DOI: 10.1002/ejic.2011((will be filled in))

This is an Accepted Manuscript of an article published as:

Bridging the gap: attractive 3c-4e interactions in *peri*-substituted acenaphthylenes

Diamond, L. M., Knight, F. R., Arachchige, K. S. A., Randall, R. A. M., Buehl, M., Slawin, A. M. Z. & Woollins, J. D. Mar 2014 In : European Journal of Inorganic Chemistry. 2014, 9, p. 1512-1523

Bridging the gap; attractive 3c-4e interactions in *peri*-substituted acenaphthylenes

Louise M. Diamond,^[a] Fergus R. Knight,^{*[a]} Kasun S. Athukorala Arachchige,^[a] Rebecca A. M. Randall,^[a] Michael Bühl,^[a] Alexandra M. Z. Slawin and J. Derek Woollins^[a]

Keywords: acenaphthylene /*peri*-substitution /3c-4e interaction /X-ray crystallography / DFT calculations/non-covalent

A series of *peri*-substituted acenaphthylenes containing mixed halogen-chalcogen functionalities at the 5,6-positions in **1-6** (Acenapyl[X][EPh] (Acenap = acenaphthylene-5,6-diyl; X = Br, I; E = S, Se, Te) and chalcogen-chalcogen moieties in **7-11** (Acenap[EPh][E'Ph] (Acenap = acenaphthene-5,6-diyl; E/E' = S, Se, Te), have been prepared from their corresponding acenaphthene analogues **A1-A11**, utilizing 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) for the dehydrogenation of the ethane backbone. The related dihalide compounds **13** and **14** Acenapyl[XX'] (XX' = BrBr, II) have also been prepared following a similar procedure and 1,2,5,6-tetrabromo-1,2-dihydroacenaphthylene **A0** was prepared as an intermediate following an alternative route to **13**. The series of acenaphthylene compounds have remarkably similar molecular structures to their acenaphthene counterparts, exhibiting an expected increase in *peri*-separation as heavier congeners occupy the close *peri*-positions.

The presence of the ethene bridge, however, naturally compresses the nearest bay angle whilst increasing the splay of the exocyclic *peri*-atoms, resulting in a minor increase in separation compared with equivalent acenaphthenes. The structures of **1-11**, **13** and **14** are discussed and compared with previously reported analogous naphthalene and acenaphthene compounds. Similar to acenaphthene derivatives, aromatic ring conformations and the location of *p*-type lone-pairs influences the geometry of the *peri*-region. Under appropriate geometric conditions quasi-linear three-body C_{ph}-E...Z (E = Te, Se, S; Z = Br/E) fragments provide an attractive component for the E...Z interaction. DFT studies confirm the onset of formation of three-center, four-electron bonding, similar in extent as observed in analogous acenaphthenes, despite an increase in the *peri*-distances.

Introduction

Understanding how atoms interact in different bonding situations and the ability to quantify the extent of bonding between two atoms is an ongoing challenge for chemists, and one which dates back to the origins of the electronic theory of valence proposed by Lewis and Langmuir in the early 1900s.[1,2] The stability of molecules was originally ascribed to their ability to pair valence electrons off in chemical bonds to achieve 'stable octets', with the concept of covalence introduced as 'the number of pairs of electrons an atom can share with its neighbor'.[1-3] Ambiguity over the bonding in molecules of heavier main-block elements (period 3 and higher), in which an 'octet expansion' would be required in order to conform to conventional Lewis 2c-2e covalent bonding theory, was thus rationalized by the availability of unfilled low-lying *d*-orbitals.[1] Langmuir, however, accounted for the legitimacy of the octet rule by suggesting the bonding in these species, termed hypervalent,[4] was now ionic rather than covalent in nature.[2]

The advancement of molecular orbital theory in the latter half of the last century led to a greater understanding of the bonding in hypervalent compounds, favoring the octet rule rather than conventional Lewis 2c-2e theory as a valid first approximation for

the bonding in molecules of the main-block.[3] The concept of a three centre four-electron bond (3c-4e) subsequently introduced by Rundle[5] and Pimental[6] was able to explain the bonding without either violating the octet rule or invoking ionic bonding and later evolved to include four- and five-centre, six electron bonds (4c-6e, 5c-6e).[7] With the help of increasingly sophisticated calculations, novel bonding scenarios are continuing to be uncovered,[8] however identifying synthetic routes to these systems is essential for corroborating theoretical predictions, which are not always unambiguous.

The chemistry of 1,8-disubstituted naphthalenes is well developed[9] with many groups utilizing the rigidity of the backbone and close proximity of the substituted moieties for studying weak non-covalent interactions in main group systems.[10,11] The geometric constraints unique to *peri*-substituted species, allows large heteroatoms to occupy unusually close positions within van der Waals radii. The subsequent nonbonded intramolecular interactions which result from the direct overlap of orbitals can either be repulsive due to steric hindrance or attractive in the form of weak or strong bonding.[12,13] When electron density is delocalized over formally nonbonded atoms, the degree to which the delocalization contributes to the bonding between these atoms is of particular interest.[8,14-19] Heavier third and fourth row *peri*-substituents, susceptible to hypervalent bonding, can be forced to interact well within the sum of van der Waals radii. However, the nature, size and number of the substituents attached to the *peri*-atoms and the makeup of the rigid backbone can have a notable affect on the formally non-bonded *peri*-separations. Such tendencies are observed in naphthalenes **N1-N12**[18] and their acenaphthene analogues **A1-A12**. [17] Under

[a] EaStCHEM, School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, UK
Fax: (+44)1334 463829
E-mail: frk@st-andrews.ac.uk
<http://chemistry.st-and.ac.uk/staff/jdw/group/home.html>
Supporting information for this article is available on the WWW under <http://www.eurjic.org/> or from the author.

appropriate geometric configurations, 3c-4e type interactions provide an attractive component for the E...Z interaction, which becomes less prominent for the lighter, second-row congeners. However, the variation in *peri*-separation between compounds with different aromatic ring configurations can be correlated to the ability of frontier orbitals to take part in attractive or repulsive interactions. In addition, the introduction of the ethane linker ensures *peri*-substituted acenaphthenes naturally display greater molecular distortion than corresponding naphthalene derivatives, resulting in longer *peri*-distances and less interaction between the *peri*-atoms.[17,18]

The ease of synthesising the valuable precursor 5,6-dibromoacenaphthene[20] compared to the more laborious method for preparing the naphthalene equivalent,[21] has seen an increasing rise in the use of the acenaphthene scaffold for preparing *peri*-substituted species.[22-27] The related acenaphthylene backbone incorporating a C=C double bond on the bridging moiety, however, has seen limited use. Herein, we report the synthesis and structural characterisation of a series of halogen and chalcogen *peri*-substituted acenaphthylenes **1-12**, analogues of previously reported naphthalenes **N1-N12**[18] and acenaphthenes **A1-A12**,[17] along with 5,6-dihaloacenaphthylenes **13** (Br)[28,29] and **14** (I).

Figure 1. Sterically crowded *peri*-substituted acenaphthylenes **1-14**, acenaphthenes **A1-A12**[17] and naphthalenes **N1-N12**. [18]

Results and Discussion

Acenaphthylenes **1-11**, **13**[28,29] and **14** were synthesized, with crystal structures determined for **2**, **3**, **5**, **6**, **8-10** and **13**. In addition, 1,2,5,6-tetrabromo-1,2-dihydroacenaphthylene **A0**[28] was synthesized as an intermediate in the preparation of **13** and its

crystal structure determined. The structure of 5,6-dibromoacenaphthene **A13** is also reported for completeness and for comparison with **13** and **A0**. All compounds obtained (**1-11**, **13**, **14** and **A0**) were characterized by multinuclear magnetic resonance and IR spectroscopy and mass spectrometry, and the homogeneity of the new compounds was where possible confirmed by microanalysis. ^{77}Se and ^{125}Te NMR spectroscopic data can be found in Table 1.

Previous work undertaken on analogous naphthalene[18] and acenaphthene[17] compounds highlighted 5,6-dibromoacenaphthylene **13**[28,29] as a potential starting material for the preparation of chalcogen substituted acenaphthylenes **1-12**. 1,8-dibromonaphthalene **N13** and 5,6-dibromoacenaphthene **A13** both readily undergo lithium-halogen exchange reactions to form mono- and di-lithiated precursors for many metal-substitution reactions, and have previously been shown to react with diphenyl dichalcogenides to form substituted chalcogen compounds.[17,18,30,31]

13 was initially prepared following a modified version of the route reported by Meinwald and Chiang.[28] A chloroform solution of 5,6-dibromoacenaphthene **A13**[32] was treated with 2.2 equivalents of N-bromosuccinimide (NBS) and 0.22 equivalents of benzoyl peroxide and heated under reflux for five hours affording **A0** (yield 74%). Debromination to the target compound **13** was subsequently achieved by treating **A0** with five equivalents of zinc and refluxing in glacial acetic acid for four hours (yield 86%, Scheme 1).[33] An alternative route to **13**, reported by Mitchell and co-workers,[34] converts 5,6-dibromoacenaphthene **A13** directly to the product in one step, using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing benzene (24 h) to dehydrogenate the ethane bridge (yield 25%, Scheme 1).

Scheme 1. Alternative routes for the synthesis of 5,6-dibromoacenaphthylene **13**; i) N-bromosuccinimide, benzoyl peroxide, chloroform, 80 °C, 5 h; ii) zinc powder, glacial acetic acid, 120 °C, 4 h; iii) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), benzene, 90 °C, 24 h.

The preparation of 5,6-bis(phenylsulfanyl)acenaphthylene **7** was initially attempted following the procedure outlined previously for the synthesis of analogous 5,6-bis(phenylchalcogeno)acenaphthenes **A7-A10**. [17] **13** was first treated with TMEDA (2.7 equivalents) and *n*-butyllithium (2.4 equivalents) to afford the corresponding 5,6-dilithioacenaphthylene·2TMEDA complex, which was subsequently reacted with two equivalents of diphenyl disulfide. The reaction, however, was unsuccessful and an alternative route to acenaphthylenes **1-12** was explored.

Prompted by the ease of conversion of **A13** into acenaphthylene **13**, it was decided to first prepare acenaphthenes **A1-A12**[17] and then treat them with DDQ to dehydrogenate the ethane backbone and afford the desired acenaphthylenes **1-12**. **A1-**

Table 1. ^{77}Se and ^{125}Te NMR spectroscopic data, δ (ppm).[17,18]

	2	N2	A2	5	N5	A5	8	N8	A8	10	N10	A10
<i>peri</i> -atoms	Br,Se	Br,Se	Br,Se	I,Se	I,Se	I,Se	Se,Se	Se,Se	Se,Se	Se,S	Se,S	Se,S
^{77}Se NMR	448	448	424	427	431	401	427	429	408	456	455	434
	3	N3	A3	6	N6	A6	9	N9	A9	11	N11	A11
<i>peri</i> -atoms	Br,Te	Br,Te	Br,Te	I,Te	I,Te	I,Te	Te,Te	Te,Te	Te,Te	Te,S	Te,S	Te,S
^{125}Te NMR	723	731	696	687	698	662	618	620	586	951	715	689

A12 were thus reacted with DDQ (1.5 eq.) following the same procedure outlined above for the preparation of **13**,[34] with 5,6-diiodoacenaphthene **A14** converted to acenaphthylene **14** in a similar fashion. Conversion to the corresponding acenaphthylene was successful in each case and in moderate to good yields (12–71%), except, surprisingly for the reaction of mixed tellurium-selenium compound **A12**, which was unsuccessful. ^1H NMR revealed that the reaction had formed an unsymmetrical acenaphthylene, as the characteristic pair of doublets which represent the two *CH* peaks of the ethene double bond were present (6.94 (1 H, d, $^3J_{\text{HH}}$ 5.2 Hz, *CH*), 6.91 (1 H, d, $^3J_{\text{HH}}$ 5.2 Hz, *CH*)). However, ^1H NMR and HSQC revealed that peaks for only one phenyl group were present, indicating that only one chalcogen-phenyl group remained. In addition, no signal was observed in the ^{125}Te NMR spectrum, however the ^{77}Se NMR displayed a singlet at 446 ppm. Mass spectrometry confirmed the presence of a mono-substituted selenium-phenyl acenaphthylene with a mass: charge ratio of 307.0. Attempts to recrystallise the unknown product were unsuccessful, we speculate that the reaction has proceeded with loss of PhTe to give acenaphthyl(SePh).

^{77}Se and ^{125}Te NMR spectroscopic data for the series of acenaphthylene derivatives and their acenaphthene and naphthalene analogues is displayed in Table 1. The acenaphthylene derivatives display NMR signals with similar chemical shifts to their naphthalene counterparts. This is in contrast with equivalent acenaphthene compounds, whose signals lie noticeably upfield at much lower chemical shifts. The exception is mixed tellurium-sulfur derivative **11** which displays a significantly higher chemical shift of 952 ppm (*cf.* **N11** 715 ppm; **A11** 589 ppm).

X-ray investigations

Suitable single crystals were obtained for **2**, **3**, **5**, **6**, **8** and **13** by diffusion of hexane into a saturated solution of the compound in dichloromethane. Crystals for **9** and **10** were obtained by slow evaporation of a saturated dichloromethane solution of the product and for **A0** by evaporation of a saturated hexane solution. Compound **13** contains two nearly identical molecules in the asymmetric unit, in contrast to the remaining members of the series which crystallize with one molecule in the asymmetric unit. The molecular structures of **2**, **3**, **5**, **6**, **8–10** and **13** are analysed together here and compared with the structures of naphthalene and acenaphthene derivatives previously reported.[17,18] The molecular structures of **A0** and **A13** are also discussed. Selected interatomic bond lengths and angles are listed in Tables 2 and 3. Further crystallographic information can be found in the Supporting Information.

The molecular structures of acenaphthylenes **2**, **3**, **5**, **6**, **8–10** and **13** are remarkably similar to their acenaphthene counterparts (**A2**, **A3**, **A5**, **A6**, **A8–10** and **A13**),[17] exhibiting identical phenyl and ‘naphthalene’ ring configurations and with comparable degrees of molecular distortion between corresponding compounds. Naturally,

the ethane and ethene backbones of the acenaphthene and acenaphthylene derivatives have a noticeable impact on their molecular geometry compared to the equivalent substituted naphthalenes (**N2**, **N3**, **N5**, **N6**, **N8–10** and **N13**).[18] This is most apparent when contrasting the degree to which each set of compounds deviates from an ideal geometry[36–38] upon the introduction of the large chalcogen and halogen heteroatoms. The substituted naphthalene systems, without the restriction of a semi-rigid linker, have greater freedom to deform in order to reduce the steric crowding occurring within the *peri*-region. Elongation of the bonds around C10 (average 1.44 Å compared with the ideal 1.42 Å),[18,36] close to the site of steric repulsion, is accompanied by a natural increase in the C1–C10–C9 angular splay (average 128° compared with the ideal 118°),[18,36] although this is offset by a minor reduction in the C4–C5–C6 angle (average 118° compared with the ideal 122°).[18,36] The most conspicuous deviation from ideality in the naphthalene systems is the reduction in planarity of the carbon framework, with central naphthalene C–C–C–C torsion angles indicating a significant buckling of the ring system is taking place (average 5° compared with the ideal 0°).[18,36]

The introduction of bridging ethane/ethene organic linkers at the 1- and 2- positions of the naphthalene skeleton in acenaphthene and acenaphthylene results in a minor reduction in the planarity of the carbon framework, and naturally compresses the C4–C5–C6 angle (naphthalene 122°, acenaphthene 112°, acenaphthylene 109°).[36–38] In both compounds this coincides with a significant widening of the bay-region, augmented by an increase in the C1–C10–C9 angle (acenaphthene 127°, acenaphthylene 128°, *cf.* naphthalene 122°).[36–38] The exocyclic *peri*-H-atoms are thus divergent and no longer parallel, subsequently increasing the ideal *peri*-distance to ~2.7 Å in both acenaphthene and acenaphthylene (*cf.* naphthalene 2.4 Å).[36–38] This natural increase in *peri*-separation in the unsubstituted compounds is reflected in the series of substituted acenaphthenes (**A2**, **A3**, **A5**, **A6**, **A8–10** and **A13**)[17] and acenaphthylenes (**2**, **3**, **5**, **6**, **8–10** and **13**), which exhibit less deviation from ideality compared to analogous naphthalene derivatives. Nevertheless, in both series, and in line with their naphthalene analogues, substitution of the heavy halogen and chalcogen moieties requires further widening of the C1–C10–C9 angle (average 131° (acenaphthene) and 132° (acenaphthylene) compared with the ideal 127° and 128°, respectively)[17,37,38] however, unlike the naphthalenes, the bonds around C10 retain their ideal length (average 1.43 Å and 1.44 Å, respectively).[17,37,38] In addition, the presence of the ethane and ethene bridges blocks any possible distortion of the C4–C5–C6 angle, which remains close to ideal in both sets of compounds (average 112° and 109°, respectively).[17,37,38] The rigidity of the organic linkers also helps to reduce the distortion occurring within the acenaphthene and acenaphthylene carbon frameworks, with central C–C–C–C torsion angles averaging only 3° compared with 5° in the naphthalene derivatives.

Table 2. Selected interatomic distances [Å] and angles [°] for compounds **2**, **3**, **5**, **6**, **8-10**.

