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FLUORINE NMR PARAMETERS OF TWO-CARBON CHLOROFLUOROHYDROCARBONS

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SUMMARY

A complete database of fluorine nmr parameters for compounds with two carbons and all possible combinations of fluorine, chlorine, and hydrogen substituents now exists. These include the saturated compounds from CH_3CH_2F to CF_3CF_3 and olefins from $CH_2=CHF$ to $CF_2=CF_2$.

The chemical shifts cannot all be explained in terms of simple additive substituent effects. With this database as a guide, nmr analysis of mixtures can be made down to the 0.1% level.

INTRODUCTION

Fluorine-19 nmr is a powerful analytical tool to aid in the elucidation of the structure of fluorine containing molecules. It can also be used as both a qualitative and quantitative analysis of complex mixtures if the spectra of the individual components can be established.

There is renewed interest worldwide in the synthesis of two-carbon chlorofluorohydrocarbons as replacements for the fully halogenated one-carbon molecules $CFCl_3$ and CF_2Cl_2. Carefully chosen two-carbon compounds may provide the necessary physical and chemical properties to function in the applications now dominated by one-carbon, fully halogenated species. Non-chlorinated compounds would not affect the earth's ozone layer. Hydrogen containing compounds which still contain chlorine would have a less deleterious effect than fully halogenated compounds.

Novel catalytic reactions produce new by-product distributions. The necessity of recycling in some process designs makes identification of by-products essential. The toxicological properties of 99% pure materials may differ if some impurities are more toxic than the major product.

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The primary analytical tools in our synthetic effort are GC and GC/MS. Distinguishing isomers is not always possible using these two techniques, and F-19 nmr is a valuable adjunct.

Some of the required data can already be found in books which tabulate fluorine nmr data [1,2,3]. However, there are many gaps in this literature. The many mixtures which turned up in our synthetic work provided more compounds. Finally, deliberately synthesized compounds completed the list.

RESULTS

Table 1 gives the fluorine chemical shifts and coupling constants for saturated, two-carbon, chlorofluorohydrocarbons. Table 2 contains similar data for the two-carbon olefins. Chemical shifts are reported to the nearest ppm, coupling constants to the nearest Hz. Solvent and temperature effects suggest that greater precision is neither useful nor needed to decipher our mixtures.

The structure of our database is somewhat different from the one previously described for perfluorocarbons [4]. In that database each compound was a record, each chemical shift was a sub-record, and no coupling information was stored. In the current database each fluorine chemical shift is a record and the coupling information is the sub-record.

The database is stored on a VAX-cluster within the program Datatrieve[r]. The structure of the database is:

```
RECORD FS2 USING
01    FLUORINE.
      03    DESG.
            04    NAME PIC X(20).
            04    CODE PIC X(6).
      03    FORMULA QUERY_NAME FORM.
            06    C PIC 9(1).
            06    F PIC 9(1).
            06    H PIC 9(1).
            06    CL PIC 9(1).
            06    ALPHA PIC X(3).
            06    BETA  PIC X(3).
            06    GAMMA PIC X(3).
            06    SHIFT PIC 999V9 EDIT_STRING IS ZZ9.9.
      03    NUMBER_J QUERY_NAME NOJ  PIC 9(1).
      03    COUP  OCCURS 0 TO 6 TIMES DEPENDING ON NUMBER_J.
      04    EACH_COUP QUERY_NAME NUC.
            06    SPLIT PIC 9(1).
            06    J PIC 999V9 EDIT_STRING IS ZZZ9.9.
```

