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Synthetic and Structural Studies of 1,8-Chalcogen Naphthalene Derivatives

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Abstract: Four novel 1,8-disubstituted naphthalene derivatives **4**–**7** that contain chalcogen atoms occupying the *peri* positions have been prepared and fully characterised by using X-ray crystallography, multinuclear NMR spectroscopy, IR spectroscopy and MS. Molecular distortion due to noncovalent substituent interactions was studied as a function of the bulk of the interacting chalcogen atoms and the size and nature of the alkyl group attached to them. X-ray data for **4**–**7** was compared to the series of known 1,8-bis(phenylchalcogeno)naphthalenes **1**–**3**, which were themselves prepared from novel synthetic routes. A general increase in the E⋯E′ distance was observed for molecules containing bulkier atoms at the *peri* positions. The decreased S⋯S distance from phenyl-**1** and ethyl-**4** analogues is ascribed to a weaker chalcogen lone pair–lone pair repulsion acting in the ethyl analogue due to the presence of two equatorial S(naphthyl) ring conformations. Two novel *peri*-substituted naphthalene sulfoxides of **1**, Nap(O=SPh)(SPh) **8** and Nap(O=SPh)$_2$ **9**, which contain different valence states of sulfur, were prepared and fully characterised by using X-ray crystallography and multinuclear NMR spectroscopy, IR spectroscopy and MS. Molecular structures were analysed by using naphthalene ring torsions, *peri*-atom displacement, splay angle magnitude, S⋯S interactions, aromatic ring orientations and quasi-linear O=S⋯S arrangements. The axial S-(naphthyl) rings in **8** and **9** are unfavourable for S⋯S contacts due to stronger chalcogen lone pair–lone pair repulsion. Although quasi-linear O=S⋯S alignments suggest attractive interaction is conceivable, analysis of the B3LYP wavefunctions affords no evidence for direct bonding interactions between the S atoms.

Keywords: ab initio calculations · chalcogens · density functional calculations · naphthalene · *peri*-substitution · X-ray diffraction

Introduction

Atomic interactions are a fundamental aspect of chemistry, biology and materials science.[1] Great advances have been made in the area of strong covalent and ionic bonding, but the major challenge for chemists of developing a full understanding of weak intra- and intermolecular forces still remains. *peri*-Substituted naphthalenes are able to constrain heavy polarisable elements in close proximity through a rigid C_2 backbone and, therefore, are ideal models for studying such non-covalent interactions.

The *peri*-carbon atoms of "ideal" naphthalene are separated by a distance of 2.44 Å,[2] which is sufficient for accommodating two hydrogen atoms, but it is reasonable to expect that larger substituents at the *peri* positions will experience considerable steric hindrance.[3] Although this is true, intramolecular interactions between *peri* substituents can also be attractive due to the presence of weak or strong bonding.[4] The ease of forming sterically crowded *peri*-substituted naphthalenes is influenced by the steric strain. This is relieved either through bond formation or interaction between *peri* atoms, or through naphthalene distortion that effectively changes the geometry away from that of ideal naphthalene. The most common forms of naphthalene distortion are in-plane and out-of-plane deviations of the exocyclic bonds and buckling of the naphthalene ring system.[3]

The availability of X-ray structural data plays a crucial role in assessing the repulsive steric effects between heavy *peri* substituents and, therefore, quantifying the distortion in

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902523, and contains X-ray crystallographic files for compounds **4**–**9**, experimental procedures for compounds **1**–**3** and ^{77}Se chemical shift calculations for **2**, **2**$^{2+}$ and a number of mono- and diprotonated variants of **2**.

non-ideal naphthalenes.[5] Molecular structures also help to elucidate attractive effects between *peri* atoms and verify the existence of weak intra- and intermolecular interactions. To quantify the extent of naphthalene distortion taking place in a given molecule, the naphthalene geometry is compared with that of ideal, or un-substituted, naphthalene.[2] In-plane distortion is calculated by observing the sum of angles in the bay region (splay angles); in the ideal geometry these angles total 357.2° (Figure 1b).[2] If the sum of the splay angles is greater than this value (positive splay angle) we can conclude the bonds have moved apart, which indicates steric repulsion, but if the sum is lower (negative splay angle), then the atoms have come closer as a result of favourable interactions.[2,5,6]

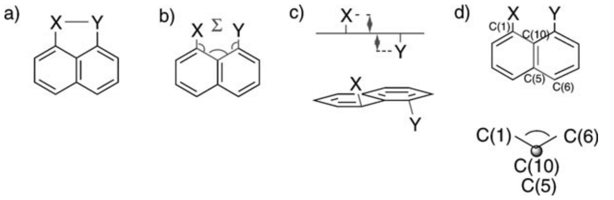
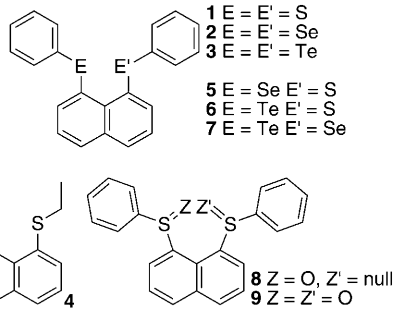


Figure 1. Measuring steric interactions and naphthalene distortions: a) *peri* distance, b) sum of the bay region angles, c) distance of the *peri* atoms from the mean naphthalene plane and d) torsion angles around the C(5)−C(10) bond.

Likewise, out-of-plane distortion can be measured from the distance that the *peri* substituents reside above and below the naphthalene plane (Figure 1c); in ideal naphthalene the *peri* hydrogens lie on the naphthyl plane.[2] Lastly, torsion angles can indicate the level of planarity in the molecule and give an insight into the degree of buckling taking place in the naphthalene ring system (as depicted by the C(1)-C(10)-C(5)-C(6) angle in Figure 1d). In ideal naphthalene, the torsion angles are either 0 or 180°, depicting total planarity.[2,5] The three types of distortion are cumulatively expressed by the value of the *peri* distance, which is used as the primary parameter when describing the distortion away from ideal and also indicates the presence of *peri*-atom interaction (Figure 1a).[5]

A number of groups have been investigating *peri*-substituted naphthalenes involving two heavy atoms at the 1,8 positions, in an effort to understand the factors that influence the degree of distortion.[7] During our own studies, we have investigated some sterically crowded 1,8-disubstituted naphthalenes.[5,8,9]

Positioning chalcogen atoms at the naphthalene 1,8 positions provides a good system with which to study the naphthalene distortion and the emergence of non-covalent *peri*-atom interactions. An ideal naphthalene model that places chalcogen atoms in the *peri* positions would result in very short non-bonded distances, smaller than the sum of the van der Waals (vdW) radii for the two atoms minus roughly 1 Å.[1,7h,10–13] The resulting steric strain occurring in non-bonded *peri*-substituted systems would be expected to cause the naphthalene to distort away from the idealised geometry; however, as non-bonded distances decrease relative to the sum of vdW radii, weak non-covalent interactions become more covalent in nature, thus reducing the steric hindrance between two heavy atoms.[14]



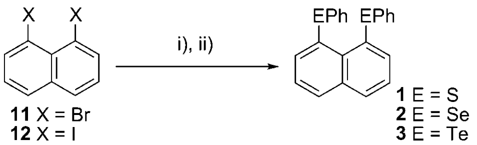
Herein we report the synthesis and structural analysis of six novel *peri*-substituted chalcogen systems **4**–**9** and compare the degree of molecular distortion and the occurrence of non-covalent intramolecular chalcogen–chalcogen interactions with the known series of compounds 1,8-bis(phenylsulfanyl)naphthalene (**1**),[14,15] 1,8-bis(phenylselanyl)naphthalene (**2**)[14,16] and 1,8-bis(phenyltelluro)naphthalene (**3**).[14,17] Compounds **1**–**3** were prepared by using new synthetic routes that were replicated for the synthesis of the novel S-(ethyl) analogue of **1**, 1,8-bis(ethylsulfanyl)naphthalene (**4**), and an analogous series of related novel mixed 1,8-(phenylchalcogeno)naphthalenes **5**–**7**. Oxidation of **1** with different molar equivalents of *meta*-chloroperoxybenzoic acid (MCPBA) afforded two novel oxides **8** and **9**. Molecular structures of **1**, **2** and **4**–**9** were determined by X-ray crystallographic analysis, although **1**[14,15] and **2**[14,16] have been previously reported.

The structures of a series of Nap[G][ZR] (nap = naphthalene-1,8-diyl; G = Cl, Br, F, H, SeMe) have been well documented by Nakanishi et al. into three geometrical types A (in which the Z−R bond lies perpendicular to the naphthyl plane), B (in which the Z−R bond lies with the naphthyl plane) and C (intermediate between A and B).[1,11,13,18] The structures for Nap[RZ][R′Z] compounds can also be classified by a pairing of geometrical types denoted by AA-*t*, AA-*c*, AB, BB or CC (-*t* denotes a *trans* conformation, -*c* denotes *cis*).[1,12–14,17,19] The molecular structures of **1**–**9** were analysed for naphthalene ring torsions, *peri*-atom displacement, splay angle magnitude, E···E′ interactions, aromatic ring orientations and quasi-linear X−E···E′ arrangements to establish geometric controlling factors. The structural conformations of **1**–**9** were characterised based on the classification system reported by Nakanishi et al.[1,12–14]

Results and Discussion

Compounds **1**–**9** were synthesised and their crystal structures were determined. Additionally, except for the three previously reported compounds (**1**–**3**),[14–17] all the new compounds were characterised by multinuclear NMR and IR spectroscopies and mass spectrometry, and the homogeneity of the new compounds was, where possible, confirmed by microanalysis.

The series of 1,8-bis(phenylchalcogeno)naphthalene compounds (**1**–**3**) was prepared through stepwise halogen–lithium exchange reactions of analogous 1,8-dibromonaphthalene (**11**)[20] and 1,8-diiodonaphthalene (**12**)[21] (Scheme 1).

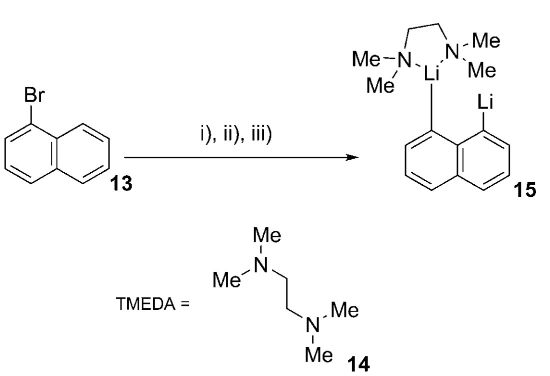


Scheme 1. The preparation of 1,8-bis(phenylchalocgeno)naphthalenes **1**–**3**. Conditions: i) *n*BuLi (2 equiv), Et_2O, −78 °C, 1 h; ii) PhEEPh (2 equiv), Et_2O, −78 °C, 1 h.

