SOME SELENIUM-77 AND TELLURIUM-125 NMR SPECTROSCOPIC STUDIES

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Abstract Correlations between chemical shifts, the electro-
nagativities of X and the ΔE value, respectively, allow the
prediction of chemical shifts for CF_3SeX compounds and com-
pounds containing a C=Se moiety. Coupling constants
$^1J(Se-C)$, $^1J(Te-C)$, and $^1J(Se-Se)$ of CF_3Se and CF_3Te com-
pounds are considerably larger than those of corresponding
CH_3 compounds. The isotope effect of ^{13}C on ^{77}Se,
$^1\Delta^{77}Se(^{13/12}C)$, extends over a wide range. The first corre-
lation between isotope shifts and bond lengths was estab-
lished with the aid of these data. The isotope effect of
all Se isotopes in diselenides $R^{77}Se^nSeR$ (n = 74, 76, 77,
78, 80, 82), and $^1\Delta^{125}Te(^{127.7/123}Te)$ and
$^1\Delta^{123}Te(^{127.9/125}Te)$ values for $CF_3TeTeCF_3$ could be measured.

INTRODUCTION

The development of pulsed Fourier transform NMR spectrometers
operating at high magnetic fields enables the chemists to study
NMR spectra of more and more elements in compounds of their
interest. Of the group VI elements selenium and tellurium are
best suited for a NMR study. The author's interest in the
chemistry of sulfenic acid fluorides (e.g. CF_3SF), the fact that
a large number of CF_3 or perhalogenomethyl substituted sulfur and
selenium compounds were known[1] and available, gave the impetus
for a systematic multinuclear (^{77}Se, ^{19}F, ^{13}C and others) inves-
tigation of CF_3Se (and CF_3S) compounds[2]. In addition, some CF_3Te
compounds[3] and compounds containing C=Se (and C=S) double bonds
were studied to find general trends. The results show that the

presence of fluorine changes the electronic structure of these
molecules considerably, as is apparent from a comparison of CF
derivatives with their corresponding CH analogues. Trends in
chemical shifts, coupling constants and isotope effects are
briefly summarized in this paper.

^{77}Se CHEMICAL SHIFTS

In early papers on ^{77}Se chemical shifts of organoselenium com-
pounds, the electron excitation energy ΔE[4] and the electronega-
tivity of substituents[5] were proposed to be the dominant factor
in Ramsey's paramagnetic term for the ^{77}Se nuclear shielding. A
series of closely related compounds of type CF_3SeX, with X a
series of substituents with wide variations in their electro-
negativities, appeared to be well suited to study the inductive
effect on the ^{77}Se shielding while compounds containing a C=Se
moiety were of interest to investigate the influence of ΔE due
to low energy n→π* transitions in these colored compounds.

CF_3 Substituted Selenium Compounds[6]

An excellent linear correlation between $\delta(^{77}Se)$ and Huggins
electronegativity values χ was established for CF_3SeX compounds
using only well defined χ_x values of Cl, Br, CN, H, and Ag
(Fig. 1) while no dependence of $\delta(^{77}Se)$ on the lowest ΔE values
was observed.

$$\delta(^{77}Se) = 829,8 \; \chi_x - 1549 \tag{1}$$

The conclusions are:
- In CF_3SeX compounds the electronegativity of X is dominating
  the ^{77}Se shielding.
- Eq. (1) allows the estimation of effective group electronega-
  tivities of substituents X from $\delta(^{77}Se)$ measurements.
- ^{77}Se chemical shifts of new compounds can be predicted using
  Eq. (1) and known χ_x values.

