Selenium and Proton Nuclear Magnetic Resonance Measurements on Organic Selenium Compounds[1]

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Abstract: The chemical shift of ^{77}Se was measured in symmetric dialkyl and diphenyl selenides and diselenides by conventional nmr techniques on samples containing the isotope in its natural abundance of 7.5%. The organic selenium compounds exhibited chemical shifts ranging from 822 ppm for PhSeSePh to 1282 ppm for $(CH_3)_2Se$ upfield from an external standard of H_2SeO_3(aq). Large differences in chemical shift between selenides and diselenides having the same organic groups were observed (226 ppm for methyl and 58 ppm for phenyl compounds). The main contribution to the ^{77}Se chemical shift arose from the paramagnetic term of the shielding coefficient and this in turn was correlated with the lowest electronic transitions of the molecule considered. Proton chemical shifts in the alkyl compounds were shown to be dependent on the electronegativity of -Se- or -SeSe- substituents and, therefore, dominated by the diamagnetic term of the shielding coefficient.

Naturally occurring selenium contains an isotope, ^{77}Se, possessing a nuclear magnetic moment that makes it suitable for nmr experiments. But low natural abundance (7.50%) combined with low sensitivity (6.97×10^{-3} relative to that of protons at constant field) made it not very attractive for selenium nmr experiments in the past. Several ways to improve the unfavorable situation can be considered. An increase in sample volume and the use of specimens enriched in ^{77}Se would increase the number of nuclei suitable for the experiment. Time averaging and use of the proton noise decoupling technique and Overhauser effect are possibilities to improve the signal to noise ratio.

Only very few data on *selenium nmr* experiments were reported in the literature prior to 1965[2] but, more recently, with the availability of more powerful techniques, Birchall, *et al.*,[3] have measured selenium chemical shifts of a number of inorganic selenium compounds by using a side-band technique and McFarlane has reported selenium chemical shifts and coupling constants obtained using the INDOR method.[4]

Proton nmr is more accessible and a number of papers have been published on the application of this tool for the elucidation of the structure of organic selenium compounds.[5-14]

We examined a number of organic selenium compounds by proton and selenium nmr techniques. Proton and selenium chemical shifts as well as proton-proton and proton-selenium coupling constants were determined. Literature data on proton chemical shifts and coupling constants were confirmed. Additional data on dialkyl and diphenyl selenides and diselenides were obtained. The proton chemical shifts of the alkyl compounds were then correlated with the apparent electronegativity of the substituents.

The large spread in chemical shift of selenium reported by Birchall, *et al.*,[3] led us to expect relatively large shifts even within the limited range of organic selenium compounds. We found this to be true. The selenium nucleus is very sensitive to environmental changes and its chemical shift, therefore, is suitable as a tool to probe the chemical environment of a selenium atom within a molecule. The chemical shift differences were attributed to the predominance of the paramagnetic part of the shielding coefficient and correlated with the electronic energy levels of the organic selenides. Long-range coupling between the selenium and protons separated by two and three bonds was observed.

Experimental Section

The samples were used as received when commercially available; their purity was judged by the proton nmr spectrum. The spectra were obtained on neat liquids at room temperature or on melts at an elevated temperature. TMS was used as internal standard for the room-temperature proton spectra. In case of the melt spectra, 1,1,2,2-tetrachloroethane served as external standard which was in turn calibrated at room temperature against internal TMS. The Jeolco spectrometer[15] operating at 14,000 G was used for all the measurements. Proton nmr spectra were recorded with samples in 5-mm o.d. tubes using the internal lock system and a frequency counter for the accurate determination of the position of the lines. Selenium nmr measurements were made with 8-mm o.d. sample tubes, using the NSS attachment[15] and a selenium probe operating at 11.45454 MHz. The field was calibrated with the usual side-band method. Since chemical shifts of selenium are large, a wide sweep (1000 ppm) had to be used. No locking system was available for this mode of operation. The chemical shift was determined by obtaining sample and reference spectra consecutively several times. The results were then checked by running the spectra of sample and reference compounds simultaneously in a coaxial arrangement of nmr tubes having the sample in a 5-mm tube surrounded by the reference solution [H_2SeO_3(aq)] in the 8-mm tube. Since both methods gave the same results within a few ppm, it was decided to use the first method in order to obtain a better signal to noise ratio. This yielded reproducible results for the selenium chemical shifts of the various compounds considered. Details of the spectrum, such as, *e.g.*, ^{1}H-^{77}Se coupling constants, were observed in the

