Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2012, **22**, 297–298

Mendeleev
Communications

Synthesis, X-ray structure and mass spectrum of C_s-$C_{60}(CF_3)_6$

Natalia A. Romanova, Nadezhda B. Tamm, Vitaliy Yu. Markov,
Alexey A. Goryunkov, Lev N. Sidorov and Sergey I. Troyanov*

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.
Fax: +7 495 939 1240; e-mail: stroyano@thermo.chem.msu.ru

DOI: 10.1016/j.mencom.2012.11.005

C_s-$C_{60}(CF_3)_6$ was synthesized by the reaction of S_6-$C_{60}(CF_3)_{12}$ with C_{60} at 530 °C. Its molecular structure with skew-pentagonal-pyramidal addition pattern was elucidated by single crystal X-ray diffraction. Theoretical DFT calculations were performed to account for a high degree of fragmentation in negative-ion mass spectra.

Trifluoromethylated fullerenes belong to the most numerous and well studied fullerene derivatives. They are characterized by high chemical and thermal stability and may be considered as prospective compounds with strong acceptor properties. The usual synthesis methods are based on the reactions of fullerenes with CF_3 radicals, which are produced by UV irradiation[1] or thermally, for example, by heating CF_3I[2] or decomposition of metal trifluoroacetates.[3] The alternative method of reacting higher fullerene$(CF_3)_{2n}$ with pristine fullerene was proposed recently for derivatives of C_{70}.[4] By now, more than 35 $C_{60}(CF_3)_{2n}$ compounds including different isomers with $2n$ ranging from 2 to 18 were isolated and structurally characterized by ^{19}F NMR spectroscopy and/or a direct method of single crystal X-ray diffraction.[3,5]

For the $C_{60}(CF_3)_6$ composition, there are four isomers with known molecular structures.[2,3] While the molecular structures of three isomers have been unambiguously elucidated by X-ray crystallography, one isomer was only investigated by ^{19}F NMR spectroscopy. Its C_s symmetric molecular structure with the so-called skew-pentagonal-pyramidal (SPP) addition pattern was deduced taking into account variable-temperature ^{19}F NMR spectra, a high fragmentation degree in the mass spectrum and the similarity of the electronic spectrum to those of other $C_{60}X_6$ compounds with SPP attachment of six atoms or groups. Here, we report the synthesis, isolation and X-ray crystallographic characterization of SPP C_s-$C_{60}(CF_3)_6$ and discuss its molecular structure and mass spectrum.[†]

A mixture of $C_{60}(CF_3)_{2n}$ compounds was prepared by a modified two-step synthesis. In the first step, the known S_6-$C_{60}(CF_3)_{12}$ was obtained by a selective reaction of C_{60} with gaseous CF_3I in a glass ampoule at 400 °C, as described in detail elsewhere.[6] In the second step, a finely ground mixture of S_6-$C_{60}(CF_3)_{12}$ and C_{60} in a molar ratio of (2–4) : 1 was pressed into a pellet and heated at 530 °C in a sealed quartz ampoule for 20 min. The reaction product appeared as a glossy cake, which indicated the melting of the pellet in the course of the reaction. It contained $C_{60}(CF_3)_{2n}$ ($2n$ = 2–10) with the predominant abundance of compounds with n = 4–6 according to MALDI mass-spectrometric analysis performed in the negative ion mode using a Bruker AutoFlex II time-of-flight reflectron instrument (with DCTB as a matrix material). Note that the reaction product did not contain unreacted C_{60}. The compound mixture was dissolved in toluene and separated by HPLC using a Cosmosil Buckyprep column (10 mm i.d. × 250 mm) and toluene (or toluene–hexane mixtures) as an eluent (flow rate, 4.6 ml min^{-1}), monitored at 290 nm.

