Preparation, crystallographic characterization and theoretical study of $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$†

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$C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$, the first trifluoromethylated fullerene derivatives to comprise a pair of adjacent CF_3 groups, have been isolated from a mixture obtained *via* reaction of C_{70} with CF_3I, characterized in a single crystal XRD study and theoretically investigated at the DFT level of theory.

Following 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 or metal trifluoroacetates,[1,2] 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 means of fractional sublimation and high performance liquid chromatography (HPLC)[3] can provide individual compounds for further structural investigations by means of vibrational and NMR spectroscopy or X-ray crystallography. Only one trifluoromethylated fullerene, $C_{60}(CF_3)_{12}$, can be prepared selectively.[4] The list of individual compounds obtained so far includes $C_{60}(CF_3)_n$ with n = 2–12[4–7] and $C_{70}(CF_3)_m$ with m = 2–14.[8–13] Direct structural determinations have been carried out for $C_{60}(CF_3)_{10}$,[7] $C_{60}(CF_3)_{12}$,[4] $C_{70}(CF_3)_8$,[10] $C_{70}(CF_3)_{10}$,[11] two isomers of $C_{70}(CF_3)_{12}$,[12] and four isomers of $C_{70}(CF_3)_{14}$.[13] Here, we report the isolation, X-ray crystallography and a theoretical study of $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$ that continue the series of well-characterized trifluoromethylated C_{70} derivatives with sequentially growing numbers of CF_3-groups.

C_{70} (36 mg, Term-USA) was placed into a glass ampoule and *ca.* 0.5 ml of CF_3I (98%, Apollo) was condensed into it under cooling with liquid nitrogen. The sealed ampoule was placed into 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 developed 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. Separation by HPLC (Cosmosil Buckyprep column 10 mm ID × 25 cm) using hexane as eluent (4.6 ml min^{-1}) allowed the isolation of two fractions containing $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$ (retention times 3.0 and 3.7 min, respectively). The abundance of these compounds in the mixture was *ca.* 17% and 9%, respectively, based on HPLC integrated intensities.[13] It should be noted that $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$ were also detected as admixtures in some other fractions eluted between 2.8 and 3.9 min, but these isomers were not isolated in the present study.

The isolated fractions were slowly evaporated to give 0.1–0.3 mm orange crystals. An X-ray single-crystal diffraction study revealed closely related C_1 molecular structures of $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$ shown in Fig. 1.‡ The addition pattern in $C_{70}(CF_3)_{16}$ can be described as incorporating the substructure of $C_{70}(CF_3)_{10}$[11]

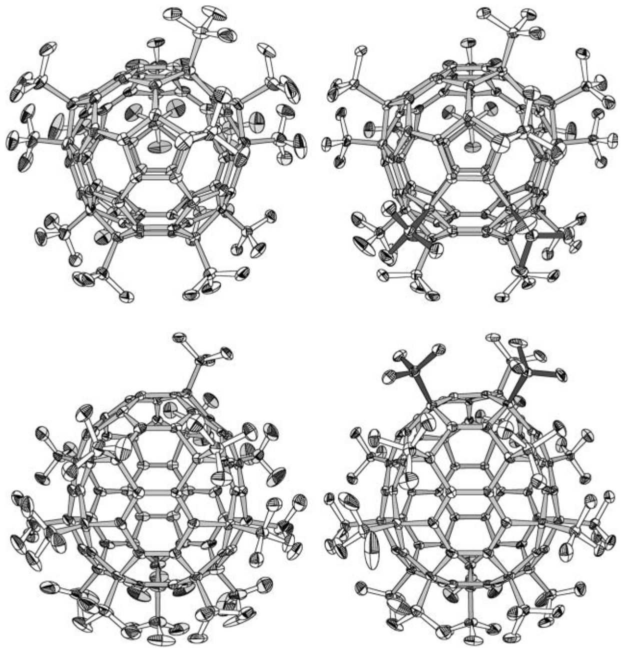

Fig. 1 Top and side ORTEP views of the $C_{70}(CF_3)_{16}$ (left, 45% probability ellipsoids) and $C_{70}(CF_3)_{18}$ (right, 55% probability ellipsoids) molecules. The bonds of the two additional CF_3 groups of $C_{70}(CF_3)_{18}$ are shown in black.

