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^{19}F NMR SPECTRA OF MESOMERIC CARBANIONS GENERATED FROM POLYFLUORODIARYLACETONITRILES. THE ELECTRONIC EFFECT OF PERFLUOROALKYL GROUPS

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SUMMARY

^{19}F NMR spectra of 1,2-dimethoxyethane solutions of Na- and Li-salts of polyfluorinated carbanions $[p\text{-}RC_6F_4\bar{C}(CN)C_6F_4R'\text{-}p]\ Na^+$ (Li^+) and of their neutral precursors $p\text{-}RC_6F_4CH(CN)C_6F_4R'\text{-}p$ / R = F or CF_3 and R' = CF_3, CF_2CF_3, $CF(CF_3)_2$ and $C(CF_3)_3$ / have been studied. The values of changes in the chemical shifts of fluorine atoms in the ring and in the side chain are practically the same when going from the precursor to carbanion with the perfluoroalkyl group being varied. This gave grounds to conclude that the electronic effect of the perfluoroalkyl groups is rather similar. The ^{19}F NMR method has revealed no differences in the predominant mechanism of the negative charge distribution by these groups.

INTRODUCTION

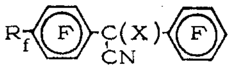
As is known, in the case of benzotrifluorides either deshielding or shielding of the fluorine atoms of the CF_3 group is observed in the ^{19}F NMR spectra of these compounds, depending on whether an electron-donor substituent is found in or an electron-acceptor substituent is introduced into the para-position [1,2]. This phenomenon is characteristic not only for benzotrifluorides, but also for benzyl- and naphthylmethyl fluorides, alicyclic, cyclic and bicyclic fluorides [3]. Though no convincing explanation of this phenomenon can be offered, in one of the studies the spectral behaviour of the fluorine atoms in substituted benzotrifluorides was attributed to the effect of negative hyperconjugation of the CF_3 group [1]. Later this point of view was subjected to criticism, since the effects of the substituent on the values of chemical shifts of the fluorine atoms in the CF_3 group in substituted benzotrifluorides are by an order of magnitude smaller than those for substituted fluorobenzenes and, hence, the contribution of the resonance structure of type (A) to the ground state of the molecule is not great [4].

A

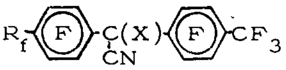
At the same time in the above-cited article it was pointed out that checking of the role of the effect of negative hyperconjugation of the CF_3 group by various methods (including the NMR method) is more effective on models containing anions, since such models better approximate transition states in organic reactions. Thus, for enolate anions generated from polyfluorinated isobutenol and propenol ethers, deshielding of the fluorine atoms of the CF_3 groups (10 ppm. downfield shift) is observed [5]. The study of Meisenheimer complexes containing CF_3 group showed that in the case of the CF_3 group being in para-position to the geminal node the signal of the fluorine atoms of this group in the ^{19}F NMR spectrum is observed to be 0.27 ppm. downfield as compared to the location of the same signal in the ^{19}F NMR spectrum for the case of the CF_3 group being in ortho-position to the geminal node [6]. Taking into consideration that in Meisenheimer complexes a larger portion of the negative charge is located on that carbon atom of the ring, which is in para-position to the geminal node [7], relative deshielding of the fluorine atoms of the CF_3 group in the para-position is identical with the above-cited data concerning the behaviour of the same group in substituted benzotrifluorides and enolate anions. Previously we have also indicated deshielding of the fluorine atoms of the CF_3 group to take place when passing from para-trifluoromethyl-substituted derivatives of polyfluorophenylmalonic acid, triarylmethanes and diarylacetonitriles over to the corresponding carbanions [8, 9].

RESULTS AND DISCUSSION

For checking the connection between deshielding of the fluorine atoms of the CF_3 group in the ^{19}F NMR spectra of carbanions and the effect of negative hyperconjugationo of this group, we have undertaken spectral studies of two series of polyfluorinated diarylacetonitriles and their salts of carbanions containing perfluoroalkyl groups in para-position.



