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^{19}F nuclear magnetic resonance studies of halogenated propanes

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Abstract

The relationship between ^{19}F chemical shifts in halogenated propanes and their structures are elucidated using MNDO calculations to determine the population of rotamers The pairs of atoms gauche to a fluorine atom and van der Waals interaction between the two terminal substituents are responsible for the ^{19}F chemical shifts The differences among chemical shifts in diastereomers are also discussed in terms of the conformation of the molecule

Introduction

In a previous paper [1] we described the correlation between the ^{19}F chemical shifts and the structures of halogenated propanes by conformational analysis using MNDO calculations [2]: van der Waals interaction between the fluorine atoms in the trifluoromethyl group and the substituent R lead to high-frequency shifts of the ^{19}F signals for the trifluoromethyl group in pentafluoropropane systems (CF_3CF_2–R). The ^{19}F chemical shifts for the difluoromethylene group in halogenated propanes (R^1–CF_2–R^2) are more affected by the conformation of the molecule than the electron density on fluorine.

We now report further investigations not only on halogenated propanes with a difluoromethylene group but also on halogenated propanes with other methylene groups. First, the effect of vicinal atoms on the ^{19}F chemical shift will be discussed. Second, we will describe the long-range effect, which means the effect of terminal substituents on the chemical shifts for the trifluoromethyl or chlorodifluoromethyl group. Third, ^{19}F chemical shifts of diastereomers will be discussed The investigated compounds are chlorofluoropropanes, hydrochlorofluoropropanes, and hydrofluoropropanes.

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Results and discussion

Vicinal effect

Effect of methylene groups on the ^{19}F chemical shifts for trifluoromethyl groups

Table 1 shows the ^{19}F chemical shifts for trifluoromethyl groups in 2,2-substituted 1,1,1,3,3,3-hexafluoropropane (CF_3–CXY–CF_3) and 2,2-substituted 3,3-dichloro-1,1,1-trifluoropropane (CF_3–CXY–$CHCl_2$).

In order to elucidate the effect of the neighboring atoms, we first analyze the ^{19}F chemical shifts of 1,1,1-trifluoroethane systems (CF_3–CXYZ). We here consider only gauche neighbors because gauche effects are more significant in ^{19}F chemical shifts [3]. For the three fluorine atoms in the trifluoromethyl group, as shown in Fig. 1, there are three pairs of gauche positions. Also, for any pair of gauche positions, there are six possible combinations of H, Cl or F, *i.e.* H–H, H–Cl, H–F, Cl–Cl, Cl–F and F–F. The observed chemical shifts for trifluoromethyl groups and the numbers of gauche pairs are listed in Table 2.

TABLE 1

^{19}F chemical shifts (ppm) for CF_3 in CF_3–CXY–R

–CXY–	R	
	CF_3	$CHCl_2$
CF_2	−83.0[a]	−80.1
CClF	−79.2	−77.1
CHF	−76.6[b]	−75.0
CCl_2	−75.8[c]	−73.1
CHCl	−70.0[d]	−69.1
CH_2	−63.9[e]	−64.8
$CHCF_3$	−64.5[b]	–

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[a] [4].

[b] [5].

[c] [6].

[d] [7].

[e] [8].

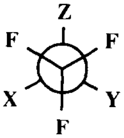

Fig. 1. CF_3CXYZ.

TABLE 2

^{19}F chemical shifts for CF_3 in CF_3–R and the number of gauche pairs

R	δ_F (ppm)	G(H–H)	G(H–Cl)	G(H–F)	G(Cl–Cl)	G(Cl–F)	G(F–F)
CF_3	−88.2	0	0	0	0	0	3
$CClF_2$	−86.7	0	0	0	0	2	1
CHF_2	−86.2	0	0	2	0	0	1
CCl_2F	−84.1	0	0	0	1	2	0
CHClF	−82.3	0	1	1	0	1	0
CCl_3	−82.2	0	0	0	3	0	0
$CHCl_2$	−78.5	0	2	0	1	0	0
CH_2F	−78.5	1	0	2	0	0	0
CH_2Cl	−72.1	1	2	0	0	0	0
CH_3	−65.0	3	0	0	0	0	0

The observed chemical shifts are correlated with six explanatory variables by multiple regression analysis, which gives eqn. (1), in which G(F–F), G(H–F), G(Cl–F), G(H–Cl), G(Cl–Cl) and G(H–H) are the number of pairs of atoms gauche to a fluorine atom in a trifluoromethyl group. The regression coefficients shown in eqn. (1) are presumed to include the effect of magnetic anisotropy, which is divided into two parts; diamagnetic, arising from the interaction of the magnetic field with the electron spin, and paramagnetic, arising from the interaction of the magnetic field with the orbital angular momentum of the electron.

$$\delta_F(CF_3) = -29.42G(F\text{–}F) - 28.49G(Cl\text{–}F) - 28.41G(H\text{–}F) - 27.40G(Cl\text{–}Cl) - 25.39G(H\text{–}Cl) - 21.63G(H\text{–}H) \qquad (1)$$

In practice, however, anisotropy of the diamagnetic components in ^{19}F NMR is considered to be smaller than that of the paramagnetic components [9]. The effects of the pairs of atoms on the low-frequency shift are in the following order, from eqn. (1):

$$F\text{–}F > Cl\text{–}F > H\text{–}F > Cl\text{–}Cl > H\text{–}Cl > H\text{–}H \qquad (2)$$

This order indicates that when a fluorine atom is gauche to a fluorine atom in the trifluoromethyl group, it leads to a lower-frequency shift than does a chlorine or a hydrogen atom.

In the case of 2,2-substituted halogenated propanes (CF_3–CXY–R), we can also observe the same effect on the ^{19}F chemical shifts for trifluoromethyl groups as shown in Table 1. X and Y are gauche to fluorine atoms of trifluoromethyl groups (see Fig. 1: Z = R) and the ^{19}F chemical shift for the trifluoromethyl group is low-frequency shifted as the pairs of atoms X, Y change in the same order as in eqn. (2). Considering that the ^{19}F chemical shift for the trifluoromethyl groups in 2-trifluoromethyl-

1,1,1,3,3,3-hexafluoropropane is almost the same as that in 1,1,1,3,3,3-hexafluoropropane, the ^{19}F chemical shift for a trifluoromethyl group depends on the magnetic anisotropy of neighboring halogen atoms X, Y rather than the steric effect of X, Y.

^{19}F chemical shifts for difluoromethylene groups in halogenated propanes

There are 55 halogenated propanes with a difluoromethylene group (R^1–CF_2–R^2) in which the two substituents ($R^1 = CX^1Y^1Z^1$, $R^2 = CX^2Y^2Z^2$) can be any combination of H, Cl or F. 2,2-Substituted halogenated propanes are shown in a Newman projection formula in Fig. 2. In a previous paper [1] we reported the results of a statistical analysis of 46 halogenated propanes and the conformational analysis of 24 halogenated propanes. This paper presents further conformational analysis of 47 compounds of the 55 halogenated propanes, 177 rotamers in total. We applied the same method as previously on these compounds to assess the conformational effect on ^{19}F chemical shifts for difluoromethylene groups. Here, both gauche and *trans* positions are considered because there are enough data compared with the number of variables. For the two fluorine atoms in a difluoromethylene group, there are four pairs of gauche positions and four *trans* positions in each rotamer, as shown in Fig. 3. There are six possible combinations of H, Cl or F for a pair of gauche positions; they are H–H, H–Cl, H–F, Cl–Cl, Cl–F and F–F. In addition, three atoms (H, Cl or F) are possible for the *trans* position. MNDO calculations were applied on all possible rotamers of each molecule to optimize the heats of formation and molecular geometries. On the basis of the population of rotamers, we calculated the average number of pairs of atoms, *i.e.* H–H, H–Cl, H–F, Cl–Cl, Cl–F and F–F, gauche to F in a difluoromethylene group and the average number of H, Cl and F *trans* to F in a difluoromethylene group. The results for 47 halogenated propanes are listed

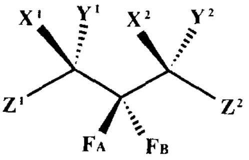

Fig. 2. $CX^1Y^1Z^1$–CF_2–$CX^2Y^2Z^2$.

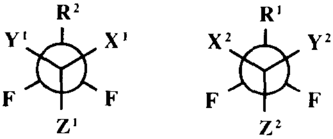

Fig. 3. $CX^1Y^1Z^1$–CF_2–$CX^2Y^2Z^2$.

in Table 3. The observed ^{19}F chemical shifts (see spectral data section) for the difluoromethylene group are given by:

$$\begin{aligned}\delta_F(\mathrm{ppm}) = {} & 60.41G(F\text{–}F) + 61.13G(H\text{–}F) + 63.89G(Cl\text{–}F) \\ & + 66.06G(H\text{–}Cl) + 66.68G(Cl\text{–}Cl) + 75.01G(H\text{–}H) \\ & - 97.11T(H) - 91.94T(Cl) - 93.12T(F) \end{aligned} \tag{3}$$

where G(F–F), G(H–F), G(Cl–F), G(H–Cl), G(Cl–Cl) and G(H–H) are the average number of pairs of atoms gauche to F atoms in a difluoromethylene group, and T(H), T(Cl) and T(F) are the average number of atoms *trans* to F in a difluoromethylene group. The regression coefficients and the relationship between the calculated and observed ^{19}F chemical shifts for difluoromethylene groups are shown in eqn. (3) and Fig. 4, respectively.

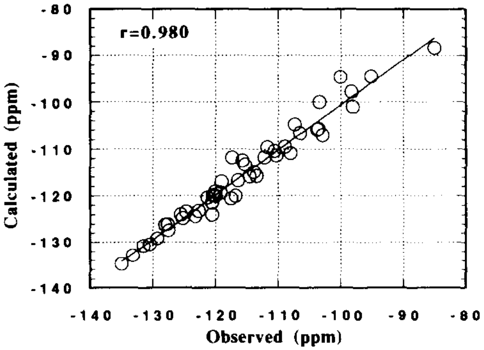

Fig. 4. Observed *vs.* calculated ^{19}F chemical shifts for CF_2 in $R^1\text{–}CF_2\text{–}R^2$.

Equation (3) shows that the pairs of atoms gauche to F in a difluoromethylene group contribute to the low frequency shift of a difluoromethylene group in the following order:

$$F\text{–}F > H\text{–}F > Cl\text{–}F > H\text{–}Cl > Cl\text{–}Cl > H\text{–}H \tag{4}$$

For the atoms *trans* to F in the difluoromethylene group, H leads to lower-frequency shifts than does Cl or F.