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(1) Presented, in part, at the Pacific Conference on Chemistry and Spectroscopy, Anaheim, Calif., Oct 6-10, 1969.

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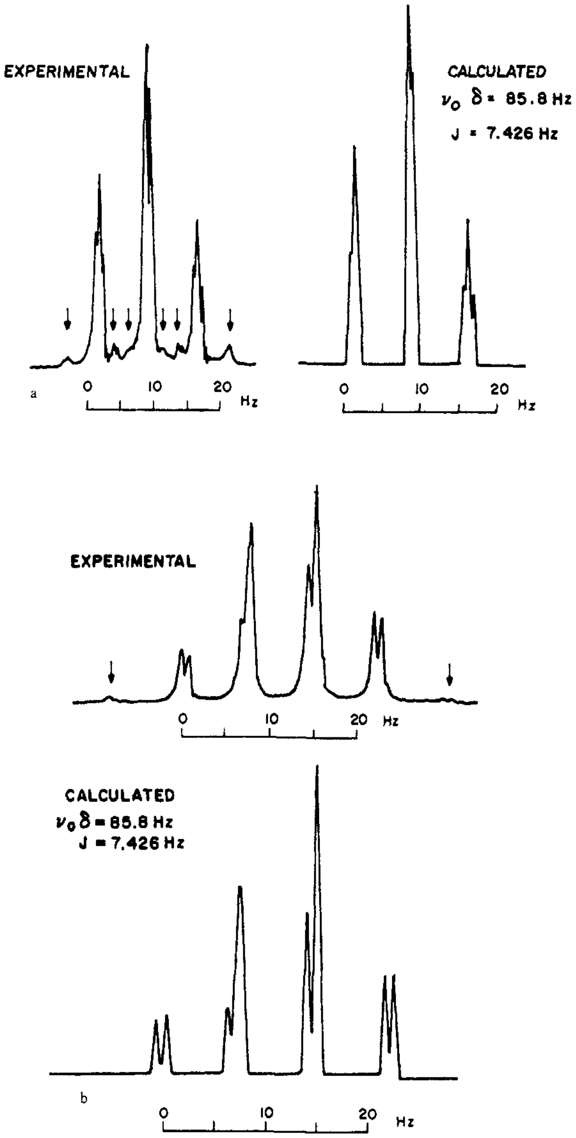

Figure 1. Comparison of experimental and calculated proton nmr spectra of diethyl diselenide in the region of (a) methyl protons, (b) methylene protons. The side bands arising from the coupling between ^{77}Se and ^{1}H are indicated by arrows.

selenium nmr spectrum but were more conveniently determined from the proton spectrum.

Since most of the compounds investigated are highly toxic and volatile they were handled with due caution in vacuum-sealed nmr tubes.

Results

The *proton nmr* spectrum of diethyl diselenide is shown in Figures 1a and 1b as a typical example for the proton spectrum of an organic selenium compound. The A_3B_2 pattern of the five ethyl protons was simulated on a small computer and agreed very well with the experimental proton spectrum. Both the experimental and the calculated patterns for the methylene and the methyl protons are shown in Figures 1a and 1b, respectively. The discrepancies between theoretical and observed spectra (arrows) arise from the fact that the interactions of ^{77}Se with protons were neglected in the calculation. Low-intensity doublets arising from the coupling of the protons to the selenium nucleus appear in both experimental spectra shown and were used to calculate the proton–selenium coupling constants.

