New trifluoromethylated derivatives of [60]fullerene, $C_{60}(CF_3)_n$ with n = 12 and 14†

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New isomers of $C_{60}(CF_3)_{12}$ and $C_{60}(CF_3)_{14}$ have been isolated from mixtures obtained *via* reaction of C_{60} or S_6-$C_{60}(CF_3)_{12}$ with CF_3I; they were characterized by single crystal XRD study and investigated theoretically by means of DFT calculations.

Recent progress in the synthesis and isolation of trifluoromethylated fullerene derivatives led to the structural characterization of numerous $C_{60}(CF_3)_n$ compounds in the range of n = 2–18. This variety of molecules encompasses lower (n = 2–8),[1,2] intermediate (n = 10, 12),[3,4] and higher (n = 16, 18)[5] CF_3 derivatives of [60]fullerene. Frequently occurring isomerism of addend distribution on the carbon cage has stimulated extensive discussion of possible pathways of trifluoromethylation.

To date, four isomers of $C_{60}(CF_3)_{10}$ have been characterized, exhibiting rather different addition patterns.[3] None of them, however, can be considered as a precursor for the known S_6 isomers of $C_{60}(CF_3)_{12}$,[4,6] if restricting the trifluoromethylation process to simple sequential addition without migration of addends. Moreover, crystalline S_6-$C_{60}(CF_3)_{12}$, which uniquely can be prepared with a high selectivity, drastically differs from all other $C_{60}(CF_3)_n$ compounds in its low solubility in most organic solvents.[4] Even more obscure are further trifluoromethylation pathways since no isomer of $C_{60}(CF_3)_{14}$ has been structurally investigated so far in spite of detection of this compound among the synthetic products.[3a,5] This constitutes an essential gap in our knowledge of products and possible pathways of fullerene trifluoromethylation.

Here, we report the preparation, isolation, X-ray crystallography and theoretical study of a new isomer of $C_{60}(CF_3)_{12}$ and two isomers of $C_{60}(CF_3)_{14}$, thus filling a gap in the range of structurally characterized trifluoromethylated C_{60} derivatives with sequentially increasing number of CF_3 groups.

Two series of experiments have been carried out. In the first series, C_{60} (99.98%, Term-USA) was reacted with CF_3I (98%, Apollo) in a glass ampoule at 400–440 °C for 2–4 days, as described previously.[4,5] The products were analyzed by means of negative-ion MALDI MS analysis using 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB, ≥99%, Fluka) as a matrix. As a whole, the product mixture comprised $C_{60}(CF_3)_n$ compounds with n ranging from 12 to 18, *i.e.* it had a composition close to that obtained in similar experiments previously.[5] Separation by HPLC (Cosmosil Buckyprep column 10 mm ID × 25 cm) using hexane as eluent (4.6 ml min^{-1}) provided two fractions with retention times of 6.00 and 3.63 min containing mainly $C_{60}(CF_3)_n$ compounds with n = 12 and n = 14, respectively (see MALDI mass spectra in Fig. 1). Slow concentration of these fractions afforded, in both cases, small yellow crystals, their X-ray investigation revealing molecular structures of a new isomer of $C_{60}(CF_3)_{12}$ ($C_{60}(CF_3)_{12}$-III) and the first isomer of $C_{60}(CF_3)_{14}$ ($C_{60}(CF_3)_{14}$-I).‡ See ESI for their UV/Vis spectra.†

In the second series of experiments, C_{60} was replaced as a starting material with S_6-$C_{60}(CF_3)_{12}$, prepared according to the known method.[4] The latter was subjected to trifluoromethylation with CF_3I in ampoules at 320–360 °C, *i.e.* under relatively mild conditions, in order to slow down sublimation of unreacted starting material and to prevent possible rearrangement reactions. This process, traced *via* the rate of deposition of volatile products in the cooler zone of the ampoules, was found to be considerably slower than trifluoromethylation of C_{60} at higher temperatures and thus required 7–20 days to achieve complete transport of the

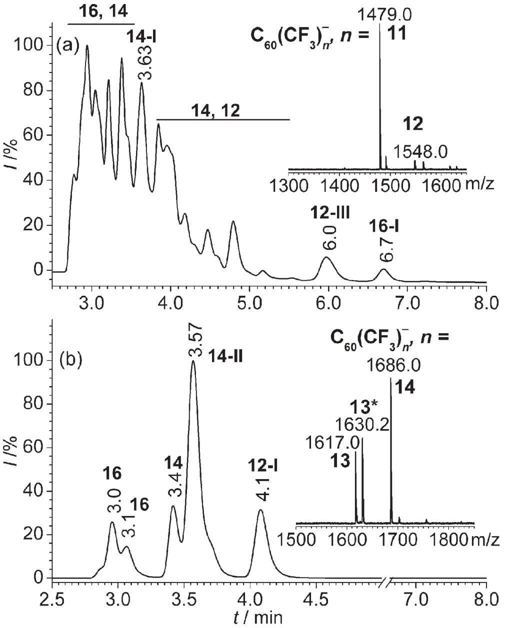

Fig. 1 HPLC traces of trifluoromethylation products of C_{60} at 400 °C (a) and S_6-$C_{60}(CF_3)_{12}$ at 360 °C (b). MALDI MS spectra of 12-III and 14-II isomers are also given.

