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Comparative studies in the ^{19}F and ^{1}H NMR chemical shifts in 2,2-difluorohalogenated propanes

T. Tanuma *, K. Ohnishi, H. Okamoto, S. Morikawa

Research Center, Asahi Glass Co., 1150 Hazawa-cho, Kanagawa-ku, Yokohama-shi, Kanagawa 221, Japan

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Abstract

Fluorine-19 chemical shifts were compared with ^{1}H chemical shifts in CF_3–CF_2–R versus CH_3–CF_2–R, CF_2Cl–CF_2–R versus CH_2Cl–CF_2–R and $CFCl_2$–CF_2–R versus $CHCl_2$–CF_2–R, where R is a substituted methyl group containing all combinations of H, Cl and F. A good linear relationship was found between the ^{19}F and ^{1}H NMR chemical shifts. Conformational analysis using MNDO calculations was applied to the CF_3–CF_2–R and CH_3–CF_2–R series to clarify the interaction between the terminal substituents. In halogenated propanes, ^{19}F and ^{1}H chemical shifts are mainly affected by the through-space interaction between the terminal substituents rather than the electronegativity.

Keywords: NMR spectroscopy; Mass spectrometry; Difluorohalogenated propanes; MNDO calculations; Through-space interaction

1. Introduction

We reported [1,2] the correlation between ^{19}F NMR chemical shifts and the molecular structures of halogenated propanes by conformational analysis using MNDO calculations. Although a large number of studies have been made on ^{19}F and ^{1}H NMR spectroscopic data respectively, no studies have ever tried to compare ^{19}F chemical shifts with ^{1}H chemical shifts systematically.

We have made an investigation into the relationship between ^{19}F and ^{1}H NMR chemical shifts in 2,2-difluorohalogenated propanes. Proton chemicals shifts were compared with ^{19}F NMR chemical shifts in CF_3–CF_2–R versus CH_3–CF_2–R, CF_2Cl–CF_2–R versus CH_2Cl–CF_2–R and $CFCl_2$–CF_2–R versus $CHCl_2$–CF_2–R, where R is a substituted methyl group containing all combinations of H, Cl and F.

2. Results and discussion

We have examined the ^{19}F NMR chemical shifts of trifluoromethyl groups and ^{1}H NMR chemical shifts of methyl groups. Table 1 shows a comparison of the ^{19}F chemical shifts in decreasing order of magnitude of trifluoromethyl groups in halogenated propane and ethanes. The order of substituent is completely different in both cases. We reported [1,2] the reasons for this difference as follows. In halogenated propanes the ^{19}F chemical shift of the trifluoromethyl group is mainly affected by the steric interaction with the terminal substituent. In contrast, the paramagnetic component of the neighboring atoms is responsible for the ^{19}F chemical shift of the trifluoromethyl group in halogenated ethanes.

Table 1
^{19}F chemical shift [a] of CF_3 group in CF_3–CF_2–R and CF_3–R

R	CF_3–CF_2–R	R	CF_3–R
CH_3	−87.2	CF_3	−88.2
CH_2F	−84.5	$CClF_2$	−86.7
CH_2Cl	−84.1	CHF_2	−86.2
CHF_2	−83.0	CCl_2F	−84.1
CF_3	−82.8	$CHClF$	−82.3
$CHClF$	−81.9	CCl_3	−82.2
$CClF_2$	−80.9	$CHCl_2$	−78.5
$CHCl_2$	−80.1	CH_2F	−78.5
CCl_2F	−78.1	CH_2Cl	−72.1
CCl_3	−75.6	CH_3	−65.0

[a] δ_F (ppm) from CCl_3F.

A comparison of the ^{1}H NMR chemical shifts of the methyl groups in halogenated propanes and ethanes is given in Table 2. In contrast with the case of the trifluoromethyl group, there is very little difference between the substituent order for halogenated propanes and ethanes. It appears that the bulkier the substituent, the larger the chemical shift. If additivity of the atoms in R is assumed, interesting results are obtained. Thus,

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* Corresponding author.

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Table 2
^{1}H chemical shift [a] of CH_3 group in CH_3–CF_2–R and CH_3–R

R	CH_3–CF_2–R	R	CH_3–R
CH_3	1.61	CH_3	0.88 [b]
CHF_2	1.67	CH_2F	1.35
CH_2F	1.69	CH_2Cl	1.48
CH_2Cl	1.74	CHF_2	1.55
CHClF	1.78	CHClF	1.86
CF_3	1.79	CF_3	1.87
$CClF_2$	1.83	$CHCl_2$	2.06
$CHCl_2$	1.85	$CClF_2$	2.16
CCl_2F	1.94	CCl_2F	2.46
CCl_3	2.04	CCl_3	2.73

[a] δ_H (ppm) from TMS.
[b] Measured in the gaseous state. See Ref. [3].

