Journal of Fluorine Chemistry, *35* (1987) 359–371

Received: May 7, 1986; accepted July 6, 1986

^{17}O AND ^{13}C NUCLEAR MAGNETIC RESONANCE STUDY OF POLYFLUORINATED CARBONYL COMPOUNDS

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SUMMARY

$\delta^{17}O$- and $\delta^{13}C$ values are reported for 15 polyfluorinated carbonyl compounds. If the R_f group is separated from the carbonyl group by less than two carbon atoms a marked increase in the nuclear shielding of $^{13}C(C{=}O)$ and a marked decrease in the nuclear shielding of the $^{17}O(C{=}O)$ nucleus is observed. This is ascribed to the differing effects of the R_f group on the σ and the π system of the carbonyl unit. The effect on the σ-manifold leads to increase in shielding but it may be offset (as in the case of the ^{17}O nucleus) by destabilization of the π system. UV spectroscopic data for some polyfluorinated carbonyl compounds support these arguments.

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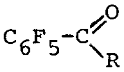
0022-1139/87/$3.50

INTRODUCTION

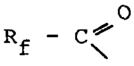
The electronic structure of carbonyl compounds is of prime interest for many different lines of research. Therefore, the investigation of spectroscopic properties of the C=O bond has been a major object for many years [1]. Our current interest in the influence of polyfluorinated alkyl groups upon NMR spectroscopic parameters [2,3] prompted us to study polyfluorinated carbonyl compounds by ^{17}O- and ^{13}C NMR. The ^{13}C NMR measurements are continuing a previous more general study [2] whereas ^{17}O NMR for this type of compounds is studied in a systematic way for the first time. Thus far, some ^{17}O-chemical shifts ($\delta^{17}O$) have been reported for pentafluorophenyl carbonyl compounds [4], and a few other data are scattered in the literature [5]. The comparison of the $\delta^{17}O$ values for the pentafluorophenyl carbonyl compounds with those of their hydrocarbon analogues shows the deshielding influence of the C_6F_5-group [4].



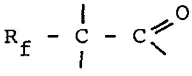
R	H	Me	CF_3	Cl	OMe
$\delta^{17}O$ [4] (C=O)	612	615	627	552	379

The effect of perfluoroalkyl groups (R_f effect) on unsaturated linkages was found to be thermodynamically destabilizing. Thus, it was concluded that the enormous thermal stability of many perfluorinated compounds is completely kinetic in nature [6,7]. From the spectroscopic point of view the changes in the electronic structure induced by the R_f group are important. The electron withdrawing power (-I effect) of the R_f group is expected to stabilize σ-orbitals (including n-orbitals). However, π-orbitals may be destabilized owing to the repulsing effects of the fluorine non-bonding electrons [8]. In order to shed some light on these problems we have selected different types of carbonyl compounds with the structures **A**, **B**, **C**.

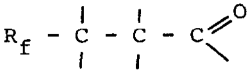
These should allow to study the influence of the R_f group on the ^{17}O- and ^{13}C-chemical shifts.



A
(1 - 9)



B
(1o - 14)



C
(15)

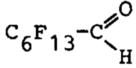
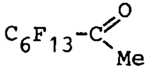
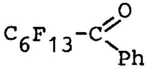
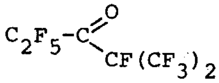
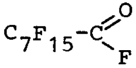
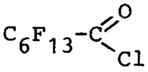
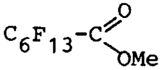
RESULTS AND DISCUSSION

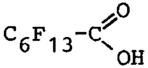
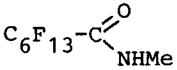
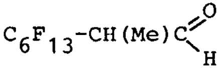
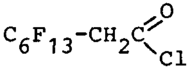
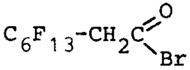
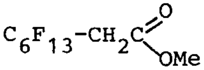
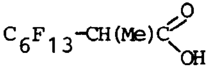
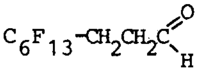
Table 1 collates δ^{17}O and δ^{13}C data together with chemical shift differences (Δ^{17}O, Δ^{13}C) with respect to the corresponding hydrocarbon analogues. The inspection of the δ^{17}O and δ^{13}C data for the C=O group shows that the shielding of the ^{13}C-nucleus increases markedly in the presence of an R_f group (type A or B), whereas the shielding of the ^{17}O-nucleus decreases. In general these effects are more pronounced for type A (1-9) than for type B (1o-14). In type C (15) the influence of the R_f group is very small, both on δ^{13}C and δ^{17}O, as expected from previous observations [2,3 It also appears that the effects of the R_f group is compensated to some extent in the carboxylic acids, esters and in the amide (8, 14, 7, 13, 9) as compared to the aldehydes, ketones and halides. The additivity of the effects exerted by the R_f groups is shown by the Δ^{13}C and Δ^{17}O values for compound 4 .

