***Peri*-Interactions in 8-Diphenylphosphino-1-bromonaphthalene,
6-Diphenylphosphino-5-bromoacenaphthene and Derivatives**

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Abstract

The syntheses and full characterizations of the *peri*-substituted naphthalenes (Nap) and acenaphthenes (Ace) 1-Br-8-(Ph₂P)-Nap (**1a**) and 5-Br-6-(Ph₂P)-Ace (**1b**), as well as their derivatives 1-Br-8-[Ph₂P(E)]-Nap (**2a**, E = CH₃⁺ (counter ion Γ); **3a**, E = O; **4a**, E = S; **5a**, E = Se) and 5-Br-6-[Ph₂P(E)]-Ace (**2b**, E = CH₃⁺ (counter ion Γ); **3b**, E = O; **4b**, E = S; **5b**, E = Se) are reported. In order to quantify the energetic and electronic effects of the *peri*-interactions, an additional set of molecules, **1c-5c**, with the Br atom and the Ph₂P(E) fragment on opposite sides of the naphthalene group was generated which serves as reference because **1c-5c** exhibit negligible *peri*-interactions. The molecular geometries of all 15 compounds were optimized at the B3PW91/6-311+G(2df,p) level of theory.

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The analysis of the *peri*-interactions was not only based on the inspection of the molecular geometries and energies alone, but extended to a set of real-space bonding indicators (RSBI). These indicators were derived from theoretically calculated electron densities and pair densities, respectively. Particularly, the stockholder, Atoms-In-Molecules (AIM) and Electron-Localizability-Indicator (ELI-D) space partitioning schemes were used to produce Hirshfeld surfaces (HS), bond topological properties and basins of localized bonding and nonbonding electron pairs. Since **1c-5c** are 35-58 kJ/mol lower in energy than their counterparts **1a-5a**, the hypothesis of a mainly repulsive *peri*-interaction in **1a/b-5a/b** was confirmed. The shapes and contact patterns of the HSs of atoms and fragments involved in the *peri*-interactions (Br, P, E = CH₃⁺, O, S, Se) reveal that only in **1a** and **1b** are *peri*-interactions exhibited between the Br and the P atoms. In all other cases (**2a/b-5a/b**), the interaction mainly occurs between the Br atom and the E atom/fragment. According to the bond topological properties and the electron populations the (non)bonding ELI-D basins, are almost unaffected by the Br-P/E *peri*-interactions.

Introduction

Peri-substituted naphthalenes (Nap) and acenaphthenes (Ace) feature prominent transannular interactions between the substituents in 1,8- and 5,6-positions that can be repulsive due to steric congestion or attractive due to weak or strong bonding. The close proximity of the *peri*-substituents may also give rise to cooperative effects, for instance in the concomitant binding of other atoms in a chelating mode.^[1-3] Much of the earlier work on *peri*-substituted naphthalenes revolved around 1,8-dimethylaminonaphthalene, (1,8-Me₂N)₂-Nap, (**A**), which has found applications as a proton sponge (Scheme 1).^[4]

Scheme 1. *Peri*-substituted naphthalenes and acenaphthenes.

The facile C-H lithiation of dimethylnaphthylamine Me_2N -Nap (**B**) using *n*-butyllithium^[5] and subsequent salt metathesis with (organo)element halides proved to be a straight-forward route for the synthesis of intramolecularly coordinating 8-dimethylaminonaphthylelement species 1-(R_nE)-8-(Me_2N)-Nap (**C**) featuring the elements E = B,^[6,7] Al,^[8-12] Ga,^[10] In,^[10,13] Tl,^[13] Si,^[14-20] Sn,^[14, 21-24] P,^[25-28] As,^[30, 31] Sb,^[31,32] Bi,^[31,33] S, ^[34-38] Se,^[39-41] and Te.^[30-48] Within these compounds, short $\text{E} \cdots \text{N}$ transannular distances are frequently observed, which are indicative of strong attractive interactions.

A natural progression of this chemistry involves the replacement of nitrogen by phosphorous. Consequently, a vast number of 1,8-diphosphino-substituted naphthalenes-, (1,8- X_2P)₂-Nap, (**D**, X = R, H, Cl, OR, NR₂) has been prepared over the years.^[49-61]

Amongst those, 1,8-(Ph₂P)₂-Nap is the most prominent example, and has been utilized as chelating ligand for a number of transition metals.[62,63] Unlike **B**, the C-H lithiation of diphenylphosphinonaphthalene (**E**)[64] with various organolithium species is not a feasible strategy for the preparation of the intramolecularly coordinated 8-diphenylphosphinonaphthylelement species 1-(R_nE)-8-(Ph₂P)-Nap (**F**), which is presumably the reason why the chemistry of these derivatives has not been extensively investigated. In fact, we are aware of only a few examples of type **F** compounds bearing E = Si[65], O, S and Se[66, 67]. The recently introduced 5,6-disubstituted acenaphthenes [68-72] provide an alternative to 1,8-disubstituted naphthalenes since they offer the advantage that the starting material 5,6-dibromoacenaphthene is much easier to obtain than 1,8-dibromonaphthalene, which is usually prepared by a tedious Sandmeyer reaction.[73,74] Furthermore, the tricyclic acenaphthene ring system is more rigid and possesses smaller conformational flexibility than the bicyclic naphthalene ring system, which gives rise to slightly different *peri*-distances of approximately 2.5 than 2.7 Å for the parent compounds (Scheme 1).[3] This slight variation allows the study of minute effects of the bonding situation encountered for *peri*-bonded elements by choosing the same substituents in order to minimize electronic differences. Surprisingly, 1,8-disubstituted naphthalenes and 5,6-disubstituted acenaphthenes with the same substituents in the *peri*-positions have not yet been investigated in a comparative study. In the present work we describe the synthesis and structural characterization of both 1-Br-8-(Ph₂P)-Nap (**1a**) and 5-Br-6-(Ph₂P)-Ace (**1b**), as well as their derivatives 1-Br-8-[Ph₂P(E)]-Nap (**2a**, E = CH₃⁺; **3a**, E = O; **4a**, E = S; **5a**, E = Se) and 5-Br-6-[Ph₂P(E)]-Ace (**2b**, E = CH₃⁺; **3b**, E = O; **4b**, E = S; **5b**, E = Se) (Scheme 2), which hold potential as starting materials for compounds of type **F** and related acenaphthenes derivatives.

The bonding situation in sterically crowded molecular systems is almost exclusively interpreted in terms of molecular geometries, occasionally supported by NBO (natural bond orbital) analysis from density functional calculations.[75]

However, the analysis of so-called real-space bonding indicators derived either from the electron density (ED) or from the pair density (or density matrix) provide complementary information. Most common indicators are related to the Atoms-In-Molecules theory (AIM),[\[76\]](#) the stockholder partitioning[\[77\]](#) and the localization functions ELF[\[78\]](#) and ELI.[\[79\]](#) Utilizing AIM theory, a rigorous definition of chemical bonding based on the electron density is available. Atomic basins and a corresponding pattern of bond paths as well as bond-, ring- and cage-critical points (bcp's, rcp's, ccp's) are generated by introducing surfaces of zero electron flux, which provides consistent atomic as well as bonding properties. This space-filling topological approach has found wide application as a complement to molecular orbital analyses, because the electron density can in principle be obtained from both theoretical calculations and high-resolution X-ray diffraction data.[\[80\]](#)

The Electron Localizability Indicator (ELI) is a further development of the electron localization function (ELF). Both concepts divide space into regions of localized electron pairs instead of atoms and therefore eminently complement AIM theory. The mathematical method of space partitioning is equivalent to the one used in AIM theory. Therefore, the partitioning is likewise space filling and discrete, providing consistent integrated electron counts of both core shells and (non)bonded valence electrons. For the interpretation of atom-atom interactions, the calculation of overlap of ELI valence basins with AIM atoms is very helpful. It was developed by Raub and Jansen based on the ELF and used primarily for the estimation of bond polarities.[\[81\]](#) The visualization of density-based surfaces of atoms, functional groups and molecules in crystals aids understanding of steric demands, while mapping electronic properties (e.g. the electrostatic potential; ESP) onto the same surfaces provides insight into the electron distribution. The most prominent surface types are the zfs-boundaries within the AIM scheme, the 001-isosurface of the electron density (the ED is cut at 0.001 au) and the Hirshfeld Surface[\[82\]](#) which is defined by stockholder partitioning.

In this work, the *peri*-interactions between the Br atom and the PPh₂E fragment (E = none, CH₃⁺, O, S, Se) of **1a** - **5a** and **1b** - **5b** are analyzed in terms of experimentally and theoretically obtained molecular geometries, Hirshfeld surfaces based on experimental geometries from the crystal structures and theoretically obtained real-space bonding indicators derived from the AIM and ELI-D partitioning schemes. Due to the significant out-of-plane shifts of the Br and P atoms, the *peri*-interaction is assumed to be mainly of a repulsive character in **1a** - **5a** and **1b** - **5b**. In order to quantify these effects a comparative analysis of the naphthalene and acenaphthene derivatives is extended to include an analysis of the 1,6-bis-substituted naphthalene compounds **1c** - **5c**. They serve as reference molecules (hereafter abbreviated “Ref”) because they are considered to have “standard” (and much weaker) *peri*-interactions between the Br and the H atoms as well as between the PPh₂E fragments and the H atoms (Scheme 3).

