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Stable trifluoromethylated fullerene radicals $C_{60}(CF_3)_{15}$ and $C_{60}(CF_3)_{17}$

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Stable $C_{60}(CF_3)_{15}$ and $C_{60}(CF_3)_{17}$ radicals were generated by UV irradiation of $C_{60}(CF_3)_n$ mixture and characterized by ESR spectroscopy and MALDI mass spectrometry revealing the presence of pentakis- and tris(trifluoromethyl) moieties, respectively.

Several free radical C_{60} derivatives with methyl,[1] trichloromethyl and C(O)OMe[2] addends were observed by ESR spectroscopy. The existence of $^{\bullet}CF{=}CFC(CF_3)_3$ and $^{\bullet}C(O)CF(CF_3)_2$ radical adducts with C_{60} was also reported.[3] Allylic $C_{60}R_3^{\bullet}$ and cyclopentadienyl $C_{60}R_5^{\bullet}$ ($R = PhCH_2$) radical adducts were observed by ESR spectroscopy as relatively stable products.[4] However, the observed species were found to be less stable in solution and to be degraded in the presence of oxygen. Perfluorinated carbon-centered radicals often demonstrate higher stability in comparison with ordinary alkyl analogues.[5,6]

Many trifluoromethylated [60]- and [70]fullerenes, $C_{60/70}(CF_3)_n$, with even number of addends ($n = 2$–18) have been synthesized, isolated and structurally investigated,[7,8] whereas the compounds with odd *n* have not been isolated up to now. However, it was mentioned[9] that the crude product of the reaction between C_{60} and CF_3COOAg contained species with odd number of CF_3 groups, which possessed high reactivity and could be removed from the mixture by sublimation *in vacuo*. In the present work, we report the formation of stable trifluoromethyl radical derivatives of C_{60} and their investigation by methods of ESR spectroscopy and MALDI mass spectrometry.

A mixture of $C_{60}(CF_3)_n$ ($n = 12$–18) was synthesized by the reaction of C_{60} (99.98%, Term-USA) with CF_3I (98%, Apollo) in a glass ampoule at 410–420 °C for 2 days as described elsewhere.[10] The MALDI mass spectrum for this sample was constituted by the peaks of $C_{60}(CF_3)_n^-$ ions with $n = 12$–18, those with even *n* considerably dominating (not shown).[†] The ESR spectra of the initial $C_{60}(CF_3)_n$ mixture in solid state and in hexane solution (not shown) revealed the presence of stable radical species with $g = 2.0031$; however, with the content as low as ~0.2 mol%.[‡]

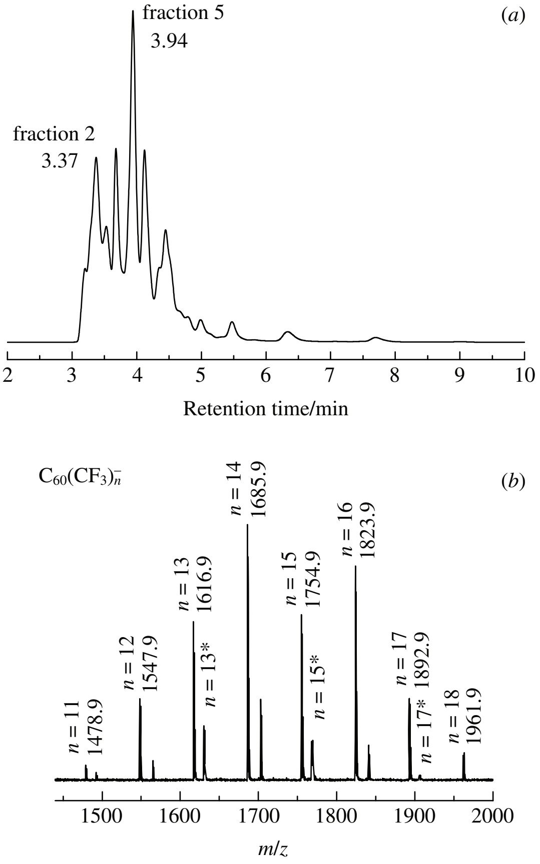

Figure 1 HPLC trace (*a*) and MALDI mass spectrum (*b*) of the mixture of trifluoromethylated fullerenes after UV irradiation. The metastable peaks are marked with asterisk.