I,Ia,b- IV,IVa,b



V,Va,b - VIII, VIIIa,b

	X	R_f
I,V	H	CF_3
Ia,Va	Na	
Ib,Vb	Li	
II,VI	H	CF_2CF_3
IIa,VIa	Na	
IIb,VIb	Li	
III,VII	H	$CF(CF_3)_2$
IIIa,VIIa	Na	
VIIb	Li	
IV,VIII	H	$C(CF_3)_3$
IVa,VIIIa	Na	
IVb,VIIIb	Li	

In the choice of these series of compounds we were guided by the consideration that their study offered a possibility to compare changes in the values of chemical shifts of the fluorine α-atoms in perfluoroalkyl groups R_f and of the fluorine atoms in the CF_3 group when the R_f substituent in the other benzene ring is varied. If the mechanism of hyperconjugation of the CF_3 group is associated with the value of deshielding of the fluorine atoms in this group, then, as we go from compounds (I,V) containing only CF_3 groups over to compounds (II- IV, VI,- VIII) containing other perfluoroalkyl groups, changes must be observed in the values of chemical shifts of the fluorine α-atoms in the side chain. Investigation of the two types of salts of carbanions (Ia,b - VIIIa,b) makes possible a more reliable evaluation of the character of changes in the values of chemical shifts of the fluorine atoms.

The parameters of the ^{19}F NMR spectra of the series of compounds (I- VIII), as well as of their Na- and Li- salts of carbanions (Ia,b - VIIIa,b) are given in Tables 1 and 2, where $\Delta\delta_F$ stands for the shift of the signal of the corresponding fluorine atom in carbanion with respect to the same in the precursor. The ^{19}F NMR spectra of compounds (II,IIb) and (VIII,VIIIb) are presented in Figs 1,2. Assignment of the signals of the fluorine atoms in compounds (I,Ia,b) and (V,Va) was carried out earlier in [9]. Assignment of the signals of the fluorine atoms in compounds (II, IIa,b- IV,IVa,b) and (VI,VIa,b - VIII,VIIIa,b) is carried out both on the

TABLE 1

Parameters of ^{19}F NMR spectra of compounds type

Compound			Chemical shifts of fluorine atoms δ and shifts of fluorine atoms when going from precursor						
No.	X	R_f	δ_F^2	$\Delta\delta_F^2$	$\delta_F^{2'}$	$\Delta\delta_F^{2'}$	δ_F^3	$\Delta\delta_F^3$	$\delta_F^{3'}$
I**	H	$\overset{\alpha}{C}F_3$	+ 25.5		+ 23.6***		+ 23.6		+ 2.1
Ia	Na		+ 15.0*****	-10.5	+ 21.5	-2.1	+ 15.0	-8.6	-4.3**
Ib	Li		+ 15.5*****	-10.0	+ 21.2	-2.4	+ 15.5	-8.1	-3.6**
II	H	$\overset{\alpha}{C}F_2\overset{\beta}{C}F_3$	+ 25.8		+ 23.6		+ 25.4		+ 2.1
IIa	Na		+ 15.2	-10.6	+ 21.6	-2.0	+ 16.1	-9.3	-3.8**
IIb	Li		+ 15.6	-10.2	+ 21.4	-2.2	+ 16.6	-8.8	-3.5**
III	H	$\overset{\alpha}{C}F(\overset{\beta}{C}F_3)_2$	+ 26.1		+ 23.6		+ 28.4		+ 2.0
IIIa	Na		+ 15.8	-10.3	+ 21.6	-2.0	+ 20.0	-8.4	-4.0**
IV	H	$C(\overset{\beta}{C}F_3)_3$	+ 26.6		+ 23.4		+ 36.4		+ 1.8
IVa	Na		+ 16.2	-10.4	+ 21.6	-1.8	+ 27.1	-9.3	-3.6**
IVb	Li		+ 16.9	-9.7	+ 21.8	-1.6	+ 27.7	-8.7	-3.3**

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* Ratio of signal intensities is correct.

