerene **2** with ~ 75% yield.



2

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Catalytic [2+1]-cycloaddition of diazoacetates to [60]fullerene

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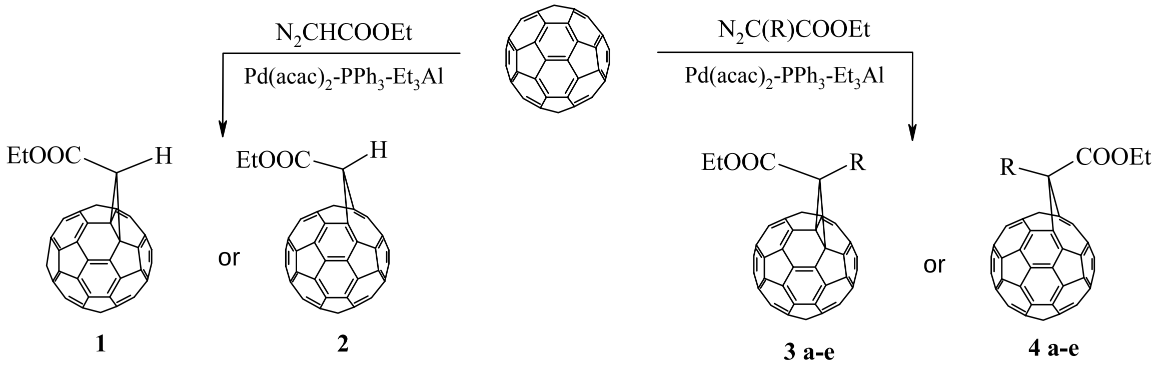
In the report the effective method of the selective [2+1]-cycloaddition of diazoacetates to carbon clusters in the presence of three-component catalytic system Pd(acac)$_2$-PPh$_3$-Et$_3$Al is presented. The suggested method allows to obtain functional substituted methanofullerenes with high yield and selectivity.

The cycloaddition of ethyldiazoacetate to [60]fullerene (80°C, 1 h) assisted by three-component catalytic system Pd(acac)$_2$-PPh$_3$-Et$_3$Al was found to selectively produce 6,6-closed methanofullerene **1** or 5,6-open fulleroid **2** in ~ 80% yield and > 95% selectivity, depending on ratio of initial components of catalytic system and the nature of a solvent. On the basis of spectra of ^{13}C and ^{1}H, it was shown, that carboalkoxy group of 5,6-open fulleroid **2** located above five-membered ring.

With the purpose of expansion of area of the application of developed catalytic systems, substituted diazoacetates have been involved in the reaction with [60]fullerene. Depending on ratio of components of three-component catalytic system Pd(acac)$_2$-PPh$_3$-Et$_3$Al and the solvent, the reaction of substituted diazoacetates with C$_{60}$ (40°C, 1 h) selectively produced either corresponding 6,6-closed **3 a-e** or 5,6-open **4 a-e** adducts of fullerene. On the basis of spectra of ^{13}C and ^{1}H it was shown, that carboalkoxy group of 5,6-open fulleroids **4 a-e** is located above six-membered ring.

Now researches on studying influence of structure of the substitutant (including natural compounds) in carboalkoxy group on selectivity of reaction are carrying out.



3a: R= Me
3b: R= Et
3c: R=*i*-Pr
3d: R= *i*-Bu
3e: R= Bn

4a: R= Me
4b: R= Et
4c: R=*i*-Pr
4d: R= *i*-Bu
4e: R= Bn

The research work was financially supported by President of Russian Federation (Grant NSh-2349.2008.3).

Methods of combination and functionalization of organolithium polymer derivatives of fullerene in the precise synthesis of regular star-shaped structures

