CHEMICAL SHIFTS OF F^{19} NUCLEAR MAGNETIC RESONANCE IN ORGANOFLUORINE COMPOUNDS

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Abstract

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CHEMICAL SHIFTS OF F^{19} NUCLEAR MAGNETIC RESONANCE IN ORGANOFLUORINE COMPOUNDS

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The discovery and investigation of chemical shifts in nuclear magnetic resonance (NMR), caused by different magnetic shielding of nuclei occupying structurally nonequivalent positions in a molecule, made it possible successfully to apply the NMR method to the structural and qualitative analysis of organic, and in particular organofluorine, compounds ([1–4]).

Since at present the possibility of theoretical calculation of chemical-shift magnitudes is practically absent, in order to carry out qualitative analysis by means of NMR it is necessary first to determine the ranges of chemical shifts characteristic of individual fluorine-containing groups occurring in organic molecules. For this purpose, in the present work the F^{19} NMR spectra of about 100 organofluorine molecules of known structure were investigated. This made it possible to refine the limits of the chemical-shift ranges for some groups studied previously ([3,4]), and also to find shift values for groups not investigated or only little investigated, including CF_2H—, —CFH—, CFH_2—. The measurements were carried out with a synchronized self-oscillating spectroscope ([5]) with resolving power $\Delta H/H \cong 10^{-6}$, a detailed description of which is given in ([6]).

The substances studied were sealed in cylindrical glass ampoules with an internal diameter of 4 mm. The sample volume was about 0.1 cm^3; diamagnetic corrections for the shape of the sample were not introduced.

The measure of the chemical shift is a relative quantity, determined as follows:

$$\delta = \frac{H_{\text{sample}} - H_{\text{std}}}{H_{\text{std}}} 10^6.$$

Here H_{sample} and H_{std} are the resonance values of the intensity of the constant magnetic field for the substance studied and the reference sample, respectively, at a fixed value of the spectroscope frequency. Freon CF_2Cl_2 was used as the reference sample. The results of the measurements are given in Table 1. For each of the fluorine-containing groups studied, the minimum and maximum values of δ are indicated, determining the range of chemical shifts characteristic of the given group, as well as the arithmetic mean value of the shift in each

range. The shift values in repeated measurements were reproduced with an accuracy of $\pm 1 \cdot 10^{-6}$. To convert to chemical-shift values relative to F_2 and CF_3COOH, used as reference samples in works ([3,4]), one may use the relations ([2]): $\delta_{F_2} = \delta_{CF_2Cl_2} + 434.8$; $\delta_{CF_3COOH} = \delta_{CF_2Cl_2} - 72.8$.

The groups investigated are arranged in Table 1 in order of increasing shift. The total change in the shift for all molecules whose NMR spectra were recorded in the present work is $293 \cdot 10^{-6}$. In this case the least-

the smallest shift occurs for fluorine in the group $-C(=O)F$, the largest in $-CFH_2$. In the groups CF_2H-, $-CFH-$, $-CFH_2$ the shift increases with an increase in the number of hydrogen atoms per fluorine atom $\left(\frac{n_H}{n_F}\right)$. An analogous picture was observed in work ([2]) for the series: CF_4, CF_3H, CF_2H_2, CFH_3. It is interesting to note that in this series there is an almost linear dependence of the chemical shift (measured relative to CF_4) on $\frac{n_H}{n_F}$.

Table 1

Ranges of NMR chemical shifts of F^{19} for individual fluorine-containing groups

$$\left(\delta_{CF_2Cl_2} = \frac{H_{\text{sample}} - H_{CF_2Cl_2}}{H_{CF_2Cl_2}} \cdot 10^6\right)$$

Group	Shift range $\delta_{\min}$	Shift range $\delta_{\max}$	Number of groups studied	Mean shift value	Group	Shift range $\delta_{\min}$	Shift range $\delta_{\max}$	Number of groups studied	Mean shift value
$-C(=O)F$	−63	−27	3	−38	$)C-CF_2-C$	93	105	2	99
$-CF_2Br$	38	55	10	46	$-CFCl-$	90	119	4	104
$-CF_2Cl$	43	59	13	51	$-CF_2H$	105	133	17	116
$-CFCl_2$	57	61	3	56	$-CFBr-$	104	136	15	117
$C=(CF_3)_2$	53	67	13	58	$-CFBrH$	126	136	3	131

Group	Shift range δ_{min}	Shift range δ_{max}	Number of groups studied	Mean shift value	Group	Shift range δ_{min}	Shift range δ_{max}	Number of groups studied	Mean shift value
–CF-ClBr	58	58	1	58	–CF-ClH	135	135	1	135
–CF-ClJ	60	60	1	60	a) C–CFH–S	168	171 (doublet)	1	169
–CF_3	53	74	30	66	) C–CFH–C	176	203	11	192
a) C–CF_2–O	50	77	9	68	a) S–CFH_2	193	200	2	196
) C–CF_2–N	78	85	5	81	) C–CFH_2	216	230	3	223
) C–CF_2–S	93	97	3	94					

The large magnitude of the shift characteristic of the groups –CFH–and –CFH_2 makes it possible to determine readily the presence of these groups in a molecule by the NMR method. Identification of –CF_2H is more difficult, since the ranges of chemical shifts of this group and of the groups –CF_2–, –CFCl–, CFBr–, –CFBrH, and –CFClH overlap with one another. In most cases the problem is facilitated by the fact that the NMR signals from fluorine in –CF_2H are split into a doublet owing to indirect spin-spin interaction of the fluorine and hydrogen nuclei ([7]). Multiplet splittings were also observed for the groups –CFH–and –CFH_2.

Changes in the chemical shift for a given fluorine-containing group, caused by the influence of neighboring atoms in the aliphatic chain, were noted. For example, for the grouping C–CF_2–X, the magnitude of the NMR shift of fluorine in the –CF_2–group depends on X and increases in the series X = O, N, S, C from 50 to 105. The same dependence was found in C–CFH–X and CFH_2–X, where X = S, C. In some cases it is possible to observe small changes in δ due to the

influence of more remote parts of the molecule. Thus, in the grouping C–CF_2–OR, the magnitude of the shift, other conditions being equal, depends on R.

This gives grounds to hope that the accumulation of experimental data will lead to the establishment of a relationship, important for structural analysis, between the magnitude of the NMR chemical shift of fluorine for a given group and

composition of the neighboring groups. Detailed data on the fluorine NMR spectra for all the compounds studied will be published later.

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Note: Figure translations are in progress. See original paper for figures.