Journal of Fluorine Chemistry, 60 (1993) 103–108

Fluorine nuclear magnetic resonance parameters for hydrochlorofluoropropanes with one terminal hydrogen atom and all possible combinations of fluorine and chlorine atoms in the other positions

F. J. Weigert

Central Research and Development Department, EI Du Pont de Nemours & Co., Wilmington, DE 19880-0328 (USA)

(Received November 23, 1991; accepted March 23, 1992)

Abstract

This paper presents the ^{19}F nuclear magnetic resonance chemical shifts and coupling constants for all saturated compounds with three carbon atoms at least one fluorine atom, one terminal hydrogen atom and all possible combinations of fluorine and chlorine atoms in the remaining six positions.

Introduction

Chlorofluorocarbons (CFCs) have been technologically important compounds for the past 50 years [1]. Their use is being phased out worldwide because they are implicated in stratospheric ozone destruction. Perfluorocarbons (FCs) are unlikely replacements because they have long atmospheric lifetimes and are greenhouse gases. One strategically placed hydrogen can reduce the atmospheric lifetime, making hydrochlorofluorocarbons (HCFCs) more environmentally acceptable materials than CFCs. Hydrofluorocarbons (HFCs) have zero ozone depletion potential because they contain no chlorine. They are, however, greenhouse gases.

A high hydrogen-to-halogen ratio makes HCFCs flammable. While this also means a short atmospheric life, it is an undesirable property in products intended for home use. Fluorine is expensive, and minimizing the amount of this element in the products is desirable. After exhaustively examining two-carbon alternatives, the industry is looking at longer chains for the desired combination of physical and chemical properties, cost and toxicity.

During our work, all saturated HCFCs with three carbon atoms and one terminal hydrogen atom have crossed our path. Gas chromatography (GC) and GC–mass spectroscopy are the primary analytical tools in the volatile fluorocarbon field. GC is superb at distinguishing between compounds with different boiling points and molecular weights, but sometimes does not separate isomeric pairs. Mass spectral isomer assignments may be ambiguous. Here, ^{19}F nuclear magnetic resonance (NMR) emerges as the tool of choice.

0022-1139/93/$6.00

Databases of fluorine NMR parameters are useful tools in the analysis of complex mixtures. With their information we can complete both qualitative and quantitative analyses down to the 0.1% level. Previous work described several such databases. These include fluorine chemical shifts of FCs [2], a complete tabulation of all two-carbon CFCs, HCFCs and HFCs [3] and a nearly complete tabulation of the ^{19}F NMR parameters of saturated three-carbon CFCs [4]. We present here the ^{19}F NMR chemical shifts and coupling constants for all compounds with three carbon atoms, at least one fluorine atom, one terminal hydrogen atom, and all possible combinations of fluorine and chlorine atoms in the remaining six positions (F-22x).

Results

Compound enumeration

Table 1 lists the compounds which fall within the scope of this paper in the order of the number of fluorine atoms. Also included are the number of unique fluorine chemical shifts expected for these compounds and the structure of the individual isomers. These are identified with a three-number designator for the number of fluorine atoms on each of the three carbon atoms. The carbon atom with the hydrogen atom is on the right. There are four pairs of diastereomers: $CF_3CFClCFHCl$, $CF_2ClCFClCFHCl$, $CFCl_2CFClCFHCl$ and $CCl_3CFClCFHCl$. These result from two asymmetric centers –CFCl– and –CFHCl and the four possible combinations of fluorine and chlorine on the other terminal carbon atom. The present NMR information is not sufficient to assign stereochemistry unambiguously.