A factor which has been thought to contribute importantly to shielding is magnetic anisotropy [11]. ^{19}F magnetic shielding is especially affected by the paramagnetic terms [12], which depend on the details of the excited electronic states of the molecule. In this conformational analysis, magnetic anisotropy around a fluorine atom is represented as the number of gauche pairs of atoms, *i.e.* as a sum of C–X bond anisotropy. This order shows the magnitude of magnetic anisotropy given by neighboring atoms; the ^{19}F chemical shifts for a difluoromethylene group are mainly affected by the conformation of the molecule, in other words, by neighboring atoms.

TABLE 3

Average number of gauche pairs of atoms and atoms *trans* to fluorine atoms in CF_2

Compound	Gauche						*Trans*		
	H–H	H–Cl	H–F	Cl–Cl	Cl–F	F–F	H	Cl	F
$CF_3CF_2CCl_3$	0	0	0	2	0	2	0	2	2
$CF_3CF_2CCl_2F$	0	0	0	0.916	1.084	2	0	1.084	2.916
$CF_3CF_2CClF_2$	0	0	0	0	1.619	2.381	0	0.381	3.619
$CF_3CF_2CF_3$	0	0	0	0	0	4	0	0	4
$CF_3CF_2CHCl_2$	0	1.071	0	0.929	0	2	0.929	1.071	2
CF_3CF_2CHClF	0	0.809	0.324	0	0.867	2	0.867	0.324	2.809
$CF_3CF_2CHF_2$	0	0	1.240	0	0	2.760	0.760	0	3.240
$CF_3CF_2CH_2Cl$	0.249	1.751	0	0	0	2	1.751	0.249	2
$CF_3CF_2CH_2F$	0.558	0	1.442	0	0	2	1.442	0	2.558
$CF_3CF_2CH_3$	2	0	0	0	0	2	2	0	2
$CCl_3CF_2CCl_3$	0	0	0	4	0	0	0	4	0
$CCl_3CF_2CCl_2F$	0	0	0	2.546	1.454	0	0	3.454	0.546
$CCl_3CF_2CClF_2$	0	0	0	2	1.172	0.828	0	2.828	1.172
$CCl_3CF_2CHCl_2$	0	1.029	0	2.971	0	0	0.971	3.029	0
CCl_3CF_2CHClF	0	0.319	0.703	2	0.978	0	0.978	2.703	1
$CCl_3CF_2CHF_2$	0	0	1.013	2	0	0.987	0.987	2	1.013
$CCl_3CF_2CH_2Cl$	0.155	1.845	0	2	0	0	1.845	2.155	0
$CCl_3CF_2CH_3$	2	0	0	2	0	0	2	2	0
$CH_3CF_2CCl_2F$	2	0	0	0.197	1.803	0	2	1.803	0.197
$CH_3CF_2CClF_2$	2	0	0	0	1.051	0.949	2	0.949	1.051
$CH_3CF_2CHCl_2$	2	1.592	0	0.408	0	0	2.408	1.592	0
CH_3CF_2CHClF	2	0.414	0.936	0	0.650	0	2.650	0.936	0.414
$CH_3CF_2CH_2Cl$	2.831	1.168	0	0	0	0	3.168	0.831	0
$CH_3CF_2CH_2F$	2.511	0	1.489	0	0	0	3.484	0	0.511
$CH_3CF_2CH_3$	4	0	0	0	0	0	4	0	0

$CClF_2CF_2CHF_2$	0	0	1 089	0	1	1 911	0 957	1	2 043
$CClF_2CF_2CH_2F$	0.518	0	1.48	0	1 069	0 929	1 480	0 929	1 587
$CClF_2CF_2CHCl_2$	0	1 031	0	0.969	1.066	0 934	0 969	1 965	1 066
$CClF_2CF_2CH_2Cl$	0 197	1 805	0	0	1 054	0 948	1 805	1 145	1 054
$CClF_2CF_2CHClF$	0	0 488	0 578	0	1 653	1 277	0 973	1 123	1.9
$CClF_2CF_2CClF_2$	0	0	0	0	3 023	0 981	0	0 981	3.023
$CClF_2CF_2CCl_2F$	0	0	0	0 892	2 434	0 682	0	1.794	2.214
$CCl_2FCF_2CCl_2F$	0	0	0	1 639	2 361	0	0	2 361	1 639
$CCl_2FCF_2CH_2Cl$	0 146	1 854	0	0 2	1 8	0	1 854	1 946	0.2
$CCl_2FCF_2CHCl_2$	0	1.025	0	1 288	1 687	0	0 975	2 712	0.313
$CCl_2FCF_2CHF_2$	0	0	1.039	0.722	1 278	0 961	0 961	1.278	1.761
CCl_2FCF_2CHClF	0	0.566	0 475	0 566	2 393	0	0 959	1 909	1 132
$CHCl_2CF_2CH_2F$	0 296	1.518	1 704	0 482	0	0	2 186	1.518	0 296
$CHCl_2CF_2CHF_2$	0	1 162	1 035	0 836	0	0 963	1 799	1 162	1 035
$CHCl_2CF_2CHCl_2$	0	2.165	0	1 835	0	0	1 835	2 165	0
$CHCl_2CF_2CHClF$	0	1 229	0 977	0 929	0.905	0	1 834	2 068	0 138
$CHF_2CF_2CH_2Cl$	0.727	1 273	1 138	0	0	0 862	2 135	0.727	1 138
$CHF_2CF_2CH_2F$	0 845	0	2 435	0	0	0 72	2 351	0	1 649
CHF_2CF_2CHClF	0	0 443	1.993	0	0 155	1 435	1.59	0 871	1 543
$CHF_2CF_2CHF_2$	0	0	2 525	0	0	1 475	1 475	0	2.525
$CH_2ClCF_2CH_2Cl$	1.565	2 435	0	0	0	0	2 435	1 565	0
CH_2ClCF_2CHClF	0.708	1 547	0.912	0	0.837	0	1 531	1 62	0 853
$CH_2FCF_2CH_2Cl$	1 267	1 168	1 565	0	0	0	2 061	1 168	0.771

Long range effects

Effect of the halogenated methylene group and the terminal substituent on the ^{19}F chemical shifts for the trifluoromethyl or chlorodifluoromethyl groups

We reported in a previous paper [1] that van der Waals interaction is responsible for the ^{19}F chemical shift for the trifluoromethyl group in pentafluoropropane derivatives. We have made a further investigation of the ^{19}F chemical shifts for trifluoromethyl or chlorodifluoromethyl groups in halogenated propanes, not only with a difluoromethylene group but also with a chlorofluoromethylene or dichloromethylene group. Tables 4(a) and 4(b) show the ^{19}F chemical shifts for trifluoromethyl and chlorodifluoromethyl groups in halogenated propanes. The figures in parentheses are the predicted values calculated by the method described below.

TABLE 4(a)

^{19}F chemical shifts (ppm) for CF_3 in halogenated propanes

R	CF_3–CF_2–R	CF_3–CClF–R^a	CF_3–CCl_2–R
CH_3	−87.2	(−83.8)	(−80.2)
CH_2F	−84.5	(−81.6)	(−78.0)
CH_2Cl	−84.1	(−80.7)	(−77.7)
CF_3	−83.0	−79.2	−75.8
CHF_2	−82.8	(−79.6)	−76.2
CHClF	−81.9	−78.1, −79.1^b	−75.1
$CClF_2$	−80.9	−77.7	−73.5
$CHCl_2$	−80.1	−77.1	−73.1
CCl_2F	−78.1	−74.5	−71.0
CCl_3	−75.6	−71.9	−68.7

^{a}Figures in parentheses are the predicted values.
^{b}Diastereomers.

TABLE 4(b)

^{19}F chemical shifts (ppm) for $CClF_2$ in halogenated propanes

R	$CClF_2$–CF_2–R	$CClF_2$–CClF–R^a	$CClF_2$–CCl_2–R
CH_3	−72.5	(−67.9)	(−63.2)
CH_2F	−71.0	(−66.4)	(−61.7)
CH_2Cl	−70.4	(−65.8)	(−61.1)
CF_3	−70.0	−64.7, −65.9	−61.1
CHF_2	−70.3	−65.8	−61.0
CHClF	−69.1	(I) −64.3, −64.6	−59.2
		(II) −63.8, −64.0	
$CClF_2$	−67.7	−62.6, −63.6	−58.6
$CHCl_2$	−66.3	−60.8, −61.7	−55.8
CCl_2F	−64.6	−59.2, −61.2	−55.9
CCl_3	−61.3	−56.4, −58.7	(−52.4)

^{a}Figures in parentheses are the predicted values. (**I**), (**II**): diastereomers.

MNDO calculations were applied for 1-chloro-1,1,2,2-tetrafluoropropane derivatives ($CClF_2CF_2$–R) as follows: the interatomic distances of X^1(F or Cl)–X^2, Y^1(F or Cl)–Y^2, Z^1(F or Cl)–F$_A$ and Z^1–F$_B$ in Fig. 2 were calculated in each rotamer. The populations of the rotamers were calculated on the basis of the differences in their heats of formation. The product of the interatomic distances of X^1–X^2, Y^1–Y^2, Z^1–F$_A$, Z^1–F$_B$ and populations of each rotamer then gives the average interatomic distances d(F–H), d(F–Cl), d(F–F), d(F–F$_A$) and d(F–F$_B$), which are the weighted means of the individual values for each rotamer. The results are summarized in Table 5(a). On deriving the ^{19}F chemical shifts for the chlorodifluoromethyl group by using these five variables, we found a good correlation (Fig. 5) between the chemical shifts and the parameters, as we

TABLE 5(a)

Observed ^{19}F chemical shifts for $CClF_2$ and average interatomic distances[a] in $CClF_2CF_2$–R

R	δ (ppm)	d(F–H)	d(F–Cl)	d(F–F)	d(F–F$_A$)	d(F–F$_B$)
CH_3	−72.5	2.978	0	0	2.678	2.690
CH_2F	−71.0	2.875	0	0.121	2.628	2.638
CH_2Cl	−70.4	2.516	0.503	0	2.665	2.686
CHF_2	−70.3	0.239	0	2.684	2.815	2.860
CF_3	−70.0	0	0	4.721	1.049	1.081
CHClF	−69.1	0.278	0.531	2.386	2.553	2.619
$CClF_2$	−67.7	0	0.711	3.675	1.346	1.431
$CHCl_2$	−66.3	0.603	2.674	0	2.562	2.680
CCl_2F	−64.6	0	1.585	2.298	1.848	1.974
CCl_3	−61.3	0	3.669	0	2.188	2.332

[a] In angstroms

TABLE 5(b)

Observed ^{19}F chemical shifts for CF_3 and average interatomic distances[a] in CF_3CF_2–R