Some separated fractions gave small crystals by the slow evaporation of the solvent. In other cases, the crystals were obtained by recrystallization from other solvent. Single crystal X-ray diffraction with the use of synchrotron radiation allowed us to confirm the known molecular structures of $C_{60}(CF_3)_4$-II,[3] $C_{60}(CF_3)_4O$,[2,3] $C_{60}(CF_3)_6$-III[3] (as a solvate with *p*-xylene),[†] and $C_{60}(CF_3)_{10}$-5.[5] Crystals grown from the chromatographic fraction eluted at 39.2 min in a toluene–hexane mixture (4:6, v/v) revealed the structure of SPP C_s-1,6,9,12,15,18-$C_{60}(CF_3)_6$.[†] The UV-VIS spectrum of the compound recorded in toluene is consistent with that published.[2]

Figure 1 shows the molecular structure and Schlegel diagram of 1,6,9,12,15,18-$C_{60}(CF_3)_6$. The same SPP addition pattern was found previously in $C_{60}X_6$ compounds with X = Cl,[7,8] Br[9,10] and Me.[11] The fully ordered structure of SPP C_s-$C_{60}(CF_3)_6$ is of sufficient quality (esd's of C–C bond lengths are 0.004–0.005 Å) for a detailed analysis of interatomic distances and a comparison with the DFT calculated structure,[2] as well as other $C_{60}X_6$. Special features of the SPP addition pattern are the existence of sp^3–sp^3 (*ortho*) attachment of two CF_3 groups and the presence of the *cis*-butadiene-like C^2=C^3–C^4=C^5 fragment in the central cage pentagon. The experimental sp^3–sp^3 C^1–C^9 bond length of 1.602(4) Å is in excellent agreement with the calculated value of 1.603 Å, whereas slight deviations were found for the butadiene-like fragment with an alternation of double and single C–C bonds: 1.333, 1.478, 1.344(4) Å *vs.* 1.358, 1.479, 1.358 Å in the DFT calculated structure.[2] Noteworthy, the C^1–C^9 bond is significantly shorter in the $C_{60}Br_6$ molecule, 1.557(4) Å, due to the smaller size of Br atoms compared with that of the CF_3 group thus diminishing the repulsion of addends attached in adjacent positions.[10] At the same time, the C–C distances in the *cis*-butadiene-like fragment, 1.348, 1.462, 1.351(4) Å, are almost the same as those in the CF_3 derivative.

[†] *Crystal data.* C_s-$C_{60}(CF_3)_6$, monoclinic, space group $P2_1/n$, a = 11.816(1), b = 16.867(1) and c = 19.196(1) Å, β = 101.811(8)°, V = 3744.8(4) Å^3, Z = 4. Anisotropic refinement with 8433 reflections and 758 parameters converged to wR_2 = 0.172 and R_1 = 0.068 for 5623 reflections with $I > 2\sigma(I)$.

C_1-$C_{60}(CF_3)_6O_{0.12}\cdot 0.5p$-xylene, monoclinic, space group $P2_1/n$, a = = 10.0651(5), b = 35.543(1) and c = 12.2302(6) Å, β = 111.889(4)°, V = = 4059.9(3) Å^3, Z = 4. Anisotropic refinement with 8352 reflections and 799 parameters converged to wR_2 = 0.169 and R_1 = 0.068 for 6797 reflections with $I > 2\sigma(I)$.

Synchrotron X-ray data were collected at 100 K at the BL14.2 at the BESSY storage ring (PSF at the Free University of Berlin, Germany) using a MAR225 CCD detector, λ = 0.8856 Å. Structures were solved by SHELXD and refined with SHELXL.

CCDC 907787 and 907788 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2012.

