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High-Temperature Synthesis of the Surprisingly Stable C_1-$C_{70}(CF_3)_{10}$ Isomer with a *para*^{7}–*meta*–*para* Ribbon of Nine $C_6(CF_3)_2$ Edge-Sharing Hexagons**

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With one exception, isolable $C_{70}X_{10}$ derivatives, which include $C_{70}H_{10}$,[1] $C_{70}Me_{10}$,[2] $C_{70}Ph_{10}$,[3] $C_{70}Ph_9(OH)$,[4] $C_{70}Ph_8(OH)_2$,[4] $C_{70}Cl_{10}$,[5] and $C_{70}Br_{10}$,[6] have the "equatorial-belt" C_s structure shown in Figure 1, with the ten substituents[7] positioned on a closed loop of ten edge-sharing hexagons, nine of which are *para*-C_6X_2 fragments and one of which is an *ortho*-C_6X_2 fragment (p^9o(loop)).[8–10] The exception is the recently described compound $C_{70}(t\text{BuOO})_{10}$, which has the C_2 structure also shown in Figure 1 with an all-*para* ribbon of nine edge-sharing $C_6(t\text{BuOO})_2$ hexagons (p^9), presumably because the *t*BuOO groups are too large to be on adjacent cage C atoms.[11]

We recently reported the synthesis of batches (more than 10 mg) of a single isomer of $C_{70}(CF_3)_{10}$ at 470 °C in 27 % overall yield based on converted C_{70}.[12] A combination of 1D- and 2D-COSY ^{19}F NMR spectroscopy showed that this derivative has C_1 symmetry and, by analogy with the structure of a spectroscopically similar C_1 isomer of $C_{60}(CF_3)_{10}$, most probably has its ten CF_3 groups arranged in the form of a ribbon of nine *meta*-$C_6(CF_3)_2$ and/or *para*-$C_6(CF_3)_2$ edge-sharing hexagons.[12] We now report an X-ray diffraction study of this high-yield, high-temperature C_1-$C_{70}(CF_3)_{10}$ isomer, which demonstrates that the ribbon of hexagons is the

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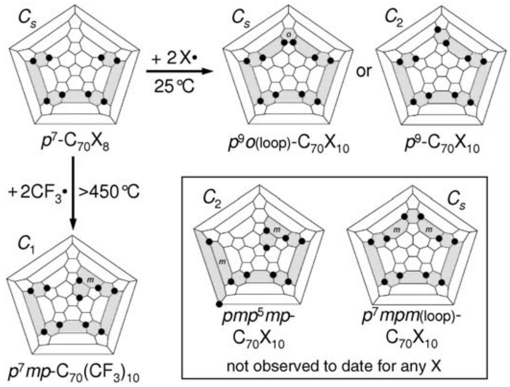

Figure 1. The transformation of C_s-p^7-$C_{70}X_8$, the structure of which has been proven by single-crystal X-ray diffraction (XRD) for X = Me, into either C_s-p^9o(loop)-$C_{70}X_{10}$ (proven by XRD for X = Br; proven by ^{13}C NMR for X = H, Cl, and Ph), C_2-p^9-$C_{70}X_{10}$ (proven by ^{13}C NMR for X = *t*BuOO), or C_1-p^7mp-$C_{70}(CF_3)_{10}$ (proven by XRD; this work). The inset shows the structures of two $C_{70}X_{10}$ isomers that have not yet been observed for any isolable compound. See text for references.

unprecedented C_1-symmetric p^7mp ribbon shown in Figure 1. Like the hypothetical C_s-p^9o(loop)- and C_2-p^9-$C_{70}(CF_3)_{10}$ structures, the C_1-p^7mp-$C_{70}(CF_3)_{10}$ structure includes the C_s-p^7-$C_{70}X_8$ motif that has been observed for $C_{70}Me_8$[13] and $C_{70}Ph_8$.[3]

