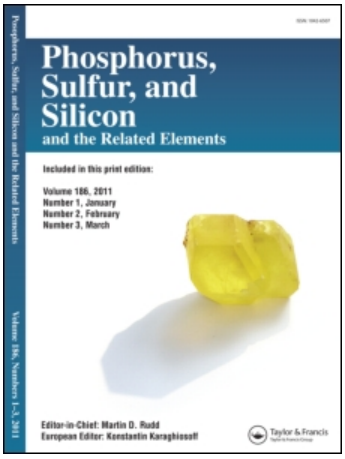


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

H/D Isotope Effect on ^{77}Se NMR Chemical Shifts in 8-Methyl-1-(arylselanyl)naphthalenes and Related Selenides: Nonbonded CH—Se Through-Space Versus Through-Bond Mechanisms

Satoko Hayashi[a]; Kentaro Yamane[a]; Waro Nakanishi[a]
[a] Department of Material Science and Chemistry, Faculty of Systems Engineering, Wakayama University, Wakayama, Japan

To cite this Article Hayashi, Satoko , Yamane, Kentaro and Nakanishi, Waro(2009) 'H/D Isotope Effect on ^{77}Se NMR Chemical Shifts in 8-Methyl-1-(arylselanyl)naphthalenes and Related Selenides: Nonbonded CH—Se Through-Space Versus Through-Bond Mechanisms', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 6, 1481 — 1495
To link to this Article: DOI: 10.1080/10426500902947807
URL: http://dx.doi.org/10.1080/10426500902947807

Phosphorus, Sulfur, and Silicon, 184:1481–1495, 2009

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902947807

Taylor & Francis
Taylor & Francis Group

H/D Isotope Effect on ^{77}Se NMR Chemical Shifts in 8-Methyl-1-(arylselanyl)naphthalenes and Related Selenides: Nonbonded C—H—Se Through-Space Versus Through-Bond Mechanisms

Satoko Hayashi, Kentaro Yamane, and Waro Nakanishi
Department of Material Science and Chemistry, Faculty of Systems Engineering, Wakayama University, Wakayama, Japan

*^{77}Se NMR chemical shifts of methyl-d_3 derivatives of 8-methyl-1-(phenylselanyl) naphthalene (**1**) and 8-methyl-1-(p-anisylselanyl)naphthalene (**2**) are observed 0.25 and 0.20 ppm upfield from **1** and **2**, respectively. The observations must be the reflection of the nonbonded interactions of the C—H—Se 3c–4e type in **1** and **2**. The mechanism is elucidated by means of crystallographic and theoretical investigations. The nonbonded distance between Se and C_{Me} (2.989 Å) is observed to be shorter than the sum of the van der Waals radii of the two by 0.91 Å in **2**. **1** and **2** may be in equilibrium between conformers **A** and **B** in solution, where Se—C_i is perpendicular to the naphthyl plane in **A** and it is on the plane in **B**. Natural bond orbital (NBO) analysis on **1** revealed that the nonbonded n_p(Se)—σ^*(C—H) interaction contributes in **A**, whereas nonbonded n_s(Se)—σ^*(C—H) and double σ(C—H)—σ^*(Se–C) interactions operate in **B**.*

Keywords Ab initio calculations; H/D isotopic effect; natural bond orbital analysis; NMR; nonbonded C—H—Se interaction; structures

INTRODUCTION

Nonbonded interactions containing group 16 elements are of current interest.[1–3] Naphthalene 1,8-positions serve as a good system to study the interactions. Lone pair orbitals of heteroatoms play an important role in the nonbonded interactions. They have much effect on the energy

Received 7 January 2008; accepted 3 February 2008.
Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.
This work was partially supported by a Grant-in-Aid for Scientific Research (Nos. 16550038 and 19550041) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.
Address correspondence to Waro Nakanishi, Department of Material Science and Chemistry, Faculty of Systems Engineering, Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan. E-mail: nakanisi@sys.wakayama-u.ac.jp

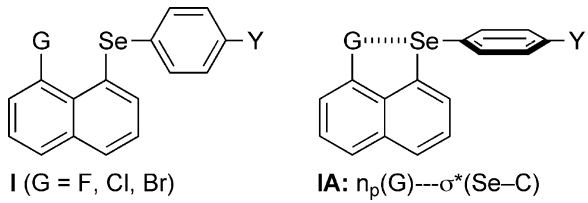


FIGURE 1 Compounds **I** and the n_p(G)—σ^*(Se—C) interaction.

of the system and the NMR parameters, such as chemical shifts and the nuclear spin–spin couplings containing the atoms.[1d,g,2,3] We have demonstrated the attractive nonbonded linear G—Se—C interactions in 8-G-1-(arylselanyl)naphthalenes (**I**), where G are Br and Cl and even F.[2a,e] p-Type lone pair orbitals of halogens [n_p(G)] and the anti-bonding orbitals of the Se—C bonds (σ^*(Se—C)) play an important role in the attractive interactions of the n_p(G)—σ^*(Se—C) form (**IA**) (Figure 1).

We have also been interested in the nonbonded C—H—Se and/or H—Se—C interactions in relation to the nonbonded linear G—Se—C interactions in **I**. Although the G—Se—C interactions for G of halogens are well explained by hypervalent n_p(G)—σ^*(Se—C) 3c–4e type interactions, such contribution would be small for G = Me. Nevertheless, large downfield shifts in δ (Se) are detected for 8-methyl-1-(phenylselanyl)-naphthalene (**1**) and 8-methyl-1-(*p*-anisylselanyl)naphthalene (**2**), relative to 1-(phenylselanyl)naphthalene (**3**)[4] and 1-(*p*-anisylselanyl)naphthalene (**4**),[4] respectively (Figure 2). The values amounted to 81–92 ppm. What happens in ^{77}Se NMR chemical shifts [δ (Se)], when selanyl and methyl groups are placed proximity in space? The results must come from the large steric effect of the methyl group on the neighboring selenium atom by the through-space interaction in **1** and **2**.

