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Synthesis and structures of poly(perfluoroethyl)[60]fullerenes: 1,7,16,36,46,49-$C_{60}(C_2F_5)_6$ and 1,6,11,18,24,27,32,35-$C_{60}(C_2F_5)_8$

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The high-temperature reaction of C_{60} and C_2F_5I produced poly(perfluoroethyl)fullerenes with unprecedented addition patterns.

Our recent work has shown that both [60]- and [70]fullerene can be trifluoromethylated with CF_3I at 400–500 °C to yield 10+ mg amounts of compositionally and isomerically pure poly(trifluoromethyl)fullerenes, including the crystallographically characterized C_1 isomers of $C_{60}(CF_3)_{10}$[1] and $C_{70}(CF_3)_{10}$.[1,2] For the particular isomer of $C_{70}(CF_3)_{10}$ studied, the yield was 27% based on converted C_{70} (*i.e.*, 12 mg of 95% pure C_1-$C_{70}(CF_3)_{10}$ was isolated).[1] Significantly, neither addition pattern had been investigated by any previous computational study of isomers of $C_{60}X_{10}$ or $C_{70}X_{10}$.

In addition to their potential value as thermally[1,3] and electrochemically stable[4] acceptor moieties for photovoltaic devices, these and other[5–8] poly(trifluoromethyl)fullerenes exhibit significant NMR ${}^{6,7}J_{FF}$ coupling between CF_3 groups that are mutually *meta* and/or *para* on $C_6(CF_3)_2$ hexagons. This coupling is predominantly mediated by through-space Fermi-contact interactions between lone-pair electrons on the F atoms of proximate CF_3 groups.[1,9,10] In many cases, the $C_6(CF_3)_2$ hexagons share C–C(CF_3) edges, forming a continuous ribbon. In some cases, 1D and 2D ${}^{19}F$ NMR spectra have revealed that some of the CF_3 groups in some $C_{60,70}(CF_3)_n$ isomers are arranged on isolated $C_6(CF_3)_2$ hexagons. For example, one of the C_1 isomers of $C_{60}(CF_3)_{10}$ has two CF_3 groups on an isolated *para*-$C_6(CF_3)_2$ hexagon and the remaining eight on a ribbon of seven *meta*- and/or *para*-$C_6(CF_3)_2$ edge-sharing hexagons.[1]

Compounds with perfluoroethyl groups, such as $C_{60}(C_2F_5)_n$ and $[C_{60}(C_2F_5)]_2$, were isolated as mixtures (n = 9–16) or generated in solution ($C_{60}(C_2F_5)$/$[C_{60}(C_2F_5)]_2$) in the seminal work by the DuPont group by treating C_{60} with C_2F_5I or perfluoropropionyl peroxide.[11] We now report that the high-temperature reaction of C_{60} with C_2F_5I gas followed by HPLC purification of the cold-zone condensate yields, among other compounds, milligram amounts of single C_1 isomers of $C_{60}(C_2F_5)_6$ and $C_{60}(C_2F_5)_8$ (*i.e.*, the title compounds).† In addition to demonstrating the efficacy of hot tube reactions between fullerenes and perfluoroalkyl iodides other than CF_3I, these results are also significant because the two new compounds exhibit C_{60} addition patterns that are unprecedented.

The two compounds were structurally characterized by X-ray diffraction.‡ Drawings of each are shown in Fig. 1. Neither the molecules nor the individual C_2F_5 groups exhibit any significant disorder. The lack of conformational disorder of the C_2F_5 groups about their C_{cage}–CF_2 bonds is especially remarkable since the four isolated *para*-$C_6(C_2F_5)_2$ hexagons in the two structures have their perfluoroethyl CF_3 moieties positioned over both adjacent pentagons and adjacent hexagons. This demonstrates that both types of staggered conformations are possible within a given molecule.

The "*p,p,p*" addition pattern in 1,7,16,36,46,49-$C_{60}(C_2F_5)_6$ is unprecedented for $C_{60}X_6$ derivatives and, to our knowledge, has not been investigated computationally by any fullerene theorist. It

