

# X-ray structure and DFT study of $C_1-C_{60}(CF_3)_{12}$ . A high-energy, kinetically-stable isomer prepared at $500\text{ }^\circ\text{C}^\dagger$

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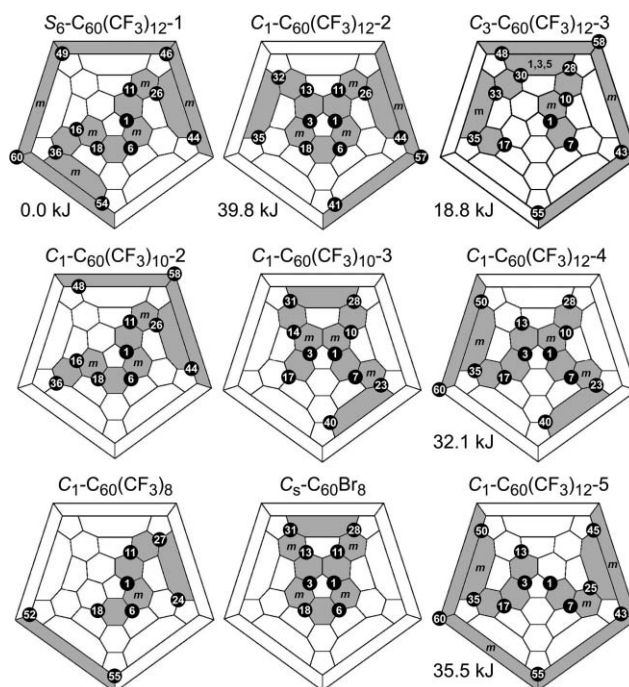
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The title compound, prepared from  $C_{60}$  and  $CF_3I$  at  $500\text{ }^\circ\text{C}$ , exhibits an unusual fullerene( $X$ )<sub>12</sub> addition pattern that is  $40\text{ kJ mol}^{-1}$  less stable than the previously reported  $C_{60}(CF_3)_{12}$  isomer.

Perfluoroalkylfullerenes ( $C_{60+x}(R_f)_n$ ) have become one of the broadest classes of well-characterized  $C_{60+x}Y_n$  compounds, with  $n = 2-18$ . Twenty X-ray structures have appeared since mid-2005,<sup>†</sup> some of which exhibit little or no disorder and have esd's for cage C-C distances as low as  $0.0010-0.0016\text{ \AA}$ .<sup>1,2</sup> More than twenty additional derivatives have had their structures elucidated by <sup>19</sup>F NMR spectroscopy and DFT calculations and several more have not yet had their structures determined.<sup>3,4</sup> Unlike most well-characterized  $C_{60,70}Y_n$  derivatives ( $Y = H, F, Cl, Br, R, Ar$ ), the addition patterns observed for most of the  $C_{60,70}(R_f)_n$  derivatives ( $R_f = CF_3, C_2F_5$ ) are asymmetric. The only exceptions among the compounds characterized by X-ray crystallography are  $C_s-C_{70}(CF_3)_8$ ,<sup>5</sup>  $C_2-C_{60}(CF_3)_{10}$ ,<sup>6</sup> and  $S_6-C_{60}(CF_3)_{12}$  ( $C_{60}(CF_3)_{12-1}$ ).<sup>2</sup> The last compound was reported to be formed in 84% yield in a sealed ampoule reaction of  $C_{60}$  and  $CF_3I$  at  $440\text{ }^\circ\text{C}$  for 2 days.<sup>2</sup>

We now report that the reaction of  $C_{60}$  and  $CF_3I$  in a continuous flow apparatus<sup>7</sup> at  $500\text{ }^\circ\text{C}$  produced not just one but several isomers of  $C_{60}(CF_3)_{12}$ .<sup>‡</sup> One asymmetric isomer has been isolated with *ca.* 90% purity and its structure has been determined by X-ray crystallography.<sup>§</sup> The compound  $C_{60}(CF_3)_{12-2}$ , shown as a Schlegel diagram in Fig. 1 (top center), crystallized from benzene with two independent fullerenes and three solvent molecules in the asymmetric unit. The independent molecules exhibit only minor differences in  $CF_3$  conformations with respect to the  $C_{60}$  cage. The independent molecules exhibit only minor differences in  $CF_3$  conformations with respect to the  $C_{60}$  cage. Some F atom thermal ellipsoids indicate substantial libration and/or disorder, but only one  $CF_3$  group could be satisfactorily modeled assuming a simple two-site disorder.