A thermal-ellipsoid plot, excluding the molecule of lattice-bound toluene, is shown in Figure 2. The poly(trifluoromethyl)fullerene itself is not disordered. The CF_3 groups containing C73 and C74 each exhibit a two-fold librational disorder; the other CF_3 groups, including the four CF_3 groups on the two *p*-$C_6(CF_3)_2$ hexagons at opposite ends of the ribbon, exhibit unexceptional F-atom thermal ellipsoids. Distances and angles within the ordered CF_3 groups are normal. The estimated standard deviations (esds) for individual C–C and C–F distances in this structure are all 0.003 Å (except for the C–F distances in the two disordered CF_3 groups), making this one of the most precisely determined C_{70}-containing structures reported to date (the ranges of esd's for C–C bonds within the cage of known structures include 0.002–0.004 Å for two Diels–Alder monoadducts,[14] 0.004–0.006 and 0.006–0.007 Å for $C_{70}(CH_3)_8$[13] and $C_{70}F_{38}$,[15] respectively, and 0.02–0.03 Å for $C_{70}Br_{10}$,[6] $C_{70}(IrCl(PPh_3)_2)$,[16] and $C_{70}(Ru_3(CO)_9)$[17]).

In addition to further supporting[12] our earlier conclusion[18] that fullerene$(CF_3)_n$ compounds in general have their

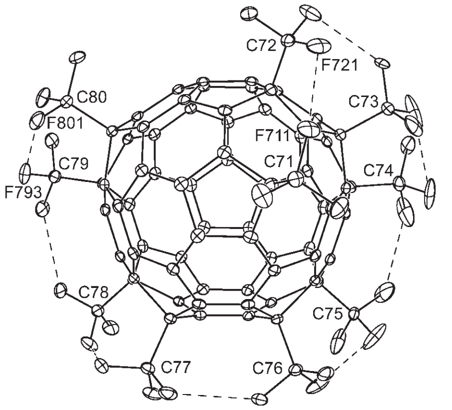

Figure 2. Drawing of C_1-$C_{70}(CF_3)_{10}$ looking down the former C_5 axis of the empty C_{70} cage (50% probability ellipsoids; only one of the two disordered CF_3 conformers is shown for each of the C73 and C74 CF_3 groups). Starting with the C80 CF_3 group, the CF_3 groups are arranged on a *para*^{7}–*meta*–*para* ribbon of $C_6(CF_3)_2$ edge-sharing hexagons. Atoms C71–C80 are connected to the fullerene cage at C25, C10, C1, C4, C19, C41, C60, C69, C66, and C49, respectively. The F801···F793 and F711···F721 distances are 2.570(2) and 2.744(2) Å, respectively.

CF_3 groups arranged on *m*- and *p*-$C_6(CF_3)_2$ hexagons (most of which form a continuous ribbon through edge sharing) and are not arranged on adjacent (i.e., *ortho*) cage C atoms as suggested by others,[19–21] the structure of C_1-$C_{70}(CF_3)_{10}$ has revealed several interesting and unanticipated aspects of $C_{70}X_n$ stereochemistry. In 1999, Clare and Kepert predicted the relative ΔH_f^0 values for a (necessarily) limited number of isomers of $C_{70}X_{10}$ at the AM1 level of theory, including the C_s-p^9o(loop) and C_2-p^9 isomers for X = H, F, Br, Ph, and *t*Bu.[10] They did not consider any $C_{70}X_{10}$ isomer with one or more *m*-C_6X_2 hexagons. Except for X = *t*Bu, the C_s-p^9o(loop) isomer was found to be more stable than the C_2-p^9 isomer for these substituents (Table 1; Schlegel diagrams for the five isomers are shown in Figure 1). However, all isolable C_s-p^9o(loop)-$C_{70}X_{10}$ compounds[1,3–6] and the one isolable C_2-p^9-$C_{70}X_{10}$ compound, $C_{70}(t\text{BuOO})_{10}$,[11] were prepared at 25 °C and may, at least in some cases, be a kinetically stable isomer and not the isomer with the lowest ΔH_f^0 value. On the other hand, C_1-$C_{70}(CF_3)_{10}$ was prepared at 470 °C,[12] a temperature that may be high enough for facile CF_3 migration to occur on the fullerene surface, a process that could conceivably result in the transformation of a less stable isomer to a more stable

Table 1: AM1 relative enthalpies ΔH_f^0 [kJ mol^{-1}] of formation of $C_{70}X_{10}$ isomers.[a]