Compound	2	3	5	6
X, E	Br,Se	Br,Te	I,Se	I,Te
Peri-region-distances				
X(1)···E(1)	3.189(2)	3.260(4)	3.3324(9)	3.366(3)
% $\Sigma r_{vdW}[a]$	85	83	86	83
Peri-region bond angles				
X(1)–C(1)–C(10)	124.0(8)	122.6(18)	125.4(3)	121.2(12)
C(1)–C(10)–C(9)	131.3(9)	134(3)	132.2(4)	131.7(17)
E(1)–C(9)–C(10)	121.2(7)	118.0(18)	121.7(3)	126.5(14)
Σ of bay angles	376.5(14)	374.6(22)	379.3(6)	379.4(25)
Splay angle[b]	16.5	14.6	19.3	19.4
C(4)–C(5)–C(6)	109.0(9)	109(3)	109.5(4)	109.0(2)
X(1)–E(1)–C(13)	177.07(1)	169.40(1)	174.72(1)	170.03(1)
Out-of-plane displacement				
X(1)	-0.217(1)	-0.258(1)	-0.245(1)	0.357(1)
E(1)	0.190(1)	0.382(1)	0.183(1)	-0.417(1)
Central naphthalene ring torsion angles				
C:(6)–(5)–(10)–(1)	-175.1(8)	-174(2)	175.6(4)	177.4(19)
C:(4)–(5)–(10)–(9)	179.8(8)	-178(2)	-179.7(4)	172.4(19)
Compound	8	9	10	
X, E	Se,Se	Te,Te	Se,S	
Peri-region-distances				
E(1)···E(2)	3.191(3)	3.393(3)	3.144(3)	
% $\Sigma r_{vdW}[a]$	84	82	85	
Peri-region bond angles				
E(1)–C(1)–C(10)	123.4(11)	124.5(10)	122.8(6)	
C(1)–C(10)–C(9)	130.5(12)	131.2(13)	129.9(6)	
E(2)–C(9)–C(10)	122.5(12)	124.1(10)	123.0(5)	
Σ of bay angles	376.4(20)	379.8(19)	375.7(10)	
Splay angle[b]	16.4	19.8	15.7	
C(4)–C(5)–C(6)	109.0(12)	108.7(13)	108.4(6)	
E(2)–E(1)–C(13)	84.47(1)	92.99(1)	172.72(1)	
E(1)–E(2)–C(19)	176.6(1)	174.06(1)	94.35(1)	
Out-of-plane displacement				
X(1)	-0.213(1)	0.306(1)	0.276(1)	
E(1)	0.245(1)	-0.387(1)	-0.260(1)	
Central naphthalene ring torsion angles				
C:(6)–(5)–(10)–(1)	-177.1(14)	177.5(8)	178.5(6)	
C:(4)–(5)–(10)–(9)	-177.0(14)	175.2(8)	177.4(6)	

[a] van der Waals radii used for calculations: $r_{vdW}(\text{Br})$ 1.85 Å, $r_{vdW}(\text{I})$ 1.98 Å, $r_{vdW}(\text{S})$ 1.80 Å, $r_{vdW}(\text{Se})$ 1.90 Å, $r_{vdW}(\text{Te})$ 2.06 Å; [35] [b] Splay angle: Σ of the three bay region angles – 360.

Akin to their naphthalene and acenaphthene analogues, substituted acenaphthylenes **2**, **3**, **5**, **6**, **8-10** and **13** experience additional out-of-plane displacement, with the *peri*-atoms lying 0.18-0.42 Å from the mean plane depending upon the bulk of the *peri*-substituents. Further separation is provided by in-plane tilting of the exocyclic *peri*-bonds with angles around C1 and C9 averaging 123° compared to 120° in the ideal acenaphthylene structure.[38] This, coupled with the natural increase in the C1–C10–C9 angular splay from the inclusion of the ethene bridge, results in greater bay region angles in the acenaphthylene compounds compared to analogous acenaphthenes and naphthalenes (average splay angles 17°, 16° and 14°, respectively).[17,18] This is reflected in the magnitude of the *peri*-distances observed in each set of compounds which increase in the order naphthalenes to acenaphthenes to acenaphthylenes (3.06-3.31 Å in **N2**, **N3**, **N5**, **N6**, **N8-10** and **N13**:[18] 3.11-3.38 Å in **A2**, **A3**, **A5**, **A6**, **A8-10** and **A13**:[17] 3.14-3.39 Å in **2**, **3**, **5**, **6**, **8-10** and **13**). Nevertheless, *peri*-separations are still shorter than the sum of

van der Waals radii [3.60–4.12 Å][35] for the two interacting atoms in all of the compounds studied.

Figure 2. The molecular structure of **2** (H atoms omitted for clarity). The structures of **3**, **5** and **6** (adopting similar conformations) are omitted here but can be found in the ESI (Figure S1).

Table 3. Selected interatomic distances [$\text{\AA}$] and angles [$^\circ$] for compounds **13**, **A0** and **A13** [values in parentheses are for independent molecules].

Compound	13	A0	A13
X, X	Br, Br	Br, Br	Br, Br
Peri-region-distances			
X(1)⋯X(2)	3.3387(6) [3.3195(6)]	3.462(3)	3.3052(11)
% Σr_{vdw}^a	90 [90]	94	89
Peri-region bond angles			
Br(1)–C(1)–C(10)	124.0(2) [123.6(2)]	120.2(12)	124.3(3)
C(1)–C(10)–C(9)	133.3(3) [133.6(3)]	142.2(13)	132.5(4)
Br(2)–C(9)–C(10)	124.44(19) [123.5(3)]	119.6(11)	123.8(4)
Σ of bay angles	381.74(19) [380.7(5)]	382.0(21)	380.6(6)
Splay angle ^b	21.7 [20.7]	22.0	20.6
C(4)–C(5)–C(6)	124.0(2) [123.6(2)]	120.2(12)	111.0(4)
Out-of-plane displacement			
X(1)	-0.006(1) [-0.011(1)]	0.192(1)	0.028(1)
X(2)	0.042(1) [0.029(1)]	-0.196(1)	-0.061(1)
Central naphthalene ring torsion angles			
C(6)–(5)–(10)–(1)	178.7(3) [-178.5(2)]	179.3(12)	179.8(3)
C(4)–(5)–(10)–(9)	-178.1(3) [179.7(2)]	179.4(13)	178.9(3)

[a] van der Waals radii used for calculations: $r_{vdw}(\text{Br})$ 1.85 $\text{\AA}$;³⁵ [b] Splay angle: Σ of the three bay region angles – 360.

Acenaphthylenes **2**, **3**, **5**, **6**, **8–10** adopt identical configurations to their acenaphthene counterparts,[17] previously characterised, along with the naphthalene series,[18] according to the related classification systems devised by Nakanishi *et al.*[10] and Nagy *et al.*[39] The absolute conformation of each structure is calculated from torsion angles θ and γ (Tables 4 and 5; Figures 4 and S4), which describe the relative alignment of the E('naphthalene') and E(phenyl) rings with respect to the C(ar)–E–C(ar) planes.[10,39]

The equatorial type B configuration adopted by mono-substituted acenaphthylenes **2**, **3**, **5** and **6** (Table 4, Figure 4), in which the E-C_{Ph} bond aligns along the mean plane of the molecule,[10,39] corresponds to the general trend observed for analogous Se and Te acenaphthene and naphthalene derivatives.[17,18] This promotes a quasi-linear three-body fragment with X⋯E-C_{Ph} angles (ψ) in the range 169–177° (Figure 4). Independent of the form of the 'naphthalene' backbone, substitution of larger congeners into the congested *peri*-region leads to a buildup of steric pressure, which is alleviated via molecular distortion. In each class of compounds, a steady increase in the *peri*-distance is observed as bromine and selenium are sequentially replaced by iodine and tellurium, respectively (**N2** 3.1136(6) $\text{\AA}$ to **N6** 3.3146(6) $\text{\AA}$;^[18] **A2** 3.1588(16) $\text{\AA}$ to **A6** 3.3721(17) $\text{\AA}$;^[17] **2** 3.189(2) $\text{\AA}$ to **6** 3.366(3) $\text{\AA}$; Figure 3), influenced in part by an increasingly large and positive splay of the exocyclic X–C_{Acenapyl} and E–C_{Acenapyl} bonds (**N2–N6** 13–16°;^[18] **A2–A6** 15–18°;^[17] **2–6** 17–19°). These figures also reflect the influence of the ethane and ethene backbones, with significantly wider *peri*-separations observed for the acenaphthenes and acenaphthylenes compared with their naphthalene equivalents.

The mutual axial-equatorial orientation of the acenaphthyl and phenyl rings, characteristic of the type AB configuration,[10] gives the structures of **8–10** an 'aircraft-like' appearance, commonly associated with diaryl sulfides[39] and seen in previously reported bis- and mixed-chalcogen naphthalene and acenaphthene analogues (Table 5, Figure 4).[17,18] The AB conformation positions one of the E-C_{Ph} bonds perpendicular to the mean acenaphthylene plane whilst aligning the other E-C_{Ph} bond along the plane of the molecule, and gives rise to a quasi-linear three-centre E⋯E'-C_{Ph} type fragment. In all cases ψ approaches 180° (173–177°), and non-bonded *peri*-distances are within the sum of van der Waals radii for

the two interacting chalcogen atoms. It is worth noting that 5,6-bis(phenyltelluro)naphthalene **N9** is the one anomaly amongst this group of compounds choosing to adopt the marginally different CC-*t* type configuration.[17]

Figure 3. Independent of the backbone, increasing *peri*-distances are observed as larger heteroatoms occupy the close *peri*-positions, although acenaphthenes and acenaphthylenes display greater separations compared to naphthalene derivatives (naphthalenes: diamonds; acenaphthenes: squares; acenaphthylenes: triangles).

Acenaphthylenes **8–10**, which differ only by chalcogen type and not by configuration, conform to the accepted rule that increasing the bulk of the substituents residing in the *peri*-region will result in an increase in molecular distortion. When compared in conjunction with their acenaphthene and naphthalene counterparts, this trend is extended to each set of compounds irrespective of the backbone, with *peri*-distances (**N10** 3.063(2) $\text{\AA}$ to **N9** 3.3287(1) $\text{\AA}$; **A10** 3.113(4) $\text{\AA}$ to **A9** 3.3674(19) $\text{\AA}$; **10** 3.144(3) $\text{\AA}$ to **9** 3.393(3) $\text{\AA}$)[17,18] and corresponding splay angles (**N10** 12.4° to **N9** 15.0°; **A10** 12.7° to **A9** 18.4°; **10** 15.7° to **9** 19.8°)[17,18] steadily

Figure 4. The orientation of the E(phenyl) groups, the quasi-linear arrangements and structural conformations of acenaphthylenes **2**, **3**, **5**, **6**, **8-10**.

increasing in each case as the heavier congeners are located in close proximity. This coincides with the expected change in structural deformation across the series for corresponding compounds, with a notable increase in distortion associated with changing the naphthalene backbone for acenaphthene and acenaphthylene, respectively (**N10** 3.063(2) Å, **A10** 3.113(4) Å, **10** 3.144(3) Å; **N8** 3.1322(9) Å, **A8** 3.1834(10) Å, **8** 3.191(3) Å; **N9** 3.287(1) Å, **A9** 3.3674(19) Å, **9** 3.393(3) Å).[17,18]

Whilst the nature of the organic backbone and the size of the heteroatoms located at the *peri*-positions play an important role in

determining the molecular geometry of these systems, the number, size and location of the functional groups attached to the *peri*-atoms is also highly influential.[17] The conformation of the aromatic ring systems and by inference the location and interaction of the chalcogen and halogen lone-pairs has been shown to dictate the geometry of the *peri*-region in naphthalenes **N1-N12** and acenaphthenes **A1-A12**. [18,17] The contrast observed in *peri*-separation between differing conformers of the *peri*-substituted phenyl group can be correlated to the ability of the frontier orbitals of the halogen or chalcogen atoms to take part in attractive or

Table 4. Torsion angles [°] categorizing the acenaphthylene and phenyl ring conformations in **2**, **3**, **5** and **6**.

Compound	Acenaphthylene ring conformations	Phenyl ring conformations
Torsion angle	C10-C9-E1-C13	C9-E1-C13-C14
2	θ_1 -167.8(7) Acenapyl ₁ ^[a] : equatorial ^[d]	γ_1 84.8(7) Ph ₁ ^[b] : axial ^[c]
3	θ_1 -161.4(17) Acenapyl ₁ : equatorial	γ_1 100.4(18) Ph ₁ : axial
5	θ_1 -167.7(3) Acenapyl ₁ : equatorial	γ_1 84.4(3) Ph ₁ : axial

[a] **Acenapyl₁**: acenaphthylene ring E(1); [b]**Ph₁**: E(1) phenyl ring; [c]**axial**: perpendicular to C(ar)-E-C(ar) plane; [d]**equatorial**: coplanar with C(ar)-E-C(ar) plane.[39]

Table 5. Torsion angles [°] categorizing the acenaphthylene and phenyl ring conformations in **8**, **9** and **10**

Compound	Acenaphthylene ring conformations		Phenyl ring conformations	
Torsion angle	C10-C1-E1-C13	C10-C9-E2-C19	C1-E1-C13-C14	C9-E2-C19-C20
8	θ_1 -75.7(13)	θ_2 -174.0(12)	γ_1 156.2(14)	γ_2 84.6(10)
	Acenapyl ₁ ^[a] : axial ^[e]	Acenapyl ₂ ^[b] : equatorial ^[f]	Ph ₁ ^[c] : equatorial	Ph ₂ ^[d] : axial
9	θ_1 78.8(7)	θ_2 166.2(7)	γ_1 -159.2(8)	γ_2 86.1(10)
	Acenapyl ₁ : axial	Acenapyl ₂ : equatorial	Ph ₁ : equatorial	Ph ₂ : axial
10	θ_1 161.9(5)	θ_2 82.1(5)	γ_1 99.2(6)	γ_2 -165.8(5)
	Acenap ₁ : equatorial	Acenap ₂ : axial	Ph ₁ : axial	Ph ₂ : equatorial

[a] **Acenapyl₁**: acenaphthylene ring E(1); [b]**Acenapyl₂**: acenaphthylene ring E(2); [c]**Ph₁**: E(1) phenyl ring; [d]**Ph₂**: E(2) phenyl ring; [e]**axial**: perpendicular to C(ar)-E-C(ar) plane; [f]**equatorial**: coplanar with C(ar)-E-C(ar) plane.[39]

repulsive interactions. Repulsion between *p*-type lone-pairs was found to be less pronounced when the conformation of the respective compound conformed to a type B or type AB configuration.[10,17,18,39]

In this situation, torsion angles (θ) approach 180°, corresponding to an equatorial ‘naphthalene’ ring conformation, and the axis of the *p*-orbitals aligns parallel and vertical to the aromatic system.[39] In addition, the existence of a quasi-linear G...E-C_{Ph} (G = Br, I, S, Se, Te) three-body fragment exhibited by this type of configuration was shown to provide an attractive component for the G...E interaction. Density functional studies confirmed these weak donor-acceptor interactions in type AB conformers, which promoted the delocalisation of a *p*-type lone-pair (G) to the antibonding $\sigma^*(E-C)$ orbital, thus forming an attractive three-centre four-electron (3c-4e) type interaction.[16,17,18] This was shown to become more prevalent as heavier congeners were introduced along the series, with increasingly large Wiberg bond index (WBI)[40] values obtained, up to a value of 0.14 for the tellurium species **A9**. [17,18] Similar, attractive donor-acceptor 3c-4e type interactions are predicted to occur in acenaphthylenes **2**, **3**, **5**, **6**, **8-10**, all of which adopt either the type B or type AB configuration.

To complement our previous results on the naphthalene and acenaphthene series, we optimized the ditelluride **9** in both AB and CC-*t* conformations at the B3LYP/SDD/6-31+G* level of density functional theory (DFT). At that level, (chosen for compatibility with our previous calculations on the naphthalene and acenaphthene series),[17] both are very close in energy, within less than 1 kJ/mol, the AB form observed in the crystal being the more stable (see Table S14 in the ESI). The trend towards longer Te...Te separations on going from **N9** to **9** is captured well in the computations (from 3.34 Å to 3.44 Å, respectively, **A9** lying in between). However, the calculated WBI decreases only marginally, from 0.14 to 0.13, within this series; the same trends are seen for

the other dichalcogenides from the present study that have been structurally characterised (see Table S14). The donor-acceptor interaction from a lone pair on one Te into a $\sigma^*(Te-C)$ antibonding orbital of the other TePh moiety, which was identified for **A9**,[17] is thus present in the acenaphthylene derivative as well. According to second-order perturbation analysis of the natural bond orbitals (NBOs),[41] the energy of this interaction is essentially the same in **A9** and **9**, namely 47 kJ/mol.

Figure 5. Short intermolecular contacts between neighbouring molecules of **9** form planar Te₄ parallelogram units with Te...Te separations within the sum of vander Waals radii. The structures of **8** and **10**, displaying similar AB configurations, can be found in the ESI.

An additional calculation on the elusive mixed Te-Se compound **12** furnished no apparent reason why it should not be formed: structural properties are as expected, i.e. in between those of the

bis-selenium and bis-tellurium congeners (see Table S14), and the stability relative to the latter (eq 2) is comparable to the corresponding driving force leading to the Te-S species **11** (eq 1), which can be isolated:[42]

Similar to its acenaphthene analogue, bis-telluride **9** packs with short intermolecular contacts between Te atoms of neighbouring molecules to construct Te₄ parallelograms. The strictly planar Te₄ rhombus core contains two unequal Te...Te non-bonded distances and interior angles sum to 360°. The intermolecular Te...Te separation (3.843(1) Å) is longer than the non-bonded intramolecular *peri*-distance (3.393(3) Å), however both distances are shorter than twice the van der Waals radius of tellurium (4.12 Å) (Figure 5).[35] No similar intermolecular arrangement is observed in SeSe (**8**) or SeS (**10**) derivatives.

13 and **A0** were first prepared by G. P. Pretenko *et al.*[29] in 1967 and despite their use in the years to follow, no molecular structure data have yet been published. The structure of **13** is, at first sight, remarkably similar to its acenaphthene analogue **A13**; a planar molecule containing negligible out-of-plane distortion in which the bromine atoms are essentially located on the mean acenaphthylene plane (displacements < 0.1 Å; C-C-C-C torsion angles < 2°; Figure 6). On closer inspection, structural changes are observed within the carbon skeleton caused by the presence of the C=C double bond (1.322(5) Å [1.359(5) Å]), which coincides with a greater in-plane distortion occurring in the bay-region.

Figure 6. The structure of **13** contains two independent molecules in the asymmetric unit (H atoms omitted for clarity). The corresponding structure of **A13** is omitted here but can be found in the ESI (Figure S3).

Contraction of the C4-C5-C6 angle (**13** 109.5(2)° [109.5(3)°]; **A13** 111.0(4)°) is accompanied by a natural increase in the C1-C10-C9 angular splay (**13** 133.3(3)° [133.6(3)°]; **A13** 132.5(4)°) with the C5-C10 bond reducing accordingly from 1.418(6) in **A13**[17] to 1.410(4) Å [1.417(5) Å] in **13**. Further widening of the exocyclic Br-C_{Acenap} bonds results in a larger observed splay angle (**13** 21.7° [20.7°]; *cf.* **A13** 20.6°) and increases the separation between the two bromine atoms which now lie 3.3387(6) Å [3.3195(6) Å] apart (*cf.* **A13** 3.3052(11) Å).

The substitution of two additional bromine atoms onto the ethane bridge in 1,2,5,6-tetrabromoacenaphthene **A0** dramatically transforms the geometry of the carbon framework, inducing greater molecular distortion in order to accommodate the extra steric bulk (Figure 7). A marked expansion of the C4-C5-C6 angle

Figure 7. The molecular structure of **A0** (H atoms omitted for clarity).

