^{29}Si, ^{13}C, ^{19}F, AND ^{1}H-NMR SPECTRA
# OF FLUOROALKYLSILANES*

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^{29}Si, ^{13}C, ^{19}F, and ^{1}H chemical shifts and coupling constants are presented for five fluoroalkyl-silanes of the type $R_3Si(CH_2)_mF$ ($R = CH_3$, $m = 1, 3$, and 5; $R = Cl$, $m = 2$, and 3), neopentyl fluoride, and fluoroheptane. According to these data the α derivatives, fluoromethyltrimethylsilane and neopentyl fluoride appear different from all the other fluoroalkylsilanes and fluoroalkanes. An interpretation of the observed trends in structural terms is offered.

The previous NMR study[1] of compounds of the type *I* with

$$(CH_3)_{3-n}X_nSi(CH_2)_mY \qquad I$$
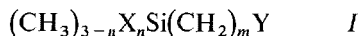
$Y = NH_2$ revealed no indication of Si$\cdots$Y interaction though such interactions, especially in the α derivative, have been reported in literature[2]. According to the theoretical considerations[3] the "through space" interaction between silicon and the substituent Y in α position decreases in the order $NH_2 > OH > F$, in the case of the "through bond" interaction, however, the order would be reversed and the inter-action would be strongest in the fluoro derivative. Therefore, it represented an interest to continue our NMR study[1,4] of the compounds of the type *I* and investigate the spectra of the compounds having $Y = F$. In these compounds, similarly as in the aminoalkylsilanes[1], NMR spectra of the first atom in the substituent Y can be measured in addition to the spectra of ^{29}Si, ^{13}C, and ^{1}H nuclei. Thus a more complete picture can be obtained than in the other compounds of the same type but with NMR inactive first atoms of the substituents Y. Owing to the preparative difficulties the series of fluoroalkylsilanes is severely limited but still some important conclusions can be derived even from the necessarily limited set of data.

EXPERIMENTAL

The preparation of the studied compounds[5-7] as well as the measurements of their ^{19}F-NMR spectra[5] were described previously. All the compounds, except for neopentyl fluoride, were NMR pure. Neopentyl fluoride contained some 10% of an impurity that could not be removed. According to the spectra and method of preparation the impurity was 2-methyl-2-butene. In the course of the present work ^{19}F-NMR spectra of (fluoromethyl)trimethylsilane, (γ-fluoropropyl)trimethyl-silane, and neopentyl fluoride were remeasured in order to verify the large diamagnetic shift reported for the first of the compounds. The three spectra were measured at 94·1 MHz in FT mode.

^{29}Si and ^{13}C-NMR spectra (Table I) were measured in the FT mode on a JEOL-PFT-100 spectrometer interfaced to a Nicolet 1085 data system. The former spectra were recorded at 19·87 MHz in neat compounds using tetramethylsilane (TMS) in a separate sample as a reference. The spectrometer was locked to ^{19}F-NMR signal of C_6F_6 in a capillary through measurements of [29]Si and to [2]D-Signal of $CDCl_3$ for ^{13}C-NMR spectra, which were measured at 25·15 MHz in carbon tetrachloride solutions (approximately 70% v/v), the solvent served also as an internal reference. The shifts were converted into δ-scale using the shift $\delta = 95\cdot98$ of CCl_4 as determined in this laboratory (literature[8] value $\delta = 96\cdot0$).

^{1}H-NMR spectra (Table II) were measured in the CW mode on a modified Tesla BS 467 spectrometer operating at 60 MHz. The proton chemical shifts were measured in tetrachloro-methane solutions (20% v/v) containing 10% (v/v) of chloroform to provide a lock signal. The shifts were calculated using the chemical shift of chloroform[9] $\delta = 7\cdot25$.

Del Re calculations were carried out for fluoroalkyltrimethylsilanes as described previously[1], the calculations could not be performed for chlorosilanes because of the lack of empirical parameters.

