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Synthesis and characterization of difluoromethylene-homo[60]fullerene, $C_{60}(CF_2)$

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Refluxing of the *o*-DCB solution of C_{60} with $CF_2ClCOONa$ and 18-crown-6 leads to formation of $C_{60}(CF_2)_n$ (*n* = 1–3); the monoadduct $C_{60}(CF_2)$ has been found to consist of the main [6,6]- and minor [5,6]-isomers, both having an open structure.

In spite of considerable advances in synthesis and characterization of fluoro- and trifluoromethylfullerenes,[1,2] difluoromethylene adducts have so far remained essentially missing from a large family of fullerene-based fluorocarbons. At the same time, CCl_2, CBr_2, and CI_2 derivatives have already been described in the literature.[3–5] Depending on the reaction conditions and dihalocarbene involved, one can obtain either methanofullerenes with cyclopropane fused to the carbon cage or homofullerenes, *i.e.* products of insertion of a CR_2 bridging group into a C–C bond. Methanofullerenes usually form upon addition to a double [6,6]-bond, while homofullerenes generally result from cleavage of a single [5,6]-bond. So far, all the available dihalomethylene fullerene derivatives but one have been shown to be [6,6]-closed isomers;[3–5] the only known example of a [5,6]-open isomer is $C_{70}(CCl_2)$.[6] To date, no information has been reported regarding the two other possible types of dihalocarbene (CCl_2, CBr_2, CI_2) monoaddition, *i.e.* formation of [6,6]-open and [5,6]-closed isomers, although for polyadducts of some other types of fullerene derivatives [6,6]-bond cleavage has nevertheless been observed.[7,8]

In the present work we report preparation of a mixture of difluoromethylenated fullerenes $C_{60}(CF_2)_n$ (*n* = 1–3) and isolation and characterization of the monoadduct $C_{60}(CF_2)$. The synthetic methodology employed included refluxing of C_{60} (125 mg, 0.174 mmol) with $CF_2ClCOONa$ (80 mg, 0.525 mmol) and 18-crown-6 (15 mg, 0.057 mmol) in *o*-dichlorobenzene (250 ml) for 1 hour. This was found to result in *ca.* 55% conversion of C_{60} and 45% yield of the monoadduct. The yield was estimated by the integration of HPLC traces. After some further loss of the desired product at the HPLC separation stage, *ca.* 24 mg (19% yield) of purified $C_{60}(CF_2)$ were obtained.

The negative ion MALDI mass spectrum (Fig. 1, *trans*-2-(3-(4-*t*-butylphenyl)-2-methyl-2-propenylidene)malononitrile (DCTB) matrix) of the crude synthetic mixture contains four very prominent peaks due to $C_{60}(CF_2)_n$ adducts (*n* = 1–3) and to unreacted [60]fullerene. The isolation of the individual adducts was carried out by means of HPLC (10 mm × 25 cm Cosmosil Buckyprep column, 4.6 ml min^{-1} flow rate, toluene eluent). The fraction eluted at 8.7 min (C_{60}: 8.3 min) was found to comprise $C_{60}(CF_2)$ monoadduct as its major component. This fraction was then subjected to further HPLC purification (toluene–hexane, 4 : 1 v/v) and the fractions collected were subsequently analyzed by HPLC (4.6 mm × 25 cm Cosmosil Buckyprep column, 2 ml min^{-1} flow rate, toluene–hexane, 3 : 2 v/v). The chromatographic and MALDI data for the $C_{60}(CF_2)$ fraction thus obtained are given in Fig. 2. According to the MALDI mass spectrum, it contains only a minor amount of $C_{60}(CF_2)_2$ impurity, which proved difficult to completely eliminate.

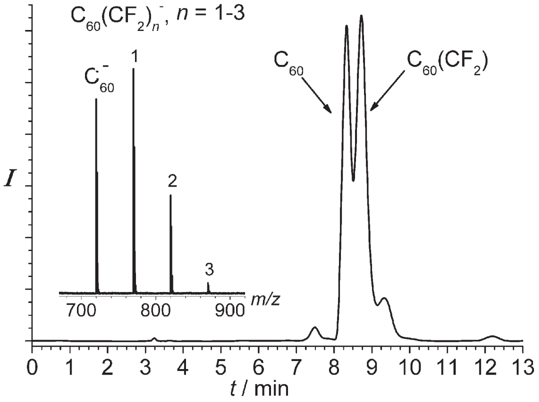

Fig. 1 HPLC trace and MALDI mass spectrum of the crude $C_{60}(CF_2)_n$.

