FLUORINE-19 AND CARBON-13 SPECTROSCOPY OF FLUORINATED ORGANIC MOLECULES

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Introduction

Fluorinated organic molecules are of great practical significance because of their uses as monomers for polymers, refrigerants, lubricants, anesthetics and biochemical tracers, and of scientific interest with respect to the nature of their bonding and geometry. Nuclear magnetic resonance is the premier technique for analyzing these molecules and studying their structures. To some extent, \(^{19}\text{F}\) NMR behavior resembles that of \(^{1}\text{H}\) nuclei as it reflects molecular structure, but \(^{19}\text{F}\) chemical shifts are much more sensitive to the environment and indirect spin-spin coupling extends over a much longer range, primarily because of the participation of unshared electrons. An advantage of \(^{19}\text{F}\) application in following the behavior of fluorine-containing molecules in biological systems is the absence of natural background.

Results and Discussion

Our laboratory has a library of various fluorinated materials, acquired thru consulting arrangements with Wright-Patterson Air Force Laboratories and with a number of industrial firms, as well as from syntheses by faculty research groups at the University of Florida. The availability of the Varian 500-MHz NMR spectrometer, to the acquisition of which the NHMFL made a substantial financial contribution, has permitted a much more detailed study of these materials than was possible with earlier lower-frequency instruments. Two areas of this work have been completed and described in 2004 publications in which the contribution of the NHMFL is acknowledged [1, 2], and a manuscript describing a third set of results has been submitted.

High-resolution fluorine-19 and carbon-13 NMR methods, utilizing such techniques as selective decoupling and 2D nuclear Overhauser (NOE) and correlation spectroscopy (COSY) experiments, were applied to study of geometry and bonding in 1,3,5-triazines with fluorinated side-chains, including amino linkages [1]. The patterns of structural effects on chemical shift and on spin-spin coupling in these molecules have been worked out. Remote effects of unsymmetrical substitution are observed in the fluorine-19 and carbon-13 spectra, in some molecules indicating restricted rotation about the bond joining an amino group to a ring carbon.

In a second area, similar procedures have been applied to chlorofluorocarbons with chains of seven to ten carbon atoms [2]. The steric effects of chlorine modify the fluorine chemical shifts, with the largest effect being on fluorines on carbons two atoms away from the chlorine substituent. These results give information about the molecular geometry. A scale of chlorine substituent effects on the fluorine shifts was developed. COSY patterns show that the fluorines in terminal CF₃ groups have no measurable coupling to the fluorines on the neighboring carbon, but that the small triplet splitting which is observed arises instead from coupling to fluorines on the fourth carbon atom from the end of the chain.

The third field of research concerns the structure and NMR spectra of vinyl ethers containing one or more fluorines. Presence of fluorines in these molecules interferes with the conjugation of the olefinic \(\pi\) electrons with the unshared electrons on the oxygen that is observed in protonated molecules. Long-range coupling effects are also important in analysis of the carbon-13 and fluorine-19 spectra of these molecules. Fluorine shifts resulting from the presence of chlorine isotopes are found only when the fluorine and chlorine atoms are attached to the same carbon. Support of NHMFL is acknowledged in a manuscript which has been submitted to the Journal of Fluorine Chemistry.

References