RESULTS AND DISCUSSION

On the brief inspection of Table I, where the experimental results are summarized, it is apparent that most of the data for the α derivative, fluoromethyltrimethylsilane, stands out as different from the data of other fluoroalkylsilanes. One would be tempted to explain this difference by the so-called "α-effect". But we should first see if the difference could be explained without the recourse to this special effect.

^{19}F-NMR. The difference between the α and the other derivatives is most striking in the case of ^{19}F chemical shifts; in fluoromethyltrimethylsilane the fluorine nucleus is shielded by some 55 p.p.m. more than it is in all the other studied compounds. Comparison with the available ^{19}F chemical shifts[10] reveals that the shielding in (fluoromethyl)trimethylsilane is essentially the same as that in methyl fluoride; in the chemical shift range $-210 - -220$ p.p.m. in which the fluoroalkylsilanes studied here resonate some other β substituted ethyl fluorides are also found[10], most notably ethyl fluoride $(\delta = -213)$. With the regards to the following discussion of ^{13}C chemical shifts it should be emphasized that the ^{19}F shift in neopentyl fluoride (Table I) is very close to the indicated range. Our value for (β-fluoroethyl)trichloro-silane agrees reasonably well with the value $(\delta = -209$ after conversion into our scale) obtained in a different solvent earlier by other authors[11].

TABLE I

^{29}Si, ^{19}F, and ^{13}C-NMR Data^a

Compound	δ(Si)	δ(F)	J(Si—F)	^1J(F—C)	^2J(F—C)	^3J(F—C)
$(CH_3)_3SiCH_2F^b$	−1·49	−270·37	21·0	161·0	—	2·2
$Cl_3Si(CH_2)_2F$	9·64	−210·51	28·2	171·3	22·1	—
$(CH_3)_3Si(CH_2)_3F$	2·16	−215·09	1·0	169·9	19·8	4·4
$Cl_3Si(CH_2)_3F$	13·34^d	−219·85		169·9	21·3	5·1
$(CH_3)_3Si(CH_2)_5F$	1·45	−218·06	—			
n-$C_7H_{15}F$	—	−218·19	—	164·8	19·5	4·9
$(CH_3)_3CCH_2F$	—	−222·23	—	173·5	17·6^g	4·4

^{a} Chemical shifts are in δ scale (*i.e.* p.p.m. units, positive values denote paramagnetic shift). The shifts of ^{29}Si, ^{13}C and ^{1}H nuclei are relative to TMS line, the shifts of ^{19}F are relative to CFCl$_3$ line. Coupling constants are in Hz, the signs of the coupling constants have not been determined. The nuclei are identified by their symbols only; Si, F, C and H stand for ^{29}Si, ^{19}F, ^{13}C and ^{1}H nuclei resp. Estimated errors are: 0·10 p.p.m. for ^{29}Si and ^{13}C chemical shifts, 0·05 p.p.m. for ^{13}F chemical shifts, 0·2 Hz for J(Si—F) and J(F—H) and 1·2 Hz for J(C—H) coupling constants. ^{b} Coupling constants of protons deteimined from ^{1}H-NMR spectrum of the

For a long time the fluorine chemical shifts have been known[10] to depend on the electronegativity of the atom to which the fluorine is bonded. Recent inductive effect theory[12] of ^{19}F chemical shifts is based on the assumption that the chemical shift of a fluorine bonded to a carbon atom is proportional to the ionic character if the C—F bond, which, in turn, is supposed to be proportional to the difference of effective electronegativities of the fluorine and carbon atoms in the molecule. The effective electronegativities are evaluated from Huggins electronegativities (E_X) by considering their modification due to other substituents. For compounds of the type F—CH$_2$—X the theory (which considers monoatomic substituents only) gives the following equation for the chemical shift in the scale adopted here

$$\delta(F) = 208·81 - E_X(154·12 + 4·4k^{HX}),$$

where k^{HX} is a constant for the substituent X. From this equation it is clear that when plotting fluorine chemical shift as linearly dependent on E_X the variation in k^{HX} is neglected. Also if such a plot involves composite substituent groups for which E_X is equated with the electronegativity of the first atom other assumptions are being tacitly made. Therefore, one is not surprised to see the large scatter around the line drawn through the points corresponding to compounds with X = H and F as shown on Fig. 1.