A drawing of one of the  $C_{60}(CF_3)_{12-2}$  molecules showing all F-atom and some C-atom thermal ellipsoids is shown in Fig. 2. The  $CF_3$ -group addition pattern is a single ribbon of



**Fig. 1** Schlegel diagrams for relevant  $C_{60}(CF_3)_n$  derivatives ( $n = 8, 10, 12$ ) and for  $C_{60}Br_8$ . For the five  $C_{60}(CF_3)_{12}$  isomers, the relative  $\Delta H_f^\circ$  values are shown in  $\text{kJ mol}^{-1}$ . Except for the three compounds  $C_{60}(CF_3)_{12-3, -4, -5}$ , which are not yet known experimentally (but may be present in our mixtures of  $C_{60}(CF_3)_{12}$ ), the compounds shown have been structurally characterized by single-crystal X-ray diffraction. The  $C_3-C_{60}(CF_3)_{12-3}$  isomer is the lowest energy isomer of this composition after the  $S_6$  isomer.

11 edge-sharing *meta*- and *para*- $C_6(CF_3)_2$  hexagons (by definition, each shared edge has one  $sp^3$  and one  $sp^2$  C atom); the molecule is  $C_1-p^3mpmpmpmp-C_{60}(CF_3)_{12}$  or 1,3,6,11,13,18,26,32,35,41,44,57- $C_{60}(CF_3)_{12}$  (IUPAC locants<sup>8</sup>). A single ribbon of edge-sharing *m*- and/or *p*- $C_6(CF_3)_2$  hexagons (as just defined) is the most common addition pattern for  $C_{60+x}(R_f)_n$  derivatives,<sup>†</sup> although a ribbon plus an isolated *p*- $C_6(CF_3)_2$  hexagon,<sup>9,10</sup> two ribbons,<sup>4</sup> a loop,<sup>2</sup> two loops,<sup>6</sup> a loop plus an isolated hexagon,<sup>4</sup> and a loop plus a ribbon<sup>4</sup> are also known (each shared edge of a loop of edge-shared  $C_6(CF_3)_2$  hexagons must also have one  $sp^3$  and one  $sp^2$  cage C atom; therefore,  $C_{60}(CF_3)_{12-2}$  and  $C_{60}(CF_3)_{10-3}$  are *single-ribbon isomers* and do not contain loops, while  $C_{60}(CF_3)_{12-1}$  and  $C_{60}Br_8$  are *single-loop isomers*).

By definition, a fullerene always has 12 pentagons.<sup>11</sup> For compounds with more than 12  $R_f$  groups (*e.g.*,  $C_{70}(CF_3)_{14}$ ,

