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Isolation and Structural Characterization of the Most Stable, Highly Symmetric Isomer of $C_{60}(CF_3)_{18}$

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The high thermal and chemical stability of C_{3v}-$C_{60}(CF_3)_{18}$ allowed its isolation from a complex $C_{60}(CF_3)_n$ isomer mixture followed by characterization with ^{19}F NMR spectroscopy and single-crystal X-ray crystallography.

Introduction

Trifluoromethyl derivatives of fullerenes (TFMF) belong to the compounds extensively investigated during the last few years. The first synthesis of $C_{60}(CF_3)_n$ with n up to 14 was reported as early as in 1993.[1] Later on, mass spectrometric studies enabled the detection of compounds with 2–22 CF_3 groups.[2] Preparative methods including a reaction of fullerene with reagents, which easily release CF_3 radicals (CF_3COOAg, CF_3I), resulted in the isolation and structural characterization of more than two dozens of $C_{60}(CF_3)_n$ isomers containing not more than 18 CF_3 groups.[3–8]

In the case of higher isomers with n = 16, 18, the data are scarce. Three isomers of $C_{60}(CF_3)_{16}$ and one isomer of $C_{60}(CF_3)_{18}$ have been isolated by HPLC from a mixture prepared by trifluoromethylation of C_{60} with CF_3I in a glass ampoule at 380–400 °C. Their molecular structures have been determined by means of single-crystal XRD and discussed in terms of mechanistic pathways of their formation and relative energy stability calculated by DFT methods.[4]

For $C_{60}(CF_3)_{18}$, the single HPLC-isolated C_1 isomer occupies the sixth place in the relative stability row and is much higher in energy than the theoretically predicted most stable C_{3v} isomer.[4] Although $C_{60}(CF_3)_{18}$ isomers were also present in other chromatographic fractions, especially in the first hexane fraction, their isolation failed due to the difficulties in separation from other components, mostly from $C_{60}(CF_3)_{16}$.[4] In the present work we report synthesis, partial isolation and X-ray structure determination of C_{3v}-$C_{60}(CF_3)_{18}$, the most stable and symmetric isomer of this composition.

Results and Discussion

The synthetic methodology employed a reaction of C_{60} (99.98%, Term-USA) with CF_3I (98%, Apollo) in a glass ampoule at 440 °C for 2–3 d as described elsewhere.[3] The reaction product was only partially (90%) soluble in hexane. According to MALDI MS analysis {negative ion mode, Bruker AutoFlex II TOF (N_2 laser, 337 nm, 1 ns pulse), 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB, ≥ 99%, Fluka) as a matrix}, the hexane extract contained $C_{60}(CF_3)_n$ compounds with n = 10–18, whereas the insoluble part contained compounds with n = 16 and 18. HPLC separation [Cosmosil Buckyprep (Nakalai Tesque Inc.), 10 mm i.d. × 25 cm, hexane as the eluent, 4.6 $mL\,min^{-1}$ flow rate, 290 nm] of the hexane extract resulted in the isolation of the first (practically unretained) fraction with an elution time of 2.7 min that contained mainly $C_{60}(CF_3)_{18}$. The ^{19}F NMR spectrum (Bruker, Avance-400, 376.5 MHz, $CDCl_3$, 25 °C) of this fraction (Figure S1 in the Supporting Information) showed, however, that it practically did not contain the C_{3v} isomer of $C_{60}(CF_3)_{18}$, which should be characterized by only three signals of equal intensities due to the high symmetry of the C_{3v} molecule.

The part of the reaction product, which was insoluble in hexane (ca. 10%), was extracted with chloroform. The ^{19}F NMR spectrum of the chloroform solution (Figure S1) showed three main signals of equal intensities in the typical CF_3-group spectral region, which could be attributed to the

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C_{3v}-$C_{60}(CF_3)_{18}$ isomer. Other lower-intensity signals were also observed in the NMR spectrum due to the presence of other low-symmetry TFMFs, mainly $C_{60}(CF_3)_{16}$ isomer(s). It follows from MALDI and NMR spectroscopic data that the isomer C_{3v}-$C_{60}(CF_3)_{18}$ is always present in the products of trifluoromethylation in the part, as a mixture with $C_{60}(CF_3)_{16}$, that is hardly soluble in hexane.