To enlarge the content of paramagnetic derivatives, the mixture of $C_{60}(CF_3)_n$ (5 mg) was dissolved in liquid CF_3I in sealed quartz ampoule and irradiated by low-pressure mercury lamp (254 nm) during 24 h. In fact, free radicals content in the irradiated sample was found to increase up to 4 mol%. Correspondingly, its MALDI mass spectrum (Figure 1) showed the considerable increase of relative intensities for stable odd numbered peaks as compared with the untreated sample. The even numbered peaks are known to originate from the corresponding molecules while the odd ones can be either fragments formed by the loss of a CF_3 group or due to stable odd numbered molecules. The formation of fragments is always accompanied by the appearance of metastable peaks (of comparable intensities) shifted from the stable odd numbered peaks by ≅ 13 Da.[11]

[†] MALDI mass spectra in the negative ion mode were obtained with a Bruker AutoFlex II time-of-flight reflectron device, N_2 laser, 337 nm, 1 ns pulse; 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB, ≥ 99%, Fluka) was used as a matrix.

[‡] ESR spectra were recorded using a Varian E-3 (USA) spectrometer. ESR signal of Mn^{2+} in MgO was used for magnetic field calibration. The ESR spectra of fraction 2 and fraction 5 were unchanged up to 333 K where slow degradation of ESR signals was observed. To avoid the influence of oxygen ESR spectra were recorded under argon or in solutions deaerated by vacuum. A numerical simulation of ESR spectra was carried out with the use of the spin Hamiltonian that includes second-order terms with regard to the energy of nuclear Zeeman interaction. The non-linear least-squares method was used for determination of individual line width and hyperfine constants (hfc).

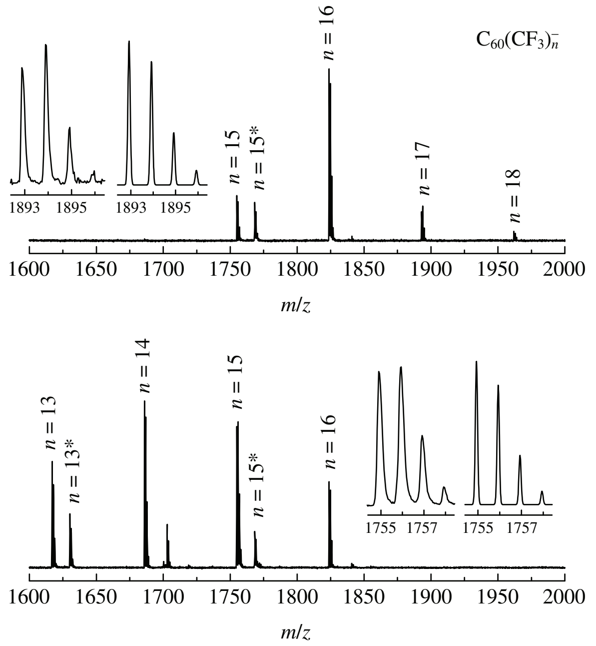

Figure 2 Negative ion MALDI mass spectra of HPLC fractions 2 (top) and 5 (bottom). The insets present the zooms of top and bottom spectra in mass ranges of 1892.4–1896.4 and 1754.4–1758.4, respectively (on the left), and the calculated isotopic abundances for $C_{60}(CF_3)_{17}$ and $C_{60}(CF_3)_{15}$ (on the right). The metastable peaks are marked with asterisks.