Table 2 lists each magnetically unique fluorine atom in this data set. They are sorted by the number of fluorine atoms in each of the compounds. Also presented are fluorine–fluorine and fluorine–proton coupling constants, if any. The shifts are in parts per million upfield from $CFCl_3$. The multiplicities are indicated by a number: a doublet is 2, a triplet 3 etc. Coupling constants

TABLE 1

^{19}F nuclear magnetic resonance parameters for F-22x

Number of fluorine atoms	Number of isomers	Number of resonances	Formulae
1	3	3	100, 010, 001
2	7	11	200, 020, 002, 110, 101, 011
3	9	23	300, 210, 201, 120, 102, 012, 021, 111
4	9	26	310, 301, 220, 202, 022, 121, 112, 211
5	7	23	320, 302, 221, 212, 122, 311
6	3	11	321, 212, 222
7	1	3	322
	39	100	

TABLE 2

^{19}F nuclear magnetic resonance parameters for F-22x

Name	Shift	Splittings, couplings
$\mathrm{CCl_3CCl_2C\mathit{F}HCl}$	126.6	2, 49.6
$\mathrm{CCl_3C\mathit{F}ClCHCl_2}$	100.2	2, 2.0
$\mathrm{C\mathit{F}Cl_2CCl_2CHCl_2}$	53.8	0
$\mathrm{CCl_3C\mathit{F}ClCFHCl}$	121.9	2, 17.4 2, 9.4
$\mathrm{CCl_3CFClC\mathit{F}HCl}$	137.2	2, 48.4 2, 17.4
$\mathrm{CCl_3CFClC\mathit{F}HCl}$	135.6	2, 48.4 2, 22.1
$\mathrm{CCl_3C\mathit{F}ClCFHCl}$	109.5	2, 22.1
$\mathrm{C\mathit{F}_2ClCCl_2CHCl_2}$	55.9	0
$\mathrm{CCl_3CCl_2C\mathit{F}_2H}$	117.2	2, 55.3
$\mathrm{C\mathit{F}Cl_2CCl_2CFHCl}$	57.8	2, 25.0
$\mathrm{CFCl_2CCl_2C\mathit{F}HCl}$	131.7	2, 48.7 2, 25.0
$\mathrm{C\mathit{F}Cl_2CFClCHCl_2}$	60.0	2, 10.0
$\mathrm{CFCl_2C\mathit{F}ClCHCl_2}$	108.5	2, 11.7 2, 2.1
$\mathrm{CCl_3C\mathit{F}_2CHCl_2}$	106.5	2, 9.2
$\mathrm{CF_2ClCCl_2C\mathit{F}HCl}$	133.9	2, 48.7 2, 14.1 2, 16.6
$\mathrm{C\mathit{F}_2ClCCl_2CFHCl}$	58.6	2, 163.0 2, 14.0
$\mathrm{C\mathit{F}_2ClCCl_2CFHCl}$	59.7	2, 163.0 2, 17.0
$\mathrm{C\mathit{F}_2ClCFClCHCl_2}$	61.7	2, 170.0 2, 7.0
$\mathrm{C\mathit{F}_2ClCFClCHCl_2}$	60.8	2, 170.0 2, 8.0
$\mathrm{CF_2ClC\mathit{F}ClCHCl_2}$	114.9	2, 7.0 2, 8.0 2, 4.0
$\mathrm{CCl_3CFClC\mathit{F}_2H}$	127.3	2, 295.0 2, 55.0 2, 14.0
$\mathrm{CCl_3CFClC\mathit{F}_2H}$	121.3	2, 295.0 2, 55.0 2, 7.0
$\mathrm{CCl_3C\mathit{F}ClCF_2H}$	121.7	2, 7.0 2, 14.0 2, 2.0
$\mathrm{C\mathit{F}_3CCl_2CHCl_2}$	73.1	0
$\mathrm{CFCl_2CCl_2C\mathit{F}_2H}$	120.7	2, 54.5 2, 13.0
$\mathrm{C\mathit{F}Cl_2CCl_2CF_2H}$	60.4	3, 3.0
$\mathrm{C\mathit{F}Cl_2CF_2CCl_2H}$	68.0	3, 7.4
$\mathrm{CFCl_2C\mathit{F}_2CCl_2H}$	113.8	2, 7.4 2, 9.0
$\mathrm{C\mathit{F}Cl_2CFClCFHCl}$	65.3	2, 16.3 2, 16.5
$\mathrm{CFCl_2C\mathit{F}ClCFHCl}$	118.2	2, 16.3 2, 24.0 2, 6.6
$\mathrm{CFCl_2CFClC\mathit{F}HCl}$	142.1	2, 48.6 2, 19.0 2, 19.0
$\mathrm{CFCl_2C\mathit{F}ClCFHCl}$	127.2	2, 15.2 2, 19.0 2, 10.1
$\mathrm{C\mathit{F}Cl_2CFClCFHCl}$	63.5	2, 15.2 2, 19.0
$\mathrm{CFCl_2CFClC\mathit{F}HCl}$	141.5	2, 48.5 2, 24.0 2, 16.5
$\mathrm{CCl_3C\mathit{F}_2CFHCl}$	123.6	2, 251.0 2, 11.0 2, 0.8
$\mathrm{CCl_3CF_2C\mathit{F}HCl}$	147.0	2, 47.0 2, 11.0 2, 15.0
$\mathrm{CCl_3C\mathit{F}_2CFHCl}$	107.0	2, 251.0 2, 13.5 2, 15.0
$\mathrm{C\mathit{F}_2ClCCl_2CF_2H}$	61.1	3, 9.5
$\mathrm{CF_2ClCCl_2C\mathit{F}_2H}$	123.0	2, 54.3 3, 9.5
$\mathrm{C\mathit{F}_2ClCF_2CHCl_2}$	65.8	3, 2.0
$\mathrm{CF_2ClC\mathit{F}_2CHCl_2}$	115.9	3, 2.0 2, 9.0
$\mathrm{CF_2ClCFClC\mathit{F}HCl}$	144.2	2, 48.4 3, 12.3 2, 24.6
$\mathrm{C\mathit{F}_2ClCFClCFHCl}$	63.7	2, 171.5 2, 12.0 2, 10.0
$\mathrm{CF_2ClCFClC\mathit{F}HCl}$	144.7	2, 48.4 3, 12.1 2, 19.1
$\mathrm{CF_2ClC\mathit{F}ClCFHCl}$	132.5	2, 19.0 3, 9.8 2, 9.0
$\mathrm{C\mathit{F}_2ClCFClCFHCl}$	63.9	2, 173.6 2, 12.0 2, 10.0
$\mathrm{CF_2ClC\mathit{F}ClCFHCl}$	125.0	2, 24.6 3, 10.3 2, 0.8
$\mathrm{C\mathit{F}_2ClCFClCFHCl}$	64.0	2, 171.5 2, 10.0 2, 12.0
$\mathrm{C\mathit{F}_2ClCFClCFHCl}$	64.0	2, 173.6 2, 12.0 2, 10.0