TABLE I

(*Continued*)

^2J(F—H)	CH₃		Si-CH₂		C—CH₂—C		CH₂—F	
	δ(C)	J(C—H)	δ(C)	^1J(C—H)	δ(C)	^1J(C—H)	δ(C)	^1J(C—H)
47·0	—4·25	119·44	80·03	137·1	—	—	80·03	137·1
47·0	—	—	26·45	124·3	—	—	77·77	153·3ᶜ
48·0	—1·96	116·9	11·33	115·8	24·79	123·9	84·88	143·5
46·5	—	—	19·85	120·2	23·39	ᵉ	83·10	150·6
48·0								
47·5					ᶠ		83·91	
48·0	25·45		ᵍ				92·32	139·2ʰ

neat compound, ^2J(F—H) = 47·53 ± 0·07 Hz, ^4J(F—H) = 0·64 ± 0·07 Hz. ᶜ ^3J(C—H) = = 5·9 Hz (¹³C in CH₂F group, for ¹³C of SiCH₂ group is not seen in the spectrum). ᵈ From 80% (v/v) solution in CCl₄. ᵉ Not determined from the complex spectrum. ᶠ Carbons at β and γ positions occure at δ = 30·93 and 25·59, resp., other resonances have not been assigned. ᵍ Tertiary carbon is found at δ = 32·37 but a line of impurity present, 2-methyl-1-butene, reso-nates in this region too. If the given assignment were wrong the shift would be δ = 31·40 and the coupling constant 31·6 Hz. ʰ Determined from one satelite only, error ±0·5 Hz.

On the other hand, the ionic character of the C—F bond can be approximated by net charges on fluorine atom (Q_F) as calculated by Del Re method. Linear dependences between the charges calculated by this method and chemical shifts of ¹H and ¹³C nuclei have been reported[13,14]. The plot of this type is also shown on Fig. 1.

FIG. 1

Fluorine-19 Chemical Shift, δ(F), Dependences on the Total Net Charge on the Fluorine Atom, Q_F, and on the Electronegativity, E_X, of the Substituent X in the Compounds of the Type FCH₂X

(Values taken from ref.[10], charges calculated here. The vertical bar indicates the range of the shifts in alkyl fluorides. The substituent X indicated in the figure.) The solid lines are drawn through the points corresponding to X = H and F.
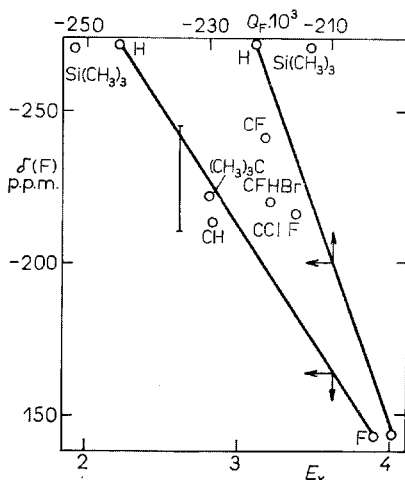
Considerably less scattered are the points in the dependence of fluorine chemical shift on the difference $(Q_C - Q_F)$ shown on Fig. 2. This quantity involves in addition to the ionic character of the C—F bond also the net charge on the carbon atom due to the polarization of other bonds of this carbon.

