First linear alignment of five C–Se⋯O⋯Se–C atoms in anthraquinone and 9-(methoxy)anthracene bearing phenylselanyl groups at 1,8-positions†

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Five C_i–Se⋯O⋯Se–C_i atoms in anthraquinone and 9-(methoxy)anthracene bearing phenylselanyl groups at 1,8-positions align linearly, the origin of which is shown to be a non-bonded 5c–6e interaction of the five atoms.

Non-bonded interactions[1] are of great interest. This is especially so if they lead to linear bonds longer than the three center–four electron bond (3c–4e) through direct orbital overlaps containing group 16 elements.[2] Naphthalene 1,8-positions supply a good system to study such non-bonded interactions, containing 2c–4e, 3c–4e and 4c–6e interactions.[2–5] However, the nature of the 5c–6e interaction is as yet not well understood. Anthracene 1,8,9-positions also serve as a good system for such interactions.[6]

Five C–Se⋯O⋯Se–C atoms are shown to align linearly for 1,8-bis(phenylselanyl)anthraquinone (**1**)† and 9-(methoxy)-1,8-bis(phenylselanyl)anthracene (**2**).†The linear alignment can be analyzed by the 5c–6e model. The structure of 1,8-bis-(phenylselanyl)anthracene (**3**)†is also investigated for convenience of comparison, in which five C–Se⋯H⋯Se–C atoms are not aligned linearly.

1   **2** (R = OMe), **3** (R = H)
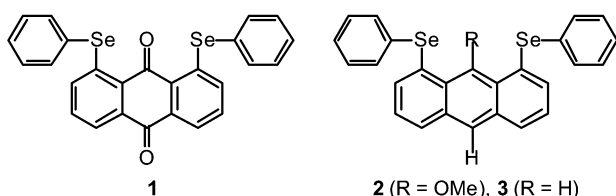
Figs. 1–3‡ show the structures of **1**–**3**, respectively.[7] Conformations around the two Se atoms are both type **B**[8] (**1** (**BB**)). Consequently, the five C–Se⋯O⋯Se–C atoms align linearly with Se(1)–O(1)–Se(2) 153°. The slightly bent alignment is a reflection of the differences in the r(C,O) and r(C,Se) values. The structure of **1** is close to C_2 symmetry. The two phenyl planes in **1** are perpendicular to the anthraquinone plane. Conformations around the Se atoms of **2** are also both type **B**[8] (**2** (**BB**)). The five atoms in **2** also align linearly with Se(1)–O(1)–Se(2) 148°. Indeed, the structure of **2** is very similar to that of **1**, but is closer to C_s symmetry. However, the structure of **3** is very different from those of **1** and **2**. The conformations around the Se atoms are both type **A**[8] (**3** (**AA**)). Two phenyl groups are located at the same sides of the plane (**3** (**AA-cis**)). It is well demonstrated that the double type **A** structure in **3** changes dramatically to the double type **B** in **1** and **2** with each O atom at the 9-position.

The p-type lone pair orbitals of the O atoms (n_{p_x}(O)) in **1** and **2** extend toward the Se atoms (the axes in **1** (and **2**) are defined in Fig. 4). Observed non-bonded Se⋯O distances of 2.67–2.74 Å are about 0.7 Å shorter than the sum of their van der Waals radii (3.40 Å).[9] Therefore, n_{p_x}(O) directly overlaps with the σ*(Se–C) orbitals at both sides of n_{p_x}(O). If the two non-bonded O⋯Se–C 3c–4e interactions are connected effectively through the central n_{p_x}(O), the non-bonded σ*(C–Se)⋯n_{p_x}(O)⋯σ*(Se–C) 5c–6e arrangement is formed. The 5c–6e interaction must play an important role in the double type **B** structures of **1** and **2**.