(120.2(12)° *cf.* **A13** 111.0(4)°) and the C1-C10-C9 angular splay (142.2(13)° *cf.* **A13** 132.5(4)°) naturally constricts the C5-C10 bond which compresses to 1.239(18) Å, comparable in length to a standard C=C double bond and much shorter than that found in **A13** (1.418(6) Å). The increased splay of the two exocyclic Br-C_{Acenap} bonds (22.0° *cf.* **A13** 20.6°), coupled with the displacement of the *peri*-bromine atoms to opposite sides of the mean acenaphthene plane (~0.2 Å), increases the separation across the bay-region to 3.462(3) Å (*cf.* **A13** 3.3052(11) Å), only 6% shorter than the sum of the van der Waals radii (3.70 Å).[35] The presence of the two additional bromine atoms, which occupy remote positions 2.114(1) Å above (Br3) and 2.077(1) Å below (Br4) the plane respectively, causes the C11-C12 bond of the ethane bridge to extend to 1.59(2) Å (*cf.* **A13** 1.561(8) Å). Interestingly, the Br3-C11 (2.066(15) Å) and the Br4-C12 (2.078(14) Å) bonds are considerably longer than those associated with the *peri*-bromine atoms (Br1-C1 1.724(17) Å; Br2-C9 1.694(14) Å).

Conclusions

Peri-substituted acenaphthylenes [Acenapyl(X)(EPh)] (X = Br, I; E = S, Se, Te) **1-6**, [Acenapyl(EPh)(E'Ph)] (E/E' = S, Se, Te) **7-11** and [Acenapyl(X)₂] (X = Br, I) **13, 14** have been prepared from corresponding acenaphthenes **A1-A14** using DDQ to perform the dehydrogenation of the ethane backbone.[34] Crystal structures determined for **2, 3, 5, 6, 8-10** were analyzed and compared with previously reported analogous naphthalenes **N1-N12**[18] and acenaphthenes **A1-A12**. [17] In addition, 1,2,5,6-tetrabromo-1,2-dihydroacenaphthylene **A0**[28] was synthesized as an intermediate in the preparation of **13** and crystal structures determined for **13** and **A0** were contrasted with the structure of 5,6-dibromoacenaphthene **A13**.

The series of acenaphthylenes are unremarkable and reveal similar trends to those found in acenaphthene analogues, with increased molecular distortion associated with an increase in steric bulk within the *peri*-region. Under appropriate geometric conditions quasi-linear three-body C_{Ph}-E...Z (E = Te, Se, S; Z = Br/E) fragments provide an attractive component for the E...Z interaction. DFT studies map the trend towards longer E...E separations on going from naphthalenes to acenaphthenes to acenaphthylenes, however, calculated WBIs decrease only marginally between series. DFT calculations also confirm the onset of formation of 3c-4e bonding, with the donor-acceptor interaction (from a Te lone pair into a σ*(Te-C) antibonding orbital of the neighbouring TePh) reported for **A9**,[17] also identified in the acenaphthylene derivatives and similar in extent, despite an increase in the *peri*-distances.

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 Stephen Boyer at the London Metropolitan University. Infra-red spectra were recorded for solids as KBr discs and oils on NaCl plates in the range 4000–300 cm^{-1} on a Perkin-Elmer System 2000 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer with $\delta(\text{H})$ and $\delta(\text{C})$ referenced to external Me_4Si . ^{77}Se and ^{125}Te NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with $\delta(\text{Se})$ and $\delta(\text{Te})$ referenced to external Me_2Se and Me_2Te respectively, with a secondary reference for $\delta(\text{Te})$ to diphenyl ditelluride ($\delta(\text{Te}) = 428$ ppm). Assignments of ^{13}C 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 for **2**, **3**, **5**, **6**, **8–10** and **A0**. Electrospray Mass Spectrometry (ESMS) was carried out on a Micromass LCT orthogonal accelerator time of flight mass spectrometer. Mass spectrometry for **13** and **14** was carried out at EPSRC National Mass Spectrometry Service in Swansea. The isotopic distribution patterns of the respective fragment ions were confirmed using IsoPro 3.1 MS simulation software,[43] however, in each case only the most abundant isotopic peak for each fragment ion is reported. Acenaphthene precursors (**A1–A12**,[17] 5,6-dibromoacenaphthene **A13**[20] and 5,6-diiodoacenaphthene **A14**[30] were prepared following standard literature procedures.

1,2,5,6-tetrabromoacenaphthene (A0): A solution of 5,6-dibromoacenaphthene (1.18 g, 3.77 mmol), *N*-bromosuccinimide (1.48 g, 8.29 mmol), benzoyl peroxide (0.20 g, 0.83 mmol) and chloroform (40 mL) was heated to reflux for 5 h under an atmosphere of nitrogen, cooled, washed with saturated aqueous sodium hydrogen carbonate (3 x 50 mL), dried (MgSO_4), filtered and concentrated under reduced pressure to give an orange solid. The crude solid was purified by column chromatography with a hexane eluent and an analytically pure sample was obtained by recrystallization from hexane (1.30 g, 74%); mp 148–150 °C. ^1H NMR (300 MHz; CDCl_3 ; 25 °C; Me_4Si) $\delta = 8.00$ (2 H, d, $^3J(\text{H,H}) = 7.5$, Acenap 4,7-H), 7.42 (2 H, d, $^3J(\text{H,H}) = 7.5$, Acenap 3,8-H), 5.86 (2 H, s, Acenap 9,10-H). ^{13}C NMR (75.5 MHz; CDCl_3 ; 25 °C; Me_4Si) $\delta = 141.5(\text{q})$, 137.0(s), 136.7(q), 127.7(q), 124.2(s), 119.3(q), 53.2(s). MS (ES^+): m/z (%) 309.76 (100) [$\text{M} + \text{H}$]. Anal. Calcd for $\text{C}_{12}\text{H}_6\text{Br}_4$: C, 30.9; H, 1.3. Found: C, 31.1; H, 1.3.

[Acenapyl(Br_2)] (13): A solution of **A0** (0.32 g, 0.69 mmol), zinc powder (0.22 g, 3.43 mmol) and glacial acetic acid (50 mL) was heated to reflux for 4 h, cooled and filtered. The yellow filtrate was washed with saturated aqueous sodium hydrogen carbonate (2 x 50 mL), dried (MgSO_4), filtered and concentrated under reduced pressure to give an orange solid. An analytically pure sample was obtained by recrystallization from hexane (0.18 g, 86%); mp 80–82 °C. ^1H NMR (300 MHz; CDCl_3 ; 25 °C; Me_4Si) $\delta = 7.86$ (2 H, d, $^3J(\text{H,H}) = 7.4$, Acenapyl 4,7-H), 7.39 (2 H, d, $^3J(\text{H,H}) = 7.4$, Acenapyl 3,8-H), 6.91 (2 H, s, Acenapyl 9,10-H). ^{13}C NMR (75.5 MHz; CDCl_3 ; 25 °C; Me_4Si) $\delta = 140.4(\text{q})$, 135.5(s), 129.6(q),

129.2(s), 126.5(q), 125.3(s), 121.1(q). MS (ES^+): m/z (%) 310.89 (100) [$\text{M} + \text{H}$]. Anal. Calcd for $\text{C}_{12}\text{H}_6\text{Br}_2$: C, 46.5; H, 1.95. Found: C, 46.4; H, 2.0.

Alternative route to **13** following a modification of the procedure described by Mitchell and co-workers:[34] DDQ (10.9 g, 48.1 mmol) was added to a stirred solution of 5,6-dibromoacenaphthene **A13** (10.0 g, 32.1 mmol) in benzene (250 mL) and the mixture was heated under reflux for 24 h. After cooling to room temperature, pentane (200 mL) was added and the mixture was filtered. The filtrate was passed through a short column of silica with a pentane eluent. The resulting solution was then evaporated under reduced pressure to yield the title compound as a yellow solid. An analytically pure sample was obtained by recrystallisation from diffusion of hexane into a saturated solution of the compound in dichloromethane to give yellow crystals (0.16 g, 20%).

[Acenapyl(SPh)(Br)] (1): Compound **1** was synthesized by the method described for **13** but with DDQ (1.05 g, 4.63 mmol) and [Acenap(SPh)(Br)] **A1** (1.00 g, 2.93 mmol) to yield a red solid (0.48 g, 48%); mp 80–82 °C. ^1H NMR (300 MHz; CDCl_3 ; 25 °C; Me_4Si) $\delta = 7.69$ (1 H, d, $^3J(\text{H,H}) = 7.4$, Acenapyl 4-H), 7.36–7.23 (7 H, m, Acenapyl 3,8-H, SPh 12–16-H) 7.05 (1 H, d, $^3J(\text{H,H}) = 7.4$, Acenapyl 7-H), 6.79 (2 H, s, 2 x CH). ^{13}C NMR (75.5 MHz; CDCl_3 ; 25 °C; Me_4Si) $\delta = 140.3(\text{q})$, 139.1(q), 138.6(q), 135.8(q), 134.7(s), 133.8(s), 13.3(q), 131.0(s), 129.3(s, CH x 2), 128.7(s), 128.65(s), 127.1(q), 125.3(s), 125.25(s), 120.7(q). MS (ES^+): m/z (%) 701.09 (100) [$2\text{M} + \text{Na}$], 260.12 (50) [$\text{M} - \text{Br}$]. Anal. Calcd for $\text{C}_{18}\text{H}_{11}\text{BrS}$: C, 63.7; H, 3.3. Found: C, 63.7; H, 3.4.

[Acenapyl(SePh)(Br)] (2): Compound **2** was synthesized by the method described for **13** but with DDQ (0.86 g, 3.81 mmol) and [Acenap(SePh)(Br)] **A2** (1.00 g, 2.59 mmol) to yield an orange solid which was recrystallized from evaporation of dichloromethane to give yellow crystals (0.18 g, 18%); mp 100–102 °C. ^1H NMR (300 MHz; CDCl_3 ; 25 °C; Me_4Si) $\delta = 7.86$ (1 H, d, $^3J(\text{H,H}) = 7.2$, Acenapyl 4-H), 7.84–7.82 (2 H, m, SePh 12,16-H), 7.55–7.51 (3 H, m, SePh 13–15-H), 7.43 (1 H, d, $^3J(\text{H,H}) = 7.3$, Acenapyl 3-H), 7.32 (1 H, d, $^3J(\text{H,H}) = 7.6$, Acenapyl 7-H), 7.23 (1 H, d, $^3J(\text{H,H}) = 7.6$, Acenapyl 8-H), 6.97 (1 H, d, $^3J(\text{H,H}) = 5.3$, CH), 6.94 (1 H, d, $^3J(\text{H,H}) = 5.3$, CH). ^{13}C NMR (75.5 MHz; CDCl_3 ; 25 °C; Me_4Si) $\delta = 140.6(\text{q})$, 138.7(q), 137.6(s), 137.1(q), 133.9(s), 131.6(q), 130.6(s), 130.5(q), 130.4(s), 129.7(s), 129.5(s, CH), 128.2(q), 128.1(s, CH), 125.6(s), 125.2(s), 121.8(q). ^{77}Se NMR (51.5 MHz; CDCl_3 ; 25 °C; MeSeSeMe) $\delta = 448(\text{s})$. MS (ES^+): m/z (%) 386.95 (50) [$\text{M} + \text{H}$]. Anal. Calcd for $\text{C}_{18}\text{H}_{11}\text{BrSe}$: C, 56.0; H, 2.9. Found: C, 55.9; H, 2.85.

[Acenapyl(TePh)(Br)] (3): Compound **3** was synthesized by the method described for **13** but with DDQ (0.57 g, 2.49 mmol) and [Acenap(TePh)(Br)] **A3** (0.73 g, 1.66 mmol) to yield an orange solid which was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give red crystals (0.17 g, 23%); mp 105–107 °C. ^1H NMR (300 MHz; CDCl_3 ; 25 °C; Me_4Si) $\delta = 7.91$ –7.86 (2 H, m, TePh 12,16-H), 7.67 (1 H, d, $^3J(\text{H,H}) = 7.3$, Acenapyl 4-H), 7.42–7.36 (1 H, m, TePh 14-H), 7.33–7.25 (3 H, m, Acenapyl 3-H, TePh 13,15-H), 7.23 (1 H, d, $^3J(\text{H,H}) = 7.4$, Acenapyl 7-H), 7.08 (1 H, d, $^3J(\text{H,H}) = 7.4$, Acenapyl 8-H), 6.81 (1 H, d, $^3J(\text{H,H}) = 5.3$, CH), 6.74 (1 H, d, $^3J(\text{H,H}) = 5.3$, CH). ^{13}C NMR (75.5 MHz; CDCl_3 ; 25 °C; Me_4Si) $\delta = 141.9(\text{s})$, 141.1(q), 139.3(q), 135.0(s), 133.1(s), 131.8(q), 130.6(s), 129.7(s), 129.5(s), 127.8(s, CH), 125.6(s, CH), 125.0(s), 123.4(q), 121.8(q), 118.8(q), 30.5(q). ^{125}Te NMR (81.2 MHz; CDCl_3 ; 25 °C;

MeTeTeMe) δ = 724(s). MS (ES⁺): m/z (%) 466.87 (100) [M + OMe], 435.90 (40), [M + H]. Anal. Calcd for C₁₈H₁₁BrTe: C, 49.7; H, 2.6. Found: C, 49.6; H, 2.6.

[Acenapyl(SPh)(I)] (4): Compound **4** was synthesized by the method described for **13** but with DDQ (0.41 g, 1.81 mmol) and [Acenap(SPh)(I)] **A4** (0.46 g, 1.19 mmol) to yield a brown oil (0.17 g, 37%). ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 8.38 (1 H, d, ³J (H,H) 7.3, Acenapyl 4-H), 7.60-7.38 (7 H, m, Acenapyl 7,8-H, SPh 12-16-H), 7.30 (1 H, d, ³J (H,H) 7.3, Acenapyl 3-H), 7.05 (1 H, d, ³J (H,H) 5.3, CH), 6.99 (1 H, d, ³J (H,H) 5.3, CH). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 143.9(s), 141.3(q), 140.8(q), 137.1(q), 136.8(q), 134.1(s), 132.2(s), 131.1(q), 130.2(s), 129.7(q), 129.5(s, CH), 129.4(s, CH), 128.0(s), 126.0(s), 125.42(s), 92.5(q). MS (ES⁺): m/z (%) 259.03 (100) [M – I]. Anal. Calcd for C₁₈H₁₁BrS: C, 56.0; H, 2.9. Found: C, 55.9; H, 2.8.

[Acenapyl(SePh)(I)] (5): Compound **5** was synthesized by the method described for **13** but with DDQ (0.18 g, 0.78 mmol) and [Acenap(SePh)(I)] **A5** (0.22 g, 0.51 mmol) to yield an orange solid which was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give yellow crystals (0.08 g, 34%); mp 83-85 °C. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 8.10 (1 H, d, ³J (H,H) 7.3, Acenapyl 4-H), 7.55-7.52 (2 H, m, SePh 12,16-H), 7.32-7.23 (3 H, m, SePh 13-15-H), 7.17-7.09 (3 H, m, Acenapyl 3,7,8-H), 6.75 (1 H, d, ³J (H,H) 5.3, CH), 6.72 (1 H, d, ³J (H,H) 5.3, CH). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 142.6(s), 141.3(q), 139.6(q), 136.8(s), 131.9(s), 131.7(q), 131.5(q), 131.2(q), 130.4(s), 129.3 (s, CH), 128.8(s), 128.3 (s, CH), 125.6(s), 125.4(s), 30.2(q). ⁷⁷Se NMR (51.5 MHz; CDCl₃; 25 °C; MeSeSeMe) δ = 427(s). MS (ES⁺): m/z (%) 464.89 (100) [M + OMe]. Anal. Calcd for C₁₈H₁₁IS: C, 49.9; H, 2.6. Found: C, 49.8; H, 2.6.

[Acenapyl(TePh)(I)] (6): Compound **6** was synthesized by the method described for **13** but with DDQ (0.88 g, 3.85 mmol) and [Acenap(TePh)(I)] **A6** (1.22 g, 2.52 mmol) to yield an orange solid which was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give orange crystals (0.87 g, 71%); mp 134-136 °C. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 8.03 (1 H, d, ³J (H,H) 7.3, Acenapyl 4-H), 7.85-7.83 (2 H, m, TePh 12, 16-H), 7.66 (1 H, d, ³J (H,H) 7.3, Acenapyl 7-H), 7.41-7.21 (4 H, m, acenapyl 8-H, TePh 13-15H), 7.14 (1 H, d, ³J (H,H) 7.3, Acenapyl 3-H), 6.74 (1 H, d, ³J (H,H) 5.3, CH), 6.71 (1 H, d, ³J (H,H) 5.3, CH). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 141.9(s), 141.5(s), 141.1(q), 140.0(q), 139.3(q), 136.0(s), 135.0(s), 133.8(q), 133.1(s), 130.6(s), 129.6(s, CH), 127.9(s, CH), 125.6(s), 120.7(q), 118.8(q), 97.7(q). ¹²⁵Te NMR (81.2 MHz; CDCl₃; 25 °C; MeTeTeMe) δ = 687(s). MS (ES⁺): m/z (%) 512.91 (95) [M + OMe]. Anal. Calcd for C₁₈H₁₁ITe: C, 44.9; H, 2.3. Found: C, 44.9; H, 2.3.

[Acenapyl(SPh)₂] (7): Compound **7** was synthesized by the method described for **13** but with DDQ (0.93 g, 4.11 mmol) and [Acenap(SPh)₂] **A7** (1.04 g, 2.81 mmol), affording a dark yellow solid (0.61 g, 58%); mp 169-171 °C. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 7.38 (2 H, d, ³J (H,H) 7.3, Acenapyl 4,7-H), 7.33-7.16 (12 H, m, Acenapyl 3,8-H, SPh 12-16-H), 6.87 (2 H, s, Acenapyl 9,10-H). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 148.2(q), 136.4(q), 132.6(s), 132.4(s), 131.1(q), 129.8(s), 129.6(q), 129.0(s, CH x 2), 127.9(s), 127.0(q), 125.0(s), 120.8(q). MS (ES⁺): m/z (%) 390.79 (100) [M + Na]. Anal. Calcd for C₂₄H₁₆S₂: C, 78.2; H, 4.4. Found: C, 78.1; H, 4.5.