– If Eq. (1) does not apply, an unusual electronic structure at the Se atom is suggested.
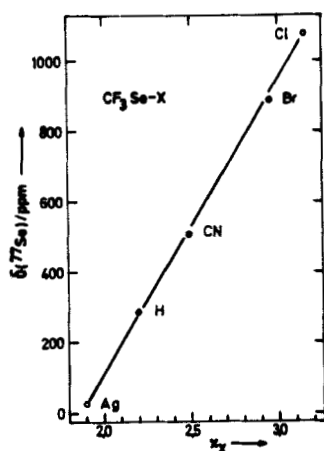
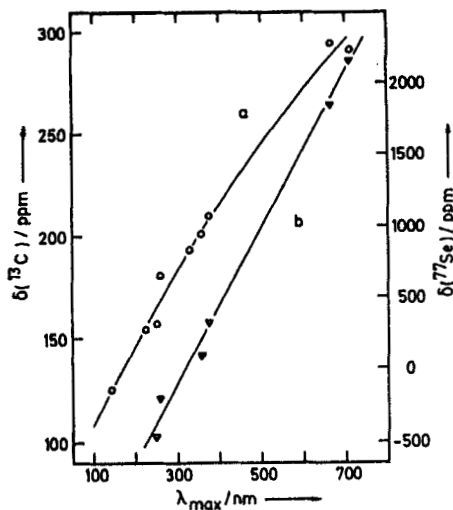FIGURE 1. Dependence of δ(^{77}Se) on the electronegativity of X in CF$_3$SeX compounds [6].

FIGURE 2. Dependence of δ(^{13}C), a, and δ(^{77}Se), b, on the low energy electron excitation in C=Se group containing compounds [7].

E.g., the δ(^{77}Se) values in the series CF$_3$SeX (X = SCF$_3$, SCF$_2$Cl, SCFCl$_2$, SCCl$_3$) show an opposite trend to that expected from the group electronegativities of X. A lower ^{77}Se shielding is related to decreasing ΔE values. Thus, the electron excitation energy ΔE is now the overwhelming factor. This can be rationalized by the involvement of the lone pair electrons at sulfur and selenium. The investigation of the ^{77}Se–^{77}Se coupling constants in the analogous compounds with X = SeCF$_3$, SeCF$_2$Cl, SeCH$_3$ and in CF$_2$ClSeSeCF$_2$Cl allows one to conclude that a π-type interaction is involved in the Se-Se bonds (vide infra). Thirty-five CF$_3$Se (II, IV) compounds have been studied by multinuclear NMR^2, the majority of the chemical shifts are published in reference 6.

Compounds Containing C=Se Double Bonds[7]

Shielding of both the ^{77}Se and ^{13}C nuclei in the C=Se moiety of
the compounds E=C=E' (E, E' = O, S, Se), Se=CF$_2$, Se=C(NH$_2$)$_2$,
Se=C(t-Bu)$_2$, and 1,1,3,3-tetramethyl-2-indanselon is dominated
by the electronic excitation energy, ΔE, of the n$\rightarrow\pi$* transition
(Fig. 2). Correlations with the electronegativities of substitu-
ents show an inverse dependence to that expected. $\delta(^{77}$Se)
values range from -447 to 2162 ppm, and $\delta(^{13}$C) from 156,6 to
293,7 ppm. Similar results have been obtained for other seleno-
ketones[8].

In conclusion, the ^{77}Se chemical shift is dominated

- by the electronegativity of substituents in compounds in which
  selenium forms single bonds and

- by the low energy n$\rightarrow\pi$* electron excitation in compounds con-
  taining C=Se double bonds.

- Weak π-type interactions, e.g., in Se-Se and Se-S bonds, can
  lead to a compensation of the inductive effect through the
  lower ΔE term.

^{125}Te CHEMICAL SHIFTS

Only a few CF$_3$Te compounds have been investigated by multi-
nuclear NMR[2]. The compounds have been synthesized by Naumann and
coworkers[3]. Their chemical shifts are listed in Table I.

TABLE I ^{125}Te chemical shifts of CF$_3$Te compounds com-
pared with ^{77}Se chemical shifts of analogous CF$_3$Se com-
pounds. E = Te, Se. Ref. (CH$_3$)$_2$Te, (CH$_3$)$_2$Se.

