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Trifluoromethyl derivatives of fullerene C_{70}, $C_{70}(CF_3)_2$, $C_{70}(CF_3)_8$ and $C_{70}(CF_3)_{14}$

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The reaction of C_{70} with higher $C_{70}(CF_3)_n$ or annealing of the latter followed by HPLC separation of reaction products resulted in an isolation of $C_{70}(CF_3)_2$, $C_{70}(CF_3)_8$ and $C_{70}(CF_3)_{14}$. X-ray diffraction study revealed molecular structure of the three isomers that are compared with other known $C_{70}(CF_3)_n$ derivatives.

The trifluoromethylation of fullerenes was proven as effective method of their functionalization. More than 20 of either $C_{60}(CF_3)_n$ or $C_{70}(CF_3)_n$ isomers with $n = 2$–18 have been isolated and structurally characterized by ^{19}F NMR spectroscopy and X-ray crystallography. The common synthesis techniques for trifluoromethylation of fullerenes are based on reactions of fullerene with compounds that release CF_3 radicals upon heating like silver trifluoroacetate[1,2] or CF_3I.[3–5] Here, we report an alternative synthetic approach, which includes a reaction of fullerene C_{70} with a mixture of higher $C_{70}(CF_3)_n$ derivatives or a partial decomposition of the latter by annealing. Molecular structures of $C_{70}(CF_3)_2$, $C_{70}(CF_3)_8$ and $C_{70}(CF_3)_{14}$ were determined by X-ray crystallography and compared with other known $C_{70}(CF_3)_n$ representatives.

A mixture of higher $C_{70}(CF_3)_n$ derivatives ($n = 14$–18) was produced *via* an ampoule reaction of C_{70} with CF_3I as described elsewhere.[4–6] 15–40 mg of C_{70} (98.5%, TermUSA) and 40 mg of the $C_{70}(CF_3)_n$ mixture were placed in a subsequently evacuated and sealed glass ampoule. The ampoule was heated at 440–450 °C for 100 h. MALDI MS analysis of the deep-brown cake performed in a negative ion mode using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, ≥ 99%, Fluka) as a matrix revealed the formation of a mixture of lower $C_{70}(CF_3)_n$ derivatives with $n = 2$–10. The composition of the resulting mixture of lower $C_{70}(CF_3)_n$ compounds was dependent on the amount of C_{70}. When 15 mg of C_{70} was used, the reaction product did not contain unreacted C_{70}; only $C_{70}(CF_3)_n$ compounds with $n = 4$–10 were found in the mixture. The use of a larger amount of C_{70} (40 mg) led to the products containing C_{70}, whereas resulting mixtures of $C_{70}(CF_3)_n$ compounds were characterized by lower CF_3 content with $n = 2$–10, isomers with $n = 8$ being dominant in the both cases. HPLC analysis performed with a Cosmosil Buckyprep column (10 mm ID × 25 cm) and toluene as an eluent demonstrated additionally that the two known C_s- and C_2-$C_{70}(CF_3)_8$ isomers[1,7,8] were most abundant among $C_{70}(CF_3)_n$ isomers.

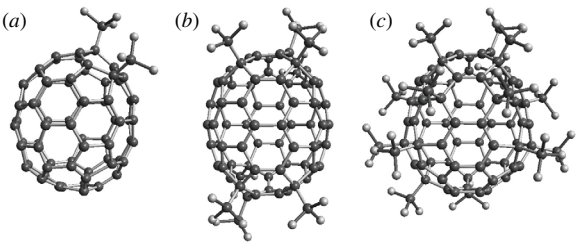

Figure 1 Side projections of the (*a*) C_1-$C_{70}(CF_3)_2$, (*b*) C_2-$C_{70}(CF_3)_8$ and (*c*) C_1-$C_{70}(CF_3)_{14}$ molecules. A non-crystallographic C_2 symmetry axis of the $C_{70}(CF_3)_8$ molecule is oriented in the view direction.

