Studies in selenium-77 and tellurium-125 nuclear magnetic resonance. Substituent effects and polarizability

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Abstract

Selenium-77 substituent-caused chemical shifts, where the substituents are alkyl groups, have been studied for a series of selenols, selenides and diselenides, respectively. An understanding of the origin of these shifts was obtained by examining solvent effects on [77]Se chemical shifts of dialkyl selenides and dialkyl diselenides in ten halocarbon solvents of varying molecular polarizabilities as well as in 2,2,2-trifluoroethanol. Based on these results of intermolecular polarizability, an *intramolecular* polarizability concept is proposed whereby dispersion forces within a molecule exerted by neighboring alkyl and haloalkyl groups influence selenium shielding. This effect along with the well-known "γ effect" offer a clear understanding of a large number of [77]Se chemical shifts. The same intramolecular polarizability concept can be used when examining the chemical shifts of tellurides and ditellurides. Here, even larger substituent caused chemical shifts are observed. Solvent effects on [125]Te chemical shifts of dimethyl telluride were also examined in solvents of varying polarizability. As in the case of several selenides and diselenides studied, the [125]Te chemical shift of dimethyl telluride can be correlated with the polarizability of the solvent.

The interpretation and analysis of substituent caused chemical shifts (SCS) in nuclear magnetic resonance spectroscopy have yielded tremendous insight into the electronic structure of many molecules [1]. The study of substituent effects on chemical shifts has been particularly rewarding in ^{13}C and ^{31}P NMR spectroscopy [1–7], although similar studies with other nuclei with low natural abundance (e.g. [15]N, [17]O, [77]Se, [125]Te) have begun to appear [8,9]. The [77]Se and [125]Te nuclei are especially conducive to such substituent effect NMR studies due to their very large chemical shift ranges [10,11]. For example, the known chemical shift range of [77]Se is presently about 2800 ppm with the most shielded resonance occurring at −665 ppm [12] (disilyl selenide) and the most deshielded resonance at 2135 ppm [13] (tetrahy-

dro-3,3,5,5-tetramethyl-4-*H*-thiopyran-4-selone) with respect to dimethyl selenide. Within this chemical shift range some rather extraordinary substituent effects are observed. In what could be considered the most "subtle" substituent effect, secondary deuterium-induced isotope shifts of more than 7 ppm have been observed in the ^{77}Se NMR spectrum of a solution of $H_{2-n}D_nSe$ ($n = 0, 1, 2$); these are the largest secondary isotope shifts observed in high resolution NMR spectroscopy for any spin isotope [14]. Similarly, the substitution of a hydrogen atom for a methyl group (i.e. CH_3SeCH_3 to CH_3SeH) results in a shielding of the ^{77}Se resonance of 115 ppm, and the substitution of two ethyl groups for two methyl groups (i.e. CH_3SeCH_3 to $C_2H_5SeC_2H_5$) deshields the ^{77}Se resonance by 230 ppm (vide infra). Even when substituents are well removed from the selenium atom, the ^{77}Se chemical shift is usually quite sensitive to the transmission of electronic effects. In our laboratories we have found this to be the case in a series of organic selenyl sulfides [15], 4-substituted phenyl selenobenzoates [16] and selenocyanates [17] and 4,4'-disubstituted diphenyl diselenides [17].

It is generally considered that the shielding of selenium is dominated by the paramagnetic term, σ^P, which is related to several factors [18,19] as shown in expression (1)

$$\sigma^P \propto \frac{-\langle r^{-3}\rangle_{4p}}{\Delta E} \sum Q \qquad (1)$$