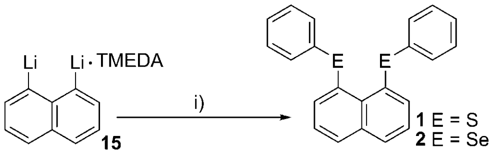
For their synthesis, compounds **11** and **12** were independently treated with two equivalents of *n*-butyllithium in diethyl ether to give the precursor, 1,8-dilithionaphthalene. Addition of diphenyl disulfide, diphenyl diselenide and diphenyl ditelluride afforded the respective doubly substituted 1,8-bis(chalcogenide) product (yield of **1**: 22, 20%; yield of **2**: 75, 82%; yield of **3**: 37, 23%; first yield for each compound based on **11** and second yield based on **12**).

Due to the laborious and low-yielding route to both 1,8-dibromo-[20] and 1,8-diiodonaphthalene,[21] a more efficient synthesis of compounds **1**–**3** was undertaken by preparing 1,8-dilithionaphthalene directly from commercially available 1-bromonaphthalene (**13**) in the presence of tetramethylethylenediamine (TMEDA; **14** Scheme 2).[22]

Dilithionaphthalene·TMEDA (**15**), formed as the exclusive product following the reflux of 1-naphthyllithium with BuLi·TMEDA (Scheme 2),[22] reacted with diphenyl disulfide and diphenyl diselenide to afford **1** (13% yield) and **2** (14% yield), respectively (Scheme 3). However, the preparation of tellurium analogue **3** from 1-bromonaphthalene and diphenyl ditelluride by using the same method was unsuccessful.



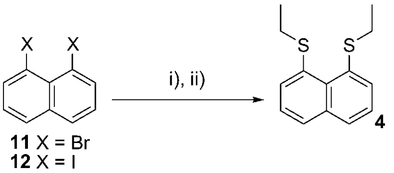
Scheme 2. The preparation of 1,8-dilithionaphthalene·TMEDA (**15**).[22] Conditions: i) *n*BuLi (1 equiv), Et_2O, −30 °C; ii) TMEDA, hexane, −30 °C; iii) *n*BuLi (1 equiv), −30 °C.



Scheme 3. The preparation of **1** and **2** from 1,8-dilithionaphthalene·TMEDA (**15**). Conditions: PhEEPh, Et_2O, −78 °C.

Compounds **1**–**3** were characterised by using elemental analysis, IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.[14–17] Compound **2** was analysed by using ^{77}Se NMR spectroscopy ($\delta = 428.6$ ppm; lit. value: $\delta = 435.4$ ppm[14]) and **3** was analysed by using ^{125}Te NMR spectroscopy ($\delta = 619.4$ ppm; lit. value: $\delta = 617$ ppm[17]).

Stepwise halogen–lithium exchange reactions of **11** and **12** were utilised for the preparation of the novel compound 1,8-bis(ethylsulfanyl)naphthalene **4** in yields of 27 and 80% based on **11** and **12**, respectively (Scheme 4).



Scheme 4. The preparation of 1,8-bis(ethylsulfanyl)naphthalene (**4**). Conditions: i) *n*BuLi (2 equiv), Et_2O, −78 °C, 1 h; ii) EtSSEt (2 equiv), Et_2O, −78 °C, 1 h.

As part of our ongoing investigation of molecular distortion in *peri*-substituted naphthalenes and intramolecular interactions, we have recently synthesised and investigated the structures of the series of compounds Nap[X][EPh] (X = Br, I; E = S, Se, Te; Figure 2).[23] Upon treatment with one molar equivalent of *n*-butyllithium followed by one equivalent of an appropriate diphenyl dichalcogenide, **11** and **12** undergo stepwise halogen–lithium exchange reactions to form singly substituted 1-halo-8-(phenylchalcogeno)naphthalenes **16**–**21** (Figure 2).[23] Further reaction of **16**–**21** with *n*-butyllithium and a suitable diphenyl dichalcogenide afforded three novel mixed chalcogen ligands (**5**–**7**).

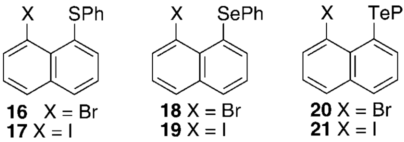
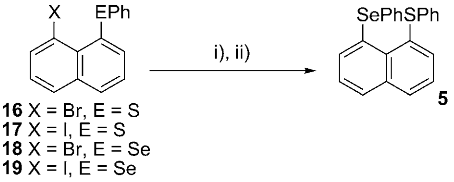


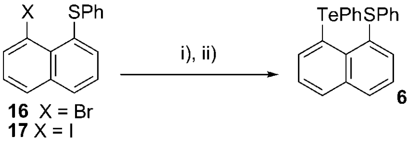
Figure 2. The products of single substitution reactions of 1,8-dibromo- and 1,8-diiodonaphthalene with diphenyl dichalcogenides.[23]

1-Bromo-8-(phenylsulfanyl)naphthalene (**16**) and 1-iodo-8-(phenylsulfanyl)naphthalene (**17**) were treated with *n*-butyllithium and diphenyl diselenide to afford the novel compound 1-(phenylselanyl)-8-(phenylsulfanyl)naphthalene **5** in 75 and 63 % yield based on **16** and **17**, respectively (Scheme 5). Analogous reactions starting from 1-bromo-8-(phenylselanyl)naphthalene (**18**) and 1-iodo-8-(phenylselanyl)naphthalene (**19**) afforded desired product **5** upon treatment with diphenyl disulfide, but in lower yields of 34 and 15 % based on **18** and **19**, respectively (Scheme 5). The ^{77}Se NMR spectrum (in $CDCl_3$) shows a single peak at $\delta=$ 455.3 ppm. Other details are given in the Experimental Section.



Scheme 5. The preparation of 1-(phenylselanyl)-8-(phenylsulfanyl)naphthalene (**5**) from 1-halo-8-(phenylsulfanyl)naphthalenes **16**, **17**, **18** and **19**. Conditions: i) *n*BuLi (1 equiv), Et_2O, −78 °C, 1 h; ii) PhEEPh (1 equiv), Et_2O, −78 °C, 1 h.

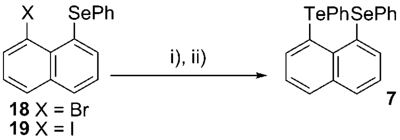
Similar halogen–lithium exchange reactions of **16** and **17** afforded compound **6** in 51 and 88 % yield, respectively (Scheme 6). The ^{125}Te NMR spectrum of **6** (in $CDCl_3$) shows a single peak at $\delta=715.2$ ppm. The preparation of **6** starting from 1-bromo-8-(phenyltelluro)naphthalene (**20**) and diphenyl disulfide was unsuccessful and may indicate that the facile cleavage of the $Te-C_{Nap}$ bond is more susceptible to attack by *n*-butyllithium rather than the bromine substituent.



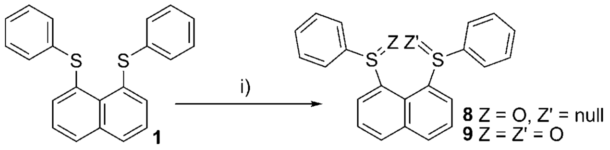
Scheme 6. The preparation of 1-(phenyltelluro)-8-(phenylsulfanyl)naphthalene (**6**). Conditions: i) *n*BuLi (1 equiv), Et_2O, −78 °C, 1 h; ii) PhTeTePh (1 equiv), Et_2O, −78 °C, 1 h.

Compound **7** was prepared by treating bromo derivative **18** and iodo derivative **19** with *n*-butyllithium and diphenyl ditelluride (81, 18 % yield based on **18** and **19**, respectively; Scheme 7). The ^{77}Se and ^{125}Te NMR spectra of **7** (in $CDCl_3$) show single peaks at $\delta=362.8$ and 687.6 ppm, respectively, with chemical shifts that are similar to those recorded for **5** (^{77}Se NMR: $\delta=455.3$ ppm) and **6** (^{125}Te NMR: $\delta=$ 715.2 ppm).

Treatment of **1** with one equivalent of *meta*-chloroperbenzoic acid (MCPBA) in diethyl ether afforded novel monosubstituted oxide **8** (Scheme 8). Reacting two equivalents of MCPBA with **1** produced dioxide **9** with both sulfur atoms mono-oxidised (Scheme 8). The treatment of **1** with further equivalents (3–6) of MCPBA gave compound **9** exclusively, and no higher oxidation to give the tri- or tetraoxide was observed.



Scheme 7. The preparation of 1-(phenyltelluro)-8-(phenylselanyl)naphthalene (**7**). Conditions: i) *n*BuLi (1 equiv), Et_2O, −78 °C, 1 h; ii) PhTeTePh (1 equiv), Et_2O, −78 °C, 1 h.



Scheme 8. The preparation of oxidised compounds **8** and **9**. Conditions: i) MCPBA (1 equiv (**8**) or 2–6 equiv (**9**)), Et_2O.

X-ray investigations: Suitable single crystals of **1**, **2** and **4**–**9** were obtained by diffusion of pentane into saturated solutions of the individual compound in dichloromethane. The molecular structures of **1**–**9** were analysed, although **1**,[14,15] **2**[14,16] and **3**[14,17] have been previously reported. Compounds **1**, **2**, **4**, **5**, **8** and **9** crystallise with one molecule in the asymmetric unit, and compounds **6** and **7** contain two nearly identical molecules in the asymmetric unit (Figure 3 shows the structures of **4**–**9**). Selected interatomic distances, angles and torsion angles are listed in Table 1. Further crystallographic information can be found in the Supporting Information.