HPLC separation of $C_{70}(CF_3)_n$ mixtures using the same column with toluene as a mobile phase and a flow rate of 4.6 ml min^{-1} allowed the isolation of several fractions containing $C_{70}(CF_3)_n$ isomers with $n = 2$, 6 and 8. Some of these isomers have been already structurally characterized by X-ray crystallography in previous studies, for example, $C_{70}(CF_3)_6$,[9] C_s-$C_{70}(CF_3)_8$,[7] and C_2-$C_{70}(CF_3)_8$.[8] Two fractions eluted at 11.9 and 16.2 min containing respectively $C_{70}(CF_3)_2$ and $C_{70}(CF_3)_8$ gave crystalline materials after slow evaporation of solvent. X-ray single crystal diffraction study with the use of synchrotron radiation allowed elucidation of their molecular structures (Figure 1).†

In another type of experiments, a mixture of higher $C_{70}(CF_3)_n$ derivatives ($n = 12$–18, with $n = 16$ most abundant) was subjected to annealing in ampoules at 350–380 °C with periodical control of the remaining mixture composition by MALDI MS analysis. It was noticed that the overall composition was gradually shifted

† *Crystal data.* Data collection for single crystals was performed on a MAR225 image plate with a CCD detector using synchrotron radiation ($\lambda = 0.9050$ Å) at the BESSY storage ring (PSF of the Free University Berlin). Structures were solved with SHELXS97[14] and anisotropically refined with SHELXL97.[15] For $C_{70}(CF_3)_2 \cdot C_6H_5CH_3$: $M = 1070.85$, orthorhombic, space group $P2_12_12_1$, $a = 10.5281(7)$, $b = 18.1615(8)$ and $c = 21.124(1)$ Å, $V = 4039.0(4)$ Å^3, $\mu = 0.121$ mm^{-1}, $Z = 4$. Reflections collected 38885, independent 7685, $R_{int} = 0.104$. Refinement with 744 parameters yielded a conventional $R_1(F) = 0.127$ for 6942 reflections with $I > 2\sigma(I)$ and $wR_2(F^2) = 0.273$ for all reflections. Toluene molecule of solvation is disordered over two positions. For C_2-$C_{70}(CF_3)_8$: $M = 1392.78$, triclinic, space group $P\bar{1}$, $a = 10.348(1)$, $b = 12.563(1)$ and $c = 19.177(1)$ Å, $\alpha = 103.41(1)°$, $\beta = 91.68(1)°$ and $\gamma = 107.09(1)°$, $V = 2305.2(3)$ Å^3, $\mu = 0.185$ mm^{-1}, $Z = 2$. Reflections collected 29829, independent 8893, $R_{int} = 0.087$. Refinement with 1089 parameters yielded a conventional $R_1(F) = 0.158$ for 6054 reflections with $I > 2\sigma(I)$ and $wR_2(F^2) = 0.377$ for all reflections. For $C_{70}(CF_3)_{14} \cdot 0.5C_6H_{14}$: $M = 1849.83$, triclinic, space group $P\bar{1}$, $a = 13.9568(7)$, $b = 14.9835(8)$ and $c = 16.0484(9)$ Å, $\alpha = 74.613(1)°$, $\beta = 88.732°$ and $\gamma = 88.237°$, $V = 2305.2(3)$ Å^3, $\mu = 0.196$ mm^{-1}, $Z = 2$. Reflections collected 42589, independent 11876, $R_{int} = 0.163$. Refinement with 1187 parameters yielded a conventional $R_1(F) = 0.109$ for 5921 reflections with $I > 2\sigma(I)$ and $wR_2(F^2) = 0.282$ for all reflections. One CF_3 group and hexane molecule are disordered.

CCDC 713078–713080 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, 2009.

to the lower CF_3 content resulting after 40 h in a $C_{70}(CF_3)_n$ mixture containing $C_{70}(CF_3)_{14}$ as the most abundant species. This mixture was HPLC separated to several fractions using a Cosmosil Buckyprep column (10 mm × 25 cm) and hexane as an eluent at a flow rate of 4.6 ml min^{-1}. The fractions eluted between 7 and 16 min showed the presence of $C_{70}(CF_3)_{12}$ and $C_{70}(CF_3)_{14}$ isomers according to MALDI MS analysis. They should represent new isomers of these compositions because the retention times of all known isomers are below 7 min.[4,5] After slow concentration of the fraction eluted at 7.7 min, small crystals were obtained that were subjected to X-ray single crystal diffraction study. Actually, crystal structure elucidation established a new isomer of $C_{70}(CF_3)_{14}$ (Figure 1).†