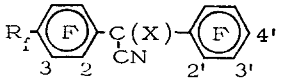
** Chemical shift values are estimated with greater precision by calibration (cf. [9]).

*** Because of superposition of signals the accuracy of determining chemical shift value is ± 0.7 ppm.

**** Because of superposition of signals the accuracy of determining chemical shift value is ± 0.2 ppm.

***** Because of superposition of signals the accuracy of determining chemical shift value is ± 0.5 ppm.

basis of the values of chemical shifts of the fluorine atoms, of the relative intensity of the signals, and with the use of the spin-spin coupling constants of the fluorine atoms. Assignment of the signals of the fluorine atoms $F_{3'}$ and $F_{4'}$ in compounds (II, IIa, b - IV, IVa, b) is similar to the assignment of the same signals in compounds (I, Ia, b) [9]. Assignment of the signals of the fluorine atoms $F_{3'}$ in compounds (VI, VIa, b - VIII, VIIIa, b) is carried out due to a considerable complication of the fine structure of these signals because of the spin-spin coupling of the fluorine atoms $F_{3'}$ and CF_3 group ($J(CF_3 - F_{3'})$ 20.5 - 23 Hz), (cf. [10])



(I,Ia,b - IV,IVa,b)

changes in values of chemical to carbanion $\Delta\delta^{*}$							Absolute values of spin-spin coupling constants, J (F- F) (Hz)
$\Delta\delta^{3'}_{F}$	$\delta^{4'}_{F}$	$\Delta\delta^{4'}_{F}$	δ^{α}_{R}	$\Delta\delta^{\alpha}_{R}$	δ^{β}_{R}	$\Delta\delta^{\beta}_{R}$	
	+11.0		+107.2		-		
-6.4	-4.3^{****}	-15.3	+110.2	+3.0	-	-	
-5.7	-3.6^{****}	-14.6	+110.3	+3.1	-	-	
	+10.9		+52.8		+77.6		J(α,3) 31.7; J(β,3) 6; J(α,β) 2.2; J(2',4')3.5; J(3',4') 21.4
-5.9	-3.8^{***}	-14.7	+55.4	+2.6	+77.2	-0.4	J(α,3) 29
-5.6	-3.5^{***}	-14.4	+55.1	+2.3	+77.1	-0.5	J(α,3) 29; J(α,β)3.3; J(β,3) 7
	+10.9		-14.3		+88.4		J(α,3) 46.5; J(β,3)13.5; J(α,β) 5.8; J(2',4') 3; J(3',4') 21.2
-6.0	-4.0^{***}	-14.9	-11.4	+2.9	+87.9	-0.5	
	+10.7		-		+102.7		J(β,3) 26.4; J(2',4') 3.5; J(2',3') 20.7
-5.4	-3.6	-14.3	-	-	+101.5	-1.2	
-5.1	-3.3	-14.0	-	-	+102.0	-0.7	J(β,3) 25.7; J(2,3) 14.5

the values of the chemical shifts of the fluorine atoms $F_{3'}$ being close to those in compounds (V, Va,b) respectively. Similarly, complication of the fine structure of the signal of the fluorine atoms F_3 in compounds (II, IIa,b - IV, IVa,b, VIa,b, VII, VIIb, VIII, VIIIa,b) together with the growth in the value of the spin-spin coupling constant J (R - F_3) to 26-46 Hz (cf. [11-12]) facilitates the assignment of these signals. The signals of the fluorine atoms F_2 and $F_{2'}$ in the both series of compounds were assigned as follows: in compounds (II - IV, IVa,b, VIIIb) the assignment was conducted in accordance with the spin-spin coupling constants J ($F_{2'}$ - $F_{4'}$) and J (F_2 - F_3); in carbanions (IIa,b) and (IIIa,b), as well as in compound (VIII), by comparing the values of chemical shifts of these fluorine atoms with the corresponding values in carbanions (Ia,b), (IVa,b) and in compounds (IV) and (V) respectively. In the case of compounds (VI, VIa,