Results and discussion

Synthetic aspects

1,8-Dibromonaphthalene was prepared by the reaction of 1,8-bis(tributylstannyl)-naphthalene[83] with bromine in 67% yield. We found this procedure more convenient than the more usual Sandmeyer reaction,[73,74] which has been noted as being painstaking.[3,62] 5,6-Dibromoacenaphthene was readily available by bromination of the parent acenaphthene.[84] The lithiation of 1,8-dibromonaphthalene and 5,6-dibromoacenaphthene using *n*-butyllithium at –78°C proceeded with a single metal-halide exchange. The subsequent reaction with diphenylchlorophosphine afforded 8-diphenylphosphino-1-bromonaphthalene, 1-Br-8-(Ph₂P)-Nap (**1a**), and 6-diphenylphosphino-5-bromonaphthalene, 6-Br-5-(Ph₂P)-Ace (**1b**), in 51% and 54% yield (Scheme 2).

Scheme 2 Syntheses and ^{31}P NMR chemical shifts (CDCl_3) of **1a** - **5a** and **1b** - **5b**.

We note that the preparation of **1a** has previously been reported,^[65,85] but apart from the ^{31}P NMR chemical shift, neither spectroscopic nor structural data were reported at the time. In **1a** and **1b**, both substituents in the *peri*-positions may be susceptible to undergo chemical transformations. The Br atoms in 1- and 5-positions may be replaced by other heteroatoms, such as B, Si, Sn, Sb, Te and Hg. However, the chemistry of these compounds will be reported elsewhere in due course. In this work, we describe the properties of those compounds bearing P atoms in the 6- and 8-positions. **1a** and **1b** were reacted with methyl iodide to produce the corresponding methylphosphonium iodides [1-Br-8-(Ph_2PCH_3)-Nap]I (**2a**·I) and [1-Br-8-(Ph_2PCH_3)-Ace]I (**2b**·I) in 79 and 89% yield (Scheme 2).

The oxidation of **1a** and **1b** with hydrogen peroxide, sulfur and selenium powder gave rise to the formation of the phosphine oxides 1-Br-8-(Ph₂PO)-Nap (**3a**) and 6-Br-5-(Ph₂PO)-Ace (**3b**) in 77 and 96% yield, the phosphine sulfides 1-Br-8-(Ph₂PS)-Nap (**4a**) and 6-Br-5-(Ph₂PS)-Ace (**4b**) in 50 and 77% yield and the phosphine selenides 1-Br-8-(Ph₂PSe)-Nap (**5a**) and 6-Br-5-(Ph₂PSe)-Ace (**5b**) in 38 and 67% yield, respectively (Scheme 2). Compounds **1a** - **5a** and **1b** - **5b** were characterized by ³¹P NMR spectroscopy (Scheme 2) as well as ¹³C- and ¹H-NMR spectroscopy and MS spectrometry (Experimental Section).

Molecular geometries and Hirshfeld surfaces.

The molecular structures of **1a** - **5a** and **1b** - **5b** determined by X-ray crystallography are shown in Figures 1 - 5. Additionally, the molecular structures of **1a/b/c** - **5a/b/c** were obtained by geometry optimization at the DFT/B3PW91/TZ level of theory. Figures of these theoretical models are given in the supplementary material. Experimentally and computationally obtained geometric parameters, which were introduced by Woollins and co-workers and are typically reported for structural analyses of this compound class (see for example reference [86]) are collected in Table 1. Considering the five reference compounds **1c-5c**, the given geometrical parameters reveal almost unstrained geometries with Br(1)-C(10)-C(19) and P(1)-C(18)-C(19) angles close to 120°. Accordingly, the C(10)-C(19)-C(18) angle is ca. 123° and the torsion angles C(13)-C(14)-C(19)-C(18) and C(15)-C(14)-C(19)-C(10) are ca. 179°. In contrast, the C(20)-P(1)-C(30) angle shows a dependency against the nature of E, which follows the same trend as in the naphthalene and acenaphthene derivatives. However, in **1a/b-5a/b** this angle is slightly smaller which may be related to the *peri*-interactions as it is found for both the experimental and theoretically-optimized geometries.

Figure 1. Molecular structures of **1a** and **1b** showing 30% probability ellipsoids and the crystallographic numbering scheme.

Figure 2. Molecular structures of **2a** and **2b** showing 30% probability ellipsoids and the crystallographic numbering scheme.

Figure 3. Molecular structure of **3a** and **3b** showing 30% probability ellipsoids and the crystallographic numbering scheme.

Figure 4. Molecular structures of **4a** and **4b** showing 30% probability ellipsoids and the crystallographic numbering scheme.

Figure 5. Molecular structure of **5a** and **5b** showing 30% probability ellipsoids and the crystallographic numbering scheme.

In cases of $E = \text{CH}_3^+$ (**2c**) and **O** (**3c**), considerable out-of-plane-shifts $d(\text{P})$ of ca. 0.1 Å are observed for the P atoms. In all other cases, the $d(\text{P})$ and $d(\text{Br})$ values are below 0.04 Å. In comparison to the reference values for **1c** to **5c**, systematic changes of some geometric parameters are observed for the naphthalenes and acenaphthenes **1a/b-5a/b**:

The Br(1)-C(10)-C(19) and P(1)-C(18)-C(19) angles are about 2-6° larger, whereas the intramannulene torsions angles C(13)-C(14)-C(19)-C(18) and C(15)-C(14)-C(19)-C(10) are smaller by 3-10° in most cases. All geometrical results compare very well with 1-SePh-8-[Ph₂P(E)]-Nap (E = O, S, Se), which was recently published by Woollins and co-workers.^[67]

Scheme 3 Computed 1,6-substituted naphthalenes used as reference (Ref) compounds

As expected, the phenyl group attached to the Se atom does not increase the sterical strain, as it is not directed towards the *peri*-region. Due to the ethylene bridge on the opposite side of the *peri*-interaction, the bay angle C(10)-C(19)-C(18) is always larger in the acenaphthene than in naphthalene species.^[3] In the presented compounds, this angle is ca. 5° larger for the naphthalenes and 9° for the acenaphthenes than observed in the reference compounds **1c** - **5c**. The out-of-plane shifts of the Br and P atoms show a significant increase of up to 0.79 Å for d(P) in **5a** (theoretically optimized geometry). With few exceptions, both the d(P) and d(Br) values from theoretical models of **1a/b** to **5a/b** follow a trend depending on the nature of E: none < O < CH₃⁺ < S < Se.

However, in the experimentally obtained X-ray structures no such trend is found. Due to the ca. 0.05 Å larger *peri*-distance in the acenaphthenes compared to the naphthalenes, out-of-plane shifts are much less pronounced in the former. In case of **1** only a very small shift from 0.027 Å (**1c**) to 0.043 Å (**1b**, theoretical model) is observed for d(Br) which points to a weak *peri*-interaction between Br and P in this compound. In the experimental solid-state structure of **1b** two molecules are located in the unit cell. The corresponding d(P) values are 0.019 and –0.195 Å which points towards an influence of the crystalline environment.

The surface curvednesses mapped on the Hirshfeld surfaces of atomic fragments derived from the experimental crystal structures of compounds **1a** and **5b** are displayed in Figure 6.[\[82\]](#)

Considering **1a**, the atomic Hirshfeld surfaces of the Br and the P atoms are found to be in contact with each other as expected for two atoms being in close proximity (Figure 6a).

Further intermolecular contact sites of the bromine atoms can be identified, delineated by the blue colored edges. Interestingly, in all other compounds except **1a** and **1b**, there is no contact patch between the Br and P atoms, and the surface shape is rather convex for the P atom facing the Br atom (wedge shape), as exemplified for **5b** in Figure 6b and shown in the Supporting Information for the remaining compounds. The absence of a contact patch between two atoms being in such close proximity is very unusual - we are not aware of another example where this phenomenon has been observed. This means that the situation occurring in **2a/b** to **5a/b**, where two atoms try to avoid contact, implies the interaction is strongly repulsive as expected. The intramolecular through-space contacts are mainly observed between the Br and the Se atoms (Figure 6c) and the Br atom and the equatorial phenyl ring (not shown). This is supported by the bond topologies (see below).

Figure 6. Curvedness mapped on the Hirshfeld surfaces of atomic fragments derived from the experimental crystal structures of compounds **1a** (a) and **5b** (b,c). In (a) and (b), the surfaces are shown for the Br and the P atoms; in (c), the surfaces are shown for the Br and the Se atoms.

Energies

The bond topologies, the shapes of the ELI-basins (see below) and to a lesser degree the molecular geometries reveal that in the reference species a weak *peri*-interaction is exhibited between the Br and H atom as well as between the PPh₂E fragment and the H atom opposite to the Br atom. However, since the naphthalene fragments are almost planar in the reference cases (**1c** - **5c**), these effects are negligible. Accordingly, for the estimation of relative energies of the steric stress introduced by close proximity of the Br atoms to the PPh₂E fragment, species **1c** - **5c** serve as references. Disregarding **2a** which is only 35.05 kJ/mol higher in energy than **2c**, the other compounds follow the same trend to that of the geometrical changes: **1a/c** (38.59 kJ/mol) < **3a/c** (52.92 kJ/mol) < **4a/c** (58.49 kJ/mol). The lower energy difference between **2a** and **2c** may be the result of a weak attractive interaction between the Br atom and an H atom of the methyl group in **2a**. Due to the larger *peri*-distance in the acenaphthene derivatives, these differences in energy are expected to be lower.

Bond topology

The relevant bond topological properties for 6 of the 15 theoretically analyzed models **1a-c** and **5a-c** are collected in Table 2.