The molecular structure of 7,24-$C_{70}(CF_3)_2$ isolated in this work corresponds to the most thermodynamically stable isomer with two CF_3 groups in 1,4 positions in a cage hexagon (Figure 2). Earlier, this addition pattern for $C_{70}(CF_3)_2$ produced by the reaction of C_{70} and CF_3COOAg and separated by HPLC was deduced on the basis of an ^{19}F NMR spectrum.[1] CF_3 groups are in perfect staggered positions relative to the three C–C bonds of the fullerene cage with the shortest intramolecular F···F distance of 2.67 Å. A similar staggered geometry of two CF_3 groups was found recently in 1,7-$C_{60}(CF_3)_2$ isomer with an intramolecular F···F distance of 2.58 Å.[2]

The molecular structure of 7,15,24,34,44,47,53,56-$C_{70}(CF_3)_8$ determined in this study (Figure 2) is substantially different from structures of the two so far structurally characterized 1,4,11,19,31,41,51,64- and 1,4,11,19,31,41,51,60-$C_{70}(CF_3)_8$.[7,8] While the latter have all CF_3 groups attached in the equatorial region, the former contains two by four groups on the both poles of the molecule with C_2 symmetry of the addition pattern. Notably, the same addition pattern was recently found in the one of four isolated $C_{70}(n\text{-}C_3F_7)_8$ isomers.[11] While so far known $C_{70}(CF_3)_8$ isomers with relative formation energies 0.0 and 6.0 kJ mol^{-1} are most thermodynamically stable and therefore most abundant isomers in synthetic mixtures, the new isomer has a much higher relative energy of 26.1 kJ mol^{-1} (ref. 11) and a very low content. Probably, its formation was only possible due to decomposition of the higher $C_{70}(CF_3)_n$ compounds.

The molecular structure of 1,4,8,11,19,24,27,31,41,43,51,53, 56,64-$C_{70}(CF_3)_{14}$ [$C_{70}(CF_3)_{14}$-VI, Figure 2] has many common features with the four already known $C_{70}(CF_3)_{14}$ isomers.[5,12] Addition patterns of all these molecules contain a substructure of C_1-$C_{70}(CF_3)_{10}$ (ref. 3) and some of them can be derived from the addition patterns of two known $C_{70}(CF_3)_{12}$ isomers.[4,13]

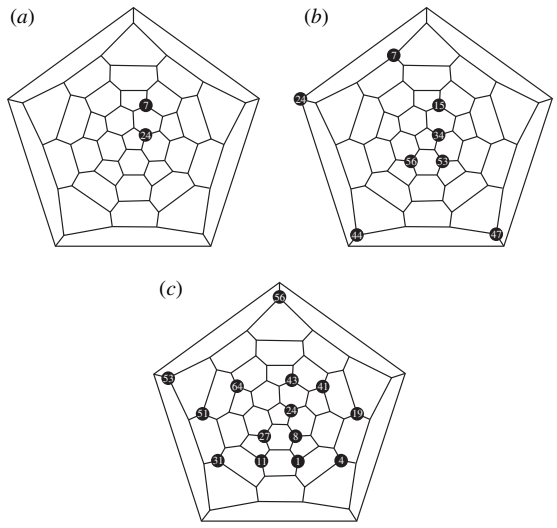

Figure 2 Schlegel diagrams of (*a*) C_1-$C_{70}(CF_3)_2$, (*b*) C_2-$C_{70}(CF_3)_8$ and (*c*) C_1-$C_{70}(CF_3)_{14}$ molecules. Numbers in black circles correspond to the lowest-locant IUPAC notation for fullerene derivatives.[10]

According to quantum-chemical calculations,[5] the relative energy of $C_{70}(CF_3)_{14}$-VI amounts to only 1.7 kJ mol^{-1}. Therefore, it is one of the most stable $C_{70}(CF_3)_{14}$ isomers occupying the third place in a stability row. This isomer, however, has not been found in the product of direct reaction of C_{70} with CF_3I in ampoules. Most probably, it was consumed due to further trifluoromethylation to $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$. Though four $C_{70}(CF_3)_{16}$ isomers with suitable addition patterns and low relative energies between 3.5 and 23.4 kJ mol^{-1} can be found by theoretical calculations,[5] no such isomer has been experimentally isolated. In contrast, the $C_{70}(CF_3)_{18}$ isomer with the addition pattern which can be obtained from $C_{70}(CF_3)_{14}$-VI by attachment of four CF_3 groups has been HPLC isolated from a mixture of higher $C_{70}(CF_3)_n$ derivatives and structurally characterized in the X-ray diffraction study.[6]

