NMR Spectra of Some Fluorine Compounds

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The F^{19} nuclear magnetic resonance (NMR) spectra of 12 fluorocarbons and hydrofluorocarbons have been studied, and chemical shifts have been measured in relation to the inert solvent trichlorofluoromethane (Freon-11). CF_3, CF_2, and CF groups were found to give fluorine resonances which fall in distinct regions of the spectrum without overlap, indicating possible analytical value. The relative diamagnetic shielding of the various groups was found to increase the following order: CF_3 (branched) < CF_3 (terminal) < CF_2<CF. Terminal CF_2H groups showed, an F^{19} doublet of 52 c.p.s. separation in four different compounds. Some suggestions are made regarding possible solutions to particular fluorine spectra patterns.

THE PROTON resonance spectra of many hydrocarbons have been reported and chemical shifts have been measured in relation to various reference standards. This is not true for the F^{19} resonance spectra of the fluorocarbons, possibly because they are fewer in number and have been less available. In some instances, the F^{19} spectra of fluorocarbons are similar to the proton spectra of the corresponding hydrocarbons, except for the larger spin-spin couplings and chemical shifts in the former cases. Chemical shifts and spin-spin couplings tend to be greater by an order of magnitude in the case of the F^{19} spectra; hence interpretation is frequently simplified. Most NMR spectrometers capable of determining proton resonance spectra can be used for fluorine work by a slight increase in magnetic field.

In the course of some work on fluorine compounds, the NMR spectra of several fluorocarbons and hydrofluorocarbons were determined and approximate values of chemical shifts were measured and tabulated. Previous work on this type of compound includes Tiers (*5*), who noted the reasonable consistency of the position of the F^{19} resonances from CF_3 groups. Muller, Lauterbur, and Svatos (*3*) studied the effects of fluorine atoms on the diamagnetic shielding in such compounds as $(CF_3)_3CF$ and $(CF_3)_4C$. Feeney and Sutcliffe (*1*) studied in some detail the chemical shift of the fluorine atoms in perfluoromethylcyclohexane. Where this work overlaps the present work, suitable agreement is obtained. The present work includes a greater variety and number of fluorine compounds than previously reported. Certain generalizations with possible analytical value are drawn from the data reported here, and some suggestions are made regarding possible interpretations of the resolvable fine structure.

EXPERIMENTAL

Samples for experimentation were contained in borosilicate tubes, 4.95-mm. o.d. and 3-mm. i.d., by freezing the proper amount of material with liquid nitrogen and sealing off under vacuum. Many of the samples were purged for 5 minutes with a stream of dry nitrogen to exclude as much oxygen as possible, in order to improve resolution. Sources of the fluorochemicals are listed in Table I. These chemicals were examined by NMR without any special purification.

The NMR spectra were determined using a Varian Associates V-4300-B high resolution nuclear magnetic resonance spectrometer with superstabilizer Model V-K3506 and associated V-4012-A 12-inch electromagent system. The magnetic field used for the F^{19} measurements was approximately 10,000 gauss, corresponding to a precession frequency of 40 Mc. per second (proton spectra were measured with the same system using a field strength of approximately 9400 gauss). The sweep axis was calibrated by the audio side band technique using a Hewlett-Packard Model 200-D variable audio-oscillator. Spectra were recorded with a Varian Graphic Model G-10 recorder.

Most chemical shifts are reported in relation to the solvent, trichlorofluoromethane (Freon-11) obtained from Matheson, Coleman, and Bell; however, some are reported only in the pure state because of the limited amount available. The method of Tiers (*6*) was tried, in which a limiting chemical shift at zero concentration is obtained by extrapolating values obtained at several different concentrations in Freon-11. This method was somewhat limited because of the low signal strength of some F^{19} peaks and equipment instabilities. The chemical shifts reported here are average values obtained by using just enough CCl_3F to give a good reference signal.

