Research Article

Fine Structures of 8-G-1-(p-YC₆H₄C≡CSe)C₁₀H₆ (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-YC₆H₄C≡CSe)C₁₀H₆ [1 (G = H) and 2 (G = Cl): Y = H (a), OMe (b), Me (c), F (d), Cl (e), CN (f), and NO₂ (g)] are determined by the X-ray analysis. Structures of 1, 2, and 3 (G = Br) are called A if each Se–Csp 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-YC₆H₄Se)C₁₀H₂ (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.

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 π and π* orbitals play an important role to appear specific properties in 8-G-1-(Ph₃SiC≡C)C₁₀H₆ (G = OMe and NMe₂) [65], but the ethynyl π and π* 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, the ethynyl influence and Y- and G-dependences as the factors to control fine structures of 8-G-1-(p-YC₆H₄C≡CSe)C₁₀H₆ [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 NO₂ (g)] are elucidated (Scheme 2). The Y- and G-dependences are also discussed for 8-G-1-(p-YC₆H₄Se)C₁₀H₆ [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–Csp 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
employed for the structures around the Se–C Nap 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(sp)≡C(sp)–C(sp2) 5c–6e type interaction in 1–6 and those around Se–C(sp) 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 NO₂ [22]. We call the results Y-dependence. The magnitude of the p(Se)–n(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 n₁(G)···σ⁺(Se–C₃p) 3c–4e interaction or the G···Se–C₃p–C₃p–C₃p 5c–6e type interaction in 2 and 3. The behaviors of 1–3 in solutions are also examined, containing the selective ¹H, ¹³C-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 (Fuisyslia PSQ-100B), acidic and basic alumina (E. Merck). 1–3 were prepared by the methods described elsewhere [66, 67].

NMR spectra were recorded at 297 K on a JEOL AL-300 MHz spectrometer (¹H, 300 MHz; ⁷⁷Se, 57 MHz) on a JEOL ECP-400 MHz spectrometer (¹H, 400 MHz; ¹³C, 100 MHz) in chloroform-d solutions (0.050 M). Chemical shifts are given in ppm relative to one of TMS for ¹H NMR spectra and relative to reference compound Me₂Se for ⁷⁷Se 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 F² 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.

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 (1A) such as H (a), OMe (b), and Me (c), whereas that of 1 is B for Y of acceptors (1B) such as Cl (e), CN (f), and NO₂ (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 NO₂. The ethynyl group interrupted between p-YC₆H₄ and Se changes the structures dramatically: (B: pd) of 4b to (A: pl) of 1b, (A: pl) of 4e to (B: pd) of 1e, and (A: pl) of 4 (Y = CO₂Et) to (B: pl) of 1g, where Y = CO₂Et is employed in place of Y = NO₂ 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(a).