(*continued*)

TABLE 2 (*continued*)

Name	Shift	Splittings, couplings
$\mathrm{C}\mathit{F}_3\mathrm{CCl_2CFHCl}$	75.2	2, 12.0
$\mathrm{CF_3CCl_2C}\mathit{F}\mathrm{HCl}$	135.3	2, 49.0 4, 12.0
$\mathrm{CF_3C}\mathit{F}\mathrm{ClCHCl_2}$	122.3	4, 5.0 2, 5.0
$\mathrm{C}\mathit{F}_3\mathrm{CFClCHCl_2}$	80.5	2, 5.0
$\mathrm{CFCl_2CF_2C}\mathit{F}\mathrm{HCl}$	150.4	2, 48.0 2, 14.0 2, 13.0 2, 16.0
$\mathrm{CFCl_2C}\mathit{F}_2\mathrm{CFHCl}$	124.6	2, 263.0 2, 10.0 2, 14.0
$\mathrm{CFCl_2C}\mathit{F}_2\mathrm{CFHCl}$	112.5	2, 263.0 2, 8.0 2, 13.0
$\mathrm{C}\mathit{F}\mathrm{Cl_2CF_2CFHCl}$	70.9	2, 16.0 2, 8.0 2, 10.0
$\mathrm{C}\mathit{F}\mathrm{Cl_2CFClCF_2H}$	64.1	2, 10.0 2, 10.0 2, 16.0
$\mathrm{CFCl_2CFClC}\mathit{F}_2\mathrm{H}$	126.0	2, 297.0 2, 54.0 2, 10.0 2, 10.0
$\mathrm{CFCl_2C}\mathit{F}\mathrm{ClCF_2H}$	129.6	2, 11.0 2, 14.0 2, 14.0
$\mathrm{CFCl_2CFClC}\mathit{F}_2\mathrm{H}$	129.2	2, 297.0 2, 54.0 2, 9.0 2, 14.0
$\mathrm{CCl_3C}\mathit{F}_2\mathrm{CHF_2}$	120.0	3, 7.0 2, 7.0
$\mathrm{CCl_3CF_2C}\mathit{F}_2\mathrm{H}$	131.8	2, 52.0 3, 7.0
$\mathrm{C}\mathit{F}_2\mathrm{ClCF_2CFHCl}$[a]	69.0	1, 13.0 2, 3.0
$\mathrm{CF_2ClC}\mathit{F}_2\mathrm{CFHCl}$	128.7	2, 273.0 3, 2.0 2, 13.0
$\mathrm{CF_2ClC}\mathit{F}_2\mathrm{CFHCl}$	118.0	2, 273.0 3, 2.0 2, 15.0 2, 13.0
$\mathrm{CF_2ClCF_2C}\mathit{F}\mathrm{HCl}$	153.6	2, 47.0 2, 15.0 2, 13.0 3, 13.0
$\mathrm{CF_2ClC}\mathit{F}\mathrm{ClCF_2H}$	136.0	2, 3.4 2, 10.7 2, 10.5 2, 14.0 2, 13.7
$\mathrm{CF_2ClCFClC}\mathit{F}_2\mathrm{H}$	128.3	2, 298.5 2, 53.2 2, 10.0 2, 10.0 2, 10.0
$\mathrm{CF_2ClCFClC}\mathit{F}_2\mathrm{H}$	131.3	2, 298.5 2, 53.7 2, 14.0 2, 7.0 2, 7.0
$\mathrm{C}\mathit{F}_2\mathrm{ClCFClCF_2H}$	65.9	2, 174.1 2, 10.0 2, 9.0 2, 7.0
$\mathrm{C}\mathit{F}_2\mathrm{ClCFClCF_2H}$	65.5	2, 174.1 2, 10.0 2, 9.0 2, 7.0
