

Hypervalent adducts of chalcogen containing *peri*-substituted naphthalenes; Reactions of sulfur, selenium and tellurium with dihalogens

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ABSTRACT: A range of structurally diverse compounds **1-15** {Nap[SPh]₂·Br₄ (Nap = naphthalene-1,8-diyl); Nap[SePh][EPh]·Br₄ (E = Se, S); Nap[SePh]₂·I₂; Nap[SePh][EPh]·3/2I₂ (E = Se, S); Nap[TePh][G]·X₂ (G = SePh, SPh, Br, I; X = Br, I); [Nap(PPh₂OH)(SPh)]⁺Br₃⁻} formed from the reactions between *peri*-substituted naphthalene chalcogen-donors **D1-D8** {Nap[ER][E`R] (ER/E`R = SPh, SePh, TePh); Nap[TePh][X] (X = Br, I); Nap[PPh₂][SPh]} and dibromine and diiodine were characterised by X-ray crystallography and where possible by multinuclear NMR, IR and MS. X-ray data for **1-15** were analysed by naphthalene ring torsions, *peri*-atom displacement, splay angle magnitude, *peri*-distance, aromatic ring orientations and quasi-linear three-body arrangements. The hypervalent linear moieties are considered in the context of the charge-transfer model and the 3c-4e model introduced by Pimentel and Rundle. In general the conformation of the final products obeyed the rule based on charge-transfer that ‘see-saw’ (X-ER₂-X, 10-E-4) adducts arise when the halogen (X) is more electronegative than the chalcogen (E) and if the converse is true then C.-T. ‘spoke’ (X-X-ER₂, 8-E-3) adducts are formed. Upon treatment with dibromine, selenium donor compounds **D2** {Nap[SePh]₂} and **D3** {Nap[SePh][SPh]} afford unusual tribromide salts of bromoselenyl cations containing a hypervalent

X-E...E` 3c-4e type interaction. Upon treatment with diiodine **D2** and **D3** form ‘Z-shaped’ ‘extended spoke’ adducts containing an uncommon 2:3 donor/chalcogen ratio and incorporating chains of I₂ held together by rare I...I interactions. As expected, ‘see-saw’ 10-E-4 adducts are formed following the reaction of Te-donors **D4-D7** {Nap[TePh][X] (X = Br, I); Nap[TePh][EPh] (E = Se, S)} with the dihalogens. Naphthalene distortion in general is comparable between respective donor compounds and products **1-15**. Ionic species **2** and **3** display a noticeable reduction in molecular distortion explained by the relief of steric strain via weak *peri*-interactions and the onset of 3c-4e bonding.

KEYWORDS Hypervalency, chalcogen, halogen, adduct, 3c-4e, *peri*-substituted naphthalene, distortion.

1. Introduction

Hypervalency of the heavier main group elements has attracted considerable attention due to the extraordinary structures and reactivity their compounds exhibit. The ambiguity over the bonding in these species continues to intrigue chemists and has been debated upon since the pioneering work on the electronic theory of the covalent bond by Lewis and Langmuir in the early 1900s.^{1,2,3,4} Whilst elements of Period 2 and atoms in their lowest valences conformed readily to the octet rule, the bonding in molecules formed by heavier atoms of the Periodic Table in their higher valences (e.g. PCl₅) conflicted with this theory and was the topic of a contentious debate.^{2,4} Lewis persisted with his traditional theory of the 2c-2e covalent bond but proposed that the bonding was accompanied by an expansion of the octet.^{2,5} Conversely, Langmuir favored the octet rule and argued that the bonding was now ionic rather than covalent.^{2,6}

With the emergence of quantum mechanical theory, the bonding in hypervalent compounds was generally assumed to be covalent in nature and rationalized by the acceptance of the supplementary electrons into the unfilled low-lying *d*-orbitals, thus violating the octet rule.^{3,4,7,8,9} The absence of 2d orbitals therefore justified the lack of hypervalency in compounds of Period 2.^{3,4} With the advancement of molecular orbital theory, Rundle and Pimentel developed the earlier work undertaken by Sugden¹⁰ and introduced the notion of a three centre four-electron bond (3c-4e) to explain the hypervalency in the trihalide ions.^{7,11} This concept has become a favored method for explaining the existence of hypervalency without violating the octet rule or invoking ionic bonding.^{12,13} The four electrons occupy bonding and non-bonding molecular orbitals;^{2,7,11,14,15} as only one bonding pair is available for the two bonds, hypervalent bonds are weaker than single electron pair bonds (2c-2e) between the same elements. Bond orders of apical bonds in hypervalent 3c-4e species are typically less

than one (~ 0.5) with bond distances predicted to be 0.18 Å longer than for single electron pair bonds with bond orders of 1.0.^{7,9,11,14,15}

In 1969 Musher classified “hypervalent” molecules as those “*formed by elements in Groups V-VIII of the periodic table in any of their valences other than their lowest stable chemical valence of 3, 2, 1, and 0 respectively.*”³ The pertinence of the term “hypervalence” has recently been under dispute following the advancement of quantum mechanical calculations which reinforce the 3c-4e theory proposed by Rundle and Pimentel and conform to the octet rule.^{2,7,11,13,16} As a consequence the use of octet expansion of the heavier main group elements has diminished from current bonding descriptions.^{13,16,17} Nonetheless, hypervalency is a topic of continued interest to chemists with numerous compounds containing linear arrangements of three main group elements having been well documented recently in the literature.^{14,15,18,19,20,21,22} The nature of the bonding in these linear species can be described by the Rundle-Pimentel 3c-4e model and a charge-transfer model and has recently been thoroughly reviewed.²³

Organic molecules containing the Group 16 donor atoms sulfur, selenium and tellurium react with dihalogens (Br_2 , I_2) and inter-halogens (IBr , ICl) to form a variety of addition complexes with wide structural diversity. Experimental conditions control the pathway these reactions take and subsequently the structural motifs and geometry around the Group 16 atoms in the final structure. Factors such as the type of chalcogen donor atom, the form of the dihalogen or inter-halogen, the stoichiometry of the reactants and the nature of the donor atoms’ R group(s) all play a significant role.^{15,22} A slight adjustment to any one of these variables could lead to subtle modifications in molecular geometry so it is unsurprising that a diverse combination of structures have been synthesised; charge-transfer (C.-T.) ‘spoke’ and ‘extended spoke’ adducts, polyiodide, ‘see-saw’, ionic, ‘T-shaped’, bent, mixed-valence, dication-bridged and dimeric structural motifs.^{15,22} Ionic compounds, often accompanied by counteranions of polyhalides adopting unusual and sometimes complex structures are also known.^{15,22,24,25,26,27,28,29,30,31,32,33} The neutral charge-transfer (C.-T.) ‘spoke’ adduct ($\text{R}_2\text{E}-\text{X}-\text{Y}$, 8-E-3) and the ‘see-saw’ ($\text{X}-\text{ER}_2-\text{Y}$, 10-E-4) insertion adduct, characteristic of quasi-linear hypervalent $\text{E}-\text{X}-\text{Y}$ ^{15,22,28,34,35} and $\text{X}-\text{E}-\text{Y}$ ^{14,15,22,28,31,36,37} fragments respectively are the most common structural motifs generated from the reaction of diorganochalcogen-donors [R_2E] with inter- or dihalogens.

With variations in the reaction conditions affecting the outcome of reactions between chalcogen-donors [R_2E] with di- and inter-halogens, predicting the conformation of the final solid state structures continues to be a challenge to chemists. In solution, the C.-T. ‘spoke’ adduct and the ‘see-saw’ adduct of $\text{RR}'\text{E}-\text{X}_2$ type compounds are in equilibrium.^{14,38,39} Husebye and co-workers suggested that all the products in these reactions are derived from a common intermediate species $[\text{R}_2\text{E}-\text{X}]^+$

and progress via a general reaction pathway,^{15,22,40} with nucleophilic attack occurring at the halogen and the chalcogen sites of the $[R_2E-X]^+$ cation affording the C.-T. ‘spoke’ and ‘see-saw’ hypervalent adducts respectively.^{14,15,22,41} The structure of the final product can therefore be predicted with a generalization based on the degree of charge-transfer between the non-bonding orbitals of the chalcogen donor $n(E)$ to the LUMO of the di- or inter-halogen acceptor $\sigma^*(X-X')$.^{14,39,42} This can be estimated from the electronegativity (χ) of the elements and follows the loose rule that the ‘see-saw’ adducts will be formed if halide X is more electronegative than chalcogen E $[R_2E^{\delta+}-X^{\delta-}]$ whilst if the converse is true then the C.-T. ‘spoke’ adducts will predominate.^{14,39,42} This is exemplified by the fact that no C.-T. adducts are known for Te-donors $[\chi(\text{Te}) 2.08]^{43}$ with any di- or inter-halogen $[\chi(\text{F}) 3.94- \chi(\text{I}) 2.36]$.^{14,15,22,43} It must be recognized however, that the electronegativity of the chalcogen atom and the electronic properties of R_2E can be affected by the R groups thus influencing the outcome of the reaction. Compounds with bulky groups around E will favor the 3 coordinate chalcogen environment of the C.-T. ‘spoke’ adduct over the more congested 4 coordinate atom in the ‘see-saw’ form.^{14,39}

‘Spoke’ adducts are formed via the transfer of electron density from non-bonding orbitals of the chalcogen donor atom into the LUMO of the di- or inter-halogen acceptor molecule (and hence termed charge-transfer adducts). This generally occurs when $\chi(E) > \chi(X)$, *i.e.* the chalcogen atom is a stronger donor and more electron density is available to donate into the empty orbitals on X.^{15,22} The majority of neutral C.-T. ‘spoke’ adducts reported in the literature are formed by reaction of organosulfur $[\chi(\text{S}) 2.58]^{43}$ donors with diiodine $[\chi(\text{I}) 2.36]$,^{15,22,30,35,43,44} for example benzyl sulfide diiodine.⁴⁵

Organoselenium diiodine C.-T. adducts are less common^{15,22,46,47} but those reported in the literature exhibit a considerable increase in the iodine-iodine bond length from free iodine $[2.66 \text{ \AA}]^{48}$ compared to similar sulfur compounds showing organoselenides are better donor molecules than organosulfides $[\chi(\text{Se}) 2.35, \chi(\text{S}) 2.58]$.^{15,22,43} Reaction of dibromine with diorganosulfur- and diorganoselenium-donors produces adducts of different geometries. Following the general rule based on electronegativity values, both R_2S- $[\chi(\text{S}) 2.58]^{43}$ and R_2Se- $[\chi(\text{Se}) 2.35]^{43}$ donors are expected to form ‘see-saw’ compounds $[\chi(X) > \chi(E); \chi(\text{Br}) 2.68]$.^{14,15,22,39,42,43} Whilst all structurally reported diorganoselenium dibromine compounds exclusively adopt ‘see-saw’ structures,^{14,15,22,47,49,50} diorganosulfur dibromine compounds are known to adopt C.-T. ‘spoke’ arrangements^{15,22,28,42,51,52} (‘T-shaped’ adducts have been reported from the reaction of S-donor compounds with dibromine).^{41,53}

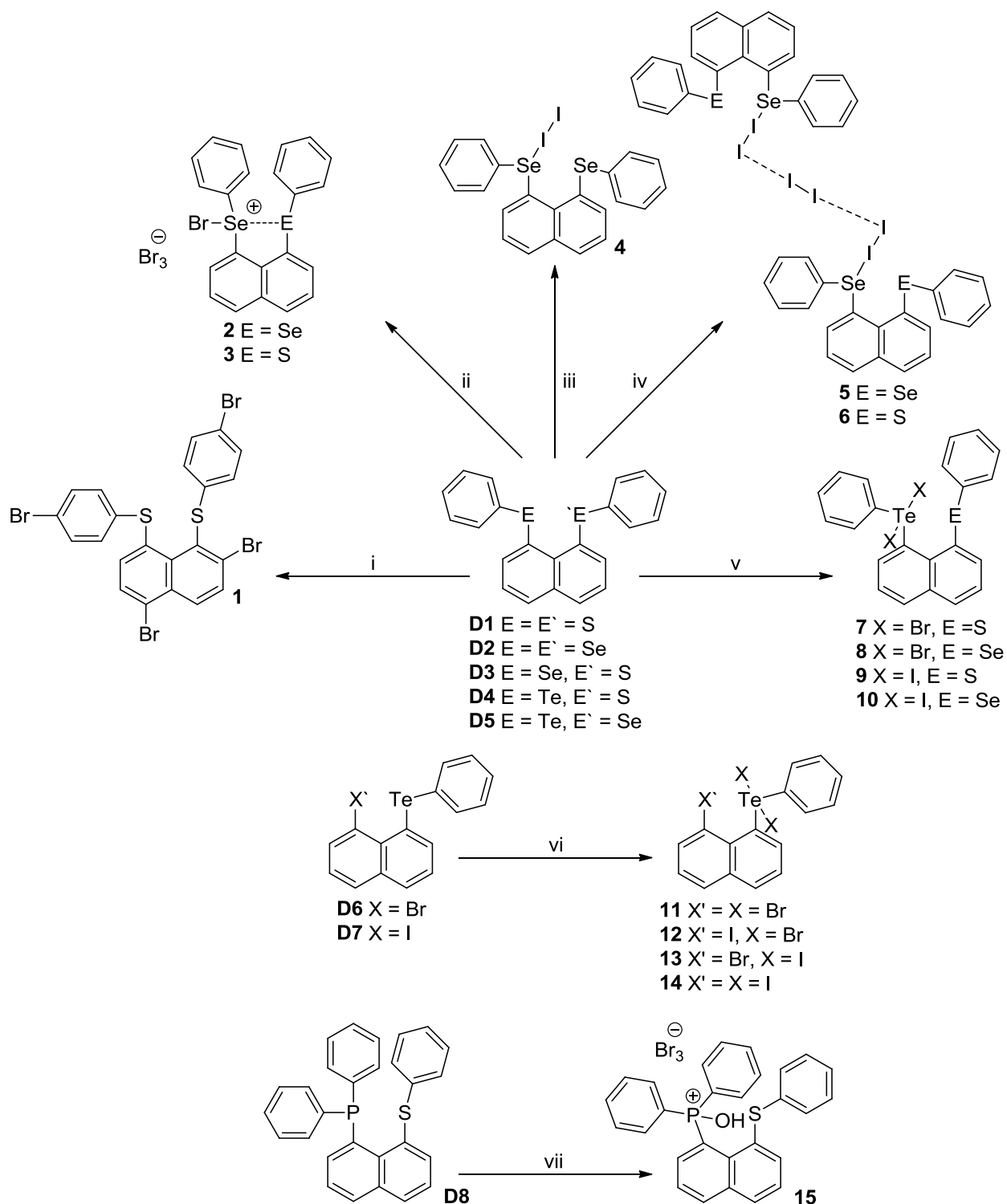
Generally, when the halide species (X) is more electronegative than the chalcogen atom (E), ‘T-shaped’ or ‘see-saw’ adducts are formed.^{14,39,42} Consequently, all the known reactions between tellurium-donors $[\chi(\text{Te}) 2.08]^{43}$ and di- or inter-halogens $[\chi(\text{F}) 3.94- \chi(\text{I}) 2.36]^{43}$ form ‘T-shaped’ or ‘see-saw’ adducts with no tellurium C.-T. ‘spoke’ adducts

known.^{15,22,42} Tellurium forms strong donor-strong acceptor systems with the dihalogens, strong enough to cleave the X-X bond and oxidize tellurium.^{14,15,22} Subsequent nucleophilic attack occurring at the tellurium site of the $[R_2Te-X]^+$ cation affords the ‘see-saw’/‘T-shaped’ hypervalent adduct with a quasi linear X-Te-X alignment.^{14,15,22}

Partial negative charge acting on the terminal Y atom of R_2E-X-Y linear fragment can be sufficient for C.-T. ‘spoke’ adducts to act as donors towards other acceptors (A). This produces adducts which are structurally more complex, known as C.-T. ‘extended spoke’ adducts $[R_2E-X-Y\cdots A]$ (where A is normally another XY molecule and $XY\cdots A$ angles are typically close to 90°).^{15,22} The terminal atom-acceptor ($Y\cdots A$) interaction delocalizes negative charge onto Y which in turn strengthens the E-X bond. With an extremely strong $Y\cdots A$ interaction, systems of the type $[RE-X]^+[Y-A]^-$ can be envisaged (for example the adduct formed by reaction of N-methylbenzothiazole-2(3*H*)-selone with IBr).^{2,15}

We have previously explored sterically crowded 1,8-disubstituted naphthalenes.^{54,55} Our early work focused on di-chalcogenide ligands⁵⁴ and unusual phosphorus compounds.⁵⁵ More recently we have reported the synthesis and structural study of mixed phosphorus-chalcogen,⁵⁶ chalcogen-chalcogen⁵⁷ and halogen-chalcogen systems.⁵⁸ During our investigations of *peri*-substituted naphthalenes we prepared a number of chalcogen-donors **D1-D8** (Scheme 1).^{57,58} The work reported here complements our previous study of chalcogen-naphthalene derivatives,^{56,57,58} expanding the knowledge of naphthalene distortion and contributing to the exciting field of hypervalence that occurs in linear species formed from the reactions between chalcogen-donors and dihalogens. Here we present the reactions between chalcogen-donors **D1-D8** and dibromine and diiodine and a full structural study of the geometrically diverse products formed **1-15** (Scheme 1).

