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FLUORINE NMR INVESTIGATIONS ON TRIFLUOROMETHYLGERMANES

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SUMMARY

The ^{19}F nmr spectra of trifluoromethylgermanes $(CF_3)_nGeX_{4-n}$ (X = Cl,Br,I,$OCOCF_3$,CH_3,$N(CH_3)_2$; n=1-4), $(CF_3)_nGeF_mX_{4-m-n}$ (X = Cl,Br,I; n,m=1-3) and $(CF_3)_nGeH_mX_{4-m-n}$ (X = F,Cl,Br,I; n,m=1-3) are reported. Chemical shifts $\delta(CF_3)$ and $\delta(GeF)$ as well as coupling constants are compared with those of analogous carbon compounds and are analyzed for substitution effects. The ^{13}C nmr spectra as well as the u.v. spectra are reported for the iodides $(CF_3)_nMI_{4-n}$ (M = C,Ge; n=1-4).

INTRODUCTION

The wide range of ^{19}F chemical shifts and their sensitivity to substitution effects makes ^{19}F nmr spectroscopy a very useful tool in the characterization of fluorinated materials [1,2]. However, fluorine chemical shifts are not readily interpretable and usually result from a superposition of several, quite often opposing, effects. The main contributions arise from paramagnetic terms. Their calculation, however, requires detailed knowledge of the electronic states which is usually not available for polyatomic molecules. It is therefore desirable to reduce complex mathematical terms to descriptive terms such as ionicity, the influence of low-lying excited electronic states, electric fields, van der Waals interactions etc.

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The coupling constants encountered in fluorine nmr are as complex as the chemical shifts. Besides the Fermi contact term, orbital and spin-dipole contributions have to be considered [3-5]. Since relative signs of these terms are often different, small couplings of different signs may result. On the other hand coupling through several bonds or 'through space' may yield large values. Though resonances are usually sufficiently separated to allow for the X approximation, magnetic inequivalence due to long-range coupling quite often imposes severe problems in the interpretation of ^{19}F nmr spectra [1,6].

Until recently the investigation of trifluoromethyl derivatives of group IV B elements was mainly restricted to fluorinated alkanes. The synthesis of the series CF_3SiF_2X [7] and $(CF_3)_nGeX_{4-n}$ [8-10] now offers the possibility of a more systematic analysis of trends. In particular the similarity of the carbon and germanium atoms leads one to expect that the origins of shifts and couplings constants should be basically similar, while contributing to different extents.

RESULTS AND DISCUSSION

^{19}F chemical shifts

Ge-F shifts

The presence of ^{19}F chemical shift contributions with different signs is demonstrated in Fig.1 for the series $(CF_3)_nMF_{4-n}$ and $(CH_3)_nMF_{4-n}$ (M = C and Ge). The minimum for n = 1 in the germane series is attributed to a predominant paramagnetic term which is associated with increasing Ge-F double-bond character or with the lower energy necessary to excite to the first unoccupied orbital carrying mainly σ^*(Ge-C) along with some F 2p character. For n = 2 or 3 the shielding component dominates as expected as the negative charge on the fluorine atom or atoms increases. In accordance both with the reduced importance of $R^-R_2C{=}F^+$ resonance structures and larger ΔE values, the deshielding component is less pronounced for the carbon series.

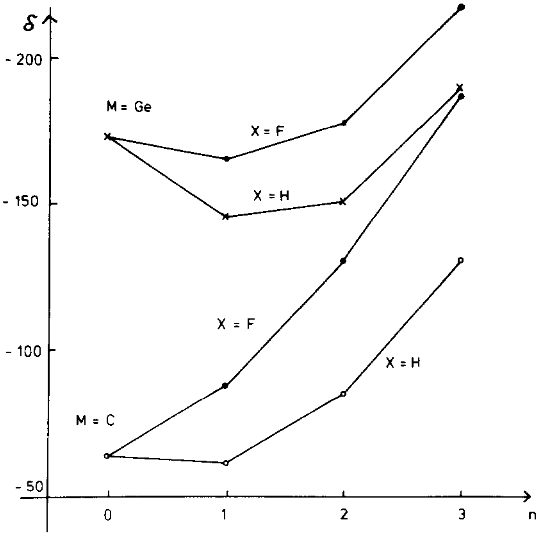

Fig. 1. Variations in chemical shifts of Ge- or C-bonded fluorines in the series $(CX_3)_nMF_{4-n}$ (M = C,Ge; n=0-3).