TABLE 2

Parameters of ^{19}F NMR spectra of compounds type

Compound			Chemical shifts of fluorine atoms δ and shifts of fluorine atoms when going from						
No.	X	R_f	δ^2_F	$\Delta\delta^2_F$	$\delta^{2'}_F$	$\Delta\delta^{2'}_F$	δ^3_F	$\Delta\delta^3_F$	$\delta^{3'}_F$
V	H	$\overset{\alpha}{CF_3}$	+ 25.9		+ 25.9		+ 23.6		+ 23.6
Va	Na		+ 19.5	-6.4	+ 19.5	-6.4	+ 16.1	-7.5	+ 16.1
Vb	Li		+ 19.9	-6.0	+ 19.9	-6.0	+ 16.5	-7.1	+ 16.5
VI	H	$\overset{\alpha}{CF_2}\overset{\beta}{CF_3}$	- 26.1**		+ 26.1		+ 26.1		+ 23.6
VIa	Na		+ 19.9***	-6.2	+ 19.9	-6.2	+ 17.5	-8.6	+ 16.8
VI b	Li		+ 20.0***	-6.1	+ 20.0	-6.1	+ 18.0	-8.1	+ 16.7
VII	H	$\overset{\alpha}{CF}(\overset{\beta}{CF_3})_2$	- 26.2**		+ 26.2		+ 28.5		+ 23.8
VIIa	Na		+ 20.1****	-6.1	+ 20.1	-6.1	+ 20.1	-8.4	+ 16.5
VIIb	Li		+ 20.2****	-6.0	+ 20.2	-6.0	+ 21.1	-7.4	+ 16.8
VIII	H	$C(\overset{\beta}{CF_3})_3$	- 27.2		+ 25.8		+ 36.4		+ 23.7
VIIIa	Na		+ 20.4*****	-6.8	+ 20.4	5.4	+ 28.2	- 8.2	+ 16.3
VIIIb	Li		+ 20.9	-6.3	+ 20.6	5.2	+ 28.9	- 7.5	+ 16.8

* Ratio of signal intensities is correct.

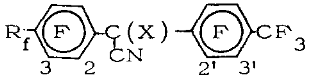
** Because of superposition of signals the accuracy of determining chemical shift value is ± 0.9ppm.

*** Because of superposition of signals the accuracy of determining chemical shift value is ± 0.6ppm.

**** Because of superposition of signals the accuracy of determining chemical shift value is ± 0.5ppm.

***** Because of poor resolution of signals the chemical shift value could not be determined accurately.

b, VII, VIIa, b) superposition of signals of the atoms F_2 and $F_{2'}$ or F_2, $F_{2'}$ and F_3 is observed. Assignment of the signals of the fluorine atoms in the perfluoroalkyl groups R_f in compounds (II - IV) and (VI - VIII) is unambiguous [10 - 12].



(V, Va, b - VIII, VIIIa, b)

changes in the values of chemical precursor to carbanion Δδ *							Absolute values of spin-spin coupling constants, J(F - F) (Hz)
$\Delta\delta_F^{3'}$	δ_{CF_3}	$\Delta\delta_{CF_3}$	δ_R^{α}	$\Delta\delta_R^{\alpha}$	δ_R^{β}	$\Delta\delta_R^{\beta}$	
	+107.1		+107.1	-			J(α, 3)21.9
-7.5	+108.8	+1.7	+108.8	+1.7	-	-	J(α, 3)21.2
-7.1	+108.6	+1.5	+108.6	+1.5	-	-	J(α, 3)21.5
	+106.7		+52.7		+77.8		$J(CF_3, 3')$22.8 J(α, 3)31.7 J(β, 3)6; J(α, β)2.2
-6.8	+108.9	+.2.2	+54.7	+2.0	+77.3	-0.5	
-6.9	+108.2	+1.5	+54.4	+1.7	+77.2	-0.6	$J(CF_3, 3')$20.5 J(α, 3)29.5
	+107.0		-14.5		+88.8		$J(CF_3, 3')$22.2 J(α, 3)44.5 J(β, 3)13.5 ; J(α, β)6
-7.3	+109.0	+2.0	-12.5	+2.0	+87.9	-0.9	
-7.0	+109.1	+2.1	-12.8	+1.7	+88.0	-0.8	$J(CF_3, 3')$21.0; J(α, 3)39.5; J(β, 3)12.5; J(α, β)6
	+106.7		-		+102.8		$J(CF_3, 3')$23.0; J(β, 3)26.5
-7.4	+108.9	+2.2	-		+101.8	-1.0	
-6.9	+109.0	+2.3	-		+102.4	-0.4	$J(CF_3, 3')$21.5; J(β, 3)25.9; J(2, 3)11.0

