

## Research Article

# Fine Structures of 8-G-1-(*p*-YC<sub>6</sub>H<sub>4</sub>C≡CSe)C<sub>10</sub>H<sub>6</sub> (G = H, Cl, and Br) in Crystals and Solutions: Ethynyl Influence and Y- and G-Dependences

Satoko Hayashi, Kentaro Yamane, and Waro Nakanishi

Department of Material Science and Chemistry, Faculty of Systems Engineering, Wakayama University,  
930 Sakaedani, Wakayama 640-8510, Japan

Correspondence should be addressed to Waro Nakanishi, nakanisi@sys.wakayama-u.ac.jp

Received 18 January 2009; Revised 14 April 2009; Accepted 24 June 2009

Recommended by Govindasamy Mugesh

Fine structures of 8-G-1-(*p*-YC<sub>6</sub>H<sub>4</sub>C≡CSe)C<sub>10</sub>H<sub>6</sub> [**1** (G = H) and **2** (G = Cl): Y = H (**a**), OMe (**b**), Me (**c**), F (**d**), Cl (**e**), CN (**f**), and NO<sub>2</sub> (**g**)] are determined by the X-ray analysis. Structures of **1**, **2**, and **3** (G = Br) are called **A** if each Se–C<sub>sp</sub> bond is perpendicular to the naphthyl plane, whereas they are **B** when the bond is placed on the plane. Structures are observed as **A** for **1a–c** bearing Y of nonacceptors, whereas they are **B** for **1e–g** with Y of strong acceptors. The change in the structures of **1e–g** versus those of **1a–c** is called Y-dependence in **1**. The Y-dependence is very specific in **1** relative to 1-(*p*-YC<sub>6</sub>H<sub>4</sub>Se)C<sub>10</sub>H<sub>7</sub> (**4**) due to the ethynyl group: the Y-dependence in **1** is almost inverse to the case of **4** due to the ethynyl group. We call the specific effect “Ethynyl Influence.” Structures of **2** are observed as **B**: the **A**-type structure of **1b** changes dramatically to **B** of **2b** by G = Cl at the 8-position, which is called G-dependence. The structures of **2** and **3** are examined in solutions based on the NMR parameters.

Copyright © 2009 Satoko Hayashi et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

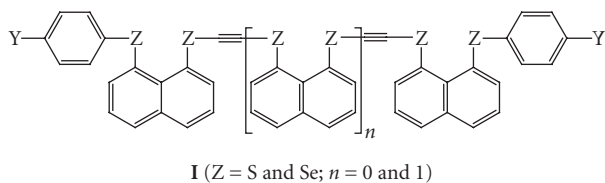
## 1. Introduction

We are much interested in extended hypervalent bonds [*m* center–*n* electron bonds (*mc–ne* : *m* ≥ 4) [1–11] higher than 3c–4e [1, 12–14]. The nature of 4c–6e [1–5] is demonstrated to be very different from that of 3c–4e [1, 12–18]. Our strategy to construct the extended hypervalent bonds is to employ the interactions caused by direct orbital overlaps between nonbonded atoms [1–11, 19–21]. Weak interactions control fine structures and create delicate functionalities of materials [15, 22–40]. Recently, extended hypervalent bonds are shown to play an important role in physical, chemical and biological properties of the compounds [41–50]. On the other hand, the ethynyl group and the derivatives are of great importance as building blocks in the material design of high functionality [51–64]. Indeed, the ethynyl  $\pi$  and  $\pi^*$  orbitals play an important role to appear specific properties in 8-G-1-(Ph<sub>3</sub>SiC≡C)C<sub>10</sub>H<sub>6</sub> (G = OMe and NMe<sub>2</sub>) [65], but the ethynyl  $\sigma$  and  $\sigma^*$  orbitals must also be of interest to originate the functionalities of materials. It will be great interest if

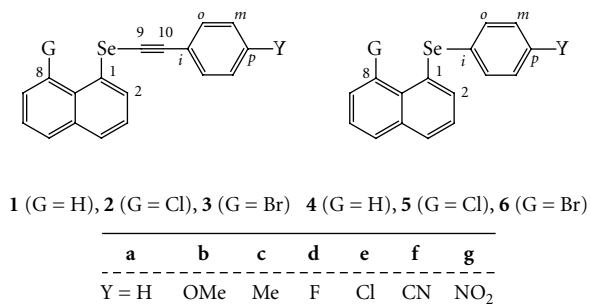
the ethynyl group is joined to the extended hypervalent bonds constructed by the group 16 elements, such as **I** (Scheme 1).

As the first step to clarify the factors to control the fine structures of the ethynyl joined extended hypervalent compounds such as **I**<sup>1</sup>, the ethynyl influence and Y- and G-dependences as the factors to control fine structures of 8-G-1-(*p*-YC<sub>6</sub>H<sub>4</sub>C≡CSe)C<sub>10</sub>H<sub>6</sub> [**1** (G = H) [66], **2** (G = Cl) [67], and **3** (G = Br) [67]: Y = H (**a**), OMe (**b**), Me (**c**), F (**d**), Cl (**e**), CN (**f**), and NO<sub>2</sub> (**g**)] are elucidated (Scheme 2). The Y- and G-dependences are also discussed for 8-G-1-(*p*-YC<sub>6</sub>H<sub>4</sub>Se)C<sub>10</sub>H<sub>6</sub> [**4** (G = H) [22], **5** (G = Cl) [16], and **6** (G = Br) [16] for convenience of comparison. **1–3** are prepared and the structures of some compounds are determined by the X-ray crystallographic analysis.

Structures of the naphthalene system are well explained by the three types, **A**, **B**, and **C**, in our definition, where the Se–C<sub>sp</sub> bond is perpendicular to the naphthyl plane in **A**, it is placed on the plane in **B**, and **C** is intermediate between **A** and **B** [4, 15, 16, 22, 23, 68]. The **A**, **B**, and **C** notations are



SCHEME 1



SCHEME 2

employed for the structures around the Se–C<sub>Nap</sub> bonds in **1–6**. The planar (**pl**) and perpendicular (**pd**) notations are also used to specify the structures of **1–6**, where they specify the conformers around the Se–C≡C–C<sub>Ar</sub> (abbreviated Se–C<sub>Ar</sub>) bonds in **1–3** and those around Se–C<sub>Ar</sub> in **4–6**. Scheme 3 illustrates plausible structures of **1–3**. Combined notations such as (**A: pl**) and (**B: pd**) are employed for the structures. The structures of **4** are **B** for Y of donating groups such as OMe, whereas they are **A** for Y of accepting groups such as NO<sub>2</sub> [22]. We call the results Y-dependence. The magnitude of the p(Se)–π(Ar/Nap) conjugation must be the origin of Y-dependence in **4**.

Here, we report the fine structures of **1** and **2** determined by the X-ray crystallographic analysis as a factor to control the fine structures. We call the factor “*Ethynyl Influence*” in **1** and the G-dependence arise from the nonbonded n<sub>p</sub>(G) ··· σ\*(Se–C<sub>sp</sub>) 3c–4e interaction or the G ··· Se–C<sub>sp</sub>–C<sub>sp</sub>–C<sub>sp</sub><sup>2</sup> 5c–6e type interaction in **2** and **3**. The behaviors of **1–3** in solutions are also examined, containing the selective <sup>1</sup>H, <sup>13</sup>C–NOE difference spectroscopic measurements, to estimate the efficiency of the factors based on NMR parameters.

## 2. Experimental

**2.1. Materials and Measurements.** Manipulations were performed under an argon atmosphere with standard vacuum-line techniques. Glassware was dried at 130°C overnight. Solvents and reagents were purified by standard procedures as necessary.

Melting points were measured with a Yanaco-MP apparatus of uncollected. Flash column chromatography was performed on silica gel (Fujisilysia PSQ-100B), acidic and basic alumina (E. Merck). **1–3** were prepared by the methods described elsewhere [67, 68].

NMR spectra were recorded at 297 K on a JEOL AL-300 MHz spectrometer (<sup>1</sup>H, 300 MHz; <sup>77</sup>Se, 57 MHz) on a JEOL ECP-400 MHz spectrometer (<sup>1</sup>H, 400 MHz; <sup>13</sup>C, 100 MHz) in chloroform-*d* solutions (0.050 M)<sup>2</sup>. Chemical shifts are given in ppm relative to one of TMS for <sup>1</sup>H NMR spectra and relative to reference compound Me<sub>2</sub>Se for <sup>77</sup>Se NMR spectra.