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† Electronic supplementary information (ESI) available: UV/Vis spectra of the four isolated compounds, Schlegel diagrams, relative energies, and IUPAC numbering for the most stable isomers of $C_{60}(CF_3)_{12}$ and $C_{60}(CF_3)_{14}$. See DOI: 10.1039/b709684d

mixture of products and unreacted S_6-$C_{60}(CF_3)_{12}$ (light-yellow powder) to the cooler zone. The powder was only partly soluble in toluene and the IR spectrum of the insoluble part was identical to that of pure S_6-$C_{60}(CF_3)_{12}$, while the HPLC (hexane) and MALDI analyses of the soluble part revealed the presence of new fractions of $C_{60}(CF_3)_{14}$ (3.57 min) and $C_{60}(CF_3)_{12}$ (4.08 min) (Fig. 1b). It is noteworthy that neither of these fractions was observed in the products of the abovementioned trifluoromethylation of C_{60}. Slow evaporation of the first fraction provided yellow crystals of one more isomer of $C_{60}(CF_3)_{14}$ ($C_{60}(CF_3)_{14}$-II), as determined by means of single-crystal X-ray study, whereas the crystals grown from the second fraction were identified as S_6-$C_{60}(CF_3)_{12}$ on the basis of unit cell parameters.[4]‡

The molecular structure of $C_{60}(CF_3)_{12}$-III isolated from the mixture of higher $C_{60}(CF_3)_n$ compounds is quite remarkable (Fig. 2). It contains two so-called "skew-pentagonal-pyramids" (SPP) of six CF_3 groups on the opposite poles of the fullerene cage. Three possible isomers of such type differ by rotation of one pyramid (*i.e.* the position of the addend in the central pentagon) with respect to the other one. The most symmetric isomer (1,6,9,12,15,18,43,46,49,52,55,60-$C_{60}(CF_3)_{12}$ according to the IUPAC notation[7]) possesses C_{2h} symmetry, while the other two are enantiomeric pairs of C_2 symmetry. Our DFT calculations demonstrate that the C_{2h} structure is considerably higher in energy than S_6-$C_{60}(CF_3)_{12}$ (+32.5 kJ mol^{-1}) and the two C_2 isomers are only 0.2 and 1.6 kJ mol^{-1} higher than their C_{2h} analog (see ESI†).§ One can thus suggest that the mixture of all three almost isoenergetic isomers accounts for the observed disorder in the positions of the CF_3 group attached to the polar pentagons. The discussed structures are, in their turn, slightly (by *ca.* 7 kJ mol^{-1}) more stable than the recently reported C_1-$C_{60}(CF_3)_{12}$ (+39.8 kJ mol^{-1}) obtained under strongly non-equilibrium conditions.[6] It is worth noting that double-skew-pyramid structures become the most stable ones for hypothetical $C_{60}Cl_{12}$ and $C_{60}Br_{12}$ according to theoretical calculations,[8] because steric repulsion of adjacently attached addends is, perhaps, not that significant for less bulky Cl or Br atoms. Analogous observations remain true for the $C_{60}X_6$ structures: the SPP isomer of $C_{60}(CF_3)_6$ is 13.8 kJ mol^{-1} less stable than the 1,6,11,18,24,27-$C_{60}(CF_3)_6$,[1b,9] and has been, so far, characterized only spectroscopically,[10] whereas the isostructural SPP isomers $C_{60}Cl_6$[11] and $C_{60}Br_6$[12] represent the only isolable compounds of $C_{60}Hal_6$ composition.

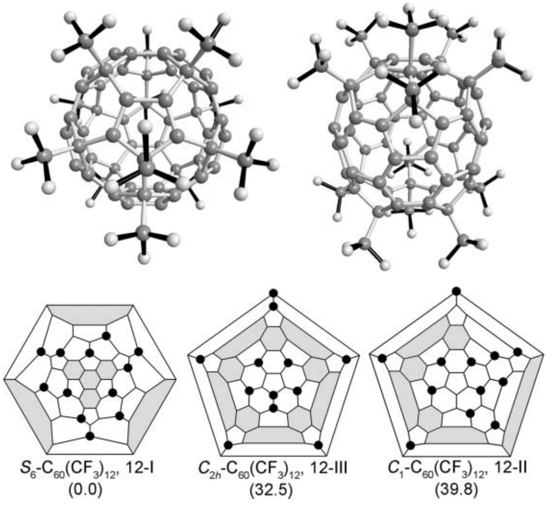

Fig. 2 Two views of the $C_{60}(CF_3)_{12}$-III molecule and Schlegel diagrams of S_6-$C_{60}(CF_3)_{12}$ (left), C_{2h}-$C_{60}(CF_3)_{12}$ (middle), and C_1-$C_{60}(CF_3)_{12}$. Energy is given in kJ mol^{-1}. Hexagons without attachment are shown grey.

