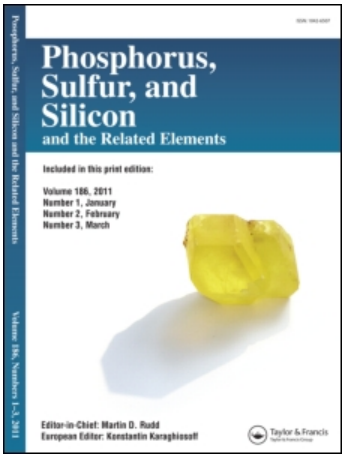

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How Do G–Se Nonbonded and Y–Se Through π-Bond Interactions Determine the Structures of 8-G-1-(*p*-YC_6H_4Se)$C_{10}H_6$?

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*Structures of 8-G-1-(*p-YC_6H_4Se)$C_{10}H_6$ (G = H (**1**), SeMe (**2**), Cl (**3**), and Br (**4**)) bearing various Y are determined by the X-ray crystallographic analysis. While Y dependence in the structures originates from the through π interaction between n_p(Se) and n_p(Y), G dependence is based on the nonbonded $n_p(G)\cdots\sigma^*(Se{-}C)$ 3c–4e interaction. QC calculations reveal that the specific stability appears when the π 2c–4e is distorted (Möbius type stability).*

Keywords 2c–4e; 3c–4e; lone pair; naphthalene-1,8-positions; nonbonded interactions; QC calculations; selenides

INTRODUCTION

Various types of structures will be observed in 8-G-1-(*p*-YC_6H_4Se)$C_{10}H_6$ (**1**–**4**) bearing various Y (Scheme 1). However, it has been difficult to tell the origin of the structures. Nonbonded interactions play an important role to determine the fine structures, especially for those with short nonbonded distances. The structures of **1**–**4** are of great interest, since selenium has both s-type and p-type lone pairs, which results in various types of nonbonded interactions. We have started our project to clarify the fine structures of **1**–**4**, together with factors to determine the structures in detail.[1–5] Nonbonded interactions are sometimes so weak. Therefore, it is important to support and explain the experimental results. QC calculations are widely employed in this study.

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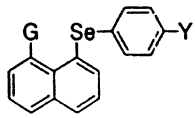


1 (G =H), **2** (G = SeMe), **3** (G = Cl), **4** (G = Br)

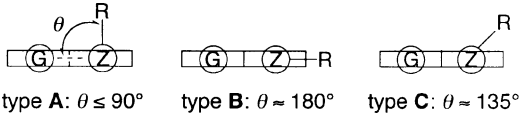
	a	**b**	**c**	**d**	**e**	**f**	**g**
Y =	H	OMe	Me	Cl	Br	CO_2Et	NO_2

SCHEME 1

RESULTS AND DISCUSSION

Structures of 1–4

The structure around the Se atom of the naphthalene system is well classified by type **A** (**A**), **B**, and **C** (Scheme 2).[1–4] The structures of **1**–**4** are determined by the X-ray crystallographic analysis. For example, the characters of **1b**, **1d**, **2a**, **2b**, **2d**, **3d**, and **4d** are **B**, **A**, **CC**, pseudo-**AB**, **AB**, **B**, and **B**, respectively. The factor to determine **A** and **B** is the through π interaction of the n_p(Se)-π(Nap) type.[4] **BB** is controlled by the p(Se)-π(Nap) through bond interaction, **CC** appears when the non-bonded Se–Se interaction is substantially large, and **AB** is controlled by the CT of the n(Se)—σ^*(Se–C) type, together with the p(Se)–π(Nap) interaction (Scheme 3). Scheme 4 summarizes the results, containing the structures of **1b**, **1d**, **2a**, **2b**, **2d**, and **4d**.[5]



type **A**: $\theta \leq 90°$ type **B**: $\theta \approx 180°$ type **C**: $\theta \approx 135°$

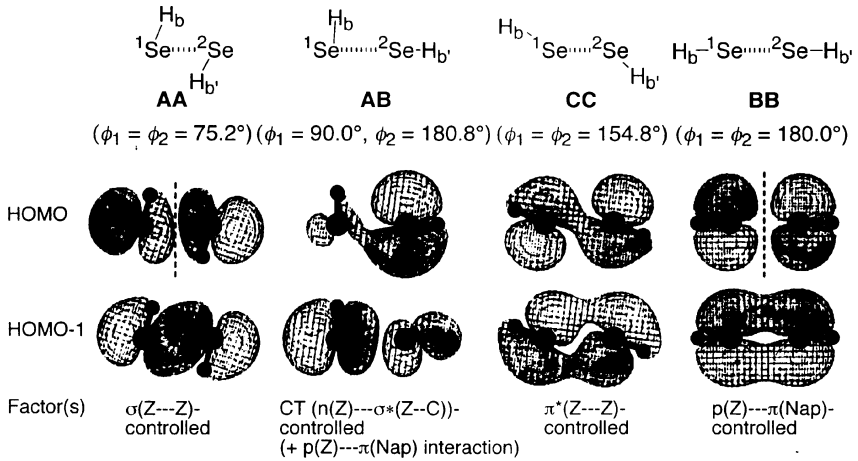
θ stand for the projected angles of GZR. Namely, the meanings are ϕ(GC_1ZR).

