SHORT COMMUNICATION

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Synthesis and Structural Characterization of Four Isomers of $C_{70}(n\text{-}C_3F_7)_8$

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The first four isomers of $C_{70}(n\text{-}C_3F_7)_8$ synthesized by the ampoule reaction of C_{70} with $n\text{-}C_3F_7I$, isolated by HPLC, and characterized by X-ray crystallography possess unprecedented addition patterns among $C_{70}X_8$ compounds.

Introduction

In the last years, a large number of thermally stable perfluoroalkylated derivatives of C_{60} and C_{70} has been synthesized and structurally characterized, and some of them show interesting electrochemical behavior.[1,2] The largest group of compounds is represented by trifluoromethyl derivatives, $C_{60/70}(CF_3)_n$, with n ranging from 2 to 18.[3,4] Among perfluoroethylated fullerenes, several representatives of $C_{60}(C_2F_5)_n$ (n = 6–10)[5] and $C_{70}(C_2F_5)_n$ (n = 10)[6] are known so far. Noteworthy, addition patterns of isolated pentafluoroethylated isomers seldom coincide with those of trifluoromethylated ones, which thus reveals an influence of the size of the perfluoroalkyl group on the relative stability of the isomers. For example, only one addition pattern is common for six known (or suggested) isomers of $C_{70}(CF_3)_{10}$[2,7] and seven known isomers of $C_{70}(C_2F_5)_{10}$.[6] One can therefore assume that even larger fluoroalkyl groups would produce derivatives with new addition patterns.

The synthesis of n-perfluorohexyl derivatives by heating C_{60} with perfluorohexyl iodide in trichlorobenzene solution resulted in a mixture of $C_{60}(C_6F_{13})_n$ compounds with n = 6–12, but no individual isomers were obtained.[8] Recently, the first isomer of $C_{60}(i\text{-}C_3F_7)_6$ was isolated from a mixture produced by an ampoule reaction of C_{60} with $i\text{-}C_3F_7I$ and characterized by X-ray crystallography.[9] Here we report the preparation, HPLC separation, and crystallographic characterization of four isomers of $C_{70}(n\text{-}C_3F_7)_8$ possessing unprecedented addition patterns.

Results and Discussion

C_{70} (30 mg, 98.5%, Term-USA) and an excess amount of $n\text{-}C_3F_7I$ (0.4 mL, 98%, FluoroChem) were heated at 300–310 °C in a sealed glass ampoule for 90 h. After opening the ampoule, the excess of $n\text{-}C_3F_7I$ and iodine was removed from a brown-colored reaction product by heating at ca. 100 °C in open air for 20 h. MS (MALDI) analysis by using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malonitrile (DCTB) as matrix showed, besides a small amount of unreacted C_{70}, the presence of $C_{70}(C_3F_7)_n$ compounds with n = 2–10, in which those with n = 8 prevailed. The mixture was roughly divided into three fractions by using HPLC with toluene as the eluent (Cosmosil Buckyprep column, 10 mm ID × 25 cm, flow rate 4.6 mL min^{-1}, detection at 290 nm). An admixture of C_{70} was removed at this stage (See Supporting Information for more details). Fraction 1 collected between 2.5 and 3.1 min contained $C_{70}(C_3F_7)_n$ compounds with n = 6–10, whereas fraction 2

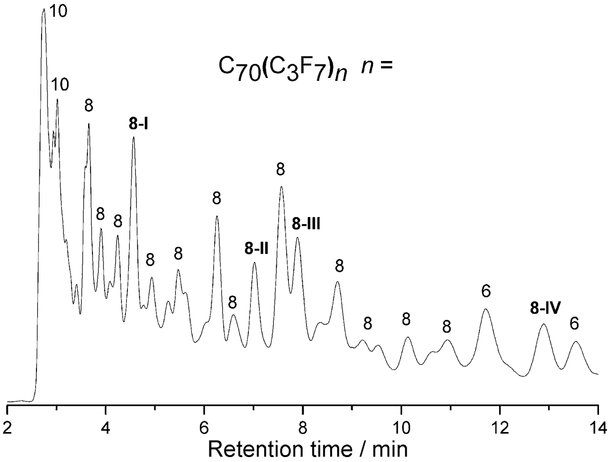

Figure 1. HPLC chromatogram of the $C_{70}(C_3F_7)_n$ mixture with hexane as eluent, 4.6 mL min^{-1}. Composition of chromatographic fractions was established by MS (MALDI). The structurally characterized isomers are indicated with roman letters.