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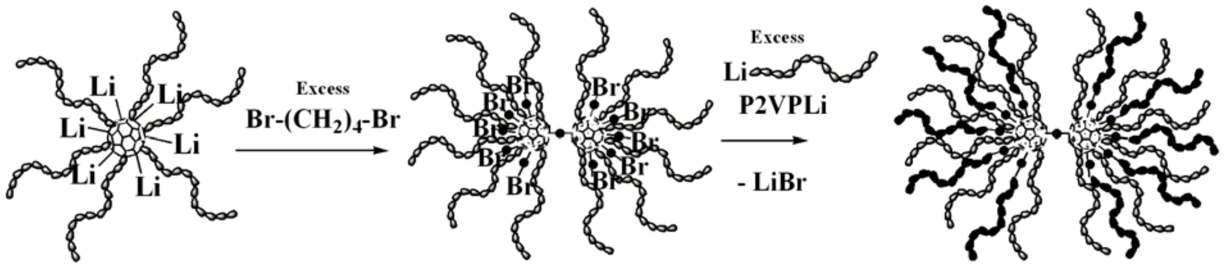
Star-shaped heteroarm polymers, combining polar and non-polar chains at the common branching center, possess a tendency to form (mono)macromicellar and complex nanostructures. The ability for self-organization, inherent in such systems, opens a way to synthesis of materials with micro-domain morphology and pronounced periodic ordering at molecular level. This is related mainly to the “stars” having a structure approaching as much as possible to perfect (model) structure.

The methods presented allow to synthesize the “stars” of reference (perfect) structure formed due to high regioselectivity of reactions of “living” anionic polymers with fullerene C_{60}, strictly preset bonding number and regulated reactivity of anionic centers C_{60}–Li created on fullerene core. The synthesis of homo- and heteroarm star-shaped polymers with double branching fullerene (C_{60}–C_{60})-center, polar and non-polar arms with well-defined chain lengths was carried out. Synthetic techniques are based on the complex approach, including several stages. These stages are: 1) using dihalogenides to bond active organolithium derivatives of fullerene C_{60} (hexa-adducts based on polystyrene, $(PS^-)_6C_{60}(Li^+)_6$) and obtain 12-arm macromolecules with double core; 2) substitution of lithium atoms to halogen-containing groups (functionalization); 3) reaction of functionalized 12-arm “stars” with “living” chains of polar and non-polar polymer (formation of 22-arm macromolecules).



The formation of regular star-shaped macromolecules of well-defined functionality was confirmed by size exclusion chromatography, molecular hydrodynamics and light scattering methods.

The work was supported by the Program of Fundamental Researches of Presidium RAS № 27.

The mechanism of interaction of azides with $C_{60}NR$

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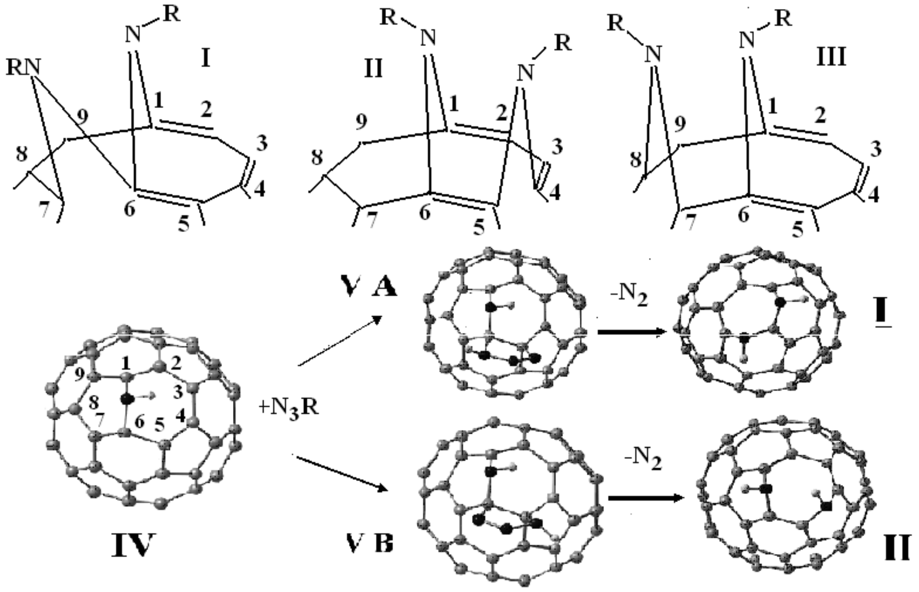
Studying the interaction of C_{60} with azides, we have shown both high selectivity of the reaction and the contradiction between stability and the yield of regioisomers $C60(NR)_2$ [1]. Strained I (*1,6; 6,7*) and stable II (*1,6; 4,5*) isomers has been obtained, though most stable isomer III (*1,6; 7,8)* and some other isomers (*1,6; m, n*) did not isolated [1,2].



