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An Experimental Study of ^{19}F–^{19}F and ^{13}C–^{19}F Spin–Spin Coupling in Molecules of Difluoro(fluorosulfonyl)- and Difluoro(fluorosulfonyloxy)acetyl Fluorides

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Abstract—High-resolution ^{19}F and ^{13}C NMR spectra of difluoro(fluorosulfonyl)- and difluoro(fluorosulfonyloxy)acetyl fluorides were studied, and specific features of complex spin–spin coupling of fluorine and carbon nuclei were characterized. The mechanisms of ^{19}F and ^{13}C coupling were interpreted.

Today analysis of the contributions of nuclear spins, covalent bonds, and lone electron pairs does not allow detailed understanding of the coupling mechanisms manifested in the ^{19}F and ^{13}C NMR spectra, which is indicated in numerous papers [1–10]. In attempts to unambiguously interpret the available data, from the set of numerous and interrelated factors the researchers choose those that do not contradict the existing views on the nature of the spin–spin coupling.

Two principal concepts of spin–spin coupling of nuclei have been suggested: transfer of the spin–spin information from one nucleus to another through covalent bonds or through lone electron pairs within the framework of the space-filling model along the straight line linking the coupled nuclei. Both concepts as applied to ^{19}F were presented in most detail by Ng and Sederholm [11]. They stated that spin–spin coupling involving ^{19}F requires no further explanations.

Along with F–F coupling, researchers also attempt to develop unambiguous interpretation for the ^{13}C–^{19}F coupling. As the main criteria for identification of the coupling mechanism, through covalent bonds or lone electron pair orbitals, they consider the dependence of J^{FF} and J^{CF} on the molecular geometry in π systems (polyconjugated, unsaturated, and aromatic compounds) [12–14] or the dependence of J on the electronegativity

of substituents [15]. For example, if J^{FF} in a system with overlapping lone electron pairs depends on the molecular geometry, whereas J^{CF} does not depend, the remote F–F coupling is assigned to through-space interaction, and the C–F coupling, on the contrary, to through-bond interaction [12]. At the same time, Jaime–Figueroa et al. [14] interpret the C–F coupling in substituted aromatic compounds as through-space coupling, owing to the dependence of J^{CF} on the inductive effect of the substituent. Thus, today there is no commonly accepted opinion on the mechanism of spin–spin coupling involving ^{19}F and ^{13}C.

Despite apparent simplicity of studying the spin systems of ^{19}F nuclei, the majority of the data obtained are insufficient for predicting in detail the spectral characteristics of new fluorinated organic compounds by semiempirical calculations. At the same time, quantum-chemical calculations do not take into account in full measure the specific features of the behavior of real molecules in real media and are not always correct, either. Therefore, understanding of the coupling mechanism in fluorinated organic compounds is the key point both for interpreting the available spectra and for predicting the spectral features of newly synthesized substances.

It should be noted that the main problem in recording high-resolution ^{19}F NMR spectra is the
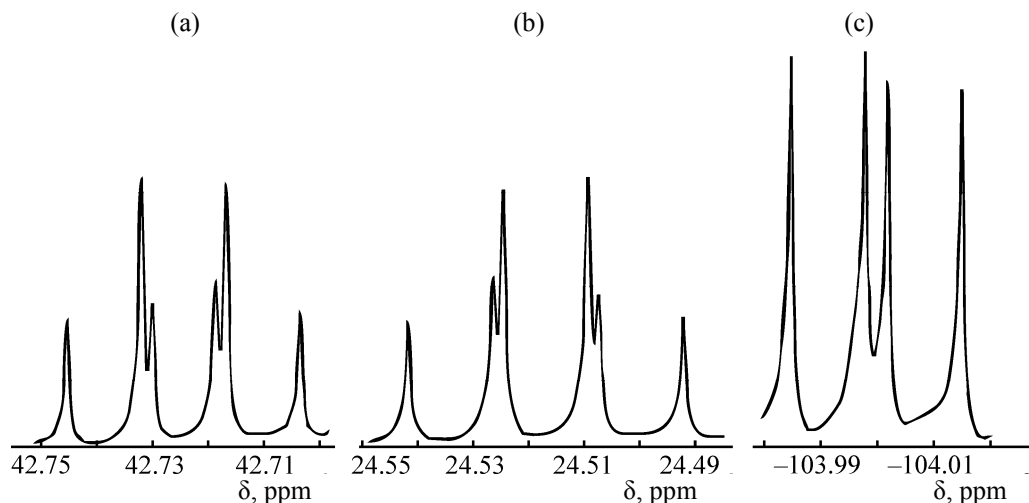
Fig. 1. ^{19}F NMR spectrum of difluoro(fluorosulfonyl)acetyl fluoride. (δ) Chemical shift; the same for Figs. 2–4. Group: (a) FSO$_2$, (b) COF, and (c) CF$_2$.