Molecular structures of $C_{60}(CF_3)_{14}$-I and II are similar in that they both inherit one of two triphenylene fragments of S_6-$C_{60}(CF_3)_{12}$ surrounded by CF_3 groups (Fig. 3) and are coupled *via* relocation of only two CF_3 groups. $C_{60}(CF_3)_{14}$-II can be obtained by simple (*i.e.* without any further rearrangement) addition of two CF_3 groups to S_6-$C_{60}(CF_3)_{12}$, as would be expected for trifluoromethylation of the latter compound under milder conditions. In contrast to the above case, $C_{60}(CF_3)_{14}$-I cannot be connected to S_6-$C_{60}(CF_3)_{12}$ *via* attachment of two extra addends only but also requires migration of two more groups. It is, thus, not surprising that isomer I was isolated from the mixture obtained at higher temperatures. The two characterized isomers of $C_{60}(CF_3)_{14}$ occupy (in the order of their numbering) the first and the third places in the isomeric stability list with the gap of 2.2 kJ mol^{-1} only (see ESI†). Both of them can be regarded as possible precursors of the previously reported $C_{60}(CF_3)_{16}$-II and -III, which still retain one unoccupied triphenylene fragment.[5] It is noteworthy that the latter compounds were also detected among the products of trifluoromethylation of S_6-$C_{60}(CF_3)_{12}$, while $C_{60}(CF_3)_{16}$-I and $C_{60}(CF_3)_{18}$-I,[5] which do not incorporate triphenylene substructure, were absent.

As we mentioned above, one of the hexane fractions separated by HPLC afforded crystalline S_6-$C_{60}(CF_3)_{12}$ after evaporation of the solvent. Significantly, it could not be dissolved again in hexane or other solvent. Earlier,[4] insolubility of crystalline S_6-$C_{60}(CF_3)_{12}$ in such solvents as hexane, benzene, toluene, and even 1,2-dichlorobenzene (also under ultrasound treatment) was accounted for by the peculiarities of crystal packing. It contains chains of

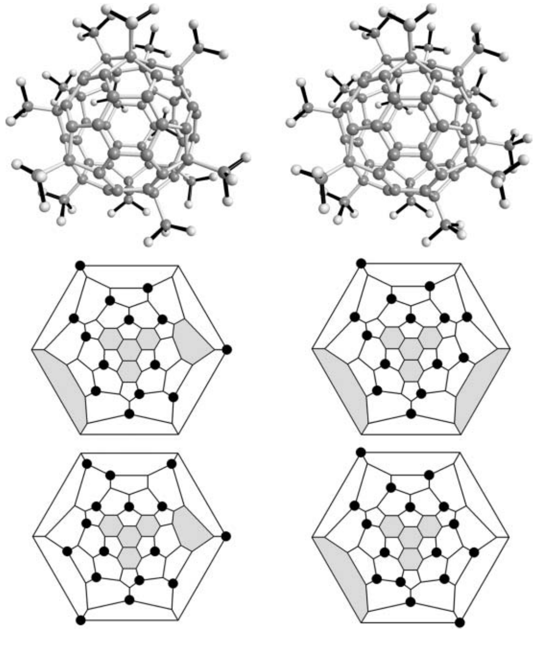

Fig. 3 Views of $C_{60}(CF_3)_{14}$-I (left) and -II molecules, their Schlegel diagrams (middle row), and those of $C_{60}(CF_3)_{16}$-II and -III (bottom row). Hexagons without attachment are shown grey.

$C_{60}(CF_3)_{12}$ molecules with very short intermolecular contacts due to the stacking interaction of the central hexagons of triphenylene fragments (Fig. 2) accompanied by shielding of these contacts by surrounding CF_3 groups. However, the NMR spectrum of this compound recorded in benzene has been reported recently.[13] We, therefore, suppose that insolubility of S_6-$C_{60}(CF_3)_{12}$ crystals is merely a kinetic effect of inaccessibility of stacking contacts in a crystal for solvent molecules and that the equilibrium solubility can be achieved in the case of non-crystalline material. Indeed, our additional experiments with rapidly sublimed S_6-$C_{60}(CF_3)_{12}$ clearly revealed a correlation between the sublimation rate and the amount of soluble fraction in the condensed product. Obviously, trifluoromethylation of a complex fullerene mixture performed in a flow reactor followed by fast condensation in the cold zone[13] effectively prevented the formation of crystalline phases, thus accounting for dissolution of S_6-$C_{60}(CF_3)_{12}$ in benzene.