To explain selectivity of bis-adducts formation, we investigated the stability $C_{60}(NR)_2$ and C_{60} $(NR)N_3R$ regioisomers and the mechanism of addition of azides to C60NR (IV) by DFT/PBE/TZ2P method. Addition of azides to *5=6* bond dominate with formation of (*1,6; 5,6*) - regioisomers C_{60} $(NR)N_3R$ (V). All other bisadducts (*1,6; m, n*) are less stable more than by 12 kcal/mole and presumably are not formed. Eliminating of N_2 from VA and VB irreversibly yields products I and II which have been isolated.

[1] I.P. Romanova, G.G. Yusupova, O.A. Larionova, A.A. Balandina, Sh.K. Latypov, D.G. Yakhvarov, V.V Zverev, O.G. Sinyashin. *Rus. Chem. Bull.* 697 (2006).

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DFT study of cycloaddition of alkyl azides to C_{60} and elimination of N_2 from adducts $C60N_3R$

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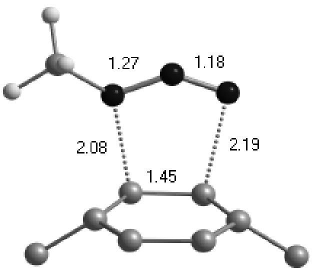
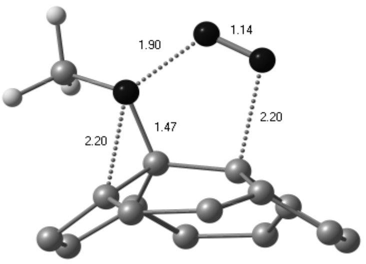
Earlier we investigated N-bridged isomers $C_{60}NH$ by HF and DFT methods with BLYP, B3LYP and PBE functional at the 6-311G ** and TZ2P basis sets and have found a good agreement between the results [1]. Recently stable and unstable isomers of various C60 adducts have been investigated by DFT/PBE/TZ2P method; we showed consistency of our theoretical results and experimental ones [2].

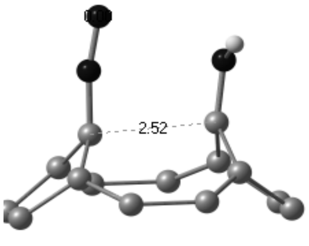
In this work the method DFT/PBE/TZ2P (Priroda package) is applied to the research of the mechanism of azides cycloaddition to C_{60}. We have found, that both reaction - azide N_3R (R=H, Me) addition to C_{60} and eliminating N_2 from the adducts are optimal in one step with the synchronous formation and cleavage of the corresponding bonds, activation barriers TS1 and TS2 being 15 and 27 kcal/mole (R=Me), accordingly. At the first reaction azides joined to the double bond of C60 and the most stable 6,6-closed adduct $C60N_3R$ is formed. At the second reaction at eliminating N_2 5,6-opened isomer C60NR is formed. Both reactions proceed with heat production:



TS1



TS2



IM

$$C60 + NNNMe \rightarrow TS1 \rightarrow [6,6]C60NNNMe \quad TS1\ 15.4,\ \Delta E\ -5.9,\ \Delta H\ -3.5$$

$$[6,6]C60NNNMe \rightarrow TS2 \rightarrow [5,6]C60NMe + N_2 \quad TS2\ 27.3,\ \Delta E\ -28.3,\ \Delta H\ -30.3$$

Earlier two-step mechanism of eliminating N2 through intermediate IM (method AM1) was reported [3], but according to our data, this two-step route is by about 15 kcal/mole higher then the proposed here synchronous route.

[1] V.V. Zverev, V.I. Kovalenko, I. P. Romanova, O.G. Sinyashin. *Int. J. Quant. Chem.* **107**, 2442 (2007).

[2] V. V. Zverev, V. I. Kovalenko. *Fullerene, Nanotubes and Carbon Nanostructures.* **16,** 555 (2008).

[3] M. Cases, M.Duran, J.Mestres, N.Martin, M.Sola. *J.Org. Chem.***66**, 433 (2001).