Table 3
Observed and calculated ^{1}H chemical shifts [a] of CH_3 group in halogenated propanes and ethanes

R	CH_3–CF_2–R		CH_3–R	
	Obs.	Calc.	Obs.	Calc.
CH_3	1.61	1.60	0.88 [b]	0.91
CHF_2	1.67	1.71	1.35	1.57
CH_2F	1.69	1.66	1.48	1.24
CH_2Cl	1.74	1.74	1.55	1.51
CHClF	1.78	1.79	1.86	1.84
CF_3	1.79	1.76	1.87	1.90
$CClF_2$	1.83	1.85	2.06	2.17
$CHCl_2$	1.85	1.88	2.16	2.11
CCl_2F	1.94	1.93	2.46	2.44
CCl_3	2.04	2.02	2.73	2.71
r	0.981		0.996	
rms error	0.0736		0.137	

[a] δ_H (ppm) from TMS.
[b] Measured in the gaseous state. See Ref. [3].

Table 4
Observed ^{19}F and ^{1}H chemical shifts [a] of CF_3 and CH_3 groups in CF_3CF_2–CXYZ and CH_3CF_2–CXYZ and the average number of atoms in X, Y positions of CF_3CF_2–CXYZ and CH_3CF_2–CXYZ as depicted in Fig. 2

	CF_3 δ_F (ppm)	CH_3 δ_H (ppm)	Average number of atoms in X and Y positions					
			CF_3CF_2–CXYZ			CH_3CF_2–CXYZ		
			H	F	Cl	H	F	Cl
CCl_3	−75.6	2.04			2.000			2.000
CCl_2F	−78.1	1.94		0.916	1.084		0.197	1.803
$CHCl_2$	−80.1	1.85	0.929		1.071	0.408		1.592
$CClF_2$	−80.9	1.83		1.619	0.381		1.051	0.949
CHClF	−81.9	1.79	0.867	0.809	0.324	0.650	0.414	0.936
CF_3	−82.8	1.78		2.000			2.000	
CHF_2	−83.0	1.74	0.760	1.240		0.727	1.273	
CH_2Cl	−84.1	1.69	1.751		0.249	1.168		0.831
CH_2F	−84.5	1.67	1.442	0.558		1.489	0.511	
CH_3	−87.2	1.61	2.000			2.000		

[a] δ_H (ppm) from TMS; δ_F (ppm) from CCl_3F.

the ^{1}H chemical shifts of methyl groups in halogenated propanes and ethanes may be expressed by the number of H, F and Cl atoms [n(H), n(F) and n(Cl)] in R as shown in Eqs. (1) and (2).

Hence, for halogenated propanes:

$$d_H(CH_3) = 0.535n(H) + 0.587n(F) + 0.672n(Cl) \qquad (1)$$

and for halogenated ethanes

$$d_H(CH_3) = 0.302n(H) + 0.637n(F) + 0.902n(Cl) \qquad (2)$$

The relationships between the observed and calculated ^{1}H chemical shifts are listed in Table 3.

These results agree with those obtained by us for the CF_3–CF_2–R system and we presume that the order of the coefficient is related to the bulkiness of the atom. It is generally known that ^{1}H chemical shifts are affected by the electronegativity, steric effects or magnetic anisotropic effects of the substituent. In these halogenated propanes and ethanes, the ^{1}H chemical shifts are mainly affected by the steric factor associated with the terminal substituent R.

Let us now compare the ^{19}F chemical shift with the ^{1}H chemical shift in halogenated propanes. The left-hand column of Table 4 lists the ^{19}F chemical shifts of the trifluoromethyl group and the ^{1}H chemical shifts of the methyl group in halogenated propanes. Bulkier substituents tend to lead to larger value shifts for the substituted methyl group in halogenated propanes. A plot of the ^{19}F chemical shifts of the trifluoromethyl group versus the ^{1}H chemical shifts of the methyl group in halogenated propanes gives an approximately linear relationship (Fig. 1). This indicates that both the ^{19}F and the ^{1}H chemical shifts are affected by the same factor, presumably one of steric origin.

