Preparation, crystallographic characterization and theoretical study of two isomers of $C_{70}(CF_3)_{12}$†

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Two isomers of $C_{70}(CF_3)_{12}$ have been isolated from a mixture obtained by trifluoromethylation of C_{70} with CF_3I; their molecular structures determined by X-ray crystallography are in good agreement with the results of theoretical DFT calculations for the most stable $C_{70}(CF_3)_{12}$ isomers.

Known synthetic methods for preparation of trifluoromethylated fullerenes are based on reactions of fullerenes with compounds that easily produce CF_3 radicals, such as CF_3I[1] or metal trifluoroacetates.[2] As a rule, these methods yield complex mixtures of CF_3 derivatives that need to be separated by means of fractional sublimation and high pressure liquid chromatography (HPLC).[3] To date, isolation of $C_{60}(CF_3)_n$ compounds with n = 2–10 and $C_{70}(CF_3)_m$ compounds with m = 2–10 has been reported.[4–7] The majority of these compounds were studied only by means of ^{19}F NMR and vibrational spectroscopy. A few of them, $C_{60}(CF_3)_{10}$,[6] $C_{70}(CF_3)_8$,[8] and $C_{70}(CF_3)_{10}$,[9] have been characterized by means of X-ray crystallography. Recently, the first selective synthesis of a trifluoromethylated [60]fullerene was described, which resulted in the preparation of $C_{60}(CF_3)_{12}$ and determination of its molecular and crystal structure.[10] The addition pattern in all the compounds characterized can be formally broken down into pairs of CF_3-groups attached to hexagons in *para*-positions. These pairs are all connected by either *para*- or 1,3-contacts in hexagons (*meta*) or pentagons. In the present communication, we report isolation, X-ray crystallography, and theoretical study of two $C_{70}(CF_3)_{12}$ isomers, which provide the first examples of a somewhat different addition pattern.

A reaction of C_{70} (36 mg, Term-USA) with gaseous (*ca.* 5 bar) CF_3I (Apollo) was carried out in a glass ampoule at 390(±5) °C for 24 h. More than 95% of the fullerene was consumed and an orange coloured sublimate (*ca.* 60 mg) was found in the zone at *ca.* 300 °C, whereas crystalline I_2 was deposited in the cooler zone at *ca.* 100 °C. The sublimate was shown to be a mixture of $C_{70}(CF_3)_m$ with m = 12–20 by negative-ion MALDI MS analysis performed using *trans*-2-(3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene)malononitrile (DCTB, Fluka) as matrix. Hence the approach employed provides a higher degree of trifluoromethylation than the flow reaction at 460 °C described in ref. 6, where the number of CF_3-groups attached was between 8 and 14.

HPLC separation of the sublimate resulted in isolation of two fractions (in *ca.* 1 : 1 ratio) containing $C_{70}(CF_3)_{12}$-I and $C_{70}(CF_3)_{12}$-II (retention times 4.9 and 5.7 min, respectively) (Fig. 1). MALDI analysis did not reveal the presence of $C_{70}(CF_3)_{12}$ in other fractions isolated.

The isolated solutions with $C_{70}(CF_3)_{12}$ were slowly evaporated to give 0.2–0.5 mm orange crystals. An X-ray single-crystal study revealed two unsymmetric structures of the isomeric molecules, 1,4,10,19,25,32,41,49,54,60,66,69-$C_{70}(CF_3)_{12}$ (I) and 1,4,10,14,19,25,35,41,49,60,66,69-$C_{70}(CF_3)_{12}$ (II) presented in Fig. 2 and Fig. 3 (numbering is given according to IUPAC recommendations).[11]‡ Both molecules contain a p^7mp ribbon of nine $C_6(CF_3)_2$ hexagons as reported earlier for the $C_{70}(CF_3)_{10}$ molecule.[9] Two additional

