Extended Hypervalent 5c-6e Interactions: Linear Alignment of Five CZ- - -O- - -ZC (Z = S, Se) Atoms in Anthraquinone and Anthracene Systems

Warô Nakanishi[a]; Satoko Hayashi[a]; Takashi Furuta[a]; Norio Itoh[a]; Yusaku Nishina[b]; Makoto Yamashita[b]; Yohsuke Yamamoto[b]

[a] Department of Chemistry, Faculty of Systems Engineering, Wakayama University, Wakayama, Japan
[b] Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Japan

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Warô Nakanishi
Satoko Hayashi
Takashi Furuta
Norio Itoh
Department of Chemistry, Faculty of Systems Engineering,
Wakayama University, Wakayama, Japan

Yusaku Nishina
Makoto Yamashita
Yohsuke Yamamoto
Department of Chemistry, Graduate School of Science,
Hiroshima University, Higashi-Hiroshima, Japan

Structures of 1,8-(ArZ)$_2$C$_{14}$H$_6$O$_2$ and 9-(MeO)-1,8-(ArZ)$_2$C$_{14}$H$_7$ (Z = S, Se) are determined by X-ray crystallographic analysis. Five C—Z---O---Z—C atoms of the compounds align linearly, which are analyzed by the extended hypervalent 5c–6e model, based on QC calculations. CT of the 5c–6e occurs as the $\sigma^*(C—Z) \leftarrow n_p(O) \rightarrow \sigma^*(Z—C)$ direction.

Keywords 5c–6e; anthracene; anthraquinone; extended hypervalent interaction; QC calculations; selenide; structure; sulfide

INTRODUCTION

Extended hypervalent bonds mc–ne ($m \geq 4$) are of great interest, where mc–ne are the σ-type linear bonds constructed by m (≥ 4) atoms with n ($\geq m$) electrons. After substantial development of 4c–6e,[1] the next extension of our investigations is to reveal the nature of 5c–6e.[2] Scheme 1 shows the approximate molecular orbital model of 5c–6e.

ψ_5 ——

ψ_4 ——

ψ_3 -OO-

ψ_2 -OO-

ψ_1 -OO-
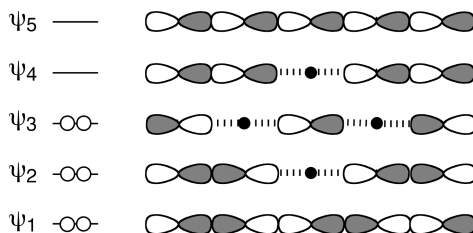
SCHEME 1 Approximate molecular orbital model of Z_5 5c–6e.

Our strategy to construct the *mc–ne* system is to employ the nonbonded interactions arising from direct orbital overlaps containing lone pair orbitals.[1–3]
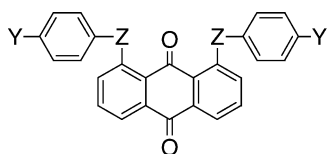
RESULTS AND DISCUSSION

Structures are determined for 1,8-bis(arylthio)anthraquinones (**1**), 9-methoxy-1,8-bis(arylthio)anthracenes (**2**), and 1,8-bis(arylthio)anthracenes (**3**), together with the selenium derivatives (**4–6**), by X-ray crystallographic analysis.
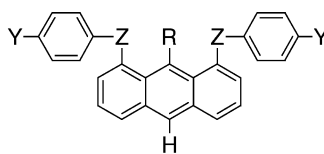
1 (Z = S), **4** (Z = Se)　　　　**2** (Z = S, R = OMe), **3** (Z = S, R = H)
a (Y = H), **b** (Y = Me), **c** (Y = Cl)　　**5** (Z = Se, R = OMe), **6** (Z = Se, R = H)

Figures 1–3 show the structures of **4a–6a**, respectively.[2] Those of **1a–3a** are shown in the abstracts of ISOCS-XXI.[4] Five C—Z---O---Z—C

FIGURE 1 Structure of **4a**. Nonbonded lengths (Å) and angles (°): Se(1)—O(1), 2.688(4); Se(2)–O(1), 2.673(4); Se(1)–O(1)–Se(2), 152.5(2).