We have applied conformational analysis using MNDO calculations to elucidate the steric interaction in the molecules. The heats of formation of all rotamers of CF_3CF_2–CXYZ and CH_3CF_2–CXYZ (X, Y, Z = H, Cl, F) were calculated in order to estimate the rotamer population as described previously [2]. Then the average number of atoms

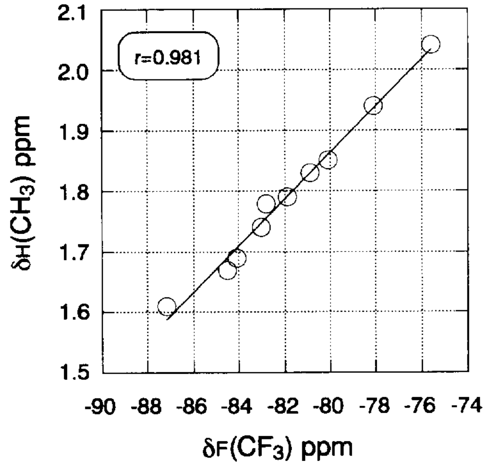

Fig. 1. Correlation between ^{19}F chemical shifts of CF_3 in CF_3CF_2–R and ^{1}H chemical shifts of CH_3 in CH_3CF_2–R.

in the X and Y positions depicted in Fig. 2 was calculated as listed in Table 4. The right-hand column of Table 4 shows that the greater the number of large atoms located in the X and Y positions in Fig. 2, the larger the magnitude of the chemical shift. If large substituent atoms are located in the X and Y positions, they would have a through-space interaction with the other terminal substituent; this is known as the anisotropic and steric effect [8].

Table 5 lists the ^{19}F chemical shifts of chlorodifluoromethyl and dichlorofluoromethyl groups and the ^{1}H chemical shifts of chloromethyl and dichloromethyl groups in halogenated propanes and their relationships. An approximately linear relationship (Figs. 3 and 4) also exists between these ^{19}F and ^{1}H chemical shifts.

A similar observation applies to the ^{1}H NMR chemical shifts of the methyl groups and the H atom of the 10-position in the 1,2,3,4-halogenated methyltriptycene (Fig. 5) system

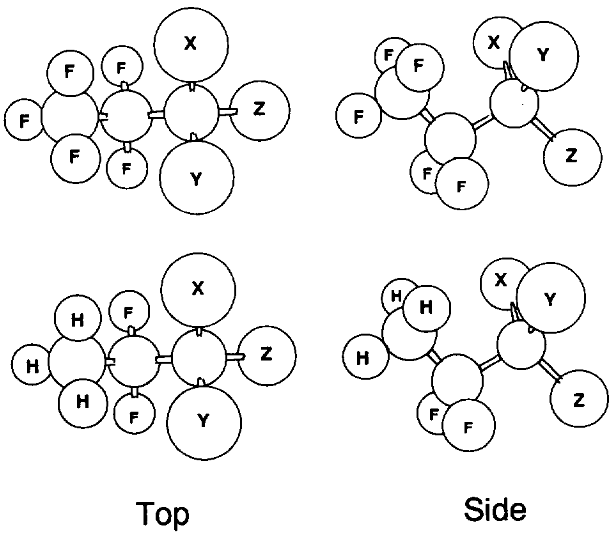

Fig. 2. Top and side view of CF_3–CF_2–CXYZ and CH_3–CF_2–CXYZ.

Table 5
^{19}F chemical shifts of CF_2Cl and $CFCl_2$ groups and ^{1}H chemical shifts of CH_2Cl and $CHCl_2$ groups in halogenated propanes [a]

R^2	CX_2Cl–CF_2–R^2		$CXCl_2$–CF_2–R^2	
	δ_F (CF_2Cl)	δ_H (CH_2Cl)	δ_F ($CFCl_2$)	δ_H ($CHCl_2$)
CCl_3	−61.3	4.30	−63.9	6.47
CCl_2F	−64.6	4.08	−66.7	6.25
$CHCl_2$	−66.3	–	−66.4	6.24
$CClF_2$	−67.7	3.94	−70.9	6.04
CHClF	−69.1	3.91	−71.4	6.00
CF_3	−70.0	3.88	−73.1	5.93
CH_2Cl	−70.4	3.79	−72.1	–
CHF_2	−70.3	3.82	−73.4	5.90
CH_2F	−71.0	3.80	–	5.92
CH_3	−72.5	3.66	−73.5	5.77
r	0.986		0.978	

[a] δ_H (ppm) from TMS; δ_F (ppm) from CCl_3F.