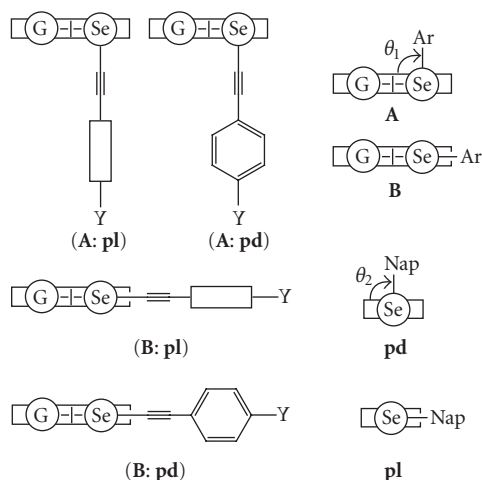
**2.2. X-Ray Crystal Structure Determination.** Single crystals of some of **1** and **2** were obtained by slow evaporation of dichloromethane-hexane and/or ethyl acetate solutions at room temperature. X-ray diffraction data were collected on a Rigaku/MSC Mercury CCD diffractometer equipped with a graphite-monochromated MoKα radiation source (λ = 0.71070 Å) at 103(2) K. The structures were solved by direct methods (SIR97) [69] for **1a–c**, **1e–g**, and **2e** and (SHELXS-97) [70] for **2b**, and (SIR2004) [71] for **2g** and refined by the full-matrix least squares method on F<sup>2</sup> for all reflections (SHELXL-97) [72]. All of the nonhydrogen atoms were refined anisotropically. CCDC-666789 (**1a**), CCDC-666790 (**1b**), CCDC-666791 (**1c**), CCDC-666792 (**1e**), CCDC-666793 (**1f**), CCDC-666794 (**1g**), CCDC-687206 (**2b**), CCDC-687207 (**2e**), and CCDC-687208 (**2g**) are available. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

## 3. Results and Discussion

**3.1. Structures of 1 and 2 in Crystals.** Single crystals were obtained for **1a–c**, **1e–g**, **2b**, **2e**, and **2g** via slow evaporation of dichloromethane-hexane or ethyl acetate solutions. The X-ray crystallographic analyses were carried out for a suitable crystal of each compound. One type of structure corresponds to **1b**, **1c**, **1e–g**, **2b**, **2e**, and **2g** and two-type ones to **1a** in the crystals. The crystallographic data and the structures are reported elsewhere [66, 67]. Figure 1 summarizes structures of **1** and **2**, relative to **4–6**. Table 1 collects the selected interatomic distances, angles, and torsional angles, necessary for the discussion. The atomic numbering scheme is shown for **1b** in Figure 1, as an example.

As shown in Figure 1 and Table 1, the structure of **1** is **A** for Y of nonacceptors (**1 (A)**) such as H (**a**), OMe (**b**), and Me (**c**), whereas that of **1** is **B** for Y of acceptors (**1 (B)**) such as Cl (**e**), CN (**f**), and NO<sub>2</sub> (**g**) (Scheme 2). The results are quite a contrast to the case of **4**, where the structure of **4** is **B** with Y = OMe, and they are **A** when Y = Cl and NO<sub>2</sub>. The ethynyl group interrupted between *p*-YC<sub>6</sub>H<sub>4</sub> and Se changes the structures dramatically: (**B: pd**) of **4b** to (**A: pd**) of **1b**, (**A: pl**) of **4e** to (**B: pd**) of **1e**, and (**A: pl**) of **4 (Y = CO<sub>2</sub>Et)** to (**B: pl**) of **1g**, where Y = CO<sub>2</sub>Et is employed in place of Y = NO<sub>2</sub> for **4** [22]. The direction of Y-dependence in **1** is just the inverse to the case of **4**. We call the factor to determine the fine structure of **1** “*Ethynyl Influence*”.

The change in the structures of **1e–g** versus those of **1a–c** is called Y-dependence in **1**. The Y-dependence is very

SCHEME 3: Plausible structures of 1–3: **A** and **B** notation for naphthyl group, **pd** and **pl** for phenyl group, and the combined one for 1–3.TABLE 1: Selected bond distances, angles, and torsional angles around Se atom, observed in **1** and **2**<sup>(a)</sup>.

	<b>1a<sub>A</sub></b>	<b>1a<sub>B</sub></b>	<b>1b</b>	<b>1c</b>	<b>1e</b>	<b>1f</b>	<b>1g</b>
$r(\text{Se1}, \text{C1})$ (Å)	1.9321(19)1.9315(15)	1.9243(18) <sup>(b)</sup>	1.936(2)	1.933(2)	1.935(2)	1.9335(19)	
$r(\text{Se1}, \text{C11})$ (Å)	1.8406(18)1.8233(15)	1.8381(19) <sup>(c)</sup>	1.847(2)	1.844(2)	1.829(3)	1.825(2)	
$\angle \text{C1Se1C11}$ (°)	98.07(7)	99.68(8) <sup>(d)</sup>	98.46(9)	99.07(10)	98.92(11)	98.93(9)	98.41(6)
$\angle \text{C2C1Se1}$ (°)	117.37(14)122.17(11)	116.77(15) <sup>(e)</sup>	117.61(16)	117.61(17)	121.26(19)	122.02(15)	
$\angle \text{C10C1Se1}$ (°)	121.12(13)116.44(11)	121.74(14) <sup>(f)</sup>	120.89(15)	120.84(17)	116.86(18)	116.32(14)	
$\angle \text{C10C1Se1C11}$ (°)	60.64(15)171.42(11)	62.36(15) <sup>(g)</sup>	-79.69(17)	-78.92(19)	-169.24(19)	171.59(15)	
$\angle \text{C1Se1C13C14}$ (°)	-54.80	-135.72 <sup>(h)</sup>	-58.78	126.88	-123.63	176.47	2.61
Structure	( <b>A: pd</b> )	( <b>A: np</b> ) <sup>(i)</sup>	( <b>A: pd</b> )	( <b>A: pd</b> )	( <b>B: pd</b> )	( <b>B: pl</b> )	( <b>B: pl</b> )
	<b>2b</b>		<b>2e</b>		<b>2g</b>		
$r(\text{Se1}, \text{Cl1})$ (Å)	2.9495(16)		2.9753(17)		2.9454(15)		
$r(\text{Se1}, \text{C1})$ (Å)	1.946(4)		1.9458(18)		1.945(2)		
$r(\text{Se1}, \text{C11})$ (Å)	1.831(5)		1.8383(19)		1.829(2)		
$r(\text{Cl1}, \text{C9})$ (Å)	1.749(4)		1.7443(18)		1.744(2)		
$\angle \text{Cl1Se1C11}$ (°)	179.18(15)		165.51(17)		175.70(15)		
$\angle \text{Se1C11C12}$ (°)	167.2(4)		173.07(17)		170.6(2)		
$\angle \text{C1Se1C11}$ (°)	99.7(2)		98.47(8)		99.32(10)		
$\angle \text{C2C1Se1}$ (°)	118.0(3)		117.64(14)		117.70(17)		
$\angle \text{C10C1Se1}$ (°)	121.7(3)		122.39(13)		122.21(16)		
$\angle \text{C10C1Se1C11}$ (°)	170.5(3)		-164.16(15)		171.80(19)		
$\angle \text{C1Se1C13C14}$ (°)	104.41(6)		102.59(8)		3.68(7)		
Structure	( <b>B: pd</b> )		( <b>B: pd</b> )		( <b>B: pl</b> )		

<sup>(a)</sup> The atomic numbering scheme is shown for **1b** in Figure 1, as an example. <sup>(b)</sup>  $r(\text{Se2}, \text{C19})$ . <sup>(c)</sup>  $r(\text{Se2}, \text{C29})$ . <sup>(d)</sup>  $\angle \text{C19Se2C29}$ . <sup>(e)</sup>  $\angle \text{C20C19Se2}$ . <sup>(f)</sup>  $\angle \text{C28C19Se2}$ . <sup>(g)</sup>  $\angle \text{C28C19Se2C29}$ . <sup>(h)</sup>  $\angle \text{C19Se2C31C32}$ . <sup>(i)</sup> Intermediate structure between (**A: pd**) and (**A: pl**).

specific in **1** relative to **4** due to the ethynyl group: the Y-dependence in **1** is almost inverse to the case of **4** due to the ethynyl group. We call the specific effect “*Ethynyl Influence*.”

In the case of the structures of **2**, they are (**B: pd**) for **2b** and **2e** and (**B: pl**) for **2g**. The results exhibit that **1b** (**A: pd**) changes dramatically to **2b** (**B: pd**) by G = Cl at the 8-position in **2**. We call the effect G-dependence in **2**. The effect fixes the structure of **2** to **B**. While the variety of structures

such as (**A: pd**), (**B: pd**), and (**B: pl**) are observed in **1**, the observed structure is only **B** in **2**. The observation is quite different from that in **1**, again. The observed structure of **1g** is substantially different from that of **6g**. Y-dependence in **2** must be very similar to that in **1**.

After explanation of the observed structures of **1** in crystals, the role of crystal packing forces is examined in relation to the fine structures of **1**.