choice of the optimal concentration for each compound because of differences in intermolecular interaction of fluorinated organic molecules and solvation effects. This leads to signal broadening and complicates the determination of remote coupling constants. Proper recording of ^{19}F spectra is still a complex experimental problem, even for known substances. Therefore, until recently ^{19}F NMR spectroscopy of fluorinated organic compounds was in most cases merely an identification tool, so that the ^{19}F NMR spectra of many known fluorinated organic compounds require refinement. Difluoro(fluorosulfonyl)acetyl fluoride **I** is a known compound [16], but detailed characteristics of its NMR spectra have not been examined to sufficient extent. Difluoro(fluorosulfonyloxy)acetyl fluoride **II** is a new compound synthesized in our laboratory. In addition, both compounds chosen for the study demonstrate in total how the spectral pattern of a fluorinated organic compound changes in going from fluorosulfonyl to fluorosulfonyloxy group.

The goal of this study was to interpret theoretically the high-resolution ^{19}F and ^{13}C NMR spectra of **I** and **II** and to reveal specific features of the coupling of fluorine and carbon nuclei in these compounds.

EXPERIMENTAL

The ^{19}F and ^{13}C NMR spectra were recorded on a Bruker Spectrospin AM-500 spectrometer operating at 470.60 (^{19}F) and 125.76 MHz (^{13}C). The signals were accumulated in 8 to 512 scans. Samples were placed in standard ampules 5 mm in diameter. As solvent and internal reference for ^{13}C we used CDCl$_3$ (77.12 ppm). For ^{19}F the internal reference was hexafluorobenzene (–162.9 ppm).

Below are the structural formulas of compounds **I** and **II** with fluorine atoms denoted by Arabic numerals and carbon atoms, by capital Roman letters:
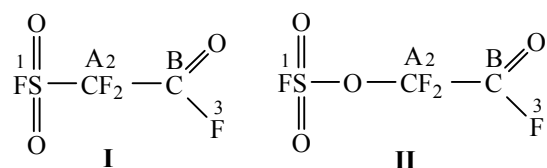
The ^{19}F NMR spectrum of **I** (Fig. 1) consists of three multiplets from –FSO$_2$, –COF, and –CF$_2$ groups. The fluorosulfonyl group –FSO$_2$ (Fig. 1a) gives a triplet of doublets at 42.7 ppm with the coupling constants $^3J_{12} = 6.2$ and $^4J_{13} = 7.2$ Hz. The signal from the –COF group (Fig. 1b) is shifted to 24.5 ppm and is also a triplet of doublets with the coupling constants $^4J_{31} = 7.2$ and $^3J_{32} = 8.1$ Hz.

It has been noted that remote F–F coupling constants can be larger than vicinal constants [17]. This fact was attributed to the contribution of through-space coupling of fluorine nuclei due to overlap of the electronic shells of the fluorine atoms in the case when these atoms are closely located in space.