The ^{19}F NMR spectrum of $C_{60}(CF_2)$ presented in Fig. 3a (Bruker Avance 400, 376.5 MHz; benzene-d_6/*o*-DCB; C_6F_6) contains a singlet at δ_F −119.20 ppm and a signature of an AB spin system (enlarged in the right hand inset) with δ_F −121.30 ppm and −121.64 ppm and J_{FF} = 181 Hz, as found on the basis of multiplet modeling, the integral intensity ratio between the singlet peak and the AB signals being *ca.* 9.5 : 1. The observed chemical shifts fall into a range typical for a CF_2 group but are well upfield from what can be expected for a CF_2Cl moiety. A homonuclear coupling constant of such magnitude is also typical for a CF_2 group with slightly inequivalent fluorine atoms. We attribute both singlet peak and AB signals to the two isomers of $C_{60}(CF_2)$ but not to the traces of $C_{60}(CF_2)_2$ on the basis of the following MALDI observations: a) although some of our preliminary syntheses that were carried out with the use of a more time-consuming crown ether-free technique resulted in higher relative abundance of the "AB system" compound (up to 60% of the main signal intensity in the NMR spectra), no increase of the relative intensity of the

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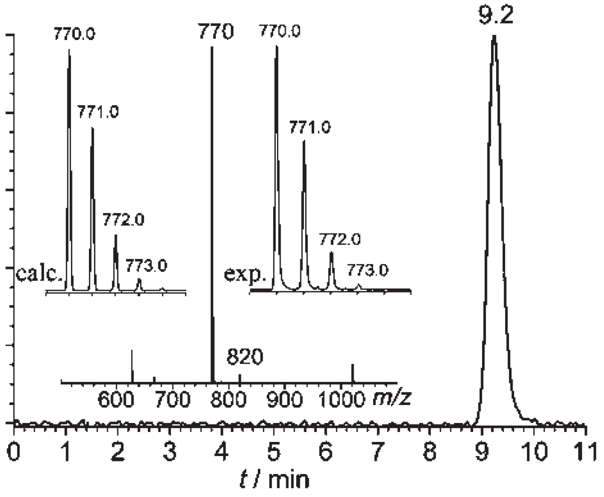

Fig. 2 HPLC trace and MALDI mass spectrum of the purified $C_{60}(CF_2)$. Experimental and calculated isotopic distributions are given in the insets.

$C_{60}(CF_2)_2$ peaks in the MALDI spectra was observed; b) absolutely no fragmentation of $C_{60}(CF_2)_2$ from the respective isolated chromatographic fraction has been observed both in positive and negative ion MALDI spectra. Of the two possible carbene addition patterns, [6,6]-$C_{60}(CF_2)$ contains equivalent fluorine atoms coupled by a mirror plane, while in [5,6]-$C_{60}(CF_2)$ there is no symmetry equivalence of these atoms and hence a certain magnetic inequivalence could be expected. Thus, the main singlet signal observed in the NMR spectrum is obviously due to the more symmetric [6,6]-isomer, whereas the AB system is due to the [5,6]-structure.

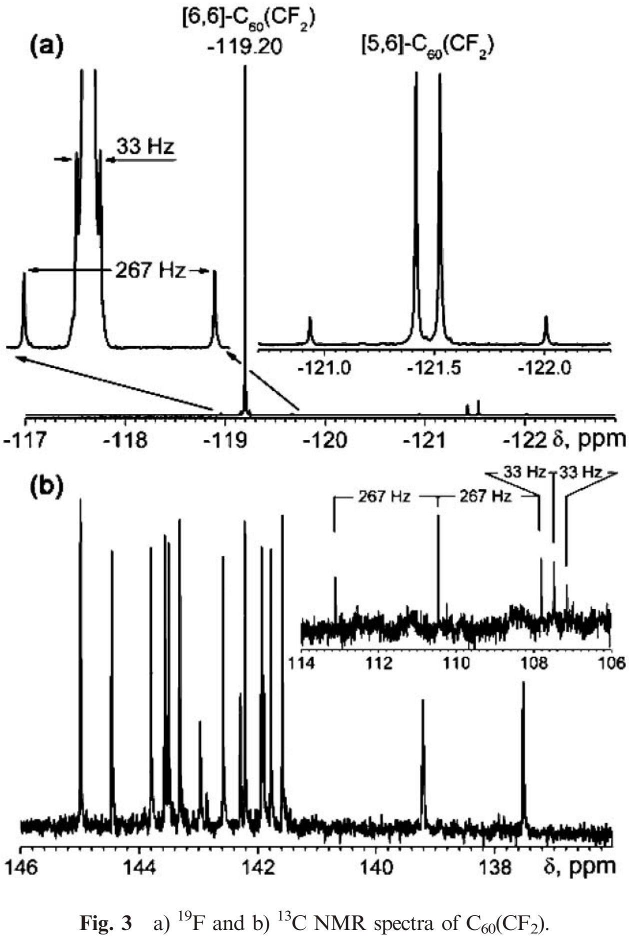

Fig. 3 a) ^{19}F and b) ^{13}C NMR spectra of $C_{60}(CF_2)$.