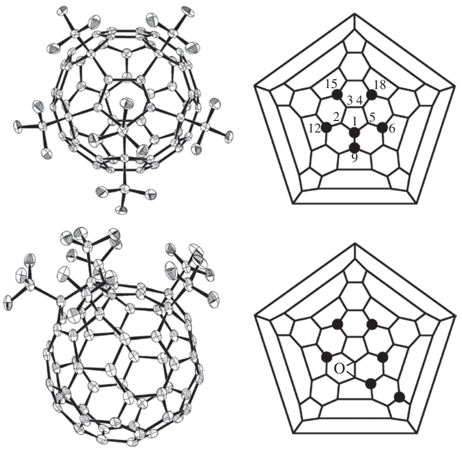

Figure 1 Left: two views of the SPP C_s-$C_{60}(CF_3)_6$ molecule. Thermal ellipsoids are given with 50% probability. Right: Schlegel diagrams of SPP C_s-$C_{60}(CF_3)_6$ (top) and C_1-$C_{60}(CF_3)_6O$ (bottom). Black circles denote the positions of attached CF_3 groups. Epoxy compound co-crystallized with C_1-$C_{60}(CF_3)_6$-III possessing the same attachment of CF_3 groups.

The closest experimental (though less precise) structure of SPP C_s-$C_{60}Me_6$ shows similar values of 1.571(9) Å (C^1–C^9) and 1.349, 1.460, 1.364(9) Å (C^2=C^3–C^4=C^5) because of roughly similar sizes of Me and CF_3 groups (atoms numbering corresponds to that depicted in Figure 1).[11] The further similarity concerns the lengths of the C(cage)–CX_3 bonds with a small but noticeable elongation of the distances to C^1 and C^9 [1.576(5) and 1.553(5) Å], as compared to the averaged value of 1.542 Å for four other such bonds (to C^6, C^{12}, C^{15}, and C^{18}), which are not in adjacent positions to one another. The corresponding C–Me distances in the methylated derivative are 1.575, 1.552 and 1.533 Å.

The second molecular structure determined in this work corresponds roughly to the most stable isomer, C_1-1,6,11,18,24,27-$C_{60}(CF_3)_6$-III (Figure 1).[3] Interestingly, an epoxide compound, $C_{60}(CF_3)_6O$, with the same attachment of CF_3 groups is present as an admixture (12%) to C_1-$C_{60}(CF_3)_6$ in the same crystallographic site. A similar epoxide-type attachment is characteristic of $C_{60}(R^F)_4O$ with $R^F = CF_3$ and C_2F_5.[2,3]

The negative-ion MALDI mass spectrum of SPP C_s-$C_{60}(CF_3)_6$ contains the peaks of $C_{60}(CF_3)_6^-$ molecular and $C_{60}(CF_3)_5^-$ fragment ions of close intensities, as well as that of a metastable ion corresponding to the loss of a CF_3 group in the field free region of mass analyzer (Figure 2). The latter is indicative of the fragment origin of the $C_{60}(CF_3)_5^-$ ion. This high degree of fragmentation is untypical of the MALDI mass spectra of trifluoromethylated C_{60} and C_{70} fullerenes with 2–10 attached CF_3 groups.[12] However, the positive ion spectrum contains only the molecular ion peak, the fragment ones being almost absent, which is quite usual for lower trifluoromethylated fullerenes. A similar phenomenon was observed in the negative-ion APCI mass spectrum of SPP $C_{60}(CF_3)_6$, which was qualitatively explained by the formation of a stable $C_{60}(CF_3)_5^-$ anion with the cyclopentadienide structure.[2]

To account quantitatively for the high fragmentation degree of SPP C_s-$C_{60}(CF_3)_6$ in MALDI mass spectra, the minimum energies of ion dissociation with the loss of a CF_3 group were calculated by the DFT method at the PBE/TZ2P level.[13,14] These calculations were performed for the cations and anions of SPP C_s and C_1 isomers [1,6,9,12,15,18- and 1,6,11,18,24,27-$C_{60}(CF_3)_6$, respectively].[2] In the case of the SPP $C_{60}(CF_3)_6^-$ anion, the minimum dissociation energy was extremely low (0.9 eV), whereas in other cases the values (1.8–2.0 eV) were insignificantly lower than the average C_{60}(cage)–CF_3 bond energies (2.1–3.0 eV).[15] The loss of a CF_3 group by SPP $C_{60}(CF_3)_6^-$ with a minimum energy corresponds to the detachment from the C^1 position (*i.e.*, the break of the most elongated C–CF_3 bond) resulting in a C_{5v}-$C_{60}(CF_3)_5^-$ fragment anion, which possesses the stabilizing aromatic ring of the cyclopentadienide type (see Figure 2). Thus, it is the structural feature of SPP C_s-$C_{60}(CF_3)_6$ that causes a high fragmentation degree in its negative-ion MALDI mass spectrum.

