Metallic Fe and Co nanoparticles in powder mixtures with fullerene-containing materials

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Carbon plasma is a perspective method of synthesis of carbon nanosized materials, containing metallic clusters. However as a rule, extraction of metal-containing particles from initial soot condensate is a difficult process. The authors [1] showed that iron clusters banded with fullerene can be isolated from soot by benzene extraction. In the present work for isolation of metallic Fe and Co clusters we used termooxidation of soot impurities at the presence of Fe, Co or Na acetylacetonates. It was shown in our earlier papers, that the thermal interaction of fullerene-containing soot and metal acetylacetonates as powder mixtures proceeds in a catalytic combustion regime.

X-ray diffraction analysis and electron magnetic resonance (EÌ R) of powder materials burned previously showed that the materials contain metallic Fe or Co and nanoparticles of metal oxides connected with fullerenes. The combustion products were boiled in HCl acid, where metal oxides are dissolved. The nanoparticles of Fe and Co (1-100 nm size) and fullerenes remained in insoluble residue. Metal particles are coated probably with carbon shell, which makes difficult their dissolving in HCl acid. Following action by HNO_3 leaded to partial dissolving of the solid residue. Water soluble powders were obtained from this solution. According to the data of EMR, IR spectroscopy and element analysis the synthesized powder materials consist of polyhydroxylated fullerenes and metal (1-1.5 %). According to [2], these powders are similar to water-soluble materials which contain polyhydroxylated fullerenes and small nanoparticles (1-2 nm) of platinum and iridium. Water-soluble metal-containing fullerene derivatives are very promising for medicine, biology and pharmaceutics.

[1] N.V. Bulina, E.A. Petrakovskaya, A.V. Marachevsky, I.S. Lityaeva, I.V. Osipova, G.A. Glushenko, W. Kratschmer, G.N. Churilov, *Physics of the Solid State* **48** (5), 1012 (2006).

[2] V.G. Isakova, E.A. Petrakovskaya, V.P. Isakov, Å.A. Goncharova, Yu.E. Tolokonnikova, Joint International Conference Nanocarbon & Nanodiamond, St. Petersburg, p.75 (2006).

NMR investigations of several trifluoromethylated [70]fullerrenes

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Trifluoromethylated fullerenes constitute a particularly promising class of fullerene derivatives due to combination of remarkable electron withdrawing properties with stability towards heating and hydrolysis. One of the most useful tools for characterization of these compounds is ^{19}F NMR spectroscopy that features high “sensitivity” to addition pattern variations and to dynamics of CF_3 groups.

In the present work we report ^{19}F NMR 1D and 2D COSY spectra of two isomers of $C_{70}(CF_3)_{12}$ [1] and one isomer of $C_{70}(CF_3)_{16}$ [2]. Accurate and comprehensive analysis of the 1D spectra and topology of CF_3 interactions, as revealed by the 2D COSY spectra, combined with simulation of multiplets with the use of the WINDNMR software [3] has resulted in assignment and determination of all J_{FF} spin-spin coupling constants. Analysis of correlations between $J_{F\text{-}F}$ values and XRD- and DFT-based interatomic distances has been found to provide additional helpful means for the attribution of the ^{19}F NMR multiplets to the CF_3 positions on the carbon cage.

[1] D.V. Ignat’eva, A.A. Goruynkov, N.B. Tamm, I.N. Ioffe, S.M. Avdoshenko, L.N. Sidorov, A. Dimitrov, E. Kemnitz, and S.I. Troyanov *Chem. Commun.* 1778 (2006).

[2] S.M. Avdoshenko, A.A. Goryunkov, I.N. Ioffe, D.V. Ignat’eva, L.N. Sidorov, P. Patisson, E. Kemnitz, and S.I. Troyanov, *Chem. Commun.* 2463 (2006).

[3] H.J. Reich. WINDNMR: NMR spectrum calculations Version 7.1.12, Aug 15, 2005, reich@chem.wisc.edu.

^{19}F and ^{13}C NMR studies and DFT calculations of $C_{60}(CF_2)_n$ (n=1, 2) and their Bingel monoadducts

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Difluoromethylene adducts of C_{60}, a recently discovered class of fullerene derivatives [1], are of particular interest due to unusual trend to form [6,6]-open isomers with all carbon cage atoms remaining in the sp^2 state and consequential diverse possibilities for their chemical modification. Herein, we report ^{19}F and ^{13}C NMR spectra of $C_{60}CF_2$ that confirm predominance of [6,6]-isomer over the [5,6]-one and its open, homofullerene, nature. The NMR conclusions are supported by quantum-chemical calculations at the DFT level of theory. We also provide first ^{19}F NMR spectrum of the $C_{60}(CF_2)_2$ bis-adduct.

[6,6]-$C_{60}CF_2$ has been further chemically modified via Bingel reaction with diethyl bromomalonate and three chromatographically separated fractions of products have been examined by ^{19}F NMR spectroscopy. The spectra contained two singlet resonances, seven AB-systems and, additionally, three more pairs of AB systems of equal minor intensity. The number and type of main signals probably evidence the accessibility of all remaining [6,6]-bonds in $C_{60}CF_2$ for the malonate moiety attack since there are exactly nine different Bingel monoadducts of [6,6]-type, two of them having equivalent mirror plane-coupled fluorine atoms. The three minor paired signals are, possibly, due to Bingel addition to a $C_{60}(CF_2)_2$ admixture. Relative stability of the isomers obtained has been studied by means of ^{19}F NMR analysis of refluxed dichlorobenzene solutions and DFT calculations.

[1] A.S. Pimenova, A.A. Kozlov, A.A. Goryunkov, V.Yu. Markov, P.A. Khavrel, S.M. Avdoshenko, I.N. Ioffe, S.G. Sakharov, S.I. Troyanov, and L.N. Sidorov, *Chem. Commun.*, 374 (2007).

Synthesis of fullerene[C_{60}]-gold nanoparticle by non-ionic surfactants; polysorbate80, Brij97

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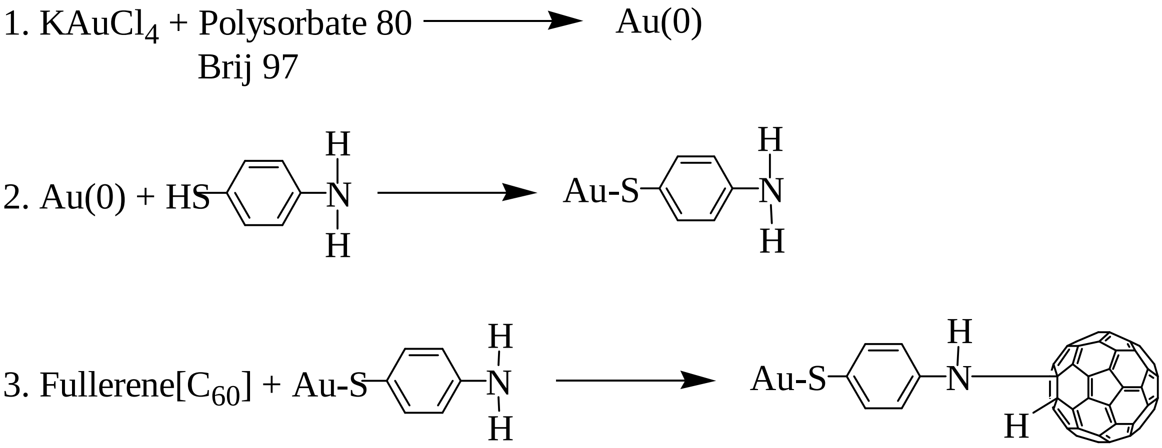
The synthesis of gold nanoparticle showed with non-ionic surfactants such as polysorbate 80, Brij 97 and $KAuCl_4$ in water. The products well dispersed gold nanoparticle in water. Gold nanoparticle reacted with 4-aminothiophenol in water and then, added diethylether, fullerene[C_{60}] in toluene and stirred for 24hr. UV-vis spectra, TEM, XRD analysis confirmed that the products were fullerene[C_{60}]-gold nanoparticle.

Scheme



[1] Y.S. Shon, H. Choo, *J. Chem. Soc., Chem. Commun.* 2560 (2002).
[2] S.R. Isaacs, H. Choo, W.B. Ko, Y.S. Shon, *Chem. Mater.* **18**, 107 (2006).

Synthesis of Various 2?-Azidoethyl per-*O*-acetyl Glycosides to Fullerene[C_{70}] Under Ultrasonication

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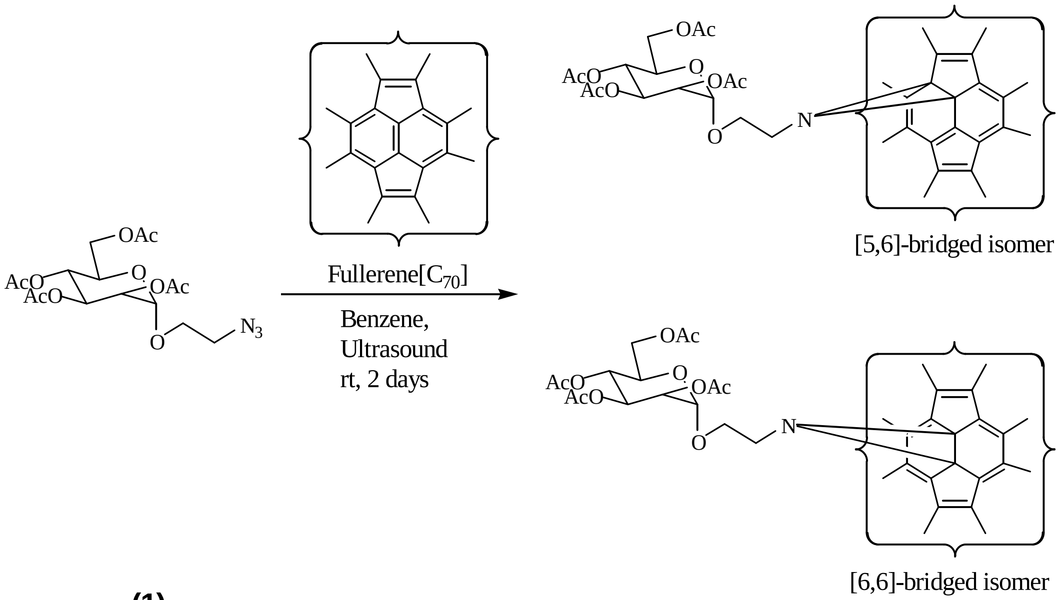
Cycloaddition of fullerene[C_{70}] with various 2?-azidoethyl per-*O*-acetyl glycoside of D-mannopyranose (**1**), D-galactopyranose, D-glucopyranose, D-xylopyranose and maltose, respectively, gave the glycosyl fullerene[C_{70}] derivatives such as α-D-mannosyl fullerene[C_{70}] (**2**) under ultrasonication. Based on analyses using of ^{1}H- and ^{13}C-NMR, UV-vis, FT-IR, and FAB-MS spectroscopies the glycosyl fullerene[C_{70}] derivatives, the products were a 1:1 glycoside-fullerene[C_{70}] adduct.

