

Structures in 8-(methylselanyl)-1-(methylseleninyl)- and 1,8-bis(methylseleninyl)naphthalenes: Transition states involving simultaneous rotation around Se–C bonds, together with stable structures

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Abstract

The energy profile of 8-(methylselanyl)-1-(methylseleninyl)naphthalene (**1**) is revealed to clarify how the Se(O)Me and SeMe groups control the stereochemistry of **1**, through the nonbonded Se–Se=O interaction. Six stable structures (SSs) and eight transition states (TSs) are optimized for **1**. Frequency analysis is carried out for all SSs and TSs. The global minimum of **1** is the *trans*-form of **1** (**1** (*t*-AA)), which reproduces the structure determined by the X-ray crystallographic analysis. Three Se–Se=O atoms in **1** (*t*-AA) are on the naphthyl plane and two Me groups are in *trans*. Next stable one is the *cis*-form (**1** (*c*-AC')). Motions in the imaginary frequencies of six TSs correspond to the rotation around an Se–C_{Nap} bond, whereas those of the two to the simultaneous rotations around the two Se–C_{Nap} bonds. Attractive interactions must play an important but additional role in the simultaneous rotations in TS. The observed structure in 1,8-bis(methylseleninyl)naphthalene (**2**) is also reproduced by the global minimum, where the four O=Se–Se=O atoms align linearly. NBO analysis reveals that $\sigma(3c-4e)$ of the nonbonded Se–Se=O interaction controls the structure of **1** whereas $\sigma(4c-4e)$ of the O=Se–Se=O interaction will not in **2**.

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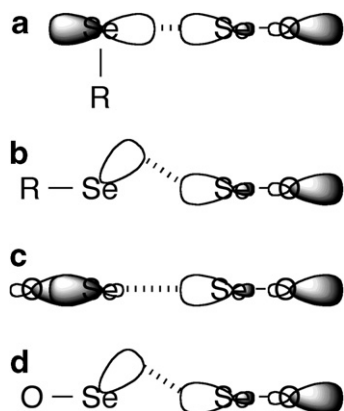
1. Introduction

To control the stereochemistry of selenoxides [RSe(O)R'] is one of current interests [1–7]. Although selenoxides afford optically active enantiomers if R and R' are not the same, the racemization is usually very fast. Efforts have been made to decrease the rate of racemization through the nonbonded coordination by the neighboring groups (G) to the cationic Se atom, utilizing the energy lowering effect of the G–Se–O 3c–4e interaction [7]. Among various G, divalent selanyl groups will cause intriguing phenomena around Se in selenoxides, since G of divalent

selanyl groups supply two directions of interactions, related to those of the Se–C_R bond in Se–R: One direction is brought by the p-type lone pair orbital of Se ($n_p(\text{Se})$) and the other is by the orbitals perpendicular to it, such as $n_s(\text{Se})$, $\sigma(\text{Se}-\text{C}_R)$, and $\sigma^*(\text{Se}-\text{C}_R)$. Scheme 1 shows $n_p(\text{Se})-\sigma^*(\text{Se}-\text{O})$ and $n_s(\text{Se})-\sigma^*(\text{Se}-\text{O})$ 3c–4e interactions with $G = \text{SeR}$, together with mutual $\sigma(\text{Se}-\text{O})-\sigma^*(\text{Se}-\text{O})$ 4c–4e and $n_s(\text{Se})-\sigma^*(\text{Se}-\text{O})$ 3c–4e interactions with $G = \text{Se(O)R}$.

To clarify how the Se–Se–O 3c–4e interaction controls the fine structures of selenoxides, we examined the fine structures of 8-(methylselanyl)-1-(methylseleninyl)naphthalene (**1**) and 1,8-bis(methylseleninyl)naphthalene (**2**) (Chart 1). Quantum chemical (QC) calculations are performed on **1** and **2**, to reveal the factors to control the fine

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Scheme 1. G–Se–O interactions: (a) $n_p(\text{Se})-\sigma^*(\text{Se}-\text{O})$ 3c–4e with $G = \text{SeR}$, (b) $n_s(\text{Se})-\sigma^*(\text{Se}-\text{O})$ 3c–4e with $G = \text{SeR}$, (c) mutual $\sigma(\text{Se}-\text{O})-\sigma^*(\text{Se}-\text{O})$ 4c–4e with $G = \text{Se(O)R}$, and (d) $n_s(\text{Se})-\sigma^*(\text{Se}-\text{O})$ 3c–4e with $G = \text{Se(O)R}$.

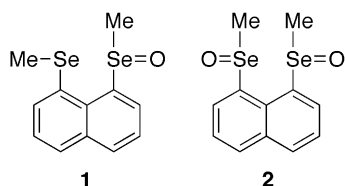
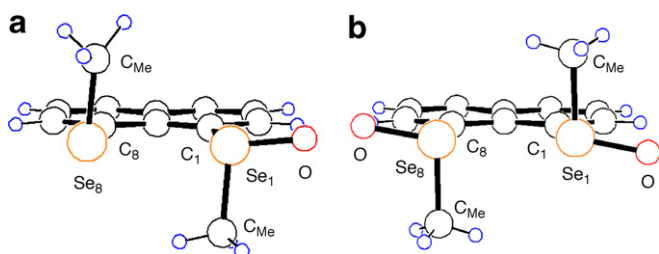


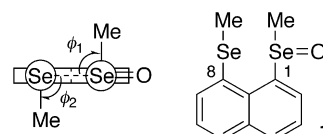
Chart 1.

structures. Stable structures (SSs) and transition states (TSs) between them are examined for **1** and SSs are for **2**. The characters of TSs in **1** are also clarified.