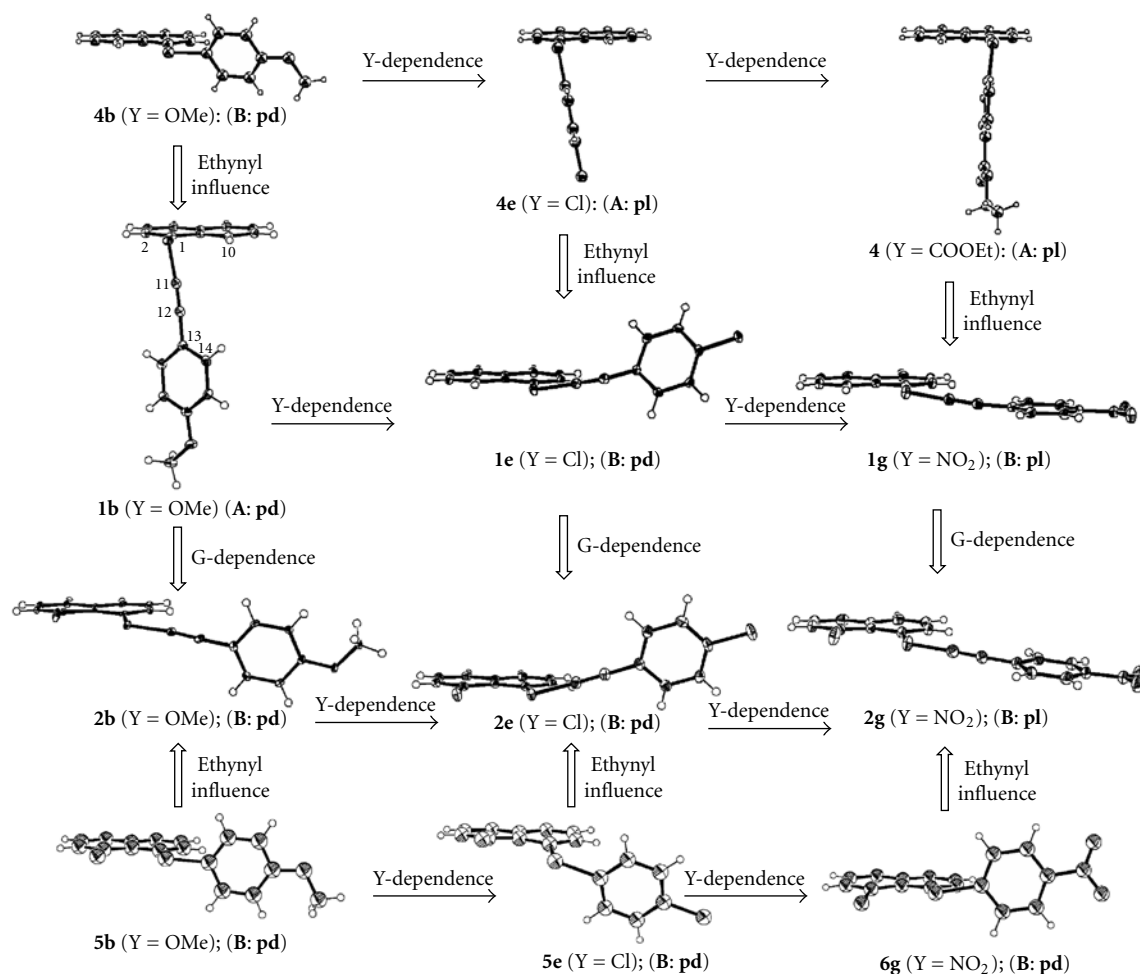


FIGURE 1: Ethynyl Influence in 1 and 2 and Y-dependence in 1, 2, and 4-6.

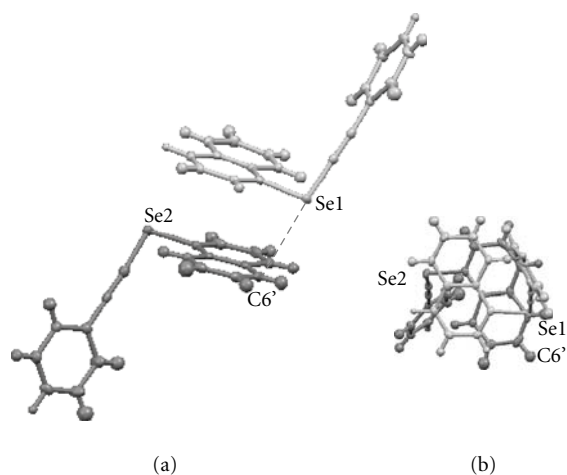
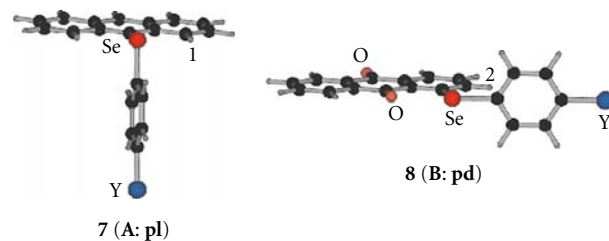


FIGURE 2: Dimer formed in **1a**, which contains **1a<sub>A</sub>** and **1a<sub>B</sub>**: (a) a side view ( $r(\text{Se1}-\text{C6}')$ : 3.392 Å) and (b) a top view.

3.2. Crystal Packing Forces as Factor to Determine Fine Structure of **1**. The structures of **1a-c** are observed as dimers. Figure 2 shows the dimer formed from **1a**, which contains



SCHEME 4: Illustration for the structures of **7** (A: pl) and **8** (B: pd).

**1a<sub>A</sub>** and **1a<sub>B</sub>**. Se atoms in the **1a** dimer are in short contact with C at the 6' position of the partner molecule, and the Se1—C6' distance is 3.392 Å. Dimers of **1b** and **1c** are essentially the same as that of **1a**. An Se atom in the **1b** dimer is in short contact with C at the 4' position of the partner molecule. The overlap between two naphthyl planes seems larger for the **1b** dimer relative to the **1a** dimer. The driving force of the dimer formation must be the energy lowering effect by the  $\pi$ -stacking of the naphthyl groups. The  $\pi(\text{C}) \cdots \sigma^*(\text{Se}-\text{C}_{\text{sp}})$  3c-4e interaction must

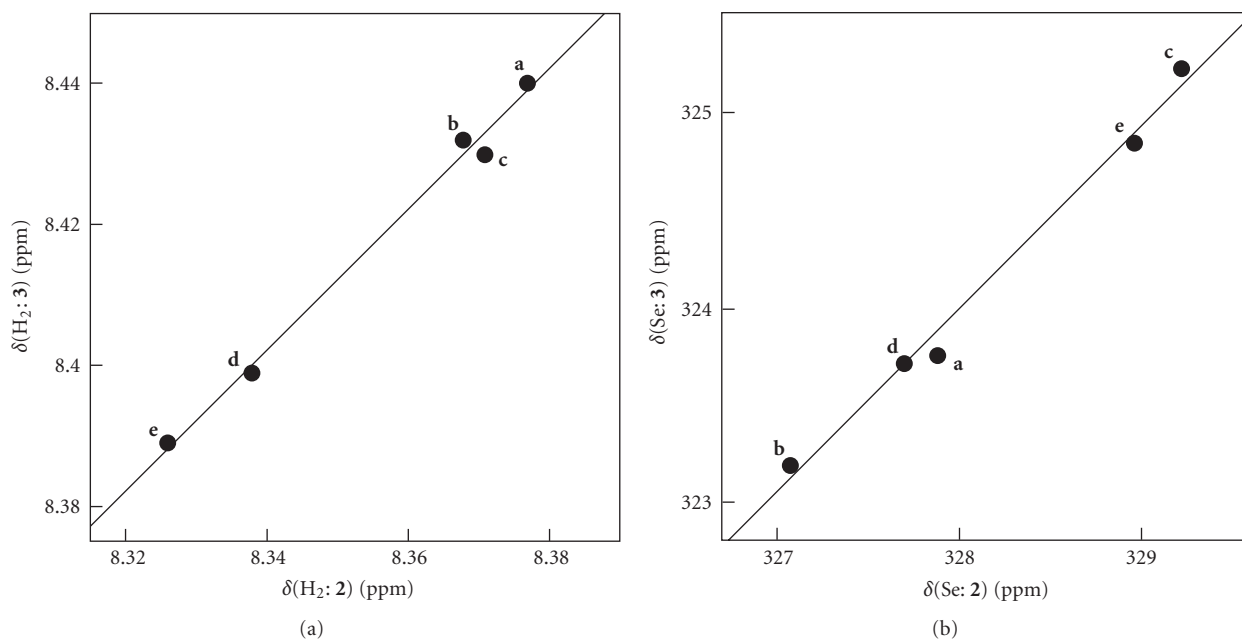


FIGURE 3: Plots of  $\delta(\text{H}_2: 3)$  versus  $\delta(\text{H}_2: 2)$  (a) and  $\delta(\text{Se}: 3)$  versus  $\delta(\text{Se}: 2)$  (b).

also contribute to stabilize the dimers. The dimer formation must stabilize the **A** structure for **1a–c**. It would be difficult to conclude whether the structures are **A** or **B** without such dimer formation. However, the **A** structure of **1a–c** would be suggested without the aid of the dimer formation by considering the electron affinity of naphthalene (NapH) and the evaluated values for *p*- $\text{YC}_6\text{H}_4\text{CCH}$  ( $\text{Y} = \text{H}$ , OMe, and Me), which are the components of **1**.

After the establishment of the structures of **1** and **2** in crystals, next extension is to examine the structures of **1–3** in solutions.