The high-frequency shifts of the CH_3 derivatives with respect to their CF_3 counterparts oppose the predictions made on the basis of charges or double-bond character. The contributions arising from electric fields [11-13], 1 ppm or less, are too small to be of importance. An explanation of this CF_3/CH_3 substitution effect presumably requires detailed studies of the electronic states with emphasis on long-range H..F contacts.

Substitution of the fluorines of GeF_4 by heavier halides (Table 1) causes deshielding in a similar way as in SiF_nX_{4-n} [14] or CF_nX_{4-n} [2]. That Si$\underline{F}$ and Ge$\underline{F}$ shifts, including the series CF_3SiF_2X [7], are well correlated by the equation

$$\delta(Si\underline{F}) = 0.89\ \delta(Ge\underline{F}) - 4\ \ [ppm],$$

indicates the principal similarity of the factors determining GeF and SiF shifts, whereas a good CF/GeF correlation does not exist. The magnitude of the 'inverse' halide shift decreases along the series GeF_3X, CF_3GeF_2X and $(CF_3)_2GeFX$.

TABLE 1

Chemical shifts of germanium-bonded fluorine in $(CF_3)_nGeF_mX_{4-m-n}$ (X = Cl, Br, I; n,m = 0-3)[a]

X =	F	Cl	Br	I
GeF_3X	-173.5[b,c]	-144.1[c]	132.2	-115.6[b]
GeF_2X_2		-120.6[c]	102.3	-81.3[b]
$GeFX_3$		-101.8[c]	-81.5	-67.7[b]
CF_3GeF_2X	-166.1	-150.5	-143.9	-133.5
CF_3GeFX_2[d]		-140.9	-133.3	-130.0
$(CF_3)_2GeFX$	-178.7	-178.9	-178.1	-179.2
$(CF_3)_3GeX$	-218.8			

[a] in ppm relative to internal SiF_4 at δ -163.1 ppm.
[b] internal $CFCl_3$. [c] ref. [15]: $\delta(GeF_4)$ -171.4, $\delta(GeF_3Cl)$ -141.9, $\delta(GeF_2Cl_2)$ -116.2, $\delta(GeFCl_3)$ -100.9 ppm.
[d] $\delta(CF_3Ge\underline{F}ClBr)$ -136.6, $\delta(CF_3Ge\underline{F}ClI)$ -130.5, $\delta(CF_3Ge\underline{F}BrI)$ -130.2 ppm.

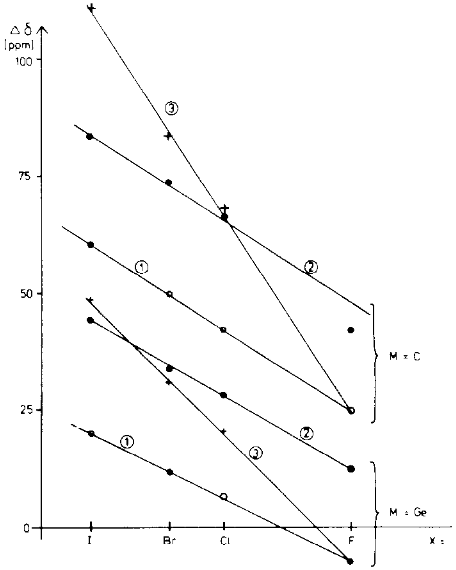

Fig.2. F/CF_3 substitution effects in FMF_2X (1), $FMF(CF_3)X$ (2) and $FMFX_2$ (3). The halides X are arranged following Sanderson's electronegativity scale.

Shielding and deshielding contributions just compensate in the series $(CF_3)_2GeFX$, and all δ(GeF) values fall in the narrow range of -178.7±0.6 ppm, the variations being non-systematic for the order X = F, Cl,Br, and I. A similar pattern is observed for the carbon series where a 'normal' halogen dependence is obtained for $(CF_3)_2CFX$ (Table 2). The latter confirms the less relative importance of the paramagnetic contributions in the carbon series. The halogen and CF_3 dependence is evident from the CF_3/F substitution pattern. Replacing one F atom by a CF_3 group will shift the M$\underline{F}$ resonance to lower frequencies, except in case of GeF_4. Figure 2 shows the change in the chemical shifts for the series $(CF_3/F)MF_2X$, $(CF_3/F)M(CF_3)FX$ and $(CF_3/F)MFX_2$, labelled 1, 2 and 3, respectively. In general, the change is significantly greater for M = C. This is ascribed to the greater π-acceptor capability of germanium and thus more pronounced GeF double-bond character. The figure also nicely demonstrates that the changes caused by one X atom (lines 1 and 2) approximately double for two X atoms (line 3).