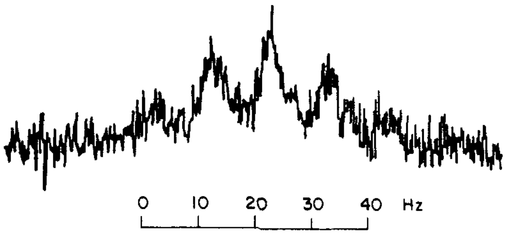

Figure 2. Selenium nmr spectrum of dimethyl selenide (ν 11.45454 MHz, J_{Se-C-H} = 10.4 ± 0.1 Hz).

The *selenium nmr* spectrum of dimethyl selenide is shown in Figure 2 as an example of a selenium spectrum. These spectra were normally obtained using the wide sweep of 1000 ppm for the determination of the resonance positions of reference and sample compounds. In the spectrum shown, however, a sweep width of only 18 ppm was used in order to examine the fine structure. Five lines are observed and these are part of the heptet expected from the coupling of the six equivalent protons with the selenium nucleus.

The experimental results for the series of six compounds are summarized in Tables I, II, and III. The proton chemical shifts from internal TMS reference are shown in Table I. A significant dilution effect was observed in the proton spectrum of diphenyl compounds. The values given for the aromatic protons in *ortho* position to the selenium correspond approximately to the center of the band observed in dilute solution. The *para* and *meta* protons experience a larger dilution shift to lower fields than the *ortho* protons.

Table I. Proton Chemical Shifts Downfield from Internal TMS Reference and Differences (Δ) in Chemical Shifts of Selenides and Diselenides

Organic group	–Se–, ppm	–Se–Se–, ppm	Δ, ppm
CH_3–	1.955	2.548	0.593
CH_3–CH_2– (*H* italic)	2.529	2.863	0.334
CH_3–CH_2–	1.367	1.433	0.066
Ph, *ortho* protons	7.45	7.60	0.15

Table II. Selenium Chemical Shifts Upfield from External H_2SeO_3(aq) Reference and Difference (Δ) in Chemical Shifts of Selenides and Diselenides

Organic group	–Se–, ppm	–Se–Se–, ppm	Δ, ppm
CH_3–	1282	1016	266
CH_3CH_2–	1065	967	98
Ph–	880	822	58

Table III. ^{77}Se–^{1}H Coupling Constants

Compound	*J*, Hz[a]	Range of coupling
CH_3–Se–CH_3	10.4	*Se*-C-*H*
CH_3–Se–Se–CH_3	12.0	*Se*-C-*H*
	2.3	*Se*-Se-C-*H*
CH_3CH_2–Se–CH_2CH_3	10.8	*Se*-C-*H*
	10.8	*Se*-C-C-*H*
CH_3CH_2–Se–Se–CH_2CH_3	15.6	*Se*-C-*H*
	9.6	*Se*-C-C-*H*

[a] Accuracy, ±0.1 Hz.

Chemical shifts of the selenium resonance relative to external $H_2SeO_3(aq)$ are shown in Table II. The signals of the compounds considered here all occur at a higher field than the H_2SeO_3 resonance. Dimethyl selenide shows the highest shielding of our series (1282 ppm) but is still considerably lower than H_2Se (1507 ppm).[3]

Coupling between protons and ^{77}Se was observed in all aliphatic compounds and the results are compiled in Table III. Literature data on the dimethyl compounds[4,9] and on the diethyl selenide[8] were confirmed. Both the methylene as well as the methyl protons are coupled equally with the selenium nucleus in diethyl selenide. In the analogous diselenide, however, two different coupling constants are observed as might be expected.

