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^{13}C-NMR CHEMICAL SHIFTS OF DIFLUOROMETHYLENE GROUPS

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The carbon-13 chemical shifts are reported for difluoromethylene groups. These carbons resonate in a small range between 109 - 117 ppm. Triple resonance technique, ^{13}C-{^{1}H}{^{19}F} was used in the case of compounds including hydrogen and fluorine.

Carbon-13 NMR spectra of carbon compounds containing fluorines should give valuable structual informations. However, little work has been published on this subject[1-4]. ^{13}C-^{19}F couplings are relatively large ($J_{C-F} = 200 \sim 400$ Hz) and a range of fluorine chemical shifts is extremely wide (about 300 ppm) compared with that of ^{1}H chemical shifts. Briggs and Randall have reported ^{13}C chemical shifts of some phenyl derivatives[2], and Ovenall and Chang have studied chemical shifts of some perfluoro-compounds[3]. Although chemical shifts of trifluoromethyl groups was studied by DeMarco et al.[4], few ^{13}C chemical shifts of difluoromethylene groups ($-CF_2-$) have been reported.

We report the ^{13}C chemical shifts of difluoromethylene groups for several highly fluorinated compounds. Substituents and chemical shifts are given in Table 1. In the case of the substituent containing hydrogen ($X = H$, CF_2H), the spectrum is extremely complicated due to ^{13}C-^{1}H couplings as well as ^{13}C-^{19}F couplings. We could obtain simple spectra with triple resonance technique ^{13}C-{^{1}H}{^{19}F}, that is ^{1}H and ^{19}F simultanous decoupling[5].

From these results it is evident that the difluoromethylene carbons of several substituents resonate in surprisingly small ranges from 109 to 117 ppm. The range of chemical shifts for difluoromethylene carbons is within 9 ppm, and this range is outstandingly smaller than that of a similar series of methylene groups of hydrocarbons.

Table 1. Chemical Shifts of Difluoromethylene Groups
($X-\underline{CF_2}-CF_2-CF_2-$)

Substituents (X)	Chemical Shifts (δppm)[a]
CF_3	109.4[b]
C_nF_{2n+1} (n = 2)	111.8[b]
C_nF_{2n+1} (n ≧ 3)	112.2[b]
H	109.5[c]
CF_2H	112.8[c]
CO_2H	109.8[c]
CO_2CH_3	108.2[d]
$CH{=}CH_2$	114.4[d]
$N(n\text{-}C_4F_9)_2$	116.8[b]
CH_2OH	117.3[c]

a. from TMS, b. neat, c. solvent: acetone-d_6,
d. solvent: chloroform-d

References and Note

1) G. E. Howkes and R. J. Abraham, Org. Magn. Reson., 6, 552 (1974).

2) J. M. Briggs and E. W. Randall, J. Chem. Soc., Perkin Trans. 2, 1973, 1789.

3) D. W. Ovenall and J. J. Chang, J. Magn. Reson., 25, 361 (1977).

4) R. A. DeMarco, W. B. Fox, W. B. Moniz, and S. A. Sojka, J. Magn. Reson., 18, 552 (1975).

5) A JEOL FX-100 spectrometer equipped with multi-irradiation unit NM-IRR1, multi-irradiation power amplifier NM-IRR2, ^{19}F irradiation unit NM-3620G and 5mm probe NM-3800A was used. The practical noise ^{19}F decoupling range was about 7 kHz or 75 ppm at 93.7 MHz. Deuterio chloroform and Deuterio acetone served as both solvent and lock signal. In the case of undissolved samples, deuterium external lock was used. Internal tetramethylsilane was used as reference. Signal accumulation was 1000 times and spectra width was 4000 Hz or 5000 Hz at 25 MHz.

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