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Synthesis, HPLC isolation and structural characterization of three new $C_{60}(CF_3)_{18}$ isomers

Nadezhda B. Tamm,* Vitaliy Yu. Markov and Sergey I. Troyanov

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

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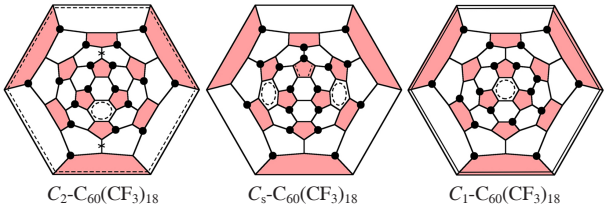
Three new $C_{60}(CF_3)_{18}$ isomers have been synthesized by high-temperature trifluoromethylation of [60]fullerene with gaseous CF_3I, isolated by HPLC, and structurally characterized by single crystal X-ray diffraction using synchrotron radiation.



Keywords: fullerene C_{60}, trifluoromethylation, HPLC separation, synchrotron radiation, structure elucidation.

Trifluoromethylated fullerenes C_{60} and C_{70} represent the large group of compounds which are obtained, separated and structurally characterized experimentally and considered theoretically.[1–3] Until recently, the numbers of structurally studied isomers $C_{60}(CF_3)_n$ were 13 (n = 10),[1,4] 6 (n = 12),[5,6] 3 (n = 14),[1] 3 (n = 16),[7] and 2 (n = 18).[7,8] According to MS data of raw trifluoromethylation products, the maximum number of attached CF_3 groups is 20[9] but no molecular structure of $C_{60}(CF_3)_{20}$ is known. In the last few years, owing to the development of HPLC separation methods and X-ray structure determination facilities, the number of isolated and structurally characterized $C_{60}(CF_3)_n$ (n = 12, 14, 16) has been increased considerably and has reached 9,[10] 15,[11] and 11,[12] respectively. In the present communication, we report the synthesis, isolation, and structural studies of three new $C_{60}(CF_3)_{18}$ isomers, thus increasing the number of structurally characterized isomers to five.

The synthesis of $C_{60}(CF_3)_n$ derivatives was performed in ampoules by the reaction of C_{60} fullerene with CF_3I at 420 °C for 36–48 h as previously described.[11] The reaction product was dissolved in *n*-hexane and subjected to HPLC separation in *n*-hexane using a semipreparative Cosmosyl Buckyprep column, 2.3 ml min^{-1}. The composition of the HPLC fractions was controlled by MALDI–TOF mass spectrometry.† In the first HPLC separation stage, several fractions gave crystals of the early reported isomers of $C_{60}(CF_3)_{12}$-III and -V, $C_{60}(CF_3)_{14}$-III, $C_{60}(CF_3)_{16}$-I and $C_{60}(CF_3)_{18}$-I (Roman figures correspond to the isomers numeration used in refs. 7, 10–12).

The fraction with retention time 6.7 min was additionally separated using a semipreparative Cosmosyl Buckyprep-D column thus producing isomerically pure or nearly pure subfractions of $C_{60}(CF_3)_{18}$ and $C_{60}(CF_3)_{18}O_n$ compounds (n = 1, 2) (Figure 1).†

$C_{60}(CF_3)_{18}$ crystals were grown from the solutions in hexane; because of typically very small size of the crystals their X-ray diffraction study was performed with the use of synchrotron radiation.‡

New isomers were designated as 18-III, -IV and -V according to increasing elution times; their IUPAC lowest-locant abbreviations[13] are 1, 3, 6, 11, 13, 18, 22, 25, 28, 31, 34, 37, 41,

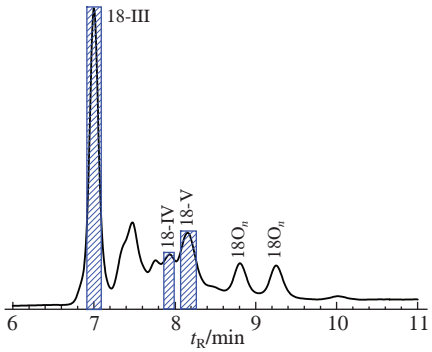


Figure 1 Second step HPLC separation using a semipreparative Cosmosyl Buckyprep-D column, *n*-hexane, 2.3 ml min^{-1}. The composition of HPLC fractions was determined by MALDI-MS and confirmed for fraction 18-III–18-V by X-ray crystallography. The fractions eluted at 7.5 and 7.7 min contained $C_{60}(CF_3)_{18}$ species of unknown molecular structures.

