On the Factors to Determine ^{77}Se NMR Chemical Shifts of Organic Selenium Compounds: Application of GIAO Magnetic Schielding Tensor to the ^{77}Se NMR Spectroscopy

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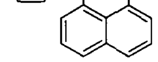
The magnetic shielding tensor was calculated with the GIAO theory for some selenium compounds of versatile structures. The calculated chemical shifts of the selenium nucleus (δ_c(Se)) correlated well with the observed ones (δ_o(Se)), showing the reliability of the method. The δ_c(Se) values for *p*-substituted benzeneselenols also explained the δ_o(Se) values of aryl selenides of various structures around the Se-C bonds.

Observed ^{77}Se NMR chemical shifts (δ_o(Se)) of organic selenium compounds have been interpreted based on the Karplus-Pople's equation.[1] The ΔE factor, for example, is expected to play an important role in δ_o(Se) of diselenides, while the $<r^{-3}>$ factor would be operating in hypervalent compounds or oxides relative to the corresponding selenides.[2] Since the values are governed by the complex conjugation of many factors, the chemical shifts would not be proportional to either the ΔE or the $<r^{-3}>$ factor in some cases.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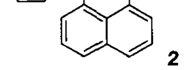
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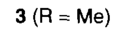
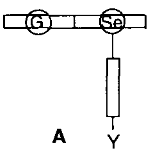
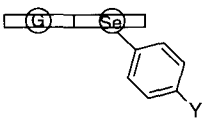

3 (R = Me)
4 (R = Ph)
5 (R = H)

		a	b	c	d	e	f	g	h	i
Y	=	H	OMe	Me	Cl	Br	CO_2Et	NO_2	NH_2	CHO


A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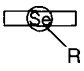
C


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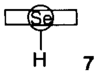
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We have encountered a good correlation in the plot of δ_o(Se) of ArSe groups in bis[8-(arylselanyl)naphthyl] diselenides (**1**) against those of 8-(arylselanyl)-1-(methylselanyl)naphthalenes (**2**).[3] We wondered why the correlation was good irrespective of their different structures. The Se-C(Nap) bond is on the phenyl plane in **1a** (**A**)[4a] but it is perpendicular to the plane in **2a** (**B**).[4b] The δ_o(Se) values of **1** and **2** also correlated well with those of *p*-substituted selenoanisoles (**3**)[5] and diphenyl selenides (**4**).[6] The structure of **3** and **4** is shown by **C**: the dihedral angles of the Se-C(R) bonds to the aryl plane in **3a** and in ditolyl selenide are reported to be about 40[7] and 55[8] deg, respectively.

Recently the magnetic shielding tensor calculated with the gauge including atomic orbitals (GIAO) theory for the carbon nucleus is shown to be reliable.[9] This encouraged us to calculate the GIAO magnetic shielding tensor for the ^{77}Se nucleus (σ(Se)). Although the contribution of relativistic terms has been pointed out for heavier atoms,[10] the perturbation would be small for the selenium nucleus. Here we would like to present the results of the calculations emphasizing how it is useful to explain the observed ^{77}Se NMR chemical shifts and to understand the organic selenium chemistry based on the spectroscopy.

Table 1. The δ_c(Se), Qn, and $\Delta\varepsilon$ Values for Some Selenium Compounds, Together with the δ_o(Se) Values[a]

Compound	δ_c(Se)	Qn(Se)	$\Delta\varepsilon$	δ_o(Se)	Solvent
MeSeMe	0.0	0.2719	0.203	0.0	$CDCl_3$
MeSeSeMe	340.7	0.1270	0.179	281	$CDCl_3$
$MeSeCl_2Me$	401.9	1.0477	0.193	448	CH_2Cl_2
Me_3Se^+	220.9	1.0229	0.309	253	H_2O
Me_2SeO	768.0	1.3485	0.221	812	H_2O
F_4Se	1115.0	2.1805	0.257	1083	CH_3F
F_6Se	632.7	2.9570	0.295	610.3	neat
F_2SeO	1353.0	1.9940	0.252	1378.2	neat
F_2SeO_2	914.6	2.7655	0.247	948	neat

[a] The δc(Se) values are from MeSeMe of which σ(Se) is 1656.4 (ppm).