The points corresponding to fluoromethyltrimethylsilane fit reasonably well into the dependences on Figs 1 and 2. Apparently the large diamagnetic shift of fluorine in this compound can be in the large part accounted for by the inductive effect of the trimethylsilyl group. The shift of fluorine in neopentyl fluoride fits very well the line on Fig. 2, but in the dependence on Q_F (Fig. 1) it represents one extreme deviation while the point for fluoromethyltrimethylsilane represents the other. According to the calculated value of Q_F the fluorine nucleus should be shielded considerably more in the former compound and less in the latter than it indeed is.

Of all the fluorine coupling constants reported in Tables I and II only one-bond $^{19}F-^{13}C$ coupling constants can be discussed, others are either not available for important compounds (e.g. $^2J(^{19}F-^{13}C)$, $^3J(^{19}F-^1H)$) or are not comparable (^3J . $(^{19}F-^{13}C)$). The small changes in $^2J(^{19}F-^1H)$ coupling constants are hard to
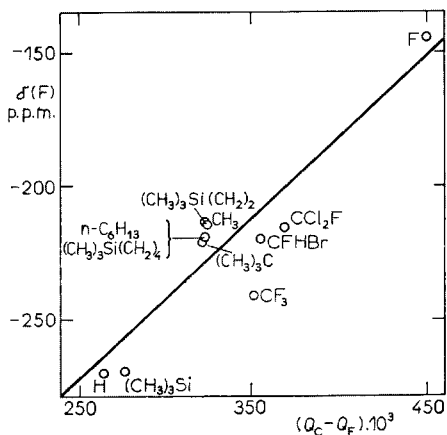

Fig. 2

Fluorine-19 Chemical Shift, $\delta(F)$, Dependence on the Difference of the Total Net Charges on Carbon and Fluorine Atoms, $(Q_C - Q_F)$, in the Compounds of the Type FCH_2X

(Values taken from ref.[10], charges calculated here. The substituent X indicated in the figure.) The solid line is a least-squares fit of all the indicated points.
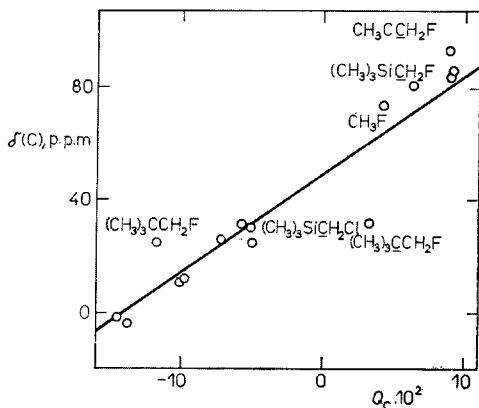
Fig. 3

Correlation of Carbon-13 Chemical Shift, $\delta(C)$, with the Total Net Charge on the Carbon Atom, Q_C

(NMR data of Table I and from refs[1,24,35], the charges calculated here. The solid line taken from ref.[1]. Where indicated the shift of the underlined carbon is shown.)

discuss. Among the fluoroalkylsilanes the trend in $^1J(^{19}F - ^{13}C)$ coupling constants parallels that in ^{19}F shielding, in accord with a general tendency for the absolute value of this coupling constants (which are now believed to have negative values[15]) to decrease with increased ^{19}F shielding[15]. The coupling constant in the α derivative is considerably smaller than the coupling in the other compounds, in contrast, in the carbon analogue (neopentyl fluoride) this coupling is almost by 10 Hz larger than in fluoroheptane. Worth mentioning feature of $^{19}F - ^{29}Si$ couplings is their order. The two-bond coupling constant in the α-derivative is smaller than the three-bond coupling in the β-derivative.