Scheme 1 Hypervalent adducts formed from the reactions of chalcogen containing *peri*-substituted naphthalenes **D1-D8** with dibromine and diiodine.



conditions: i-vii X_2 ($\text{X} = \text{Br}, \text{I}$), CH_2Cl_2 , 2 h, RT: i (4 equiv) Br_2 ; ii (2 equiv) X_2 ; iii/iv (1 equiv) I_2 ; v/vi (1 equiv) X_2 ; vii (4 equiv) Br_2 .

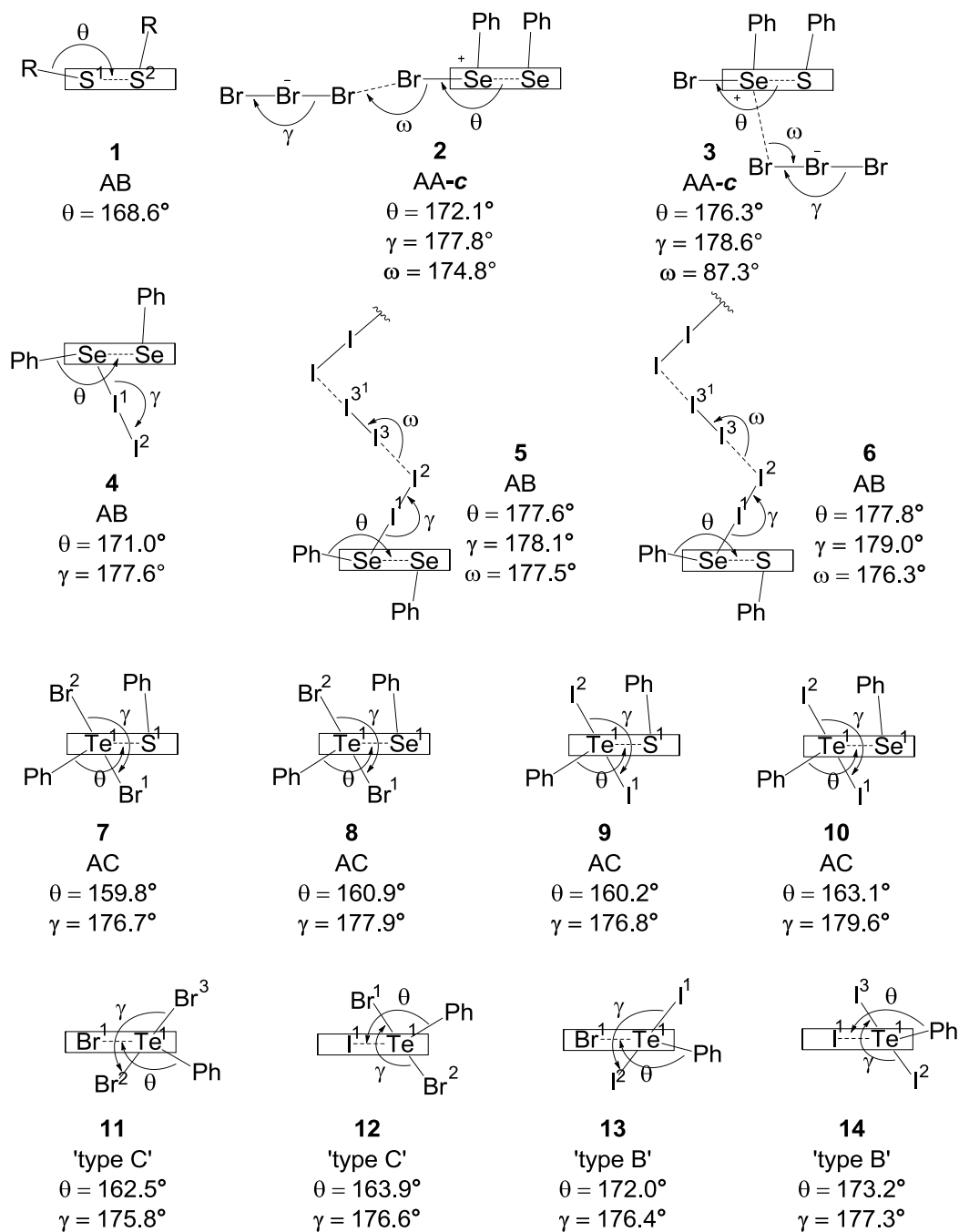


Figure 1 The orientation of the naphthyl and phenyl rings, the type of structure and the quasi-linear arrangements in compounds **1-14**.⁶⁵

2. Results and discussion

Compounds **1-15** were synthesised and where possible the derivatives were characterized by multinuclear NMR and IR spectroscopy and mass spectrometry and the homogeneity of the new compounds was confirmed by microanalysis. ³¹P, ⁷⁷Se and ¹²⁵Te NMR spectroscopy data for compounds **4-15** is compared in Table 1 with donors **D2-D8**.^{57,58} The tribromide salts

2 and **3** are insoluble in all common NMR solvents, hence no NMR spectroscopic data for these compounds is given.

Suitable single crystals were obtained for **1-15** by diffusion of pentane into saturated solutions of the individual compound in dichloromethane. All compounds **1-15** crystallise with one molecule in the asymmetric unit. Selected interatomic distances, angles and torsion angles are listed in Tables 1-6. Further crystallographic information can be found in Tables 8-11 and the Supporting Information.

Adducts formed from the reaction of diorganosulfur compounds with dibromine are rare. The majority of those reported and structurally characterised by single crystal X-ray diffraction adopt the C.-T. ‘spoke’ structure with an S-Br-Br linear arrangement.^{15,22,28,42,51} Upon treatment of 1,8-bis(phenylsulfanyl)naphthalene **D1** with dibromine, no adduct is isolated but electrophilic aromatic substitution dominates. Aromatic groups bearing -SR groups are strongly activated by delocalization of resonance lone-pairs into the aromatic π -system and are therefore highly reactive towards electrophilic substitution.⁵⁹ The delocalization of the lone pair on sulfur into the aromatic system in **D1** makes it unavailable for donation into the empty orbitals of the dibromine molecule. The naphthalene ring system being less aromatic than the phenyl moieties are thus more susceptible towards electrophilic substitution. The activating S(phenyl) group donates electrons into the π -system and directs incoming electrophiles to the *ortho* or *para* positions. Attack at the *para* position is sterically more favorable placing the large bromine atom further from the bulk of the molecule.⁵⁹ The second bromination is directed by the second S(phenyl) moiety to the *ortho* (C7) position to avoid the inevitable steric interaction between the bromine atoms upon *para* substitution. Final bromination of the phenyl rings occurs with the sulfur atoms directing the substitution to the two *para* positions, away from the steric bulk of the molecule to produce 1,8-bis(4-bromophenylsulfanyl)-2,5-dibromonaphthalene **1** (Scheme 1).⁵⁹ Varying the loading of dibromine (1-6 equiv), produced **1** exclusively.

Substitution of the heavier main group elements at the *peri*-positions in naphthalene causes considerable steric hindrance giving rise to structurally distorted compounds with unusual bonding and geometry.^{56,57,58,60} The bulky atoms are constrained in close proximity by the rigid backbone at a distance shorter than the sum of van der Waals radii for the two interacting atoms.^{56,57,58} Steric strain caused by the crowding of substituents can be released through bond formation or if weak attractive non-covalent interactions exist between tightly packed atoms.^{60,61} As non-bonded distances decrease relative

to the sum of van der Waals radii, weak non-covalent interactions become more covalent in nature and the steric interaction is reduced.⁶² Distortion away from the ‘ideal’ naphthalene geometry also helps alleviate steric strain and occurs via in-plane and out-of-plane deviations of the exocyclic bonds and buckling of the usually rigid backbone.^{56,57,58,60,61,63} X-ray structural data plays a fundamental role in determining naphthalene distortion and therefore assessing steric strain.^{56,57,58}

The structural geometry of compounds **1-15** can be described by the orientation of the naphthyl and phenyl rings relative to the C(ar)-G(1)-C(ar) and the C(ar)-Z(2)-CI planes, calculated from torsion angles θ and γ respectively (see Table 7, Figure 1).⁶⁴ When θ and γ approach 90° the orientation is categorized as axial whilst an equatorial conformation is denoted by angles close to 180° .⁶⁴ Conformations in between axial and equatorial are classified as twist.⁶⁴ For angle θ , axial conformations correspond to the ‘type A’ structure presented by Nakanishi *et al.* (G-C_{Ph}/Z-C_{Ph} bond lies perpendicular to the naphthyl plane).⁶⁵ An equatorial conformation for θ aligns the G-C_{Ph}/Z-C_{Ph} bond on or close to the plane (‘type B’)⁶⁵ and a twist conformation relates to Nakanishi’s ‘type C’ (Figure 1).^{64,65}

Compound **1** (Figure 2) displays a mixed equatorial-axial and axial-equatorial conformation of naphthyl and phenyl rings around the two individual sulfur atoms, matching that observed for **D1** and classified as ‘AB-type’ structure (Figure 1).^{57,65} The sulfur atoms are displaced to even distances but to opposite sides of the naphthalene least squares plane with a deviation comparable to that displayed by **D1**.⁵⁷ The sulfur atoms are further accommodated by in-plane distortions in the C-C-C group between the *peri*-atoms indicated by a positive splay angle of 9.9° . The resulting non-bonded S...S *peri*-distance [2.935(4) Å] is 18 % shorter than the sum of the van der Waals radii for two sulfur atoms [3.60 Å]⁶⁶ and marginally shorter than observed in **D1** [3.0036(13) Å].⁵⁷

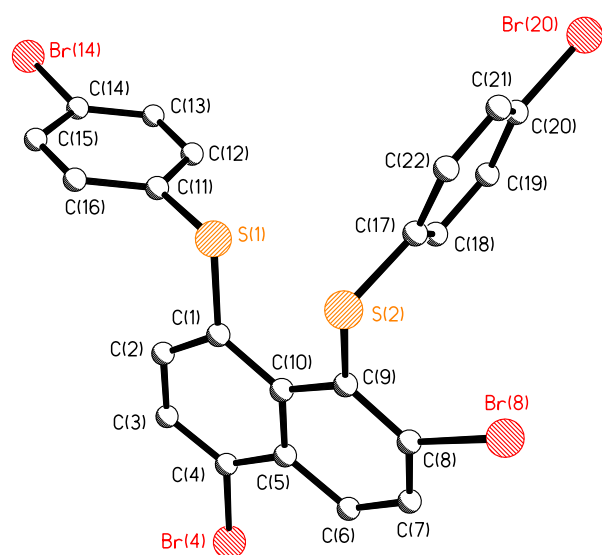


Figure 2 The molecular structure of 1,8-bis(4-bromophenylsulfanyl)-2,5-dibromonaphthalene **1**.

A more pronounced distortion of the naphthalene skeleton is observed in **1** which exhibits larger maximum C-C-C-C torsion angles [*ca.* 4°] compared to **D1** [*ca.* 1-3°].⁵⁷ Br(4) and Br(8) atoms lie 0.025(13) Å and 0.103(11) Å above the naphthyl plane respectively and Br-C [1.90-1.91 Å] and S-C [1.79-1.76 Å] bond lengths are within the usual ranges [1.90, 1.77 ± 0.05 Å]. Intermolecular short contacts exist between bromine atoms [Br(4)⋯Br(8)]¹ 3.63(1) Å; Br(4)⋯Br(14)¹¹ 3.65(1) Å; Br(14)⋯Br(20)¹¹¹ 3.63(1) Å] but no significant overlap of phenyl or naphthyl rings is observed.

All structurally reported adducts formed from the reaction of diorganoselenium compounds with dibromine adopt the ‘see-saw’ geometry.^{14,15,22,47,49,50} The donor compounds 1,8-bis(phenylselenenyl)naphthalene **D2** and 1-(phenylselenenyl)-8-(phenylsulfanyl)naphthalene **D3** react with dibromine to form similar tribromide salts of analogous bromoselenenyl cations which can be represented by the formula [RSe-Br]⁺⋯[Br-Br₂]⁻ (Scheme 1).¹⁵ The lower electronegativity and hence greater electron donor ability of selenium over sulfur allows for a strong donor-strong acceptor system to form with dibromine sufficient to cleave the Br-Br bond and oxidise the selenium atom.^{15,22,43} In both **D2** and **D3** the Se(1) atom reacts with the first molecule of Br₂ simultaneously weakening the Br(1)-Br(2) bond. The partial negative charge acting on the terminal Br(2) atom could be sufficient to act as a donor towards a second (acceptor) molecule of Br₂. Delocalization of negative charge onto the terminal Br(2) atom would strengthen the Se(1)-Br(1) bond to the extent that the Br(1)-Br(2) bond is cleaved forming the cation [RSe-Br]⁺ and a quasi-linear hypervalent 3c-4e Br₃⁻ counteranion.¹⁵

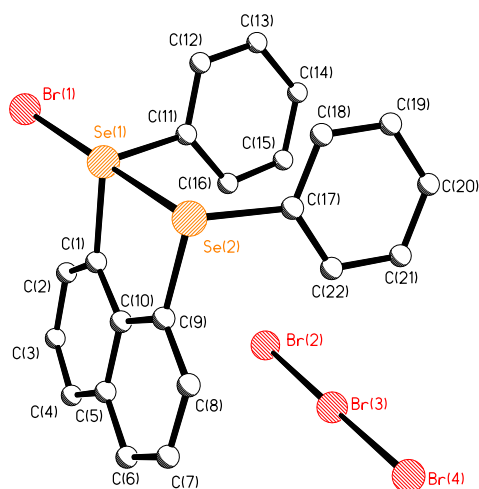


Figure 3 The molecular structure of the ionic C.-T. ‘extended spoke’ adduct **2** formed from the reaction of **D2** with dibromine (compound **3** adopts a similar structure, see the supporting information).

The ionic ‘extended spoke’ adducts **2** and **3** adopt a similar conformation in their molecular structures (Figure 3). The naphthyl and phenyl rings orientate with an axial-equatorial arrangement around each chalcogen *peri*-atom with both E- C_{ph} bonds aligning perpendicular to and on the same side of the naphthyl plane (‘AA-*c* type’, Figure 1).^{64,65} The phenyl rings overlap in a face-to-face offset arrangement with centroid-centroid distances [**2**: 3.691(1) Å; **3**: 3.79(1) Å] within the usual range for typical π - π -stacking [3.3-3.8 Å].⁶⁷ Each adduct displays one quasi-linear X-E...E’ arrangement of three atoms [**2**: 172.1°; **3**: 176.3°], the nature of the bonding in which can be described by the Rundle-Pimentel 3c-4e model.^{7,11} The Se...Se and Se...S *peri*-distances in **2** and **3** [2.7619(7) Å; 2.721(2) Å] are 27 % and 26 % shorter than the sum of van der Waals radii for the two interacting atoms respectively. These values lie between those of a single electron pair Se-Se and Se-S bond [2.3639(5) Å; 2.24(1) Å]^{68,69} and the non-bonding interactions observed in **D2** and **D3** [3.1332(9) Å; 3.063(2) Å] respectively.⁵⁷

The significant reduction in the *peri*-distance in both adducts relative to **D2** and **D3** suggests that a weak attractive non-covalent interaction is operating between the *peri*-atoms thus decreasing steric hindrance. As expected, naphthalene distortion in **2** and **3** although still influential due to the absence of a strong *peri*-covalent bond,⁶⁸ is notably diminished compared with **D2** and **D3** respectively. The inclination of the exocyclic E- C_{Nap} bonds within the naphthyl plane is minimal with small, but not negligible, positive splay angles [**2** 6.1°; **3** 5.3°] considerably reduced compared with donor compounds **D2** [13.9°] and **D3** [12.4°]. The displacement of the *peri*-atoms from the naphthyl plane is relatively low in both compounds, with the Se(2) atom of **2** lying virtually on the plane. The *peri*-atoms of **3** are displaced to the same side of the plane. The naphthalene skeleton for **2** shows a minor deviation from planarity with central naphthalene ring torsion angles *ca.* 3-5°, whilst the backbone of **3** is essentially planar *ca.* 0.7-0.8°.

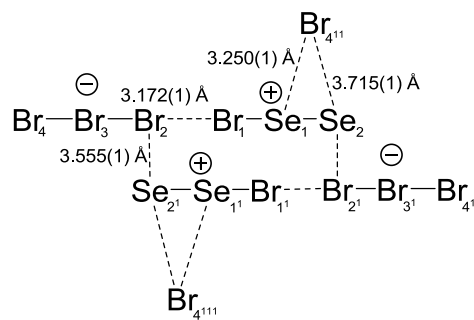
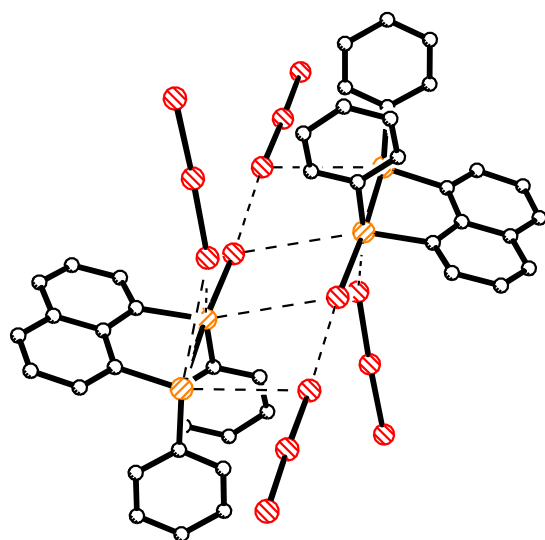


Figure 4 Intermolecular short contacts in the molecular structure of the ionic C.-T. ‘extended spoke’ adduct **2** produce a quasi-linear rectangular arrangement of 8 atoms.

