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$^{13}\text{C}$ -NMR STUDIES OF POLYFLUORINATED HYDROCARBONS, CARBOXYLIC  
ACID DERIVATIVES, ALCOHOLS AND ETHERS

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SUMMARY

$\delta^{13}\text{C}$  values and coupling constants ( $^1\text{J}(^{13}\text{C}^1\text{H})$ ,  $^1\text{J}(^{13}\text{C}^{13}\text{C})$ ,  $^n\text{J}(^{19}\text{F}^{13}\text{C})$ ) are reported for 19 polyfluorinated organic compounds. It is shown that the shielding of carbon depends upon the number of fluorine atoms in  $\gamma$ -position. If the  $\text{R}_\text{F}$ -group is linked to a  $\pi$ -system hyperconjugative and  $n-\pi$  interaction accounts for the  $\delta^{13}\text{C}$  data. The values  $^1\text{J}(^{13}\text{C}^1\text{H})$  and  $^1\text{J}(^{13}\text{C}^{13}\text{C})$  are in qualitative agreement with changes of the s-character of the respective bonds.

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## INTRODUCTION

It is well known that polyfluorinated alkyl substituents take a strong influence on the spectroscopic properties of the remaining part of the molecule.  $^{13}\text{C}$ -NMR spectroscopy provides a means to obtain information on both the fluorinated and the nonfluorinated part of the molecule. Although perfluorinated hydrocarbons have been studied by  $^{13}\text{C}$ -NMR using  $^{13}\text{C} \{^{19}\text{F}\}$  double resonance in order to assign chemical shifts [1] and/or to obtain  $T_1(^{13}\text{C})$  values [2] little is known about the influence of perfluorinated groups  $\text{C}_n\text{F}_{2n+1}$  on the  $^{13}\text{C}$ -NMR parameters of the nonfluorinated part of the molecule [3 - 8].

Therefore, in the present work we report on  $\delta^{13}\text{C}$  data and coupling constants  $^nJ(^{13}\text{C}\text{X})$  ( $\text{X} = ^1\text{H}, ^{13}\text{H}, ^{19}\text{F}$ ) in the compounds of type I to IV defined below.

<u>I</u>	$\text{R} - \text{C}_n\text{F}_{2n+1}$	<u>II</u>	$\text{R} - \text{C}(0) - \text{C}_6\text{F}_{13}$
( <u>a</u> )	$\text{CH}_3\text{CH}_2$ (6)	( <u>a</u> )	$\text{CH}_3$
( <u>b</u> )	$\text{CH}_2=\text{CHCH}_2$ (6)	( <u>b</u> )	$\text{C} 1$
( <u>c</u> )	$\text{CH}_2=\text{CH}$ (6)		
( <u>d</u> )	$\text{CH}_3\text{CH}=\text{CH}$ (6) ( <u>cis</u> )	<u>III</u>	$\text{HO}(\text{CH}_2)_n - \text{C}_6\text{F}_{13}$
( <u>e</u> )	$\text{CH}_3\text{CH}=\text{CH}$ (6) ( <u>trans</u> )	( <u>a</u> )	(1)
( <u>f</u> )	$\text{HC}\equiv\text{C}$ (5)	( <u>b</u> )	(2)
	$\text{R} - \text{C}_n\text{F}_{2n} - \text{R}$	( <u>c</u> )	(3)
( <u>g</u> )	$\text{CH}_2=\text{CH}$ (4)	( <u>d</u> )	(4)
( <u>h</u> )	$\text{CH}_2=\text{CH}$ (6)	( <u>e</u> )	$\text{HS}(\text{CH}_2)_2 - \text{C}_6\text{F}_{13}$
( <u>i</u> )	$\text{CH}_2=\text{CH}-\text{CF}_2\text{CF}_2\text{Br}$		
<u>IV</u>	$\text{R} - \text{O} - \text{CF}_2\text{CF}_2\text{H}$		
( <u>a</u> )	$\text{CH}_3$	( <u>b</u> )	$\text{CH}_2=\text{CHCH}_2$
		( <u>c</u> )	$\text{CH}_2=\text{CH}$

$\delta^{13}\text{C}$  values are given in Table 1, together with shift differences relative to the parent hydrocarbons. Coupling constants  ${}^n\text{J}(^{13}\text{C-X})$  are listed in Table 2.