The corresponding molecular graphs are shown in Figure 7. Topological properties and molecular graphs of the remaining models are given in the supporting information. All Br-C and P-C bond topological properties show the characteristics of polar-covalent interactions. The electron density at the bcp varies between ca. 1.1 to 1.2 e/Å³ for all cases. Interestingly, the Br-C bond topological parameters of the 15 theoretically analyzed models are virtually identical, although the Br atom lies in the naphthalene plane in the reference species and significantly out-of-plane for naphthalene and acenaphthene derivatives (up to 0.606 Å for **5a**). This observation points towards a quite flexible Br-C bond character with delocalization of the Br valence electrons and leads to the assumption that the energy costs of an out-of-plane shift of the Br atom are also quite low. In contrast, the P-C(naphthyl) bond lengths depend slightly on the sterical strain as they are ca. 0.02 Å shorter in the relaxed geometries of **1c-5c**. However, these effects are small. Moreover, the P-E bonds (E = CH₃⁺, O, S, Se) are also completely unaffected by the structural variation so it can be concluded that the steric strain is barely observable within the AIM-topology. In all models Br-P, Br-E, Br-C(phenyl) and/or Br-H(methyl) contacts are observed because of the presence of bond critical points. As expected, they show small electron density values of 0.05-0.13 e/Å³ at the bcp and a positive Laplacian close to zero. Their extraordinarily large bond ellipticities reflect a somewhat smeared electron density between the Br atom and its sterically close neighbours.

Atomic properties

Like for the AIM bond topology, the sterical strain has only a small influence on the atomic AIM charges. The charges of the relevant fragments - the naphthyl ring, the axial and equatorial phenyl rings, the Br atom, the P atom and the E fragment (X = CH₃⁺, O, S, Se) - are collected in Table 3.

Figure 7. AIM bond topology of compounds **1a-c** and **5a-c**. Red dots: bond critical points; yellow dots: ring critical points.

As expected, the charge of the P atom shows pronounced effects depending on the nature of the E atom/fragment attached to it, but the effect of the increased sterical hindrance within the series Ref < Ace < Nap is hardly distinguishable. Pertaining to the charges of the E atom/fragment, only when E = Se is a small increase of charge observed (Ref = -0.40 e < Ace = -0.56 e < Nap = -0.62 e). However, the three organic residues (naphthyl ring, axial/equatorial phenyl ring) are almost unaffected by both the nature of E and by the magnitude of steric hindrance. The same is true for the Br atoms.

ELI-D analysis

Since all non-terminal atoms are by definition involved in more than one chemical contact, atomic AIM charges may in some cases hinder the evaluation of substituent effects because shifts of electron populations may cancel out and produce similar atomic AIM charges despite

different chemical environments. However, a more detailed view is provided by the analysis of integrated electron populations within distinct bonding or lone pair basins generated by space partitioning according to the ELI-D scheme. In this work, the analysis is divided into two parts: first, the bonding and lone pair basins of the Br atoms and the PPh₂E fragments are calculated, and second, the C-C bonds in the naphthalene and acenaphthene groups are analysed. The electron populations of the ELI-D basins in the Br-C bond, the summed values of the lone pairs of the Br atoms, the values of the three P-C bonds, the summed values of the P-E bonds, the summed values of the lone pairs of the E atoms (for E = O, S, Se) and the summed values of the populations of the H atoms for E = CH₃⁺ are listed in Table 4. The number of contributing basins is additionally given for the lone pairs and the P-E bonds. With regards to the Br-C bond and the lone pairs of the Br atom, the observed changes in the electron populations are remarkably small. The maximum change for these basin types is 0.03 e. This is especially noteworthy for the summed electron populations in the lone pairs of the Br atom which seem to be totally unaffected by the nature of E in the PPh₂E fragment and the degree of geometrical distortion. Compound **2** is an exception, for which a slight decrease in the Br-C bond population is accompanied by a corresponding increase in the lone pair population. This is in accordance with the assumption of a weak attractive interaction between the Br atom and an H atom of the methyl group in compounds **2a** and **2b** as mentioned above. Inspection of the remaining basin types uncovers distinct effects depending on the nature of E, but the differences between the *trans*-species and the naphthalene and acenaphthene derivatives are negligible. Up to this point the results indicate that significant geometrical changes are accompanied by negligible changes in the electron densities and pair densities in the *peri*-region which we assert is characteristic of any type of repulsive interaction. This is supported by the combined analysis of the AIM and ELI-D space partitioning schemes: The partial electron population of the P or E atoms lone pair ELI-D basins within the atomic Br atom never exceeds 1% of the total value.

This means that sterically repelling atoms are characterized by an almost similar location and shape of both the AIM zero-flux-surfaces and the boundaries of the ELI-D basins. Iso-surface representations ($Y = 1.3$) of the ELI-D for compounds **1a**, **2a** and **5c** are shown in Figure 8. A characteristic feature of the *peri*-interaction is the fact that the lone-pair basins of the Br atom are split into two to three fragments with one or two small and flattened parts pointing towards the *peri*-partners (H, P, E, equatorial phenyl ring) and a larger part pointing to the opposite site. also In addition, the basins of the *peri*-partners are also flattened in direction of the Br atom. The degree of flattening depends on the electronegativity of atom E and is only very small for E = O (see supporting information for the remaining ELI-D Figures).

In the following, the electronic properties of the C-C bonding basins of the naphthalene fragments will be analyzed in order to uncover the effects of the geometrical distortion. The basin volumes and electron populations both with a 0.001 a.u. cutoff, the ELI-D value at the attractor position (max), and the perpendicular distance of the attractor position to the C-C axis (d_{ELI}) are reported in Table 5. The electron distribution within the annulene ring system indicates that the mesomeric structure shown in Figure 9 is the dominant one for all cases. The central bond connecting the two rings, is similar, however, to the four C-C bonds attached to it and therefore no double bond has been drawn here. The d_{ELI} values are in the range of 0.002-0.030 Å for the almost planar reference species and with few exceptions increases for the strained C-C bonds. The largest value found is 0.067 Å for the C(10)-C(19) bond in **5b**.

Figure 8. ELI-D iso-surface representations (side and top view) of compounds **1a** (first row), **2a** (second row) and **5c** (third row). The surfaces are color-coded according to the basin

size: green (small) through to blue (large). For clarity, protonated valence basins (H atoms) are in transparent.

Figure 9. Dominant mesomeric structure in compounds **1a-5c**.

Conclusions

Two related series of *peri*-substituted naphthalenes 1-Br-8-[Ph₂P(E)]-Nap (**1a**, E = none; **2a**, E = CH₃⁺; **3a**, E = O; **4a**, E = S; **5a**, E = Se) and acenaphthenes 5-Br-6-[Ph₂P(E)]-Ace (**1b**, E = none; **2b**, E = CH₃⁺; **3b**, E = O; **4b**, E = S; **5b**, E = Se) were prepared and fully characterized. Sterical interactions between the substituents in 1,8- and 5,6-positions lead to considerable geometrical distortions which are the subject of a large range of experimental studies. In a Hirshfeld surface analysis, which is based on only geometry and promolecule densities, these distortions clearly are the result of two neighbouring atoms avoiding each other intramolecularly, which can be interpreted in terms of pronounced repulsion. Such strong distortions are also expected to be paralleled by concomitant changes in real-space bonding descriptors derived from the electron or pair densities. But this study reveals that for purely repulsive interactions these changes are very small in spite of the significant geometrical distortions. In the compounds presented, steric repulsion is characterized solely by geometrical and Hirshfeld surface changes and is not paralleled by electronic bonding properties.

Hence, for future studies on strained molecular systems atom-atom repulsion may be distinguished from atom-atom attraction by a combined analysis of the molecular geometries, the molecular energies referenced to corresponding unstrained models (if possible) and details in real-space bonding indicators. Starting from **1a** - **5a** and **1b** - **5b** we are currently preparing naphthalenes of type F (Scheme 1) and related acenaphthenes containing attractive and repulsive *peri*-interactions between phosphorous and elements (e.g. E = B, Si, Sn, Sb, Te, Hg) other than bromine.

Experimental Section

General. Reagents were obtained commercially (Sigma-Aldrich, Germany) and were used as received. Dry Solvents were collected from a SPS800 mBraun solvent system.

1,8-Bis(tributylstannyl)naphthalene[83] and 5,6-dibromoacenaphthene[84] were prepared according to literature procedures. ^1H -, ^{13}C -, ^{31}P - and ^{77}Se -NMR spectra were recorded in CDCl_3 at r.t. using a Bruker Avance-360 spectrometer and are referenced to tetramethylsilane (^1H , ^{13}C), phosphoric acid (85% in water) (^{31}P) and diphenyldiselenide (^{77}Se). Chemical shifts are reported in parts per million (ppm) and coupling constants (J) are given in Hertz (Hz).

Electron impact mass spectroscopy (EIMS) was carried out using a Finnigan MAT 95. The ESI MS spectra were obtained with a Bruker Esquire-LC MS. Methanol solutions (unless otherwise stated, $c = 1 \cdot 10^{-6} \text{ mol L}^{-1}$) were injected directly into the spectrometer at a flow rate of $3 \mu\text{L min}^{-1}$. Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 5 L min^{-1} and a pressure of 5 psi, respectively. Pressure in the mass analyzer region was usually about $1 \cdot 10^{-5} \text{ mbar}$. Spectra were collected for one minute and averaged. The nozzle-skimmer voltage was adjusted individually for each measurement.