The nonbonded interactions between the methyl and selanyl groups are investigated by means of the H/D isotope effect on δ (Se), employing naphthalene 1,8-positions in **1**–**4** and benzene 1,2-positions in *o*-tolyl phenyl selenide (**5**) and diphenyl selenide (**6**) (Figure 2). The mechanism of the H/D isotope effect is demonstrated to be pure through-space for **1** and **2**, whereas that of **6** is through-bond. The difference between the through-space and the through-bond mechanisms must supply the information on the nonbonded C—H—Se and/or H—Se—C interactions.

The structure of **2** is determined by the X-ray crystallographic analysis to clarify the structural environments in the H/D isotope effect. Structures of **1** and **2** are optimized employing the 6-311+G(2d,p) basis sets of the Gaussian 03 program[5] at the density functional theory (DFT:

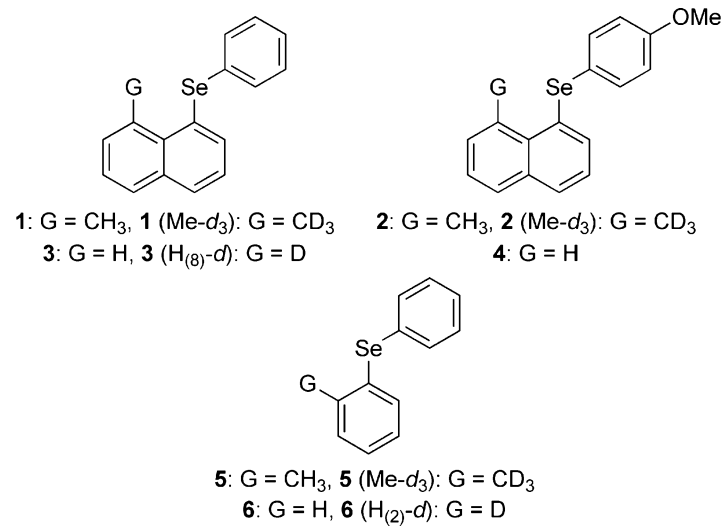
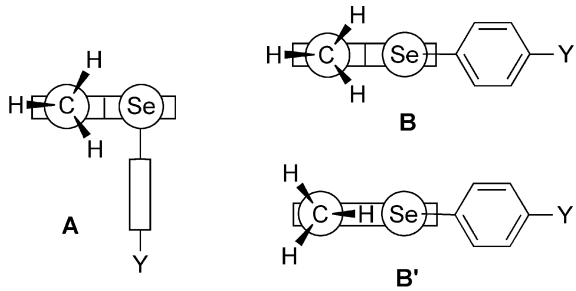


FIGURE 2 Compounds with which the H/D isotope effect examined.

B3LYP).[6,7] Natural bond orbital (NBO) analysis[8,9] is carried out for the plausible structures of **1**, **A**, and **B** (see Scheme 1). The observations are explained based on the observed and the calculated structures.

Here, we report the nature of the C–H—Se and/or H—Se–C interactions based on the H/D isotope effect, together with the results of QC calculations, employing **1**–**6**.



SCHEME 1 Plausible structures of **1** and **2**.

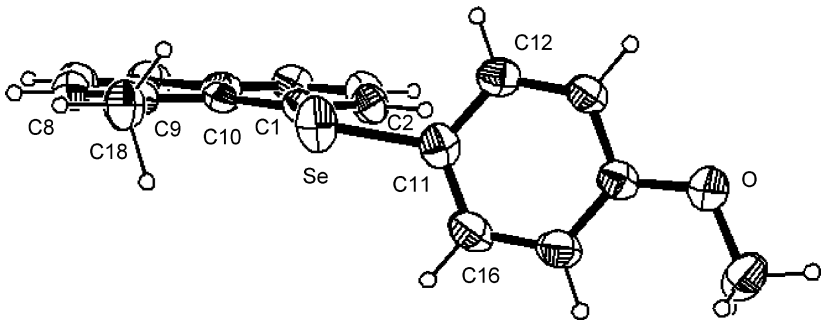


FIGURE 3 Structure of **2**, showing the numbering scheme (thermal ellipsoids are shown at 30% probability levels).

RESULTS AND DISCUSSION

Structure of 1-Methyl-8-(*p*-anisylselanyl)naphthalene (2)

The structure of **2** was determined by the X-ray crystallographic analysis, whereas that of **1** was not due to its oily nature. Single crystals of **2** were obtained via slow evaporation of a hexane solution and one of suitable crystals was subjected to the analysis. Table I shows the crystallographic data. Figure 3 shows the structure of **2**[10] and Table II collects the selected interatomic distances, angles, and torsional angles, necessary for the discussion.

The planarity of the naphthyl and anisyl planes is very good. The anisyl plane is almost perpendicular to the naphthyl plane, the torsional angle of C1-Se-C11-C12 being 86.7(4) degrees. The methyl carbon and the Se—C11 bond lay on the naphthyl plane: the torsional angles of

TABLE I Crystallographic Data for 2

Formula	$C_{18}H_{16}OSe$	Z	8
Mol wt	327.28	D_{calcd} (g cm^{-3})	1.455
T (K)	292(1)	F(000)	1328
Cryst. syst.	monoclinic	no. of rflns collected	4313
Space group	$C2/c$ (#15)	no. of ind rflns	3591
a (Å)	14.033(4)	no. of data/restraints/params	1829/0/181
b (Å)	11.903(5)	goodness of fit, F_2	1.45
c (Å)	17.970(4)	R_1, wR_2	0.043, 0.051
β (°)	95.54(2)		[$I > 1.5\sigma$ (I)]
V (Å^{-3})	2987(1)	largest diff peak (e Å^{-3})	0.38 to –0.29

