Inverse Substituent Effect on ^{77}Se NMR Chemical Shifts in Naphthalene Systems with Linear 4c-6e Se$_4$ Bond: 1-[8-(p-YC$_6$H$_4$Se)C$_{10}$H$_6$]SeSe[C$_{10}$H$_6$(SeC$_6$H$_4$Y-p)-8']-1' *vs.* 1-(MeSe)-8-(p-YC$_6$H$_4$Se)C$_{10}$H$_6$

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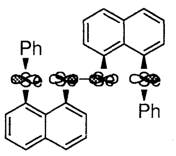
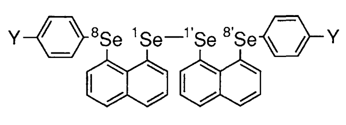
The substituent effect on δ(^{1}Se) *vs.* δ(^{8}Se) in bis[8-(arylselanyl)naphthyl] diselenides (**1**) was opposite to that for 1-(methylselanyl)-8-(phenylselanyl)naphthalene and its p-substituted derivatives. The observation must be the reflection of the 4c-6e interaction between the p-orbitals of the four Se atoms in **1**.

In a previous paper,[1] we reported the linear alignment of four selenium atoms in bis[8-(phenylselanyl)naphthyl] diselenide (**1**(Y=H)), revealed by the X-ray crystallographic analysis. This alignment was also shown to come from the energy lowering by the construction of the four-center six-electron (4c-6e) bond with the linear four selenium 4p atomic orbitals of **1**(Y=H) based on MO calculations.[1]





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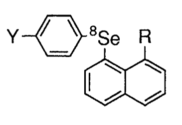


2 (R = ^{1}SeMe), **3** (R = H)

Y = OMe, Me, H, Cl, Br, COOEt, NO$_2$

As a next extension of the study, we looked for novel properties owing to the linear 4c-6e Se$_4$ bond and found an inverse substituent effect on the ^{77}Se NMR chemical shifts of the diselenide Se atoms in **1**[2] bearing substituents at the phenyl *para*-positions, relative to those in 1-(methylselena)-8-(phenylselena)naphthalene and its phenyl *para*-substituted derivatives (**2**).[2] The methyl selenides **2** are expected to show a substituent effect arising from the lone pair-lone pair interaction. Here we would like to present the inverse substituent effect on the diselenide Se atoms in **1** relative to the case in **2**, considering their structures for the better understanding of the substituent effect.

Tables 1 and 2 show ^{77}Se NMR chemical shifts and coupling constants of **1** and **2**, respectively. Table 1 contains ^{77}Se NMR chemical shifts of similarly substituted naphthyl phenyl selenides (**3**) (δ(Se)) and Table 2 also exhibits ^{13}C NMR chemical shifts and coupling constants in connection with the ^{77}Se NMR data of **2**.

Table 1. ^{77}Se NMR chemical shifts and coupling constants of **1**, together with those of **3**[a]

Y	δ(^{8}Se)	δ(^{1}Se)	^4J(^{8}Se,^{1}Se)	^5J(^{8}Se,$^{1'}$Se)	δ(Se)[b]
OMe	416.2	541.4	371.6	12.4	354.3
Me	422.0	537.4	354.4	11.9	356.2
H	429.0	534.2	341.4	13.6	361.0
Cl	429.1	534.7	330.1	14.0	359.4
Br	429.6	534.0	327.1	c	359.4
COOEt	442.5	530.2	311.4	13.7	368.1
NO$_2$	456.1	529.6	294.1	13.5	379.6

[a] Chemical shifts are from external MeSeMe and coupling constants are in Hz. [b] Values for **3**. [c] Not observed due to low solubility and low sensitivity.

Table 2. ^{77}Se NMR chemical shifts and coupling constants of **2**, together with the selected ^{13}C NMR data[a,b]

Y	δ(^{8}Se)	δ(^{1}Se)	δ(C$_{Me}$)	^4J(^{8}Se,^{1}Se)	^1J(^{1}Se,C$_{Me}$)
OMe	424.5	233.1	13.9	341.6	71.2
Me	427.7	234.5	13.7	330.9	72.8
H	434.3	235.4	13.4	322.4	72.8
Cl	431.6	234.7	13.5	316.7	72.8
Br	432.4	235.2	13.4	313.9	72.7
COOEt	442.4	239.2	12.9	294.7	74.5
NO$_2$	453.9	240.1	12.5	272.5	76.1

[a] Chemical shifts are from external MeSeMe or TMS and coupling constants are in Hz. [b] Values of ^5J(^{8}Se,C$_{Me}$) were observed to be 15.0-16.1 Hz.