	$\delta(^{125}$Te)	$\delta(^{77}$Se)		$\delta(^{125}$Te)	$\delta(^{77}$Se)
CF$_3$ECF$_3$	1368	717	(CF$_3$)$_2$EBr$_2$	1180	–
CF$_3$ECF$_2$Cl	1566	815	(CF$_3$)$_2$EO	1063	1095
CF$_3$EECF$_3$	686	550	(CF$_3$)$_2$E(CF$_3$COO)$_2$	1176	–
(CF$_3$)$_2$EF$_2$	1187	830	(CF$_3$)$_2$E(NO$_3$)$_2$	1202	–
(CF$_3$)$_2$ECl$_2$	1114	–			

Trends in chemical shift values appear to be in general similar for both nuclei. However, compounds of type $(CF_3)_2EX_2$ and CF_3EECF_3 exhibit unexpected values when compared with $(CF_3)_2EO$. The NMR parameters of $(CF_3)_2TeCl_2$, in particular the coupling constant $^2J(^{125}Te-^{19}F)$, are strongly temperature dependent. This can be rationalized in terms of the ionic dissociation equilibrium below:

$$(CF_3)_2TeCl_2 \rightleftharpoons (CF_3)_2TeCl^+ + Cl^-$$

COUPLING CONSTANTS INVOLVING ^{77}Se AND ^{125}Te

### $J(^{77}Se-^{13}C)$ and $J(^{125}Te-^{13}C)$ in CF_3Se and CF_3Te Compounds

The coupling constants are much larger in $CF_3Se(II)$ (127-195 Hz) and $CF_3Te(II)$ (420-523 Hz)[2] compounds than in analogous $CH_3Se(II)$ (46-73 Hz) and $CH_3Te(II)$ (162Hz in $(CH_3)_2Te$) compounds[9] (Fig. 4). A preliminary relationship between $^1J(SeC)$ and the s-character in the orbitals forming the Se-C bond is suggested based on the limited structural data available[2].

$$CH_3Se(II): \quad ^1J(SeC) = -0.23 \text{ \%s(Se) \%s(C)} \qquad (2)$$

$$CF_3Se(II): \quad ^1J(SeC) = -0.32 \text{ \%s(Se) \%s(C)} - 64 \qquad (3)$$

Eq. (3) indicates a non Fermi contact contribution in CF_3Se compounds of about 64 Hz which can be interpreted in terms of π-bond participation in the C-Se bond. The unexpected trend of ^{19}F chemical shifts in compounds of type CF_3-E-R (E = O, S, Se, R = substituent)[6] and E=CXY (X,Y = Halogen)[10] could also be explained by C-F π-type interactions. Instead of resonance formula the following simplified formulae I and II containing partial double bonds and one weak bond describe the electronic structures. NMR parameters are found to be extremely sensitive to the participation of π-type interactions.

$$F \cdots \underset{F}{\overset{F}{\diagdown}} C = E - R \quad (I) \qquad\qquad E = C \overset{F}{\underset{F}{\diagup}} \quad (II)$$
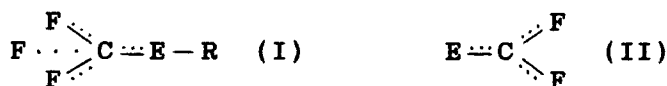
$^1J(^{77}Se-^{13}C)$ in Compounds Containing C=Se Double Bonds

The values vary between about 200 and 290 Hz[7,8]. Compounds containing sp-hybridized carbon show in general larger values than those containing sp^2-carbon. Thus, the Fermi contact term plays an important role.

$^2J(SeF)$ and $^2J(TeF)$ in CF_3Se and CF_3Te Compounds[2]

The coupling constants for $CF_3Se(II)$ (2-52 Hz), $CF_3Se(IV)$ (2-69 Hz), $CF_3Te(II)$ (37-95 Hz), and $CF_3Te(IV)$ (17-97 Hz) compounds vary considerably. A correlation with bonding or structural properties is not apparent.