From the data concerning various reaction series it follows that the electronic effect of the perfluoroalkyl groups in the form of the Hammett σ- constant is practically the same [13, 14]. This point of view is confirmed also by kinetic data for the nucleophilic substitution reaction in perfluoromonoalkyl- substituted derivatives of benzene [15]. The same result ensues likewise from the data concerning the equilibrium of the series of carbanions of the type $(p\text{-}RC_6F_4\bar{C}(CN)C_6F_5)Na^+$ with the use of the correlation equation $\Delta\delta_F^{4'} = -9.5\,\sigma_p + 20.7$ which relates the value $\Delta\delta_F$ for the para-atom of fluorine and the σ_p - constant of the substituent [9].From the fact that the values of $\Delta\delta_F^{4'}$ (Table 1) are close for all the

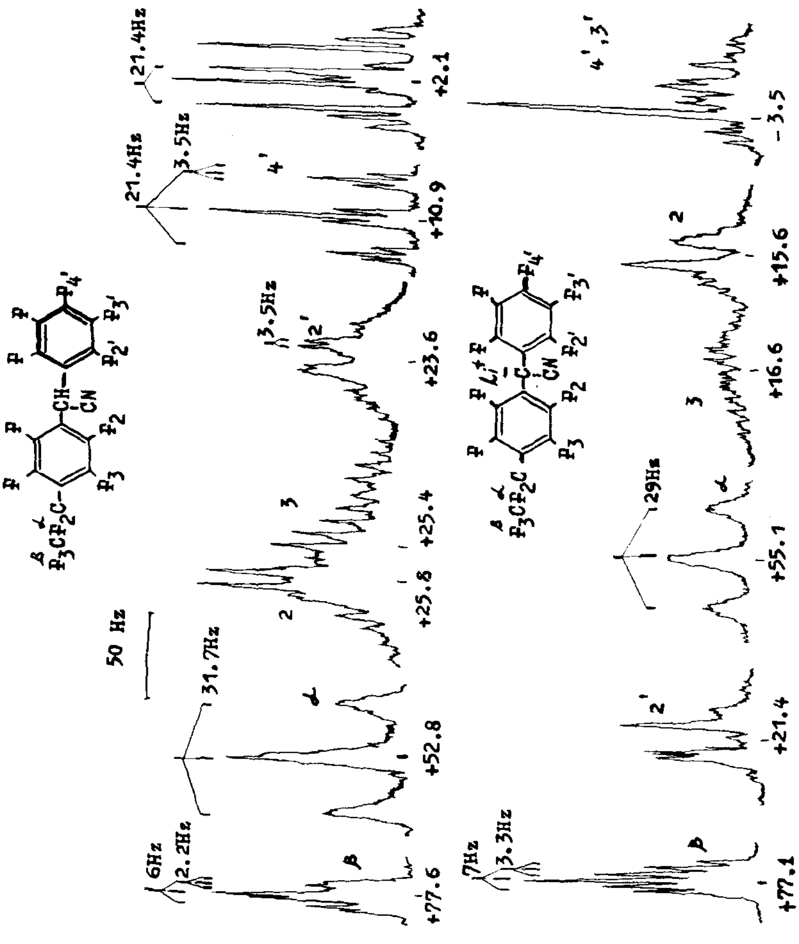


Fig. 1. ^{19}F NMR spectra of a solution of the compounds (II) and (IIb) in DME.

