

T_h -C₆₀F₂₄

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We previously reported that fluorinations of C₆₀ with F₂ (315–355 °C) or metal fluorides (MF_x; 300–500 °C) yielded C₆₀F₄₈, C₆₀F₃₆, or C₆₀F₁₈^{1,2} and that the fluorination of C₇₄ with K₂PtF₆ at 500 °C selectively produced D₃-C₇₄F₃₈.³ In all cases, the thermodynamically most stable isomer or set of isomers was produced, each exhibiting a contiguous pattern of F-bearing sp³ C atoms and (except for C₆₀F₄₈) one or more stabilizing isolated benzenoid rings.^{3–7}

One might expect that milder reaction conditions could produce kinetically stable fluorofullerenes with completely different structures, but until now this has not been demonstrated. Fluorinations of C₆₀ or C₆₀(Cl,Br)_n at low temperatures (25–70 °C) have been reported, but in each case complex mixtures of products were produced, and pure compounds were not isolated.⁸

We now report that fluorination of T_h -C₆₀Br₂₄⁹ with XeF₂¹⁰ in anhydrous HF (aHF) at 25 °C produced T_h -C₆₀F₂₄, the first fluorofullerene with a noncontiguous addition pattern of F atoms.^{11,12} Figure 1 shows the EI and ESI mass spectra of the pale yellow crude product and HPLC-purified C₆₀F₂₄, respectively.¹³ No significant peaks with *m/z* > 1300 were observed in either spectrum. Comparison of the EI mass spectra in Figure 1 and from the product of the reaction without aHF solvent¹² demonstrates the substantial improvement in compositional purity caused by the addition of aHF. The ESI mass spectrum of HPLC-purified C₆₀F₂₄ in Figure 1 shows parent negative ions assigned to three new compounds that coeluted: C₆₀F₂₄ (1176 *m/z* for C₆₀F₂₄⁻), significantly less C₆₀F₂₅Br (1276 *m/z* for C₆₀F₂₅Br⁻), and ≤5% C₆₀F₂₄O (1192 *m/z* for C₆₀F₂₄O⁻). Note that the EI and ESI spectra in Figure 1 are the first reported direct observations of a fullerene derivative with a C _{cage}-Br bond by mass spectrometry.

The ¹⁹F NMR spectrum of HPLC-purified C₆₀F₂₄, shown in Figure 2, consists of a single resonance at δ -144.8, indicating that all 24 F atoms are equivalent.¹³ Carbon-13 NMR spectra (with and without ¹⁹F decoupling; not shown) revealed two resonances at δ 145.9 (C=C) and δ 83.5 (C-F; *J*_{CF} = 212 Hz) in an approximately 3:2 ratio. Only a *T_h*-symmetry isomer of C₆₀F₂₄ is consistent with these spectra, and only two such isomers are geometrically possible. These are shown as Schlegel diagrams **1** and **2** in Figure 2. Isomer **1** has the noncontiguous addend pattern of T_h -C₆₀Br₂₄ (determined by single-crystal X-ray diffraction^{9,14}) and could conceivably arise by concerted Br/F exchanges at sp³ C atoms. Isomer **2** is an alternative structure with a noncontiguous series of 1,2 additions across 12 hexagon-pentagon edges. We studied these two structures at the DFT level of theory.^{15–17} Upon geometry optimization, the initial *T_h* structure of **2** was found to