| Structure   | 1a_A | 1a_B | 1b  | 1c  | 1e  | 1f  | 1g  |
|-------------|------|------|-----|-----|-----|-----|-----|
| r(Se1, C1) (Å) | 1.9321(19) | 1.9335(19) | 1.93(2) | 1.935(2) | 1.935(2) | 1.9335(19) |
| r(Se1, C11) (Å) | 1.846(18) | 1.847(2) | 1.844(2) | 1.829(3) | 1.825(2) |
| r(Se1, C13) (Å) | 1.9315(15) | 1.9243(18) | 1.9458(18) | 1.946(9) | 98.07(7) |
| r(Se1, C1) (Å)  | 1.936(2) | 1.933(2) | 1.935(2) | 1.9335(19) |
| ∠C1Se1C11 (°) | 99.68(8) | 98.46(9) | 99.07(10) | 98.92(11) |
| ∠C2C1Se1 (°)  | 117.37(14) | 116.77(15) | 117.61(16) | 117.61(17) |
| ∠C10C1Se1 (°) | 121.12(13) | 121.74(14) | 120.89(15) | 120.84(17) |
| ∠C1Se1C13C14 (°) | 60.64(15) | 121.74(14) | 116.86(18) | 116.32(14) |
| Structure     |      |      |      |      |      |      |      |
| (A: pd)       | 2b   | 2e   | 2g   | 2f   | 2g   | 1b   | 1c   |
| r(Se1, C1) (Å) | 1.946(4) | 1.9458(18) | 1.945(2) | 1.945(2) | 1.945(2) | 1.945(2) |
| r(Se1, C11) (Å) | 1.831(5) | 1.8383(19) | 1.8383(19) | 1.829(3) | 1.829(3) | 1.829(3) |
| r(Se1, C13) (Å) | 1.749(4) | 1.7443(18) | 1.744(2) | 1.744(2) | 1.744(2) | 1.744(2) |
| ∠C1Se1C11 (°) | 179.18(15) | 167.2(4) | 170.6(2) | 170.6(2) | 170.6(2) | 170.6(2) |
| ∠C7Se1C12 (°) | 167.2(4) | 173.07(17) | 170.6(2) | 170.6(2) | 170.6(2) | 170.6(2) |
| ∠C2C1Se1 (°)  | 99.7(2) | 98.47(8) | 99.32(10) | 99.32(10) | 99.32(10) | 99.32(10) |
| ∠C1Se1C13C14 (°) | 118.0(3) | 117.64(14) | 117.70(17) | 117.70(17) | 117.70(17) | 117.70(17) |
| Structure     |      |      |      |      |      |      |      |
| (B: pd)       |      |      |      |      |      |      |      |
| r(Se1, C1) (Å) | 2.9495(16) | 2.9458(18) | 2.945(2) | 2.945(2) | 2.945(2) | 2.945(2) |
| r(Se1, C11) (Å) | 1.946(4) | 1.9458(18) | 1.945(2) | 1.945(2) | 1.945(2) | 1.945(2) |
| r(Se1, C13) (Å) | 1.831(5) | 1.8383(19) | 1.8383(19) | 1.829(3) | 1.829(3) | 1.829(3) |
| ∠C1Se1C11 (°) | 179.18(15) | 167.2(4) | 170.6(2) | 170.6(2) | 170.6(2) | 170.6(2) |
| ∠C7Se1C12 (°) | 167.2(4) | 173.07(17) | 170.6(2) | 170.6(2) | 170.6(2) | 170.6(2) |
| ∠C2C1Se1 (°)  | 99.7(2) | 98.47(8) | 99.32(10) | 99.32(10) | 99.32(10) | 99.32(10) |
| ∠C1Se1C13C14 (°) | 118.0(3) | 117.64(14) | 117.70(17) | 117.70(17) | 117.70(17) | 117.70(17) |
| Structure     |      |      |      |      |      |      |      |
| (B: pd)       |      |      |      |      |      |      |      |

(a) The atomic numbering scheme is shown for 1b in Figure 1, as an example. (b) r(Se2, C19). (c) r(Se2, C29). (d) ∠ClSe1C11. (e) ∠ClSe1C12. (f) ∠ClSe1C13. (g) ∠ClSe1C14. (h) ∠ClSe1C13C14. (i) 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 1aA and 1aB: (a) a side view (r(Se1—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 1aA and 1aB. 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 π-stacking of the naphthyl groups. The π(C)···σ*(Se–Csp) 3c–4e interaction must...
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-YC₆H₄CCH (Y = 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-YC₆H₄Se)C₆H₅: 7] and 1-(arylselanyl)anthraquinones [9-(p-YC₆H₄Se)C₆H₄O₂: 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, ¹H and ⁷⁷Se 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).

¹H and ⁷⁷Se NMR chemical shifts of 1–3 were measured in chloroform-d solutions (0.050 M) at 297 K. Table 2 collects the substituent induced δ(H₂), δ(H₈), and δ(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, δ(H₂: 3) and δ(Se: 3) are plotted versus δ(H₂: 2) and δ(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 ≥ 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 C≡C bond in 3 (G = Br) might be stronger than that in 2 (G = Cl), since δ(H₂) 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 δ(H₂) 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 H₂ 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, δ(H₂) 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 δ(H₂), since H atoms above the C≡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 that 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 δ(H₂: 1 and 2) versus δ(H₂: 7) and δ(H₂: 8). The plots appear from downfield to upfield in an order of δ(H₂: 1) ≪ δ(H₂: 2). The correlations are given in Table 3 (entries 3–6), which support above discussion.