Synthesis of 1,8-dibromonaphthalene. Bromine (250 mg, 1.57 mmol) was added at r.t. to a solution of 1,8-bis(tributylstannyl)naphthalene (500 mg, 0.71 mmol) in *n*-hexane (5 ml) and stirred overnight. The solvent was removed by rotary evaporation and the residue was left for crystallization at 5°C. The obtained crystals were filtered, washed with cold *n*-hexane and dried in vacuum yielding 1,8-Br₂-Nap as colourless crystals (100 mg, 0.48 mmol, 67%).

¹H-NMR: δ = 7.96 (dd, $^3J(^1\text{H}-^1\text{H}) = 7$ Hz, $^4J(^1\text{H}-^1\text{H}) = 2$ Hz, 2H, H-2,7), 7.83 (dd, $^3J(^1\text{H}-^1\text{H}) = 8$ Hz, $^4J(^1\text{H}-^1\text{H}) = 1$ Hz, 2H, H-4,5); 7.28 ppm (t, $^3J(^1\text{H}-^1\text{H}) = 8$ Hz, 2H, H-3,6). **¹³C{¹H}-NMR:** δ = 136.8 (s, C_b), 135.1 (s, C₂ and C₇), 129.4 (s, C₄ and C₅), 128.6 (s, C_a), 126.2 (s, C₃ and C₆), 119.3 ppm (s, C₁ and C₈). **MS (EI⁺):** *m/z*: 284 [M⁺].

Synthesis of 1-bromo-8-diphenylphosphino-naphthalene (1a). *n*-Butyllithium (5.25 mmol, 2.5 M in *n*-hexane) was added to a solution of 1,8-dibromonaphthalene (1.50 g, 5.25 mmol) in diethyl ether (20 ml) at -78°C. After 1 h Ph₂PCl (1.16 g, 5.25 mmol) was added and stirring was continued at -78°C for 60 minutes. The mixture was allowed to warm to r.t. overnight. The solvent was removed and CH₂Cl₂ (30 ml) was added. The resulting suspension was washed three times with water. The organic layer was separated, dried over Mg₂SO₄ and the solvent was removed by rotary evaporation. The resulting yellow precipitate was recrystallized by CH₂Cl₂/*n*-hexane affording 1-Br-8-(Ph₂P)-Nap (**1a**) as pale yellow crystals (1.04 g, 2.66 mmol, 51%).

¹H-NMR : δ = 7.88-7.81 (m, 3H), 7.36-7.29 ppm (m, 13H). **¹³C{¹H}-NMR:** δ = 139.3 (d, $^2J(^{31}\text{P}-^{13}\text{C}) = 14$ Hz, C₂), 137.2 (d, $^4J(^{31}\text{P}-^{13}\text{C}) = 1$ Hz, C₄), 136.4 (d, $^3J(^{31}\text{P}-^{13}\text{C}) = 3$ Hz, C_b), 134.7 (d, $^1J(^{31}\text{P}-^{13}\text{C}) = 17$ Hz, C₁), 134.1 (d, $^2J(^{31}\text{P}-^{13}\text{C}) = 21$ Hz, C_o), 131.6 (d, $^1J(^{31}\text{P}-^{13}\text{C}) = 31$ Hz, C_i), 130.6 (s, C₆ or C₇), 129.4 (d, $^4J(^{31}\text{P}-^{13}\text{C}) = 1$ Hz, C₅), 128.5 (d, $^3J(^{31}\text{P}-^{13}\text{C}) = 7$ Hz,

C_m), 128.4 (s, C_p), 125.8 (d, $^3J(^{31}\text{P}-^{13}\text{C}) = 15\text{ Hz}$, C₃), 120.8 ppm (d, $^3J(^{31}\text{P}-^{13}\text{C}) = 1\text{ Hz}$, C₈).

$^{31}\text{P}\{^1\text{H}\}$ -NMR: $\delta = -5.3\text{ ppm}$ (s). MS (EI⁺): m/z : 390 [M⁺].

Synthesis of 5-bromo-6-diphenylphosphino-acenaphthene (1b). To a suspension of 5,6-dibromoacenaphthene (4.00 g, 12.8 mmol) in diethyl ether (40 ml), *n*-butyllithium (12.8 mmol, 2.5 M in *n*-hexane) was added at -78°C . After 1 h Ph₂PCl (2.83 g, 12.8 mmol) was added dropwise. Stirring was continued for 1 h at -78°C and the suspension was allowed to warm to r.t. overnight. The solvent was removed under vacuum and CH₂Cl₂ (50 ml) was added. After aqueous workup the solvent was concentrated by rotary evaporation and the solution was left for crystallization. The resulting pale yellow crystals were filtrated, washed with *n*-hexane and dried in vacuum affording 5-Br-6-(Ph₂P)-Ace (**1b**), as yellow crystals (2.87 g, 6.88 mmol, 54%).

^1H -NMR: $\delta = 7.74$ (d, $J = 7\text{ Hz}$, 1H), 7.38-7.36 (m, 10H), 7.16-7.11 (m, 3H), 3.35 ppm (s, 4H, H-1,2). $^{13}\text{C}\{^1\text{H}\}$ -NMR: $\delta = 148.4$ (s, C_b), 146.7 (d, $^4J(^{31}\text{P}-^{13}\text{C}) = 2\text{ Hz}$, C_d), 141.4 (d, $^4J(^{31}\text{P}-^{13}\text{C}) = 4\text{ Hz}$, C_c), 139.1 (d, $^2J(^{31}\text{P}-^{13}\text{C}) = 13\text{ Hz}$, C₄), 137.7 (s, C₇ or C₈), 134.6 (s, C₇ or C₈), 134.1 (d, $^2J(^{31}\text{P}-^{13}\text{C}) = 20\text{ Hz}$, C_o), 133.2 (d, $^1J(^{31}\text{P}-^{13}\text{C}) = 19\text{ Hz}$, C₅), 129.8 (d, $^1J(^{31}\text{P}-^{13}\text{C}) = 29\text{ Hz}$, C_i), 128.4 (d, $^3J(^{31}\text{P}-^{13}\text{C}) = 7\text{ Hz}$, C_m), 128.3 (s, C_p), 120.4 (d, $^3J(^{31}\text{P}-^{13}\text{C}) = 23\text{ Hz}$, C₃), 115.7 (s, C₆), 30.0 (s, C₁ or C₂), 29.8 ppm (s, C₁ or C₂). $^{31}\text{P}\{^1\text{H}\}$ -NMR: $\delta = -8.1\text{ ppm}$ (s). MS (EI⁺): m/z : 416 [M⁺].

Synthesis of 1-bromo-8-naphthyl-methyldiphenylphosphonium iodide (2a). Methyl iodide (23.4 mg, 0.16 mmol) was added to a solution of **1a** (54.5 mg, 0.14 mmol) in toluene (2 ml) and stirred at r.t. overnight. The precipitate was filtered, washed three times with toluene and dried in vacuum yielding [1-Br-8-Ph₂P(CH₃)-Nap]⁺I⁻ (**2a**) as a yellow solid (68.6 mg,

0.11 mmol, 79%). Crystals suitable for X-ray crystallography were obtained by recrystallization by CH₂Cl₂/toluene.

¹H-NMR: δ = 8.32 (d, J = 8 Hz, 1H), 8.10 (d, J = 8 Hz, 1H), 7.89-7.50 (m, 14H), 3.30 ppm (d, $^2J(^1\text{H}-^{31}\text{P})$ = 13 Hz, 3H, CH₃). **¹³C{¹H}-NMR:** 142.9 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 12 Hz, C₂), 138.2 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 3 Hz, C₄), 136.9 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 9 Hz, C_b), 136.0 (s, C₇), 134.1 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 3 Hz, C_p), 132.3 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 10 Hz, C_o), 130.9 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 1 Hz, C₅), 130.1 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 13 Hz, C_m), 128.3 (s, C₆), 125.4 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 15 Hz, C₃), 123.6 (d, $^1J(^{31}\text{P}-^{13}\text{C})$ = 91 Hz, C_i), 117.3 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 4 Hz, C₈), 113.8 (d, $^1J(^{31}\text{P}-^{13}\text{C})$ = 86 Hz, C₁), 16.6 ppm (d, $^1J(^{31}\text{P}-^{13}\text{C})$ = 60 Hz, CH₃). **³¹P{¹H}-NMR:** δ = 29.7 ppm (s). **ESI MS** (MeOH, positive mode): m/z = 405.3 (C₂₃H₁₉BrP) for [1-Br-8-Ph₂PCH₃-C₁₀H₆]⁺ (**2a**).

Synthesis of 5-bromo-6-acenaphthyl-methyldiphenylphosphonium iodide (2b). Methyl iodide (340 mg, 2.40 mmol) was added to a solution of **1b** (1.00 g, 2.40 mmol) in toluene (10 ml) and stirred at r.t. overnight. The precipitate was filtered, washed three times with toluene and dried in vacuum yielding [5-Br-6-Ph₂P(CH₃)-Ace]⁺I⁻ (**2b**) as colourless solid (1.19 g, 2.13 mmol, 89%). Crystals suitable for X-ray crystallography were obtained by recrystallization by CH₂Cl₂/*n*-hexane.

