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Preparation, Crystallographic Characterization, and Theoretical Study of $C_{70}(CF_3)_{14}$

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Dedicated to the memory of Roger Tayler

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Five $C_{70}(CF_3)_{14}$ isomers have been isolated chromatographically from the mixture produced in the ampoule reaction between C_{70} and CF_3I at 390 °C. Molecular structures of four isomers have been determined in a single-crystal X-ray diffraction study. A quantum chemical survey of the theoretically possible isomers demonstrated that the structures obtained are energetically favorable but that there is probably no full thermodynamic control in the trifluoromethylation process.

Introduction

After fullerene fluorides, trifluoromethylated fullerene derivatives have attracted considerable attention since the early 1990s as prospective building blocks for novel fullerene-based materials with useful properties. Commonly used methods for preparation of trifluoromethylated fullerenes employ agents such as CF_3I[1] or metal trifluoroacetates,[2] which easily release CF_3 radicals upon heating. Usually, these methods yield complex mixtures of $C_{60/70}$ derivatives containing up to 22 CF_3 groups per fullerene cage. Subsequent separation by fractional sublimation followed by high performance liquid chromatography (HPLC)[3] can provide individual compounds for further structural investigations by vibrational and NMR spectroscopy or X-ray crystallography. The library of individual compounds thus obtained includes $C_{60}(CF_3)_n$ with n = 2–10[4] and $C_{70}(CF_3)_m$ with m = 2–12.[5,6] Because of the small available amounts of these substances and other technical difficulties, however, only in a very few cases has it appeared feasible to go beyond a typical ^{19}F NMR characterization and to perform an X-ray crystallographic investigation: direct structural determination has so far been carried out only for $C_{60}(CF_3)_{10}$,[4] $C_{70}(CF_3)_8$,[7] $C_{70}(CF_3)_{10}$,[8] and two isomers of $C_{70}(CF_3)_{12}$.[6] In addition, the first selective synthesis of a trifluoromethylated $C_{60}(CF_3)_{12}$ molecule and determination of its molecular and crystal structure have recently been reported.[9]

Here we report the isolation, X-ray crystallographic characterization, and theoretical study of four $C_{70}(CF_3)_{14}$ isomers that continue the series of well characterized trifluoromethylated C_{70} derivatives with sequentially growing number of CF_3 groups.

Results and Discussion

A mixture of trifluoromethylated $C_{70}(CF_3)_m$ isomers with m ranging from 12 to 20 was obtained by treatment of C_{70} with gaseous CF_3I in a sealed ampoule at 390 °C. HPLC separation of the mixture and matrix-assisted laser desorption/ionization (MALDI) negative ion mass spectrometry of the fractions revealed the presence of $C_{70}(CF_3)_{14}$ isomers in five fractions eluted between 3.9 and 4.8 min (Figure 1). In spite of the rather narrow range of retention times, all five $C_{70}(CF_3)_{14}$-containing fractions were successfully isolated. Further HPLC and MALDI investigations additionally confirmed that all five isolated fractions contained different individual isomers (as demonstrated for one of the isomers in Figure 1) and that they were the only fractions containing $C_{70}(CF_3)_{14}$ [except for a small admixture of $C_{70}(CF_3)_{14}$ to the fraction with $C_{70}(CF_3)_{16}$-**II**]. It should be noted that $C_{70}(CF_3)_{14}$ has recently been observed as the highest product of C_{70} trifluoromethylation in a flow of CF_3I at 470 °C [the lowest was

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$C_{70}(CF_3)_8$];[4] however, only a single isomer of $C_{70}(CF_3)_{10}$[8] and two isomers of $C_{70}(CF_3)_{12}$[6b] have so far been reported to have been isolated from the mixture obtained by this method.