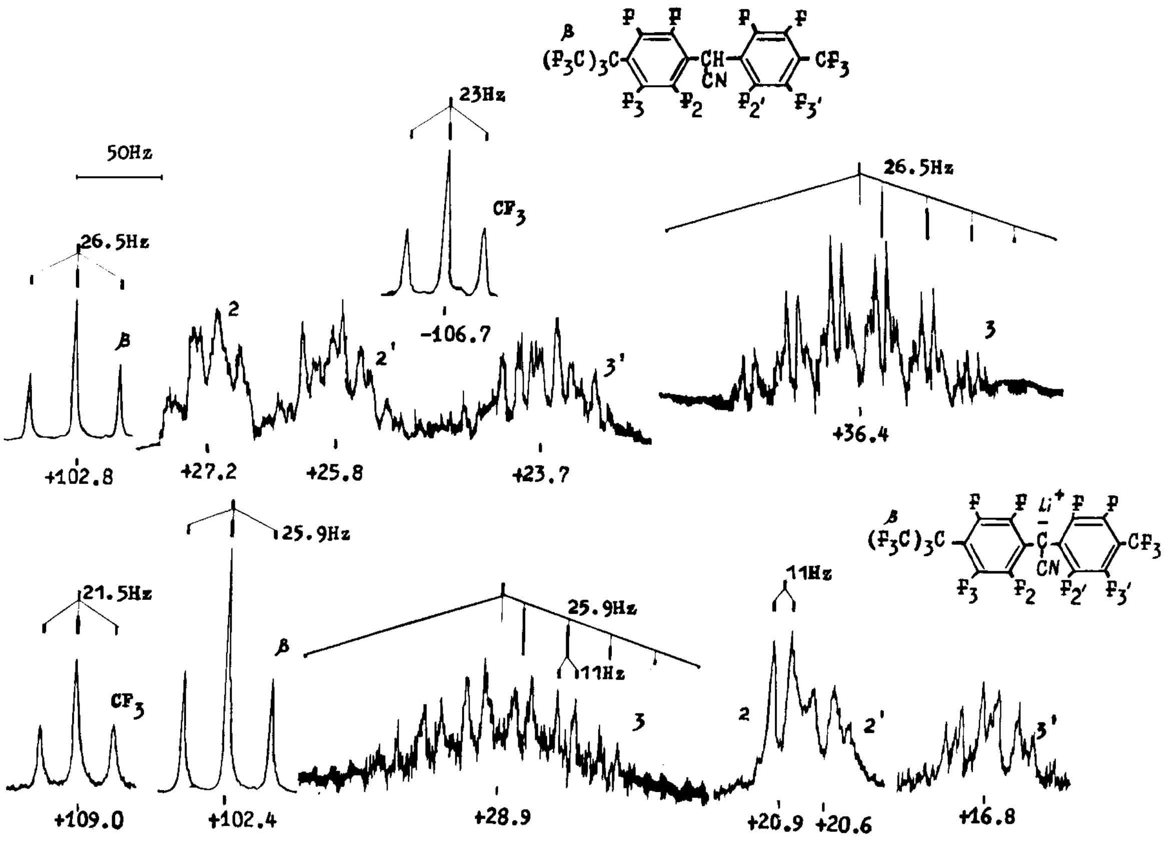


Fig. 2. ^{19}F NMR spectra of a solution of the compounds (VIII) and (VIIIb) in DME.