^{13}C-NMR. Similarly to ^{19}F chemical shift, carbon-13 chemical shifts can be rationalized in the terms of inductive effect. This fact is demonstrated on Fig. 3 which shows a linear correlation between δ and the total net atomic charge on the carbon atom Q_C calculated by the Del Re method. The solid line shown on Fig. 3 has been derived previously for the shifts in aminoalkylsilanes[1] and is essentially identical with the line reported by Lazzaretti and Taddei[14] for a more general class of compounds. It was recognized[1] that deviations from the solid line might be indicative of special effects which were not taken into account by the simple Del Re approach. As it is apparent from Fig. 3 the points corresponding to fluoroalkyltrimethylsilanes fit the line rather well, the only noticeable deviation to be seen is for methylene carbon atom of the α derivative. This carbon atom is shielded slightly less than it corresponds to its Q_C value. A similar deviation is, however, observed in methyl fluoride, that is in the compound with the same ^{19}F chemical shift. The largest deviations are observed, however, for all the three carbons of neopentyl fluoride. According to the Del Re charges α and γ carbon nuclei should be shielded more while β carbon less than observed.

TABLE II
^1H-NMR Data[a]

	CH$_3$		SiCH$_2$		CH$_2$F	
	δ	J(F—H)	δ	J(F—H)	δ	^2J(F—H)
(CH$_3$)$_3$SiCH$_2$F	0·07	0·64	4·38	47·07	4·38	47·07
Cl$_3$Si(CH$_2$)$_2$F	—	—	1·98[b]	20·42	4·71[b]	46·92
(CH$_3$)$_3$Si(CH$_2$)$_3$F	0·01	0·3	[c]	[c]	4·32[d]	46·16
(CH$_3$)$_3$CCH$_2$F	0·87[e]	1·72	—	—	3·90[e]	48·04
n-C$_7$H$_{15}$F					4·37[f]	47·50

TABLE III

Total Net σ-Electron Charges Q Calculated by the Del Re Method

Compound	CH$_3$			SiCH$_2$		CH$_2$F			
	Q_H	Q_C	Q_{Si}	Q_C	Q_H	Q_C	Q_H	Q_F	$Q_C - Q_F$
(CH$_3$)$_3$SiCH$_2$F	0.051	−0.138	−0.023	0.063	0.066	0.063	0.066	−0.214	0.277
(CH$_3$)$_3$Si(CH$_2$)$_3$F	0.046	−0.145	0.020	−0.097	0.044	0.092^a	0.056^a	−0.230	0.322
(CH$_3$)$_3$Si(CH$_2$)$_5$F	0.046	−0.145	0.021	−0.099	0.044	0.091	0.056	−0.230	0.321
(CH$_3$)$_3$CCH$_2$F	0.039	−0.117	0.0321^b			0.089	0.056	−0.230	0.319
n-C$_7$H$_{15}$F	0.039	−0.118				0.091^c	0.056^c	−0.230^c	0.321

^{a} In the middle CH$_2$ group Q$_C$ = −0.050 and Q_H = 0.041. ^{b} Central carbon atom. ^{c} In the β CH$_2$ group Q$_C$ = −0.057 and Q_H = 0.040 and in γ CH$_2$ group Q$_C$ = −0.072 and Q_H = 0.038.

Recent criticism of interpretations of one-bond $^{13}C-^1H$ coupling constants in the terms of *s*-character[16] does not invalidate the three arguments set forth by Matwiyoff and Drago[17] as the theoretical basis of a linear relationship between this coupling and proton chemical shifts. As the same arguments apply to these coupling constants and carbon chemical shifts (which, in addition, were shown to depend on inductive effect) a linear relationship between these two quantities would be expected to hold in a series of similar compounds. It is demonstrated on Fig. 4 that such a relationship holds for the data reported here. Included are also literature data for fluoromethane[18,19] and difluoromethane[18,19]. As far as we know, relationship of this type has not yet been reported in literature. (Similar relationship used by Pehk, Alla and Lippmaa[20] to demonstrate the dependence of carbon chemical shift on the hybridisation of the neighbouring carbon atom employed the coupling of one carbon atom and the shift of another one.) In contrast to the analogous relationships (described *e.g.* in refs[17,21]) holding for the proton chemical shifts the deviations from the streight line of Fig. 4 cannot be explained by magnetic anisotropy effects which are known to be of minor importance in determining carbon chemical shifts. As in the case of the dependence on the net charge, again among the studied compounds the α derivative and neopentyl fluoride exhibit the largest deviations from the least-square line on Fig. 4 and again the carbon atoms are shielded less than they should according to this plot.