Further treatment of the initial $C_{60}(CF_3)_n$ mixture was carried out in two different ways. One procedure included thermal treatment with slow sublimation of the material performed in an ampoule in a temperature gradient of 440 to 25 °C for ca. 20 h. The composition of the orange-colored sublimate (soluble part) was found to be shifted to the lower CF_3 derivatives. Most of the lower derivatives were removed by extraction with hexane. The remaining product (ca. 20%) was recrystallized from hot toluene to partly afford needle-shaped yellow crystals suitable for X-ray investigation with the use of synchrotron radiation. The latter has revealed the structure of the C_{3v}-$C_{60}(CF_3)_{18}$ isomer (Figure 2).[9]

The product of a treatment with toluene was partially dissolved in chloroform, and the solution showed a ^{19}F NMR spectrum of C_{3v}-$C_{60}(CF_3)_{18}$ with the same three main lines of equal intensities and a much better signal-to-noise ratio (Figure 1). In the respective 2D COSY spectrum (Figure S2 in Supporting Information) two cross-peaks were found, which confirmed attribution of all three main signals to the same molecule. This information about the topology of spin-spin-coupled CF_3 groups together with the calculated values of ^{19}F NMR chemical shifts enabled the assignment of the NMR signals to the specific classes of equivalent CF_3 groups in the molecule: δ_F = –59.84 (br. s, 18 F, A), –61.62 (br. s, 18 F, B) and –64.38 (br. m, 18 F, C) ppm labeled as A, B and C in Figures 1 and 2 (bottom left). Noteworthy, no spin-spin splittings could be extracted from the ^{19}F NMR spectrum recorded at room temperature due to significant broadening of the resonances. This indicates higher energy barriers of CF_3 rotations than in the majority of other TFMFs studied earlier where most of the multiplets were clearly resolvable.[10,11] A number of less intense NMR signals found in the spectrum are likely due to other unidentified TFMF molecules.

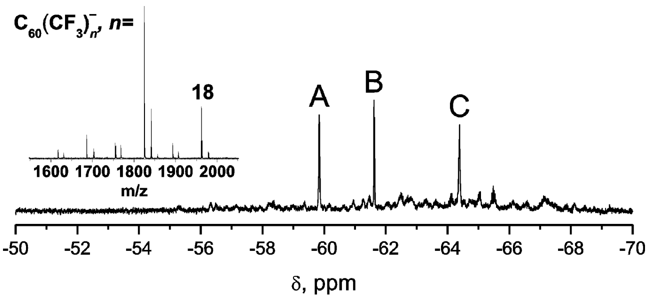

Figure 1. ^{19}F NMR spectrum and MALDI mass spectrum (inset) of the chloroform extract from the product insoluble in hexane after its thermal treatment.

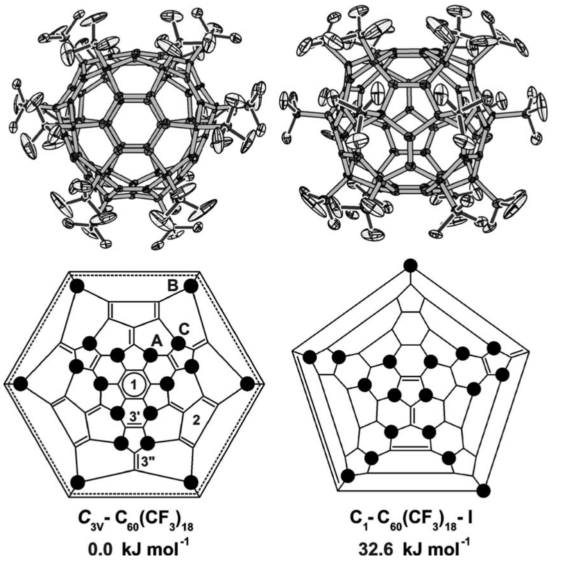

Figure 2. Top and side perspective views and Schlegel diagrams of the C_{3v}-$C_{60}(CF_3)_{18}$ molecule (bottom left) and C_1-$C_{60}(CF_3)_{18}$-I (bottom right).