### CHEMICAL SHIFTS $\delta^{13}\text{C}$

The data in Table 1 for compounds I (a, b) and III (a - e) show that the  $\text{C}_6\text{F}_{13}$ -group exerts only a small deshielding influence upon the carbon atom directly attached to it. This is in contrast to the finding for  $\delta^{13}\text{C}(1,3)$  in 2,2-difluoro norbornane [ 8 ] with respect to  $\delta^{13}\text{C}(1,3)$  in norbornane [ 7 ] or for  $\delta^{13}\text{C}(2,4)$  in 1,1,1,3,3-pentafluorobutane [ 4 ] with respect to  $\delta^{13}\text{C}(2,4)$  of n-butane [ 7 ] . The  $^{13}\text{C}$  resonances of carbons in  $\beta$ -position relative to the  $\text{C}_6\text{F}_{13}$ -group in the compounds I (a, b) and III (a - e) are generally shifted to lower frequencies (higher field) as compared to the parent hydrocarbons. The  $\Delta^{13}\text{C}$  values range from -13.7 (I (b)) to -8.4 (III (d)). This effect is due to the fluorine atoms in  $\gamma$ -position relative to the carbon atom in question. These low frequency shifts have received much attention in rigid systems and they are ascribed to hyperconjugative type interaction between lone electron pairs on fluorine and the neighboured C - C bond which will lead to an increase in electron density at  $^{13}\text{C}$  [ 9 ] .

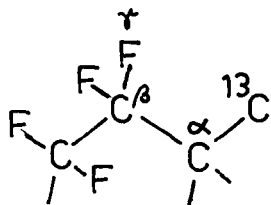


TABLE I

 $^{13}\text{C}$  - chemical shifts  $\delta^{13}\text{C}$ , [ppm] of polyfluorinated compounds

Nr.	Compound	RF	R
I (a)	$\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_3$	118.4 110.0 112.4 112.4 112.4 119.3 (+104.4) (+87.0) (+80.0) (+82.7) (+82.7) (+86.9)	29.9 3.5 (+6.9) (-11.5)
I (b)	$\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}=\text{CH}_2$	118.1 110.0 112.5 112.5 112.5 117.9 (+104.4) (+87.0) (+80.0) (+82.7) (+82.7) (+86.8)	36.2 125.5 121.9 (+1.2) (-13.7) (+6.9)
I (c)	$\text{C}_6\text{F}_{13}\text{CH}=\text{CH}_2$	118.1 109.4 112.0 111.7 111.7 114.9 (+102.7) (+85.1) (+78.2) (+80.6) (+80.6) (+79.9)	125.6 125.1 (-13.6) (+10.1)
I (d)	$\text{C}_6\text{F}_{13}\text{CH}=\text{CHCH}_3$	----- <sup>b</sup> -----	117.8 138.3 13.9 (-13.1) (+14.6) (+0.9)
I (e)	$\text{C}_6\text{F}_{13}\text{CH}=\text{CHCH}_3$ (cis)	----- <sup>b</sup> -----	118.9 139.8 16.8 (-13.6) (+14.6) (-2.2)
I (e)	$\text{C}_6\text{F}_{13}\text{CH}=\text{CHCH}_3$ (trans)	----- <sup>b</sup> -----	69.9 80.1 (-14.1) (+11.3)
I (f)	$\text{C}_5\text{F}_{11}\text{C}\equiv\text{C}-\text{H}$	118.3 111.0 111.0 111.0 107.6 (+103.1) (+87.4) (+79.1) (+81.7) (+88.7)	126.0 124.8 (-13.2) (+ 9.6)
I (g)	$\text{CH}_2=\text{CH}(\text{CF}_2)_4\text{CH}=\text{CH}_2$	114.9 112.0 112.0 114.9 (+ 79.9) (+81.0) (+81.0) (+79.9)	125.7 124.6 (-13.5) (+ 9.6)
I (h)	$\text{CH}_2=\text{CH}(\text{CF}_2)_6\text{CH}=\text{CH}_2$	114.4 111.6 111.4 111.4 111.6 114.6 (+ 79.4) (+80.6) (+80.4) (+80.4) (+80.6) (+79.4)	125.9 126.0 125.9 126.0
I (i)	$8\text{FCF}_2\text{CF}_2\text{CH}=\text{CH}_2$	118.1 114.5	190.9 24.1 (-15.9) (- 5.3)
II (a)	$\text{C}_6\text{F}_{13}\text{C}(0)\text{CH}_3$	117.7 109.2 111.8 111.8 111.2 109.8 (+102.2) (+85.1) (+78.4) (+81.0) (+86.2) (+65.2)	162.9 (- 8.4)
II (b)	$\text{C}_6\text{F}_{13}\text{C}(0)\text{Cl}$	118.1 109.1 111.7 111.7 111.3 109.0 (+102.4) (+85.0) (+78.6) (+81.2) (+86.0) (+62.3)	