$\mathrm{CFCl_2CF_2C}\mathit{F}_2\mathrm{H}$	134.9	2, 52.0 2, 10.0 3, 7.0
$\mathrm{C}\mathit{F}\mathrm{Cl_2CF_2CF_2H}$	73.4	4, 8.0
$\mathrm{CFCl_2C}\mathit{F}_2\mathrm{CF_2H}$	124.7	2, 7.0 4, 8.0
$\mathrm{C}\mathit{F}_3\mathrm{CCl_2CF_2H}$	76.2	3, 8.0
$\mathrm{CF_3CCl_2C}\mathit{F}_2\mathrm{H}$	124.5	2, 54.0 4, 8.0
$\mathrm{C}\mathit{F}_3\mathrm{CF_2CCl_2H}$	80.0	0
$\mathrm{CF_3C}\mathit{F}_2\mathrm{CCl_2H}$	121.1	2, 9.0
$\mathrm{C}\mathit{F}_3\mathrm{CFClCFHCl}$	79.2	2, 7.1 2, 9.3
$\mathrm{CF_3C}\mathit{F}\mathrm{ClCFHCl}$	138.7	4, 5.6 2, 19.3 2, 11.0
$\mathrm{CF_3CFClC}\mathit{F}\mathrm{HCl}$	145.7	2, 48.0 2, 24.4 4, 9.5
$\mathrm{CF_3C}\mathit{F}\mathrm{ClCFHCl}$	132.5	2, 20.0 2, 24.4 4, 7.1
$\mathrm{C}\mathit{F}_3\mathrm{CFClCFHCl}$	78.2	2, 5.6 2, 10.1
$\mathrm{CF_3CFClC}\mathit{F}\mathrm{HCl}$	146.0	2, 48.0 4, 10.1 2, 19.3
$\mathrm{C}\mathit{F}_2\mathrm{ClCF_2CF_2H}$	70.4	3, 4.0 3, 7.8
$\mathrm{CF_2ClC}\mathit{F}_2\mathrm{CF_2H}$	128.8	3, 4.0 3, 6.7 2, 5.0
$\mathrm{CF_2ClCF_2C}\mathit{F}_2\mathrm{H}$	136.8	2, 52.0 3, 6.7 3, 7.8
$\mathrm{CF_3CF_2C}\mathit{F}\mathrm{HCl}$	155.3	2, 47.4 2, 15.0 2, 13.0 4, 9.2
$\mathrm{C}\mathit{F}_3\mathrm{CF_2CFHCl}$	82.0	2, 9.0
$\mathrm{CF_3C}\mathit{F}_2\mathrm{CFHCl}$	124.0	2, 280.0 2, 13.0
$\mathrm{CF_3C}\mathit{F}_2\mathrm{CFHCl}$	132.0	3, 280.0 2, 15.0
$\mathrm{C}\mathit{F}_3\mathrm{CFClCF_2H}$	79.5	4, 8.0
$\mathrm{CF_3C}\mathit{F}\mathrm{ClCF_2H}$	143.2	4, 8.0 2, 16.0 2, 12.0 2, 9.0
$\mathrm{CF_3CFClC}\mathit{F}_2\mathrm{H}$	130.0	2, 300.0 2, 53.0 4, 8.0 2, 12.0
$\mathrm{CF_3CFClC}\mathit{F}_2\mathrm{H}$	132.6	2, 300.0 2, 53.0 2, 16.0 4, 8.0
$\mathrm{C}\mathit{F}_3\mathrm{CF_2CF_2H}$	82.7	3, 7.2
$\mathrm{CF_3C}\mathit{F}_2\mathrm{CF_2H}$	133.0	2, 4.5 3, 4.5
$\mathrm{CF_3CF_2C}\mathit{F}_2\mathrm{H}$	137.9	2, 52.2 3, 4.5 4, 7.2