The linear Br_3^- counteranions present in both molecular structures exhibit a lengthening of the Br-Br distances [2.52–2.57 Å] compared to free bromine [2.28 Å].⁴⁸ This is indicative of the three centre four-electron bond (3c-4e) model proposed by Rundle and Pimentel to explain hypervalency in the trihalide ions.^{7,11} The primary distinction between the molecular structures of **2** and **3** derives from differing intra- and intermolecular interactions and subsequent molecular packing. Short Br(1)⋯Br(2) [3.172(1) Å] and Se(2)¹⋯Br(2) [3.555(1) Å] contacts present in **2** lock two neighboring molecules together forming a quasi-planar rectangular arrangement of eight atoms (Figure 4). Two further non-bonded intermolecular interactions are observed between a terminal Br(4¹¹) atom of a Br_3^- ion and the two selenium *peri*-atoms [Se(1)⋯Br(4¹¹) 3.250(1) Å and Se(2)⋯Br(4¹¹) 3.715(1) Å]. The linear tribromide counteranion in **3** adopts a position above the *peri*-atoms. There is no Br(1)⋯ Br_3^- interaction but instead a non-bonded intramolecular interaction between Se(1)⋯Br(2) [3.562(1) Å]. Although a number of short contacts exist, there is no significant overlap of phenyl or naphthyl rings in either adduct and no $\pi\cdots\pi$ stacking.

Diorganoselenium compounds are known to form C.-T. ‘spoke’ adducts upon treatment with diiodine.^{15,22,46,47} 1,8-Bis(phenylselenyl)naphthalene **D2** reacts with one molar equivalence of diiodine to form the neutral C.-T. ‘spoke’ adduct **4** containing a quasi-linear Se-I-I fragment [177.6(1)°] (Scheme 1). Iodine [$\chi(\text{I})$ 2.36],⁴³ unlike bromine [$\chi(\text{Br})$ 2.68],⁴³ has a similar electronegativity to selenium [$\chi(\text{Se})$ 2.35]⁴³ and accepts electron density from non-bonding orbitals of the selenium donor to form the charge-transfer adduct. This has the effect of lowering the bond order and consequently weakening the I-I bond which extends from 2.66 Å (free iodine)⁴⁸ to 2.7987(6) Å.^{15,22} The partial negative charge delocalized on the terminal I(2) atom in the hypervalent 3c-4e Se(1)–I(1)–I(2) bond allows I(2) to act as a donor towards a second molecule of diiodine to afford a C.-T. ‘extended spoke’ adduct **5** (Scheme 1).¹⁵

Adduct **5** adopts a similar structure to that formed by the reaction of triphenylphosphine sulfide with I_2 .⁷⁰ The terminal iodine atoms of two molecules of adduct **4** (D2- I_2) act as donors towards the same diiodine molecule which bridges via soft-soft I⋯I interactions [3.543(1) Å] constructing a ‘Z-shaped’ system with a D2- $\text{I}_2\cdots\text{I}_2\cdots\text{I}_2$ -D2 configuration. Compounds with extended poly(I_2) chains held by weak $\text{I}_2\cdots\text{I}_2$ interactions and adducts formed with a donor/dihalogen composition greater than 1:1 are extremely rare.^{15,71}

The treatment of 1-(phenylselenenyl)-8-(phenylsulfanyl)naphthalene **D3** with two equivalents of diiodine produces an analogous ‘Z-shaped’ adduct to that of **5** (Scheme 1). Two ‘spoke’ like adduct units constructed from the selenium donor moiety of **D3** and diiodine are bridged by the same diiodine molecule with weak I...I interactions of a similar magnitude as observed in adduct **5** [3.526(1) Å].¹⁵

The ⁷⁷Se NMR spectra for adducts **4** and **5** display a downfield shift compared to **D2** [δ = 428.6 ppm].⁵⁷ Both spectra exhibit two signals, each corresponding to a different selenium environment [**4** δ = 436.9, 436.7 ppm; **5** δ = 445.1, 444.3 ppm]. The ⁷⁷Se NMR spectrum for adduct **6** reveals a similar downfield shift compared to **D3** [δ = 455.3 ppm]⁵⁷ with a single peak at δ = 476.9 ppm.

Following the treatment of selenium donor **D2** with diiodine, no significant alteration to the naphthalene geometry is observed upon the formation of the C.-T. ‘spoke’ addition product **4** (Figure 5).⁵⁷ The naphthyl and phenyl rings orientate with the same mixed equatorial-axial/axial-equatorial conformation as observed for **D2**, with one E-C_{Ph} bond aligning perpendicular to the naphthyl plane and one aligning with the plane (‘AB-type’, Figure 1).^{57,64,65} Displacement of the *peri*-atoms from the naphthalene mean plane in **4** is comparable to **D2** [*ca.* 0.3-0.5 Å]⁵⁷ and reveals steric strain operating between the selenium atoms in the two compounds is of a similar magnitude. Deviation of the *peri*-atoms within the naphthyl plane also corresponds, with the divergence of the exocyclic bonds illustrated by the splay angle [**4** 13.3°; **D2** 13.9°].⁵⁷ Despite the amount of naphthalene distortion, interatomic non-bonded Se...Se separations for **4** [3.1339(6)] and **D2** [3.1332(9)]⁵⁷ are 18% shorter than double the van der Waals radii of selenium [3.80].⁶⁶ Maximum C-C-C-C central naphthalene ring torsion angles in the range 4-7° show both naphthalene backbones are significantly buckled.

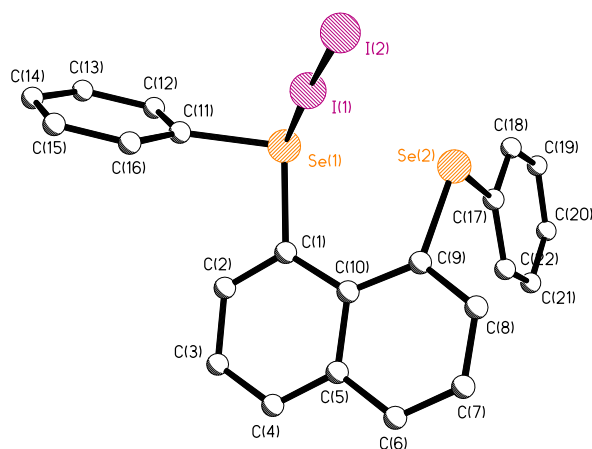


Figure 5 The molecular structure of the neutral C.-T. ‘spoke’ adduct **4**.

The hypervalent quasi-linear Se(1)-I(1)-I(2) fragment [Se-I-I angle 177.6°], characteristic of the weaker 3c-4e bond, displays an increase in the I(1)-I(2) bond length [2.7987(6) Å] compared to free diiodine [2.66 Å].⁴⁸ It is situated at 97.0(1)° to the Se(1)-C(11) bond and lies quasi-perpendicular to the C(11)-Se(1)-C(1) plane [76.6(1)°] due to steric crowding around the selenium lone-pairs.^{72,73} This results in a close intramolecular I(1)⋯Se(2) contact [3.6956(7) Å] which is within the sum of van der Waals radii for interacting selenium and iodine atoms [3.88 Å].⁶⁶ Adduct **4** also exhibits an intermolecular non-bonded interaction between the I(2) and Se(2) atoms of neighboring molecules (A and B) with an I(2A)⋯Se(2B) distance of 3.663(1) Å (Figure 6).

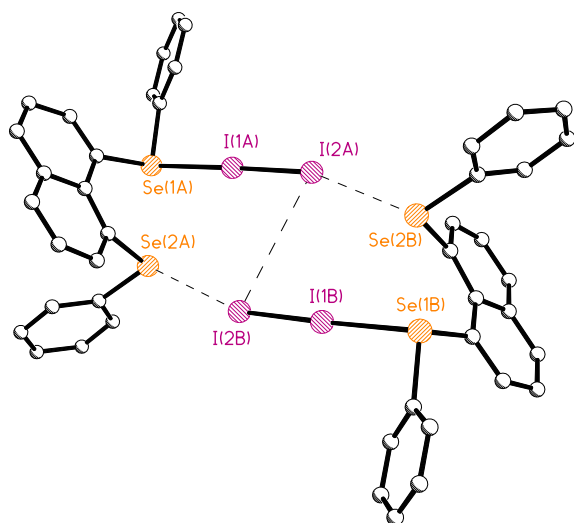


Figure 6 The intermolecular non-bonded short contacts between two neighbouring molecules of adduct **4**.

The C.-T. ‘extended spoke’ adducts **5** and **6** are characterised by a ‘Z-shaped’ D-I₂⋯I₂⋯I₂-D system constructed from two ‘spoke’ like adduct units and a bridging diiodine molecule held by weak I⋯I interactions [5 3.543(1) Å; 6 3.526(1) Å] (Figure 7). In both cases the linear Se-I-I fragment [**5** 178.1(1)°; **6** 179.0(1)°] has the same orientation as described for adduct **4**; situated at 99.4(1)° and 99.3(1)° to the Se(1)-C(11) bond and lying 80.4(1)° and 76.9(1)° to the C(11)-Se(1)-C(1) plane respectively. I(1) is positioned in the *peri*-gap with I(1)⋯E(2) separations [**5** 3.8730(9) Å; **6** 3.8527(13) Å] within the sum of van der Waals radii.⁶⁶

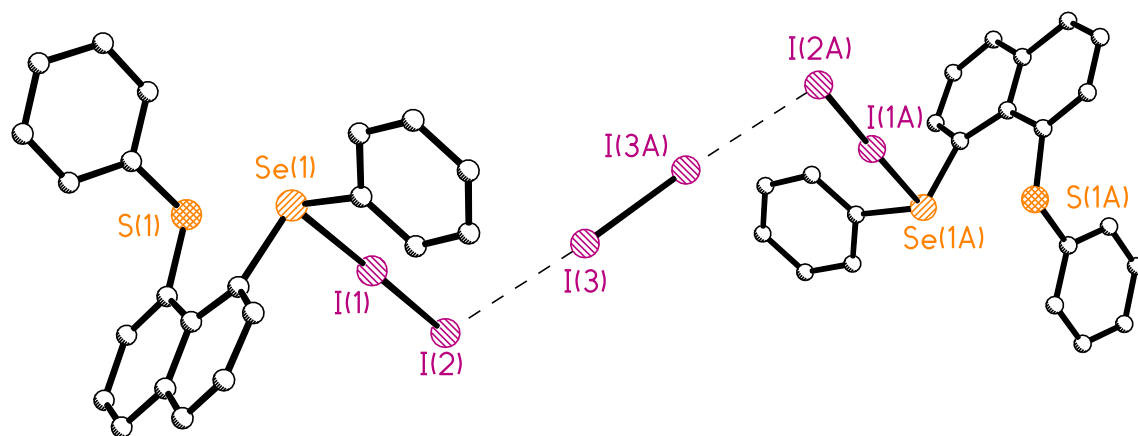


Figure 7 The molecular structure of the C.-T. ‘extended spoke’ adduct **6** characterised by a ‘Z-shaped’ D-I₂...I₂...I₂-D system (adduct **5** adopts a similar structure, see supporting information).

The interaction between the terminal I(2) atom of the ‘spoke’ adduct and the second I₂ molecule weakens and extends the I(1)-I(2) bond [**5** 2.8672(8) Å; **6** 2.8706(5) (*cf.* **4** 2.7987(6) Å)], concurrent with shortening the Se(1)-I(1) bond [**5** 2.8497(9) Å; **6** 2.8436(6) Å (*cf.* **4** 2.9795(8) Å)].^{15,22} I(1)-I(2)...I₂ angles [**5** 107.9(1)°; **6** 108.0(1)°] are slightly more obtuse than average values [90°] for known ‘extended spoke’ compounds.^{15,22} As expected, the I(3)-I(3¹) bond length of the bridging diiodine molecule is extended in both adducts [**5** 2.7402(11) Å; **6** 2.7418(7) Å] compared with free iodine [2.66 Å]⁴⁸ due to the existence of the weak I...I interactions.

The naphthalene components of each ‘Z-shaped’ adduct display a minor decrease in molecular distortion compared with donor compounds **D2** and **D3**, with a greater distortion observed in adduct **5** compared with **6**. In both compounds the non-bonded Se(1)...E(2) distance [**5** 3.0756(14) Å; **6** 2.9798(18) Å] is 19% shorter than the sum of van der Waals radii for the two interacting atoms [*cf.* **D2** 18%; **D3** 17%].⁵⁷ The displacement of the *peri*-atoms from the naphthalene mean plane [0.2-0.4 Å] is comparable in the two adducts to the out-of-plane distortion observed for **D2** and **D3**.⁵⁷ The substitution of heavier elements in the bay region of **5** compared with **6** causes a larger positive splay of the two E-C_{Nap} bonds within the least squares plane and thus exhibits a greater splay angle [**5** 13.6°; **6** 10.9°]. Maximum C-C-C-C central ring torsion angles are in the range 3-5° for both compounds showing the deviation of the naphthalene backbones from planarity is comparable. The conformation of the naphthyl and phenyl rings in both adducts is comparable to donor compounds **D2** and **D3**, with an equatorial-axial/axial-equatorial orientation described as an ‘AB-type’ structure.^{57,64,65}

‘See-saw’ and ‘T-shaped’ adducts are formed if halide X is more electronegative than chalcogen E [R₂E^{δ+}-X^{δ-}].

Consequently, all known reactions between tellurium-donors [χ(Te) 2.08]⁴³ and di- or inter-halogens [χ(F) 3.94- χ(I) 2.36]⁴³

afford ‘T-shaped’/‘see-saw’ adducts with no tellurium C.-T. ‘spoke’ adducts having been reported.^{15,22} Tellurium forms a strong donor-strong acceptor system with dihalogen molecules sufficient to cleave the X-X bond and oxidize tellurium.^{15,22} Nucleophilic attack occurring at the chalcogen site of a diorganotellurium $[R_2Te-X]^+$ cation affords a ‘see-saw’ hypervalent adduct containing the quasi linear X-Te-X alignment.^{15,22}

Tellurium-donor compounds 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene **D4** and 1-(phenyltellurenyl)-8-(phenylselenenyl)naphthalene **D5** react conventionally with dibromine and diiodine affording a series of ‘see-saw’ insertion adducts (Scheme 1). In all four reactions the dihalogen reacts at the larger, less electronegative tellurium atom due to its greater electron donor ability over sulfur and selenium.^{43,48}

The formation of the X-Te-X fragment is confirmed by a significant downfield shift in the ^{125}Te NMR spectra for **7-10** compared to **D4** [$\delta = 715.2$ ppm]⁵⁷ and **D5** [$\delta = 687.6$ ppm].⁵⁷ Single peaks are observed in all four spectra with the signals for the bromine compounds **7** [$\delta = 958.9$ ppm] and **8** [$\delta = 941.4$ ppm] lying at expected higher chemical shifts to their iodine analogues **9** [$\delta = 790.9$ ppm] and **10** [$\delta = 747.0$ ppm]. A downfield shift is also observed in the ^{77}Se NMR spectra of **8** and **10** compared to **D5** [$\delta = 362.8$ ppm]⁵⁷ with single peaks at $\delta = 500.0$ ppm and $\delta = 428.8$ ppm respectively.

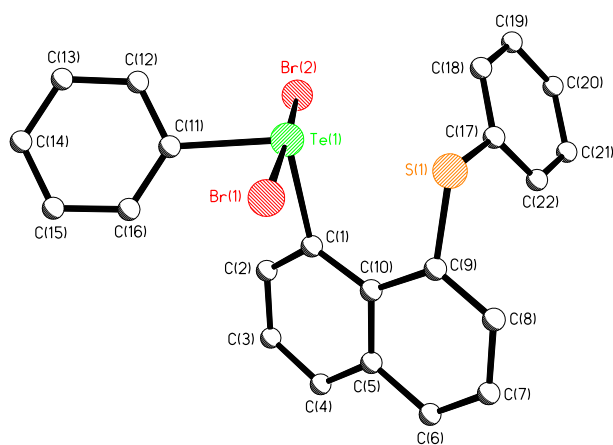


Figure 8 The molecular structure of the ‘see-saw’ adduct **7** (adducts **8-10** display similar molecular structures, see supporting information).