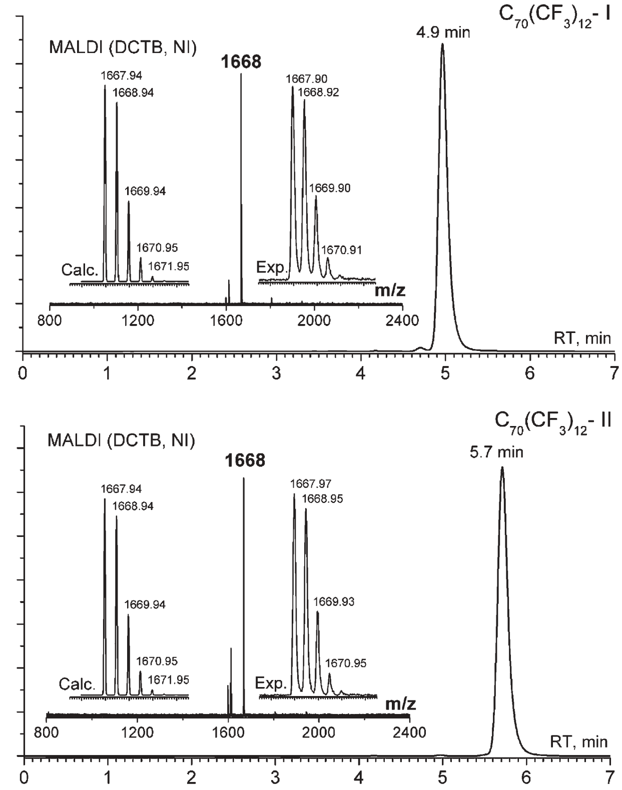

Fig. 1 HPLC chromatograms (Cosmosil Backyprep, 10 mm id × 25 cm, 4.6 ml min^{-1}, hexane, 290 nm) of two isomers of $C_{70}(CF_3)_{12}$. Insets show the MALDI mass spectra (DCTB, NI) of the purified isomers as well as the calculated and experimental isotopic distributions for $C_{70}(CF_3)_{12}$.

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† Electronic supplementary information (ESI) available: Schlegel diagrams, relative energies (AM1 and DFT levels of theory) and IUPAC numbering for the most stable isomers. See DOI: 10.1039/b518422c

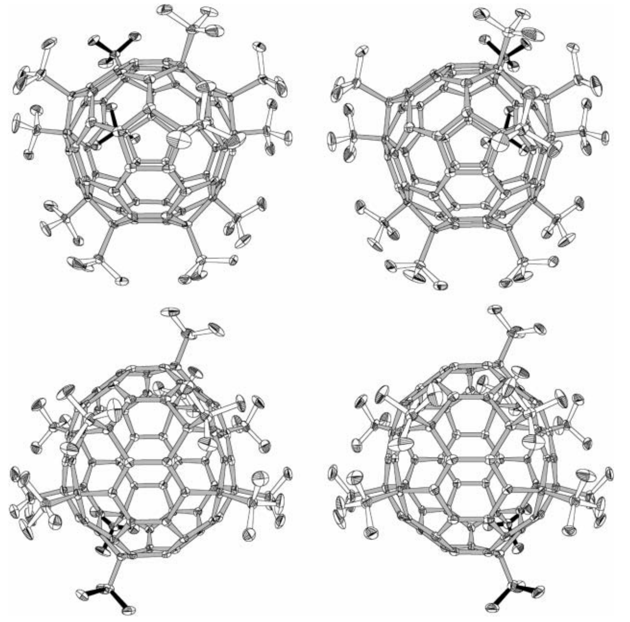

Fig. 2 Two views of $C_{70}(CF_3)_{12}$-I (left) and $C_{70}(CF_3)_{12}$-II (right) molecules given at the 50% probability level. C–F bonds belonging to the $C_{70}(CF_3)_{10}$ pattern are shown in white; those of two additional CF_3 groups are black. Only the most abundant components of the disordered CF_3 groups are shown.