III(a)	$C_6F_{13}CH_2OH$	118.8	109.4	112.0	112.0	111.5	117.4	61.1
		(+104.6)	(+86.3)	(+79.6)	(+82.3)	(+85.1)	(+84.2)	(- 1.1)
III(b)	$C_6F_{13}(CH_2)_2OH$	119.1	109.4	111.8	111.8	111.8	119.9	35.4
		(+104.9)	(+86.3)	(+79.4)	(+81.9)	(+81.8)	(+93.5)	(+ 2.2)
III(c)	$C_6F_{13}(CH_2)_3OH$	119.0	109.3	112.0	112.0	112.0	120.2	29.0
		(+104.7)	(+86.1)	(+79.5)	(+82.1)	(+81.8)	(+90.1)	(+ 2.5)
III(d)	$C_6F_{13}(CH_2)_4OH$	119.1	109.5	112.0	112.0	112.0	119.9	31.9
		(+104.8)	(+86.4)	(+79.5)	(+82.1)	(+81.8)	(+89.8)	(+ 1.8)
III(e)	$C_6F_{13}(CH_2)_2SH$	118.8	109.4	111.8	111.8	111.8	118.7	37.2
IV(a)	$HCF_2CF_2OCH_3$	109.8	119.4					51.3
		(+ 92.8)	(+53.2)					(- 6.6)
IV(b)	$HCF_2CF_2OCH_2CH=CH_2$	109.4	118.9					66.2
		(+ 94.6)	(+53.0)					132.7
IV(c)	$HCF_2CF_2OCH=CH_2$	109.2	117.8					119.3
		(+ 94.5)	(+53.2)					(- 5.4)
								(-2.7)
								(+2.9)
								140.9
								101.1
								(-11.6)
								(+14.9)

a to low field of internal  $(CH_3)_4Si$ ,  $\pm 0.1$  ppm; values in paranthesis are the shift differences  $\Delta^{13}C$  relative to the corresponding hydrocarbons

b mixture of isomers, ca. 3:1 (trans : cis)

TABLE 2

Coupling constants [Hz]  $^1J(^{13}C^1H)$ ,  $^nJ(^{19}F^{13}C)$ ,  $^1J(^{13}C^{13}C)$ 

Compound	$^1J(^{13}C^1H)$	$^nJ(^{19}F^{13}C)$	$^1J(^{13}C^{13}C)$
<u>I (a)</u>	127.0 (CH <sub>2</sub> )	CH <sub>3</sub> <sup>-</sup> 4.9 CH <sub>2</sub> <sup>-</sup> 23.8 CF <sub>2</sub> <sup>-</sup> 251.0	(CF <sub>2</sub> ) <sub>3</sub> <sup>-</sup> 262.0 CF <sub>2</sub> <sup>-</sup> 268.0 CF <sub>3</sub> 285.0
	127.0 (CH <sub>3</sub> )	31.2	33.2
<u>I (b)</u>	130.0 (CH <sub>2</sub> )	CH <sub>2</sub> =CH- 5.0 CH <sub>2</sub> <sup>-</sup> 23.5	(CF <sub>2</sub> ) <sub>3</sub> <sup>-</sup> 262.0 CF <sub>2</sub> <sup>-</sup> 267.0 CF <sub>3</sub> 288.0
	157.5 (CH)	157.0 (=CH <sub>2</sub> )	--
	172.0 (CH)	CH <sub>2</sub> = 9.8 CH- 24.5	(CF <sub>2</sub> ) <sub>3</sub> <sup>-</sup> 265.0 CF <sub>2</sub> <sup>-</sup> 268.0 CF <sub>3</sub> 287.5
163.4 (CH <sub>2</sub> )	31.0	33.5	
<u>I (c)</u>	128.9 (CH <sub>3</sub> )	CH <sub>3</sub> <sup>-</sup> 1.4 CH= 7.0	(CF <sub>2</sub> ) <sub>5</sub> <sup>-</sup> ----- CF <sub>3</sub>
	164.4 (CH)	23.6	--
<u>I (d)</u> (cis)	155.5 (CHCH <sub>3</sub> )	CH <sub>3</sub> <sup>-</sup> 1.2 CH= 9.0	(CF <sub>2</sub> ) <sub>5</sub> <sup>-</sup> ----- CF <sub>3</sub>
	127.0 (CH <sub>3</sub> )	22.0	--
<u>I (e)</u> (trans)	164.0 (CH)	2.0	--
	156.5 (CHCH <sub>3</sub> )	2.0	--
<u>I (f)</u>	50.5 (CCH)	H-C≡ 6.3 C- 36.3	(CF <sub>2</sub> ) <sub>3</sub> <sup>-</sup> 265.0 CF <sub>3</sub> 284.0
	261.5 (CH)	32.3	33.0
		2.0	32.3
		2.0	185.0 (C≡C)
			80.0 (≡C-CF <sub>2</sub> )