The four adducts **7-10** are characterized by the well-known ‘see-saw’ structure and incorporate an asymmetric linear X-Te-X fragment [**7** $176.7(1)^\circ$; **8** $177.9(1)^\circ$; **9** $176.8(1)^\circ$; **10** $179.6(1)^\circ$] characterized by unequal X-Te bond lengths (Figure 8).²³ The central tellurium atom adopts a distorted trigonal bipyramidal (TBP) geometry with angles around tellurium for all four adducts in the range $87-98^\circ$. The formation of the linear fragment is accompanied by a minor adjustment to the

naphthyl and phenyl ring conformations compared to the tellurium donor compounds **D4** and **D5**.⁵⁷ A slight rotation round the Te(1)-C(1) bond positions the Te-C_{Ph} bond intermediate between perpendicular and coplanar with the naphthyl plane and both phenyl rings adopt twist conformations.⁶⁴ This affords a twist-twist and axial-twist arrangement corresponding to the ‘AC-type’ structure (Figure 1).^{64,65} The alignment of the ‘see-saw’ moiety positions one of the terminal halide atoms of X-Te-X in the *peri*-gap and in close proximity to E(2). Non-covalent X...E(2) distances [**7** 3.486(2) Å; **8** 3.542(2) Å; **9** 3.6136(16) Å; **10** 3.696(2) Å] are marginally shorter than the sum of van der Waals radii for the two interacting atoms [94-96%].⁶⁶ Te-Br [2.67-2.72 Å] and Te-I [2.89-2.95 Å] bond lengths are within the usual ranges [2.68, 2.99 ± 0.05 Å].⁷⁴

The naphthalene moieties of the ‘see-saw’ adducts experience a similar degree of molecular distortion compared to donor compounds **D4** and **D5**.⁵⁷ As expected, the deformation of the naphthalene unit is greater in adducts **8** and **10** (TeSe) compared with compounds **7** and **9** (TeS). Intramolecular Te...S [**7** 3.075(2) Å; **9** 3.0767(17) Å] and Te...Se [**8** 3.141(2) Å; **10** 3.137(2) Å] *peri*-distances are 20-22% shorter than the sum of van der Waals radii for the two chalcogen atoms and comparable to the separations in the independent molecules of **D4** [3.0684(13) Å (3.0984(11) Å)]⁵⁷ and **D5** [3.1919(11) Å (3.1580(12) Å)]⁵⁷ respectively. Deviation of the *peri*-atoms within the naphthyl plane is marginally greater in the selenium compounds **8** and **10** with large positive splay angles of the magnitude 13.5° and 12.4° [*cf.* 12.0°, 12.3° for **7** and **9**]. Distortion out-of-the plane is comparable throughout the series with atoms lying at distances between 0.3-0.4 Å and the deviation of the central naphthalene ring torsion angles from planarity is also consistent 0-7°. Short intermolecular contacts exist in each of the four adducts between Te and X atoms of neighboring molecules constructing planar Te₂X₂ squares (Figure 9). In all cases the Te...X distance is 93-95% of the sum of van der Waals radii for the two interacting atoms.

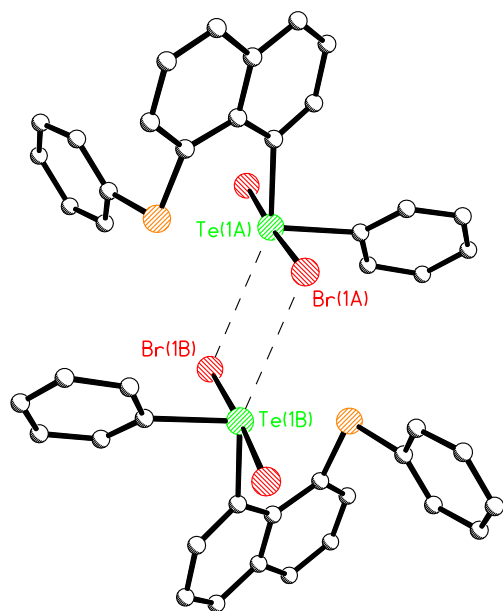


Figure 9 Short intermolecular contacts between neighbouring molecules of the ‘T-shaped’ adduct **7** form planar Te₂X₂ square units (**8**, **9** and **10** adopt identical arrangements, see supporting information).

The comparable reactions of 1-bromo-8-(phenyltellurenyl)naphthalene **D6** and 1-iodo-8-(phenyltellurenyl)naphthalene **D7** with dihalogens (Br₂, I₂) afforded a similar array of ‘see-saw’ insertion adducts **11-14** (Scheme 1). The ¹²⁵Te NMR spectra for **11-14** show a similar trend to that previously described for **7-10** with an expected downfield shift compared to their respective donor compounds **D6** [δ = 731.2 ppm]⁵⁸ and **D7** [δ = 698.3 ppm].⁵⁸ Single peaks are observed in all spectra, with bromine compounds **11** [δ = 942.8 ppm] and **12** [δ = 903.0 ppm] possessing higher chemical shifts compared to their iodine counterparts **13** [δ = 887.5 ppm] and **14** [δ = 848.0 ppm].

Adducts **11-14** adopt similar ‘see-saw’ geometries to those observed for **7-10** but the linear X-Te-X fragments are more symmetrical (Figure 10). Tellurium adopts a quasi-trigonal bipyramidal conformation with angles around the central atom in the range 87.4-99.4°. Adducts **11** and **12** containing Te and Br *peri*-atoms adopt a twist-twist orientation of naphthyl and phenyl rings (‘C-type’), whilst in adducts **13** and **14** (TeI) the Te-C_{Ph} bond aligns along the naphthyl plane and the compounds display an equatorial-twist conformation (‘B-type’) (Figure 1).^{64,65} The arrangement of the linear species in all four adducts positions one of the X atoms in the *peri*-gap, but X...X’ separations in all cases are greater than the sum of van der Waals radii for the two interacting halogen atoms. Te-Br [2.66-2.68 Å] and Te-I [2.90-2.95 Å] bond lengths are within the usual ranges [2.68, 2.99 ± 0.05 Å].⁷⁴

The substitution of bulky halogen atoms at the second *peri*-position in **11-14** results in a greater degree of steric strain and consequently naphthalene distortion compared with adducts **7-10**. Additionally, the deformation of the naphthalene unit is greatest in adducts with an iodine *peri*-atom **12** and **14** compared with **11** and **13** (Br). The intramolecular Te...Br *peri*-distance in **11** [3.2397(15) Å] is larger than the separation in the tellurium donor compound **D6** [3.1909(10) Å]⁵⁸ whilst the distance in **13** is marginally shorter [3.1563(6) Å]. Conversely, the Te...I distances in **12** and **14** [3.3810(7) Å; 3.3608(11) Å] are longer than the separation in **D7** [3.3146(6) Å].⁵⁸ In all cases the Te...X separation is less than the sum of van der Waals radii for the two interacting atoms by 16-19%.

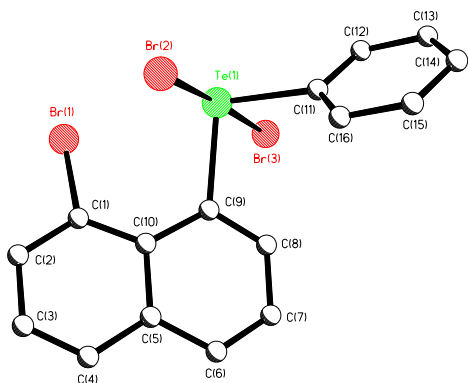


Figure 10 The molecular structure of the ‘see-saw’ insertion adduct **11** (**12-14** adopt identical arrangements, see supporting information).

The increased congestion in the *peri*-region of adducts **12** and **14** causes a larger divergence of the Te-C and X-C bonds within the naphthyl plane compared with **11** and **13**. Large positive splay angles are observed for all four adducts with those for **11** and **13** [13.1°; 12.4°] similar in size to **D6** [13.6°]⁵⁸ and those for **12** and **14** [15.9°; 18.7°] comparable to the splay in **D7** [16.2°].⁵⁸ Adducts **11** and **12** containing the Br-Te-Br linear fragment display the greatest out-of-plane distortion with atoms lying ~0.6 Å to opposite sides of the naphthalene least squares plane. Adducts **11** and **12** also display a major distortion to the naphthalene ring system with maximum central naphthalene ring torsion angles ~10-11°. Short intermolecular contacts between Te and I atoms of neighboring I-Te-I units in **12** and **14** form similar planar Te₂X₂ square units to **7-10**. Although a number of short contacts exist in adducts **11** and **13**, no similar intermolecular arrangement is observed.

We have recently reported the synthesis and structural study of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **D8**, a complete series of phosphorus(V) oxygen, sulfur and selenium chalcogenides and a study of its coordination chemistry.⁵⁶ Treatment of **D8** with excess dibromine in dichloromethane led to the formation of the air-stable phosphonium salt **15**. Phosphorus forms a 4 co-ordinate cationic fragment via the addition of a hydroxyl group which is balanced by a linear Br₃⁻ counteranion (Scheme 1). The ³¹P NMR spectrum shows a single peak at $\delta = 52.48$ ppm.

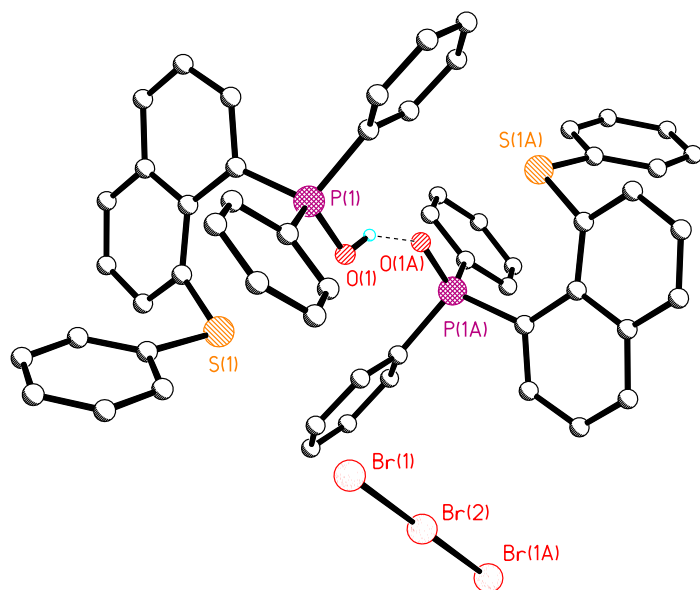


Figure 11 The molecular structure of hydroxydiphenyl[(8-phenylsulfanyl)naphthalene-1-yl]phosphonium tribromide **15**.

The molecular structure of **15** is shown in Figure 11. In the asymmetric unit, two molecules of **15** share the proton situated between the oxygen atoms and form a ‘Z-shaped’ P-O-H-O-P bridge. All five atoms lie on the same plane with P-O-H angles of 131.2(1)° and the O-H-O angle of 180.0(1)°. P-O bond lengths are identical in both molecules [1.527(6) Å] with a value in between the observed P=O bond length in the phosphine oxide of **D8** (**D8=O**) [1.492(2) Å]⁵⁶ and a standard single P-OH bond [1.56 Å].⁷⁵ This suggests the structure is an average of a phosphine oxide and a phosphonium cation as depicted in Figure 12. The charge of the cation is balanced by the presence of a linear Br₃[−] counteranion [180.00(6)°] which exhibits elongated Br-Br bond lengths [2.5984(12) Å] compared to free bromine [2.28 Å].⁴⁸

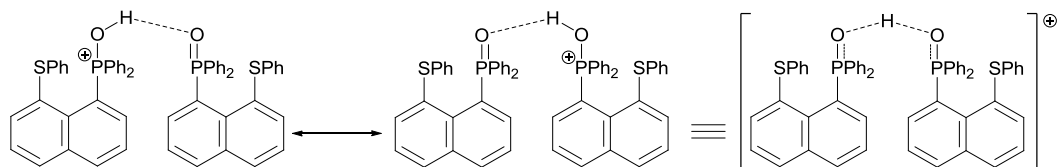


Figure 12 In the crystal structure of **15**, two molecules share a proton to form a P-O-H-O-P bridge; explained by an average structure of a phosphine oxide and a phosphonium cation.

The naphthalene component of the phosphonium salt **15** exhibits greater strain relief and naphthalene distortion compared to phosphine **D8** and its phosphine oxide **D8=O**.⁵⁶ The *peri*-atoms are accommodated by an intramolecular non-bonded P...S distance of 3.165(2) Å, notably larger than the separation in **D8** [3.0330(7) Å] and **D8=O** [3.1489(9) Å].⁵⁶

The divergence of the P-C and S-C bonds within the naphthyl plane is also more pronounced in **15** with a large positive splay angle of 15.5° [*cf.* **D8** 14.1; **D8=O** 12.4].⁵⁶ Additionally, the *peri*-atoms are displaced to opposite sides of the mean naphthalene by 0.436(11) Å (P) and -0.466(11) Å (S). The naphthalene backbone in the phosphonium salt displays a significant deformation from planarity, with maximum C-C-C-C torsion angles lying in the range 5-8°. One short intramolecular S...O contact exists with a separation 11% shorter than the sum of van der Waals radii for the two atoms. Although a number of short intermolecular interactions exist, there is no significant overlap of phenyl or naphthyl rings and no π - π -stacking is observed.

3. DFT Calculations

Of the compounds presented here, only **2** and **3** display a reduction in naphthalene distortion and by inference the degree of steric strain operating between the *peri*-atoms, compared with parent donor compounds (**D2** and **D3**).⁵⁷ This can be rationalized by the presence of an attractive weak interaction between the *peri*-atoms, inferred by the noticeable shrinkage of the *peri*-distance in both adducts. In addition the two *peri*-atoms align with one bromine atom to form a quasi-linear Br(1)-Se(1)...E(2) arrangement, suggesting the nature of the bonding could be represented by the 3c-4e mode. To try and assess the possibility of direct Se(1)...E(2) bonding interactions that would indicate an onset of 3c-4e bonding in **2** and **3**, density functional theory computations were performed for the possible reaction products between 1,8-(SePh)₂-C₁₀H₆ (**D2**) and Br₂, optimized at the B3LYP/962(+d)/6-31+G* level (Figure 13).

Structure **A** (Figure 13) corresponds to that observed in the solid for **2**, **A**⁺ is the isolated cationic fragment of this ion pair, **B** corresponds to the analogue where Se^a is replaced with Te (**8**), and **C** to that where Br is replaced with I (**4** and **5**). Optimizations starting from the two different conformations found in the latter two solids converged to the same minimum. Optimisations for **A** starting from the coordinates of **2** and its S-analogue **3** afforded two distinct minima, which differ in the exact position of the Br₃ moiety. Both are very close in energy, within *ca.* 1 kcal/mol, and only the results for the most stable conformer (derived from solid **3**) will be discussed in the following. As expected, the Se...Se contacts are shortest in **A** and **A**⁺ with substantial bonding interactions indicated by Wiberg bond indices (WBI)⁷⁶ of *ca.* 0.3 - 0.4. 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. The optimized Se-Se distance for **A**, 2.807 Å, is in very good agreement with that observed in solid **2**, 2.762 Å, even though the Br₃ moiety has moved somewhat closer to the cationic fragment in the gas-phase optimization (Se^a...Br and Se^b...Br of 3.42 Å and 3.87 Å, respectively), as compared to the solid (where Se^a...Br and Se^b...Br are 3.55 Å and 4.40 Å, respectively). In **B** and **C** the

Se...Se distances are larger than in **A** and **A**⁺, and weaker but still noticeable bonding is found (WBI \approx 0.1). The refined selenium-selenium distances for species **2** and **3** suggest 3c-4e bonding is present in both cases.

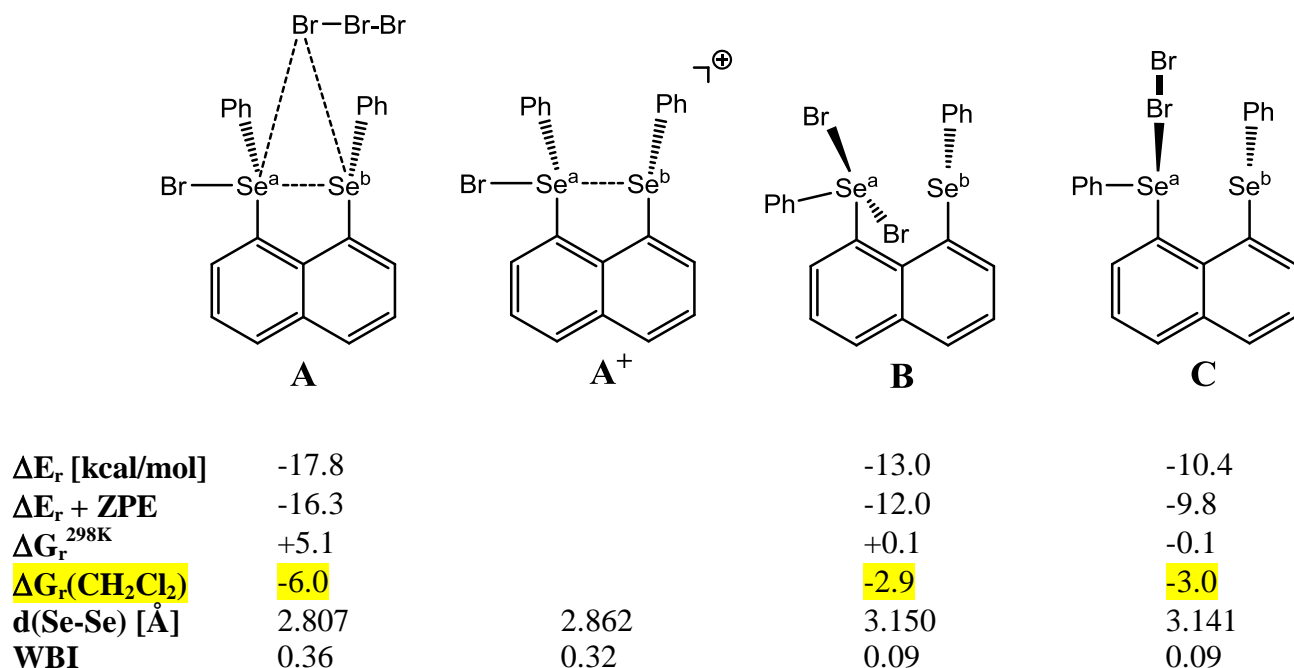


Figure 13: DFT computations performed at the B3LYP level for the possible reaction products between **D2** and Br₂. ΔE_r , $\Delta E_r + \text{ZPE}$, and ΔG_r^{298K} are gas-phase relative energies, zero-point corrected energies, and free energies, respectively, relative to **D2** + *n* Br₂; $\Delta G_r(\text{CH}_2\text{Cl}_2)$ are free energies (at 298K) corrected for solvation effects.

