Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2010, **20**, 229–230

Mendeleev Communications

Trifluoromethyl derivatives of fullerene C_{76}, $C_{76}(CF_3)_{14–18}$

Nadezhda B. Tamm 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.2010.06.016

The trifluoromethylation of a higher fullerene mixture followed by the HPLC separation of CF_3 derivatives resulted in the isolation of $C_{76}(CF_3)_{14}$, $C_{76}(CF_3)_{16}$ and $C_{76}(CF_3)_{18}$ (two isomers), the crystal and molecular structures of which were determined by X-ray diffraction with the use of synchrotron radiation.

Higher fullerenes are difficult to study not only due to the small amounts of available test materials but also because of the existence of cage isomers for each higher fullerene. From two possible IPR isomers of C_{76}, the D_2 isomer has much higher stability than the T_d isomer.[1,2] Multifunctionalized derivatives of D_2-C_{76} were isolated for chlorides, $C_{76}Cl_{18}$,[3(*a*)] $C_{76}Cl_{34}$,[3(*b*)] and $C_{76}(CF_3)_n$ with $n = 6–12$.[4] Whereas the cage connectivity of D_2-C_{76} has been confirmed by an X-ray diffraction study,[3] assumptions concerning the addition patterns of CF_3 derivatives were made on the basis of ^{19}F NMR spectra in solution.[4] Recently, the cage rearrangement of D_2-C_{76} to a non-IPR C_2-$^{\#18917}C_{76}$ in the course of chlorination has been discovered.[5] Here, we report the results of the synthesis, isolation and structural characterization of polytrifluoromethyl derivatives of D_2-C_{76}. The addition patterns of the $C_{76}(CF_3)_n$ molecules with 14–18 attached CF_3 groups are discussed and compared with published data.

A mixture of higher fullerenes C_{76}–C_{96} also containing small amounts of C_{60} and C_{70} (MER Corp.) was used as a starting material in this work. The higher fullerene mixture (15 mg) reacted with CF_3I in a sealed glass ampoule at 380–400 °C and a reagent pressure of ~6 bar for 50–100 h. The resulting CF_3 derivatives were sublimed into a colder part of the ampoule. MALDI mass-spectrometric analysis of the reaction product (~28 mg) was performed on an AutoFlex reflectron TOF spectrometer (Bruker) equipped with a N_2 laser (337 nm, 1 ns pulse) with the use of 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB, ≥ 99%, Fluka AG) as the matrix. The reaction product contained a wide variety of trifluoromethyl derivatives of C_{60}, C_{70} and C_{76}–C_{96} with 12–20 attached CF_3 groups. The sublimed $C_m(CF_3)_n$ mixture was dissolved in hexane and separated by HPLC with the use of a WATERS 1500 chromatographic system, a Cosmosil Buckyprep column (10×250 mm, Nacalai Tesque Corp.) and hexane as an eluent (detection at 290 nm). Figure 1 represents a chromatogram of the mixture. The peak positions of fractions eluted between 3 and 25 min containing $C_{76}(CF_3)_n$ compounds with $n = 14–18$ as main components are shown. Slow concentration of four separated fractions with elution times of 3.8, 4.0, 6.2, and 11.4 min afforded crystalline materials.

Data collection for the single crystals of $C_{76}(CF_3)_n$ was carried out with a MAR225 CCD detector at 100 K using synchrotron radiation at the BESSY storage ring, BL 14.2 ($\lambda = 0.9050$ Å, PSF of the Free University of Berlin, Germany). The structures were solved using direct methods (SHELXS97) or with the shake-and-bake program SHELXD and anisotropically refined with SHELXL97.[6] Crystallographic data and some details of data collection and structure refinement are given in Table 1S of Online Supplementary Materials.[†]

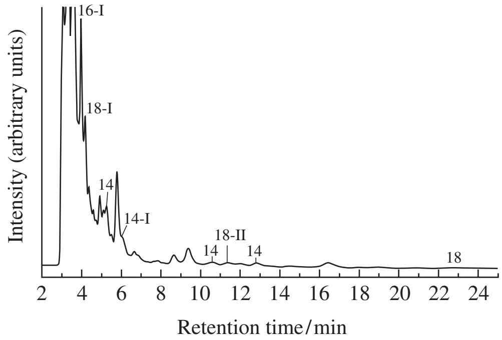

Figure 1 Chromatogram of the $C_m(CF_3)_n$ mixture recorded in hexane. Arabic figures denote the numbers of attached CF_3 groups for fractions containing predominantly $C_{76}(CF_3)_n$. Roman numerals denote consecutive numbers of isomers with known structures.