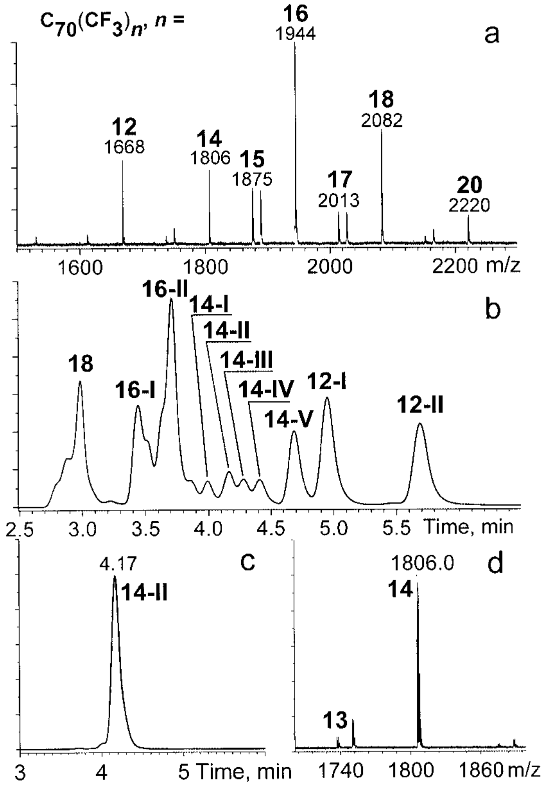

Figure 1. Negative ion MALDI mass spectrum of the mixture of $C_{70}(CF_3)_m$ isomers (m = 12–20) (a), HPLC chromatogram of the mixture (b), HPLC chromatogram of the purified fraction containing isomer $C_{70}(CF_3)_{14}$-**II** (c), and the corresponding MALDI mass spectrum (d).

The isolated solutions of isomers **I**–**V** of $C_{70}(CF_3)_{14}$ were concentrated by slow evaporation of hexane to give crystalline material. Because of the differences in size and quality of the crystals thus formed, only isomers **II**–**V** were subjected to X-ray diffraction study, as the sizes of the crystals of isomer **I** were found to be insufficient. Still rather small crystals of isomers **II** and **III** were studied with use of synchrotron radiation, whilst somewhat larger crystals of isomers **IV** and **V** were investigated with use of conventional laboratory X-ray equipment (see Supporting Information). The crystal structures of isomers **II**–**V** were determined at different levels of accuracy: the most precise data were obtained for isomer **IV** (esds of C–F and C–C bond lengths $\leq$ 0.003 Å) and the least precise for isomer **V** (esds of bond lengths 0.014–0.019 Å), due to partial loss of solvate molecules (hexane).

The molecular structures of isomers **II**–**V** appear to be rather similar (Figure 2), all including a substructure of $C_{70}(CF_3)_{10}$,[8] and we therefore use the same numbering scheme for all four isomers (alternative numbering according to IUPAC recommendations[10] is given in the Supporting Information). Moreover, the structures of isomers **II**–**IV** each include one of the addition patterns of the two isolated isomers of $C_{70}(CF_3)_{12}$.[6] Isomers **II** and **III** can be regarded as derived from $C_{70}(CF_3)_{12}$-**I** [which contains a substructure of $C_{70}(CF_3)_{10}$ plus CF_3 groups attached to positions 32 and 54] by further addition to positions 23 and 44 (isomer **II**, Figure 2) or 37 and 56 (isomer **III**). Analogously, isomer **IV** can be derived from $C_{70}(CF_3)_{12}$-**II** [$C_{70}(CF_3)_{10}$ plus CF_3 groups at positions 14 and 35] by attachment to positions 23 and 44. Isomer **V**, the only one to exhibit a nontrivial C_2 symmetry (see view in Figure 2), comprises a substructure of $C_{70}(CF_3)_{10}$ plus four CF_3 groups linked to positions 13, 15, 29, and 34. Notably, isomers **II** and **IV** exhibit a certain "complementarity": they have the same extra addition sites occupied with respect to the parent $C_{70}(CF_3)_{12}$ substructures, thus differing only in the attachment of two CF_3 groups on the left (positions 32 and 54) or on the right side (positions 14 and 35) of the Schlegel diagrams. One might thus expect a similar "complementarity" of isomers **III** and **I** (i.e., the unknown structure of the latter may contain two CF_3 groups attached in positions 14 and 35 instead of 32 and 54 in the former; Figure 2).