† *Experimental details.* HPLC separation was carried out by means of a Waters LC system equipped with semipreparative Cosmosyl Buckyprep and Cosmosyl Buckyprep-D columns (both 10 I.D.×250 mm). The negative-ion MALDI mass spectra were acquired using a Bruker AutoFlex II reflector time-of-flight mass spectrometer (N_2 laser, 337 nm, 2.5 ns pulse). 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]-malononitrile (DCTB) employed as a matrix.

‡ *Crystal data.* Synchrotron X-ray diffraction data for 18-III–18-V were collected at 100 K at the BESSY storage ring (BL14.3, Berlin, Germany) using a MAR225 CCD detector (λ = 0.8950 Å). The crystal structures were solved by SHELXD and anisotropically refined with SHELXL.

$C_{60}(CF_3)_{18}$ (18-III), monoclinic, $P2_1/n$, a = 13.811(1), b = 21.518(2) and c = 20.874(2) Å, β = 96.947(8)°, V = 6157.9(9) Å^3, Z = 4, R_1 = 0.062 with 7502 reflections [$I > 2\sigma(I)$], wR_2 = 0.189 with 10099 reflections and 1217 parameters.

$C_{60}(CF_3)_{18}$ (18-IV), triclinic, $P\bar{1}$, a = 11.985(1), b = 14.117(1) and c = 20.6921(8) Å, α = 89.893(5)°, β = 74.823(4)°, γ = 65.627(7)°, V = 3055.2(4) Å^3, Z = 2, R_1 = 0.047 with 10623 reflections [$I > 2\sigma(I)$], wR_2 = 0.136 with 12035 reflections and 1189 parameters.

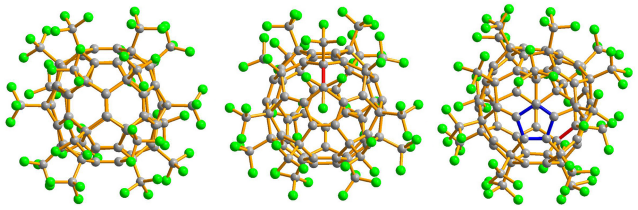


Figure 2 Projections of C_2-$C_{60}(CF_3)_{18}$-III, C_s-$C_{60}(CF_3)_{18}$-IV and C_1-$C_{60}(CF_3)_{18}$-V molecules. Isomer 18-III is viewed along a C_2 axis whereas isomer 18-IV is presented parallel to the mirror plane. C–C bonds with *ortho* CF_3 attachments are shown in red. In C_1-$C_{60}(CF_3)_{18}$-V molecule, the cage pentagon unoccupied with CF_3 groups are indicated with blue color.

43, 45, 50, 53, 60-$C_{60}(CF_3)_{18}$, 1, 3, 6, 11, 13, 18, 21, 26, 33, 38, 42, 44, 46, 49, 51, 53, 55, 56-$C_{60}(CF_3)_{18}$, and 1, 3, 6, 11, 13, 18, 22, 24, 27, 32, 33, 37, 41, 43, 46, 51, 54, 59-$C_{60}(CF_3)_{18}$, respectively.

Molecular structures of C_2-$C_{60}(CF_3)_{18}$-III, C_s-$C_{60}(CF_3)_{18}$-IV and C_1-$C_{60}(CF_3)_{18}$-V are presented in Figure 2. The axis and mirror symmetries indicated for isomers 18-III and 18-IV correspond to the idealized geometry of the respective molecules. The results of X-ray structure determination revealed only very small deviations of symmetry connected bond lengths (less or equal to 2 esd's) from the idealized geometry of both molecules. In structure 18-IV, rotation angles of some CF_3 groups around C–CF_3 bonds distort the strict C_s symmetry more considerably.

Formation energies of $C_{60}(CF_3)_{18}$ molecules were calculated on the DFT level of theory.[14–16] Overall, relative formation energy are close to the data reported previously[17] with the most stable isomer C_{3v}-$C_{60}(CF_3)_{18}$-II (18-II) and the least stable isomer C_1-$C_{60}(CF_3)_{18}$-V (18-V) (see Figure 3). The addition patterns of all five $C_{60}(CF_3)_{18}$ isomers are presented as Schlegel diagrams in Figure 3. Characteristic structural fragments are isolated double C=C bonds surrounded by four C atoms with sp^3 hybridization. Partially isolated C=C bonds have only three sp^3 carbon neighbours. Both types of isolated C=C bonds have lengths in the range of 1.33–1.35 Å. Another stabilizing structural fragment is a benzenoid ring *i.e.*, hexagon surrounded by six (or only five) sp^3 carbon atoms as shown in Figure 3. Two fully isolated benzenoid rings are found in isomer 18-II. Carbon cage of isomer 18-V contains one completely isolated benzenoid ring whereas benzenoid rings of other isomers are partially isolated: 18-I (1 ring), 18-III (2), 18-IV (2) and 18-V (1). Averaged C–C bond lengths in benzenoid rings are in the range of 1.39–1.40 Å. The attachment of CF_3 groups (as comparatively bulky addends) in *ortho* position of the cage is believed to be a destabilizing factor. Such *ortho* contacts are present in isomers 18-IV and 18-V (see Figure 2). The *ortho* contact in isomer 18-IV (1.573 Å) is a part of a so-called skewed pentagonal pyramid (SPP) arrangement[18] with butadiene-like C=C–C=C fragment in the pentagon (bond lengths of 1.34, 1.46, and 1.35 Å) as depicted in Figure 3. An *ortho* contact in SPP is likely to facilitate a detachment of one CF_3 group. That is why isomer 18-IV gives the fragment ion $C_{60}(CF_3)_{17}^-$ as a main peak in the MALDI mass