X	C_s-p^9o(loop)	C_2-p^9	C_1-p^7mp	C_s-p^7mpm(loop)	C_2-pmp^5mp
CF_3	0.0	−14.1	$\underline{-36.2}$[b]	132.0	−17.2
Ph	0.0 [0.0][b]	6.2 [3.1]	$\underline{-16.0}$	156.5	2.8
Br	0.0 [0.0][b]	11.6 [11.6]	$\underline{-2.9}$	145.1	20.6
Cl	$\underline{0.0}$[b]	13.7	0.6	149.7	26.2
H	$\underline{0.0\ [0.0]}$[b]	26.8 [26.9[c]]	14.4	158.4	40.7
F	$\underline{0.0\ [0.0]}$	33.7 [33.7]	20.3	183.9	47.8
*t*BuOO	$\underline{0.0}$	24.7[b]	13.7		
*t*Bu	0.0 [0.0]	$\underline{-230.2\ [-230.0]}$	−202.2		

[a] All values from this work except values in square brackets, which are from reference [10]. The lowest relative ΔH_f^0 value for each composition is underlined. [b] The principal or only isomer observed by X-ray crystallography or ^{13}C NMR spectroscopy. [c] The next most stable structure reported in reference [10], $p^4opopop$(loop)-$C_{70}H_{10}$, had a relative ΔH_f^0 value of 46.4 kJ mol^{-1}.

one. The facile migration of F atoms on the surface of $C_{60}F_n$ isomers at 300–350 °C is well documented.[22]

The relative stabilities of various fullerene$(CF_3)_n$ isomers are determined by at least four factors: 1) the degree of delocalization/aromatization of the remaining fullerene π bonds; 2) the presence or absence of double bonds in pentagons; 3) steric repulsions between proximate substituents; and, in the case of nonlinear polyatomic substituents such as CF_3 groups, 4) the rotational conformation of each substituent with respect to its underlying cage C−C bonds. To examine the possibility that C_1-p^7mp-$C_{70}(CF_3)_{10}$ is truly more stable than the alternative C_s-p^9o(loop) and C_2-p^9 isomers, we also carried out calculations at the AM1 level of theory. The AM1-predicted relative ΔH_f^0 values for five isomers of $C_{70}(CF_3)_{10}$ and selected $C_{70}X_{10}$ derivatives (X = H, F, Cl, Br, Ph, *t*BuOO, and *t*Bu) are also listed in Table 1. (We also optimized the geometry of C_1-p^7mp-$C_{70}(CF_3)_{10}$ at the DFT level of theory for comparison with the X-ray structure.) Note that C_1-p^7mp-$C_{70}(CF_3)_{10}$ is predicted to be 36 kJ mol^{-1} more stable than the C_s-p^9o(loop) isomer and 22 kJ mol^{-1} more stable than the C_2-p^9 isomer, despite the fact that the C_s and C_2 isomers do not have any double bonds in pentagons and the C_1 isomer has several (the three shortest 6–5 junctions in C_1-p^7mp-$C_{70}(CF_3)_{10}$ are C8-C9 (1.347(3) Å X-ray, 1.357 Å DFT), C6-C7 (1.397(3) Å X-ray, 1.403 Å DFT), and C11-C29 (1.391(3) Å X-ray, 1.399 Å DFT)).

The difference in energy between the C_1 and C_2 isomers may be explained by the fact that two bulky CF_3 groups can be farther apart on a p-$C_6(CF_3)_2$ hexagon in the more highly curved polar region of the C_{70} cage than on a relatively flat equatorial hexagon. For example, the $F_3C\cdots CF_3$ distance is 4.412(3) Å for the end-of-ribbon polar p-$C_6(CF_3)_2$ hexagon (i.e., C71···C72) and 3.935(3) Å for the end-of-ribbon equatorial p-$C_6(CF_3)_2$ hexagon (C79···C80); the corresponding DFT distances are 4.502 and 3.992 Å, respectively. Consistent with this, the X-ray and DFT results reveal that every other CF_3 group on the equatorial part of the ribbon of p-$C_6(CF_3)_2$ edge-sharing hexagons in C_1-p^7mp-$C_{70}(CF_3)_{10}$ is partially or very-nearly eclipsed, in contrast to the [60]fullerene derivative C_1-pmp^3mpmp-$C_{60}(CF_3)_{10}$, in which all but one of the CF_3 groups along the ribbon are staggered or nearly so.[12] Note that both of the CF_3 groups on the end-of-ribbon polar hexagon in the structure of C_1-$C_{70}(CF_3)_{10}$ adopt the staggered conformation.