In order to explain the formation of five specific $C_{70}(CF_3)_{14}$ isomers out of the great variety of possible structures, we undertook a theoretical study of all possible isomers incorporating the addition patterns of the two most stable $C_{70}(CF_3)_8$ isomers and containing no adjacent carbon sites with bonded CF_3 groups (see details in the Experimental Section). All five isolated isomers (**II**–**V** and the suggested isomer **I**) appeared to number among the most stable structures, within a range of only 11 kJ·mol^{-1}; however, six more structures [all incorporating the $C_{70}(CF_3)_{10}$ substructure] were found to fall in the same range. Such selective formation of a restricted group of isomers within a set of comparably stable structures suggests that trifluoromethylation at the corresponding stage is at least partially kinetically controlled. Notably, possible precursors of isomers **I**–**IV** include the two isolated isomers of $C_{70}(CF_3)_{12}$ shown by a similar quantum chemical survey to be the most energetically stable,[6] whereas possible $C_{70}(CF_3)_{12}$ precursors of isomer **V** were, on the contrary, calculated to be even less stable than potential precursors of the missing energetically favorable $C_{70}(CF_3)_{14}$ isomers mentioned above (see supplement to[6a]). Two possible schemes of trifluoromethylation can therefore be suggested. In the first scheme, which includes only consecutive CF_3 addition stages, some of the compounds formed during the synthesis should not accumulate in the sample due to higher reactivity. Such isomers may include missing precursors of isomer **V** and, possibly, both missing energetically stable $C_{70}(CF_3)_{14}$ isomers and their potential precursors. The second scheme additionally takes possible migration of CF_3 groups on the carbon cage into consideration. It has recently been demonstrated that there is no direct addition pathway from the single isolated isomer of $C_{70}(CF_3)_2$ and one of the isolated isomers of $C_{70}(CF_3)_4$ to the two characterized isomers of $C_{70}(CF_3)_8$;[5] this may point to possible migration of CF_3 groups under the high-temperature synthetic conditions, similarly to the directly established migrations of fluorine