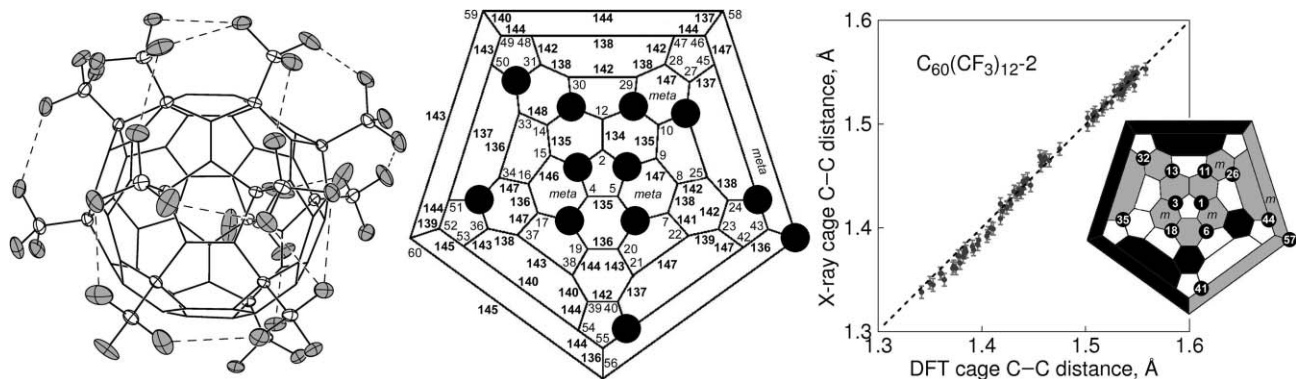
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<sup>†</sup> Electronic supplementary information (ESI) available: Complete list of references for X-ray structures of fullerene( $R_f$ )<sub>n</sub> compounds ( $n > 1$ ); IUPAC-numbered and thermal ellipsoid plots; table of DFT relative  $\Delta H_f^\circ$  values for numerous  $C_{60}(CF_3)_{12}$  isomers. See DOI: 10.1039/b617489b



**Fig. 2** (left) Drawing of the  $^{f_5}A$  isomer of  $C_1-p^3mpmpmpmp-C_{60}(CF_3)_{12}$  in ( $^{f_5}C-C_{60}(CF_3)_{12}$ )( $^{f_5}A-C_{60}(CF_3)_{12}$ )- $3C_6H_6$  (50% probability ellipsoids for the 12  $CF_3$  groups and the cage C atoms to which they are attached; F atoms are highlighted). The  $F\cdots F$  contacts between  $CF_3$  groups that share the same hexagon or pentagon are shown as dashed lines and range from 2.558(2) to 2.857(2) Å. (middle left) Schlegel diagram showing cage C atom numbering and all  $C(sp^2)-C(sp^2)$  distances in pm (the distances are known to better than  $\pm 1$  pm since  $3\sigma = 0.6$  pm). (middle right) Plot of X-ray vs. DFT-optimized cage C-C distances for  $C_{60}(CF_3)_{12-2}$  (the error bars are  $\pm 3\sigma$ ). (right) Schlegel diagram showing the seven remaining  $C(sp^2)_6$  hexagons in  $C_{60}(CF_3)_{12-2}$ .

$C_{70}(CF_3)_{16}$ , and  $C_{70}(CF_3)_{18}$ ,<sup>12,13</sup> some pentagons must have more than one substituent. However, of the *ca.* 40 well-characterized  $C_{60+x}(R)_n$  compounds with  $n \leq 12$ ,  $C_{60}(CF_3)_{12-2}$  is only the second example with a  $1,3-C_5(R)_2$  pentagon (the first was  $C_{60}(CF_3)_{10-3}$ ,<sup>7</sup> shown in Fig. 1), and it is the first example with two  $1,3-C_5(R)_2$  pentagons. The  $C_1-p^3mpmpmpmp$  ribbon in  $C_{60}(CF_3)_{10-2}$  is related to the  $C_1-p^3mpmpmpmpmp$  ribbon in  $C_{60}(CF_3)_{12-2}$  except that the final  $-mp$  fragment in  $C_{60}(CF_3)_{10-2}$ , unlike the third  $-mp-$  fragment in  $C_{12}(CF_3)_{12-2}$ , involves a  $m-C_6(CF_3)_2$  hexagon that does not lead to the formation of two  $1,3-C_5(CF_3)_2$  pentagons.

The estimated standard deviation for all 90 cage C-C bonds is 0.002 Å, making a meaningful analysis of the cage  $C(sp^2)-C(sp^2)$  bond distances possible. These are shown, to the nearest pm (for clarity), in the Schlegel diagram in Fig. 2. The ten shortest bonds range from 1.338(2) (C2-C12) to 1.366(2) Å (C27-C45), and six of these are pent-hex junctions (PHJs) that have been shortened from *ca.*  $1.45 \pm 0.01$  Å in  $C_{60}$ <sup>14</sup> to  $1.35 \pm 0.01$  Å in  $C_{60}(CF_3)_{12-2}$ . The hex-hex junction (HHJ) C2-C12 and the PHJ C4-C5, 1.345(2) Å, are unique in that they are isolated double bonds. Although double bonds on PHJs are normally considered destabilizing, each *pmp* or  $p^3$  fragment in a  $C_{60}(CF_3)_n$  derivative with a ribbon of edge-sharing  $C_6(CF_3)_2$  hexagons requires that at least one very short cage C-C bond be located in a pentagon. For this reason, the isomer  $C_{60}(CF_3)_{12-1}$ , with an  $S_6-pmpmpmpmpmpmpmp$  loop, also has six double bonds in pentagons.<sup>2</sup>

