A Carbon-13 Nuclear Magnetic Resonance Study of Compounds Substituted by a Perfluoroalkyl Chain

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The ¹³C NMR spectra of alkanes, alkanones and cyclohexanones substituted by perfluoroalkyl groups, R_F , have been studied. The influence of the perfluoroalkyl group on the chemical shifts of other carbons of the molecules is the same regardless of the R_F chain length.

INTRODUCTION

Studies using ¹³C NMR of compounds containing an electronegative substituent have shown that the γ -carbon generally undergoes a shift towards high field. This necessitates a privileged orientation of the carbon-heteroatom bond in relation to the bond be-tween the β - and γ -carbons (antiperiplanar form or gauche form).^{1,2} In particular, this effect has been observed in the monofluorinated derivatives of cyclohexane³ and cyclohexanone.⁴ In gem-difluoronor-bornanes, the signals corresponding to the different γ -carbons are not all shifted in the same direction.⁵

We have examined the ¹³C NMR spectra of various compounds substituted by three or more fluorine atoms. These compounds were alkanes or ketones having a perfluoroalkyl chain $R_F = CF_3(CF_2)_n$ with *n* varying from 0 to 5. We observed high-field shifts for the carbons located in the γ -position to the fluorine atoms.

RESULTS

The shift increments produced on the introduction of fluorine atoms into the studied molecules have been calculated. Each compound was of the RY type in which Y was a substituent such as methyl, trifluoromethyl or linear perfluoroalkyl R_F . The comparison of various RY compounds with respect to the R—CH₃ compound allowed the calculation of the increment due to the replacement of CH₃ by Y.

When a methyl group is replaced by an R_F group the α -carbon generally undergoes a shift of 8–10 ppm towards low field, while the β -carbons have a shift of similar amplitude towards high field. The effects due to the R_F group are practically independent of the length of the fluorinated chain. In hydrogenated series the shifts induced by substitutions in α , β , γ or δ positions are of variable amplitude.⁶ This is due to the different electronic effects of C—H and C—CH₂ bonds. On the contrary, in the polyfluorinated series the electronic effects of C—F and C—CF₂ bonds are not very different and induce similar shifts.

The dodecanes 2, 3, 4 and 5 (Table 1) are long enough to assume that the non-fluorinated extremity of the chain has no influence. The presence of three fluorine atoms in 2 induces a low-field shift of 8.3 ppm for the α -carbon and a high-field shift of -10.1 ppm for the β -carbon. One finds practically the same effect on the α -carbon in propanone 7 (Table 2). The carbonyl in β -position is shifted -11.9 ppm towards high field. The methyl in γ -position is shifted 2 ppm towards low field. The carbon α to the trifluoromethyl group in cyclohexanone 11 (Table 3) undergoes a shift of 8.4 ppm and the carbonyl experiences a high-field shift of -10.1 ppm; C-3, also located in the β position, shifts -8.3 ppm to high field. A low-field shift of 1.1 ppm was noted for C-6.

EXPERIMENTAL

Perfluorinated dodecanes 2, 3, 4 and 5 were furnished by Nguyen Thoai.⁹ α -Perfluoroalkylcyclohexanones **11–14** were prepared according to Ref. 10. The α -perfluoroalkylpropanones were synthesized by the photosensitized addition of perfluoroalkyl iodides to isopropenyl methyl ether, followed by acidic hydrolysis. The experimental conditions for this enol ether were the same as those for the enamines (Ref. 10, procedure A).

Compound 7, b.p. 94 °C. Yield 5%. Microanalysis was not possible owing to its high vapour pressure. Compound 8, b.p. 108 °C. Yield 25%. Calculated C:34.10%, H:2.86%; found C:33.95%, H:2.96%. Compound 9, b.p. 45 °C at 0.5 torr. Yield 25%. Calculated C:28.74, H:1.34%; found C:28.80%, H:1.39%.