Fig. 2 Structure of **2**. Selected bond lengths (Å), angles (°) and torsion angles (°): Se(1)–C(1), 1.930(4), Se(1)–C(15) 1.921(5), Se(2)–C(11) 1.932(5), Se(2)–C(21) 1.938(5), C(13)–O 1.387(5), C(27)–O 1.436(6), Se(1)–O 2.731(3), Se(2)–O 2.744(3); C(1)–Se(1)–C(15) 99.2(2), C(11)–Se(2)–C(21) 99.9(2), C(13)–O–C(27) 111.7(4), Se(1)–O–Se(2) 147.9(1); C(14)–C(1)–Se(1)–C(15) –163.1(4), C(12)–C(11)–Se(2)–C(21) 175.8(4), C(1)–Se(1)–C(15)–C(16) –104.2(5), C(11)–Se(2)–C(21)–C(22) 88.3(5), C(14)–C(13)–O–C(27) 89.1(5).
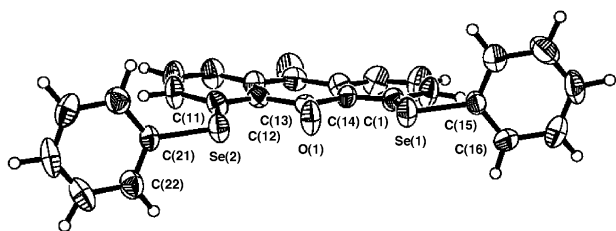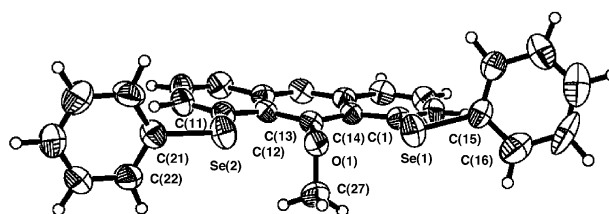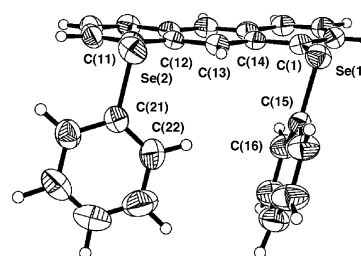

Fig. 1 Structure of **1**. Selected bond lengths (Å), angles (°) and torsion angles (°): Se(1)–C(1), 1.922(7), Se(1)–C(15) 1.924(6), Se(2)–C(11) 1.917(6), Se(2)–C(21) 1.927(6), C(13)–O(1) 1.225(7), Se(1)–O(1) 2.688(4), Se(2)–O(1) 2.673(4); C(1)–Se(1)–C(15) 98.5(3), C(11)–Se(2)–C(21) 100.2(3), Se(1)–O(1)–Se(2) 152.5(2); C(14)–C(1)–Se(1)–C(15) –172.8(6), C(12)–C(11)–Se(2)–C(21) –171.3(5), C(1)–Se(1)–C(15)–C(16) 90.5(6), C(11)–Se(2)–C(21)–C(22) 103.5(6).

Fig. 3 Structure of **3**. Selected bond lengths (Å), angles (°) and torsion angles (°): Se(1)–C(1) 1.923(3), Se(1)–C(15) 1.923(3), Se(2)–C(11) 1.943(3), Se(2)–C(21) 1.931(3); C(1)–Se(1)–C(15) 100.3(1), C(11)–Se(2)–C(21) 98.3(1); C(14)–C(1)–Se(1)–C(15) 72.6(3), C(12)–C(11)–Se(2)–C(21) –103.0(3), C(1)–Se(1)–C(15)–C(16) 6.7(3), C(11)–Se(2)–C(21)–C(22) 85.8(3).
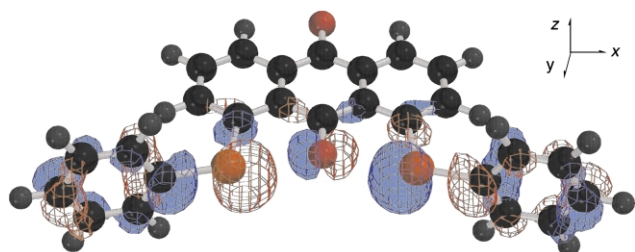
**Fig. 4** HOMO − 2 drawn on the optimized structure of **1** (**BB**).