The dependence of the vicinal coupling constants of the fluorine nuclei on the hybridization of the carbon atoms was noted for a compound in which the coupling of fluorine nuclei can be considered principally similar to that in **I** [18]:
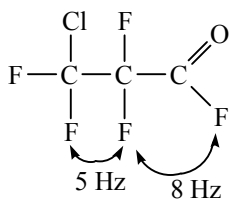
Comparison of this example with **I** demonstrates similar trends for the vicinal coupling constants. For example, the constant $^3J_{12}$ determined by contact of fluorine nuclei through covalent bonds with an sp^3 carbon atom and with an electron-depleted sulfur atom is lower than the constant $^3J_{32}$ involving the contribution of the free electron of the sp^2 carbon atom. Thus, the influence of the structure of the electronic shells of the intermediate atoms on the spin–spin coupling of the fluorine atoms indicates that the coupling of the vicinal nuclei mainly occurs through covalent bonds.

The –CF$_2$ group (Fig. 1c) is a doublet of doublets with a chemical shift of –104.0 ppm and vicinal coupling constants $^3J_{21} = 6.2$ and $^3J_{23} = 8.1$ Hz. The ^{19}F nuclei of this group are magnetically equivalent.

The ^{19}F NMR spectrum of **II** is shown in Fig. 2. The molecular structure of **II** differs from that of **I** in the presence of an ester bond, which leads to an upfield shift of the ^{19}F signals of the F^1 and F^2 atoms. The spectrum of **II** consists of three multiplets from the –FSO$_2$, –COF, and –OCF$_2$ groups. The ^{19}F signal of the –FSO$_2$ group (Fig. 2a) at 50.0 ppm is a broadened triplet with the coupling constants $^3J_{32} = 2.9$ and $^5J_{31} = 0.7$ Hz. The –COF signal (Fig. 2b) at 15.7 ppm is also a broadened triplet with $^3J_{32} = 2.9$ and $^5J_{31} = 0.7$ Hz. The ^{19}F signal of the –OCF$_2$ group at –77.5 ppm (Fig. 2c) is a doublet of doublets with $^4J_{21} = 7.3$ and $^3J_{23} = 2.9$ Hz. Comparison of the spectra of both compounds shows that the chemical shifts of **II** are in agreement with the theoretical concepts.

The remote coupling of fluorine nuclei in **II** is suppressed by two lone electron pairs of the ester oxygen atom, but the vicinal coupling constant ^3J between –CF$_2$ and –COF ($^3J_{23}$) is also considerably smaller (by a factor of almost 3) than in **I**. At the same time, the remote coupling constant $^4J_{21}$ in **II** is larger by 1 Hz than the vicinal coupling constant $^3J_{21}$ in **I**. Taking into account indications made by Liu et al. [19] that the F–F coupling becomes weaker in higher fields, we can conclude that shielding by oxygen limits the fluorine coupling, but the contribution of the through-space interaction to the remote coupling constant $^4J_{12}$ is possible owing to higher flexibility of the molecular chain with the hinge oxygen atom.