SCHEME 2 Types of structures in naphthalene system.

Y and G Dependence in 1–4

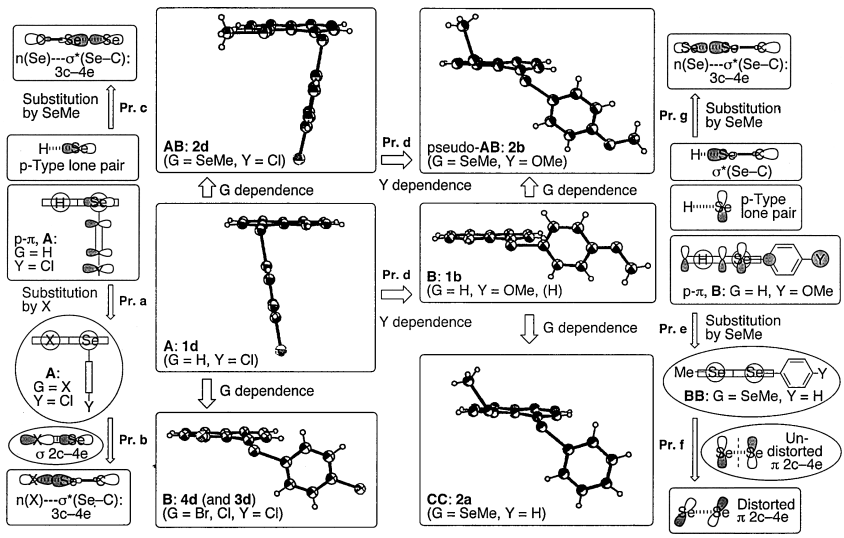
As shown in Scheme 4, structures are drawn exemplified by **1b**, **1d**, **2a**, **2b**, **2d**, and **4d** (and **3d**). Observed structures are shown in rectangles, while tentative ones are in circles. The structural change by Y and G are called Y dependence and G dependence, respectively. The processes shown in the Scheme are as follows. Process a (Pr. **a**) shows the substitution by X. Pr. **b** and Pr. **f** stand for G dependence of the structure. Pr. **c**, Pr. **e**, and Pr. **g** exhibit the substitution by SeMe and the formation of the pairings. Pr. **d** exhibits Y dependence of the structure.

The halogen substitution at the 8-position in **1d** of type **A** (**A**: **1d**) will generate the nonbonded Se–X σ 2c–4e interaction in **4d**, which must



SCHEME 3 Factors to control the structures: Nonbonded 2c–4e and 3c–4e interactions.

destabilize the compound very much (Pr. **a**). Rotation around the Se–C bonds takes place to yield **B** in this case (Pr. **b**). The new structure generates the nonbonded n(X)—σ^*(Se–C) 3c–4e interaction, which stabilize **B**. The destabilizing effect by the nonbonded π 2c–4e interaction simultaneously operating in **4d** must be smaller than the stabilizing effect by the nonbonded 3c–4e.



SCHEME 4 Structures of **1b**, **1d**, **2a**, **2b**, **2d**, and **4d** and factors to determine them.

The SeMe substitution at the 8-position in **1d** (Pr. **c**) results in the nonbonded 3c–4e Se—Se–C_{Me} interaction. But the SeMe group affects little on the conformation around the *p*-ClC_6H_4Se group in **2d**. The role of SeMe in **2d** of **AB** makes the structure more stable, although the conformations around the *p*-ClC_6H_4Se group in **1d** and **2d** are both **A**. **1d** of **A** changes to **B** if Y = Cl goes to Y = OMe, for example (Y dependence: Pr. **d**). The SeMe group in **2a** yields **AB** or **BB** according to the conformation of the SeMe group. The latter is shown in Scheme 4. If **BB** is generated in **2a**, it will be destabilized by the nonbonded π 2c–4e. The rotation around the Se–C_{Nap} bonds occurs to avoid the destabilizing effect, which results in the formation of **CC**.

It is worthwhile to comment the stabilizing factor in **CC**. The character of the orbital interaction in **CC** is the distorted π 2c–4e. The explicit nodal plane between the nonbonded Se–Se bond in π^* of **BB** disappears in **CC**. The disappearance of the nodal plane must stabilize **CC**, which may avoid the severe exchange repulsion of the π 2c–4e interaction more effectively. It must be the driving force for **CC**. The orbital interaction accompanied by the disappearance of the nodal plane in **CC** remembers Möbius type interaction in cyclic π systems. It is named Möbius type stabilization in the distorted π 2c–4e, although the π 2c–4e interaction does not form a ring.

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