I(i)	170.3 (CH)	CH <sub>2</sub> =	CH-	CF <sub>2</sub> -	CF <sub>2</sub> Br	--
	164.0 (CH <sub>2</sub> )	9.2	24.6	251.5	311.1	
II(a)	131.2 (CH <sub>3</sub> )	CH <sub>3</sub> -	C(O)-	CF <sub>2</sub> -	(CF <sub>2</sub> ) <sub>3</sub> -	CF <sub>3</sub>
	6.0 (C(O))	1.5	26.6	267.0	265.0	287.4
				32.0	32.5	33.0
II(b)	--	Cl-	C(O)-	CF <sub>2</sub> -	(CF <sub>2</sub> ) <sub>3</sub> -	CF <sub>3</sub>
			36.6	273.0	265.0	267.0
III(a)	145.8 (CH <sub>2</sub> )	HO-	CH <sub>2</sub> -	CF <sub>2</sub> -	(CF <sub>2</sub> ) <sub>3</sub> -	CF <sub>3</sub>
			26.8	258.0	265.0	267.0
				30.5	33.0	33.3
III(b)	130.4 (CH <sub>2</sub> )	HO-CH <sub>2</sub> -	CH <sub>2</sub> -	CF <sub>2</sub> -	(CF <sub>2</sub> ) <sub>3</sub> -	CF <sub>3</sub>
	144.0 (OCH <sub>2</sub> )	5.1	21.3	254.3	265.0	287.6
				31.5	33.0	33.3
III(c)	126.5 (CF <sub>2</sub> CH <sub>2</sub> )	HOCH <sub>2</sub> -	CH <sub>2</sub> -	CF <sub>2</sub> -	(CF <sub>2</sub> ) <sub>3</sub> -	CF <sub>3</sub>
	126.5 (CH <sub>2</sub> CH <sub>2</sub> )	3.5	22.5	253.9	265.0	287.5
	142.0 (OCH <sub>2</sub> )			31.0	33.0	33.0
						1.5
III(d)	126.5 (CF <sub>2</sub> CH <sub>2</sub> )	HO(CH <sub>2</sub> ) <sub>2</sub> -	CH <sub>2</sub> -	CF <sub>2</sub> -	(CF <sub>2</sub> ) <sub>3</sub> -	CF <sub>3</sub>
	128.0 (CH <sub>2</sub> CH <sub>2</sub> )	3.9	23.0	253.5	265.0	287.0
	127.4 (CH <sub>2</sub> CH <sub>2</sub> )			31.3	33.0	33.3
	140.7 (OCH <sub>2</sub> )					1.3

TABLE 2 (cont.)

Compound	$J(^{13}C^1H)$	$J(^{19}F^{13}C)$	$J(^{13}C^{13}C)$
III(e)	130.0 (CH <sub>2</sub> )	HS-CH <sub>2</sub> -CH <sub>2</sub> - 5.0 22.0	CF <sub>2</sub> <sup>-</sup> 255.4
	143.0 (SCH <sub>2</sub> )	1.1	CF <sub>2</sub> <sup>-</sup> 31.5
IV(a)	147.9 (OCH <sub>3</sub> )	CH <sub>3</sub> - 0-	(CF <sub>2</sub> ) <sub>3</sub> - 265.0
	192.6 (CF <sub>2</sub> H)	6.9 --	CF <sub>2</sub> <sup>-</sup> 265.9
IV(b)	147.5 (OCH <sub>2</sub> )	CH <sub>2</sub> =CH-CH <sub>2</sub> - 0-	CF <sub>2</sub> <sup>-</sup> 28.2
		6.1 --	CF <sub>2</sub> <sup>-</sup> 267.5
	156.7 (CH)		CF <sub>2</sub> <sup>-</sup> 27.5
	192.3 (CF <sub>2</sub> H)		CF <sub>2</sub> <sup>-</sup> 249.5
IV(c)	192.3 (CH)	CH <sub>2</sub> =CH- 0-	CF <sub>2</sub> <sup>-</sup> 270.6
	160.7 (CH <sub>2</sub> )	6.6 --	CF <sub>2</sub> <sup>-</sup> 29.0
CH <sub>3</sub> CH <sub>2</sub> -O-CH=CH <sub>2</sub>	192.5 (CF <sub>2</sub> H)		CF <sub>2</sub> <sup>-</sup> 250.2
			CF <sub>2</sub> <sup>-</sup> 41.2
CH <sub>3</sub> CH <sub>2</sub> -O-C(CH <sub>3</sub> )=CH <sub>2</sub>			CF <sub>2</sub> <sup>-</sup> 83.6 (CH=CH <sub>2</sub> )
			CF <sub>2</sub> <sup>-</sup> 39.2 (CH <sub>2</sub> -CH <sub>3</sub> )
			CF <sub>2</sub> <sup>-</sup> 78.5 (CH=CH <sub>2</sub> )
			CF <sub>2</sub> <sup>-</sup> 80.9 (C=CH <sub>2</sub> )

<sup>a</sup> mixture of isomers

<sup>b</sup> ref. [13]



Although this interaction is most effective in an anti-periplanar arrangement we expect an averaged influence of this type in case of less rigid molecules.

In fact the comparatively small deshielding of the  $\alpha$ -carbons can be accounted for considering that there are also two fluorine atoms in  $\gamma$ -position. These are not present in 2,2-difluoro-norbornane or in 1,1,1,3,3-pentafluorobutane where a significant deshielding for the respective C  $\alpha$ -atoms is observed.

The data for  $\text{II}$  ( $\underline{c}$ ,  $\underline{d}$ ) show that the influence of the  $\text{C}_6\text{F}_{13}$  group on  $\delta^{13}\text{C}$  is completely attenuated by two intervening  $\text{CH}_2$ -groups.