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Table 1. ¹³C shifts^a and increments^{a,b} (in parentheses) of dodecanes

C _n F _{2n+}	1C _{12-n} H _{2(12-n)+1}	1	2	3	4	5	6	7	8	9	10	11	12	J ^{c,d}
1	Dodecane	14.1	22.8	32.1	←		29. 9 –29.6	;			32.1	22.8	14.1	
2	<i>n</i> = 1		31.1 (8.3)	22 (-10.1)	·		29.7–29.4	,		>	32.1	22.8	14.1	27
3	n = 2			30.9 (8.1)	20.4 + (−11.7)		- 29.8–29.4	۱ <u> </u>		>	32	22.8	14.1	
4	n = 3				30.9 (8.1)	20.3 (–11.8)	29.829.4	ļ ——		>	32.1	22.9	14.1	
5	n = 4					31.3 (8.5)	20.4 ← (−11.7)		29.6	;>	32.2	22.9	14.1	

^a In ppm. ^b The carbon α to the perfluorinated group is compared with C-2 of the dodecane etc. ^c The carbon α to the perfluorinated group is a triplet for $n \ge 2$. The lateral signals of this triplet generally appear as shoulders on other carbon signals. ^d In hertz.

Table 2. ^{13}C Shifts* and increments* (in parentheses) of α -perfluoroalkyl propanones and the related ketone

	Ő.	1	2	3	4	² J(CF) ^b ¹ J(CF) ^b
6	2 3 1 4 CH ₃	28.8° 28.4 ^d	206.3° 209.5ª	36.4° 36.3 ^d	7.4 ^c 7.9 ^d	
7	0 CF ₃	30.4 (2.0)	197.6 (–11.9)	47.3 (11)	123.9	28 276
8	C_2F_5	31.3 (2.9)	197.8 (–11.7)	44.2 (7.9)		22
9	2 3 1 4 C ₆ F ₁₃	31.4 (3.0)	197.6 (11.9)	44.4 (8.1)		22

^a In ppm. ^b In hertz. ^d Our measurement. ° Ref. 7.

Table 3.	¹³ C shifts ^a	and increments*	(in parentheses)	of	cyclohexanones
	C Shints		(in parenticoco)	ΨI.	Cyclonexanone:

	5 6	1	2	3	4	5	6	7	²J(CF) [♭]	¹J(CF) [⊳]
10		210.3° 213.2ª	44.3° 45.4 ^d	35.2° 36.2ª	24.5° 25.2 ^d	27.3° 28.0 ^d	40.9° 41.3 ^ª	14.8ª		
11	$4 \sqrt{\frac{5}{3}} \frac{6}{2} \frac{1}{2} 0$ CF ₃	203.1 (-10.1)	53.8 (8.4)	27.9 (-8.3)	24.0 (1.2)	27.4 (~0.6)	42.4 (1.1)	125.2	25	280
12	$4 \underbrace{5}_{3} \underbrace{6}_{1} \underbrace{0}_{2} \underbrace{0}_{2}$	203.2 (-10)	52 (6.6)	27.7 (-8.5)	23.8 (-1.4)	27.7 (-0.3)	42.8 (1.5)		20	
13	$4 \underbrace{\overbrace{}_{3}}_{3} \underbrace{\overbrace{}_{2}}_{C_{3}} F_{7}$	203.2 (-10)	52.3 (6.9)	27.8 (-8.4)	23.9 (-1.3)	27.8 (0.2)	42.9 (1.6)		20	
14	4 5 6 3 2 C ₆ F ₁₃	203.1 (10.1)	52.5 (7.1)	27.9 (-8.3)	23.8 (-1.4)	27.9 (-0.1)	42.8 (1.5)		20	

^a in ppm. ^b in hertz. ^c Ref. 8. ^d Our measurement.

¹³C NMR spectra (20 MHz) were recorded on a Varian CFT 20 spectrometer at 37 °C in deuterochloroform with TMS as internal standard. The spectral width was 8000 Hz, and the pulse angle was 30° with an acquisition time of 0.5 s; the delay was 1.5 s. Offresonance spectra were recorded at 4000 Hz with an acquisition time of 1 s.

Acknowledgements

We wish to thank Nguyen Thoaï for providing compounds 2-5.

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Received 29 October 1979; accepted (revised) 13 March 1980

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