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

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Crystal structure determination for $C_{70}(CF_3)_8$·PhMe revealed that the eight CF_3 groups in the $C_{70}(CF_3)_8$ molecule are situated in a *para*(7) string around the equator of the C_{70} cage; the molecule of $C_{70}(CF_3)_8$ is isostructural with the known methylated and phenylated derivatives of C_{70}, $C_{70}Me_8$ and $C_{70}Ph_8$.

Trifluoromethylated derivatives of fullerenes together with fluorinated derivatives have attracted considerable attention because these compounds are prospective building blocks for new materials with useful properties. Similar to fluorides, CF_3 derivatives possess high thermal stability and good solubility in organic solvents that allows their investigation by mass-spectrometric methods in a gas phase and by NMR spectroscopy in solutions. Known synthetic methods are based on reactions of fullerenes with compounds easily producing CF_3 radicals, such as silver or copper trifluoroacetates[1] or CF_3I.[2] As a rule, these methods result in complex mixtures of CF_3 derivatives, which need to be separated by fractional sublimation and high-pressure liquid chromatography (HPLC).[3]

An effective synthesis of C_{60} and C_{70} derivatives by flow reactions with CF_3I on heating was reported.[4] After separation by HPLC, the crystals of one of the $C_{60}(CF_3)_{10}$ isomers were grown and its molecular structure was determined by X-ray crystallography. Here, we report the results of the first X-ray crystallographic study of the trifluoromethylated [70]fullerene $C_{70}(CF_3)_8$. A mixture of CF_3 derivatives was obtained by a reaction of C_{70} (TERMUSA, 99.5%) with CF_3COOAg (Aldrich, 98%) at 320 °C for 1 h. The crude product was sublimed at 420–520 °C under dynamic vacuum (10^{-1} Torr). The sublimate was separated by HPLC with toluene as an eluent (Cosmosil Buckyprep column 4.6 mm×25 cm, 2 ml min^{-1} flow rate, 290 nm). The fraction containing the main $C_{70}(CF_3)_8$ isomer (retention time of 1.9 min) was collected and characterised by MALDI mass spectrometry. The synthesis, chromatographic separation and NMR spectroscopy will be considered in detail elsewhere.[5]

Using a toluene solution of $C_{70}(CF_3)_8$ **1**, we were unable to grow single crystals suitable for X-ray structure determination by conventional methods. However, very small brown crystals were obtained, and they were used for a crystallographic investigation using synchrotron radiation. Note that the crystal structure could not be solved using conventional direct methods (SHELXS97) even with a wide variation of starting parameters. However, a five hour run of the program XM (alias SHELXD)[6] that employs the shake-and-bake algorithm resulted in the localization of nearly all atoms of the structure; the asymmetric unit consisted of **1** and a toluene solvent molecule.[†] The quality of the structure determination for $C_{70}(CF_3)_8$·PhMe can be estimated as rather high as compared with those of other fullerene derivatives.

The top and side views of the $C_{70}(CF_3)_8$ molecule are shown in Figure 1; the Schlegel diagram is presented in Figure 2. In order to facilitate a comparison of the molecular structures of **1** and isostructural methylated compound,[7] the same numbering scheme for carbon atoms in the C_{70} cage (suggested in ref. 8) was chosen. The arrangement of eight trifluoromethyl groups on a [70]fullerene carbon cage corresponds to that predicted in a theoretical study of addition patterns of various atoms or groups.[9] It was found that the relative stabilities of the structure with *para* string increase with the effective volume of addend X: H < F < Br < Ph. Although CF_3 derivatives of C_{70} were not studied by Clare and Kepert,[9] the conclusion on a greater stability of a *para*(7) string for $C_{70}X_8$ derivatives is also valid for a trifluoromethylated compound because the effective volume of the CF_3 group is larger than that of the Br atom and

