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First Br_4 four centre–six electron and Se_2Br_5 seven centre–ten electron bonds in nonionic bromine adducts of selenanthrene

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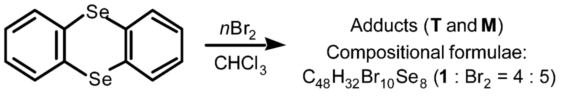
Extended hypervalent Br_4 4c–6e and Se_2Br_5 7c–10e bonds are detected in nonionic bromine adducts of selenanthrene, where the four Br_4 and seven Se_2Br_5 atoms align linearly.

Extended hypervalent bonds (*mc*–*ne* ($m \geqslant 4$))[1] are of great interest. The nature of 4c–6e bonds is very different from that of 3c–4e bonds.[2,3] Linear Z_4 atoms, where Z = Br,[4] I,[5] Se[6] and S,[7] are reported to contain some 4c–6e bonds. However, linear Br_4 atoms are ionic species whilst Se_4 and S_4 exist by fixing suitable nonbonding distances. Our strategy to construct *mc*–*ne* ($m \geqslant 4$) bonds is to employ nonbonding interactions[8] arising from direct orbital overlappings containing lone pairs.[6,9] Here, we report the first thermally stable and nonionic linear Br_4 4c–6e species of a bromine adduct of selenanthrene (**1**). The first example of 7c–10e bonds in a molecular complex (MC) of a selenide with bromine as a component is also reported.



1 (1)

Two kinds of single crystals are obtained as shown in eqn. (1).† The crystals are triclinic (**T**) when the evaporation temperature is lower than 15 °C, and are monoclinic (**M**) if the temperature is higher than 20 °C. Both crystal types have the compositional formula $C_{48}H_{32}Br_{10}Se_8$ and have a ratio of **1** : Br_2 = 4 : 5. The X-ray crystallographic analyses were carried out for **T** and **M** crystals at −70 °C and 15 °C, respectively.‡ Both adducts are represented by (**1**·Br_2–Br_2–**1**·Br_2) + 2(**1**·Br_2), with the adduct **1**·Br_2 having a trigonal bipyramidal structure (TB).

Figs. 1 and 2 show partial structures of **T** and **M** (**1**·Br_2–Br_2–**1**·Br_2), respectively, which are denoted by **2** and **3**, respectively. The bromine molecule is evidently included between Br(1) and Br(1)* atoms in **2**, with no significant secondary Se–Br interactions (Fig. 1). The formation of the Z-shaped Br(2)–Se(1)–Br(1)–Br(3)–Br(3)*–Br(1)*–Se(1)*–Br(2)* skeleton linkage is the driving force for the formation of **2**. The internal Br(1)–Br(3)–Br(3)*–Br(1)* bond is linear with *r*(Br(1)–Br(3)) = 3.134(1) Å, *r*(Br(3)–Br(3)*) = 2.331(2) Å and ∠Br(1)Br(3)Br(3)* = 172.02(6)°.[10] To the best of our knowledge this observation is the first example of linear Br_4 atoms forming a nonionic species. The angle between the two external bonds [Br(1)–Se(1)–Br(2) and Br(1)*–Se(1)*–Br(2)*] and the internal bond, *i.e.*, ∠Se(1)Br(1)Br(3), is 102.60(3)°.

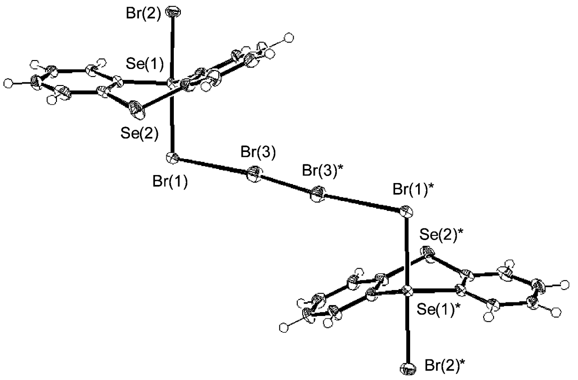


Fig. 1 Structure of **2**, the partial structure of **T**, with displacement ellipsoids shown at the 50% probability level. The * symbol in the atom labels refers to atoms at equivalent position (2 − *x*, 1 − *y*, 2 − *z*).