The isomers of higher fullerenes are difficult to separate due to their very similar properties. In contrast, higher fullerene derivatives can be separated much more easily because cage differences result in more pronounced differences in the composition and shape of derivatized molecules. Therefore, the separation of a complex mixture of trifluoromethylated C_{60}, C_{70} and C_{76}–C_{96} performed in this work resulted in the isolation and structural characterization of four $C_{76}(CF_3)_{14–18}$ compounds and other CF_3 derivatives of higher fullerenes, such as $C_{84}(CF_3)_{12,16}$,[7] $C_{86}(CF_3)_{16,18}$,[8] $C_{88}(CF_3)_{18}$ and $C_{92}(CF_3)_{16}$.[9] Earlier, a similar method was used for the isolation and characterization of the CF_3 derivatives of C_{76}, C_{78}, C_{84} and C_{90}.[4] In this case, the reaction between fullerene and CF_3I in a flow at 520 °C, *i.e.*, at a lower pressure (~1 bar) and a higher temperature, resulted in compounds with a smaller number of attached CF_3 groups. Thus, $C_{76}(CF_3)_n$ isomers with n of 6–12 have been observed, and suggestions concerning molecular structures of these compounds have been made on the basis of ^{19}F NMR spectra.[4] The compounds obtained in our ampoule syntheses under a higher CF_3I pressure and for a much longer reaction time contained 12–18 attached CF_3 groups. The X-ray crystallographic structure determination of $C_{76}(CF_3)_n$ isomers has been performed for the first time.

The molecular structures of the four $C_{76}(CF_3)_n$ isomers with $n = 14$, 16 and 18 (two isomers) are shown in Figure 2. Addition patterns of four molecules denoted as 76-14-I, 76-16-I, 76-18-I and 76-18-II, respectively, are presented in Figure 3 as

---

[†] CCDC 743440–743443 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, 2010.

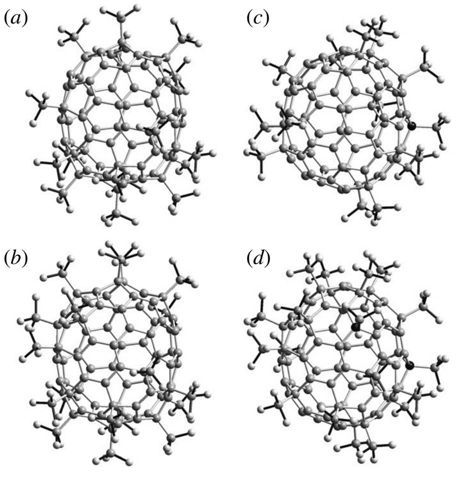

Figure 2 Molecules of (*a*) $C_{76}(CF_3)_{16}$-I, (*b*) $C_{76}(CF_3)_{18}$-I, (*c*) $C_{76}(CF_3)_{14}$-I and (*d*) $C_{76}(CF_3)_{18}$-II shown along the shortest cage axes. The attachments of CF_3 groups at the THJ positions in the molecules of $C_{76}(CF_3)_{14}$-I and $C_{76}(CF_3)_{18}$-II are indicated by the black colour of corresponding C atoms.

Schlegel diagrams. As expected, all of the four isomers are the derivatives of D_2-C_{76}. Taking into account the addition patterns, the four isomers can be divided into two groups. In the isomers 76-16-I and 76-18-I, CF_3 groups are attached to the C_{76} fullerene cage at the positions where junctions of one pentagon and two hexagons occur (PHH positions). Addition patterns of 76-14-I and 76-18-II also contain one and two CF_3 attachments, respectively, in the positions of triple hexagon junctions (HHH or THJ). The latter type of addition has been regarded as hardly accessible owing to strong steric strain.[4] However, additions in THJs become more probable in overcrowded molecules with a large number of addends. Such additions were first observed in $C_{70}Cl_{28}$[10] and in two isomers of $C_{70}F_{38}$.[11,12] Recently, the addition of two CF_3 groups in THJ positions has been found in the structure of the $C_{94}(CF_3)_{20}$ molecule, which can also be regarded as overcrowded.[13]

The isomers 76-16-I and 76-18-I possess similar addition patterns in that 14 CF_3 groups are attached at the same positions on the D_2-C_{76} cage. Therefore, it could be assumed that 76-16-I is a precursor of 76-18-I at its formation in the course of trifluoromethylation, if a rearrangement of only two CF_3 groups on the fullerene cage is allowed to proceed.[14] As indicated in Figure 3, several isolated C–C double bonds are formed on the fullerene cages, which are 1.33 Å long, whereas two conjugated C–C bonds in the structure of 76-16-I have an average bond length of 1.34 Å. The 76-18-I molecule has two additions in the *ortho* position in the region of the highest surface curvature of the D_2-C_{76} cage, *i.e.*, near to the longest cage ellipsoid axis.

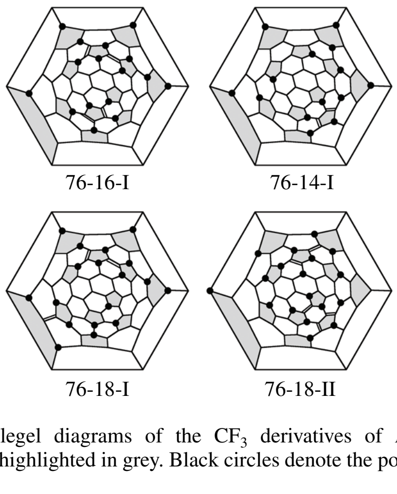

Figure 3 Schlegel diagrams of the CF_3 derivatives of D_2-C_{76}. Cage pentagons are highlighted in grey. Black circles denote the positions of CF_3 attachments.