¹H-NMR: δ = 7.75-7.48 (m, 10H), 7.39-7.31 (m, 2H), 7.12-7.02 (m, 2H), 3.40 (m, 4H, H-1,2), 3.24 ppm (d, $^2J(^1\text{H}-^{31}\text{P})$ = 13 Hz, 3H, CH₃). **¹³C{¹H}-NMR:** δ = 157.9 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 3 Hz, C_d), 148.7 (s, C_b), 143.7 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 13 Hz, C₄), 141.8 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 10 Hz, C_c), 137.2 (s, C₇), 134.0 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 3 Hz, C_p), 132.3 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 10 Hz, C_o), 130.8 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 7 Hz, C_a), 129.9 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 13 Hz, C_m), 123.2 (d, $^1J(^{31}\text{P}-^{13}\text{C})$ = 91 Hz, C_i), 123.1 (s, C₈), 120.0 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 15 Hz, C₃), 112.0 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 3 Hz, C₆), 107.7 (d, $^1J(^{31}\text{P}-^{13}\text{C})$ = 88 Hz, C₅), 30.4 (s, C₁ or C₂), 29.6 (s, C₁ or C₂), 16.3 (d, $^1J(^{31}\text{P}-^{13}\text{C})$ = 60 Hz,

CH₃). **³¹P{¹H}-NMR:** δ = 27.7 ppm (s). **ESI MS** (MeOH, positive mode): m/z = 431.1

(C₂₅H₂₁BrP) for [5-Br-6-Ph₂PCH₃-C₁₂H₈]⁺ (**2b**).

Synthesis of 5-bromo-6-diphenyloxophosphino-naphthalene (3a). Hydrogen peroxide (100 μ L, 30%-solution) was added to a solution of **1a** (50.2 mg, 0.13 mmol) in THF (2 ml) and stirred at r.t. overnight. The solvent was removed by rotary evaporation and the residue was recrystallized by CH₂Cl₂/*n*-hexane affording 1-Br-8-Ph₂P(O)-Nap (**3a**) as colourless crystals (42.4 mg, 0.10 mmol, 77%).

¹H-NMR: δ = 7.98 (d, J = 8 Hz, 1H), 7.88 (d, J = 8 Hz, 2H), 7.67-7.58 (m, 5H), 7.54-7.27 ppm (m, 8H). **¹³C{¹H}-NMR:** δ = 139.1 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 13 Hz, C₂), 136.5 (d, $^1J(^{31}\text{P}-^{13}\text{C})$ = 108 Hz, C_i), 136.6 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 8 Hz, C_b), 135.1 (s, C₇), 134.5 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 3 Hz, C₄), 133.9 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 6 Hz, C_a), 131.5 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 9 Hz, C_o), 131.1 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 3 Hz, C_p), 129.3 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 1 Hz, C₅), 128.5 (d, $^1J(^{31}\text{P}-^{13}\text{C})$ = 98 Hz, C₁), 128.3 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 12 Hz, C_m), 126.8 (s, C₆), 124.2 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 15 Hz, C₃), 120.2 ppm (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 4 Hz, C₈). **³¹P{¹H}-NMR:** δ = 36.8 ppm (s). **MS (EI⁺):** m/z : 327 [M-Br]⁺.

Synthesis of 5-bromo-6-diphenyloxophosphino-acenaphthene (3b). Hydrogen peroxide (200 μ L, 30%-solution) was added to a solution of **1b** (100 mg, 0.24 mmol) in THF (2 ml) and stirred at r.t. overnight. The solvent was removed by rotary evaporation and the residue was recrystallized by CH₂Cl₂/*n*-hexane affording 5-Br-6-Ph₂P(O)-Ace (**3b**) as colourless crystals (100 mg, 0.23 mmol, 96%).

¹H-NMR: δ = 7.77 (d, J = 7 Hz, 1H), 7.68-7.37 (m, 11H), 7.21-7.11 (m, 2H), 3.36 ppm (s, 4H, H-1,2). **¹³C{¹H}-NMR:** δ = 153.3 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 2 Hz, C_d), 146.8 (s, C_b), 141.7 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 9 Hz, C_c), 140.5 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 14 Hz, C₄), 136.3 (s, C₇), 136.0 (d, $^1J(^{31}\text{P}-^{13}\text{C})$

= 108 Hz, C_i), 132.5 (d, $^2J(^{31}\text{P}-^{13}\text{C}) = 7$ Hz, C_a), 131.7 (d, $^2J(^{31}\text{P}-^{13}\text{C}) = 9$ Hz, C_o), 131.1 (d, $^4J(^{31}\text{P}-^{13}\text{C}) = 2$ Hz, C_p), 128.3 (d, $^3J(^{31}\text{P}-^{13}\text{C}) = 12$ Hz, C_m), 123.4 (d, $^1J(^{31}\text{P}-^{13}\text{C}) = 102$ Hz, C₅), 121.7 (s, C₈), 118.7 (d, $^3J(^{31}\text{P}-^{13}\text{C}) = 15$ Hz, C₃), 115.0 (d, $^3J(^{31}\text{P}-^{13}\text{C}) = 4$ Hz, C₆), 30.2 (s, C₁ or C₂), 29.6 ppm (s, C₁ or C₂). **$^{31}\text{P}\{^1\text{H}\}$ -NMR:** $\delta = 36.3$ ppm (s). **MS (EI⁺):** m/z : 353 [M-Br]⁺.

Synthesis of 1-bromo-8-diphenylsulfidophosphino-naphthalene (4a). Sulfur (9.83 mg, 0.31 mmol) was added to a solution of **1a** (50.0 mg, 0.14 mmol) in THF (2 ml) and stirred at r.t. overnight. The solvent was removed by rotary evaporation and the residue was recrystallized by CH₂Cl₂/*n*-hexane affording 1-Br-8-Ph₂P(S)-Nap (**4a**) as colourless crystals (30.9 mg, 0.07 mmol, 50%).

^1H -NMR: $\delta = 7.94$ -7.76 (m, 7H), 7.55-7.20 ppm (m, 7H). **$^{13}\text{C}\{^1\text{H}\}$ -NMR:** $\delta = 138.3$ (d, $^2J(^{31}\text{P}-^{13}\text{C}) = 11$ Hz, C₂), 136.9 (d, $^3J(^{31}\text{P}-^{13}\text{C}) = 8$ Hz, C_b), 136.4 (d, $^1J(^{31}\text{P}-^{13}\text{C}) = 88$ Hz, C_i), 135.1 (s, C₇), 134.1 (d, $^4J(^{31}\text{P}-^{13}\text{C}) = 3$ Hz, C₄), 132.9 (d, $^2J(^{31}\text{P}-^{13}\text{C}) = 6$ Hz, C_a), 131.8 (d, $^2J(^{31}\text{P}-^{13}\text{C}) = 10$ Hz, C_o), 130.8 (d, $^4J(^{31}\text{P}-^{13}\text{C}) = 3$ Hz, C_p), 129.5 (d, $^1J(^{31}\text{P}-^{13}\text{C}) = 80$ Hz, C₁), 129.4 (d, $^4J(^{31}\text{P}-^{13}\text{C}) = 1$ Hz, C₅), 128.2 (d, $^3J(^{31}\text{P}-^{13}\text{C}) = 13$ Hz, C_m), 126.8 (s, C₆), 124.2 (d, $^3J(^{31}\text{P}-^{13}\text{C}) = 14$ Hz, C₃), 120.0 ppm (d, $^3J(^{31}\text{P}-^{13}\text{C}) = 4$ Hz, C₈). **$^{31}\text{P}\{^1\text{H}\}$ -NMR:** $\delta = 52.0$ ppm (s). **MS (EI⁺):** m/z : 343 [M-Br]⁺.

Synthesis of 5-bromo-6-diphenylsulfidophosphino-acenaphthene (4b). Sulfur (10.0 mg, 0.29 mmol) was added to a solution of **1b** (100 mg, 0.24 mmol) in THF (2 ml) and stirred at r.t. overnight. The solvent was removed by rotary evaporation and the residue was recrystallized from CH₂Cl₂/*n*-hexane affording 5-Br-6-Ph₂P(S)-Ace (**4b**) as yellow crystals (82.2 mg, 0.19 mmol, 77%).

^1H -NMR: δ = 7.89-7.75 (m, 5H), 7.53-7.34 (m, 7H), 7.20 (d, J = 7 Hz, 1H), 7.10 (d, J = 7 Hz, 1H), 3.34 ppm (s, 4H, H-1,2). **$^{13}\text{C}\{^1\text{H}\}$ -NMR:** δ = 152.9 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 3 Hz, C_d), 145.0 (s, C_b), 142.1 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 9 Hz, C_c), 139.4 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 13 Hz, C₄), 136.7 (s, C₇), 136.2 (d, $^1J(^{31}\text{P}-^{13}\text{C})$ = 87 Hz, C_i), 132.0 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 10 Hz, C_o), 131.4 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 7 Hz, C_a), 130.8 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 3 Hz, C_p), 128.3 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 13 Hz, C_m), 124.7 (d, $^1J(^{31}\text{P}-^{13}\text{C})$ = 83 Hz, C₅), 121.7 (s, C₈), 118.8 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 14 Hz, C₃), 114.7 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 3 Hz, C₆), 30.1 (s, C₁ or C₂), 29.6 ppm (s, C₁ or C₂). **$^{31}\text{P}\{^1\text{H}\}$ -NMR:** δ = 50.2 ppm (s). **MS (EI⁺):** m/z : 369 [M-Br]⁺.