The steric strain introduced in **1**–**3** and **5**–**7** by the substitution of heavy chalcogen atoms in the bay region is released by out-of-plane and in-plane distortions associated with significant twisting of the naphthalene backbone (see the central torsion angles of the naphthalene ring in Table 1). The degree of geometrical distortion is related to the size of the chalcogen atoms that occupy the *peri* positions in the naphthalene molecules. This is best observed when comparing the magnitude of the *peri* distance parameter for the six compounds. The E(phenyl) groups lie in close proximity, with non-bonded interatomic *peri* distances (E···E′) that display a general increase when larger atoms occupy the close-contact 1,8-positions (see Table 1). The E···E′ distances (3.00–3.29 Å) are less than the respective sum of the vdW radii for the two interacting atoms (3.60–4.12 Å);[10] in all cases this distance is between 79 and 83 % of the vdW sum (Table 1). These short non-bonded *peri* distances indicate the possible existence of weak intramolecular interactions.[24]

In each of the six compounds, the individual chalcogen atoms are displaced to different sides of the naphthalene

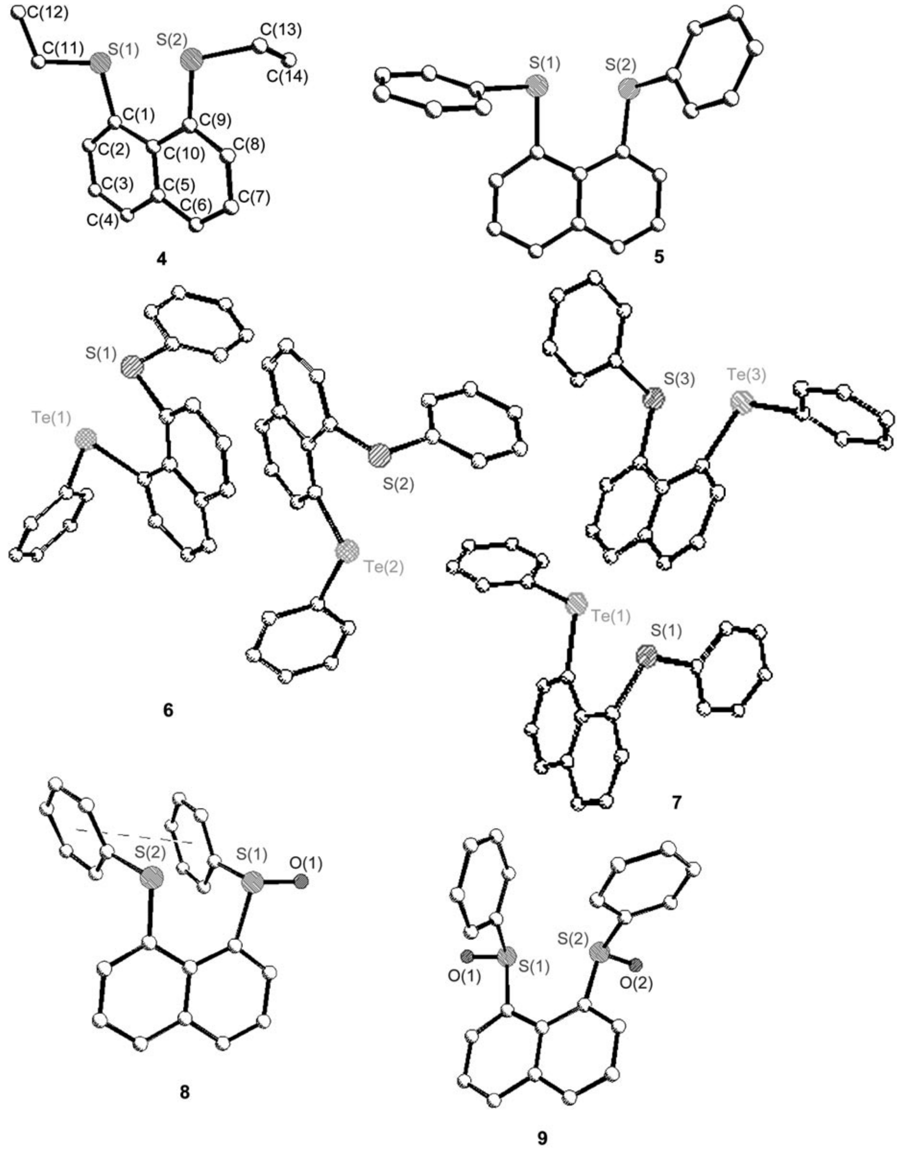


Figure 3. The crystal structures of 1,8-bis(ethylsulfanyl)naphthalene (**4**), 1-(phenylselanyl)-8-(phenylsulfanyl)-naphthalene (**5**), 1-(phenyltelluro)-8-(phenylsulfanyl)naphthalene (**6**; two independent molecules in the unit cell), 1-(phenyltelluro)-8-(phenylselanyl)naphthalene (**7**), 1-(phenylsulfinyl)-8-(phenylsulfanyl)naphthalene (**8**) and 1,8-bis(phenylsulfinyl)naphthalene (**9**).

least-squares plane. The displacement of the E atoms from this plane ranges from 0.15 to 0.57 Å, with an overall increase in the out-of-plane distortion observed as the size of the chalcogen atoms increases. The least amount of steric strain is observed in **1**, as indicated by the relatively small displacement of the two small sulfur atoms ($\Sigma r_{\mathrm{vdW}} = 3.60$ Å)[10] from the naphthyl plane by −0.16 and 0.27 Å. The out-of-plane distortion is most pronounced and observed to the greatest extent in **3**, in which the displacement of the two large tellurium atoms ($\Sigma r_{\mathrm{vdW}} = 4.12$ Å)[10] is −0.51 and 0.57 Å. Considerable distortion of the bay area geometry within the naphthyl plane is observed in all six compounds, with positive splay angles of 11.8 to 15.0° that ensure that the E−C bonds are tilted in opposite directions to minimise the steric repulsion between the two bulky chalcogen atoms ("*peri*-space crowding").[25]

Like analogues **1**–**3**, compounds **5**–**7** can be thought of as structural "Siamese twins" that are instead formed from two, non-identical diphenyl dichalcogenide parts fused through one benzene ring.[15] The conformation and arrangement of the E(naphthyl) and E(phenyl) rings relative to the C(ar)-E(1)-C(ar) and C(ar)-E(2)-C(ar) planes can be categorised from torsion angles θ and γ, respectively (see Table 2). When θ and γ approach 90° the orientation is denoted axial, and when the angles indicate a quasi-planar arrangement (close to 180°) they are termed equatorial.[15]

Compounds **5**–**7** display a mixed axial–equatorial conformation of the naphthyl and phenyl rings around the chalcogen atom in each independent half of the molecule. This orientation, which matches that of **1**[15] and **2**[14] and is commonly found in diaryl sulfides,[26] gives these compounds an "aircraft-like" shape (Figure 4).[15]

The S···Se, Te···S and Te···Se atoms in naphthalene derivatives **5**–**7**, with separations shorter than the sum of vdW radii (3.70, 3.86 and 3.96 Å),[10] are fixed in unavoidably close proximity. Repulsive E···E′ interactions between the *peri* atoms transpire and force the distortion of the naphthalene geometry by stretching the C−C bonds and C-C-C angles together with a buckling of the naphthalene skeleton. Bond lengths around C(10), which is closer to the repulsive interactions, are on average longer than those around C(5) (average lengths 1.44 and 1.42 Å, respectively) and C(1)-C(10)-C(9) bond angles splay to a mean 126° away from the ideal geometry observed for C(4)-C(5)-C(6) (average 119°).[2] The aforementioned bond stretching and angle widening distortions alone are insufficient to overcome the steric strain between the *peri* atoms. Supplementary widening of the E(1)-C(1)-C(10) and E(2)-C(9)-C(10) angles and displacement of the E atoms from the mean naphthyl plane takes place to aid the alleviation of steric pressure.

Table 1. Selected interatomic distances [Å] and angles [°] for **1–9**.[a]

	1	**2**	**3**[14,17]	**4**	**5**	**6**	**7**	**8**	**9**
peri-region distances									
E(1)···E′(9)	3.0036(13)	3.1332(9)	3.287(1)	2.9323(13)	3.063(2)	3.0684(13) (3.0984(11))	3.1919(11) (3.1580(12))	3.0460(11)	3.0757(13)
Σr_{vdW}−E···E′[b]	0.6	0.67	0.83	0.67	0.64	0.79 (0.76)	0.77 (0.80)	0.55	0.52
Σr_{vdW}[b] [%]	83	82	80	81	83	79 (80)	81 (80)	85	85
E(1)−C(1)	1.794(3)	1.922(7)	2.14(1)	1.776(4)	1.907(9)	2.141(5) (2.100(5))	2.137(11) (2.124(10))	1.830(3)	1.814(3)
E′(9)−C(9)	1.783(4)	1.930(7)	2.14(2)	1.778(4)	1.813(8)	1.770(5) (1.771(5))	1.920(12) (1.925(10))	1.774(3)	1.804(3)
naphthalene bond lengths									
C(1)−C(2)	1.379(5)	1.381(10)	1.34(1)	1.383(5)	1.367(12)	1.379(6) (1.386(8))	1.388(18) (1.415(13))	1.376(4)	1.365(5)
C(2)−C(3)	1.408(5)	1.400(11)	1.38(1)	1.402(5)	1.372(14)	1.424(8) (1.404(8))	1.414(19) (1.426(16))	1.413(5)	1.408(5)
C(3)-C(4)	1.348(6)	1.357(11)	1.34(1)	1.352(5)	1.375(15)	1.357(9) (1.367(6))	1.367(15) (1.335(18))	1.359(4)	1.344(6)
C(4)−C(5)	1.428(5)	1.420(10)	1.46(1)	1.415(5)	1.426(14)	1.413(7) (1.423(8))	1.428(18) (1.393(14))	1.416(5)	1.427(5)
C(5)−C(10)	1.442(5)	1.423(10)	1.42(1)	1.439(5)	1.435(12)	1.440(7) (1.433(8))	1.409(17) (1.449(16))	1.436(4)	1.438(5)
C(5)−C(6)	1.416(5)	1.436(10)	1.39(1)	1.423(5)	1.413(14)	1.408(8) (1.416(6))	1.437(13) (1.412(18))	1.421(4)	1.407(6)
C(6)−C(7)	1.362(5)	1.371(10)	1.35(1)	1.355(6)	1.363(15)	1.362(7) (1.356(9))	1.402(18) (1.362(15))	1.366(5)	1.359(5)
C(7)−C(8)	1.405(5)	1.381(12)	1.38(1)	1.402(6)	1.435(14)	1.395(8) (1.399(9))	1.355(19) (1.392(17))	1.401(5)	1.397(5)
C(8)−C(9)	1.374(5)	1.368(10)	1.37(1)	1.379(5)	1.381(13)	1.380(8) (1.381(6))	1.360(14) (1.378(18))	1.387(4)	1.386(5)
C(9)−C(10)	1.431(5)	1.436(9)	1.41(2)	1.439(5)	1.423(12)	1.437(6) (1.433(7))	1.451(16) (1.428(14))	1.424(4)	1.432(4)
C(10)−C(1)	1.446(5)	1.461(9)	1.45(1)	1.453(5)	1.447(12)	1.441(7) (1.436(6))	1.449(12) (1.470(16))	1.439(4)	1.433(5)
S(1)−O(1)	–	–	–	–	–	–	–	1.500(2)	1.497(3)
S(2)−O(2)	–	–	–	–	–	–	–	–	1.486(3)
peri-region bond angles									
E(1)-C(1)-C(10)	121.8(2)	123.5(5)	123(1)	122.6(2)	122.3(6)	122.9(3) (123.2(4))	125.2(9) (126.4(6))	126.8(2)	125.7(2)
C(1)-C(10)-C(9)	126.8(3)	126.6(6)	128(1)	126.1(3)	127.8(7)	126.1(4) (126.1(5))	125.5(10) (124.9(9))	126.4(3)	128.0(3)
E(9)-C(9)-C(10)	124.5(2)	123.8(5)	124(1)	122.1(2)	122.3(6)	122.8(4) (122.9(3))	123.6(7) (123.4(9))	122.1(2)	121.5(3)
Σ of bay angles	373.1	373.9	375.0	370.8	372.4	371.8 (372.2)	374.3 (374.7)	375.3	375.2
splay angle[c]	13.1	13.9	15.0	10.8	12.4	11.8 (12.2)	14.3 (14.7)	15.3	15.2
C(4)-C(5)-C(6)	118.8(3)	117.3(6)	118.0(1)	118.8(3)	177.6(8)	117.4(10) (120.4(10))	119.4(4) (119.0(5))	119.6(3)	119.4(3)
O(1)-S(1)-C(1)	–	–	–	–	–	–	–	105.0(1)	105.3(2)
O(1)-S(1)-C(11)	–	–	–	–	–	–	–	104.3(2)	105.3(2)
O(1)-S(1)···S(2)	–	–	–	–	–	–	–	174.3(1)	171.9(1)
O(2)-S(2)-C(9)	–	–	–	–	–	–	–	–	106.9(2)
O(2)-S(2)-C(17)	–	–	–	–	–	–	–	–	106.8(2)
O(2)-S(2)···S(1)	–	–	–	–	–	–	–	–	120.8(1)
out-of-plane displacement									
E(1)	0.270(4)	0.468(9)	−0.51(1)	0.182(4)	0.432(11)	−0.565(7) (−0.406(7))	0.372(15) (−0.50(1))	0.010(4)	0.121(5)
E(9)	−0.163(4)	−0.327(9)	0.57(1)	−0.176(5)	−0.320(11)	0.146(7) (0.449(7))	−0.43(2) (0.17(1))	0.210(4)	−0.213(4)
O(1)	–	–	–	–	–	–	–	0.020(5)	0.129(6)
O(2)	–	–	–	–	–	–	–	–	−0.1545(6)
central naphthalene ring torsion angles									
C(6)-C(5)-C(10)-C(1)	178.6(3)	173.5(6)	174.2(1)	−178.7(3)	−175.2(8)	−176.9(6) (176.7(6))	−177.4(1) (−174.8(1))	−179.4(3)	−179.5(3)
C(4)-C(5)-C(10)-C(9)	177.2(3)	174.6(6)	175.1(1)	−178.9(3)	−174.5(8)	−174.6(6) (173.8(5))	−175.0(1) (−176.9(1))	−177.7(3)	179.0(3)

