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Structure and Bonding in Bis(1-naphthyl) Diselenide and Bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} Tetraselenide, and Their Brominated Derivatives

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Abstract. The formation and crystal structures of bis(1-naphthyl) diselenide (**1**) and bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} tetraselenide (**2**) are described. Whereas **1** can be produced in good yields, **2** is formed only as a minor product together with the known main product, bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} diselenide. The composition of the reaction mixture is semi-quantitatively estimated by ^{77}Se NMR spectroscopy and DFT calculations. The effect of the $n^2 \rightarrow \sigma^*$(Se–Se) and $\pi \rightarrow \sigma^*$(Se–Se) secondary bonding interactions on the Se–Se bonds is discussed both by DFT calculations and comparison with literature, as available. The bromination of **1** yields monomeric (1-naphthyl)selenenyl bromide (**3**) in good yields. That of the reaction mixture of $(C_6H_4CH_2NMe_2)Se_x$ (x = 2–4) and Se_8 afforded $(C_6H_4CH_2NMe_2H)_2[SeBr_4]$ (**4**) and $(C_6H_4CH_2NMe_2H)_2[SeBr_6]$ (**5**) in addition to $(C_6H_4CH_2NMe_2)SeBr$, which has been previously reported.

Introduction

Diaryl diselenides and ditellurides are useful reagents in chemistry, since they can conveniently be oxidized and reduced (see, for instance Refs. [1–4] and references cited therein). The oxidation of diaryl diselenides and ditellurides by SO_2Cl_2, Br_2, or I_2 is known to lead to the cleavage of the chalcogen–chalcogen bond with the formation of Ar*EX* or ArEX_3 (Ar = aryl group; *E* = Se, Te; *X* = Cl, Br, I; for some illustrative examples, see Refs. [5–10] and references cited therein). The final products depend on the identity of the organic group, chalcogen, and halogen as well as on the molar ratio of the chalcogen and halogen (see Scheme 1). With bulky aryl groups or if the chalcogen atom is also involved in secondary bonding interactions, Ar*EX* is stable and has been isolated and structurally characterized, but the reaction often continues and affords ArEX_3[5–10] or also cyclic species.[11–14] In case of tellurium, mixed valence compounds of the type *R*TeTEX_2*R* are also formed.[15–18] Both Ar*EX* and ArEX_3 have also been long known as versatile electrophilic reagents for organic transformations.[1–4]

In this contribution, we report the preparation and structural characterization of a solvent-free crystal modification of bis(1-naphthyl) diselenide (**1**). We have also revisited the formation of bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} diselenide, the preparation and structural characterization of which have been reported by *Kaur* et al.[5] Recently, *Kulcsar* et al.[19] have deduced that bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} triselenide is also formed in the reaction. We were interested in seeing, whether polyselenides of a longer chain length are also formed in the reaction, and report the formation and structural characterization of bis{[2-(*N*,*N*-dimethylamino)methyl]-phenyl} tetraselenide (**2**). The experimental work is supported by high-level DFT calculations.

The oxidation of **1** by Br_2 expectedly leads to (1-naphthyl)-selenenyl bromide (**3**). The related reaction involving the product mixture from the bis{[2-(*N*,*N*-dimethylamino)methyl]-phenyl} diselenide preparation resulted in the formation of a mixture containing, in addition to the main product, bis{[2-(*N*,*N*′-dimethylamino)methyl]phenyl}selenenyl bromide,[5] also bis[(phenylmethyl)(dimethyl)ammonium] tetrabromidoselenate (**4**) and hexabromidoselenate (**5**).

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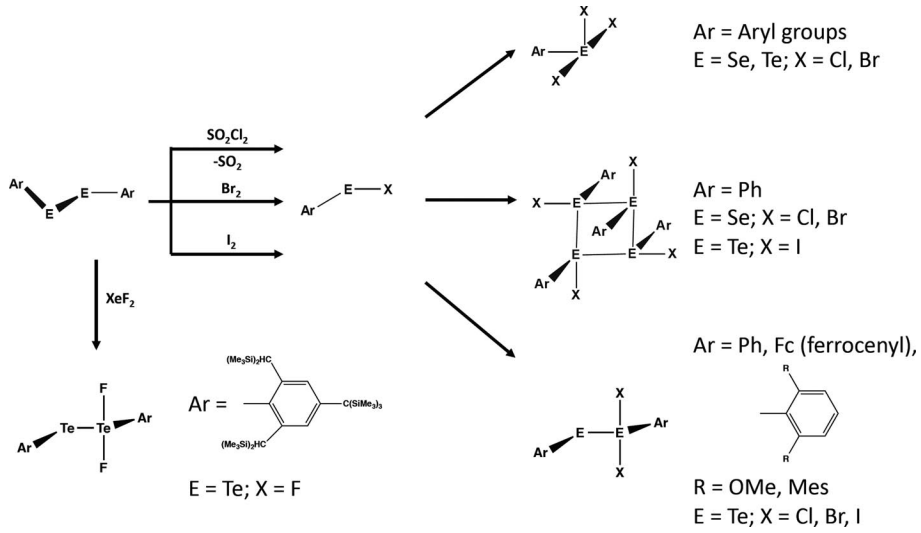
Results and Discussion

Bis(1-naphthyl) Diselenide (1)

Bis(1-naphthyl) diselenide (**1**) was prepared in a good yield by following the methods described for analogous bis(1-naphthyl) ditelluride.[20] The crystal structure of **1** together with the numbering of the atoms and selected bond parameters is shown in Figure 1.