CF_3Ge shifts

The ^{19}F resonances of a CF_3 group attached to germanium are typically found in the region of -50 to -65 ppm. Coupling to the isotope ^{73}Ge (spin 9/2, natural abundance 7.76%) can only be observed for spherical molecules [16]. The ^{19}F spectrum of $(CF_3)_4Ge$ (Fig. 3) shows ten additional lines of equal intensities with a spacing of $^2J(^{73}GeF)$=26.3

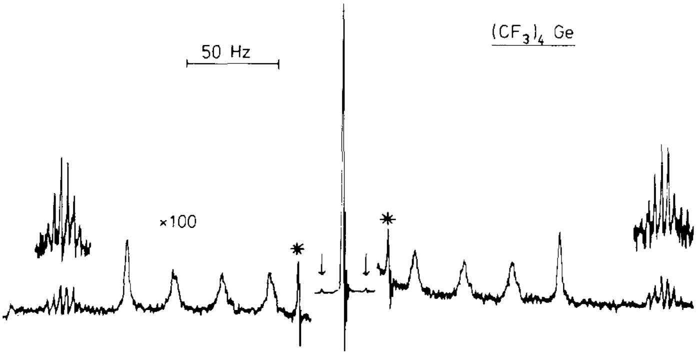

Fig. 3. ^{19}F nmr spectrum of $(CF_3)_4Ge$. Spinning side bands are marked with an asterisk.

Hz, the centre of this system coinciding with the main signal. The line widths of the outer peaks with $m_I = \pm 9/2$ ($W_{1/2}$= 2 Hz) are approximately half of those of the inner lines, the broadening being caused by electric quadrupole relaxation. Application of the formulae derived by Pople [17,18] for the transition probabilities ($\Delta m = \pm 1, \pm 2$) to the 9/2 spin system yields relative line widths of 1.0, 2.1, 2.2, 1.9, and 1.7 for the transitions with $m_I = \pm 9/2$, ±7/2, ±5/2, ±3/2, and ±1/2, respectively, which agrees well with the experiment. The origin of the ^{13}C satellite system is shifted 0.15 ppm to lower frequency, each satellite being split into a decet due to $^4J(FF)$.

A systematization of CF_3 shifts is complicated by the fact that they result from the average of rotational isomers [19,20] which may differ by as much as 20 ppm for gauche and trans conformations. In contrast to CF_3-C derivatives, the small barrier to internal rotation [21] prevents the isolation of distinct rotamers in trifluoromethylgermanes and thus the assignment of individual resonances. In general, increasing the number of CF_3 groups attached to carbon (Table 2) or germanium (Tables 3 and 4) causes deshielding of the fluorine atoms, both $(CF_3)_4M$ molecules resonating at the high-frequency end of the scales. Only in molecules with rather bulky substituents such as $(CF_3)_3GeGe(CF_3)_3$ or $(CF_3)_3GeSi(CH_3)_3$ ($\delta(CF_3)$-48.5 ppm [22]) are the fluorines less shielded. Both vibrational [30] and x-ray excited photoelectron spectroscopy [31] have demonstrated that bonding parameters and charges do not vary significantly across the chloride series, $(CF_3)_nGeCl_{4-n}$. Consequently, the contributions due to changing ionicity may be assumed to be negligible for the $(CF_3)_nMCl_{4-n}$ series. The high-frequency offset of ca. 5.5 ppm/CF_3 group for M = C is usually ascribed to non-bonded fluorine-fluorine interactions (repulsive deshielding). This concept, however, is made questionable by the corresponding offsets in the germane series also being ca. 4.5 ppm despite the fact that F...F contacts between different CF_3 groups are much shorter in $(CF_3)_4C$ (272 pm [32]) than in $(CF_3)_4Ge$ (331 pm [21]).