R	δ (ppm)	d(F–H)	d(F–Cl)	d(F–F)	d(tF–F)
CH_3	−87.2	5.669	0	0	2.842
CH_2F	−85.0	4.039	0	1.653	2.846
CH_2Cl	−84.1	4.893	0.808	0	2.835
CHF_2	−84.5	2.105	0	3.661	2.855
CF_3	−83.0	0	0	5.867	2.858
CHClF	−81.9	2.426	1.040	2.352	2.836
$CClF_2$	−80.9	0	1.121	4.699	2.840
$CHCl_2$	−80.1	2.530	3.409	0	2.825
CCl_2F	−78.1	0	3.420	2.627	2.818
CCl_3	−75.6	0	6.237	0	2.793

[a] In angstroms

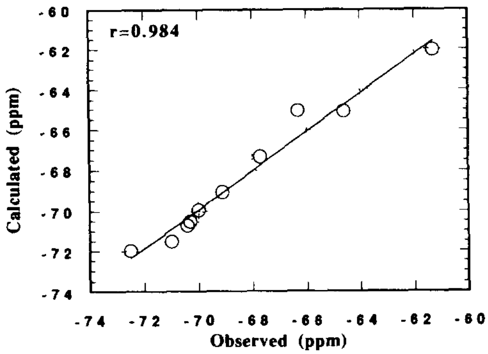

Fig. 5 Observed *vs* calculated ^{19}F chemical shifts for $CClF_2$ in $CClF_2CF_2$-R

did for pentafluoropropane derivatives (CF_3CF_2-R). The following equation was obtained:

$$\delta_F(CClF_2) = -12.85d(F\text{-}H) - 9.93d(F\text{-}Cl) - 12.10d(F\text{-}F) - 27.16d(F\text{-}F_A) + 14.51d(F\text{-}F_B) \tag{5}$$

The results for pentafluoropropane derivatives are also shown in Table 5(b) and eqn. (6) for reference. In this case, *d*(tF–F) is the mean value of $d(F\text{-}F_A)$ and $d(F\text{-}F_B)$, as there is little difference between them.

$$\delta_F(CF_3) = -25.19d(F\text{-}H) - 23.66d(F\text{-}F) - 20.96d(F\text{-}Cl) + 19.70d(tF\text{-}F) \tag{6}$$

As for 1-chloro-1,1,2,2-tetrafluoropropane derivatives ($CClF_2CF_2$-R), eqn. (5) shows that the presence of *d*(F–Cl) leads to higher-frequency shifts than that of *d*(F–F) or *d*(F–H), which is the same result found for pentafluoropropane derivatives.

Next, we applied another statistical analysis (multiple regression) to the halogenated propanes listed in Tables 4(a) and 4(b). Ten methyl groups and three methylene groups in the halogenated propanes were used as variables to predict the chemical shifts of trifluoromethyl and chlorodifluoromethyl groups. The chemical shift data were expressed, as a result, by a simple linear combination of the substituents, which further allowed the prediction of ^{19}F chemical shifts of halogenated propanes whose chemical shifts have not been reported. Table 6 shows the substituent parameters (regression coefficients) of the multiple regression equation. Values are determined so that the value of the difluoromethylene group may become zero. The relationships between the observed and calculated ^{19}F chemical shifts are shown in Figs 6(a) and 6(b).

The substituent parameters for trifluoromethyl and chlorodifluoromethyl groups are of the same order. As for the methylene groups, the order agrees with the vicinal effect mentioned above. Also, values of the

TABLE 6

Substituent parameters (regression coefficients) for CF_3 and $CClF_2$ in halogenated propanes

R	CF_3	$CClF_2$
CH_3	−45.79	−38.62
CH_2F	−43.59	−37.12
CH_2Cl	−42.69	−36.52
CHF_2	−41.59	−36.48
CF_3	−41.39	−36.18
$CHClF$	−40.59	−34.91
$CClF_2$	−39.43	−33.88
$CHCl_2$	−38.83	−31.87
CCl_2F	−36.59	−30.98
CCl_3	−34.13	−27.82
CF_2	0	0
$CClF$	+3.40	+4.56
CCl_2	+5.25	+9.33

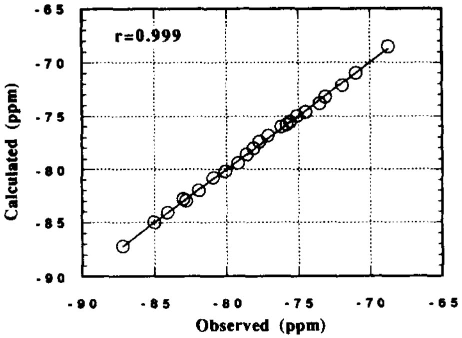

Fig. 6. (a) Observed *vs.* calculated ^{19}F chemical shifts for CF_3 in CF_3CXY–R.

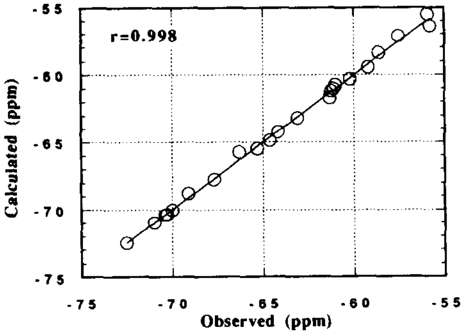

Fig. 6. (b) Observed *vs.* calculated ^{19}F chemical shifts for $CClF_2$ in $CClF_2CXY$–R.

methyl groups lie in order of substituent bulkiness; the bulkier the substituent, the higher the induced frequency shift.

These results led us to conclude that van der Waals interaction [13–15] between X^1-Y^1 and X^2-Y^2, *i.e.* the interaction between the two terminal substituents, plays an important role in determining the ^{19}F chemical shifts for the terminal substituents. Van der Waals forces in the molecule affect the neighboring fluorine atoms by distorting their electron clouds and decreasing the shielding of any attached fluorine atoms.

The ^{19}F chemical shifts for fluoromethyl, difluoromethyl and chlorofluoromethyl groups

As described so far, the ^{19}F chemical shifts of trifluoromethyl and chlorodifluoromethyl groups are affected by the bulkiness of the terminal substituents because of van der Waals interaction between the fluorine atom and the terminal substituent. However, this is not the case for the ^{19}F chemical shifts of fluoromethyl, difluoromethyl and chlorofluoromethyl groups, as shown in Table 7. In order to clarify the reason for the inconsistency, conformational analysis using MNDO calculations was performed on the 15 compounds in Table 7. The following two populations were determined from the populations of rotamers in each compound, calculated on the basis of the differences in their heats of formation.

TABLE 7

^{19}F chemical shifts for CH_2F, CHF_2, CHClF and *r*(F-X), *r*(*trans*) in halogenated propanes

Compounds	δ_F (ppm)	*r*(F-H)	*r*(F-Cl)	*r*(F-F)	*r*(*trans*)
CH_2F-CF_2CH_3	−233.7	0.509	0	0	0.491
CH_2F-CF_2CF_3	−243.7	0	0	0.558	0.442
CH_2F-CF_2CHCl_2	−239.2	0.231	0.065	0	0.704
CHF_2-CF_2CH_3	-	1	0	0	0.727
CHF_2-CF_2CF_3	−138.0	0	0	1	0.760
CHF_2-CF_2CHCl_2	−138.1	0.812	0.222	0	0.963
CHF_2-CF_2CCl_3	−131.8	0	1	0	0.987
CHClF-CF_2CH_3	−151.7	0.413	0	0	0.587
CHClF-CF_2CF_3	−155.6	0	0	0.809	0.191
CHClF-CF_2CHCl_2	−155.9	0.012	0.078	0	0.970
CHClF-CF_2CCl_3	−145.3	0	0.297	0	0.703
$CClF_2$-CF_2CH_3	−72.5	1	0	0	0.949
$CClF_2$-CF_2CF_3	−70.0	0	0	1	0.381
$CClF_2$-CF_2CHCl_2	−66.3	0.224	0.837	0	0.934
$CClF_2$-CF_2CCl_3	−61.3	0	1	0	0.813

***r*(F–X), X = H, Cl, F**: *r*(F–X) is the sum of the rotamer population where a fluorine atom of fluoromethyl, difluoromethyl or chlorofluoromethyl group and a halogen or hydrogen atom of the terminal substituent is in the X^1–X^2 or Y^1–Y^2 position of Fig. 2. Van der Waals interaction is supposed to exist between F and X in this case.

***r(trans)*:** *r(trans)* is the sum of the rotamer population where a fluorine atom of fluoromethyl, difluoromethyl or chlorofluoromethyl group is in the Z^2 position of Fig. 2. In this position the fluorine atom would have little interaction with the terminal substituent.

Although the dichloromethyl group is one of the bulkiest substituents, ^{19}F chemical shifts for fluoromethyl or chlorofluoromethyl groups are low-frequency shifted when the terminal substituent changes from a methyl group to a dichloromethyl group, contrary to our expectations. On the other hand, when the terminal substituent is a trichloromethyl group, the ^{19}F chemical shifts for difluoromethyl or chlorofluoromethyl groups are high-frequency shifted, as we would expect. The *r*(F–Cl) values in Table 7 show the difference between the two substituents; *r*(F–Cl) values of the compounds with a dichloromethyl group are much smaller than those of the compounds with a trichloromethyl group, which means a fluorine atom of fluoromethyl, difluoromethyl or chlorofluoromethyl groups favors the position that has less interaction with the terminal substituent. The ^{19}F chemical shifts of the fluoromethyl, difluoromethyl or chlorofluoromethyl group, therefore, cannot be necessarily related with the bulkiness of the terminal substituent.

^{19}F chemical shifts of diastereomers

Diastereomers may be defined as stereoisomers that are not enantiomers. They have different physical, chemical and spectral properties. We report the ^{19}F NMR data and the results of conformational analysis of diastereomers of 2,3-dichloro-1,1,2,3-tetrafluoropropane (225ba), 1,2,3-trichloro-1,1,2,3-tetrafluoropropane (224bb) and 1,3-dichloro-1,1,2,3-tetrafluoropropane (234eb)*.

There are four isomers of 225ba and 224bb: two pairs of enantiomers, and these pairs are diastereomers, as shown in Fig. 7. One of the enantiomers is shown. A part of the ^{19}F NMR data for diastereomers of 225ba, 224bb and 234eb is listed in Table 8. At ordinary temperature the C–C bond in a molecule rotates rapidly, though it still spends most of its time

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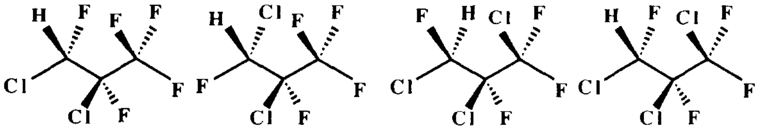
*American Society of Refrigerating Engineers (ASRE) devised the ASRE Standard 34 [16(a)] for methane, ethane and cycloalkane refrigerants. The coding system has been extended [16(b)] unofficially to include other fluoroaliphatics.