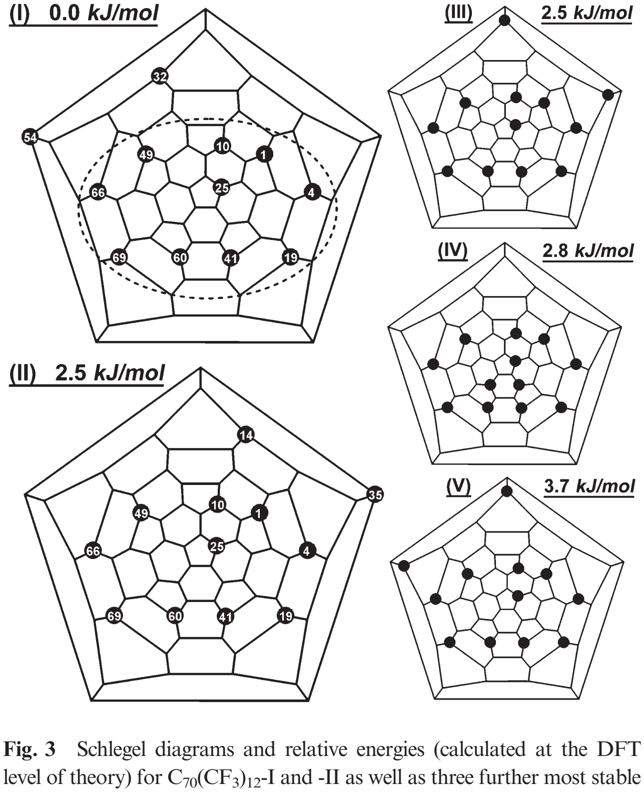

Fig. 3 Schlegel diagrams and relative energies (calculated at the DFT level of theory) for $C_{70}(CF_3)_{12}$-I and -II as well as three further most stable $C_{70}(CF_3)_{12}$ isomers (III–V). Black circles denote the attached CF_3 groups (the numbering of the addition sites is given inside the circles). The dashed line encircles the $C_{70}(CF_3)_{10}$ substructure.

CF_3-groups (marked with black C–F bonds in Fig. 2), which form a *para*-pair, do not share the same pentagons or hexagons with the groups from the p^7mp ribbon. Structures I and II represent the only two possibilities of such placement of an additional pair of groups and thus provide rare examples of compounds where not all of the *p*-$C_6(CF_3)_2$ units are connected.§

As shown in ref. 7, trifluoromethylation of C_{70} with trifluoroacetates is likely to yield the most thermodynamically stable $C_{70}(CF_3)_m$ isomers at least for $m \leqslant 10$. One can thus suggest that trifluoromethylation is thermodynamically controlled *via* a sort of "CF_3 dance" analogous to fluorine[12] and chlorine[13] dances. In order to find out whether the isomeric composition of $C_{70}(CF_3)_{12}$ obtained in the present work is governed by thermodynamic stability, a theoretical study of the possible $C_{70}(CF_3)_{12}$ structures has been undertaken. We have restricted ourselves to the structures containing a substructure of either of the two main $C_{70}(CF_3)_8$ isomers.[7,8] This choice was justified by the *ca.* 20 kJ mol^{-1} gap between these two isomers and the next stable ones[7] and by the presence of such substructure in the isolated isomer of $C_{70}(CF_3)_{10}$.[9] All the possible isomers incorporating one of the above substructures plus two more *p*-pairs of CF_3-groups and containing no 1,2-contacts between the groups have been considered. After the preliminary geometry optimization of all 261 structures of this type at the AM1 level of theory (PC-GAMESS software[14]), the most stable isomers within the gap of 50 kJ mol^{-1} were reoptimized at the DFT level of theory (PRIRODA software[15]) with the use of a TZ2P basis set and PBE exchange-correlation functional.[16] The discrepancies between the relative stability of the isomers at the DFT and AM1 levels of theory did not exceed 26 kJ mol^{-1}, thus demonstrating good applicability of the latter semiempirical method to trifluoromethylated fullerene molecules (the details of calculation results are given in the supporting information).