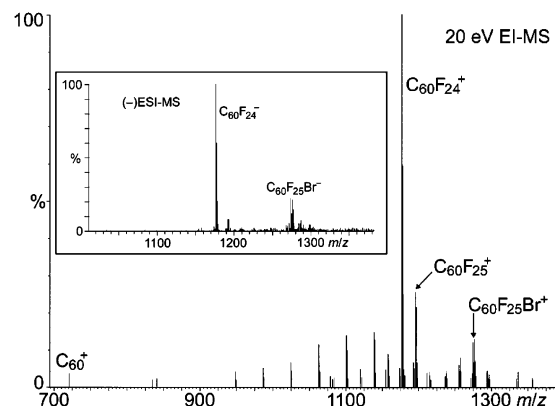


Figure 1. EI mass spectrum (20 eV) of the crude product of reaction of C₆₀Br₂₄ with XeF₂ in aHF. Raising *U_e* to 70 eV resulted in an increase in the C₆₀F₂₅⁺-fragment intensity and disappearance of the C₆₀F₂₅Br⁺ peak. (Inset) Negative-ion ESI mass spectrum of an HPLC-purified sample of C₆₀F₂₄. Collision-induced dissociation of the *m/z* 1276 C₆₀F₂₅Br⁻ ion produced the *m/z* 1195 C₆₀F₂₅⁻ ion via Br loss, confirming the peak assignment. An aliquot of the ESI sample was used to obtain the NMR and FTIR spectra of this compound.

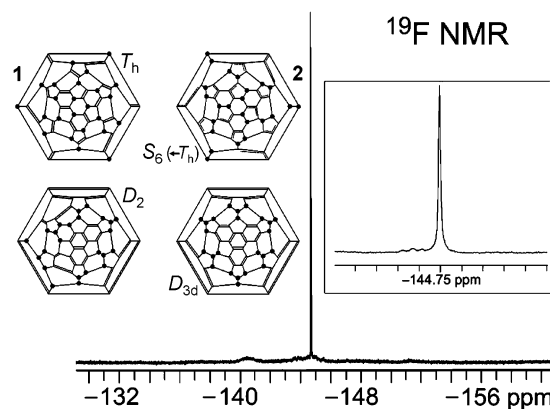


Figure 2. ¹⁹F NMR spectrum of the HPLC-purified sample of C₆₀F₂₄. The Schlegel diagrams show four possible isomers of C₆₀F₂₄. • = fluorine-bearing carbon atoms. Only isomer **1** is consistent with this spectrum and the ¹³C NMR spectra.

be unstable with respect to an *S₆* distortion of the C₆₀ core. Furthermore, *S₆*-distorted **2** was found to be 430 kJ mol⁻¹ less stable than geometry-optimized **1**, which retained its *T_h* symmetry. Therefore, since **1** is the only DFT-consistent *T_h* isomer of C₆₀F₂₄, we conclude that **1** corresponds to the structure of C₆₀F₂₄ synthesized in this work.

Further support for structure **1** is provided by comparing the experimental and calculated IR spectra for T_h -C₆₀F₂₄, which are shown in Figure 3.^{13,15} Our previous study of C₆₀F₁₈ revealed that

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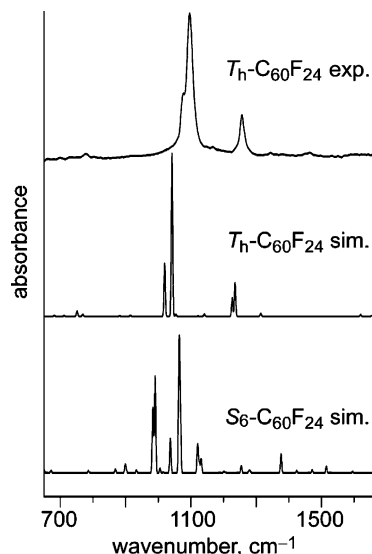


Figure 3. Experimental FTIR spectrum of T_h - $C_{60}F_{24}$ and simulated IR spectra of the T_h and S_6 ($\leftarrow T_h$) isomers **1** and **2**, respectively.