RESULTS AND DISCUSSION

The fluorine NMR fast-scanned spectra at room temperature of the 12 compounds listed in Table I are summarized schematically in Figure 1. Each peak is shown in its proper position and proper height in relation to all other peaks in the figure. Chemical shifts accurate to ±1% are given in Table II, with the numbers for each compound corresponding to those in Figure 1. Chemical shifts are defined as

Table I. Fluorine Compounds

Name of Compound	Formula	Boiling Point, ° C.	Source
Perfluoroheptane	n-C_7F_{16}	82.4	Oak Ridge National Laboratories
Perfluorohexane (pure)	n-C_6F_{14}	56.5	R.D. Dunlap University of Maine
Perfluorohexane (impure)	n-C_6F_{14}	. . .	Minnesota Mining and Mfg. Co.
Perfluoro(2-methylpentane)	*Iso*-C_6F_{14}	57.7	G. Cady, Univ. of Washington
1-Hydropentadecafluoroheptane	n-$C_7F_{15}H$	94.1	Matheson, Coleman and Bell
1,4-Dihydro-octafluorobutane	$H(CF_2)_4H$	42.0	Du Pont, Jackson Laboratory
Perfluoromethylcyclohexane	$CF_3C_6F_{11}$	76.3	Du Pont, Jackson Laboratory
Perfluorodimethylcyclohexane	$(CF_3)_2C_6F_{10}$	101–02.6	Du Pont, Jackson Laboratory
1,5,5-Trihydro-octafluoropentanol	$H(CF_2)_4CH_2OH$	142.0	Du Pont, Jackson Laboratory
1,3,3-Trihydrotetrafluoroproponal	$H(CF_2)_2CH_2OH$	108.5	Du Pont, Jackson Laboratory
Tri-*n*-perfluorobutylamine (N-43)	$(C_4F_9)_3N$	179.1	Minnesota Mining and Mfg. Co.
f-*α*-*n*-Propyltetrahydropyran (0-75)	$(C_8F_{16}O)$ isomers	99–107	Minnesota Mining and Mfg. Co.

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$$\text{Chemical shift (p.p.m.)} = \frac{[H_{\text{obsd.}} - H_{\text{CCl}_3\text{F}}] \times 10^6}{H_{\text{CCl}_3\text{F}}}$$

where

$H_{\text{obsd.}}$ = field at which resonance occurs for peak in question.

and

$H_{\text{CCl}_3\text{F}}$ = field at which resonance occurs for reference, CCl_3F.

The F^{19} resonances from the various perfluoro groups—i.e., CF_3, CF_2, and CF—fall into distinct regions of the spectrum. There is no overlap of the group regions for the relatively small number of compounds studied here. These results have been summarized in Table III, which shows the ranges of chemical shifts for the F^{19} resonances in relation to trichlorofluoromethane. This result could be of analytical value for a fast determination of the type of fluorine groups present in an unknown fluorine compound.

The relative diamagnetic shielding of the fluoro groups increases in the following order: $CF_3 < CF_2 < CF$. Branched CF_3 groups fall at even lower fields than terminal CF_3 groups, indicating less shielding in the former case. The CF_3 groups attached to the perfluorocyclohexane rings show even further decreases in shielding. The perfluoromethylcyclohexane compound has been studied by Feeney and Sutcliffe (*1*), who find essentially the same results reported here. The perfluoromethyl group in this compound is in an equatorial position and remains relatively unshielded.