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† Electronic supplementary information (ESI) available: Schlegel diagrams, relative energies (AM1 and DFT level of theory), and IUPAC numbering for the most stable isomers of $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$. See DOI: 10.1039/b603201j

and a so-called "skew pentagonal pyramid" arrangement of the remaining six CF_3 groups around a polar pentagon analogous to that observed in $C_{60}Br_6$ and $C_{60}Cl_6$.[14] Two additional CF_3 groups in $C_{70}(CF_3)_{18}$ are attached to positions 23 and 44 (Fig. 1 and 2). Surprisingly, contrary to the cases of $C_{70}(CF_3)_{14}$ and $C_{70}(CF_3)_{12}$, $C_{70}(CF_3)_{16}$ does not incorporate a substructure of any of the four characterized isomers of its direct precursor, namely $C_{70}(CF_3)_{14}$ (see supporting information for ref. 13).

The most striking structural feature of both characterized molecules is a pair of 1,2-adjacent CF_3 groups attached to positions 33 and 34. Contrary to earlier suggestions,[5] all the $C_{60}(CF_3)_n$ and $C_{70}(CF_3)_m$ derivatives studied so far are currently known to have only 1,3-contacts in hexagons (*meta*) or pentagons and *para*-contacts of CF_3 groups.[4,7,9–13] The only possible exception is the "$C_{60}(CF_3)_6$ isomer from fraction 2" from ref. 5, which may be reattributed in the light of recent findings as isostructural to $C_{60}Br_6$ and $C_{60}Cl_6$.[14] Although theory predicted a double skew pentagonal arrangement of addends at the opposite poles of the [70]fullerene cage for $C_{70}Cl_{12}$ and $C_{70}Br_{12}$ molecules,[15] *ortho*-contacts of the more bulky CF_3 groups, shown to be comparatively less favorable [not dramatically, however, in the case of $C_{60}(CF_3)_6$],[6] were not observed in $C_{70}(CF_3)_{12}$[12] and $C_{70}(CF_3)_{14}$.[13] Nevertheless, $C_{70}(CF_3)_{16}$ appears to reveal considerable similarity with the recently reported isomers of $C_{70}Cl_{16}$.[16] Both of them comprise a *para*^{9}*ortho* equatorial belt of ten Cl atoms around the equator and a skew pentagonal cap of six Cl atoms on the pole. While $C_{70}(CF_3)_{16}$ comprises a substructure of $C_{70}(CF_3)_{10}$, the above belt in $C_{70}Cl_{16}$ is inherited from $C_{70}Cl_{10}$. In the case of CF_3 groups, such a closed type of belt containing an *ortho*-contact was calculated to be less favorable than a contiguous sequence of edge-sharing *para*- and *meta*-$C_6(CF_3)_2$ hexagons forming a p^7mp ribbon,[9] which has been observed in the whole series of isolated $C_{70}(CF_3)_n$ isomers with $n \geqslant 10$.[9,11–13] Therefore, the energetics of *ortho*-contacts in C_{70} derivatives can be expected to depend on their position on the carbon cage.