Scheme



(1)

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[1] A. Yashiro, Y. Nishida, M. Ohno, S. Eguchi, and K. Kobayashi, *Tetrahedron. Lett.* **39**, 9031 (1998).
[2] W.B. Ko, J.H. Nam, S.H Hwang, *Ultrasonics* **42**, 611 (2004).

Supramolecular approach to the synthesis of [60]fullerene - metal dithiocarbamate complexes, $\{(M^{II}(R_2dtc)_2)_x{}^{\chi}L\}^{\chi}C_{60}$ (M= Zn, Cd, Hg, Fe and Mn; x = 1 and 2). The study of magnetic properties and photoconductivity

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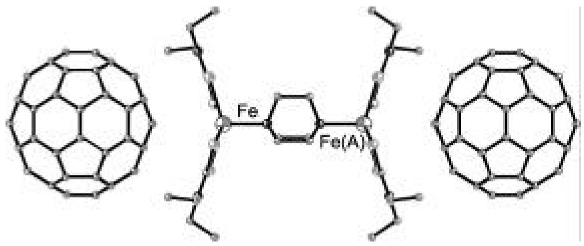
Coordination dimers and monomers formed by metal (II) dithiocarbamates, $M^{II}(R_2dtc)_2$ (M = Zn, Cd, Hg, Mn, and Fe; R = Me, Et, *i*Pr, *n*Pr and *n*Bu) and nitrogen-containing ligands (L = DABCO, DMP, and HMTA) effectively co-crystallize with fullerene to form complexes $\{(M^{II}(R_2dtc)_2)_x{\cdot}L\}{\cdot}C_{60}$ (x = 1 and 2) with layered and 3D packing of fullerene molecules (**1-11**) [1]. Metal atoms are five-coordinated in $\{M^{II}(R_2dtc)_2\}_2{\cdot}L$ units with one short axial M-N(L) bond and four longer equatorial M-S(dtc) bonds.



Crystal structure of C_{60} complex with $\{Fe^{II}(Et_2dtc)_2\}_2{\cdot}$DABCO dimer

According to optical and EPR spectra **1-11** have a neutral ground state. Magnetic susceptibilities of $\{[M^{II}(Et_2dtc)_2]_2{\cdot}DABCO\}{\cdot}C_{60}{\cdot}(DABCO)_2$ (M = Mn and Fe) follow the Curie-Weiss law in the 50-300 K range with the Weiss constants Q = 0.35 and 1.70 K, respectively. Magnetic moments of the complexes are 8.23 and 6.88 μ_B at 300 K and correspond to the high-spin state of the Mn^{II} (S = 5/2) and Fe^{II} (S = 2) ions. The increase of $\mu_{eff.}$ below 35 and 50 K up to 8.5 μ_B (at 3 K) and 7.4 μ_B (at 6 K) proves a short-range ferromagnetic interaction of spins in the $[M^{II}(Et_2dtc)_2]_2{\cdot}$DABCO dimers.

The complexes show up to 10^2 times enhance of photocurrent under the illumination of the crystals by white light. The main contribution to the generation of free charge carriers is provided by direct charge transfer from $\{M^{II}(R_2dtc)_2\}_2{\cdot}L$ to C_{60}. It was found that photocurrent increases in magnetic field with induction B < 1 T.

The work was supported by the Russian Science Support Foundation, INTAS YSF 05-109-4653 and RFBR grants N 06-03-32824 and 06-03-91361.

[1] D.V. Konarev, S.S. Khasanov, A.Yu. Kovalevsky, V.V. Lopatin, V.V. Rodaev, G. Saito, and R.N. Lyubovskaya, *Cryst. Growth Des*., 2007, in press.

Unexpected formation of pyrrolinofullerenes in the acid-catalyzed [2+3]cycloaddition reactions of [60]fullerene with imines

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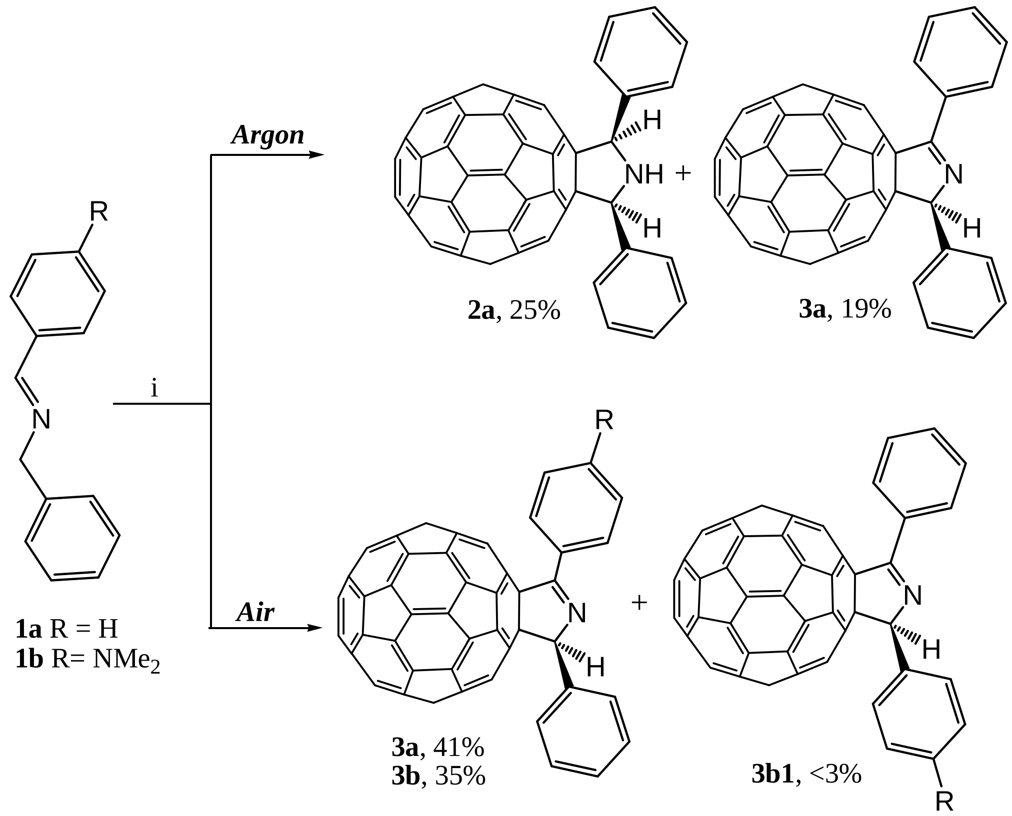
We report for the first time on the acid-catalyzed reactions of [60]fullerene with imines of benzylamine that yield 2,5-disubstituted pyrrolidinofullerenes or pyrrolinofullerenes depending on the reaction conditions. The developed synthetic methods provide easy route for fullerene derivatization and might be also used in general organic synthesis for preparation of various pyrrolidine- or pyrroline ring containing targets.



Theoretical research of poly-[2+1]-cycloaddition to $Ñ_{60}ÑF_2$

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The lasting interest of researchers in the field of $Ñ_{60}$ derivates is due to potential applications of fullerene compounds as constituents of energy-harvesting complexes. A proven and most commonly used method of organic functionalization of fullerene cage is [2+*n*]-cycloaddition, where *n*=1-4. However most of the products of such reactions appear to be weaker electron acceptors than C_{60} itself, which strongly limits their practical value. The recently discovered CF_2 derivatives of $Ñ_{60}$ that can be synthesized via attachment of difluorocarbene constitute a promising exception. In addition to the negative inductive effect of the CF_2 moiety, the $C_{60}CF_2$ monoadduct exhibits unusual molecular structure with a cleaved [6,6]-bond [1]. Thus, all 60 carbon atoms of the fullerene cage retain their sp^2 nature and can take part in electron delocalization.

Although, further cycloaddition of CF_2 groups results in formation of complex mixture of $C_{60}(ÑF_2)_n$ compounds (*n*=1-6) and their characterization is far from completion, a quantum-chemical survey of stability and structures of their possible isomers at the DFT level of theory has been undertaken. We report the theoretically observed trends in sequential CF_2 addition and the expected isomeric composition of the products of thermodynamically governed synthesis.

We have also studied some related processes of $Ñ_{60}ÑF_2$ functionalization with some divalent groups like CH_2, $C(COOEt)_2$, NH. Systhematic elucidation of structure and properties of such compounds may help to find novel promising targets for synthetic chemist and designers of photovoltaic devices.

[1] A.S. Pimenova, A.A. Kozlov, A.A. Goryunkov, V.Yu. Markov, P.A. Khavrel, S.M. Avdoshenko, I.N. Ioffe, S.G. Sakharov, S.I. Troyanov and L.N. Sidorov, *Chem. Commun.* 374 (2007).

Crystallosolvates of fullerene C_{60} with individual and mixed solvents

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The interactions of fullerenes with organic solvents have become a significant part of fullerene chemistry related to the technological synthesis of these class of compounds. The formation of solid solvates with different classes of solvent molecules (aromatics, alkanes, halogenated alkanes etc.) is a characteristic feature of fullerenes. Dramatic changes in crystalline lattice and decomposition of these van der Waals complexes with temperature result in anomalous temperature dependence of solubility, in particular. Absolute values of solubility of fullerenes also depend upon the thermodynamic stability of these solids.

This work has been focused on experimental study of the systems C_{60} with pure o-dichlorobenzene, tetrachloromethane, toluene, tetralin and mixtures tetrachloromethane with toluene, o-dichlorobenzene and tetralin by means of solubility measurement (298.15–368.15K temperature interval) and differential scanning calorimetry (DSC 204 F1 Phoenix NETZSCH instrument).

We found that C_{60} solubility in pure tetrachloromethane is temperature independent in the studied temperature range. In pure toluene and o-dichlorobenzene we observed a decrease of C_{60} solubility with increasing of temperature. In pure tetralin we observed the maximum of solubility at 341K. We have suggested the equation to evaluate the C_{60} solubility dependence on temperature and composition of mixed solvent. The thermodynamic functions of C_{60} solution process have been calculated using this equation.

We were able to identify the solid solvates in all studied systems. The thermodynamic parameters (temperatures T_{imp}, enthalpies $?_{\mathrm{r}}H$, and entropies $?_{\mathrm{r}}S$) of observed crystallosolvates were determined using differential scanning calorimetry. We supposed that these solvates contain both components of mixed solvent. The thermodynamic characteristics of the incongruent melting process and influence of solvate formation on solubility of C_{60} have been discussed.

We also calculated the thermodynamic functions of solution and solvation of C_{60} in the individual tetrachloromethane, toluene, tetralin and 1,2-dichlorobenzene. It was shown that temperature dependence of the Gibbs free energy of C_{60} solvation in the individual solvents is controlled by the entropy term.

This work has been done under the financial support of Russian Foundation for Basic Research (RFBR), project ¹ 05-03-32696.