Significant energetic driving forces are computed for all products **A** - **C** already in the gas phase (*cf.* the negative $\Delta E_r + \text{ZPE}$ values). The largest such driving force is computed for **A**, the actual, crystallized product, but compounds **B** and **C** are only a few kcal/mol less stable. Standard entropic and enthalpic corrections would reduce the free energy of bromination to essentially zero for **B** and **C**, and would make formation of **A** endergonic (see ΔG_r^{298K} values). Immersion in a polarisable continuum favors formation of **B** and **C** slightly, by *ca.* -3 kcal/mol, and stabilises the highly polar ion pair **A** significantly, by *ca.* -11 kcal/mol. Judging from the $\Delta G_r(\text{CH}_2\text{Cl}_2)$ values, formation of all products is exergonic in a condensed phase, with a slight preference for the observed product **A**. These results therefore suggest that the occurrence of **A** may not be due to its intrinsic stability, but would rather arise from its favorable interaction with the polar environment of the crystal.

Notwithstanding the crude nature of some approximations involved (ideal-gas entropies, continuum solvation model), the

relative free energies in solution are computed to be rather similar for all products. This would help to rationalize the rather diverse chemistry encountered upon varying the chalcogen and/or the halogen in this system.

Because the relative free energies of the various products appear to be rather closely spaced, it is conceivable that complex equilibria rather than a single product might occur in solution, and that, thus, the nature of the species present in solution could be different from that in the solid state. This is in agreement with the generally accepted mechanism to describe the formation of adducts from the reaction of diorganochalcogen donors with the dihalogens;^{14,38,39} in solution the C.-T. ‘spoke’ and the ‘see-saw’ adduct of type $RR'E\cdot X_2$ are in equilibrium and as reported by Husebye and co-workers, all the products in these reactions are derived from a common intermediate species $[R_2E-X]^+$.^{15,22,40}

4. Conclusions

The structural conformation of the products formed from the reactions between donor compounds **D1-D8** and the dihalogens is dependent on several factors; most importantly the donor ability of the chalcogen atom, the acceptor ability of the dihalogen species and the stoichiometry of the reactants. When two donor atoms are available (**D3**, **D4**, **D5**) reaction occurs explicitly between the dihalogen and the least electronegative element. The neutral charge-transfer (C.-T.) ‘spoke’ adduct and the ‘see-saw’ insertion adduct, characteristic of quasi-linear hypervalent $E-X-Y$ ^{15,22,28,34,35} and $X-E-Y$ ^{14,15,22,28,31,36,37} fragments respectively are the most common structural motifs generated from the reaction of diorganochalcogen-donors $[R_2E]$ with inter- or dihalogens.^{15,22} In general the reactions between **D1-D8** and the dihalogens conform to the charge-transfer rule and form ‘see-saw’ adducts when the halogen (X) species is more electronegative than the chalcogen-donor (E) $[R_2E^{\delta+}-X^{\delta-}]$ and form C.-T. ‘spoke’ adducts if the converse is true.^{20,21,22}

Reactions between Te-donors $[\chi(\text{Te}) 2.08]$ ⁴³ and any dihalogen $[\chi(\text{F}) 3.94-\chi(\text{I}) 2.36]$ ⁴³ explicitly afford ‘see-saw’ or ‘T-shaped’ adducts with no C.-T. adducts known for any tellurium compound.^{14,15,22,43} Tellurium donor compounds **D4-D7** react conventionally to form strong donor-strong acceptor systems with the dihalogens, the X-X bond is cleaved and the Te atom is oxidised.^{14,15,22} In each case, nucleophilic attack occurs at the tellurium site of the $[R_2\text{Te}-X]^+$ cation affording a series of ‘see-saw’ hypervalent adducts **7-14** characterized by the quasi-linear X-Te-X alignment.^{14,15,22}

As expected from electronegativity values, all structurally reported adducts formed from the reaction of diorganoselenium compounds $[\chi(\text{Se}) 2.35]$ ⁴³ with dibromine $[\chi(\text{Br}) 2.58]$ ⁴³ adopt the ‘see-saw’ geometry.^{14,15,22,47,49,50} The decrease in the electronegativity difference between selenium and iodine $[\chi(\text{Br}) 2.36]$ ⁴³ favors the formation of C.-T. ‘spoke’

adducts.^{15,22,46,47} The selenium-donor compounds **D2** and **D3** react to form strong donor-strong acceptor systems with dibromine sufficient to cleave the Br-Br bond and oxidize the selenium atom.^{15,22} The hypervalent 3c-4e interaction operating between the quasi-linear Br-Se...E arrangement in both compounds blocks the nucleophilic attack at the selenium site of the $[R_2Se-X]^+$ cation so no 'see-saw' adduct is formed. Instead a hypervalent linear tribromide counteranion balances the charge and the ionic tribromide salts **2** and **3** are formed which can be represented by the formula $[RSe-Br]^+ \cdots [Br-Br_2]^-$.^{2,34}

D2 reacts conventionally with a single equivalent of diiodine to form the C.-T. 'spoke' adduct **4** characterized by the quasi-linear Se-I-I alignment. Reaction with a higher equivalent of diiodine (1:2) affords a structurally more complex 'extended spoke' adduct **5** incorporating I_2 chains. Two molecules of adduct **4** acting as donors interact with a single bridging diiodine molecule via soft-soft I...I interactions to construct a 'Z-shaped' system with a $D-I_2 \cdots I_2 \cdots I_2-D$ configuration. **D3** reacts to form a comparable system **6**. These 'Z-shaped' systems are of great interest as compounds with extended poly(I_2) chains held by weak $I_2 \cdots I_2$ interactions and also adducts formed with a donor/dihalogen composition greater than 1:1 are extremely rare.^{15,71}

Adducts formed from the reaction of organosulfur compounds with dibromine are rare.^{15,22,28,42,51} Resonance lone-pairs on sulfur in **D1** and **D8** are delocalized into the aromatic π -system reducing the donor ability of the compound for reaction with the dihalogens. The aromatic groups in **D1** are strongly activated and highly reactive towards electrophilic substitution.⁵⁹ Upon treatment with dibromine **D1** undergoes a standard electrophilic aromatic substitution reaction which substitutes bromine atoms in the 4- and 8-positions on the naphthyl ring and in the *para* positions on the two phenyl rings. Phosphine **D8** neither reacts to form an adduct or undergoes electrophilic aromatic substitution. Instead treatment with dibromine affords the tetravalent phosphonium salt **15** which packs via a 'Z-shaped' P-O-H-O-P bridge and is charge balanced by the presence of a tribromide counteranion.

M. Carla Aragoni *et al.* have recently reviewed the nature of the bonding in linear three-body systems including the E-X-X and X-E-X arrangements of the C.-T. 'spoke' and 'see-saw' adducts.²³ They concluded these linear moieties can be accounted for by a charge-transfer model and the three centre four-electron bond (3c-4e) model introduced by Rundle-Pimentel to explain the hypervalency in the trihalide ions.^{7,11} The linear three-body systems present in **2-14** conform to the 3c-4e model and as such have weaker and by inference longer bond lengths compared with the distances between atoms in standard single electron pair 2c-2e bonds. The tribromide anions present in compounds **2**, **3** and **15** all display elongated Br-Br bond distances [2.52-2.60 Å] compared to free dibromine [2.28 Å]⁴⁸ but within the usual range for Br_3^- ions [2.5-2.6

Å].⁷⁴ Similarly, I-I bond lengths exhibit a noticeable lengthening in the Se-I-I fragments of compounds **4-6** [2.80-2.87 Å] compared with free diiodine [2.66 Å].⁴⁸ Te-Br and Te-I bond lengths in the linear Br-Te-Br and I-Te-I fragments of the ‘see-saw’ insertion adducts **7-14** are within the usual range.²³

Following treatment with dibromine and diiodine, the degree of distortion and by inference the steric strain operating between the *peri*-atoms in their addition products **2-15** (and the substitution product **1**) in general appears unchanged. The exceptions to this are the two tribromide salts of bromoselenyl cations (**2**, **3**) which display a reduction in the distortion of the naphthalene geometry compared to parent donor compounds **D2** and **D3** respectively. This can be rationalized by the existence of the quasi-linear Br(1)-Se(1)···E(2) interaction in both compounds which can be represented by the 3c-4e model. The attractive weak interaction between the *peri*-atoms, inferred by the noticeable shrinkage of the *peri*-distance in both adducts, reduces the steric hindrance and therefore the required distortion of the naphthalene scaffold. From DFT calculations performed on **2**, the optimized Se-Se distance [2.746 Å] is in excellent agreement with that observed in the solid [2.762 Å] and the WBI value⁷⁶ of 0.4 indicates a considerable bonding interaction and the onset of 3c-4e bonding in the quasi-linear three-body system.

5. Experimental Section

All experiments were carried out under an oxygen- and moisture-free nitrogen atmosphere using standard Schlenk techniques and glassware. Reagents were obtained from commercial sources and used as received. Dry solvents were collected from a MBraun solvent system. Elemental analyses were performed by the University of St. Andrews School of Chemistry Microanalysis Service. Infra-red spectra were recorded as KBr discs in the range 4000-300 cm⁻¹ on a Perkin-Elmer System 2000 Fourier transform spectrometer. ¹H and ¹³C NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with δ(H) and δ(C) referenced to external tetramethylsilane. ³¹P, ⁷⁷Se and ¹²⁵Te NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with δ(P), δ(Se) and δ(Te) referenced to external phosphoric acid, dimethylselenide and diphenyl ditelluride respectively. Assignments of ¹³C and ¹H 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 on a Micromass GCT orthogonal acceleration time of flight mass spectrometer. Electrospray Mass Spectrometry (ESMS) was carried out on a Micromass LCT orthogonal accelerator time of flight mass spectrometer.

1,8-bis(4-bromophenylsulfanyl)-2,5-dibromonaphthalene (1): A solution of 1,8-diphenylsulfanylnaphthalene **D1** (0.22 g, 0.63 mmol) in dichloromethane (20 mL) was cooled to 0 °C and slowly treated with bromine (0.2 g, 0.06 mL, 1.3 mmol). An analytically pure sample was obtained by crystallization from diffusion of pentane into a dichloromethane solution of the product (0.3 g, 75 %); (Found: C, 41.2; H, 1.8. Calc. for C₂₂H₁₂S₂Br₄: C, 40.3; H, 1.8 %); $\nu_{\max}(\text{KBr disc})/\text{cm}^{-1}$: 3401w, 3075w, 2920w, 2848w, 2362w, 1881w, 1570s, 1558s, 1470vs, 1400w, 1382s, 1320w, 1282s, 1268s, 1185s, 1083s, 1065s, 1018w, 1006vs, 805vs, 765w, 745s, 688w, 641w, 608w, 561w, 517w, 497w, 471s, 417w, 396w, 373w, 352w; $\delta_{\text{H}}(270 \text{ MHz, CDCl}_3)$ 8.19 (1 H, d, *J* 9.1 Hz, nap 4-H), 7.80 (1 H, d, *J* 9.1 Hz, nap 3-H), 7.46 (1 H, d, *J* 8.2 Hz, nap 6-H), 7.33 (2 H, d, *J* 8.4 Hz, *SPhBr* 3,5-H), 7.21 (2 H, d, *J* 8.6 Hz, *SPhBr* 9,11-H), 7.05 (2 H, d, *J* 8.4 Hz, *SPhBr* 2,6-H), 6.95 (1 H, d, *J* 8.2 Hz, nap 2-H), 6.74 (2 H, d, *J* 8.6 Hz, *SPhBr* 8,12-H); $\delta_{\text{C}}(67.9 \text{ MHz, CDCl}_3)$ 135.4(s), 132.9(s), 132.5(s), 132.1(s), 131.8(s), 130.7(s), 128.3(s); *m/z* (EI⁺) 659.69 ([M]⁺, 100 %, 347.80 ([M-2(ArBr)]⁺, 98 %).

(2): A solution of 1,8-bis(phenylselenenyl)naphthalene **D2** (0.21 g, 0.47 mmol) in dichloromethane (20 mL) was cooled to 0 °C and slowly treated with bromine (0.15 g, 0.05 mL, 0.93 mmol). An analytically pure sample was obtained by crystallization from diffusion of dichloromethane into a pentane solution of the product (0.2 g, 57 %); (Found: C, 39.6; H, 1.3. Calc. for C₂₂H₁₆Se₂Br₄: C, 40.3; H, 2.5 %); $\nu_{\max}(\text{KBr disc})/\text{cm}^{-1}$: 3396w, 3050w, 2920w, 2848w, 2356w, 2325w, 1589w, 1566w, 1486s, 1470s, 1438s, 1346s, 1261w, 1212w, 1194w, 1176w, 1083w, 1047s, 1016w, 992s, 825s, 812vs, 757w, 744vs, 730vs, 679vs, 659w, 533w, 484w, 463s, 457s, 442w, 378w; *m/z* (ES⁺) 539.11 ([M-Br₃+Na]⁺, 100 %).

(3): A solution of 1-(phenylselenenyl)-8-(phenylsulfanyl)naphthalene **D3** (0.02 g, 0.051 mmol) in dichloromethane (5 mL) was cooled to 0 °C and slowly treated with bromine (0.02 g, 0.005 mL, 0.10 mmol). An analytically pure sample was obtained by crystallization from diffusion of dichloromethane into a pentane solution of the product (0.01 g, 33 %); $\nu_{\max}(\text{KBr disc})/\text{cm}^{-1}$: 3447vs, 3418vs, 2924vs, 2848s, 2372w, 1985w, 1918w, 1773w, 1735s, 1718s, 1703s, 1686s, 1654s, 1636s, 1578s, 1543s, 1523w, 1459s, 1436s, 1383w, 1343w, 1261w, 1203w, 1177w, 1148w, 1087s, 1020w, 913w, 814vs, 751vs, 735vs, 692w, 602w, 541w, 456s, 398w; *m/z* (ES⁺) 422.83 ([M-Br₄+OMe]⁺, 97 %), 391.83 ([M-Br₄]⁺, 100 %).

(4): A solution of 1,8-bis(phenylselenenyl)naphthalene **D2** (0.23 g, 0.53 mmol) in dichloromethane (20 mL) was cooled to 0 °C and slowly treated with iodine (0.13 g, 0.53 mmol). An analytically pure sample was obtained by crystallization from diffusion of dichloromethane into a pentane solution of the product (0.2 g, 66 %); (Found: C, 39.5; H, 2.2. Calc. for C₂₂H₁₆Se₂I₂: C, 38.2; H, 2.3 %); $\nu_{\max}(\text{KBr disc})/\text{cm}^{-1}$: 3406w, 3050w, 2920w, 2848w, 2382w, 1690w, 1659w, 1573s,

1550w, 1473s, 1435s, 1331w, 1191w, 1137w, 1088w, 1060s, 1018s, 995w, 956w, 912w, 838w, 811vs, 750s, 737vs, 687vs, 662s, 613w, 471w, 453w; δ_{H} (270 MHz, CDCl_3) 7.82 (2 H, dd, J 1.0 and 8.2 Hz, nap 4,5-H), 7.72 (2 H, dd, J 1.2 and 7.4 Hz, nap 2,7-H), 7.47-7.37 (4 H, m, *SePh* 2,6-H), 7.36-7.20 (8 H, m, nap 3,6-H, *SePh* 3-5-H); δ_{C} (67.9 MHz, CDCl_3) 136.2(s), 133.1(s), 130.1(s), 129.7(s), 128.0(s), 126.4(s); δ_{Se} (51.5 MHz, CDCl_3) 436.9, 436.7; m/z (EI^+) 565.99 ($[\text{M-I}]^+$, 5 %), 440.12 ($[\text{M-I}_2]^+$, 100 %).

(5): A solution of compound **4** (0.24 g, 0.35 mmol) in dichloromethane (20 mL) was cooled to 0 °C and slowly treated with iodine (0.09 g, 0.35 mmol). An analytically pure sample was obtained by crystallization from diffusion of dichloromethane into a pentane solution of the product; δ_{H} (270 MHz, CDCl_3) 7.74 (2 H, dd, J 1.0 and 8.2 Hz, nap 4,5-H), 7.63 (2 H, dd, J 1.2 and 7.4 Hz, nap 2,7-H), 7.44-7.37 (4 H, m, *SePh* 2,6-H), 7.28-7.20 (8 H, m, nap 3,6-H, *SePh* 3-5-H); δ_{Se} (51.5 MHz, CDCl_3) 445.1, 444.3.