where $\langle r^3\rangle_{4p}$ is the mean inverse cube of the radius of the $4p$ orbitals, the Q terms denote the imbalance of charge in the valence shell of selenium and ΔE is the effective excitation energy. From expression (1), it is evident that deshielding of selenium will increase (i) as the valence shell electrons get closer to the nucleus, i.e. the larger the radial factor $\langle r^{-3}\rangle_{4p}$, (ii) as the asymmetry of the valence cloud increases, i.e. the greater the ΣQ term and (iii) as ΔE becomes smaller and excitation becomes easier. An increase in the electron-withdrawing ability of the groups attached to selenium should decrease the value of r, thereby increasing $\langle r^{-3}\rangle$ and increasing the deshielding. Such a correlation is demonstrated [20] by the ^{77}Se chemical shifts for a series of methyl derivatives in which selenium shielding increases in the order $CH_3SeOOH < (CH_3)_2SeO_2 < (CH_3)_2SeCl_2 < (CH_3)_2SeBr_2 < (CH_3)_2Se_2 < CH_3SeCH_3 < CH_3SeH < CH_3Se^-$. This is also the order of decreasing electronegativity of the substituents attached to selenium. A similar order is found when the chemical shifts of a series of phenyl derivatives are compared [12]. For example, the shielding increases in the order $C_6H_5SeOOH < C_6H_5SeCl < C_6H_5SeBr < C_6H_5SeSC_6H_5 < C_6H_5SeSeC_6H_5 < C_6H_5SeCH_3 < C_6H_5SeH < C_6H_6Se^-$.

The ultimate objective of our ^{77}Se NMR studies is to obtain and provide meaningful interpretations of ^{77}Se spectra of selenium containing biomolecules. To this end we have attempted to build a solid foundation of ^{77}Se NMR parameters through a series of relatively basic investigations including relaxation time studies [21,22], model system studies [15,16], a careful study of dimethyl selenide as a chemical shift reference [23] and ^{77}Se NMR studies of the association of selenium-containing compounds with selected enzymes and proteins [24–26].

To date, ^{77}Se and ^{125}Te chemical shifts have received limited theoretical attention; however, in examining our data and ^{77}Se and ^{125}Te chemical shifts reported from other laboratories, we have attempted to understand these shifts and various substituent effects on, at least, an empirical basis. As chemical shift data of these

"heavy" nuclei accumulated, it appeared that alkyl substituent effects were related to the polarizability of the electron cloud of the relatively "soft" selenium and tellurium atoms. To establish this relationship we have examined [77]Se and [125]Te chemical shifts in solvents of varying polarizability and have then extrapolated these intermolecular results to explain intramolecular substituent effects on [77]Se and [125]Te chemical shifts. The results of this study and the interpretation of a large number of [77]Se chemical shifts of selenols, selenides and diselenides are presented herein.

Results and discussion

[77]Se chemical shifts

McFarlane has noted previously that the correlation of selenium shielding with the electronegativity of attached substituents breaks down in the series of selenium compounds where substituents are only alkyl groups or hydrogen [20]. Thus in the series R_2Se, R_2Se_2, RSeH, RSe⁻, where R is an alkyl group, the shielding of selenium increases in the order t-Bu < i-Pr < Et < Me. These organic groups possess essentially identical electronegativity values [27]; therefore, the inductive effect can not be used as the rationale for the [77]Se chemical shift trends observed in these compounds.

In alkane selenols, we observed the same deshielding trend found by McFarlane [20]. In this series, a deshielding, varying from 110–151 ppm, of the [77]Se resonance occurred upon the replacement of an α-hydrogen by a methyl group with CH_3SeH possessing the most shielded [77]Se resonance at −115 ppm (Table 1) and t-C_4H_9SeH being the most deshielded with the [77]Se resonance occurring at 272 ppm (Table 1).

In alkyl selenides, a deshielding of the [77]Se resonance is once again observed each time a hydrogen atom in the parent compound, CH_3SeCH_3 (0 ppm) is replaced by a methyl group (Table 1); for example, in the series CH_3SeCH_3 (0 ppm), $CH_3SeCH_2CH_3$ (112 ppm), $CH_3SeCH(CH_3)_2$ (206 ppm), $CH_3SeC(CH_3)_3$ (295 ppm) where deshielding ranges from 89–112 ppm for each α-substitution of a hydrogen by a methyl group. Symmetrical selenides display an even larger deshielding; this can be explained by the fact that these compounds features two α-substitutions of a hydrogen by a methyl group, e.g. CH_3SeCH_3 to $CH_3CH_2SeCH_2CH_3$. In the series CH_3SeCH_3 (0 ppm), $CH_3CH_2SeCH_2CH_3$ (230 ppm), $(CH_3)_2CHSeCH(CH_3)_2$ (429 ppm), and $(CH_3)_3CSeC(CH_3)_3$ (614 ppm), the deshielding resulting from the two α-substitutions varies from 185–230 ppm.