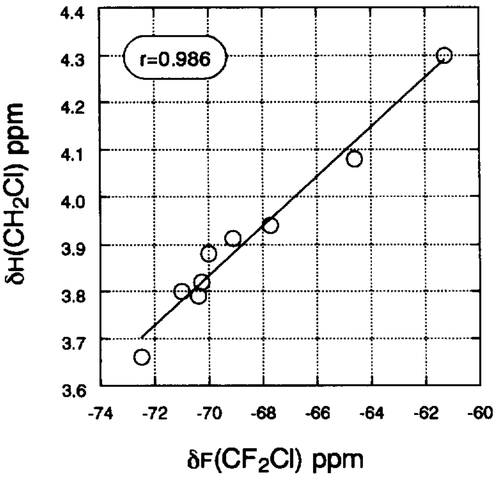

Fig. 3. Correlation between ^{19}F chemical shifts of CF_2Cl in CF_2ClCF_2–R and ^{1}H chemical shifts of CH_2Cl in CH_2ClCF_2–R.

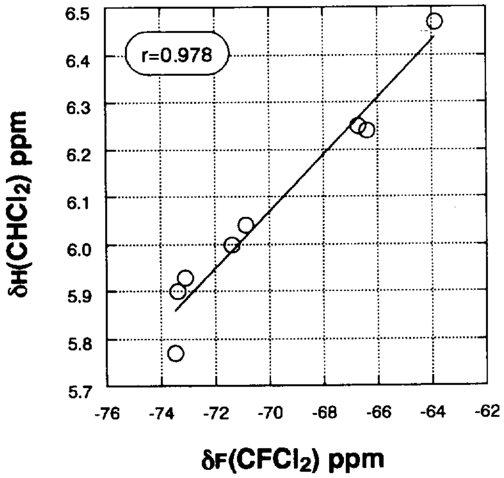

Fig. 4. Correlation between ^{19}F chemical shifts of $CFCl_2$ in $CFCl_2CF_2$–R and ^{1}H chemical shifts of $CHCl_2$ in $CHCl_2CF_2$–R.

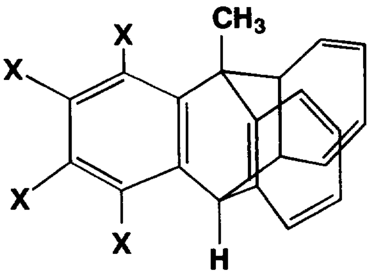

Fig. 5. 1,2,3,4-Halogenated 9-methyltriptycene.

Table 6
^{1}H chemical shifts [a] of CH_3 and 10-H in 1,2,3,4-halogenated methyltriptycene

X	CH_3	10-H
H [4]	2.36	5.38
F [5]	2.56	5.77
Cl [6]	2.73	6.03
Br [7]	2.75	6.10

[6–8]. As indicated by the data in Table 6, ^{1}H chemical shifts of the methyl group and the H atom at the 10-position are shifted to larger values in the order of X = H, F, Cl, Br, which is the same as the order of ionic radii.

The through-space interaction, therefore, is responsible for the larger values of the ^{19}F and ^{1}H NMR chemical shifts of the substituted methyl group in halogenated propanes.

3. Experimental details

3.1. Spectral data

The ^{19}F and ^{1}H NMR chemical shift data for halogenated propanes and halogenated ethanes containing the trifluoromethyl group were extracted from a previous paper [2]. All the halogenated ethanes listed in Tables 1 and 2 were obtained commercially (PCR Inc.) except for 1-chloro-1-fluoroethane. Some of the chemical shift data for halogenated ethanes have already been quoted in the literature [9,10], but there are some gaps due to changes in the experimental conditions such as the solvent or concentration so we have remeasured the NMR spectra under the same conditions. The NMR spectra were obtained in the pulse Fourier transform mode using a JNM-EX-90 (JEOL) instrument operating at 84.2 MHz (^{19}F) and 89.5 MHz (^{1}H) respectively. The spectral data were recorded in $CDCl_3$ solution (0.05–0.2 M) with CCl_3F (^{19}F) and TMS (^{1}H) as internal references. Chemical shifts are given in parts per million (ppm) from CCl_3F (^{19}F) and TMS (^{1}H).

Mass spectra were recorded on a gas chromatograph/mass spectrometer (M-80B, Hitachi, Ltd.).

3.2. Calculations

MNDO calculations were performed on a Titan 3000 computer with full geometry optimization using a MOPAC 5.0 program [11–13].

3.3. Purification and identification of products

The reaction mixture was distilled to obtain pure products, then separated and collected by gas chromatographic methods (Silicone KF-96, GL Sciences). Identification of products was effected by ^{19}F and ^{1}H NMR spectroscopy, and mass spectrometry.