**3.3. Behavior of 1–3 in Solutions Based on NMR Spectroscopy.** 9-(Arylselanyl)anthracenes [9-(*p*- $\text{YC}_6\text{H}_4\text{Se}$ ) $\text{C}_{14}\text{H}_9$ : **7**] and 1-(arylselanyl)anthraquinones [9-(*p*- $\text{YC}_6\text{H}_4\text{Se}$ ) $\text{C}_{14}\text{H}_7\text{O}_2$ : **8**] with all Y shown in Scheme 2 are demonstrated to serve as the standards for the structures of (**A**: **pl**) and (**B**: **pd**) in solutions, respectively [73, 74]. Scheme 3 illustrates the structures of **7** (**A**: **pl**) and **8** (**B**: **pd**). Consequently,  $^1\text{H}$  and  $^{77}\text{Se}$  NMR chemical shifts of **1–3** are also served as the standards to determine the (**A**: **pl**) and (**B**: **pd**) structures in solutions. The structures and the behaviors of **1–3** are investigated in solutions based on the NMR chemical shifts of **1–3** by comparing those of **7** (**A**: **pl**) and **8** (**B**: **pd**).

$^1\text{H}$  and  $^{77}\text{Se}$  NMR chemical shifts of **1–3** were measured in chloroform-*d* solutions (0.050 M) at 297 K<sup>2</sup>. Table 2 collects the substituent induced  $\delta\delta(\text{H}_2)$ ,  $\delta(\text{H}_8)$ , and  $\delta(\text{Se})$  values for **1–3**. Table 2 also collects the values for **7** (**A**: **pl**) and **8** (**B**: **pd**). The values of **1–3** change depending on Y, although the magnitudes are not so large. How are the changes in the chemical shifts depending on Y correlated to the structural changes in solutions? The changes in **1–3** are examined by comparing those in **7** (**A**: **pl**) and **8** (**B**: **pd**).

To organize the process for the analysis,  $\delta(\text{H}_2: 3)$  and  $\delta(\text{Se}: 3)$  are plotted versus  $\delta(\text{H}_2: 2)$  and  $\delta(\text{Se}: 2)$ , respectively. Figure 2 shows the plots. The correlations are given in Table 3 (entries 1 and 2, resp.). The correlations are very good ( $r \geq 0.995$ ). The results show that the structure of each member in **3** is very close to that of **2**, in solutions. Therefore, the structures of **2** should be analyzed from the viewpoint of the orientational effect, together with those of **1**. The anisotropic effect of the  $\text{C} \equiv \text{C}$  bond in **3** ( $\text{G} = \text{Br}$ ) might be stronger than that in **2** ( $\text{G} = \text{Cl}$ ), since  $\delta(\text{H}_2)$  values of **3** (8.39–8.44) are observed slightly more downfield than those of **2** (8.30–8.38).

As shown in Table 2, the  $\delta(\text{H}_2)$  values of **7** (**A**: **pl**) and **8** (**B**: **pd**) appear at 8.67–8.93 and 7.18–7.26, respectively, which should be the anisotropic effect of the phenyl group: the  $\text{H}_2$  atom in **7** (**A**: **pl**) exists on the in-plane area of the phenyl group, whereas it resides upside of the group in **8** (**B**: **pd**). On the other hand,  $\delta(\text{H}_2)$  of **1** appear at 7.78–7.86, whereas those of **2** are 8.30–8.38. We must be careful when the structures of **1–3** are considered based on  $\delta(\text{H}_2)$ , since H atoms above the  $\text{C} \equiv \text{C}$  bond is more deshielded which is just the inverse anisotropic effect by the phenyl group. The magnitudes of the former must be smaller than of the latter. Namely, the structures of **2** and **3** are expected to be **B** in solutions, although the slight equilibrium between **A** and **B** could not be neglected. The structures of **1** would be **A** in solutions, although **A** may equilibrate with **B** to some extent. Figure 4 shows the plots of  $\delta(\text{H}_2: 1)$  and  $\delta(\text{H}_2: 2)$  versus  $\delta(\text{H}_1: 7)$  and  $\delta(\text{H}_2: 8)$ . The plots appear from downfield to upfield in an order of  $\delta(\text{H}_2: 1) \ll \delta(\text{H}_2: 2)$ . The correlations are given in Table 3 (entries 3–6), which support above discussion.

$\delta(\text{H}_8: 1)$  and  $\delta(\text{Se}: 1)$  are plotted versus  $\delta(\text{H}_1: 7)$  and  $\delta(\text{Se}: 7)$ , respectively. Figure 5 shows the results. The

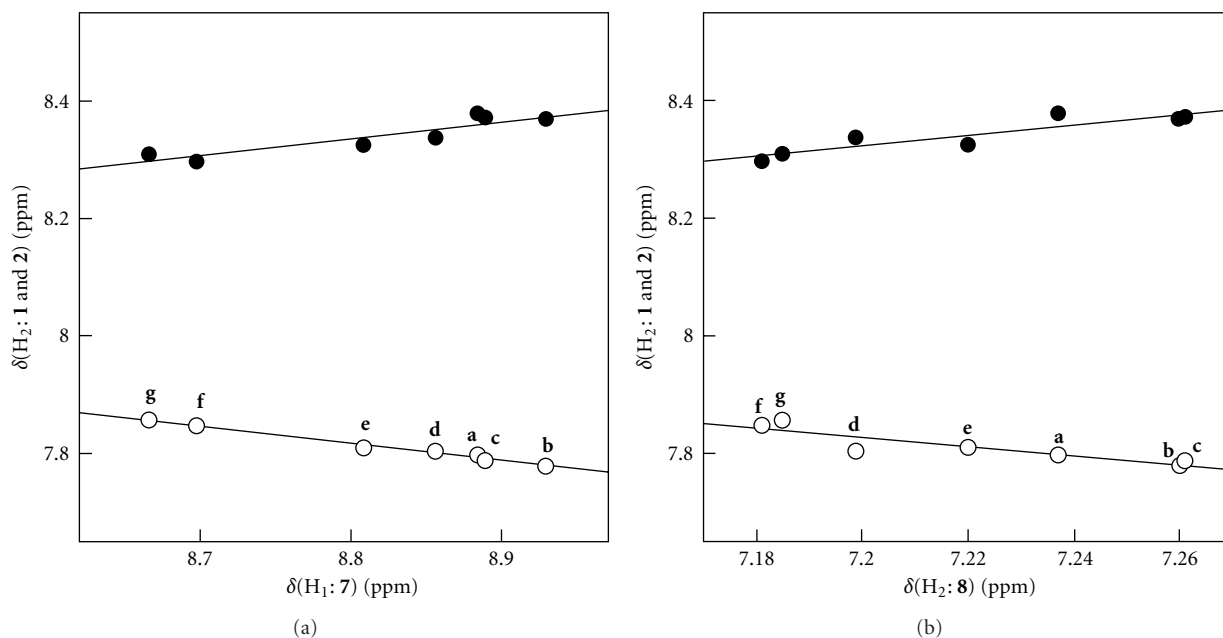


FIGURE 4: Plots of  $\delta(\text{H}_2: \mathbf{1}$  and  $\mathbf{2})$  versus  $\delta(\text{H}_1: \mathbf{7})$  (a) and  $\delta(\text{H}_2: \mathbf{8})$  (b):  $\circ$  for  $\mathbf{1}$  and  $\bullet$  for  $\mathbf{2}$ .

TABLE 2:  $^1\text{H}$  and  $^{77}\text{Se}$  NMR chemical shifts in  $\mathbf{1}$ – $\mathbf{3}$ , together with those in  $\mathbf{7}$  and  $\mathbf{8}^{(a,b)}$ .

Y	OMe	Me	H	F	Cl	CN	$\text{NO}_2$
	<b>b</b>	<b>c</b>	<b>a</b>	<b>d</b>	<b>e</b>	<b>f</b>	<b>g</b>
<b>1</b>							
$\delta(\text{H}_2)$	7.779	7.787	7.798	7.803	7.809	7.845	7.857
$\delta(\text{H}_8)$	8.010	8.019	8.033	8.038	8.045	8.087	8.102
$\delta(\text{Se})$	240.9	241.4	241.4	240.5	241.3	243.9	244.9
<b>2</b>							
$\delta(\text{H}_2)$	8.368	8.371	8.377	8.338	8.326	8.298	8.309
$\delta(\text{Se})$	327.1	329.2	327.9	327.7	329.0	332.7	334.2
<b>3</b>							
$\delta(\text{H}_2)$	8.432	8.430	8.440	8.399	8.389		
$\delta(\text{Se})$	323.1	325.2	323.7	323.7	324.8		
<b>7</b>							
$\delta(\text{H}_1)$	8.929	8.889	8.884	8.856	8.809	8.698	8.666
$\delta(\text{Se})$	236.8	242.4	249.0	245.4	247.5	275.2	279.3
<b>8</b>							
$\delta(\text{H}_2)$	7.260	7.261	7.237	7.199	7.220	7.181	7.185
$\delta(\text{H}_8)$	8.374	8.365	8.352	8.357	8.363	8.363	8.370
$\delta(\text{Se})$	497.3	503.4	512.3	502.2	505.3	504.1	509.8

<sup>(a)</sup> In  $\text{CDCl}_3$ . <sup>(b)</sup> From TMS for  $\delta(\text{H})$  and from  $\text{Me}_2\text{Se}$  for  $\delta(\text{Se})$ .

correlations are shown in Table 3 (entries 7 and 8, resp.). The correlation of the former is good, which means that (**A: pl**) contributes predominantly to the structures of **1**, although the correlation constant is a negative value of  $-0.34$ . The negative value would be the reflection of the inverse anisotropic effect between the phenyl  $\pi$  system and the ethynyl group. It is concluded that the structures of **1** in solutions are substantially (**A: pl**) with some contributions of

(**B: pd**) and/or (**B: pl**) through the equilibrium. The correlation for the plot of  $\delta(\text{Se}: \mathbf{1})$  versus  $\delta(\text{Se}: \mathbf{7})$  also supports the conclusion, although **A** is suggested to equilibrate with **B** in solutions.