Electronic structure and optical properties of charge-transfer fullerene-porphyrin complexes: ab initio calculations

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The organic fullerene derivatives have attracted considerable attention as perspective materials for microelectronic devices [1-3]. In this work, *ab initio* calculations of optimized geometry, electronic structure, and vibrational properties of meso-tetraphenylporphyrin H_2TPP, MgTPP, ZnTPP and fullerene based complexes, H_2TPP-C_{60}, MgTPP-C_{60} and ZnTPP-C_{60} are carried out. The method of density functional theory with B3LYP hybrid functional was employed. All the calculations have been performed at the 3-21G and, partly, at 6-31G* levels.

It is found that H_2TPP-C_{60} is a molecular complex with dissociation energy $E_{\rm dis}$=0.15 eV, and TPMgP-$C_{60,}$ TPZnP-C_{60} are charged transfer complexes with $E_{\rm dis}$= 0.4 eV and 0.6 eV, respectively. The calculated values of HOMO-LUMO gap $E_{\rm g}$ for the complexes (1.68 eV in H_2TPP-C_{60}, 1.48 eV in MgTPP-C_{60} and 1.38 eV in ZnTPP-C_{60}) are in excellent agreement with those values found from tunneling spectroscopy data [4]. The origin of a narrowing of a HOMO-LUMO gap in the complexes as against that in the molecular components (2.73 eV in H_2TPP, 2.87 eV in MgTPP, 2.95 eV in ZnTPP and 2.94 eV in C_{60}) is elucidated. The excited electron states of the H_2TPP, MgTPP and ZnTPP-C_{60} are examined using time-dependent DFT method. The vibrational frequencies and their IR intensities for the both H_2TPP and H_2TPP-C_{60} are calculated. The results are in an a good agreement with experimental data [1, 5]. The work is supported by the Russian Foundation for Basic Research (Grants 05-02-17779 and 06-02-17305).

[1] M.E. Milanesio, M. Gervaldo, L.A. Otero, L. Sereno, J.J. Silber and E.N. Durantini. *J. Phys. Org. Chem.* **15**, 844 (2002).

[2] D.M. Guldi, I. Zilbermann, G. Anderson, N.A. Kotov, N. Tagmatarchis and M. Prato *J. Mater. Chem.* **15**, 114 (2005).

[3] D.M. Guldi. *Pure Appl. Chem.* **75**, 1069 (2003).

[4] T. Nishino, T. Ito, and Y. Umezawa, Proceedings of the National Academy of Sciences of the United States of America (PNAS). **102**, 5659 (2005).

[5] I.B. Zakharova, E.G. Donenko, Yu.F. Biryulin, L.V. Sharonova. This conference.

Aggregation in C_{60}/NMP, C_{60}/NMP/water and C_{60}/NMP/toluene mixtures by UV-Vis spectroscopy and SANS

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Solutions of fullerenes in nitrogen-containing solvents (e.g. N-methyl-2-pyrrolidon (NMP), pyridine and etc.) constitute a specific class of C_{60} solutions characterized by the formation of fullerene clusters. NMP is supposed to form electron donor-acceptor complexes with fullerenes and dissolve them. N-methyl-2-pyrrolidon dissolves C_{60} quite well (solubility 1240 μM) and is miscible with water. So, it can be used for fullerene transfer into aqueous media, which is of current interest with respect to employing biological activity of fullerenes in medical applications.

In the present paper the aggregation of C_{60} in the solvent *N*-methyl-2-pyrrolidinone (NMP) and in the binary mixtures NMP/water and NMP/toluene by UV-Vis spectroscopy and small-angle neutron scattering (SANS) is investigated. The intensity of characteristic peaks of fullerenes in the UV-Vis spectrum of the C_{60}/NMP solution changes with time, which reflects the cluster formation. The addition of water into C_{60}/NMP system leads to changes in spectroscopic and SANS data. This effect is the result of the cluster reorganization at the scale of 1-100nm. The effect has a critical character and takes place if the water relative content is higher than 40 %. With binary mixtures of miscible polar and non-polar solvents it is possible to change the size of a cluster by changing the composition of the liquid media. An increase in the polar solvent content leads to the clusters growth. The critical value of permittivity in solution (at which clusters form) is $e = 13\pm1$. The example of such a binary solvent is a mixture of NMP ($e = 32$) and toluene ($e = 2.37$). The change in the toluene content in the system $\tilde{N}_{60}$/NMP/toluene makes it possible to vary permittivity of the whole solution in a wide interval. Spectra of $\tilde{N}_{60}$/NMP/toluene solutions at different toluene content are analyzed. Also, results of fullerenes extraction by hexane (non-miscible with NMP) from $\tilde{N}_{60}$/NMP are reported.

Oxidation and polymerization of fullerenes Ñ$_{60}$, Ñ$_{70}$ and Ñ$_{60}$/C$_{70}$ mixtures

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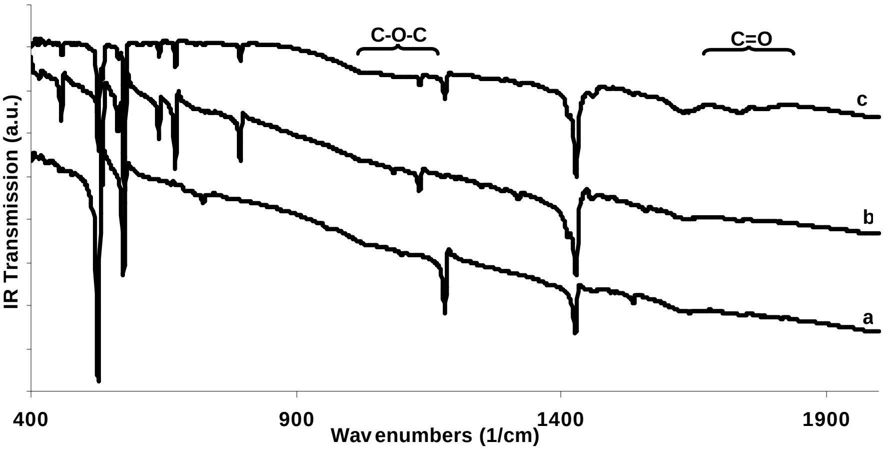
A great number of papers on low-temperature destruction of fullerenes have mostly been aimed at studying pure (mainly Ñ$_{60}$) fullerenes, the influence of various impurities (residues of solvents, adsorbed gases, etc.) being the subject for study. Meanwhile oxidation/polymerization of a mixture of fullerenes Ñ$_{60}$/Ñ$_{70}$, their solid solutions formed by rapid crystallization from solution is a great interest.

The results of research on oxidation/polymerization of powders pure Ñ$_{60}$, Ñ$_{70}$ fullerenes, after being annealed at 473 K ambient condition, the fullerene 20% Ñ$_{70}$ mixture recrystallizated from toluene solution as well as the mixture received obtained without preliminary chromatographic separation are presented in this paper. Comparative research has been carried out by x-ray diffraction and optical spectroscopy. Formation of the dimers linked by the furanoid bridge (stretching mode of C-O-C group exhibit the bands in region 1200-1000 ñì $^{-1}$) and possible fullerene molecule destruction (stretching mode of C=O group exhibit the bands in a region 1780-1715 ñì $^{-1}$) has been determined by FT-IR spectroscopy.



IR transmission spectra of recrystallized samples pure (Ñ$_{60}$), Ñ$_{70}$ (b) and Ñ$_{60}$/Ñ$_{70}$ mixtures (c) after being annealed at 473Ê.

The studies have revealed that oxidation and polymerization are not observed for pure Ñ$_{60}$, Ñ$_{70}$, including samples recrystallized from toluene solution. They have been found only in case of Ñ$_{60}$/Ñ$_{70}$ mixtures recrystallization. It has been shown, that oxidation/polymerization is defined by the initial crystal state of the samples.

The work was supported by the fundamental research program of Presidium of the Russian Academy of Science.

Supramolecular complexes of oligophenylvynil resorcinarene-dendrimers and fullerene C_{60}

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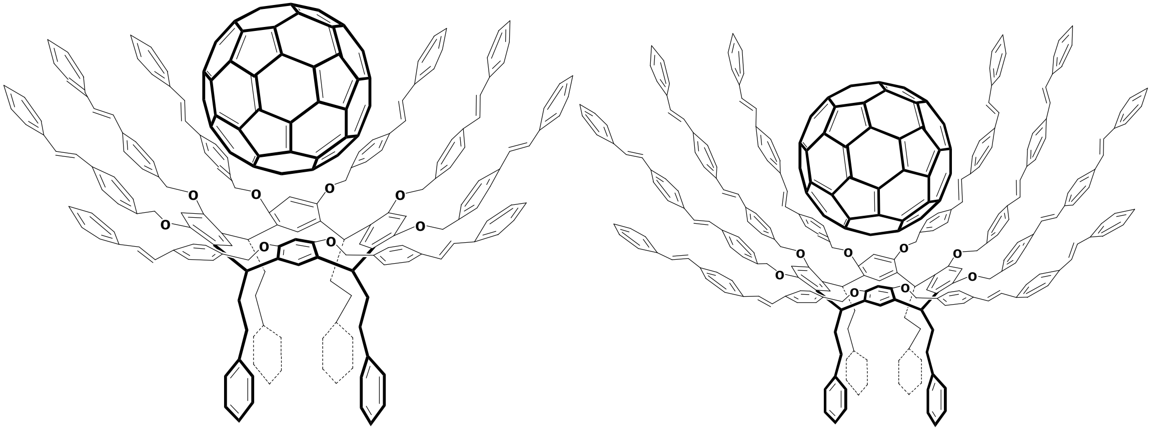
Resorcinarenes, readily available in the form of their rccc (all cis) isomers by acid catalyzed condensation of resorcinol with high molecular weight aldehydes, are easily substituted in the hydroxy groups of the resorcinol units by alkylating reagents. Dendrimers are three-dimensional macromolecules with well defined structures. In the last years a number of synthetic approaches for producing dendrimers have been described in the literature.[1] The convergent method starts from the periphery towards the central core.[1] In the present work we report the convergent synthesis of two generations of dendrimers using resorcinarenes as an eight focal point core molecule with oligophenylvinyl dendrons and their novel supramolecular complexes with [60] fullerene.

The resorcinarenes were synthesized following a synthetic methodology described previously[2] and only “crown” conformation was observed by ^1H NMR spectroscopy. The dendrons were carried out in several steps from styrene and 4-bromobenzaldehyde using Heck and Wittig reactions. The dendrimers were obtained from resorcinarenes and the dendrons in acetone at reflux for 3 days in presence of K_2CO_3. The structures of first and second generation of dendrimers were confirmed by ^1H, ^{13}C NMR spectroscopy, elemental analysis, FAB+ and MALDI-TOF mass spectra.



The supramolecular complexes **1** and **2** were obtained from the dendrimers and fullerene C_{60}, the reaction was carried out in toluene at reflux for 7 days. The elemental analysis showed 1:1 relation, π-π, CH-π and n-π interactions were observed by ^{13}C CP-MAS, FTIR, analysis

[1] G.R. Newkome, C.N. Moorefield, F. Vogtle, Dendritic molecules: concepts, syntheses, perspectives, VCH,Weinheim 1996.