Table 1 shows calculated chemical shifts ($\delta_c(Se) = -(\sigma(Se) - \sigma(Se)_{MeSeMe})$) for some selenium compounds with the 6-311++G(3df,2pd) basis sets at the DFT (B3LYP) level,[11] together with the δ_o(Se) values. Natural charges (Qn) and the energy differences ($\Delta\varepsilon$) between HOMO and LUMO were also given for convenience of comparison. Figure 1 and eq 1 show the plot of δ_o(Se) against δ_c(Se) given in Table 1 and its correlation, respectively. These results exhibit that the method must be a powerful tool to support the ^{77}Se NMR spectroscopy.

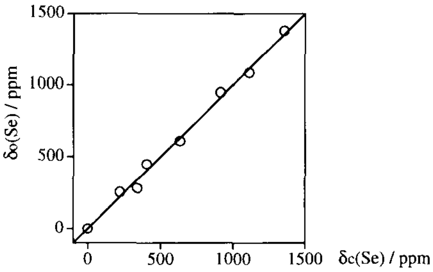

Figure 1. Plot of δo(Se) *vs* δc(Se) shown in Table 1.

$$\delta_o(\mathrm{Se}) = 1.00 \times \delta_c(\mathrm{Se}) + 0.4 \qquad (r = 0.997) \quad (1)$$

$$\delta_c(\mathrm{Se})\ \text{of}\ \mathbf{7} = 0.875 \times \delta_c(\mathrm{Se})\ \text{of}\ \mathbf{6} - 41.1 \qquad (\mathrm{G_A}\text{: } r = 0.980) \quad (2)$$

$$\delta_c(\mathrm{Se})\ \text{of}\ \mathbf{7} = 0.421 \times \delta_c(\mathrm{Se})\ \text{of}\ \mathbf{6} + 5.5 \qquad (\mathrm{G_B}\text{: } r = 0.988) \quad (3)$$

$$\delta_c(\mathrm{Se}:\chi) = \chi\delta_c(\mathrm{Se})\ \text{of}\ \mathbf{6} + (1 - \chi)\delta_c(\mathrm{Se})\ \text{of}\ \mathbf{7} \quad (4)$$

$$\delta_o(\mathrm{Se})\ \text{of}\ \mathbf{1} = 0.812 \times \delta_c(\mathrm{Se}:0.75) + 371.2 \qquad (r = 0.997) \quad (5)$$

$$\delta_o(\mathrm{Se})\ \text{of}\ \mathbf{2} = 0.615 \times \delta_c(\mathrm{Se}:0.70) + 390.7 \qquad (r = 0.990) \quad (6)$$

$$\delta_o(\mathrm{Se})\ \text{of}\ \mathbf{3} = 0.851 \times \delta_c(\mathrm{Se}:0.95) + 140.1 \qquad (r = 0.990) \quad (7)$$

$$\delta_o(\mathrm{Se})\ \text{of}\ \mathbf{4} = 0.819 \times \delta_c(\mathrm{Se}:0.50) + 373.4 \qquad (r = 0.994) \quad (8)$$

Similar calculations were also performed on selenols **5** with the 6-311+G(d,p) basis sets at the DFT (B3LYP) level: each selenol was optimized to exist as two structures shown in **6** and **7**:[12] the Se-H bond placed in the aryl plane in **6** and the bond being perpendicular to the plane in **7**. Table 2 collects the δ_c(Se), Qn, and $\Delta\varepsilon$ values, together with the δ_o(Se) values of **1** - **4**.