TABLE II Selected Interatomic Distances, Angles, and Torsional Angles of 2[a]

Interatomic distances (Å)			
Se-C1	1.933 (4)	Se-C11	1.914 (5)
Se-C18	2.989 (5)	C9-C18	1.504 (7)
Angles (°)			
Se-C1-C2	117.6 (3)	Se-C1-C10	122.1 (3)
Se-C11-C12	120.8 (4)	Se-C11-C16	120.1 (4)
C1-Se-C11	101.8 (2)	C11-Se-C18	175.1 (2)
C10-C9-C18	125.0 (4)		
Torsional angles (°)			
C10-C1-Se-C11	173.7 (4)	C1-Se-C11-C12	86.7 (4)
Se-C1-C10-C9	0.8 (6)	C1-C10-C9-C18	2.3 (7)

[a]The atomic numbering scheme for **2** is defined in Figure 1.

C1-C10-C9-C18, Se-C1-C10-C9, and C10-C1-Se-C11 are 2.3(7), 0.8(6), and 173.7(4) degrees, respectively. The nonbonded distance between Se and C18 atoms [r(Se, C_{Me})] is 2.989(5) Å, which is shorter than the sum of the van der Waals radii[11] of Me group and Se atom by 0.91 Å [Δr_v(Se, C_{Me}) = 0.91 Å]. Since the methyl group is not spherical, the interpretation of the van der Waals radii must be considered carefully in this case (the gear effect).[12] The methyl carbon (C_{Me}), selenium, and ipso carbon (C_i) of the *p*-anisyl group in **2** align linearly: the C11-Se-C18 angle is 175.1(2) degrees. The linear alignment in **2** would be mainly controlled by the n_p(Se)–π (Nap) conjugation.

H/D Isotope Effect on δ (Se)

The ^{77}Se NMR spectrum was measured for **1** in chloroform-*d* at an ambient NMR probe temperature of 25°C. The resolution of ^{77}Se NMR spectra was 0.7 Hz (0.01 ppm) measured at 76 MHz. The signal was observed at δ (Se) = 452.57. A new signal appeared at the 0.25 ppm upfield from that of **1** when the CD_3 derivative of **1** [**1** (Me-d_3)] was added to the solution. The new signal grew up as the addition of **1** (Me-d_3). The half value widths ($\nu_{1/2}$) of the ^{77}Se NMR signals in **1** and **1** (Me-d_3) are 2.8 and 5.7 Hz, respectively. The H/D isotope effect of **1** was –0.25 ppm [= δ (Se: **1** (Me-d_3)) – δ (Se: **1**)]. The H/D isotope effect of **2** was also measured. The effect was –0.20 ppm. The $\nu_{1/2}$ values for **2** and **2** (Me-d_3) are 2.8 and 6.2 Hz, respectively. Figure 4 shows the ^{77}Se NMR spectra recorded at a 1:1 mixture of **2** and **2** (Me-d_3). The H/D

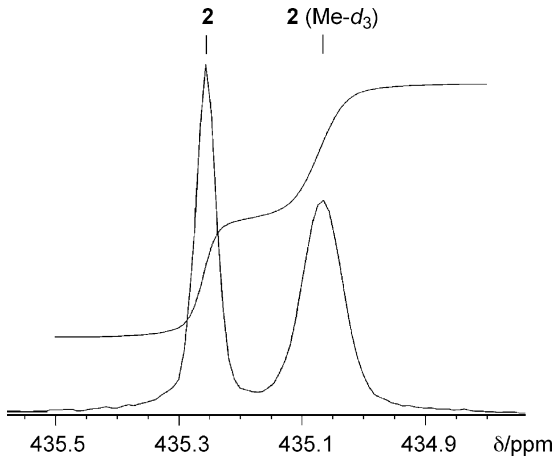


FIGURE 4 ^{77}Se NMR spectra recorded at a 1:1 mixture of **2** and **2** (Me-d_3).

isotope effect was similarly measured for **3**, **5**, and **6**. Table III collects the results, together with the $\nu_{1/2}$ values.

Before discussion of the H/D isotope effect on δ (Se) in the naphthalene system, that of the benzene system is discussed, first.

As shown in Table III, the H/D isotope effect on δ (Se) of **6** is 0.93 ppm. The $\nu_{1/2}$ values of **6** and **6** ($H_{(2)}$–*d*) are both 3.8 Hz. The same $\nu_{1/2}$ values show that the nuclear spin–spin coupling between Se and $D_{(2)}$ in **6** ($H_{(2)}$–*d*) is very small, so is that between Se and $D_{(2)}$ in **6**. The H/D isotope effects were reported to be –7.0 and –14.0 ppm for HDSe and D_2Se relative to H_2Se, respectively.[13] It is –7.0 ppm per D. The effect is large since D is joined directly to Se in place of the Se–H bond in these cases. The effect of –1.68 ppm was reported for 2-deuterioselenophene relative to selenophene[14] and the –3.78 ppm for

TABLE III H/D Isotope Effects on ^{77}Se NMR Chemical Shifts and the Half-Value Widths of 1–3, 5, and 6

	δ (Se: *d*)	δ (Se)	$\Delta\delta$ (Se)[a]	$\nu_{1/2}$(Se: *d*) (Hz)	$\nu_{1/2}$(Se) (Hz)	$\Delta\nu_{1/2}$[b] (Hz)
1	452.32	452.57	–0.25	5.7	2.8	2.9
2	435.07	435.27	–0.20	6.2	2.8	3.4
3	361.10	361.02	0.08	3.6	3.2	0.4
5	382.55	382.66	–0.11	3.4	3.4	0.0
6	422.36	423.29	–0.93	3.8	3.8	0.0

[a] δ (Se: with *d*) – δ (Se).
[b] $\nu_{1/2}$(Se: with *d*) – $\nu_{1/2}$(Se).

