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Mendeleev Commun., 2007, **17**, 172–174

Mendeleev
Communications

Synthesis and molecular structure of seven isomers of $C_{70}(C_2F_5)_{10}$

Nadezhda B. Tamm and Sergey I. Troyanov*

Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation. Fax: +7 495 939 1240; e-mail: stroyano@thermo.chem.msu.ru

DOI: 10.1016/j.mencom.2007.05.014

A mixture of $C_{70}(C_2F_5)_n$ (n = 8, 10, 12) compounds was synthesised by a reaction of C_{70} with C_2F_5I at 350 °C followed by HPLC separation; crystal structure determination for seven isomers of $C_{70}(C_2F_5)_{10}$ revealed a large variety of addition patterns most of which are unprecedented in the regiochemistry of [70]fullerene.

The perfluoroalkylated derivatives of fullerenes attract considerable attention because they may serve as chemically and thermally stable acceptors in light-harvesting systems.[1] A large number of trifluoromethylated derivatives of C_{60} and C_{70} has been synthesized and structurally characterized. The maximum number of the attached CF_3 groups reaches 22,[2,3] but the yet isolated and characterized isomers contained 18 CF_3 groups both for C_{60}[4] and C_{70}.[5] The mixtures of $C_{60}(C_2F_5)_n$ (n = 2–16) were produced by treating fullerene with C_2F_5I.[2] The high-temperature reaction of C_{60} with a flow of C_2F_5I followed by HPLC separation resulted in isolation of two individual compounds, $C_{60}(C_2F_5)_6$ and $C_{60}(C_2F_5)_8$, and determination of their molecular structures by X-ray diffraction.[6]

Here, we report the preparation, isolation and crystallographic characterization of seven isomers of $C_{70}(C_2F_5)_{10}$.

Experimental procedure for producing $C_{70}(C_2F_5)_n$ compounds by a high-temperature reaction of C_{70} with C_2F_5I closely resembles that for preparation of $C_{70}(CF_3)_n$.[7,8] Typically, 30 mg of C_{70} (98.5%, Term-USA) reacted with an excess of C_2F_5I (98%, Apollo) in a glass ampoule placed in a furnace in a temperature gradient of 350–100 °C for 40–60 h. A brown product was found in the hot and colder zones. A toluene extract was analyzed by MALDI mass spectrometry showing the presence of mainly $C_{70}(C_2F_5)_{10}$ and a small amount of $C_{70}(C_2F_5)_{12}$ and C_{70}. The $C_{70}(C_2F_5)_n$ compounds were separated from C_{70} by HPLC using toluene as an eluent (Cosmosil Buckyprep column 10 mm i.d. × 25 cm, 4.6 ml min^{-1} flow rate, 290 nm). The toluene solution of the C_2F_5 derivatives was evaporated to dryness and then dissolved in hexane. The hexane solution was subjected to separation by HPLC on the same column at a 4.6 ml min^{-1} flow rate using hexane as an eluent (Figure 1). According to the MALDI mass spectra, the chromatographic fractions collected between 2.7 and 6.1 min contained predominantly $C_{70}(C_2F_5)_{10}$ with a small admixture of $C_{70}(C_2F_5)_{12}$ in some fractions. The results of a similar synthetic experiment carried out at a higher temperature of the hot zone (400 °C) showed the additional presence of $C_{70}(C_2F_5)_8$ in some hexane fractions eluted at longer retention times (5.6–8.2 min).

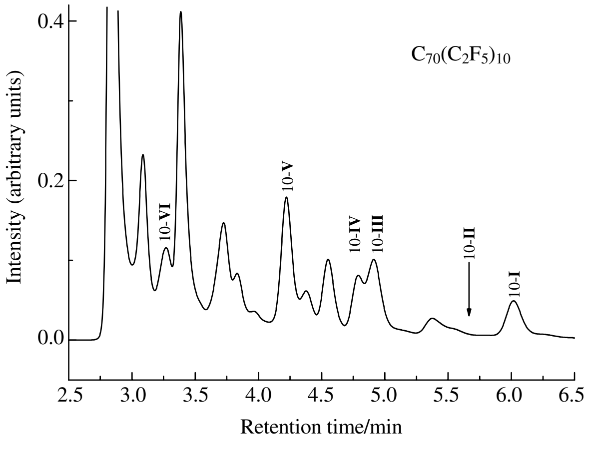

Figure 1 HPLC chromatogram of the $C_{70}(C_2F_5)_n$ mixture (after separation of fullerene) with hexane as an eluent, 4.6 ml min^{-1}. The labels designate the isomers with known structures. The arrow shows the position of the additional peak at 5.66 min in another chromatographic separation experiment.