Surprisingly, the relative ΔH_f^0 results in Table 1 suggest that the isolable and well-characterized C_s-p^9o(loop) isomers of $C_{70}Br_{10}$ and $C_{70}Ph_{10}$ may only be kinetically stable with respect to their respective, thermodynamically more stable, C_1-p^7mp isomers. Even more surprisingly, it appears that C_2-p^9-$C_{70}(t\text{BuOO})_{10}$[11] may be a kinetic isomer with respect to *both* C_1-p^7mp-$C_{70}(t\text{BuOO})_{10}$ and C_s-p^9o(loop)-$C_{70}(t\text{BuOO})_{10}$, and would ultimately rearrange to C_s-p^9o(loop)-$C_{70}(t\text{BuOO})_{10}$ if sufficient activation energy were available (and if the compound did not decompose when that activation energy was added). It is also possible that C_2-p^9-$C_{70}(CF_3)_{10}$, like C_2-p^9-$C_{70}(t\text{BuOO})_{10}$, is formed during the reaction of C_{70} and the $X^{\bullet}$ precursor (CF_3I or *t*BuOOH) and rearranges to the high-yield product C_1-p^7mp-$C_{70}(CF_3)_{10}$ at 470 °C.[12] These and other issues relating to the mechanisms of multiple additions to C_{70}, including the kinetic vs. thermodynamic importance of the density of unpaired spins on the various C atoms of putative $C_{70}X_9^{\bullet}$ radical intermediates,[9] will be addressed in future experimental work and with additional calculations at the DFT level.

It is significant that the stability of C_1-p^7mp-$C_{70}(CF_3)_{10}$ relative to the hypothetical isomers C_s-p^9o-$C_{70}(CF_3)_{10}$ and C_2-p^9-$C_{70}(CF_3)_{10}$ would not have been discovered were it not for the fact that poly(trifluoromethyl)fullerenes are thermally stable at 400–500 °C,[12,18] a property that is unparalleled in exohedral fullerene chemistry except for a few fluorofullerenes.[23] Therefore, we expect that the study of poly(perfluoroalkyl)fullerenes at high temperatures will reveal additional unanticipated aspects of kinetically vs. thermodynamically controlled addition reactions for C_{60} and higher fullerenes.

We have also calculated ΔH_f^0 values at the AM1 level for two loop/ribbon $C_{70}X_{10}$ isomers that have not been observed experimentally, the equatorial C_s-p^7mpm(loop) isomer and the "pole-to-pole" C_2-pmp^5mp isomer. The C_s-p^7mpm(loop) isomer is ≥ 140 kJ mol^{-1} less stable than the most stable isomer listed in Table 1 for X = H, F, Cl, Br, Ph, and CF_3. This extreme instability is because the formation of C_s-p^7mpm(loop)-$C_{70}X_{10}$ from C_s-$C_{70}X_8$ requires the pyramidalization of two triple-hexagon junctions, the most planar C atoms in C_{70}.[24] In the structure of C_s-p^7-$C_{70}Me_8$,[13] for example, the triple-hexagon-junction C atoms are only 0.19 Å above the least-squares planes formed by their three nearest-neighbor cage C atoms. Other sp^2 C atoms involved in forming the four other isomers in Table 1 are displaced 0.26–0.31 Å from their respective nearest-neighbor planes (the largest values in this range are for the C atoms that comprise the polar pentagons). For comparison, out-of-plane displacements for the sp^3 cage C atoms are 0.58–0.59 Å in $C_{70}Me_8$ and are 0.583(3) and 0.561(3) for C25 and C49 in C_1-$C_{70}(CF_3)_{10}$. The high energy cost involved in adding X groups to the triple-hexagon junctions of C_{70} was previously noted.[10] The pole-to-pole isomers C_2-pmp^5mp-$C_{70}(CF_3)_{10}$ and -$C_{70}Ph_{10}$ are marginally more stable than the all-*para*, all-equatorial ribbon isomers C_2-p^9-$C_{70}(CF_3)_{10}$ and -$C_{70}Ph_{10}$. They are not more stable than the C_1-p^7mp isomers, possibly because the formation of the pole-to-pole isomer would disrupt the polar corannulene-like π system of C_1-p^7mp-$C_{70}(CF_3)_{10}$.