$PhSeCD_2Ph$ from $PhSeCH_2Ph$ (–1.89 ppm per D).[15,16] The effect in benzyl phenyl selenide is close to that in selenophene. The H/D isotope effect of –0.93 ppm in **6** is about a half of those in selenophene and benzyl phenyl selenide. The smaller effect in **6** must be the reflection of one bond longer between Se and H(D) in **6** relative to selenophene and benzyl phenyl selenide. The mechanism of the H/D isotope effect in hydrogen selenide is through-bond and those in selenophene and benzyl phenyl selenide must be mainly through-bond.[17] Consequently, the mechanism in **6** should also be through-bond in the analogy with above cases.

The H/D isotope effect of –0.11 ppm is observed for **5**, which is much smaller than that in **6**. The value observed for **3** is 0.08 ppm. The magnitudes of the effect in **3** and **5** are very close to each other, although the signs are different. The $\nu_{1/2}$ values for δ (Se) of **3**, **5**, and the deuterated compounds were almost the same (3.2–3.8 Hz). The magnitude of the H/D isotope effect decreases as the bond number between Se and H(D) in question increases.[18] Therefore, the H/D isotope effect in **3**–**6** can be explained by the through-bond mechanism. Indeed, the through-space mechanism could operate in **3** and **5**, but the contributions seem small.

The H/D isotope effects of –0.25 ppm in **1** and –0.20 ppm in **2** are substantially larger than those observed in **3** and **5**, respectively, in magnitude. The $\nu_{1/2}$ values of 5.7 Hz in **1** (Me-d_3) and 6.2 Hz in **2** (Me-d_3) are also substantially larger than those of 2.8 Hz in **1** and **2**. It is difficult to explain such a large H/D isotope effect by the through-bond mechanism. The effect in **1** and **2** must be smaller than that in **3** and **5**, if only through-bond mechanism operates: The numbers of the bonds between the atoms in **1** and **2** are five, whereas they are three in **3** and **5**. Namely, the through-space mechanism is demonstrated to operate in the H/D isotope effect in **1** and **2**. The nonbonded nuclear spin–spin couplings in **1** and **2** can be similarly explained by the through-space mechanism.

Why is the H/D isotope effect in **1** and **2** negative? The effect would arise from the very slight difference between the r(Se, D_{Me}) and r(Se, H_{Me}) in **1** and **2**. The potential surfaces around the atoms must be essentially the same with each other in **1** and **2**. The mass of deuterium is twice of that of hydrogen. Therefore, the zero-point energy for a C–D bond is about 0.71 ($\approx 2^{-1/2}$) times larger than that of the C—H bond, which results in a slightly shorter bond distance for C–D relative to C—H, in the average.[19] Namely, the C–D bonds in **1** (Me-d_3) and **2** (Me-d_3) would be slightly shorter than the C—H bonds in **1** and **2**, respectively, which will decrease slightly the steric conjunction[20] around Se in **1** (Me-d_3) and **2** (Me-d_3), relative to **1** and **2**, respectively.

This consideration supports the conclusion that the negative H/D isotope effect in **1** and **2** arises from the through-space mechanism, where the steric compression between Me-d_3 and Se in **1** (Me-d_3) and **2** (Me-d_3) is slightly released, relative to **1** and **2**, respectively. Although the H/D isotope effect in **1** and **2** is small, the intrinsic steric compression between Se and Me must be very large judging from the Δr(Se, C_{Me}) value of 0.91 Å in **2**. The Δr(Se, C_{Me}) values affect on of δ (Se) in **1** and **2** from **3** and **4**, respectively. The conclusion in the H/D isotope effect is in accordance with $\Delta\delta$ (Se) in **1** and **2**.

The through-space mechanism is well demonstrated for the negative H/D isotope effect in **1** and **2**. How does the effect originate through the C—H—Se and/or H—Se—C interactions? Quantum chemical (QC) calculations are performed on **1** and **2**, containing the NBO analysis, to elucidate the nature of the nonbonded interaction.

QC Calculations on 1 and 2

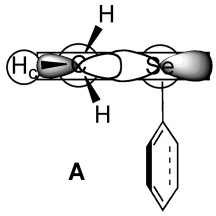
QC calculations were performed on **1** and **2** by the B3LYP/6-311+G(2d,p) method. Scheme 1 shows plausible structures, **A**, **B**, and **B'** for **1** and **2**, where Se—C_i is perpendicular to the naphthyl plane in **A** and it is on the plane in **B**. **A** and **B** are stable, whereas **B'** is expected to be a transition state.[10]

Calculations are performed on **1** (**A**), **1** (**B**), **1** (**B'**), **2** (**A**), and **2** (**B**). Table IV shows the results, containing the relative energies.[21] While the energies of **1** (**A**) and **1** (**B**) are very close with each other, **1** (**B'**) is less stable than **1** (**B**) by 15.2 kJ mol^{-1}. On the other hand, **2** (**B**) is predicted to be substantially stable than **2** (**A**) (E(**2** (**B**)) – E(**2** (**A**)) = –7.1 kJ mol^{-1}). The global minimum of **2** (**B**) well reproduced the structure of **2** determined by the X-ray crystallographic analysis. **2** (**B**) is expected to contribute much in the solution.

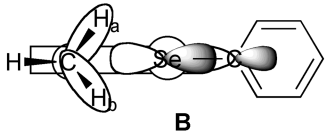
TABLE IV Results of QC Calculations on 1 and 2 with the B3LYP/6-311+G(2d,p) Method

	E (au)	ΔE (kJ mol^{-1})
1 (**A**)	–3057.9673	0.0
1 (**B**)	–3057.9683	–2.6
1 (**B'**)	–3057.9625	15.2
2 (**A**)	–3172.5261	0.0
2 (**B**)[a]	–3172.5288	–7.1

[a] **2** (**B**) is optimized even if starting from **2** (**B'**).