[2] M.A. Garcia, C.J.G. Dominguez, E. Klimova, T. Klimova, N.M. Gutierrez, G.M. Martinez, *Fullerenes, Nanotub. And Carbon Nanostruc.* **14**(2,3), 357-363 (2006).

Synthesis and crystal structure of new molecular complex of C_{60} with [Re(CO)$_3$Cl(DEAS-BPy)]: C_{60}·[Re(CO)$_3$Cl(DEAS-BPy)]·$C_6H_4Cl_2$

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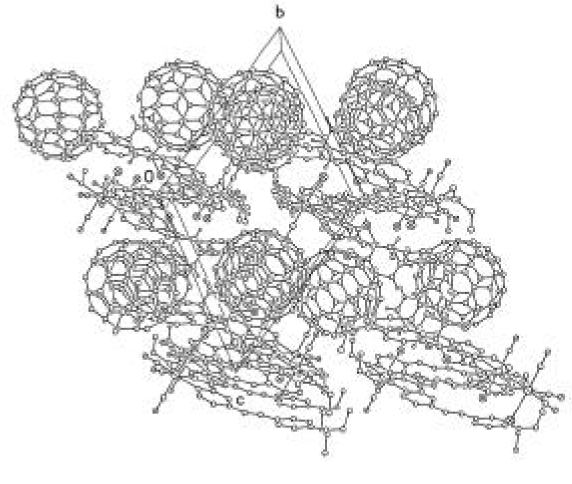
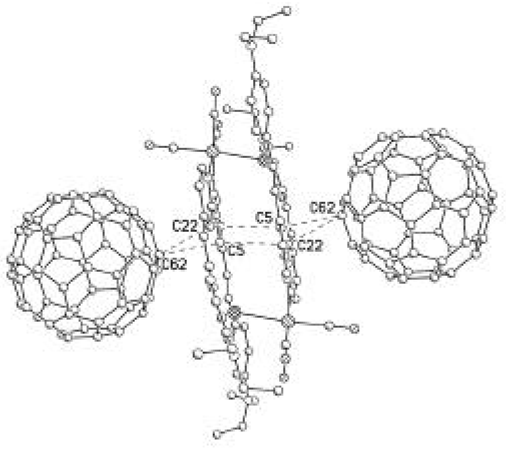
New C_{60} molecular complex with [Re(CO)$_3$Cl(DEAS-BPy)]: C_{60}·([Re(CO)$_3$Cl(DEAS-BPy)]·$C_6H_4Cl_2$ (**1**) ([Re(CO)$_3$Cl(DEAS-BPy)] = 4,4'-bis[?-(diethylamino)-?-styryl]-2,2'-bipyridine}-tricarbonylchlororhenium(I)) has been synthesized by evaporation of *o*-di-chlorobenzene solution containing [Re(CO)$_3$Cl(DEAS-BPy)] and C_{60} at a 2:1 molar ratio.

Crystal data for **1** are: $C_{103}H_{42}N_4O_3Cl_3Re_2$, M=1675.96 g·mol^{-1}, dark red parallelepipeds, triclinic, space group P1?, a=15.8794(4), b=15.9922(4), c=16.0080(4), ?=111.984(1) , ?=112.382(1) , ?=98.0280(10) , V =3291.4(1) A^3, Z=2, D$_c$=1.691 g·cm^{-3}. In the crystal, C_{60} and [Re(CO)$_3$Cl(DEAS-BPy)] form alternating layers, which make an angle of 49° with the crystallographic plane ***ab***. In a C_{60} layer, the fullerenes are arranged into hexagonal honeycomb, so that each molecule has three neighbours with the center-to-center distances of 9.835 A, 9.863 A and 10.290 A. Inside these hexagons, formed by the fullerenes, the solvent molecules reside as dimers with short Cl…Cl interactions C…C of 3.530 A (the sum of van der Waals radii is 3.80 A^3). These dimers stick out of the fullerene layer into the Re molecules layer. The other chlorine atom of the *o*-dichlorobenzene makes short van der Waals contacts with a neighbouring C_{60}, Cl…C 3.57A (the sum of van der Waals radii is 3.61 A^3). The Re molecules form a lot of interactions with the fullerenes by their DEAS-BPy ligand. The interactions between the π-conjugated systems of DEAS-BPy ligands in a dimer and with the fullerene molecules result in the formation of π-stacked tetramers.

The work was supported by the RFBR (grant 06-03-32824a).





Charge transfer complexes of fullerene C_{60} with N,N-dimethylaniline derivatives

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The charge transfer (CT) complexes of C_{60} with N-aromatic donors are the important objects for the photoinductivity process investigation. The influence of the X substituents on the energies of the CT bands ($h?_{CT}$) in the electronic absorption spectra was investigated in CH_2Cl_2 solution:

$1,4\text{-}XC_6H_4N(CH_3)_2 + C_{60}$ - $1,4\text{-}XC_6H_4N(CH_3)_2^{\bullet+} \bullet C_{60}^{\bullet-}$ ($h?_{CT}$; solvent CH_2Cl_2)

The X substituents and $h?_{CT}$ values (eV) are as follows: $(CH_3)_2N$(1.823); CH_3O(2.137); CH_3(2.296); H(2.34); Br(2.442); CHO (2.504); CN (2.61).

It has been known [1], that equations of the type (1)-(3) are valid for CT complexes

$$h?_{CT} = h?_{CT}^{H} + a?_{I} + b?_{R} + c?_{?} \qquad (1)$$

$$h?_{CT} = d + k\,IP \qquad (2)$$

$$h?_{CT} = l + mE_{1/2}^{ox} \qquad (3)$$

where $?_I$, $?_R$, $?_?$ are inductive, resonance and polarizability (ion-dipole interaction of the radical cation charge with the induced dipole of the X substituent) constants of the X substitutes, IP is the ionization potentials of the N-aromatic donors, $E_{1/2}^{ox}$ is electrochemical oxidation potentials. Parameters of the correlation equations are displayed in the Table:

Equation (1)			Equation (2)		Equation (3)			
a	b	c	d	k	l	m	S_y	r
0.33	0.58	-0.1					0.04	0.99
0.34*	1.43*	-0.64*	-3.85*	0.84*			0.05	0.98
1.25**	-1.04**	0.82**			1.72	0.85	0.05	0.98

*Values $h?_{CT}$ and IP are taken from Ref.[2]; ** Values $h?_{CT}$ are taken from Ref.[3].

The electronic absorption spectra of the $1,4\text{-}CH_3C_6H_4NR_2$ (R = H, CH_3, C_2H_5) complexes with the C_{60} (solvent toluene) [2] and with the C_{70} (solvent CCl_4) [3] were analyzed.

It was shown that the $h?_{CT}$ values of all investigated weak complexes depend on the inductive, resonance and polarizability constants of the X substituents in the N,N-dimethylanilines. The resulting linear relationships are described by the expression (1). The analysis shows the dominating role of the resonance effects in the complexes.

[1] A.N. Egorochkin, O.V. Zderenova, S.E. Skobeleva, *Russ. Chem. Bull.* **49**(6), 997 (2000).

[2] S.P. Sibley, R.L. Campbell, H.B. Silber, *J. Phys .Chem.* **99**(15), 5274 (1995).

[3] S. Bhattacharya, S.K. Noyak, S. Chattopadhyay et al., *J. Phys. Chem.A*, **106**(29), 6710 (2002).

Homolytic reactive mass spectrometry of fullerenes: interaction of C_{60} with radical generating compounds from different classes in the EI ion source of a mass spectrometer

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We already reported reactions of Ñ$_{60}$ and C_{70} (substrates) with representatives of various classes of compounds (for example, ketones, aldehydes and organosilanes) (reagents) occurring under EI in the ionization chamber (IC) of a mass spectrometer *via* a mechanism involving the homolytic dissociation of the reagents. Now we have introduced another pack of the compounds capable of providing reactive radicals under EI into the reactions with C_{60} in the IC. It comprises benzene (**1**), chlorobenzene (**2**), *o*-, *m*-, *p*-carboranes (**3o**,**m**,**p**, respectively), 9-iodo-*o*-carborane (**4**), 1-*o*-carboranylmethyl bromide (**5**), benzylamine (**6**), and benzylmethylamine (**7**).

C_{60} reacted with species **1** and **2** in the IC at 300°C acquiring phenyl radicals, the paramagnetic products being stabilized by addition of the next radical or a hydrogen atom [1]. In both cases, the single phenyl addition was predominant; however, the double one also occurred though to a small extent. We failed to reliably detect the products of addition reactions with carboranes **3o**,**m**,**p** and **4** taken as reagents, probably, because did not manage to achieve sufficient partial pressures of the corresponding radicals in the IC. In accord with this, when compound **5** was used that under EI produced a relatively more stable radical $\bullet CH_2CCHB_{10}H_{10}$, and thus, with a higher partial pressure in the IC, the product of addition of this radical to C_{60} was found.

Analogously to **1** and **2,** amines **6** and **7** furnished the product of phenyl and a hydrogen atom addition to the fullerene core when reacted with C_{60} in the IC at 300°C. For **7**, the monomethylated fullerenes, stabilized by both the addition and the loss of hydrogen atoms were also registered.

[1] The ion/molecule adducts $[C_{60}\text{-}C_6H_6]^+$ and $[Nd@C_{82}\text{-}C_6H_6]^+$ formed in the gas phase under self-CI conditions (~ 10 Pa, 200°C, 100 eV) were reported (D. Sun, Zi. Liu, Zh. Liu, X. Guo, C. Hao, W. Xu and S. Liu. *Fullerene Sci. Technol.*, 1977, **5**, No. 7, 1461-1477). However, this is not our case since $HC_{60}Ph$ obtained under our conditions was shown as evaporating from the walls of the IC to be registered in the form of the molecular ion after EI.

(Fullerene)(Cyclopentadienyl)dicarbonylmanganese

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C_{60} reacts with cymantrene (CTM) on irradiation by UV-light, in decaline or î -$C_6H_4Cl_2$, at 293 K and forms a mixture of compounds, from which the green compound (**I**) is separated by chromatography on Al_2O_3. The compound (**I**) is soluble in aromatic solvents, sparingly soluble in ÑÍ ${}_2$Ñl$_2$, insoluble in hexane, is stable at presence of air in darkness. The IR spectrum of **I** indicates absorption bands, which are characteristic for C_{60} and CTM at 493, 525, 577, 838 and 1181 cm^{-1}. In comparison with CTM the CO-stretching frequencies for the **I** is shifted to a lower energy (to 1930 and 1984 cm^{-1}) on 17 and 42 ñm^{-1}, characteristic for the derivatives of CTM with CO replaced. The UV-vis spectroscopy of **I** in CH_2Cl_2 (Fig.1) has shown the presence of absorption bands which are characteristic for C_{60} at 595, 329, 253 nm and for fullerene adducts (430 nm). In comparison with CTM (3.89 ppm, C_6D_6), the resonances of C_5H_5 ring protons are shifted to a lower field in ^{1}H NMR spectrum of **I** (4.29 ppm, C_6D_6), characteristic for the derivatives of CTM with CO replaced. The solid sample **I** decomposes above 423Ê in vacuum 10^{-2} torr with formation of gas and loses 14% of weight on heating to 623K. The solid residue of thermal decomposition has molar ratio Ñ$_{60}$/Mn is close to 1. The compound **I** decomposes on irradiation by light at the air presence to form Ñ$_{60}$ and manganese oxides. Thus, **I** is the fullerene ?-complex - CpMn(η^2–C_{60})(CO)$_2$ (**I**).