In order to elucidate the nature of the 4c–6e bonds in **2**, quantum chemical calculations were performed on ^{B}Br–H_2Se–^{A}Br–Br–Br–^{A}Br–H_2Se–^{B}Br (**4**), H_2SeBr_2 (TB) (**5**) and Br_2, employing the MP2/6-311+G(3d,2p) method.[11] Species **4** was optimized with C_i symmetry and was evaluated to be more stable than its components: $\Delta E(\mathbf{4}) = E(\mathbf{4}) - \{2E(\mathbf{5}) + E(Br_2)\} = -53.3$ kJ mol^{-1}.[12] Fig. 3 exhibits the optimized structure of **4**, together with the natural charges (*Qn*).[13] HOMO-2 is also depicted in Fig. 3. Its character of the Br_4 4c–6e bonds is ψ_3.[14,15] These results demonstrate that the linear Br_4 bond is well fitted by the 4c–6e model. The driving force for the formation of Br_4 4c–6e bonds must be the large negative charge development at the ^{A}Br atoms of the ^{A}Br–Se–^{B}Br 3c–4e bonds.

In the case of **3**, the bromine molecule is clearly joined to the divalent Se atom of **1**·Br_2 to yield an MC (**1**·Br_4 (TB, MC)) with *r*(Se(2)–Br(3)) = 2.641(2) Å (Fig. 2).[10] The divalent Se atom in **1**·Br_2 reacts with bromine to give the MC. To the best of our knowledge, this is the first example of MC formation of a selenide with bromine determined by X-ray crystallographic analysis.[16] The effective electronegativity of the divalent Se atom in **1**·Br_2 is large enough to give an MC with bromine due to the strong electron-withdrawing ability of the neighboring $SeBr_2$ group. The bulkiness of the group must also be advantageous for MC formation since the MC is tri-coordinated whereas the TB structure is tetra-coordinated. The Br(2) atom is placed close to the trivalent Se atom

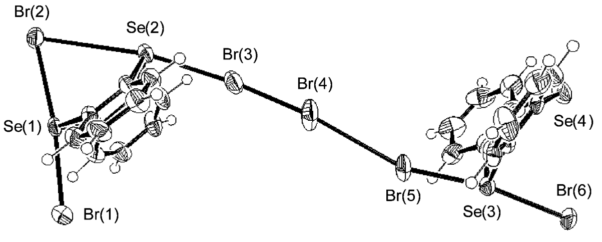


Fig. 2 Structure of **3**, the partial structure of **M**, with displacement ellipsoids shown at the 50% probability level.

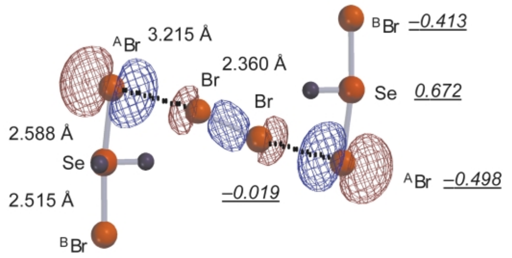


Fig. 3 Optimized structure of **4** with bond distances and *Qn* (underlined) (∠BrSeBr = 170.5°, ∠SeBrBr = 80.6° and ∠BrBrBr = 168.4°), together with the HOMO-2 (ψ_3 of Br_4) drawn on the structure.

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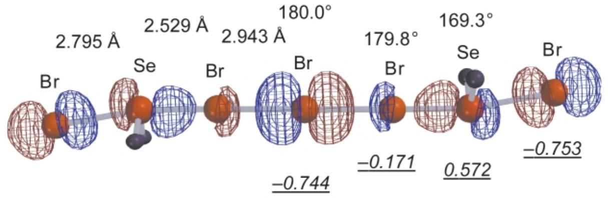

Fig. 4 Optimized structure of **6** with bond distances, angles and *Qn* (underlined), together with HOMO (ψ_5 of Se_2Br_5) drawn on the structure.

in **1**·Br_4 (r(Se(2)–Br(2)) = 3.206(2) Å), which results in the formation of a new linear Br(2)–Se(2)–Br(3)–Br(4) 4c–6e bond. The electrostatic force between the positively charged Se(2) in Se(2)–Br(3)–Br(4) and the highly negatively charged Br(2) in Br(1)–Se(1)–Br(2) must also contribute to such a short r(Se–Br(2)) distance.