For the compounds  $\text{I}$  ( $\underline{c}$  -  $\underline{i}$ ) and  $\text{II}$  ( $\underline{a}$ ,  $\underline{b}$ ) the  $^{13}\text{C}\alpha$ -resonance is shifted to significantly lower frequencies with respect to the parent hydrocarbon (-15.9 to -13.1 ppm) while the resonance of  $^{13}\text{C}\beta$  in  $\text{I}$  ( $\underline{c}$  -  $\underline{i}$ ) is shifted to higher frequencies (+10.1 to 14.6 ppm). In compound  $\text{II}$  ( $\underline{a}$ ) the methyl  $^{13}\text{C}$ -resonance is shifted to low frequencies (-5.2 ppm) in contrast to the corresponding carbon atoms in  $\text{I}$  ( $\underline{c}$  -  $\underline{i}$ ) which are  $\text{sp}^2$ - oder  $\text{sp}$ -hybridized. We conclude that the perfluoroalkyl group changes the nature of the  $\pi$ -system since this is believed to take a major influence on the shielding of the carbon atoms concerned [ 7 ] . Both, inductive and hyperconjugative effects, may produce the shielding pattern observed here. There is a possibility that a  $\pi$ -type n-orbital of fluorine interacts through space with a  $\pi^*$  orbital of the  $\pi$ -system. This attenuates the hyperconjugative through bond interaction from fluorine but may induce the release of  $\pi$ -electron density from the  $\pi$ -system into the C-F bond [ 10 ] .

This argument agrees with the finding that the low frequency shift of the methyl  $^{13}\text{C}$ -resonance in the ketone II (a) is much smaller than in compounds I (a, b) and III (a - e).



The  $\delta^{13}\text{C}$  values for the compounds IV should reveal in which way a heteroatom changes the influence of fluorine atoms in  $\gamma$ -position. We observe low frequency shifts for the  $^{13}\text{C}$ -resonances in IV (a) ( $^{13}\text{CH}_3$ ), IV (b) ( $^{13}\text{CH}_2$ ) and IV (c) ( $^{13}\text{CH}=\text{}$ ). However, it is difficult to evaluate the influence of oxygen on the basis of the present data. The comparison of the  $\delta^{13}\text{C}$  data for the olefinic carbons in ethyl vinyl ether and in IV (c) shows that the bonding situation changes significantly. With the  $\text{CH}_2$ -group between the vinyl group and the  $\text{C}_6\text{F}_{13}$  rest (I (b)) the  $^{13}\text{CH}_2=\text{}$  resonance is shifted by only +6.9 ppm to high frequency (relative to 1-nonene). In compound IV (c) the  $^{13}\text{CH}_2=\text{}$  resonance is shifted by +15.0 ppm (relative to ethylvinyl ether). This is suggestive of reduced  $\pi$ -donation from oxygen to the  $\text{C}=\text{C}$   $\pi$  system due to the  $\text{HCF}_2\text{CF}_2$ -group in IV (c). The situation is very complex since the increase in  $\sigma$ -polarization of the  $=\text{HC}-\text{O}$  bond has also to be taken into account. The latter effect, the  $\sigma$ -polarization of the  $\text{H}_2\text{C}-\text{O}$  bond in IV (b) may be responsible for the high frequency shift of the  $^{13}\text{CH}_2=\text{}$  resonance in IV (b) with respect to the alkyl ethyl ether.

The  $\delta^{13}\text{C}$  values of the polyfluoroalkyl groups cover a narrow range. As shown in Fig. 1 the assignment of the resonance signals is fairly straightforward even without decoupling of  $^{19}\text{F}$ . In addition to  ${}^n\text{J}(^{19}\text{F}^{13}\text{C})$  the long range  $^{13}\text{C}$ - $^1\text{H}$  coupling constants in the  $^1\text{H}$ -coupled spectra serve in this respect.

The effect of substituents X on  $\delta^{13}\text{C}$  of  $\text{C}_6\text{F}_{13}\text{X}$  is similar as in hydrocarbons for the carbon atom directly linked to X (range from 94.0 (X = I) to 118.5 ppm (X = F) [ 1 ] . However, the  $^{13}\text{C}$  resonances for carbon atoms in  $\beta$ -position to X are already very similar (range from 110.0 (X = I) [ 1 ] to 112.0 (X =  $\text{C}_2\text{H}_5$ ) and the same is true for the carbons in  $\gamma$ -position.

It has been noted [ 1 ] that  $\delta^{13}\text{C}$  of perfluorohydrocarbons can be calculated by substituent parameters similar as in hydrocarbons [ 7 ] . We would like to show that the shift differences  $\Delta^{13}\text{C}$  between the two classes of compounds depend on the number of fluorine atoms in  $\gamma$ -position in the perfluorinated hydrocarbon. Relevant data in Table 1\* show that the shift differences  $\Delta^{13}\text{C}$  decrease in magnitude with increasing number of  $\gamma$ -fluorine atoms.