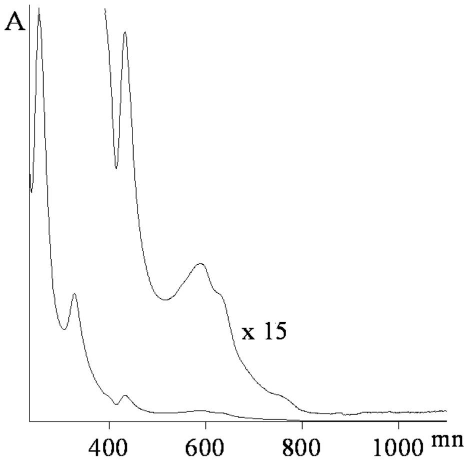

Fig. 1. UV-vis spectra of CpMn(η^2–C_{60})(CO)$_2$ in CH_2Cl_2.

This work was supported by the Grants of the RF President (Scientific School, NSh-8017.2006.3), the Federal Science and Innovation Agency, the RFBR (project 06-03-32728a), and programs of the Presidium of the RAS and of the Division of Chemistry and Materials Science, RAS.

Bis(arene)vanadium(I) fullerides

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Ñ$_{60}$ reacts with bis(mesitylene)vanadium(0) and mixture of compounds $[(\eta^6–C_6H_{6–n}Et_n)(\eta^6–C_6H_{6–m}Et_m)V]^0$ n=1-3; m=1-3 in PhMe or î–$C_6H_4Cl_2$ at 293K and forms microcrystalline black compounds (**I**) and (**II**) correspondingly. The compounds **I** and **II** are insoluble in hexane, sparingly soluble in PhMe, soluble in PhCN. Analysis of the V content in the **I**, **II** and in the initial organometallic compounds (OMC) shows that the OMC : C_{60} molar ratio in **I** and **II** is close to 1. The visible spectroscopy of **I** and **II** in PhCN has shown presence of absorption band which is characteristic for $[C_{60}]^{-\bullet}$ at 1079 nm. The decomposition of **II** was performed in evacuated systems (10^{-2} Torr). Volatiles were trapped using liquid N_2. Complex **II** begins to decompose above 393Ê. According to the data of ^{1}H NMR spectroscopy and chromatography, ethylbenzene, diethylbenzenes and symm-triethylbenzene are liquid products of the thermal decomposition, and they are completely isolated when complexes **II** was heated above 493 K. The composition of this mixture and of the liquid products of oxidizing decomposition of initial OMC is equal. Diethylbenzenes are the main component. Compound **II**, in difference from starting OMC, is EPR-silent. The magnetic moment of **II** is close to 3.6 µB at 293K, which corresponds to three electron spins. Thus, taking into account that the $(\eta^6–arene)_2V^+$ cation has two electron spins, **II** is the mixture of salt-like, ion-radical type fullerides (with n=1-3; m=1-3) $[(\eta^6–C_6H_{6–n}Et_n)(\eta^6–C_6H_{6–m}Et_m)V]^+[C_{60}]^{-\bullet}$.

Ñ$_{60}$ reacts with bis(t-butylbenzene)chromium(0) and bis(fluorobenzene)chromium(0) in PhMe at 293 K and forms microcrystalline black compounds - salt-like, ion-radical type fullerides $[(\eta^6–tBuPh)_2Cr]^+[C_{60}]^{-\bullet}$ and $[(\eta^6–PhF)_2Cr]^+[C_{60}]^{-\bullet}$. Bis(arene)chromium(I) and (azulenium)(azuleniat)chromium(I) fullerids reacts with sodium at 373 K, intensive stirring in toluene and forms sodium fullerides as black precipitate and solution of bis(arene)chromium(0).

$$[(\eta^6\text{–arene})_2\mathrm{Cr}]^+[\mathrm{C}_{60}]^{-\bullet} + \underset{\text{excess}}{n\mathrm{Na}} \xrightarrow{\text{373K, toluene, stirring}} \mathrm{Na}_n\mathrm{C}_{60} + [(\eta^6\text{–arene})_2\mathrm{Cr}]^0$$

arene = PhH, PhMe, tetralin

This work was supported by the Grants of the RF President (Scientific School, NSh-8017.2006.3), the Federal Science and Innovation Agency, RFBR 06-03-32728a, and programs of the Presidium of the RAS and of the Division of Chemistry and Materials Science, RAS.

Bis- and tris- thiophosphorylated aldehydes and synthesis of new fulleropyrrolidines C_{60}

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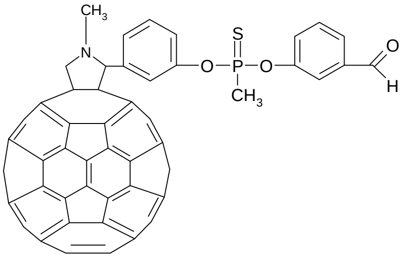
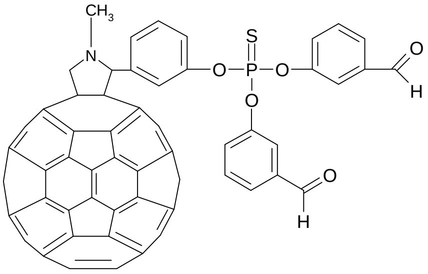
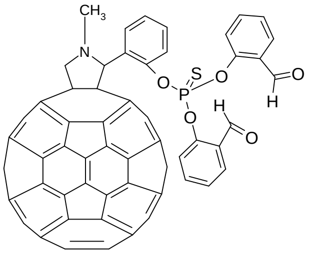
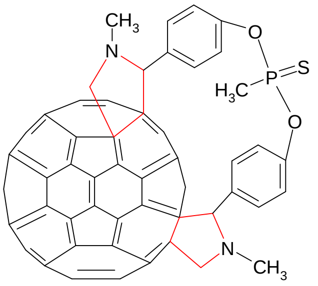
Synthesis of new functionally substituted fullerene derivatives is important for creating new materials for nanodevices. Thiophosphorylated derivatives of *para*- [1], *meta*- and *orto*-hydroxybenzadehydes are synthesized. In conditions of Prato reaction on the basis of synthesized bis-and –tris-aldehydes we obtained the new mono-fulleropyrrolidines with free reactive aldehyde groups and bis-fulleropyrro-lidines, in which two pyrrolidine fragments linked by a bridge.









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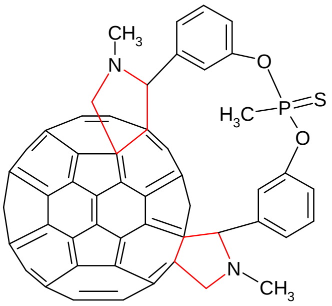

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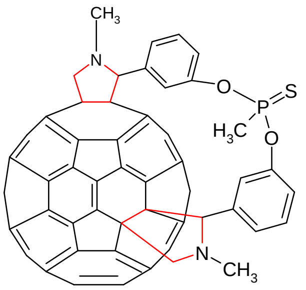

trans-4

The parent aldehydes and new fullerene derivatives were studied using RCA and quantum chemistry methods.

We studied reactions of fullerene derivatives with primary amines to obtain Shiff base that can used for preparation of water-soluble fullerene derivatives [2].

[1] G.M. Fazleeva, V.P. Gubskaya, F.G. Sibgatullina, V.V. Yanilkin, N.V. Nastapova, Sh.K. Latypov, A.A. Balandina, I.E. Ismaev, Ju.Ja. Efremov, I.A. Nuretdinov. *Russ.Chem.Bull. Int.Ed.*, **55**(3), 507-506 (2006)

[2] O.V. Nazarova, I.A. Nuretdinov, A.V. Slita, G.M. Pavlov, N.P. Evlampieva, L.S. Litvinova, V.P. Gubskaya, G.M. Fazleeva, L.Sh. Berezhnaya, A.V. Pronina, O.I. Kiselev, E.F. Panarin, *Russ. J. Appl. Chem.*, ^{1} 12, 2011-2016 (2005).

Synthesis and structure of the complexes of osmium with fullerene Ñ$_{70}$

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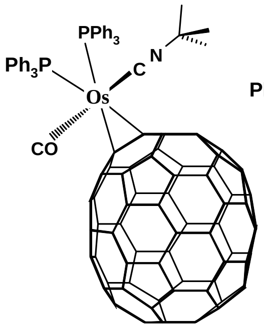
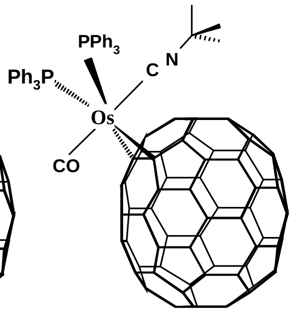
The majority of known metal-fullerene complexes belong to Ñ$_{60}$ derivatives. In contrast, complexes of fullerene Ñ$_{70}$ with transition metals are scarce and limited to a few metals.

We have found that, in the reaction of Ñ$_{70}$ with cis-$OsH_2(CO)(PPh_3)_3$ in the presence of t-BuNC, the complex (?^{2}-C$_{70}$)Os(ÑÎ)(*t*-BuNC)(PPh_3)$_2$ is arisen in the form of a mixture of two position isomers (**I** and **II,** in the ratio 10:1), where isomer **II** represents a mixture of two geometric isomers *a* and *b* in the ratio 1:1. Contrary to Ñ$_{60}$, in the case of Ñ$_{70}$ binuclear complex (?^{2}-C$_{70}$)[Os(ÑÎ)(*t*-BuNC)(PPh_3)$_2$]$_2$ (**III**) consisting of the mixture of isomers is also formed along with mononuclear compound.

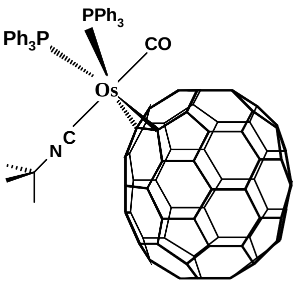
Mono-adducts I and II have been separated from bis-adducts **III** by chromatography. Structure and configuration of obtained complexes were determined using the data of elemental analysis, UV, IR and NMR ^{1}Í and ^{31}Ð spectroscopy. Structure of complex **I** has been determined by single-crystal X-Ray analysis.