Either slow concentration of the hexane fractions obtained in two experiments or recrystallization from toluene allowed the isolation of crystalline solids. Due to a very small size of crystals, the X-ray diffraction study was performed with the use of synchrotron radiation [the BESSY storage ring, PSF BL 14.1 (or 14.2) of the Free University of Berlin, Germany]. The crystallographic investigation was successful for the chromatographic fractions isolated at the retention times of 3.27, 4.22, 4.55, 4.79, 4.91 and 6.02 min in the first experiment and at a retention time of 5.66 min in the second one (arrow in Figure 1). These fractions are designated by Arabic and Roman numerals, the former being for the number of the C_2F_5 group in the $C_{70}(C_2F_5)_n$ molecule and the latter for sequential number of isomer in order of decreasing retention time.

The structures were solved using the SHELXD[9] program and then extended and anisotropically refined using SHELXL97.[10,†] Selected crystallographic data and details of data collection and refinement are given as Supplementary Material. All the structures contain isomeric molecules **I**–**VII** of the same composition, $C_{70}(C_2F_5)_{10}$, in some cases with a solvent molecule in the crystal lattice: $C_{70}(C_2F_5)_{10}\cdot 0.25PhMe$ (**I**), $C_{70}(C_2F_5)_{10}\cdot 0.5C_6H_{14}$ (**II**), and $C_{70}(C_2F_5)_{10}\cdot PhMe$ (**V**). Despite of different levels of the achieved accuracy (esd's of the C–C distances are within 0.003–0.02 Å), the addition patterns of all investigated $C_{70}(C_2F_5)_{10}$ molecules were determined unambiguously. Schlegel

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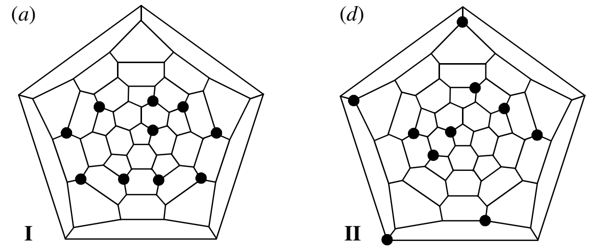
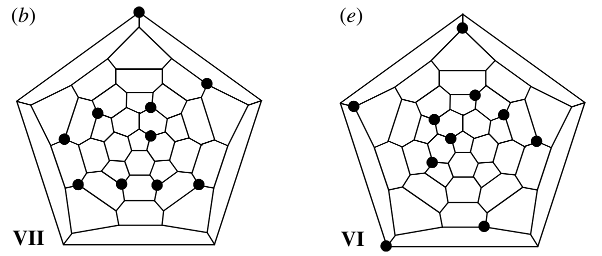
[†] Selected crystallographic data along with some details of data collection and refinement are available as Online Supplementary Materials.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 643896–643903. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2007.



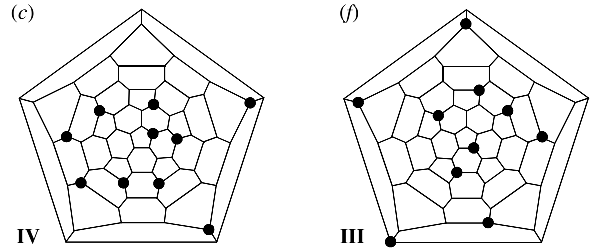
1,4,10,19,25,41,49, 60,66,69-$C_{70}(C_2F_5)_{10}$