The first digit on the right is the number of fluorine atoms, the second digit from the right is one more than the number of hydrogen atoms, and the third digit from the right is one less than the number of carbon atoms in the compound. The first appended letter indicates the substitution on the central carbon. The second appended letter indicates the substitution at C1 and C3 carbons.



(2R,3S)-225ba (2R,3R)-225ba (2S,3R)-224bb (2S,3S)-224bb

Fig. 7. Diastereomers of 225ba and 224bb.

TABLE 8

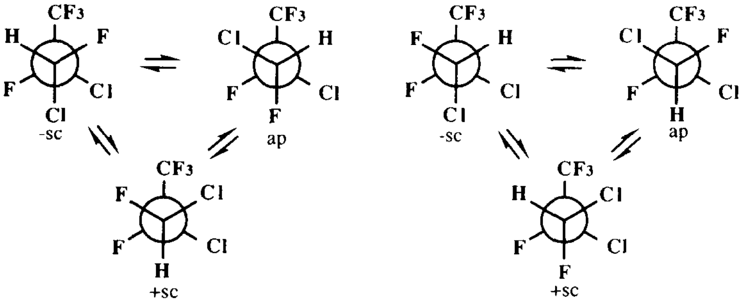
^{19}F chemical shifts (ppm) for methylene F and coupling constants ^3J (Hz)[a]

$CF_3CClFCHClF$					
225ba (I)	−132.6	J(F–H) = 2	J(F–F) = 24		
225ba (II)	−138.6	J(F–H) = 10	J(F–F) = 20		
$CClF_2CClFCHClF$					
224bb (I)	−124.9	J(F–H) = 1	J(F–F) = 24		
224bb (II)	−132.4	J(F–H) = 10	J(F–F) = 19		
$CClF_2CHFCHClF$					
234eb (I)	−195.4	J(H–H) = 6	J(H–F) = 6	J(F–H) = 7	J(F–F) = 25
234eb (II)	−201.8	J(H–H) = 3	J(H–F) = 15	J(F–H) = 13	J(F–F) = 12

[a] J(X–Y): X in the methylene, Y in the chlorofluoromethyl group.

at or near the energy minimum. Consideration of rotamers at the energy minimum is sufficient to discuss the conformation of molecules at ambient temperature. Figure 8 shows three rotamers of 225ba. As for 224bb and 234eb, there are three rotamers for both the 1-carbon and 3-carbon, as shown in Fig. 9, therefore 224bb and 234eb have nine rotamers in total. Table 9 shows the populations of rotamers determined on the basis of the differences in their heats of formation calculated by AM1 [17].

H–F coupling constants are sometimes very useful in determining molecular structures. ^3J (H–F) in saturated compounds is dependent on



225ba(I) 225ba(II)

Fig. 8. Rotamers of 225ba.

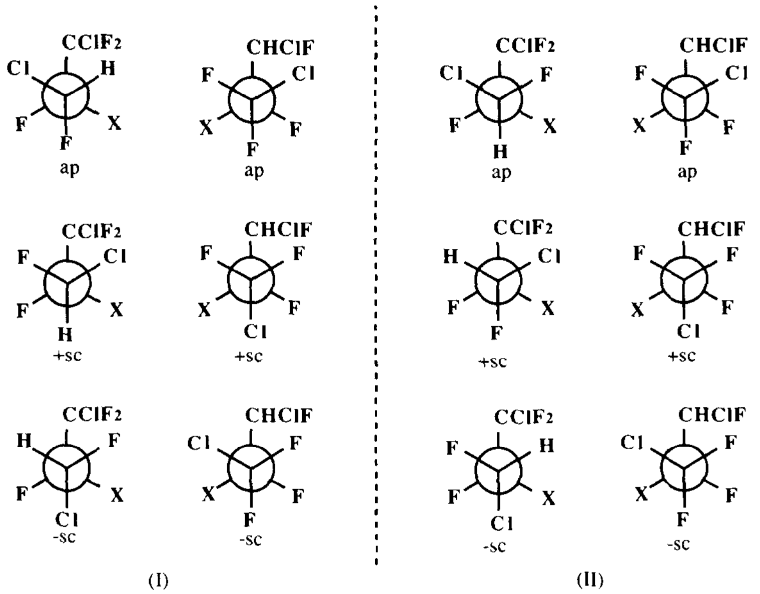


Fig 9 Rotamers of 224bb (X = Cl) and 234eb (X = H)

TABLE 9

Calculated populations of rotamers

$CF_3CClFCHClF$ (I)[a]	ap	0.049	$CF_3CClFCHClF$ (II)[a]	ap	0.010
225ba(I)	+sc	0.170	225ba(II)	+sc	0.271
	−sc	0.781		−sc	0.719
$CClF_2CClFCHClF$ (I)[b]	ap, ap	0.002	$CClF_2CClFCHClF$ (II)[b]	ap, ap	0.001
224bb(I)	ap, +sc	0.021	224bb(II)	ap, +sc	0.006
	ap, −sc	0.055		ap, −sc	0.001
	+sc, ap	0.006		+sc, ap	0.013
	+sc, +sc	0.050		+sc, +sc	0.055
	+sc, −sc	0.188		+sc, −sc	0.174
	−sc, ap	0.118		−sc, ap	0.004
	−sc, +sc	0.423		−sc, +sc	0.323
	−sc, −sc	0.138		−sc, −sc	0.424
$CClF_2CHFCHClF$ (I)[b]	ap, ap	0.054	$CClF_2CHFCHClF$ (II)[b]	ap, ap	0.004
234eb(I)	ap, +sc	0.005	234eb(II)	ap, +sc	0.068
	ap, −sc	0.320		ap, −sc	0.071
	+sc, ap	0.051		+sc, ap	0.008
	+sc, +sc	0.053		+sc, +sc	0.141
	+sc, −sc	0.177		+sc, −sc	0.152
	−sc, ap	0.067		−sc ap	0.005
	−sc, +sc	0.125		−sc, +sc	0.200
	−sc, −sc	0.147		−sc, −sc	0.349

[a] See Fig 8

[b] See Fig 9, combination of left and right (ap, ±sc) rotamers.

TABLE 10

^{19}F chemical shifts for F in the methylene group and average number of gauche pairs of atoms in F in CF_2

Compounds	δ_F (ppm)	Gauche pairs					
		H–H	H–Cl	H–F	Cl–Cl	Cl–F	F–F
$CF_3CClFCHClF$ (I)	−132.6	0	0.781	0.17	0	0.049	1
$CF_3CClFCHClF$ (II)	−138.6	0	0.01	0.271	0	0.719	1
$CClF_2CClFCHClF$ (I)	−124.9	0	0.679	0.244	0	0.698	0.381
$CClF_2CClFCHClF$ (II)	−132.4	0	0.008	0.242	0	1.153	0.599
$CClF_2CHFCHClF$ (I)	−195.4	0	0.645	0.183	0	0.832	0.340
$CClF_2CHFCHClF$ (II)	−201.8	0	0.017	0.408	0	1.015	0.554

the dihedral angle, ϕ, between C–H and C–F bonds [18, 19] as given by eqn. (7), well known as Karplus' equation:

$$^3J(\text{H–F}) = A + B\cos\phi + C\cos^2\phi \qquad (7)$$

In this equation, ^3J(H–F) is at a maximum when F is *trans* to H. Comparision of the ^3J(H–F) value with the population of rotamers has assigned 225ba(II) to (2*RS*, 3*SR*)-225ba, which has the larger ^3J(H–F) value (10.2 Hz), and 225ba(I) to (2*RS*, 3*RS*)-225ba. 224bb(I) and 224bb(II) were assigned to (2*SR*, 3*RS*)-224bb, (2*SR*, 3*SR*)-224bb, respectively. Also, diastereomers of 234eb were assigned in the same way.

^{19}F chemical shifts for a fluorine atom in the methylene group and the average number of gauche pairs of atoms to a fluorine atom of the methylene group are listed in Table 10. A fluorine atom that has more Cl–F or F–F gauche pairs gives a lower-frequency chemical shift than a fluorine atom that has more H–Cl gauche pairs. This agrees with the results, as described above, that the pairs of atoms gauche to a fluorine atom in a difluoromethylene group contribute to low-frequency shifts of a difluoromethylene group in ^{19}F NMR.

Conclusion

Vicinal effect

The ^{19}F chemical shifts for the trifluoromethyl groups in 2,2-substituted-1,1,1-trifluoropropanes (CF_3–CXY–R) depend on the magnetic anisotropy of the methylene substituents.

The pairs of atoms gauche to a fluorine atom of a difluoromethylene group in 2,2-difluoropropanes (R^1–CF_2–R^2) contribute to low-frequency shifts of a difluoromethylene group in the order:

F–F > H–F > Cl–F > H–Cl > Cl–Cl > H–H

Long range effects

van der Waals interaction between the two terminal substituents is responsible for the ^{19}F chemical shifts for the terminal fluorine-containing substituents.

^{19}F chemical shifts of diastereomers

In diastereomers of halogenated propanes, a methylene fluorine atom that has more Cl–F or F–F gauche pairs shows lower-frequency ^{19}F chemical shifts than a fluorine atom that has more H–Cl gauche pairs.

Experimental

NMR spectra

NMR spectra were measured in the pulse Fourier transform mode with a JNM-EX-90 (JEOL) operating at 84.2 MHz (^{19}F) and 89.5 MHz (^{1}H). 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) upfield from CCl_3F (^{19}F) and downfield from TMS (^{1}H).

Mass spectra

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

Calculations

MNDO and AM1 calculations were performed on a Titan 3000 computer with full geometry optimization using a MOPAC 5.0 program [20].

Purification and identification of products

The reaction mixture was distilled to obtain pure products or the mixture of isomers. Each isomer was separated and collected by gas chromatography (silicone KF-96, GL Sciences). The identification of the products was made by ^{19}F NMR, ^{1}H NMR and mass spectroscopy.

Preparation of 3-chloro-1,1,2,2-tetrafluoropropane (244ca)

3-Chloro-1,1,2,2-tetrafluoropropane was prepared by the reaction of 1,1,2,2-tetrafluoropropanol (20 g, 0.15 mol) with tolysulfonyl chloride (30.7 g, 0.16 mol) followed by chlorination with lithium chloride as in the literature [21] (total yield: 80%).