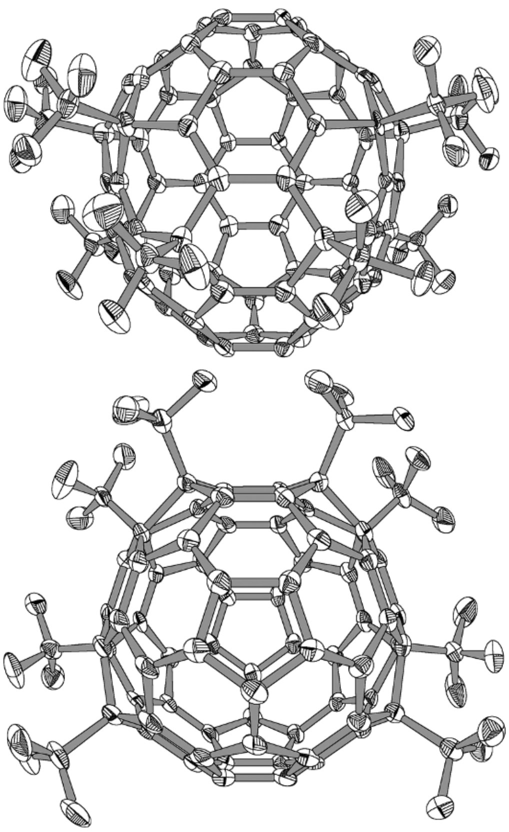

Figure 1 Side (above) and top (below) views of the $C_{70}(CF_3)_8$ molecule. Thermal ellipsoids are given with a 50% probability.

[†] *Crystal data*: $C_{70}(CF_3)_8$·PhMe, $M = 1484.91$, orthorhombic, space group $P2_12_12_1$, $a = 14.2386(4)$, $b = 15.0361(8)$ and $c = 24.3570(1)$ Å, $V = 5214.7(4)$ Å^3, $\mu = 0.170$ mm^{-1}, $Z = 4$. Data collection was performed on a MAR345 image plate at 100 K using synchrotron radiation at the BESSY storage ring ($\lambda = 0.9100$ Å), PSF BL 14.2 of the Free University of Berlin, Germany. Reflections collected 21928, independent 7472, $R_{int} = 0.062$. Anisotropic refinement with 984 parameters yielded a conventional $R_1(F) = 0.045$ for 5538 reflections with $I > 2\sigma(I)$ and $wR_2(F^2) = 0.101$ for all reflections.

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.ac.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 number 289404. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.

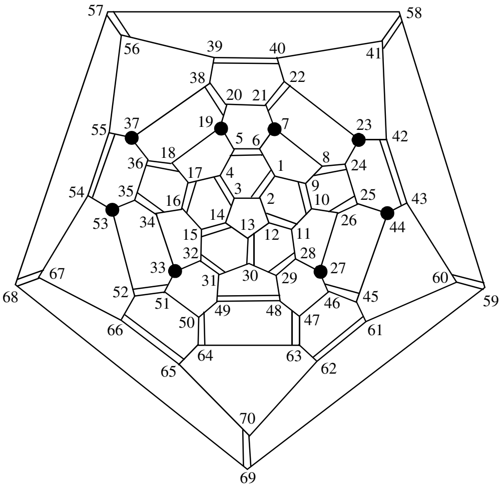

Figure 2 Schlegel diagram for $C_{70}(CF_3)_8$. Carbon atom numbering is the same as for the $C_{70}(CH_3)_8$ molecule in ref. 7.

smaller than that of the phenyl group.[10] The addition pattern of $C_{70}Ph_8$ was experimentally determined as a *para*(7) string by NMR spectroscopy.[11]

In compound **1**, all of the CF_3 groups are situated around the molecular equator at the 1,4 positions in the adjacent hexagons, *e.g.*, forming a *para*(7) string. Thus, this molecule is isostructural with methylated compound $C_{70}Me_8$ **2** (crystallographic data for the cyclohexane solvate[7]) and the phenylated derivative $C_{70}Ph_8$.[11,‡] In the carbon cage, sp^3 C atoms (bearing CF_3 groups) are pushed out from the centre of the molecule to an average distance of 3.989 Å (3.988 Å in **2**; 3.674 Å in a C_{70} molecule) resulting in a pronounced boat conformation of the corresponding $C_6(CF_3)_2$ hexagons (see the top view in Figure 1). Therefore, the fullerene cage in **1** is expanded in the equatorial region and slightly compressed in the polar regions, as compared with the [70]fullerene cage; the distances between the pole pentagons are 7.883 Å in **1**, 7.888 Å in **2**, and 7.937 Å in the C_{70} molecule (in the $C_{70}\cdot 2TiCl_4$ solvate[12]).