Compound **1** is isomorphic with bis(1-naphthyl ditelluride). The Se–Se bond length is 2.3542(9) Å, the C–Se–Se bond angle is 99.7(2)°, and the C–Se–Se-C torsional angle about the Se–Se bond is 82.646(9)°. The previously reported crystal structure of **1**·($C_{10}H_8$) shows the respective values of



Scheme 1. Oxidation of diaryl dichalcogenides by SO_2Cl_2, X_2 (X = Br, I), or XeF_2.[5–18]

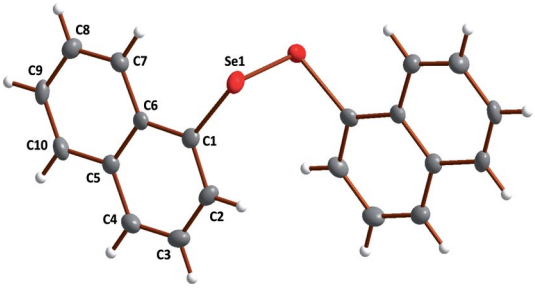


Figure 1. Molecular structure of bis(1-naphthyl) diselenide together with the atomic labeling scheme. The anisotropic displacement parameters are shown at 50% probability level. Selected bond lengths /Å and angles /°: Se1–C1 1.932(4), Se1–Se1^i 2.3545(10), C1–Se1–Se1^i 99.53(12), C1–Se1–Se1^i–C1^i –82.66(18). ^{i} Symmetry operation: $-x$, $-y$, $-z$.

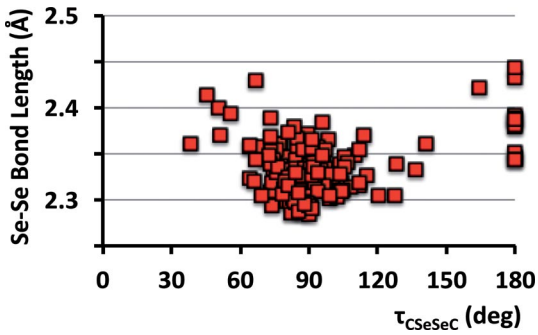


Figure 2. Distribution of Se–Se bond lengths as a function of C–Se–Se-C torsional angles in acyclic diorganyl diselenides (structural data taken from Cambridge Crystallographic Data Base[22]).

2.3429(10) Å, 100.30(8)°, and 84.29(11)°.[21] These values are quite typical for organic diselenides. The distribution of Se–Se bond lengths and the torsional angles of the structurally characterized simple diselenides are shown in Figure 2.[22] It can be seen that the majority of known diselenides show the torsional angle near to the value of 90°, as expected from the minimized repulsion of the p lone-pair of electrons of the adjacent selenium atoms, which should also render the Se–Se bond as short as possible. The range of the bond lengths, however, clearly shows that there must be other factors such as steric bulkiness of the organic groups and both intra- and intermolecular interactions, which contribute to the bond lengths observed in the solid state. The average metrical values of 2.33 Å and 94.7° calculated from the data in Figure 2, however, are close to the expected single bond parameters.

There are some clear outliers in the data, in which the torsional angle is 180° (see Figure 2). They are either caused by strong steric demand of the organic substituent or by secondary bonding $n^2 \rightarrow \sigma^*$(Se–Se) interactions.

The molecules of **1** are linked together by the $\pi \rightarrow \sigma^*$(Se–Se) interactions and the $\pi \rightarrow \pi$ interactions between the aromatic rings (see Figure 3). These interactions result in

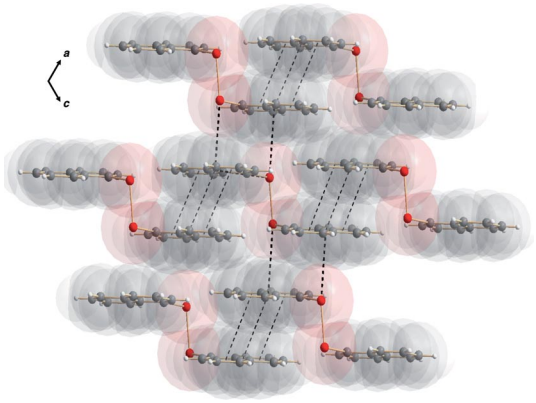


Figure 3. The $\pi \rightarrow \sigma^*$(Se–Se) and $\pi \rightarrow \pi$ interactions in bis(1-naphthyl) diselenide (**1**).

the Se···Ct (Ct = naphthyl ring centroid) close contact of 3.525 Å and the Ct···Ct close contacts ranging 4.071–4.073 Å. The Se–Se···Ct angle is 170.4°. The isomorphic bis(1-naphthyl) ditelluride shows the corresponding metrical values of 3.556 Å (Te···Ct), 4.018–4.019 Å (Ct···Ct), and 166.1° (Te–Te···Ct).[20]

Interestingly, bis(1-naphthyl) diselenide–naphthalene(1/1) adduct **1**·($C_{10}H_8$) does not show as strong π→σ*(Se–Se) interactions [the Ct···Se contacts span a range of 3.9901(14)–4.3264(14) Å].[21] Consequently, the Se–Se bond is somewhat shorter in **1**·($C_{10}H_8$) than in solvent-free **1**. There are no significant π→π interactions in **1**·($C_{10}H_8$) and the Ct···Ct contacts are 3.7272(11) Å, but the solvent naphthalene molecules link the diselenide molecules into ribbons by weak H···Ct hydrogen bonds of 2.812–2.863 Å.[21]