In symmetrical dialkyl diselenides, a similar but smaller deshielding (66–87 ppm per replacement of a hydrogen by a methyl group per selenium atom) is observed (Table 1) in the [77]Se chemical shifts of $CH_3SeSeCH_3$ (270 ppm), CH_3CH_2SeSe-CH_2CH_3 (336 ppm), $(CH_3)_2CHSeSeCH(CH_3)_2$ (404 ppm), $(CH_3)_3CSeSeC(CH_3)_3$ (491 ppm) [28]. In all cases each methyl group causes an additional deshielding to the [77]Se resonance which is surprisingly large for a relatively small change in the electronic nature and electronegativity of these groups. This trend, which has been highlighted above for the alkane selenols, selenides, and diselenides, has also been observed in phenyl alkyl selenides [29], and alkyl tellurides [29] and ditellurides [30]. In these previous studies, it was noted that the extent of α-branching on the carbon adjacent to the chalcogen was the major influence upon the [77]Se (or [125]Te) chemical shift [29,30].

Table 1

[77]Se chemical shifts of alkyl selenols, selenides and diselenides

Compound	δ (ppm) [a]
Selenols	
CH_3SeH	-115
C_2H_5SeH	36
$i\text{-}C_3H_7SeH$	161
$t\text{-}C_4H_9SeH$	289
$n\text{-}C_3H_7SeH$	27
$n\text{-}C_4H_9SeH$	82
Selenides	
$(CH_3)_2Se$	0
$(C_2H_5)_2Se$	230
$(i\text{-}C_3H_7)_2Se$	429
$(t\text{-}C_4H_9)_2Se$	614
$(n\text{-}C_3H_7)_2Se$	155
$(n\text{-}C_4H_9)_2Se$	161
$CH_3Se(C_2H_5)$	112
$CH_3Se(i\text{-}C_3H_7)$	206
$CH_3Se(t\text{-}C_4H_9)$	295
$CH_3Se(n\text{-}C_3H_7)$	75
$CH_3Se(n\text{-}C_4H_9)$	79
Diselenides	
$CH_3SeSeCH_3$	270
$(C_2H_5)_2Se_2$	336
$(i\text{-}C_3H_7)_2Se_2$	404
$(t\text{-}C_4H_9)_2Se_2$	491
$(n\text{-}C_3H_7)_2Se_2$	305
$(n\text{-}C_4H_9)_2Se_2$	346
$C_2H_5Se^\star SeCH_3$	399*; 208
$i\text{-}C_3H_7Se^\star SeCH_3$	493*; 178
$t\text{-}C_4H_9Se^\star SeCH_3$	584*; 179
$n\text{-}C_3H_7Se^\star SeCH_3$	358*; 219
$n\text{-}C_4H_9Se^\star SeCH_3$	362*; 218

[a] All shifts are measured relative to $(CH_3)_2Se$ in $CDCl_3$ (60% v/v). Also, $CDCl_3$ was used as the lock solvents in all samples.

An understanding of these [77]Se substituent-caused chemical shifts can be obtained by more closely examining solvent effects on the [77]Se chemical shifts of these alkyl selenides and diselenides. The solvents shifts of three dialkyl selenides and three dialkyl diselenides in ten halocarbons and 2,2,2,-trifluoroethanol are provided in Table 2. In order to eliminate solute–solute interactions as much as possible, dilute solutions (5% v/v) were employed. Values of the bulk susceptibility correction for each solvent were derived from molar susceptibility and density data [31]. When molar susceptibility data were not available, values were obtained with the aid of Pascal's constants [32,33]. The bulk susceptibility value of the standard solution (60% $(CH_3)_2Se$ in $CDCl_3$) was calculated using the additivity law of volume susceptibilities [32,33]. The solvents which were chosen were all tetrahedral one-carbon molecules (with the exception of CF_3CH_2OH) which are in general nonpolar, have negligible diamagnetic anisotropy and span a wide range of molecu-

lar polarizabilities. Since molecular polarizability is a function of the refractive index [34], an attempt was made to correlate solvent polarizability with the solvent-induced shifts. For example, 2,2,2-trifluoroethanol was chosen because it has a very low value of refractive index [31] and methylene iodide was chosen for its corresponding high value [31]. Trifluoroacetic acid was initially used because of its low refractive index; however, it appeared that a reaction may have been occurring between the selected selenides and diselenides and the CF_3COOH solvent. A solvent with a comparable refractive index was needed; therefore, 2,2,2-trifluoroethanol was chosen for this study.