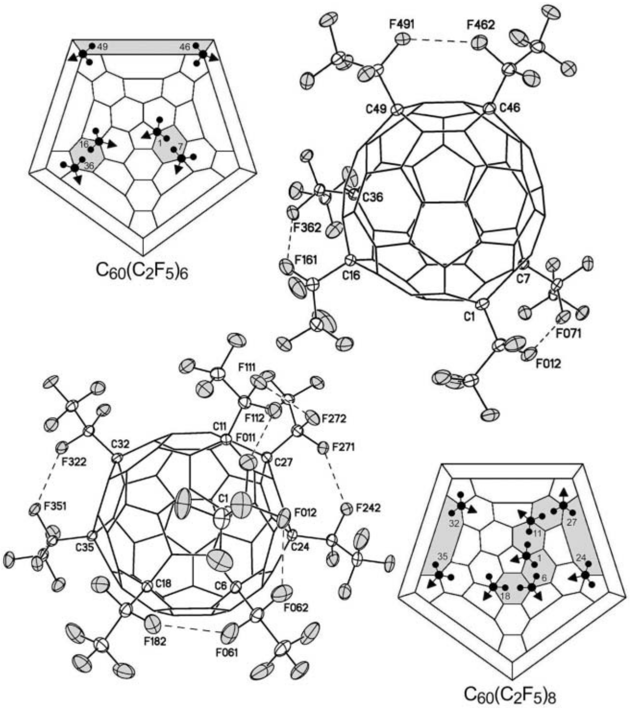

Fig. 1 Drawings (50% probability ellipsoids where shown) of 1,7,16,36,46,49-$C_{60}(C_2F_5)_6$ and 1,6,11,18,24,27,32,35-$C_{60}(C_2F_5)_8$. The larger and smaller circles in the Schlegel diagrams represent CF_2 carbon and fluorine atoms, respectively, and the triangles represent CF_3 groups. The C_2F_5 groups on C1, C6, C11, and C27 in $C_{60}(C_2F_5)_8$ are not as perfectly staggered as shown in the idealized Schlegel diagram.

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consists of three isolated *para*-$C_6(C_2F_5)_2$ hexagons. The esd's for individual cage C–C and C–F bonds are 0.004 and 0.003/0.004 Å, respectively. The conformations around the $F_3C–CF_2(C_{60})$ and $(CF_3)F_2C–C_{cage}$ bonds are staggered, leading to a relatively planar C–F···F–C trapezoid formed by CF_2 groups in each *para*-$C_6(C_2F_5)_2$ hexagon that are similar to the C–F···F–C trapezoids formed by staggered CF_3 groups in the *para*-$C_6(CF_3)_2$ hexagons in $C_{60}(CF_3)_{10}$ and $C_{70}(CF_3)_{10}$.[1,2] The F161···F362, F071···F012, and F491···F462 distances shown in Fig. 1 are 2.585(3), 2.577(3), and 2.579(3) Å, respectively. The shortest such distances involving a terminal, end-of-ribbon CF_3 group in $C_{60}(CF_3)_{10}$ and $C_{70}(CF_3)_{10}$ are 2.640(3), and 2.570(2) Å, respectively.[1,2]

The addition pattern for 1,6,11,18,24,27,32,35-$C_{60}(C_2F_5)_8$ consists of an isolated *para*-$C_6(C_2F_5)_2$ hexagon and a *para–para–para–meta–para* ribbon of five edge-sharing $C_6(C_2F_5)_2$ hexagons. The esd's for nearly all of the individual cage C–C and C–F bonds are 0.003 Å. The four C_2F_5 groups attached to C1, C6, C11, and C27 have conformations with respect to the C_{60} cage that are midway between staggered and eclipsed, in contrast to the staggered conformation of the C_2F_5 groups at either terminus of the ribbon or in the isolated $C_6(C_2F_5)_2$ hexagons in either structure. In addition to the expected F···F contacts between CF_2 fluorine atoms across the one *meta*- and four *para*-$C_6(C_2F_5)_2$ hexagons on the p^3mp ribbon, there are four additional F···F contacts $\leqslant 3.0$ Å involving the perfluoroethyl CF_3 moieties, as shown in Fig. 2.

The p^3mp ribbon in $C_{60}(C_2F_5)_8$ clearly demonstrates that the absence of such a ribbon in *p,p,p*-$C_{60}(C_2F_5)_6$ is not because C_2F_5 groups are too bulky to allow such ribbons to form. In this regard, we note that *p,p,p*-$C_{60}(C_2F_5)_6$ is not the only isomer of $C_{60}(C_2F_5)_6$ in the cold-zone-condensed reaction product, and it may not be the most stable isomer that has this composition. It is only the first $C_{60}(C_2F_5)_6$ isomer we have purified to $\geqslant 90\%$ and therefore the first to be structurally characterized. Interestingly, a reaction of C_{60} with AgTFA at 300 °C was reported to produce 13 isomers of $C_{60}(CF_3)_6$, and none of those that were charaterized by ^{19}F NMR had spectra consistent with three isolated pairs of proximate CF_3 groups ($TFA^- = CF_3CO_2^-$).[7]