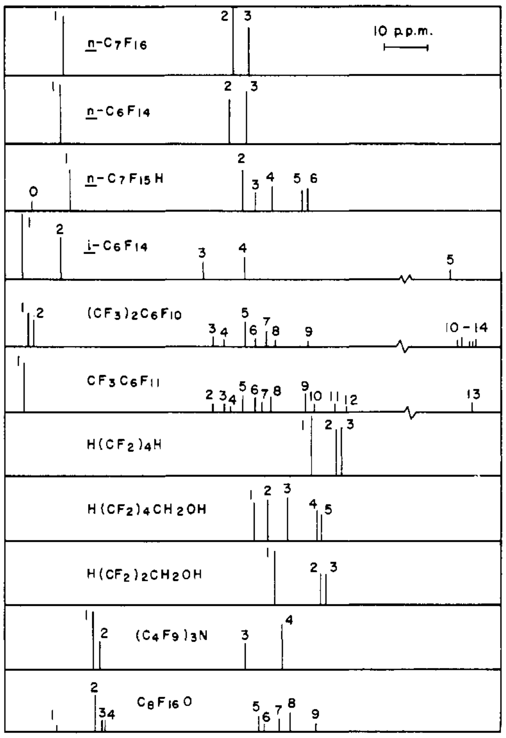

Figure 1. Relative intensities and positions for F^{19} NMR peaks in fluorine compounds

Table II. Chemical Shifts for F^{19} Resonances of Fluorocarbons

Compound	Peak No.	Reference	Chem. Shift, P.P.M.
n-C_7F_{16}	1	CCl_3F	82.9
	2	CCl_3F	125.3
	3	CCl_3F	128.9
n-C_6F_{14}	1	CCl_3F	82.8
	2	CCl_3F	125.7
	3	CCl_3F	129.3
Iso-C_6F_{14}	1	CCl_3F	71.4
	2	CCl_3F	80.3
	3	CCl_3F	114.2
	4	CCl_3F	123.9
	5	CCl_3F	184.4
n-$C_7F_{15}H$	0	CCl_3F	73.3
	1	CCl_3F	83.1
	2	CCl_3F	125.8
	3	CCl_3F	128.8
	4	CCl_3F	132.0
	5	CCl_3F	139.3
	6	CCl_3F	140.6
$(CF_3)_2C_6F_{10}$	0	Peak 1	−4.94
	1	Peak 1	0.00[a]
	2	Peak 1	1.13
	3	Peak 1	44.5
	4	Peak 1	46.4
	5	Peak 1	51.6
	6	Peak 1	54.0
	7	Peak 1	56.6
	8	Peak 1	59.0
	9	Peak 1	67.1
	10	Peak 1	114.0
	11	Peak 1	115.1
	12	Peak 1	116.3
	13	Peak 1	117.2
	14	Peak 1	118.5
$CF_3C_6F_{11}$	1	CCl_3F	71.0
	2	CCl_3F	116.7
$CF_3C_6F_{11}$	3	CCl_3F	120.2
	4	CCl_3F	121.6
	5	CCl_3F	124.3
	6	CCl_3F	127.2
	7	CCl_3F	128.7
	8	CCl_3F	130.9
	9	CCl_3F	139.0
	10	CCl_3F	141.1
	11	CCl_3F	146.0
	12	CCl_3F	148.4
	13	CCl_3F	189.8
$C_4F_8H_2$	1	CCl_3F	139.4
	2	CCl_3F	145.4
	3	CCl_3F	146.7
$H(CF_2)_4CH_2OH$	1	CCl_3F	125.2
	2	CCl_3F	128.1
	3	CCl_3F	132.9
	4	CCl_3F	139.5
	5	CCl_3F	140.8
$H(CF_2)_2CH_2OH$	1	CCl_3F	129.8
	2	CCl_3F	140.7
	3	CCl_3F	142.0
$(C_4F_9)_3N$	1	Peak 1	0.0[b]
	2	Peak 1	1.78
	3	Peak 1	38.2
	4	Peak 1	46.9
$C_8F_{16}O$	1	Peak 1	0.0[c]
	2	Peak 1	8.9
	3	Peak 1	11.1
	4	Peak 1	11.7
	5	Peak 1	48.5
	6	Peak 1	50.0
	7	Peak 1	53.0
	8	Peak 1	55.7
	9	Peak 1	61.8

[a] Ca. + 72 p.p.m. relative to CCl_3F. [b] Ca. 87 p.p.m. relative to CCl_3F. [c] Ca. 88 p.p.m. relative to CCl_3F.