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collected at 3.1–5.0 min showed the presence of compounds with $n = 2$–6. HPLC separation of fraction 1 by using the same column and hexane as the eluent (flow rate 4.6 mL min^{-1}) resulted in several fractions containing presumably compositionally pure $C_{70}(C_3F_7)_n$ derivatives (Figure 1; see also Supporting Information).

A chromatogram of fraction 1 demonstrates that the $C_{70}(C_3F_7)_{10}$ isomers are eluted at the beginning (between 2.5 and 3.5 min) and numerous compounds with eight perfluoropropyl groups eluted between 3.5 and 13.0 min. MS (MALDI) analysis proved the presence of at least 16 $C_{70}(C_3F_7)_8$ isomers in this fraction. The last chromatographic peaks of fraction 1 (11.7–14.0 min) contained mostly $C_{70}(C_3F_7)_6$. Slow concentration of four fractions eluted at 4.6, 7.0, 7.9, and 12.9 min containing $C_{70}(C_3F_7)_8$ (denoted as isomers I, II, III, and IV, respectively) gave small crystals suitable for X-ray study with the use of synchrotron radiation.[10]

Molecular structures of all four $C_{70}(n\text{-}C_3F_7)_8$ isomers determined by single-crystal X-ray crystallography (Figure 2) show unprecedented addition patterns among known $C_{70}X_8$ derivatives. Addition patterns of isomers I and II are characterized by the presence of four *n*-fluoropropyl groups on the opposite poles of the molecules (Figure 2a,b). In both molecules of isomers III and IV, two fluoropropyl groups are “displaced” to the equatorial region, whereas the other two and four groups remain in the polar regions (Figure 2c,d). The molecule of isomer I has approximate C_2 symmetry with a twofold axis passing through the midpoint of the equatorial C–C bond and the center of the opposite hexagon (the view direction on a side projection in Figure 2a). Small deviations from twofold symmetry can be seen in the conformation of some perfluoropropyl groups. The molecule of isomer II possesses an idealized C_s symmetry with a noncrystallographic mirror plane on the molecule equator (situated horizontally on the side view in Figure 2b). Very small deviations from idealized symmetry can be found in the positions of the outmost fragments of the perfluoropropyl groups. Isomers III and IV have only trivial C_1 symmetry.

Addition patterns of the four investigated $C_{70}(n\text{-}C_3F_7)_8$ isomers are shown as Schlegel diagrams in Figure 3 together with two others that are typical for known $C_{70}X_8$ derivatives. It can be clearly seen that the difference between C_2- and C_s-$C_{70}(n\text{-}C_3F_7)_8$ isomers consists in the attachment of only two *n*-perfluoropropyl groups on one of the poles (Figure 3a,b). The difference in the addition patterns of both isomers is also reflected in their IUPAC lowest-locant numbering for the cage carbon atoms bearing n-C_3F_7 groups: C_s-7,17,24,36,44,47,53,56- and C_2-7,15,24,34,44,47,53,56-$C_{70}(n\text{-}C_3F_7)_8$.[11] Either set of the four n-C_3F_7 groups can also be described as the *para–meta–para* (*pmp*) arrangement of the three edge-sharing $C_6(n\text{-}C_3F_7)_2$ hexagons, which results in the *pmp*,*pmp* notation for both the C_2- and C_s-$C_{70}(n\text{-}C_3F_7)_8$ isomers.