Indeed, the preferential contribution of **B** is predicted for **2**, but, the plots of  $\delta(\text{H}_2: \mathbf{2})$  versus  $\delta(\text{H}_2: \mathbf{8})$  do not give good correlations (Panel (b) of Figure 4 and entry 6 in Table 3). Although not shown, the plot of  $\delta(\text{Se}: \mathbf{2})$  versus

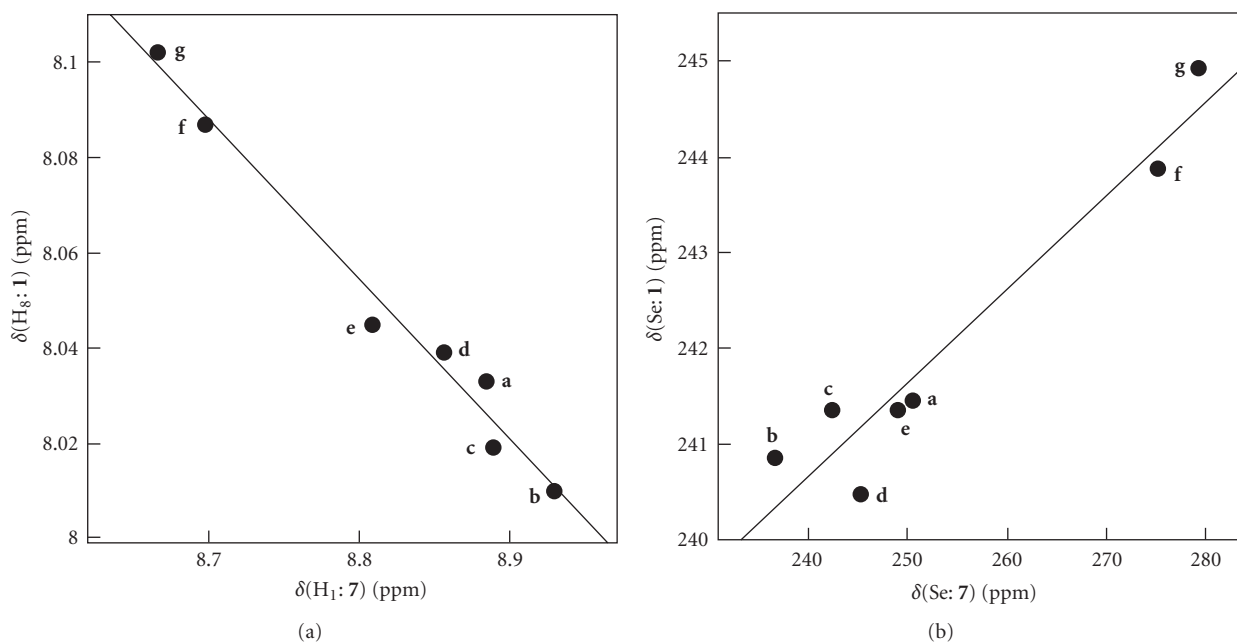
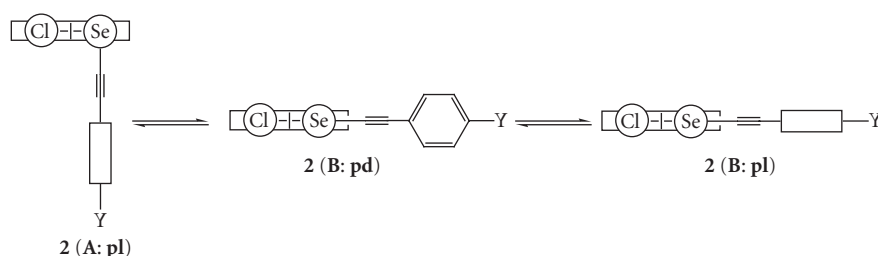


FIGURE 5: Plots of  $\delta(\text{H}_8: 1)$  versus  $\delta(\text{H}_1: 7)$  (a) and  $\delta(\text{Se}: 1)$  versus  $\delta(\text{Se}: 7)$  (b).



SCHEME 5: Equilibrium in **2**: **2 (B: pd)** is expected to be the substantial structure in solutions.

$\delta(\text{Se}: 8)$  did not give good correlation either (entry 10 in Table 3). The plots of  $\delta(\text{Se}: 2)$  versus  $\delta(\text{Se}: 7)$  gave rather good correlation (entry 9 in Table 3). The discrepancy must come mainly from the equilibrium between (**B: pd**) and (**B: pl**). Namely, the structures of **2** are predominantly **B**, which are in equilibrium between (**B: pd**) and (**B: pl**) especially for Y of strong electron accepted groups (Scheme 5). The equilibrium with **A** would exist but the contribution must be small for most of Y.

The **B** structures of **2** and **3** in solutions are determined based on the large downfield shifts of  $\delta(\text{H}_2: 2)$  and  $\delta(\text{H}_2: 3)$  versus  $\delta(\text{H}_2: 1)$ . The reason for the structural determination in solutions will be discussed, next.

**3.4. Selective  $^1\text{H}$ ,  $^{13}\text{C}$ -NOE Difference Spectroscopy for **1e** and **2e** in Solutions.** **1e** (G = H, Y = Cl) and **2e** (G = Y = Cl) were employed for the selective  $^1\text{H}$ ,  $^{13}\text{C}$ -NOE difference spectroscopy.  $^{13}\text{C}$  NMR spectra were measured for **1e** and **2e** under the completely  $^1\text{H}$  decoupling mode, the off-resonance decoupling mode, and the selective  $^1\text{H}$ ,  $^{13}\text{C}$ -NOE difference mode at the  $\delta(\text{H}_2)$  frequency: The atom

numbers are shown in Scheme 2. Figure 6 shows the  $^{13}\text{C}$  NMR spectra for **2e**. Panels (a)–(c) of Figure 6 correspond to the selective  $^1\text{H}$ ,  $^{13}\text{C}$ -NOE difference spectroscopy, off-resonance decoupling spectroscopy, and completely decoupling spectroscopy, respectively. As shown in Panel (a) of Figure 6, the selective irradiation at the  $\delta(\text{H}_2)$  frequency of **2e** enhances exclusively the  $^{13}\text{C}$  NMR signals of  $\text{C}_2$  and  $\text{C}_9$  of **2e**, relative to others. On the other hand, only  $^{13}\text{C}$  NMR signal of  $\text{C}_2$  of **1e** is enhanced relative to others, when the  $\delta(\text{H}_2)$  frequency of **1e** is selectively irradiated, although not shown. The results must be the reflection of the expectation that  $\text{H}_2$  is very close to  $\text{C}_9$  in **2e** to arise the nuclear interaction resulting in the NOE enhancement, whereas such interaction does not appear between  $\text{H}_2$  and  $\text{C}_9$  in **1e** due to the long distance between them. Namely, structures of **1e** and **2e** are demonstrated to be **A** and **B**, respectively, in solutions on the basis of the homonuclear NOE difference spectroscopy. The structure of **3e** must also **B** in solutions on the analogy of the case in **2e**. The results strongly support above conclusion derived from the  $\delta(\text{H}_2)$  values of **1–3**.

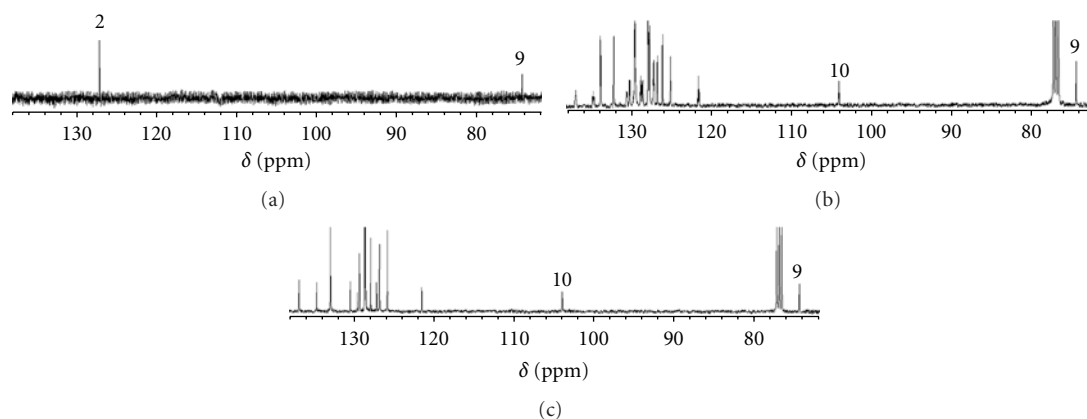


FIGURE 6: (a) Selective  $^1\text{H}$ ,  $^{13}\text{C}$ -NOE difference spectrum, (b) off-resonance decoupling spectrum, and (c) completely  $^1\text{H}$  decoupled spectrum for **2e**.