$^1J(SeSe)$ in Diselenides and $^1J(TeTe)$ in $CF_3TeTeCF_3$

$^{77}Se-^{77}Se$ coupling constants in perhalogenomethyl diselenides have been determined to find out whether π-type interactions are involved in these bonds. The values obtained are considerably larger ($CF_3SeSeCF_3$ 48.5 Hz, $CF_3SeSeCF_2Cl$ 57.9 Hz, $CF_2ClSeSeCF_2Cl$ 66.5 Hz) than those found for organyl diselenides[11-14]. The relative sign is positive in $C_6H_5SeSeCH_3$ (+22 Hz)[11]. The small J-value in $CF_3SeSeCH_3$ (11 Hz[15]) can be understood only if the relative sign in halogenated diselenides is negative because this value should lie between those for organyl and halogenated diselenides. Therefore, the relative sign of $^1J(SeSe)$ in $CF_3SeSeCH_3$ has now been determined and is indeed found to be **negative**. If the Fermi contact term is positive and the orbital contribution resulting from π-type interactions negative, then the $^1J(SeSe)$ values should be more negative for diselenides with the lower mean ^{77}Se shielding through lower ΔE values. Figure 3
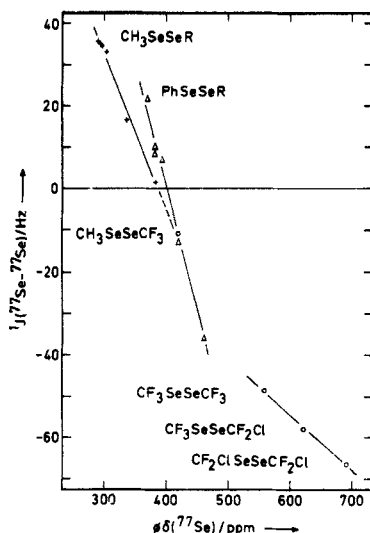
**FIGURE 3. Plot of Se-Se coupling constants versus the
mean ^{77}Se chemical shift of both Se nuclei in
diselenides.**

demonstrates that this assumption is reasonable. The analogous
plot for compounds CH_3SeSeR and C_6H_5SeSeR supports the presumption
of Odom et al.[13] that a sign inversion of $^1J(SeSe)$ could occur.

The conclusion is that in perhalogenomethyl diselenides a
weak π-type interaction occurs not only in the F-C-Se moiety but
extends over the whole molecule as well:

$$F \cdots \overset{\overset{\displaystyle F}{\diagdown}}{\underset{\underset{\displaystyle F}{\diagup}}{C}} = Se = Se = \overset{\overset{\displaystyle F}{\diagup}}{\underset{\underset{\displaystyle F}{\diagdown}}{C}} \cdots Cl$$

$^1J(^{125}Te-^{125}Te)$ in $CF_3TeTeCF_3$ (249,3 Hz, calculated from
$^1J(^{125}Te-^{123}Te)$ = 206,5 Hz[16]) is much larger than the analogous
Se-Se coupling constant in $CF_3SeSeCF_3$ (48,5 Hz). The reduced
coupling constants are: $^1K(TeTe)$ = 20.8$\cdot 10^{20}$, $^1K(SeSe)$ = 11.1$\cdot$
10^{20} $NA^{-2}m^{-3}$ (cf. ^1K-values).

Diverse Coupling Constants[2]

For the first time coupling constants $^1J(^{77}Se\,^{15}N)$ have been measured in the ^{15}N-enriched compounds $(CF_3Se)_3N$, $(CF_3Se)_2NH$ and CF_3SeNH_2. Further couplings including $^2J_{NC}$, $^3J_{FN}$ and $^5J_{FC}$ could also be detected. $^1J_{TeF}$, $^2J_{TeF}$, and $^3J_{TeF}$ are found in $(CF_3)_2TeF_2$ and $CF_3TeTeCF_3$, $^1J_{SeP}$ and $^3J_{SeP}$ in $(CF_3Se)_3P$.

$(CF_3Se)_3N$ $^1J_{SeN}$ 78,4, $^2J_{NC}$ 2,4, $^5J_{FC}$ 0,9

$(CF_3Se)_2NH$ $^1J_{SeN}$ 74,7, $^1J_{NH}$ 85,6, $^2J_{SeH}$ 4,8,

$^2J_{NC}$ 3,8, $^3J_{FN}$ 0,54, $^5J_{FC}$ 1,1

CF_3SeNH_2 $^1J_{SeN}$ 60,1, $^1J_{NH}$ 70,8, $^2J_{NC}$ 4,0, $^5J_{FC}$ 1,1

$(CF_3Se)_3P$ $^1J_{SeP}$ 203,1, $^3J_{SeP}$ 5,6

$(CF_3)_2TeF_2$ $^1J_{TeF}$ 234, $^2J_{TeF}$ 97

$CF_3TeTeCF_3$ $^2J_{TeF}$ 95,0, $^3J_{TeF}$ 12,4

Comparison of Reduced Coupling Constants K[2]

K values are of interest to compare the energy of spin-spin inter-
actions. $K(AB) = 4\pi^2 J_{AB}/(h \cdot \gamma_A \cdot \gamma_B)$.[17] The reduced coupling
constants $^1K(TeC)$ and $^2K(TeF)$ are larger than the corresponding
values of $^1K(SeC)$ and $^2K(SeF)$ (Table II). Thus, spin-spin inter-
actions are stronger for tellurium than for selenium in analogous
compounds.