predicted $\nu(\text{CF})$ values are generally somewhat lower than experimental values, but the relative positions and relative intensities of the $\nu(\text{CF})$ peaks in the experimental spectrum were well reproduced in the calculated spectrum.^{18,19} By these criteria, there is a good correspondence of the topologies of the experimental and calculated spectra for T_h - $C_{60}F_{24}$ in Figure 3. By comparison, the calculated IR spectrum of S_6 - $C_{60}F_{24}$ (derived from **2** by geometry optimization) is a poor match for the topology of the experimental spectrum, as shown in Figure 3. There is also a good correspondence between the experimental and calculated Raman spectra of **1**.¹²

Our DFT calculations predict that the D_2 and D_{3d} contiguous-F-atom isomers of $C_{60}F_{24}$ shown in Figure 2 are more stable than T_h - $C_{60}F_{24}$ by 340 and 280 kJ mol^{-1} , respectively. There may be other isomers that are more stable, but our intention in this initial computational study was not to predict the most stable isomer but to demonstrate that T_h - $C_{60}F_{24}$ is not the most stable isomer of $C_{60}F_{24}$, making it a rare example of an isolable kinetically stable fluorofullerene as well as the first isolable noncontiguous fluorofullerene. Although it may spontaneously isomerize to a more stable structure over time at elevated temperature (experiments in progress), the ^{19}F NMR spectrum of T_h - $C_{60}F_{24}$ dissolved in oxygenated toluene remained unchanged after a period of more than two months at 25 $^\circ\text{C}$ (i.e., no rearrangement, oxidation, or oxygenation was observed).

In summary, we have shown that T_h - $C_{60}\text{Br}_{24}$ reacts with XeF_2 dissolved in aHF to produce T_h - $C_{60}F_{24}$ with ca. 80% compositional purity. This kinetically stable (months) isomer represents the first example of a new family of fluorofullerenes with noncontiguous addition patterns. It remains to be seen if the reaction proceeds by concerted Br/F exchanges at sp^3 C atoms or by a series of addition–elimination reactions. Regardless of the mechanism, it is clear that some transformations of fullerene derivatives to fluorofullerenes can be highly regioselective and lead to relatively pure samples of novel fluorofullerenes and fluorofullerene derivatives (e.g., $C_{60}F_{25}\text{-Br}$), and such reactions deserve further study.

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Supporting Information Available: Additional references on the nonselective fluorination of C_{60} and $C_{60}(\text{Cl},\text{Br})_n$ under mild conditions and details of the reaction of C_{60} and XeF_2 in the absence of aHF (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) In a typical aHF solution reaction, $C_{60}\text{Br}_{24}$ (70 mg, 0.027 mmol) was stirred with an aHF solution of XeF_2 (500 mg, 2.96 mmol in 3 mL of aHF) in a FEP reactor at 25 $^\circ\text{C}$ for 5 d. [CAUTION: aHF is hazardous and should only be handled by trained personnel.] The color changed from dark orange to pale yellow almost immediately, and gas, presumably Xe, evolved continuously over 5 d. Removal of aHF and other volatile compounds under vacuum (2 h) afforded 30 mg of a pale-yellow powder that was analyzed by EI mass spectrometry. This reaction product was processed by HPLC (10 mm \times 250 mm Cosmosil Buckyprep column; 5 mL of toluene/min). The fraction that eluted at 2.89 min was analyzed by ESI mass spectrometry and by NMR and ATR-FTIR spectroscopy.
- (12) See Supporting Information for details of the reaction of $C_{60}\text{Br}_{24}$ with XeF_2 in the absence of HF and IR calculations and for the Raman spectra.
- (13) The EI and ESI mass spectra were recorded with a Fisons VG Quattro single quadrupole mass spectrometer and a Finnigan LCQ Duo mass spectrometer, respectively. Fluorine-19 and ^{13}C NMR spectra (toluene- d_8 and 20:80 v:v benzene- d_6 :1,2-dichlorobenzene solutions, respectively) were recorded with a Bruker IVONA-400 spectrometer. The FTIR spectrum was recorded with an ASI ReactIR-1000 ATR-FTIR spectrometer.
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