[Acenapyl(SePh)₂] (8): Compound **8** was synthesized by the method described for **13** but with DDQ (0.74 g, 3.26 mmol) and [Acenap(SePh)₂] **A8** (1.01 g, 2.16 mmol) to yield an orange solid which was recrystallised from diffusion of hexane into a saturated solution of the compound in dichloromethane to give orange crystals (0.53 g, 53%); mp 82-84 °C. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 7.73-7.69 (2 H, m, SePh 12,16-H), 7.67 (2 H, d, ³J (H,H) 7.7, Acenapyl 3,8-H), 7.50 (2 H, d, ³J (H,H) 7.7, Acenapyl 4,7-H), 7.46-7.44 (3 H, m, SePh 13-15-H), 7.05 (2 H, s, Acenapyl 9,10-H). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 140.3(q), 135.05(s), 134.7(s), 134.3(q), 133.6(q), 131.4(q), 131.2(q), 130.2(s), 129.2(s, CH x 2), 128.5(s), 125.3(s). ⁷⁷Se NMR (51.5 MHz; CDCl₃; 25 °C; MeSeSeMe) δ = 428(s). MS (ES⁺): m/z (%) 463.78 (100) [M + H]. Anal. Calcd for C₂₄H₁₆Se₂: C, 62.4; H, 3.5. Found: C, 62.3; H, 3.55.

[Acenapyl(TePh)₂] (9): Compound **9** was synthesized by the method described for **13** but with DDQ (0.30 g, 1.32 mmol) and [Acenap(TePh)₂] **A9** (0.50 g, 0.89 mmol) to yield a red solid which was recrystallized by evaporation of dichloromethane affording red crystals (0.22 g, 45%); mp 123-125 °C. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 7.80 (2 H, d, ³J (H,H) 7.2, Acenapyl 4,7-H), 7.69-7.62 (2 H, m, TePh 12,16-H), 7.23-7.13 (5 H, m, Acenapyl 3,8-H, TePh 13-15-H), 6.78 (2 H, s, Acenapyl 9,10-H); ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 141.4(s), 138.6(s), 136.4(q), 131.0(q), 130.2(s), 129.2(s, CH x 2), 128.6(s), 125.3(s), 121.9(q), 121.6(q), 120.0(q). ¹²⁵Te NMR (81.2 MHz; CDCl₃; 25 °C; MeTeTeMe) δ = 618(s). ¹²³Te NMR (70.7 MHz; CDCl₃; 25 °C; MeTeTeMe) δ = 619(s, ⁴J (¹²³Te, ¹²⁵Te) 1706). MS (ES⁺): m/z (%) 590.96 (100) [M + OMe], 484.93 (62) [M – Ph]. Anal. Calcd for C₂₄H₁₆Te₂: C, 51.5; H, 2.9. Found: C, 51.2; H, 3.0.

[Acenapyl(SePh)(SPh)] (10): Compound **10** was synthesized by the method described for **13** but with DDQ (0.45 g, 1.98 mmol) and [Acenap(SePh)(SPh)] **A10** (0.52 g, 1.25 mmol) to yield an yellow solid which was recrystallized from evaporation of dichloromethane to give red crystals (0.16 g, 31%); mp 75-77 °C. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 7.88 (1 H, d, ³J (H,H) 7.2, Acenapyl 4-H), 7.87-7.82 (2 H, m, SePh 12,16-H), 7.68 (1 H, d, ³J (H,H) 7.2, Acenapyl 3-H), 7.60-7.48 (3 H, m, SePh 13-15-H), 7.48-7.30 (7 H, m, Acenapyl 7,8-H, SPh 12-16-H), 7.12 (1 H, d, ³J (H,H) 5.3, CH), 7.06 (1 H, d, ³J (H,H) 5.3, CH). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 142.0(q), 139.0(q), 138.6(q), 137.6(s), 137.3(s), 133.1(q), 131.8(q), 131.3(q), 130.7(s), 130.4(s, CH), 130.2(q), 129.8(s), 129.6(s), 129.4(s), 129.0(s), 128.2 (s, CH), 126.9 (s), 125.7(s), 124.9(s), 124.6(q). ⁷⁷Se NMR (51.5 MHz; CDCl₃; 25 °C; MeSeSeMe) δ = 456(s). MS (ES⁺): m/z (%) 416.01 (100) [M + H]. Anal. Calcd for C₂₄H₁₆SSe: C, 69.4; H, 3.9. Found: C, 69.3; H, 3.9.

[Acenapyl(TePh)(SPh)] (11): Compound **11** was synthesized by the method described for **13** but with DDQ (0.78 g, 1.67 mmol) and [Acenap(TePh)(SPh)] **A11** (0.57 g, 2.53 mmol) to yield an oily yellow solid (0.09 g, 12%); mp 113-115 °C. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 8.36-8.32 (2 H, m, TePh 12,16-H), 7.88 (1 H, d, ³J (H,H) 7.1 Hz, Acenapyl 4-H), 7.83 (1 H, d, ³J (H,H) 7.3, Acenapyl 7-H), 7.61 (1 H, d, ³J (H,H) 7.0, Acenapyl 3-H), 7.58-7.42 (4 H, m, Acenapyl 8-H, TePh 13-15-H), 7.22-7.14 (5 H, m, SPh 12-16-H), 7.01 (1 H, d, ³J (H,H) 5.3, CH), 6.96 (1 H, d, ³J (H,H) 5.3, CH). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 140.4(s), 136.6(s), 136.4(q), 136.2(s), 136.1(s), 135.0(q), 132.6(q), 132.5(q), 132.3(s, CH), 132.0(s), 130.7 (s, CH), 130.6(q), 130.4(s),

129.8(s), 129.6(q), 129.3(s), 127.6(s), 126.2(q), 125.8(s), 125.6(q). ^{125}Te NMR (81.2 MHz; CDCl_3 ; 25 °C; MeTeTeMe) δ = 951(s). MS (ES^+): m/z (%) 495.02 (95) [$\text{M} + \text{OMe}$].

[Acenapyl(I_2)] (14): Compound **14** was synthesized by the method described for **13** but with DDQ (0.94 g, 4.12 mmol) and [Acenap(I_2)] **A14** (1.08 g, 2.67 mmol) to yield a yellow solid (0.16 g, 15%); mp 109–111 °C. ^1H NMR (300 MHz; CDCl_3 ; 25 °C; Me_4Si) δ = 8.29 (2 H, d, $^3J(\text{H,H})$ 7.4, Acenapyl 4,7-H), 7.15 (2 H, d, $^3J(\text{H,H})$ 7.4, Acenapyl 3,8-H), 6.80 (s, $\text{CH} \times 2$); ^{13}C NMR (75.5 MHz; CDCl_3 ; 25 °C; Me_4Si) δ = 144.8(s), 144.7(q), 153.7(q), 129.6(q), 129.44(s, $\text{CH} \times 2$), 125.9(s), 125.5(q). MS (ES^+): m/z (%) 404.86 (100) [$\text{M} + \text{H}$]. Anal. Calcd for $\text{C}_{12}\text{H}_6\text{I}_2$: C, 35.7; H, 1.5. Found: C, 35.6; H, 1.6.

Crystal Structure Analyses

X-ray crystal structures for **A0** and **6** were determined at –148(1) °C on the St Andrews Robotic Diffractometer,[44] a Rigaku ACTOR-SM, Saturn 724 CCD area detector with graphite-monochromated Mo $\text{K}\alpha$ radiation (λ = 0.71073 Å). Data was corrected for Lorentz, polarization, and absorption. Data for compound **10** were collected at –148(1) °C using a Rigaku MM007 high-brilliance RA generator (Mo $\text{K}\alpha$ radiation, confocal optic) and Saturn CCD system. At least a full hemisphere of data was collected using ω scans. Intensities were corrected for Lorentz, polarization, and absorption. Data for compounds **13** and **A13** were collected at –148(1) °C on a Rigaku SCXmini CCD area detector with graphite-monochromated Mo $\text{K}\alpha$ radiation (λ = 0.71073 Å). Data were corrected for Lorentz, polarization, and absorption. Data for **2**, **3**, **5**, **8** and **9** were collected at –180(1) °C using a Rigaku MM007 high-brilliance RA generator (Mo $\text{K}\alpha$ radiation, confocal optic) and Mercury CCD system. At least a full hemisphere of data was collected using ω scans. Data for the complexes analyzed was collected and processed using CrystalClear (Rigaku).[45] Structures were solved by direct methods[46] and expanded using Fourier techniques.[47] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[48] crystallographic software package except for refinement, which was performed using SHELXL-97.[49]

CCDC-975710 (**2**), -975711 (**3**), -975712 (**5**), -975713 (**6**), -975714 (**8**), -975715 (**9**), -975716 (**10**), -976268 (**13**), -976269 (**A0**), -976270 (**A13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details

The same methods were employed as in our previous study,[17] i.e. geometries were fully optimised in the gas phase at the B3LYP level[50] using the Stuttgart-Dresden effective core potential along with its double zeta valence basis sets for Te[51] (augmented with a set of d-polarisation functions), and 6-31+G(d) basis elsewhere. Wiberg bond indices[40] were obtained in an NBO analysis[41] at the same level. See the ESI for more details.

Supporting Information (see footnote on the first page of this article): Full experimental details, crystallographic data and figures, and computational details.

Acknowledgments

Elemental analyses were performed by Stephen Boyer at the London Metropolitan University. Mass spectrometry was performed by Caroline Horsburgh at the University of St. Andrews Mass Spectrometry Service and by the EPSRC National Mass Spectrometry Service in Swansea. Calculations were performed using the EaStCHEM Research Computing Facility maintained by Dr. H. Früchtl. The work in this project was supported by the Engineering and Physical Sciences Research Council (EPSRC). M.B. wishes to thank EaStCHEM and the University of St Andrews for support.

- [1] a) G. N. Lewis, *J. Am. Chem. Soc.* **1916**, *38*, 762-785; (b) G. N. Lewis, *Valence and the Structure of Atoms and Molecules*; The Chemical Catalog Co: New York, NY, **1923**; Chapter 8.
- [2] a) I. Langmuir, *J. Am. Chem. Soc.* **1916**, *41*, 868-934; (b) I. Langmuir, *Science* **1921**, *54*, 59-67.
- [3] W. B. Jensen, *J. Chem. Educ.* **2006**, *83*, 1751-1752.
- [4] J. I. Musher, *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54-68.
- [5] a) R. J. Hatch, R. E. Rundle, *J. Am. Chem. Soc.* **1951**, *73*, 4321-4324; (b) R. E. Rundle, *J. Am. Chem. Soc.* **1963**, *85*, 112-113; (c) R. E. Rundle, *J. Am. Chem. Soc.* **1947**, *69*, 1327-1331.
- [6] G. C. Pimental, *J. Chem. Phys.* **1951**, *19*, 446-448.
- [7] W. Nakanishi, in *Handbook of Chalcogen Chemistry, New Perspectives in Sulfur, Selenium and Tellurium*, (Eds.: F. A. Devillanova), RSC Publishing, Cambridge, **2007**, ch. 10.3 and references cited therein.
- [8] M. Bühl, P. Kilian, J. D. Woollins, *ChemPhysChem* **2011**, *12*, 2405-2408.
- [9] a) P. Kilian, F. R. Knight, J. D. Woollins, *Chem. Eur. J.* **2011**, *17*, 2302-2328; (b) P. Kilian, F. R. Knight, J. D. Woollins, *Coord. Chem. Rev.* **2011**, *255*, 1387-1413.
- [10] a) W. Nakanishi, S. Hayashi, S. Toyota, *Chem. Commun.* **1996**, 371-372; (b) W. Nakanishi, S. Hayashi, A. Sakaue, G. Ono, Y. Kawada, *J. Am. Chem. Soc.* **1998**, *120*, 3635-3640; (c) W. Nakanishi, S. Hayashi, S. Toyota, *J. Org. Chem.* **1998**, *63*, 8790-8800; (d) S. Hayashi, W. Nakanishi, *J. Org. Chem.* **1999**, *64*, 6688-6696; (e) W. Nakanishi, S. Hayashi, T. Uehara, *J. Phys. Chem.* **1999**, *103*, 9906-9912; (f) W. Nakanishi, S. Hayashi, *Phosphorus, Sulfur, Silicon Relat. Elem.* **2002**, *177*, 1833-1837; (g) S. Hayashi, W. Nakanishi, *J. Org. Chem.* **2002**, *67*, 38-48; (h) S. Hayashi, W. Nakanishi, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1605-1615.
- [11] For example: a) G. P. Schiemenz, S. Pörksen, C. Näther, Z. *Naturforsch. B* **2000**, *55*, 841-854; (b) G. Dyker, M. Hagel, G. Henkel, M. Köckerling, C. Näther, S. Peterson, G. P. Schiemenz, Z. *Naturforsch. B* **2001**, *56*, 1109-1116; (c) G. P. Schiemenz, C. Näther, S. Pörksen, Z. *Naturforsch. B* **2003**, *58*, 663-671; (d) C. Chuit, R. J. P. Corriu, C. Reyé, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371-1448; (e) C. Breliere, F. Carré, R. J. P. Corriu, M. Poirier, G. Royo, J. Zwecker, *Organometallics* **1989**, *8*, 1831-1833; (f) R. J. P. Corriu, J. C. Young, in *The Chemistry of Organic Silicon Compounds*, (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1989**, pp. 1242.
- [12] V. Balasubramanian, *Chem. Rev.* **1966**, *66*, 567-641.
- [13] a) H. E. Katz, *J. Am. Chem. Soc.* **1985**, *107*, 1420-1421; (b) R. W. Alder, P. S. Bowman, W. R. S. Steel, D. R. Winterman, *Chem. Commun.* **1968**, 723-724; (c) T. Costa, H. Schmidbaur, *Chem. Ber.* **1982**, *115*, 1374-1378; (d) A. Karacar, M. Freytag, H. Thönnessen, J. Omelanczuk, P. G. Jones, R. Bartsch, R. Schmutzler, *Heteroat. Chem.* **2001**, *12*, 102-113; (e) J. Meinwald, D. Dauplaise, F. Wudl, J. J. Hauser, *J. Am. Chem. Soc.* **1977**, *99*, 255-257; (f) R. S. Glass, S. W. Andruski, J. L. Broeker, H. Firouzabadi, L. K. Steffen, G. S. Wilson, *J. Am. Chem. Soc.* **1989**, *111*, 4036-4045; (g) T. Fuji, T. Kimura, N. Furukawa, *Tetrahedron Lett.* **1995**, *36*, 1075-1078.
- [14] M.-L. Lechner, K. S. Athukorala Arachchige, R. A. M. Randall, F. R. Knight, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Organometallics* **2012**, *31*, 2922-2930.

- [15] F. R. Knight, R. A. M. Randall, K. S. Athukorala Arachchige, L. Wakefield, J. M. Griffin, S. E. Ashbrook, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chem.* **2012**, *51*, 11087-11097.
- [16] F. R. Knight, K. S. Athukorala Arachchige, R. A. M. Randall, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2012**, *41*, 3154-3165.
- [17] L. K. Aschenbach, F. R. Knight, R. A. M. Randall, D. B. Cordes, A. Baggott, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2012**, *41*, 3141-3153.
- [18] a) F. R. Knight, A. L. Fuller, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Chem. Eur. J.* **2010**, *16*, 7503-7516; b) F. R. Knight, A. L. Fuller, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Chem. Eur. J.* **2010**, *16*, 7605-7616.
- [19] F. R. Knight, A. L. Fuller, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Chem. Eur. J.* **2010**, *16*, 7617-7634.
- [20] W. D. Neudorff, D. Lentz, M. Anibarro, A. D. Schlüter, *Chem. Eur. J.* **2003**, *9*, 2745-2757.
- [21] D. Seyferth, S. C. Vick, *J. Organomet. Chem.* **1977**, *141*, 173.
- [22] B. A. Surgenor, M. Bühl, A. M. Z. Slawin, J. D. Woollins, P. Kilian, *Angew. Chem. Int. Ed.* **2012**, *51*, 10150-10153.
- [23] C. G. M. Benson, C. M. Schofield, R. A. M. Randall, L. Wakefield, F. R. Knight, A. M. Z. Slawin, J. D. Woollins, *Eur. J. Inorg. Chem.* **2013**, 427-437.
- [24] a) F. R. Knight, R. A. M. Randall, L. Wakefield, A. M. Z. Slawin, J. D. Woollins, *Molecules* **2012**, *17*, 13307; b) F. R. Knight, R. A. M. Randall, L. Wakefield, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2013**, 42, 143.
- [25] F. R. Knight, R. A. M. Randall, T. L. Roemmele, R. T. Boeré, B. E. Bode, L. Crawford, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *ChemPhysChem* **2013**, *14*, 3199-3203.
- [26] a) M. J. Ray, A. M. Z. Slawin, M. Bühl, P. Kilian, *Organometallics* **2013**, *32*, 3481-3492; b) M. J. Ray, R. A. M. Randall, K. S. Athukorala Arachchige, A. M. Z. Slawin, M. Bühl, T. Lebl, P. Kilian, *Inorg. Chem.* **2013**, *52*, 4346-4359; c) P. Wawrzyniak, A. L. Fuller, A. M. Z. Slawin, P. Kilian, *Inorg. Chem.* **2009**, *48*, 2500-2506; d) P. Wawrzyniak, A. M. Z. Slawin, J. D. Woollins, P. Kilian, *Dalton Trans.* **2010**, 39, 85-92; e) P. Wawrzyniak, A. M. Z. Slawin, A. L. Fuller, J. D. Woollins, P. Kilian, *Dalton Trans.* **2009**, 38, 7883-7884.
- [27] J. Beckmann, T. G. Do, S. Grabowsky, E. Hupf, E. Lork, S. Mebs, *Z. Anorg. Allg. Chem.* **2013**, *639*, 2233-2249.
- [28] L. Chiang, J. Meinwald, *Tetrahedron Lett.* **1980**, *21*, 4565-4568.
- [29] G. P. Petrenko, E. N. Tel'nyuk, *Zh. Org. Khim.* **1967**, *3*, 180-.
- [30] N. Tanaka, T. Kasai, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3020-3026.
- [31] a) W. Neugebauer, T. Clark, P. von Ragué Schleyer, *Chem. Ber.* **1983**, *116*, 3283-3292; b) L. Brandsma, H. D. Verkruijsse, *Preparative Polar Organometallic Chemistry*, 1st ed.; Springer-Verlag: Heidelberg, **1987**.
- [32] W. D. Neudorff, D. Lentz, M. Anibarro, A. D. Schlüter, *Chem. Eur. J.* **2003**, *9*, 2745-2757.
- [33] A. Ashnagar, J. M. Bruce, *Int. J. Chem. Tech. Res.* **2011**, *3*, 39-42.
- [34] R. H. Mitchell, M. Chaudhary, R. Vaughan Williams, R. Fyles, J. Gibson, M. J. Ashwood-Smith, A. J. Fry, *Can. J. Chem.* **1992**, *70*, 1015-1021.
- [35] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441-451.
- [36] a) C. A. Coulson, R. Daudel, J. M. Robertson, *Proc. R. Soc. London, Ser. A* **1951**, *207*, 306-320; b) D. W. Cruickshank, *Acta Crystallogr.* **1957**, *10*, 504-508; c) C. P. Brock, J. D. Dunitz, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *38*, 2218-2228; d) J. Oddershede, S. Larsen, *J. Phys. Chem. A* **2004**, *108*, 1057-1063.
- [37] A. C. Hazell, R. G. Hazell, L. Norskov-Lauritsen, C. E. Briant, D. W. Jones, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *42*, 690-693.
- [38] R. A. Wood, T. R. Welberry, A. D. Rae, *J. Chem. Soc. Perkin Trans. II* **1985**, 451-456.
- [39] P. Nagy, D. Szabó, I. Kapovits, Á. Kucsman, G. Argay, A. Kálmán, *J. Mol. Struct.* **2002**, *606*, 61-76.
- [40] The extent of covalent bonding is conveniently probed by the Wiberg bond index (WBI), which usually approaches a value of one for a true single bond: K. B. Wiberg, *Tetrahedron*, **1968**, *24*, 1083-1096.
- [41] A. E. Reed, F. Curtiss, L. A. F. Weinhold, *Chem. Rev.* **1988**, *88*, 899-926.
- [42] The most stable isomers (**BA**) were employed in eqs 1 and 2, which are meant to gauge thermodynamic stability of the mixed systems with respect to the known homo-dichalocogenides **7 - 9**, rather than kinetic barriers toward possible decomposition products.
- [43] <https://sites.google.com/site/isoproms/home>
- [44] A. L. Fuller, L. A. S. Scott-Hayward, Y. Li, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *J. Am. Chem. Soc.* **2010**, *132*, 5799-5802.
- [45] CrystalClear 1.6: Rigaku Corporation, 1999. CrystalClear Software User's Guide, Molecular Structure Corporation, (c) 2000. J. W. P. Flurath, *Acta Crystallogr., Sect. D* **1999**, *D55*, 1718-1725.
- [46] SIR97: A. Altomare, M. Burla, M. Camalli, G. Casciaro, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* **1999**, *32*, 115-119.
- [47] DIRDIF99: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, **1999**. The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
- [48] CrystalStructure 3.8.1: Crystal Structure Analysis Package, Rigaku and Rigaku/MS (2000-2006). 9009 New Trails Dr. The Woodlands TX 77381 USA.
- [49] SHELX97: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112-122.
- [50] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789.
- [51] a) P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker, P. D. W. Boyd, *J. Chem. Phys.* **1989**, *91*, 1762-1774; b) A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431-1441; c) for I the valence basis by Kaupp *et al.* (including diffuse functions) was employed: M. Kaupp, R. V. R. Schleyer, H. Stoll, H. Preuss, *J. Am. Chem. Soc.* **1991**, *113*, 6012-6020.

Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

Entry for the Table of Contents (Please choose one layout)

Layout 1:

Non-covalent interactions

Peri-substituted acenaphthylenes [Acenapyl(X)(EPh)] and [Acenapyl(EPh)(E'Ph)] have been prepared and molecular structures determined where possible. Comparison with analogous naphthalene and acenaphthene compounds reveals similar trends. Under appropriate geometric conditions quasi-linear C_{Ph}-E...Z (E = Te, Se, S; Z = Br/E) fragments exist promoting attractive 3c-4e interactions.

Louise M. Diamond, Fergus R. Knight,* Kasun S. Athukorala Arachchige, Rebecca A. M. Randall, Michael Bühl, Alexandra M. Z. Slawin and J. Derek Woollins
Page No. – Page No.

Bridging the gap; attractive 3c-4e interactions in *peri*-substituted acenaphthylenes.

Layout 2:

Key Topic

((Please adjust TOC Graphic to the size of this area; max. width 11.5 cm; max. height 2.5 cm))

Text for Table of Contents.

Text for Table of Contents, Continued – max. 350 characters; not the same text as the Abstract.

Author(s), with * for Corresponding Author(s) Page No. – Page No.

Title

Keywords: Keyword 1 / Keyword 2 / Keyword 3 / Keyword 4 / Keyword 5

Supporting Information

1. 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 Stephen Boyer at the London Metropolitan University. Infra-red spectra were recorded for solids as KBr discs and oils on NaCl plates in the range 4000-300 cm^{-1} on a Perkin-Elmer System 2000 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer with $\delta(\text{H})$ and $\delta(\text{C})$ referenced to external Me_4Si . ^{77}Se and ^{125}Te NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with $\delta(\text{Se})$ and $\delta(\text{Te})$ referenced to external Me_2Se and Me_2Te respectively, with a secondary reference for $\delta(\text{Te})$ to diphenyl ditelluride ($\delta(\text{Te}) = 428 \text{ ppm}$). Assignments of ^{13}C 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 for **2**, **3**, **5**, **6**, **8-10** and **A0**. Electrospray Mass Spectrometry (ESMS) was carried out on a Micromass LCT orthogonal accelerator time of flight mass spectrometer. Mass spectrometry for **13** and **14** was carried out at EPSRC National Mass Spectrometry Service in Swansea. The isotopic distribution patterns of the respective fragment ions were confirmed using IsoPro 3.1 MS simulation software,[1] however, in each case only the most abundant isotopic peak for each fragment ion is reported. Acenaphthene precursors (**A1-A12**,[2] 5,6-dibromoacenaphthene **A13**[3] and 5,6-diiodoacenaphthene **A14**[4] were prepared following standard literature procedures.

1,2,5,6-tetrabromoacenaphthene (A0): A solution of 5,6-dibromoacenaphthene **A13** (1.18 g, 3.77 mmol), *N*-bromosuccinimide (1.48 g, 8.29 mmol), benzoyl peroxide (0.20 g, 0.83 mmol) and chloroform (40 mL) was heated to reflux for 5 h under an atmosphere of nitrogen, cooled, washed with saturated aqueous sodium hydrogen carbonate (3 x 50 mL), dried (MgSO_4), filtered and concentrated under reduced pressure to give an orange solid. The crude solid was purified by column chromatography with a hexane eluent and an analytically pure sample was obtained by recrystallization from hexane (1.30 g, 74%); mp 148-150 °C. ν_{max} (KBr disk)/ cm^{-1} : 3420w, 3072w, 3002w, 2954w, 2922w, 2852w, 1879w, 1718w, 1669w, 1607w, 1560s, 1482w, 1461w, 1440w, 1413s, 1320s, 1245w, 1231w, 1205vs, 1160w, 1140vs, 1112s, 1050w, 1028vs, 984s, 876s, 838vs, 827vs, 795s, 737w, 714vs, 665vs, 614s, 576w, 527s, 491w, 475w, 349s, 310w. ^1H NMR (300 MHz; CDCl_3 ; 25 °C; Me_4Si) $\delta = 8.00$ (2 H, d, $^3J(\text{H,H}) = 7.5$, Acenap 4,7-H), 7.42 (2 H, d, $^3J(\text{H,H}) = 7.5$, Acenap 3,8-H), 5.86 (2 H, s, Acenap 9,10-H). ^{13}C NMR (75.5 MHz; CDCl_3 ; 25 °C; Me_4Si) $\delta = 141.5(\text{q})$, 137.0(s), 136.7(q), 127.7(q), 124.2(s), 119.3(q), 53.2(s). MS (ES^+): m/z (%) 309.76 (100) [$\text{M} + \text{H}$]. Anal. Calcd for $\text{C}_{12}\text{H}_6\text{Br}_4$: C, 30.9; H, 1.3. Found: C, 31.1; H, 1.3.

[Acenapyl(Br_2)] (13): A solution of **A0** (0.32 g, 0.69 mmol), zinc powder (0.22 g, 3.43 mmol) and glacial acetic acid (50 mL) was heated to reflux for 4 h, cooled and filtered. The yellow filtrate was washed with saturated aqueous sodium hydrogen carbonate (2 x 50 mL), dried (MgSO_4), filtered and concentrated under reduced pressure to give an orange solid. An analytically pure sample was obtained by recrystallization from hexane (0.18 g, 86%); mp 80-82 °C. ν_{max} (KBr disk)/ cm^{-1} : 3421w, 3071w, 3035w, 2924w, 2377w, 2345w, 1876w, 1799w, 1719w, 1664w, 1609w, 1569s, 1492s, 1461s, 1434w, 1409vs, 1362s, 1328w, 1231w, 1205w, 1186w, 1163w, 1102w, 1078vs, 1045s, 1018vs, 940w, 879s, 830vs, 764s, 722s, 629s, 560w, 524w, 492w, 473w, 305w. ^1H NMR (300 MHz; CDCl_3 ; 25 °C; Me_4Si) $\delta = 7.86$ (2 H, d, $^3J(\text{H,H}) = 7.4$, Acenapyl 4,7-H), 7.39 (2 H, d, $^3J(\text{H,H}) = 7.4$, Acenapyl 3,8-H), 6.91 (2 H, s, Acenapyl 9,10-H). ^{13}C NMR (75.5 MHz; CDCl_3 ; 25 °C; Me_4Si) $\delta =$

140.4(q), 135.5(s), 129.6(q), 129.2(s), 126.5(q), 125.3(s), 121.1(q). MS (ES⁺): *m/z* (%) 310.89 (100) [M + H]. Anal. Calcd for C₁₂H₆Br₂: C, 46.5; H, 1.95. Found: C, 46.4; H, 2.0.

Alternative route to 13 following a modification of the procedure described by Mitchell and co-workers:[4] DDQ (10.9 g, 48.1 mmol) was added to a stirred solution of 5,6-dibromoacenaphthene A13 (10.0 g, 32.1 mmol) in benzene (250 mL) and the mixture was heated under reflux for 24 h. After cooling to room temperature, pentane (200 mL) was added and the mixture was filtered. The filtrate was passed through a short column of silica with a pentane eluent. The resulting solution was then evaporated under reduced pressure to yield the title compound as a yellow solid. An analytically pure sample was obtained by recrystallisation from diffusion of hexane into a saturated solution of the compound in dichloromethane to give yellow crystals (0.16 g, 20%).

[Acenapyl(SPh)(Br)] (1): Compound 1 was synthesized by the method described for 13 but with DDQ (1.05 g, 4.63 mmol) and [Acenap(SPh)(Br)] A1 (1.00 g, 2.93 mmol) to yield a red solid (0.48 g, 48%); mp 80-82 °C. *v*_{max} (KBr disk)/cm⁻¹: 3054w, 2921w, 1719w, 1574s, 1475vs, 1438s, 1411vs, 1322s, 1232w, 1199w, 1079s, 1024vs, 891s, 831vs, 735vs, 688vs, 663s, 640s, 474w. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 7.69 (1 H, d, ³*J* (H,H) 7.4, Acenapyl 4-H), 7.36-7.23 (7 H, m, Acenapyl 3,8-H, SPh 12-16-H) 7.05 (1 H, d, ³*J* (H,H) 7.4, Acenapyl 7-H), 6.79 (2 H, s, 2 x CH). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 140.3(q), 139.1(q), 138.6(q), 135.8(q), 134.7(s), 133.8(s), 13.3(q), 131.0(s), 129.3(s, CH x 2), 128.7(s), 128.65(s), 127.1(q), 125.3(s), 125.25(s), 120.7(q). MS (ES⁺): *m/z* (%) 701.09 (100) [2M + Na], 260.12 (50) [M – Br]. Anal. Calcd for C₁₈H₁₁BrS: C, 63.7; H, 3.3. Found: C, 63.7; H, 3.4.

[Acenapyl(SePh)(Br)] (2): Compound 2 was synthesized by the method described for 13 but with DDQ (0.86 g, 3.81 mmol) and [Acenap(SePh)(Br)] A2 (1.00 g, 2.59 mmol) to yield an orange solid which was recrystallized from evaporation of dichloromethane to give yellow crystals (0.18 g, 18%); mp 100-102 °C. *v*_{max} (KBr disk)/cm⁻¹: 3044w, 1629w, 1597w, 1567s, 1485s, 1469s, 1435w, 1409vs, 1362w, 1079s, 1019s, 883s, 830vs, 745vs, 728s, 691s, 635s, 468w. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 7.86 (1 H, d, ³*J* (H,H) 7.2, Acenapyl 4-H), 7.84-7.82 (2 H, m, SePh 12,16-H), 7.55-7.51 (3 H, m, SePh 13-15-H), 7.43 (1 H, d, ³*J* (H,H) 7.3, Acenapyl 3-H), 7.32 (1 H, d, ³*J* (H,H) 7.6, Acenapyl 7-H), 7.23 (1 H, d, ³*J* (H,H) 7.6, Acenapyl 8-H), 6.97 (1 H, d, ³*J* (H,H) 5.3, CH), 6.94 (1 H, d, ³*J* (H,H) 5.3, CH). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 140.6(q), 138.7(q), 137.6(s), 137.1(q), 133.9(s), 131.6(q), 130.6(s), 130.5(q), 130.4(s), 129.7(s), 129.5(s, CH), 128.2(q), 128.1(s, CH), 125.6(s), 125.2(s), 121.8(q). ⁷⁷Se NMR (51.5 MHz; CDCl₃; 25 °C; MeSeSeMe) δ = 448(s). MS (ES⁺): *m/z* (%) 386.95 (50) [M + H]. Anal. Calcd for C₁₈H₁₁BrSe: C, 56.0; H, 2.9. Found: C, 55.9; H, 2.85.

[Acenapyl(TePh)(Br)] (3): Compound 3 was synthesized by the method described for 13 but with DDQ (0.57 g, 2.49 mmol) and [Acenap(TePh)(Br)] A3 (0.73 g, 1.66 mmol) to yield an orange solid which was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give red crystals (0.17 g, 23%); mp 105-107 °C. *v*_{max} (KBr disk)/cm⁻¹: 3042w, 1872w, 1595w, 1564s, 1487s, 1470w, 1433w, 1406vs, 1364w, 135w, 1079s, 1015s, 998w, 880w, 833vs, 732vs, 692s, 633s, 456w. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 7.91-7.86 (2 H, m, TePh 12,16-H), 7.67 (1 H, d, ³*J* (H,H) 7.3, Acenapyl 4-H), 7.42-7.36 (1 H, m, TePh 14-H), 7.33-7.25 (3 H, m, Acenapyl 3-H, TePh 13,15-H), 7.23 (1 H, d, ³*J* (H,H) 7.4, Acenapyl 7-H), 7.08 (1 H, d, ³*J* (H,H) 7.4, Acenapyl 8-H), 6.81 (1 H, d, ³*J* (H,H) 5.3, CH), 6.74 (1 H, d, ³*J* (H,H) 5.3, CH). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 141.9(s), 141.1(q), 139.3(q), 135.0(s), 133.1(s), 131.8(q), 130.6(s), 129.7(s), 129.5(s), 127.8(s, CH), 125.6(s, CH), 125.0(s), 123.4(q), 121.8(q), 118.8(q), 30.5(q). ¹²⁵Te NMR (81.2

MHz; CDCl₃; 25 °C; MeTeTeMe) δ = 724(s). MS (ES⁺): m/z (%) 466.87 (100) [M + OMe], 435.90 (40), [M + H]. Anal. Calcd for C₁₈H₁₁BrTe: C, 49.7; H, 2.6. Found: C, 49.6; H, 2.6.

[Acenapyl(SPh)(I)] (4): Compound 4 was synthesized by the method described for 13 but with DDQ (0.41 g, 1.81 mmol) and [Acenap(SPh)(I)] A4 (0.46 g, 1.19 mmol) to yield a brown oil (0.17 g, 37%). $\nu_{\max}$ (NaCl Plate)/cm⁻¹: 3071s, 2919w, 1881w, 1597s, 1570vs, 1491vs, 1476vs, 1457vs, 1409vs, 1360s, 1325s, 1200s, 1080vs, 1022vs, 889vs, 837vs, 735vs, 641vs, 372vs. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 8.38 (1 H, d, ³J (H,H) 7.3, Acenapyl 4-H), 7.60-7.38 (7 H, m, Acenapyl 7,8-H, SPh 12-16-H), 7.30 (1 H, d, ³J (H,H) 7.3, Acenapyl 3-H), 7.05 (1 H, d, ³J (H,H) 5.3, CH), 6.99 (1 H, d, ³J (H,H) 5.3, CH). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 143.9(s), 141.3(q), 140.8(q), 137.1(q), 136.8(q), 134.1(s), 132.2(s), 131.1(q), 130.2(s), 129.7(q), 129.5(s, CH), 129.4(s, CH), 128.0(s), 126.0(s), 125.42(s), 92.5(q). MS (ES⁺): m/z (%) 259.03 (100) [M – I]. Anal. Calcd for C₁₈H₁₁BrS: C, 56.0; H, 2.9. Found: C, 55.9; H, 2.8.

[Acenapyl(SePh)(I)] (5): Compound 5 was synthesized by the method described for 13 but with DDQ (0.18 g, 0.78 mmol) and [Acenap(SePh)(I)] A5 (0.22 g, 0.51 mmol) to yield an orange solid which was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give yellow crystals (0.08 g, 34%); mp 83-85 °C. $\nu_{\max}$ (KBr disk)/cm⁻¹: 2922w, 2367w, 1865w, 1561s, 1485s, 1468w, 1435w, 1405vs, 1359w, 1077s, 1017vs, 878s, 829vs, 744vs, 692vs, 633s, 467s, 307w. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 8.10 (1 H, d, ³J (H,H) 7.3, Acenapyl 4-H), 7.55-7.52 (2 H, m, SePh 12,16-H), 7.32-7.23 (3 H, m, SePh 13-15-H), 7.17-7.09 (3 H, m, Acenapyl 3,7,8-H), 6.75 (1 H, d, ³J (H,H) 5.3, CH), 6.72 (1 H, d, ³J (H,H) 5.3, CH). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 142.6(s), 141.3(q), 139.6(q), 136.8(s), 131.9(s), 131.7(q), 131.5(q), 131.2(q), 130.4(s), 129.3 (s, CH), 128.8(s), 128.3 (s, CH), 125.6(s), 125.4(s), 30.2(q). ⁷⁷Se NMR (51.5 MHz; CDCl₃; 25 °C; MeSeSeMe) δ = 427(s). MS (ES⁺): m/z (%) 464.89 (100) [M + OMe]. Anal. Calcd for C₁₈H₁₁IS: C, 49.9; H, 2.6. Found: C, 49.8; H, 2.6.