Various models have been developed to understand the ^{13}C-nuclear shielding of carbonyl compounds [9]. From solid state NMR measurements it is known that the principal axis corresponding to the largest paramagnetic shift is parallel to the C=O bond and the largest diamagnetic shift is perpendicular to the $\rangle$C=O plane [1o]. Recently, the same picture has been established experimentally for ^{17}O-nuclear shielding in benzophenone [11]. Clearly, this implies

TABLE 1

^{17}O- and ^{13}C NMR Data [a,b] of R_f- Carbonyl Compounds

Nr	Compound	$\delta^{17}O$	h1/2 Hz	Solvent/°C	$\delta^{13}C$ (C=O)	$J(^{19}F^{13}C)$ [Hz]	$\delta^{13}C$ [c] (other)	
1	 $C_6F_{13}-C(=O)H$	+633	230	$CDCl_3$/30	182.4 [d]	31.7	---	
		(+46)			(-18.9)			
2	 $C_6F_{13}-C(=O)Me$	+594	500	C_6D_6/30	190.9	26.6	24.1	
		(+31)			(-15.9)		(-5.3)	
3	 $C_6F_{13}-C(=O)Ph$	+585	>800	$CDCl_3$/30	183.4	26.0	131.8(i),	130.2(o)
		(+30)			(-16.5)		(-5.5)	(1.5)
							129.0(m),	135.4(p)
							(1.0)	(2.6)
4	 $C_2F_5-C(=O)CF(CF_3)_2$	+637	200	$CDCl_3$/30	180.7	29.0, 29.0	119.5($(CF_3)_2$),	118.3(CF_3)
		(+93)			(-32.3)		93.0(CF),	108.4(CF_2)
5	 $C_7F_{15}-C(=O)F$	+397	150	$CDCl_3$/50	148.9	375.7, 34.6	---	
		(+24)						
6	 $C_6F_{13}-C(=O)Cl$	+543	250	$CDCl_3$/50	162.9	36.6	---	
		(+48)			(- 8.4)			
7	 $C_6F_{13}-C(=O)OMe$	+362	450	$CDCl_3$/30	159.3	29.1	54.0	
		(+12)			(-12.9)			
		+131(OMe)	600					

8	 $C_6F_{13}-C(=O)OH$	+270 (+26)	>500	$CDCl_3$/40	164.0 (-16.6)	30.0	---
9	 $C_6F_{13}-C(=O)NHMe$	+314 (+ 6)	>800	$CDCl_3$/70	159.1 (-13[e])	25.8	26.1
10	 $C_6F_{13}-CH(Me)C(=O)H$	+605 (+21[e])	350	$CDCl_3$/30	194.0[f] (-10[e])	1.5	49.3(CH), 6.7(Me)
11	 $C_6F_{13}-CH_2C(=O)Cl$	+525 (+30)	500	$CDCl_3$/70	163.9 (- 7.4)	1.5	47.2 (+1.2)
12	 $C_6F_{13}-CH_2C(=O)Br$	+560 (+34)	>800	$CDCl_3$/70	157.6	1.5	52.2
13	 $C_6F_{13}-CH_2C(=O)OMe$	+355 (+ 5) +135(OMe)	400 400	$CDCl_3$/40	164.4 (- 7.8)	1.5	36.4(CH_2), 51.9(OMe)
14	 $C_6F_{13}-CH(Me)C(=O)OH$	+260 (+16)	>800	$CDCl_3$/70	174.9 (- 8[e])	1.5	43.0(CH), 10.3(Me)
15	 $C_6F_{13}-CH_2CH_2C(=O)H$	+590 (+ 3)	400	$CDCl_3$/50	198.1[g] (- 3.3)	1.5	34.7(CH_2), 23.7($\underline{C}H_2CF_2$) (-8.9) (+1.6)

Footnotes to Table 1

[a] In 10 mm (o.d.) tubes; ^{13}C NMR at 27 - 28°C; chemical shift differences with respect to the hydrocarbon analogues are given in parentheses.

[b] The accuracy of the δ^{17}O values depends on the line widths h1/2: $\pm$ 1 ppm (h1/2 $\leq$ 300 Hz), $\pm$ 3 ppm (h1/2 $\leq$ 600 Hz), $\pm$ 5 ppm (h1/2 $\leq$ 60 Hz).

[c] For typical $\delta^{13}C(R_f)$ values see Ref [2].