Comparison of the observed ^{19}F chemical shifts and coupling constants for both compounds shows that in **II** there is an intermolecular region of space within which the coupling constants J_{FF} are increased. For **I**, all the coupling constants are similar in value
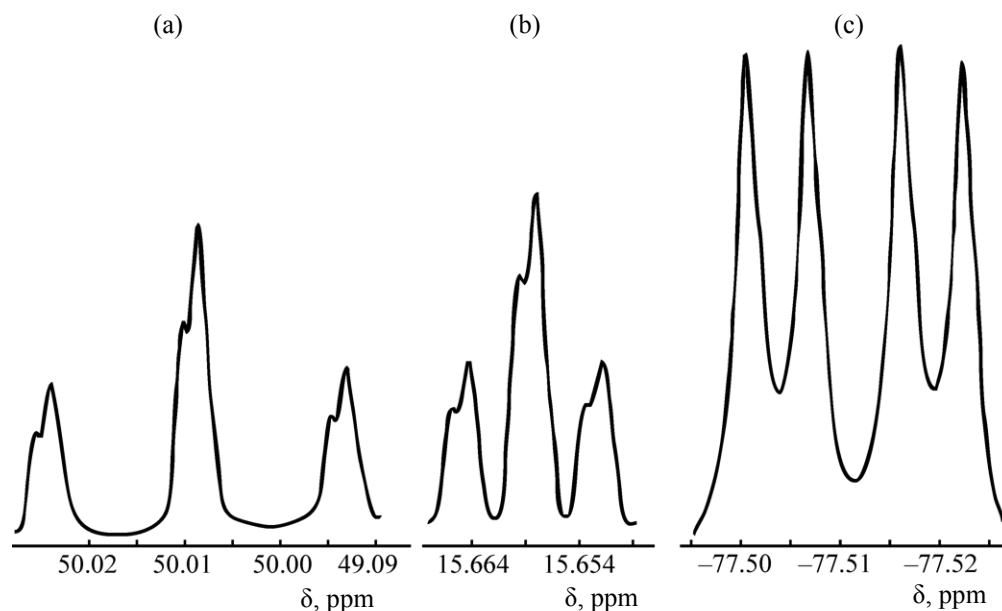

Fig. 2. ^{19}F NMR spectrum of difluoro(fluorosulfonyloxy)acetyl fluoride. Group: (a) FSO$_2$, (b) COF, and (c) OCF$_2$.

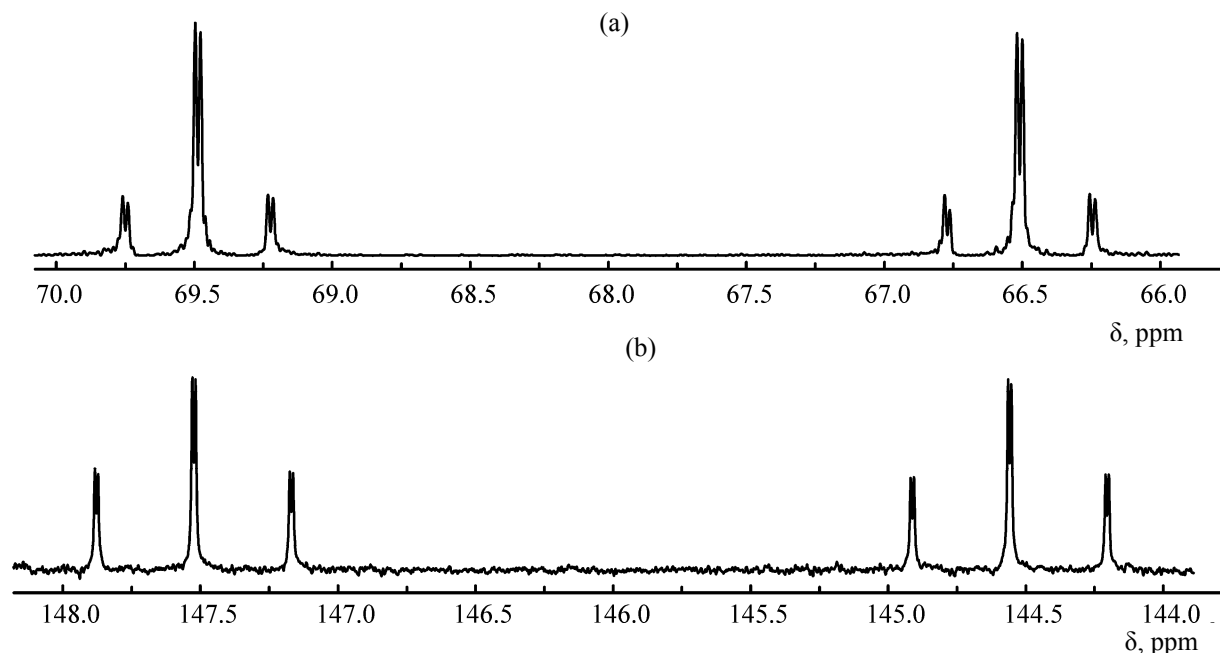**Fig. 3.** ^{13}C signals from the –COF group of (a) difluoro(fluorosulfonyl)acetyl and (b) difluoro(fluorosulfonyloxy)acetyl fluorides.