It, therefore, becomes evident that both selective formation and poor (kinetic) solubility of S_6-$C_{60}(CF_3)_{12}$ are due to its unique crystal packing, *i.e.* unavailability of triphenylene fragments both for further addition and for interaction with solvent. The selectivity effects may thus be quite sensitive to a large number of subtle effects that influence crystallization kinetics in the reaction ampoules. Fast formation of high-quality crystals of S_6-$C_{60}(CF_3)_{12}$ in the initial period of synthesis can be expected to promote further selective accumulation of this isomer; in the opposite case it will form only on an equal basis with the rest of the possible isomers.

In conclusion, one novel isomer of $C_{60}(CF_3)_{12}$ and two novel isomers of $C_{60}(CF_3)_{14}$ have been isolated and characterized by means of X-ray crystallography. The observed differences in formation conditions of these isomers, particularly in starting material employed, provide valuable insights into trifluoromethylation pathways. It now becomes more clear that milder reaction conditions may increase the role of structural relations between precursors and products. The growing number of $C_{60}(CF_3)_n$ isomers with known molecular structures now provides stronger hope for better understanding of complex trifluoromethylation routes.

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Notes and references

‡ *Crystal data*: synchrotron X-ray data for all crystals were collected at 100 K at the BL14.1 or 14.2 at the BESSY storage ring (PSF at the Free University of Berlin, Germany) using a MAR225 detector, $\lambda = 0.9050$ Å. $C_{60}(CF_3)_{12}$-III: orthorhombic, *Pbca*, $a = 17.2319(5)$, $b = 16.5102(3)$, $c = 17.6880(5)$ Å, $V = 5032.3(2)$ Å^3, $D_c = 2.044$ g cm^{-1}, $Z = 4$. Anisotropic refinement with 4219 reflections and 546 parameters yielded a conventional $R_1(F) = 0.095$ for 3676 reflections with $I > 2\sigma(I)$ and $wR_2(F^2) = 0.232$ for all reflections. One CF_3 group is disordered between four positions, which reflects overlap of similar double-skew-pyramidal isomers with different relative positions of pyramids on the poles. $C_{60}(CF_3)_{14}$-I: monoclinic, $P2_1/c$, $a = 11.2190(2)$, $b = 13.8820(2)$, $c = 35.5411(5)$ Å, $\beta = 90.544(1)°$, $V = 5535.0(2)$ Å^3, $D_c = 2.024$ g cm^{-1}, $Z = 4$. Anisotropic refinement with 8031 reflections and 1111 parameters yielded a conventional $R_1 = 0.152$ for 6826 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.358$ for all reflections. The crystal showed twinning (β near to 90°). The molecule is strongly disordered due to overlap of two enantiomers. $C_{60}(CF_3)_{14}$-II: triclinic, $P1$, $a = 11.1180(3)$, $b = 11.1525(3)$, $c = 12.2892(3)$ Å, $\alpha = 69.872(1)$, $\beta = 70.133(1)$, $\gamma = 76.892(1)°$, $V = 1335.12(6)$ Å^3, $D_c = 2.098$ g cm^{-1}, $Z = 1$. Anisotropic refinement with 8341 reflections and 1046 parameters yielded a conventional $R_1 = 0.072$ for 8015 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.187$ for all reflections. CCDC 652165–652167. For crystallographic data in CIF format see DOI: 10.1039/b709684d

§ The theoretical survey included all the structures of $C_{60}(CF_3)_{12}$ and $C_{60}(CF_3)_{14}$ free of *ortho*-$C_6(CF_3)_2$ fragments and formally constructable of 6 or 7 *para*-$C_6(CF_3)_2$ hexagons. The set of $C_{60}(CF_3)_{12}$ isomers was further extended by all possible isomers with two skew-pentagonal-pyramids. Preliminary geometry optimization of 10172 generated $C_{60}(CF_3)_{12}$ isomers and 7889 $C_{60}(CF_3)_{14}$ isomers was carried out at the AM1 level of theory with the use of the PC-GAMESS software.[14] The most stable $C_{60}(CF_3)_{12}$ and $C_{60}(CF_3)_{14}$ isomers within the gap of 50 kJ mol^{-1} and 25 kJ mol^{-1}, respectively, were then reoptimized at the DFT level of theory with the use of PRIRODA software,[15] employing an original TZ2P basis set and PBE exchange–correlation functional.[16]

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