The second treatment method applied for the initial trifluoromethylated product consisted of its chlorination with $SbCl_5$ at elevated temperature. Initially, this method was aimed at the preparation of mixed chloro(trifluoromethyl)-fullerenes, $C_{60}(CF_3)_nCl_m$, represented so far by the only stucturally characterized example of $C_{60}(CF_3)_{12}Cl_{12}$.[12] In fact, the products of such treatment performed in ampoules at 300–350 °C for 2–3 d consisted of a complex mixture of chloro(trifluoromethyl) derivatives according to MALDI MS analysis. In addition, a second phase was detected in the reaction product consisting of yellow crystals, which were shown by single-crystal XRD analysis to contain the same C_{3v}-$C_{60}(CF_3)_{18}$ isomer. The crystals obtained by this method were of somewhat better quality than those produced by recrystallization from toluene. Diffraction data from the former were used for the final structure refinement.[9]

The molecular structure of C_{3v}-$C_{60}(CF_3)_{18}$ is quite remarkable due to its high symmetry and rather uniform distribution of CF_3 addends on the [60]fullerene cage. The IUPAC lowest-locant abbreviation[13] for C_{3v}-$C_{60}(CF_3)_{18}$ is: 1,3,6,11,13,18,22,24,27,32,35,37,41,43,46,49,52,54-$C_{60}(CF_3)_{18}$. The Schlegel diagram in Figure 2 demonstrates that there are no CF_3 groups attached to *ortho* positions in $C_6(CF_3)_2$ hexagons. The structure is further stabilized by the formation of two benzenoid rings on opposite sides (poles) of the fullerene cage (regions 1 in the Schlegel diagram). Three fulvene fragments (regions 2) and six isolated C–C double bonds (regions 3′ and 3′′) are present in the equatorial area. C–C bonds in aromatic hexagons (1) have typical (averaged) bond lengths of 1.39 Å, whereas the lenghts of isolated double bonds (3′, 3′′) and nearly double bonds in fulvene fragments (2) amount to 1.34 and 1.35 Å, respectively. The cage C–C bonds at sp^3-carbon atoms bearing CF_3 groups are signficantly longer, 1.52 Å. The energetically next favorable $C_{60}(CF_3)_{18}$ isomers contain either CF_3 groups attached to *ortho* positions (9.4–28.3 kJ mol^{-1}) or three CF_3 groups in the same hexagon [isomer $C_{60}(CF_3)_{18}$-I, 32.6 kJ mol^{-1}, Figure 2].[4]

Molecular packing diagram of C_{3v}-$C_{60}(CF_3)_{18}$ in the crystal is shown in Figure 3. It can be described as consisting of approximately closest-packed *ab* layers of molecules with a roughly spheric shape. The layers are further packed in the *c* direction forming a distorted hexagonal *ABAB* sequence. In spite of the rotational disorder of most CF_3 groups, which could results in an increase of an effective molecular volume, the crystal packing of the C_{3v} isomer is slightly more dense than that of $C_{60}(CF_3)_{18}$-I; the molecular volumes at 100 K are 1489 and 1526 Å^3, respectively.