[d] $^{1}J(^{13}C^{1}H)$ = 200.3 Hz $\pm$ 1.

[e] Estimated values from data for closely related compounds.

[f] $^{1}J(^{13}C^{1}H)$ = 187.0 Hz $\pm$1.

[g] $^{1}J(^{13}C^{1}H)$ = 177.4 Hz $\pm$1.

that magnetic field (B_o) induced paramagnetic charge circulations involving the oxygen lone electron pair control a large part of the isotropic values δ^{13}C(C=O) and δ^{17}O(C=O). Although there is a parallel trend for δ^{13}C and δ^{17}O values in most carbonyl compounds, it is difficult to predict changes in the anisotropic shielding tensors. Therefore, the participation of the oxygen lone electron pair in the changes of δ^{13}C and δ^{17}O values is not obvious.

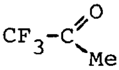
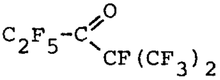
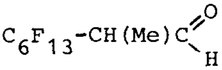
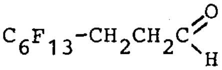
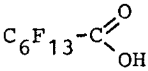
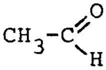
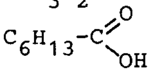
Considering solely the δ^{13}C and δ^{17}O values for the compounds 1-15 the changes in δ^{13}C and δ^{17}O values are similar to those for other carbonyl compounds [9,5], especially if we look at the δ^{13}C, δ^{17}O values for 2, 6, 7, 9 or for 10, 11, 13. However, it is unusual to find a marked shielding of the ^{13}C(C=O) nucleus and, at the same time, a considerable deshielding of the ^{17}O nucleus by introducing a new substituent, in our case by replacing R with R_f.

It has been shown that the isotropic nuclear shielding of $^{13}C(C=O)$ and $^{17}O(C=O)$ increases with gain in electronic charge on both nuclei (in contrast to $^{13}C(sp^3)$ and to two-cordinate oxygen) [12]. The discrepancy with the behaviour of $\delta^{13}C(sp^3)$ arises because of the inverse changes of σ- and π-electron densities in many π systems [12]. In the case of the polyfluorinated carbonyl compounds the R_f group is expected to reduce the electron population at the $^{13}C(C=O)$ nucleus, both by σ- and π effects. The importance of the σ effects for $\delta^{13}C$ has been noted [12], and the observed increase in nuclear shielding of $^{13}C(C=O)$ in 1-14 (with respect to the hydrocarbon analogues) is in accord with the analysis of the electron population in the C=O bond. In the absence of other influences a shielding effect of the R_f group on the $^{17}O(C=O)$ nucleus would also be expected. However, the σ effect of the R_f group may be offset by the possible interaction between the fluorine lone electron pairs and the antibonding C=O π^*orbital [13]. This may be particularly important for the $^{17}O(C=O)$ resonance since the σ effect of the R_f group will be somewhat attenuated by the intervening carbonyl carbon atom (e.g. in type A).

These qualitative arguments are corroborated by UV spectroscopic data (Table 2) of some polyfluorinated carbonyl compounds. The absorption band at longest wave length (small extinction), usually assigned to the $n\rightarrow\pi^*$ transition, is slightly shifted to longer wave lengths with respect to the hydrocarbon analogues, in agreement with other observations [14]. This proves the complex influence of the R_f group on the C=O bond. Clearly, there is considerable delocalization of the oxygen lone electron pair and a direct relationship between λ_{max} $(n\rightarrow\pi^*)$ and $\delta^{17}O$ would be fortuitous. On the other hand, the fairly small effect of the R_f group (with respect to R) on the UV absorption bands in the region between *ca.* 19o-3oo nm may be regarded as an

TABLE 2

UV Spectroscopic Data for some R_f Carbonyl Compounds [a]

Nr	Compound	$n\rightarrow\pi^*$ λ_{max} nm	condition, solvent
	$(CF_3)_2C=O$	308[b]	vapour
	 $CF_3-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow Me}$	288[b]	heptane
4	 $C_2F_5-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow CF(CF_3)_2}$	306.5	hexane
10	 $C_6F_{13}-CH(Me)C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow H}$	297	hexane
15	 $C_6F_{13}-CH_2CH_2C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow H}$	290.6	hexane
8	 $C_6F_{13}-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH}$	215[c]	hexane
	 $CH_3-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow H}$	290[b]	heptane
	$(CH_3)_2C=O$	279	
	 $C_6H_{13}-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH}$	204[c]	hexane

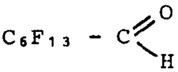
[a] Extinction $\varepsilon < 20$; absorption bands assigned to $\pi\rightarrow\pi^*$ transitions are observed at $\lambda_{max} = 219$ ($\varepsilon = 242$) (**10**) and at $\lambda_{max} < 200$ for the other compounds.