TABLE 2

^{19}F nmr parameters of perfluoroalkyl halides

	$\delta(CF_3)^a$	$\delta(CF/CF_2)^a$	$\|^3J(FF)\|^b$	$\|^1J(CF)\|^b$	$\|^4J(FF)\|^b$
CF_3CF_3	-88.2		3.9[c]	283.5	
CF_3CCl_3[d]	-82.2			282.0	
CF_3CBr_3[d]	-79.3			279.4	
CF_3CI_3[d]	-77.0			277.4	
CF_3CH_3[d]	-61.8			272.3	
$(CF_3)_2CF_2$	-83.4	-131.0	0.8	285[e]	7.6[e]
$(CF_3)_2CCl_2$	-77.0			283.7	10.0
$(CF_3)_2CBr_2$	-72.7			283.5	10.5
$(CF_3)_2CI_2$	-68.3			280.5	11.3
$(CF_3)_2CH_2$[i]	-63.9				
$(CF_3)_3CF$	-75.0	-188.0	6.1		
$(CF_3)_3CCl$	-71.5			285.8	11.0
$(CF_3)_3CBr$	-67.5			285.0	11.0
$(CF_3)_3CI$	-65.9			283.8	11.3
$(CF_3)_3CH$[k]	-64.5				
$(CF_3)_4C$	-65.4			289.9[f]	
CF_3CF_2Cl	-87.0	-74.9	0.8		
CF_3CF_2Br	-85.9	-70.3	2.2		
CF_3CF_2I	-85.4	-65.2	4.6		
$(CF_3)_2CFCl$	-79.8	-141.8	5.5		
$(CF_3)_2CFBr$	-78.0	-144.2	8.7		
$(CF_3)_2CFI$	-76.0	-148.9	12.5		
CF_3CFCl_2[g]	-84.6	-76.8	5.5		
$CF_3CFClBr$[g]	-84.3	-77.0	7.8		
CF_3CFBr_2	-82.2	-77.1	9.7		
CF_3CFClI[h]	-82.6	-78.3	10.6		
CF_3CFBrI[h]	-81.0	-85.9	13.0		
CF_3CFI_2[h]	-81.4	-87.5	16.4		

[a] in ppm from internal $CFCl_3$. [b] in Hz. [c] $^1J(CF)$ 281.3 Hz, $^3J(FF)$ 3.5 Hz at -80°C [23]. [d] ref. 24. [e] ref. 25. [f] ref. 26. [g] ref. 27. [h] ref. 20. [i] ref. 28. [k] ref. 29.

TABLE 3

^{19}F nmr data of trifluoromethylgermanes CF_3GeXYZ

X	Y	Z	$\delta(CF_3)^a$	$\lvert ^1J(CF)\rvert ^b$	$\lvert ^3J(HF)\rvert ^b$
F	F	F	-54.8	324.8	
F	F	Cl	-57.9	329.5	
F	F	Br	-58.5		
F	F	I	-61.0		
F	Cl	Cl	-60.5		
F	Cl	Br	-60.9		
F	Cl	I	-63.1		
F	Br	Br	-61.7		
F	Br	I	-63.4		
F	I	I	-65.2	341.8	
Cl	Cl	Cl	-62.6	335.2	
Cl	Cl	Br	-63.2		
Cl	Cl	I	-64.8	339.7	
Cl	Br	Br	-63.6		
Cl	Br	I	-65.3		
Cl	I	I	-66.8	343.5	
Br	Br	Br	-64.2	339.4	
Br	Br	I	-65.7		
Br	I	I	-67.1		
I	I	I	-68.2	345.7	
CH_3	CH_3	CH_3	-62.6	336.8	
$OCOCF_3$	$OCOCF_3$	$OCOCF_3$	-56.0	331.6	
H	H	H	-49.2	331.6	8.7
H	H	F	-58.8		8.2
H	H	Cl	-57.6		8.1
H	H	Br	-56.7		8.3
H	H	I	-55.4		8.4
H	Cl	Cl	-62.1		8.6
H	Br	Br	-61.9		9.
H	I	I	-61.7		8.9

[a] in ppm from $CFCl_3$. [b] in Hz.

TABLE 4

^{19}F nmr data of trifluoromethylgermanes $(CF_3)_2GeXY$

X	Y	$\delta(CF_3)^a$	$\lvert ^1J(CF)\rvert ^b$	$\lvert ^4J(FF)\rvert ^b$	$\lvert ^3J(HF)\rvert ^b$
CF_3	CF_3	-49.2	330.5	3.53	$^2J(^{73}GeF)$ 26.3
CF_3	F	-54.1	328.5	3.20	
CF_3	Cl	-54.1	331.0	3.56	
CF_3	Br	-53.9	332.3	3.70	
CF_3	I	-53.7	334.0	3.95	
CF_3	H	-50.1	330.2	4.1(2)	6.7
CF_3	CH_3	-54.6	330.2	3.93	
CF_3	$Ge(CF_3)_3$	-46.4			
CF_3	$OGe(CF_3)_3$	-54.7	331^c		
CF_3	$OCOCF_3$	-52.8	331.3	3.50	
CF_3	$N(CH_3)_2$	-52.3	334.2	3.60	
F	F	-56.0	327(1)		
F	Cl	-57.4			
F	Br	-57.6			
F	I	-58.6			
Cl	Cl	-58.6	332.7	3.61	
Cl	Br	-58.7			
Cl	I	-59.5			
Br	Br	-58.9	335.3	3.92	
Br	I	-59.4			
I	I	-59.7	339.7	4.32	
CH_3	CH_3	-58.9	333.0	4.12	
$OCOCF_3$	$OCOCF_3$	-54.8	331.7	3.53	
$N(CH_3)_2$	$N(CH_3)_2$	-53.9	336.9	3.75	
$N(CH_3)_2$	I	-65.5	336.2	4.15	
H	H	-50.3	330.2	4.72	7.7
H	F	-56.8			7.9
H	Cl	-56.5			7.7
H	Br	-55.9			7.6
H	I	-55.2			7.3

[a] in ppm from $CFCl_3$. [b] in Hz. [c] broadened by long-range FF coupling.