Discussion

Chemical Shift in General. The chemical shift (δ) is defined as the difference in the shielding coefficients of the sample (σ) and a reference compound (σ_R).

$$\sigma = \sigma - \sigma_R \tag{1}$$

The shielding coefficient for the atom A within the molecule is usually written as the sum of a number of contributions as follows[16]

$$\sigma_A = \sigma_A{}^{dia} + \sigma_A{}^{para} + \sum_{A \neq B} \sigma_{AB} + \sigma_A{}^{deloc} \tag{2}$$

Induced diamagnetic currents on the atom A whose nucleus is subject to the nmr experiment depend upon the electron density around the nucleus of A. The first term of eq 2, $\sigma_A{}^{dia}$, therefore, depends strongly on the electronegativity of any substituent of A. The second term, $\sigma_A{}^{para}$, arises from paramagnetic currents induced on atom A. It is nonzero only for nuclei where a mixing of ground and excited electronic states by the applied field results in a nonspherical distribution of the electrons. The third term, $\Sigma\sigma_{AB}$, represents the influence of local induced currents on nuclei other than A and depends on the nature of their susceptibility tensor. Only nuclei having an anisotropic susceptibility tensor contribute to this term, which is, therefore, also referred to as the neighbor anisotropy effect. Delocalized electrons give rise to the last term, $\sigma_A{}^{deloc}$.

The theoretical interpretation of proton chemical shifts is generally complex since all the terms of eq 2 can become important. It is possible, however, to study the effect of one of the terms by an appropriate selection of closely related compounds such as, *e.g.*, the dialkyl selenides and diselenides.

It is known from data published on the chemical shifts of nuclei other than protons that the paramagnetic contribution ($\sigma_A{}^{para}$) to the shielding coefficient is the dominant term for these nuclei. A similar pattern is expected for the chemical shift of ^{77}Se.

Proton Chemical Shifts. Proton chemical shifts of alkyl groups (alkyl–X) are known to depend essentially on the diamagnetic term ($\sigma_A{}^{dia}$) of eq 2 and, therefore, on the electronegativity (x) of the substituents and on the neighbor diamagnetic anisotropy effects.

Dailey and Shoolery[17] reported a simple correlation between Huggins'[18] electronegativities and the difference in chemical shift between the methylene and the methyl protons of the ethyl halides. The equation was later revised by Cavanaugh and Dailey[19] to include previously neglected solvent effects. The equation best describing the experimental correlation between electronegativity (x) and chemical shift difference was given as follows

$$x = (1.14 \times 10^{-2})\Delta + 1.78 \tag{3}$$

$\Delta = \nu_0\delta$, δ = difference in chemical shift (ppm) between $-CH_3$ and $-CH_2-$, ν = rf frequency (60 MHz).

Cavanaugh and Dailey calculated apparent electronegativities of substituents in ethyl derivatives by means of this equation. Using the resulting data, they then determined the chemical shift of substituted methyl derivatives in a similar way by means of a second equation (4). They found good agreement between calculated and experimental data.

$$\delta_{CH_3} = 1.667x - 2.30 \text{ ppm} \tag{4}$$

We measured the proton chemical shifts in dialkyl selenides and diselenides and interpreted the results in terms of this model.

The differences (Δ) in chemical shifts of the methylene and methyl protons in diethyl compounds were determined with an accuracy of 0.1 Hz (69.6 Hz for Et_2Se, 85.8 Hz for $(EtSe)_2$) by means of the exact solution of the eigenvalue problem for an A_3B_2 system. Using these values and eq 3, the apparent electronegativities (x) of the –Se– and –SeSe– substituents were calculated and the chemical shifts of the corresponding methyl derivatives were computed by means of eq 4. The results are compared with experimental data in Table IV. Good agreement was found between the calculated electronegativity (2.57) and Huggins' values (2.55) for diethyl selenide. The chemical shift of the dimethyl selenide as determined by eq 4 was also very close to the experimental value. A discrepancy of the order of 10% was found between calculated and measured values for the proton chemical shift of dimethyl diselenide. This is not quite unexpected, since the chemical shift is known to depend on magnetic anisotropy in neighbor groups as well as on the electronegativity.[17,19,20] The model used so far may be limited by the fact that the chemical shift is considered to reflect the sum of several atomic contributions. A simultaneous treatment of all the different effects on the chemical shift has not been re-

Table IV. Internal Difference (Δ) in Chemical Shift of Ethyl Protons and Calculated Electronegativity (x) in Diethyl Selenides and Diselenides. Calculated and Observed Chemical Shifts in Dimethyl Selenides and Diselenides

Substituent	Δ, Hz	x	δ_{CH_3}(calcd), ppm	δ_{CH_3}(obsd), ppm
–Se–	69.6	2.57	1.983	1.955
–Se–Se–	85.8	2.76	2.300	2.548

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ported to our knowledge for molecules of the size considered here.