TABLE 3: Correlations of  $\delta(\text{H})$  and  $\delta(\text{Se})$  in **1–3**, **7**, and **8** in solutions<sup>(a)</sup>.

Entries	Correlation	$a$	$b$	$r^2$	$n(\text{Y})$
1	$\delta(\text{H}_2: \mathbf{3})$ versus $\delta(\text{H}_2: \mathbf{2})$	0.994	0.11	0.996	5 <sup>(c)</sup>
2	$\delta(\text{Se}: \mathbf{3})$ versus $\delta(\text{Se}: \mathbf{2})$	0.939	16.1	0.995	5 <sup>(c)</sup>
3	$\delta(\text{H}_2: \mathbf{1})$ versus $\delta(\text{H}_1: \mathbf{7})$	-0.290	10.37	0.992	7 <sup>(b)</sup>
4	$\delta(\text{H}_2: \mathbf{2})$ versus $\delta(\text{H}_1: \mathbf{7})$	0.289	5.79	0.917	7 <sup>(b)</sup>
5	$\delta(\text{H}_2: \mathbf{1})$ versus $\delta(\text{H}_2: \mathbf{8})$	-0.784	13.47	0.895	7 <sup>(b)</sup>
6	$\delta(\text{H}_2: \mathbf{2})$ versus $\delta(\text{H}_2: \mathbf{8})$	0.856	2.16	0.906	7 <sup>(b)</sup>
7	$\delta(\text{H}_8: \mathbf{1})$ versus $\delta(\text{H}_1: \mathbf{7})$	-0.337	11.02	0.990	7 <sup>(b)</sup>
8	$\delta(\text{Se}: \mathbf{1})$ versus $\delta(\text{Se}: \mathbf{7})$	0.098	217.2	0.961	7 <sup>(b)</sup>
9	$\delta(\text{Se}: \mathbf{2})$ versus $\delta(\text{Se}: \mathbf{7})$	0.157	289.8	0.957	7 <sup>(b)</sup>
10	$\delta(\text{Se}: \mathbf{2})$ versus $\delta(\text{Se}: \mathbf{8})$	0.261	197.0	0.786	7 <sup>(b)</sup>

<sup>(a)</sup> The constants ( $a$ ,  $b$ ,  $r$ ) are defined by  $y = ax + b$  ( $r$ : correlation coefficient). <sup>(b)</sup> Y = OMe, Me, H, F, Cl, CN, and NO<sub>2</sub>. <sup>(c)</sup> Y = OMe, Me, H, F, and Cl.

## 4. Conclusions

The behavior of ethynylchalcogenyl groups is examined as the factor to control fine structures. Fine structures of 8-G-1-(*p*-YC<sub>6</sub>H<sub>4</sub>C $\equiv$ CSe)C<sub>10</sub>H<sub>6</sub> [**1** (G = H) and **2** (G = Cl): Y = H (**a**), OMe (**b**), Me (**c**), F (**d**), Cl (**e**), CN (**f**), and NO<sub>2</sub> (**g**)] are determined by the X-ray crystallographic analysis. Structures are (**A**: **pd**) or (**A**: **np**) for **1a–c** bearing Y of nonacceptors, it is (**B**: **pd**) for **1e** with Y = Cl, and they are (**B**: **pl**) for **1f** and **1g** having Y of strong acceptors of CN and NO<sub>2</sub>. The Y-dependence observed in **1** is just the opposite to the case of 1-(*p*-YC<sub>6</sub>H<sub>4</sub>Se)C<sub>10</sub>H<sub>7</sub> (**4**). The factor to control the fine structures of **1** is called “*Ethynyl Influence*.” The structures are determined by the X-ray crystallographic analysis for **2b**, **2e**, and **2g**. The structures are all **B** around the Se–C<sub>Nap</sub> bonds, in our definition. The structures around the Se–C<sub>Ar</sub> bonds are **pd** for **2b** and **2e** and **pl** for **2g**. The **1b** (**A**: **pd**) structure with Y = OMe changes dramatically to **2b** (**B**: **pd**) by G = Cl at the 8-position in **2**. The effect is called G-dependence. The G-dependence must arise from the energy lowering effect of the  $n_p(\text{Cl}) \cdots \sigma^*(\text{Se}-\text{C}_{\text{sp}}) 3c-4e$  interaction. The

$n_p(\text{Cl})-\pi(\text{Nap})-n_p(\text{Se})-\pi(\text{C}\equiv\text{C})$  interaction may also contribute to stabilize the structure. The structures of **1**, **2**, and **3** (G = Br) are also examined in solutions based on the NMR parameters for (**A**: **pl**) of 9-(arylselanyl)anthracenes (**7**) and (**B**: **pd**) of 1-(arylselanyl)anthraquinones (**8**). The results show that **2** and **3** behave very similarly in solutions, and the structures of **2** and **3** are predominantly **B** in solutions with some equilibrium between **pd** and **pl** for the aryl groups. The selective  $^1\text{H}$ ,  $^{13}\text{C}$ -NOE difference spectroscopic measurements strongly support that the structures are **A** for **1** and **B** for **2** and **3** in solutions derived from the  $\delta(\text{H}_2)$  values of **1–3**.

## Acknowledgments

This work was partially supported by a Grant-in-Aid for Scientific Research (nos. 16550038, 19550041, and 20550042) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. The authors are grateful to Professor Norihiro Tokitoh and Dr. Takahiro Sasamori, Institute for Chemical Research, Kyoto University, for the X-ray analysis.