As for the M$\underline{F}$ resonances, deshielding relative to the halides is apparent for molecules with hydrogen in adjacent positions; e.g. the resonance frequency increases along the series $(CF_3)_nCH_{4-n}$ with increasing number of hydrogens. An analogous hydrogen effect is observed for the trifluoromethylgermanes, $(CF_3)_nGeH_{4-n}$, the CF_3 groups resonating at appreciably higher frequencies ($\delta(CF_3)$ -49.7±0.6 ppm) than the halides with the same number of CF_3 groups.

The Tables 2-4 exhibit a further basic difference between the carbon and germanium derivatives. The CF_3 shifts of the carbon compounds are characterized by an inverse halogen dependence, CF_3CF_3 resonating at the lowest frequency. This trend has been rationalized in terms of van der Waals interactions [13] which, due to the r^{-6} dependence, are much less important for the trifluoromethylgermanes and are obviously overruled by the inductive effect. Consequently, a normal halogen shift results for CF_3GeX_3 and $(CF_3)_2GeX_2$, the most negative δ-value being recorded for CF_3GeI_3. The halide substitution pattern is such that introduction of a heavier halide will increase the CF_3 shielding. The magnitude of the shift difference $\Delta(XY)$ upon replacement of a halide X by another halide Y depends on the δ-value itself and decreases linearily with increased shielding:

$$\Delta(XY) = \delta(CF_3GeR_2X) - \delta(CF_3GeR_2Y) = a \cdot \delta(CF_3GeR_2X) + b$$
$$(R, X, Y = \text{halogen})$$

The values of a and b for the different pairs of X and Y are listed in Table 5. All slopes intersect at approximately

TABLE 5

Halide substitution shifts $\Delta(XY)$ in the ^{19}F spectra of (trifluoromethyl)trihalogermanes CF_3GeR_2X (R, X, Y = F, Cl, Br, I)

XY =	FI	FBr	FCl	ClI	ClBr	BrI
a	0.302	0.174	0.147	0.181	0.033	0.167
b	22.6	13.3	11.1	13.6	2.6	12.3
$\delta(\Delta=0)$	-75.2	-76.1	-75.5	-75.0	-78.1	-73.4
r^*	0.996	0.990	0.979	0.989	0.60	0.968

*Correlation coefficient $r = a \cdot \sigma_x / \sigma_y$.

$\Delta(XY) = 0$ and $\delta(CF_3) = -75.4$ ppm, which points towards an almost pure inductive effect. An electropositive ligand will increase the negative charge of the fluorines and cause a shielding contribution, which however will be reduced by the concomitantly increased repulsive interaction of the fluorines which are only ca. 216 pm apart. Both terms will cancel at a hypothetical value of ca. -75.4 ppm. These correlations do not include R = H or CF_3, both of which reduce $\Delta(XY)$ and eventually lead to negative values (inverse halogen dependence) for the series $(CF_3)_3GeX$, $(CF_3)_2GeHX$, CF_3GeH_2X and CF_3GeHX_2. Correspondingly, the points of intersection are shifted to higher frequencies, e.g. $\delta(\Delta=0)$ is ca. -61.2 ppm for $(CF_3)_2GeX_2$ and -53.5 ppm for $(CF_3)_3GeX$.

An inductive effect comparable to that of germanes should also be valid for the carbon compounds, which implies that the B values in the van der Waals expression [13] are too small. The large difference in the shifts of the individual fluorines of a CF_3 group, for example in CF_3CF_2I [19], are indicative of van der Waals and inductive contributions. There the fluorine trans to iodine, which is too far removed for significant 'through space' interactions, resonates at a lower frequency than the other fluorines with their shorter F..I gauche contacts or than the fluorines in CF_3CF_3.