When the mixture of $C_{60}(CF_3)_n$ products of a different reaction of C_{60} and AgTFA at 280 °C was heated to 500 °C under vacuum, 1D and 2D ^{19}F NMR spectra and DFT calculations revealed that the abundant $C_{60}(CF_3)_6$ isomer in the HPLC-purified sublimate was a C_1 isomer with a ribbon of five edge-sharing $C_6(CF_3)_6$ hexagons (presumably some isomers reported in ref. 7 that are formed at 280–300 °C rearrange to fewer, more stable isomers upon heating to 500 °C).[5] Significantly, the p^3mp pattern of the ribbon of edge-sharing $C_6(CF_3)_2$ hexagons in $C_{60}(CF_3)_6$ predicted to be the most stable by DFT calculations,[6] also shown in Fig. 2, is identical to the p^3mp pattern of the ribbon of edge-sharing $C_6(C_2F_5)_2$ hexagons in the structure of *p,p*^{3}*mp*-$C_{60}(C_2F_5)_8$.

Twenty-one isomers of $C_{60}(CF_3)_8$ were identified from the aforementioned 300 °C C_{60}–AgTFA reaction mixture.[7] The ^{19}F NMR spectrum of one of these (the major isomer in "Fraction 13") exhibited four quartets and four quartets of quartets. The authors of that study concluded that this isomer of $C_{60}(CF_3)_8$ has an isolated pair of CF_3 groups on *adjacent* cage carbon atoms and six CF_3 groups on a string of six *contiguous* cage carbon atoms.[7] However, DFT calculations have shown that $C_{60,70}(CF_3)_n$ derivatives with CF_3 groups on adjacent cage carbon atoms are significantly less stable than alternative structures derived from 1,4 additions.[1,2,6] Based on this, on the structures and NMR spectra of *pmp*^{3}*mpmp*-$C_{60}(CF_3)_{10}$[1] and p^7mp-$C_{70}(CF_3)_{10}$,[1,2] and on the two structures reported herein, it is more likely that the major isomer in their Fraction 13 has an addition pattern similar to, if not congruent with, the *p,p*^{3}*mp*-$C_{60}(C_2F_5)_8$ addition pattern (alternatively, it may be one of several possible *p,pmpmp* isomers). Therefore, p^3mp-$C_{60}(C_2F_5)_8$ may be the second, and not the first, $C_{60}X_8$ derivative with this addition pattern.

The ^{19}F NMR spectrum of *p,p,p*-$C_{60}(C_2F_5)_6$ at −50 °C is shown in Fig. 3. The six narrow resonances between δ −80.2 and −81.2 are assigned to the six CF_3 groups. The absence of observable coupling between the CF_3 and CF_2 groups is consistent with $^3J_{FF}$ values of ~0 Hz for a wide variety of perfluoroalkyl groups. Furthermore, the narrow linewidths of the CF_3 resonances at all temperatures strongly suggest rapid exchange between the two staggered conformers for each C_2F_5 group that have a CF_2

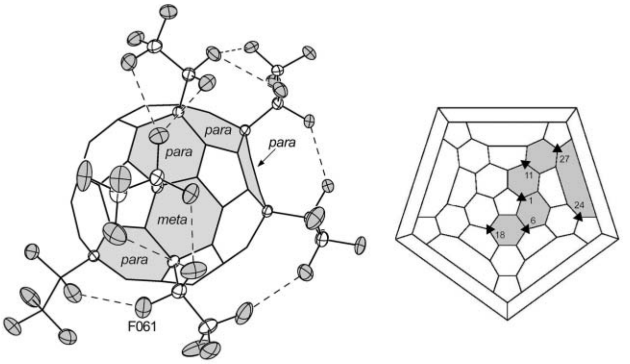

Fig. 2 Left: Part of the structure of 1,6,11,18,24,27,32,35-$C_{60}(C_2F_5)_8$ (*p,p*^{3}*mp*-$C_{60}(C_2F_5)_8$) that includes the p^3mp ribbon of six $C_6(C_2F_5)_2$ edge-sharing hexagons (50% probability ellipsoids where shown). The F···F distances shown range from 2.518(3) to 2.939(3) Å. The F322···F352 distance in the isolated $C_6(C_2F_5)_2$ hexagon (not shown) is 2.683(3) Å. Right: Schlegel diagram for the DFT-predicted[6] stable isomer of p^3mp-$C_{60}(CF_3)_6$.