Preparation of 1,1-dichloro-2,2,3,3-tetrafluoropropane (234cb) and 1,1,1-trichloro-2,2,3,3-tetrafluoropropane (224cc)

A solution of 3-chloro-1,1,2,2-tetrafluoropropane (0.66 g, 4.4 mmol) and chlorine gas (0.32 g, 0.45 mmol) in 4 g of tetrachloromethane was exposed to an ultraviolet lamp at 0 °C for 2 h. The conversion of the starting material was 57% and the selectivities of the products were as follows: 1,1-dichloro-2,2,3,3,-tetrafluoropropane (234cb, 72%), 1,1,1-trichloro-2,2,3,3-tetrafluoropropane (224cc, 21%), 1,3-dichloro-1,1,2,2-tetrafluoropropane (234cc, 3%), 1,1,3-trichloro-2,2,3,3-tetrafluoropropane (224ca, 2%), 1,1,1,3-tetrachlorotetrafluoropropane (214cb, 2%).

Reaction of chlorotrifluoroethylene and chlorodifluoromethane

Chlorotrifluoroethylene (200 g, 1.72 mol) and aluminum trichloride (16 g, 0.12 mol) were charged into a 500 ml autoclave. The autoclave was cooled to -30 °C and chlorodifluoromethane (100 g, 1.16 mol) was added slowly. Then the mixture was kept stirring at 0–10 °C for 10 h. The products were as follows: 2,2-dichloro-1,1,1,3,3-pentafluoropropane (225aa, 2.4%), 2,3-dichloro-1,1,1,2,3-pentafluoropropane (225ba, diastereomer **I**, 6.9%), 2,3-dichloro-1,1,1,2,3-pentafluoropropane (225ba, diastereomer **II**, 6.6%), 2,3-dichloro-1,1,2,3,3-pentafluoropropane (225bb, 2.3%), 3,3-dichloro-1,1,1,2,2-pentafluoropropane (225ca, 0.6%), 1,3-dichloro-1,1,2,2,3-pentafluoropropane (225cb, 12.4%), 1,1-dichloro-1,2,2,3,3,-pentafluoropropane (225cc, 1.5%). 2,2,3-trichloro-1,1,1,3-tetrafluoropropane (224aa, 4.4%), 1,2,2-trichloro-1,1,3,3-tetrafluoropropane (224ab, 0.5%), 2,3,3-trichloro-1,1,1,2-tetrafluoropropane (224ba, 12.5%), 1,2,3-trichloro-1,1,2,3-tetrafluoropropane (224bb, diastereomer **I**, 3.6%), 1,2,3-trichloro-1,1,2,3-tetrafluoropropane (224bb, diastereomer **II**, 6.3%), 1,3,3-trichloro-1,1,2,2-tetrafluoropropane (224ca, 30.5%), 1,1,3-trichloro-1,2,2,3-tetrafluoropropane (224cb, 8.9%), chloroform (1.3%); others (1.4%).

Reaction of 1,1-dichloro-2,2-difluoroethylene and dichlorofluoromethane

A 1 000 ml three-necked flask fitted with a stirrer and a reflux condenser was charged with 1,1-dichloro-2,2-difluoroethylene (665 g, 5.0 mol) and aluminum trichloride (66 g, 0.5 mol). The mixture was cooled to 0 °C in an ice bath and stirred vigorously. Then dichlorofluoromethane (515 g, 5.0 mol) was added carefully. After stirring 10 h at 0 °C, the reaction mixture was distilled to give tetrachlorotrifluoropropanes (yield, 98%). The products were as follows: 2,2,3,3-tetrachloro-1,1,1-trifluoropropane (223aa, 5.3%), 1,2,2,3-tetrachloro-1,1,3-trifluoropropane (223ab, 16.1%), 1,1,3,3-tetrachloro-1,2,2-trifluoropropane (223ca, 78.5%), 1,1,1,3-tetrachloro-2,2,3-trifluoropropane (223cb, trace); others (1.2%).

Hydrogenation of 1,1,3,3-tetrachloro-1,2,2-trifluoropropane (223ca)

At 0.5 inch i.d. and 24 inch long Inconel tube reactor was charged with 100 ml of Pt/C (granules, Pt = 0.5 wt.%) catalyst and heated at 120 °C. 1,1,3,3-Tetrachloro-1,2,2-trifluoropropane (223ca) and hydrogen were fed at the rate of 75 and 225 ml/min, respectively. The reactant gas was passed through the aqueous alkali (Na_2CO_3) solution and trapped in a dry ice–acetone bath. The products were distilled to give several compounds as follows: 1,1,3-trichloro-2,2,3-trifluoropropane (233ca, 11%), 1,1,3-trichloro-1,2,2,-trifluoropropane (233cb, 29%), 1,3-dichloro-1,2,2-trifluoropropane (243ca, 1%), 1,1-dichloro-2,2,3-trifluoropropane (243cb, 1%), 1,1-dichloro-1,2,2-trifluoropropane (243cc, 17%), 1,1-dichloro-2,2-difluoropropane (252cb, 1%), 1,1,3,3-tetrachloro-1,2,2-trifluoropropane (starting material, 223ca, 35%); others (5%).

Hydrogenation of 1,1,3-trichloro-1,2,2-trifluoropropane (233cb)

A 0.5 inch i.d. and 24 inch long Inconel tube reactor was charged with 100 ml of Pt/C (granules, Pt = 0.5 wt.%) catalyst and heated at 200 °C. 1,1,3-Trichloro-1,2,2-trifluoropropane (233cb) and hydrogen were fed at the rate of 75 and 225 ml/min, respectively. The reactant gas was passed through the aqueous alkali (Na_2CO_3) solution and trapped in a dry ice–acetone bath. The products were distilled to give several compounds as follows: 1,1-dichloro-1,2,2-trifluoropropane (243ca, 62%), 1,1-dichloro-1,2,2,-trifluoropropane (243cc, 1%), 1-chloro-2,2,3-trifluoropropane (253ca, 7%), 1-chloro-1,2,2-trifluoropropane (253cb, 9%), 1,2,2-trifluoropropane (263ca, 11%), 1,1,3-trichloro-1,2,2-trifluoropropane (starting material 233cb, 8%); others (2%).

Fluorination of 1,3,3-trichloro-1,1,2,2-tetrafluoropropane (224ca)

A 0.5 inch i.d. and 24 inch long Inconel tube reactor was charged with 100 ml of Cr_2O_3 catalyst and heated at 280 °C. 1,3,3-trichloro-1,1,2,2-tetrafluoropropane (224ca) and hydrogen fluoride were fed at a rate of 200 ml/min. The molar ratio HF/224ca was 3. The reactant gas was passed through the aqueous alkali (Na_2CO_3) solution and trapped in a dry ice–acetone bath. The products were distilled to give several compounds as follows: 1,3,3-trichloro-1,1,2,2-tetrafluoropropane (224ca, 30%), 3,3-dichloro-1,1,1,2,2-pentafluoropropane (225ca, 5%), 1,3-dichloro-1,1,2,2,3-pentafluoropropane (225cb, 44%), 3-chloro-1,1,1,2,2,3-hexafluoropropane (226ca, 3%), 1-chloro-1,1,2,2,3,3-hexafluoropropane (226cb, 16%); others (2%).

Reaction of tetrafluoroethylene and trichlorofluoromethane

Trichlorofluoromethane (700 g, 5.1 mol) and aluminum trichloride (28 g, 0.21 mol) were charged into a 1000 ml autoclave. The autoclave was cooled to −30 °C and tetrafluoroethylene (530 g, 0.53 mol) was added slowly, keeping the temperature in the range from 30 to 50 °C. After adding tetrafluoroethylene, the autoclave was kept stirring for 10 h. The reaction mixture was distilled to give several compounds as follows: 1,3-dichlorohexafluoropropane (216ca, 0.3%), 1,1-dichlorohexafluoropropane (216cb, 2.7%), 1,1,1-trichloropentafluoropropane (215cb, 74%), 1,1,1,3-tetrachlorotetrafluoropropane (214cb, 13%); others (10%).

Hydrogenation of 1,3,3-trichloro-1,1,2,2-tetrafluoropropane (244ca)

A 0.5 inch i.d. and 24 inch long Inconel tube reactor was charged with 100 ml of Pd/C (granules, Pd = 0.5 wt.%) catalyst and heated at 200 °C. 1,3,3-trichloro-1,1,2,2-tetrafluoropropane (224ca) and hydrogen were fed at the rate of 60 and 240 ml/min, respectively. The reactant gas was passed through the aqueous alkali (Na_2CO_3) solution and trapped in a dry ice–acetone bath. The products were distilled to give several compounds as follows: 1,3-dichloro-1,1,2,2-tetrafluoropropane (234cc, 28%), 1-chloro-1,1,2,2-tetrafluoropropane (244cc, 69%); others (3%).

Preparation of 2,3,3-trichloro-1,1,1-trifluoropropane (233da)

2,3,3-Trichloro-1,1,1-trifluoropropene (8.0 g, 0.04 mol) in 50 g of ethanol and 3 g of Pt/C (powder, Pt = 0.5 wt.%) catalyst were charged in a 200 ml autoclave. Then hydrogen was charged slowly into the reactor to a pressure of 8 atm. After the reaction mixture was stirred for 5 h at ambient temperature, the reactant was washed with water. 2,3,3-trichloro-1,1,1-trifluoropropane (233da) was obtained in 10% yield.

Reaction of trifluoroethylene and dichlorofluoromethane

Dichlorofluoromethane (167 g, 1.62 mol) and aluminum trichloride (8 g, 0.06 mol) were charged into a 200 ml autoclave. The autoclave was cooled to −30 °C and trifluoroethylene (140 g, 1.7 mol) was added slowly, keeping the temperature in the range from 0 to 10 °C. The autoclave was kept stirred for 2 h. The reaction mixture then was distilled to give several compounds as follows: 3,3-dichloro-1,1,1,2-tetrafluoropropane (234ea, 52%), 1,3-dichloro-1,1,2,3-tetrafluoropropane (234eb **I** diastereomer, 22%), 1,3-dichloro-1,1,2,3-tetrafluoropropane (234eb **II** diastereomer, 14%), chloroform (5%); others (7%).

Reaction of 1,1-difluoroethylene and dichlorofluoromethane

Dichlorofluoromethane (500 g, 4.85 mol) and aluminum trichloride (30 g, 0.23 mol) were charged into a 500 ml autoclave. The autoclave was cooled to −30 °C and 1,1-difluoroethylene (320 g, 5.0 mol) was added slowly, keeping the temperature in the range from 0 to 10 °C. The autoclave was kept stirred for 5 h. The reaction mixture was then distilled to give 3,3-dichloro-1,1,1-trifluoropropane (243fa) in 50% yield.

