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A full analysis of the NMR spectra of H^1 and F^{19} mixtures of the cis and trans isomers of β -fluorostyrene was carried out. The chemical shifts of H^1 and F^{19} and the spin-spin interaction constants in systems of the CFH= CHX type, the differences for the various isomers, and the effect of the X substituent are discussed.

NMR has proved quite effective in the study of the isomers of various compounds [1]. The reasons for the appearance of the isomers in the NMR spectra of H^1 and F^{19} are connected either with the effect of the anisotropic diamagnetic susceptibility or with the effect of the internal electrical fields. The difference in the shielding of the nuclei in the cis and trans isomers can amount to 20 ppm [2,3] in the NMR spectra of F^{19} .

Results of the investigation of the NMR spectra of H^1 and F^{19} in β -fluorostyrene are reported in this article. This compound can be found principly in two isomeric forms, cis (I) and trans (II):



Bergman was the first to deal with the question of cis-trans isomerization in β -fluorostyrene and concluded that β -fluorostyrene (nD²⁰ = 1.5284) is found basically in the trans form [4]. This conclusion was based chiefly on infrared spectroscopic data.

The β -fluorostyrene investigated in this work was synthesized according to work [5] and had an $n_D^{20} = 1.5262$ which is adequately close to the constant reported by Bergman.

The NMR-H¹ and F¹⁹ spectra of β -fluorostyrene are presented in Figs. 1a and 2c. The spectra were taken on an SYaMR-63 spectrometer with the frequency for the protons equal to 22.68 Mcps and for the F¹⁹ nucleus, 21.35 Mcps. The chemical shifts of F¹⁹ are reported relative to benzotrifluoride, C₆H₅CF₃. The protonic chemical shifts are given relative to hexamethyldisiloxane (HMS). The reference compounds in both cases were used as internal standards. The utilization of literature data for F¹⁹ shifts, which are often given relative to CFCl₃ (F-scale) [6], was carried out according to the relation: $F(C_{6}H_5CF_3) = -63.773$ ppm. In the same way the utilization of data presented on the τ -scale (TMS = 0) was carried out according to the relation $\tau(HMS) = -0.05$ [7] for the proton resonance.

The precision of the measurement of the H¹ chemical shift amounts to ± 0.05 ppm, F¹⁹ ± 0.2 ppm. The relative positions of the low resonance lines in the H¹ spectrum was measured with a precision of ± 0.2 cps, and in the F¹⁹ spectrum, ± 1 cps.

ANALYSIS OF THE SPECTRA

In accordance with the accepted classification of NMR spectra, each of the β -fluorostyrene isomers should be attributed to the ABX system [3]. It is known that the spectrum of an ABX system has a portion, AB, consisting of two quartets, each of which should give a constant J_{AB} , and a portion, X, which contains a maximum of six lines from which there are two lines of a combination type. In this way, it directly follows from the F¹⁹ spectrum (see Fig. 2a) that the sample studied contained two isomers: from the symmetry and intensities, it is easy to conclude

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Fig. 1. The NMR- H^1 spectrum of a mixture of β -fluorostyrene isomers: a) experimental, numbering of the lines in accordance with Table 1, shifts are given relative to HMS: b) calculation for the trans-isomer, c) calculation for the cis-isomer; d) for the mixture of isomers.



Fig. 2. The NMR- F^{19} spectrum of a mixture of β -fluorostyrene isomers: a) experimental, numbering of the lines in accordance with Table 2, scale in cps is given relative to $C_6H_5CF_3$: b) calculation for cis isomer; c) for the trans isomer; d) for the mixture of isomers.

that lines 1-6 and 7-12 belong to the different isomers, and, consequently, the F^{19} spectra do not overlap.

It can be concluded that just such lines are attributable to the isomer being identified if the distance between the maximum (by intensity) lines in the X portion of the ABX spectrum is found equal to $|J_{AX} + J_{BX}|$. It was established from the spectrum that this distance equals 130 cps for one isomer (lines 1-6), and for the other, 105 cps (lines 7-12).

