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Crystal and molecular structures of C_2-$C_{70}(CF_3)_8$·1.5PhMe

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An X-ray diffraction study of $C_{70}(CF_3)_8$·1.5PhMe resulted in the first structure determination of C_2-$C_{70}(CF_3)_8$, the isomer with a *para*[7] string of eight CF_3 groups around the equator of the carbon cage.

Trifluoromethylated fullerenes are prospective chemically and thermally stable compounds for use in the material chemistry. In the case of C_{60}, many $C_{60}(CF_3)_n$ isomers with n ranging from 2 to 18 have been already isolated and structurally characterised by X-ray crystallography.[1–4] The range of X-ray characterised $C_{70}(CF_3)_m$ derivatives is somewhat narrower with m between 6 and 18.[5–10] However, addition patterns for lower $C_{70}(CF_3)_m$ compounds with m = 2–12 have been deduced from the ^{19}F NMR data.[11] The most abundant C_s-isomer of $C_{70}(CF_3)_8$ is among those characterised by both NMR[11] and XRD.[6] Here, we report single crystal X-ray structure for the second isomer of $C_{70}(CF_3)_8$, which has C_2 symmetry.

The common synthetic techniques for trifluoromethylation of fullerenes are based on reactions with compounds that release CF_3 radicals upon heating like silver trifluoroacetate[1,5,11(a)] or CF_3I.[2–4,8–10,12] These techniques usually result in complex mixtures of CF_3 derivatives that require further separation by fractional sublimation and HPLC. We used a new synthetic approach, which involved reaction of C_{70} with a mixture of higher $C_{70}(CF_3)_m$ derivatives (m = 12–18), the latter having been produced *via* an ampoule reaction of C_{70} with CF_3I as described elsewhere.[8–10] 15 mg of C_{70} (98.5%, TermUSA) and 50 mg of the $C_{70}(CF_3)_m$ mixture were placed in a subsequently evacuated and sealed glass ampoule. The ampoule was heated at 440–450 °C for 60 h. The MALDI MS analysis of the deep-brown cake performed in a negative ion mode using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, ≥99%, Fluka) as a matrix revealed the formation of a mixture of lower $C_{70}(CF_3)_m$ derivatives with m = 4–10. Note that the product did not contain unreacted C_{70}, *i.e.*, formation of the above products was due to a transfer of addends between the constituents of the reaction mixture rather than decomposition of the original higher trifluoromethylated reactants. A chromatogram of the mixture (Figure 1) demonstrates that the isomeric distribution, at least at the beginning, is similar to that reported for the reaction of C_{70} with $Ag(CF_3COO)$.[11(a)]

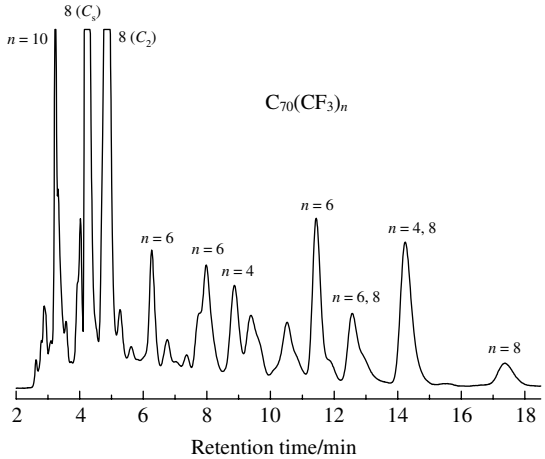

Figure 1 HPLC trace of the reaction product with Cosmosil Buckyprep column (10 mm i.d.×25 cm) and toluene as an eluent (4.6 ml min^{-1}), monitored at 290 nm. Composition of chromatographic fractions was established by MALDI MS.

The HPLC separation using a Cosmosil Buckyprep column (10 mm ID × 25 cm) and toluene as an eluent afforded several compositionally pure fractions according to MALDI MS analyses. Crystallization of fraction 1 (retention time, 3.24 min) by the evaporation of toluene yielded yellow crystals of the $C_{70}(CF_3)_{10}$·1.5PhMe solvate of the well known 1,4,10,19,25,41, 49,60,66,69-$C_{70}(CF_3)_{10}$ isomer, as revealed by the single crystal X-ray study.† The above solvate differs from the previously characterised 1:1 compound.[7] The position of chromatographic peak 2 (retention time, 4.23 min) was indicative of the known C_s isomer of $C_{70}(CF_3)_8$.[11] This assignment has been additionally confirmed by determination of unit cell parameters for the yellow crystals obtained from fraction 2: the latter appeared to coincide with those known for $C_{70}(CF_3)_8$·PhMe.[6] Finally, slow evaporation of toluene from fraction 3 (retention time, 4.85 min) afforded deep green crystals of $C_{70}(CF_3)_8$·1.5PhMe, which were found to contain the second abundant isomer of $C_{70}(CF_3)_8$ with C_2 molecular symmetry.† IR spectra of the C_s- and C_2-$C_{70}(CF_3)_8$