Spectral data

All compounds in Table 2 were obtained commercially (PCR Inc.). The following data were recorded in our laboratory (except 218ca, 232ca, 232cb, 236ca, 236cb, 242cb, and 272ca). Literature references are given for the compounds that have been previously reported.

1,1,1,3,3,3-Hexachlorodifluoropropane (212ca) [4]: ^{19}F NMR $\delta = -98.1$ (s).

1,1,1,2,2-Pentachlorotrifluoropropane (213ab) [6]: ^{19}F NMR $\delta = -68.7$ (s).

1,1,1,3,3-Pentachlorotrifluoropropane (213ca) [4]: ^{19}F NMR $\delta = -63.7$ (1F, t, $^3J = 4$ Hz), -103.5 (2F, d, $^3J = 4$ Hz).

1,2,2,3-Tetrachlorotetrafluoropropane (214aa) [6]: ^{19}F NMR $\delta = -58.6$ (s).

1,1,3,3-Tetrachlorotetrafluoropropane (214ca) [6]: ^{19}F NMR $\delta = -66.6$ (2F, t, $^3J = 7$ Hz), -108.7 (2F, d, $^3J = 7$ Hz).

*1,1,1,3-*Tetrachlorotetrafluoropropane (214cb) [6]: ^{19}F NMR $\delta = -61.3$ (2F, s), -108.0 (2F, s).

1,2,2-Trichlorotetrafluoropropane (215aa) [6]: ^{19}F NMR $\delta = -61.0$ (2F, q, $^4J = 11.9$ Hz), -73.5 (3F, t, $^4J = 11.9$ Hz).

1,1,3-Trichloropentafluoropropane (215ca) [6]: ^{19}F NMR $\delta = -64.6$ (2F, d, $^4J = 13.7$ Hz), -70.9 (1F, dt, $^3J = 7.0$, $^4J = 13.7$ Hz), -113.8 (2F, d $^3J = 7.0$ Hz).

1,1,1-Trichloropentafluoropropane (215cb) ([21], no NMR data): ^{19}F NMR $\delta = -75.6$ (3F, s), -114.5 (2F, s); *m/e*: 69($CF_3{}^+$), 117,119($CCl_3{}^+$), 201($M^{+\cdot} - Cl$).

1,3-Dichlorohexafluoropropane (216ca) [6]: ^{19}F NMR $\delta = -67.7$ (4F, s), -119.2 (2F, s).

1,1-Dichlorohexafluoropropane (216cb): ^{19}F NMR $\delta = -73.1$ (1F, sext, $^3J = 7.7$ and $^4J = 10.4$ Hz), -78.2 (3F, d, $^4J = 10.4$ Hz), -120.0 (2F, d, $^3J = 7.7$ Hz); *m/e*: 69($CF_3{}^+$), 151($CCl_2FCF_2{}^+$), 201 ($M^+ - F$).

2-Chloroheptafluoropropane (217ba): ^{19}F NMR $\delta = -79.2$ (6F, d, $^3J = 7.2$ Hz), -141.4 (1F, hept, $^3J = 7.2$ Hz).

1-Chloroheptafluoropropane (217ca) [4]: ^{19}F NMR $\delta = -69.8$ (2F, q, $^4J = 9.3$ Hz), -80.9 (3F, t, $^4J = 9.3$ Hz), -125.3 (2F, s).

1,1,2,2,3-Pentachloro-3,3-difluoropropane (222aa) ([23], no NMR data): ^{19}F NMR $\delta = -55.9$ (s); ^{1}H NMR $\delta = 6.23$ (s).

Octafluoropropane (218ca) [4]: ^{19}F NMR $\delta = -83.0$ (6F, t, $^4J = 7.3$ Hz), -131.5 (2F, t, $^4J = 7.3$ Hz).

1,1,1,3,3-Pentachloro-2,2-difluoropropane (222ca) [10]: ^{19}F NMR $\delta = -106.2$ (d, $^3J = 10.3$ Hz); ^{1}H NMR $\delta = 6.38$ (t, $^3J = 9.0$ Hz).

2,2,3,3-Tetrachloro-1,1,1-trifluoropropane (223aa): ^{19}F NMR $\delta = -73.1$ (s); ^{1}H NMR $\delta = 6.10$ (s); *m/e*: 69($CF_3{}^+$), 83($CHCl_2{}^+$), 151($CF_3CCl_2{}^+$).

1,2,2,3-Tetrachloro-1,1,3-trifluoropropane (223ab): ^{19}F NMR $\delta = -59.0$ and -59.3 (2F, apparent dd, $^4J = 16.5$ and 14.4 Hz), -134.0 (1F ddd, $^2J = 49.4$, $^4J = 16.5$ and 14.4 Hz); ^{1}H NMR $\delta = 6.56$ (d, $^2J = 48.8$ Hz); *m/e*: 67 ($CHClF^+$), 85($CClF_2{}^+$), 199($M - Cl$).

1,2,3,3-Tetrachloro-1,1,2-trifluoropropane (223ba) [24]: ^{19}F NMR $\delta = -60.8$ (1F, dd, $^2J = 169$, $^3J = 9.3$ Hz), -61.7 (1F, dd, $^2J = 169$, $^3J = 7.2$ Hz), -114.9 (1F, ddd, $^3J = 9.3$, 7.2 and 4.3 Hz); ^{1}H NMR $\delta = 6.21$ (d, $^3J = 4.3$ Hz).

1,1,3,3-Tetrachloro-1,2,2-trifluoropropane (223ca) [25]: ^{19}F NMR $\delta = -66.4$ (1F, t, $^3J = 7.2$ Hz), -112.2 (2F, dd, $^3J = 7.2$ and 9.0 Hz); ^{1}H NMR $\delta = 6.26$ (t, $^3J = 9.0$ Hz).

1,1,1,3-Tetrachloro-2,2,3-trifluoropropane (223cb) [25]: ^{19}F NMR $\delta = -105.7$ (1F, dd, $^2J = 251$, $^3J = 11.3$ Hz), -121.8 (1F, dt, $^2J = 251$,

$^{3}J = 14.4$ Hz), -145.3 (1F, ddd, $^{2}J = 47.4$, $^{3}J = 14.7$ and 10.8 Hz); ^{1}H NMR $\delta = 6.49$ (ddd, $^{2}J = 46.4$, $^{3}J = 15.1$ and 1.0 Hz).

2,2,3-Trichloro-1,1,1,3-tetrafluoropropane (224aa): ^{19}F NMR $\delta = -75.1$ (3F, d, $^{4}J = 11.3$ Hz), -135.2 (1F, dq, $^{2}J = 48.8$, $^{4}J = 11.3$ Hz); ^{1}H NMR $\delta = 6.45$ (d, $^{2}J = 48.4$ Hz); *m/e*: 67($CHClF^{+}$), 69(CF_3^{+}), 183($M^{+} - Cl$).

1,2,2-Trichloro-1,1,3,3-tetrafluoropropane (224ab): ^{19}F NMR $\delta = -61.1$ (2F, t, $^{4}J = 9.8$ Hz), -123.0 (2F, dt, $^{2}J = 54.1$, $^{4}J = 9.5$ Hz); ^{1}H NMR $\delta = 6.12$ (t, $^{2}J = 54.4$ Hz); *m/e*: 51(CHF_2^{-}), 85($CClF_2^{-}$), 183($M^{+} - Cl$).

2,3,3-Trichloro-1,1,1,2-tetrafluoropropane (224ba) [24]: ^{19}F NMR $\delta = -77.1$ (3F, d, $^{3}J = 5.1$ Hz), -122.3 (1F, qd, $^{3}J = 5.1$ Hz); ^{1}H NMR $\delta = 6.08$ (d, $^{3}J = 5.1$ Hz).

1,2,3-Trichloro-1,1,2,3-tetrafluoropropane, diastereomer **I** (224bb): ^{19}F NMR $\delta = -64.3$ (1F, dd, $^{4}J = 13.1$, $^{3}J = 10.7$ Hz), -64.6 (1F, dd, $^{4}J = 13.1$, $^{3}J = 10.7$ Hz), -124.9 (1F, dt, $^{3}J = 23.7$ and 10.0 Hz), -143.8 (1F, m, $^{2}J = 48.5$, $^{3}J = 24.8$, $^{4}J = 12.4$ Hz); ^{1}H NMR $\delta = 6.59$ (dd, $^{2}J = 48.3$, $^{3}J = 1$ Hz); *m/e*: 67($CHClF^{+}$), 85($CClF_2^{+}$), 116($CClF_2CF^{-}$).

1,2,3-Trichloro-1,1,2,3-tetrafluoropropane, diastereomer **II** (224bb): ^{19}F NMR $\delta = -63.8$ (1F, td, $^{4}J = 11.3$, $^{3}J = 9.3$ Hz), -64.0 (1F, td, $^{4}J = 11.3$, $^{3}J = 9.3$ Hz), -132.4 (1F, dtd, $^{3}J = 19.1$ and 9.3 Hz), -144.7 (1F, ddt, $^{2}J = 48.4$, $^{3}J = 18.6$, $^{4}J = 12.3$ Hz); ^{1}H NMR $\delta = 6.49$ (dd, $^{2}J = 46.5$, $^{3}J = 9.9$ Hz); *m/e*: 67($CHClF^{+}$), 85($CClF_2^{+}$), 116($CClF_2CF^{+}$).

1,3,3-Trichloro-1,1,2,2-tetrafluoropropane (224ca) [24]: ^{19}F NMR $\delta = -66.3$ (2F, s); ^{1}H NMR $\delta = 6.04$ (t, $^{3}J = 9.0$ Hz).

1,1,3-Trichloro-1,2,2,3-tetrafluoropropane (224cb) [24]: ^{19}F NMR $\delta = -71.4$ (1F, ddd, $^{3}J = 10.3$ and 7.2, $^{4}J = 17.5$ Hz), -112.9 (1F, dd, $^{2}J = 263$, $^{3}J = 11.6$ and 7.5 Hz), -125.1 (1F, ddd, $^{2}J = 263$, $^{3}J = 12.9$, 12.6 and 10.4 Hz), -150.9 (1F, m); ^{1}H NMR $\delta = 6.64$ (ddd, $^{2}J = 47.4$, $^{3}J = 12.5$ and 2 Hz).

1,1,1-Trichloro-2,2,3,3-tetrafluoropropane (224cc): ^{19}F NMR $\delta = -120.0$ (2F, dt, $^{3}J = 7$ and 6 Hz), -131.8 (2F, dt, $^{2}J = 53$, $^{3}J = 7$ Hz); ^{1}H NMR $\delta = 6.32$ (tt, $^{2}J = 52.5$, $^{3}J = 5.7$ Hz); *m/e*: 51(CHF_2^{+}), 117, 119(CCl_3^{+}), 183 ($M^{+} - Cl$).