Synthesis of 8-bromo-1-diphenylselenidophosphino-naphthalene. Selenium (12.6 mg, 0.16 mmol) was added to a solution of **1a** (51.9 mg, 0.13 mmol) in THF (2 ml) and stirred at r.t. overnight. The solvent was removed by rotary evaporation and the residue was recrystallized by CH₂Cl₂/*n*-hexane affording 1-Br-8-Ph₂P(Se)-Nap (**5a**) as yellow crystals (22.9 mg, 0.05 mmol, 38%).

^1H -NMR: δ = 7.96-7.80 (m, 7H), 7.53-7.23 ppm (m, 9H). **$^{13}\text{C}\{^1\text{H}\}$ -NMR:** δ = 138.2 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 11 Hz, C₂), 137.0 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 8 Hz, C_b), 135.3 (s, C₇), 135.2 (d, $^1J(^{31}\text{P}-^{13}\text{C})$ = 79 Hz, C_i), 134.2 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 3 Hz, C₄), 132.9 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 6 Hz, C_a), 132.5 (d, $^2J(^{31}\text{P}-^{13}\text{C})$ = 10 Hz, C_o), 131.0 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 3 Hz, C_p), 129.5 (d, $^4J(^{31}\text{P}-^{13}\text{C})$ = 1 Hz, C₅), 128.4 (d, $^1J(^{31}\text{P}-^{13}\text{C})$ = 71 Hz, C₁), 128.3 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 13 Hz, C_m), 126.9 (s, C₆), 124.2 (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 14 Hz, C₃), 120.1 ppm (d, $^3J(^{31}\text{P}-^{13}\text{C})$ = 4 Hz, C₈). **$^{31}\text{P}\{^1\text{H}\}$ -NMR:** δ = 42.9 ppm (s, $^1J(^{77}\text{Se}-^{31}\text{P})$ = 742 Hz). **$^{77}\text{Se}\{^1\text{H}\}$ -NMR:** δ = -178.3 ppm (d, $^1J(^{31}\text{P}-^{77}\text{Se})$ = 746 Hz). **MS (EI⁺):** m/z : 391 [M-Br]⁺.

Synthesis of 5-bromo-6-diphenylselenidophosphino-acenaphthalene. Selenium (23.0 mg, 0.29 mmol) was added to a solution of **1b** (100 mg, 0.24 mmol) in THF (2 ml) and stirred at

r.t. overnight. The solvent was removed by rotary evaporation and the residue was recrystallized by CH₂Cl₂/*n*-hexane affording 5-Br-6-Ph₂P(Se)-Ace (**5b**) as yellow crystals (80.0 mg, 0.16 mmol, 67%).

¹H-NMR: δ = 7.93-7.83 (m, 4H), 7.77 (d, *J* = 7 Hz, 1H), 7.52-7.30 (m, 7H), 7.20 (d, *J* = 7 Hz, 1H), 7.10 (d, *J* = 7 Hz, 1H), 3.34 ppm (s, 4H, H-1,2). **¹³C{¹H}-NMR:** δ = 153.1 (d, ⁴*J*(³¹P-¹³C) = 3 Hz, C_d), 147.0 (s, C_b), 142.2 (d, ⁴*J*(³¹P-¹³C) = 10 Hz, C_c), 139.3 (d, ²*J*(³¹P-¹³C) = 12 Hz, C₄), 136.9 (s, C₇), 134.9 (d, ¹*J*(³¹P-¹³C) = 79 Hz, C_i), 132.6 (d, ²*J*(³¹P-¹³C) = 10 Hz, C_o), 131.3 (d, ²*J*(³¹P-¹³C) = 8 Hz, C_a), 130.9 (d, ⁴*J*(³¹P-¹³C) = 3 Hz, C_p), 128.3 (d, ³*J*(³¹P-¹³C) = 13 Hz, C_m), 123.5 (d, ¹*J*(³¹P-¹³C) = 72 Hz, C₅), 121.8 (s, C₈), 118.9 (d, ³*J*(³¹P-¹³C) = 14 Hz, C₃), 114.6 (d, ³*J*(³¹P-¹³C) = 3 Hz, C₆), 30.1 (s, C₁ or C₂), 29.7 ppm (s, C₁ or C₂). **³¹P{¹H}-NMR:** δ = 40.7 ppm (s, ¹*J*(⁷⁷Se-³¹P) = 735 Hz). **⁷⁷Se{¹H}-NMR:** δ = -170.5 ppm (d, ¹*J*(³¹P-⁷⁷Se) = 721 Hz). **ESI MS** (CH₂Cl₂/MeOH 1:10, positive mode): *m/z* = 479.0 (C₂₄H₁₉BrPSe) for [5-Br-6-Ph₂PSe-C₁₂H₈+H]⁺.

X-ray crystallography. Intensity data were collected on a STOE IPDS 2T area detector (**3a**, **3b**, **4a**, **5a**) and a Siemens P4 diffractometer (**1a**, **1b**, **2a**, **2b**, **4b**, **5b**) fitted with a Siemens LTII at 173 K with graphite-monochromated Mo-Kα (0.7107 Å) radiation. All structures were solved by direct methods and refined based on F² using the SHELX program package.^[87] All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. Crystal and refinement data are collected in Table 6. Figures were created using ORTEP.^[88] Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 941919 - 9412928.

Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Theoretical calculations. For all 15 models, the molecular geometries were optimized at the B3PW91/6-311++G(2df,p) level of theory using GAUSSIAN09[89]. Frequency calculations were carried out to check that all optimized geometries correspond to energy minima. The wavefunctions were analyzed with AIM2000[90] and DGRID-4.6[91] in order to obtain all the required real-space bonding indicators based on the AIM and ELI-D space partitioning. The Hirshfeld surfaces were generated with the program CrystalExplorer[92] from the promolecule densities. Isosurface representations of the ELI-D were made using the program MOLISO[93].

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Table 1. Selected experimental (first row) and computational (second row, *italics*) distances [Å] and angles [°] for **1a** - **5a**, **1b** - **5b** and **1c** - **5c**.

Compound	1a	2a ·I [−]	3a	4a	5a
E	-	CH ₃	O	S	Se
<i>Peri-region-distances</i>					
P(1)-Br(1)	3.139(2) <i>3.147</i>	3.350(2) <i>3.386</i>	3.302(1) <i>3.297</i>	3.417(2), 3.386(2) <i>3.391</i>	3.388(2) <i>3.399</i>
<i>Peri-region bond angles</i>					
Br(1)-C(10)-C(19)	124.2(3) <i>123.52</i>	122.6(4) <i>122.75</i>	123.5(2) <i>123.30</i>	122.7(3), 122.9(3) <i>123.20</i>	123.2(3) <i>123.14</i>
C(10)-C(19)-C(18)	126.8(4) <i>127.66</i>	129.2(5) <i>128.59</i>	128.5(3) <i>127.84</i>	128.8(4), 128.2(4) <i>128.11</i>	128.4(3) <i>128.13</i>
P(1)-C(18)-C(19)	123.3(3) <i>123.52</i>	127.0(4) <i>127.55</i>	125.0(2) <i>125.56</i>	125.4(3), 126.2(3) <i>125.76</i>	126.3(3) <i>123.14</i>
Σ of bay angles	374(1) <i>374.70</i>	379(2) <i>378.89</i>	377.0(7) <i>376.70</i>	377(2), 377(2) <i>377.07</i>	377.9(9) <i>374.41</i>
Splay angle ^a	14 <i>14.70</i>	19 <i>18.89</i>	17 <i>16.70</i>	17, 17 <i>17.07</i>	17.9 <i>14.41</i>
C(20)-P(1)-C(30)	101.1(3) <i>101.48</i>	107.8(3) <i>106.67</i>	103.8(2) <i>103.21</i>	105.3(3), 104.7(2) <i>102.22</i>	102.9(3) <i>102.23</i>
<i>Out-of-plane displacement</i>					
P(1)	−0.364(2) <i>0.420</i>	0.548(2) <i>0.666</i>	−0.571(1) <i>0.639</i>	−0.701(2), −0.640(2) <i>0.777</i>	0.570(2) <i>0.786</i>
Br(1)	0.472(1) <i>−0.268</i>	−0.557(1) <i>−0.581</i>	0.431(1) <i>−0.504</i>	0.691(1), 0.645(1) <i>−0.601</i>	−0.636(1) <i>−0.606</i>
<i>Central naphthalene ring torsion angles</i>					
C:(13)-(14)-(19)-(18)	174.2(4) <i>−176.46</i>	172.3(7) <i>−173.01</i>	178.0(4) <i>−173.42</i>	171.6(5), 173.1(5) <i>−172.34</i>	176.0(4) <i>−172.29</i>
C:(15)-(14)-(19)-(10)	174.6(5) <i>−175.88</i>	172.4(7) <i>−170.01</i>	173.4(3) <i>−172.15</i>	169.3(5), 169.8(5) <i>−170.41</i>	172.5(5) <i>−170.26</i>

Table 1. cont.