† *Crystal data.* Data collection was carried out on an image plate diffractometer (Stoe) with MoKα radiation (λ = 0.71073 Å). $C_{70}(CF_3)_{10}$·1.5PhMe at 100 K, M = 1669.00, monoclinic, space group $P2_1/n$, a = 14.3810(4), b = 22.0101(4) and c = 18.3313(5) Å, β = 95.791(2)°, V = 5772.7(2) Å^3, μ = 0.180 mm^{-1}, Z = 4. Reflections collected 77199, independent 17537, R_{int} = 0.082. Anisotropic refinement with 1199 parameters yielded a conventional $R_1(F)$ = 0.059 for 14240 reflections with $I > 2\sigma(I)$ and $wR_2(F^2)$ = 0.141 for all reflections. One CF_3 group and the both toluene molecules are disordered.

C_2-$C_{70}(CF_3)_8$·1.5PhMe at 150 K: M = 1530.98, orthorhombic, space group $C222$, a = 20.604(2), b = 21.369(2) and c = 25.330(3) Å, V = = 11152(2) Å^3, μ = 0.162 mm^{-1}, Z = 8. Reflections collected 44943, independent 14069, R_{int} = 0.049. Anisotropic refinement with 1089 parameters yielded a conventional $R_1(F)$ = 0.061 for 10433 reflections with $I > 2\sigma(I)$ and $wR_2(F^2)$ = 0.169 for all reflections. Several CF_3 groups and all toluene molecules are disordered.

CCDC 680557 and 680558 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, 2008.

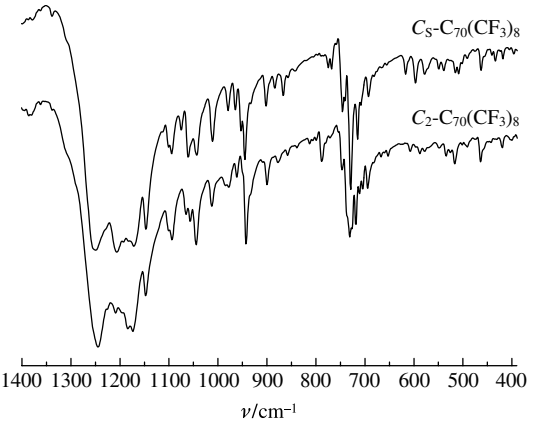

Figure 2 IR spectra of C_s and C_2 isomers of $C_{70}(CF_3)_8$ recorded in KBr pellets.

are very similar (Figure 2). Characteristic vibrations of CF_3 groups occur at 1150–1250 cm^{-1}. Main absorption bands for C_s-$C_{70}(CF_3)_8$ are found at 1095, 1061, 1043, 1011, 947, 901, 866, 714, 692, 595 and 464 cm^{-1}; main bands for C_2-$C_{70}(CF_3)_8$ are observed at 1093, 1044, 1012, 943, 900, 788, 731, 719, 693, 515 and 464 cm^{-1}. The observed small differences between the IR spectra of the C_s and C_2 isomers were found to be satisfactorily reproducible at the DFT level of theory by using the PRIRODA package[13] and the PBE functional.[14]

Previously, the addition pattern for C_2-$C_{70}(CF_3)_8$ was suggested on the basis of ^{19}F NMR spectra.[11] Our X-ray crystallographic study has confirmed this suggestion. Crystal structure contains two independent $C_{70}(CF_3)_8$ molecules on the crystallographic two-fold axis and four disordered toluene molecules that occupy the sites of C_2 or D_2 symmetry. Thus, the idealised symmetry of the C_2-$C_{70}(CF_3)_8$ molecule coincides with its crystallographic symmetry in the $C_{70}(CF_3)_8$·1.5PhMe solvate (Figure 3). Addition patterns of both C_2- and C_s-$C_{70}(CF_3)_8$ shown as Schlegel diagrams in Figure 3 are characterised by the presence of a string of seven adjacent 1,4-$C_6(CF_3)_2$ hexagons around the equatorial zone of the carbon cage (a *para*[7] string). These two isomers differ by the position of only one CF_3 group, as additionally reflected by very similar IUPAC notations for these isomers, 1,4,11,19,31,41,51,60- and 1,4,11,19,31,41,51,64-$C_{70}(CF_3)_8$, respectively. The C_2 isomer is only 6 kJ mol^{-1} higher in energy than the C_s one, the most stable isomer of $C_{70}(CF_3)_8$.[11] Nevertheless, only the C_s isomers have been reported so far for the other known $C_{70}X_8$ derivatives like $C_{70}H_8$,[15] $C_{70}Me_8$,[16] $C_{70}Ph_8$[17] and $C_{70}(OOBu^t)_8$.[18]