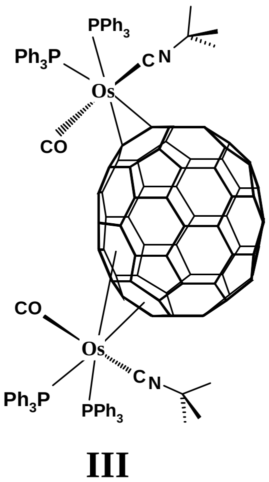
I



IIa



IIb



III

New nitroxyde methanofullerenes C_{60} and C_{70}. Synthesis and properties

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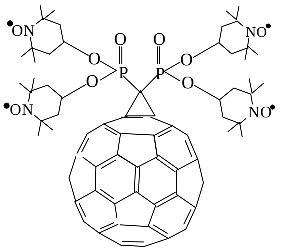
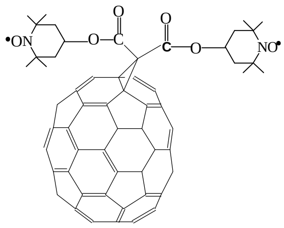
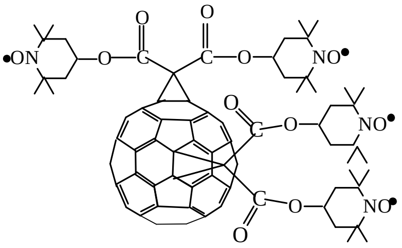
The nitroxide fullerene derivatives are perspective for obtain of new biologically active compounds, for study of pharmacokinetics of fullerene derivatives in alive and study of their optophysical properties. We obtained for the first time the new methanofullerenes containing various number of nitroxyde groups on fullerene core and investigated their some properties [1-3].







[1] L. Franco, M. Mazzoni, C. Corvaja, V.P. Gubskaya, L.Sh. Berezhnaya and I.A. Nuretdinov, *Chem. Commun.*, 2128 (2005).

[4] V.P. Gubskaya, L.Sh. Berezhnaya, V.V. Yanilkin, V.I. Morozov, N.V. Nastapova, Yu.Ya. Efremov, I.A. Nuretdinov. *Russ.Chem.Bull. Int.Ed.* **54**(7), 1594 (2005).

[5] V.P. Gubskaya, L.Sh. Berezhnaya, A.T. Gubaidullin, I.I. Faingold, R.A. Kotelnikova, N.P. Konovalova, V.I. Morozov, I.A. Litvinov and I.A. Nuretdinov**,** *Org. Biomol. Chem.***,** 2007 DOI: 10.1039/b617892h.

Molecular transformations in higher trifluoromethylated [60]fullerenes

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Trifluoromethylated fullerenes are strong electron acceptors due to the presence of electron withdrawing CF_3 group. This is the reason why trifluoromethyl derivatives of [60]- and [70]fullerenes attract attention as prospective building blocks for novel fullerene-based materials with useful properties.

Reactions of C_{60} with CF_3I vapor at 350-450°C usually result in complex mixtures of $Ñ_{60}(ÑF_3)_n$ (n=8-18) [1,2]. Only one trifluoromethylated fullerene, S_6-$C_{60}(CF_3)_{12}$, can be prepared selectively [3]. This compound possesses a unique molecular and crystal structure which defines its physical properties such as low solubility and volatility. The S_6-$C_{60}(CF_3)_{12}$ isomer is presumably more thermodynamically stable than other isomers, and it is also generated from higher trifluoromethylated derivatives and kinetically stable isomers.

The trifluoromethylation reaction of $C_{60}(CF_3)_{12}$ carried out at 420°Ñ produced a mixture of $Ñ_{60}(ÑF_3)_n$ with n = 12-18 according to MALDI MS analysis. The mixture was then separated by means of HPLC using a half-preparative column Cosmosil Buckyprep and hexane as an eluent. From some chromatographic fractions, crystals were grown by slow evaporation of solvent. Crystal structures were determined by X-ray crystallography using laboratory equipment or synchrotron radiation. This allowed us to draw some conclusions concerning trifluoromethylation reaction pathways. It could be shown that some transformations of molecular structure occur that mimic CF_3 groups migration on fullerene cage.

Analogous trifluoromethylation experiments were carried out with mixtures of trifluoromethylated derivatives, $Ñ_{60}(ÑF_3)_n$, where n = 10-16. According to MALDI MS analysis, the mixture composition shifts to higher level of trifluoromethylation (n = 12-18).

[1] I.E. Kareev, I.V. Kuvychko, S.F. Lebedkin, S.M. Miller, O.P. Anderson, K. Seppelt, S.H. Strauss, O.V. Boltalina, *J. Am. Chem. Soc.* **127**, 8362 (2005).

[2] S.I. Troyanov, A.A. Goryunkov, E.I. Dorozhkin, D.V. Ignat'eva, N.B. Tamm, S.M. Avdoshenko, I.N. Ioffe, L.N. Sidorov, K. Scheurel, E. Kemnitz, *J. Fluorine Chem.* **128**, in press, (2007).

[3] S.I. Troyanov, A. Dimitrov, E. Kemnitz, *Angew. Chem. Int. Ed.* **45**, 1971 (2006).

Selective synthesis and crystal structure of the $C_{70}(CF_3)_{10}[C(COOEt)_2]$ Bingel monoadduct

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S.I. Troyanov, and M. A. Yurovskaya

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The one of the most versatile and efficient methodologies to functionalize fullerenes and their derivatives is the cyclopropanation by stabilized α-halogenocarboanions (Bingel reaction) [1]. Here we report the first example of successful application of poly(trifluoromethyl)fullerene 1,4,10,19,25,41,49,60,66,69-$C_{70}(CF_3)_{10}$ (further p^7mp-$C_{70}(CF_3)_{10}$) [2] as building block for novel fullerene-based compound obtained via the Bingel reaction.

The mixture of trifluoromethylated [60]fullerene containing $C_{70}(CF_3)_{10}$ and $C_{70}(CF_3)_{10}$ compounds was prepared by reaction of C_{70} with CF_3I in ampoule at 400°C by technique described in [3]. Isolation of the individual p^7mp-$C_{70}(CF_3)_{10}$ was carried out by means of HPLC.

The Bingel reaction performed with p^7mp-$C_{70}(CF_3)_{10}$ as starting compound leads to the formation of monoadduct, $C_{70}(CF_3)_{10}[C(CO_2Et)_2]$, as the major product according to MALDI mass spectra and HPLC analysis. The HPLC separation of the crude reaction mixture resulted in the main product, $C_{70}(CF_3)_{10}[C(CO_2Et)_2]$, and two fractions containing isomeric minor by-products $C_{70}(CF_3)_{10}[CH(CO_2Et)]$. Probably, the latter products formed in the course of reaction of $C_{70}(CF_3)_{10}$ with traces of the monoethylmalonate followed by decarboxylation. Slow evaporation of toluene solution of $C_{70}(CF_3)_{10}[C(CO_2Et)_2]$ gave yellow crystalline material suitable for X-ray crystallographic study.

Single crystal X-ray diffraction study using synchrotron radiation revealed the molecular structure of the monoadduct with diethylmalonate group attached to sites 33 and 34 on the fullerene cage, whereas the attachment of all CF_3 groups remained unchanged. The structures of the $C_{70}(CF_3)_{10}[C(CO_2Et)_2]$ and $C_{70}(CF_3)_{10}[CH(CO_2Et)]$ cycloadducts will be discussed using theoretical calculations.

[1] C. Bingel, *Chem. Ber.* **126**, 1957 (1993).

[2] I. Kareev, I. Kuvychko, A. Popov, S. Lebedkin, S. Miller, O. Anderson, S. Strauss, O. Boltalina, *Angew. Chem. Int. Ed.* **44**, 7984 (2005).

[3] S.I. Troyanov, A. Dimitrov, E. Kemnitz, *Angew. Chem. Int. Ed.* **45**, 1971 (2006).

Difluoromethylene[60]fullerenes: synthesis, structure and properties

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Fullerenes being spheroidal closed-cage carbon molecules reveal the features of both polyenes and aromatic compounds. Hence they readily enter nucleophilic and radical addition reactions. [2+1]-Cycloaddition, considered to be one of common ways for fullerene sphere modification, results in formation of either methanofullerenes or homofullerenes. In general there can be four possible isomers of [60]fullerene derivatives: [5,6]-open and [6,6]-closed, predicted to be the most stable and experimentally observed [1], [5,6]-closed, known only for addition of germanene [:GeR_2] to C_{60}, and [6,6]-open isomer, never observed before.

Here we report of preparation of CF_2-fullerene derivatives. The developed synthetic approach allows to obtain adducts with up to five CF_2-groups added to fullerene sphere [2]. By the moment we have succeeded in isolation and characterization of the monoadduct $C_{60}(CF_2)$. According to ^{19}F- and ^{13}C-NMR spectra this compound was proved to be [6,6]-open isomer. This result was confirmed by quantum chemical calculations (at the DFT level) and UV/Vis-spectrum, obtained for $C_{60}(CF_2)$. An interesting feature of $C_{60}(CF_2)$, shown by our calculations, is the possibility of controlling the cage opening by means of electronic excitation and ionization.

In order to study the reactivity of diflurometylene[60]fullerene, it was subjected to the reaction with diethyl bromomalonate in the presence of base, giving as a result several monoadducts $Ñ_{60}(ÑF_2)C(CO_2Et)_2$. Isolation of the individual adducts was carried out by means of HPLC, isomeric composition of each fraction was established by ^{19}F-NMR spectroscopy.

Thus, formation of the [6,6]-open fullerene derivative is believed to be unusual fact in fullerene chemistry, and this unique structure will probably give rise to observation of specific properties of such molecules.

[1] B.W. Clare and D.L. Kepert, *J. Mol. Struct. (Theochem).* **548**, 61 (2001).

[2] A.S. Pimenova, A.A. Kozlov, A.A. Goryunkov, V.Yu. Markov, P.A. Khavrel, S.M. Avdoshenko, I.N. Ioffe, S.G. Sakharov, S.I. Troyanov, L.N. Sidorov, *Chem. Commun.* 374 (2007).

Scheme of the fullerenoaziridines and azahomofullerenes formation

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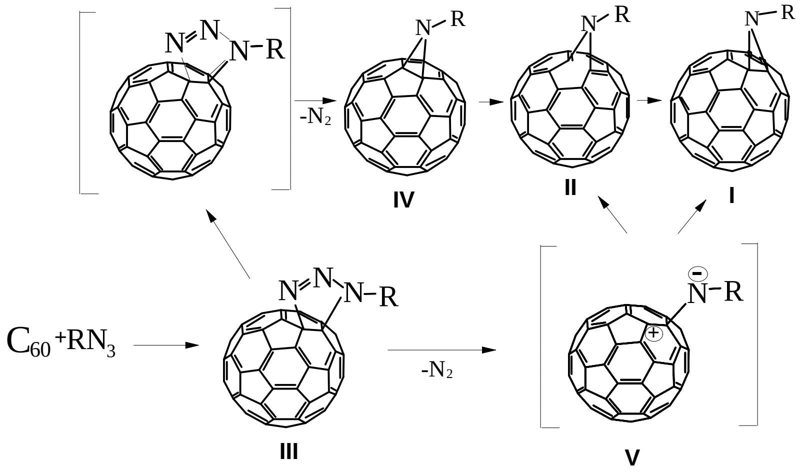
Fulleroaziridines **I** (6,6-closed adducts) and azahomofullerenes **II** (5,6-opend adducts) are “mysterious fullerenes derivatives”. The large quantities of such compounds were synthesized by the reactions of fullerenes with organic azides. But the scheme of this adducts formation is darkly so far.