If the literature data are turned to for the spin-spin bond constants of the bond on the fluoroethylenes [1], the variation of the values $J_{HF}_{trans} = 40$ cps, $J_{HF}_{cis} = 20$ cps, and $J_{HF}_{gem} = 80$ cps clearly leads to the following conclusions: 1) lines 1-6 are attributable to the cis-isomer, lines 7-12 to the trans isomer, 2) the J_{HF} constants have the same signs for each of the isomers.

An analysis of the proton spectrum is complicated by the overlapping of the lines of the various isomers (see Fig. 1a). It can also be assumed that part of the lines from the protons of the vinyl group are superimposed on the multiplet of the ring protons (K, see Fig. 1a). The H¹-spectrum of β -fluorostyrene was taken at 40 Mcps* with the idea of possibly simplifying the analysis of the spectra. However, this spectrum did not yield

the expected simplification. Therefore, while carrying out the analysis, we basically depended on the data from the spectrum (Fig. 1a) (f = 22.68 Mcps). The calculation performed was then also checked for a frequency of 40 Mcps and agreed well with the experimental value.

Based on the reasonable values of the J_{AB} constants, which are known from the literature [1], it can be proposed that lines 9 and 10 are attributable to the quartets of the AB portion of the spectra of the cis and trans isomers respectively. This is also confirmed by the fact that the ratio of the overall intensities of curve 1, 2 to 9, 10 agrees

^{*}We take this opportunity to express our appreciation to É. I. Fedin for taking the spectrum.



Fig. 3. The NMR-H¹ spectrum of the fraction obtained after the reaction of β -fluorostyrene with o-tolyllithium. The scale is in ppm relative to HMS. Peaks I and II are attributable to impurities.

TABLE 1.	Analysi	s of the	ΝM	IR−H ¹	Spectrum
(22.68 Mc	ps) of a	Mixture	of	β-Fluo	prostyrene
Isomers					

Spectrum line	Exp. fre- quency*	Exp. in- tensity†	Calc.fre- quency	Calc. in- tensity [‡]	Calc. in - tensity with allowance for structure				
		trans-Is	omer						
1 2 3 4 5 6 7 8	$\begin{array}{r} -45,7 \\ -33,8 \\ ** \\ +15,3 \\ +21,4 \\ +33,1 \\ +42,2 \\ +54,0 \end{array}$	0,25 0,35 **) 0,28 0,15 0,43 0,43 0,15	$\begin{array}{r} -45,7\\ -33,9\\ +3,6\\ +15,4\\ +21,3\\ +33,1\\ +41,9\\ +53,7\end{array}$	0,76 1,24 1,24 0,76 0,43 1,57 1,57 0,43					
cis-Isomer									
9 10 11 12 13 14 15 16	-29,0-23,5+14,4+19,9**)+59,4+61,1+66,6	0,16 0,23 0,23 0,16 ** 0,32 0,32 0,05	$\begin{array}{r} -28,9 \\ -23,4 \\ +14,2 \\ +19,8 \\ +54,0 \\ +59,5 \\ +60,9 \\ +66,4 \end{array}$	0,87 1,13 1,13 0,87 0,20 1,80 1,80 0,20	0,17 0,23 0,23 0,17 0,04 0,36 0,36 0,36 0,05				

*The frequencies are corrected relative to the center of the multiplet of the ring (K) in cps. The shift for (K) is relative to HMS-6.93 ppm.

†From an estimate that the overall intensity of lines 1 and 2 equals 0.60 (trans-isomer content equals 60%).

 \ddagger From an estimate that the overall intensity of lines 1 and 2 is equal to 2.00.

**Partial or total overlapping of the lines.

with the ratio of the cis-trans isomers which were determined from the F^{19} spectrum (41% cis form).