It also appeared possible to derive some heteronuclear ^{19}F–^{13}C coupling constants for the [6,6]-$C_{60}(CF_2)$ from the positions of the satellite signals to the main peak in the ^{19}F NMR spectrum. The $^{1}J_{C-F}$ coupling constant in the $-CF_2-$ group was found to be 267 Hz while the weaker $^{2}J_{C-F}$ coupling with the C–(CF_2) carbon atoms was found to be of 33 Hz magnitude (see left hand inset to Fig. 3a). The satellite signals are somewhat asymmetric with respect to the main signal, which is probably due to the isotope effect in chemical shifts.[9] The same coupling constants were reproduced in the ^{13}C NMR spectrum presented in Fig. 3b (Bruker Avance 400, 100.6 MHz; benzene-d_6/*o*-DCB). The spectrum contains 16 singlet signals in the typical sp^2 fullerene range between 137 and 145 ppm, three of them being of roughly halved intensity with respect to the other 13, plus five signals between 105 and 113 ppm. Careful analysis of the latter signals revealed that they represent two triplets with J_{CX} of 267 Hz and 33 Hz centered at 110.5 ppm and 107.5 ppm, respectively, with coincidentally overlapping upfield component of the first and downfield component of the second triplet. Thus, these two triplets can be unambiguously attributed to the CF_2-carbon atom and to the adjacent C–(CF_2) carbon atoms, respectively. Although it is impossible to state with confidence that the strongest solvent signals between 126 and 133 ppm did not mask any weaker signals of interest, there is a perfect coincidence between the experimental observations and the theoretically expected number of signals for the [6,6]-$C_{60}(CF_2)$ molecule of C_{2v} symmetry, namely one for CF_2-carbon, one more for the neighboring C–(CF_2) atoms from the carbon cage and $13 \times 2C + 3 \times 1C$ signals for the rest of the C_{60} cage. Any signals due to [5,6]-$C_{60}(CF_2)$ could not be observed because of the much lower abundance and lower symmetry of the said isomer and not very high signal-to-noise ratio of the spectrum.

It is noteworthy that the observed chemical shift of the C–(CF_2) carbon atoms of 107.5 ppm was markedly downfield from the region typical for cyclopropane sp^3 carbon atoms, *i.e.* 20–40 ppm. This observation strongly suggests sp^2 nature of these atoms and, consequently, an unprecedented [6,6]-homofullerene structure of the [6,6]-$C_{60}(CF_2)$. In order to compare this suggestion with theoretical predictions, quantum chemical calculations at the DFT level of theory have been carried out (PRIRODA software,[10] RI approach, PBE exchange-correlation functional and an original basis set of triple zeta quality[11]). The computational results have confirmed that both [6,6]- and [5,6]-$C_{60}(CF_2)$, unlike $C_{60}(CCl_2)$ isomers also taken into consideration, have only open forms characterized by C_{2v} and C_s symmetry, respectively, but no potential energy minima corresponding to the closed cyclopropane geometries. Such an observation, although expected for the [5,6]-isomer, is very unusual for the [6,6]-one since, as we mentioned, all other [6,6]-$CHal_2$ fullerene derivatives are known to have methanofullerene rather than homofullerene structure.[3] Indeed, we found the DFT calculated distance between the C–(CCl_2) carbon atoms in the [6,6]-$C_{60}(CCl_2)$ to be 1.65 Å, which corresponds to a single C–C bond, though considerably elongated. At the same time, the similar distances in $C_{60}(CF_2)$ turned out to be 2.06 Å for the cleaved [6,6]-bond and even 2.23 Å for the [5,6]-bond. Thus, CF_2 derivatives of C_{60} are unique among other $CHal_2$

fullerene compounds that reveal a methanofullerene rather than a homofullerene addition pattern.[3] One should note, however, that the cross-section of the potential energy surface along the cleaved [6,6]-bond stretching coordinate (with the other degrees of freedom being instantly optimized) is unusually flat: in the range of 1.65–2.20 Å the energy remains within the gap of 6 kJ mol^{-1} from the energy minimum.

The [6,6]-open and [5,6]-open isomers of $C_{60}(CF_2)$ were found to be of comparable stability. Although relocation of double bonds into pentagons is generally anticipated to be energetically unfavorable,[12] redistribution of the π-electron density of the cleaved [6,6]-bond to the adjacent pentagonal rings makes the [6,6]-isomer only 3.2 kJ mol^{-1} less stable than the [5,6]-isomer. An interesting feature of [6,6]-$C_{60}(CF_2)$, as revealed by our calculations, is the possibility of controlling the cage opening by means of electronic excitation and ionization. Both the positively charged state and several lowest excited singlet states exhibit a closed configuration with a C–C distance of 1.67 Å, whereas negative charging leads to further cage opening to 2.23 Å.