The reactions of fullerene C_{60} with azides having both electron donor and electron acceptors organic fragments were systematically studied by us. As a result the sufficient evidences of azides decomposition to nitrens and the following nitrens [2+1]-cycloaddition to fullerene with the formation of isomers were not obtained. We suppose that the reaction of fullerene with organic azides is a [3+2]-cylcloaddition reaction with the thermal unstable triazolinofullerenes **III** formation. The final products structure depends on the triazolinofullerenes decomposition mechanism. In turn, the triazolinofullerenes decomposition scheme depends on the structure (electron donor or acceptor properties, volume characteristics) of azides organic fragments and conditions of the process. When using electron donor or poor electron acceptor organic fragments, the triazolinofullerenes decompose by synchronous mechanism with the formation of fulleroaziridines **IV** and isomers **II**[1]. At that the isomers **I** are the products of thermal transformation of isomers **II**. In case of electron acceptor organic fragments nonsynchronous mechanism of the triazolinofullerenes decomposition with the formation of bipolar ion **V** is most likely. **V** become stable with simultaneous formation of both isomers **I** and **II**, which do not undergo mutual thermal transformations.

This work was financially supported by the RFBR (¹ 05-03-32418à) and the RAS (Program ¹ 7-Okh).



[1] A Hirsch, and M. Brettreich, *Fullerens: Chemistry and Reactions*, Wiley-VCH Verlag, Wienheim, 2005, 422 P.

Electron acceptor phosphorylated fullerene containing materials for flexible organic photovoltaic cells

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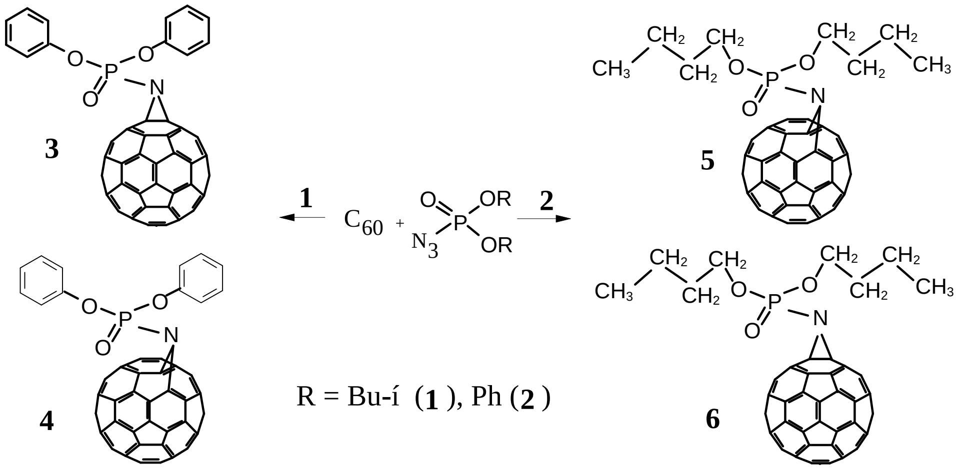
Fullerenes hold much promise for the use as a component of flexible organic photovoltaic cells.[1] However the pristine fullerenes aggregate very easily and are poorly soluble in most common solvents. As a result the efficacy of fullerene cells is low. In this view well soluble organofullerenes, which can accept electrons easier than that pristine fullerenes, are more attractive. In this work we have shown that the last-named organofullerenes may be obtained by the reaction of fullerene C_{60} with phosphorelated azides.

The reactions of fullerene C_{60} with azides **1** and **2** were carried out in o-DCB at 130 and 180°Ñ. Both the 5,6-opend and 6,6-closed monoadducts **3-6** were synthesized. The 5,6-opend monoadducts were the main products at any temperatures. The structures of adducts **3-6** were established by MALDI, ^{13}C and ^{1}H NMR (COSY, HSQC, HMBC), IR and UV spectroscopy.

The electrochemical properties of adducts 3-6 were studied at room temperature by cyclic voltammetry (CVA). It has been determined that the electron affinities of these adducts are higher than that of pristine fullerene C_{60}.

Well soluble adducts 3-6 with unusual electrochemical properties are perspective electron acceptor materials for flexible organic photovoltaic cells.



This work was financially supported by the RFBR (¹ 05-03-32418à and ¹ 05-03-32558à) and the RAS (Program ¹ 7-Okh).

[1] M.G. Nava, S. Setayash, A.Rameau, P. Masson, and J.-F. Nerengarten, *New J.Chem.* **26**, 1584 (2002).

Tether-directed bis-adducts vs dimers of [60]Fullerene with triphenylamine

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Considering the number of reactive double bonds the control of the degree of additions to fullerenes is a very challenging task. Nevertheless, sophisticated approaches have been developed in order to chemically control the topological formation of isomers with the most outstanding methodology being the tether-directed remote functionalization. The novelty of the method is based on the ability for the synthesis of fullerene bis-adducts with addition patterns that are otherwise difficult and/or improbable to be obtained under standard, thermodynamically and/or kinetically controlled, reaction conditions in moderate to high yields. On the other hand, the synthesis of all-carbon fullerene dimers as well as dumbbell shaped bis-fullerenes where two fullerene cages are interconnected by bridging organic addends represents an important frontier in fullerenes chemistry not only from the morphological point of view but most importantly as far as technological applications concern, for example when the bridging organic unit is an electron donor and/or electron transporter. Herein, we present the regioselective synthesis of an *equatorial* C_{60} bis-adduct with triphenylamine as well as the preparation of a novel C_{60} dimer in which the two buckyspheres are interconnected via a triphenylamine unit. Moreover, our research is directed towards the preparation of a series of new push-pull hybrid material consisting of the good electron acceptor C_{60} and triphenylamine as electron donor as well as efficient hole-transporter and electroluminescence material for nanotechnological applications.

We are deeply indebted to Dr Dina Yannakopoulou (Inst. Physical Chemistry, Demokritos) for obtaining some NMR spectra. Financial support from ESF/EUROHORCs through the EURYI Award is kindly acknowledged.

The thermodinamics properties of the dimeric derivatives of Ñ$_{60}$ fullerene with elementorganic ligands

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Firstly, the temperature dependences of heat capacities $C_p^o = f(T)$ of dimeric derivatives of C_{60} fullerene – $[(Me_3Si)_3C_{60}]_2$ (I), $[(Me_3Si)_7C_{60}]_2$ (II) and $[(Me_3Si)_9C_{60}]_2$ (III) in the range from 6 to 650K by adiabatic vacuum and precise differential scanning calorimetry were measured. The irreversible endothermic transitions that connecting with opening of the dimeric bond between fullerene fragments and destruction of the tested complexes on its heating were observed as well as their thermodynamic characteristics were calculated.

The low-temperature heat capacity (Ò< 50K) was analyzed on based of the multifractal variant of the heat capacity solids Deby's theory and as results the conclusion about the structure heterodynamicity of compexes was estimated.

The experimental data were used for calculating the standard thermodynamic functions C_p^o(Ò), H^o(Ô)$-H^o(0)$, S^o(Ô) and G^o(Ô)$-H^o(0)$ in the range from $T \to 0$ to 400-450K. The value of standard entropy of formation of the complex from simple substances at $T = 298.15$K has been determined.

The standard thermodynamic properties of the studied dimeric derivatives C_{60} fullerene, neutral $(C_{60})_2$ dimer and C_{60} fullerite were comprised and discussed.

On the based of the our thermodynamic data, information about the structure and the composition of their and the respective data for the neutral dimer $(C_{60})_2$ the assumption about the bound nature between fullerene fragments in the complexes was made.

The work was performed with the financial support of the Russian Foundation of Basic Research (project No. 05-03-32363), FCNTP Program (St. Contr. No. 02.442.11.7486).

[1] A.V. Markin, B.V. Lebedev, N.N. Smirnova, V.A. Davydov, AV. Rakhmanina, *Thermochim. Acta* **421**, 73 (2004).

Structure state and magnetic properties of CNM produced by the exploding wires technique

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Exploding wires (EW) technique is one of the most prominent technology for synthesis of wide spectra of carbon nanomaterials (CNM) – fullerene-like clusters, carbon nanotubes, nanodiamonds, etc. [1]. The main advantages of the above mentioned technique in comparison with traditionally used ones – laser evaporation of graphite, electrical arc process, etc.,- are a decrease of an amount of technological stages of CNM production and a possibility to fulfil the process at the atmospheric pressure. It results in essential decrease of prime cost of CNM. Moreover, EW technology enables to produce fullerene-like clusters with big masses (more than 1000 a.m.u.) and endofullerenes.

Phase composition and structural state of the produced CNM is controlled by time-energy parameters of an electrical explosion process, material of an exploding wire, and type of a surrounding medium. So, depending on an electrical explosion energetic regime (the ratio between a specific storage energy and specific energy of wire sublimation ? = w/w_s) it is possible to produce amorphous graphite (? ? 0.5), carbon nanotubes and fullerene-like clusters (?? 0.5-0.8), and nanodiamonds (? > 1.2).

It is worthy of note, that EW products have very strong ferromagnetic properties in a number of cases. The experimentally measured magnetization curves are typical to those of ferromagnetics. The values of saturation magnetization ? and Curie temperature T_c for the magnetic fraction separated from produced CNM are 57 $A\cdot m^2/kg$ and 473K, accordingly.

[1] A.D. Rud, A.E. Perekos, K.V. Chuistov, A.P. Shpak, V.N. Uvarov, V.Z. Voynash, V.M. Ogenko, N.I. Kuskova, Zh.N. Ishchenko, Extended Abstracts of IX Int. Conf. “Hydrogen Materials Science and Chemistry of Carbon Nanomaterials”. *(ICHMS’2005)*, Sevastopol, Crimea, Ukraine, 5-11 September 2005, 388-389 (2005).

Addition of ozone to C_{60} fullerene: a DFT study

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The molozonide $C_{60}O_3$ (MO) has been detected as a product of C_{60} ozonolysis. Similarly to alkene molozonides the structure with 1,2,3-trioxalane functionality of the 6.6 fullerene bond has been declared for this matter. But mechanism of ozonolysis has not been clear till now.