Relative Signs of Coupling Constants

The following signs have been determined in the compounds
CF_3SeCH_3, $Se=CF_2$, $(CF_3Se)_2NH$, $CF_3SeSeCH_3$ and CF_3TeCF_3 relative to
the negative sign of $^1J_{FC}$.[18]

$^1J_{FC}$ neg., $^1J_{SeC}$ neg., $^1J_{TeC}$ pos. $(^1K_{TeC}$ neg.$)$,

$^2J_{SeF}$ neg., $^2J_{Se-N-H}$ pos., $^1J_{SeN}$ pos. $(^1K_{SeN}$ neg.$)$,

$^1J_{NH}$ neg. $(^1K_{NH}$ pos.$)$, $^1J_{SeSe}$ neg.

TABLE II Reduced coupling constants (K in 10^{20} $NA^{-2}m^{-3}$

	$^1K(SeC)$ $^1K(TeC)$	$^2K(SeF)$ $^2K(TeF)$
CH_3SeCH_3	– 10,8	–
CH_3TeCH_3	– 17,0	–
CF_3SeCF_3	– 23,3	– 0,487
CF_3TeCF_3	– 44,1	– 1,042
$CF_3SeSeCF_3$	– 30,0	– 0,301
$CF_3TeTeCF_3$	– 54,8	– 2,661
$(CF_3)_2SeO$	– 32,5	– 0,097
$(CF_3)_2TeO$	– 45,8	– 0,479

ISOTOPE EFFECTS ON THE NUCLEAR SHIELDING OF ^{77}Se AND ^{125}Te

__Definition:__ $^n\Delta N(^{k/1}N')/ppm = \delta_N(^kN') - \delta_N(^1N')$

$^n\Delta$: isotope shift via n bonds; N: resonant nucleus; $(^{k/1}N')$: pair of isotopes for which the effect is observed; k and l are given in the order of decreasing masses. If a signal is due to several isotopomers which contain isotopes without a magnetic moment, then the weighted average mass for the isotopes should be given, e.g., $^1\Delta^{125}Te(^{127.7/123}Te)$.[16]

$^1\Delta^{77}Se(^{13/12}C)$, Its Correlation with C-Se Bond Distances and Force Constants, and Its Temperature Dependence[16]

Thirty values for Se(II) and Se(IV) compounds containing sp^3-, sp^2-, and sp-hybridized carbon were measured (Fig. 4). A wide range of low frequency shifts was found between −0,012 and −1,099 ppm. A correlation between the isotope shift and the C-Se bond length was established for CF_3 and CH_3 substituted selenium compounds and for SeCO, SeCS, and SeCSe. Furthermore, the isotope shift of the latter compounds is inversely dependent on the
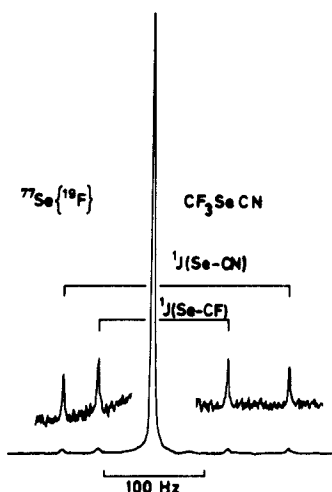
FIGURE 4. ^{19}F decoupled ^{77}Se NMR spectrum of CF$_3$SeCN showing the ^{77}Se-^{13}C coupling and $^{13/12}$C isotope shifts on δ^{77}(Se).