δ(H₂: 1) and δ(Se: 1) are plotted versus δ(H₂: 7) and δ(Se: 7), respectively. Figure 5 shows the results. The
correlations are shown in Table 3 (entries 7 and 8, resp.). The correlation of the former is good, which means that \((A: \text{pl})\) 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 \((A: \text{pl})\) with some contributions of \((B: \text{pd})\) and/or \((B: \text{pl})\) through the equilibrium. The correlation for the plot of \(\delta(\text{Se: 1})\) versus \(\delta(\text{Se: 7})\) 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 \(\delta(H_2: 2)\) versus \(\delta(H_1: 8)\) do not give good correlations (Panel (b) of Figure 4 and entry 6 in Table 3). Although not shown, the plot of \(\delta(\text{Se: 2})\) versus

---

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

| Y | OMe | Me | H | F | Cl | CN | NO\(_2\) |
|---|-----|----|---|---|---|----|---------|
| 1 |     |    |   |   |    |
| \(\delta(H_1)\) | 7.779 | 7.879 | 7.798 | 7.803 | 7.809 | 7.845 | 7.857 |
| \(\delta(H_4)\) | 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 |
| 2 |     |    |   |   |    |
| \(\delta(H_1)\) | 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 |
| 3 |     |    |   |   |    |
| \(\delta(H_1)\) | 8.432 | 8.430 | 8.440 | 8.399 | 8.389 |
| \(\delta(\text{Se})\) | 323.1 | 325.2 | 323.7 | 323.7 | 324.8 |
| 7 |     |    |   |   |    |
| \(\delta(H_1)\) | 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 |
| 8 |     |    |   |   |    |
| \(\delta(H_1)\) | 7.260 | 7.261 | 7.237 | 7.199 | 7.220 | 7.181 | 7.185 |
| \(\delta(H_4)\) | 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 |

\(^{\text{a}}\) In CDCl\(_3\). \(^{\text{b}}\) From TMS for \(\delta(\text{H})\) and from Me\(_2\)Se for \(\delta(\text{Se})\).
δ(Se: 8) did not give good correlation either (entry 10 in Table 3). The plots of δ(Se: 2) versus δ(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 δ(H2: 2) and δ(H2: 3) versus δ(H2: 1). The reason for the structural determination in solutions will be discussed, next.

3.4. Selective 1H, 13C-NOE Difference Spectroscopy for 1e and 2e in Solutions. 1e (G = H, Y = Cl) and 2e (G = Y = Cl) were employed for the selective 1H, 13C-NOE difference spectroscopy. 13C NMR spectra were measured for 1e and 2e under the completely 1H decoupling mode, the off-resonance decoupling mode, and the selective 1H, 13C -NOE difference mode at the δ(H2) frequency: The atom numbers are shown in Scheme 2. Figure 6 shows the 13C NMR spectra for 2e. Panels (a)–(c) of Figure 6 correspond to the selective 1H, 13C -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 δ(H2) frequency of 2e enhances exclusively the 13C NMR signals of C2 and C9 of 2e, relative to others. On the other hand, only 13C NMR signal of C2 of 1e is enhanced relative to others, when the δ(H2) frequency of 1e is selectively irradiated, although not shown. The results must be the reflection of the expectation that H2 is very close to C9 in 2e to arise the nuclear interaction resulting in the NOE enhancement, whereas such interaction does not appear between H2 and C9 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 δ(H2) values of 1–3.
The structures around the Se–C Ar bonds 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 NO₂. The δ(H2) values observed in 1 is just the opposite to the case of 1-(p-YC₆H₄Se)C₁₀H₇ (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–C₃Nap bonds, in our definition. The structures around the Se–C₃Ar 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 nₓ(Cl)–π(Nap)–nₓ(Se–C₅p) 3c-4e interaction. The nₓ(Cl)–π(Nap)–nₓ(Se–C₅p) 3c-4e 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)anthraquiones (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 ¹H, ¹³C-NOE difference spectroscopic measurements strongly support that the structures are A for 1 and B for 2 and 3 in solutions derived from the δ(H₂) values of 1–3.