FIGURE 2 Structure of **5a**. Nonbonded lengths (Å) and angles (°): Se(1)–O(1), 2.731(3); Se(2)–O(1), 2.744(3); Se(1)–O(1)–Se(2), 147.9(1).
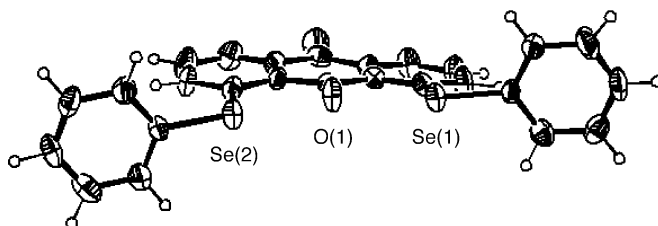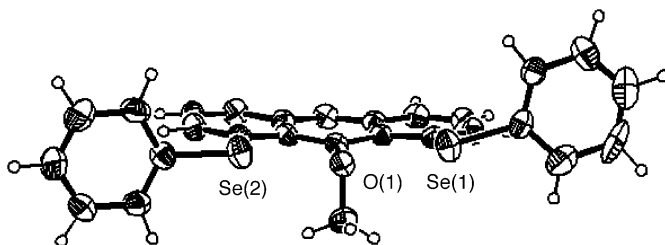
(Z = S, Se) atoms in **1**, **2**, **4**, and **5** align linearly, however, five C—Z---H---Z—C atoms in **3** and **6** never align linearly.

What is the origin of the linear alignment? The results suggest that the p-type lone pair orbital directed toward Z at the central O atom [$n_p(O)$] must play an important role in the linear alignment. Quantum Chemical (QC) calculations are performed on **1a**–**6a** and the models.

Figure 4 shows optimized structures of **1a**–**6a**, together with the relative energies. The relative energies of **1a** (**AA**-trans), **1a** (**AB**), and **1a** (**BB**) are 0.0, –21.5, and –40.7 kJ mol^{-1}, respectively. These values for **1a** are approximately 68% of those corresponding conformers in **4a**. Similarly, **2a** (**AA**-cis) becomes more stable by 15.0 and 20.0 kJ mol^{-1} when it goes to **2a** (**AB**) then **2a** (**BB**), respectively. The values in **2a** are 55–61% of those in the corresponding process in **5a**. Conformer **A** changes to **B** in each process. The characters of **AA**, **AB**, and **BB** in **1**, **2**, **4**, and **5** are 3c–6e, 4c–6e, and 5c–6e, respectively.[2] These results demonstrate that the change in each conformer from **A** to **B** stabilizes **1**, **2**, **4**, and **5**.

On the other hand, **3a** (**AA**-trans) is more stable than any other conformers, **3a** (**AB**), **3a** (**AA**-cis), and **3a** (**BB**). The energy differences
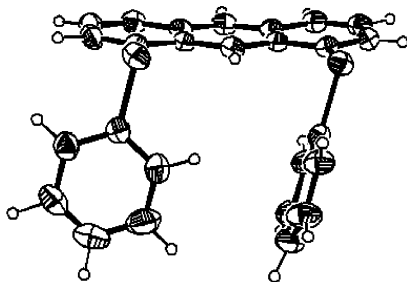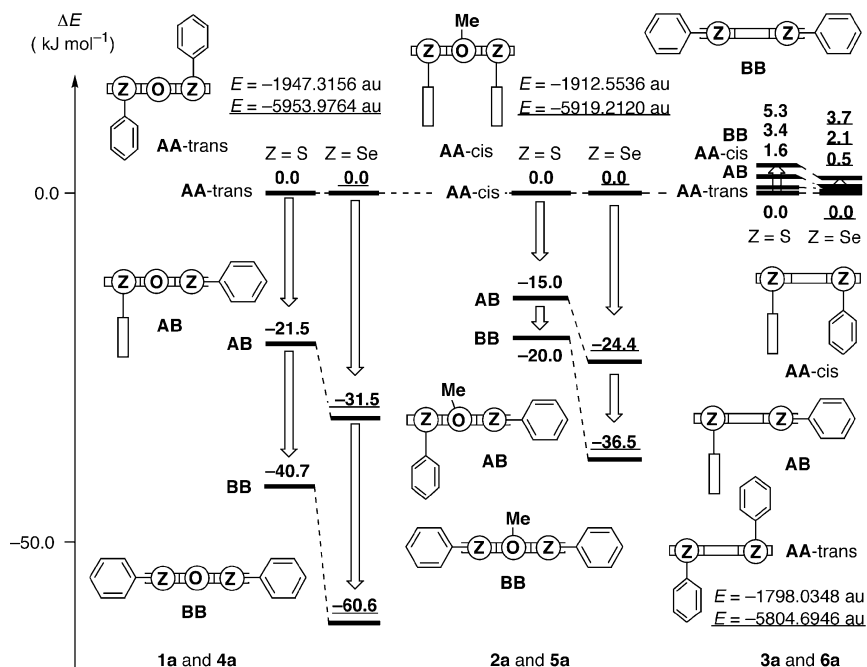