perfluoroalkyl substituents in compounds (I - IV) it follows that the values of the σ_p - constants for these substituents are also close, though for the CF_3 group the value of σ_p is somewhat smaller than for the rest of the perfluoroalkyl groups. If the change in the chemical shift of the para-atom of fluorine $\Delta\delta_F^{4'}$ is determined predominantly by the interaction of this fluorine atom with the carbanion substituent in the π- system, then practically the same values of $\Delta\delta_F^{2'}$ for the ortho-atoms of fluorine are also indicative of the same relative contribution of the interaction of this substituent with the ortho-atoms of fluorine in the π- system in the series of compounds (I - IV) (Table 1) [9]. Moreover, in this series of compounds similar changes in the values $\Delta\delta_F^2$ are observed for the ortho-atoms of fluorine F_2 and also for the meta-atoms of fluorine $\Delta\delta_F^3$ and $\Delta\delta_F^{3'}$ (Table 1), this once again confirming the similarity of the electronic effect of the perfluoroalkyl groups. The fact that the absolute values of $\Delta\delta_F^2$ and $\Delta\delta_F^3$ are greater than those of $\Delta\delta_F^{2'}$ and $\Delta\delta_F^{3'}$ respectively is conditioned both by the presence of the electron-acceptor group R_f and, probably, by the conformational behaviour of the carbanions (cf. [9]).

In the series of compounds (V - VIII) close changes in the values of $\Delta\delta_F^2$ and $\Delta\delta_F^{2'}$ for the ortho-atoms of fluorine and of $\Delta\delta_{CF_3}$ for the CF_3 group are observed, this also indicating that the electronic effect of the perfluoroalkyl groups is approximately the same. It should be noted that in this series of compounds somewhat greater values of $\Delta\delta_F^3$ are observed as compared with the values of $\Delta\delta_F^{3'}$ for the meta-atoms of fluorine as one goes from compound (V) with the CF_3 group over to compounds (VI - VIII) containing other perfluoroalkyl groups. This fact is associated with a somewhat greater electronic effect of the perfluoroalkyl groups as compared to that of the CF_3 group, though the difference in the effects is small (cf. [13]).

It could be expected that, the electronic effect of all the perfluoroalkyl groups being similar, the differences in the delocalization mechanism of the negative charge by the CF_3 group and by the other perfluoroalkyl groups CF_2CF_3, $CF(CF_3)_2$ and $C(CF_3)_3$ could be revealed by comparing the values of $\Delta\delta_F^{\alpha}$ for the α- atoms of fluorine in the side chain in the series of compounds (I - IV). However, as it follows from the data presented in Table 1, the value of $\Delta\delta_F^{\alpha}$ for the CF_3 group is very close to those for the groups

CF_2CF_3 and $CF(CF_3)$. A similar comparison of the values of $\Delta\delta^{\alpha}_{F}$ for the same groups in the series of compounds (V - VIII) (Table 2) gives the same result, though in the absolute value the deshielding effect diminishes as was pointed out earlier [9]. No differences in the spectral behaviour of the perfluoroalkyl groups can be revealed either when comparing the values of $\Delta\delta^{\beta}_{F}$ for the β- atoms of fluorine in these groups in the both series of compounds (Tables 1 and 2).

Thus, consideration of the $\Delta\delta_{F}$ values both for the aromatically bonded fluorine atoms and for side chain fluorine atoms in the series of compounds (I - VIII) shows that no differences (if they exist!) in the negative charge delocalization mechanisms by the CF_3 group and by other perfluoroalkyl groups can be revealed by the ^{19}F NMR method. No such differences have been revealed either when studying the kinetics of the reaction of nucleophilic substitution of the fluorine atom in pentafluoro- substituted benzene derivatives [15] and the kinetics of base- catalyzed deutero- exchange in 2- (para- $R_f$phenyl)- 1.1.1.3.3.3-hexafluoropropanes [16].