1,4,11,33,38,46,53, 55,62,64-$C_{70}(C_2F_5)_{10}$



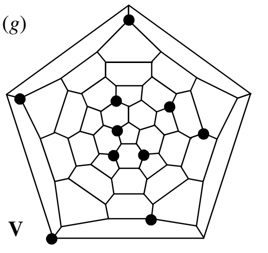
1,4,11,19,31,41,46, 55,62,67-$C_{70}(C_2F_5)_{10}$

1,4,11,33,38,46,48, 53,55,62-$C_{70}(C_2F_5)_{10}$



1,4,11,19,23,31,44, 55,57,67-$C_{70}(C_2F_5)_{10}$

1,4,11,24,33,38,43, 48,53,55-$C_{70}(C_2F_5)_{10}$



1,4,23,28,33,38,44, 46,53,55-$C_{70}(C_2F_5)_{10}$

Figure 2 Schlegel diagrams and IUPAC lowest-locant abbreviations for the seven structurally characterized isomers of $C_{70}(C_2F_5)_{10}$. Black circles denote attached C_2F_5 groups.

diagrams for isomers **I–VII** are shown in Figure 2 along with their IUPAC lowest-locant abbreviations.[11]

The addition pattern of isomer **I** [Figure 2(*a*)] is exactly the same as that in $C_{70}(CF_3)_{10}$.[12] The arrangement of the ten pentafluoroethyl groups on a [70]fullerene carbon cage can be represented as a *para-para-para-para-para-para-para-meta-para* ribbon (a p^7mp ribbon) formed by nine edge-sharing $C_6(C_2F_5)_2$ hexagons. All but one addition patterns of other investigated isomers can also be represented in this way, for example, as p^4,pm,p for isomer **IV** or p^5,p,p for **VII** [Figure 2(*c*) and (*b*)]. As a feature in common, they contain several (three or four) isolated domains of the attached C_2F_5 groups that have no edge-sharing $C_6(C_2F_5)_2$ hexagons in between. Alternatively, we can denote each isomer by pointing out the number of C_2F_5 groups in such domains present in a $C_{70}(C_2F_5)_{10}$ molecule. Therefore, isomer **I** with all ten C_2F_5 groups in the same domain has the notation ‘10’. The addition patterns of isomers **VII** (6;2;2) and **IV** (5;3;2) have some similarity with that of **I** due to the presence of eight and seven C_2F_5 groups, respectively, in the same positions on a fullerene cage. These three isomers have in common that several C_2F_5 groups (8, 6 and 5 for isomers **I**, **VII** and **IV**, respectively) are attached as a ribbon in the positions around the C_{70} cage equator. The addition pattern of isomer **VII** (but not the whole molecule) possesses a C_2 symmetry [Figure 3(*a*)].

The isomers **II**, **III** and **VI** constitute another type with their addition patterns having only two edge-sharing $C_6(C_2F_5)_2$ hexagons near to the cage equator [Figure 2(*d*),(*f*) and (*e*)]. In another domain near to the cage pole, there are three edge-sharing $C_6(C_2F_5)_2$ hexagons, *i.e.*, four C_2F_5 groups. Both isomers **II** and **VI** have the same notation, 4;3;3, the difference being the position of only one C_2F_5 group; this is also reflected in their lowest-locant abbreviations. The highest number of domains has isomer **III** (4;3;2;1) [Figure 2(*f*)]; the difference from isomer **VI** is the positions of two C_2F_5 groups.

Finaly, isomer **V** contains only two attached C_2F_5 groups near to the equator, whereas the both poles contain four C_2F_5 groups each [Figure 2(*g*)]. The domain structure is (4;4;2). The addition pattern of this isomer (but not the molecule as a whole) possesses a molecular C_2 symmetry [Figure 3(*b*)].