Quantum chemical calculations are performed on **1**–**3**, together with 1-(phenylselanyl)anthraquinone (**4**) and 9-(methoxy)-1-(phenylselanyl)anthracene (**5**), at the DFT (B3LYP) level.[10] Conformers, **AA**, **AB** and **BB**, are optimized to be stable for **1** and **2**, which correspond to 3c–6e, 4c–6e and 5c–6e, respectively. The results are collected in Table 1.[11] Energies evaluated for each process from **1** (**AA**) to **1** (**BB**) (32–29 kJ mol^{-1}) are very close to that in **4**.[12] The average value from **2** (**AA**) to **2** (**BB**) (18 kJ mol^{-1}) is close to that in **5**.[12] These results demonstrate that the non-bonded σ*(C–Se)···n$_{p_x}$(O)···σ*(Se–C) 5c–6e interaction is effectively present in **1** and **2**.[13] The two non-bonded 3c–4e interactions are well connected through the central n$_{p_x}$(O) orbital. Some MOs in **1** and **2** extend over the five C–Se···O···Se–C atoms as shown in Fig. 4, exemplified by HOMO − 2 in **1** (**BB**),[14] which supports the above discussion.

Table 1 Relative energies of the conformers in **1**–**3**[a]

Conformation	1	2	3
AA-*trans*	0.0[b]		0.0[c]
AA-*cis*		0.0[d]	2.1
AB	−31.5	−24.4	0.5
BB	−60.6	−36.5	3.7

[a] kJ mol^{-1}. [b] $E = -5953.9764$ au. [c] $E = -5804.6946$ au. [d] $E = -5919.2120$ au.

It is worthwhile to comment on the through π-bond interactions between n$_{p_z}$(Se) and n$_{p_z}$(O) *via* the π-framework of anthracene in **1**. Since the carbonyl group acts as a good electron acceptor, electron densities at O and Se atoms in **1** become larger and smaller, relative to those without such interactions, respectively. This will create advantageous conditions for the non-bonded 5c–6e interaction, since the character of CT is of the type σ*(C–Se)←n$_{p_x}$(O)→σ*(Se–C). The rigid structure in **1**, except for the rotation around the Se–C bonds, must be advantageous for the π-conjugation. Almost equal stabilization energies calculated in each process from **1** (**AA**) to **1** (**BB**) must arise from the rigid structure. Lack of the effective π-conjugation between n$_{p_z}$(Se) and n$_p$(O) through the π-framework in **2** must be responsible for the smaller stabilization energies evaluated for the corresponding processes relative to those in **1**. The additional flexibility around C–O bonds in **2** would also play an important role in its characteristic energy profile.
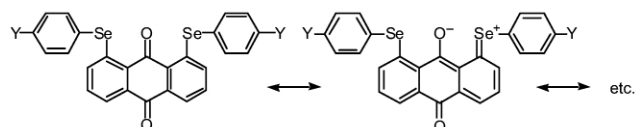
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Notes and references