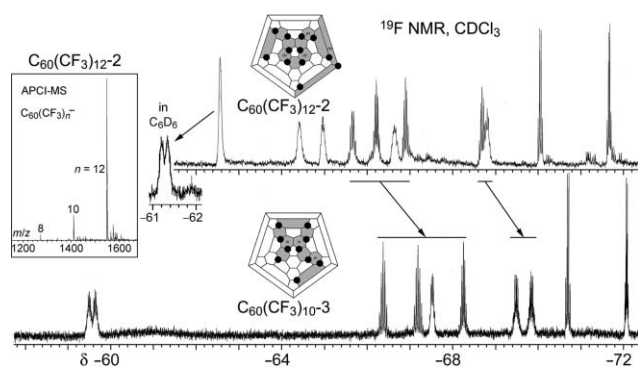
Of the seven remaining  $C(sp^2)_6$  hexagons in  $C_{60}(CF_3)_{12-2}$ , six are fused into a curved benzo[*c*]picene (zig-zag polyhexacene) fragment,<sup>15</sup> as shown in Fig. 2.

We have calculated the relative  $\Delta H_f$  values for more than 10000 isomers of  $C_{60}(CF_3)_{12}$  at the AM1 level of theory followed by full optimization of the most stable isomers at the DFT level of theory (PRIRODA package,<sup>16</sup> PBE functional,<sup>17</sup> TZ2P Gaussian basis set). All isomers that can be made (i) by a series of 1,4 additions of two  $CF_3$  groups (which leads to interior  $m-C_6(CF_3)_2$  hexagons if the ribbon has more than four  $CF_3$  groups), (ii) by adding three 1,4 additions plus a skew-pentagonal pyramid (SPP) unit of six  $CF_3$  groups (as in 1,6,9,12,15,18- $C_{60}(CF_3)_6$ ,<sup>18</sup>), (iii) by adding two SPP units, or (iv) by adding a  $p-C_6(CF_3)_2$  hexagon to  $C_2-(p^3m^2-loop)^2-C_{60}(CF_3)_{10}$ <sup>6</sup> were considered. (These constraints are based on the

addition-pattern motifs observed for more than forty well-characterized fullerene( $CF_3$ )<sub>n</sub> derivatives; it is possible that other stable addition-pattern motifs will be discovered in the future.) Ten isomers were found to have relative  $\Delta H_f$  values of 0.0–39.8 kJ mol<sup>-1</sup>, and five of these are shown in Fig. 1. There are two additional isomers (not shown) with  $\Delta H_f$  values of *ca.* 20 kJ mol<sup>-1</sup> that, like  $C_{60}(CF_3)_{12-3}$ , have a  $1,3,5-C_6(CF_3)_3$  hexagon. The isomers  $C_{60}(CF_3)_{12-4}$  and -5, which are predicted to be more stable than  $C_{60}(CF_3)_{12-2}$ , each have one  $1,3-C_5(CF_3)_2$  pentagon. The fifth isomer, like  $C_{60}(CF_3)_{12-2}$ , has a  $C_1-p^3mpmpmpmpmp$  ribbon and is structurally related to  $C_{60}(CF_3)_{10-2}$ . The fourth isomer is composed of two ribbons, a  $p^3mp$  ribbon and a *pmpmp* ribbon. The  $C_{2h}$  addition-pattern isomer with two SPP fragments on opposite poles has a relative  $\Delta H_f$  value of 32.6 kJ mol<sup>-1</sup>. Single point B3LYP/6-31G\*//PBE/TZ2P calculations only changed the energy difference between the  $S_6$  and  $C_{60}(CF_3)_{12-2}$  isomers from 39.8 to 36.6 kJ mol<sup>-1</sup>. Furthermore, a plot of the 90 X-ray vs. PBE-DFT cage C-C distances is shown in Fig. 2. The correlation to within  $\pm 3\sigma$  is very good to excellent.