We are not citing those numerous modifications which were examined during attempts at a complete interpretation of the spectra. In a short time, we just decided on those considerations which were used in the final modification. Lines 14 and 15 are the central lines of one of the quartets in the AB portion of the ABX spectrum of the trans isomer. J_{AB} was obtained from the splitting of lines 1-2 for the trans and 9-10 (H^1 -spectrum) for the cis isomer (11.8 and 5.5 cps). Then, through the parameters D₊ and D₋ of the F¹⁹ spectrum, the values of $\Delta \nu = \nu_A - \nu_B$ and $|J_{AX} - J_{BX}|$ [1] were found from a system of equations, simultaneously $|J_{AX} + J_{BX}|$ can be determined from the F¹⁹ spectrum from the splittings of 1-6 and 7-12 (for the cis and trans isomer respectively). Further, the constants JAX and JBX are found from the values of $|J_{AX} + J_{BX}|$ and $|J_{AX} + J_{BX}|$. During the determination of the intensities, attention was paid to the fact that the inner lines with a splitting of $2 | D_+ - D_- |$ are greater in intensity than the outer (combined) lines with a splitting of $2 | D_{+} - D_{-} |$ (lines 2 and 5). This fact concerns the cis isomer. In the case of the trans isomer, the reverse situation is observed: the intensity of combined lines 8 and 11 is more intense than lines 9 and 10. Therefore, during the determination of φ_{+} [1],

it is necessary to consider φ_+ as 2π - arc sin $(\frac{J_{AB}}{2D_{t}})$, and not as

arc sin
$$(\frac{JAB}{2D_+})$$
.

Data from the calculations of the H^1 and F^{19} spectra are presented in Tables 1 and 2. In addition, spectra calculated for each of the isomers (1b, 2c - trans) and (1c, 2b - cis) are given in Fig. 1 and 2. Spectra, plotted in accordance with the isomer content of the mixture, are presented in Figs. 1 and 2. Intensities are given in the last columns of Tables 1 and 2; experimental intensities, for comparison, are presented in the second columns.

The data on the analysis of the NMR spectra (in part, concerning the assignment of the lines to the specific isomer) were confirmed by the curious behavior of β -fluorostyrene in the reaction with o-tolyllithium. The following products were isolated upon carrying out this reaction in ether at 0°: α, α' -diphenylethylene, b.p. 120°/0 mm and $nD^{20} = 1.6294$, and a fraction with a b.p. of 76-78°/70 mm and $nD^{20} = 1.5340$. From the NMR-H¹ spectrum of this fraction (Fig. 3), it follows that as a result of the reaction, the ratio of β -fluorostyrene isomers changed (59% - trans isomer before the reaction, 28% - after the reaction). Lines (I and II) observed in the spectrum in Fig. 3 are attributable to impurities (toluene, etc.). In this way, it can be concluded that the trans-isomer reacts more energetically, and this, apparently, leads primarily to trans-stilbene.

TABLE 2. Analysis of the NMR- F^{19} Spectrum (21.35 Mcps) of a Mixture of β -Fluorostyrene Isomers

Spectrun line	Exp. fre- quency*	tensity†	Calc. fre quency	Calc. in- tensity‡	Calc. in - tensity with allowance for structure			
		cis-Is	omer					
1 2 3 4 5 6	1210 1250 1255 1290 1300 1340	0,40 0,10 0,33 0,33 0,10 0,40	1210 1249 1255 1283 1299 1340	1,00 0,10 0,85 0,85 0,10 1,00	0,40 0,06 0,34 0,06 0,06 0,40			
trans-Isomer								
7 8 9 10 11 12	1390 1400 1430 1455 1475 1475 1495	0,60 0,47 0,15 0,15 0,47 0,60	1390 1407 1429 1456 1476 1495	1,00 0,82 0,18 0,18 0,82 1,00	0,60 0,49 0,11 0,11 0,49 0,60			

*Relative to benzotrifluoride ($C_6H_5CF_3$) as the internal standard in cps.

†From an estimate that the overall intensity of lines 1 and 7 is equal to 1.00. ‡The intensities of lines 1 and 7 was assumed to be equal to 1.00.