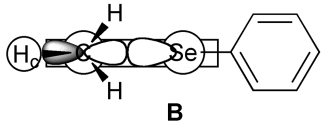


$n_p(Se)$---$\sigma^*(C–H_c)$: 4.5 kJ mol^{-1}



$\sigma(C–H_a)$---$\sigma^*(Se–C)$: 4.2 kJ mol^{-1}

$\sigma(C–H_b)$---$\sigma^*(Se–C)$: 4.2 kJ mol^{-1}



$n_s(Se)$---$\sigma^*(C–H_c)$: 3.8 kJ mol^{-1}

SCHEME 2 Nonbonded interactions in **1**, contributing to **A** and **B**.

Charge-transfer interactions from donor NBO(i) to acceptor NBO(j) can be evaluated through the second order perturbation theory analysis in the NBO basis. They are evaluated by Equation 1, where $E(2)$ is the second order perturbation energy, q_i is the donor orbital occupancy, $F(i,j)$ is the off-diagonal NBO Fock matrix element, and $(\varepsilon_i - \varepsilon_j)$ is the energy difference between donor NBO(i) and acceptor NBO(j).

$$E(2) = \Delta E_{ij} = q_i F(i,j)^2/(E(j) - E(i)) \quad (1)$$

Natural bond orbital (NBO) analysis is carried out on **1** (**A**) and**1** (**B**). Table V shows the results of NBO analysis, and Scheme 2 illustrates the results.[21] The n_p(Se)—σ^*(C—H) interaction contributes 4.5 kJ mol^{-1} for **1** (**A**). In the case of **1** (**B**), the n_s(Se)—σ^*(C—H) interaction contributes 3.8 kJ mol^{-1}, together with the double σ(C—H)—σ^*(Se—C) type interactions by 8.4 kJ mol^{-1} (4.2 kJ mol^{-1} for each). Why is the contribution of the nonbonded n_s(Se)—σ^*(C—H) interaction (3.8 kJ mol^{-1}) in **1** (**B**) close to that of the n_p(Se)—σ^*(C—H) type (4.5 kJ mol^{-1}) in **1** (**A**)? The nonbonded distance between Se and C_{Me} must be an important factor to control the values. The r(Se, C_{Me}) values optimized for **1** (**A**) and **1** (**B**) are 3.211 and 3.025 Å, respectively. The former is longer than the latter by 0.186 Å, which makes the contributions almost equal.

Are there some differences between the nonbonded interactions described by C—H—Se and H—Se—C? The image of the nonbonded C—H—Se interaction may be close to the n_p(Se)—σ^*(C—H) and n_s(Se)—σ^*(C—H) interactions, whereas the H—Se—C interaction would be

TABLE V Results of NBO Analysis for 1 with the B3LYP/6-311+G(2d,p) Method[a]

Donor NBO(i)[b]	Acceptor NBO(j)[c]	$E(2)$[d] (kJ mol^{-1})	$E(j)$–$E(i)$[e] (au)	F(i,j)[f] (au)
1 (**A**): r(Se, C_{Me}) = 3.211 Å[g]				
n_p(Se)	σ* (C_{Me}–H_c)	4.5	0.63	0.024
1 (**B**): r(Se, C_{Me}) = 3.025 Å[g]				
σ (C_{Me}–H_a)	σ* (Se—C_i)	4.2	0.63	0.023
σ (C_{Me}–H_b)	σ* (Se—C_i)	4.2	0.63	0.023
n_s(Se)	σ* (C_{Me}–H_c)	3.8	1.12	0.029

[a]Second order perturbation of Fock matrix (threshold being 2.1 kJ mol^{-1}).[21]
[b]Donor orbitals. [c]Acceptor orbitals.
[d]The values are the estimated strengths of the donor–acceptor interactions. The stabilization energy associated with these interactions is evaluated by Equation 1 in the text.
[e]Energy difference between donor NBO(i) and acceptor NBO(j).
[f] The element of the Fock (or Kohn-Sham) matrix describing the donor–acceptor interaction.
[g]Calculated values.

understood by the σ (C—H)—σ *(Se—C) type. The results of the NBO analysis show that the nonbonded n(Se)—σ *(C—H) interaction operates in both **A** and **B**, whereas the nonbonded σ(C—H)—σ *(Se—C) type interaction contributes only in **B**. The contribution of σ *(C—H)—σ (Se—C) would be negligible, which is less than the threshold value of 2.1 kJ mol^{-1}.

CONCLUSION

It is elucidated how the C—H bonds, with very stable σ (C—H) and high energy σ *(C—H) orbitals, interact with neighboring groups, such as n(Se) and/or σ *(Se—C) orbitals of the ArSe group, employing the naphthalene 1,8-positions of **1** and **2**. The structure of **2** is determined by the X-ray crystallographic analysis. The nonbonded distance between Se and C_{Me} in **2** is 2.989 Å, which is shorter than the sum of the van der Waals radii of the atoms by 0.91 Å. The δ (Se) values of methyl-d_3 derivatives of **1** and **2** are observed 0.25 and 0.20 ppm upfield from **1** and **2**, respectively, in chloroform-*d*. The H/D isotope effect must occur through the C—H—Se and/or H—Se—C interactions. The mechanism for the nonbonded interactions is elucidated based on the NOB analysis of **1**. While the nonbonded n_p(Se)—σ *(C—H) interaction contributes in

A, both nonbonded n_s(Se)—σ^*(C—H) and double σ (C—H)—σ^*(Se—C) interactions operate in **B**.