Selenium Chemical Shifts. The most significant result of the measurement of selenium chemical shifts is the wide range of values found for the relatively narrow selection of organic selenium compounds. Although part of the differences in the resonance position must be attributed to differences in the bulk diamagnetic susceptibility of the samples, it seems reasonable to assume that this contribution is negligible compared with the large effects observed for compounds of very similar chemical structure.

The shielding coefficient for selenium is dominated by the paramagnetic term of eq 2 (σ_A^{para}) giving rise to large negative shifts. The situation here is different from that of proton nmr where deformation of the spherical symmetry of the orbital is more difficult to achieve and the paramagnetic contribution is normally small and certainly not the dominating factor. Behavior similar to that found in selenium nmr has been reported for other nuclei such as, *e.g.*, ^{19}F and ^{31}P and, according to Lauterbur,[21] even ^{13}C exhibits a large paramagnetic shielding effect in spite of its tetrahedral symmetry.

An inspection of the chemical shift data presented in Table II shows that (a) there are large differences among the selenides and diselenides having various organic groups and (b) the selenium resonance is shifted to lower fields whenever a diselenide is compared with its corresponding selenide.

These results are interpreted qualitatively in terms of Ramsey's[22] expression for the correlation of energy differences between ground and excited states with the paramagnetic contribution (σ_A^{para}) to the shielding coefficient.

$$\sigma_A^{para} \propto \sum_{n\neq 0} \frac{B}{E_n - E_0} \tag{5}$$

The summation extends over all excited states. The factor B contains matrix elements of the angular momentum operator and has to be averaged for all the possible orientations of the molecule. Since the wave functions of the excited states needed for calculating the factor B are not known at the present time this factor is tentatively assumed to be constant.

The electronic excitation energies $E_n - E_0$ of the molecules considered here are known.[23] They can be approximated by an average value ΔE.[24] This mean electronic transition energy is lower for phenyl selenide than for alkyl selenides; a larger paramagnetic contribution and a resonance position downfield from that of the alkyl compounds is therefore expected for the phenyl selenide. This prediction is borne out by the experiment.

Similarly the mean transition energy of alkyl diselenides is lower than that of the corresponding selenides, since diselenides in general exhibit an additional long-wavelength absorption band typical for the –Se–Se– configuration.[23] The selenium resonance of the diselenides is, therefore, expected to occur at a lower field than that of the corresponding selenides. This was found to be true for all three diselenides considered. The diselenide shift was largest for dimethyl diselenide and decreased in the order of methyl > ethyl > phenyl compounds.

Conclusions

Proton nmr spectroscopy of organic selenium compounds has shown that the chemical shift of ethylene protons in alkyl monoselenides is essentially determined by electronegativity of the substituents. This implies that the diamagnetic term is the dominant factor in determining the chemical shift. In diselenides, however, the direct correlation between electronegativity and chemical shift broke down. Magnetic anisotropy was apparently important here and must be taken into account.

Long-range coupling between ^1H and ^{77}Se was observed to extend over several bonds. Coupling constants for molecules with one or two carbon atoms between the coupled nuclei were of the order of 10–16 Hz. The coupling constant was reduced to 2.3 Hz when the two nuclei considered were connected by a –C–Se– linkage.

The selenium chemical shifts of even the limited variety of compounds considered were spread over a range of 460 ppm. The main contribution to the selenium chemical shift arises from the paramagnetic term of the shielding coefficient. This paramagnetic factor is in turn related to the electronic spectrum of the compounds and particularly sensitive to the energy of the lowest electronic transitions.

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