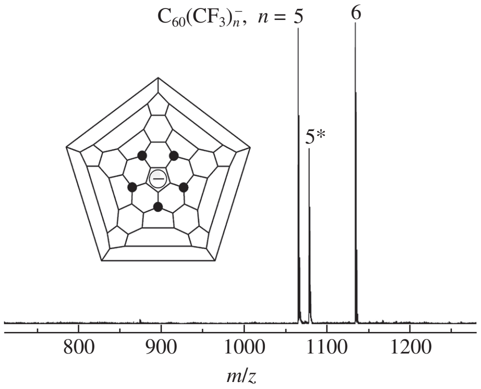

Figure 2 Negative-ion MALDI mass spectrum; the peak of a metastable ion is marked by an asterisk. Schlegel diagram shows the structure of the C_{5v}-$C_{60}(CF_3)_5^-$ fragment ion.

In summary, the reaction between S_6-$C_{60}(CF_3)_{12}$ and C_{60} in a quartz ampoule produces $C_{60}(CF_3)_n$ with the predominance of compounds with $n = 4$–6. HPLC separation followed by X-ray diffraction study resulted in the structure determination of C_s-$C_{60}(CF_3)_6$ with the skew-pentagonal-pyramidal addition pattern. According to quantum chemical calculations, the low energy of detachment of one CF_3 group is the reason for the high fragmentation degree in the negative-ion MALDI mass spectrum.

This work was supported in part by the Russian Foundation for Basic Research (project no. 12-03-00324).

References

1 N. B. Shustova, I. E. Kareev, I. V. Kuvychko, J. B. Whitaker, S. F. Lebedkin, A. A. Popov, L. Dunsch, Y.-S. Chen, K. Seppelt, S. H. Strauss and O. V. Boltalina, *J. Fluorine Chem.*, 2010, **131**, 1198.

2 I. E. Kareev, N. B. Shustova, I. V. Kuvychko, S. F. Lebedkin, S. M. Miller, O. P. Anderson, A. A. Popov, S. H. Strauss and O. V. Boltalina, *J. Am. Chem. Soc.*, 2006, **128**, 12268.

3 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.

4 T. Mutig, E. Kemnitz and S. I. Troyanov, *Mendeleev Commun.*, 2009, 30.

5 A. A. Popov, I. E. Kareev, N. B. Shustova, E. B. Stukalin, S. F. Lebedkin, K. Seppelt, S. H. Strauss, O. V. Boltalina and L. Dunsch, *J. Am. Chem. Soc.*, 2007, **129**, 11551.

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

7 P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1993, 1230.

8 S. I. Troyanov, A. V. Burtsev and E. Kemnitz, *Crystallogr. Rep.*, 2009, **54**, 242.

9 P. R. Birkett, P. B. Hitchcock, H. W. Kroto, R. Taylor and D. R. M. Walton, *Nature*, 1992, **357**, 479.

10 S. I. Troyanov, A. A. Popov, N. I. Denisenko, O. V. Boltalina, L. N. Sidorov and E. Kemnitz, *Angew. Chem. Int. Ed.*, 2003, **42**, 2395.

11 H. Al-Matar, A. K. Abdul-Sada, A. G. Avent, P. W. Fowler, P. B. Hitchcock, K. M. Rogers and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 2002, 53.

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.

13 D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.

14 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

15 S. M. Avdoshenko, I. N. Ioffe and L. N. Sidorov, *J. Phys. Chem. A*, 2009, **13**, 10833.

Received: 21st June 2012; Com. 12/3947