FIGURE 3 Structure of **6a**.

FIGURE 4 Optimized structures of **1a**–**6a** and the relative energies. Energies are given for **AA**-trans of **1a**, **3a**, **4a**, and **6a** and **AA**-cis of **2a** and **5a**. Values for **4a**–**6a** are given by underlines.

are slightly larger than those corresponding conformers in **6a**. This may show that the steric repulsion between phenyl group and the H atom at the 2-position is responsible for the stability of **3a** and **6a**.

The hypervalent $n_p(O)\text{---}\sigma^*(Z\text{—}C)$ 3c–4e interactions will occur at both sides of the O atom in **1**, **2**, **4**, and **5**. If the two 3c–4e are connected effectively at the O atom, both $\sigma^*(Z\text{—}C)$ interact together through $n_p(O)$, resulting in the formation of extended hypervalent 5c–6e of the $\sigma^*(C\text{—}Z)\text{---}n_p(O)\text{---}\sigma^*(Z\text{—}C)$ type. Figure 5 shows the proposed extended hypervalent 5c–6e interaction of the type. The direction of CT in the 5c–6e must be $\sigma^*(C\text{—}Z) \leftarrow n_p(O) \rightarrow \sigma^*(Z\text{—}C)$, which is well supported by QC calculations on the models, although not shown here.

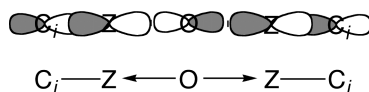$$C_i\text{—}Z \longleftarrow O \longrightarrow Z\text{—}C_i$$

FIGURE 5 Extended hypervalent 5c–6e interactions in **1**, **2**, **4**, and **5**.

The formation and the energy-lowering effect of the extended hypervalent 5c–6e interactions are well established based on the experimental and theoretical investigations.

Dedicated to Prof. Michinori Ōki on occasion of his 77th birthday.

REFERENCES

[1] W. Nakanishi, S. Hayashi, and S. Toyota, *Chem. Commun.,* 371–372 (1996); W. Nakanishi, S. Hayashi, and S. Toyota, *J. Org. Chem.*, **63,** 8790–8800 (1998); W. Nakanishi and S. Hayashi, *J. Org. Chem.*, **64,** 6688–6696 (1999); W. Nakanishi, S. Hayashi, and T. Arai, *Chem. Commun.*, 2416–2417 (2002).
[2] W. Nakanishi, S. Hayashi, and N. Itoh, *Chem. Commun.*, 124–125 (2003); W. Nakanishi, S. Hayashi, and N. Itoh, *J. Org. Chem.*, **69,** 1676–1684 (2004).
[3] W. Nakanishi, S. Hayashi, S. Yamaguchi, and K. Tamao, *Chem. Commun.*, 140–141 (2004).
[4] W. Nakanishi, S. Hayashi, T. Furuta, N. Itoh, Y. Nishina, M. Yamashita, and Y. Yamamoto, ISOCS-XXI, Madrid, Spain, July 4–9, 2004, Abstracts p. 78.