TABLE 1

Fluorine Chemical Shifts of Saturated C-2 Chlorofluorohydrocarbons

Alpha	CF_3	CF_2Cl	$CFCl_2$	CF_2H	CFHCl	CFH_2
Beta						
CF_3	**F116** 89 --	**F115** 75 q 1	**F114a** 77 q 6	**F125** 142 d 53 q 3	**F124** 156 d 48 q 11	**F134a** 241 t 46 q 16
CF_2Cl	**F115** 87 t 1	**F114** 71 --	**F113** 73 t 6	**F124a** 133 d 53 t 7	**F123a** 148 d 48 t 15	**F133b** 227 t 46 t 21
$CFCl_2$	**F114a** 84 d 6	**F113** 68 d 6	**F112** 68 --	**F123b** 127 d 56 d 15	**F122a** 140 d 48 d 23	**F132c** 210 d 46 t 23
CF_2H	**F125** 90 t 3 d 3	**F124a** 74 t 7	**F123b** 67 t 15	**F134** 138 d 53 d 3	**F133** 156 d 48 t 16 d 3	**F143** 239 t 46 t 18 d 6
CFHCl	**F124** 82 d 11 d 4	**F123a** 67 70 d 15 d 16 d 3 d 5 d 172	**F122a** 70 d 23 d 4	**F133** 131 132 d 55 d 54 d 14 d 16 d 5 d 5 d 295	**F132** 146 147 d 49 d 49 d 26 d 21 d 8 d 7	**F142** 220 t 47 d 21 d 9
CFH_2	**F134a** 78 d 16 t 8	**F133b** 66 d 21 t 11	**F132c** 73 d 22 t 14	**F143** 130 d 55 d 18 t 13	**F142** 146 d 51 d 21 d 20 d 18	**F152** 226 t 45 t 17

(continued)

CH_3	**F143a**	**F142b**	**F141b**	**F152a**	**F151a**	**F161**
	64 q 13	47 q 15	46 q 16	110 d 57 q 21	123 d 50 q 21	212 t 49 q 27
CH_2Cl	**F133a**	**F132b**	**F131a**	**F142**	**F141**	**F151**
	73 t 8	59 t 11	60 t 13	120 d 55 t 13	138 d 51 d 22 d 14	220 t 48 t 25
$CHCl_2$	**F123**	**F122**	**F121**	**F132a**	**F131**	**F141a**
	78 d 6	62 d 6	61 d 1	124 d 55 d 8	137 d 49 d 9	208 t 46 d 8
CCl_3	**F113a**	**F112a**	**F111**	**F122b**	**F121a**	**F131b**
	82 --	65 --	63 --	122 d 55	130 d 49 d 1	198 t 46

The two records for the compound CF_3CFHCl are:

NAME	CODE	C	F	H	CL	ALPHA	BETA	SHIFT	NUMBER J	SPLIT	J
CF3CFHCL	124a	2	4	1	1	FF6	FHC	82.3	2	2	4.0
										2	11.0
CF3CFHCL	124a	2	4	1	1	HC6	FFF	156.3	2	2	48.0
										4	11.0

The first entry is the structural formula written without subscripts, and in no particular order of which carbon is on the left. The second entry is the mysterious fluorocarbon code which all people knowledgable in the field use, but which was specifically designed to mystify outsiders. The secret is to first add 90 to the number given.

The four possible digits then each have individual meaning. The thousands digit is the number of double bonds. The hundreds digit is the number of carbon atoms (two for all the compounds in this paper). The tens digit is the number of hydrogens. The units digit is the number of fluorines. All other atoms to fill the carbon valencies are chlorine.

The next four entries are redundant formula information, but make some questions easier to ask.

TABLE 2

Fluorine Chemical Shifts of Unsaturated C-2 Chlorofluorohydrocarbons

Alpha	$=CF_2$		=CFCl		=CFH	
Beta						
CF_2	**F1114**		**F1113**		**F1123**	
	134		143		205	
	---		d 58		d 33	
			d 115		d 119	
					d 71	
CFCl	**F1113**		**F1112**		**F1122**	
			c	t	c	t
	101	119	105	120	156	173
	d 78	d 115	---	---	d 72	d 73
	d 58	d 78			d 10	d 132
CFH	**F1123**		**F1122**		**F1132**	
			c	t	c	t
	100	126	104	130	165	186
	d 87	d 87	d 23	d 0	d 73	d 74
	d 33	d 119	d 10	d 132	d 20	d 4
	d 13	d 4			d 19	d 125
CHCl	**F1122a**		**F1121**		**F1131**	
			c	t	c	t
	90	95	84	79	128	131
	d 42	d 42	d 4	d 17	d 77	d 79
	d 17	d 1			d 28	d 9
CH_2	**F1132a**		**F1131a**		**F1141**	
	81		68		113	
	d 1		d 39		d 85	
	d 34		d 7		d 20	
	d 0				d 52	
CCl_2	**F1112a**		**F1111**		**F1121**	
	89		79		122	
	--		--		d 76	