Figures 1a and 1b show the plots of the ^{77}Se chemical shifts of diselenide Se atoms (δ(^{1}Se)) *vs.* those of arylselanyl groups at 8,8'- or 8-positions (δ(^{8}Se)[3]) in **1** and **2**, respectively, and the correlations are given in eqs 1 and 2, respectively. Although a good correlation was held with a positive proportionality constant for **2** (regular correlation), the proportionality constant in **1** was negative or the plots had better be analyzed as inversely proportional as shown by a dotted line (inverse correlation).

$$\delta(^1\mathrm{Se})\ \text{of}\ \mathbf{1} = -0.282 \times \delta(^8\mathrm{Se})\ \text{of}\ \mathbf{1} + 656.2 \qquad (r = 0.924) \qquad (1)$$

$$\delta(^1\mathrm{Se})\ \text{of}\ \mathbf{2} = 0.252 \times \delta(^8\mathrm{Se})\ \text{of}\ \mathbf{2} + 126.5 \qquad (r = 0.965) \qquad (2)$$

$$^4J(\mathrm{Se,Se})\ \text{of}\ \mathbf{1} = -1.87 \times \delta(^8\mathrm{Se})\ \text{of}\ \mathbf{1} + 1141.4 \qquad (r = 0.960) \qquad (3)$$

$$^4J(\mathrm{Se,Se})\ \text{of}\ \mathbf{2} = -2.28 \times \delta(^8\mathrm{Se})\ \text{of}\ \mathbf{2} + 1305.5 \qquad (r = 0.980) \qquad (4)$$

The structure of 1,8-bis(methylsulfanyl)naphthalene[4] has been reported. Its HOMO and next HOMO were shown to be the π*- and π-type lone pairs, respectively, extended mainly on the two sulfur atoms, interacting with π-orbitals of the naphthyl ring. The structure of **2** (Y = H) is very close to that of the bis-sulfide, especially around the hetero atoms.[5] Therefore the lone pair-lone pair interaction between the Se atoms in **2**, must be mainly responsible for the regular correlation. The electron density on the ^{8}Se atom decreases as the electron-withdrawing

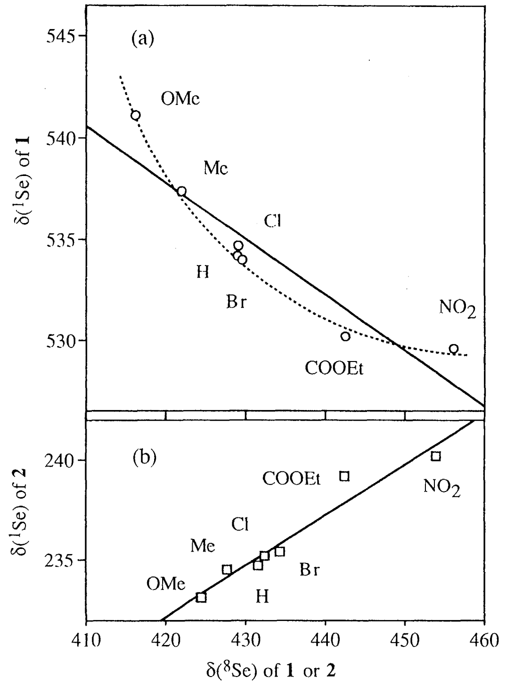


Figure 1. Plots of δ(^{1}Se) *vs.* δ(^{8}Se). (a): in **1** and (b): in **2**.

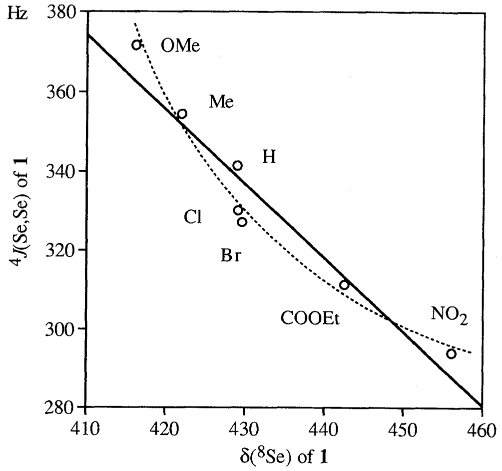
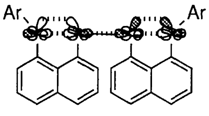


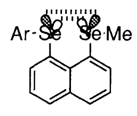
Figure 2. Plots of ^4J(Se,Se) *vs.* δ(^{8}Se) in **1**.

ability of the substituent at the *para*-position becomes stronger, and in turn the ^{8}Se atom may pull electrons more effectively on the ^{1}Se atom, resulting in the downfield shifts for both ^{8}Se and ^{1}Se atoms in **2** (see eq 2).