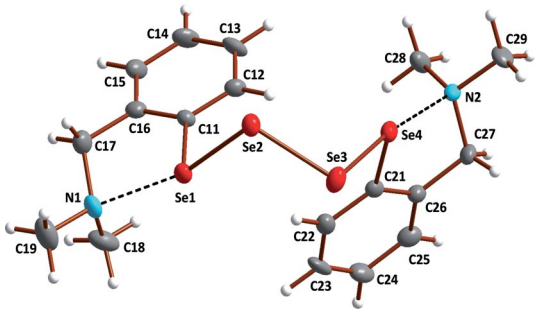


Figure 4. Molecular structure of bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} tetraselenide (**2**) together with the atomic labeling scheme. The anisotropic displacement parameters are shown at 50% probability level. Selected bond lengths /Å and angles /°: Se1–C11 1.948(5), Se4–C21 1.950(5), Se1–Se2 2.3578(9), Se2–Se3 2.3388(8), Se3–Se4 2.3814(11), C11–Se1–Se2 99.05(15), Se1–Se2–Se3 107.63(3), Se2–Se3–Se4 106.54(3), Se3–Se4–C21 99.81(15), C11–Se1–Se2–Se3 –100.51(15), Se1–Se2–Se3–Se4 92.63(3), Se2–Se3–Se4–C21 –101.60(15).

Bis{[2-(N,N-dimethylamino)methyl]phenyl} Tetraselenide (2)

Upon the reported preparation of bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} diselenide,[5] a small crop of crystals of bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} tetraselenide (**2**) was obtained by the treatment of *N*,*N*-dimethylbenzylamine with *n*-butyllithium and elemental selenium, followed by oxidation in aqueous conditions. The crystal structure of **2** together with labeling of the atoms and selected bond parameters is shown in Figure 4.

The terminal bonds of the Se_4 chain (Se1–Se2 and Se3–Se4), which show the respective lengths of 2.3578(9) and 2.3814(11) Å, are significantly longer than the Se–Se single bond (the sum of the covalent radii is 2.34 Å[23]). By contrast, the middle bond Se2–Se3 of 2.3388(8) Å is a normal single bond. The torsional angles are in the range 92.63(15) and –[100.51–101.60(15)]° (positive value clockwise, negative value counterclockwise) as expected because of p lone pair interactions. The only acyclic organyl tetraselenides, for which the crystal structures are known, are dipiperidino and dimorpholino tetraselenide.[24] The former shows the terminal and middle Se–Se bond lengths of 2.327(2) and 2.347(2) Å, respectively, and the latter 2.336(2) and 2.356(2) Å, respectively. With lack of secondary bonding interactions all Se–Se bond show normal single bond lengths in these two molecules.

We have employed DFT calculations to explore in detail the effect of the N···Se interactions on the Se–Se bonds by considering the first five members of the bis{[2-(*N*,*N*′-dimethylamino)methyl]phenyl} polyselenides. Their optimized structures together with experimental information, where available, are shown in Figure 5.

The lengthening of the terminal Se–Se bonds can be understood in terms of the $n^2(N)\rightarrow\sigma^*$ secondary bonding interactions, as shown schematically in Figure 6. The NBO analysis of $(C_6H_4CH_2NMe_2)_2Se_x$ indicates that there is a clear correlation between the extent of delocalization of the nitrogen lone

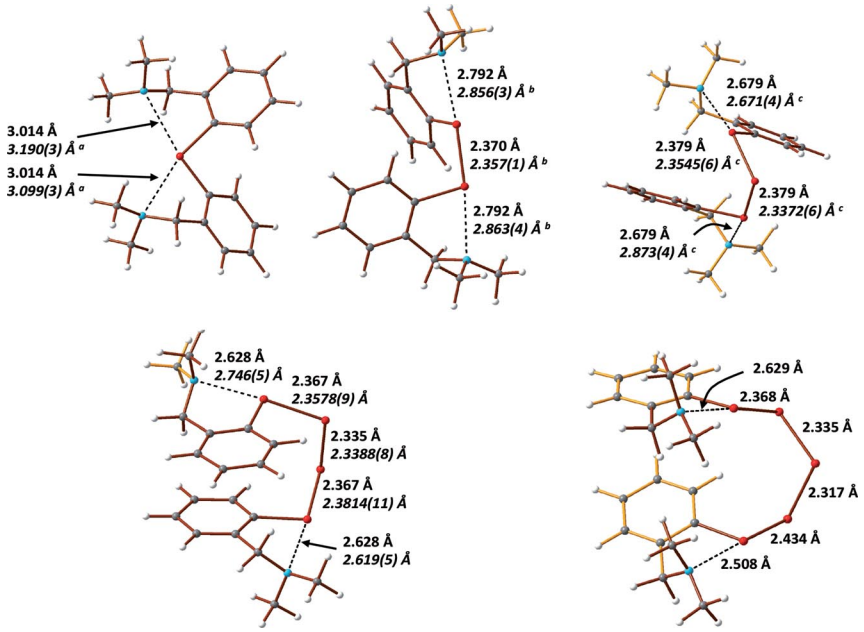


Figure 5. Selected interatomic distances in the PBE0/def2-TZVPP optimized geometries of $(C_6H_4CH_2NMe_2)_2Se_x$ (x = 1–5). The values in italics have been taken from the crystal structure determinations (this work, and [a] Ref. [25], [b] Ref. [5], [c] Ref. [19]).

Table 1. The AIM and NBO analysis of $(C_6H_4CH_2NMe_2)_2Se_2$.