Coupling constants

The $^1J(CF)$ coupling constants may be obtained either from the ^{13}C nmr or the ^{13}C satellites in the ^{19}F nmr spectra. In principal, these spectra of $(CF_3)_nMR_{4-n}$ derivatives have to be analyzed as $A_3B_{3-n}X$ systems. In the case of the germanes, the ratio $^1J(CF)/2 \cdot J(FF)$ is approximately 40:1 and with the given resolution both the A (^{19}F) and X (^{13}C) subspectra appear as first order. In all cases the B part was hidden by the main singlet. For the carbon series, however, the ratio decreases to ca 14:1 and high order splittings are clearly resolved both in the ^{19}F and ^{13}C spectra, which were analyzed by computer simulation [33].

The one-bond CF coupling constant depends on the atom attached to the CF_3 group [34], its absolute value increasing with the size of the central atom. As with all couplings involving fluorine, orbital and dipolar terms add considerable contributions to the total value [4]. Substituent effects are consequently not directly related to bonding parameters such as bond lengths or force constants. The presence of contributions with different signs is apparent from the comparison of the carbon and germanium series. The germanes span a range from 324.7 Hz in CF_3GeF_3 to 345.7 Hz in CF_3GeI_3 (Table 3). In contrast, $|^1J(CF)|$ decreases with increasing size of the halide in CF_3CX_3 (Table 2), and the largest coupling is found for $(CF_3)_4C$. Because of the longer bonds in the trifluoromethylgermanes steric interactions are expected to be less important than inductive effects. The electronegativity of the atom or group attached to germanium seems to exhibit a major influence, an electron-withdrawing group contracting the effective size of the germanium atom and thus decreasing $|^1J(CF)|$.

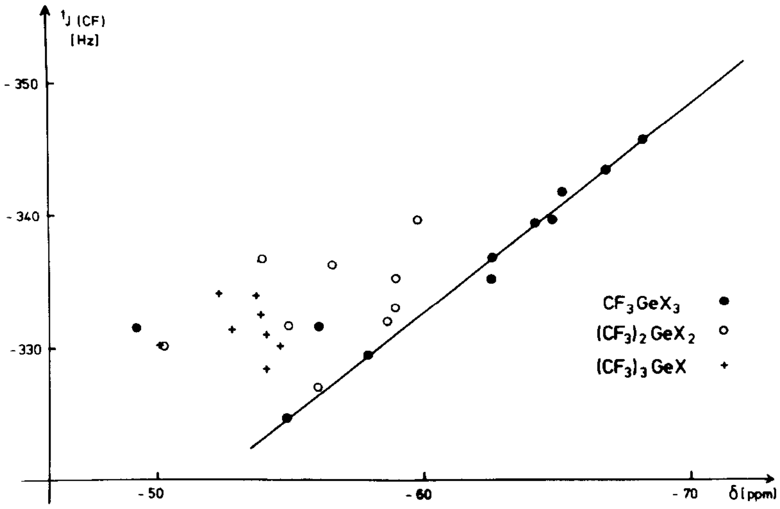

Fig. 4. Plot of $^1J(CF)$ vs. $\delta(CF_3)$ in trifluoromethylgermanes

A linear correlation between $\delta(CF_3)$ and $^1J(CF)$ is obtained for CF_3GeX_3 derivatives (X = halogen), which however does not include the high-frequency shifted hydride. The Figure also demonstrates the absence of a more general $\delta(CF_3)/^1J(CF)$ relation, which indicates that long-range

F..F or F..H contacts do not contribute uniformly to $\delta(CF_3)$ and $^1J(CF)$. Considering again the chloride series $(CF_3)_nMCl_{4-n}$, which is expected to have the least electronic changes in the CF_3M part, a slight decrease in $|^1J(CF)|$ is found with increasing n for M = Ge. This is in contrast to the carbon analogues, and the large coupling constant in $(CF_3)_4C$ presumably arises from steric hindrance of the CF_3 groups. In a simple MO description, interaction between the CF_3 groups will stabilize the virtual C-F antibonding orbitals and destabilize the non-bonding p_F orbitals, thus reducing ΔE and increasing the predominant contact and orbital terms.

The ^{13}C satellites of compounds with more than one CF_3 group are split due to $^4J(FF)$, and the multiplicity of the satellites may be used as a valuable aid in establishing the number of the CF_3 groups. The time-averaged value of $^4J(FF)$ was shown to be positive for $(CF_3)_2CI_2$ [19] though specific interactions such as the trans-gauche coupling may adopt a negative sign. These long-range couplings have been calculated to decrease with increasing F..F distances [5], in principal agreement with the smaller absolute value of 4 ± 1 Hz found for the germanes (Table 4). As a general trend the magnitude of this coupling constant decreases with increasing electronegativity of the ligands which suggest the same sign for the carbon and the germanium series. The largest value is found for the hydrides, again confirming the exceptional role of hydrogen.