On the other hand, the inverse correlation in **1** could not be well explained by the lone pair-lone pair interaction between the Se atoms. It must, we believe, come from the 4c-6e interaction of the linear four selenium atoms which is constructed by the p-orbitals of the outside selenium atoms with the σ*-orbital of the inside Se-Se bond in **1**.[1] The 4c-6e interaction in **1** would inversely transfer the magnetic or electronic change at the ^{8}Se atom to the ^{1}Se atom. The observation of the long range ^5J(^{8}Se,1'Se) (and ^5J(^{1}Se,8'Se)) couplings in **1** also supports the effective orbital interaction between the four Se atoms.

Such inverse correlation was also partly observed in the plots of ^4J(Se,Se) *vs.* δ(^{8}Se) in **1** as shown in Figure 2 (see a dotted line). The correlations for **1** and **2** are given in eqs 3 and 4, respectively. The correlation coefficient for **2** were larger than that for **1** again, with negative proportionality constants. Comparing Figure 2 with Figure 1a, one may recognize that the inverse correlation partly observed in the plots of ^4J(Se,Se) *vs.* δ(^{8}Se) must be the reflection of the inverse correlation in δ(^{1}Se) *vs.* δ(^{8}Se) in **1**. The negative signs must show that ^4J(Se,Se) in **1** and **2** become smaller when δ(^{8}Se) shift downfield, namely, the *J*-values become smaller as the electron density of the ^{8}Se atoms decreases.[6] These results show that the 4c-6e interaction plays an important role to determine the properties of **1**.





The plots of the δ(C_{Me}) *vs.* δ(^{8}Se) in **2** also gave a good correlation with a negative proportionality constant of -0.048 (r = 0.993), which would be explained by the contribution of the unsymmetrical 3c-4e Se---Se-C bond[7] or by the contribution of the interaction between the lone pair electrons of the ^{8}Se atom and the σ*(Se-C) orbital similar to the case of the lone pair orbitals of ^{8}Se atoms with the σ*(Se-Se) orbital in **1**. Further study on the nonbonded interaction containing Se atoms is in progress.

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References and Notes

1 W. Nakanishi, S. Hayashi, and S. Toyota, *J. Chem. Soc., Chem. Commun.*, **1996**, 371.

2 Elemental analyses were satisfactory for all the new selenides **1** - **3** with Y = OMe, Me, H, Cl, Br, COOEt, NO$_2$. ^{1}H, ^{13}C, and ^{77}Se NMR spectra were measured with a Bruker-WM 360 and/or a JEOL JNM-LA 400, spectrometers.

3 The correlations of δ(^{8}Se) in **1** and **2** with δ(Se) in **3** were as follows (The substituent effect of δ(^{8}Se) *vs.* δ(Se) was very similar to those observed in *p*-YC_6H_4SeMe[8a], *p*-YC_6H_4SePh[9], and (p-$YC_6H_4)_2Se$.[8b]):
δ(^{8}Se) of **1** = 1.51 x δ(Se) of **3** - 116.7 (r = 0.987)
δ(^{8}Se) of **2** = 1.14 x δ(Se) of **3** + 21.3 (r = 0.996)

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5 The X-ray crystallographic analysis has been carried out for **2**. The details will be reported elsewhere.

6 The ^4J(Se,Se) values of 1-(methylseleninyl)-8-(methylselanyl)-naphthalene and 1-(acetoxymethylselanyl)-8-(methylselanyl)naphthalene were reported to be 203 and 310 Hz, respectively.[10] This may come from the more favorable orientation of the lone pairs for the latter. It could also be explained by assuming that the electron density of the selenoxide Se atom of the former is less than the selenide Se atom of the latter, irrespective of the expected magnitude of interactions.

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