Compounds (I - VIII) were obtained according to the scheme:

$$\underset{IX,\ X}{p\text{-}RC_6F_4CH_2CN} \xrightarrow[DMF]{NaH} \left[p\text{-}RC_6F_4\overset{-}{C}HCN\right]Na^+ \longrightarrow$$

$$\xrightarrow[2.\ H_2O,\ HCl]{1.\ C_6F_5R_f(XI\ -\ XIV)} \quad I\ -\ VIII$$

$R = F\ (IX),\ CF_3\ (X)$

$R_f = CF_3\ (XI),\ CF_2CF_3\ (XII),\ CF(CF_3)_2\ (XIII),\ C(CF_3)_3\ (XIV)$

EXPERIMENTAL

^{19}F NMR spectra have been recorded on a "Varian A 56- 60A" spectrometer at 56.4 MHz with a 10 mol. % DME solution (hexafluorobenzene as an internal standart), measuring accuracy of ± 0.1 ppm. and precision of chemical shifts of ± 0.2 ppm.

Compounds (I), (V) and (X) were prepared by following the procedure described in [9], compound (IX) was prepared by following the same procedure as in [17], compound (XII) was pre-

TABLE 3

Synthesis of polyfluorodiarylacetonitriles p-$R_fC_6F_4CH(CN)C_6F_5$ (II - IV) and p-$R_fC_6F_4CH(CN)C_6F_4CF_3$-p (VI - VIII) by reacting polyfluorinated arylacetonitriles p-$RC_6F_4CH_2CN$ (IX, X) with polyfluoroalkylbenzenes $C_6F_5R_f$ (XII - XIV) in the presence of sodium hydride in DMF

Initial compounds		Reaction products				Elementary analysis								
R in p-R-$C_6F_4CH_2CN$	R_f in $C_6F_5R_f$	No	Yield, %	B.p. (mm Hg)	M.p. (solvent for crystallization)	Found, %				Formula	Calculated, %			
						C	H	F	N		C	H	F	N
F (IX)	CF_2CF_3 (XII)	II	44	165-166° (4)	-	40.4	0.4	56.1	3.2	$C_{16}HF_{14}N$	40.3	0.2	56.3	3.0
F (IX)	$CF(CF_3)_2$ (XIII)	III	30	-	56-58° (petroleum ether with b.p. 40-60°)	39.0	traces	58.1	2.9	$C_{17}HF_{16}N$	39.0	0.2	58.2	2.7
F (IX)	$C(CF_3)_3$ (XIV)	IV	20	-	82-84° (petroleum ether with b.p. 40-60°)	37.9	traces	59.5	2.4	$C_{18}HF_{18}N$	37.7	0.2	59.7	2.5
CF_3 (X)	CF_2CF_3 (XII)	VI	18	168-170° (4)	-	39.4	0.3	58.6	2.9	$C_{17}HF_{16}N$	39.0	0.2	58.2	2.7
CF_3 (X)	$CF(CF_3)_2$ (XIII)	VII	24	-	114-115° (EtOH)	37.4	traces	59.6	2.6	$C_{18}HF_{18}N$	37.7	0.2	59.7	2.5
CF_3 (X)	$C(CF_3)_3$ (XIV)	VIII	19	-	146-148° (EtOH)	36.5	0.1	60.9	2.4	$C_{19}HF_{20}N$	36.6	0.2	61.0	2.3

pared by following the procedure described in [18], compound (XIII) was prepared by following the procedure in [11],and compound (XIV), by following the procedure described in [12]. Purification of the DMF and DME solvents and generation of the salts of carbanions (Ia, b - VIII) were carried out by following the procedures described in [9].

Synthesis of polyfluorodiarylacetonitriles (II - IV, VI - VIII) (nc)

Synthesis of polyfluorodiarylacetonitriles (II - IV, VI - VIII) was conducted by following the procedure described in [9]. To a suspension of 0.013 mol. NaH in 20 ml of DMF 0.013 mol. of polyfluoroalkylbenzene (XII - XIV) in a stream of dry nitrogen were added. Then 0.0086 mol. of compound (IX) or (X) was added gradually at 20- 25^{o} during 30 min. Then the reaction mixture was kept at the same temperature for 3 hours and neutralized with a 5% HCl solution. After that extraction with ether was performed, the extract was washed with water and dried with $MgSO_4$. Tte product was isolated by distillation. The results of the experiments and data of the elementary analysis are given in Table 3.

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