## References

- [1] W. Nakanishi, "Hypervalent chalcogen compounds," in *Handbook of Chalcogen Chemistry: New Perspectives in Sulfur, Selenium and Tellurium*, F. A. Devillanova, Ed., chapter 10.3, Royal Society of Chemistry, London, UK, 2006.
- [2] W. Nakanishi, S. Hayashi, and S. Toyota, "Structure of bis(8-(phenylselanyl)naphthyl)diselenide: first linear alignment of four Se atoms as a four-centre six-electron bond," *Chemical Communications*, no. 3, pp. 371–372, 1996.
- [3] W. Nakanishi, S. Hayashi, and H. Yamaguchi, *Chemistry Letters*, no. 25, pp. 947–948, 1996.
- [4] W. Nakanishi, S. Hayashi, and S. Toyota, "Four-center six-electron interaction versus lone pair-lone pair interaction between selenium atoms in naphthalene peri positions," *Journal of Organic Chemistry*, vol. 63, no. 24, pp. 8790–8800, 1998.
- [5] S. Hayashi and W. Nakanishi, "Novel substituent effect on  $^{77}\text{Se}$  NMR chemical shifts caused by 4c–6e versus 2c–4e and 3c–4e in naphthalene peri positions: spectroscopic and theoretical study," *Journal of Organic Chemistry*, vol. 64, no. 18, pp. 6688–6696, 1999.
- [6] W. Nakanishi, S. Hayashi, and T. Arai, "Linear alignment of four sulfur atoms in bis[(8-phenylthio)naphthyl] disulfide: contribution of linear  $\text{S}_4$  hypervalent four-centre six-electron bond to the structure," *Chemical Communications*, no. 20, pp. 2416–2417, 2002.
- [7] W. Nakanishi, S. Hayashi, and N. Itoh, "First linear alignment of five C–Se···O···Se–C atoms in anthraquinone and 9-(methoxy)anthracene bearing phenylselanyl groups at 1,8-positions," *Chemical Communications*, vol. 9, no. 1, pp. 124–125, 2003.
- [8] W. Nakanishi, S. Hayashi, and N. Itoh, "Extend hypervalent 5c–6e interactions: linear alignment of five C–Se···O···Se–C atoms in anthraquinone and 9-methoxyanthracene bearing arylselanyl groups at the 1,8-positions," *Journal of Organic Chemistry*, vol. 69, no. 5, pp. 1676–1684, 2004.
- [9] W. Nakanishi, S. Hayashi, T. Furuta, et al., "Extended hypervalent 5c–6e interactions: linear alignment of five C—Z···O···Z—C (Z = S, Se) atoms in anthraquinone and anthracene systems," *Phosphorus, Sulfur and Silicon and the Related Elements*, vol. 180, no. 5–6, pp. 1351–1355, 2005.
- [10] W. Nakanishi, T. Nakamoto, S. Hayashi, T. Sasamori, and N. Tokitoh, "Atoms-in-molecules analysis of extended hypervalent five-center, six-electron (5c–6e)  $\text{C}_2\text{Z}_2\text{O}$  interactions at the 1,8,9-positions of anthraquinone and 9-methoxyanthracene systems," *Chemistry*, vol. 13, no. 1, pp. 255–268, 2007.
- [11] W. Nakanishi, S. Hayashi, S. Yamaguchi, and K. Tamao, "First  $\text{Br}_4$  four centre-six electron and  $\text{Se}_2\text{Br}_5$  seven centre-ten electron bonds in nonionic bromine adducts of selenanthrene," *Chemical Communications*, vol. 10, no. 2, pp. 140–141, 2004.
- [12] G. C. Pimentel, "The bonding of trihalide and bifluoride ions by the molecular orbital method," *The Journal of Chemical Physics*, vol. 19, no. 4, pp. 446–448, 1951.
- [13] J. I. Musher, "The chemistry of hypervalent molecules," *Angewandte Chemie International Edition in English*, vol. 8, no. 1, pp. 54–68, 1969.
- [14] K.-Y. Akiba, Ed., *Chemistry of Hypervalent Compounds*, Wiley-VCH, New York, NY, USA, 1999.
- [15] W. Nakanishi, S. Hayashi, and T. Uehara, "Successive change in conformation caused by  $p$ -Y groups in 1-(MeSe)-8-( $p$ - $\text{YC}_6\text{H}_4\text{Se}$ ) $\text{C}_{10}\text{H}_6$ : role of linear  $\text{Se}\cdots\text{Se}-\text{C}$  three-center-four-electron versus  $n(\text{Se})\cdots n(\text{Se})$  two-center-four-electron nonbonded interactions," *Journal of Physical Chemistry A*, vol. 103, no. 48, pp. 9906–9912, 1999.
- [16] W. Nakanishi and S. Hayashi, "Structure of 1-(arylselanyl)naphthalenes. 2. G dependence in 8-G-1-( $p$ - $\text{YC}_6\text{H}_4\text{Se}$ ) $\text{C}_{10}\text{H}_6$ ," *Journal of Organic Chemistry*, vol. 67, no. 1, pp. 38–48, 2002.
- [17] R. A. Hayes and J. C. Martin, "Sulfurane chemistry," in *Organic Sulfur Chemistry: Theoretical and Experimental Advances*, F. Bernardi, I. G. Csizmadia, and A. Mangini, Eds., Elsevier, Amsterdam, The Netherlands, 1985.
- [18] W. Nakanishi, S. Hayashi, A. Sakae, G. Ono, and Y. Kawada, "Attractive interaction caused by the linear  $\text{F}\cdots\text{Se}-\text{C}$  alignment in naphthalene peri positions," *Journal of the American Chemical Society*, vol. 120, no. 15, pp. 3635–3640, 1998.
- [19] S. Scheiner, Ed., *Molecular Interactions. From van der Waals to Strongly Bound Complexes*, John Wiley & Sons, New York, NY, USA, 1997.
- [20] K.-D. Asmus, "Stabilization of oxidized sulfur centers in organic sulfides. Radical cations and odd-electron sulfur-sulfur bonds," *Accounts of Chemical Research*, vol. 12, no. 12, pp. 436–442, 1979.
- [21] W. K. Musker, "Chemistry of aliphatic thioether cation radicals and dications," *Accounts of Chemical Research*, vol. 13, no. 7, pp. 200–206, 1980.
- [22] W. Nakanishi, S. Hayashi, and T. Uehara, "Structure of 1-(arylselanyl)naphthalenes—Y dependence in 1-( $p$ - $\text{YC}_6\text{H}_4\text{Se}$ ) $\text{C}_{10}\text{H}_7$ ," *European Journal of Organic Chemistry*, no. 20, pp. 3933–3943, 2001.
- [23] S. Hayashi, H. Wada, T. Ueno, and W. Nakanishi, "Structures of 1-(arylseleninyl)naphthalenes: O, G, and Y dependences in 8-G-1-[ $p$ - $\text{YC}_6\text{H}_4\text{Se}(\text{O})$ ] $\text{C}_{10}\text{H}_6$ ," *Journal of Organic Chemistry*, vol. 71, no. 15, pp. 5574–5585, 2006.
- [24] A. Kucsman and I. Kapovits, "Nonbonded sulfur-oxygen interaction," in *Organic Sulfur Chemistry: Theoretical and Experimental Advances*, F. Bernardi, I. G. Csizmadia, and A. Mangini, Eds., Elsevier, Amsterdam, The Netherlands, 1985.
- [25] R. S. Glass, S. W. Andruski, and J. L. Broeker, "Geometric effects in sulfur lone pair interactions," in *Reviews on Heteroatom Chemistry*, S. Oae, Ed., vol. 1, pp. 31–45, MYU, Tokyo, Japan, 1988.
- [26] R. S. Glass, S. W. Andruski, J. L. Broeker, H. Firouzabadi, L. K. Steffen, and G. S. Wilson, "Sulfur-sulfur lone pair and sulfur-naphthalene interactions in naphtho[1,8- $b,c$ ]-1,5-dithiocin," *Journal of the American Chemical Society*, vol. 111, no. 11, pp. 4036–4045, 1989.
- [27] R. S. Glass, L. Adamowicz, and J. L. Broeker, "Theoretical studies on transannular  $\text{S}\cdots\text{S}$  interactions in geometrically constrained 1,5-dithiocane derivatives," *Journal of the American Chemical Society*, vol. 113, no. 4, pp. 1065–1072, 1991.
- [28] N. Furukawa, "Studies on dichalcogena dications of 2-center-2-electron and 3-center-4-electron bonds: isolation and intermediary formation," *Bulletin of the Chemical Society of Japan*, vol. 70, no. 11, pp. 2571–2591, 1997.
- [29] N. Furukawa, K. Kobayashi, and S. Sato, "Transannular and intermolecular interactions between chalcogen atoms: syntheses and properties of dichalcogena dications and trichalcogena hypervalent dications," *Journal of Organometallic Chemistry*, vol. 611, no. 1–2, pp. 116–126, 2000.
- [30] W. Nakanishi, "Facile C–Se and C–S bond cleavages in diorganyl selenides and sulfides by iodine," *Chemistry Letters*, vol. 22, no. 12, pp. 2121–2122, 1993.
- [31] M. Iwaoka, S. Takemoto, M. Okada, and S. Tomoda, "Statistical characterization of nonbonded  $\text{S}\cdots\text{O}$  interactions in proteins," *Chemistry Letters*, vol. 30, no. 2, pp. 132–133, 2001.