From the data in Table 2 it can be seen that the solvent shifts cover a range of 28–54 ppm for the selenides and 20–23 ppm for the diselenides. It should also be noted that the extreme values for these solvent shifts for alkyl selenides and diselenides occur for the solvents 2,2,2-trifluoroethanol (maximum shielding) and diiodomethane (maximum deshielding). Thus it appears that dispersion forces may dominate the intermolecular shielding. To further demonstrate that these dispersive interactions are important, the solvent shifts were plotted against the following parameters: 1) refractive index, η, 2) refractive index function [35,36], $\eta^2 - 1/2\eta^2 + 1$ and, 3) polarizability/molar volume (b/V_M) of solvents. For selenides and diselenides, the best correlations of solvent-induced shifts were obtained with the polarizability/molar volume function of the solvent, and plots of ^{77}Se NMR chemical shifts versus the (b/V_M) function for dimethyl selenide and diisopropyl diselenide (Fig. 1) reveal several features of the systems under study. First, as the polarizability/molar volume of the solvent increases, the deshielding of the selenium resonance increases in a linear fashion, i.e. more electron density is being withdrawn from the selenium atom by the more polarizable solvent. Second, excess deshielding of selenium occurs with CCl_4, CCl_3Br and CCl_2Br_2. As shown in Fig. 1, the ^{77}Se chemical shifts observed for these three solvent systems correlate linearly. The rationale for this behavior is not evident and should receive further attention. If we disregard these three solvents, a good linear correlation exists for the remaining eight solvents (Fig. 1).

Based on these results of intermolecular polarizability, we propose an *intramolecular* polarizability concept where dispersion forces within a molecule exerted by neighboring alkyl groups influence selenium shielding. Alkyl groups have been shown to be very polarizable in the gas phase in that they stabilize a positive or a negative charge [37,38]. This is nicely illustrated in the gas phase acidities [37,38] (an intrinsic property as in NMR shielding) of alcohols. The observed order of gas phase acidities of alkyl alcohols is $(CH_3)_3COH > (CH_3)_2CHOH > CH_3CH_2OH > CH_3OH > H_2O$ which is exactly the reverse of the solution order. This polarizability effect is based on the charge-induced dipole interaction and attenuates rapidly with distance (proportional to r^{-4}) between the centers of polarizability and of charge. Since the polarizability of a molecule is an additive property [39], successive additions of a methyl group at a fixed distance should exert nearly the same influence. Thus in going from $CH_3SeCH_3 \rightarrow CH_3SeCH_2CH_3 \rightarrow CH_3CH_2SeCH_2$ $CH_3 \rightarrow CH_3SeC(CH_3)_3 \rightarrow (CH_3)_2CHSeCH(CH_3)_2 \rightarrow (CH_3)_3CSeC(CH_3)_3$, successive replacement of a methyl group at a fixed distance disperses the electron density at the highly polarizable selenium atom by approximately the same magnitude which correspondingly increases the $\langle r^{-3} \rangle$ factor (r decreases) and may also increase the asymmetry factor, ΣQ, in expression (1). The net result is an increased

Table 2

^{77}Se chemical shifts of selenides and diselenides in selected halocarbon solvents