The compounds in Fig. 1 have different addition patterns but many similarities that may not be clear at first: (i)  $C_{60}Br_8$  and  $C_{60}(CF_3)_{12-2}$  have six addition positions in common; (ii)  $C_{60}(CF_3)_{10-2}$  and  $C_{60}(CF_3)_{12-1}$  have eight common  $CF_3$  groups, as do  $C_{60}(CF_3)_{10-3}$  and  $C_{60}(CF_3)_{12-4}$ ; (iii) the  $p^3mp$  ribbon in  $C_{60}(CF_3)_8$  is common to  $C_{60}(CF_3)_{12-3}$ ,  $C_{60}(CF_3)_{12-4}$ ,  $C_{60}(CF_3)_{10-2}$ , and  $C_{60}(CF_3)_{10-3}$  as well as to  $C_1-C_{70}(CF_3)_6$ ; (iv)  $C_{60}(CF_3)_{12-5}$  is closely related to  $C_{60}(CF_3)_{12-1}$  in that they have ten  $CF_3$  groups in common. Moving the  $CF_3$  groups on C3 and C13 in  $C_{60}(CF_3)_{12-5}$  to adjacent C atoms would transform it into  $C_{60}(CF_3)_{12-1}$ .

The compound  $C_{60}(CF_3)_{12-2}$  is predicted to be nearly 40 kJ mol<sup>-1</sup> less stable than  $C_{60}(CF_3)_{12-1}$ , which is the most stable isomer. In all previous computational studies of  $C_{60+x}(CF_3)_n$  derivatives, all well-characterized isomers of a given composition that were prepared at or above 400 °C were within the first 15 kJ mol<sup>-1</sup> of the most stable isomer, and all but one were within the first 10 kJ mol<sup>-1</sup>.<sup>3,4,6,18–20</sup> We have proposed that  $C_{60+x}(CF_3)_n$  derivatives can undergo facile isomerization above 400 °C.<sup>3,7</sup> This has not yet been proven, however, and the extent to which the relative amounts of various isomers of a given composition in a high-temperature product mixture are controlled by



**Fig. 3** Fluorine-19 NMR spectra. The boxed inset is the APCI mass spectrum of an HPLC purified sample of  $C_{60}(CF_3)_{12-2}$ .

thermodynamic and/or kinetic factors is not clear in any study published to date. The isolation of  $C_{60}(CF_3)_{12-2}$ , which is predicted to be far from equilibrium with respect to isomerization, is the first unambiguous experimental evidence that kinetically-stable  $C_{60+x}(CF_3)_n$  isomers are possible, even at 500 °C. Its further study may lead to new insights about the rates and mechanisms of (i) multiple radical additions to fullerenes as well as (ii) high-temperature  $C_{60+x}(CF_3)_n$  isomerizations.

Since  $C_{60}(CF_3)_{12-1}$ , -2, -3, -4, and -5 all have six *PHJ* double bonds, their significantly different DFT-predicted  $\Delta H_f$  values must be attributed to other electronic and/or steric factors. The  $S_6$  isomer has eight remaining  $C(sp^2)_6$  hexagons in two nearly-isolated triphenylene fragments on opposite poles, each of which has three vinyl-like moieties. On the other hand,  $C_{60}(CF_3)_{12-2}$  has the benzo[*c*]picene fragment, a  $C(sp^2)_6$  hexagon, a  $C(sp^2)_5$  pentagon, plus a number of vinyl-like moieties. The difference in energy for the two isomers may be due to (i) different electronic stabilities of the remaining  $\pi$  systems, including different strain energies in the polycyclic hydrocarbon fragments, (ii) different steric repulsions between proximate F atoms, and (iii) differences in the degree to which the  $CF_3$  groups are eclipsed or staggered with respect to the cage. All of these possibilities are being explored.