Geometry differences for the carbon cages in molecules **1** and **2** are small. Taking into account C_s symmetry of the carbon cage, it is justified to average bond distances for two hemispheres left and right on the Schlegel diagram (Figure 2). Among averaged bond distances, there are 12 elongated bonds for sp^3 C atoms (with numbers 7, 23, 27, and 44) ranging from 1.515 to 1.571 Å (1.520–1.554 Å in **2**). The sp^2–sp^2 C–C bonds with predominantly single character (single lines in Figure 2) have a length between 1.407 and 1.457 Å (average 1.436 Å), whereas the bonds of a predominantly double character (double lines in Figure 2) are shorter (except for the 48,49 bond) lying in the range 1.369–1.407 Å (average 1.388 Å). Significantly, the maximum length for formally double bonds, 1.418(6) Å, occurred in the C(48)–C(49) bond, which can be accounted for a tendency of avoiding double bonds in pentagons. Notably, the C(48)–C(49) bond in **2** is the shortest C–C bond of the 5/6 type (*i.e.*, in a pentagon), whereas in **1** there are some shorter bonds of this type: 8,9 (1.411 Å), 11,28 (1.413 Å) and 22,40 (1.407 Å).

Our DFT calculations for the molecules of **1** and **2** revealed small differences in their optimised geometry.[§] According to the calculation, the C(48)–C(49) bond is 1.415 Å in **1** and 1.416 Å in **2** (experimental value[8] is 1.402 Å), whereas some other 5/6 bonds have similar lengths (8,9) or are slightly shorter (22,40 1.413 Å); this qualitatively reflects the relations found experimentally for **1**. Further addition of two CF_3 groups to $C_{70}(CF_3)_8$ could proceed under formation of a *para*(8)-*ortho*-*para* belt. Such $C_{70}X_{10}$ molecules are known for X = Cl,[14] Br[15] and Ph.[11] However, most probably the larger effective volume of CF_3 groups will prevent their addition in *ortho* position.

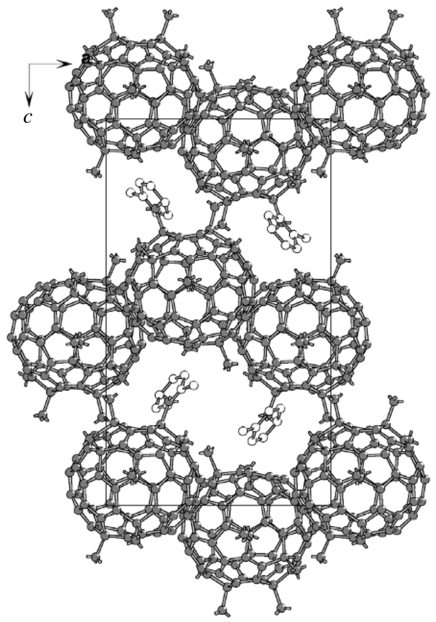

Figure 3 $C_{70}(CF_3)_8$ and toluene molecules in the crystal lattice. For clarity, F atoms are not shown.

The lengths of single C–CF_3 bonds in **1** are in the range 1.515–1.549 Å (average 1.534 Å). The similar bonds in $C_{60}(CF_3)_{10}$ **3**[4] (1.528–1.565 Å, average 1.541 Å) and C–Me bonds in **2** (1.539–1.559 Å, average 1.547 Å) are slightly shorter. The C–F distances in **1** are in the range 1.296–1.355 Å (average 1.332 Å), which is typical of such bonds. Nine shortest intramolecular F···F contacts range from 2.505 to 2.867 Å (the next shortest F···F distance is 3.259 Å). These values are comparable with intramolecular F···F contacts, 2.541–2.992 Å, in the more crowded structure of **3**.

Molecular packing in **1** is shown in Figure 3. Toluene molecules are incorporated between corrugated *ab* layers of the $C_{70}(CF_3)_8$ molecules that elongate the *c* axis. Eight shortest intermolecular F···F contacts 2.68–2.99 Å are only slightly longer than the intramolecular ones (see above).

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[‡] Esd's for most C–F and C–C bonds in **1** are 0.005 and 0.006 Å, respectively. For the molecule of **2** in a crystal of the cyclohexane solvate, $C_{70}Me_8\cdot 2C_6H_{12}$, esd's of C–C bonds vary from 0.006 to 0.009 Å as calculated from the CIF file for CSD 'OJUQIT'.

[§] Geometry optimization of the $C_{70}(CF_3)_8$ molecule was carried out at the AM1 level of theory. The obtained structure was reoptimised by DFT using the program PRIRODA,[13] the TZ2P basis set and the PBE exchange-correlation functional.

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