The two p-$C_6(CF_3)_2$ hexagons at opposite ends of the ribbon of edge-sharing hexagons in C_1-$C_{70}(CF_3)_{10}$ give rise to two different F···F distances between nearest-neighbor CF_3 groups, 2.744(2) Å for the polar end-of-ribbon hexagon and 2.570(2) Å for the equatorial end-of-ribbon hexagon. These F···F distances are fully consistent with different through-space Fermi-contact $^7J_{FF}$ values reported earlier for the two terminal CF_3 groups in C_1-$C_{70}(CF_3)_{10}$, 10.3 and 15.9 Hz,[12] which can now be assigned to the polar and equatorial end-of-ribbon CF_3 groups, respectively. Note that one of the end-of-ribbon p-$C_6(CF_3)_2$ hexagons in C_1-$C_{60}(CF_3)_{10}$ exhibited an F···F distance of 2.640(3) Å and a $^7J_{FF}$ value of 12.8 Hz,[12] both intermediate values when compared with the above-listed values for C_1-$C_{70}(CF_3)_{10}$. The conclusions reached by others, that through-space J_{FF} coupling in fullerene$(CF_3)_n$ derivatives is unimportant[19,20] and that, in general, 1,4-addition of CF_3 groups to C_{70} "does not account for the large coupling constant variations" (i.e., $J_{FF} = 9.1–17.7$ Hz),[19,21] are not supported by the data presented here.

In summary, the precise structure of C_1-$C_{70}(CF_3)_{10}$ and the new computational results have added significant new information to the small but growing fullerene$(CF_3)_n$ and $C_{70}X_{10}$ databases. More importantly, it has shown that low-temperature exohedral addition on C_{70} may frequently produce kinetic, not thermodynamic, products.

Experimental Section

The compound C_1-$C_{70}(CF_3)_{10}$ was prepared as previously described (no other isomers of this composition were obtained).[12] Crystals suitable for X-ray diffraction were grown by slow evaporation of a toluene solution. Diffraction data from a single crystal were recorded on a Bruker SMART CCD diffractometer employing MoK_α radiation (graphite monochromator). Unit cell parameters were obtained from a least-squares fit to the angular coordinates of all reflections. An empirical absorption correction was applied by using SADABS.[25] The structure was solved by using direct methods and was refined (on F^2, using all data) by a full-matrix, weighted least-squares process.[26] All C and F atoms were refined using anisotropic atomic displacement parameters. Two of the CF_3 groups (C73, C74) were treated as disordered by rotation about the C–C bond connecting them to the fullerene cage. The disorder model allowed for variation of the C-F distance within each disordered group while preserving the tetrahedral geometry about the C atom. Standard Bruker software was employed for structure solution, refinement, and graphics.[27]

The DFT-optimized structure of C_1-p^7mp-$C_{70}(CF_3)_{10}$ was determined with the PRIRODA package[28] using the GGA functional of Perdew, Burke, and Ernzerhof (PBE)[29] and the TZ2P {6,1,1,1,1,1/4,1,1/1,1} basis set. Semi-empirical AM1 calculations were performed with the PC version[30] of the GAMESS(US) package.[31]

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[26] For C_1-$C_{70}(CF_3)_{10}$: $0.31 \times 0.26 \times 0.12$ mm; monoclinic; $P2_1/c$; $a = 20.9959(14)$, $b = 16.0478(13)$, $c = 17.0276(11)$ Å, $\beta = 100.628(7)°$; $V = 5638.8(7)$ Å^3 $(Z = 4)$; $\rho_{calcd} = 1.912$ Mg m^{-3}; $2\theta_{max} = 28.32°$; $-27 \leq h \leq 28$, $-21 \leq k \leq 21$, $-22 \leq l \leq 22$; $\lambda = 0.71073$ Å; $T = 100(1)$ K; number of reflections = 53979; number of independent reflections = 13877 (R(int) = 0.0571); restraints/parameters = 24/1077; full-matrix least-squares refinement on F^2; semi-empirical absorption correction from equivalents; $\mu = 0.181$ mm^{-1}; final R indices $(I > 2\sigma(I))$ are $R_1 = 0.0568$ and $wR_2 = 0.1324$; largest difference peak and hole = 1.174 and −1.008e Å^{-3}. CCDC-277466 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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