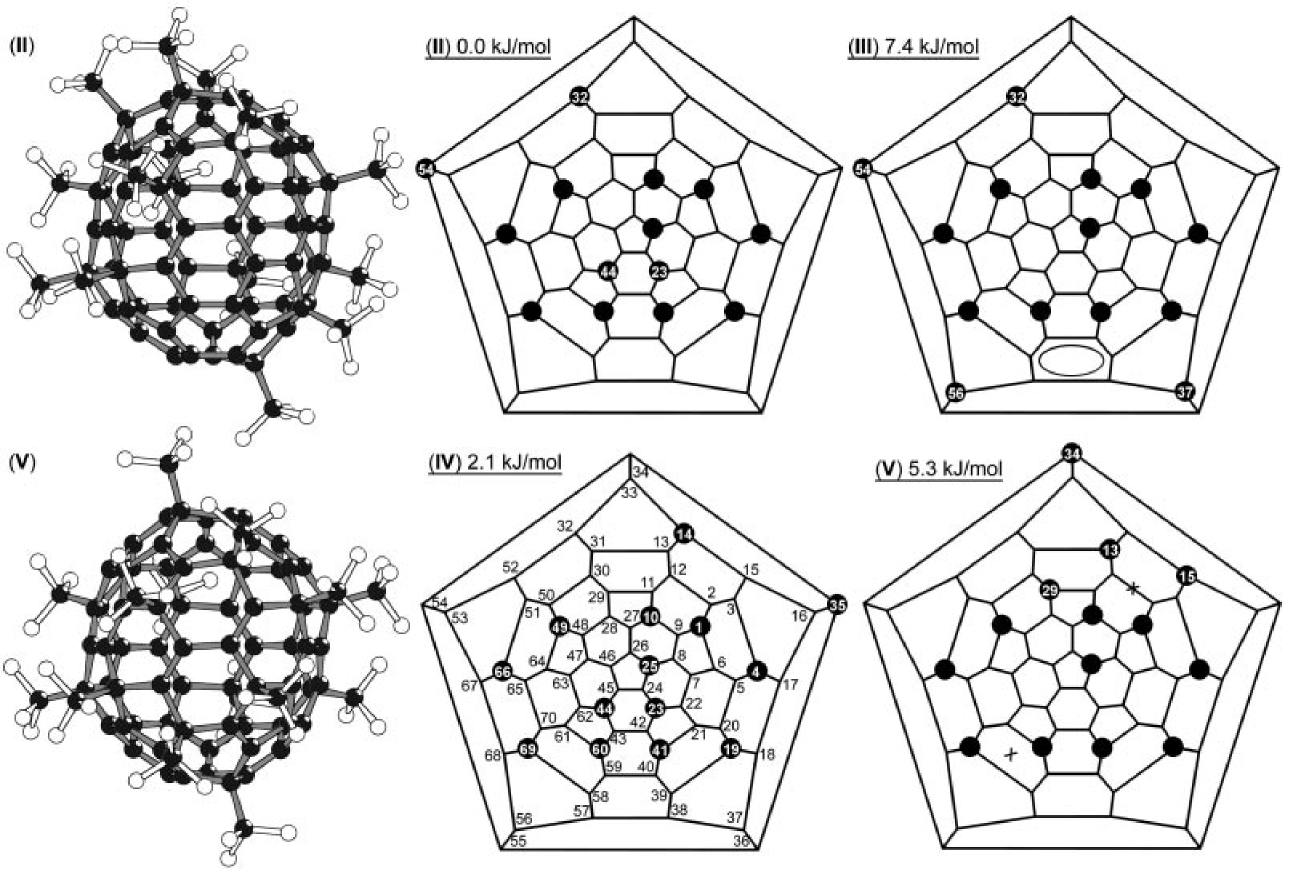

Figure 2. Schlegel diagrams and relative energies of isomers **II**–**V** of $C_{70}(CF_3)_{14}$ and molecular structures of isomers **II** and **V**. The diagram of isomer **IV** demonstrates the numbering scheme used in this work; for the rest of isomers only the addition sites not occupied in the parent $C_{70}(CF_3)_{10}$ are numbered. Both ellipsoid representations of isomers **II** and **V** show these molecules in the same orientation. The molecule **V** is viewed along a twofold axis, also denoted with crosses on its Schlegel diagram.

("fluorine dance"[11]) and chlorine.[12] Then, isomer **V** may be a product of rearrangement of CF_3 shells of other isomers. Again, to explain the absence of the remaining energetically stable isomers of $C_{70}(CF_3)_{14}$, one has to introduce kinetic arguments, such as higher reactivity of these isomers. Unfortunately, the case of $C_{70}(CF_3)_{12}$ adds nothing to verification of the migration hypothesis, since not only the isomers isolated but all the comparably stable structures appear to be based on a $C_{70}(CF_3)_{10}$ addition pattern.[6] The mechanism of trifluoromethylation and its rearrangement-related aspects thus require additional investigation and we expect further study of higher CF_3 derivatives containing 16 and more CF_3 groups to provide relevant evidence.

It seems interesting to compare some characteristic bond lengths in isomers **II**–**IV** (isomer **V** is excluded from comparison due to the low accuracy of the experimental data). The majority of the unsaturated bonds in all three isomers lie in the 1.36–1.42 Å range, thus indicating their conjugated natures. Indeed, the greater part of the π-system of $C_{70}(CF_3)_{14}$ forms conjugated aromatic fragments, though coordination of atoms involved is quite far from planar. However, there are several exceptions. Each of the three isomers considered contains a nearly isolated double bond C(8)–C(9) ranging from 1.331 to 1.351 Å and inherited from $C_{70}(CF_3)_{12}$ (1.344 Å)[6] and even $C_{70}(CF_3)_{10}$ (1.347 Å).[8] Another nearly isolated double bond, C(24)–C(45), is observed only in isomers **II** and **IV** (1.337–1.338 Å), whereas in isomer **III** this bond appears to be much longer (1.424 Å); finally, isomers **II** and **IV** also each contain a completely isolated double bond, C(42)–C(43) [1.328(5) and 1.332(3) Å, respectively], which is again much longer in isomer **III** [1.382(9) Å] and also in $C_{70}(CF_3)_{10}$ and $C_{70}(CF_3)_{12}$ (1.363–1.367 Å).

One more structural fragment of special interest is the completely isolated six-membered ring C(38)–C(39)–C(40)–C(59)–C(58)–C(57) in isomer **III**. Four C–C bonds in this ring are characterized by typical benzenoid lengths of 1.395–1.401 Å and another is even a bit shorter (1.376 Å), but the remaining C(40)–C(59) bond appears to be significantly elongated (1.440 Å). Similar elongation of equatorial bonds has also been observed in all $C_{70}(CF_3)_{10}$-based molecules characterized so far,[4,6] and thus seems to be a common effect due to C_{70} cage inflation upon addition of a large number of CF_3 groups. On the other hand, the same six-membered ring in all other $C_{70}(CF_3)_{10}$-based molecules, in which this ring has neighboring sp^2 atoms, shows a distinct alternation in the bond lengths. Notably, all the experimentally obtained structural data are in good agreement with the DFT-calculated molecular geometries: the discrepancies between the observed and computed bond lengths, for instance, are typically within 0.010 Å and rarely exceed 0.015 Å.

In conclusion, five $C_{70}(CF_3)_{14}$ isomers were chromatographically isolated from the mixture produced in the ampoule reaction between C_{70} and CF_3I at 390 °C, and the molecular structures of four isomers have been elucidated by single-crystal X-ray crystallography. Theoretical AM1 and DFT study showed the five isolated isomers to be thermodynamically favorable and in most cases to have corresponding $C_{70}(CF_3)_{12}$ precursors. The absence of other possible energetically favorable isomers can be accounted for by their high reactivity towards further trifluoromethylation.