Additional confirmation of the open structure of the synthesized compound is provided by the UV/Vis spectrum (Fig. 4). It appears to be very similar to that of pristine C_{60} and known homofullerenes.[3,10] The spectrum does not contain any characteristic feature at 424–432 nm, which is typical for closed isomers, *e.g.* in epoxide $C_{60}O$, cyclopropanated $C_{60}(CH_2)$,[13] and dihalomethylene[60]fullerenes $C_{60}(CCl_2)$,[4] $C_{60}(CBr_2)$.[5]

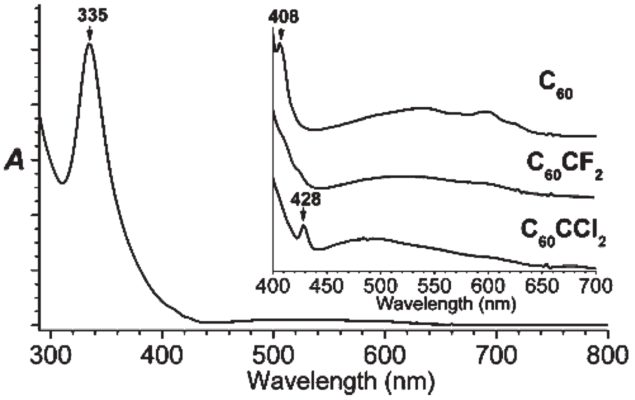

Fig. 4 UV/Vis-spectrum of $C_{60}(CF_2)$ toluene solution.

IR study (KBr) of $C_{60}(CF_2)$ provides additional evidence in favor of the predominant formation of the [6,6]-isomer based on the comparison of the experimental spectrum (Fig. 5, center) and the calculated spectra for [6,6]- (Fig. 5, bottom) and [5,6]-structures (Fig. 5, top). As one can see, the spectrum calculated for the [6,6]-isomer shows a better agreement with the experimental one, though the experimental IR intensities are not reproduced very well. Additional weaker bands in the experimental spectrum are possibly due to admixture of the [5,6]-isomer.

Attempts to determine the molecular structure of $C_{60}(CF_2)$ by X-ray crystallography have not been entirely successful. Crystallization from toluene, chloroform and *o*-xylene resulted in the formation of crystals where the molecules were strongly disordered. Crystallization from mesitylene or 1,2,4-trichlorobenzene gave crystals with ordered solvent molecule and disordered $C_{60}(CF_2)$. In crystals with the composition $C_{60}(CF_2){\cdot}C_6H_3Cl_3$, the $C_{60}(CF_2)$ molecules appeared to be disordered between two positions, so that reliable determination of the C…C distance was not possible.

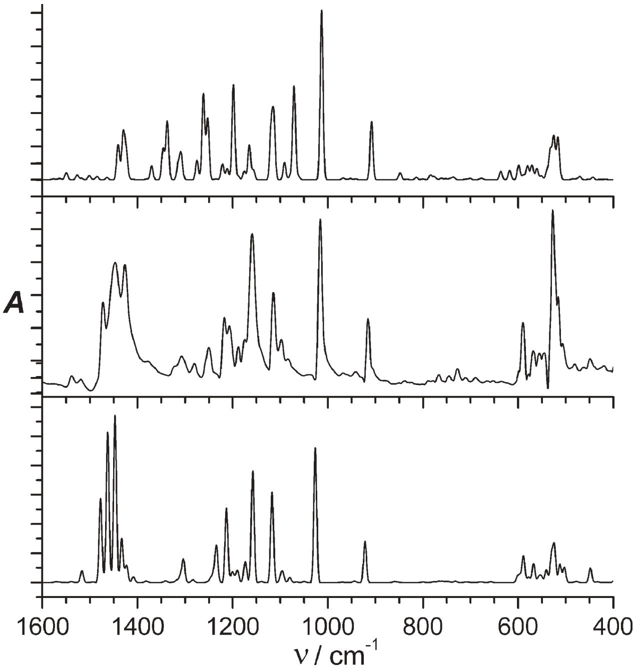

Fig. 5 The experimental IR spectrum of $C_{60}(CF_2)$ (center) and calculated spectra for [5,6] (top) and [6,6] (bottom) isomers.

Summarizing all the experimental and theoretical data for the considered compound, we report the formation of the first difluoromethylene derivative of C_{60}, $C_{60}(CF_2)$, which has been proved to be the first homofullerene with a cleaved [6,6]-bond. Further study of difluoromethylene polyadducts is currently underway.

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