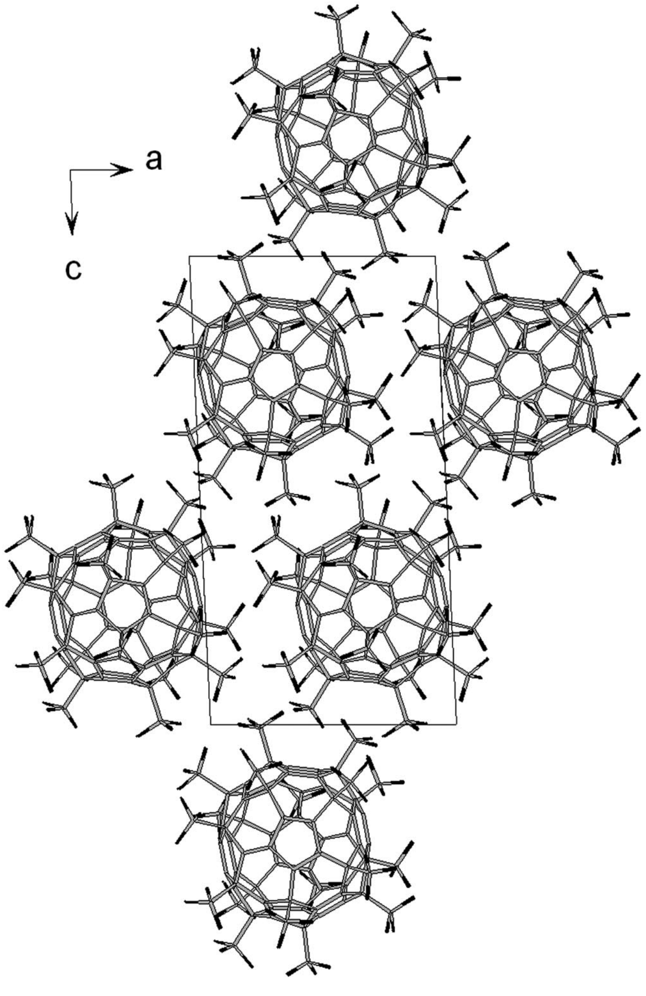

Figure 3. Packing diagram of C_{3v}-$C_{60}(CF_3)_{18}$ in the crystal shown along the *b* axis.

In spite of the highest energetic stability of C_{3v}-$C_{60}(CF_3)_{18}$ among other $C_{60}(CF_3)_{18}$ isomers, its isolation appeared rather challenging. It is noteworthy that the formation of the C_{3v}-$C_{60}(CF_3)_{18}$ isomer in the course of trifluoromethylation is difficult to explain in terms of successive attachements of pairs of CF_3 groups to the fullerene cage. Analysis of possible $C_{60}(CF_3)_{16}$ precursors did not reveal any suitable one among all isomers surveyed in the range of 0–20 kJ mol^{-1}.[4] Schlegel diagrams of the two possible lowest-energy precursors with 22.4 and 30.2 kJ mol^{-1} are given in the Supporting Information Therefore, the formation of C_{3v}-$C_{60}(CF_3)_{18}$ may include an addend rearrangement on the fullerene cage during the synthesis or additional thermal treatment. There are some examples of this phenomenon in the fullerene chemistry reported in the literature as "fluorine dance",[14] 1,3-fluorine shift,[15] or "chlorine dance".[16] Rearrangments of CF_3 groups on the [70]fullerene cage have been experimentally proved for trifluoromethylation of two $C_{70}(CF_3)_{12}$ isomers.[17]

Conclusions

The molecular structure of the C_{3v} isomer with 18 CF_3 groups nearly uniformly covering the [60]fullerene cage accounts for its inertness against thermal and chemical impacts due to an effective shielding of the cage by CF_3 groups. Thus, its reactivity may be significantly lower than that of all other isomers. In the treatment of the complex mixture of the $C_{60}(CF_3)_n$ isomers, two ways of isomer destruction have been applied, thermal impact and chlorination. In both cases, thermal or chemical transformation of most isomers took place, leaving only C_{3v}-$C_{60}(CF_3)_{18}$ molecules unchanged. This circumstance allowed the obtainment of single crystals and X-ray structure determination of the energetically most stable $C_{60}(CF_3)_{18}$ isomer whose addition pattern was predicted by us earlier.

Supporting Information (see footnote on the first page of this article): 1D and 2D COSY ^{19}F NMR spectra, Schlegel diagrams of possible precursors.

Acknowledgments

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[9] Synchrotron X-ray data for the crystal obtained by the chlorination method were collected at 100 K at the BL14.2 at the BESSY storage ring (PSF at the Free University of Berlin, Germany) by using a MAR225 detector, $\lambda = 0.9050$ Å. $C_{60}(CF_3)_{18}$: triclinic, $P\bar{1}$, $a = 11.6968(1)$, $b = 12.7295(1)$, $c = 21.1230(2)$ Å, $\alpha = 85.8595(6)$, $\beta = 86.2822(6)$, $\gamma = 71.8412(4)°$, $V = 2977.68(4)$ Å^3, $D_{calcd.} = 2.189$ g cm^{-1}, $Z = 2$. Anisotropic refinement with 10354 reflections and 1502 parameters yielded a conventional $R_1(F) = 0.096$ for 9344 reflections with $I > 2\sigma(I)$ and $wR_2(F^2) = 0.256$ for all reflections. Most CF_3 groups are rotationally disordered around C–CF_3 axes. Typical esd values of C–C cage distances are 0.006–0.007 Å. CCDC-715269 contains 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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