‡ *Crystal data*: for **1**: monoclinic, space group $P2_1/n$ (#14), $a = 7.412(2)$, $b = 16.002(2)$, $c = 17.682(2)$ Å, $\beta = 93.58(2)°$, $V = 2092.9(7)$ Å^3, $Z = 4$. For **2**: triclinic, space group $P\bar{1}$ (#2), $a = 10.930(3)$, $b = 13.673(4)$, $c = 8.052(2)$ Å, $\alpha = 96.64(2)$, $\beta = 102.20(3)$, $\gamma = 106.48(2)°$, $V = 1107.9(6)$ Å^3, $Z = 2$. For **3**: triclinic, space group $P\bar{1}$ (#2), $a = 10.598(3)$, $b = 11.575(3)$, $c = 9.947(3)$ Å, $\alpha = 113.59(2)$, $\beta = 95.42(2)$, $\gamma = 109.39(2)°$, $V = 1017.6(6)$ Å^3, $Z = 2$. Rigaku AFC5R four-circle diffractometer, Mo-Kα radiation ($\lambda = 0.71069$ Å). The structure analyses are based on 2756 observed reflections with $I > 1.50\sigma(I)$ for **1**, on 2795 for **2** and on 3395 for **3** and 271 variable parameters for **1**, 271 for **2** and 253 for **3**. The structures of **1**–**3** were solved by heavy-atom Patterson methods (PATTY) and expanded using Fourier techniques (DIRDIF94) and refined by full-matrix least squares on $|F|^2$. $R = 0.046$, $R_w = 0.029$, GOF = 1.51 for **1**, $R = 0.040$, $R_w = 0.030$, GOF = 1.59 for **2** and $R = 0.034$, $R_w = 0.026$, GOF = 2.46 for **3**. CCDC reference numbers 175767 (**1**), 175768 (**2**) and 175769 (**3**). See http://www.rsc.org/suppdata/cc/b2/b209261a/ for crystallographic data in CIF or other electronic format.

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6 For example, Akiba *et al.* reported the 1,8-dimethoxy-9-dimethoxymethylanthracene monocation as a model of the transition state of the S_N2 reaction: K-y. Akiba, M. Yamashita, Y. Yamamoto and S. Nagase, *J. Am. Chem. Soc.*, 1999, **121**, 10644–10645; see also: M. Yamashita, Y. Yamamoto, K-y. Akiba and S. Nagase, *Angew. Chem., Int. Ed.*, 2002, **39**, 4055–4058.

7 The structures of *p,p′*-dichloro derivatives of **1** and **3** are substantially the same as those of **1** and **3**, respectively.

8 Structures of the naphthalene system, 8-G-1-(ArSe)C$_{10}$H$_6$, are well classified using type **A**, type **B** and type **C**, where the Se–C$_{Ar}$ bond is placed almost perpendicular to the naphthyl plane in type **A**, the bond is located on the plane in type **B** and type **C** is intermediate between type **A** and type **B**. The notation is applied to the structures of **1**–**3**. See ref. 2 and W. Nakanishi and S. Hayashi, *Eur. J. Org. Chem.*, 2001, **20**, 3933–3943.

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10 Gaussian 98, Revision A.9 is employed for the calculations (J. A. Pople *et al.*, Gaussian, Inc., Pittsburgh PA, 1998).[11] The 6-311+G(d) basis sets are employed for Se and O atoms and the 6-31G(d) basis sets for C and H atoms.

11 Details are shown in the ESI†.

12 **4** (**B**) and **5** (**B**) are more stable than **4** (**A**) and **5** (**A**) by 30.5 and 14.7 kJ mol^{-1}, respectively.

13 Model calculations are also performed on model **a** (H$_a$·H$_b$,^{B}Se···(H$_2$C=)O···^{A}SeH$_a$H$_b$) and model **b** (H$_a$·H$_b$,^{B}Se···(H$_2$)O···^{A}SeH$_a$H$_b$) with the B3LYP/6-311++G(3df,2pd) method. The non-bonded Se···O distances in the models are fixed at 2.658 Å, observed in the phenyl *p,p′*-dichloro derivative of **1**. No noticeable saturation is predicted in the energy lowering effect in each conformational change from type **A** to type **B** in the models. The results also support the 5c–6e nature of the σ*(H–Se)···n$_{p_x}$(O)···σ*(Se–H) interaction in the models.

14 The MacSpartan Plus program Ver. 1.0 is used (H. J. Hehre, Wavefunction Inc., Irvine, CA 92612, USA).