The isomers 76-14-I and 76-18-II have eight attachment positions of CF_3 groups in common including one attachment in the THJ position. Isolated and conjugated C–C double bonds have the lengths of 1.33 and 1.34 Å, respectively. In the structure of the 76-18-II isomer, the aromatic (benzenoid) ring isolated by six CF_3 attachments on the fullerene cage has an average C–C bond length of 1.40 Å. Due to different curvatures of cage regions, two sp^3 carbons at THJs in the molecule of 76-18-II have significantly different averaged C–C–CF_3 angles of 110.2° and 112.1°.

Addition patterns established in $C_{76}(CF_3)_{14-18}$ differ drastically from those suggested for $C_{76}(CF_3)_{8-12}$[4] in that many interpentagonal C–C bond positions are occupied by CF_3 groups in the former, whereas no such a kind of attachments were found in the latter. In the suggested $C_{76}(CF_3)_{8-12}$ structures, most CF_3 groups are attached at the *para* positions in hexagons; no 1,2 or THJ attachments are present.

It can be suggested that, in the attachment of a large number of such bulky groups as CF_3, some less energetically favourable (overcrowded) addition fragments are realized. This is the case of 1,2 addition as in the isomer 76-18-I or of addition in the positions of triple hexagon junctions as in the structure of the isomer 76-18-II. Theoretical calculations of relative energy for these two isomers at the DFT level of theory revealed the difference of 67.6 kJ mol^{-1} in favour of the 76-18-I molecule. Such a high energy difference for the isomers $C_m(CF_3)_n$ obtained under the same experimental conditions has not been observed before. The largest energy difference of about 40 kJ mol^{-1} was reported for S_6 and C_1 isomers of $C_{60}(CF_3)_{12}$.[15]

This work was supported in part by the Russian Foundation for Basic Research (project nos. 09-03-00433 and 09-03-91337). We are grateful to Dr. A. A. Goryunkov for the use of the drawing program for Schlegel diagrams and Dr. P. A. Khavrel for theoretical calculations.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2010.06.016.

References

1 P. W. Fowler and D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon, Oxford, 1995, p. 392.

2 R. Ettl, I. Chao, F. Diederich and R. L. Wetten, *Nature*, 1991, **353**, 149.

3 (*a*) K. S. Simeonov, K. Yu. Amsharov and M. Jansen, *Angew. Chem. Int. Ed.*, 2007, **46**, 8419; (*b*) H. Liang, Y.-Z. Tan, T. Zhou, Z.-L. Chen, S.-Y. Xie, R.-B. Huang and L.-S. Zheng, *Inorg. Chem.*, 2010, **47**, 3089.

4 I. E. Kareev, A. A. Popov, I. V. Kuvychko, N. B. Shustova, S. F. Lebedkin, V. P. Bubnov, O. P. Anderson, K. Seppelt, S. H. Strauss and O. V. Boltalina, *J. Am. Chem. Soc.*, 2008, **130**, 13471.

5 I. N. Ioffe, A. A. Goryunkov, N. B. Tamm, L. N. Sidorov, E. Kemnitz and S. I. Troyanov, *Angew. Chem. Int. Ed.*, 2009, **48**, 5904.

6 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

7 N. B. Tamm, L. N. Sidorov, E. Kemnitz and S. I. Troyanov, *Chem. Eur. J.*, 2009, **15**, 10486.

8 S. I. Troyanov and N. B. Tamm, *Kristallografiya*, 2009, **54**, 637 (*Crystallogr. Rep*., 2009, **54**, 598).

9 N. B. Tamm and S. I. Troyanov, *Chem. Commun.*, 2009, 6035.

10 S. I. Troyanov, N. B. Shustova, I. N. Ioffe, A. P. Turnbull and E. Kemnitz, *Chem. Commun.*, 2005, 72.

11 P. B. Hitchcock, A. G. Avent, N. Martsinovich, P. A. Troshin and R. Taylor, *Chem. Commun.*, 2005, 75.

12 P. B. Hitchcock, A. G. Avent, N. Martsinovich, P. A. Troshin and R. Taylor, *Org. Lett.*, 2005, **7**, 1975.

13 N. B. Tamm, L. N. Sidorov, E. Kemnitz and S. I. Troyanov, *Angew. Chem. Int. Ed.*, 2009, **48**, 9102.

14 D. V. Ignat'eva, T. Mutig, A. A. Goryunkov, N. B. Tamm, E. Kemnitz, S. I. Troyanov and L. N. Sidorov, *Izv. Akad. Nauk, Ser. Khim.*, 2009, 1117 (*Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 1146).

15 I. E. Kareev, N. B. Shustova, D. V. Peryshkov, S. F. Lebedkin, S. M. Miller, O. P. Anderson, A. A. Popov, O. V. Boltalina and S. H. Strauss, *Chem. Commun.*, 2007, 1650.

Received: 18th January 2010; Com. 10/3454