The  $^{19}F$  NMR spectra of  $C_{60}(CF_3)_{12-2}$  and  $C_{60}(CF_3)_{10-3}$  in  $CDCl_3$  are shown in Fig. 3. The multiplets are either quartets, quartets of quartets (some are apparent septets), or unresolved multiplets, as found for a variety of  $C_{60+x}(CF_3)_n$  compounds.<sup>3,4,7</sup> The observed<sup>6,7</sup>  $J_{FF}$  coupling between  $CF_3$  groups sharing the same hexagon or, in the case of these two compounds, the same pentagon, is primarily mediated by the overlap of lone pairs of electrons on proximate  $CF_3$  F atoms (*i.e.*, through-space Fermi-contact coupling), as previously described.<sup>3,4,7</sup> A complete analysis of  $\delta$  vs. (i) addition pattern and (ii)  $CF_3$  conformation for these and other  $C_{60+x}(CF_3)_n$  derivatives will be reported in the near future.

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## Notes and references

‡ Synthesis of  $C_{60}(CF_3)_{12-2}$ : The procedure published in 2005<sup>7</sup> was used with the following changes: 100 mg  $C_{60}$ , 500 °C, 1 h. The combined crude products from several preparations (600 mg total) were processed by HPLC (Cosmosil Buckyprep column; 18 mL heptane  $min^{-1}$ ).<sup>7</sup> The 12.8 min fraction was collected and reprocessed three times. Further HPLC

purification resulted in 3–5 mg of *ca.* 90% pure  $C_{60}(CF_3)_{12-2}$  (see APCI mass spectrum<sup>4</sup> in Fig. 3).  $^{19}F$  NMR (376.48 MHz,  $CDCl_3$ , 25 °C,  $C_6F_6$  int. std. ( $\delta$  –164.9)): –62.6, unresolved multiplet (*um*), int. 2; –64.4, *um*, int. 1; –65.0, unresolved *um*, int. 1; –65.6, apparent septet (*as*),  $J = 14$  Hz, int. 1; –66.2, *as*,  $J = 12$  Hz, int. 1; –66.6, *um*, int. 1; –66.9, *as*,  $J = 12$  Hz, int. 1; –68.7, *as*,  $J = 12$  Hz, int. 1; –68.8, *as*,  $J = 12$  Hz, int. 1; –70.0, quartet (*q*),  $J = 13$  Hz, int. 1; –71.7, *q*,  $J = 11$  Hz, int. 1.

§ Crystal data. Bruker Kappa APEX II CCD diffractometer (Mo-K $\alpha$   $\lambda = 0.71073$  Å; graphite monochromator;  $T = 100(2)$  K). Empirical absorption correction was applied using SADABS.<sup>21</sup> Structures were solved using direct methods and refined using full-matrix least squares on  $F^2$  using SHELXTL.<sup>22</sup> For 1,3,6,11,13,18,26,32,35,41,44,57- $C_{60}(CF_3)_{12-1.5}C_6H_6$ ,  $C_{81}H_9F_{36}$ ,  $M = 1665.88$ , triclinic, space group  $P\bar{1}$  (No. 2),  $a = 13.3366(3)$ ,  $b = 19.2741(5)$ ,  $c = 22.5169(6)$  Å,  $\alpha = 86.810(2)^\circ$ ,  $\beta = 88.954(2)^\circ$ ,  $\gamma = 85.636(2)^\circ$ ,  $V = 5761.7(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{calc} = 1.920$  Mg  $m^{-3}$ ,  $\mu = 0.194$  mm<sup>-1</sup>,  $2\theta_{max} = 65.16^\circ$ , final  $R$  indices ( $I > 2\sigma(I)$ ):  $R_1 = 0.056$ ,  $wR_2 = 0.157$  (262111 total reflections, 41972 unique reflections (28477 with  $I > 2\sigma(I)$ ),  $R_{int} = 0.0516$ . CCDC 629289. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617489b

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