The next two fields describe the environment around the nucleus of interest. FF6 identifies the fluorine as a part of a FCF_2 group (attached to carbon). HC6 identifies the fluorine as part of a FCHCl group. The three substituents on the beta carbons are identified in the next field. FHC signifies a CFHCl group, FFF a CF_3 group.

The chemical shift is in ppm from the $CFCl_3$ internal reference. The conventional minus sign to signify upfield shifts is understood and is not stored.

The coupling information is stored in two parts. NOJ is the number of coupling constants. This is zero for a singlet, one if there is one coupling, etc. For each coupling, the next two entries are the splitting pattern, 2 for doublet, 3 for triplet... and the value of the coupling constant.

The database does not distinguish between fluorine-fluorine and fluorine-proton couplings. However, homonuclear couplings can be identified because they will appear in both fluorines. Proton-fluorine couplings appear only once. The 11 Hz. coupling which appears in both sets is $^3J(FF)$.

The database does not have bibliographical information.

Datatrieve allows searching any combination of fields using all Boolean logic operations. The database can be used to analyze complex mixtures which sometimes result from catalytic reactions [5].

The usual logic is to choose a resonance with an unusual chemical shift and ask the database for possible structures with shifts in that neighborhood. Next, check the coupling pattern for consistency with the observed resonance.

If the compound identified has more than one type of fluorine, search the database by name to find the other expected resonances. Inspect the spectrum to see if all the other expected fluorines are present, and have the proper coupling patterns and integrals. If all criteria are met, the resonances are deemed to be assigned, and the process repeated.

In particularly complicated spectra, COSY experiments unambiguously assign resonances pairs to coupled fluorines in the same molecule. In most cases the chemical shift suffices to characterize a resonance; coupling data is redundant.

Using this database we can usually identify compounds in mixtures down to the 0.1% level. The major assumption that must be made is there is no really unusual chemistry going on which produces compounds outside the scope of the database. Compounds whose partial spectra are similar to those in the database cause trouble in the assignments.

CORRELATIONS

Saturated Compounds

There have been many attempts to find correlations between structure and fluorine nmr parameters [6]. Individual authors generally found regularities in the compounds they investigated, but attempts to generalize from these observations have not been very successful. Part of the reason may be that conformational effects are never explicitly considered in such simple analyses. A CF_3 group such as the one in CF_3CFHCl really has three individual chemical shifts. The typical spectrum gives only the average chemical shift [7].

With this wealth of easily searchable data, we find that not all the effects are simply additive.

There are 63 unique -CF< environments on an ethane where the other substituents can be any combination of H, Cl or F. There are six environments for a fluorine in an ethane if only the alpha carbon substituents are considered. For each of these there are ten possible beta environments. The extra three environments are either geometric isomers or individually identifiable CF_2 resonances adjacent to an asymmetric CHFCl group.

Let us consider ethyl fluoride, CH_3CH_2F as the base point. If the substitutent effects are additive, we should be able to correlate the chemical shift data with four parameters. These are the alpha and beta effects of chlorine and fluorine. The correlation found is:

$$\text{Shift} = 205.8 - 71.2 * X1 - 73.7 * X2 + 7.5 * X3$$

where X1 is the number of alpha fluorines, X2 is the number of alpha chlorines and X3 is the number of beta fluorines. The parameter for the number of beta chlorines is not statistically significant. The estimated error for each parameter is 1.9 ppm. The R^2 of the fit is 0.97 and the standard error of the regression is 9.8 ppm.

The alpha effects for chlorine and fluorine are nearly the same, and are much larger than the beta effect. The data cluster depending mainly on the number of beta halogens, independent of their nature. The scatter within these clusters suggests other parameters may be operable.