[a] Values in parentheses are for independent molecules. [b] vdW radii used for calculations: $r_{vdW}(S) = 1.80$ Å, $r_{vdW}(Se) = 1.90$ Å, $r_{vdW}(Te) = 2.06$ Å.[10] [c] Splay angle: Sum of the three bay region angles−360.

Table 2. Torsion angles [°] categorising the naphthalene and phenyl ring conformations in **5–7**.[a]

	5		**6**		**7**	
	Torsion angle	Conformation	Torsion angle	Conformation	Torsion angle	Conformation
naphthalene ring conformations						
C(10)-C(1)-E(1)-C(11)	$\theta_1 = -156.4(7)$	Nap_1: equatorial	$\theta_1 = -160.5(11)$ $(-168.1(11))$	Nap_1: equatorial	$\theta_1 = -165.3(5)$ $(160.8(5))$	Nap_1: equatorial
C(10)-C(9)-E(2)-C(17)	$\theta_2 = 111.3(7)$	Nap_2: axial	$\theta_2 = -83.1(11)$ $(-82.3(12))$	Nap_2: axial	$\theta_2 = -84.0(5)$ $(81.9(5))$	Nap_2: axial
phenyl ring conformations						
C(1)-E(1)-C(11)-C(12)	$\gamma_1 = -98.0(8)$	Ph_1: axial	$\gamma_1 = 108.0(11)$ $(-91.0(8))$	Ph_1: axial	$\gamma_1 = -89.5(4)$ $(108.1(6))$	Ph_1: axial
C(9)-E(2)-C(17)-C(18)	$\gamma_2 = -9.3(9)$	Ph_2: equatorial	$\gamma_2 = -12.3(9)$ $(-17.5(9))$	Ph_2: equatorial	$\gamma_2 = -12.5(5)$ $(10.6(4))$	Ph_2: equatorial

[a] Values in parentheses are for independent molecules. Definitions: Nap_1: naphthalene ring E(1); Nap_2: naphthalene ring E(2); Ph_1: E(1) phenyl ring; Ph_2: E(2) phenyl ring; axial: perpendicular to C(ar)-E-C(ar) plane; equatorial: coplanar with C(ar)-E-C(ar) plane.

A similar displacement of the *peri* atoms to either side of the naphthalene least-squares plane in **5** and **6** (**5**: 0.43 and −0.32 Å; **6**: −0.57 (−0.41) and 0.15 Å (0.45 Å)) reveals that steric strain in the two compounds is roughly equivalent.

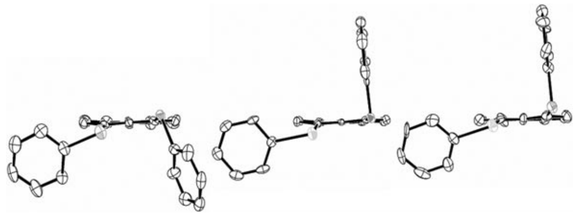


Figure 4. The crystal structures of **5**–**7** (from left to right) showing the conformation of the E(naphthyl) and E(phenyl) rings.

Corresponding splay angles for **5** (12.4°) and **6** (11.8° (12.2°)) also implies that the E–C bonds are tilted away from each other to a similar extent to minimise the steric repulsion operating between the chalcogen atoms. Non-bonded E···E′ interatomic distances in **5** (3.063(2) Å) and **6** (3.0684(13) Å (3.0984(11) Å)) are 0.64 and 0.79 Å (0.76 Å) shorter than the sum of vdW radii for the two interacting atoms (3.70, 3.86 Å),[10] that is, only 83 and 79% (80%) of the vdW sum for **5** and **6**, respectively. The deviation of the central naphthalene ring torsion angles from planarity is similar in the two compounds but with a greater range in **6** (≈5–6° in **5** and ≈2–6° in **6**).

The increased congestion in the *peri* space of **7** causes a larger positive splay of the E–C bonds within the naphthyl plane and an increased angle of 14.3° (14.7°). The displacement of the tellurium and selenium atoms from the naphthalene best plane (0.37 (−0.50), −0.43 Å (0.17 Å)) is comparable to the out-of-plane distortion that occurs in **5** and **6** (0.15–0.57 Å). The naphthalene unit in **7** also shows a similar deviation from planarity to **5** and **6**, with a maximum C-C-C-C torsion angle of 5.2°. The resulting geometry repels the Te and Se atoms to a non-bonded interatomic distance of 3.1919(11) Å (3.1580(12) Å), but this gap is still 19% (20%) shorter than the sum of their collective vdW radii. The S–C (1.72–1.82 Å), Se–C (1.88–1.98 Å) and Te–C (2.07–2.17 Å) bond lengths are within the usual ranges ((1.77±0.05), (1.93±0.05) and (2.12±0.05) Å, respectively)[27] in all three compounds. Although intermolecular short contacts exist in all three derivatives in the molecular structures, there is no significant overlap of phenyl or naphthalene rings and no π stacking.

Steric strain operating between the *peri* atoms in **1**–**3** and **5**–**7** is dominated by the repulsion of chalcogen p-type lone pairs, which thus have a big influence on non-bonded E···E′ distances. When the conformation of the E(naphthyl) group is axial (torsion angles θ_1 and θ_2 approach 90°; Table 2), the axis of the p orbitals of the chalcogen atom lie in the plane of the aromatic system and repulsion is relatively high.[15,19b] Conversely, when torsion angles θ_1 and θ_2 approach 180° (E-(naphthyl) conformation being equatorial), the p orbitals are arranged parallel and vertical to the aromatic plane and less lone pair–lone pair repulsion is observed.[15] The presence of a quasi-linear X–E···E′ alignment of atoms allows for the possible occurrence of an attractive E···E′ interaction. Following the promotion of a chalcogen lone pair into the antibonding σ*(S–X) orbital,[28] a noncovalent three-centre–four-electron (3c–4e) interaction emerges[29] and influences the conformation of the molecule.[14]

The structures for Nap[RZ][R′Z] compounds can be classified by a pairing of geometrical types denoted by AA-*t*, AA-*c*, AB, BB or CC.[1,12–14,17,19] Compounds **1**[14,15] and **2**[14,16] have been reported to adopt similar AB type conformations with one E–C_{Ph} bond aligning close to the naphthyl plane and one aligning roughly perpendicular to the plane.[1,12–14] Bulkier tellurium analogue **3**[14,17] adopts a CC type structure with both E–C_{Ph} bonds lying at roughly 135° to the naphthyl plane (Figure 5).[1,12–14]

One attractive quasi-linear arrangement (C(11)–S(1)···S(2)) is observed in **1** with an angle of 168.4° and one C(11)–Se(1)···Se(2) alignment appears in **2** with an angle of 171.3°. No similar linear arrangements are found in **3**, which has angles of 145.7 (C(11)–Te(1)···Te(2)) and 154.2° (C(17)–Te(2)···Te(1)) (Figure 5).[17] The molecular structures of **5**–**7**

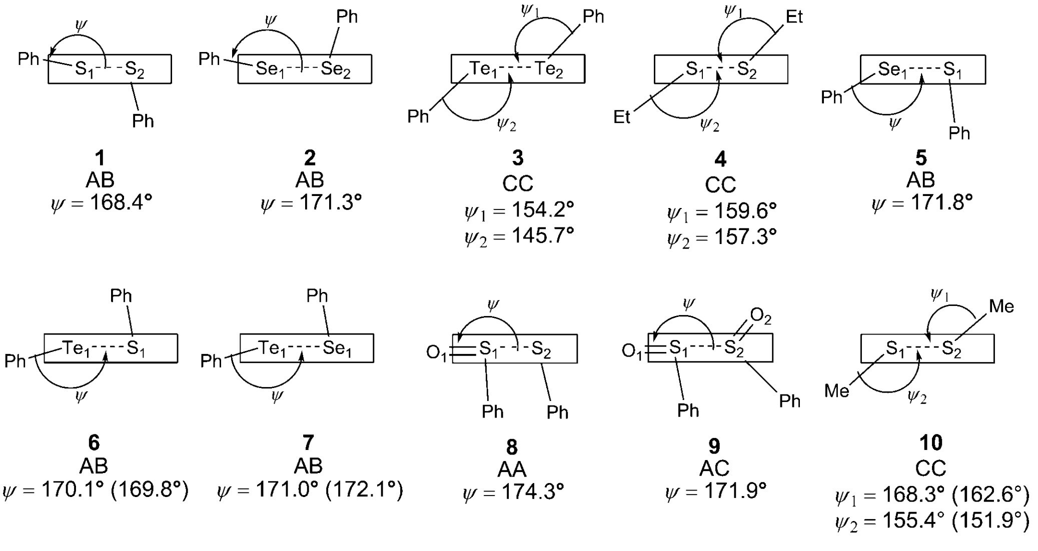


Figure 5. The orientation of the E(phenyl) groups and structure types of **1**–**10** and the quasi-linear arrangements.[12–17,19b]

display an AB-type arrangement[1,12–14] equivalent to that reported for **1** and **2**.[14–16] In all cases one quasi-linear arrangement of the type C–E···E′ is observed with angles in the range of 169–172° (Figure 5).