#### COUPLING CONSTANTS ${}^1\text{J}(^{13}\text{C}^1\text{H})$ , ${}^n\text{J}(^{13}\text{CF})$ , ${}^1\text{J}(^{13}\text{C}^{13}\text{C})$

The data  ${}^1\text{J}(^{13}\text{C}^1\text{H})$  in Table 2 for compounds I (a, b) show the following trends:

- (i) The magnitude of  ${}^1\text{J}(^{13}\text{C}^1\text{H})$  increases slightly with respect to hydrocarbons in case of  $\text{sp}^3$ -hybridized carbon in  $\alpha$  or in  $\beta$ -position to the fluoroalkyl group.

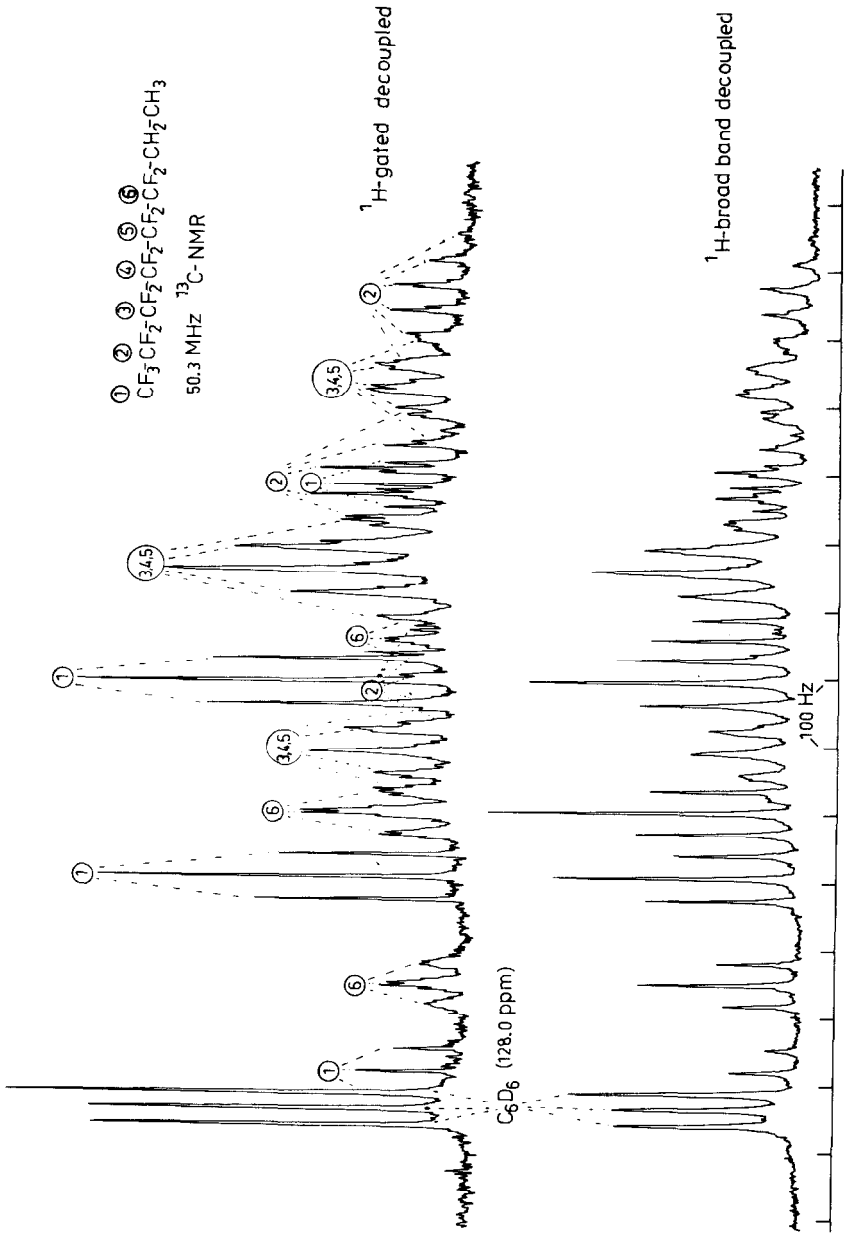


Fig. 1.  $^{13}\text{C}$ -NMR spectra of the  $\text{C}_6\text{F}_{13}$  group in (I(a)). The assignment follows from the splitting pattern due to  $n_{\text{J}}(^{19}\text{F}^{13}\text{C})$  and  $n_{\text{J}}(^{1}\text{H})$ .