^{29}Si-NMR. Previous works on compounds of the type $(CH_3)_{3-n}Cl_nSi(CH_2)_mY$ have shown that the substituent effect of electronegative substituents Y on silicon shielding is negative (increasing the shielding) if $n > 0(Y = NH_2$ (ref.[1]), Cl (ref.[22]), and $OC(O)CH_3$ (refs[23,24])). In trimethylsilyl derivatives $(n = 0)$ the substituent effects were small and positive (*i.e.* the electronegative substituent brought about a small
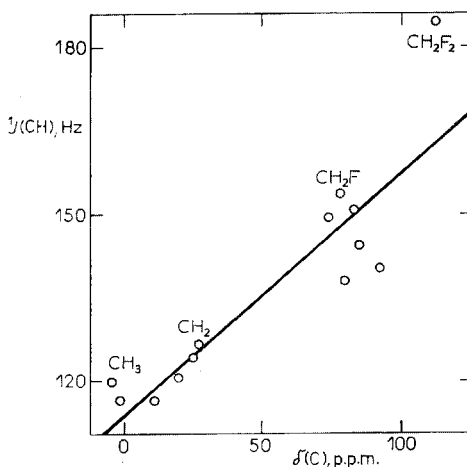

FIG. 4

Correlation of One-Bond Coupling Constant, $^1J(C-H)$, with Carbon Chemical Shift, $\delta(C)$

The solid line is a least-squares fit of all the points in the graph.

decrease in the shielding). Some illustrative examples are given in Table IV. The mentioned trends are easily interpreted by the existing theories[25] of silicon shielding.

It is apparent from Table IV that the ^{29}Si shifts and the substituent effects of fluorine in fluoroalkylsilanes studied here are in harmony with the trends just described. Only the α derivative appears anomalous, substitution of one hydrogen atom in tetramethylsilane by fluorine leads to an increase in the shielding (by 1·49 p.p.m.). Such an effect was expected[26] to occur if an interaction Si···Y took place. Most recently we noticed the substituent effect of the same sign in methoxymethyl- and hydroxymethyl trimethylsilanes[27].

^1H-NMR. Proton chemical shifts and coupling constant reported in Table II for fluoroalkylsilanes vary in the way one would expect on the basis of known trends in similar compounds. Neopentyl fluoride is, however, a notable exception. Its methylene protons are shielded by 0·5 p.p.m. more than the corresponding protons in fluoromethyltrimethylsilane. As far as we know, this is the first report of methylene protons being more shielded in a carbon analogue than in the organosilicon compounds. It is clear from data of the Table II and from literature values of proton shifts in methyl[28] and ethyl[29] fluorides that the anomaly lies in the carbon compound.

Structural Considerations

The above discussion of NMR parameters has shown that both fluoromethyltrimethylsilane and its carbon analogue, neopentyl fluoride, differ from the compounds which have fluorine atom attached to a longer methylene chain. Fluoroethyl-,
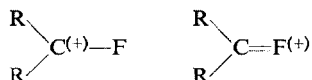
TABLE IV
^{29}Si-NMR Chemical Shifts in Related Compounds

Compound	Y	δ	Compound	Y	δ
$(CH_3)_3SiCH_2Y$	H	0·00[a]	$Cl_3Si(CH_2)_2Y$	H	14·6[b]
	$OC(O)CH_3$	0·3[c]		$OC(O)CH_3$	10·4[c]
	NH_2	0·5[d]		CH_3	12·8[b]
	Cl	2·79[e]		Cl	8·3[e]
	F	−1·49		F	9·64
$(CH_3)_3Si(CH_2)_3Y$	H	0·7[f]	$Cl_3Si(CH_2)_3Y$	H	12·8[f]
	Cl	1·5[e]		Cl	12·4[f]
	F	2·16		F	13·34

[a] Reference compound. Value taken from: [b] ref.[27]. [c] ref.[23]. [d] ref.[1]. [e] ref.[22]. [f] ref.[24].

fluoropropyl- and fluoropentylsilanes have their NMR spectra similar to those of fluoroalkanes represented here by fluoroheptane.