The Br(2)–Se(2)–Br(3)–Br(4)–Br(5)–Se(3)–Br(6) skeleton linkage in **3** is close to being linear. How is the linear Se_2Br_5 bond constructed? Model calculations were performed on $[Br–H_2Se–Br–Br–Br–SeH_2–Br]^-$ (**6**) using the MP2/6-311+G(3d,2p) method. Fig. 4 shows the results, together with *Qn*[13] values. Species **6** was optimized to be linear with C_{2h} symmetry and evaluated to be more stable than its components: $\Delta E(\mathbf{6}) = E(\mathbf{6}) - \{2E(\mathbf{5}) + E(Br^-)\} = -87.7$ kJ mol^{-1}.[12] The HOMO is depicted which has the typical ψ_5 character of 7c–10e bonds.[14] The 7c–10e character plays an important role in making the Se_2Br_5 atoms linear.[17] The linear bond in **3** is formed by CT interactions between **1**·Br_4 and **1**·Br_2,[18] although the characters of 3c–4e in Br–Se–Br and 4c–6e in Br–Se–Br–Br are partially retained. This will be discussed in further detail elsewhere.

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Notes and references

† Selenanthrene (**1**) was prepared according to the literature.[16a] 72% yield, mp 178.6 °C (DSC); δ_H($CDCl_3$) 3.86 (s, 3H), 7.24 (t, *J* 7.7, 2H), 7.85 (d, *J* 7.2, 2H), 7.91 (d, *J* 8.3, 2H), 8.23 (s, 1H). **T** was formed as deep red crystals from $CHCl_3$ at below 15 °C. Anal. calcd for **T** ($C_{48}H_{32}Se_8Br_{10}$): C, 28.27; H, 1.58. Found: C, 28.51; H, 1.59%. **M** was formed as deep red crystals from $CHCl_3$ at more than 20 °C. Anal. calcd for **M** ($C_{48}H_{32}Se_8Br_{10}$): C, 28.27; H, 1.58. Found: C, 28.41; H, 1.57%.

‡ Crystal data for **T**: triclinic, space group *P1*(#2), a = 10.6128(5) Å, b = 13.0950(6) Å, c = 10.4855(4) Å, α = 99.762(3)°, β = 106.388(4)°, γ = 79.458(3)°, V = 1363.64 Å^3, Z = 1, T = −70 °C and for **M**: monoclinic, space group *P2₁/n*(#14), a = 9.0412(2) Å, b = 20.6912(6) Å, c = 14.7923(4) Å, β = 94.369(2)°, V = 2759.20 Å^3, Z = 2, T = 15 °C, Rigaku/RAXIS-IV diffractometer, Mo-Kα radiation (λ = 0.71070 Å), $2\theta_{max}$ = 55.1°. The structure analyses are based on 4209 observed reflections with $I > 3.00\sigma(I)$ for **T** and on 4920 reflections for **M** with 299 variable parameters for **T** and 484 for **M**. The structures were solved by direct methods (SIR92) and refined by full-matrix least squares on $|F|^2$. R = 0.047, R_W = 0.071, GOF = 1.23 for **T** and R = 0.038, R_W = 0.050, GOF = 1.07 for **M**. CCDC 219237 and 219238. See http://www.rsc.org/suppdata/cc/b3/b310655a/ for crystallographic data in cif or other electronic format.

1 The meaning of the word "hypervalent" is not so clear for *m*c–*n*e ($m \geqq 4$) bonds. There must be $(n - m)$ $^{10}X^L$ atoms[2b] in an *m*c–*n*e bond. For example, there are two $^{10}Br^2$ atoms in Br_4^{2-} 4c–6e, as shown by $[^8Br^1–^{10}Br^2–^{10}Br^2–^8Br^1]^{2-}$. An extended hypervalent bond can be defined as a linear σ-type bond which contains at least one hypervalent $^{10}X^L$ (or $^9X^L$) atom (*m*c–*n*e with $m < n$). However, it is difficult to identify which atom is hypervalent if hypervalent atoms appear only in resonance structures, although the external atoms in a linear bond cannot be hypervalent.

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18 CT mainly contributing to the interactions are ψ_3(Br–Se–Br–Br) in **1**·$Br_4 \rightarrow \psi_3$(Br–Se–Br) in **1**·Br_2 and ψ_2(Br–Se–Br) in **1**·$Br_2 \rightarrow \psi_4$(Br–Se–Br–Br) in **1**·Br_4.