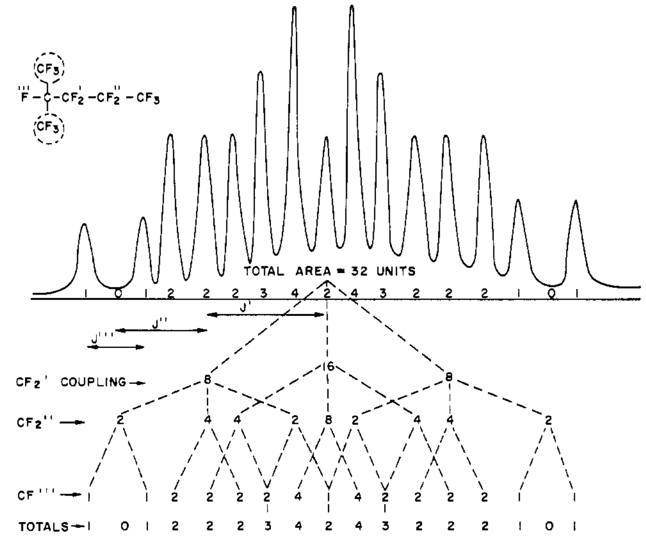

Figure 2. Perfluoro(2-methylpentane)
Detailed F^{19} NMR spectrum of branched perfluoromethyl groups

Another feature relating to the hydrofluorocarbon compounds appears to be of potential analytical value. A terminal proton attached to two or more CF_2 groups gives a doublet in the F^{19} spectra of approximately 52-cycle separation. This also shows up in the proton spectra as a triplet with the same coupling constant. Four compounds exhibit this feature in the present work—namely, n-$C_7F_{15}H$, $C_4F_8H_2$, $H(CF_2)_4CH_2OH$, and $H(CF_2)_2CH_2OH$. Substitution of a proton in a CF_3 group results in a shift to high field of the resulting terminal CF_2 fluorine resonances (*3*). In all cases where the F^{19} doublet appears, it is at highest field in relation to the other CF_2 group resonances within the molecule.

PERFLUORO(2-METHYLPENTANE)

The F^{19} NMR spectrum of perfluoro(2-methylpentane) shows five main peaks, corresponding to five different types of fluorine in the compound. The largest peak is at lowest field and represents the branched CF_3 groups. Under high resolution, this peak shows a peculiar 15-line pattern as indicated in Figure 2. A possible solution to this particular pattern is also indicated in this figure. There is a strong spin-spin coupling (11.6 c./s.) of the branched CF_3 fluorines with one of the CF_2 groups, producing a triplet, and a weaker coupling (8.7 c./s.) with the other CF_2 group. Finally there is a still weaker coupling (5.8 c./s.) with the single tertiary fluorine atom. This analysis reproduces the measured spectrum as shown in the bottom part of Figure 2. This analysis requires the respective coupling constants, J', J'', and J''', to have the ratios, 4:3:2, which is unlikely on a probability basis. Additionally, it requires that fluorine nuclei separated by five chemical bonds have larger spin-spin coupling constants than those separated by three chemical bonds. This feature was first found by Gutowsky and Saika (*2*) in the molecule $(CF_3)_2NCF_2CF_3$. Later Petrakis and Sederholm (*4*) found this long-range coupling to be a common feature of many saturated organic fluorine compounds and suggested that the proper explanation of its cause concerns itself with direct-through-space coupling rather than through-the-bonds coupling. Such a phenomenon would seldom, if ever, be of importance for proton-proton couplings, but may well provide the answer in the case of some F-F or H-F couplings.

Table III. Ranges of Chemical Shifts for F^{19} NMR Spectra of Fluorocarbon Groups

Group	Chemical Shift,[a] P.P.M.
CF_3	73–93
CF_2	116–151
CF	118–194.5

[a] Reference, trichlorofluoromethane.

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