**Table 3: Correlations of δ(H) and δ(Se) in 1–3, 7, and 8 in solutionsa.)**

| Entries | Correlation                  | a    | b    | r²  | n  |
|---------|------------------------------|------|------|-----|----|
| 1       | δ(H₂; 3) versus δ(H₂; 2)    | 0.994| 0.11 | 0.996| 5  |
| 2       | δ(Se; 3) versus δ(Se; 2)    | 0.784| 1.34 | 0.895| 7  |
| 3       | δ(H₂; 1) versus δ(H₂; 7)    | -0.290| 10.37 | 0.992| 7  |
| 4       | δ(H₂; 2) versus δ(H₂; 7)    | 0.289| 5.79 | 0.917| 7  |
| 5       | δ(H₂; 1) versus δ(H₂; 8)    | -0.784| 13.47 | 0.895| 7  |
| 6       | δ(H₂; 2) versus δ(H₂; 8)    | 0.856| 2.16 | 0.906| 7  |
| 7       | δ(H₂; 1) versus δ(H₂; 7)    | -0.337| 11.02 | 0.990| 7  |
| 8       | δ(Se; 1) versus δ(Se; 7)    | 0.279| 217.2| 0.961| 7  |
| 9       | δ(Se; 2) versus δ(Se; 8)    | 0.261| 197.0| 0.786| 7  |

a.) The constants (a, b, r) are defined by y = ax + b (r: correlation coefficient).b.) Y = OMe, Me, H, F, Cl, CN, and NO₂, c.) 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-YC₆H₄C≡CSe)C₁₀H₆ (1 (G = H) and 2 (G = Cl): Y = H (a), OMe (b), Me (c), F (d), Cl (e), CN (f), and NO₂ (g)) are determined by the X-ray crystallographic analysis. The structures of 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 NO₂. The δ(H₂) values observed in 1 is just the opposite to the case of 1-(p-YC₆H₄Se)C₁₀H₇ (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–C₃Nap bonds, in our definition. The structures around the Se–C₃Ar 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 nₓ(Cl)–π(Nap)–nₓ(Se–C₅p) 3c-4e interaction. The nₓ(Cl)–π(Nap)–nₓ(Se–C₅p) 3c-4e 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)anthraquiones (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 ¹H, ¹³C-NOE difference spectroscopic measurements strongly support that the structures are A for 1 and B for 2 and 3 in solutions derived from the δ(H₂) 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-phenylselenyl)naphthyl disulfide: 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 ?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 S 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···O···Se–C atoms in anthraquinone and 9-(methoxy)anthracene bearing phenylselenyl group 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···O···Se–C atoms in anthraquinone and 9-methoxyanthracene bearing arylselenyl 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. Tokiho, “Atoms-in-molecules analysis of extended hypervalent five-center, six-electron (5c–6e) C2Z2O 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 Br4 four centre-six electron and Se4Br3 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-(MeS)2-8-(p-YC6H4Se)2C10H7: role of linear Se···Se–C three-center-four-electron versus n(Se)···n(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-(arylselenyl)naphthalenes. 2. G dependence in 8-G-1-(p-YC6H4Se)C10H7,” 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. Cziszmadia, and A. Mangini, Eds., Elsevier, Amsterdam, The Netherlands, 1985.

[18] W. Nakanishi, S. Hayashi, A. Sakaue, G. Ono, and Y. Kawada, “Attractive interaction caused by the linear F···Se–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 dicitons,” Accounts of Chemical Research, vol. 13, no. 7, pp. 200–206, 1980.

[22] W. Nakanishi, S. Hayashi, and T. Uehara, “Structure of 1-(arylselenyl)naphthalenes—Y dependence in 1-(p-YC6H4Se)C10H7,” 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-YC6H4Se(O)C10H7],” Journal of Organic Chemistry, vol. 71, no. 15, pp. 5574–5585, 2006.