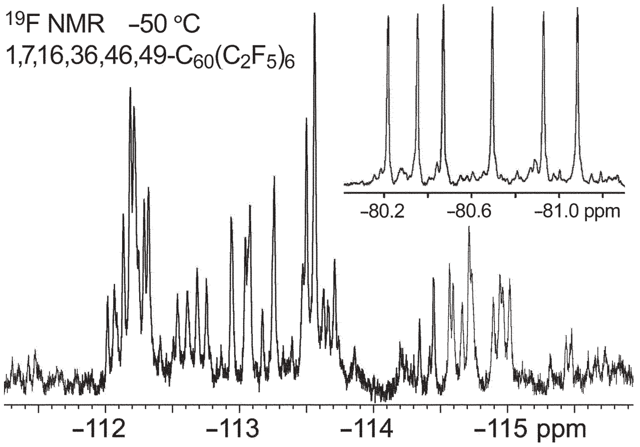

Fig. 3 ^{19}F NMR spectrum of *p,p,p*-$C_{60}(C_2F_5)_6$ (376 MHz, $C_6D_5CD_3$–C_6F_6, −50 °C; $\delta(C_6F_6)$ int. std. −164.9). Except for minor changes in δ values and relative intensities, the spectrum was unchanged at 25 °C and 75 °C.

fluorine atom positioned over the shared hexagon. The complex CF_2 region from δ −112 to −116 is assigned to three superimposed ABCD patterns for the three pairs of through-space-coupled (and conformationally averaged) CF_2 groups and cannot be deconvoluted at this time. The ^{19}F NMR spectrum of *p,p*^{3}*mp*-$C_{60}(C_2F_5)_8$ (not shown) is even more complex. Nevertheless, these spectra contain a wealth of $^{\geqslant 6}J_{FF}$ coupling information that will be of value, once they are better understood, to NMR theorists[10] and other chemists/biochemists[12] interested in through-space NMR coupling. We are continuing to investigate these and other poly(perfluoroalkyl)fullerenes by variable-temperature 1D and 2D ^{19}F NMR spectroscopy and single-crystal X-ray crystallography for this reason as well as because they (i) may continue to reveal new, unanticipated features of fullerene addition regiochemistry and (ii) may eventually find application in one or more electrooptical devices.

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Notes and references

† In a typical synthesis, a finely ground 90 mg portion of C_{60} (Hoechst, 99.9+% Super Gold Grade) mixed with copper powder was heated in a glass tube to 400–430 °C under an atmosphere of argon and then treated with gaseous C_2F_5I (Sigma-Aldrich, 97%) for 2–4 h [**CAUTION**: C_2F_5I decomposes above 300 °C when exposed to air and produces toxic HF, HI, COF_2, and I_2; handle only in a well-ventilated fume hood]. The mixture of dark brown $C_{60}(C_2F_5)_n$ compounds that condensed inside the glass tube in the cold zone was dissolved in toluene and processed by HPLC (20 mm I.D. × 250 mm long Cosmosil Buckyprep column (Nacalai Tesque, Inc.), 300 nm UV detector, hexane eluent, 18 mL min^{-1} flow rate). Among other products that have not yet been fully characterized were 2–3 mg each of 90+% pure 1,7,16,36,46,49-$C_{60}(C_2F_5)_6$ and *ca.* 80% pure 1,6,11,18,24,27,32,35-$C_{60}(C_2F_5)_8$, which were recrystallized from toluene to afford single crystals suitable for diffraction. Detailed descriptions of the synthetic apparatus and the chromatographic purification procedure are given in ref. 1.

‡ *Crystal data.* For both compounds, measurements were made on a Bruker SMART diffractometer (Mo-Kα, λ = 0.71073 Å; graphite monochromator; T = 100(2) K). An empirical absorption correction was applied using the SADABS program.[13] Structures were solved using direct methods and refined using full-matrix least squares on F^2 using SHELXTL.[14] 1,7,16,36,46,49-$C_{60}(C_2F_5)_6$, $C_{72}F_{30}$, M = 1434.72, triclinic, space group $P\bar{1}$ (no. 2), a = 9.8807(8), b = 14.6719(13), c = 16.5397(14) Å, α = 89.944(2), β = 84.994(2), γ = 75.915(2)°, V = 2316.3(3) Å^3, Z = 2, ρ_{calc} = 2.057 Mg m^{-3}, μ = 0.205 mm^{-1}, $2\theta_{max}$ = 56.58°, final R indices ($I > 2\sigma(I)$): R_1 = 0.060, wR_2 = 0.173 (22 234 total reflections, 11 001 unique reflections, R_{int} = 0.0280). 1,6,11,18,24,27,32,35-$C_{60}(C_2F_5)_8$, $C_{76}F_{40}$, M = 1672.76, monoclinic, space group $P2_1/c$ (no. 14), a = 18.9559(18), b = 13.5701(13), c = 21.425(2) Å, β = 98.424(2)°, V = 5451.7(9) Å^3, Z = 4, ρ_{calc} = 2.038 Mg m^{-3}, μ = 0.215 mm^{-1}, $2\theta_{max}$ = 56.72°, final R indices ($I > 2\sigma(I)$): R_1 = 0.052, wR_2 = 0.155 (51 080 total reflections, 13 374 unique reflections, R_{int} = 0.0404). CCDC 284722 and 284773. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513477c

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