(6–8 Hz), i.e., the spin–spin couplings are distributed among ^{19}F nuclei in accordance with the electronic structure of atoms of this molecule. However, in **II** the coupling constants of the fluorocarbonyl group are beyond the region of high J values and are in the range 0.7–3.0 Hz. Thus, the presence of an ester bond in **II** leads to spatial differentiation of the J_{FF} constants of the nuclei located within and beyond the revealed region, which may be due to changes in the molecular geometry or to the effect of certain specific factors.

Let us consider the C–F coupling in **I** (Figs. 3a, 4a). The –COF group (Fig. 3a) of **I** gives a doublet of triplets of doublets at 146.5 ppm with $^{1}J_{B3} = 374.5$, $^{2}J_{B2} = 33.4$, and $^{3}J_{B1} = 1.6$ Hz. The signal of the –CF$_2$ group (Fig. 4a) is a triplet of doublets of doublets at 110.5 ppm with $^{1}J_{A2} = 300.0$, $^{2}J_{A1} = 39.5$, and $^{2}J_{A3} = 84.4$ Hz.

Comparison of the direct C–F coupling constants in **I** shows that the sp^2 carbon atom additionally contributes to the C–F coupling ($^{1}J_{B3} > ^{1}J_{A2}$) owing to the presence of the π-electron pair.

As for geminal coupling constants, $^{2}J_{A3}$ for the C and F nuclei coupled via sp^2 carbon atom is more than 2 times larger than $^{2}J_{B2}$ for the C and F nuclei coupled via sp^3 carbon atom. This fact means that the C–F coupling is transferred through covalent bonds and

therefore depends on the electronic shell of the atoms participating in this interaction. The other geminal coupling constant, $^{2}J_{A1}$, is almost 2 times smaller than $^{2}J_{A3}$, because the A–1 coupling is transferred through the electron-depleted sulfur atom.

The 6.1 Hz lower value of $^{2}J_{B2}$ compared to $^{2}J_{A1}$ can be attributed to high total electronegativity of the fluorine atoms in the –CF$_2$ group, preventing the B–2 coupling through covalent bonds.

In the ^{13}C MNR spectrum of **II** (Figs. 3b, 4b), there are two complex signals at 146.0 and 111.5 ppm. As compared to **I**, no significant changes in the chemical shifts are observed: the –OCF$_2$ signal is slightly shifted upfield under the action of the ester oxygen, whereas the –COF signal is, on the contrary, slightly shifted downfield.

The –COF group (Fig. 3b) gives a doublet of triplets of doublets at 146.0 ppm with $^{1}J_{B3} = 372.8$, $^{2}J_{B2} = 44.5$, and $^{4}J_{B1} = 1.5$ Hz. The –OCF$_2$ signal at 111.7 ppm (Fig. 4b) is a triplet of doublets with $^{1}J_{A2} = 289.36$, $^{2}J_{A3} = 94.8$, and $^{3}J_{A1} = 1.5$ Hz.