In fluoroalkanes, fluorine is now recognized[30] strong σ electron attractor, removing electrons from the carbon to which it is bonded. It is also a weak π electron donor, π electrons going to the atoms in the β position relative to the fluorine atom. The effects of these interactions on coupling constants[31] and carbon-13 chemical shifts[18] have been described. NMR manifestations of back-donation $(2p\text{-}2p$ interaction$)$ to carbon/atom are apparently best documented for carbonium ions $(e.g.$[32,33]$)$ in which the charge is delocalized onto the fluorine atom

$$\begin{array}{cc} \begin{array}{c} R \\ \diagdown \\ \diagup C^{(+)}\!\!-\!\!F \\ R \end{array} & \begin{array}{c} R \\ \diagdown \\ \diagup C\!\!=\!\!F^{(+)} \\ R \end{array} \end{array}$$

and fluorine is considerably deshielded[32] (from the resonance of the parent compound) and the couplings of the fluorine nucleus to other nuclei in the molecule are greater[33] than in the covalent precursor. The values of $^1J(^{13}C-^1H)$ coupling constants $(e.g.$ 169 Hz in isopropyl cation$)$ are considered to be indicative of sp^2 hybridization of the central carbon atom[34,35].

Apparently the two interactions are balanced in the fluoroalkylsilanes similarly as they are in the fluoroalkanes. In fluoromethyltrimethylsilane and neopentyl fluoride, however, the situation is modified by the proximity of fluorine to trimethylsilyl or tert-butyl group.

The results of simple Del Re calculations (Table III) do not shed much light on the anomalous NMR parameters of fluoromethyltrimethylsilane and neopentyl fluoride as compared to the other fluoroalkanes but, to some extent, they illustrate the difference between the two compounds. Replacement of the tertiary carbon atom in neopentyl fluoride by a silicon atom leads to an increase of the total electron density on all α atoms and to a decrease of the density on all β atoms. The predicted increases in charges are parralelled by the corresponding shifts of carbon resonances (α atoms) to higher field and the anomaly of CH_2F proton (β atom) being shielded more in the carbon analogue is thus accounted for. On the other hand the charges calculated for the other β atoms, $i.e.$ hydrogen atoms of the methyl groups and fluorine atom, do not provide basis on which alone their chemical shifts could be easily explained. We shall not discuss the shift of the protons of the methyl groups because the difference between the proton shifts in the two compounds is smaller than that between the fluorines and also because of the known difficulties in interpreting these shifts in Group IV B methyl derivatives[36].

In the discussion of fluorine chemical shifts we have shown that the shifts are essentially determined by the inductive effect. According to the basic assumption of the theory[12] the maximum ^{19}F shielding is indicative of the maximum ionic character in fluoromethyltrimethylsilane. The fact that the deviations in $\delta(^{19}F)$ vs

$(Q_C - Q_F)$ plot (Fig. 2) are much smaller than those in Fig. 1 suggests that an additional effect which is apparently associated with other bonds of carbon contributes to the shielding of fluorine in these compounds.

Muller and Carr[37] have suggested, however, that the degree of C—F double bond character is the most important single parameter influencing both fluorine chemical shift and spin-spin coupling constant between fluorine and directly bonded carbon in organofluorine compounds. The ionic character was considered to be less important in determining the shift and the coupling constant[37]. According to these authors[37] the coupling constant was also reduced by increasing the s-character of carbon orbital used in the C—F bond but others[38] adopted the oposite view.