Solvent	Compound												b/V_M ($\times 10^{24}$)
	$(CH_3)_2Se$		$(CH_3)_2Se_2$		$(C_2H_5)_2Se$		$(C_2H_5)_2Se_2$		$(i\text{-}C_3H_7)_2Se$		$(i\text{-}C_3H_7)_2Se_2$		
	Obs.	Corr.[a]	Obs.	Corr.	Obs.	Corr.	Obs.	Corr.	Obs.	Corr.	Obs.	Corr.	
CH_2Cl_2	−4.5	−4.4	267.3	267.2	230.5	230.4	332.5	332.4	426.9	426.8	396.1	396.0	0.1012
CH_2ClBr	−2.8	−3.1	268.9	268.6	231.1	230.8	334.3	334.0	427.2	426.9	402.9	402.6	0.1134
$CHCl_3$	−4.8	−4.9	268.4	268.3	227.7	227.6	333.5	333.4	424.1	424.0	402.0	401.9	0.1057
CH_2Br_2	−0.9	−1.4	270.6	270.1	231.9	231.4	336.3	335.8	427.4	426.9	404.0	403.5	0.1247
$CHCl_2Br$	−2.2	−2.4	270.2	270.0	228.2	228.0	335.7	335.5	424.0	423.8	404.5	404.3	0.1159
$CHClBr_2$	−0.5	−0.9	271.6	271.2	228.6	228.2	337.4	337.0	424.2	423.8	406.4	406.0	0.1259
CCl_4	5.4	5.4	275.2	275.2	238.4	238.4	340.9	340.9	435.5	435.5	409.3	409.3	0.1086
CCl_3Br	8.4	8.3	276.7	276.6	235.9	235.8	342.9	342.8	431.5	431.4	412.0	411.9	0.1178
CCl_2Br_2	11.4	11.2	273.8	273.6	239.7	239.5	344.5	344.3	428.5	428.3	414.1	413.9	0.1269
CH_2I_2	11.5	10.6	279.1	278.2	235.8	234.9	336.1	335.2	429.6	428.7	413.4	412.5	0.1603
CF_3CH_2OH	−23.2	−22.8	257.5	257.9	210.8	211.2	323.4	323.8	381.6	382.0	390.1	390.5	0.07184

[a] Bulk susceptibility corrections were derived from molar susceptibility and density data or from Pascal's constants (see Results and Discussion).
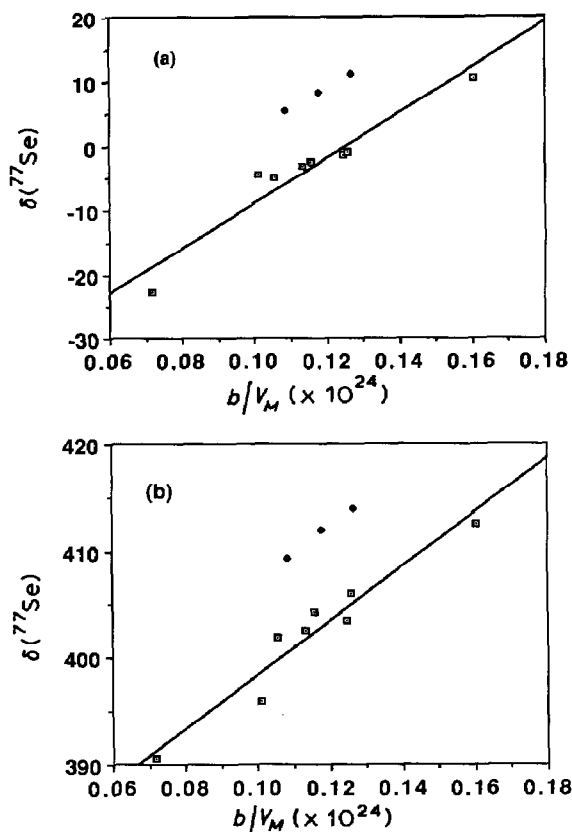
Fig. 1. ^{77}Se chemical shift of (a) dimethyl selenide and (b) di-isopropyl diselenide vs. polarizability/molar volume ($b/V_M \times 10^{24}$) in solvents listed in Table 2. The correlation coefficient for dimethyl selenide in (□) solvents = 0.96; the correlation coefficient for di-isopropyldiselenide in (□) solvents = 0.97. In (a) and (b), ■ represents ^{77}Se chemical shifts in CCl_4, CCl_3Br, CCl_2Br_2 (see Results and discussion).

deshielding of about equal magnitude in each case. The deshielding observed in alkane selenols (Table 1) can be explained in a similar manner as the methyl hydrogens in methyl selenol are successively replaced by methyl groups.