The irradiated mixture was then fractionated by HPLC resulting in 16 chromatographic fractions.[§] Fractions 2 (at 3.37 min) and 5 (3.94 min) gave the most intense ESR spectra. Their MALDI mass spectra are presented in Figure 2. Both spectra contained stable odd-numbered peaks, $C_{60}(CF_3)_{17}^-$ and $C_{60}(CF_3)_{15}^-$, respectively, which intensities considerably exceeded those of minor even numbered peaks, $C_{60}(CF_3)_{18}^-$ and $C_{60}(CF_3)_{16}^-$, respectively. The metastable peaks corresponding to the detachment of a CF_3 group from $C_{60}(CF_3)_{18}^-$ or $C_{60}(CF_3)_{16}^-$ are either completely absent (fraction 2) or have the much lower intensity relatively to the stable odd-numbered peak. Moreover, these prominent odd-numbered peaks were characterized by deviations from theoretical isotopic abundances (see insets in Figure 2), so the both spectra unambiguously indicated the presence of hydrogenated ions, $\{C_{60}(CF_3)_{17} + H\}^-$ and $\{C_{60}(CF_3)_{15} + H\}^-$, respectively. The appearance of hydrogenated peaks is untypical of MALDI mass spectra of trifluoromethylated fullerenes with the use of DCTB matrix.[12] Therefore, it can be concluded that the $C_{60}(CF_3)_{17}^-$ and $C_{60}(CF_3)_{15}^-$ stable peaks in the spectra of fractions 2 and 5, respectively, have radical precursors, namely, $C_{60}(CF_3)_{17}^{\bullet}$ and $C_{60}(CF_3)_{15}^{\bullet}$. The hydrogenated species are likely to be formed in the reactions of these radicals with the solvent or matrix occurring during the solution storage or sample preparation prior to the MALDI experiment.

ESR spectrum for fraction 2 [main radical component $C_{60}(CF_3)_{17}$] presented in Figure 3 (spectrum *1*) demonstrates hyperfine structure due to interaction of unpaired electron with fluorine atoms. The ESR spectra were observed during weeks without significant changes, thus demonstrating a high stability of paramagnetic species in solution in the presence of air. It was satisfactory simulated (spectrum *2* in Figure 3) using following parameters: $a_F(5F) = 1.72$ G, $a_{F'}(5F) = 0.71$ G, $a_{F''}(5F) = 0.35$ G and width of Lorenzian line 0.4 G. Due to similarity to the spectrum observed earlier[1] for $C_{60}Me_5$ radicals, it can be attributed to cyclopentadienyl-type radical. Note stronger hyperfine interaction (hfi) constants and higher stability of CF_3 derivatives in comparison with Me analogues. Similar to the data[1] for $C_{60}Me_5^{\bullet}$, rotation of trifluoromethyl groups in $C_{60}(CF_3)_{17}$ radical is hindered.

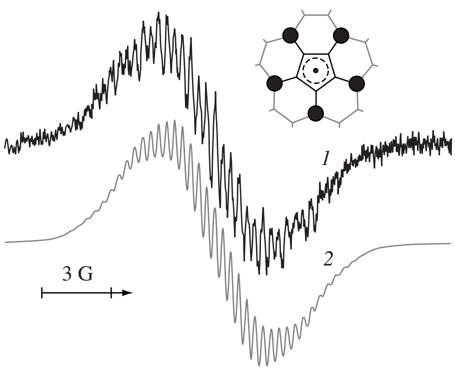

Figure 3 (*1*) Experimental and (*2*) calculated ESR spectra of fraction 2 at 293 K. Insert shows the presumable paramagnetic moiety; black circles denote CF_3 groups.

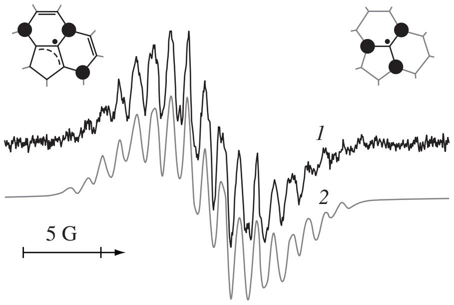

Figure 4 (*1*) Experimental and (*2*) calculated ESR spectra of fraction 5 at 293 K. Inserts show the possible paramagnetic moieties; black circles denote attached CF_3 groups.