TABLE I\*

$\delta^{13}\text{C}$ , data and shift differences  $\Delta^{13}\text{C}$  (in ppm) of some perfluoroalkanes [1] and corresponding alkanes [7]

Compound	$\delta^{13}\text{C}$				$\Delta^{13}\text{C}(\delta\text{-F})$			
	C(1)	C(2)	C(3)	C(4)	C(1)	C(2)	C(3)	C(4)
$\text{C}_5\text{F}_{12}$	118.5	109.8	111.1		104.8 (2)	87.2 (2)	76.6 (6)	
$\text{C}_5\text{H}_{12}$	13.7	22.6	34.5					
$\text{C}_6\text{F}_{14}$	118.5	109.9	111.6		104.6 (2)	87.0 (2)	79.6 (5)	
$\text{C}_6\text{H}_{14}$	13.9	22.9	32.0					
$\text{C}_7\text{F}_{16}$	118.5	109.9	111.7	112.1	104.6 (2)	85.9 (2)	79.3 (5)	82.6 (4)
$\text{C}_7\text{H}_{16}$	13.9	23.0	32.4	29.5				
$\text{C}_8\text{F}_{18}$	118.1	109.4	111.2	111.8	104.1 (2)	85.4 (2)	78.8 (5)	82.1 (4)
$\text{C}_8\text{H}_{18}$	14.0	23.0	32.4	29.7				
$\text{C}_6\text{F}_{12}$	108.8				81.0 (4)			
$\text{C}_6\text{H}_{12}$	27.8							

- (ii) This increase becomes more apparent in the olefinic compounds I (c, d, e, i) and in the alkyne I (f).
- (iii) There is no significant influence of the  $\text{HCF}_2\text{-CF}_2$ -group upon  $^1\text{J}(^{13}\text{C}^1\text{H})$  in the ether compounds IV.

The strong influence of the perfluoroalkyl substituents upon the magnitude of  $^1\text{J}(^{13}\text{C}^1\text{H})$  is in agreement with the assumption that the  $\sigma$ -polarization changes the nature of the  $\pi$ -system. Thus increase in  $^1\text{J}(^{13}\text{C}^1\text{H})$  is qualitatively in accord with the expected increase in the s-character of the C-H bond.

It is interesting to compare the change in  $^1\text{J}(^{13}\text{C}^1\text{H})$  with that in  $^1\text{J}(^{13}\text{C}^{13}\text{C})$ . The coupling constants  $^1\text{J}(^{13}\text{C}^{13}\text{C})$  have been obtained for compound I (a), I (f), IV (b), IV (e) and ethyl vinyl ether from natural abundance  $^{13}\text{C}$ -NMR spectra. Because of the small shift differences  $\Delta^{13}\text{C}$  and partial overlap of the  $^{13}\text{C}$  resonances of the olefinic carbons with those of the perfluoroalkyl group it proved impossible to obtain  $^1\text{J}(^{13}\text{C}^{13}\text{C})$  for the compounds I (c, d, e, g, h, i).

The data for I f have already been reported and discussed in another context [ 11 ]. Similar to  $^1\text{J}(^{13}\text{C}^1\text{H})$  there is no significant change of  $^1\text{J}(^{13}\text{CH}_2^{13}\text{CH}_3)$  in I (a) as compared to ethane (34.6 Hz [ 13 ]). This is noteworthy since there is a range of 16 Hz for  $^1\text{J}(^{13}\text{C}^{13}\text{C})$  in ethyl derivatives  $\text{CH}_3\text{-CH}_2\text{-X}$  with  $\text{X} = \text{Li}$  (22.1 Hz) [ 12 ] and  $\text{X} = \text{F}$  (38.2 Hz) [ 13 ] at the extreme ends. On the other hand the value for  $^1\text{J}(^{13}\text{CH}_2^{13}\text{CF}_2)$  in I (a) is according to expectations. We expect increased s-participation in the  $\text{F}_2\text{C-CH}_2$ -bond from the  $\text{CF}_2$ -carbon because of the electronegative fluorine atoms.

Corresponding to the marked increase in  $^1J(^{13}C^1H)$  in compound I (f) with respect to other alkynes we find a significant increase in  $^1J(^{13}C^{13}C)$ . This must be attributed mainly to the  $\sigma$ -polarizing ability of the perfluoroalkyl group [11]. As for I (a) we find in I (f) that the magnitude of  $^1J(^{13}CF_2-^{13}C\equiv)$  is increased with respect to  $^1J(^{13}CH_3-^{13}C\equiv)$  in propyne (67.4 Hz [13]).

In compound IV (b) the  $HCF_2CF_2$ -group is rather far removed from the carbon atoms in question. The values  $^1J(^{13}C^{13}C)$  are in the expected range. In compound IV (c) it is expected that the  $\sigma$ -polarizing  $HCF_2-CF_2$  group will cause a small increase in the magnitude of  $^1J(^{13}C=^{13}C)$  with respect to alkyl vinyl ethers. This was found to be the case.

The values of the coupling constants  $^nJ(^{19}F^{13}C)$  of the fluorinated alkyl groups fall in the range already reported for numerous compounds [7]. Other coupling constants  $^2J(^{19}F^{13}C)$  and  $^3J(^{19}F^{13}C)$  are not particularly informative. There is no significant difference between  $^2J(^{19}F^{13}C)$  for  $sp^3$ - and  $sp^2$ -hybridized carbon. The increase in magnitude of  $^2J(^{19}F^{13}C)$  observed for the carbonyl carbon atoms in III (a, b) and for the  $sp$ -hybridized carbon in I (f) is also in agreement with literature data of similar compounds [7]. The complex nature of the coupling constants  $^nJ(^{19}F^{13}C)$  precludes a detailed interpretation of the observed trends.