Compound	N···Se Length[a)]	NBO[b)]	BCP[c)]	Se–Se Length[a)]	BCP[c)]
$(C_6H_4CH_2NMe_2)_2Se_2$	2.818	1.81	0.026	2.370	0.101
$(C_6H_4CH_2NMe_2)_2Se_3$	2.741	1.79	0.032	2.379	0.098
$(C_6H_4CH_2NMe_2)_2Se_4$	2.707	1.78	0.036	2.367	0.101
$(C_6H_4CH_2NMe_2)_2Se_5$	2.508	1.78	0.046	2.434	0.091
	2.629	1.75	0.036	2.368	0.100

a) PBE0/def2-TZVPP optimization. b) Delocalization of nitrogen p lone pair. c) Electron density at bond critical point.

pairs to the σ*(Se–Se) orbital and the length of the Se–Se bond (see Table 1). Similarly, the AIM results indicate that as the electron density at the bond critical point of the N···Se interaction increases, the terminal Se–Se bond lengthens. These deductions can be extended to the related $C_6H_4CH_2NR_2SeX$ species (*X* = Cl, Br, I, S*R′*, Se*R′*) for which a number of crystal structures are known.[22] It can be seen from Figure 6 that the Se–*X* bond order correlates inversely with the strength of the N···Se interaction. Furthermore, the increasing electronegativity of the *X* moiety increases the N···Se interaction and therefore weakens the Se–*X* bond.

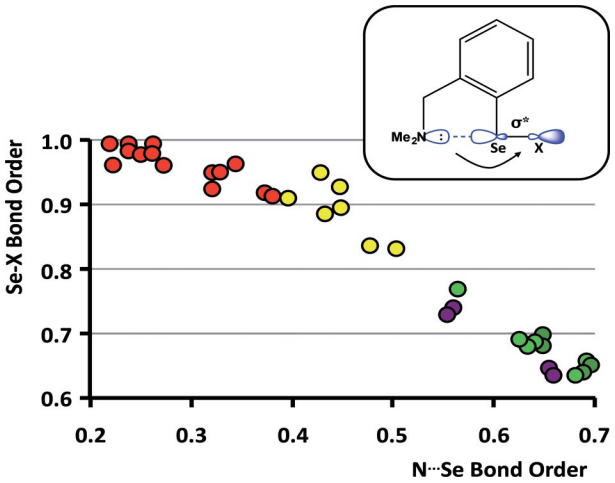


Figure 6. The inverse relationship between the Pauling bond orders of the N···Se interaction and the Se–*X* bonds in $(C_6H_4CH_2NMe_2)SeX$ [*X* = Se*R* (red), S*R* (yellow), I (violet), Br (dark green), Cl (bright green)]. Crystal structures are taken from this work and from the Cambridge Crystallographic Data Base.[22] The bond orders are calculated by utilizing the Pauling relationship:[26] $BO = e^{-(D-R)/0.71}$, where *D* is the sum of covalent radii of the two atoms in question, and *R* the actual distance between them. The covalent radii are taken from Ref. [23].

The composition of the product mixture, which was formed in the preparation of bis{[2-(*N*,*N*-dimethylamino)methyl]-phenyl} diselenide could be inferred by ^{77}Se NMR spectroscopy and DFT calculations. The ^{77}Se NMR spectrum indicated that the main product was the expected bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} diselenide (δ = 422 ppm[5]). Bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} triselenide [δ = 583 and 614 ppm (the intensity ratio of 2:1)], and bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} tetraselenide (**2**) [δ = 634 and 643 ppm (the intensity ratio of 1:1)] were only formed in small amounts. In addition, the presence of Se_8 (δ = 612 ppm[27,28]), and one, yet unidentified species exhibiting a ^{77}Se resonance at δ = 485 ppm could be observed. The logical candidate for the assignment of this resonance would be bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} selenide, but its chemical shift in $CDCl_3$ has been reported to be 340.8 ppm.[25]

The relative intensities of the ^{77}Se NMR resonances also facilitated the semi-quantitative estimation of the product distribution, as shown in Table 2.

The energetics based on the DFT calculations can be utilized to rationalize the molecular distribution of $(C_6H_4CH_2NMe_2)_2Se_x$. The PBE0/Def2-TZVPP total energies of the optimized geometries of relevant polyselenides are shown in Table 3. These values can be used to calculate the change in Gibbs' energy in the course of the following disproportionation reactions:

$$(C_6H_4CH_2NMe_2)_2Se_2 \rightleftarrows (C_6H_4CH_2NMe_2)_2Se + {}^1/_8Se_8; \quad \Delta G_1^\circ = 11.19\ kJ{\cdot}mol^{-1} \quad (1)$$

$$(C_6H_4CH_2NMe_2)_2Se_2 \rightleftarrows (C_6H_4CH_2NMe_2)_2Se + (C_6H_4CH_2NMe_2)_2Se_3; \quad \Delta G_2^\circ = 14.77\ kJ{\cdot}mol^{-1} \quad (2)$$

$$(C_6H_4CH_2NMe_2)_2Se_3 \rightleftarrows (C_6H_4CH_2NMe_2)_2Se_2 + (C_6H_4CH_2NMe_2)_2Se_4; \quad \Delta G_3^\circ = -2.68\ kJ{\cdot}mol^{-1} \quad (3)$$

$$(C_6H_4CH_2NMe_2)_2Se_4 \rightleftarrows (C_6H_4CH_2NMe_2)_2Se_3 + (C_6H_4CH_2NMe_2)_2Se_5; \quad \Delta G_4^\circ = 24.38\ kJ{\cdot}mol^{-1} \quad (4)$$

Table 2. The product distribution in the reaction mixture obtained in the preparation of bis[2-(*N*,*N*-dimethylamino)methylphenyl] diselenide.