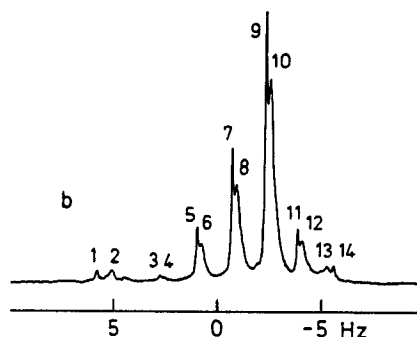FIGURE 5. ^{19}F and ^{1}H decoupled ^{77}Se NMR spectrum of the CH$_3$Se group of CF$_3$SeSeCH$_3$ showing the $^{n/74}$Se isotope effect on $\delta(^{77}$Se) and the presence of two conformers [15].

stretching force constant of the C=Se bond. After this first correlation between isotope shifts and bond distances three further examples for such a dependence were found for other isotope shifts[19-21].

The isotope effect can be temperature dependent; this was shown, for example, on liquid samples of CF$_3$SeCN and SeCO[16].

As expected, the analogous isotope effect $^1\Delta^{125}$Te($^{13/12}$C) in five Te(II) and Te(IV) compounds was found to be larger than in the corresponding selenium compounds due to the larger chemical shift range[16].

$^1\Delta^{77}$Se($^{n/74}$Se) (n = 76,77,78,80,82) in Diselenides[15]

For the first time the effect of Se isotopes on the adjacent ^{77}Se nuclear shielding was detected in CH$_3$SeSeCH$_3$, although not all Se

isotopes could be resolved[22]. A study of this isotope effect in

$CF_3SeSeCF_3$, $CF_3SeSeCH_3$ and $CH_3SeSeCH_3$ with a 5.9 T NMR spectro-

meter showed that not only all Se isotopes can be resolved but

that the isotope effect per unit mass difference decreases with

increasing mass of the Se isotopes. This is the first experi-

mental proof for the dependence of isotope shifts on the relative

mass fraction[15] as is expected theoretically. An excellent

linear correlation of the isotope shift with (n-74)/n was estab-

lished based on these data[23].

The presence of two different species of $CF_3SeSeCH_3$ was

deduced from the highly resolved ^1H and ^{19}F decoupled ^{77}Se NMR

spectrum. $^{77}Se-^{77}Se$ coupling constants of 10.4 and 11.5 Hz were

obtained for these two species (lines 1, 14 and 2, 13, respec-

tively, Fig. 5) which are assigned to two conformers[15].

Diverse Isotope Effects

The measurement of the $^{125}Te-^{123}Te$ coupling constant in the ^{125}Te

and ^{123}Te NMR spectra of $CF_3TeTeCF_3$ allowed evaluation of the iso-

tope shifts $^1\Delta^{125}Te(^{127.7/123}Te) = -0.042$ ppm and

$^1\Delta^{123}Te(^{127.9/125}Te) = -0.018$ ppm[16]. Weighted average masses of

127.7 and 127.9 of several isotopomers were used. The difference

in isotope shift reflects the different fractional changes in

mass. It is noteworthy that tellurium is the heaviest element so

far for which isotope effects have been observed.

The two-bond isotope shifts of $^{37/35}Cl$ on ^{77}Se and ^{125}Te in

$CF_3SeCFCl_2$ and CF_3TeCF_2Cl are: $^2\Delta^{77}Se(^{37/35}Cl) = -0.0124$ ppm,

$^2\Delta^{125}Te(^{37/35}Cl) = -0.0266$ ppm[2].

$^2\Delta^{77}Se(^{15/14}N)$ values of -0.070 ppm for N_{ax} and -0.098 ppm

for N_{eq} were found in Phenylamino-selenoxodioxaphosphorinanes[19].

EXPERIMENTAL

Some compounds were prepared after literature methods, some

especially synthesized for this NMR study and some synthesized

for a thesis in the group of Prof. Haas, Bochum. The CF_3Te compounds have been synthesized in the group of Prof. Naumann, Dortmund, two selones in the group of Prof. Voss, Hamburg.

The NMR spectra were recorded on a Bruker WM 250 spectrometer operating at 47.71, 62.90, 65.61, 78.92, 235.36, and 250.13 MHz for ^{77}Se, ^{13}C, ^{123}Te, ^{125}Te, ^{19}F, and ^{1}H, respectively. A homemade ^{19}F decoupling device was used.

ACKNOWLEDGMENTS

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