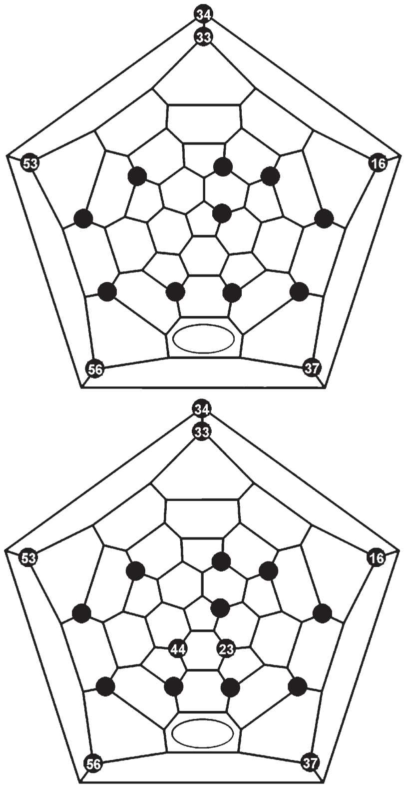

Fig. 2 Schlegel diagrams for $C_{70}(CF_3)_{16}$ (top) and $C_{70}(CF_3)_{18}$ (bottom). The numbering is given only for the sites not occupied in the $C_{70}(CF_3)_{10}$ substructure.

In development of the discussion of the mechanism of high-temperature radical trifluoromethylation started in ref. 12 and 13, we undertook a DFT study of a large group of isomers of $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$.§ The total number of possible $C_{70}X_{18}$ structures being enormous, some reasonable restrictions on the set of structures to investigate are inevitable. First of all, it was necessary to understand which types of *ortho*-contacts, with respect to their location on the C_{70} cage, are more energetically favorable and thus need to be taken into account. We, therefore, started from computations of the possible *ortho*-isomers of $C_{70}(CF_3)_2$. It was found that the most stable *ortho*-isomer of $C_{70}(CF_3)_2$ exhibits a 6–6 *ortho*-contact located similarly to those observed in the presently reported $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$ (*i.e.* radiating from the polar pentagon) but this *ortho*-isomer of $C_{70}(CF_3)_2$ is still *ca.* 24 kJ mol^{-1} less stable than the best *para*-isomer. Accordingly, our further survey was restricted to those structures of $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$ which comprised no more than one similarly located *ortho*-contact plus a substructure of either of the two most stable isomers of $C_{70}(CF_3)_8$.[9] The C_s-$C_{70}(CF_3)_8$ motif can be observed in $C_{70}(CF_3)_{10}$ and in the isolated isomers of $C_{70}(CF_3)_{12}$ and $C_{70}(CF_3)_{14}$ as well as in the presently reported $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$ [the isomers of the latter four compounds are, in fact, even $C_{70}(CF_3)_{10}$-based[11–13]], while the C_2-$C_{70}(CF_3)_8$ motif was also taken into consideration due to its being closely structurally related and comparable in stability to C_s-$C_{70}(CF_3)_8$.

According to the DFT results obtained, the XRD characterized isomers of both $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$ appear to be the most stable among all the structures considered. However, at least four more isomers of both $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$, with and without *ortho*-contacts, were found to be only a few kJ mol^{-1} less stable than the reported ones (see ESI†). Formation of the most stable isomers of $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$ can be regarded as evidence of at least partial thermodynamic control in trifluoromethylation. Nevertheless, taking into account that other stable isomers found theoretically should also form in case of such control, structural characterization of those additional isomers which were detected in the chromatographic fractions would be helpful. An additional argument in favor of thermodynamic control is *ortho*-addition, which looks kinetically unfavorable from the steric point of view, taking into account the availability of less hindered addition sites. However, *ortho*-positions are generally more activated in the precursor radicals with an odd number of addends and the relative rate of addition to such sites may, in principle, correlate with the relative thermodynamic favorability of the corresponding addition products.