Table 2. The δ_c(Se), Qn, and $\Delta\varepsilon$ Values of **6** and **7**, Together with the δ_0(Se) Values for **1** - **4**[a,b]

Y	**6**: δ_c(Se)	Qn(Se)	$\Delta\varepsilon$	**7**: δ_c(Se)	Qn(Se)	$\Delta\varepsilon$	δ_0(Se) of **1**[c]	δ_0(Se) of **2**[c]	δ_0(Se) of **3**[d]	δ_0(Se) of **4**[d]
a	81.7	0.1346	0.1971	40.0	0.0773	0.2018	429.0	434.3	207.8	423.6
b[e]	69.9	0.1262	0.1827	16.9	0.0794	0.2062	416.2	424.5	197.4	408.1
c	73.5	0.1292	0.1921	25.1	0.0760	0.2029	422.0	427.7	200.6	415.0
d	84.3	0.1439	0.1889	32.4	0.0855	0.1991	429.1	431.6	210.3	421.9
e	84.5	0.1453	0.1886	33.3	0.0859	0.1795	429.6	432.4	210.6	422.3
f[f]	104.6	0.1612	0.1677	47.8	0.0861	0.1707	442.5	442.4	222.3	433.3
g	119.0	0.1786	0.1428	55.3	0.0959	0.1444	456.1	453.9	241.2	446.3

[a] The σ(Se) of MeSeMe being 1624.4 ppm. [b] The δc(Se) (ppm) are from MeSeMe. [c] Ref. 3. [d] This work. [e] Calculated for OH. [f] Calculated for COOH.

Since the electronic effect of Y at the *para*-position is transmitted through both inductive and mesomeric mechanisms,[13] the charges developed on the Se atoms in **1** - **4** must not be the same, which should affect their δ_0(Se) values in different trends. The plots of Qn and $\Delta\varepsilon$ of **6** *vs* those of **7** did not give good correlations, which must be the reflection of the different mechanism to transmit the effect of Y on the Se atom, as expected.

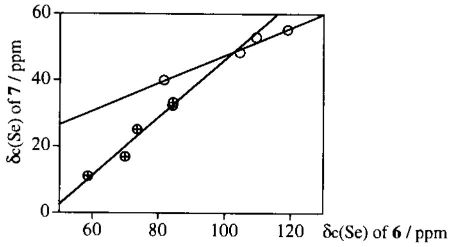

Figure 2. Plot of δc(Se) of **7** *vs* δc(Se) of **6**.

Figure 2 shows the plot of δ_c(Se) of **7** against those of **6**. Although the plot can be variously understood, it was analyzed as the two groups here. Group A consists of **5b** - **5e** and **5h**, of which Y act as electron donors with the lone pairs or the hyperconjugation by the methyl group. Group B contains **5a**, **5f**, **5g**, and **5i**, of which Y are electron accepting groups or a hydrogen. The correlations for Group A and Group B are shown in eqs 2 and 3, respectively.[14] The proportionality constants were 0.875 and 0.421, respectively. The latter value must be the results from the significant contribution of the mesomeric effect on **6**, which would not be effective in Group A.

Indeed a good correlation was obtained in the plot of δ_0(Se) of **1** *vs* δ_c(Se) of **6**, but a better correlation was obtained with a new parameter, $\delta_c(\mathrm{Se}:\chi)$,[15] which is defined in eq 4. The δ_0(Se) values of **1** - **4** were plotted *vs* δ_c(Se:0.75), δ_c(Se:0.70), δ_c(Se:0.95), and δ_c(Se:0.50), respectively. Eqs 5 - 8 show the correlations. The good correlations observed in **1** and **4** are well explained by the predominant structures for the compounds shown in **A** and **C**, respectively. The correlation in **2** may show that structures other than **B**, such as **A**, may contribute in solutions. The contribution of δ_c(Se) of **6** to those of **3** is larger than that expected based on structure **C**: it may be closer to that of **6** in solutions and/or such character might be enhanced by the electron donating methyl ligand in **3**. The reason why δ_0(Se) of **1** - **4** correlate with each other is now clarified to be the large contributions of δ_c(Se) of **6** to the values.