[b] Ref. [14].

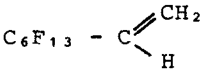
[c] The $n\rightarrow\pi^*$ absorption band is partially hidden by the long wave shoulder of the intense $\pi\rightarrow\pi^*$ absorption band.

indication for the proposed different influence of the R_f group on the σ- and π system of the C=O bond. Recent work (^{15}N, ^{17}O NMR) on N-sulphinyl-polyfluoroarylamines [15] has led to similar conclusions.

Finally, a comparison between $\delta^{13}C$ of alkenes and $\delta^{13}C$, $\delta^{17}O$ of carbonyl compounds should help to assess the influence of the oxygen lone electron pair on changes in $\delta^{17}O$. In principle the nuclear shielding of ^{17}O and ^{13}C should be related by the ratio of the radial expansion terms $\langle r^{-3}_{2p} \rangle$ for both nuclei, assuming the dominance of the local paramagnetic term, σ_p^{loc}, in Pople's approximation [16]. This will be the case if the shielding of both nuclei is controlled by the same effects. Then the ratio of $\Delta^{17}O/\Delta^{13}C$ should correspond to the ratio of $\langle r^{-3}_{2p} \rangle_O / \langle r^{-3}_{2p} \rangle_C$ which is in the order of 3 to 4 [17] :

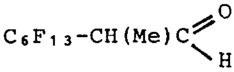


$C_6F_{13}-CHO$

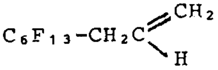


$C_6F_{13}-CH=CH_2$

$\Delta^{17}O = +46$	$\Delta^{17}O/\Delta^{13}C = 4.6$	$\Delta^{13}C(=CH_2) = +10.1$
$\Delta^{13}C = -18.9$		$\Delta^{13}C(=CH) = -13.6$
$\Delta^{17}O = +21$	$\Delta^{17}O/\Delta^{13}C = 3.1$	$\Delta^{13}C(=CH_2) = +6.9$
$\Delta^{13}C = -10.6$		$\Delta^{13}C(=CH) = -13.7$



$C_6F_{13}-CH(Me)CHO$



$C_6F_{13}-CH_2CH=CH_2$

The examples available show the parallel trend in the change of $\delta^{13}C$ and $\delta^{17}O$ in the carbonyl compounds and alkenes upon introduction of the R_f group. Furthermore, the ratio $\Delta^{17}O/\Delta^{13}C(=CH_2)$ is close to the ratio predicted by theory. That indicates a small influence of the oxygen lone electron pair on the changes in the ^{17}O-nuclear shielding induced by the R_f group.

EXPERIMENTAL

The NMR spectra (^{13}C, ^{17}O) have been recorded with a Bruker WP 200 spectrometer (see Table 1). ^{17}O NMR spectra of concentrated solutions (ca. 50-60 %) were obtained after 10^4 to 10^5 scans (acquisition time ca. 0.02 s, pulse angle ca. 70° = 35 μs). A fairly straight base line was observed when a pre-acquisition delay of 35 to 80 μs was used. The UV spectra have been measured with a Perkin-Elmer Lamda-5 spectrophotometer.

The aldehyde 1 has been obtained from perfluoroheptanyl chloride by Rosenmund reduction, followed by purification through a slot tube column. The ketones 2 and 3 have been prepared in moderate yields by slowly adding an ether solution of methyl- or phenyl magnesium bromide, respectively, to perfluoroheptanoyl chloride in ether at -20°C. The compounds 6, 7, 9, and 13 were prepared by standard procedures. Compound 12 has been obtained by photobromination of 2-perfluorohexyl-ethanol, similarly to the preparation of the corresponding acid chloride 11 (c.f. [18]). A hydroformylation reaction of 1.1.2-trihydro-1-perfluorooctene in benzene (catalyst: $[Rh(CO)H(PPh_3)_3]$; 2h, 80°C; $p(CO) = p(H_2)$ = 40 bar) yielded after distillation the aldehydes 14 (54%, b.p. 45-47°/13 mbar) and 15 (32%, b.p. 65-67°/15 mbar). The aldehyde 15 is the major product in the cobalt-catalyzed hydroformylation (c.f. [18]). The compounds 4, 5, and 11 have been prepared according to literature procedures[18]

ACKNOWLEDGMENT

We thank the Deutsche Forschungsgemeinschaft and the Fond der Chemischen Industrie for support of this work.

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