The results are discussed based on the structures determined by the X-ray crystallographic analysis. The structures of **1** and **2** are illustrated in Scheme 2 [8]. They are well specified using type **A** (**A**), type **B** (**B**), and type **C** (**C**), together with type **A'** (**A'**), type **B'** (**B'**), and type **C'** (**C'**), for the torsional angles of $\phi_1(\text{C}_8\text{C}_1\text{Se}_1\text{C}_{\text{Me}})$ and $\phi_2(\text{C}_1\text{C}_8\text{Se}_8\text{C}_{\text{Me}})$. Scheme 3 shows the notation, exemplified by **1**. The structures of **1** and **2** are both **AA** for the methyl groups in our definition, where both $\text{Se}-\text{C}_{\text{Me}}$ bonds are perpendicular to the naphthyl planes. Three $\text{Se}-\text{Se}-\text{O}$ atoms in **1** and four $\text{O}=\text{Se}-\text{Se}=\text{O}$ atoms in **2** align linearly. The $\text{Se}-\text{Se}-\text{O}$ 3c–4e interaction is strongly suggested to control the fine structure of **1**. Although the $\text{O}-\text{Se}-\text{Se}-\text{O}$ 4c–4e interaction is expected to determine the fine structure of **2**, we must be careful since the interaction would not stabilize the system. The fine structure of **2** can be controlled by the O-dependence of the $n_p(\text{Se})-\pi(\text{Nap})$ interactions [7].



Scheme 2. Structures of **1** (a) and **2** (b).



$$\phi_1(\text{C}_8\text{C}_1\text{Se}_1\text{C}_{\text{Me}}), \phi_2(\text{C}_1\text{C}_8\text{Se}_8\text{C}_{\text{Me}})$$

type **A**: $60^\circ < \phi < 105^\circ$; type **A'**: $255^\circ < \phi < 300^\circ$

type **B**: $150^\circ < \phi \leq 180^\circ$; type **B'**: $180^\circ < \phi < 210^\circ$

type **C**: $105^\circ \leq \phi \leq 150^\circ$; type **C'**: $210^\circ \leq \phi \leq 255^\circ$

Scheme 3. Notation for the structures of **1** and **2**, exemplified by **1**.

During the course of our investigations into the non-bonded interactions at naphthalene 1,8-positions [9], we encountered such transition states that involve simultaneous rotations around both Se_1-C_1 and Se_8-C_8 bonds in **1**. Here, we report the whole picture of the interconversions in **1**, together with the factors to control the fine structures of **1**, such as the $\text{Se}-\text{Se}-\text{O}$ 3c–4e interaction. The role of the $\text{O}-\text{Se}-\text{Se}-\text{O}$ 4c–4e interaction in the structure of **2** is also discussed. The interactions are examined based on the natural bond orbital (NBO) analysis [10,11].

2. Computational

QC calculations are performed on **1** and **2**, employing the 6-311G(d), 6-311+G(d,p), and/or 6-311+G(2d,p) basis sets of the Gaussian 98 program [12]. Calculations are performed at the density functional theory (DFT) level of the Becke three parameter hybrid functionals with the Lee–Yang–Parr correlation functional (B3LYP) [13,14]. SSs and TSs are searched for **1** and SSs for **2**. To search SSs, calculations are performed starting from initial structures with $\phi_1(\text{C}_8\text{C}_1\text{Se}_1\text{C}_{\text{Me}})$ of every 30° and $\phi_2(\text{C}_1\text{C}_8\text{Se}_8\text{C}_{\text{Me}})$ of every 45° . TSs are optimized between SSs. Some of them are identical with each other (see also Scheme 5). Frequency analysis is carried out for all structures in **1**. Optimized structures are drawn using MolStudio R3.2 [15]. Natural bond orbital (NBO) analysis [10,11] is carried out to clarify how the global minima are stabilized through the nonbonded interactions with the Gaussian 03 program [16].

3. Results and discussion

3.1. QC Calculations on **1** and **2**

SSs and TSs are searched for **1** to clarify the energy profile with the 6-311G(d), 6-311+G(d,p), and/or 6-311+G(2d,p) basis sets at the DFT (B3LYP) level [17]. The *trans*-**AA** structure (*t*-**AA**) is optimized as the global minimum for **1**, where both ϕ_1 and ϕ_2 of *t*-**AA** are in the **A** region for the two Me groups, which are in *trans*. The global minimum of **1** (*t*-**AA**) reproduces well the observed structure of **1**. The next stable structure is *c*-**AC'**, which corresponds to the *cis*-form of *t*-**AA**, although ϕ_2 is in the **C'** region. The structures of *t*-**AA** and *c*-**AC'** optimized

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