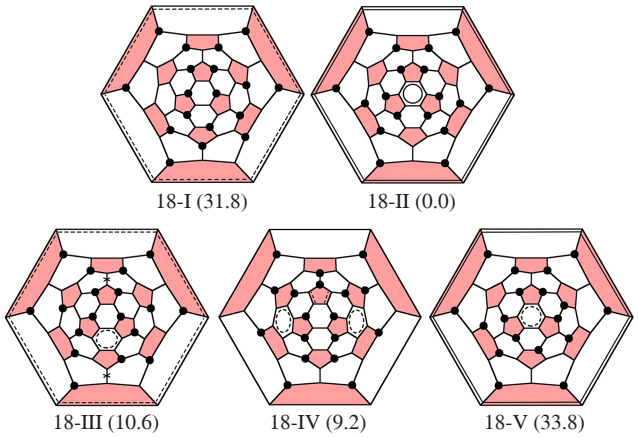


Figure 3 Schlegel diagrams of five $C_{60}(CF_3)_{18}$ isomers, three of which, 18-III–18-V, were structurally characterized in this work. Cage pentagons are highlighted in red. Black circles denote the positions of CF_3 attachments. Depositions of completely and partially isolated benzenoid rings are indicated by solid and dashed ellipses, respectively. The butadiene-like fragment in the SPP arrangement is also shown. The positions of two-fold axes in isomer C_2-$C_{60}(CF_3)_{18}$ (18-III) are indicated by small crosses. Theoretically calculated relative formation energies are given in parentheses in kJ mol^{-1}.

spectrum whereas molecular species $C_{60}(CF_3)_{18}^-$ dominate in the mass spectra of other isomers. It is of interest that the most stable isomer 18-II contains three unoccupied pentagons on a carbon cage whereas non such pentagons are found in 18-III, 18-IV and only one such pentagon is present in the least stable isomers 18-I and 18-V (see Figure 2). In fact, destabilizing effect of the presence of unoccupied pentagons is compensated by the formation of additional partially isolated C=C bonds in such pentagons.

Most similar are the addition pattern of isomers 18-II and 18-V with 15 common CF_3 attachment positions as can be seen in Figure 3. Isomers 18-I and 18-III have 14 common CF_3 attachments. The addition pattern of isomer 18-IV differs from that of other isomers more considerably because it possesses only 11 common CF_3 attachments with isomers 18-I, 18-III and 18-V. Note that the addition patterns of isomers 18-I and 18-V have 16 common CF_3 attachment positions with known isomers 16-I and 16-III, respectively,[12] which can be regarded as possible precursors of the corresponding $C_{60}(CF_3)_{18}$ isomers.

In summary, three new $C_{60}(CF_3)_{18}$ isomers have been synthesized, chromatographically isolated, and structurally characterized by X-ray crystallography. The addition patterns and relative formation energies of all five known $C_{60}(CF_3)_{18}$ isomers are discussed in terms of molecular symmetry, the presence of isolated C–C bonds, benzenoid rings, SPP substructures and unoccupied pentagons on the C_{60} carbon cage. With this and our recently published works on $C_{60}(CF_3)_{12,14,16}$, the number of structurally characterized isomers $C_{60}(CF_3)_{2n}$ ($2n$ = 2–18) reached as many as 68.

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$C_{60}(CF_3)_{18}$ (18-V), monoclinic, $P2_1/n$, a = 11.649(1), b = 21.8909(6) and c = 24.2141(8) Å, β = 102.770(9)°, V = 6022.0(6) $Å^3$, Z = 4, R_1 = 0.116 with 9390 reflections [$I > 2\sigma(I)$], wR_2 = 0.326 with 13744 reflections and 1590 parameters. In the crystal packing, two enantiomeric molecules are overlapped in the same crystallographic site.

CCDC 2369558–2369560 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

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