#### EXPERIMENTAL

$^{13}C$ -NMR spectra (50.3 MHz) were recorded with a BRUKER WP 200 NMR spectrometer. The measurements have been carried out at 27° C in 10 mm (o.d.) tubes using solutions

(50 - 60 %) in  $C_6D_6$  (+1 %  $(CH_3)_4Si$ ). For compound III (a) a 1:1 mixture of  $C_6D_6$  /  $CH_3OH$  was used as solvent. In general ca. 1000 transients (sweep width 10 000 Hz, acquisition time 0.8 s, pulse angle ca.  $20^\circ$ ) were necessary to obtain a sufficient S/N ratio in order to assign the signals of  $R_F$ -group. The  $^{13}C$ - $^{13}C$  coupling constants have been obtained by accumulation of ca. 30 000 scans (the same parameters as above but acquisition time 1.6 s).

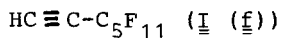
Most compounds have been prepared by standard procedures. The samples of I (a) and I (f) have been obtained by the following routes:

$CH_3-CH_2-C_6F_{13}$  (I (a))

A mixture consisting of 30.07 g of powdered zinc (0.46 mol), 0.84 g of copper (II) acetate (4.6 mmol) and 200 of dry DMF was stirred for 1 hour at  $100^\circ$  under nitrogen. The activated zinc was filtered off, washed with 50 ml of DMF and suspended in 450 ml of the same solvent under nitrogen.  $C_6F_{13}-CH_2-CH_2I$  (133.8 g, 0.282 mol) was added dropwise during 3 hours with rapid stirring, keeping the temperature below  $30^\circ$ . The mixture was stirred overnight, 300 ml of DMF was distilled off under reduced pressure and the residue was hydrolysed with dilute sulfuric acid. The liquid which separated as lower layer was dried over calcium chloride and purified by distillation to give 81.6 g (yield: 83 %) of I (a), boiling at  $106-7^\circ$ .

$^1H$ -NMR:  $\delta^1H$  ( $CH_3$ ) 0.93 (t); ( $CH_2$ ) 1.84 (q, t, t);  
 $^3J$  (HH) 7.6 Hz,  $^3J$  (FH) 18.7 Hz,  $^4J$  (FH) 1.7 Hz)





1.1.-dihydro-perfluorocarboxylic acids and also the corresponding chlorides and esters  $(\text{CF}_3(\text{CF}_2)_n-\text{CH}_2-\text{C}(\text{O})\text{X})$ ;  $\text{X} = \text{OH}, \text{Cl}, \text{OR}$ ), when treated with alkali hydroxides, are transformed into a mixture of the alkynes  $\text{CF}_3(\text{CF}_2)_{n-1}-\text{C}\equiv\text{CH}$  and of the 1-hydroperfluoroalkanes  $\text{CF}_3(\text{CF}_2)_{n-1}-\text{H}$  [14].

In our case,  $\text{C}_6\text{F}_{13}-\text{CH}_2-\text{C}(=\text{O})\text{Cl}$  was added dropwise to a concentrated solution of potassium hydroxide (fivefold excess) at  $100 - 120^\circ$  with stirring. The volatile products were condensed, dried over magnesium sulfate and redistilled to give a mixture of  $\underline{\text{I}} \quad (\underline{\text{f}})$  and of  $\text{C}_5\text{F}_{11}\text{H}$  boiling at  $74^\circ$ , which contained these components in a molar ratio of 6:4. Separation could be achieved by addition of  $n\text{-BuLi}$ . The solid  $\text{Li C}\equiv\text{C}-\text{C}_5\text{F}_{11}$  was filtered off and dried in high vacuo. Treatment of the solid with the required amount of methanol gave pure  $\underline{\text{I}} \quad (\underline{\text{f}})$  in a yield of 45 % based on the acid chloride. ( $^1\text{H-NMR}$ :  $\delta^1\text{H}$  2.14 (t);  $^4\text{J}$  (FH) 5.7 Hz)

Attempts at the preparation of  $\text{CF}_3(\text{CF}_2)_n-\text{C}\equiv\text{CH}$  ( $n = 4, 5$ ) by a reaction sequence similar to the one employed by Henne and Nager for the synthesis of 1.1.1-trifluoro-propyne [15] were unsuccessful since the intermediate  $\text{CF}_3(\text{CF}_2)_n\text{CBr}_2-\text{CH}_2\text{Br}$  could not be dehydrobrominated properly. Treatment of this compound with an ethanolic solution of  $\text{KOH}$  led to ether formation, while potassium tert-butoxide in  $\text{DMSO}$  mainly eliminated bromine.

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