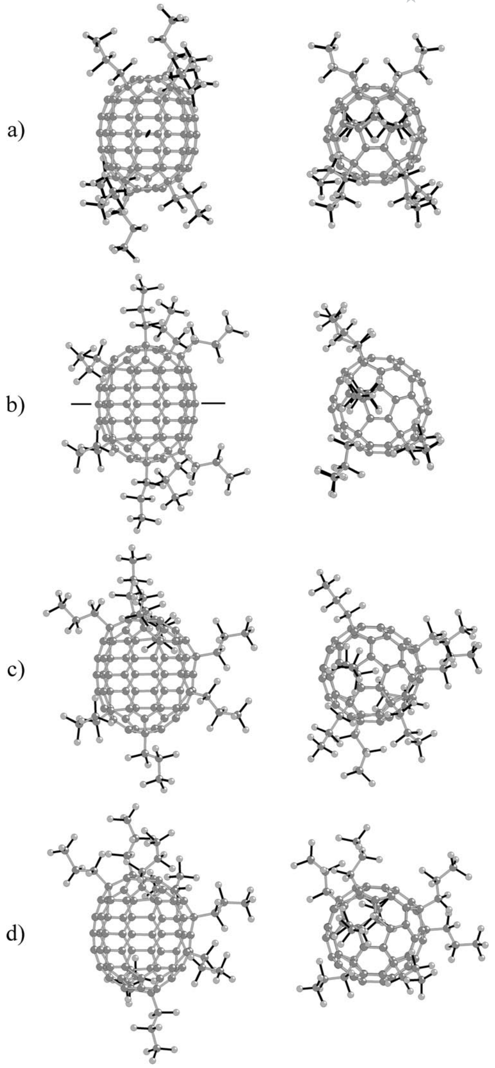

Figure 2. Side and top views of $C_{70}(n\text{-}C_3F_7)_8$-I (a), -II (b), -III (c), and -IV (d) molecules. A twofold axis for C_2 isomer I and a mirror plane for C_s isomer II are indicated.

Isomers III and IV also differ from one another in the arrangement of only two n-C_3F_7 groups on one of the poles (Figure 3c,d), which is also evident by comparison of their IUPAC notations C_1-1,4,23,28,36,44,46,57- and C_1-1,4,23,28,34,44,46,52-$C_{70}(n\text{-}C_3F_7)_8$, respectively. Both arrangements belong to the *pmp*,*p*,*p* type, which represents the presence of three edge-sharing $C_6(n\text{-}C_3F_7)_2$ hexagons and two isolated hexagons.

As a comparison with data in the literature, a typical arrangement of eight atoms or groups on a C_{70} cage is known to be a p^7 ribbon of seven edge-sharing C_6X_2 hexagons situated around the molecular equator (Figure 3f). This arrangement of C_s symmetry was theoretically shown to the preferable one for such atoms (groups) as H, F, Br, and Ph.[12] This addition pattern has been reported for most of the known $C_{70}X_8$ derivatives, such as $C_{70}H_8$,[13] $C_{70}(CH_3)_8$,[14] $C_{70}Ph_8$,[15] $C_{70}(OOtBu)_8$,[16] and $C_{70}(CF_3)_8$.[17] Recently, the less-favorable C_2-$C_{70}(CF_3)_8$ isomer with a Schlegel diagram shown in Figure 3e, which also contains a p^7 ribbon of seven edge-sharing $C_6(CF_3)_2$ hexagons, was structurally characterized.[18] Whereas the relative energies