The $^3J(FF)$ coupling constants in $(CF_3)_nGeF_mX_{4-m-n}$ derivatives (Table 6) span the range from 3 to 16 Hz, the magnitude of the values increasing with increasing electronegativity of X. A linear correlation has been found for CF_3CF_2X and CF_3SiF_2X compounds, which leads to the prediction of positive signs for the silanes [35]. The germanes correlate similarly with their carbon analogues. Figure 5 shows that all mono-CF_3 derivatives may be represented by a single line whereas the line correlating the $(CF_3)_2MFX$ compounds is clearly offset and also does not include $(CF_3)_3MF$. The data strongly suggest a positive sign for all observed $^3J(FF)$ couplings in the germane series.

TABLE 6

Coupling constants $^{3}J(FF)$ [Hz] in trifluoromethylgerman fluorides, $(CF_3)_nGeF_mX_{4-m-n}$

X =	F	Cl	Br	I
CF_3GeF_2X	16.5	13.2	11.8	9.9
CF_3GeFX_2 [a]		10.4	8.2	4.5
$(CF_3)_2GeFX$	9.5	7.1	5.8	3.9
$(CF_3)_3GeX$	3.7			

[a] $CF_3GeFClBr$ 9.3, $CF_3GeFClI$ 7.3, $CF_3GeFBrI$ 6.5 Hz.

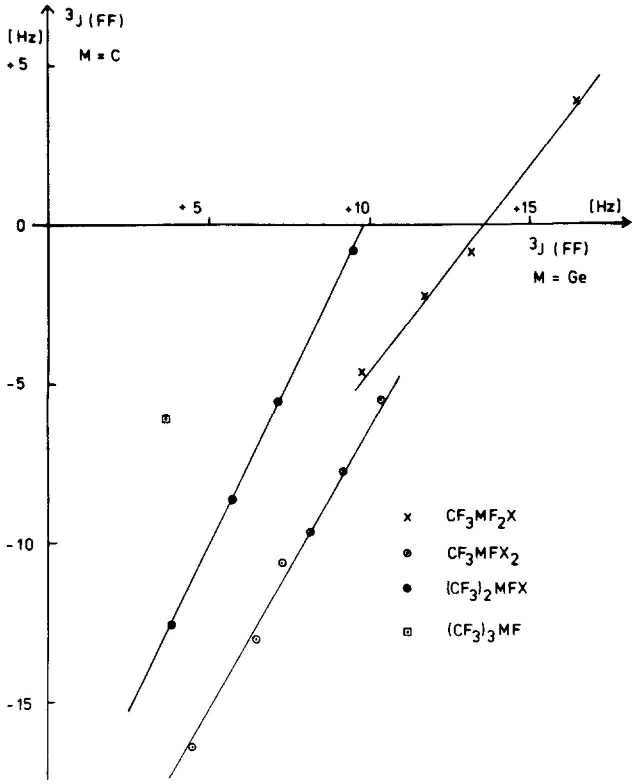

Fig. 5. Plot of $^{3}J(FF)$ in $(CF_3)_nCF_mX_{4-m-n}$ vs. $^{3}J(FF)$ in $(CF_3)_nGeF_mX_{4-m-n}$ (X = F, Cl, Br, I)

^{13}C nmr spectra

The ^{13}C spectra of the iodo derivatives $(CF_3)_nGeI_{4-n}$ (n = 1-4) and $(CF_3)_nCI_{4-n}$ (n = 1-3) are summarized in Table 7 along with their u.v. spectra. Increasing the number of iodine atoms shifts the ^{13}C resonances to lower frequencies, the changes being more pronounced for the germanes. A large shift results for the central carbon atom, e.g. the $CF_3\underline{C}I_3$ resonance is observed as low as -127.9 ppm. The high-order pattern of the $\underline{C}F_3$ resonances in the perfluoroalkanes allows the direct determination of the sign of the three-bond coupling $^3J(CF)$. Its small value of ca. 1 Hz, which is in contrast to the value of ca. 5 Hz for the germanes, indicates partly cancelling contributions for J_{av}, for example opposite signs for trans and gauche couplings.