2,2-Dichloro-1,1,1,3,3-pentafluoropropane (225aa): ^{19}F NMR $\delta = -76.2$ (3F, t, $^{4}J = 8.2$ Hz), -124.5 (2F, dq, $^{2}J = 54.2$, $^{4}J = 8.3$ Hz); ^{1}H NMR $\delta = 6.03$ (t, $^{2}J = 54.4$ Hz); *m/e*: 51 (CHF_2^{+}), 69(CF_3^{+}), 133($CHF_2CCl_2^{+}$).

2,3-Dichloro-1,1,1,2,3-pentafluoropropane, diastereomer **I** (225ba) [24]: ^{19}F NMR $\delta = -79.1$ (3F, dd, $^{4}J = 9.3$, $^{3}J = 7.2$ Hz), -132.6 (1F, dqq, $^{3}J = 23.9$, 7.3 and 2 Hz), -145.7 (1F, ddq, $^{2}J = 48.0$, $^{3}J = 24.4$, $^{4}J = 9.5$ Hz); ^{1}H NMR $\delta = 6.47$ (dd, $^{2}J = 48.3$, $^{3}J = 2.1$).

2,3-Dichloro-1,1,1,2,3-pentafluoropropane, diastereomer **II** (225ba) [24]: ^{19}F NMR $\delta = -78.1$ (3F, dd, $^{4}J = 10.3$, $^{3}J = 5.2$ Hz), -138.6 (1F, ddq, $^{3}J = 18.8$, 10.2 and 5.1 Hz), -146.1 (1F, ddq, $^{2}J = 48.4$, $^{3}J = 19.8$, $^{4}J = 10.0$ Hz); ^{1}H NMR $\delta = 6.37$ (ddq, $^{2}J = 48.3$, $^{3}J = 10.2$, $^{4}J = 0.3$ Hz).

1,2-Dichloro-1,1,2,3,3-pentafluoropropane (225bb): ^{19}F NMR $\delta = -65.7$ (2F, apparently q, $^{4}J = {}^{3}J = 9$ Hz), -136.0 (2F, apparently t, $^{3}J = 11$ Hz), $-133 \sim -135$ (m); ^{1}H NMR: not measured; *m/e*: 51 (CHF_2^{+}), 85($CClF_2^{+}$), 167($M^{-} - Cl$).

3,3-Dichloro-1,1,1,2,2-pentafluoropropane (225ca) ([21], no ^{19}F NMR data): ^{19}F NMR $\delta = -80.1$ (3F, s), -120.6 (2F, d, $^3J = 8.8$ Hz); ^{1}H NMR $\delta = 5.93$ (1H, t, $^3J = 8.9$ Hz).

1,3-Dichloro-1,1,2,2,3-pentafluoropropane (225cb) ([21], no ^{19}F NMR data): ^{19}F NMR $\delta = -69.1$ (2F, d, $^4J = 11.9$ Hz), -118.0 (1F, dd, $^2J = 273$, $^3J = 13.0$ Hz) -128.5 (1F, dd, $^2J = 273$, $^3J = 12.4$ and 15.2 Hz), -153.7 (1F, m); ^{1}H NMR $\delta = 6.45$ (qd, $^2J = 47.5$, $^3J = 12.3$ and 2.6 Hz).

1,1-Dichloro-1,2,2,3,3-pentafluoropropane (225cc): ^{19}F NMR $\delta = -73.4$ (1F, tt, $^3J = 9$, $^4J = 9$ Hz), -124.7 (2F, dtd, $^3J = 9$ and 5 Hz), -134.9 (2F, dtd, $^2J = 52$, $^3J = 9$, $^4J = 9$ Hz); ^{1}H NMR $\delta = 6.17$ (tt, $^2J = 52$, $^3J = 5$); *m/e*: 51(CHF_2^+), 101(CCl_2F^+), 167($M^+ - Cl$).

3-Chloro-1,1,1,2,2,3-hexafluoropropane (226ca): ^{19}F NMR $\delta = -81.9$ (3F, d, $^4J = 8.3$ Hz), -123.8 (1F, dd, $^2J = 281$, $^3J = 12.3$ and 4.1 Hz), -131.6 (1F, ddd, $^2J = 281$, $^3J = 15.0$ and 10.9 Hz); ^{1}H NMR $\delta = 637$ (ddd, $^2J = 47.5$, $^3J = 11.2$ and 3.3 Hz); *m/e*: 67($CHClF^+$), 69(CF_3^+), 167 ($M^+ - F$).

1-Chloro-1,1,2,2,3,3-hexafluoropropane (226cb): ^{19}F NMR $\delta = -70.3$ (2F, tt, $^4J = 8.0$ and $^3J = 3.1$ Hz), -129.3 (2F, m), -136.7 (2F, dtt, $^2J = 52.0$, $^3J = 6.3$, $^4J = 7.7$ Hz); ^{1}H NMR $\delta = 6.06$ (tt, $^2J = 52.0$ and $^3J = 5.0$ Hz); *m/e*: 51(CHF_2^+), 85($CClF_2^+$), 151($M^+ - Cl$).

1,1,1,2,2,3,3-Heptafluoropropane (227ca) [6, 26]: ^{19}F NMR $\delta = -82.8$ (3F, t, $^4J = 7.2$ Hz), -133.2 (2F, dd, $^3J = 4.8$ Hz), -138.0 (2F, dqd, $^2J = 52.0$, $^4J = 7.2$ and 4.8 Hz); ^{1}H NMR $\delta = 5.97$ (ttq, $^2J = 51.8$, $^3J = 4.5$ and $^4J = 0.8$ Hz).

1,1,3,3-Tetrachloro-2,2-difluoropropane (232ca) [10]: ^{19}F NMR $\delta = -117.4$ (t, $^3J = 8.7$ Hz); ^{1}H NMR $\delta = 6.24$ (t, $^3J = 8.7$ Hz).

1,1,1,3-Tetrachloro-2,2-difluoropropane (232cb) [10]: ^{19}F NMR $\delta = -110.6$ (t, $^3J = 14.2$ Hz); ^{1}H NMR $\delta = 4.30$ (t, $^3J = 14.2$ Hz).

1,1,3-Trichloro-2,2,3-trifluoropropane (233ca): ^{19}F NMR $\delta = -120.8$ (1F, dquint, $^2J = 251$, $^3J = 13.5$ Hz), -121.8 (1F, dsext, $^2J = 251$, $^3J = 13.5$ Hz), -155.9 (1F, dt, $^2J = 45.7$ and $^3J = 13.5$ Hz); ^{1}H NMR $\delta = 6.53$ (1H, ddd, $^2J = 47.8$, $^3J = 8.8$ and 5.6 Hz), 6.00 (1H, dd, $^3J = 9.3$ and 7.5 Hz); *m/e*: 83($CHCl_2^+$), 133($CHCl_2CF_2^+$), 165($M^+ - Cl$).

1,1,3-Trichloro-1,2,2-trifluoropropane (233cb): ^{19}F NMR $\delta = -72.1$ (1F, t, $^3J = 8.4$ Hz), -113.4 (2F, dt, $^3J = 13.4$ and 8.1 Hz); ^{1}H NMR $\delta = 4.08$ (dt, $^3J = 14.3$, $^4J = 1.2$ Hz); *m/e*: 49(CH_2Cl^+), 101(CCl_2F^+), 200(M^+).

2,3,3-Trichloro-1,1,1-trifluoropropane (233da): ^{19}F NMR $\delta = -69.1$ (dd, $^3J = 10.9$, $^4J = 10.9$ Hz); ^{1}H NMR not measured; *m/e*: not measured.

1,1-Dichloro-2,2,3,3-tetrafluoropropane (234cb): ^{19}F NMR $\delta = -125.6$ (2F, dtd, $^3J = 9$, 6 and 5 Hz), -138.1 (2F, dt, $^2J = 52$, $^3J = 6$ Hz); ^{1}H NMR $\delta = 5.90$ (1H, tt, $^3J = 9.0$, $^4J = 0.8$ Hz), 6.14 (1H, tt, $^2J = 52.7$, $^3J = 5.0$ Hz); *m/e*: 51(CHF_2^+), 83($CHCl_2^+$), 133($CHCl_2CF_2^+$).

1,3-Dichloro-1,1,2,2-tetrafluoropropane (234cc): ^{19}F NMR $\delta = -70.5$ (2F, s), -116.9 (2F, t, $^3J = 14.4$ Hz); ^{1}H NMR $\delta = 3.94$ (tt, $^3J = 14.2$, $^4J = 2$ Hz); *m/e*: 49(CH_2Cl^+), 85($CClF_2^+$), 99($CF_2CClF_2^+$).

3,3-Dichloro-1,1,1,2-tetrafluoropropane (234ea) [27]: ^{19}F NMR $\delta = -75.0$ (3F, dd, $^3J = 10.7$ and 5.4 Hz), -197.0 (1F, m); ^{1}H NMR $\delta = 4.96$

(1H, ddq, $^{2}J = 44$, $^{3}J = 5.2$ and 4.5 Hz), 5.95 (1H, dd, $^{3}J = 12.0$ and 5.2 Hz); *m/e*: 69(CF_3^+), 83($CHCl_2^+$), 165($M^+ - F$).

1,3-Dichloro-1,1,2,3-tetrafluoropropane, diastereomer **I** (234eb) [27]: ^{19}F NMR $\delta = -62.7$ (1F, m, $^{2}J = 178$, $^{3}J = 17$, $^{4}J = 11$ Hz), -64.9 (1F, m, $^{2}J = 178$, $^{3}J = 15$, $^{4}J = 15$ Hz), -147.4 (1F, m, $^{2}J = 48$, $^{3}J = 26$, $^{4}J = 12.3$ Hz), -195.4 (1F, m, $^{3}J = 24$ and 16 Hz); ^{1}H NMR $\delta = 4.86$ (1H, tdd, $^{2}J = 44.4$, $^{3}J = 6.3$ and 5.7 Hz), 6.36 (1H, ddd, $^{2}J = 48.3$, $^{3}J = 6.6$ and 5.8 Hz); *m/e*: 67($CHClF^+$), 85($CClF_2^+$), 165($M^+ - F$).