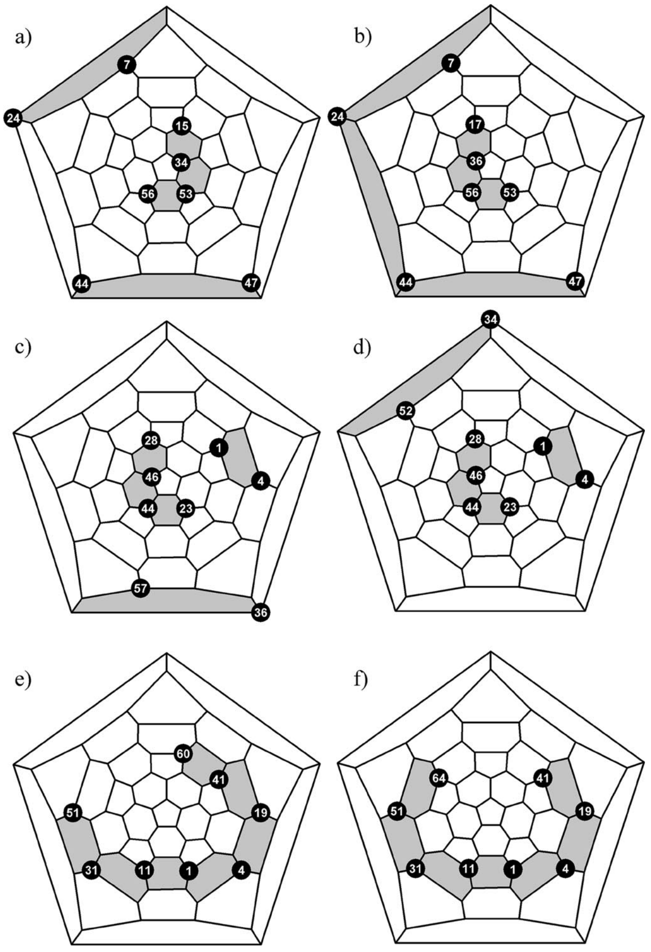

Figure 3. Schlegel diagrams for the addition patterns of the $C_{70}(n\text{-}C_3F_7)_8$-I (a), -II (b), -III (c), and -IV (d) isomers as well as those of the C_2- (e) and C_s-$C_{70}(CF_3)_8$ (f) isomers. Black circles denote attached perfluoroalkyl groups.

of the C_s- and C_2-$C_{70}(CF_3)_8$ isomers are 0.0 and 6.0 kJ mol^{-1}, respectively,[4a] the energies of the octakis(trifluoromethyl)[70]fullerenes with the addition patterns found for *n*-fluoropropyl derivatives in this work (Figure 3a–d) were calculated to be much higher: 26.1, 24.5, 33.2, and 32.6 kJ mol^{-1} for isomers I, II, III, and IV, respectively.[4a,19] Noteworthy, for $C_{70}(CF_3)_4$ isomers, the *pmp* attachment of the four CF_3 groups on the pole has a very low relative energy of only 1.0 kJ mol^{-1}.[4a]

Whereas the crystals of isomers I, II, and IV are built from $C_{70}(n\text{-}C_3F_7)_8$ molecules only, the crystal packing of isomer III contains additional, most probably, water molecules that occupy the wave-like channels in the packing (Figure 4). The most usual guests in host packings of perfluoroalkylated fullerenes are solvent molecules such as aromatic or aliphatic hydrocarbons. Because of the rather hydrophobic properties of perfluoroalkylated fullerenes, incorporation of water molecules should be considered as an unusual phenomenon, but it has been repeatedly reproduced with crystallization experiments of isomer III from hexane or toluene. Obviously, the $C_{70}(n\text{-}C_3F_7)_8$-III molecules cannot be packed without formation of small channels that are, however, too small to incorporate the larger guest molecules, whereas they are accessible for smaller water molecules.

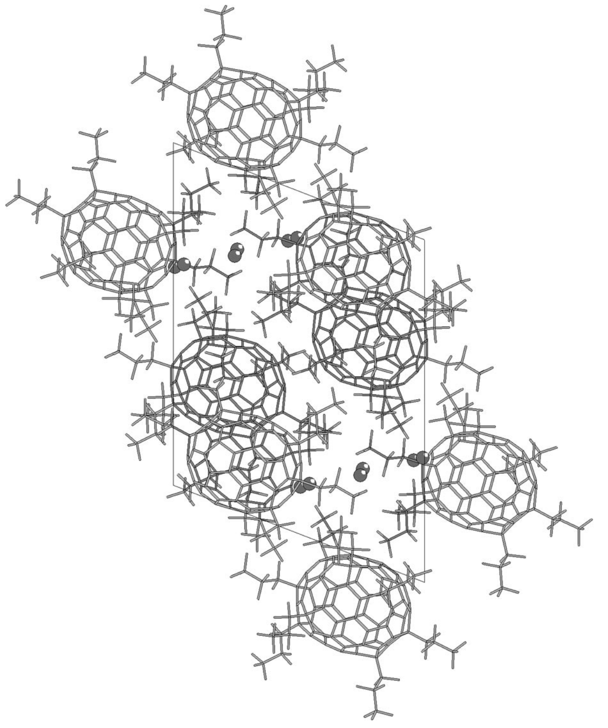

Figure 4. $C_{70}(C_3F_7)_8$-III molecules in the crystal lattice shown along the *b* axis. Black balls are for the oxygen atoms of water molecules that occupy the wave-like channels in the packing.