In molecules where the alkyl group is n-propyl, a *shielding* of selenium is observed relative to the case where the alkyl group is ethyl. For example, this is seen in the compounds CH_3SeCH_3 (0 ppm), $CH_3SeC_2H_5$ (112 ppm), $CH_3Se(i-C_3H_7)$ (206 ppm), $CH_3Se(t-C_4H_9)$ (295 ppm), and $CH_3Se(n-C_3H_7)$ (75 ppm). This shielding in n-propyl derivatives can be explained since a methyl group is now introduced two carbon atoms away from the selenium and thus the deshielding introduced by an extra methyl group is very small compared to that in $CH_3Se(i-C_3H_7)$ where the methyl group is introduced one atom removed from selenium. In addition, introduction of a methyl group in the γ-position with respect to the selenium atom causes shielding by the "γ-effect" [12,28], which is well-known and accepted in ^{13}C NMR spectroscopy [40]. Confirmation of this γ-effect in selenium NMR spectroscopy is further established by comparing the ^{77}Se NMR chemical shifts of some aryl alkyl selenides, namely, $C_6H_5SeCH_2CH(CH_3)_2$ (264 ppm) and $C_6H_5SeCH_2CH_2CH_2CH_3$ (288 ppm), and $C_6H_5SeCH(CH_3)CH_2CH_3$ (354 ppm) and $C_6H_5SeCH(CH_3)_2$ (424 ppm) [29]. In the first case the iso-butyl derivative has two γ-carbons with respect to

selenium whereas the n-butyl derivative has only one such carbon; thus an increased shielding of 24 ppm is observed with the iso-butyl derivative. In the second case, introduction of a γ-carbon in the iso-propyl compounds yields a s-butyl derivative and causes a shielding of 30 ppm. The replacement of a methyl hydrogen of the n-propyl group by an alkyl group has virtually no effect on the selenium shielding, as in the case of CH_3Se-n-C_3H_7 (75 ppm) and CH_3Se-n-C_4H_9 (79 ppm) and in (n-C_4H_9)$_2Se$ (167 ppm) and (n-C_8H_{17})$_2Se$ (168 ppm). Thus, intramolecular dispersion effects of "near neighbor" alkyl groups have a great influence on the shielding of the selenium nucleus.

An interesting example where a less electronegative group influences the shielding of selenium-77 in the reverse manner is the observed deshielding in the series CF_3SeCH_3 (370 ppm), $CF_3SeCFCl_2$ (927 ppm) and CF_3SeCCl_3 (953 ppm) [41]. This shielding order has been explained by considering carbon–fluorine and carbon–chlorine hyperconjugation [41]. However serious reservations have been expressed and reviewed [42–44] concerning this concept and conclusions have also been advanced that C–F hyperconjugation does *not* play a significant role in the stability or reactivity of aliphatic organofluorine compounds or aromatic compounds with perfluoroalkyl substituents. An attractive alternative explanation for this order of shielding is the polarizability concept. The atomic polarizabilities of F, Cl and Br are 0.53, 2.61 and 3.79 $\mathring{A}^3$, respectively [43]. Compared to fluorine, the more polarizable chlorine atom can more effectively polarize the electron density of the selenium atom and thus cause a deshielding of the selenium resonance. This concept has been used previously to explain [44] the order of gas phase acidities of halogen-substituted acetic acid molecules, i.e. $FCH_2COOH < ClCH_2COOH < BrCH_2COOH$ which is the reverse of the order in aqueous solution.

The polarizability concept can also explain the order of ^{77}Se chemical shifts observed in dialkyl diselenides. As mentioned previously, a deshielding of approximately 66–87 ppm is observed in going from $(CH_3)_2Se_2 \rightarrow (C_2H_5)_2Se_2 \rightarrow [(CH_3)_2CH]_2Se_2 \rightarrow [(CH_3)_3C]_2Se_2$. The magnitude of the deshielding is less than that observed in alkyl selenides, and this smaller deshielding in diselenides can be understood in terms of the difference in the site where substitution takes place. For $(CH_3)_2Se$ to $(C_2H_5)_2Se$, the substitution takes place at each of the α-carbons, whereas for $(CH_3)_2Se_2$ to $(C_2H_5)_2Se_2$, each of the methyl groups is introduced at the α-position with respect to one selenium atom and at the β-position with respect to the second selenium atom. Thus, in diethyl diselenide each of the selenium atoms has a methyl group in the γ-position, which induces a shielding of selenium by the γ-effect (vide supra). Therefore, in the series $(CH_3)_2Se_2 \rightarrow (C_2H_5)_2Se_2 \rightarrow [(CH_3)_2CH]_2Se_2 \rightarrow [(CH_3)_3C]_2Se_2$, each new methyl group induces *deshielding* of the β-selenium by a polarizability effect and *shielding* of the distant selenium by the γ-effect, resulting in a smaller magnitude of deshielding compared to that observed in the alkyl selenide series.