	^{77}Se chemical shifts	Observed relative content[a)] /mol %	Computed relative content[b)] /mol %
$(Me_2NCH_2C_6H_4)Se$	–		0.1
$(Me_2NCH_2C_6H_4)Se_2$	422	50	58.8
$(Me_2NCH_2C_6H_4)Se_3$	618 (*1*), 538 (*2*)[c)]	28	16.4
$(Me_2NCH_2C_6H_4)Se_4$	643 (*1*), 634 (*1*)[c)]	9	11.8
$(Me_2NCH_2C_6H_4)Se_5$	–	–	<0.01
Se_8	612	13	12.9

a) The relative content of the molecular species were estimated from the intensities of the ^{77}Se resonances. b) The calculated relative content is based on equilibrium contents calculated from the PBE0/def2-TZVP energetics (see Table 3). c) The values in parenthesis shown in italics are the relative intensities of the two resonances in question.

Table 3. The PBE0/Def2-TZVPP total energies (a.u.) of the optimized structures of $(C_6H_4CH_2NMe_2)_2Se_x$ (x = 1–4).

Compound	Total energy[a)]	Thermal energy	Thermal enthalpy	Gibb's energy
$(C_6H_4CH_2NMe_2)_2Se$	–3210.111107	–3210.089374	–3210.08843	–3210.162974
$(C_6H_4CH_2NMe_2)_2Se_2$	–5611.411612	–5611.387726	–5611.386782	–5611.468336
$(C_6H_4CH_2NMe_2)_2Se_3$	–8012.710428	–8012.684804	–8012.68386	–8012.768073
$(C_6H_4CH_2NMe_2)_2Se_4$	–10414.01407	–10413.98636	–10413.98542	–10414.07483
$(C_6H_4CH_2NMe_2)_2Se_5$	–12815.30814	–12815.27855	–12815.27761	–12815.37230

a) Zero-point correction included in total energies.

The equilibrium constants for the four reactions can be calculated from these Gibbs' energies and it enables the computation of the equilibrium composition of the five selenides and Se_8. The computed relative content of the species is also presented in Table 2. It can be seen that the calculated equilibrium composition of the reaction mixture agrees well with that deduced by ^{77}Se NMR spectroscopy. Similar equilibrium between related bis[8-(dimethylamino)naphthyl] di-, tri-, and tetratelluride has recently been reported.[29]

1-Naphthylselenenyl Bromide (3), Bis[(phenylmethyl)-dimethylammonium] Tetrabromidoselenate (4), and Hexabromidoselenate (5)

The oxidation of bis(1-naphthyl) diselenide (**1**) by bromine afforded 1-naphthylselenenyl bromide (**3**) in good yields. The crystal structure of **3** together with the labeling of atoms and selected bond parameters are shown in Figure 7.

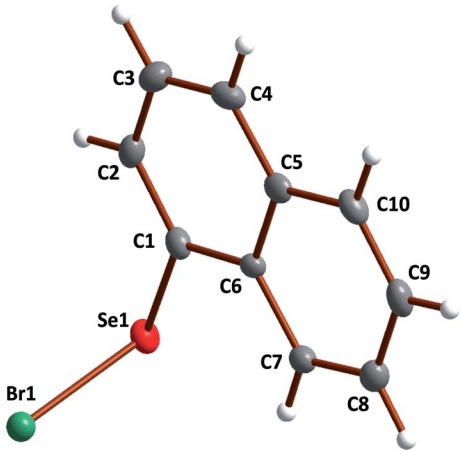


Figure 7. Molecular structure of bis(1-naphthyl)selenenyl bromide (**3**) together with the atomic labeling scheme. The anisotropic displacement parameters are shown at 50% probability level. Selected bond lengths /Å and angles /°: Se1–C1 1.916(4), Se1–Br1 2.3619(7), C1-C1–Se1–Br1 98.64(12).

The Se–Br bond in **3** shows a length of 2.3619(7) Å approaching that of a single bond (the sum of covalent radii of selenium and bromine is 2.31 Å[23]). The angle between the naphthyl ring and the Se–Br bond is 88.35(6)°. The slight lengthening of the bond is probably due to the weak π→σ*(Se–Br) interaction of 3.284(4) Å from the naphthyl ring of the adjacent molecule in the lattice (see Figure 8). The Se–Br bond length of **3** is consistent with those of the Se–Br bonds in 2,4,6-$(X)_3C_6H_2SeBr$ (X = Me, CF_3, tBu), which show the metrical values ranging 2.3101(6)–2.3358(6) Å [the angles of the Se–Br bonds and the benzene rings span a range 85.87(7)–89.29(12)°].[6] The related 1,4-(BrSe)C_6H_4 exhibits the Se–Br bond lengths and the corresponding angles of 2.3107(18)–2.3687(17) Å and 38.0(2)–75.9(2)°, respectively.[30] All these molecules show only very weak or no π→σ*(Se–Br) or n^2→σ*(Se–Br) interactions.