These results exhibit that the GIAO method can be a powerful tool to investigate the organic selenium chemistry containing the structural dependence of the δ(Se) values if one employ the method supporting the ^{77}Se NMR spectroscopy. The study containing nonbonded interactions with the method is in progress.

This paper is dedicated to Professor Michinori Ôki on the occasion of his 70th birthday. This work was partly supported by a Grant-in-Aid for Scientific Research from Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1 M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

$$\sigma_i^{\mathrm{para}} = -\frac{\mu_0\mu_B{}^2}{2\pi\,\Delta E} <r^{3}> [Q_i + \sum_{j\neq i} Q_j] \qquad \text{(a)}$$

The $<r^{-3}>$ factor of the 4p orbitals is expected to be proportional to the atomic charge on the Se atom being observed. The ΔE factor, the average excitation energy, could be estimated by the energy difference between HOMO and LUMO of the compound if the 4p atomic orbitals of the selenium atom substantially contribute to both of the orbitals. The HOMO of **6** and **7** of the A'' symmetry are mainly constructed by the p-type lone pair of the Se atom. The situation is similar for LUMO of **6** (the A'' symmetry). The p-type orbital also contributes to LUMO of **7** with the A' symmetry, which bisects its CSeH angle.

2 H. Iwamura and W. Nakanishi, *J. Syn. Org. Chem. Jpn.*, **39**, 795 (1981); S. Patai and Z. Rappoport (eds), "The Chemistry of Organic Selenium and Tellurium Compounds," Wiley, New York (1986), Chap. 6 (Vol. 1); T. M. Klapôtke and M. Broschag, "Compilation of Reported ^{77}Se NMR Chemical Shifts," Wiley, New York (1996).

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δ(Se) of 1 = 1.33 × δ(Se) of 2 - 147.1 (r = 0.994) (b)

4 a) W. Nakanishi, S. Hayashi, and S. Toyata, *J. Chem. Soc., Chem. Commun.*, **1996**, 371. b) W. Nakanishi, S. Hayashi, and S. Toyata, unpublished results.

5 Since the reported δ(Se) of 3 were determined in neat liquid by the INDOR ^{1}H-{^{77}Se} technique, the δ(Se) were reexamined using an FT NMR in $CDCl_3$. See, G. A. Kalabin, D. F. Kushnarev, V. M. Bzesovsky, and G. A. Tschmutova, Org. Mag. Res., **12**, 598 (1979).

6 The correlations of δ(Se) in **1** and **2** with those of **4** are as follows:

δ(Se) of 1 = 1.07 × δ(Se) of 4 - 21.4 (r = 0.996) (c)

δ(Se) of 2 = 0.79 × δ(Se) of 4 + 98.2 (r = 0.991) (d).

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11 *Gaussian 94, Revision D.4*; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1995. *Ab initio* MO calculations were performed on Origin and/or Power Challenge L computers.

12 a) The energy minima could not be found near the structure of **7f** and **7i**, when the selenols were full optimized. Some appropriate torsional angles were fixed in the calculations to achieve the structure. b) The δc(Se) values of (**6**: **7**) were (58.6: 11.1) for **h** and (109.5: 53.0) for **i**.

13 R. W. Taft (ed)," Progress in Physical Organic Chemistry," Wiley, New York (1976), Vol. 12.

14 The correlation becomes more complex, if the data of Y = CN is added, for example. It contains π(z)- and π(y)-orbitals which could interact with the p-type orbitals of the Se atom through the phenyl group.

15 Efforts were not made to obtain the best-fitted correlations. Details, containing the correlations in **6** and **7**, will be reported elsewhere.