[Acenapyl(TePh)(I)] (6): Compound 6 was synthesized by the method described for 13 but with DDQ (0.88 g, 3.85 mmol) and [Acenap(TePh)(I)] A6 (1.22 g, 2.52 mmol) to yield an orange solid which was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give orange crystals (0.87 g, 71%); mp 134-136 °C. $\nu_{\max}$ (KBr disk)/cm⁻¹: 3425s, 3044w, 1562s, 1487s, 1467w, 1432s, 1404vs, 1361w, 1324w, 1078s, 1012s, 876w, 833vs, 731vs, 693s, 632s, 456s. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 8.03 (1 H, d, ³J (H,H) 7.3, Acenapyl 4-H), 7.85-7.83 (2 H, m, TePh 12, 16-H), 7.66 (1 H, d, ³J (H,H) 7.3, Acenapyl 7-H), 7.41-7.21 (4 H, m, acenapyl 8-H, TePh 13-15H), 7.14 (1 H, d, ³J (H,H) 7.3, Acenapyl 3-H), 6.74 (1 H, d, ³J (H,H) 5.3, CH), 6.71 (1 H, d, ³J (H,H) 5.3, CH). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 141.9(s), 141.5(s), 141.1(q), 140.0(q), 139.3(q), 136.0(s), 135.0(s), 133.8(q), 133.1(s), 130.6(s), 129.6(s, CH), 127.9(s, CH), 125.6(s), 120.7(q), 118.8(q), 97.7(q). ¹²⁵Te NMR (81.2 MHz; CDCl₃; 25 °C; MeTeTeMe) δ = 687(s). MS (ES⁺): m/z (%) 512.91 (95) [M + OMe]. Anal. Calcd for C₁₈H₁₁ITe: C, 44.9; H, 2.3. Found: C, 44.9; H, 2.3.

[Acenapyl(SPh)₂] (7): Compound 7 was synthesized by the method described for 13 but with DDQ (0.93 g, 4.11 mmol) and [Acenap(SPh)₂] A7 (1.04 g, 2.81 mmol), affording a dark yellow solid (0.61 g, 58%); mp 169-171 °C. $\nu_{\max}$ (KBr disk)/cm⁻¹: 3054w, 2951w, 1578s, 1536s, 1475s, 1409s, 1334s, 1207w, 1151w, 1114w, 1066s, 1023s, 833vs, 753vs, 738vs, 690vs, 553w, 488w, 467w. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 7.38 (2 H, d, ³J (H,H) 7.3, Acenapyl 4,7-H), 7.33-7.16 (12 H, m, Acenapyl 3,8-H, SPh 12-16-H), 6.87 (2 H, s, Acenapyl 9,10-H). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 148.2(q), 136.4(q), 132.6(s), 132.4(s), 131.1(q), 129.8(s), 129.6(q), 129.0(s, CH x 2), 127.9(s), 127.0(q), 125.0(s), 120.8(q). MS (ES⁺): m/z (%) 390.79 (100) [M + Na]. Anal. Calcd for C₂₄H₁₆S₂: C, 78.2; H, 4.4. Found: C, 78.1; H, 4.5.

[Acenapyl(SePh)₂] (8): Compound 8 was synthesized by the method described for 13 but with DDQ (0.74 g, 3.26 mmol) and [Acenap(SePh)₂] A8 (1.01 g, 2.16 mmol) to yield an orange solid which was recrystallised from diffusion of hexane into a saturated solution of the compound in dichloromethane to give orange crystals (0.53 g, 53%); mp 82-84 °C. $\nu_{\max}$ (KBr disk)/cm⁻¹: 3053w, 1881w, 1573s, 1475s, 1460s, 1435s, 1408vs, 1360s, 1190w, 1080s, 1065s, 1019s, 997s, 889s, 838vs, 738vs, 690vs, 665s, 644s, 460s, 307w. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 7.73-7.69 (2 H, m, SePh 12,16-H), 7.67 (2 H, d, ³J (H,H) 7.7, Acenapyl 3,8-H), 7.50 (2 H, d, ³J (H,H) 7.7, Acenapyl 4,7-H), 7.46-7.44 (3 H, m, SePh 13-15-H), 7.05 (2 H, s, Acenapyl 9,10-H). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 140.3(q), 135.05(s), 134.7(s), 134.3(q), 133.6(q), 131.4(q), 131.2(q), 130.2(s), 129.2(s, CH x 2), 128.5(s), 125.3(s). ⁷⁷Se NMR (51.5 MHz; CDCl₃; 25 °C; MeSeSeMe) δ = 428(s). MS (ES⁺): m/z (%) 463.78 (100) [M + H]. Anal. Calcd for C₂₄H₁₆Se₂: C, 62.4; H, 3.5. Found: C, 62.3; H, 3.55.

[Acenapyl(TePh)₂] (9): Compound 9 was synthesized by the method described for 13 but with DDQ (0.30 g, 1.32 mmol) and [Acenap(TePh)₂] A9 (0.50 g, 0.89 mmol) to yield a red solid which was recrystallized by evaporation of dichloromethane affording red crystals (0.22 g, 45%); mp 123-125 °C. $\nu_{\max}$ (KBr disk)/cm⁻¹: 3047w, 2921w, 2363s, 1571s, 1472s, 1433s, 1405s, 1323w, 1262s, 1059s, 1015s, 997s, 837s, 803s, 730vs, 688vs, 637s, 454s. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 7.80 (2 H, d, ³J (H,H) 7.2, Acenapyl 4,7-H), 7.69-7.62 (2 H, m, TePh 12,16-H), 7.23-7.13 (5 H, m, Acenapyl 3,8-H, TePh 13-15-H), 6.78 (2 H, s, Acenapyl 9,10-H); ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 141.4(s), 138.6(s), 136.4(q), 131.0(q), 130.2(s), 129.2(s, CH x 2), 128.6(s), 125.3(s), 121.9(q), 121.6(q), 120.0(q). ¹²⁵Te NMR (81.2 MHz; CDCl₃; 25 °C; MeTeTeMe) δ = 618.3(s). ¹²³Te NMR (70.7 MHz; CDCl₃; 25 °C; MeTeTeMe) δ = 619(s, ⁴J (¹²³Te, ¹²⁵Te) 1706). MS (ES⁺): m/z (%) 590.96 (100) [M + OMe], 484.93 (62) [M - Ph]. Anal. Calcd for C₂₄H₁₆Te₂: C, 51.5; H, 2.9. Found: C, 51.2; H, 3.0.

[Acenapyl(SePh)(SPh)] (10): Compound 10 was synthesized by the method described for 13 but with DDQ (0.45 g, 1.98 mmol) and [Acenap(SePh)(SPh)] A10 (0.52 g, 1.25 mmol) to yield an yellow solid which was recrystallized from evaporation of dichloromethane to give red crystals (0.16 g, 31%); mp 75-77 °C. $\nu_{\max}$ (KBr disk)/cm⁻¹: 3070s, 2925w, 1884w, 1639w, 1576vs, 1476vs, 1438s, 1413vs, 1362s, 1333w, 1196w, 1109w, 1080vs, 1023vs, 1000w, 898s, 738vs, 691vs, 666s, 649vs. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 7.88 (1 H, d, ³J (H,H) 7.2, Acenapyl 4-H), 7.87-7.82 (2 H, m, SePh 12,16-H), 7.68 (1 H, d, ³J (H,H) 7.2, Acenapyl 3-H), 7.60-7.48 (3 H, m, SePh 13-15-H), 7.48-7.30 (7 H, m, Acenapyl 7,8-H, SPh 12-16-H), 7.12 (1 H, d, ³J (H,H) 5.3, CH), 7.06 (1 H, d, ³J (H,H) 5.3, CH). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 142.0(q), 139.0(q), 138.6(q), 137.6(s), 137.3(s), 133.1(q), 131.8(q), 131.3(q), 130.7(s), 130.4(s, CH), 130.2(q), 129.8(s), 129.6(s), 129.4(s), 129.0(s), 128.2 (s, CH), 126.9 (s), 125.7(s), 124.9(s) 124.6(q). ⁷⁷Se NMR (51.5 MHz; CDCl₃; 25 °C; MeSeSeMe) δ = 456(s). MS (ES⁺): m/z (%) 416.01 (100) [M + H]. Anal. Calcd for C₂₄H₁₆SSe: C, 69.4; H, 3.9. Found: C, 69.3; H, 3.9.

[Acenapyl(TePh)(SPh)] (11): Compound 11 was synthesized by the method described for 13 but with DDQ (0.78 g, 1.67 mmol) and [Acenap(TePh)(SPh)] A11 (0.57 g, 2.53 mmol) to yield an oily yellow solid (0.09 g, 12%); mp 113-115 °C. $\nu_{\max}$ (KBr disk)/cm⁻¹: 3450w, 3054w, 2925w, 2356w, 1576w, 1475s, 1457s, 1435s, 1416s, 1329w, 1187w, 1080w, 1051s, 1022w, 996s, 824s, 736vs, 685s, 643s, 455s. ¹H NMR (300 MHz; CDCl₃; 25 °C; Me₄Si) δ = 8.36-8.32 (2 H, m, TePh 12,16-H), 7.88 (1 H, d, ³J (H,H) 7.1 Hz, Acenapyl 4-H), 7.83 (1 H, d, ³J (H,H) 7.3, Acenapyl 7-H), 7.61 (1 H, d, ³J (H,H) 7.0, Acenapyl 3-H), 7.58-7.42 (4 H, m, Acenapyl 8-H, TePh 13-15-H), 7.22-7.14 (5 H, m, SPh 12-16-H), 7.01 (1 H, d, ³J (H,H) 5.3, CH), 6.96 (1 H, d, ³J (H,H) 5.3, CH). ¹³C NMR (75.5 MHz; CDCl₃; 25 °C; Me₄Si) δ = 140.4(s), 136.6(s), 136.4(q), 136.2(s), 136.1(s),

135.0(q), 132.6(q), 132.5(q), 132.3(s, CH), 132.0(s), 130.7 (s, CH), 130.6(q), 130.4(s), 129.8(s), 129.6(q), 129.3(s), 127.6(s), 126.2(q), 125.8(s), 125.6(q). ^{125}Te NMR (81.2 MHz; CDCl_3 ; 25 °C; MeTeTeMe) δ = 951(s). MS (ES^+): m/z (%) 495.02 (95) [M + OMe].

[Acenapyl(I_2)] (14): Compound **14** was synthesized by the method described for **13** but with DDQ (0.94 g, 4.12 mmol) and [Acenap(I_2)] **A14** (1.08 g, 2.67 mmol) to yield a yellow solid (0.16 g, 15%); mp 109–111 °C. ν_{max} (KBr disk)/ cm^{-1} : 2923s, 2853w, 2372w, 1654w, 1559s, 1493s, 1459s, 1403vs, 1360s, 1205w, 1184w, 1075vs, 1012vs, 871w, 828vs, 721s, 626s, 474w. ^1H NMR (300 MHz; CDCl_3 ; 25 °C; Me_4Si) δ = 8.29 (2 H, d, 3J (H,H) 7.4, Acenapyl 4,7-H), 7.15 (2 H, d, 3J (H,H) 7.4, Acenapyl 3,8-H), 6.80 (s, CH x 2); ^{13}C NMR (75.5 MHz; CDCl_3 ; 25 °C; Me_4Si) δ = 144.8(s), 144.7(q), 153.7(q), 129.6(q), 129.44(s, CH x 2), 125.9(s), 125.5(q). MS (ES^+): m/z (%) 404.86 (100) [M + H]. Anal. Calcd for $\text{C}_{12}\text{H}_6\text{I}_2$: C, 35.7; H, 1.5. Found: C, 35.6; H, 1.6

2. Crystal structure analyses

Figure S1. The molecular structures of **3**, **5** and **6** (H atoms omitted for clarity).

Figure S2. The molecular structures of **8** and **10** (H atoms omitted for clarity).

Figure S3. The molecular structure of **A13** (H atoms omitted for clarity).

Figure S4. The absolute conformation of aromatic rings and methyl functionalities is calculated from torsion angles θ (defining rotation around the E-C_{Acenap} bond) and γ (defining rotation around the E-C_{Ph} bond).

Table S1. Crystallographic data for compounds **2**, **3**, **5** and **6**.

	2	3	5	6
Empirical Formula	C ₁₈ H ₁₁ BrSe	C ₁₈ H ₁₁ BrTe	C ₁₈ H ₁₁ ISe	C ₁₈ H ₁₁ ITe
Formula Weight	386.15	434.79	433.15	481.79
Temperature (°C)	-180.0	-180.0	-180.0	-145.0
Crystal Colour, Habit	yellow, platelet	red, platelet	yellow, chip	orange, platelet
Crystal Dimensions (mm ³)	0.150 X 0.090 X 0.020	0.120 X 0.040 X 0.020	0.150 X 0.150 X 0.060	0.210 X 0.030 X 0.020
Crystal System	monoclinic	orthorhombic	monoclinic	orthorhombic
Lattice Parameters	a = 11.794(5) Å	a = 23.460(3) Å	a = 11.847(4) Å	a = 23.311(11) Å
	b = 5.732(3) Å	b = 10.5785(13) Å	b = 5.738(2) Å	b = 10.863(5) Å
	c = 20.549(9) Å	c = 5.796(7) Å	c = 20.993(6) Å	c = 5.884(3) Å
	-	-	-	-
	β = 92.57(2)°	-	β = 93.010(10)°	-
	-	-	-	-
Volume (Å ³)	1387.7(10)	1439(2)	1425.1(8)	1490.0(12)
Space Group	P2 ₁ /c	Pca2 ₁	P2 ₁ /c	Pca2 ₁
Z Value	4	4	4	4
D _{calc} (g/cm ³)	1.848	2.007	2.019	2.148
F ₀₀₀	752	824	824	896
μ(MoKα) (cm ⁻¹)	55.793	48.397	47.879	40.559
No. of Reflections Measured	8176	8425	8555	11989
R _{int}	0.0883	0.1219	0.0424	0.0746
Min and Max Transmissions	0.357 - 0.894	0.232 - 0.908	0.472 - 0.750	0.567 - 0.922
Independ. Reflection (No. Variables)	2518(181)	2219(181)	2563(181)	3349(181)
Reflection/Parameter Ratio	13.91	12.26	14.16	18.50
Residuals: R ₁ (I > 2.00σ(I))	0.0700	0.0694	0.0347	0.0784
Residuals: R (All Reflections)	0.0881	0.1071	0.0440	0.0956
Residuals: wR ₂ (All Reflections)	0.1981	0.2720	0.0680	0.2514
Goodness of Fit Indicator	1.131	1.057	1.042	1.218
Flack Parameter	-	0.03(3)	-	0.000(1)
Maximum peak in Final Diff. Map	1.16 e ⁻ /Å ³	1.75 e ⁻ /Å ³	1.54 e ⁻ /Å ³	1.79 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.77 e ⁻ /Å ³	-2.67 e ⁻ /Å ³	-0.82 e ⁻ /Å ³	-2.37 e ⁻ /Å ³

Table S2. Crystallographic data for compounds **8**, **9** and **10**.

	8	9	10
Empirical Formula	C ₂₄ H ₁₆ Se ₂	C ₂₄ H ₁₆ Te ₂	C ₂₄ H ₁₆ SSe
Formula Weight	462.31	559.59	415.41
Temperature (°C)	-180.0	-180.0	-148.0
Crystal Colour, Habit	orange, chunk	red, prism	red, chunk
Crystal Dimensions (mm ³)	0.050 X 0.050 X 0.050	0.060 X 0.040 X 0.030	0.120 X 0.090 X 0.030
Crystal System	Monoclinic	triclinic	monoclinic
Lattice Parameters	a = 9.292(6) Å	a = 9.968(5) Å	a = 9.680(5) Å
	b = 25.932(12) Å	b = 10.048(6) Å	b = 17.417(8) Å
	c = 8.688(5) Å	c = 11.903(7) Å	c = 11.528(5) Å
	-	α = 108.391(6)°	-
	β = 114.183(13)°	β = 114.183(13)°	β = 106.228(11)°
	-	γ = 116.885(6)°	-
Volume (Å ³)	1910(2)	953.3(9)	1866(2)
Space Group	P2 ₁ /c	P-1	P2 ₁ /c
Z Value	4	2	4
Dcalc (g/cm ³)	1.608	1.949	1.478
F000	912	528	840
μ(MoKα) (cm ⁻¹)	38.770	30.648	21.282
No. of Reflections Measured	10473	6101	13647
Rint	0.1544	0.0602	0.0701
Min and Max Transmissions	0.201 - 0.824	0.411 - 0.912	0.659 - 0.938
Independ. Reflection (No. Variables)	3167(235)	3257(235)	3243(235)
Reflection/Parameter Ratio	13.48	13.86	13.80
Residuals: R1 (I>2.00σ(I))	0.0795	0.0546	0.0736
Residuals: R (All Reflections)	0.1795	0.0842	0.0988
Residuals: wR ₂ (All Reflections)	0.3329	0.2336	0.2987
Goodness of Fit Indicator	1.012	1.050	1.256
Maximum peak in Final Diff. Map	1.65 e ⁻ /Å ³	2.35 e ⁻ /Å ³	1.29 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-1.87 e ⁻ /Å ³	-2.95 e ⁻ /Å ³	-0.99 e ⁻ /Å ³

Table S3. Crystallographic data for compounds **13**, **A0** and **A13**.

	13	A0	A13
Empirical Formula	C ₁₂ H ₆ Br ₂	C ₁₂ H ₆ Br ₄	C ₁₂ H ₆ Br ₂
Formula Weight	309.99	469.80	312.00
Temperature (°C)	-148.0	-148.0	-148.0
Crystal Colour, Habit	yellow, platelet	colorless, platelet	colorless, platelet
Crystal Dimensions (mm ³)	0.310 X 0.150 X 0.040	0.120 X 0.090 X 0.030	0.120 X 0.090 X 0.030
Crystal System	monoclinic	orthorhombic	monoclinic
Lattice Parameters	a = 16.980(2) Å	a = 10.146(5) Å	a = 7.813(3) Å
	b = 15.482(2) Å	b = 8.974(4) Å	b = 11.393(3) Å
	c = 7.6280(8) Å	c = 13.618(6) Å	c = 11.709(3) Å
	-	-	-
	β = 101.784(7)°	-	β = 107.435(10)°
	-	-	-
Volume (Å ³)	1963.0(4)	1239.8(10)	994.3(5)
Space Group	P2 ₁ /c	Pca2 ₁	P2 ₁ /n
Z Value	8	4	4
Dcalc (g/cm ³)	2.098	2.517	2.084
F000	1184	872	600
μ(MoKα) (cm ⁻¹)	82.331	129.896	81.275
No. of Reflections Measured	16043	8701	8266
Rint	0.1232	0.0866	0.0547
Min and Max Transmissions	0.325 - 0.719	0.307 - 0.677	0.544 - 0.784
Independ. Reflection (No. Variables)	3448(253)	2283(145)	1747(127)
Reflection/Parameter Ratio	13.63	15.74	13.76
Residuals: R1 (I>2.00σ(I))	0.0601	0.0611	0.0293
Residuals: R (All Reflections)	0.1107	0.0740	0.0336
Residuals: wR ₂ (All Reflections)	0.1115	0.1938	0.0971
Goodness of Fit Indicator	1.050	1.264	1.190
Maximum peak in Final Diff. Map	0.61 e ⁻ /Å ³	2.08 e ⁻ /Å ³	0.87 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.52 e ⁻ /Å ³	-2.48 e ⁻ /Å ³	-0.86 e ⁻ /Å ³

We recognise that a number of these determinations have high wR₂ values. We did not attempt to artificially improve them by removal of inconvenient reflections. The high values may reflect the challenging crystal size and shapes. Despite the high wR₂ values the structures are precise enough to enable us to draw the conclusions in the ms.

