DIGGING FOR NOVEL FLUOROFULLERENES

Collaborative team makes molecules that look like a deflated soccer ball and a ringed planet

WHAT A DIFFERENCE TWO fluorine atoms can make! One might think that the partially fluorinated fullerenes $C_{60}F_{18}$ and $C_{60}F_{20}$ would be very similar molecules. But recent research results indicate that they are dramatically different: $C_{60}F_{18}$ has been described as a tortoise shell or a partially deflated soccer ball, while $C_{60}F_{20}$ is reminiscent of the ringed planet Saturn.

The structure of $C_{60}F_{18}$ was reported last year by a Russian-British collaborative team led by chemists Olga V. Boltalina of Moscow State University and Roger Taylor of Sussex University [*Angew. Chem. Int. Ed.*, **39**, 3273 (2000); C&EN, Sept. 18, 2000, page 47]. Boltalina's group prepared both fluorofullerenes by reacting C_{60} with K_2PtF_6 at 460 °C under reduced pressure in a glass reactor. Taylor's group fished out the major product ($C_{60}F_{18}$) and characterized it. Collaborators at the Nesmeyanov Institute of Organoelement Compounds in Moscow obtained the compound's X-ray crystal structure.

The findings show that one-half of the fullerene cage—the half studded with the 18 fluorine atoms—is flattened, like a beaten-in soccer ball. In the middle of this flattened region is a hexagonal ring that appears to be fully aromatic because its six C–C bonds are all the same length. The 18 fluorine atoms are arranged like a crown around this special hexasubstituted benzene ring.

$C_{60}F_{18}$ is produced in the reactor along with many other fullerene derivatives, and one of the minor by-products was identified from its mass spectrum as $C_{60}F_{20}$. To characterize it further, the researchers needed larger amounts of this fluorofullerene, so Boltalina's group scaled up the preparation using a fluorinating mixture of manganese(III) fluoride and potassium fluoride. The larger scale synthesis enabled Taylor and coworkers to isolate several milligrams of $C_{60}F_{20}$ by high-performance liquid chromatography—enough to establish its extraordinary structure by spectroscopic means.

The infrared spectrum of $C_{60}F_{20}$ points to a highly symmetrical structure. And the ^{19}F nuclear magnetic resonance spectrum—obtained by collaborator Joan M. Street of the University of Southampton, England—shows a single, sharp line, indicating that all 20 fluorine atoms are equivalent. Only one possible structure is consistent with all the spectroscopic data, according to the researchers: a structure in which a jagged $(CF)_{20}$ chain runs along the "equator" of the cage.

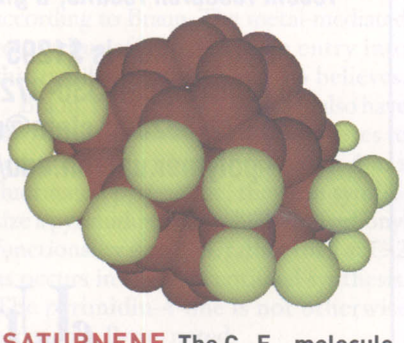
PHOTO BY RON DAGANI

PHOTO BY YVES RUBIN

BOLTALINA (left) and TAYLOR

Furthermore, calculations indicate that $C_{60}F_{20}$ is highly strained, causing the cage to be distorted: The poles are flattened and the fluorine-ringed equator is expanded, suggestive of a spinning planet. The researchers have dubbed the molecule "saturnene" [*Angew. Chem. Int. Ed.*, **40**, 787 (2001)].

They also have proposed a mechanistic scenario that explains how $C_{60}F_{18}$ and $C_{60}F_{20}$ can form under the same reaction conditions via two different but related pathways. Each pathway involves steps in which fluorines are added to a pair of contiguous carbons. But this addition can proceed according to two different patterns, one leading to $C_{60}F_{18}$ and the other to $C_{60}F_{20}$. The formation of $C_{60}F_{18}$ is favored because it contains an aromatic ring and $C_{60}F_{20}$ does not. Consistent with this scenario, the amount of $C_{60}F_{18}$ produced is 20 times that of $C_{60}F_{20}$.



SATURNENE The $C_{60}F_{20}$ molecule is depicted in an equatorial view. The fluorine atoms are shown in greenish-yellow.

THE GEOMETRY of the saturnene cage and the electron-withdrawing effect of its fluorines suggest that this molecule could be of interest for future photonic or photovoltaic applications. With this in mind, Boltalina and coworkers are trying to boost the yield of the compound so that there will be sufficient quantities of it for electrochemical and other relevant experiments. In addition, Taylor is trying to grow saturnene crystals that are large enough for X-ray analysis.

$C_{60}F_{18}$ and $C_{60}F_{20}$ are not the only unusual fluorofullerenes that the Russian and British researchers have uncovered. They also have isolated both isomers of $C_{60}F_{36}$, which look "very unfullerenelike," in Taylor's words. One isomer has three flat aromatic faces, and the other has four.

Another amazing structure in this family is $C_{60}F_{48}$, which Boltalina calls "an indented fullerene" because of "the drastic distortions" in the carbon cage around the only six double bonds that remain unfluorinated. The Moscow-Sussex team, though, was not first with this one: The synthesis and structure determination of $C_{60}F_{48}$ was first reported by an American team in 1994.

Beyond these molecules, the Boltalina-Taylor team has isolated and characterized many other fluorofullerenes, including $C_{60}F_2$, $C_{60}F_{16}$, $C_{60}F_{17}CF_3$, various monooxides and dioxides of fluorofullerenes, and fluorinated derivatives of C_{70}, C_{76}, C_{78}, C_{82}, and C_{84}. Most of these compounds have been reported within the past few years, and Boltalina presented highlights of the research last month at the 15th Winter Fluorine Conference in St. Petersburg Beach, Fla.

At that conference, Boltalina suggested that this work is like excavating at an archaeological site and never knowing what you'll turn up. In the case of some of these oddly shaped fluorofullerenes, she remarked, "we dug out something very valuable."—RON DAGANI