The degree of steric strain operating between the *peri* atoms in bis(S(ethyl)) **4** is notably reduced compared with the S(phenyl) analogue **1**,[14,15] but greater than the repulsive interaction displayed by 1,8-bis(methylsulfanyl)naphthalene **10** previously reported by Glass et al.[19b] The nature of the alkyl substituent attached to the *peri*-sulfur atoms plays a crucial role in determining the geometry of the three structures. The *peri* atoms are displaced by equal distances and in opposite directions from the naphthalene least-squares plane in both **4** (±0.18 Å) and **10** (±0.30 Å)[19b] but by unequal distances in **1** (0.27 and −0.16 Å).[14,15] Positive splay angles are comparable for **4** (10.8°) and **10** (9.9°),[19b] but there is a notable increase in the splay of the S–C bonds in **1** (13.1°)[14,15] to alleviate *peri*-space crowding.[25] The noncovalent S···S *peri* distances for **1** (3.0036(13) Å), **4** (2.9323(13) Å) and **10** (2.918(2) Å (2.934(2) Å)) are shorter than double the vdW radius of sulfur by 0.67, 0.60 and 0.68 Å (0.67 Å), respectively. No major distortion of the naphthalene scaffold is observed in **4**, which has only a minor deviation from planarity; the maximum C-C-C-C torsion angle is 1.3° for C(6)-C(5)-C(10)-C(1). The deviation of the central naphthalene ring torsion angles from planarity is more pronounced in **1** (≈1–3°) and **10** (≈4°). Short intermolecular interactions are observed between two molecules of **4** within the crystal structure: H(11b)···H(14a) (2.37(1) Å) and H(12a)···H(13a) (2.32(1) Å).

In compound **4**, all the S–C (1.78–1.82 Å) bond lengths are within the usual range ((1.77±0.05) Å).[27] The repulsion acting between the *peri* atoms is observed in the naphthalene skeleton, with bond lengths around C(10) found to be stretched and longer than those around C(5) (average: 1.45 and 1.42 Å, respectively) and the C(1)-C(10)-C(9) angle, which is most affected by the repulsion, splays to 126° away from the ideal geometry observed for C(4)-C(5)-C(6) (119°).[2]

The disparity between the larger non-bonded S···S length observed in compound **1** (3.00 Å),[14,15] compared with the distances found in the ethyl- and methyl-analogues **4** (2.93 Å) and **10** (2.93 Å),[19b] may reflect a stronger lone pair–lone pair repulsion acting in the phenyl analogue. This can be rationalised by comparing the torsion angles θ_1 and θ_2 (Table 3) associated with S(naphthyl) conformations. In bis(sulfide) **1**,[14,15] only one of these torsion angles approaches 180°, whereas in **4** and **10**[19b] both S(naphthyl) conformations are equatorial, the p orbitals are arranged parallel to the aromatic plane and less lone pair–lone pair repulsion is observed (see Table 3).[15]

Compounds **4** and **10** both adopt the CC-*t* type arrangement[1,12–14] (Figure 5) in which the S–C bonds lie on opposite sides of the naphthyl plane, intermediate between the type A (perpendicular) and type B (planar) arrangements.[1,11,13,18] Two favourable quasi-linear C–S···S moieties are present in both **4** (C(11)–S(1)···S(2) 157.32°, C(13)–S(2)···S(1) 159.60°) and **10** (C(11)–S(1)···S(2) 155.4° (151.9°), C(12)–S(2)···S(1) 168.3° (162.6°)), which suggests an attractive S···S noncovalent interaction and could explain the relatively short distances observed compared with bis(sulfide) **1**.[19b]

Oxides **8** and **9** adopt similar geometrical conformations and display a similar degree of steric strain between the sulfur *peri* atoms, but are notably different compared to the non-oxidised bis(sulfide) **1**.[14,15] The presence of oxygen atoms bonded to the *peri*-sulfur substituents plays a crucial role in determining the geometry of the oxides. Both compounds are relatively planar with no major distortion of the naphthalene scaffold observed. Only minor deviations from planarity exist for **8** and **9**, with maximum C-C-C-C torsion angles of 2.3 and 1.0°, respectively. The displacement of the sulfur atoms from the naphthalene least-squares plane in **8** is insignificant, with S(1) essentially lying on the plane (0.01, −0.16 Å). The *peri* atoms in **9** (0.12, −0.21 Å) are displaced from the naphthalene plane in opposite directions and by similar distances to **1** (0.27, −0.16 Å).[14,15] Large and positive splay angles of 15.3 (**8**) and 15.2° (**9**), however, illustrate that a big in-plane distortion is operating to alleviate *peri*-space crowding.[25] The noncovalent S···S *peri* lengths for **8** (3.0460(11) Å) and **9** (3.0757(13) Å) are longer than in **1** (3.0036(13) Å), but still 15% shorter than double the vdW radius of sulfur in both cases.[10]

In the crystal structure of **8**, there is an approximate alignment of the naphthalene rings along the *c* axis, with the closest intermolecular short contact between C(3) and C(9) (3.56(1) Å). No similar alignment is observed in the structure of **9**, but a short intermolecular distance exists between S(1) and C(3) (3.43(1) Å). All the S–C (1.77–1.83 Å) and S=O (1.49–1.50 Å) bond lengths are within the usual ranges ((1.79±0.05) and (1.50±0.05) Å, respectively).[27] Bond lengths around C(10) are stretched longer, but to a lesser extent than normal, than those around C(5) (average: 1.43 and 1.42 Å, respectively) and angle C(1)-C(10)-C(9), which

Table 3. Torsion angles [°] categorising the naphthalene ring conformations in **1**, **4** and **10**.[a]

	1		**4**		**10**[19b]	
	Torsion angle	Conformation	Torsion angle	Conformation	Torsion angle	Conformation
naphthalene ring conformations						
C(10)-C(1)-S(1)-C(11)	$\theta_1=159.8(2)$	Nap_1: equatorial	$\theta_1=-149.7(3)$	Nap_1: equatorial	$\theta_1=-143.2$ (−142.0)	Nap_1: equatorial
C(10)-C(9)-S(2)-C(17/3/2)	$\theta_2=95.0(3)$	Nap_2: axial	$\theta_2=-153.1(3)$	Nap_2: equatorial	$\theta_2=-152.3$ (−153.0)	Nap_2: equatorial

[a] Values in parentheses are for independent molecules. Definitions: Nap_1: naphthalene ring E(1); Nap_2: naphthalene ring E(2); axial: perpendicular to C-E-C plane; equatorial: coplanar with C-E-C plane.

is most affected by the repulsion, splays to a mean 127° away from the ideal geometry observed for C(4)-C(5)-C(6) (120°).[2]

The larger noncovalent S···S distances observed in oxides **8** and **9** (3.05, 3.08 Å) compared with the equivalent distance found in **1** (3.00 Å) can be rationalised by comparing the S-(naphthyl) conformations in all three molecules (Table 4). In compound **8** both S(naphthyl) conformations are axial (torsion angles θ_1 and θ_2 approach 90°, Table 4), the axis of the p orbitals of the chalcogen atom lie in the plane of the aromatic system and repulsion is relatively high.[15] Similarly, in oxide **9** one is axial and one is a twist conformation. Conversely, in bis(sulfide) **1**,[14,15] one of the torsion angles approaches 180°, the p orbitals arrange parallel to the aromatic plane and less lone pair–lone pair repulsion is observed.[15]

Compounds **8** and **9** adopt different structural arrangements compared with the AB-type arrangement[1,12–14] of non-oxidised **1** (Figure 5).[1,12–14] In compound **8**, both S$-$C$_{Ph}$ bonds lie roughly perpendicular to and on the same side of the naphthyl plane (AA-*c*-type),[1,12–14] with the quasi-linear arrangement O(1)=S(1)···S(2) lying along the naphthyl plane (174.3°; Figures 6 and 7). Compound **9** adopts a similar structure, but with the added bulk of the second oxygen atom, one of the S$-$C$_{Ph}$ bonds is distorted to ≈135° and thus classified as an AC-*c* type arrangement.[1,12–14] The same linear arrangement of the type O(1)=S(1)···S(2) (171.9°) is observed and the second oxygen atom takes up position on the opposite side of the naphthalene plane to give an S(1)···S(2)=O(2) angle of 120.8°.

The AA-*c*-type arrangement[1,12–14] in compound **8** allows for the close configuration and overlap of the two phenyl rings.[30] The alignment of the rings is a face-to-face offset arrangement with slipped packing, known as parallel displacement (Figures 3 and 7).[30] The distance between the two interacting centroids (3.821(1) Å) is at the top end of the range for typical centroid–centroid π stacking (3.3–3.8 Å),[30] so possible π–π stacking could be envisaged (Figure 3).[30]

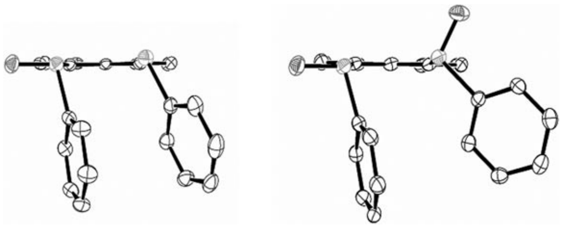


Figure 6. The crystal structures of **8** (left) and **9** (right) showing the orientation of the phenyl substituents.

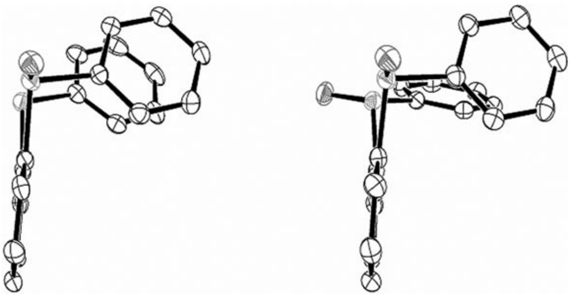


Figure 7. The crystal structures of **8** (left) and **9** (right) showing the planarity of the naphthalene backbones and the overlap of the phenyl rings.

The AC-type arrangement[1,12–14] in **9** inhibits phenyl ring overlap, with the S$-$C$_{Ph}$ moiety of the C-type arrangement being inclined at a greater angle from the naphthalene plane compared with the moiety that adopts the A-type arrangement[1,11,13,18] (phenyl ring on S(1)). The phenyl ring bonded to S(2) is also twisted upwards and impedes phenyl ring interaction, which results in no π–π stacking taking place (Figure 7).

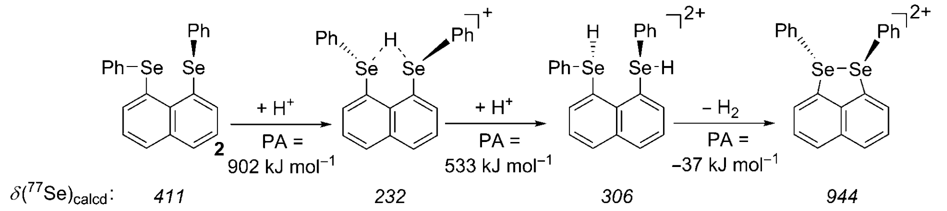
To try and assess the possibility of direct S···S bonding interactions that would indicate an onset of 3c–4e bonding, density functional theory computations were performed for derivatives **8** and **9** at the B3LYP/6-31+G* level. The Wiberg bond index (WBI),[32] which measures the covalent bond order, was calculated to be only 0.03 in both compounds, which indicates a very minor interaction taking place between these non-bonded atoms. For comparison, the fully covalent S$-$S single bond in naphtho(1,8-*cd*)(1,2-dithiole) has a WBI of 0.99 at the same level.