DISCUSSION OF RESULTS

The chemical shifts of H¹ and F¹⁹ and the spin-spin interaction constants of the protons and F¹⁹ nuclei in FHC = CHX type compounds (also including the various isomers) are presented in Table 3. The chemical shifts of H¹ were recalculated relative to ethylene for a more graphic representation of the effects of the action of fluorine on the chemical shifts of the protons in the vinyl group. A value of $\tau(C_2H_4) = -5.33$ [8] was used for the shift of ethylene.

The spin-spin interaction constants show definite regularities. A series of them show the following:

$$J_{\rm HH_{cis}} \approx 5$$
, $J_{\rm HH_{trans}} \simeq 12$, $J_{\rm HF}_{\rm trans} \simeq \mp 40 - 50$,
 $J_{\rm HF_{cis}} \simeq \pm 20$, $J_{\rm HFgem} \simeq \pm 80 - 90$ cps.

These data agree quite well with constants for a series of fluoroolefins published in the literature [1]. Notice the anomalous values of $J_{\rm HF}$ which are observed for 1,2-difluoroethylene:

$$J_{\mathrm{HF}_{\mathrm{cis}}} \simeq \pm 4.4, J_{\mathrm{HF}_{\mathrm{trans}}} = \pm 18.7 \ \mathrm{cps.}$$

The interpretation of the data on the proton resonance leads to an estimate of two effects: the inductive, connected with the drawing together of the σ -electrons with the vinyl group on the fluorine atom (-I), and the conjugation effect, consisting of the conjugation of the 2p-electrons of the fluorine atom with the π electrons of the vinyl group (+M). Thus, it follows from the experimental data that the α -hydrogen atoms yield a resonance in the

weakest fields compared with ethylene as a result of the dominant effect of -I on the α -carbon atom. A somewhat different pattern occurs for protons on the β -carbon atom. A calculation for the C-C-F structure by Hückel's method (on the assumption that $\alpha_F = 3\beta_{C-C} + \alpha_{C,\beta C-F} = 0.7 \beta_{C-C}$ [9]) was carried out to evaluate the +M effect. If it is assumed that each fluorine atom introduces two electrons into the overall π -system, then the calculation leads to the following values of the π -electron density on the atoms and the sequence of bonds:

In this way the increase in the π -electron density on the β -carbon atom by 0.075 of an electron compared to ethylene leads to a shift in the H¹ resonance of the adjacent protons in the strong fields by about 1 ppm. It is obvious that the inductive effect shows up considerably more weakly on the protons at the β -carbon atom.

The difference in the shielding of the protons at the β -carbon atom from the point of view of the existing theories can be explained either by the anisotropic diamagnetic susceptibility or by the effect of the electric field of the C-F bond dipole on the polarization of the electrons in the C-H bond. Since we do not have any data on the anisotropy of the diamagnetic susceptibility of the C-F bond available, we evaluated the different chemical



cal field. It follows from Table 3 that $\Delta \sigma = \delta H_A - \delta H_B$ is positive in all the compounds, from which the value of $\Delta \sigma$ ranges from +0.34 ppm in FHC = CH₂ to +1.02 ppm in FHC = CFH for various X. The data on the NMR shifts in

the vinyl group of H_R H_C [10] where $X = F \Delta \sigma > 0$, for $X = H \Delta \sigma = 0$, for $X = \text{metals } \Delta \sigma < 0$ are a defi-H_R X

nite argument confirming the effect of the electrical field of the bond dipole C-X. Reversal of the sign of $\Delta\sigma$ during