ESR spectrum for fraction 5 [main radical component $C_{60}(CF_3)_{15}$] is shown in Figure 4 (spectrum *1*). This spectrum can be rationalized taking into account hfi with nine fluorine atoms. The parameters obtained in the course of minimization of difference between simulated and experimental spectra are: $a_F(2F) = 2.39$ G, $a_{F'}(1F) = 2.31$ G, $a_{F''}(4F) = 1.95$ G, $a_{F'''}(2F) = 1.10$ G, width of Lorenzian line 0.59 G (spectrum *2* in Figure 4). There are two possible structures of stable free radical that imply hfi with nine fluorine atoms. These are an allyl-type radical and a triangle moiety (see inserts in Figure 4). The latter structure is in a better agreement with the parameters given above for the simulated spectrum.

In summary, the present work demonstrates the existence of paramagnetic derivatives $C_{60}(CF_3)_n$ with odd number of addends. The important feature of the discovered compounds is their high stability in solution in the presence of air and, especially, in solid state. Further structural characterization of the whole radical species is under way.

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References

1 V. V. Bashilov, F. M. Dolgushin, B. L. Tumanskii, P. V. Petrovskii and V. I. Sokolov, *Tetrahedron*, 2008, **64**, 11291.

2 B. L. Tumanskii, V. V. Bashilov, S. P. Solodovnikov, N. N. Bubnov and V. I. Sokolov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2422 (*Russ. Chem. Bull.*, 1995, **44**, 2316).

3 B. L. Tumanskii, E. N. Shaposhinikova, V. V. Bashilov, S. P. Solodovnikov, N. N. Bubnov and S. R. Sterlin, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1222 (*Russ. Chem. Bull.*, 1997, **46**, 1174).

[§] Cosmosil Buckyprep (Nakalai Tesque Inc.) column, 10 mm i.d. × 250 mm, with hexane as the eluent, 4.6 $cm^3 min^{-1}$ flow rate, UV absorption detector at 290 nm.

4 P. J. Krusic, E. Wasserman, P. N. Keizer J. R. Morton and K. F. Preston, *Science*, 1991, **254**, 1183.

5 K. V. Scherer, R. E. Fernandez, P. B. Henderson and P. J. Krusic, *J. Fluorine Chem.*, 1987, **35**, 7.

6 U. Groß, S. Rüdiger and A. Dimitrov, *J. Fluorine Chem.*, 1996, **76**, 139.

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

8 S. I. Troyanov, A. Dimitrov and E. Kemnitz, *Angew. Chem., Int. Ed. Engl.*, 2006, **45**, 1971.

9 E. I. Dorozhkin, A. A. Goryunkov, I. N. Ioffe, S. M. Avdoshenko, V. Yu. Markov, N. B. Tamm, D. V. Ignat'eva, L. N. Sidorov and S. I. Troyanov, *Eur. J. Org. Chem.*, 2007, 5082.

10 S. I. Troyanov, A. A. Goryunkov, E. I. Dorozhkin, D. V. Ignat'eva, N. B. Tamm, S. M. Avdoshenko, I. N. Ioffe, V. Yu. Markov, L. N. Sidorov, K. Scheurel and E. Kemnitz, *J. Fluorine Chem.*, 2007, **128**, 545.

11 N. S. Ovchinnikova, D. V. Ignat'eva, N. B. Tamm, S. M. Avdoshenko, A. A. Goryunkov, I. N. Ioffe, V. Yu. Markov, S. I. Troyanov, L. N. Sidorov, M. A. Yurovskaya and E. Kemnitz, *New J. Chem.*, 2008, **32**, 89.

12 V. Yu. Markov, V. E. Aleshina, A. Ya. Borschevskiy, R. V. Khatymov, R. F. Tuktarov, A. V. Pogulay, A. L. Maximov, S. V. Kardashev, I. N. Ioffe, S. M. Avdoshenko, E. I. Dorozhkin, A. A. Goryunkov, D. V. Ignat'eva, N. I. Gruzinskaya and L. N. Sidorov, *Int. J. Mass Spectrom.*, 2006, **251**, 16.

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