^{125}Te chemical shifts

If this polarizability concept successfully explains ^{77}Se chemical shifts of dialkyl selenides and dialkyl diselenides, then it should also have applicability to the corresponding chemical shifts of the more polarizable tellurium atom. Indeed the effect of replacing α-hydrogens by alkyl groups on ^{125}Te chemical shifts parallels that observed in the ^{77}Se chemical shifts for analogous compounds. A deshielding of

tellurium is observed [29] when hydrogens in $(CH_3)_2Te$ are replaced by methyl groups as shown, for example, in the following series: (1) CH_3TeCH_3 (0 ppm), $CH_3TeC_2H_5$ (185 ppm), $CH_3TeCH(CH_3)_2$ (342 ppm) and $CH_3TeC(CH_3)_3$ (497 ppm); (2) $C_2H_5TeCH_3$ (185 ppm), $C_2H_5TeC_2H_5$ (376 ppm), $C_2H_5TeCH(CH_3)_2$ (532 ppm), $C_2H_5TeC(CH_3)_3$ (690 ppm); (3) i-PrTe-i-Pr (696 ppm), i-PrTe-t-Bu (866 ppm) and (4) t-BuTe-t-Bu (999 ppm). The chemical shift values of all possible methyl derivatives of $(CH_3)_2Te$ are considered above, and in each case the deshielding introduced per replacement of a hydrogen atom by a methyl group is approximately 185 ppm. Furthermore, the shielding caused by the introduction of a γ-carbon in tellurides can be clearly seen in the ^{125}Te-chemical shifts if the following compounds are compared, i.e. $CH_3TeC_2H_5$ (185 ppm); CH_3Te-n-Pr (115 ppm); CH_3Te-i-Bu (64 ppm); CH_3Te-n-C_5H_{11} (25 ppm) [29]. Thus, the replacement of one hydrogen atom on the β-carbon of the ethyl group in $CH_3TeC_2H_5$ by a methyl group introduces a shielding of 70 ppm. Further replacement introduces additional shielding although the magnitude of the shielding decreases. A small deshielding is observed [29] if alkyl substitution takes place at the γ-carbon, and alkyl substitution more remote to tellurium than the γ-carbon has a relatively small effect on the ^{125}Te chemical shifts, e.g. (1) CH_3Te-n-Pr (95 ppm); CH_3Te-n-Bu (103 ppm); (2) $(n-Bu)_2Te$ (228 ppm); $(n-C_{16}H_{33})_2Te$ (232 ppm).

The effect of alkyl substitution on the ^{125}Te chemical shifts for phenyl methyl telluride is consistent with that observed with $(CH_3)_2Te$. Thus, for alkyl phenyl tellurides, the most shielded tellurium resonance is found in methyl phenyl telluride and the most deshielded resonance is observed for t-butyl phenyl telluride [29].

As with alkyl tellurides, ^{125}Te magnetic shielding of dialkyl ditellurides closely parallels that of selenium in analogous diselenides, but the sensitivity to changes in alkyl groups is again even greater [45]. For example, compare $(CH_3)_2Te_2$ (49 ppm); $(C_2H_5)_2Te_2$ (166 ppm); $(i-Pr)_2Te_2$ (293 ppm) and $(t-Bu)_2Te_2$ (477 ppm). The deshielding effect per replacement of a hydrogen atom by a methyl group per tellurium atom is approximately 120 ppm compared to ~ 65 ppm in the ^{77}Se chemical shifts of analogous selenium compounds. As previously discussed for ^{77}Se chemical shifts, the influence of each methyl group is two-fold, (i) to induce deshielding of the proximate tellurium by the polarizability effect and (ii) to cause shielding of the distant tellurium by the γ-effect. This two-fold influence is further illustrated if the ^{125}Te chemical shifts of the following ditellurides [45] are compared: $CH_3TeTeCH_3$ (69 ppm); $CH_3Te^{\star}TeC_2H_5$ (−28 ppm (*), 284 ppm); $CH_3Te^{\star}Te$-i-Pr (−74 ppm (*), 455 ppm); $CH_3Te^{\star}Te$-t-Bu (−48 ppm (*), 617 ppm). In these compounds the tellurium bonded to the methyl group is shielded by successive methylation of the distant methyl group, whereas the shielding of the remote tellurium decreases progressively. The tellurium atom remote to the methyl group does not have any γ-atom and thus experiences only the deshielding caused by the polarizability effect of the alkyl group in going from $(Me)_2Te_2 \rightarrow \rightarrow \rightarrow MeTe$-Te-t-Bu. On the other hand, the methyl bonded tellurium atom experiences a net shielding from the two opposing effects (shielding from the γ-effect and deshielding from the polarizability effect).