spectra of Fluoroolefins of the FHC= CHX Type
Fluo
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Refer- ence		[17]	[18]	[18]	* *	*	[61]	[19]
+4	JHF cis	$\pm 20,1$	ł	$\pm 19,9$	l	$\pm 20,5$	-	土4,4
	JHFtrans	±52,4	土41,8	ł	土 40,7	ł	±18,7	1
constants	J _{HF} gem	±84,7	±,89,9	$\pm 84,8$	±89,6	±85,3	$\pm 72,7$	$\pm 74,3$
spin bond	J _{HH} gem	-3,2	1	1	l	1	1	1
Spin-	JHHtrans	12,8	l	11,1	I	11,8	I	9,5
	JHHcis	4,7	4,5	I	2,5	l	2,0	I
H ¹	$^{\delta H_B}$	+0,96	1	+0,03	ł	+0,77	ł	-1,89
n. shifts†	βHA	+1,30	+0,65	l	+0,10	1	0,87	ł
Cher	$^{8}\mathrm{H}_{C}$	0,84	-1,13	1,13	0,94	-1,45	0,87	1,89
Chem. shift *	БЦ Q	+48,8	+67,9	+65,8	+59,4	+67,5	+101,3	+122,5
	Compound		$\mathbf{H}_{\mathbf{A}} = \left\langle \mathbf{H}_{\mathbf{F}} \right\rangle$	$\mathbf{H}_{B} \rightarrow \mathbf{H}_{F}$	$H_{Ph} \rightarrow H_{Ph} C$	$\mathbf{H}_{B} \xrightarrow{\mathbf{H}_{F}} \mathbf{H}_{C}$	$\mathbf{H}_{\mathbf{F}} = \left\langle \mathbf{H}_{\mathbf{F}} \right\rangle_{\mathbf{F}}$	$\mathbf{H}_{B} \rightarrow \mathbf{F}_{F}$
	5	I	II	III	IV	Δ	IA	ΝII

*The shifts are presented in ppm relative to $C_{g}H_{5}CF_{3}$ as the internal standard. \uparrow The shifts are presented in ppm relative to ethylene; for the recalculation, see the text. \ddagger In cps. The relative signs of the constants for JHF_{trans}, JHF_{gem}, and JHF_{cis} are presented. **This work.

the transition $F \rightarrow H \rightarrow$ metals of course is connected with a change in the sign of the dipole moment of the C-X bond. Using the formulas obtained by Buckingham [11] with the coefficients specified by Musher [12] on the assumption of the average structural parameters of work [13], and localization of the dipole in the center of the C-F bond, we estimated the dipole moment of the C-F bond in FHC= CH₂ ($\Delta \sigma$ = +0.34 ppm) to be equal to 3.5 D, which considerably exceeds other values [14]. We will arrive at still larger values for the dipole moment on comparing the shifts of H_A and H_B in the other isomers, consequently the estimate in question must be considered preferably as qualitative.

Upon considering the data in Table 3, the fact that the resonance of the protons in β -fluorostyrene shifts in the weak field (IV and V, Table 3) attracts attention. Such phenomena, as is known [1], are caused by the effect of the diamagnetic ring currents. Employing the results from work [16], corrections caused by the ring currents, were calculated: for IV-H_C (-0.25 ppm), H_A (-0.60 ppm), for V-H_C (-0.53 ppm), H_B (-0.60 ppm). The calculation of these corrections leads to the fact that the values of the chemical shifts of the protons in II and IV or in III and IV agree with each other quite closely.

It follows from Table 3 that there is additional confirmation of the conjugation effect in the F^{19} shifts [15] at this instance. Upon changing substituent X = H by F, the F^{19} signal shifts in the strong fields, although, by reason of a purely inductive effect, a shift in the weak field should have been expected. Remember that this effect is similar to the one found in trifluorovinyl compounds for the F_1 and F_2 nuclei [2]. The appearance of a cis-trans effect is small for X = H but for X = F, this effect amounts to 21.2 ppm and agrees with the variety of F^{19} shifts in the cis and trans fluoroolefin isomers [2, 3]. The diversity in the F^{19} shifts in the β -fluorostyrene isomers is possibly connected with the fact that there are certain steric hindrances in the cis-isomer leading, in the case of ortho- CH_3 -substituted fluorostilbenes [3] and of fluorostyrenes [2] for example, to a shift of resonance in the weak fields, but less markedly (7.9 ppm).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of the first issue of this year.