Separate regression analyses on the 10-12 data points within each group produce intercepts which reflect the alpha substitutent. The beta fluorine effect is relatively constant at 8±2 ppm. However, the beta chlorine effect depends additionally on the number of fluorines on the alpha carbon. The effect is -5.9 ppm for a CH_3 group, near zero for CFH_2 and CFHCl and +4 for CF_2XY, X,Y = H, Cl. The standard deviation of these parameters is also ± 2 ppm. The non-significant average effect results from the sum of these individual effects with opposite signs.

The overall correlations are still not particularly good. R^2 ranges between 0.7 and 0.9. The standard deviation of the regressions are 3 to 6 ppm out of a range of between 25 and 50 ppm. This simple additive correlation still does not take into account conformational changes which are known to affect chemical shifts.

Unsaturated Compounds

There are 27 unique =CF- environments on an ethene where the other substituents can be any combination of H, Cl or F. There are three environments for a fluorine in an ethene if only the alpha carbon substituents are considered, $=CF_2$, =CFH, and =CFCl. There are nine possible beta environments for each of these when we consider cis and trans geometries individually.

Let us consider vinyl fluoride, $CHF=CH_2$ as the base point. If the substitutent effects are additive, we should be able to correlate the chemical shift data with six parameters. These are the alpha effects of chlorine and fluorine and beta, cis and trans, effects of chlorine and fluorine. A multiple regression analysis showed that the two beta chlorine parameters are not significant. The data could be equally well fit by the four parameter equation:

$$\text{Shift} = 131.4 - 49.4 * X1 - 52.1 * X2 + 22.8 * X3 + 43.2 * X4$$

where X1 is the number of alpha fluorines, X2 is the number of alpha chlorines, and X3, X4 are the number of cis and trans beta fluorines. The estimated error for each parameter is 3.9 ppm. The R^2 of the fit is 0.95 and the standard error of the regression is 8.3 ppm.

A Literature Error

The most serious discrepancy in the literature concerns the meso and dl pair of isomers of CHFClCHFCl. With proton decoupling the two compounds give uninspiring singlets. The proton coupled spectra are each AA'XX' and can hardly be mistaken for any other compounds.

This pair first showed up as impurities in a sample of the isomer CF_2ClCH_2Cl. Bissell and Fields[8] report the chemical shifts of the two isomers as -68.4 and -89.9 (from CF_3COCF_3). Assuming a conversion factor of 78.5, their chemical shifts are -146.9 and -168.4 from $CFCl_3$. They analysed the spectra and derived the four coupling constants for each isomer.

Simulations of the two spectra using their coupling constants were a perfect match for the two observed spectra. However, the chemical shifts I observed were -147.3 and -146.3. The 20 ppm discrepancy for one of the isomers may simply be a typographical error. The error has propagated into standard reference works [1]. The meso and dl pairs cannot be unambiguously assigned to their respective resonances which are now quite close.

Syntheses

Wherever possible I remeasured the F-19 spectra on a modern spectrometer with dilute solutions in $CDCl_3$ and with $CFCl_3$ as internal reference.

The last compound needed for the database was CCl_3CH_2F. The obvious synthesis would begin with the readily available CCl_3CH_2OH and replace the hydroxyl by fluorine with one of the standard reagents available which replace OH with F. None worked in my hands.

The reaction of CCl_3CH_3 with F_2 finally produced some of the desired product. The nmr spectrum was a decoupled singlet and a coupled triplet at -198 ppm.

CONCLUSION

The complete database of fluorine nmr parameters for two-carbon compounds containing H, Cl and F substituents allows analysis of complex mixtures down to the 0.1% level as long as all the compounds in the mixture are within the scope of the database.

Availability

An ASCII version of this database on one 5 1/4" floppy disk, readable by an IBM-PC or compatible, can be obtained for $5.00 (U.S.) from:

Project Seraphim
Department of Chemistry
Eastern Michigan University
Ypsilanti, MI 48197
U.S.A.

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