3.3.1. Preparation of 1-chloro-1-fluoroethane

A 0.5 in i.d. and 24 in long Inconel tube reactor was charged with 100 ml of Pt/C (granules, Pt–0.5%) catalyst and heated at 200 °C. 1,1-Dichloro-1-fluoroethane and hydrogen were fed in at rates of 75 and 225 ml min^{-1}, respectively. The reactant gas was passed through aqueous alkali (Na_2CO_3) solution and trapped in a Dry Ice/acetone bath. The products were distilled to give several products as follows: 1-chloro-1-fluoroethane (31%), 1-fluoroethane (45%), 1-chloroethane (21%), others (3%).

3.3.2. Spectral data

1,1,1-Trichloroethane: ^{1}H NMR δ: 2.73 (s) ppm.

1,1-Dichloro-1-fluoroethane: ^{19}F NMR δ: -44.7 (q, $^3J = 16.5$ Hz) ppm. ^{1}H NMR δ: 2.46 (d, $^3J = 16.5$ Hz) ppm.

1-Chloro-1,1-difluoroethane: ^{19}F NMR δ: -45.7 (q, $^3J = 15.1$ Hz) ppm. ^{1}H NMR δ: 2.16 (t, $^3J = 15.0$ Hz) ppm.

1,1,1-Trifluoroethane: ^{19}F NMR δ: -61.2 (q, $^3J = 13.1$ Hz) ppm. ^{1}H NMR δ: 1.87 (q, $^3J = 12.8$ Hz) ppm.

1,1-Dichloroethane: ^{1}H NMR δ: 2.06 (d, $^3J = 6.0$ Hz); 5.90 (q, $^3J = 6.0$ Hz) ppm.

1-Chloro-1-fluoroethane: ^{19}F NMR δ: -124.1 (dq, $^2J = 51.0$, $^3J = 21.3$ Hz) ppm. ^{1}H NMR δ: 1.86 (dd, $^3J = 21.2$, $^3J = 5.4$ Hz); 6.29 (dq, $^2J = 50.9$, $^3J = 5.3$ Hz) ppm. MS *m/e*: 47 (CH_3CHF^+); 27 (CH_3C^+); 67 ($CHClF^+$); 82 (M^+).

1,1-Difluoroethane: ^{19}F NMR δ: -110.0 (dq, $^2J = 56.8$, $^3J = 21.0$ Hz) ppm. ^{1}H NMR δ: 1.55 (td, $^3J = 20.8$, $^3J = 4.5$ Hz); 5.93 (dq, $^2J = 56.9$, $^3J = 4.5$ Hz) ppm.

1-Chloroethane: ^{1}H NMR δ: 1.48 (t, $^3J = 7.3$ Hz); 3.56 (q, $^3J = 7.3$ Hz) ppm.

1-Fluoroethane: ^{19}F NMR δ: -212.2 (tq, $^2J = 47.0$, $^3J = 26.0$ Hz) ppm. ^{1}H NMR δ: 1.35 (dt, $^3J = 26.2$, $^3J = 7.0$ Hz); 4.50 (dq, $^2J = 47.0$, $^3J = 6.9$ Hz) ppm.

References

[1] T. Tanuma, K. Ohnishi, H. Okamoto, T. Miyajima and S. Morikawa, *Rep. Res. Lab. Asahi Glass Co. Ltd., 41* (1991) 225.

[2] T. Tanuma, K. Ohnishi, H. Okamoto, T. Miyajima and S. Morikawa, *J. Fluorine Chem., 57* (1992) 259.

[3] H. Spiesecke and W.G. Schneider, *J. Chem. Phys., 35* (1961) 722.

[4] S.T. Cristol and D.K. Pennelle, *J. Org. Chem., 35* (1970) 2357.

[5] G. Yamamoto and M. Oki, *J. Org. Chem., 49* (1984) 1913.

[6] M. Nakamura and M. Oki, *J. Am. Chem. Soc., 95* (1973) 7169.

[7] M. Nakamura, M. Oki, H. Nakanishi and O. Yamamoto, *Bull. Chem. Soc. Jpn., 47* (1974) 2415.

[8] G. Yamamoto and M. Oki, *Bull. Chem. Soc. Jpn., 63* (1990) 3550.

[9] C.H. Dungan and J.R. Van Wazer, *Compilation of Reported ^{19}F NMR Chemical Shifts*, Wiley, New York, 1990.

[10] F.J. Weigert, *J. Fluorine Chem., 46* (1990) 375.

[11] M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc., 99* (1977) 4899, 4907.

[12] M.J.S. Dewar, E.G. Zeobisch, E.F. Healy and J.J.P. Stewart, *J. Am. Chem. Soc., 107* (1985) 3902.

[13] J.J.P. Stewart, *J. Comp. Chem., 10* (1989) 209, 221.