The absence of possible direct precursors of $C_{70}(CF_3)_{16}$ among the isolated isomers of $C_{70}(CF_3)_{14}$ can also be explained from different viewpoints. The thermodynamic approach involves migration of CF_3 radicals on the fullerene cage discussed in more detail in ref. 12 and 13, while the kinetic model can be based on a supposition about the existence of trifluoromethylated molecules with various levels of reactivity. Indeed, the computational study of $C_{70}(CF_3)_{14}$ revealed the presence of a number of highly stable isomers not found experimentally.[13] The present work has revealed the presence of the addition patterns of all of these isomers as substructures in either $C_{70}(CF_3)_{16}$, or $C_{70}(CF_3)_{18}$, although some of the missing $C_{70}(CF_3)_{14}$ isomers require CF_3 addition to non-adjacent hexagons to obtain the latter compounds. Thus, one can assume $C_{70}(CF_3)_{16}$ or $C_{70}(CF_3)_{18}$ to be the products of direct trifluoromethylation of the more reactive isomers of $C_{70}(CF_3)_{14}$, which do not accumulate in the synthetic mixture unlike the less reactive isolated ones.

The above discussion demonstrates that currently it is still impossible to estimate the role of thermodynamic and kinetic factors in high temperature radical trifluoromethylation. We expect structural determination of the further isomers to help clarify the matter.

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Notes and references

‡ *Crystal data*. Synchrotron X-ray data for the crystal of $C_{70}(CF_3)_{16}$ were collected at 100 K at the Swiss-Norwegian Beam Lines at the European Synchrotron Radiation Facility, Grenoble, France using a MAR345 image plate detector, λ = 0.7500 Å. M = 1944.86, monoclinic, $P2_1/n$, a = 12.9804(7) Å, b = 20.870(1) Å, c = 22.953(1) Å, β = 93.135(4)°, V = 6208.7(5) Å^3, D_c = 2.081 g cm^{-3}, Z = 4. Reflections collected 76370, independent 12677. Anisotropic refinement with 1220 parameters yielded a conventional $R_1(F)$ = 0.121 for 12651 reflections with $I > 2\sigma(I)$ and $wR_2(F^2)$ = 0.249 for all reflections. One CF_3 group was rotationally disordered between two positions.

Data for the crystal of $C_{70}(CF_3)_{18}$ were collected on an IPDS diffractometer (Stoe) at 100 K (graphite-monochromated Mo-K$_\alpha$ radiation, λ = 0.71073 Å). M = 2082.88, triclinic, $P\bar{1}$, a = 13.3244(9) Å, b = 14.3768(9) Å, c = 20.323(1) Å, α =103.674(5)°, β = 98.521(5)°, γ = 114.658(5)°, V = 3300.8(3) Å^3, D_c = 2.096 g cm^{-3}, Z = 2. Reflections collected 38625, independent 23785. Two CF_3 groups were found to be disordered between two positions each by rotation around the $C-CF_3$ axis. Anisotropic refinement with 23777 reflections and 1334 parameters yielded a conventional $R_1(F)$ = 0.081 for 15605 reflections with $I > 2\sigma(I)$ and $wR_2(F^2)$ = 0.195 for all reflections. In both structures, the highest peaks of the rest electron density (*ca.* 1 e Å^{-3}) are in the vicinity of F atoms, indicating a small degree of disorder of some CF_3 groups.

CCDC 601105 and 601106. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603201j

§ Preliminary geometry optimization of 7494 generated $C_{70}(CF_3)_{16}$ isomers and 7780 $C_{70}(CF_3)_{18}$ isomers was carried out at the AM1 level of theory with the use of the PC-GAMESS software.[17] The most stable isomers within the gap of 30 kJ mol^{-1} were then reoptimized at the DFT level of theory with the use of the PRIRODA software[18] employing an original TZ2P basis set and PBE exchange–correlation functional.[19]

1 P. J. Fagan, P. J. Krusic, C. N. McEwen, J. Lazar, D. H. Parker, N. Herron and E. Wasserman, *Science*, 1993, **262**, 404.

2 I. S. Uzkikh, E. I. Dorozhkin, O. V. Boltalina and A. I. Boltalin, *Dokl. Akad. Nauk*, 2001, **379**, 344, *Dokl. Chem.*, 2001, **379**, 204.