More pronounced interactions could be expected as the neighbouring chalcogens become larger. This expectation is borne out by computations for **2**, which afford a WBI of 0.08 between the two Se atoms. Even stronger interactions can occur when one of the Se atoms carries an acceptor. When the "equatorial" Ph group on Se(1) in **2** is replaced with Br (for numbering see Figure 5), the Se$-$Se lengths as short as 2.516 Å have been observed.[32] A B3LYP computation for the latter molecule from the X-ray structure affords a WBI of 0.55, which suggestes a large extent of 3c–4e bonding in this case. Judging from the refined chalcogen–chalcogen distances, none of the species in the present study comes close to such a bonding situation.

Table 4. Torsion angles [°] categorising the naphthalene ring conformations in **8**, **9** and **1**.

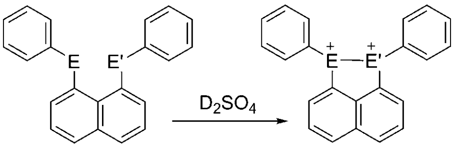
	8		**9**		**1**	
	Torsion angle	Conformation	Torsion angle	Conformation	Torsion angle	Conformation
naphthalene ring conformations						
C(10)-C(1)-S(1)-C(11)	$\theta_1=-74.3(2)$	Nap$_1$: axial	$\theta_1=-70.5(3)$	Nap$_1$: axial	$\theta_1=159.8(2)$	Nap$_1$: equatorial
C(10)-C(9)-S(2)-C(17/3/2)	$\theta_2=118.5(3)$	Nap$_2$: axial	$\theta_2=137.5(3)$	Nap$_2$: twist	$\theta_2=95.0(3)$	Nap$_2$: axial

[a] Definitions: Nap$_1$: naphthalene ring E(1); Nap$_2$: naphthalene ring E(2); axial: perpendicular to C-E-C plane; equatorial: coplanar with C-E-C plane; twist: intermediate between axial and equatorial.



Scheme 10. Computed enthalpies and mean ^{77}Se chemical shifts (δ [ppm], in italics) of **2** and selected protonation and oxidation products thereof (B3LYP level).

Compound **3** was first reported by Furukawa et al.[17] Electrochemical oxidation of **3** by cyclic voltammetry revealed one reversible oxidation peak at a very low oxidation potential of +0.16 V.[17] Furukawa et al. attributed this to the destabilisation of **3** by *peri* lone pair–lone pair repulsion and the stabilisation of the oxidised species by neighbouring-tellurium participation.[17] The ^{125}Te NMR spectrum of **3** in $CDCl_3$ has a peak at $\delta = 617$ ppm, whereas a solution of **3** in D_2SO_4 gave a downfield shift to $\delta = 964$ ppm, which suggests that it is a dication.[17] Herein we report our ^{77}Se and ^{125}Te NMR spectroscopy studies of 1,8-bis(phenylselanyl)naphthalene **2** and the three mixed chalcogen compounds **5**–**7**. Spectra for all four compounds were run in both $CDCl_3$ and D_2SO_4 to ascertain if these compounds could also afford similar cationic species (Scheme 9). The results of the ^{77}Se and ^{125}Te NMR studies are shown in Table 5. For each NMR experiment there is a significant downfield shift in the signal for spectra run in D_2SO_4 compared with the signal for spectra run in $CDCl_3$. These results suggest the formation of a dicationic species in each case (see Scheme 9).[17] To rule out protonated species as a source for the observed NMR signals, we have calculated the ^{77}Se chemical shifts for **2**, **2**$^{2+}$ and a number of mono- and diprotonated variants of **2** (see Scheme 10 and Table S15 in the Supporting Information). Protonation is predicted to result in a shielding of the Se nuclei by up to $\Delta\delta = -179$ ppm for the (symmetrically bridged) monoprotonated form. Interestingly, a substantial driving force is computed for H elimination from the diprotonated species, $\Delta H = -37$ kJ mol^{-1}, a process that will be further favoured by entropy. For the resulting oxidised dication (rightmost structure in Scheme 10), a notable deshielding of the Se resonance with respect to that of **2** is obtained ($\Delta\delta = 533$ ppm). Quantitatively, this gas-phase result overestimates the trend observed on going from the less polar solvent $CDCl_3$ to the highly polar sulfuric acid ($\Delta\delta \approx 400$ ppm, Table 5). The qualitative agreement between theory and experiment, however, can be taken as strong support for formation of **2**$^{2+}$ in D_2SO_4.



Scheme 9. The oxidation reaction of chalcogen compounds **2**, **5**–**7** with D_2SO_4.[17]

Table 5. ^{77}Se and ^{125}Te NMR spectroscopy data (δ [ppm]) run in $CDCl_3$ and D_2SO_4 for **2** and **5**–**7**.

	2	5	6	7
peri atoms	Se, Se	Se, S	Te, S	Te, Se
^{77}Se NMR ($CDCl_3$)	428.6	455.3	–	362.8
^{77}Se NMR (D_2SO_4)	828.0	927.3	–	554.7
^{125}Te NMR ($CDCl_3$)	–	–	715.2	687.6
^{125}Te NMR (D_2SO_4)	–	–	1018.3	1279.6

Conclusion

The present work is a contribution to the investigations of molecular distortion occurring in *peri*-substituted naphthalene compounds and the significance of intramolecular interactions occurring between heavy atoms when positioned at the close 1,8-positions. Repulsive steric strain caused by inserting increasingly larger atoms at the 1,8-positions in six chalcogen analogues (**1**–**3** and **5**–**7**) is shown to be relieved to a greater extent as the overall combined size of the *peri* atoms increases. The primary parameter used to quantify the amount of strain relief in non-ideal naphthalenes is the *peri* distance, which encapsulates all molecular deviations in one parameter. The largest *peri* distance for the six compounds was found in **3** (Σr_{vdW} 4.12 Å), which is substituted by two large tellurium atoms,[10] whereas the shortest *peri* gap was observed in **1** (Σr_{vdW} 3.60 Å), which contains the two smallest (sulfur) substituents.[10] Although the non-bonded distance is shorter than the sum of vdW radii for the two *peri* atoms by 21–17 % in all six compounds, no evidence of bond formation was observed.

Upon oxidation, the structure of bis(sulfide) **1** is dramatically changed and adopts either an AA-type arrangement[1,12–14] (**8**) or an AC-type arrangement[1,12–14] (**9**). The overriding factor in these two structures is a linear arrangement of the type O(1)=S(1)···S(2), which in both cases forces the two phenyl rings to align on the same side of the naphthalene plane. In compound **8** this overlap is close enough for possible π–π stacking to occur.[30] Ab initio MO calculations performed on both derivatives by using the B3LYP/6-31+G* level revealed WBI[31] values of 0.03, which indicates that only a very minor interaction exists between the non-bonded sulfur atoms.

The oxidation of chalcogenides **2** and **5**–**7** was observed by ^{77}Se and ^{125}Te NMR spectroscopy. A significant downfield shift in the signal for spectra of the three derivatives run in D_2SO_4 compared with the signal for spectra run in $CDCl_3$

reveals the formation of a *peri* bond and the presence of a dication species.[17]

Experimental Section

All experiments were carried out under an oxygen- and moisture-free nitrogen atmosphere by using standard Schlenk techniques and glassware. Reagents were obtained from commercial sources and used as received. Dry solvents were collected from an MBraun solvent system. 1,8-Dibromonaphthalene (**11**)[20] and 1,8-diiodonaphthalene (**12**)[21] were prepared by standard diazotisation reactions of 1,8-diaminonaphthalene. 1-Halo-8-(phenylchalcogeno)naphthalenes **16**–**19**[23] were prepared from **11** and **12**. Elemental analyses were performed by the University of St Andrews School of Chemistry Microanalysis Service. IR spectra were recorded as KBr discs in the range of 4000–300 cm^{-1} by using a Perkin–Elmer System 2000 Fourier transform spectrometer. ^{1}H and ^{13}C NMR spectra were recorded by using a Jeol GSX 270 MHz spectrometer with δ(H) and δ(C) referenced to external tetramethylsilane. ^{77}Se and ^{125}Te NMR spectra were recorded by using a Jeol GSX 270 MHz spectrometer with δ(Se) and δ(Te) referenced to external dimethylselenide and diphenyl ditelluride, respectively. Assignments of ^{13}C and ^{1}H NMR spectra were made with the help of H–H COSY and HSQC experiments. All measurements were performed at 25 °C. All values reported for NMR spectroscopy are in parts per million (ppm). Coupling constants (*J*) are given in Hertz (Hz). Mass spectrometry was performed by the University of St Andrews Mass Spectrometry Service. Electron impact mass spectrometry (EIMS) and chemical ionisation mass spectrometry (CIMS) was carried out by using a Micromass GCT orthogonal acceleration time-of-flight mass spectrometer. Electrospray mass spectrometry (ESMS) was carried out by using a Micromass LCT orthogonal accelerator time-of-flight mass spectrometer.

1,8-Bis(ethylsulfanyl)naphthalene (Nap(SEt)$_2$; 4)

*Synthesis of **4** from **11***: A solution of *n*-butyllithium (2.5 M, 2.4 mmol) in hexane (1.0 mL) was added dropwise to a solution of 1,8-dibromonaphthalene (0.34 g, 1.2 mmol) in diethyl ether (15 mL) at −78 °C. The mixture was stirred at this temperature for 1 h after which a solution of diethyl disulfide (0.29 g, 2.4 mmol, 0.3 mL) in diethyl ether (15 mL) was added dropwise to the mixture. The resulting mixture was stirred at −78 °C for a further 1 h. The reaction mixture was washed with 0.1 M sodium hydroxide (2×45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (hexane). Recrystallisation by diffusion of pentane into a saturated solution of the compound in dichloromethane gave colourless crystals (0.08 g, 27 %). ^{1}H NMR (270 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.65 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.2 Hz, 2H; 4,5-H), 7.55 (dd, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.3, 2H; 2,7-H), 7.39–7.30 (m, 2H; 3,6-H), 2.96 (q, ^3J(H,H) = 7.4 Hz, 2H; CH_2), 1.30 ppm (t, ^3J(H,H) = 7.4 Hz, 3H; CH_3); ^{13}C NMR (67.9 MHz, CDCl$_3$, 25 °C, TMS): δ = 130.1 (s), 127.9 (s), 125.4 (s), 31.6 (s; CH$_2$), 13.4 ppm (s; CH$_3$); IR (KBr disk): $\tilde{\nu}_{max}$ = 3047 w, 2965 s, 2924 s, 2851 s, 1932 w, 1868 w, 1784 w, 1720 w, 1597 w, 1546 s, 1490 w, 1446 s, 1420 s, 1370 w, 1313 s, 1259 vs, 1193 s, 1093 s, 1046 s, 1022 s, 985 w, 900 w, 874 s, 811 vs, 759 vs, 713 w, 579 cm^{-1} w; MS (EI$^+$): *m/z* (%): 248 (2) [*M*$^+$], 219 (4) [*M*−Et]$^+$, 189.99 (100) [*M*−Et$_2$]$^+$; elemental analysis calcd (%) for C$_{14}$H$_{16}$S$_2$: C 67.7, H 6.5; found: C 66.8, H 6.5.