1,3-Dichloro-1,1,2,3-tetrafluoropropane, diastereomer **II** (234eb) [27]: ^{19}F NMR $\delta = -63.4$ (1F, m, $^{3}J = 16$, $^{4}J = 9$ Hz), -63.5 (1F, m, $^{3}J = 16$, $^{4}J = 9$ Hz), -152.5 (1F, dm, $^{2}J = 49$, $^{3}J = 12$, $^{4}J = 9$ Hz), -201.8 (1F, dm, $^{2}J = 44$, $^{3}J = 15$ and 13 Hz); ^{1}H NMR $\delta = 4.82$ (1H, dtd, $^{2}J = 44.4$, $^{3}J = 14.9$, 7.1 and 3.2 Hz), 6.42 (1H, ddd, $^{2}J = 48.6$, $^{3}J = 13.3$ and 3.1 Hz); *m/e*: 67($CHClF^+$), 85($CClF_2^+$), 165($M^+ - F$).

1-Chloro-1,2,2,3,3-pentafluoropropane (235ca) [7]: ^{19}F NMR $\delta = -130$ (1F, dddd, $^{2}J = 286$, $^{3}J = 13$, 7 and 7 Hz), -131 (1F, dddd, $^{2}J = 286$, $^{3}J = 13$, 6 and 4 Hz), -137 (1F, ddddd, $^{2}J = 308$ and 52, $^{3}J = 6$ and 4, $^{4}J = 12$ Hz), -139 (1F, ddddd, $^{2}J = 308$ and 52, $^{3}J = 6$ and 6, $^{4}J = 3$ Hz), -158 (1F, ddddd, $^{2}J = 47$, $^{3}J = 12$ and 12, $^{4}J = 12$ and 3 Hz; ^{1}H NMR $\delta = 6.02$ (1H, tddd, $^{2}J = 52$, $^{3}J = 4$, $^{4}J = 1$ Hz), 6.29 (1H, dtt, $^{2}J = 47$, $^{3}J = 7$, $^{4}J = 1$ Hz).

3-Chloro-1,1,1,2,2-pentafluoropropane (235cb) [22]: ^{19}F NMR $\delta = -84.1$ (3F, s), -120.6 (2F, t, $^{3}J = 13.9$ Hz); ^{1}H NMR $\delta = 3.88$ (tq, $^{3}J = 13.9$, $^{4}J = 0.9$ Hz).

1-Chloro-1,1,2,2,3-pentafluoropropane (235cc) [7]: ^{19}F NMR $\delta = -71.0$ (2F, dt, $^{3}J = 3$, $^{4}J = 7$ Hz), -122.7 (2F, tdt, $^{3}J = 15$, 12.3 Hz), -225.7 (1F, ttt, $^{2}J = 47$, $^{3}J = 15$, $^{4}J = 7$ Hz); ^{1}H NMR $\delta = 4.74$ (dtt, $^{2}J = 46$, $^{3}J = 12$, $^{4}J = 1$ Hz).

1,1,2,2,3,3-Hexafluoropropane (236ca) [28]: ^{19}F NMR $\delta = -135.0$ (2F, dt, $^{2}J = 52.7$, $^{3}J = 4.1$ Hz), -138.5 (4F, dt, $^{3}J = 8.5$ and 4.3 Hz).

1,1,1,2,2,3-Hexafluoropropane (236cb) [7]: ^{19}F NMR $\delta = -84.2$ (3F, d, $^{4}J = 8.0$ Hz), -127.2 (2F, dt, $^{3}J = 15.1$ and 11.6 Hz), -243.4 (1F, dtq, $^{2}J = 45.9$, $^{3}J = 15.3$, $^{4}J = 7.7$ Hz).

1,1,1-Trichloro-2,2-difluoropropane (242cb) [10]: ^{19}F NMR $\delta = -100.0$ (q, $^{3}J = 17.4$ Hz); ^{1}H NMR $\delta = 2.07$ (t, $^{3}J = 17.4$ Hz).

1,3-Dichloro-2,2,3-trifluoropropane (243ca): ^{19}F NMR $\delta = -115.7$ (2F, m), -155.5 (1F, dt, $^{2}J = 48.4$, $^{3}J = 10.8$ Hz); ^{1}H NMR $\delta = 3.91$ (2H, dt, $^{3}J = 12.6$, $^{4}J = 1.8$ Hz); *m/e*: 67($CHClF^+$), 99($CH_2ClCF_2^+$), 166(M^+).

1,1-Dichloro-2,2,3-trifluoropropane (243cb) ([27], no ^{19}F NMR data): ^{19}F NMR $\delta = -117.5$ (2F, m), -239.2 (1F, tt, $^{2}J = 45.7$, $^{3}J = 14.8$ Hz); ^{1}H NMR $\delta = 4.78$ (2H, dt, $^{2}J = 45.7$, $^{3}J = 10.9$ Hz), 5.92 (1H, dt, $^{3}J = 8.7$, $^{4}J = 1.8$ Hz).

1,1-Dichloro-1,2,2-trifluoropropane (243cc): ^{19}F NMR $\delta = -73.5$ (1F, t, $^{3}J = 8.1$ Hz), -103.4 (2F, dq, $^{3}J = 8.1$ and 18.9 Hz); ^{1}H NMR $\delta = 1.92$ (dt, $^{3}J = 17.8$, $^{4}J = 1.4$ Hz); *m/e*: 65($CH_3CF_2^+$), 101($CCl_2F_2^+$), 131($M^+ - Cl$).

3,3-Dichloro-1,1,1-trifluoropropane (243fa): ^{19}F NMR $\delta = -64.8$ (t, $^{3}J = 9.3$ Hz); ^{1}H NMR $\delta =$ 3.08 (2H, qd, $^{3}J = 9.3$ and 6.4 Hz), 5.92 (1H, t, $^{3}J = 6.4$ Hz); *m/e*: 69(CF_3^+), 83($CF_3CH_2^+$), 131($M^+ - Cl$).

3-Chloro-1,1,2,2-tetrafluoropropane (244ca): ^{19}F NMR $\delta = -120.4$ (2F, td, $^{3}J = 13.3$ and 3.8 Hz), -138.1 (2F, d, $^{2}J = 53$ Hz); ^{1}H NMR $\delta = 3.82$ (2H, t, $^{3}J = 13.3$ Hz), 5.96 (1H, tt, $^{2}J = 53$, $^{3}J = 3.8$ Hz); *m/e*: 65($CH_3CF_2^+$), 85($CClF_2^+$), 115($M^+ - Cl$).

1-Chloro-1,1,2,2-tetrafluoropropane (244cc): ^{19}F NMR $\delta = -72.5$ (2F, s), -107.3 (2F, q, $^{3}J = 18.2$ Hz); ^{1}H NMR $\delta = 1.79$ (tt, $^{3}J = 18.2$, $^{4}J = 1.4$ Hz); *m/e*: 65($CH_3CF_2^+$), 85($CClF_2^+$), 115($M^+ - Cl$).

1,1,2,2,3-Pentafluoropropane (245ca) [7]: ^{19}F NMR $\delta = -128.1$ (2F, d, $^{3}J = 14$ Hz), -139.2 (2F, d, $^{2}J = 50$ Hz), -243.8 (1F, tt, $^{2}J = 44$, $^{3}J = 14$ Hz); ^{1}H NMR $\delta = 4.65$ (2H, dtt, $^{2}J = 46$, $^{3}J = 12$, $^{4}J = 1$ Hz), 5.89 (1H, ttd, $^{2}J = 53$, $^{3}J = 4$, $^{4}J = 2$ Hz.

1,1,1,2,2-Pentafluoropropane (245cb): ^{19}F NMR $\delta = -87.2$ (3F, s), -111.7 (2F, q, $^{3}J = 18.6$ Hz); ^{1}H NMR $\delta = 1.79$ (tq, $^{3}J = 18.5$, $^{4}J = 1.2$ Hz); *m/e*: 65($CH_3CF_2^+$), 69(CF_3^+), 133($M^+ - H$).

1,3-Dichloro-2,2-difluoropropane (252ca) ([23], no ^{19}F NMR data): ^{1}H NMR $\delta = 3.86$ (t, $^{3}J = 11.8$ Hz).

1,1-Dichloro-2,2-Difluoropropane (252cb) ([19], no ^{19}F NMR data): ^{19}F NMR $\delta = -98.3$ (qd, $^{3}J = 18.1$ and 6.4 Hz); ^{1}H NMR $\delta = 1.85$ (3H, t, 18.1 Hz), 5.70(1H, t, $^{3}J = 6.4$ Hz).

1-Chloro-2,2,3-trifluoropropane (253ca) ([27], no ^{19}F NMR data): ^{19}F NMR $\delta = -112.9$ (2F, dtt, $^{3}J = 15$, 12 and 11 Hz), -237.1 (1F, tt, $^{2}J = 45.7$, $^{3}J = 14.8$ Hz); ^{1}H NMR $\delta = 3.80$ (2H, dt, $^{3}J = 12.2$, $^{4}J = 2.3$ Hz), 4.63 (2H, dt, $^{2}J = 46.0$, $^{3}J = 11.1$ Hz).

1-Chloro-1,2,2-trifluoropropane (253cb): ^{19}F NMR $\delta = -102.6$ (1F, dm, $^{2}J = 267$ Hz), -104.7 (1F, dm, $^{2}J = 267$ Hz), -151.7 (1F, dt, $^{2}J = 48.4$, $^{3}J = 9.4$ Hz); ^{1}H NMR $\delta = 1.78$ (3H, dt, $^{3}J = 18.5$ and $^{4}J = 1.8$ Hz), 6.06 (1H, dt, $^{2}J = 49.0$, $^{3}J = 4.8$ Hz); *m/e*: 65($CH_3CF_2^+$), 132(M^+).

1-Chloro-2,2-difluoropropane (262ca) ([9], no ^{19}F NMR data): ^{19}F NMR $\delta = -95.1$ (qt, $^{3}J = 18.3$ and 11.8 Hz); ^{1}H NMR $\delta = 1.74$ (3H, t, $^{3}J = 18.3$ Hz), 3.65 (2H, t, $^{3}J = 11.8$ Hz).

1,2,2-Trifluoropropane (263ca): ^{19}F NMR $\delta = -102.9$ (2F, m), -233.7 (1F, tt, $^{2}J = 46.6$ and $^{3}J = 29.5$ Hz); ^{1}H NMR $\delta = 1.69$ (3H, dt, $^{3}J = 18.7$, $^{4}J = 2.6$ Hz), 4.40 (2H, dt, $^{2}J = 46.4$, $^{3}J = 11.3$ Hz); *m/e*: 33(CH_2F^+), 65($CH_3CF_2^+$), 83($CH_2FCF_2^+$).

2,2-Difluoropropane (272ca) [10]: ^{19}F NMR $\delta = -85.0$ (q, $^{3}J = 17.8$ Hz); ^{1}H NMR $\delta = 1.61$ (t, $^{3}J = 17.8$ Hz).

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