Table S4. Selected interatomic distances [Å] and angles [°] for compounds **2**, **3**, **5** and **6**

Compound	2	3	5	6
X, EPh	Br,SePh	Br,TePh	I,SePh	I,TePh
<i>Peri-region-distances</i>				
X(1)···E(1)	3.189(2)	3.259(4)	3.3324(9)	3.366(3)
Σr_{vdW} - X···E^[a]	0.561	0.651	0.5476	0.674
% Σr_{vdW}^[a]	85	83	86	83
X(1)-C(1)	1.881(11)	1.89(2)	2.101(4)	2.072(18)
E(1)-C(9)	1.920(10)	2.17(3)	1.929(5)	2.127(18)
<i>Acenaphthylene bond lengths</i>				
C(1)-C(2)	1.401(15)	1.41(3)	1.386(6)	1.40(3)
C(2)-C(3)	1.401(16)	1.33(4)	1.392(7)	1.43(4)
C(3)-C(4)	1.367(15)	1.41(3)	1.367(6)	1.36(4)
C(4)-C(5)	1.401(15)	1.36(3)	1.417(6)	1.44(4)
C(5)-C(10)	1.416(14)	1.41(3)	1.404(6)	1.42(3)
C(5)-C(6)	1.418(14)	1.46(3)	1.419(6)	1.37(3)
C(6)-C(7)	1.375(15)	1.39(3)	1.356(6)	1.39(4)
C(7)-C(8)	1.415(15)	1.37(3)	1.411(6)	1.39(3)
C(8)-C(9)	1.391(14)	1.33(3)	1.381(6)	1.40(3)
C(9)-C(10)	1.442(14)	1.51(3)	1.442(6)	1.41(3)
C(10)-C(1)	1.428(14)	1.39(3)	1.432(6)	1.43(3)
C(4)-C(11)	1.460(16)	1.42(3)	1.481(6)	1.44(4)
C(11)-C(12)	1.341(16)	1.39(4)	1.341(7)	1.36(4)
C(12)-C(6)	1.474(15)	1.36(3)	1.463(6)	1.47(4)
<i>Peri-region bond angles</i>				
X(1)-C(1)-C(10)	124.0(8)	122.4(14)	125.4(3)	121.2(12)
C(1)-C(10)-C(9)	131.3(9)	134.3(18)	132.2(4)	131.7(17)
E(1)-C(9)-C(10)	121.2(7)	118.2(14)	121.7(3)	126.5(14)
Σ of bay angles	376.5(14)	374.9(27)	379.3(6)	379.4(25)
Splay angle^[b]	16.5	14.9	19.3	19.4
C(4)-C(5)-C(6)	109.0(9)	108.9(18)	109.5(4)	109.0(2)
X(1)-E(1)-C(13)	177.07(1)	169.35(1)	174.72(1)	170.03(1)
<i>Out-of-plane displacement</i>				
X(1)	-0.217(1)	-0.255(1)	-0.245(1)	0.357(1)
E(1)	0.190(1)	0.388(1)	0.183(1)	-0.417(1)
<i>Central naphthalene ring torsion angles</i>				
C:(6)-(5)-(10)-(1)	-175.1(8)	-173.9(16)	-175.6(4)	177.4(19)
C:(4)-(5)-(10)-(9)	179.8(8)	-178.2(17)	-179.7(4)	172.4(19)

^a van der Waals radii used for calculations: r_{vdW}(Se) 1.90 Å, r_{vdW}(Te) 2.06 Å, r_{vdW}(Br) 1.85 Å, r_{vdW}(I) 1.98 Å; ^b Splay angle: Σ of the three bay region angles – 360.

Table S5. Selected interatomic distances [Å] and angles [°] for compounds **8**, **9** and **10**

Compound	8	9	10
E(1)Ph, E(2)Ph	SePh,SePh	TePh,TePh	SePh,SPh
<i>Peri-region-distances</i>			
E(1)···E(2)	3.191(3)	3.393(3)	3.144(3)
Σ_{r_{vdW}} - E(1)···E(2)^[a]	0.609	0.727	0.556
%Σ_{r_{vdW}}^[a]	84	82	85
E(1)-C(1)	1.926(13)	2.123(15)	1.932(7)
E(2)-C(9)	1.905(13)	2.151(14)	1.781(8)
<i>Acenaphthylene bond lengths</i>			
C(1)-C(2)	1.42(3)	1.394(19)	1.397(11)
C(2)-C(3)	1.40(2)	1.40(3)	1.443(11)
C(3)-C(4)	1.40(3)	1.383(19)	1.357(10)
C(4)-C(5)	1.44(3)	1.422(19)	1.441(11)
C(5)-C(10)	1.437(18)	1.40(2)	1.402(9)
C(5)-C(6)	1.45(3)	1.43(2)	1.421(9)
C(6)-C(7)	1.33(3)	1.387(19)	1.375(11)
C(7)-C(8)	1.42(2)	1.40(3)	1.401(10)
C(8)-C(9)	1.41(3)	1.41(2)	1.388(9)
C(9)-C(10)	1.46(3)	1.434(17)	1.428(10)
C(10)-C(1)	1.43(3)	1.425(19)	1.433(8)
C(4)-C(11)	1.47(2)	1.46(3)	1.470(9)
C(11)-C(12)	1.37(3)	1.37(2)	1.360(11)
C(12)-C(6)	1.45(2)	1.48(2)	1.458(11)
<i>Peri-region bond angles</i>			
E(1)-C(1)-C(10)	123.4(11)	124.5(10)	122.8(6)
C(1)-C(10)-C(9)	130.5(12)	131.2(13)	129.9(6)
E(2)-C(9)-C(10)	122.5(12)	124.1(10)	123.0(5)
Σ of bay angles	376.4(20)	379.8(19)	375.7(10)
Splay angle^[b]	16.4	19.8	15.7
C(4)-C(5)-C(6)	109.0(12)	108.7(13)	108.4(6)
E(2)-E(1)-C(13)	84.47(1)	92.99(1)	172.72(1)
E(1)-E(2)-C(19)	176.6(1)	174.06(1)	94.35(1)
<i>Out-of-plane displacement</i>			
E(1)	-0.213(1)	0.306(1)	0.276(1)
E(2)	0.245(1)	-0.387(1)	-0.260(1)
<i>Central naphthalene ring torsion angles</i>			
C:(6)-(5)-(10)-(1)	-177.1(14)	177.5(8)	178.5(6)
C:(4)-(5)-(10)-(9)	-177.0(14)	175.2(8)	177.4(6)

^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; ^b Splay angle: Σ of the three bay region angles – 360.

Table S6. Selected interatomic distances [Å] and angles [°] for compounds **13**, **A13** and **A0**

Compound	13	A13	A0
<i>Peri-region-distances</i>			
E(1)···E(2)	3.3387(6) [3.3195(6)]	3.3052(11)	3.462(3)
$\Sigma r_{vdW} - E(1) \cdots E(2)^{[a]}$	0.3613 [0.3805]	0.3948	0.238
$\% \Sigma r_{vdW}^{[a]}$	90 [90]	89	94
E(1)-C(1)	1.910(3) [1.907(3)]	1.904(4)	1.724(17)
E(2)-C(9)	1.901(3) [1.885(3)]	1.906(4)	1.694(14)
<i>Acenaphthylene bond lengths</i>			
C(1)-C(2)	1.384(4) [1.369(4)]	1.388(7)	1.35(3)
C(2)-C(3)	1.406(4) [1.413(5)]	1.394(6)	1.27(2)
C(3)-C(4)	1.352(5) [1.350(4)]	1.359(7)	1.43(2)
C(4)-C(5)	1.414(4) [1.419(4)]	1.420(7)	1.37(2)
C(5)-C(10)	1.410(4) [1.417(5)]	1.418(6)	1.239(18)
C(5)-C(6)	1.417(4) [1.422(5)]	1.413(7)	1.42(2)
C(6)-C(7)	1.353(4) [1.371(5)]	1.372(7)	1.40(2)
C(7)-C(8)	1.414(4) [1.413(5)]	1.400(6)	1.22(2)
C(8)-C(9)	1.373(4) [1.367(5)]	1.376(7)	1.40(3)
C(9)-C(10)	1.423(4) [1.440(4)]	1.439(7)	1.46(3)
C(10)-C(1)	1.429(4) [1.430(4)]	1.423(7)	1.49(3)
C(4)-C(11)	1.469(4) [1.481(5)]	1.513(6)	1.372(19)
C(11)-C(12)	1.322(5) [1.359(5)]	1.561(8)	1.59(2)
C(12)-C(6)	1.476(4) [1.473(5)]	1.505(6)	1.35(2)
Br(3)-C(11)			2.066(15)
Br(4)-C(12)			2.078(14)
<i>Peri-region bond angles</i>			
E(1)-C(1)-C(10)	124.0(2) [123.6(2)]	124.3(3)	120.2(12)
C(1)-C(10)-C(9)	133.3(3) [133.6(3)]	132.5(4)	142.2(13)
E(2)-C(9)-C(10)	124.44(19) [123.5(3)]	123.8(4)	119.6(11)
Σ of bay angles	381.74(19) [380.7(5)]	380.6(6)	382.0(21)
Splay angle ^[b]	21.7 [20.7]	20.6	22.0
C(4)-C(5)-C(6)	109.5(2) [109.5(3)]	111.0(4)	120.2(12)
<i>Out-of-plane displacement</i>			
E(1)	-0.006(1) [-0.011(1)]	0.028(1)	0.192(1)
E(2)	0.042(1) [0.029(1)]	-0.061(1)	-0.196(1)
<i>Central naphthalene ring torsion angles</i>			
C:(6)-(5)-(10)-(1)	178.7(3) [-178.5(2)]	179.8(3)	179.3(12)
C:(4)-(5)-(10)-(9)	-178.1(3) [179.7(2)]	178.9(3)	179.4(13)

^a van der Waals radii used for calculations: $r_{vdW}(\text{Br})$ 1.85 Å; ^b Splay angle: Σ of the three bay region angles – 360.

Table S7. Selected interatomic distances [Å] and angles [°] for compounds **N2**, **A2** and **2**

Compound	N2	A2	2
E(1)Ph, E(2)Ph	Br,SePh	Br,SePh	Br,SePh
<i>Peri-region-distances</i>			
E(1)···E(2)	3.1136(6)	3.1588(16)	3.189(2)
$\Sigma r_{vdW} - X \cdots E^{[a]}$	0.6364	0.5912	0.561
$\% \Sigma r_{vdW}^{[a]}$	83	84	85
E(1)-C(1)	1.919(3)	1.905(5)	1.881(11)
E(2)-C(9)	1.948(3)	1.943(5)	1.920(10)
<i>'Naphthalene' bond lengths</i>			
C(1)-C(2)	1.363(6)	1.361(8)	1.401(15)
C(2)-C(3)	1.402(5)	1.429(8)	1.401(16)
C(3)-C(4)	1.354(5)	1.362(8)	1.367(15)
C(4)-C(5)	1.436(6)	1.416(8)	1.401(15)
C(5)-C(10)	1.433(5)	1.423(7)	1.416(14)
C(5)-C(6)	1.420(5)	1.405(8)	1.418(14)
C(6)-C(7)	1.373(6)	1.367(8)	1.375(15)
C(7)-C(8)	1.395(5)	1.405(8)	1.415(15)
C(8)-C(9)	1.384(5)	1.377(8)	1.391(14)
C(9)-C(10)	1.434(6)	1.438(8)	1.442(14)
C(10)-C(1)	1.431(5)	1.431(8)	1.428(14)
C(4)-C(11)	-	1.514(8)	1.460(16)
C(11)-C(12)	-	1.562(9)	1.341(16)
C(12)-C(6)	-	1.510(8)	1.474(15)
<i>Peri-region bond angles</i>			
E(1)-C(1)-C(10)	122.1(3)	121.8(4)	124.0(8)
C(1)-C(10)-C(9)	128.3(3)	131.4(5)	131.3(9)
E(2)-C(9)-C(10)	122.6(2)	121.4(4)	121.2(7)
Σ of bay angles	373.0(6)	374.6(9)	376.5(14)
Splay angle ^[b]	13.0	14.6	16.5
C(4)-C(5)-C(6)	118.5(3)	111.4(5)	109.0(9)
E(2)-E(1)-C(13)	-	172.83(1)	177.07(1)
<i>Out-of-plane displacement</i>			
E(1)	0.40(1)	0.287(1)	-0.217(1)
E(2)	-0.42(1)	-0.359(1)	0.190(1)
<i>Central naphthalene ring torsion angles</i>			
C:(6)-(5)-(10)-(1)	175.8(3)	175.27(1)	-175.1(8)
C:(4)-(5)-(10)-(9)	173.8(3)	177.24(1)	179.8(8)

^a van der Waals radii used for calculations: $r_{vdW}(\text{Br})$ 1.85 Å, $r_{vdW}(\text{Se})$ 1.90 Å; ^b Splay angle: Σ of the three bay region angles – 360.

Table S8. Selected interatomic distances [Å] and angles [°] for compounds **N3**, **A3** and **3**

Compound	N3	A3	3
E(1)Ph, E(2)Ph	Br,TePh	Br,TePh	Br,TePh
<i>Peri-region-distances</i>			
E(1)···E(2)	3.1909(10)	3.2503(14)	3.259(4)
$\Sigma r_{vdW} - X \cdots E^{[a]}$	0.7191	0.6597	0.651
% $\Sigma r_{vdW}^{[a]}$	82	83	83
E(1)-C(1)	1.917(6)	1.919(10)	1.89(2)
E(2)-C(9)	2.153(6)	2.148(10)	2.17(3)
<i>'Naphthalene' bond lengths</i>			
C(1)-C(2)	1.382(12)	1.369(14)	1.41(3)
C(2)-C(3)	1.387(11)	1.389(16)	1.33(4)
C(3)-C(4)	1.352(10)	1.376(16)	1.41(3)
C(4)-C(5)	1.417(12)	1.415(14)	1.36(3)
C(5)-C(10)	1.440(9)	1.434(14)	1.41(3)
C(5)-C(6)	1.422(9)	1.420(15)	1.46(3)
C(6)-C(7)	1.399(13)	1.364(15)	1.39(3)
C(7)-C(8)	1.363(10)	1.409(14)	1.37(3)
C(8)-C(9)	1.384(9)	1.396(14)	1.33(3)
C(9)-C(10)	1.433(11)	1.434(13)	1.51(3)
C(10)-C(1)	1.419(9)	1.411(13)	1.39(3)
C(4)-C(11)	-	1.505(15)	1.42(3)
C(11)-C(12)	-	1.538(17)	1.39(4)
C(12)-C(6)	-	1.488(17)	1.36(3)
<i>Peri-region bond angles</i>			
E(1)-C(1)-C(10)	121.7(6)	121.6(7)	122.4(14)
C(1)-C(10)-C(9)	128.6(6)	131.7(9)	134.3(18)
E(2)-C(9)-C(10)	123.3(4)	123.5(7)	118.2(14)
Σ of bay angles	373.6(10)	376.8(15)	374.9(27)
Splay angle ^[b]	13.6	16.8	14.9
C(4)-C(5)-C(6)	118.9(6)	110.8(9)	108.9(18)
E(2)-E(1)-C(13)	-	169.0(1)	169.35(1)
<i>Out-of-plane displacement</i>			
E(1)	0.4058(84)	0.307(1)	-0.255(1)
E(2)	-0.529(88)	-0.298(1)	0.388(1)
<i>Central naphthalene ring torsion angles</i>			
C:(6)-(5)-(10)-(1)	174.8(6)	178.17(1)	-173.9(16)
C:(4)-(5)-(10)-(9)	173.4(6)	176.39(1)	-178.2(17)

^a van der Waals radii used for calculations: $r_{vdW}(\text{Br})$ 1.85 Å, $r_{vdW}(\text{Te})$ 2.06 Å; ^b Splay angle: Σ of the three bay region angles – 360.

Table S9. Selected interatomic distances [Å] and angles [°] for compounds **N5**, **A5** and **5**

Compound	N5	A5	5
E(1)Ph, E(2)Ph	I,SePh	I,SePh	I,SePh
<i>Peri-region-distances</i>			
E(1)···E(2)	3.2524(8)	3.3291(11)	3.3324(9)
$\Sigma r_{vdW} - X \cdots E^{[a]}$	0.6276	0.5509	0.5476
$\% \Sigma r_{vdW}^{[a]}$	84	86	86
E(1)-C(1)	2.122(4)	2.110(7)	2.101(4)
E(2)-C(9)	1.958(4)	1.930(7)	1.929(5)
<i>'Naphthalene' bond lengths</i>			
C(1)-C(2)	1.373(7)	1.360(10)	1.386(6)
C(2)-C(3)	1.402(7)	1.407(11)	1.392(7)
C(3)-C(4)	1.372(9)	1.368(11)	1.367(6)
C(4)-C(5)	1.418(7)	1.401(9)	1.417(6)
C(5)-C(10)	1.449(6)	1.417(9)	1.404(6)
C(5)-C(6)	1.414(9)	1.428(9)	1.419(6)
C(6)-C(7)	1.372(8)	1.361(10)	1.356(6)
C(7)-C(8)	1.416(7)	1.390(10)	1.411(6)
C(8)-C(9)	1.366(8)	1.391(10)	1.381(6)
C(9)-C(10)	1.452(7)	1.444(9)	1.442(6)
C(10)-C(1)	1.437(8)	1.433(10)	1.432(6)
C(4)-C(11)	-	1.513(10)	1.481(6)
C(11)-C(12)	-	1.545(11)	1.341(7)
C(12)-C(6)	-	1.510(10)	1.463(6)
<i>Peri-region bond angles</i>			
E(1)-C(1)-C(10)	124.2(3)	123.8(5)	125.4(3)
C(1)-C(10)-C(9)	128.3(4)	131.4(6)	132.2(4)
E(2)-C(9)-C(10)	122.4(4)	122.3(5)	121.7(3)
Σ of bay angles	374.9(7)	377.5(11)	379.3(6)
Splay angle ^[b]	14.9	17.5	19.3
C(4)-C(5)-C(6)	118.8(4)	111.1(6)	109.5(4)
E(2)-E(1)-C(13)	-	177.69(1)	174.72(1)
<i>Out-of-plane displacement</i>			
E(1)	0.50(1)	-0.439(1)	-0.245(1)
E(2)	-0.42(1)	0.364(1)	0.183(1)
<i>Central naphthalene ring torsion angles</i>			
C:(6)-(5)-(10)-(1)	174.9(5)	174.34(1)	-175.6(4)
C:(4)-(5)-(10)-(9)	174.6(5)	177.91(1)	-179.7(4)

^a van der Waals radii used for calculations: $r_{vdW}(I)$ 1.98 Å, $r_{vdW}(Se)$ 1.90 Å; ^b Splay angle: Σ of the three bay region angles – 360.