[24] A. Kuczman and I. Kapovits, “Nonbonded sulfur-oxygen interaction,” in Organic Sulfur Chemistry: Theoretical and Experimental Advances, F. Bernardi, I. G. Cziszmadia, 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 Hetarom 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-bc]-1,5-dithiobinc,” 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 S···S interactions in geometrically constrained 1,5-dithioane 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. 30, no. 12, pp. 2121–2122, 1993.

[31] M. Iwaoka, S. Takemoto, M. Okada, and S. Tomoda, “Statistical characterization of nonbonded S···O interactions in proteins,” Chemistry Letters, vol. 30, no. 2, pp. 132–133, 2001.
G. Mugesh, A. Panda, 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.

G. Mugesh, H. B. Singh, and R. J. Butcher, “Synthesis and characterization of monomeric tellurolato complexes of zinc and cadmium: crystal and molecular structure of bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl]ditelluride,” Journal of Organometallic Chemistry, vol. 577, no. 2, pp. 243–248, 1999.

D. Shimizu, N. Takeda, and N. Tokitoh, “Unusual carbon-sulfur bond cleavage in the reaction of a new type of bulky hexathioketoether with a zerovalent palladium complex,” Chemical Communications, no. 2, pp. 177–179, 2006.

W. Nakaniishi, S. Hayashi, S. Morinaka, T. Sasamori, and N. Tokitoh, “Extended hypervalent E′···E′···E′···E′ 4c–6e (E′ = Se, S) interactions: structure, stability and reactivity of 1-(8-PhE′C6H4H2E′E′C6H4H2E′-Ph′)-1′,” New Journal of Chemistry, vol. 32, no. 11, pp. 1881–1889, 2008.

P. J. Stang and F. Diederich, Eds., Modern Acetylene Chemistry, Wiley-VCH, Weinheim, Germany, 1995.

F. Diederich, P. J. Stang, and R. R. Tykwinski, Eds., Acetylene Chemistry: Chemistry, Biology, and Material Science, Wiley-VCH, Weinheim, Germany, 2005.

A. J. Zuccerro, 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.

E. L. Spitzer, L. D. Shirtscliff, and M. M. Haley, “Systematic structure-property investigations and ion-sensing studies of pyridine-derivatized donor/acceptor tetraakis(arylthethyl)benzenes,” Journal of Organic Chemistry, vol. 72, no. 1, pp. 86–96, 2007.

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.

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.

Y. Jiang, D. Perahia, Y. Wang, and U. H. F. Bunz, “Side chain vs main chain. Who dominates? A polyester-grafted poly(p-phenylethylene) with two different morphologies,” Macromolecules, vol. 39, no. 15, pp. 4941–4944, 2006.

K. Tahara, S. Furukawa, H. Uji-i, et al., “Two-dimensional porous molecular networks of dehydrobenzo[12]annulene derivatives via alky chain interdigitation,” Journal of the American Chemical Society, vol. 128, no. 51, pp. 16613–16625, 2006.

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 diethynylbenzenes macrocycle,” Journal of Organic Chemistry, vol. 71, no. 1, pp. 401–404, 2006.

E. E. Nesterov, Z. Zhu, and T. M. Swager, “Conjugation enhancement of intramolecular excitation migration in poly(p-phenylethylene),” 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. Petagnani, “The structure of triphenyl[a-(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-(arylethynylselenyl)naphthalenes: characteristic features brought by the ethynylselenyl 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-(arylethynylselenyl)naphthalenes (G = H, Cl, Br): factors to control the linear alignment of five G···Se=C=C C 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 $^{77}$Se NMR chemical shifts of organic selenium compounds: application of GIAO magnetic shielding tensor to the $^{77}$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 $^{77}$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 $^1$H and $^{31}$C NMR chemical shifts clarify the effect?” Journal of Organic Chemistry, vol. 72, no. 20, pp. 7387–7396, 2007.