---

[a] The expected AB pattern is not resolved even at 467 MHz.

are obtained by first-order analyses. The uncertainties from digital resolution alone are ±1.0 Hz.

Chemistry

Most of the compounds in this set have been prepared previously. Our major current interest is in the HCFC-225s as possible replacements for CFC-113. The two easiest isomers to prepare are $\mathrm{CF_2ClCF_2CFHCl}$ and $\mathrm{CF_3CF_2CHCl_2}$, both of which are products of the Lewis-acid-catalyzed addition of $\mathrm{CFHCl_2}$ to $\mathrm{CF_2{=}CF_2}$ [5, 6]. We recently reported another HCFC-225 isomer $\mathrm{CF_3CCl_2CF_2H}$, formed from the Lewis-acid-catalyzed isomerization of the initially formed isomers [7]. None of the several GC columns in common use in our laboratory separated all the HCFC-225 isomers commonly present in this reaction. Only $^{19}\mathrm{F}$ NMR gave us the true picture of the isomer distribution.

There are two HCFC-225s in which all five of the fluorine atoms are chemically distinct: $\mathrm{CF_2ClCFClCF_2H}$ and $\mathrm{CF_2ClCF_2CFHCl}$. The NMR properties result from two $\mathrm{CF_2}$ groups and an asymmetric carbon atom with one fluorine atom. There is a pair of HCFC-225 diastereomers $\mathrm{CF_3CFClCFHCl}$. At equilibrium, only the four compounds with $\mathrm{CF_3}$ groups are present at levels above 1%.

^{19}F nuclear magnetic resonance correlations

F–H coupling

Two-bond F–H coupling is generally around 50 Hz. In this set of compounds the coupling in $\mathrm{-CF_2H}$ is 53.6 ± 1.1 ($n = 16$). The coupling in $\mathrm{-CFHCl}$ is 48.3 ± 0.7 ($n = 16$).

F–F coupling

Two-bond F–F coupling is much larger. The coupling in $\mathrm{-CF_2H}$ is 297.6 ± 2.1 ($n = 4$). The coupling in $\mathrm{-CF_2Cl}$ is 170.4 ± 4.5 ($n = 5$; not measurable in $\mathrm{C}F_2\mathrm{ClCF_2CFHCl}$). The coupling in $\mathrm{-CF_2-}$ on a central carbon is 266.8 ± 12.6 ($n = 4$).