Experimental Section

Synthesis: C_{70} (36 mg, Term-USA) was placed in a glass ampoule and CF_3I (ca. 0.5 mL , 98 %, Apollo) was then condensed into it with liquid nitrogen cooling . The sealed ampoule was placed in a gradient furnace so that a section containing fullerene was heated to 390(±5) °C, whereas liquid CF_3I remained at room temperature and thus provided a vapor pressure of ca. 5 bar. During the reaction time of 24 h more than 95 % of the fullerene was consumed and two layers of products formed: an orange layer of trifluoromethylated compounds in the ca. 300 °C zone and a layer of crystalline I_2 in the ca. 100 °C zone. According to the negative ion MALDI analysis, the collected orange sublimate (ca. 60 mg) consisted of $C_{70}(CF_3)_m$ compounds with $m = 12–20$ (see Figure 1, a).

Mass Spectrometric Analysis: Negative ion MALDI mass spectrometry was applied to analyze the crude product and isolated HPLC fractions. The spectra were acquired through the use of a Bruker AutoFlex reflectron time-of-flight mass spectrometer fitted with an N_2 laser (337 nm, 1 ns pulse). *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, ≥99 %, Fluka) was chosen as a matrix, the matrix-to-analyte ratio being 1000–4000.

Isolation: The following purification protocol was applied. The synthesized mixture (25 mg) was dissolved in *n*-hexane (3 mL) and subjected to HPLC separation [10 mm I.D. × 250 mm long Cosmosil Buckyprep column (Nakalai Tesque Inc.), hexane eluent, 4.6 mL·min^{-1} flow rate, monitored at 290 nm]. Five fractions containing $C_{70}(CF_3)_{14}$ isomers **I**–**V** with the peak area ratio of **I/II/III/IV/V** = 2:3:1:3:16 characterized by the following retention time values (min) were collected: isomer **I** (4.01), **II** (4.17), **III** (4.29), **IV** (4.42), and **V** (4.69). The isolated fraction of **I** contained an insignificant admixture of $C_{70}(CF_3)_{16}$ according to the MALDI mass spectrum. The obtained fractions (ca. 30–50 mL each) were evaporated to 2–3 mL and were then transferred into vessels for further slow concentration to give crystalline material. For details of the single-crystal *X-ray crystallographic study* of the $C_{70}(CF_3)_{14}$ isomers **II**–**V** see the Supporting Information (S2).

CCDC-294635 to -294638 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/datarequest/cif.

Selection of Structures for Theoretical Study: The set of $C_{70}(CF_3)_{14}$ isomers for quantum chemical calculations was generated to satisfy the following conditions:

(*i*) CF_3 addition to adjacent sites was not permitted. As had been demonstrated in an earlier study of trifluoromethylated C_{60} derivatives,[13] isomers with CF_3 adjacency are thermodynamically less stable than those with 1,4-attached (*para*) CF_3 groups.

(*ii*) Structures including CF_3 groups sharing no hexagon with another group in the *para* position were excluded as well. Thus, any isomer generated could be regarded as a set of neighboring or nonneighboring *para*-$C_6(CF_3)_2$ hexagons somehow distributed on the fullerene cage to avoid *ortho* contacts between addends.

(*iii*) Among the structures satisfying (*i*) and (*ii*), only the isomers incorporating the addition patterns of either C_s- or C_2-$C_{70}(CF_3)_8$[5] were considered further. This restriction was due to a significant gap in stability, of 17 kJ·mol^{-1}, between the above two isomers and the rest of the $C_{70}(CF_3)_8$ structures.[5] The resulting list of isomers after the above three steps of sorting contained 1140 symmetry inequivalent structures.

Quantum Chemical Calculations: Preliminary geometry optimization of all 1140 generated isomers was carried out at the AM1 level of theory with use of PC-GAMESS software.[14] The most stable isomers within the range of 30 kJ·mol^{-1} were then reoptimized at the DFT level of theory with use of PRIRODA software[15] employing an original TZ2P basis set and PBE exchange-correlation functional.[16]

Supporting Information (see also the footnote on the first page of this article): Details of the X-ray crystallographic study of isomers **II**–**V**, full numbering schemes, including those recommended by the IUPAC for the same isomers, and a list of possible isomers within the 35 kJ·mol^{-1} range resulting from theoretical calculations at the AM1 and DFT levels.

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