(6): A solution of 1-(phenylselenyl)-8-(phenylsulfanyl)-naphthalene **D3** (0.066 g, 0.17 mmol) in dichloromethane (5 mL) was treated with iodine (0.086 g, 0.34 mmol). An analytically pure sample was obtained by crystallization from diffusion of dichloromethane into a pentane solution of the product (0.07 g, 18 %); (Found: C, 34.6; H, 2.1. Calc. for $(\text{C}_{22}\text{H}_{16}\text{SSeI}_2)\text{I}$: C, 34.2; H, 2.1 %); ν_{max} (KBr disc)/ cm^{-1} : 3434brs, 3040w, 1940w, 1880w, 1803w, 1720w, 1655w, 1575s, 1541w, 1473s, 1435s, 1350w, 1324s, 1301w, 1196s, 1139w, 1059w, 1019s, 996s, 968w, 900w, 815vs, 783s, 754s, 737vs, 687vs, 615w, 540w, 520w, 483w, 455s; δ_{H} (270 MHz, CDCl_3) 7.98-7.89 (2 H, m, nap 2,4-H), 7.76 (1 H, dd, J 1.9 and 7.2 Hz, nap 5-H), 7.68-7.60 (2 H, m, *SePh* 2,6-H), 7.50 (1 H, t, J 7.7 Hz, nap 3-H), 7.43-7.33 (3 H, m, *SePh* 3-5-H), 7.28-7.15 (4 H, m, nap 6-H, *SPh* 3-5-H), 7.15-7.06 (1 H, m, nap 7-H), 7.06-6.97 (2 H, m, *SPh* 2,6-H); δ_{C} (67.9 MHz, CDCl_3) 139.2(s), 135.9(s), 132.3(s), 131.7(s), 131.6(s), 130.1(s), 129.6(s), 129.2(s), 127.4(s), 126.5(s), 126.4(s), 126.0(s); δ_{Se} (51.5 MHz, CDCl_3) 476.9; m/z (ES^+) 391.89 ($[\text{M-I}_2]^+$, 100 %).

(7): A solution of 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene **D4** (0.032 g, 0.073 mmol) in dichloromethane (5 mL) was treated with bromine (0.023 g, 0.007 mL, 0.15 mmol). An analytically pure sample was obtained by crystallization from diffusion of dichloromethane into a pentane solution of the product (0.04 g, 80 %); (Found: C, 42.6; H, 2.7. Calc. for $\text{C}_{22}\text{H}_{16}\text{TeSBr}_2$: C, 44.0; H, 2.7 %); ν_{max} (KBr disc)/ cm^{-1} : 3441br s, 3052w, 2953w, 1944w, 1869w, 1578s, 1475s, 1437s, 1325w, 1261w, 1200w, 1180w, 1072w, 1049w, 1046w, 1023w, 991s, 907w, 814vs, 757vs, 738s, 726vs, 680vs, 619w, 564w, 538w, 480w, 448s; δ_{H} (270 MHz, CDCl_3) 8.26-7.96 (6 H, m, nap 2,4,5,7-H, *TePh* 2,6-H), 7.70-7.40 (5 H, m, nap 3,6-H, *TePh* 3-5-H), 7.32-7.00 (5 H, m, *SPh* 2-6-H); δ_{C} (67.9 MHz, CDCl_3) 139.7(s), 138.1(s), 134.3(s), 133.5(s), 132.5(s),

131.5(s), 130.3(s), 130.1(s), 129.6(s), 128.8(s), 127.4(s), 127.3(s); δ_{Te} (81.2 MHz, CDCl_3) 958.9; m/z (ES^+) 472.79 ($[\text{M}-\text{Br}_2+\text{OMe}]^+$, 100 %).

(8): A solution of 1-(phenyltellurenyl)-8-(phenylselenenyl)naphthalene **D5** (0.12 g, 0.24 mmol) in dichloromethane (5 mL) was treated with bromine (0.038 g, 0.01 mL, 0.24 mmol). An analytically pure sample was obtained by crystallization from diffusion of dichloromethane into a pentane solution of the product (0.1 g, 75 %); (Found: C, 40.7; H, 2.0. Calc. for $\text{C}_{22}\text{H}_{16}\text{TeSeBr}_2$: C, 40.9; H, 2.5 %); ν_{max} (KBr disc)/ cm^{-1} : 3441brs, 3052s, 1944w, 1869w, 1738w, 1721w, 1651w, 1604w, 1572s, 1535w, 1475s, 1436s, 1378w, 1331s, 1209w, 1195w, 1177w, 1136w, 1081w, 1064w, 1049s, 1020w, 994s, 907w, 813vs, 755vs, 727vs, 680s, 613w, 555w, 526w, 446s, 314w δ_{H} (270 MHz, CDCl_3) 8.32 (2 H, d, J 7.0 Hz, *TePh* 2,6-H), 8.28 (1 H, d, J 7.2 Hz, nap 4-H), 8.21 (1 H, d, J 7.3 Hz, nap 5-H), 8.09 (1 H, d, J 7.6 Hz, nap 7-H), 8.05 (1 H, d, J 7.7 Hz, nap 2-H), 7.64-7.44 (5 H, m, nap 3,6-H, *TePh* 3-5-H), 7.36-7.29 (2 H, m, *SePh* 2,6-H), 7.24-7.17 (3 H, m, *SePh* 3-5-H); δ_{C} (67.9 MHz, CDCl_3) 141.1(s), 138.8(s), 136.7(s), 133.6(s), 132.3(s), 131.3(s), 130.7(s), 129.9(s), 129.6(s), 127.7(s), 127.2(s), 126.9(s); δ_{Se} (51.5 MHz, CDCl_3) 500.0; δ_{Te} (81.2 MHz, CDCl_3) 941.4; m/z (ES^+) 518.69 ($[\text{M}-\text{Br}_2+\text{OMe}]^+$, 100 %).

(9): A solution of 1-(phenyltellurenyl)-8-(phenylsulfanyl)naphthalene **D4** (0.032 g, 0.073 mmol) in dichloromethane (5 mL) was treated with iodine (0.018 g, 0.073 mmol). An analytically pure sample was obtained by crystallization from diffusion of dichloromethane into a pentane solution of the product (0.04 g, 80 %); ν_{max} (KBr disc)/ cm^{-1} : 3448br s, 3045w, 2920w, 2371w, 2342w, 1720w, 1686w, 1652w, 1635w, 1578w, 1541w, 1524w, 1509w, 1475s, 1432s, 1381w, 1324s, 1261w, 1196w, 1156w, 1136w, 1073w, 1045w, 1022w, 991w, 928w, 905w, 813vs, 755vs, 734s, 723vs, 681vs, 617w, 563w, 535w, 478w, 446s, 350w; δ_{H} (270 MHz, CDCl_3) 8.37 (1 H, dd, J 0.6 and 7.5 Hz, nap 4-H), 8.22 (2 H, d, J 7.5 Hz, *TePh* 2,6-H), 8.17 (1 H, d, J 7.2 Hz, nap 2-H), 8.13-8.04 (2 H, m, nap 5,7-H), 7.66 (1 H, t, J 7.8 Hz, nap 6-H), 7.59-7.48 (2 H, m, nap 3-H, *TePh* 4-H), 7.43-7.34 (2 H, m, *TePh* 3,5-H), 7.23-7.15 (3 H, m, *SPh* 3-5-H), 7.05-6.97 (2 H, m, *SPh* 2,6-H); δ_{C} (67.9 MHz, CDCl_3) 140.1(s), 139.3(s), 138.2(s), 133.5(s), 132.6(s), 131.4(s), 130.1(s), 129.7(s), 128.1(s), 127.8(s), 127.6(s), 127.5(s); δ_{Te} (81.2 MHz, CDCl_3) 790.9; m/z (ES^+) 470.86 ($[\text{M}-\text{I}_2+\text{OMe}]^+$, 100 %).

(10): A solution of 1-(phenyltellurenyl)-8-(phenylselenenyl)naphthalene **D5** (0.13 g, 0.26 mmol) in dichloromethane (5 mL) was treated with iodine (0.065 g, 0.26 mmol). An analytically pure sample was obtained by crystallization from diffusion of dichloromethane into a pentane solution of the product (0.2 g, 85 %); (Found: C, 36.0; H, 1.7. Calc. for $\text{C}_{22}\text{H}_{16}\text{TeSeI}_2$: C, 35.7; H, 2.2 %); ν_{max} (KBr disc)/ cm^{-1} : 3441br s, 3046w, 2273w, 1572w, 1474s, 1434s, 1328s, 1189w, 1064w, 1046w, 1017w, 991w, 834w, 810vs, 752vs, 722vs, 680vs, 610w, 523w, 438s, 314w; δ_{H} (270 MHz, CDCl_3) 8.12 (1

H, d, J 7.0 Hz, nap 4-H), 8.04 (1 H, d, J 8.1 Hz, nap 2-H), 8.00 (2 H, d, J 7.5 Hz, *TePh* 2,6-H), 7.68 (1 H, d, J 7.3 Hz, nap 5-H), 7.58 (2 H, d, J 7.4 Hz, nap 3,7-H), 7.49-43 (1 H, m, *TePh* 4-H), 7.42-7.32 (4 H, m, *TePh* 3,5-H, *SePh* 2,6-H), 7.22-7.16 (4 H, m, nap 6-H, *SePh* 3-5-H); δ_{C} (67.9 MHz, CDCl_3) 139.2(s), 135.7(s), 135.6(s), 133.4(s), 132.5(s), 131.6(s), 130.5(s), 129.5(s), 129.3(s), 127.7(s), 127.5(s), 126.1(s); δ_{Se} (51.5 MHz, CDCl_3) 428.8; δ_{Te} (81.2 MHz, CDCl_3) 747.0; m/z (ES^+) 518.66 ($[\text{M-I}_2+\text{OMe}]^+$, 100 %).

(11): A solution of 1-bromo-8-(phenyltellurenyl)naphthalene **D6** (0.10 g, 0.25 mmol) in dichloromethane (5 mL) was treated with a 0.1 M solution of bromine in dichloromethane (0.25 mmol, 2.5 mL). An analytically pure sample was obtained by crystallization from diffusion of dichloromethane into a pentane solution of the product (0.1 g, 91 %); (Found: C, 33.9; H, 2.2. Calc. for $\text{C}_{16}\text{H}_{11}\text{TeBr}_3$: C, 33.7; H, 2.0 %); ν_{max} (KBr disc)/ cm^{-1} : 3424brs, 3051w, 2920w, 1655w, 1589w, 1569w, 1535w, 1470s, 1432s, 1330s, 1260s, 1186s, 1133w, 1048s, 993w, 945w, 917w, 897w, 806vs, 735vs, 681s, 453s; δ_{H} (270 MHz, CDCl_3) 8.45 (2 H, d, J 6.6 Hz, *TePh* 2,6-H), 8.08 (1 H, d, J 6.7 Hz, nap 5-H), 8.01 (2 H, d, J 7.5 Hz, nap 4,7-H), 7.91 (1 H, d, J 7.9 Hz, nap 2-H), 7.70-7.51 (3 H, m, *TePh* 3-5-H), 7.51-7.36 (2 H, m, nap 3,6-H); δ_{C} (67.9 MHz, CDCl_3) 137.2(s), 134.3(s), 133.5(s), 132.0(s), 130.2(s), 127.4(s), 126.9(s); δ_{Te} (81.2 MHz, CDCl_3) 942.8; m/z (ES^+) 442.76 ($[\text{M-Br}_2+\text{OMe}]^+$, 100 %).

(12): A solution of 1-iodo-8-(phenyltellurenyl)naphthalene **D7** (0.09 g, 0.20 mmol) in dichloromethane (5 mL) was cooled to 0 °C and slowly treated with a 0.1 M solution of bromine in dichloromethane (2.0 mL, 0.20 mmol). An analytically pure sample was obtained by crystallization from diffusion of dichloromethane into a pentane solution of the product (0.1 g, 86 %); ν_{max} (KBr disc)/ cm^{-1} : 3449br s, 3045w, 2954s, 2924s, 2851w, 1561w, 1532w, 1467w, 1432s, 1324w, 1260s, 1182w, 1094w, 1019w, 991w, 937w, 902w, 871w, 805vs, 766w, 746w, 731vs, 697w, 680s, 643w, 560w, 520w, 501w, 452s, 387w; δ_{H} (270 MHz, CDCl_3) 8.41-8.29 (3 H, m, nap 4-H, *TePh* 2,6-H), 8.12 (1 H, d, J 7.2 Hz, nap 5-H), 7.96 (1 H, d, J 8.0 Hz, nap 7-H), 7.92 (1 H, d, J 7.4 Hz, nap 2-H), 7.63-7.46 (3 H, m, *TePh* 3-5-H), 7.38 (1 H, t, J 7.7 Hz, nap 6-H), 7.28 (1 H, t, J 7.7 Hz, nap 3-H); δ_{C} (67.9 MHz, CDCl_3) 142.2(s), 138.6(s), 137.2(s), 133.9(s), 131.8(s), 130.9(s), 130.1(s), 127.9(s), 126.6(s); δ_{Te} (81.2 MHz, CDCl_3) 903.0; m/z (ES^+) 488.71 ($[\text{M-Br}_2+\text{OMe}]^+$, 100 %).

(13): A solution of 1-bromo-8-(phenyltellurenyl)naphthalene **D6** (0.039 g, 0.095 mmol) in dichloromethane (5 mL) was treated with iodine (0.0024 g, 0.095 mmol). An analytically pure sample was obtained by crystallization from diffusion of dichloromethane into a pentane solution of the product (0.03 g, 54 %); ν_{max} (KBr disc)/ cm^{-1} : 3433br s, 3040w, 2925w, 2371w, 1652w, 1638w, 1561w, 1532w, 1467s, 1432s, 1381w, 1327w, 1259w, 1207w, 1184w, 1130w, 1045s, 991w, 942w,

911w, 825w, 805vs, 746s, 729s, 680s, 603w, 526w, 446s, 432w; δ_{H} (270 MHz, CDCl_3) 8.48 (2 H, dd, J 1.1 and 8.5 Hz, *TePh* 2,6-H), 8.15 (1 H, dd, J 1.1 and 7.7 Hz, nap 4-H), 8.07 (2 H, m, nap 2,5-H), 7.92 (1 H, dd, J 0.8 and 8.3 Hz, nap 7-H), 7.67-7.59 (1 H, m, *TePh* 4-H), 7.53-7.42 (3 H, m, nap 6-H, *TePh* 3,5-H), 7.40 (1 H, t, J 7.8 Hz, nap 3-H); δ_{C} (67.9 MHz, CDCl_3) 139.7(s), 138.5(s), 134.2(s), 133.3(s), 131.8(s), 130.3(s), 130.1(s), 127.5(s), 127.1(s); δ_{Te} (81.2 MHz, CDCl_3) 887.5; m/z (ES^+) 442.76 ($[\text{M}-\text{I}_2+\text{OMe}]^+$, 100 %).

(14): A solution of 1-iodo-8-(phenyltellurenyl)naphthalene **D7** (0.11 g, 0.25 mmol) in dichloromethane (5 mL) was treated with iodine (0.063 g, 0.25 mmol). An analytically pure sample was obtained by crystallization from diffusion of dichloromethane into a pentane solution of the product (0.1 g, 81 %); (Found: C, 27.5; H, 1.3. Calc. for $\text{C}_{16}\text{H}_{11}\text{TeI}_3$: C, 26.9; H, 1.6 %); ν_{max} (KBr disc)/ cm^{-1} : 3430br s, 2959s, 2924vs, 2853s, 1735w, 1654w, 1529w, 1465w, 1430w, 1375w, 1363w, 1317w, 1261vs, 1177w, 1090vs, 1020vs, 866w, 802vs, 747w, 727w, 680w, 663w, 587w, 561w, 535w, 520w, 448w, 389w; δ_{H} (270 MHz, CDCl_3) 8.38-8.29 (2 H, m, *TePh* 2,6-H), 8.27 (1 H, dd, J 1.1 and 7.4 Hz, nap 4-H), 8.15 (1 H, dd, J 1.0 and 7.6 Hz, nap 5-H), 7.93 (1 H, d, J 8.1 Hz, nap 7-H), 7.86 (1 H, dd, J 1.0 and 8.2 Hz, nap 2-H), 7.57-7.49 (1 H, m, *TePh* 4-H), 7.44-7.34 (2 H, m, *TePh* 3,5-H), 7.30 (1 H, t, J 7.8 Hz, nap 6-H), 7.23 (1 H, t, J 7.8 Hz, nap 3-H); δ_{C} (67.9 MHz, CDCl_3) 142.1(s), 140.0(s), 139.4(s), 133.7(s), 131.6(s), 130.7(s), 130.2(s), 128.1(s), 126.9(s); δ_{Te} (81.2 MHz, CDCl_3) 848.0; m/z (ES^+) 490.68 ($[\text{M}-\text{I}_2+\text{OMe}]^+$, 100 %).