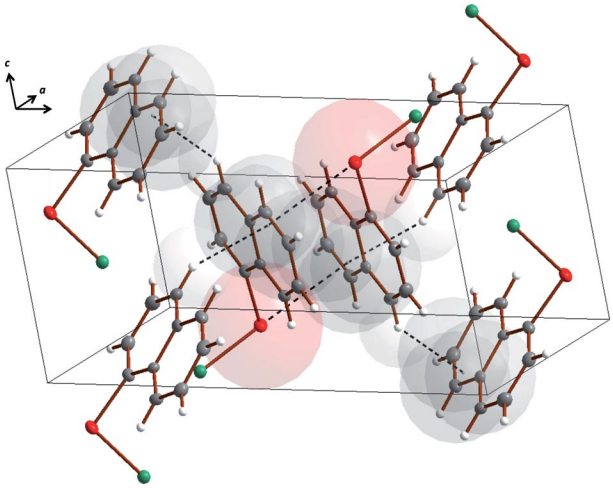


Figure 8. The π→σ*(Se–Br) interactions in (1-naphthyl)selenenyl bromide (**3**).

However, as shown in Figure 6, there are also organic selenium halides with significant secondary bonding interactions. As they get stronger, the Se–Br bond expectedly gets longer. At the same time the Se–Br bond approaches co-planarity with respect to the plane of the aromatic ring.

When the mixture of bis{[2-(*N*,*N*-dimethylamino)methyl]-phenyl} selenides and selenium was treated with Br_2, a mixture of {[2-(*N*,*N*-dimethylamino)methyl]phenyl}selenenyl bromide, bis[(phenylmethyl)dimethylammonium] tetrabromidoselenate (**4**), and hexabromidoselenate (**5**) was obtained. The crystal structures of **4** and **5** together with the labeling of atoms and selected bond parameters are shown in Figure 9. The crystal structure of {[2-(*N*,*N*-dimethylamino)methyl]phenyl}-selenenyl bromide is known.[5]

The Se–Br bonds in **4** and **5** are 2.5888(8)–2.5960(10) Å and 2.5338(17)–2.6149(17) Å. respectively. The square-planar arrangement in $[SeBr_4]^{2-}$ of **4** is well-known[31–33] and is rationalized by the six electron pair AX_4E_2 anions. While $[SeBr_6]^{2-}$ is a seven-membered AX_6E anion, it is an almost regular octahedron (for other representative crystal structures of the anion, see Refs. [34–41]). The regular arrangement can

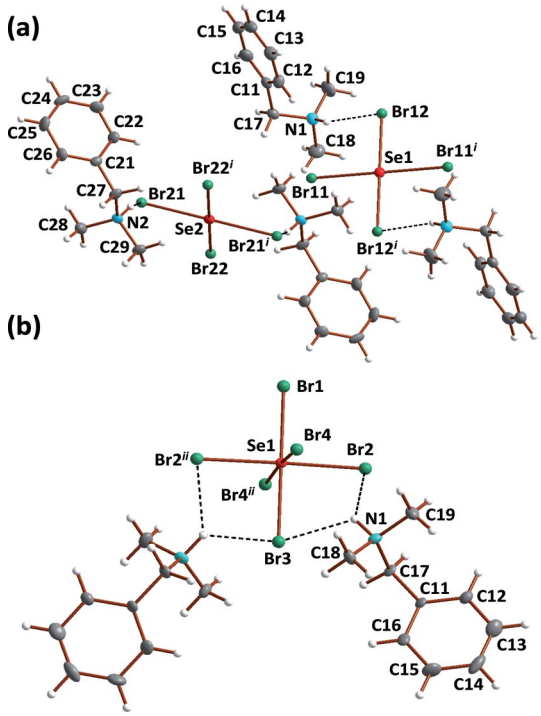


Figure 9. Molecular structure of (a) bis[(phenylmethyl)(dimethyl)ammonium] tetrabromidoselenate (**4**) and (b) bis[(phenylmethyl)(dimethyl)ammonium] hexabromidoselenate (**5**) together with the atomic labeling scheme. The anisotropic displacement parameters are shown at 50 % probability level. Selected bond lengths /Å and angles /°: (a) Se1–Br11 2.5888(8), Se1–Br12 2.5960(10), Se2–Br21 2.6024(9), Se2–Br22 2.5919(10), Br11–Se1–Br11^{i} 180.0, Br11–Se1–Br12 90.46(3), Br11–Se1–Br12^{i} 89.54(3), Br12–Se1–Br12^{i} 180.0, Br21–Se2–Br21^{i} 180.0, Br21–Se2–Br22 89.51(3), Br21–Se1–Br22^{i} 90.49(3), Br22–Se1–Br22^{i} 180.0. (b) Se1–Br1 2.5340(17), Se1–Br2 2.5751(9), Se1–Br3 2.6148(17), Se1–Br4 2.5812(9), Br1–Se1–Br2 90.61(3), Br1–Se1–Br2^{ii} 90.61(3), Br1–Se1–Br3 180.0, Br1–Se1–Br4 92.96(3), Br1–Se1–Br4^{ii} 92.96(3), Br2–Se1–Br3 89.39(3), Br2–Se1–Br3^{ii} 89.39(3), Br2–Se1–Br4 87.68(3), Br2–Se1–Br4^{ii} 87.68(3), Br3–Se1–Br4 87.04(3), Br3–Se1–Br4^{ii} 87.04(3), Br4–Se1–Br4^{ii} 174.08(6). Symmetry operations: (*i*) –*x*, –*y*, –*z*. (ii) –*x*+½, –*y*–½, *z*.

be attributed to the presence of the selenium lone pair in the stereochemically inactive 4s orbital in a similar fashion as the 5s electron pair in the case of $[TeX_6]^{2-}$ (X = Cl, Br, I).[42,43] The long Se–Br bonds can be rationalized in terms of 3c-4e bonds, in which only the selenium 4p orbitals participate.[44]