*Synthesis of **4** from **12***: A solution of *n*-butyllithium (2.5 M, 2.9 mmol) in hexane (1.2 mL) was added dropwise to a solution of 1,8-diiodonaphthalene (0.54 g, 1.4 mmol) in diethyl ether (10 mL) at −78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diethyl disulfide (0.4 mL, 0.35 g, 2.9 mmol) was added dropwise to the mixture. The resulting mixture was stirred at −78 °C for a further 1 h. The reaction mixture was washed with 0.1 M sodium hydroxide (2×45). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (hexane). Recrystallisation by diffusion of pentane into a saturated solution of the crude compound in dichloromethane gave colourless crystals (0.3 g, 80 %).

1-(Phenylselanyl)-8-(phenylsulfanyl)naphthalene (Nap(SePh)(SPh); 5)

*Synthesis of **5** from **18***: A solution of *n*-butyllithium (2.5 M, 1.1 mmol) in hexane (0.5 mL) was added dropwise to a solution of 1-bromo-8-(phenylselanyl)naphthalene (0.40 g, 1.1 mmol) in diethyl ether (20 mL) at −78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl disulfide (0.24 g, 1.1 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at −78 °C for a further 1 h. The reaction mixture was washed with 0.1 M sodium hydroxide (2×45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (hexane). Recrystallisation by diffusion of pentane into a saturated solution of the compound in dichloromethane gave the title compound as colourless crystals (0.2 g, 34 %). ^{1}H NMR (270 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.90–7.82 (m, 2H; nap 5,7-H), 7.65 (dd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.4 Hz, 1H; nap 4-H), 7.62–7.54 (m, 2H; Se*Ph* 2,6-H), 7.42 (t, ^3J(H,H) = 7.6 Hz, 1H; nap 6-H), 7.38–7.28 (m, 3H; Se*Ph* 3–5-H), 7.24–7.05 ppm (m, 7H; nap 2,3-H, S*Ph* 2–6-H); ^{13}C NMR (67.9 MHz, CDCl$_3$, 25 °C, TMS): δ = 138.2 (s), 136.6 (s), 131.2 (s), 130.8 (s), 129.7 (s), 129.0 (s), 128.5 (s), 127.9 (s), 127.4 (s), 126.3 (s), 125.9 (s), 125.8 ppm (s); ^{77}Se NMR (51.5 MHz, CDCl$_3$, 25 °C, PhSeSePh): δ = 455.3 ppm; ^{77}Se NMR (51.5 MHz, D$_2$SO$_4$, 25 °C, PhSeSePh): δ = 927.3 ppm; IR (KBr disk): $\tilde{\nu}_{max}$ = 3249 s, 3053 vs, 2957 w, 2862 w, 2638 w, 2583 w, 2386 w, 2336 w, 2168 w, 1944 s, 1876 w, 1818 w, 1773 w, 1720 w, 1644 w, 1574 vs, 1544 vs, 1474 vs, 1434 vs, 1381 w, 1353 s, 1323 s, 1261 s, 1194 s, 1152 w, 1076 s, 1618 vs, 998 w, 911 w, 861 w, 811 vs, 755 vs, 735 vs, 688 vs, 620 w, 573 w, 542 w, 472 cm^{-1} s; MS (CI$^+$): *m/z* (%): 392.01 (33) [*M*]$^+$, 314.97 (35) [*M*−Ph]$^+$, 236.07 (100) [*M*−Ph$_2$]$^+$; elemental analysis calcd (%) for C$_{22}$H$_{16}$SSe: C 67.3, H 4.1; found: C, 66.7, H 4.2.

*Synthesis of **5** from **16***: A solution of *n*-butyllithium (2.5 M, 0.72 mmol) in hexane (0.3 mL) was added dropwise to a solution of 1-bromo-8-(phenylsulfanyl)naphthalene (0.23 g, 0.72 mmol) in diethyl ether (20 mL) at −78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl diselenide (0.23 g, 0.72 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at −78 °C for a further 1 h. The reaction mixture was washed with 0.1 M sodium hydroxide (2×45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (hexane). Recrystallisation by diffusion of pentane into a saturated solution of the compound in dichloromethane gave the title compound as colourless crystals (0.2 g, 75 %).

*Synthesis of **5** from **19***: A solution of *n*-butyllithium (2.5 M, 0.3 mmol) in hexane (0.1 mL) was added dropwise to a solution of 1-iodo-8-(phenylselanyl)naphthalene (0.12 g, 0.3 mmol) in diethyl ether (15 mL) at −78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl disulfide (0.07 g, 0.3 mmol) in diethyl ether (15 mL) was added dropwise to the mixture. The resulting mixture was stirred at −78 °C for a further 1 h. The reaction mixture was washed with 0.1 M sodium hydroxide (2×45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (hexane). Recrystallisation by diffusion of pentane into a saturated solution of the compound in dichloromethane gave the title compound as colourless crystals (0.02 g, 15 %).

*Synthesis of **5** from **17***: A solution of *n*-butyllithium (2.5 M, 0.47 mmol) in hexane (0.2 mL) was added dropwise to a solution of 1-iodo-8-(phenylsulfanyl)naphthalene (0.17 g, 0.47 mmol) in diethyl ether (20 mL) at −78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl diselenide (0.15 g, 0.47 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at −78 °C for a further 1 h. The reaction mixture was washed with 0.1 M sodium hydroxide (2×45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (hexane). Recrystallisation by diffusion of pentane into a saturated solution of the compound in dichloromethane gave the title compound as colourless crystals (0.1 g, 63 %).

1-(Phenyltelluro)-8-(phenylsulfanyl)naphthalene (Nap(TePh)(SPh); 6)

*Synthesis of **6** from **16***: A solution of *n*-butyllithium (2.5 M, 1.0 mmol) in hexane (0.4 mL) was added dropwise to a solution of 1-bromo-8-(phenylsulfanyl)naphthalene (0.32 g, 1.0 mmol) in diethyl ether (20 mL) at −78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl ditelluride (0.41 g, 1.0 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at −78 °C for a further 1 h. The reaction mixture was washed with 0.1 M sodium hydroxide (2×45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (hexane). Recrystallisation by diffusion of pentane into a saturated solution of the compound in dichloromethane gave the title compound as yellow crystals (0.2 g, 51 %). ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.96–7.85 (m, 4H; nap 5,7-H, Te*Ph* 2,6-H), 7.67 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.1 Hz, 1H; nap 4-H), 7.50–7.37 (m, 3H; nap 2,6-H, Te*Ph* 4-H), 7.36–7.27 (m, 2H; Te*Ph* 3,5-H), 7.26–7.16 (m, 2H; S*Ph* 3,5-H), 7.16–7.02 ppm (m, 4H; nap 3-H, S*Ph* 2,4,6-H); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C, TMS): δ = 141.0 (s), 139.6 (q), 138.3 (s), 137.0 (s), 136.3 (s), 134.9 (s), 132.1 (s), 130.4 (q), 129.8 (s), 129.1 (s), 128.7 (s), 127.9 (s), 127.4 (s), 127.0 (s), 126.1 (s), 125.8 (s), 123.4 (q), 118.3 ppm (s); ^{125}Te NMR (81.2 MHz, $CDCl_3$, 25 °C, PhTeTePh): δ = 715.2 ppm; ^{125}Te NMR (81.2 MHz, D_2SO_4, 25 °C, PhTeTePh): δ = 1018.3 ppm; IR (KBr disk): $\tilde{\nu}_{max}$ = 3436 br, 3051 s, 2924 w, 1931 w, 1878 w, 1812 w, 1725 w, 1578 s, 1475 s, 1433 s, 1348 w, 1325 w, 1262 w, 1193 s, 1101 w, 1074 w, 1022 s, 995 w, 969 w, 898 w, 864 w, 811 vs, 758 s, 735 vs, 689 vs, 621 w, 539 s, 455 s, 405 cm^{-1} w; MS (ES$^+$): *m/z* (%): 472.84 (100) $[M+OMe]^+$; elemental analysis calcd (%) for $C_{22}H_{16}STe$: C 60.1, H 3.7; found: C 60.1, H 3.2.

*Synthesis of **6** from **17***: A solution of *n*-butyllithium (2.5 M, 0.45 mmol) in hexane (0.2 mL) was added dropwise to a solution of 1-iodo-8-(phenylsulfanyl)naphthalene (0.16 g, 0.45 mmol) in diethyl ether (20 mL) at −78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl ditelluride (0.18 g, 0.45 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at −78 °C for a further 1 h. The reaction mixture was washed with 0.1 M sodium hydroxide (2×45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (hexane). Recrystallisation by diffusion of pentane into a saturated solution of the compound in dichloromethane gave the title compound as yellow crystals (0.2 g, 88 %).

1-(Phenyltelluro)-8-(phenylselanyl)naphthalene (Nap(TePh)(SePh); 7)

*Synthesis of **7** from **18***: A solution of *n*-butyllithium (2.5 M, 0.31 mmol) in hexane (0.1 mL) was added dropwise to a solution of 1-bromo-8-(phenylselanyl)naphthalene (0.11 g, 0.31 mmol) in diethyl ether (20 mL) at −78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl ditelluride (0.13 g, 0.31 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at −78 °C for a further 1 h. The reaction mixture was washed with 0.1 M sodium hydroxide (2×45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (hexane). Recrystallisation by diffusion of pentane into a saturated solution of the compound in dichloromethane gave the title compound as yellow crystals (0.1 g, 81 %). ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.99 (dd, ^3J(H,H) = 7.1 Hz, ^4J(H,H) = 1.3 Hz, 1H; nap 4-H), 7.84–7.77 (m, 3H; nap 2-H, Se*Ph* 2,6-H), 7.60 (d, ^3J(H,H) = 7.6 Hz, 1H; nap 5-H), 7.45 (dd, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.0 Hz, 1H; nap 7-H), 7.36–7.28 (m, 2H; nap 3-H, Se*Ph* 4-H), 7.26–7.20 (m, 2H; Se*Ph* 3,5-H), 7.20–7.14 (m, 2H; Te*Ph* 2,6-H), 7.14–7.06 (m, 3H; Te*Ph* 3–5-H), 7.01 ppm (t, ^3J(H,H) = 7.7 Hz, 1H; nap 6-H); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C, TMS): δ = 140.4 (s), 139.7 (s), 136.0 (s), 131.8 (s), 130.2 (s), 129.7 (s), 129.3 (s), 128.5 (s), 128.2 (s), 126.8 (s), 126.7 (s), 125.9 ppm (s); ^{77}Se NMR (51.5 MHz, $CDCl_3$, 25 °C, PhSeSePh): δ = 362.8 ppm; ^{125}Te NMR (81.2 MHz, $CDCl_3$, 25 °C, PhTeTePh): δ = 687.6 ppm (^4J(Te,Se) = 834.0 Hz); IR (KBr disk): $\tilde{\nu}_{max}$ = 3428 br, 3042 w, 2957 w, 1969 w, 1879 w, 1809 w, 1720 w, 1655 w, 1573 s, 1535 w, 1474 s, 1431 s, 1328 w, 1261 w, 1189 w, 1138 w, 1062 s, 1019 s, 995 s, 953 w, 897 w, 839 w, 809 vs, 758 vs, 733 vs, 690 s, 665 w, 612 w, 456 cm^{-1} s; MS (ES$^+$): *m/z* (%): 410.99 (100) $[M-Ph]^+$; elemental analysis calcd (%) for $C_{22}H_{16}SeTe$: C 53.9, H 3.3; found: C 54.6, H 3.5.