(15): A solution of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **D8** (0.30 g, 0.71 mmol) in dichloromethane (15 mL) was treated with bromine (0.45 g, 0.15 mL, 2.8 mmol). An analytically pure sample was obtained by crystallization from diffusion of dichloromethane into a pentane solution of the product (0.2 g, 32 %); ν_{max} (KBr disc)/ cm^{-1} : 3430brs, 3069w, 3052w, 2691w, 2197w, 1968w, 1898w, 1814w, 1738w, 1636w, 1578s, 1543w, 1477vs, 1435vs, 1320s, 1264w, 1197s, 1151s, 1115vs, 1064w, 1023w, 988w, 921w, 887s, 825s, 765vs, 738vs, 718vs, 687vs, 625w, 613w, 581w, 561vs, 535vs, 503s, 468s, 413s, 346vs; δ_{H} (270 MHz, CDCl_3) 8.41 (1 H, d, J 8.0 Hz, nap 4-H), 8.25 (1 H, d, J 8.0 Hz, nap 5-H), 7.87 (2 H, d, J 6.8 Hz, nap 2,7-H), 7.69 (1 H, t, J 7.7 Hz, nap 6-H), 7.66-7.59 (1 H, m, nap 3-H), 7.57-7.42 (6 H, m, 2 x *PPh*₂ 3-5-H), 7.41-7.30 (4 H, m, 2 x *PPh*₂ 2,6-H), 6.96 (1 H, t, J 7.3 Hz, *SPh* 4-H), 6.92-6.83 (2 H, m, *SPh* 3,5-H), 6.15 (2 H, d, J 7.5 Hz, *SPh* 2,6-H), 2.99 (1 H, br s, -OH); δ_{C} (67.9 MHz, CDCl_3) 140.6(s), 137.3(s), 132.8(s), 132.6(s), 131.5(d, J 10.4 Hz), 129.2(d, J 13.5 Hz), 128.7(s), 128.2(s), 128.1(s), 126.2(s), 125.7(s), 125.5(s); δ_{P} (109 MHz, CDCl_3) 52.48; m/z (ES^+) 458.85 ($[\text{M}-\text{Br}_3+\text{Na}]^+$, 100 %).

5.1 Crystal Structure Analyses

X-ray crystal structures determined for compounds **8** and **10** were collected at -180(1) °C by using a Rigaku MM007 High brilliance RA generator (Mo K α radiation, confocal optic) and Mercury CCD system. At least a full hemisphere of data was collected using ω scans. Intensities were corrected for Lorentz, polarisation and absorption. Data for all other compounds [**1-5**, **7**, **9-15**] was collected at -148(1) °C on the St Andrews STANDARD system⁷⁷ Rigaku ACTOR-SM, Saturn 724 CCD area detector with confocal optic Mo-K α radiation ($\lambda = 0.71073$ Å). The data was corrected for Lorentz, polarisation and absorption. The data for the complexes analysed was collected and processed using CrystalClear (Rigaku).⁷⁸ The structure was solved by direct methods⁷⁹ and expanded using Fourier techniques.⁸⁰ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure⁸¹ crystallographic software package except for refinement, which was performed using SHELXL-97.⁸²

5.2 Computational Details

Geometries were fully optimised in the gas phase at the B3LYP level⁸³ using Curtis and Binning's 962(d) basis⁸⁴ on Se and Br (augmented with a set of diffuse s and p functions on Br) and 6-31+G(d) basis elsewhere, followed by calculation of the harmonic frequencies to confirm the minimum character of each stationary point and to evaluate standard thermodynamic corrections at 1 atm and 298 K. Wiberg bond indices⁷⁶ were obtained in a natural bond orbital⁸⁵ analysis at the same level. The optimisations were started from the experimental structures available from X-ray crystallography, substituting chalcogens and halogens where necessary. Additional single-point energy calculations were performed using the polarisable continuum model (PCM) of Tomasi and coworkers,⁸⁶ employing the same basis sets on Se and Br as before, and 6-311+G(d) elsewhere, together with the parameters of CH₂Cl₂ as a typical solvent. The resulting changes in relative energies were added as increments to the gas-phase free energies, affording the $\Delta G_r(\text{CH}_2\text{Cl}_2)$ values in Figure 13. Reaction energies have not been corrected for basis-set superposition error (BSSE). An exploratory BSSE calculation for **C** using the Counterpoise method⁸⁷ (with **D2** and Br₂ fragments) indicated a very small correction of just around 1 kcal/mol. The computations were performed using the Gaussian 03 suite of programs.⁸⁸

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Supporting Information Available: Crystal structure illustrations for compounds **3**, **5**, **8-10**, **12-14** and CIF data for **1-15**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Table 1 ^{31}P , ^{77}Se and ^{125}Te NMR spectroscopy data [δ (ppm)] for donors **D2-D8** and adducts **4-15**

	D2	4	5	D3	6	
<i>peri</i> -atoms	SeSe	SeSe	SeSe	SeS	SeS	
X-Te-X	-	Se-I-I	Se-I-I...I ₂	-	Se-I-I...I ₂	
^{77}Se NMR	428.6	436.9, 436.7	445.1, 444.3	455.3	476.9	
	D4	7	9	D5	8	10
<i>peri</i> -atoms	TeS	TeS	TeS	TeSe	TeSe	TeSe
X-Te-X	-	Br-Te-Br	I-Te-I	-	Br-Te-Br	I-Te-I
^{77}Se NMR	-	-	-	362.8	500.0	428.8
^{125}Te NMR	715.2	958.9	790.9	687.6	941.4	747.0
	D6	11	13	D7	12	14
<i>peri</i> -atoms	BrTe	BrTe	BrTe	ITe	ITe	ITe
X-Te-X	-	Br-Te-Br	I-Te-I	-	Br-Te-Br	I-Te-I
^{125}Te NMR	731.2	942.8	887.5	698.3	903.0	848.0
	D8	15				
<i>peri</i> -atoms	PS	PS				
^{31}P NMR	-5.3	52.5				

Table 2 Selected interatomic distances [\AA] and angles [$^\circ$] for **1-5**

Compound	1	2	3	4	5
<i>Peri-region distances and sub-van der Waals contacts</i>					
E(1)···E'(1)	2.935(4)	2.7619(7)	2.721(2)	3.1339(6)	3.0756(14)
$\Sigma r_{\text{vdW}} - \text{E} \cdots \text{E}'; \% \Sigma r_{\text{vdW}}^a$	0.665; 82	1.038; 73	0.979; 74	0.666; 82	0.724; 81
E(1)-C(1)	1.787(11)	1.957(6)	1.955(8)	1.953(5)	1.948(8)
E'(1)-C(9)	1.780(11)	1.918(5)	1.796(9)	1.933(5)	1.929(7)
<i>Naphthalene bond lengths</i>					
C(1)-C(2)	1.365(16)	1.372(8)	1.375(14)	1.366(7)	1.375(15)
C(2)-C(3)	1.388(16)	1.401(9)	1.390(15)	1.411(8)	1.410(12)
C(3)-C(4)	1.370(16)	1.352(9)	1.342(17)	1.383(8)	1.350(17)
C(4)-C(5)	1.417(15)	1.424(8)	1.424(14)	1.374(8)	1.428(16)
C(5)-C(10)	1.453(15)	1.430(8)	1.429(12)	1.451(7)	1.430(11)
C(5)-C(6)	1.438(16)	1.404(8)	1.422(16)	1.416(8)	1.406(14)

C(6)-C(7)	1.340(18)	1.357(9)	1.363(16)	1.350(8)	1.365(17)
C(7)-C(8)	1.386(16)	1.395(9)	1.404(15)	1.393(8)	1.411(13)
C(8)-C(9)	1.402(16)	1.374(8)	1.362(15)	1.379(7)	1.376(14)
C(9)-C(10)	1.431(15)	1.414(7)	1.395(13)	1.424(7)	1.412(14)
C(10)-C(1)	1.442(15)	1.427(7)	1.450(14)	1.435(6)	1.441(14)
<i>Peri-region bond angles</i>					
E(1)-C(1)-C(10)	122.3(8)	119.8(4)	119.5(6)	121.9(3)	122.5(7)
C(1)-C(10)-C(9)	126.0(10)	126.2(5)	126.0(8)	128.4(4)	126.9(7)
E'(1)-C(9)-C(10)	121.6(8)	120.1(4)	119.8(7)	123.0(4)	124.2(6)
Σ of bay angles	369.9(18)	366.1(9)	365.3(15)	373.3(7)	373.6(14)
Splay angle ^b	9.9	6.1	5.3	13.3	13.6
C(4)-C(5)-C(6)	121.0(10)	120.6(5)	119.0(8)	119.9(5)	119.2(8)
<i>Out-of-plane displacement</i>					
E(1)	-0.343(13)	0.2887(66)	0.112(11)	-0.3290(74)	0.415(11)
E'(1)	0.343(13)	-0.0101(66)	0.139(11)	0.5359(73)	-0.246(11)
<i>Central naphthalene ring torsion angles</i>					
C:(6)-(5)-(10)-(1)	176.1(10)	-177.4(12)	179.3(8)	-172.7(7)	176.7(6)
C:(4)-(5)-(10)-(9)	176.2(9)	-175.0(12)	-179.2(8)	-176.2(7)	174.8(7)

^a van der Waals radii used for calculations: $r_{vdW}(S)$ 1.80 Å, $r_{vdW}(Se)$ 1.90 Å;⁶¹ ^b**Splay angle:** Σ of the three bay region angles – 360.

Table 3 Selected interatomic distances [Å] and angles [°] for **6-10**

Compound	6	7	8	9	10
<i>Peri-region distances and sub-van der Waals contacts</i>					
E(1)⋯E'(1)	2.9798(18)	3.075(2)	3.141(2)	3.0767(17)	3.137(2)
$\Sigma r_{vdW} - E \cdots E'$; % Σr_{vdW}^a	0.720; 81	0.785; 80	0.819; 79	0.783; 78	0.823; 79
E(1)-C(1)	1.958(5)	2.124(10)	2.148(15)	2.138(6)	2.14(2)
E'(1)-C(9)	1.773(5)	1.782(11)	1.933(14)	1.784(6)	1.915(19)
<i>Naphthalene bond lengths</i>					
C(1)-C(2)	1.367(9)	1.355(15)	1.36(2)	1.380(9)	1.43(2)
C(2)-C(3)	1.411(8)	1.410(16)	1.37(2)	1.395(10)	1.42(2)
C(3)-C(4)	1.360(11)	1.393(15)	1.39(2)	1.363(10)	1.37(3)
C(4)-C(5)	1.416(10)	1.400(15)	1.39(2)	1.411(10)	1.43(3)
C(5)-C(10)	1.427(7)	1.421(14)	1.45(2)	1.433(9)	1.41(3)
C(5)-C(6)	1.432(10)	1.452(15)	1.52(2)	1.420(9)	1.45(2)
C(6)-C(7)	1.361(11)	1.343(15)	1.28(2)	1.360(10)	1.36(2)
C(7)-C(8)	1.399(9)	1.388(15)	1.40(2)	1.405(10)	1.43(2)
C(8)-C(9)	1.360(10)	1.362(15)	1.34(2)	1.382(9)	1.36(3)
C(9)-C(10)	1.424(9)	1.447(14)	1.43(2)	1.447(9)	1.46(3)
C(10)-C(1)	1.431(9)	1.427(13)	1.42(2)	1.433(9)	1.43(2)
<i>Peri-region bond angles</i>					
E(1)-C(1)-C(10)	121.7(4)	123.1(7)	122.2(10)	122.5(4)	122.6(14)
C(1)-C(10)-C(9)	126.8(5)	127.6(9)	130.4(15)	127.1(6)	129.4(17)

E(1)-C(9)-C(10)	122.4(4)	121.3(7)	120.9(13)	122.7(5)	120.4(14)
Σ of bay angles	370.9(9)	372.0(16)	373.5(27)	372.3(11)	372.4(31)
Splay angle ^b	10.9	12.0	13.5	12.3	12.4
C(4)-C(5)-C(6)	119.1(5)	117.7(9)	119.2(14)	119.4(6)	116.2(18)
<i>Out-of-plane displacement</i>					
E(1)	0.438(11)	-0.401(12)	-0.444(1)	-0.3690(82)	-0.372(8)
E(1)	-0.233(11)	0.250(12)	0.259(1)	0.3007(77)	0.317(8)
<i>Central naphthalene ring torsion angles</i>					
C:(6)-(5)-(10)-(1)	176.8(4)	-179.1(8)	-177.0(12)	-177.3(6)	179.7(14)
C:(4)-(5)-(10)-(9)	174.9(4)	-174.3(8)	-173.5(13)	-174.1(5)	-174.7(13)

^a van der Waals radii used for calculations: $r_{vdW}(S)$ 1.80 Å, $r_{vdW}(Se)$ 1.90 Å, $r_{vdW}(Te)$ 2.06 Å;⁶¹ ^b**Splay angle:** Σ of the three bay region angles – 360.

Table 4 Selected interatomic distances [Å] and angles [°] for **11-15**

Compound	11	12	13	14	15
<i>Peri-region distances and sub-van der Waals contacts</i>					
G(1)⋯E(1)	3.2397(15)	3.3810(7)	3.1563(6)	3.3608(11)	3.165(2)
$\Sigma r_{vdW} - G\cdots E$; % Σr_{vdW}^a	0.670; 83	0.659; 84	0.754; 81	0.679; 83	0.435; 88
G(1)-C(1)	1.900(11)	2.117(9)	1.911(6)	2.097(11)	1.796(11)
E(1)-C(9)	2.153(10)	2.150(8)	2.150(6)	2.159(9)	1.789(12)
<i>Naphthalene bond lengths</i>					
C(1)-C(2)	1.382(16)	1.361(13)	1.357(9)	1.384(17)	1.393(13)
C(2)-C(3)	1.413(16)	1.397(14)	1.390(10)	1.369(17)	1.391(17)
C(3)-C(4)	1.341(18)	1.376(14)	1.360(8)	1.36(2)	1.359(13)
C(4)-C(5)	1.423(17)	1.422(13)	1.409(10)	1.392(16)	1.423(14)
C(5)-C(10)	1.450(14)	1.453(12)	1.424(8)	1.432(13)	1.442(17)
C(5)-C(6)	1.427(18)	1.410(14)	1.419(7)	1.423(16)	1.415(13)
C(6)-C(7)	1.357(16)	1.352(14)	1.364(9)	1.345(16)	1.362(14)
C(7)-C(8)	1.390(15)	1.416(13)	1.405(8)	1.400(15)	1.414(18)
C(8)-C(9)	1.345(17)	1.374(14)	1.362(6)	1.354(16)	1.397(13)
C(9)-C(10)	1.441(16)	1.437(13)	1.444(8)	1.450(14)	1.420(12)
C(10)-C(1)	1.415(16)	1.406(13)	1.421(6)	1.415(17)	1.459(12)
<i>Peri-region bond angles</i>					
G(1)-C(1)-C(10)	121.3(8)	122.0(6)	121.5(4)	126.3(7)	126.2(7)
C(1)-C(10)-C(9)	129.3(10)	129.3(8)	128.1(5)	128.2(8)	126.4(10)
E(1)-C(9)-C(10)	122.5(8)	124.6(6)	122.8(3)	124.2(7)	122.9(7)
Σ of bay angles	373.1(18)	375.9(14)	372.4(9)	378.7(15)	375.5(17)
Splay angle ^b	13.1	15.9	12.4	18.7	15.5
C(4)-C(5)-C(6)	119.9(9)	119.8(8)	119.4(5)	120.5(10)	118.9(11)
<i>Out-of-plane displacement</i>					
G(1)	-0.550(14)	-0.644(14)	0.312(14)	-0.410(14)	0.436(11)
E(1)	0.641(15)	0.646(15)	-0.614(14)	0.436(14)	-0.466(11)

<i>Central naphthalene ring torsion angles</i>					
C:(6)-(5)-(10)-(1)	170.2(10)	-168.7(8)	174.4(5)	-175.2(9)	171.9(7)
C:(4)-(5)-(10)-(9)	174.0(10)	-175.5(8)	176.5(5)	-176.8(9)	174.9(7)
^a van der Waals radii used for calculations: $r_{vdW}(P)$ 1.80 Å, $r_{vdW}(S)$ 1.80 Å, $r_{vdW}(Br)$ 1.85 Å, $r_{vdW}(I)$ 1.98 Å, $r_{vdW}(Te)$ 2.06 Å; ⁶¹ ^b Splay angle: Σ of the three bay region angles – 360.					

Table 5 Selected interatomic X-E-E, E-X-X and X_3^- distances [Å] and angles [°] for **2-6**

Compound	2	3	4	5	6	
<i>E-Se-X and Br₃⁻ distances & sub-van der Waals contacts</i>			<i>Se-I-I and I₃⁻ distances & sub-van der Waals contacts</i>			
Br(1)-Se(1)	2.4878(8)	2.4232(15)	I(1)-Se(1)	2.9795(8)	2.8497(9)	2.8436(6)
Se(1)-E(2)	2.7619(8)	2.721(2)	I(1)-I(2)	2.7987(6)	2.8672(8)	2.8706(5)
Br(2)-Br(3)	2.5170(8)	2.5514(17)	I(2)⋯I(3)		3.543(1)	3.526(1)
Br(3)-Br(4)	2.5668(8)	2.5433(17)	I(3)-I(3) ¹		2.7402(11)	2.7418(7)
			I(1)⋯E(2)	3.6956(7)	3.8730(9)	3.8527(13)
<i>E-E-X and E-X-X bond angles</i>						
Br(1)-Se(1)-E(2)	172.10(3)	176.34(1)	I(2)-I(1)-Se(1)	177.637(15)	178.09(3)	179.04(2)
Br(2)-Br(3)-Br(4)	177.78(3)	178.57(5)	I(2)⋯I(3)-I(3)'		177.5(1)	107.9(1)
			I(1)-I(2)⋯I(3)		176.3(1)	108.0(1)
			I(1)-Se(1)-E(2)	74.33(1)	81.54(1)	82.81(1)

Table 6 Selected interatomic X-E-X distances [Å] and angles [°] for **7-14**

Compound	7	8	9	10
<i>X-E-X distances, sub-van der Waals contacts and bond angles</i>				
X(1)-Te(1)	2.7072(11)	2.719(2)	2.9457(6)	2.9538(17)
Te(1)-X(2)	2.6688(12)	2.671(2)	2.9073(6)	2.8943(17)
X(1)···G(1)^a	3.486(2)	3.542(2)	3.6136(16)	3.696(2)
X(1)-Te(1)-X(2)	176.67(4)	177.94(6)	176.81(2)	179.59(6)
	11	12	13	14
X(1)-Te(1)	2.6664(13)	2.6578(10)	2.9343(5)	2.9480(7)
Te(1)-X(2)	2.6686(13)	2.6779(11)	2.8952(4)	2.9042(7)
X(1)···G(1)^a	3.7079(17)	3.8497(11)	4.0089(6)	4.16(1)
X(1)-Te(1)-X(2)	175.80(4)	176.55(3)	176.405(19)	177.27(3)

^aG(1) = S **7,9**; Se **8,10**; Br **11,13**; I **12,14**.