- [32] M. Iwaoka, S. Takemoto, M. Okada, and S. Tomoda, "Weak nonbonded S...X (X = O, N, and S) interactions in proteins. statistical and theoretical studies," *Bulletin of the Chemical Society of Japa*, vol. 75, no. 7, pp. 1611–1625, 2002.
- [33] G. R. Desiraju, "Supramolecular synthons in crystal engineering—a new organic synthesis," *Angewandte Chemie International Edition in English*, vol. 34, no. 21, pp. 2311–2327, 1995.
- [34] V. Lippolis and F. Isaia, "Charge-transfer (C.-T.) adducts and related compound," in *Handbook of Chalcogen Chemistry: New Perspectives in Sulfur, Selenium and Tellurium*, F. A. Devillanova, Ed., chapter 8.2, Royal Society of Chemistry, London, UK, 2006.
- [35] C. Rêthorê, M. Fourmiguê, and N. Avarvari, "Tetrathiafulvalene based phosphino-oxazolines: a new family of redox active chiral ligands," *Chemical Communications*, vol. 10, no. 12, pp. 1384–1385, 2004.
- [36] C. Rêthorê, M. Fourmiguê, and N. Avarvari, "Tetrathiafulvalene-hydroxyamides and -oxazolines: hydrogen bonding, chirality, and a radical cation salt," *Tetrahedron*, vol. 61, no. 46, pp. 10935–10942, 2005.
- [37] C. Rêthorê, N. Avarvari, E. Canadell, P. Auban-Senzier, and M. Fourmiguê, "Chiral molecular metals: syntheses, structures, and properties of the  $ASF_6^-$  salts of racemic ( $\pm$ )-, (R)-, and (S)-tetrathiafulvalene-oxazoline derivatives," *Journal of the American Chemical Society*, vol. 127, no. 16, pp. 5748–5749, 2005.
- [38] T. Suzuki, H. Fujii, Y. Yamashita, et al., "Clathrate formation and molecular recognition by novel chalcogen-cyano interactions in tetracyanoquinodimethanes fused with thiazazole and selenadiazole rings," *Journal of the American Chemical Society*, vol. 114, no. 8, pp. 3034–3043, 1992.
- [39] M. Turbiez, P. Frère, M. Allain, C. Vidélot, J. Ackermann, and J. Roncali, "Design of organic semiconductors: tuning the electronic properties of  $\pi$ -conjugated oligothiophenes with the 3,4-ethylenedioxythiophene (EDOT) building block," *Chemistry: A European Journal*, vol. 11, no. 12, pp. 3742–3752, 2005.
- [40] A. F. Cozzolino, I. Vargas-Baca, S. Mansour, and A. H. Mahmoudkhani, "The nature of the supramolecular association of 1,2,5-chalcogenadiazoles," *Journal of the American Chemical Society*, vol. 127, no. 9, pp. 3184–3190, 2005.
- [41] G. Muges, A. Panda, H. B. Singh, N. S. Punekar, and R. J. Butcher, "Diferrocenyl diselenides: excellent thiol peroxidase-like antioxidants," *Chemical Communications*, no. 20, pp. 2227–2228, 1998.
- [42] G. Muges, A. Panda, H. B. Singh, N. S. Punekar, and R. J. Butcher, "Glutathione peroxidase-like antioxidant activity of diaryl diselenides: a mechanistic study," *Journal of the American Chemical Society*, vol. 123, no. 5, pp. 839–850, 2001.
- [43] J. E. Drake, M. B. Hursthouse, M. Kulcsar, M. E. Light, and A. Silvestru, "Hypervalent tellurium compounds containing Te-N interactions. Mononuclear and polynuclear derivatives," *Phosphorus, Sulfur and Silicon and Related Elements*, vol. 168–169, no. 1, pp. 293–296, 2001.
- [44] J. E. Drake, M. B. Hursthouse, M. Kulcsar, M. E. Light, and A. Silvestru, "Hypervalent tellurium compounds containing N  $\rightarrow$  Te intramolecular interactions," *Journal of Organometallic Chemistry*, vol. 623, no. 1–2, pp. 153–160, 2001.
- [45] G. Muges, A. Panda, S. Kumar, S. D. Apte, H. B. Singh, and R. J. Butcher, "Intramolecularly coordinated diorganyl ditellurides: thiol peroxidase-like antioxidants," *Organometallics*, vol. 21, no. 5, pp. 884–892, 2002.
- [46] J. R. Anaconda, J. Gómez, and D. Loroño, "Two polymorphs of bis(2-bromophenyl) disulfide," *Acta Crystallographica Section C*, vol. 59, no. 5, pp. o277–o280, 2003.
- [47] G. Muges, H. B. Singh, and R. J. Butcher, "Synthesis and structural characterization of monomeric zinc(II), cadmium(II), and mercury(II) arenethiolates with a chelating oxazoline ligand," *European Journal of Inorganic Chemistry*, no. 8, pp. 1229–1236, 1999.
- [48] G. Muges, H. B. Singh, and R. J. Butcher, "Synthesis and characterization of monomeric telluroato complexes of zinc and cadmium: crystal and molecular structure of bis[2-(4,4-dimethyl-2-oxazoliny)phenyl]ditelluride," *Journal of Organometallic Chemistry*, vol. 577, no. 2, pp. 243–248, 1999.
- [49] D. Shimizu, N. Takeda, and N. Tokitoh, "Unusual carbon-sulfur bond cleavage in the reaction of a new type of bulky hexathioether with a zerovalent palladium complex," *Chemical Communications*, no. 2, pp. 177–179, 2006.
- [50] W. Nakanishi, S. Hayashi, S. Morinaka, T. Sasamori, and N. Tokitoh, "Extended hypervalent E'...E-E...E' 4c-6e (E, E' = Se, S) interactions: structure, stability and reactivity of 1-(8-PhE'C<sub>10</sub>H<sub>6</sub>)EE(C<sub>10</sub>H<sub>6</sub>E'Ph-8')-1'," *New Journal of Chemistry*, vol. 32, no. 11, pp. 1881–1889, 2008.
- [51] P. J. Stang and F. Diederich, Eds., *Modern Acetylenic Chemistry*, Wiley-VCH, Weinheim, Germany, 1995.
- [52] F. Diederich, P. J. Stang, and R. R. Tykwinski, Eds., *Acetylene Chemistry: Chemistry, Biology, and Material Science*, Wiley-VCH, Weinheim, Germany, 2005.
- [53] A. J. Zuccherro, J. N. Wilson, and U. H. F. Bunz, "Cruciforms as functional fluorophores: response to protons and selected metal ions," *Journal of the American Chemical Society*, vol. 128, no. 36, pp. 11872–11881, 2006.
- [54] E. L. Spitler, L. D. Shirtcliff, and M. M. Haley, "Systematic structure-property investigations and ion-sensing studies of pyridine-derivatized donor/acceptor tetrakis(arylethynyl)benzenes," *Journal of Organic Chemistry*, vol. 72, no. 1, pp. 86–96, 2007.
- [55] H. Hinrichs, A. J. Boydston, P. G. Jones, K. Hess, R. Herges, M. M. Haley, and H. Hopf, "Phane properties of [2.2]paracyclophane/dehydrobenzoannulene hybrids," *Chemistry: A European Journal*, vol. 12, no. 27, pp. 7103–7115, 2006.
- [56] J. A. Marsden and M. M. Haley, "Carbon networks based on dehydrobenzoannulenes. 5. Extension of two-dimensional conjugation in graphdiyne nanoarchitectures," *Journal of Organic Chemistry*, vol. 70, no. 25, pp. 10213–10226, 2005.
- [57] Y. Jiang, D. Perahia, Y. Wang, and U. H. F. Bunz, "Side chain vs main chain. Who dominates? A polyester-grafted poly(*p*-phenyleneethynylene) with two different morphologies," *Macromolecules*, vol. 39, no. 15, pp. 4941–4944, 2006.
- [58] K. Tahara, S. Furukawa, H. Uji-i, et al., "Two-dimensional porous molecular networks of dehydrobenzo[12]annulene derivatives via alkyl chain interdigitation," *Journal of the American Chemical Society*, vol. 128, no. 51, pp. 16613–16625, 2006.
- [59] A. Nomoto, M. Sonoda, Y. Yamaguchi, T. Ichikawa, K. Hirose, and Y. Tobe, "A clue to elusive macrocycles: unusually facile, spontaneous polymerization of a hexagonal diethynylbenzene macrocycle," *Journal of Organic Chemistry*, vol. 71, no. 1, pp. 401–404, 2006.
- [60] E. E. Nesterov, Z. Zhu, and T. M. Swager, "Conjugation enhancement of intramolecular exciton migration in poly(*p*-phenylene ethynylene)s," *Journal of the American Chemical Society*, vol. 127, no. 28, pp. 10083–10088, 2005.

- [61] A. Orita, T. Nakano, D. L. An, K. Tanikawa, K. Wakamatsu, and J. Otera, "Metal-assisted assembly of pyridine-containing arylene ethynylene strands to enantiopure double helicates," *Journal of the American Chemical Society*, vol. 126, no. 33, pp. 10389–10396, 2004.
- [62] A. Orita, D. L. An, T. Nakano, J. Yaruva, N. Ma, and J. Otera, "Sulfoximine version of double elimination protocol for synthesis of chiral acetylenic cyclophanes," *Chemistry: A European Journal*, vol. 8, no. 9, pp. 2005–2010, 2002.
- [63] D. B. Werz and R. Gleiter, "Polyalkynes capped by sulfur and selenium," *Journal of Organic Chemistry*, vol. 68, no. 24, pp. 9400–9405, 2003.
- [64] S. Husebye, E. A. Meyers, R. A. Zingaro, A. L. Braga, J. V. Comasseto, and N. Petragnani, "The structure of triphenyl[ $\alpha$ -(phenylseleno)phenacylidene]phosphorane," *Acta Crystallographica Section C*, vol. 42, no. 12, pp. 90–94, 1986.
- [65] P. C. Bell, W. Skranc, X. Formosa, J. O'Leary, and J. D. Wallis, "Interactions between alkynes and methoxy or dimethylamino groups in peri-naphthalene systems," *Journal of the Chemical Society, Perkin Transactions 2*, no. 5, pp. 878–886, 2002.
- [66] K. Yamane, S. Hayashi, W. Nakanishi, T. Sasamori, and N. Tokitoh, "Fine structures of 1-(arylethynylselanyl)naphthalenes: characteristic features brought by the ethynylselanyl group," *Polyhedron*, vol. 27, no. 11, pp. 2478–2486, 2008.
- [67] K. Yamane, S. Hayashi, W. Nakanishi, T. Sasamori, and N. Tokitoh, "Fine structures of 8-G-1-(arylethynylselanyl)naphthalenes (G = H, Cl, Br): factors to control the linear alignment of five  $G \cdots \text{Se}-\text{C}\equiv\text{C}-\text{C}_{\text{Ar}}$  atoms in crystals and the behavior in solution," *Polyhedron*, vol. 27, no. 18, pp. 3557–3566, 2008.
- [68] W. Nakanishi and S. Hayashi, "On the factors to determine  $^{77}\text{Se}$  NMR chemical shifts of organic selenium compounds: application of GIAO magnetic shielding tensor to the  $^{77}\text{Se}$  NMR spectroscopy," *Chemistry Letters*, no. 6, pp. 523–524, 1998.
- [69] A. Altomare, M. C. Burla, M. Camalli, et al., "SIR97: a new tool for crystal structure determination and refinement," *Journal of Applied Crystallography*, vol. 32, no. 1, pp. 115–119, 1999.
- [70] G. M. Sheldrick, *SHELXS 97, Program for Solving Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.
- [71] M. C. Burla, R. Caliandro, M. Camalli, et al., "SIR2004: an improved tool for crystal structure determination and refinement," *Journal of Applied Crystallography*, vol. 38, no. 2, pp. 381–388, 2005.
- [72] G. M. Sheldrick, *SHELXL 97, Program for Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.
- [73] W. Nakanishi, S. Hayashi, D. Shimizu, and M. Hada, "Orientational effect of aryl groups on  $^{77}\text{Se}$  NMR chemical shifts: experimental and theoretical investigations," *Chemistry: A European Journal*, vol. 12, no. 14, pp. 3829–3846, 2006.
- [74] S. Hayashi, K. Yamane, and W. Nakanishi, "Orientational effect of aryl groups in aryl selenides: how can  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts clarify the effect?" *Journal of Organic Chemistry*, vol. 72, no. 20, pp. 7587–7596, 2007.