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

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

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Structures of 1,8-(ArZ)₂C₁₄H₆O₂ and 9-(MeO)-1,8-(ArZ)₂C₁₄H₇ (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 $\sigma^(\text{C}–\text{Z}) \leftarrow n_p(\text{O}) \rightarrow \sigma^*(\text{Z}–\text{C})$ direction.*

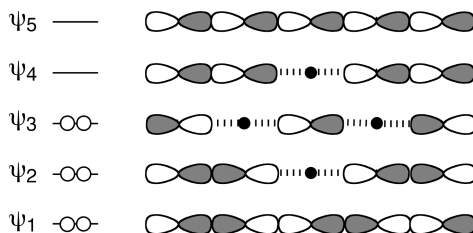
Keywords 5c–6e; anthracene; anthraquinone; extended hypervalent interaction; QC calculations; selenide; structure; sulfide

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.

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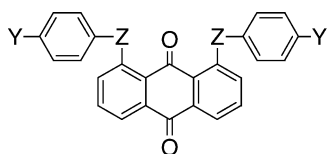


SCHEME 1 Approximate molecular orbital model of Z_5 5c–6e.

Our strategy to construct the *mc-ne* system is to employ the non-bonded interactions arising from direct orbital overlaps containing lone pair orbitals.^{1–3}

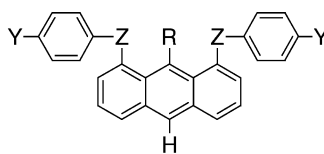
RESULTS AND DISCUSSION

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** ($Z = Se$)

a ($Y = H$), **b** ($Y = Me$), **c** ($Y = Cl$)



2 ($Z = S$, $R = OMe$), **3** ($Z = S$, $R = H$)

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

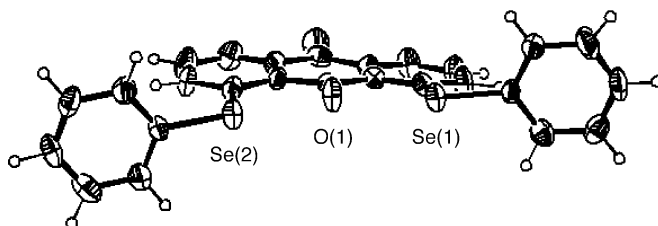


FIGURE 1 Structure of **4a**. Nonbonded lengths (Å) and angles (°): Se(1)–O(1), 2.688(4); Se(2)–O(1), 2.673(4); Se(1)–O(1)–Se(2), 152.5(2).

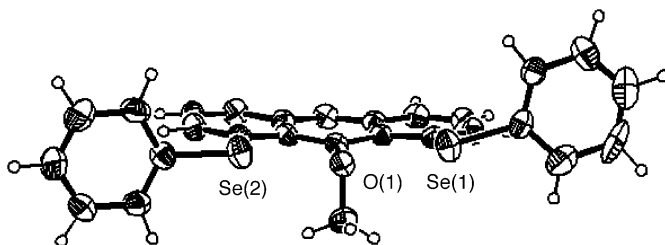


FIGURE 2 Structure of **5a**. Nonbonded lengths (Å) and angles (°): Se(1)–O(1), 2.731(3); Se(2)–O(1), 2.744(3); Se(1)–O(1)–Se(2), 147.9(1).

(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 [$n_p(\text{O})$] 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

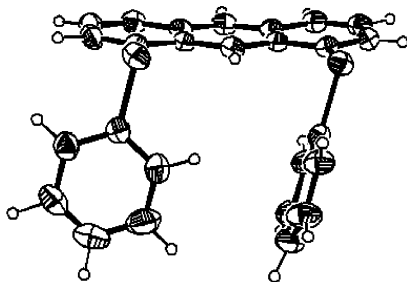


FIGURE 3 Structure of **6a**.

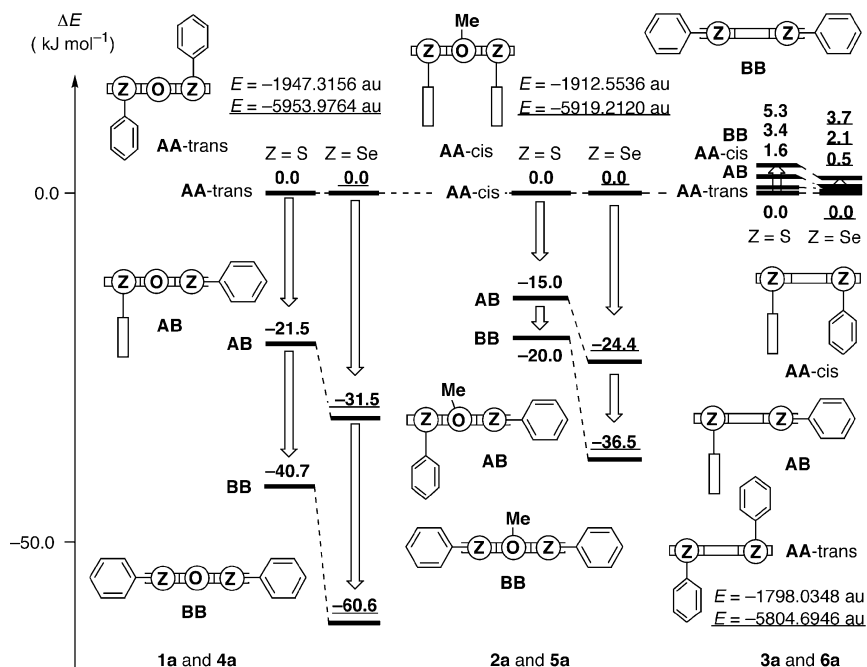


FIGURE 4 Optimized structures of **1a**–**6a** and the relative energies. Energies are given for AA-trans of **1a**, **3a**, **4a**, and **6a** and AA-cis of **2a** and **5a**. Values for **4a**–**6a** are given by underlines.

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 $n_p(\text{O}) \cdots \sigma^*(\text{Z}-\text{C})$ 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 $\sigma^*(\text{Z}-\text{C})$ interact together through $n_p(\text{O})$, resulting in the formation of extended hypervalent 5c–6e of the $\sigma^*(\text{C}-\text{Z}) \cdots n_p(\text{O}) \cdots \sigma^*(\text{Z}-\text{C})$ type. Figure 5 shows the proposed extended hypervalent 5c–6e interaction of the type. The direction of CT in the 5c–6e must be $\sigma^*(\text{C}-\text{Z}) \leftarrow n_p(\text{O}) \rightarrow \sigma^*(\text{Z}-\text{C})$, which is well supported by QC calculations on the models, although not shown here.

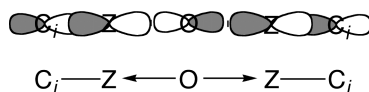


FIGURE 5 Extended hypervalent 5c–6e interactions in **1**, **2**, **4**, and **5**.

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.

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