Table 7 Torsion angles [°] categorizing the naphthalene and phenyl ring conformations in **1-15**

<i>Naphthalene ring conformations</i>		<i>Phenyl ring conformations</i>	
Nap₁: C(10)-C(1)-G(1)-C(11)	Nap₂: C(10)-C(9)-Z(9)-C(17)	Ph₁: C(1)-G(1)-C(11)-C(12)	Ph₂: C(9)-Z(9)-C(17)-C(18)
1 $\theta_1 = 155.1(9)$: eq	$\theta_2 = -105.3(9)$: ax	$\gamma_1 = -88.5(11)$: ax	$\gamma_2 = 16.8(12)$: eq
2 $\theta_1 = 99.8(4)$: ax	$\theta_2 = -101.4(4)$: ax	$\gamma_1 = 167.7(4)$: eq	$\gamma_2 = 164.4(4)$: eq

3	$\theta_1 = 87.7(7)$: ax	$\theta_2 = -116.3(7)$: ax	$\gamma_1 = -159.4(7)$: eq	$\gamma_2 = -151.5(8)$: eq
4	$\theta_1 = -155.6(5)$: eq	$\theta_2 = -88.9(5)$: ax	$\gamma_1 = -116.5(5)$: ax	$\gamma_2 = 170.2(4)$: eq
5	$\theta_1 = 166.1(5)$: eq	$\theta_2 = 75.1(6)$: ax	$\gamma_1 = -67.7(7)$: ax	$\gamma_2 = 26.2(9)$: eq
6	$\theta_1 = 166.8(3)$: eq	$\theta_2 = 75.2(4)$: ax	$\gamma_1 = 117.0(4)$: ax	$\gamma_2 = 23.2(7)$: eq
7	$\theta_1 = -145.9(7)$: twist	$\theta_2 = 85.8(8)$: ax	$\gamma_1 = -148.9(8)$: twist	$\gamma_2 = 148.3(8)$: twist
8	$\theta_1 = -147.1(12)$: twist	$\theta_2 = -86.4(13)$: ax	$\gamma_1 = 40.5(14)$: twist	$\gamma_2 = -29.5(16)$: twist
9	$\theta_1 = -146.9(5)$: twist	$\theta_2 = -87.5(5)$: ax	$\gamma_1 = -151.2(5)$: twist	$\gamma_2 = 146.2(5)$: twist
10	$\theta_1 = -148.0(12)$: twist	$\theta_2 = -86.8(13)$: ax	$\gamma_1 = 42.8(15)$: twist	$\gamma_2 = -21.8(17)$: twist
11	$\theta_1 = 141.8(8)$: twist	n/a	$\gamma_1 = 137.0(8)$: twist	n/a
12	$\theta_1 = -140.3(8)$: twist	n/a	$\gamma_1 = -136.5(7)$: twist	n/a
13	$\theta_1 = 152.8(4)$: eq	n/a	$\gamma_1 = 138.6(4)$: twist	n/a
14	$\theta_1 = -157.3(7)$: eq	n/a	$\gamma_1 = -135.7(8)$: twist	n/a
15	$\theta_1 = 160.4(7)$ Nap ₁ : eq $\theta_3 = -84.7(8)$ Nap ₃ : ax	$\theta_2 = 97.8(6)$ Nap ₂ : ax	$\gamma_1 = 101.8(10)$ Ph ₁ : ax $\gamma_3 = 153.6(6)$ Ph ₃ : twist	$\gamma_2 = -168.1(7)$ Ph ₂ : eq

Nap₁: naphthalene ring G(1); **Nap₂**: naphthalene ring Z(9); **Nap₃**: 2nd naphthalene ring G(1); **Ph₁**: G(1) phenyl ring; **Ph₂**: Z(9) phenyl ring; **Ph₃**: 2nd G(1) phenyl ring; **ax** = **axial**: perpendicular to C(ar)-G/Z-C(ar) plane; **eq** = **equatorial**: coplanar with C(ar)-G/Z-C(ar) plane; **twist**: intermediate between equatorial and axial.

Table 8 Crystallographic data for compounds **1-4**

Compound	1	2	3	4
Empirical Formula	C ₂₂ H ₁₂ Br ₄ S ₂	C ₁₆ H ₁₁ Br ₄ Se ₂	C ₂₂ H ₁₆ Br ₄ SSe	C ₂₂ H ₁₆ I ₂ Se ₂
Formula Weight	660.07	757.9	711	692.1
Temperature (°C)	-148(1)	-148(1)	-148(1)	-148(1)
Crystal Colour, Habit	yellow, prism	orange, block	orange, platelet	orange, prism
Crystal Dimensions (mm³)	0.12 X 0.06 X 0.06	0.12 X 0.12 X 0.12	0.18 X 0.12 X 0.06	0.12 X 0.12 X 0.06
Crystal System	monoclinic	monoclinic	monoclinic	triclinic
Lattice Parameters	a = 32.535(13) Å b = 5.4833(18) Å c = 27.215(9) Å - β = 92.729(11)° -	a = 9.293(3) Å b = 14.082(5) Å c = 17.212(6) Å - β = 97.177(9)° -	a = 13.555(2) Å b = 9.2381(13) Å c = 18.663(3) Å - β = 103.009(3)° -	a = 10.003(3) Å b = 10.453(2) Å c = 11.749(3) Å α = 102.307(6)° β = 84.68(3)° γ = 93.395(4)°
Volume (Å³)	V = 4850(3)	V = 2234.8(13)	V = 2277.0(6)	V = 1089.3(5)
Space Group	C2/c	P2 ₁ /n	P2 ₁ /c	P-1
Z value	8	4	4	2
Dcalc (g/cm³)	1.808	2.252	2.074	2.11
F000	2528	1424	1352	644
m(MoKa) (cm⁻¹)	68.368	104.897	87.882	62.337
No. of Reflections Measured	13347	13998	12771	11727
Rint	0.068	0.042	0.064	0.036
Min and Max Transmissions	0.406 - 0.664	0.268 - 0.284	0.294 - 0.590	0.486 - 0.688
Independent Reflections	4268	4524	3971	3715

Observed Reflection (No. Variables)	3398(254)	3974(254)	3489(254)	3557(236)
Reflection/Parameter Ratio	16.8	17.81	15.63	15.74
Residuals: R₁ (I>2.00s(I))	0.0866	0.0435	0.0699	0.0302
Residuals: R (All reflections)	0.1144	0.054	0.0813	0.0359
Residuals: wR₂ (All reflections)	0.2732	0.1236	0.1938	0.1262
Goodness of Fit Indicator	1.206	1.175	1.15	1.28
Flack Parameter	-	-	-	-
Maximum peak in Final Diff. Map	2.78 e /Å ³	1.32 e-/Å ³	2.33 e /Å ³	1.44 e /Å ³
Minimum peak in Final Diff. Map	-1.00 e /Å ³	-1.17 e-/Å ³	-1.18 e /Å ³	-1.77 e /Å ³

Table 9 Crystallographic data for compounds **5-8**

Compound	5	6	7	8
Empirical Formula	C ₄₄ H ₃₂ I ₆ Se ₄	C ₄₄ H ₃₂ I ₆ S ₂ Se ₂	C ₂₂ H ₁₆ Br ₂ STe	C ₂₂ H ₁₆ Br ₂ SeTe
Formula Weight	1638	1544.2	599.84	646.73
Temperature (°C)	-148(1)	-148(1)	-148(1)	-180(1)
Crystal Colour, Habit	red, prism	red, prism	yellow, prism	colourless, platelet
Crystal Dimensions (mm³)	0.15 X 0.09 X 0.09	0.21 X 0.15 X 0.09	0.21 X 0.03 X 0.03	0.06 X 0.06 X 0.03
Crystal System	triclinic	triclinic	monoclinic	monoclinic
Lattice Parameters	a = 9.6503(18) Å b = 11.3357(16) Å c = 11.8269(16) Å α = 65.996(10)° β = 82.763(14)° γ = 83.206(14)°	a = 9.6066(17) Å b = 11.2528(14) Å c = 11.8080(14) Å α = 65.855(9)° β = 82.839(14)° γ = 83.443(14)°	a = 18.873(10) Å b = 15.452(7) Å c = 13.922(6) Å - β = 100.423(11)° -	a = 19.172(8) Å b = 15.285(6) Å c = 14.070(7) Å - β = 100.442(13)° -
Volume (Å³)	V = 1169.3(3)	V = 1152.9(3)	V = 3993(3)	V = 4055(3)
Space Group	P-1	P-1	C2/c	C2/c
Z value	1	1	8	8
Dcalc (g/cm³)	2.326	2.224	1.995	2.119
F000	750	714	2288	2432
m(MoKa) (cm⁻¹)	71.303	57.432	56.13	7.207
No. of Reflections Measured	13845	13510	10797	12736
Rint	0.043	0.038	0.082	0.1295
Min and Max Transmissions	0.336 - 0.526	0.403 - 0.596	0.542 - 0.845	0.652 - 1.000
Independent Reflections	4628	4542	3510	3669
Observed Reflection (No. Variables)	4222(245)	4336(245)	2992(236)	2284(236)

Reflection/Parameter Ratio	18.89	18.54	14.87	15.55
Residuals: R₁ (I>2.00s(I))	0.0483	0.0429	0.0696	0.0947
Residuals: R (All reflections)	0.0569	0.0479	0.0876	0.1436
Residuals: wR₂ (All reflections)	0.1746	0.1587	0.1808	0.2625
Goodness of Fit Indicator	1.185	1.148	1.261	1.077
Flack Parameter	-	-	-	-
Maximum peak in Final Diff. Map	1.32 e-/Å ³	2.46 e-/Å ³	1.50 e-/Å ³	2.515 e-/Å ³
Minimum peak in Final Diff. Map	-1.56 e-/Å ³	-1.98 e-/Å ³	-1.67 e-/Å ³	-1.557 e-/Å ³

Table 10 Crystallographic data for compounds **9-12**

Compound	9	10	11	12
Empirical Formula	C ₂₂ H ₁₆ I ₂ STe	C ₂₂ H ₁₆ I ₂ SeTe	C ₁₆ H ₁₁ Br ₃ Te	C ₁₆ H ₁₁ Br ₂ ITe
Formula Weight	693.84	740.71	570.57	617.58
Temperature (°C)	-148(1)	-180(1)	-148(1)	-148(1)
Crystal Colour, Habit	orange, prism	colorless, platelet	colorless, platelet	yellow, prism
Crystal Dimensions (mm³)	0.15 X 0.09 X 0.09	0.05 X 0.05 X 0.05	0.12 X 0.12 X 0.01	0.15 X 0.09 X 0.09
Crystal System	monoclinic	monoclinic	orthorhombic	orthorhombic
Lattice Parameters	a = 18.909(4) Å b = 15.954(3) Å c = 14.282(3) Å - β = 99.994(5)° -	a = 19.723(9) Å b = 15.191(6) Å c = 14.463(6) Å - β = 100.692(12)° -	a = 8.4839(18) Å b = 12.041(2) Å c = 15.592(3) Å - - -	a = 8.5238(18) Å b = 12.165(3) Å c = 15.780(3) Å - - -
Volume (Å³)	V = 4243.1(15)	V = 4258(3)	V = 1592.8(6)	V = 1636.3(6)
Space Group	P2/c	C2/c	Pca2 ₁	Pca2 ₁
Z value	8	8	4	4
D_{calc} (g/cm³)	2.172	2.311	2.379	2.507
F₀₀₀	2576	2720	1056	1128
m(MoKa) (cm⁻¹)	44.16	6.011	94.028	85.916
No. of Reflections Measured	12261	13494	4898	4932
R_{int}	0.033	0.1378	0.057	0.04
Min and Max Transmissions	0.487 - 0.672	0.797 - 1.000	0.409 - 0.910	0.290 - 0.462
Independent Reflections	4204	3836	2459	2609
Observed Reflection (No. Variables)	3961(236)	2117(236)	2353(182)	2579(182)
Reflection/Parameter Ratio	17.81	16.25	13.51	14.34
Residuals: R₁ (I>2.00s(I))	0.0361	0.0823	0.0461	0.0313
Residuals: R (All reflections)	0.0429	0.1495	0.0503	0.0332
Residuals: wR₂ (All reflections)	0.1341	0.2132	0.0996	0.0967
Goodness of Fit Indicator	1.244	0.992	1.089	1.206

Flack Parameter	-	-	-	-
Maximum peak in Final Diff. Map	1.65 e-/Å ³	3.359 e-/Å ³	0.77 e-/Å ³	1.41 e-/Å ³
Minimum peak in Final Diff. Map	-1.63 e-/Å ³	-1.375 e-/Å ³	-1.09 e-/Å ³	-1.50 e-/Å ³

Table 11 Crystallographic data for compounds **13-15**

Compound	13	14	15
Empirical Formula	C ₁₆ H ₁₁ BrI ₂ Te	C ₁₆ H ₁₁ I ₃ Te	C ₅₆ H ₄₃ O ₂ P ₂ S ₂ Br ₃
Formula Weight	664.58	711.58	1113.73
Temperature (°C)	-148(1)	-148(1)	-148(1)
Crystal Colour, Habit	red, platelet	orange, prism	colorless, prism
Crystal Dimensions (mm³)	0.15 X 0.15 X 0.03	0.12 X 0.03 X 0.03	0.12 X 0.09 X 0.09
Crystal System	triclinic	triclinic	triclinic
Lattice Parameters	a = 8.221(2) Å b = 9.639(3) Å c = 11.613(3) Å α = 105.274(8)° β = 90.454(4)° γ = 102.945(9)°	a = 7.290(4) Å b = 9.642(6) Å c = 13.294(7) Å α = 104.034(9)° β = 92.232(12)° γ = 103.475(12)°	a = 9.1606(13) Å b = 11.537(3) Å c = 12.606(4) Å α = 83.21(5)° β = 71.33(4)° γ = 66.89(4)°
Volume (Å³)	V = 863.0(4)	V = 877.0(9)	V = 1160.8(7)
Space Group	P-1	P-1	P-1
Z value	2	2	1
Dcalc (g/cm³)	2.557	2.695	1.593
F000	600	636	562
m(MoKa) (cm⁻¹)	76.13	69.675	28.176
No. of Reflections Measured	9862	9605	11962
Rint	0.044	0.071	0.105
Min and Max Transmissions	0.335 - 0.796	0.632 - 0.811	0.511 - 0.776
Independent Reflections	3384	3429	4041
Observed Reflection (No. Variables)	3262(182)	3196(182)	3185(296)
Reflection/Parameter Ratio	18.59	18.84	13.65
Residuals: R₁ (I>2.00s(I))	0.0373	0.0589	0.1109
Residuals: R (All reflections)	0.0391	0.0675	0.1398
Residuals: wR₂ (All reflections)	0.1186	0.1966	0.1854
Goodness of Fit Indicator	1.144	1.134	1.241
Flack Parameter	-	-	-
Maximum peak in Final Diff. Map	1.43 e-/Å ³	2.28 e-/Å ³	0.93 e-/Å ³
Minimum peak in Final Diff. Map	-1.29 e-/Å ³	-2.40 e-/Å ³	-0.79 e-/Å ³

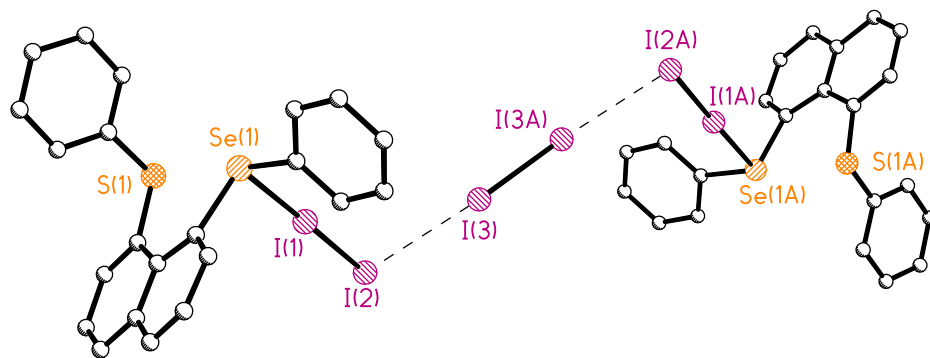
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Structurally diverse compounds {Nap[ER][E`R]} (ER/E`R = SPh, SePh, TePh); Nap[TePh][X] (X = Br, I); Nap[PPh₂][SPh]} and dibromine and diiodine have been characterised. {Nap[SePh]₂} and {Nap[SePh][SPh]} afford unusual tribromide salts of bromoselenyl cations containing a hypervalent X-E...E` 3c-4e type interaction.