# Synthesis, Isolation, and Structural Studies of $C_{60(70)}(i\text{-}C_3F_7)_n$ Derivatives

*by Natalia Shustova*

It is known that perfluoroalkylated fullerenes possess better electron-accepting properties than parent fullerenes[1,2] and therefore, these compounds can have the potential applications in energy storage and photovoltaic energy conversion. Recently, we found that the ranges of electrochemical potentials depend on the addition pattern type of the isomer.[1] Thus, this fellowship work has been focused on the studies of perfluoroalkylation reactions of $C_{60}$ and $C_{70}$ using $i\text{-}C_3F_7I$ as a bulky perfluoroalkylating agent which can form fundamentally different addition patterns in comparison with ones observed in case of $CF_3$ derivatives. The $C_{60(70)}/i\text{-}C_3F_7I$ reactions were carried out under different conditions which included photolytic and thermal methods for producing iso-heptafluoropropyl radicals. Three different reactors such as continuous flow apparatus (300–500°C), sealed glass ampules (290°C), and glass tubes (room temperature, UV-vis irradiation) were used to produce perfluoroalkylated derivatives. Experiments with $C_{60}$ in the continuous flow apparatus performed at 450–480°C led to formation of $C_{60}(CF_3)_n$ and $C_{60}(CF_3)_n(i\text{-}C_3F_7)_m$ derivatives. Thus, synthesis at these high temperatures led to decomposition of iso-heptafluoropropyl radicals with formation of $CF_3$ radicals followed by their addition to a fullerene. The next series of experiments was performed at 320–380°C, which yielded $C_{60}(i\text{-}C_3F_7)_n$ ($n$ = 6–12) compounds. In case of $C_{70}$, the synthesis with $i\text{-}C_3F_7I$ at 320°C led to formation of $C_{70}(i\text{-}C_3F_7)_n$, $n$ = 8-12, with $n$ = 12 as the most abundant compound. For the series of $C_{60}/i\text{-}C_3F_7I$ reactions in the sealed glass ampule, a lower temperature (290°C) was chosen. According to NI-APCI-MS, the $C_{60}(i\text{-}C_3F_7)_n$ ($n$ = 2-6) derivatives were obtained. Thus, the strong dependence of the composition of the $C_{60(70)}(i\text{-}C_3F_7)_n$ on the reaction conditions (temperature, reacting gas pressure) was found. We observed that in the flow apparatus increase in the temperature led to decrease in the number of attached substituents. Radical decomposition was prevented in the synthesis of $C_{60(70)}(i\text{-}C_3F_7)_n$ compounds under UV irradiation at room temperature. The brownish-orange $C_{60(70)}(i\text{-}C_3F_7)_n$ compounds have 10 $i\text{-}C_3F_7$ groups as a maximum degree of substitution. However, the yield of the obtained products was low.

The experiments in three different reactors showed that maximum number of attached $i\text{-}C_3F_7$ groups is 12 *vs.* 22 which have been observed in trifluoromethylation reactions. This fact can be explained by the steric effect, in other words, the large difference in the size of the $i\text{-}C_3F_7$ group in comparison with the $CF_3$ group.

HPLC separation of the product (sealed ampule, 290°C) led to isolation of $C_{60}(i\text{-}C_3F_7)_2$ and $C_{60}(i\text{-}C_3F_7)_4$ compounds. Slow evaporation of the toluene solutions led to formation of $C_{60}(i\text{-}C_3F_7)_2$ and $C_{60}(i\text{-}C_3F_7)_4$ crystals suitable for X-ray single crystal diffraction. Thus, two new crystal structures of $C_{60}(i\text{-}C_3F_7)_n$ derivatives were obtained (Fig. 1). $C_{60}(i\text{-}C_3F_7)_2$ has the same addition pattern as its trifluoromethylated counterpart, whereas $C_{60}(i\text{-}C_3F_7)_4$ has an unprecedented addition pattern which has not been observed in case of trifluoromethylated derivatives. Thus, use of a bulky substituent such as $i\text{-}C_3F_7$ group in the reactions with $C_{60}$ or $C_{70}$ opens the possibilities to make the compounds with new addition patterns, and hence novel electron-accepting properties.

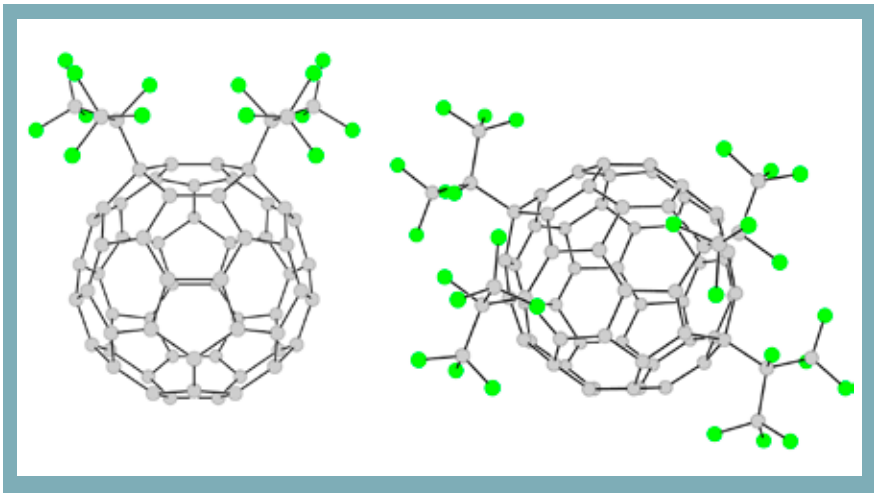

**Fig. 1.** *The X-ray structures of $C_s$- $C_{60}(i\text{-}C_3F_7)_2$ (left) and $C_2$- $C_{60}(i\text{-}C_3F_7)_4$ (right).*

## Acknowledgment

The support by ECS through the Herbert H. Uhlig Summer Research Fellowship is gratefully acknowledged.

## About the Author

**Natalia B. Shustova** is a graduate student at Colorado State University working for Steven H. Strauss and Olga V. Boltalina.

## References

1. A. A. Popov, I. E. Kareev, N. B. Shustova, S. F. Lebedkin, S. H. Strauss, O. V. Boltalina, and L. Dunsch, *Chem. Eur. J.*, **14**, 107 (2008).
2. A. A. Popov, I. E. Kareev, N. B. Shustova, E. B. Stukalin, S. F. Lebedkin, K. Seppelt, S. H. Strauss, O. V. Boltalina, and L. Dunsch, *J. Am. Chem. Soc.*, **129,** 11551 (2007).