The effect of nonbonded Se—C_{Me} interactions on the NMR parameters of **1** and **2** are also of interest. Investigations to clarify the origin of the downfield shifts by the methyl group at the 8-position in 1-(arylselanyl)naphthalenes are in progress. The results will be reported elsewhere.

EXPERIMENTAL

Chemicals were used without further purification unless otherwise noted. Solvents were purified by standard methods. Melting points were uncorrected. Column chromatography was performed on silica gel and basic alumina for the purification of compounds. ^1H, ^{13}C, and ^{77}Se NMR spectra were measured at 400, 100, and 76 MHz, respectively. The ^1H, ^{13}C, and ^{77}Se chemical shifts are given in ppm relative to those of internal $CHCl_3$ slightly contaminated in $CDCl_3$ solutions, $CDCl_3$ as the solvent, and external MeSeMe, respectively. The resolution is 0.7 Hz (0.01 ppm) for ^{77}Se NMR spectra under the conditions of measurements.

8-(Methyl)-1-(phenylselanyl)naphthalene (1)

To an ether solution of a Grignard reagent prepared from 1-bromo-8-metylnaphthalene and magnesium, an ether solution of diphenyl diselenide[22] was added under argon atmosphere. After the usual workup, the crude product was chromatographed on silica gel containing basic alumina and gave **1** as pale yellow oil in 88% yield; ^1H NMR ($CDCl_3$, 400 MHz) δ : 3.14 (s, 3H), 7.20 (t, 1H, $J = 7.8$ Hz), 7.31–7.39 (m, 5H), 7.45–7.50 (m, 2H), 7.52 (dd, 1H, $J = 7.3$ and 1.2 Hz), 7.70–7.75 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 25.6, 125.3, 125.5, 127.5, 128.0, 129.1, 129.6, 129.8, 130.2, 131.6, 132.9, 133.5, 133.6, 133.8, 135.8; ^{77}Se NMR ($CDCl_3$, 76 MHz) δ : 452.57. Anal. Calcd. For $C_{17}H_{14}Se_1$: C, 68.69; H, 4.75. Found: C, 68.53; H, 4.77.

8-(Methyl)-1-(*p*-anisylselanyl)naphthalene (2)

Following a method similar to that for **1**, **2** gave 88% yield as colorless prisms: mp 67–68°C. ^1H NMR ($CDCl_3$, 400 MHz) δ : 3.02 (s, 3H), 3.66 (s, 3H), 6.76 (dd, 2H, $J = 8.7$ and 2.5 Hz), 6.97 (t, 1H, $J = 7.7$ Hz), 7.09 (dd, 1H, $J = 7.4$ and 1.3 Hz), 7.15 (dd, 1H, $J = 7.3$ and 1.9 Hz), 7.18 (t, 1H, $J = 7.3$ Hz), 7.39 (dd, 2H, $J = 8.7$ and 2.9 Hz), 7.47 (dd, 1H, $J =$

8.0 and 1.2 Hz), 7.52 (dd, 1H, $J = 7.7$ and 1.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 25.5 ($J = 35.8$ Hz) , 55.2, 115.5, 121.2, 125.3, 125.4, 127.7, 127.8, 128.3, 129.7, 132.8, 133.0, 135.7, 135.9, 137.5 ($J = 12.0$ Hz); ^{77}Se NMR ($CDCl_3$, 76 MHz) δ : 435.27. Anal. Calcd. For $C_{18}H_{16}O_1Se_1$: C, 66.06; H, 4.93. Found: C, 65.81; H, 4.83.

1-(Phenylselanyl)naphthalene (3)

Following a method similar to that for **1**, **3** gave 82% yield as pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ : 6.82 (dd, 2H, $J = 8.9$ and 2.1 Hz), 7.15–7.22 (m, 3H), 7.32–7.37 (m, 2H), 7.37 (t, 1H, $J = 8.3$ Hz), 7.48–7.53 (m, 2H), 7.76 (dd, 1H, $J = 7.1$ and 1.2 Hz), 7.82–7.87 (m, 2H), 8.32–8.35 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 125.9, 126.2, 126.7, 126.8, 127.5 ($J = 10.8$ Hz), 128.5, 129.5, 129.2, 129.3, 131.6 ($J = 12.4$ Hz), 131.6, 133.7 ($J = 9.1$ Hz), 134.0, 134.0; ^{77}Se NMR ($CDCl_3$, 76 MHz) δ : 361.02. Anal. Calcd. For $C_{16}H_{12}Se_1$: C, 67.85; H, 4.27. Found: C, 67.93; H, 4.25.

1-(*p*-Anisylselanyl)naphthalene (**4**) was prepared by the same method in the literature.[2a] Colorless prisms: 82% yield, mp 100–101°C.

2-Tolyl Phenyl Selenide (5)

Following a method similar to that for **1**, **5** gave 84% yield as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ : 2.40 (s, 3H), 7.06 (br.t, 1H, $J = 7.4$ and 1.4 Hz), 7.19 (t, 1H, $J = 7.5$ and 1.2 Hz), 7.21–7.29 (m, 4H), 7.33 (dd, 1H, $J = 7.6$ and 1.2 Hz), 7.38–7.42 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 22.3 ($J = 10.5$ Hz), 126.7, 127.1, 127.7, 129.3, 130.2, 130.7, 131.7, 132.7 ($J = 10.9$ Hz), 133.6, 139.8 ($J = 11.4$ Hz); ^{77}Se NMR ($CDCl_3$, 76 MHz) δ : 382.66. Anal. Calcd. For $C_{13}H_{12}Se_1$: C, 63.17; H, 4.89. Found: C, 63.02; H, 4.92.

Diphenyl selenide (**6**) was prepared according to the literature.[23]

The deuterium compounds, **1** (Me-d_3), **2** (Me-d_3), and **5** (Me-d_3) were prepared in the reaction of the corresponding aryl magnesium bromides with dimethyl sulfate-d_6, and **3** ($H_{(8)}$–d) and **6** ($H_{(2)}$–d) were prepared similarly in the reaction of the magnesium bromides with D_2O.