Fluorine chemical shifts

Table 3 shows the mean and standard deviation of the chemical shifts of each fluorine-containing functional group. This mean chemical shift between $\mathrm{C}F\mathrm{HCl}$ and $\mathrm{C}F_2\mathrm{H}$ differs by just one standard deviation. Proton–fluorine coupling is a more reliable indicator of structure. Likewise, the shift difference between $\mathrm{C}F_2$ and $\mathrm{C}F\mathrm{Cl}$ is not large enough to distinguish them from each other or from $\mathrm{C}F_2\mathrm{H}$. While $\mathrm{C}F_3$ is at a higher field than $\mathrm{C}F_2\mathrm{Cl}$ and $\mathrm{C}F\mathrm{Cl_2}$, the latter two cannot be distinguished from each other by shift alone. The relatively large standard deviations of the shifts suggest that β and perhaps γ substituent effects are also important.

There are many other three-carbon molecules with only chlorine, fluorine and hydrogen substituents. Our ultimate goal is to assemble a complete catalog of their fluorine NMR parameters. We defer further analyses until a more complete data set can be assembled.

TABLE 3

^{19}F chemical shift summary of F-22x

Functional group	Mean shift	Standard deviation
$-CFHCl$	141.9	±8.0
$-CF_2H$	128.3	±6.0
$-CFCl-$	123.9	±11.7
$-CF_2-$	120.9	±8.1
$-CF_3$	75.5	±5.4
$-CFCl_2$	63.1	±6.0
$-CF_2Cl$	61.2	±4.3

General remarks

^{19}F NMR spectra in $CDCl_3$ were recorded on a Nicolet NT-220 spectrometer at 188.2 MHz and 23 °C. Trichlorofluoromethane was used as an internal standard. Many compounds were measured only as minor components in mixtures prepared for other purposes. Concentrations of the major components were generally under 10%; minor components were essentially at infinite dilution.

Acknowledgments

I thank all my colleagues who provided the pure samples and synthetic mixtures from which the NMR parameters were extracted. I thank Keith Raffell for obtaining the ^{19}F NMR results.

References

1 L. E. Manzer, *Science, 249* (1990) 31.
2 F. J. Weigert and K. J. Karel, *J. Fluorine Chem., 37* (1987) 125.
3 F. J. Weigert, *J. Fluorine Chem., 46* (1990) 375.
4 J. Kvicala, O. Paleta and V. Dedek, *J. Fluorine Chem., 43* (1989) 155.
5 O. Paleta, A. Posta and K. Tesarik, *Collect. Czech. Chem. Commun., 36* (1971) 1867; R. M. Joyce, *US Pat. 2,462,402,* 1949; D. D. Coffman, R. Cramer and G. W. Rigby, *J. Am. Chem. Soc., 71* (1949) 979.
6 H. Aoyama, T. Yasuhara, S. Kono and S. Koyama, *Eur. Pat. Appl. EP 421,322, 1991; Chem. Abstr., 115* (1991) 70901; S. Morikawa, S. Samejima, K. Ohnishi, H. Okamoto, T. Ohmori and T. Tanuma, *PCT Int. Appl. WO 91 01, 287,* 1991. *Chem. Abstr., 115* (1991) 8074; S. Morikawa, S. Samejima, M. Yoshitake, S. Tatematsu and T. Tanuma, *Jpn. Kokai Tokkyo Koho JP 02 17,133,* 1990; *Chem. Abstr., 113* (1990) 5703; S. Morikawa, S. Samejima, M. Yoshitake, S. Tatematsu and T. Tanuma, *Jpn. Kokai Tokkyo Koho JP 02 17,134,* 1990; *Chem. Abstr., 113* (1990) 5704.
7 C. G. Krespan, A. C. Sievert and F. J. Weigert, *PCT Int. Appl. WO 91 05,753,* 1991; *Chem. Abstr., 115* (1991) 70904.