TABLE 7

^{13}C nmr parameters and u.v. spectra of $(CF_3)_nMI_{4-n}$ (M = Ge,C; n = 1-4)

	$\delta(\underline{C}F_3)^a$	$^1J(CF)^b$	$^3J(CF)^b$	$\lambda_{max}{}^c$	$\sigma\cdot 10^{18}$ ^{d}
$(CF_3)_4Ge$	126.8	-330.8	±4.4	-	-
$(CF_3)_3GeI$	123.8	-335.0	±4.8	235 ^{e}	4.0
$(CF_3)_2GeI_2$	117.5	-340.3	±5.8	265 ^{e}	8.7
CF_3GeI_3	105.0	-346.7	-	310 ^{f}	7.5
$(CF_3)_3CI$ ^{g}	122.4	-283.5	+1.0 ^{k}	288 ^{e}	0.64
$(CF_3)_2CI_2$ ^{h}	121.8	-280.3	+1.3 ^{k}	302 ^{e}	3.28
CF_3CI_3 ^{i}	117.0	-278.6	-	-	-

[a] in ppm with int. $CDCl_3$ at 77.3 ppm. [b] in Hz. [c] in nm. [d] in cm^2. [e] gas phase. [f] in $CHCl_3$. [g] central carbon δ=37.7 ppm, $^2J(CF)$=30.6 Hz. [h] central carbon δ=-19.9 ppm, $^2J(CF)$= 33.6 Hz. [i] central carbon δ=-127.9 ppm, $^2J(CF)$=36.1 Hz. [k] absolute sign from computer simulation.

EXPERIMENTAL

^{19}F and ^{1}H nmr spectra were recorded on a Varian EM 390 spectrometer operating at 84.67 and 90.00 MHz, respectively. ^{19}F chemical shifts refer to $CFCl_3$, ^{13}C shifts to TMS with $\delta = 10^6(\nu_x - \nu_{ref})/\nu_{ref}$. The ^{19}F shifts were obtained from mixtures, utilizing $(CF_3)_3GeI$ or $(CF_3)_4Ge$ as internal reference for CF_3Ge groups and SiF_4 for germanium-bonded fluorine. The concentration dependence was less than 0.3 ppm for $\delta(CF_3)$ while up to 4 ppm for $\delta(GeF)$. All quoted values were averaged from at least three different samples, standard deviations being <0.3 Hz for $^{1}J(CF)$ and <0.05 Hz for $^{4}J(FF)$. ^{13}C nmr spectra were recorded on a Varian FT 80A spectrometer at 20 MHz on saturated solutions in $CDCl_3$ or with ca. 20% $CDCl_3$, serving as internal lock.

The u.v. spectra were obtained with a Beckman UV 5720 spectrometer using 1 cm gas cells. The pressure was monitored with a MKS Baratron 315 BHS manometer.

All manipulations were carried out employing a greaseless standard vacuum-line. Purification of compounds was achieved by trap-to-trap condensation and/or g.l.c. The purity of the samples was checked by their nmr and vibrational spectra.

Trifluoromethylgermanium iodides were obtained from GeI_4 and $(CF_3)_2Hg$ [10] and separated utilizing a spinning band distillation column. Conversion from the iodides to other halides or trifluoroacetates was achieved by reaction with the appropriate silver salt [8] in sealed glass ampoules. The mixed halides were prepared using excess iodogermane, the conversion always taking place to form the lighter halide. Details of the preparations, physical properties and spectroscopic data of the hithero unknown trifluoromethylgermanium trifluoroacetates, amides and hydrides will be published elsewhere. Trifluoromethyl(fluoro)germanes,

$(CF_3)_nGeF_mX_{4-m-n}$, were also obtained by the thermal decomposition of the compounds $(CF_3)_{n+m}GeX_{4-m-n}$. The reaction was carried out in sealed 4 mm glass tubes at 190°C, the progress being monitored by ^{19}F nmr spectra. Methylgermanium fluorides, $(CH_3)_nGeF_{4-n}$, were obtained from the corresponding bromides and AgF in sealed ampoules at ambient temperature and identified by their ^1H nmr and vibrational spectra [36]. Chemical shifts $\delta(Ge\underline{F})$ are: CH_3GeF_3 -146.0, $(CH_3)_2GeF_2$ -151.8, $(CH_3)_3GeF$ -190.5 ppm.

Mixtures of perfluoroalkyl halides were obtained from the reaction of CF_3 radicals, generated in a radio-frequency discharge through C_2F_6, with SnX_4 [37]. Product enrichment or separation was achieved by trap-to-trap condensation and g.l.c. utilizing a 6 mm x 7m SE 30 column on a GC Varian 3700. The compounds were identified by their nmr, mass and vibrational spectra. The samples of $(CF_3)_3CI$ and $(CF_3)_2CI_2$ were synthesized following literature methods [38]. The sample of CF_3CI_3 was kindly supplied by Dr.G.Pawelke, GHS Wuppertal.

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