As the values of one-bond proton–carbon coupling constants in the CH_2F group are very close in the two anomalous compounds it seems that the distribution of methylene carbon s-orbitals is not altered essentially by the nature of the central atom. Therefore, if we neglect any possible sterical dependence of the F—C coupling[38,39,40], the extreme values of one-bond fluorine–carbon coupling constants and of the fluorine chemical shifts in the two anomalous compounds would mean according to Muller and Carr[37] that in neopentyl fluoride the double bond character is at maximum while it is at minimum in fluoromethyltrimethylsilane.

Since in the remaining compounds the two-bond coupling constants $^2J(F—C)$ follow the same order as the one-bond coupling constants $^1J(F—C)$ (i.e. fluoroethyltrichlorosilane > fluoropropyl derivatives > n-heptyl fluoride) one can take this order for an approximate order of decreasing double bond character of the C—F bond. In these fluoroalkylsilanes the double bond character is apparently closer to that in neopentyl fluoride than to its silicon analogue because not only the $^1J(F—C)$ values are closer but also because they are reduced by an increase in the s-character in the C—H bond of the same carbon atom (see $^1J(C—H)$).

The fact that the CH_2 carbon nuclei in the two anomalous compounds are shielded less than it corresponds to their Q_C or $^1J(C—H)$ values (but carbons of the same type in chloromethyltrimethylsilane[24] and aminomethyltrimethylsilane[1] fit very well the line of Fig. 3) is in accord with the above interpretation only in the case of the silicon compound where the maximum ionic character (and or minimum double bond character) of the C—F bond could provide an additional deshielding. A similar deshielding of the CH_2 carbon would result from an interaction of the type $M–CH_2$ (with F above) which was invoked to explain the so-called "α effect" in carbofunctional organosilicon compounds. Though such interaction would explain the negative value of fluorine SCS of ^{29}Si, it cannot explain the large diamagnetic shift of fluorine in fluoromethyltrimethylsilane. Interaction of this type cannot be considered in the case of the carbon compound not only because of theoretical arguments but also because it would contradict all the other results (except the deshielding of the CH_2 carbon) for neo-

pentyl fluoride (for which the fluorine SCS on the tertiary carbon is $\Delta\delta(C) = +4.5$ p.p.m., using the data of ref.[35]).

The negative fluorine SCS on silicon in fluoromethyltrimethylsilane can be rationalised in the terms of the Del Re total charges on the silicon atom. Calculations[24] for tetramethylsilane yield $Q_{Si} = 0.0156$ while it is $Q_{Si} = -0.0228$ in fluoromethyltrimethylsilane (Table III), so the increase in the shielding is paralleled by the increase of the total electron density (in the region of Q_{Si} values in which an increase in charge corresponds to an increase in shielding[1,41,42]).

It should be mentioned here that the more elaborate calculations[3] $(CNDO/2)$ of the charge distribution in H_3SiCH_2F indicated that the substitution of a hydrogen atom in methyl fluoride by the silyl group increases the total charge on the fluorine atom less than the substitution by the methyl group though the silicon atom is an electron donor with a net positive charge and the carbon (with a net negative charge) is acceptor in H_3MCH_2F compounds with $M = C$ and Si. It was also shown[3] that the calculated total overlap population of C—F bond is smaller in ethyl fluoride than in fluoromethylsilane, in the case of the M—C bond the order of the population is reversed. From a comparison of these calculated trends with the results discussed above follows that either the substitution of methyl fluoride hydrogen by $(CH_3)_3M$ groups has different effects upon electron distribution than that calculated for H_3M groups or the NMR results cannot be so straight forwardly related to the quantum chemical terms describing the bonding situations. Since this question cannot be solved in the present paper we accept, for the time being, the above interpretation of the NMR results which is, we believe, in agreement with other NMR literature.

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