The formation of $(C_6H_4NMe_2H)_2[SeBr_4]$ (**4**) and $(C_6H_4NMe_2H)_2[SeBr_6]$ (**5**) can be explained by considering the molecular composition of the reaction mixture of $(C_6H_4CH_2NMe_2)_2Se_x$, which is shown in Table 2. *Hauge* et al.[32] have reported the preparation of $(C_6H_5NMe_3)_2[SeBr_4]$ from elemental selenium, Br_2, and $(C_6H_5NMe_3)Br$. The addition of Br_2 under ambient conditions to the solution containing $(C_6H_4CH_2NMe_2)_2Se_x$ produces significant amounts of $(C_6H_4CH_2NMe_2)SeBr$ and possibly also $(C_6H_4CH_2NMe_2)SeBr_3$, as shown in Scheme 1. Since the reaction solution contains Se_8 and it is likely that under ambient conditions it also contains HBr, all ingredients for the production of $(C_6H_4NMe_2H)_2[SeBr_4]$ (**4**) are present. $(C_6H_4NMe_2H)_2[SeBr_6]$ (**5**) may be formed from **4** by further reaction with Br_2.

Conclusions

In this contribution, we have prepared and structurally characterized bis(1-naphthyl) diselenide (**1**). The related reaction to produce bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} diselenide was found to afford, in addition to the well-known diselenide and recently characterized triselenide, also bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} tetraselenide (**2**). The composition of the product mixture could be semi-quantitatively determined by ^{77}Se NMR spectroscopy and DFT calculations. These two polyselenides together with the literature data, enabled the discussion of the effect of the $n^2 \rightarrow \sigma^*$(Se–Se) and $\pi \rightarrow \sigma^*$(Se–Se) secondary bonding interactions on the Se–Se bonds.

The bromination of **1** afforded (1-naphthyl)selenenyl bromide (**3**) in good yields. The related reaction of the mixture containing $(C_6H_4CH_2NMe_2)_2Se_x$ (x = 2–4) and Se_8 resulted in the formation of bis[(phenylmethyl)dimethylammonium] tetrabromidoselenate (**4**) and hexabromidoselenate (**5**) in addition to $(C_6H_4CH_2NMe_2)SeBr$. A reaction pathway for the formation of **4** and **5** was proposed.

Experimental Section

General Procedures: All reactions were carried out in an argon atmosphere using standard Schlenk techniques, unless otherwise stated. Diethyl ether (Baker) and THF (Rathburn chemicals) were dried over Na/benzophenone and CH_2Cl_2 (VWR) over P_2O_5. All the solvents were distilled under an argon atmosphere prior to use. 1-Naphthylbromide (Merck) was distilled before use. Se (Merck) was freshly ground before use, and bromine (Fluka), magnesium (Fluka), and *N*,*N*-dimethylbenzylamine (Aldrich) were used as received.

The ^{77}Se NMR spectra were recorded with a Bruker Avance III 400 spectrometer. A saturated D_2O solution of selenium dioxide was used as external standard. The ^{77}Se chemical shifts are reported relative to neat Me_2Se {$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$}.[45] All spectra were recorded unlocked.

X-ray Crystallography: Diffraction data for compounds **1**–**5** were collected with a Nonius Kappa CCD diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Crystal data and the details of the structure determinations are given in Table 4. The structures were solved by direct methods using SHELXS-2013 and refined using SHELXL-2013.[46] After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions. In the final refinement the calculated hydrogen atoms were riding with the carbon atom they were bonded to. The isotropic thermal parameters of the aromatic hydrogen atoms were fixed at 1.2, and those of aliphatic hydrogen atoms at 1.5 times to that of the corresponding carbon atom. The scattering factors for the neutral atoms were those incorporated with the program.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies

Table 4. Crystal data and details of the structure determinations of bis(1-naphthyl) diselenide (**1**), bis[2-(*N*,*N*-dimethylamino)methylphenyl] tetraselenide (**2**), 1-naphthylselenenyl bromide (**3**), bis[(phenylmethyl)dimethylammonium] tetrabromidoselenate (**4**), and bis[(phenylmethyl) dimethylammonium] hexabromidoselenate (**5**).