As was expected, DFT results demonstrate that the two characterized isomers of $C_{70}(CF_3)_{12}$ are indeed the most stable of all and are separated by only 2.5 kJ mol^{-1}. However, it appears that there are three other isomers within only 4 kJ mol^{-1} from the most stable one (also shown in Fig. 3) and seven more structures within 11 to 20 kJ mol^{-1}. Since all the five structures shown in Fig. 3 and the majority of the less stable ones contain a substructure of $C_{70}(CF_3)_{10}$ and thus can be expected to be easily accessible starting from the latter, it is not entirely clear whether the isomers characterized are thermodynamic or kinetic products. Two possibilities can, therefore, take place:

(a) The reaction is thermodynamically controlled but isomers III–V do not form due to a decrease of their relative stability at elevated temperatures with respect to the calculated zero-temperature relative stability. This may be, say, due to different contributions of the low-energy torsional degrees of freedom of CF_3-groups to the thermodynamic functions. In this respect, less hindered isomers may be preferable, and the two isomers isolated are somewhat less hindered since they do not contain, unlike other possible structures, 1,3-contacts of CF_3-groups in pentagons.

(b) The reaction is at least partially kinetically controlled. In this case the steric aspects of subsequent CF_3 addition should also favor the formation of less hindered isomers. Moreover, if we start from $C_{70}(CF_3)_{10}$ following the concept of Fowler and Rogers,[17] *i.e.* add a CF_3 radical to the site of highest free-valence index among those not hindered by CF_3 adjacency and subsequently add the second radical to the non-hindered site of highest spin density, the most kinetically probable structures would be again the two isomers isolated.

At present, we have insufficient data to choose between explanations a) and b). Perhaps further study of higher trifluoromethylated products of the C_{70} – CF_3I reaction might clarify the matter.

According to both experimental and theoretical results, both isomers characterized comprise carbon cage C–C bonds of the following types. Several relatively short bonds (1.34–1.36 Å) can be regarded as almost localized double bonds, although none of them is really isolated; much larger is a group of longer C–C bonds (1.38–1.47 Å) involved to an appreciable extent in aromatic conjugation. The rest are single bonds (1.51–1.56 Å), which connect sp^3 and sp^2 carbons, the 6:6 bonds being slightly shorter than the 5:6 ones. It is noteworthy that the local geometry of p^7mp substructures in both isomers appears to be very similar to the "parent" $C_{70}(CF_3)_{10}$.[9] However, in spite of this similarity, the difference in addition patterns of isomers I and II should result in somewhat different dipole moments, 0.34 and 1.40 D, respectively, as predicted by our calculations; this may serve as an explanation of the larger retention time observed for the second isomer. IR, UV, and NMR spectroscopic studies on the both isomers are underway.

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Notes and references

‡ *Crystal data*: Data for both crystals were collected on an IPDS diffractometer (Stoe) at 100 K (graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å). $C_{70}(CF_3)_{12}$-I, monoclinic, $P2_1/n$, a = 14.532(1) Å, b = 21.131(2) Å, c = 18.110(1) Å, β = 98.56(1)°, V = 5499.2(7) $Å^3$, D_c = 2.016 g cm^{-3}, Z = 4. Three CF_3 groups were found to be disordered between two positions each by rotation around the C–CF_3 axis. Anisotropic refinement with 22948 reflections and 1147 parameters yielded a conventional R_1 (F) = 0.074 for 15719 reflections with $I > 2\sigma(I)$ and wR_2 (F^2) = 0.138 for all reflections. $C_{70}(CF_3)_{12}$-II, monoclinic, $C2/c$, a = 16.6625(7) Å, b = 18.5411(5) Å, c = 35.626(1) Å, β = 99.644(3)°, V = 10870.3(6) $Å^3$, D_c = 2.016 g cm^{-3}, Z = 8. One CF_3 group was disordered between two positions. Anisotropic refinement with 20714 reflections and 1091 parameters resulted in a conventional R_1 (F) = 0.086 for 13981 reflections with $I > 2\sigma(I)$ and wR_2 (F^2) = 0.149 for all reflections. CCDC 295147 and 295148. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b518422c

§ After the submission of this paper, crystallographic data of the benzene solvates of the same two $C_{70}(CF_3)_{12}$ isomers were published in two communications: 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, **62**, o617 and o620.

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