Compound	1b	2b·I [−]	3b	4b	5b
E	-	CH ₃	O	S	Se
<i>Peri-region-distances</i>					
P(1)-Br(1)	3.225(2), 3.212(2) 3.213	3.435(4) 3.460	3.372(2) 3.353	3.445(1) 3.449	3.442(3) 3.460
<i>Peri-region bond angles</i>					
Br(1)-C(10)-C(19)	122.8(3), 123.1(3) 123.51	121.5(9) 123.73	122.9(2) 124.05	124.9(3) 124.28	125.7(4) 124.23
C(10)-C(19)-C(18)	131.1(3), 131.3(3) 131.08	132(1) 132.40	131.9(3) 131.58	132.3(3) 131.96	131.7(5) 131.98
P(1)-C(18)-C(19)	124.1(3), 123.0(3) 123.65	126.1(9) 127.87	125.9(2) 126.89	127.1(2) 126.58	127.0(4) 126.62
Σ of bay angles	378.0(9), 377.4(9) 378.24	380(3) 384.00	380.7(7) 382.52	384.3(8) 382.82	384(2) 382.83
Splay angle ^a	18, 17 18.24	20 24.00	20.7 22.52	24.3 22.82	24 22.83
C(20)-P(1)-C(30)	100.3(3), 100.9(2) 101.46	107.8(5) 106.47	102.8(2) 102.75	101.0(2) 101.71	102.2(2) 101.74
<i>Out-of-plane displacement</i>					
P(1)	0.208(2), 0.219(1) 0.177	0.671(4) 0.395	−0.466(1) 0.151	−0.050(1) 0.476	0.074(2) 0.505
Br(1)	0.019(1), −0.195(1) −0.043	−0.370(2) −0.347	0.146(1) −0.056	0.251(1) −0.314	0.011(1) −0.338
<i>Central acenaphthalene ring torsion angles</i>					
C:(13)-(14)-(19)-(18)	180.0(4), 179.4(4) −179.16	174(2) −176.71	178.5(4) −179.22	177.0(3) −176.48	176.3(6) −176.23
C:(15)-(14)-(19)-(10)	179.2(4), 177.0(4) −179.66	173(2) −174.19	174.6(4) −179.38	179.2(3) −175.27	176.7(6) −174.84

Table 1. **cont.**

Compound	1c	2c·I[−]	3c	4c	5c
E	-	CH ₃ ⁺	O	S	Se
<i>Peri-region bond angles</i>					
Br(1)-C(10)-C(19)	120.24	120.52	120.33	120.35	120.35
C(10)-C(19)-C(18)*	123.18	122.45	123.03	122.80	122.75
P(1)-C(18)-C(19)	118.60	122.06	120.09	121.24	121.48
C(20)-P(1)-C(30)	102.43	108.74	106.04	104.45	104.35
<i>Out-of-plane displacement</i>					
P(1)	0.024	−0.146	0.104	−0.020	−0.033
Br(1)	−0.027	−0.024	0.027	0.021	0.019
<i>Central acenaphthalene ring torsion angles</i>					
C:(13)-(14)-(19)-(18)	−178.71	−179.22	−178.76	−179.08	−179.23
C:(15)-(14)-(19)-(10)	−178.89	−178.18	−178.76	−179.07	−179.04

^a Splay angle: Σ of the three bay region angles − 360. * (Br)-CCC

Table 2. Bond topological parameters of computed **1a - 1c** and **5a - 5c**.

	atom-atom	$\rho(\mathbf{r})_{\text{bcp}}$ [eÅ ⁻³]	$\Delta\rho(\mathbf{r})_{\text{bcp}}$ [eÅ ⁻⁵]	d_1 [Å]	d_2 [Å]	ε	$G/\rho(\mathbf{r})_{\text{bcp}}$ [he ⁻¹]	$H/\rho(\mathbf{r})_{\text{bcp}}$ [he ⁻¹]	d [Å]
1a	Br-C10	1.10	-3.8	1.045	0.856	0.07	0.35	-0.59	1.900
	P-C18	1.03	-6.4	0.762	1.099	0.14	0.49	-0.92	1.861
	P-C20	1.07	-6.3	0.744	1.099	0.16	0.55	-0.96	1.844
	P-C30	1.08	-6.3	0.739	1.098	0.16	0.97	-0.56	1.837
	Br-P	0.13	1.0	1.639	1.516	0.09	0.56	-0.01	3.147
	Br-P (rcp)	0.08	1.2	-	-	-	0.90	0.19	-
1b	Br-C10	1.10	-3.8	1.045	0.855	0.07	0.35	-0.59	1.900
	P-C18	1.04	-6.0	0.748	1.106	0.16	0.54	-0.94	1.854
	P-C20	1.07	-6.0	0.739	1.103	0.16	0.57	-0.96	1.843
	P-C30	1.08	-6.1	0.738	1.100	0.15	0.57	-0.97	1.838
	Br-P	0.12	1.0	1.667	1.556	0.09	0.56	0.01	3.213
	Br-P (rcp)	0.07	1.1	-	-	-	0.88	0.20	-
1c	C20-H17	0.11	1.4	1.430	1.042	3.86	0.78	0.14	2.359
	C20-H17 (rcp)	0.11	1.5	-	-	-	0.83	0.15	-
1c	Br-C13	1.10	-3.8	1.047	0.855	0.07	0.35	-0.59	1.902
	P-C18	1.07	-6.0	0.742	1.102	0.17	0.56	-0.96	1.844
	P-C20	1.08	-6.0	0.736	1.101	0.14	0.59	-0.97	1.836
	P-C30	1.08	-6.1	0.739	1.100	0.15	0.57	-0.97	1.839
	Br-H15	0.10	1.2	1.673	1.046	1.71	0.77	0.14	2.690
	P-H10	0.10	1.1	1.567	1.047	1.53	0.70	0.10	2.594
	Br-H15 (rcp)	0.10	1.4	-	-	-	0.88	0.17	-
	P-H10 (rcp)	0.10	1.3	-	-	-	0.82	0.14	-
5a	Br-C10	1.12	-3.9	1.037	0.856	0.07	0.35	-0.60	1.893
	P-C18	1.08	-8.4	0.777	1.079	0.06	0.38	-0.93	1.855
	P-C20	1.12	-8.4	0.754	1.088	0.05	0.45	-0.98	1.841
	P-C30	1.15	-8.5	0.744	1.083	0.06	0.48	-1.00	1.827
	P-Se	0.93	-2.3	1.065	1.045	0.03	0.42	-0.59	2.110
	Br-P	0.08	0.8	1.786	1.632	20.65	0.63	0.08	3.399
	Br-P (r)	0.08	0.8	-	-	-	0.64	0.09	-
	Br-C30	0.08	0.9	1.778	1.528	5.04	0.65	0.13	3.264
	Br-C30 (rcp)	0.06	0.9	-	-	-	0.81	0.18	-
	C20-H17	0.12	1.5	1.382	0.977	1.68	0.76	0.13	2.324
	C20-H17 (rcp)	0.11	1.6	-	-	-	0.86	0.14	-

Table 2. cont.

5b	Br-C10	1.12	-3.9	1.037	0.856	0.07	0.35	-0.60	1.893
	P-C18	1.10	-8.7	0.785	1.062	0.07	0.36	-0.92	1.847
	P-C20	1.12	-8.6	0.761	1.082	0.05	0.42	-0.96	1.843
	P-C30	1.15	-8.5	0.744	1.084	0.07	0.48	-1.00	1.827
	P-Se	0.93	-2.3	1.065	1.046	0.01	0.42	-0.59	2.111
	Br-P (vir) [§]	0.07	0.7	1.782	1.691	2.20	0.62	0.09	3.460
	Br-C30	0.08	0.9	1.782	1.500	1.56	0.64	0.13	3.272
	Br-C30 (rcp)	0.06	0.8	-	-	-	0.82	0.20	-
	Br-Se	0.07	0.7	1.803	1.992	50.20	0.57	0.09	3.666
	Br-Se (rcp)	0.07	0.7	-	-	-	0.59	0.08	-
	C20-H17	0.12	1.5	1.369	0.944	0.99	0.75	0.12	2.291
	C20-H17 (rcp)	0.12	1.7	-	-	-	0.88	0.14	-
5c	Br-C10	1.10	-3.8	1.047	0.854	0.07	0.35	-0.59	1.901
	P-C18	1.13	-8.1	0.744	1.089	0.07	0.49	-0.99	1.833
	P-C20	1.13	-8.4	0.748	1.084	0.05	0.47	-0.99	1.832
	P-C30	1.14	-8.3	0.744	1.085	0.07	0.48	-1.00	1.828
	P-Se	0.93	-2.3	1.065	1.048	0.01	0.41	-0.59	2.113
	Br-H15	0.10	1.3	1.667	1.034	1.41	0.76	0.14	2.674
	P-H10	0.08	0.9	1.651	1.091	4.51	0.70	0.11	2.716
	Br-H15 (rcp)	0.10	1.5	-	-	-	0.89	0.17	-
	P-H10 (rcp)	0.08	1.0	-	-	-	0.77	0.13	-

For all bonds, $\rho(\mathbf{r})_{\text{bcp}}$ is the electron density at the bond critical point, $\Delta\rho(\mathbf{r})_{\text{bcp}}$ is the corresponding Laplacian, d_1 and d_2 are the distances from the atom to the bond critical point, ε is the bond ellipticity ($\varepsilon = \lambda_1/\lambda_2 - 1$; $\lambda_{1/2}$: curvatures perpendicular to the bond path), $G/\rho(\mathbf{r})_{\text{bcp}}$ and $H/\rho(\mathbf{r})_{\text{bcp}}$ are the kinetic and total energy density over $\rho(\mathbf{r})_{\text{bcp}}$ ratios. Results obtained by an analysis of the wavefunction files with AIM2000.[90] § In the corresponding viral field a Br-P bond critical point is observed.

Table 3. Atomic/fragmental AIM Q(001) charges (in e) of the theoretical models.