In the carbon cage of C_2-$C_{70}(CF_3)_8$, there are 12 considerably elongated C(sp^3)–C(sp^2) bonds with an average length of 1.537 Å, compared to 1.435 Å in a pristine C_{70} molecule.[19] The sp^3 carbon atoms are pushed out from the center of the molecule to 3.986 Å on average (3.989 Å in the C_s isomer;[6] 3.674 Å for the corresponding atoms in the C_{70} molecule[19]) thus resulting in a pronounced boat conformation of the $C_6(CF_3)_2$ hexagons (see the top view in Figure 3). Several CF_3 groups are disordered between two positions each and, in addition, some F atoms are characterised by elongation of thermal ellipsoids (tangential to C–F bonds), which may serve as an indication of static or dynamic disorder. Geometry optimization of this molecule at the DFT method reveals some deviations from idealised C_2 symmetry due to mutual repulsion of neighbouring CF_3 groups.[11(a)] Therefore, the C_2 symmetry of molecules in a crystal is only an apparent symmetry as a geometric average of molecules with less symmetric conformations of CF_3 groups. This conformational disorder is indirectly evidenced by a strong disorder of all toluene molecules in the crystal structure (Figure 4). The unit cell contains 8 molecules of C_2-$C_{70}(CF_3)_8$ and 12 toluene

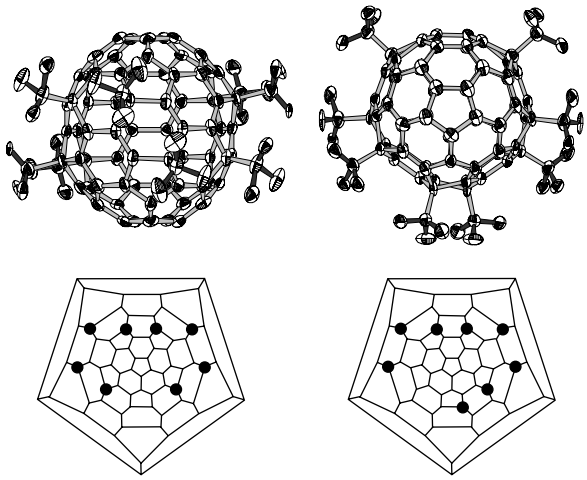

Figure 3 Side and top views of the C_2-$C_{70}(CF_3)_8$ molecule. Thermal ellipsoids are given with 45% probability. Schlegel diagrams for C_s- and C_2-$C_{70}(CF_3)_8$ are given below with black circles denoting attached CF_3 groups.

molecules, each of the latter having two orientations of equal probability to conform the site symmetries. In general, the crystal structure may be viewed as planar layers of $C_{70}(CF_3)_8$ molecules parallel to the *ac* plane with toluene molecules occupying the interlayer space.

The described synthetic technique for the lower CF_3 derivatives, though being two-step procedure, has some advantages over the conventional metal trifluoroacetate route. Apart from higher yields, it also leads to higher purity of products that form free from such admixtures as metal particles or/and oxygenated compounds typical of the silver trifluoroacetate synthesis.[1,11(a)]

A mechanism of interactions between fullerene and its higher CF_3 derivatives is not completely clear. It seems, however, quite obvious that sufficiently rapid intermolecular transfer of addends takes place. Preliminary release of the CF_3 groups into the gas phase with their subsequent re-attachment does not seem to be the case, as the concentration of active CF_3 radicals must be much lower than in the trifluoroacetate or CF_3I synthetic protocols. One can also suppose that the CF_3 exchange reaction can be facilitated by the formation of a liquid phase at elevated synthesis temperatures. Although no direct observations of such kind have been made to date, the cake-like content of the ampoules after cooling strongly resembled solidified melt.

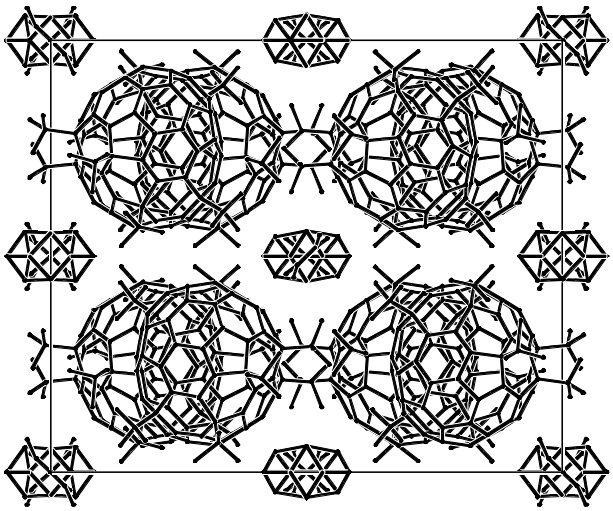

Figure 4 C_2-$C_{70}(CF_3)_8$ and toluene molecules in the crystal lattice of $C_{70}(CF_3)_8$·1.5PhMe projected along the *a* axis. Only one position is shown for each disordered CF_3 group, whereas the both positions are presented for each disordered toluene molecule.

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