Table S10. Selected interatomic distances [Å] and angles [°] for compounds **N6**, **A6** and **6**

Compound	N6	A6	6
E(1)Ph, E(2)Ph	I,TePh	I,TePh	I,TePh
<i>Peri-region-distances</i>			
E(1)···E(2)	3.3146(6)	3.3721(17) [3.3774(17)]	3.366(3)
$\Sigma r_{vdW} - X \cdots E^{[a]}$	0.7254	0.6679 [0.6626]	0.674
$\% \Sigma r_{vdW}^{[a]}$	82	83 [84]	83
E(1)-C(1)	2.108(6)	2.058(16) [2.067(16)]	2.072(18)
E(2)-C(9)	2.151(6)	2.176(17) [2.151(18)]	2.127(18)
<i>'Naphthalene' bond lengths</i>			
C(1)-C(2)	1.382(12)	1.37(2) [1.40(2)]	1.40(3)
C(2)-C(3)	1.389(10)	1.37(3) [1.37(3)]	1.43(4)
C(3)-C(4)	1.356(10)	1.39(3) [1.45(2)]	1.36(4)
C(4)-C(5)	1.400(11)	1.41(2) [1.39(2)]	1.44(4)
C(5)-C(10)	1.454(8)	1.43(2) [1.42(2)]	1.42(3)
C(5)-C(6)	1.411(9)	1.42(2) [1.40(2)]	1.37(3)
C(6)-C(7)	1.379(12)	1.40(2) [1.37(2)]	1.39(4)
C(7)-C(8)	1.365(10)	1.44(2) [1.39(2)]	1.39(3)
C(8)-C(9)	1.346(9)	1.34(2) [1.38(2)]	1.40(3)
C(9)-C(10)	1.443(11)	1.44(2) [1.47(2)]	1.41(3)
C(10)-C(1)	1.418(9)	1.44(2) [1.43(2)]	1.43(3)
C(4)-C(11)	-	1.50(3) [1.50(2)]	1.44(4)
C(11)-C(12)	-	1.48(3) [1.53(3)]	1.36(4)
C(12)-C(6)	-	1.45(2) [1.52(2)]	1.47(4)
<i>Peri-region bond angles</i>			
E(1)-C(1)-C(10)	123.4(5)	124.6(12) [123.7(11)]	121.2(12)
C(1)-C(10)-C(9)	129.2(5)	130.5(15) [130.3(14)]	131.7(17)
E(2)-C(9)-C(10)	123.6(4)	123.2(12) [124.4(10)]	126.5(14)
Σ of bay angles	376.2(9)	378.3(32) [378.4(28)]	379.4(25)
Splay angle ^[b]	16.2	18.3 [18.4]	19.4
C(4)-C(5)-C(6)	118.9(6)	110.4(15) [109.8(14)]	109.0(2)
E(2)-E(1)-C(13)	175.1(1)	171.31(1) [171.48(1)]	170.03(1)
<i>Out-of-plane displacement</i>			
E(1)	-0.4152(86)	-0.425(1) [0.333(1)]	0.357(1)
E(2)	0.5355(86)	0.334(1) [-0.395(1)]	-0.417(1)
<i>Central naphthalene ring torsion angles</i>			
C:(6)-(5)-(10)-(1)	-174.5(6)	175.29(1) [175.81(1)]	177.4(19)
C:(4)-(5)-(10)-(9)	-175.1(6)	-177.33(1) [178.08(1)]	172.4(19)

^a van der Waals radii used for calculations: $r_{vdW}(I)$ 1.98 Å, $r_{vdW}(Te)$ 2.06 Å; ^b Splay angle: Σ of the three bay region angles – 360.

Table S11. Selected interatomic distances [Å] and angles [°] for compounds **N8**, **A8** and **8**

Compound	N8	A8	8
E(1)Ph, E(2)Ph	SePh,SePh	SePh,SePh	SePh,SePh
<i>Peri-region-distances</i>			
E(1)···E(2)	3.1332(9)	3.1834(10)	3.191(3)
$\Sigma r_{vdW} - X \cdots E^{[a]}$	0.67	0.6166	0.609
$\% \Sigma r_{vdW}^{[a]}$	82	84	84
E(1)-C(1)	1.922(7)	1.928(9)	1.926(13)
E(2)-C(9)	1.930(7)	1.932(8)	1.905(13)
<i>'Naphthalene' bond lengths</i>			
C(1)-C(2)	1.381(10)	1.372(12)	1.42(3)
C(2)-C(3)	1.400(11)	1.411(12)	1.40(2)
C(3)-C(4)	1.357(11)	1.371(12)	1.40(3)
C(4)-C(5)	1.420(10)	1.420(12)	1.44(3)
C(5)-C(10)	1.423(10)	1.423(12)	1.437(18)
C(5)-C(6)	1.436(10)	1.425(12)	1.45(3)
C(6)-C(7)	1.371(10)	1.364(12)	1.33(3)
C(7)-C(8)	1.381(12)	1.412(12)	1.42(2)
C(8)-C(9)	1.368(10)	1.372(12)	1.41(3)
C(9)-C(10)	1.436(9)	1.444(12)	1.46(3)
C(10)-C(1)	1.461(9)	1.425(12)	1.43(3)
C(4)-C(11)	-	1.520(12)	1.47(2)
C(11)-C(12)	-	1.570(12)	1.37(3)
C(12)-C(6)	-	1.509(12)	1.45(2)
<i>Peri-region bond angles</i>			
E(1)-C(1)-C(10)	123.5(5)	123.4(6)	123.4(11)
C(1)-C(10)-C(9)	126.6(6)	131.1(8)	130.5(12)
E(2)-C(9)-C(10)	123.8(5)	122.0(6)	122.5(12)
Σ of bay angles	373.9(9)	376.5(13)	376.4(20)
Splay angle ^[b]	13.9	16.5	16.4
C(4)-C(5)-C(6)	117.3(6)	110.5(7)	109.0(12)
E(2)-E(1)-C(13)	-	171.28(1)	84.47 (1)
E(1)-E(2)-C(19)	-	91.48(1)	176.6(1)
<i>Out-of-plane displacement</i>			
E(1)	0.468(9)	0.176(1)	-0.213(1)
E(2)	-0.327(9)	-0.193(1)	0.245(1)
<i>Central naphthalene ring torsion angles</i>			
C:(6)-(5)-(10)-(1)	173.5(6)	178.40(1)	-177.1(14)
C:(4)-(5)-(10)-(9)	174.6(6)	179.23(1)	-177.0(14)

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

Table S12. Selected interatomic distances [Å] and angles [°] for compounds **N9**, **A9** and **9**

Compound	N9	A9	9
E(1)Ph, E(2)Ph	TePh, TePh	TePh, TePh	TePh, TePh
<i>Peri-region-distances</i>			
E(1)···E(2)	3.287(1)	3.3674(19)	3.393(3)
$\Sigma r_{vdW} - X \cdots E^{[a]}$	0.83	0.7526	0.727
$\% \Sigma r_{vdW}^{[a]}$	80	82	82
E(1)-C(1)	2.14(1)	2.180(17)	2.123(15)
E(2)-C(9)	2.14(2)	2.155(17)	2.151(14)
<i>'Naphthalene' bond lengths</i>			
C(1)-C(2)	1.34(1)	1.367(19)	1.394(19)
C(2)-C(3)	1.38(1)	1.43(3)	1.40(3)
C(3)-C(4)	1.34(1)	1.36(2)	1.383(19)
C(4)-C(5)	1.46(1)	1.410(17)	1.422(19)
C(5)-C(10)	1.42(1)	1.43(2)	1.40(2)
C(5)-C(6)	1.39(1)	1.443(20)	1.43(2)
C(6)-C(7)	1.35(1)	1.318(19)	1.387(19)
C(7)-C(8)	1.38(1)	1.42(3)	1.40(3)
C(8)-C(9)	1.37(1)	1.38(2)	1.41(2)
C(9)-C(10)	1.41(2)	1.430(18)	1.434(17)
C(10)-C(1)	1.45(1)	1.43(2)	1.425(19)
C(4)-C(11)	-	1.50(2)	1.46(3)
C(11)-C(12)	-	1.545(18)	1.37(2)
C(12)-C(6)	-	1.55(2)	1.48(2)
<i>Peri-region bond angles</i>			
E(1)-C(1)-C(10)	123(1)	123.9(10)	124.5(10)
C(1)-C(10)-C(9)	128(1)	131.7(16)	131.2(13)
E(2)-C(9)-C(10)	124(1)	122.8(12)	124.1(10)
Σ of bay angles	375.0(2)	378.4(24)	379.8(19)
Splay angle ^[b]	15.0	18.4	19.8
C(4)-C(5)-C(6)	118.0(1)	113.3(14)	108.7(13)
E(2)-E(1)-C(13)	-	174.0(4)	92.99(1)
E(1)-E(2)-C(19)	-	94.1(4)	174.06(1)
<i>Out-of-plane displacement</i>			
E(1)	-0.51(1)	0.310(1)	0.306(1)
E(2)	0.57(1)	-0.404(1)	-0.387(1)
<i>Central naphthalene ring torsion angles</i>			
C:(6)-(5)-(10)-(1)	174.2(1)	176.19(1)	177.5(8)
C:(4)-(5)-(10)-(9)	175.1(1)	179.03(1)	175.2(8)

^a van der Waals radii used for calculations: $r_{vdW}(\text{Te})$ 2.06 Å; ^b Splay angle: Σ of the three bay region angles – 360.

Table S13. Selected interatomic distances [Å] and angles [°] for compounds **N10**, **A10** and **10**

Compound	N10	A10	10
E(1)Ph, E(2)Ph	SePh,SPh	SePh,SPh	SePh,SPh
<i>Peri-region-distances</i>			
E(1)···E(2)	3.063(2)	3.113(4)	3.144(3)
$\Sigma r_{vdW} - X \cdots E^{[a]}$	0.64	0.5870	0.556
$\% \Sigma r_{vdW}^{[a]}$	83	84	85
E(1)-C(1)	1.907(9)	1.953(10)	1.932(7)
E(2)-C(9)	1.813(8)	1.798(11)	1.781(8)
<i>'Naphthalene' bond lengths</i>			
C(1)-C(2)	1.367(12)	1.393(15)	1.397(11)
C(2)-C(3)	1.372(14)	1.424(14)	1.443(11)
C(3)-C(4)	1.375(15)	1.350(16)	1.357(10)
C(4)-C(5)	1.426(14)	1.404(15)	1.441(11)
C(5)-C(10)	1.435(12)	1.450(14)	1.402(9)
C(5)-C(6)	1.413(14)	1.423(16)	1.421(9)
C(6)-C(7)	1.363(15)	1.367(16)	1.375(11)
C(7)-C(8)	1.435(14)	1.406(15)	1.401(10)
C(8)-C(9)	1.381(13)	1.361(17)	1.388(9)
C(9)-C(10)	1.423(12)	1.451(15)	1.428(10)
C(10)-C(1)	1.447(12)	1.434(16)	1.433(8)
C(4)-C(11)	-	1.522(15)	1.470(9)
C(11)-C(12)	-	1.568(17)	1.360(11)
C(12)-C(6)	-	1.525(15)	1.458(11)
<i>Peri-region bond angles</i>			
E(1)-C(1)-C(10)	122.3(6)	120.7(7)	122.8(6)
C(1)-C(10)-C(9)	127.8(7)	131.3(9)	129.9(6)
E(2)-C(9)-C(10)	122.3(6)	120.7(8)	123.0(5)
Σ of bay angles	372.4(11)	372.7(16)	375.7(10)
Splay angle ^[b]	12.4	12.7	15.7
C(4)-C(5)-C(6)	177.6(8)	113.4(9)	108.4(6)
E(2)-E(1)-C(13)	-	167.95(1)	172.72(1)
E(1)-E(2)-C(19)	-	86.58(1)	94.35(1)
<i>Out-of-plane displacement</i>			
E(1)	0.432(11)	0.274(1)	0.276(1)
E(2)	-0.320(11)	-0.416(1)	-0.260(1)
<i>Central naphthalene ring torsion angles</i>			
C:(6)-(5)-(10)-(1)	-175.2(8)	175.14(1)	178.5(6)
C:(4)-(5)-(10)-(9)	-174.5(8)	174.65(1)	177.4(6)

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

3. Computational Details.

Geometries were fully optimised in the gas phase at the B3LYP level[5] using Curtis and Binning's 962(d) basis[6] on Se and Br (augmented with a set of diffuse s and p functions on Br), the Stuttgart-Dresden effective core potential along with its double zeta valence basis sets for Te and I[7] (augmented with d-polarisation functions with an exponent of 0.237 and 0.241, respectively),[8] and 6-31+G(d) basis elsewhere. Wiberg bond indices[9] were obtained in a natural bond orbital analysis[10] at the same level. The optimisations were started from the conformers of the corresponding acenaphthene minima. The computations were performed using the Gaussian suite of programs.[11]

Table S14. Relative energies, interatomic distances [$\text{\AA}$] and WBIs for selected conformers of compounds **2**, **3**, **4**, **5**, **8-12** and their naphthalene and acenaphthene analogues.^[a]

Compound	A-N2	B-N2	A-A2	B-A2	A-2	B-2
E _{rel} , kJ/mol	9.9	0.0	6.1	0.0	11.4	0.0
Br...Se, $\text{\AA}$	3.369	3.173	3.430	3.223	3.451	3.232
WBI	0.009	0.045	0.008	0.041	0.008	0.041
Compound		B-N3	A-A3	B-A3	A-3	B-3
E _{rel} , kJ/mol		n.a. ^[b]	15.1	0.0	19.0	0.0
Br...Te, $\text{\AA}$		3.266	3.563	3.319	3.580	3.327
WBI		0.068	0.011	0.062	0.011	0.061
Compound		C-N5	A-A5	B-A5	A-5	B-5
E _{rel} , kJ/mol		n.a. ^[b]	4.8	0.0	10.1	0.0
I...Se, $\text{\AA}$		3.336	3.565	3.384	3.585	3.380
WBI		0.057	0.014	0.050	0.014	0.052
Compound		B-N6	A-A6	B-A6	A-6	B-6
E _{rel} , kJ/mol		n.a. ^[b]	15.1	0.0	19.3	0.0
I...Te, $\text{\AA}$		3.425	3.705	3.455	3.722	3.465
WBI		0.087	0.018	0.084	0.017	0.087
Compound	CCt-N8 ^[a]	AB-N8	AAt-A8	AB-A8	CCt-8	AB-8
E _{rel} , kJ/mol	0.00	1.5	11.00	0.00	1.2	0.0
Se...Se, $\text{\AA}$	3.117	3.152	3.4720	3.2170	3.179	3.237
WBI	0.082	0.081	0.0123	0.0660	0.064	0.062
Compound	AAt-N10	BA-N10	AAt-A10	BA-A10 ^[c]		BA-10
E _{rel} , kJ/mol	15.1	0.0	11.53	0.00		n.a. ^[b]
Se...S, $\text{\AA}$	3.333	3.057	3.3946	3.1313		3.147
WBI	0.012	0.068	0.0107	0.056		0.055
Compound		BA-N11	AAt-A11	BA-A11		BA-11
E _{rel} , kJ/mol		n.a. ^[b]	22.7	0.00		n.a. ^[b]
Te...S, $\text{\AA}$		3.120	3.508	3.191		3.206
WBI		0.103	0.015	0.091		0.087
Compound		BA-N12	AAt-A12	BA-A12		BA-12
E _{rel} , kJ/mol		n.a. ^[b]	23.9	0.0		n.a. ^[b]
Te...Se, $\text{\AA}$		3.204	3.586	3.267		3.284
WBI		0.130	0.018	0.116		0.109

^[a] From reference Error! Bookmark not defined.. ^[b] Only minimum found. ^[c] A(Se)...B(S) isomer higher in energy.

4. References

[1] <https://sites.google.com/site/isoproms/home>

- [2] L. K. Aschenbach, F. R. Knight, R. A. M. Randall, D. B. Cordes, A. Baggott, M. Bühl, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2012**, 41, 3141.
- [3] W. D. Neudorff, D. Lentz, M. Anibarro, A. D. Schlüter, *Chem. Eur. J.* **2003**, 9, 2745.
- [4] N. Tanaka, T. Kasai, *Bull. Chem. Soc. Jpn.* **1981**, 54, 3020.
- [5] R. H. Mitchell, M. Chaudhary, R. Vaughan Williams, R. Fyles, J. Gibson, M. J. Ashwood-Smith, A. J. Fry, *Can. J. Chem.* **1992**, 70, 1015.
- [6] a) A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, 37, 785.
- [7] R. C. Binning, L. A. Curtiss, *J. Comput. Chem.* **1990**, 11, 1206.
- [8] a) P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker, P. D. W. Boyd, *J. Chem. Phys.* **1989**, 91, 1762; b) A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, 80, 1431; c) for I the valence basis by Kaupp *et al.* (including diffuse functions) was employed: M. Kaupp, P. v. R. Schleyer, H. Stoll, H. Preuss, *J. Am. Chem. Soc.* **1991**, 113, 6012.
- [9] S. Huzinaga, J. Anzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, H. Tatewaki, in: *Gaussian Basis Sets for Molecular Calculations*, Elsevier, Amsterdam, **1984**.
- [10] K. B. Wiberg, *Tetrahedron* **1968**, 24, 1083.
- [11] A. E. Reed, F. Curtiss, L. A. F. Weinhold, *Chem. Rev.* **1988**, 88, 899.
- [12] a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford CT, **2004**; (b) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, **2009**.

((Please insert the Supporting Information here and submit the CIF and CheckCIF files for all new compounds by e-mail to EurJIC@wiley-vch.de))