X-Ray Structural Determination

The colorless single crystals of **2** were grown by slow evaporation of a hexane solution at room temperature. A crystal of dimensions 0.30 $\times$ 0.30 $\times$ 0.30 mm^3 was measured on a Rigaku AFC5R diffractometer

with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) and a rotating anode generator. The structure was solved by direct methods using *SAPI91*[24] and expanded using Fourier techniques, *DIRDIF94*.[25] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1829 observed reflections ($I > 1.50\sigma(I)$) and 181. Variable parameters and converged with unweighted and weighted agreement factors of $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $\omega R = \{\Sigma\omega(|F_o| - |F_c|)2/\Sigma\omega F_o^2\}^{1/2}$ were used to give $R = 0.043$ and $\omega R = 0.051$ for independent observed reflections. For least squares, the function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$, where $\omega = (\sigma_c^2|F_o| + p^2|F_o|^2/4)^{-1}$. Additional crystal and analysis data are listed in Table I.

CCDC-627281 contains the supplementary crystallographic data for this article. This data can be obtained free of charge form The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

COMPUTATIONAL

QC calculations were performed on **1** and **2** with 6-311+G(2d,p) basis sets of the Gaussian 03 program.[5] Calculations are performed at the density functional theory (DFT) level of the Becke three parameter hybrid functional combined with the Lee–Yang–Parr correlation functional (B3LYP).[6,7] NBO analysis[8,9] is also carried out for the plausible structures of **1**, which are type **A** and type **B** and type **B'** (see Scheme 1).

REFERENCES AND NOTES

[1] (a) R. S. Glass, S. W. Andruski, J. L. Broeker, H. Firouzabadi, L. K. Steffen, and G. S. Wilson, *J. Am. Chem. Soc.*, **111,** 4036–4045 (1989); R. S. Glass, L. Adamowicz, and J. L. Broeker, *J. Am. Chem. Soc.*, **113,** 1065–1072 (1991); (b) H. Fujihara, H. Ishitani, Y. Takaguchi, and N. Furukawa, *Chem. Lett.*, 571–572 (1995); (c) H. Fujihara, M. Yabe, J.-J. Chiu, and N. Furukawa, *Tetrahedron Lett.*, **32**, 4345–4348 (1991); N. Furukawa, T. Fujii, T. Kimura, and H. Fujihara, *Chem. Lett.*, 1007–1010 (1994); (d) H. Fujihara, R. Saito, M. Yabe, and N. Furukawa, *Chem. Lett.*, 1437–1440 (1992); (e) W. Nakanishi, *Chem. Lett.*, 2121–2122 (1993); (f) W. Nakanishi, S. Hayashi, and S. Toyota, *Chem. Comm.*, 371–372 (1996); (g) W. Nakanishi, S. Hayashi, and H. Yamaguchi, *Chem. Lett.*, 947–948 (1996); (h) W. Nakanishi, S. Hayashi, and S. Toyota, *J. Org. Chem.*, **63,** 8790–8800 (1998); (i) M. C. Aragoni, M. Arca, F. Demartin, F. A. Devillanova, A. Garau, P. Grimaldi, F. Isaia, F. Lelj, V. Lippolis, and G. Verani, *Eur. J. Inorg. Chem.*, 2363–2368 (2004); (j) M. Iwaoka, H. Komatsu, T. Katsuda, and S. Tomoda, *J. Am. Chem. Soc.*, **126,** 5309–5317 (2004); (k) G. Mugesh, A. Panda, H. B. Singh, N. S. Punekar, and R. J. Butcher, *J. Am. Chem. Soc.*, **123,** 839–850 (2001); (l) *Chemistry of Hypervalent Compounds*, K.-y. Akiba (Ed.) (Wiley-VCH,

New York, 1999); (m) W. Nakanishi, Hypervalent chalcogen compounds, In *Handbook of Chalcogen Chemistry: New Perspectives in Sulfur, Selenium and Tellurium*, F. A. Devillanova (Ed.), *Royal Society of Chemistry* (Cambridge, UK, 2006), Chapter 10.3.1, pp. 644–668.

[2] (a) W. Nakanishi, S. Hayashi, A. Sakaue, G. Ono, and Y. Kawada, *J. Am. Chem. Soc.*, **120,** 3635–3640 (1998); (b) W. Nakanishi and S. Hayashi, *J. Phys. Chem. A*, **103,** 6074–6081 (1999); (c) S. Hayashi and W. Nakanishi, *J. Org. Chem.*, **64,** 6688–6696 (1999); (d) W. Nakanishi, S. Hayashi, and T. Uehara, *J. Phys. Chem. A*, **103,** 9906–9912 (1999); (e) W. Nakanishi and S. Hayashi, *J. Org. Chem.*, **67,** 38–48 (2002); (f) W. Nakanishi, S. Hayashi, D. Shimizu, and M. Hada, *Chem. Eur. J.*, **12,** 3829–3846 (2006); (g) S. Hayashi and W. Nakanishi, *Bioinorganic Chemistry and Applications*, DOI 10.1155/BCA/2006/79327 (2006).

[3] I. Johannsen and H. Eggert, *J. Am. Chem. Soc.*, **106,** 1240–1243 (1984); I. Johannsen, H. Eggert, S. Gronowitz, and A.-B. Hörnfeldt, *Chemica Scripta*, **27**, 359–361 (1987); H. Fujihara, H. Mima, T. Erata, and N. Furukawa, *J. Am. Chem. Soc.*, **114,** 3117–3118 (1992).

[4] W. Nakanishi, S. Hayashi, and T. Uehara, *Eur. J. Org. Chem.*, 3933–3943 (2001).