	1	**2**	**3**	**4**	**5**
Empirical formula	$(C_{10}H_7Se)_2$	$C_{18}H_{24}N_2Se_4$	$C_{10}H_7NBrSe$	$C_9H_{13}NBr_4Se$	$C_{18}H_{28}N_2Br_6Se$
Relative molecular mass	412.23	584.23	286.03	671.02	830.84
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic
Space group	*C*2/*c*	$P2_1/n$	$P2_1/c$	$P\bar{1}$	*Pccn*
a /Å	16.206(3)	15.024(3)	8.7886(18)	7.6184(15)	10.951(2)
b /Å	7.6788(15)	9.546(2)	14.743(3)	10.158(2)	13.237(3)
c /Å	13.820(3)	15.064(3)	7.0938(14)	15.506(3)	17.524(4)
α /°				88.07(3)	
β /°	116.14(3)	100.07(3)	102.54(3)	89.05(3)	
γ /°				89.83(3)	
V /Å^3	1543.9(6)	2127.1(8)	897.2(3)	1199.0(4)	2540.2(9)
Z	4	4	4	2	4
F(000)	808	1128	544	648	1576
$D_{calcd.}$ /g•cm^{-3}	1.773	1.824	2.117	1.859	2.172
μ(Mo-K_α) /mm^{-1}	4.782	6.902	8.573	8.236	10.924
Crystal size /mm	0.20 × 0.10 × 0.10	0.30 × 0.10 × 0.10	0.20 × 0.15 × 0.15	0.20 × 0.20 × 0.15	0.25 × 0.05 × 0.05
θ range /°	3.00–25.97	3.00–26.00	3.25–26.00	2.96–26.00	2.98–26.00
No. reflns. collected	5057	12162	4949	10992	13724
No. unique reflns.	1508	4139	1750	4599	2493
No. observed reflns.	1324	3414	1621	4124	1896
No. of parameters / restraints	101/0	221/0	110/0	234/0	126/0
R_{int}	0.0794	0.0782	0.0655	0.0796	0.0941
R_1[a,b)]	0.0388	0.0459	0.0340	0.0515	0.0528
wR_2	0.0833	0.1051	0.0889	0.1299	0.0904
R_1 (all data)[b)]	0.0471	0.0610	0.0378	0.0579	0.0817
wR_2 (all data)	0.0878	0.1132	0.0914	0.1358	0.1014
Goodness-of-fit on F^2	1.162	1.092	1.105	1.099	1.197
$\Delta\rho_{max,\ min}$ /e•Å^{-3}	0.934, –0.662	0.796, –1.063	0.703, –0.601	1.207, –0.908	0.933, –0.897

a) $I > 2\sigma(I)$. b) $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

of the data can be obtained free of charge on quoting the depository numbers CCDC-1044700, CCDC-1044701, CCDC-1044702, CCDC-1044703, and CCDC-1044704 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Preparation of Bis(1-naphthyl) Diselenide (1): Bis(1-naphthyl) diselenide (**1**) was prepared following the method for bis(1-naphthyl) ditelluride [20]. 1-Naphthylbromide (3.00 mL, 21.5 mmol) was added to a mixture of magnesium (0.527 g, 21.7 mmol) and I_2 (0.027 g, 0.1 mmol) in diethyl ether (50 mL). The reaction mixture was refluxed for 2 h until all the Mg was consumed. Selenium (1.610 g, 20.4 mmol) was added to the solution. When selenium had reacted, the solution was poured into a saturated NH_4Cl solution and stirred for 2 h. The product was extracted into diethyl ether, the solution was dried with $MgSO_4$, and the solvent was evaporated under reduced pressure. The oily substance was treated with ice cold ethanol to give a yellow powder of bis(1-naphthyl) diselenide. Yield: 2.245 g (54 %). $C_{20}H_{14}Se_2$ (412.24): C 58.61 (calcd. 58.27); H 3.39 (3.42) %. **^{77}Se NMR** (THF, 76.31 MHz): δ = 422 ppm.

Formation of Bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} Tetraselenide (2): Upon preparation of bis{[2-(*N*,*N*-dimethylamino) methyl]phenyl} diselenide following the method of *Kaur* et al.,[5] small amounts of tri- and tetraselenide together with Se_8 were also formed. The product mixture was characterized by ^{77}Se NMR spectroscopy. Upon crystallization from the ether/hexane mixture (2:1), a small amount of the X-ray-quality crystals of bis{[2-(*N*,*N*-dimethylamino) methyl]phenyl} tetraselenide were obtained.

Preparation of 1-Naphthylselenenyl Bromide (3): Bis(1-naphthyl) diselenide **1** (0.200 g, 0.5 mmol) was dissolved in THF in air, and upon stirring, 1.0 mL of 0.5 M THF solution of Br_2 (0.5 mmol) was slowly added to the solution. After 1 h stirring the solvent was evaporated. The residue was recrystallized from THF/benzene mixture over several days giving dark well-shaped crystals. Yield: 0.273 g (98 % based on **1**). $C_{10}H_7SeBr$ (286.03): C 41.90 (calcd. 41.99); H 2.97 (2.47) %. **^{77}Se NMR** (THF, 76.31 MHz): δ = 838 ppm.

Formation of Bis[(phenylmethyl)dimethylammonium] Tetrabromidoselenate (4) and Hexabromidoselenate (5): Bromine 0.03 mL (0.6 mmol) was added to 0.200 g of the bis{[2-(*N*,*N*-dimethylamino) methyl]phenyl} polyselenide mixture in THF. The mixture was stirred for 1.5 h, after which the volume of the solution was reduced by evaporation and cooled on an ice bath. Precipitation with *n*-hexane resulted in a red powder, which was isolated and dried. Recrystallization from the THF/benzene mixture resulted in the isolation of mixture of bis[(phenylmethyl)dimethylammonium] tetrabromidoselenate (**4**) and the hexabromidoselenolate (**5**) in addition to {[2-(*N*,*N*-dimethylamino)methyl]phenyl} selenenyl bromide.

Computational Details: The structures of five first members of bis{[2-(*N*,*N*-dimethylamino)methyl]phenyl} selenides, $(C_6H_4CH_2NMe_2)_2Se_x$ (x = 1–5), were optimized using the Gaussian 09 program[47] employing the PBE0 functional.[48,49] Grimme's D3BJ dispersion correction[50] was incorporated in the calculations. Def2-TZVPP basis sets[51] obtained from the ESML basis set exchange[52,53] was used for all elements. Fundamental frequencies were calculated for all structures to establish the nature of the stationary points. Atoms in Molecules (AIM) analysis[54] was performed using the AIMAll program[55] and the nitrogen lone pair interactions and the related population analyses were performed utilizing the NBO 5.9 program.[56]

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