In the present work we have studied several ways of ozone attack on the fullerene C_{60} using quantum chemical calculations (Priroda 2.02+ program package). The density functional theory method PBE/3z has been preferred, because it correctly reproduces geometry and IR spectra of ozone and C_{60}. There are two kinds of bonds (shorter 6.6 and longer 5.6 bonds) in the structure of I_h-C_{60}. So, there are three ways of addition (Ad): 1,2-Ad (to 6.6 bond) and 2,3-Ad (to 5.6 bond), and 1,4-Ad, leading to transannular MO. We can rule out the 1,4-Ad due to its calculated endothermic effect (+27.8 kcal·mol^{-1}). Scanning of PES for exothermic ways has shown the charge transfer complex (CTC) to form as the initial step of interaction between the C_{60} and O_3 (see the table below):

$$C_{60} + O_3 > \ C_{60}^{?+}\cdots O_3^{?-} + DH_1^\circ$$

Complex	Structure of CTC, A				?	ΔH_1°, kcal·mol^{-1}
	C-C, A	C-O, A	O-O, A	OOO, ?		
1,2-$C_{60}\cdots O_3$; C_s symmetry	1.406	2.915	1.293	116.9	0.11	-2.3
2,3-$C_{60}\cdots O_3$; unsymmetric	1.458	3.124; 3.090	1.290; 1.291	117.4	0.09	-1.7

CTCs are analogous to π-complexes of arenes and alkenes, where hydrocarbon is a donor and ozone is an acceptor of electrons. Then CTCs are transformed into the MOs, described in the following table:

$$C_{60}\cdots O_3 > \ C_{60}O_3^{?} > \ C_{60}O_3 + DH_2^\circ$$

Way of addition	Structure of molozonide, A					$\Delta H^?$, kcal·mol^{-1} [b]	ΔH_2°, kcal·mol^{-1}
	C-C, A	C-O, A	O-O, A	OOO, ?	?, ?[a]		
1,2-Ad	1.609	1.449	1.458	100.5	8.9	0.0	-31.5
2,3- Ad	1.630	1.461	1.455	101.4	8.4	2.0	-16.7

[a] *The pyramidality angle for C atoms bonded with trioxalane fragment in MOs; in the C_{60} ? = 11.7? for all atoms.*

[b] *Enthalpy of activation calculated as $DH^? = H?(C_{60}O_3^?) - H?(C_{60}\cdots O_3)$.*

Comparison of calculated enthalpies shows, that 1,2-Ad is more favorable energetically and runs with negligibly low activation barrier. The 1,2-MO and transition state of its forming have a C_s symmetry structure, that is typical for alkenes. The advantage of 1,2-Ad might be explained with two reasons. First, the 6.6 bonds order in C_{60} (*1.44*) is closer to double bonds in alkenes, than that for 6.5 bonds (*1.23*). Second, 1,2-Ad makes less significant deforming of fullerene cage, which is illustrated with pyramidality angles (?) in C_{60} and its derivatives.

The work was supported by Russian Federation Ministry of Education analytical department program for special purpose “Development of higher education scientific potential”; project code DSP2.2.1.1.6332.

Continuous technology of preparation of fullerenes and atomic clusters on reaction of chlorinolysis

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It has been shown in our systematic investigations on exhaustive chlorination of hydrocarbons C_1-C_6 in boiling layer of fine-dispersed quartz sand, pumice and activated coal at temperatures 400-500°C that the formation of chlorocarbons is accompanied by the reactions of chlorinolysis, cyclization and carbonization. As a result of cyclization of carbon skeleton from C_5 and C_6 normal and isostructure hexachlorcyclopentadiene, hexachlorobenzene and fullerene clusters, yields of which depend on temperature and time of contact and molar ratio of reacting components are basically formed.

The technology of continuous preparation of valuable chlorocarbons C_1-C_6 and carbon clusters from individual hydrocarbons C_1-C_6 or their industrial mixtures has been developed. The preparation of these compounds is also possible on the base of existing chlororganic industrial wastes of various composition and structure without their preliminary identification.

Thus, the continuous technology of process of preparation of chlorocarbons C_1-C_6 and fullerene clusters has been developed and recommended for experimental realization.

The investigations on optimization of conditions of reactions of chlorinolysis of hydrocarbons of various compositions and structure providing maximum yields of products of cyclization and carbon nanostructural modifications are simultaneously continuing.

Modifying of conventional adsorbents with fullerenes

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The adsorptive properties of materials obtained by modifying active carbons with microquantities of fullerenes are examined in present work. The extract of Ñ$_{\Sigma}$ fullerenes was used as the additive agent. The adsorptive capacitance of the obtained materials has been examined in relation to the different classes of compounds: 1 – water-soluble organic compounds; 2 – cations of heavy metals; 3 – microorganisms.

By conducting a number of experiments it has been found that the insertion of fullerenes into the composition of active carbon leads to 30-60% increase of the adsorptive capacitance in relation to aromatic and chloraromatic compounds and 1.5-3 times increase in relation to spirits. This feature may be explained by the fact that the materials modified with fullerenes possess the higher degree of hydrophobicity than the initial active carbons and this leads to the decrease of the negative impact of water on the adsorption of other substances. Whereas the shift of electron density in the fullerenes leads to the redistribution of electronic density of the obtained material and this allows to increase the adsorptive capacitance for polar compounds.

Likewise while modifying the adsorptive capacitance considerably increases in relation to the cations of (2-3 times for Cu^{2+} , 1.5-3 times for Ag^{+} and 30-60% for Pb^{2+}). Such dependence may also be connected with the increase of the hydrophobicity degree of the adsorbent as well as the intensification of the donor-acceptor interaction of the adsorbed ion with the carbonic surface which is stipulated by the redistribution of electron density on the material.

In result of the work carried out, it has been found that the presence of the fullerenes on the carbonic surface causes the destruction coliform bacteria from water. We may assume that this phenomenon is explained by the destruction of cellular membrane.

Electronic structute of fluorinated fullerenes Ñ$_{60}$F$_{18}$ and Ñ$_{60}$F$_{36}$ studied by photoelectron- and absorbtion spectroscopies

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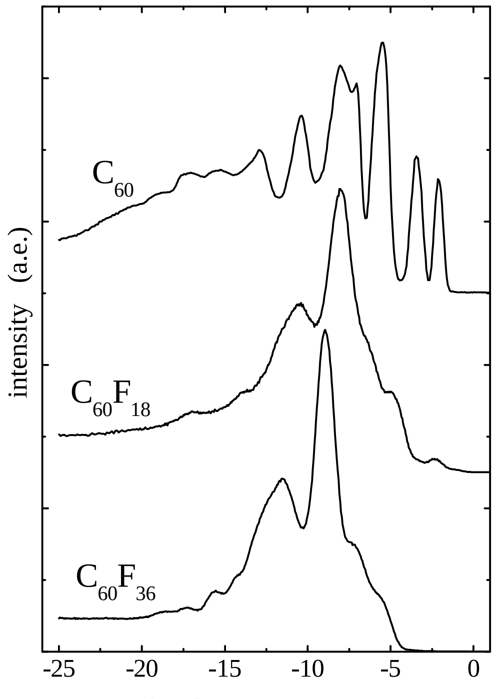
Fullerene derivatives, such as fluorinated fullerenes $C_{60}F_x$, are of particular interest to material science, as they are known to possess strong electron accepting properties. Fundamental properties of $C_{60}F_x$ films have been extensively studied recently [1-2]. However, there was a lack of information about density of occupied states (DOS), which strongly determines physical and chemical properties of materials. We bridge the gap in this research. Photoemission valence band spectra of $C_{60}F_x$ (x= 18, 36) films have been studied in comparison with those of ordinary fullerene C_{60} film by using monochromatic synchrotron radiation with photon energy h? = 120 eV. This energy seems to be high enough to go out of the region of joint DOS, which strongly depend on the photon energy, and to get into the region of DOS. Similarity of these spectra with those obtained at much higher energy h? = 370 eV indicates that these spectra reflect DOS. Figure shows VB PES of $C_{60}F_x$ (x= 0, 18. 36) indicating widening the band gap and degeneration of the molecular structure of fullerene cage in the course of its covering by fluorine atoms. The analogous degeneration effect was observed in the absorption spectra near C1s edge (NEXAFS) related to the C-local density of unoccupied states, whereas NEXAFS spectra of fluorine F1s edge demonstrate stability on the fluorine content (x). The comparative study of VB PES of ordinary fullerenes and fluorinated fullerenes with different content of fluorine atoms evidences for relatively simple atomic-like structure of fluorine derived states and for radical extinguishing the DOS near valence band top responsible for physical and chemical properties of the material.



The research was supported by the Russian-German Laboratory at BESSY and by the Russian Academy of Sciences (P-03, N2-2-14 and “Quantum nanostructures”, 5-22).

[1] O.V. Boltalina, *J. Fluorine Chem.* **101**, 273 (2000).
[6] R.Mitsumoto, T.Araki, E.Ito, YOuchi, K.Seki et al., *J.Phys.Chem.A*, **102**, 552 (1998).

Producing and properties of fullerite C_{60} intercalated with freon 32

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We have developed a technique of fullerite intercalation during its sedimentation from a solution [1]. This technique needs no high pressure, and the temperature of the process can be room. The fullerite C_{60} intercalated by freon 32 (CH_2F_2) has been obtained within the frameworks of this technique for the first time. It will be noted, that a similar sample could not be obtained by method of hot isostatical pressing (HIP), because vapor pressure of researched freon is equal to 1.5 Ì Ï à pressure at 20°Ñ and 26 Ì Ï à at 200°Ñ. Synthesis of sample ArC_{60} by HIP method needs pressure 170 Ì Ï à and temperature 200-400^{o}Ñ [2].

The sample has been studied using of the element analysis, powder X-ray diffraction, EPR, IR spectroscopy, mass spectrometry and electronic microscopy. It is established, that the composition of a sample conforms to the formula (CH_2F_2)Ñ$_{60}$. The sample crystallizes in *fcc* lattice, which parameter (14.22 A) appreciably exceeds those for pure fullerite (14.16 A). Mass spectra of the gas evolved by sample by heating in vacuum up to temperature 450°Ñ, correspond to initial freon. Products of freon destruction were not revealed at this temperature. At the same time IR spectra show, that the frequency of valence vibration C-F (1057 cm^{-1}) in researched sample (CH_2F_2)Ñ$_{60}$ is displaced on 59 cm^{-1} to the side of low wave numbers concerning those in a gas phase. Absorption bands at 1182 and 1428 cm^{-1} determined by IR active vibration modes (F_{1u}) of the C_{60} molecule with high symmetry (I_h) have not changed the position in a course of intercalation.

Acknowledgements: This work was supported by RFBR, Project No 06-03-00361.

[1] Y.M. Shul'ga, V.M. Martynenko, A.F. Shestakov, S.A. Baskakov, S.V. Kulikov, V.N. Vasilets, T.L. Makarova, Y.G. Morozov, *Russ. Chem. Bulletin* **55**(4), 687-696 (2006).

[2] G.E. Gadd, S.J. Kennedy, S. Moricca, C.J. Howard, M.M. Elcombe, P.J. Evans, M. James, *Phys. Rev. B* **55**(14), 794 (1997).