Note that the domains consisting of odd number of attached atoms or terminal groups encountered in the addition pattern of isomers **II–IV**, **VI** and **VII** are uncommon in stereochemistry of fullerene derivatives (however, note that the 1,2 attached Cl atoms in the structure of $C_{60}Cl_{30}$ form 15-membered rings[13]). For example, the structure determination for two C_2F_5 derivatives of C_{60} showed the domain structure (2;2;2) for $C_{60}(C_2F_5)_6$ and (6;2) for $C_{60}(C_2F_5)_8$.[6] Radical addition of atoms or groups to the fullerene cage occurs in pairs (as to alkenes). The addition of one atom (group) produces a radical, which transforms to a closed-shell structure by a second addition to a site with the highest spin density, the latter being *ortho* or *para* relative to the position of the first addition.[14] Addition of bulky groups such as C_2F_5 should occur preferentially in *para* positions, but some positions can be blocked sterically by the groups already attached. In addition, a high mobility of addends on the fullerene cage can take place at higher temperatures. In the case of attached halogens, this phenomenon is known as ‘chlorine’[13] or ‘fluorine dance’.[15] Apparently, kinetic factors play an important role in the stabilization of structures originally formed. In fact, several fullerene derivatives were isolated in form of different isomers, some of them being stable kinetically only. The most striking example is $C_{60}Cl_{30}$ with the C_2-isomer 78 kJ mol^{-1} less stable than the D_3-isomer.[16] The examples among perfluoroalkylated derivatives with known structure and relative energy include $C_{60}(CF_3)_8$ (two isomers; energy difference, $\Delta =$

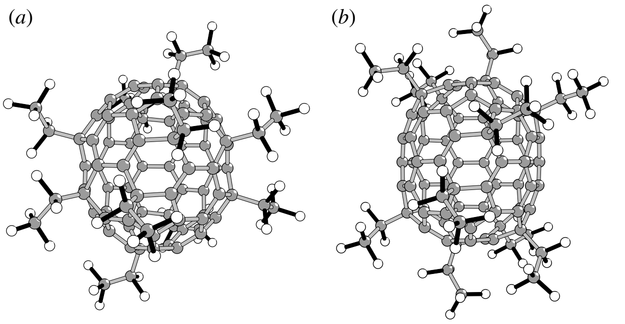


Figure 3 Views of the (*a*) $C_{70}(C_2F_5)_{10}$-**VII** and (*b*) $C_{70}(C_2F_5)_{10}$-**V** molecules demonstrating the attachment of most C_2F_5 groups around the equator for the former and on the poles for the latter. C–F bonds are shown in black. Note the cage elongation or flattening dependent on the places of most additions.

= 8.8 kJ mol^{-1}),[17] $C_{60}(CF_3)_{16}$ (three isomers; $\Delta = 11.9$ kJ mol^{-1}),[4] $C_{60}(CF_3)_{10}$ (three isomers; $\Delta = 7.6$ kJ mol^{-1}),[18] $C_{70}(CF_3)_{12}$ (two isomers; $\Delta = 2.5$ kJ mol^{-1}),[7] and $C_{70}(CF_3)_{14}$ (four isomers; $\Delta = 7.4$ kJ mol^{-1}).[8] The $C_{70}(C_2F_5)_{10}$ composition with seven structurally investigated isomers provides an example of even larger structural diversity. Theoretical calculation of these and other possible $C_{70}(C_2F_5)_{10}$ isomers has to be performed to reveal energy relationships between isomers and, possibly, to gain insight into mechanism of their formation.

In conclusion, seven isomers of $C_{70}(C_2F_5)_{10}$ isolated from the mixture produced by the reaction of C_{70} with C_2F_5I have been structurally characterized by X-ray crystallography. Only one isomer showed the known addition pattern, a p^7mp ribbon, whereas six others demonstrated unprecedented addition patterns with several isolated domains of the attached C_2F_5 groups on the fullerene cage. The reason for the formation of unusual patterns containing domains with odd number of addends should be sought in the bulkiness of the C_2F_5 group and inaccessibility of equatorial cage positions in [70]fullerene for addition of such group.

We are grateful to Dr. Alexey Goryunkov for the use of the ‘Schlegel’ program determining the IUPAC abbreviations for fullerene derivatives. This work was supported in part by the Russian Foundation for Basic Research (grant no. 05-03-04006).

Online Supplementary Materials

Supplementary data associated with this article (selected crystallographic data) can be found in the online version at doi:10.1016/j.mencom.2007.05.014.

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Received: 7th November 2006; Com. 06/2812