Conclusions

About half of the overall amount of $C_{70}(n\text{-}C_3F_7)_8$ isomers in the reaction product is represented by the four isolated isomers stucturally characterized in this study (according to HPLC), whereas two $C_{70}(CF_3)_8$ isomers with CF_3 groups attached around the equator clearly dominate in products of high-temperature reaction between C_{70} and CF_3I. Apparently, the isolation of $C_{70}(n\text{-}C_3F_7)_8$ isomers I–IV reflects the higher stability of the addition patterns with either all or most perfluoroalkyl groups attached to the C_{70} cage in the regions of higher curvature (on the poles) when compared with attachment of eight groups in the equatorial region, that is, with lower curvature. This is very probable due to the greater bulkiness of the *n*-perfluoropropyl group relative to that of the trifluoromethyl group. Further work on the synthesis and isolation of other $C_{70}(n\text{-}C_3F_7)_8$ isomers, which are present in the reaction product mixture, accompanied by theoretical calculations for perfluoropropylated [70]fullerenes, should reveal the relative stabilities of a larger number of isomers and their difference from CF_3 and C_2F_5 [70]fullerene derivatives.

Supporting Information (see footnote on the first page of this article): Details of the experimental work of the chromatographic and mass spectrometric characterization of the $C_{70}(n\text{-}C_3F_7)_8$ isomers.

Acknowledgments

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[10] Single-crystal synchrotron X-ray data were collected at 100 K at the BL14.1 at the BESSY storage ring (PSF at the Free University of Berlin, Germany) by using a MAR225 detector, λ = 0.9050 Å. Structure solution with SHELXS97 and anisotropic structure refinements with SHELXL97. Crystal data: C_2-$C_{70}(n\text{-}C_3F_7)_8$ (isomer I): triclinic, $P\bar{1}$, a = 10.1415(1) Å, b = 15.7148(2) Å, c = 23.9542(3) Å, α = 76.1413(5)°, β = 78.9409(5)°, γ = 78.6083(5)°, V = 3591.34(7) Å^3, Z = 2, wR_2 = 0.267 (for 10653 reflections and 1388 parameters) and R_1 = 0.108 [for 8977 reflections with $I > 2\sigma(I)$]. One C_3F_7 group is disordered between two positions with approximately equal occupancies. C_s-$C_{70}(n\text{-}C_3F_7)_8$ (isomer II): triclinic, $P\bar{1}$, a = 9.982(1) Å, b = 16.3630(1) Å, c = 24.200(2) Å, α = 103.28(1)°, β = 97.96(1)°, γ = 107.01(1)°, V = 3587.8(5) Å^3, Z = 2, wR_2 = 0.168 (for 12808 reflections and 1416 parameters) and R_1 = 0.062 [for 9688 reflections with $I > 2\sigma(I)$]. One fluoropropyl group is disordered between two positions with the occupancy ratio of 0.896/0.104(6). C_1-$C_{70}(n\text{-}C_3F_7)_8\cdot 2.1H_2O$ (isomer III): monoclinic, $P2_1/n$, a = 19.7053(1) Å, b = 16.5684(1) Å, c = 25.0881(1) Å, β = 111.0658(3)°, V = 7622.15(7) Å^3, Z = 4, wR_2 = 0.152 (for 15950 reflections and 1378 parameters) and R_1 = 0.061 [for 14586 reflections with $I > 2\sigma(I)$]. Three additional isolated peaks were assigned as oxygen atoms of water molecules. C_1-$C_{70}(n\text{-}C_3F_7)_8$ (isomer IV): triclinic, $P\bar{1}$, a = 16.0938(1) Å, b = 16.2716(1) Å, c = 30.7212(3) Å, α = 77.1809(5)°, β = 75.4106(4)°, γ = 74.9979(4)°, V = 7413.9(1) Å^3, Z = 2, wR_2 = 0.391 (for 26750 reflections and 2820 parameters) and R_1 = 0.175 [for 18088 reflections with $I > 2\sigma(I)$]. Several C_3F_7 groups are disordered between two positions with approximately equal occupancies. CCDC-682247, 682248, 682249, and -682250 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.

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