*Synthesis of **7** from **19***: A solution of *n*-butyllithium (2.5 M, 0.40 mmol) in hexane (0.2 mL) was added dropwise to a solution of 1-iodo-8-(phenylselanyl)naphthalene (0.16 g, 0.40 mmol) in diethyl ether (20 mL) at −78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl ditelluride (0.16 g, 0.40 mmol) in diethyl ether (20 mL) was added dropwise to the mixture. The resulting mixture was stirred at −78 °C for a further 1 h. The reaction mixture was washed with 0.1 M sodium hydroxide (2×45 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel (hexane). Recrystallisation by diffusion of pentane into a saturated solution of the compound in dichloromethane gave the title compound as yellow crystals (0.03 g, 18 %).

1-(Phenylsulfinyl)-8-(phenylsulfanyl)naphthalene (Nap(O=SPh)(SPh); 8): MCPBA (0.06 g, 0.34 mmol) was added to a solution of 1,8-(diphenylsulfanyl)naphthalene (0.12 g, 0.34 mmol) in ether (5 mL). The reaction mixture was stirred for 2 h and then concentrated under vacuum. Recrystallisation by diffusion of pentane into a saturated solution of the compound in dichloromethane gave the title compound as colourless crystals (0.05 g, 41 %). ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.75 (d, ^3J(H,H) = 7.0 Hz, 1H; nap 4-H), 8.08 (d, ^3J(H,H) = 8.0 Hz, 1H; nap 2-H), 8.03 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 1.2 Hz, 1H; nap 5-H), 7.82 (dd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.3 Hz, 1H; nap 7-H), 7.80–7.72 (m, 1H; nap 3-H), 7.56–7.48 (m, 1H; nap 6-H), 7.48–7.40 (m, 2H; SO*Ph* 2,6-H), 7.30–7.20 (m, 3H; SO*Ph* 3–5-H), 7.16–7.06 (m, 3H; S*Ph* 3–5-H), 6.84–6.74 ppm (m, 2H; S*Ph* 2,6-H); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C, TMS): δ = 139.0 (s), 132.9 (s), 131.4 (s), 130.3 (s), 129.2 (s), 129.1 (s), 127.2 (s), 127.1 (s), 126.7 (s), 126.3 (s), 126.1 ppm (s); IR (KBr disk): $\tilde{\nu}_{max}$ = 3432 br s, 3057 w, 1576 s, 1546 w, 1492 w, 1475 s, 1439 s, 1353 w, 1336 w, 1202 w, 1173 w, 1156 w, 1079 s, 1036 vs, 971 w, 928 w, 902 w, 848 w, 820 vs, 763 vs, 736 vs, 682 vs, 595 w, 558 w, 518 s, 501 w, 471 s, 433 cm^{-1} s; MS (ES$^+$): *m/z* (%): 382.89 (100) $[M+Na]^+$; elemental analysis calcd (%) for $C_{22}H_{16}S_2O$: C 73.3, H 4.5; found: C 72.2, H 5.2.>

1,8-Bis(phenylsulfinyl)naphthalene (Nap(O=SPh)$_2$; 9): MCPBA (0.18 g, 1.1 mmol) was added to a solution of 1,8-(diphenylsulfanyl)naphthalene (0.12 g, 0.35 mmol) in ether (5 mL). The reaction mixture was stirred for 2 h, after which a white precipitate was formed. The mixture was filtered and the filtrate reduced under vacuum to give a cream solid. Recrystallisation by diffusion of pentane into a saturated solution of the compound in dichloromethane gave the title compound as colourless crystals (0.06 g, 44 %). ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.58 (dd, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.4 Hz, 2H; nap 4,5-H), 8.13 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.4 Hz, 2H; nap 2,7-H), 7.83–7.74 (m, 2H; nap 3,6-H), 7.64–7.53 (m, 4H; 2×SO*Ph* 2,6-H), 7.42–7.34 ppm (m, 6H; 2×SO*Ph* 3–5-H); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C, TMS): δ = 133.5 (s), 131.2 (s), 129.6 (s), 127.4 (s), 126.7 (s), 126.2 ppm (s); IR (KBr disk): $\tilde{\nu}_{max}$ = 3445 br s, 3052 w, 1578 w, 1490 w, 1471 s, 1438 s, 1338 w, 1210 w, 1177 w, 1147 w, 1075 vs, 1045 vs, 996 w, 965 w, 911 w, 845 w, 823 vs, 753 vs, 690 vs, 621 s, 578 s, 503 s, 461 w, 438 s, 408 cm^{-1}: w; MS (ES$^+$): *m/z* (%): 398.84 (100) $[M+Na]^+$; elemental analysis calcd (%) for $C_{22}H_{16}S_2O_2$: C 70.2, H 4.3; found: C 69.3, H 4.4.

Crystal structure analyses: X-ray crystal structures were determined at −148(1) °C by using the St Andrews Robotic Diffractometer: a Rigaku ACTOR-SM, Saturn 724 CCD area detector with graphite monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The data was corrected for Lorentz, polarisation and absorption. The data for the analysed complexes was collected and processed by using CrystalClear (Rigaku).[33] The structures were solved by direct methods[34] and expanded by using Fourier techniques.[35] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by using the riding model. All calculations were performed by using the CrystalStructure[36] crystallographic software package except for refinement, which was performed by using SHELXL-97.[37] Table 6 gives the crystallographic data for compounds **4**–**9**. CCDC-759109 (**4**), -759110 (**5**), -759111 (**6**), -759112 (**7**), -759113 (**8**) and

Table 6. Crystallographic data for compounds **4**–**6**.

	4	**5**	**6**	**7**	**8**	**9**
empirical formula	$C_{14}H_{16}S_2$	$C_{22}H_{16}SSe$	$C_{22}H_{16}STe$	$C_{22}H_{16}SeTe$	$C_{22}H_{16}OS_2$	$C_{22}H_{16}O_2S_2$
M_r	248.4	391.39	440.03	486.93	360.49	376.49
T [°C]	−148(1)	−148(1)	−148(1)	−148(1)	−148(1)	−148(1)
crystal colour, habit	colourless, prism	colourless, block	yellow, prism	yellow, prism	colourless, prism	colourless, prism
crystal size [mm^3]	0.15×0.09×0.09	0.27×0.09×0.09	0.18×0.15×0.12	0.21×0.09×0.09	0.18×0.09×0.09	0.18×0.09×0.09
crystal system	orthorhombic	orthorhombic	triclinic	triclinic	monoclinic	monoclinic
a [Å]	9.0074(15)	21.150(5)	9.997(2)	10.094(4)	10.139(5)	17.275(9)
b [Å]	16.221(3)	5.7154(12)	11.2364(18)	11.2590(19)	15.379(6)	15.216(7)
c [Å]	17.386(3)	14.421(3)	17.928(3)	18.122(8)	11.575(6)	13.591(7)
α [°]	–	–	74.309(18)	73.66(4)	–	–
β [°]	–	–	87.24(2)	87.13(4)	111.083(15)	105.593(11)
γ [°]	–	–	66.344(13)	67.06(3)	–	–
V [Å^3]	2540.2(8)	1743.3(7)	1771.7(6)	1815.9(13)	1684.0(14)	3441(3)
space group	$Pbca$	$Pca2_1$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/c$
Z	8	4	4	4	4	8
ρ_{calc} [g cm^{-3}]	1.299	1.491	1.65	1.781	1.422	1.453
F(000)	1056	792	864	936	752	1568
μ(Mo$_{K\alpha}$) [cm^{-1}]	3.888	22.731	17.962	36.424	3.227	3.234
no. of reflns measured	7639	6528	19899	18410	9709	10825
R_{int}	0.076	0.063	0.032	0.05	0.054	0.059
min/max transmissions	0.942/0.966	0.397/0.815	0.718/0.806	0.461/0.720	0.943/0.971	0.961/0.981
indep. reflns	2216	2368	7014	6253	3400	3459
observed reflns (no. variables)	1963 (148)	2217 (218)	6663 (434)	5691(434)	3089(227)	3114(236)
refln/parameter ratio	14.97	10.86	16.16	14.41	14.98	14.66
R_1 ($I>2.00\sigma(I)$)	0.0764	0.0593	0.0566	0.0646	0.0693	0.0675
R (all reflns)	0.0894	0.0655	0.0599	0.0848	0.0789	0.0808
wR_2 (all reflns)	0.1333	0.1574	0.1714	0.2886	0.167	0.1995
GOF	1.245	1.14	1.099	1.211	1.169	1.312
Flack parameter	–	0.07(2)	–	–	–	–
max. peak in final diff. map [e Å^{-3}]	0.24	0.67	1.64	2.10	0.34	0.57
min. peak in final diff. map [e Å^{-3}]	−0.27	−0.68	−1.86	−2.27	−0.60	−0.55

-759114 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details: Geometries were fully optimised in the gas phase at the B3LYP level[38] by using Curtis and Binning's 962(d) basis[39] on Se and 6-31+G(d) elsewhere, followed by calculation of the harmonic frequencies to confirm the minimum character of each stationary point and to obtain thermodynamic corrections. Reaction enthalpies (including proton affinities (PAs)) and WBIs,[31] the latter obtained in a natural bond orbital analysis,[40] are given at this level. If experimental structures were available from X-ray crystallography, these were used as starting point for the optimisations. Despite noticeable differences between calculated and optimised chalcogen–chalcogen distances (the optimised ones tend to be overestimated by several picometers), essentially the same WBIs were obtained for corresponding X-Ray and DFT structures. Magnetic shielding constants (σ) were evaluated for the optimised minima at the GIAO-B3LYP/II′ level, that is, by using contracted Huzinaga basis of polarized triple-zeta quality,[41] except for the peripheral aromatic hydrogen atoms, for which a double-zeta (DZ) basis was employed. ^{77}Se chemical shifts (δ) are reported relative to Me_2Se, computed at the same level ($\delta = 1608$ ppm). The computations were performed by using the Gaussian 03 suite of programs.[41]

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