As for the direct coupling C–F coupling constants in **II**, they are smaller than those in **I**: $^{1}J_{B3}$ by 1.7 and $^{1}J_{A2}$ by 11 Hz. That is, the direct C–F coupling in the –CF$_2$ group adjacent to the ester bond becomes weaker owing to a shift of the electron density to the oxygen atom.
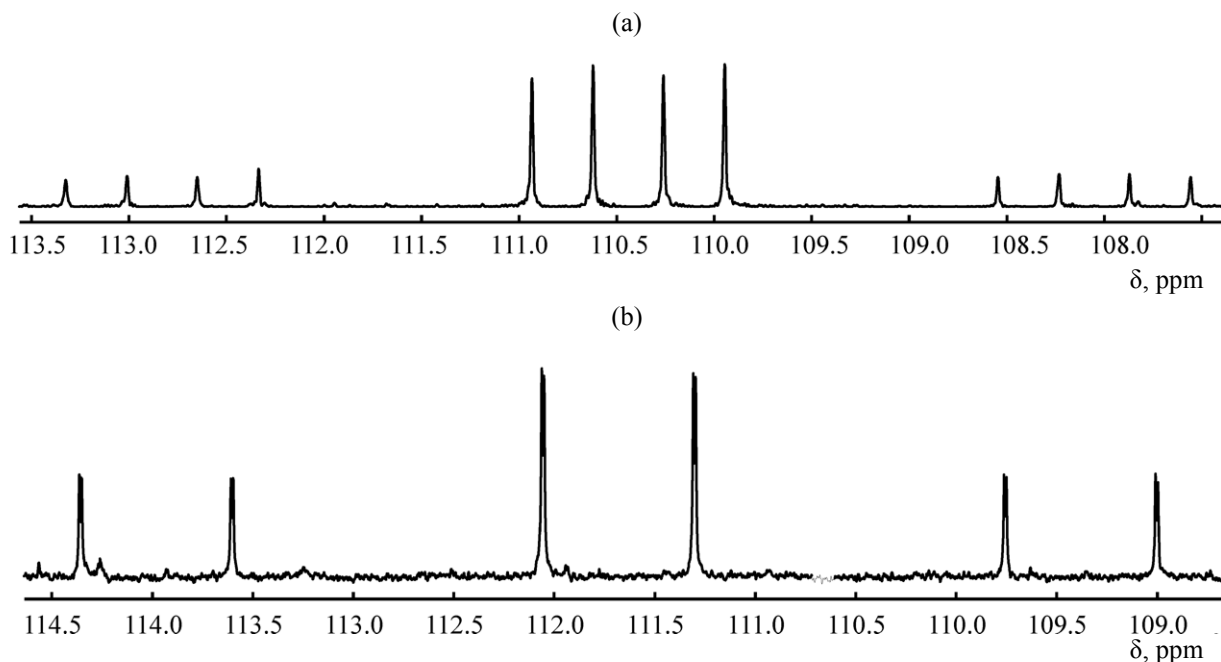
Fig. 4. ^{13}C signals from the (a) –CF$_2$ group of difluoro(fluorosulfonyl)acetyl fluoride and (b) –OCF$_2$ group of difluoro (fluorosulfonyloxy)acetyl fluoride.

The geminal coupling constant $^2J_{A3}$ in **II** is higher by 10 Hz than $^2J_{A3}$ in **I**. The same is true for $^2J_{B2}$. This fact suggests that suppression of the vicinal (2–3) F–F coupling in **II**, caused by the presence of the oxygen atom, can facilitate the geminal C–F coupling through the sequence of covalent C–C–F bonds, which leads to increased $^2J_{B2}$. As for $^2J_{A3}$, it is also increased, which does not allow the –COF group to be considered as located beyond the region of high J values and suggests enhancement of the C–F coupling at the expense of weakening of F–F coupling in the molecule. Hence, the mechanism of the transfer of the C–F spin–spin coupling is sensitive to suppression of the F–F coupling realized through covalent bonds.

The vicinal coupling A–1 is practically blocked ($^3J_{A1}$ = 1.5 Hz), which also indicates that the remote C–F coupling is transferred through covalent bonds, with the transfer suppressed by the presence of a highly electronegative atom in the molecular chain.

CONCLUSIONS

(1) The spin–spin coupling of fluorine atoms is spatially differentiated, with the coupling constants depending on the region of the molecule.

(2) The mechanism of the transfer of the C–F coupling is sensitive to suppression of the F–F coupling through covalent bonds.

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