3 A. A. Goryunkov, I. V. Kuvychko, I. N. Ioffe, D. L. Dick, L. N. Sidorov, S. H. Strauss and O. V. Boltalina, *J. Fluorine Chem.*, 2003, **124**, 61.

4 S. I. Troyanov, A. Dimitrov and E. Kemnitz, *Angew. Chem., Int. Ed.*, 2006, **45**, 1971.

5 A. D. Darwish, A. Abdul-Sada, A. G. Avent, Yu. I. Lyakhovetsky, E. A. Shilova and R. Taylor, *Org. Biomol. Chem.*, 2003, **1**, 3102.

6 A. A. Goryunkov, I. N. Ioffe, I. V. Kuvychko, T. S. Yankova, V. Yu. Markov, A. A. Streletskii, D. L. Dick, L. N. Sidorov, O. V. Boltalina and S. H. Strauss, *Fullerenes, Nanotubes, Carbon Nanostruct.*, 2004, **12**, 181.

7 I. E. Kareev, I. V. Kuvychko, S. F. Lebedkin, S. M. Miller, O. P. Anderson, K. Seppelt, S. H. Strauss and O. V. Boltalina, *J. Am. Chem. Soc.*, 2005, **127**, 8362.

8 A. D. Darwish, A. K. Abdul-Sada, A. G. Avent, N. Martsinovich, J. M. Street and R. Taylor, *J. Fluorine Chem.*, 2004, **125**, 1383.

9 E. I. Dorozhkin, D. V. Ignat'eva, N. B. Tamm, A. A. Goryunkov, P. A. Khavrel, I. N. Ioffe, A. A. Popov, I. V. Kuvychko, A. V. Streletskiy, V. Yu. Markov, J. Spandl, S. H. Strauss and O. V. Boltalina, *Chem.–Eur. J.*, 2006, **12**, 14, 3876.

10 A. A. Goryunkov, E. I. Dorozhkin, D. V. Ignat'eva, L. N. Sidorov, E. Kemnitz, G. Sheldrick and S. I. Troyanov, *Mendeleev Commun.*, 2005, 225.

11 I. E. Kareev, I. V. Kuvychko, A. A. Popov, S. F. Lebedkin, S. M. Miller, O. P. Anderson, S. H. Strauss and O. V. Boltalina, *Angew. Chem., Int. Ed.*, 2005, **44**, 7984.

12 D. V. Ignat'eva, A. A. Goryunkov, N. B. Tamm, I. N. Ioffe, S. M. Avdoshenko, L. N. Sidorov, E. Kemnitz and S. I. Troyanov, *Chem. Commun.*, 2006, 1778; I. E. Kareev, S. F. Lebedkin, S. M. Miller, O. P. Anderson, S. H. Strauss and O. V. Boltalina, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, **E62**, o617–o620.

13 A. A. Goryunkov, D. V. Ignat'eva, N. B. Tamm, N. N. Moiseeva, I. N. Ioffe, S. M. Avdoshenko, V. Yu. Markov, L. N. Sidorov, E. Kemnitz and S. I. Troyanov, *Eur. J. Org. Chem.*, 2006, DOI: 10.1002/ejoc.200600076.

14 P. R. Birkett, P. B. Hitchcock, H. W. Kroto, R. Taylor and D. R. M. Walton, *Nature*, 1992, **357**, 479; P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1993, 1230.

15 B. W. Clare and D. L. Kepert, *J. Mol. Struct. (THEOCHEM)*, 1999, **491**, 249.

16 S. I. Troyanov and A. A. Popov, *Angew. Chem., Int. Ed.*, 2005, **44**, 4215.

17 A. A. Granovsky, http://classic.chem.msu.su/gran/gamess/index.html; M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.

18 D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.

19 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.