[5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, Jr. K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03*, revision B.05; Gaussian, Inc., Pittsburgh, PA (2003).

[6] C. Lee, W. Yang, and R. G. Parr, *Phys. Rev.*, **B37,** 785–789 (1988).

[7] A. D. Becke, *Phys. Rev.*, **A38,** 3098 (1988); A. D. Becke, *J. Chem. Phys.*, **98,** 5648–5652 (1993).

[8] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.*, **83,** 735–746 (1985); J. E. Carpenter, and F. Weinhold, *J. Mol. Struct. (THEOCHEM)*, **169,** 41–62 (1988).

[9] NBO Ver. 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold. Theoretical Chemistry Institute, University of Wisconsin, Madison, WI.

[10] The structure of **2** (**B'**) would be assigned if the hydrogen atoms of the methyl group were positioned automatically. However, **2** (**B**) is reasonably determined by the X-ray crystallographic analysis, when the H atoms are positioned at those higher electron densities around the C_{Me} atom. R-values for **2** (**B**) are smaller than those for **2** (**B'**). **2** (**B**) is optimized even if started from **2** (**B'**) in the QC calculations.

[11] A. Bondi, *J. Phys. Chem.*, **68,** 441–451 (1964). See also, for Me and Ph, L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell University Press, Ithaca, NY, 1960), Chapter 7.

[12] D. Gust and K. Mislow, *J. Am. Chem. Soc.*, **95**, 1535–1547 (1973); K. Mislow, *Acc. Chem. Res.*, **9,** 26–33 (1976); H. Iwamura and K. Mislow, *Acc. Chem. Res.*, **21**, 175–182 (1988); G. Yamamoto, *Pure Appl. Chem.*, **62,** 569–574 (1990); G. Yamamoto, K. Inoue, H. Higuchi, M. Yanebayashi, Y. Nabeta, J. Ojima, *Bull. Chem. Soc. Jpn.*, **71,** 1241–1248 (1998).

[13] H. J. Jakobsen, A. J. Zozulin, P. D. Ellis, and J. D. Odom, *J. Magn. Reson.*, **38,** 219–227 (1980).
[14] H. J. Jakobsen and R. S. Hansen, *J. Magn. Reson.*, **30,** 397–399 (1978).
[15] M. Iwaoka, H. Komatsu, and S. Tomoda, *Bull. Chem. Soc. Jpn.*, **69,** 1825–1828 (1996).
[16] The isotope effect has been studied for 6*H*,12*H*-dibenzo[*b, f*][1, 5]diselenocin and concluded that the nonbonded C—H—Se interaction would be attractive based on the results.[20] However, the through-space H/D isotope effect seems not well separated from the through-bond one in the system.
[17] For the ^{12}C/^{13}C isotope effect on the δ (Se) of selenides, see W. Gombler, *J. Am. Chem. Soc.*, **104,** 6616–6620 (1982), and for the selenium isotope effect on the δ (Se) of organic selenium compounds see, W. Gombler, *J. Magn. Reson.*, **53,** 69–75 (1983).
[18] The bond number is an important factor to understand the H/D isotope effect on δ (Se) if the through-bond mechanism operates. The role of the bond number is established as the α-, β-, γ-, and δ-effects in δ (Se). The α-, β-, γ-, and δ-effects are 57,[26] 120, –37, and 3 ppm, respectively, in the series of $PhSeC_nH_{2n+1}$.[27] The γ-effect is upfield shifts and the ε-effect is negligibly small.[28] The H/D isotope effect in **6** may correspond to the γ-effect and those in **5** and **3** to the δ-effect. The H/D isotope effect of **1** and **2** must be accounted for by the ε-effect if the mechanism were through-bond.
[19] F. H. Westheimer, *Chem. Rev.*, **61,** 265–273 (1961). See also, *Mechanism and Theory in Organic Chemistry*, T. H. Lowry and K. S. Richardson (Eds.), 2nd Ed. (Harper and Row Publishers, New York, 1981), p. 205.
[20] D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89,** 5315–5318 (1967).
[21] Total energies (E) and MO energies [$E(i)$] are shown in atomic unit (au) and energy differences (ΔE) are in kJ mol^{-1}, as usual. The second order perturbation energies of the NBO analysis [$E(2)$] are also given in kJ mol^{-1}, although they are calculated in kcal mol^{-1}.
[22] G. A. Kalabin, D. F. Kushnarev, L. M. Kataeva, L. V. Kashurnikova, and R. I. Vinokurova, *Zh. Org. Khim.*, **14,** 2478–2483 (1978).
[23] B. Greenberg, E. S. Gould, and W. Burlant, *J. Am. Chem. Soc.*, **78,** 4028–4029 (1956).
[24] H.-F. Fan. *Structure analysis program with intelligent control* (Rigaku Corporation, Tokyo, Japan, 1991).
[25] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, and J. M. M. Smits, The DIRDIF-94 program system, technical report of the crystallography laboratory (University of Nijmegen, the Netherlands, 1994).
[26] The δ (Se) values of MeSeH, MeSeMe, and MeSeEt are reported to be –130, 0, and 108, respectively: the α-effect is much larger than the case of ArSeR.[27]
[27] *The Chemistry of Organic Selenium and Tellurium Compounds*, S. Patai, Z. Rappoport (Eds.), (Wiley, New York, 1986), Vol. 1, Chapter 6.
[28] The [$\delta(^A$Se), $\delta(^B$Se)] values were reported to be (392.7, 372.5) and (389.1, 370.7) for $Ph^ASe^BSeC_4H_9$–*n* and $Ph^ASe^BSeC_5H_{11}$–*n*, respectively; see, J. A. Anderson, J. D. Odom, and A. Zozulin, *J. Organometallics*, **3,** 1458–1465 (1984).