Additionally, in a preliminary study, the ^{125}Te chemical shift of $(CH_3)_2Te$, which appears to be the chemical shift standard of choice for this nucleus, was measured in solvents of varying polarizability (Table 3). The results were analogous to those found in the ^{77}Se study, i.e. the more polarizable the solvent, the more deshielded the tellurium resonance.

Table 3

^{125}Te solvent shifts of $(CH_3)_2$Te in selected halocarbon solvents

Solvent	δ	
	Obs.	Corr.
CH_2Cl_2	−15.9	−15.9
CH_2ClBr	−14.5	−14.8
$CHCl_3$	−19.9	−20.0
CH_2Br_2	−14.0	−14.2
CCl_4	0.1	0.1
CH_2I_2	−5.3	−6.2
Neat	0.0	0.0
CF_3CH_2OH	−50.8	−50.4

Conclusion

It has been shown that ^{77}Se and ^{125}Te chemical shifts of alkane selenols, dialkyl selenides, dialkyl diselenides, dialkyl tellurides and dialkyl ditellurides can be explained on the basis of the polarizability of substituents attached to these elements. Furthermore, it appears that the γ-effect also can play a part in determining the shifts of these compounds. This empirically derived treatment offers a more thorough understanding of these chemical shifts; however, a rigorous theoretical explanation for the relationship between these chemical shifts would be most welcome.

Experimental

Materials

All solvents were obtained commercially (Aldrich, Columbia Organic Chemicals) and were distilled immediately prior to use except for 2,2,2-trifluoroethanol (Aldrich, 99 + %, Gold Label) which was used as received. Dimethyl selenide, dimethyl diselenide and dimethyl telluride were obtained commercially (Alfa) and, after checking their purity by ^{77}Se (or ^{125}Te) NMR spectroscopy, were used without further purification.

Selenium compounds

All selenols were prepared by known methods [46–51]. Symmetrical selenides and diselenides were prepared from Li_2Se (or Li_2Se_2) and the corresponding alkyl halides [52], with the exception of t-Bu_2Se and t-Bu_2Se_2, which were prepared as described in the literature [28]. The preparation of unsymmetrical diselenides was described by our group previously with the exception of n-propyl methyl diselenides, which was made for this study by the reaction of $MeSe_2Li$ and n-PrBr [28].

Unsymmetrical selenides were prepared as follows. 1.0 g (12.7 mmol) of elemental Se was placed in a 50 ml, 2-neck flask fitted with a septum and evacuated. The flask was then cooled to −196°C and, under static vacuum, 10 ml of methyllithium (1.4 M in diethyl ether) was added along with 10 ml of freshly distilled THF. The flask was evacuated, thereby removing all non-condensables, and warmed to room

temperature with stirring. Within minutes a white suspension was produced. This flask was cooled once again to $-196°C$ and evacuated. The corresponding alkyl halide (14 mmol) was then condensed onto the lithium methaneselenolate. The flask was allowed to warm to room temperature and the solution stirred for several hours. The suspension was filtered and solvent removed on a rotary evaporator. The remaining unsymmetrical selenide was then condensed into an evaluated stopcock tube and its composition and purity were checked by GC/MS.

Instrumental

Natural abundance ^{77}Se NMR spectra were obtained on a Bruker WP200 NMR spectrometer, Bruker AM300 NMR spectrometer, and a Bruker WH400 spectrometer operating at 38.17, 57.24, and 76.31 MHz, respectively. All samples listed in Table 2 and Table 3 were 5% solutions (v/v) and were placed in NMR tubes coaxially inserted in a larger NMR tube containing chloroform-d, whose deuterium resonance provided the field/frequency lock. Chemical shifts were measured relative to an external 60% solution (v/v) of $(CH_3)_2Se$ in $CDCl_3$ [23]. The probe temperature was held at $22 \pm 1°C$. Generally, 3000–4000 scans were acquired using a pulse angle of $40°$ and a recycle time of 4 s. A sweep width of 2000 Hz and 16K data points resulted in a resolution of ± 0.01 ppm.

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