Apparently, the method of producing lower trifluoromethylated derivatives from the higher $C_{70}(CF_3)_n$ and C_{70} is due to transfer of addends between the constituents of the reaction mixture rather than decomposition of the original higher trifluoromethylated reactants because initial C_{70} was partially or completely consumed in such experiments.[8] On the other hand, thermal decomposition of higher $C_{70}(CF_3)_n$ at heating takes place thus resulting in some new derivatives that were not observed in the products of direct trifluoromethylation of C_{70} with CF_3I in ampoules.

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References

1 E. I. Dorozhkin, D. V. Ignat'eva, N. B. Tamm, A. A. Goryunkov, P. A. Khavrel, I. N. Ioffe, A. A. Popov, I. V. Kuvychko, A. V. Streletskiy, V. Yu. Markov, J. Spandal, S. H. Strauss and O. V. Boltalina, *Chem. Eur. J.*, 2006, **12**, 3876.
2 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.
3 I. E. Kareev, I. V. Kuvychko, A. A. Popov, S. F. Lebedkin, S. Miller, O. Anderson, S. H. Strauss and O. V. Boltalina, *Angew. Chem., Int. Ed. Engl.*, 2005, **44**, 7984.
4 D. V. Ignat'eva, A. A. Goryunkov, N. B. Tamm, I. N. Ioffe, S. M. Avdoshenko, L. N. Sidorov, A. Dimitrov, E. Kemnitz and S. I. Troyanov, *Chem. Commun.*, 2006, 1778.
5 A. A. Goryunkov, D. V. Ignat'eva, N. B. Tamm, N. N. Moiseeva, I. N. Ioffe, S. M. Avdoshenko, V. Yu. Markov, L. N. Sidorov, E. Kemnitz and S. I. Troyanov, *Eur. J. Org. Chem.*, 2006, 2508.
6 S. M. Avdoshenko, A. A. Goryunkov, I. N. Ioffe, D. V. Ignat'eva, L. N. Sidorov, Ph. Pattison, E. Kemnitz and S. I. Troyanov, *Chem. Commun.*, 2006, 2463.
7 A. A. Goryunkov, E. I. Dorozhkin, D. V. Ignat'eva, L. N. Sidorov, E. Kemnitz, G. M. Sheldrick and S. I. Troyanov, *Mendeleev Commun.*, 2005, 225.
8 T. Mutig, I. N. Ioffe, E. Kemnitz and S. I. Troyanov, *Mendeleev Commun.*, 2008, **18**, 73.
9 E. I. Dorozhkin, D. V. Ignat'eva, N. B. Tamm, N. V. Vasilyuk, A. A. Goryunkov, S. M. Avdoshenko, I. N. Ioffe, L. N. Sidorov, Ph. Pattison, E. Kemnitz and S. I. Troyanov, *J. Fluorine Chem.*, 2006, **127**, 1344.
10 F. Cozzi, W. H. Powell and C. Thilgen, *Pure Appl. Chem.*, 2005, **77**, 843.
11 T. Mutig, E. Kemnitz and S. I. Troyanov, *Eur. J. Org. Chem.*, 2008, 3256.
12 N. B. Shustova, D. V. Peryshkov, I. E. Kareev, O. V. Boltalina and S. H. Strauss, *Acta Crystallogr.*, 2007, **E63**, o3928.
13 I. E. Kareev, S. F. Lebedkin, S. M. Miller, O. P. Anderson, S. H. Strauss and O. V. Boltalina, *Acta Crystallogr.*, 2006, **E62**, o617, o620.
14 G. M. Sheldrick, *SHELXS97. Program for Solution of Crystal Structures from Diffraction Data*, Universität Göttingen, Germany, 1997.
15 G. M. Sheldrick, *SHELXL97. Program for Crystal Structure Refinement*, Universität Göttingen, Germany, 1997.

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