	Nap / Ace [§]	Ph(ax)	Ph(eq)	Br	P	E
1a	−0.17	−0.40	−0.33	0.01	1.47	—
1b	−0.13	−0.30	−0.33	0.00	1.50	—
1c	−0.18	−0.30	−0.31	0.00	1.50	—
2a	0.00	−0.19	−0.19	0.00	2.35	−0.27
2b	0.07	−0.21	−0.28	0.00	2.37	−0.29
2c	−0.09	−0.17	−0.19	0.07	2.41	−0.29
3a	−0.17	−0.31	−0.31	0.03	2.92	−1.45
3b	−0.12	−0.33	−0.31	0.03	2.93	−1.45
3c	−0.19	−0.29	−0.30	0.00	2.94	−1.46
4a	−0.12	−0.24	−0.27	0.01	2.02	−0.65
4b	−0.06	−0.30	−0.24	0.00	2.01	−0.66
4c	−0.16	−0.24	−0.28	0.01	2.08	−0.66
5a	−0.11	−0.24	−0.25	0.00	1.73	−0.62
5b	−0.07	−0.28	−0.33	−0.01	1.74	−0.56
5c	−0.14	−0.23	−0.26	0.00	1.79	−0.40

§ naphthyl or acenaphthyl fragment

Table 4. Electron populations (in e) of the bonding and lone pair basins of the Br atom and the PPh₂E fragment in the theoretical models.

model	Br-C10	Σ LP(Br)	no.	P-C18	P-C20	P-C30	P-E/LP	no.	Σ LP(E)/H	no.
1a	1.55	6.54	3	2.16	2.15	2.15	2.05	1	–	–
1b	1.54	6.55	3	2.17	2.15	2.15	2.06	1	–	–
1c	1.54	6.55	3	2.15	2.14	2.14	2.05	1	–	–
2a	1.54	6.56	3	2.28	2.23	2.25	1.99	1	5.87	3
2b	1.53	6.57	3	2.30	2.24	2.25	1.99	1	5.86	3
2c	1.60	6.50	2	2.28	2.26	2.25	1.99	1	5.85	3
3a	1.58	6.53	1	2.28	2.24	2.25	1.61	2	6.13	2
3b	1.57	6.53	3	2.28	2.25	2.24	1.58	2	6.15	2
3c	1.54	6.55	3	2.26	2.25	2.25	1.60	1	6.13	2
4a	1.58	6.56	2	2.25	2.20	2.21	2.02	1	5.76	2
4b	1.57	6.55	2	2.25	2.21	2.20	2.01	1	5.77	3
4c	1.54	6.55	3	2.22	2.21	2.22	2.00	1	5.78	3
5a	1.58	6.54	2	2.24	2.19	2.20	2.16	1	5.93	2
5b	1.57	6.55	2	2.24	2.20	2.19	2.16	1	5.92	3
5c	1.54	6.54	3	2.22	2.20	2.21	2.14	1	5.94	3

Table 5. ELI-D properties of the C–C bonding basins of the naphthalene and acenaphthene fragments in the theoretical models.

bond	$V_{(001)}$	$N_{(001)}$	$Y_{\max}$	d_{ELI}	$V_{(001)}$	$N_{(001)}$	$Y_{\max}$	d_{ELI}	$V_{(001)}$	$N_{(001)}$	$Y_{\max}$	d_{ELI}
1a				1b				1c				
C10–C19	6.5	2.65	1.86	0.030	7.0	2.68	1.86	0.063	6.9	2.68	1.86	0.051
C19–C18	6.5	2.58	1.88	0.010	6.3	2.55	1.86	0.045	6.5	2.55	1.86	0.033
C17–C18	10.2	2.95	1.82	0.005	9.0	2.94	1.80	0.023	8.6	2.92	1.80	0.035
C17–C16	6.6	2.56	1.87	0.010	6.7	2.58	1.86	0.006	6.6	2.56	1.87	0.012
C15–C16	9.2	2.94	1.80	0.003	10.2	3.00	1.82	0.040	10.2	2.96	1.82	0.016
C14–C15	5.7	2.52	1.86	0.010	6.2	2.56	1.88	0.035	6.2	2.55	1.88	0.013
C14–C13	6.6	2.60	1.88	0.006	6.5	2.59	1.87	0.038	6.4	2.58	1.88	0.012
C13–C12	10.2	2.95	1.82	0.010	10.0	2.99	1.82	0.039	10.1	2.95	1.82	0.020
C10–C12	6.7	2.57	1.86	0.007	6.9	2.60	1.86	0.003	6.8	2.59	1.86	0.016
C10–C11	9.8	3.08	1.81	0.020	9.7	3.08	1.81	0.004	9.5	3.06	1.81	0.028
C14–C19	6.7	2.57	1.87	0.001	6.5	2.58	1.87	0.003	6.7	2.57	1.86	0.002
5a				5b				5c				
C10–C19	6.5	2.65	1.87	0.029	7.1	2.70	1.86	0.067	6.6	2.68	1.86	0.056
C19–C18	6.5	2.57	1.88	0.007	6.2	2.52	1.86	0.052	6.1	2.52	1.86	0.040
C17–C18	10.2	2.95	1.82	0.006	9.4	2.96	1.80	0.048	9.1	2.95	1.80	0.064
C17–C16	6.5	2.55	1.87	0.006	6.6	2.57	1.87	0.020	6.5	2.54	1.87	0.037
C15–C16	9.4	2.95	1.80	0.019	10.1	2.99	1.82	0.042	10.2	2.96	1.82	0.036
C14–C15	5.7	2.52	1.86	0.016	6.2	2.55	1.88	0.039	6.1	2.54	1.89	0.025
C14–C13	6.6	2.60	1.88	0.008	6.5	2.60	1.87	0.039	6.5	2.58	1.88	0.016
C13–C12	10.1	2.94	1.82	0.010	9.9	2.97	1.82	0.043	10.0	2.94	1.82	0.039
C11–C12	6.7	2.57	1.86	0.006	7.0	2.62	1.86	0.018	6.9	2.59	1.86	0.033
C10–C11	9.7	3.08	1.81	0.020	9.5	3.05	1.81	0.027	9.4	3.04	1.82	0.050
C14–C19	6.8	2.58	1.87	0.002	6.6	2.58	1.87	0.004	6.9	2.59	1.86	0.005

For all basins, $V(001)$ is the basin volume cut at 0.001 a.u., $N(001)$ is the corresponding electron population in that volume, $Y_{\max}$ is the ELI-D value at the attractor position, d_{ELI} is the perpendicular distance of the attractor position to the atom-atom line. Results obtained by analysis of grid-files using DGRID-4.5.[91] The grid step size is 0.04 bohr.

Table 6. Crystal data and structure refinement of **1a** - **5a** and **1b** - **5b**

	1a	1b	2a · 1/2 hexane	2b · 1/2 CH ₂ Cl ₂
Formula	C ₂₂ H ₁₆ BrP	C ₂₄ H ₁₈ BrP	C ₂₇ H ₂₄ BrIP	C _{25.5} H ₂₂ BrClIP
Formula weight, g mol ⁻¹	391.23	417.26	586.24	601.66
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Crystal size, mm	1.0×0.8×0.6	0.8×0.5×0.3	1.0×0.6×0.5	1.0×0.2×0.1
Space group	P2 ₁ /c	P-1	C2/c	C2/c
<i>a</i> , Å	10.486(3)	9.646(2)	23.430(5)	14.399(5)
<i>b</i> , Å	15.687(3)	12.110(2)	10.232(4)	20.559(7)
<i>c</i> , Å	10.854(2)	17.271(2)	20.461(4)	16.379(8)
α , °	90	80.88(1)	90	90.00
β , °	105.95(2)	83.34(1)	98.05(1)	96.84(4)
γ , °	90	70.84(1)	90	90.00
<i>V</i> , Å ³	1716.7(7)	1877.2(5)	4857(2)	4814(3)
<i>Z</i>	4	4	8	8
ρ_{calcd} , Mg m ⁻³	1.514	1.476	1.603	1.660
μ (Mo <i>K</i> α), mm ⁻¹	2.487	2.279	3.042	3.178
<i>F</i> (000)	792	848	2312	2360
θ range, deg	2.60 to 27.50	2.61 to 27.50	2.85 to 27.50	2.50 to 22.51
Index ranges	-13 ≤ <i>h</i> ≤ 13	-12 ≤ <i>h</i> ≤ 12	-8 ≤ <i>h</i> ≤ 30	-15 ≤ <i>h</i> ≤ 9
	0 ≤ <i>h</i> ≤ 20	-15 ≤ <i>h</i> ≤ 15	-13 ≤ <i>h</i> ≤ 13	-6 ≤ <i>h</i> ≤ 22
	0 ≤ <i>h</i> ≤ 14	0 ≤ <i>h</i> ≤ 22	-26 ≤ <i>h</i> ≤ 26	-17 ≤ <i>h</i> ≤ 17
No. of reflns collected	3902	8525	6690	3904
Completeness to θ_{max}	98.9%	98.7%	98.8%	99.5%
No. indep. Reflns	3902	8525	5523	3148
No. obsd reflns with (<i>I</i> > 2 σ (<i>I</i>))	2692	6099	4102	1876
No. refined params	217	469	268	282
GooF (<i>F</i> ²)	0.840	1.075	1.024	0.971
<i>R</i> ₁ (<i>F</i>) (<i>I</i> > 2 σ (<i>I</i>))	0.0558	0.0530	0.0557	0.0670
<i>wR</i> ₂ (<i>F</i> ²) (all data)	0.1776	0.1492	0.1578	0.1643
Largest diff peak/hole, e Å ⁻³	0.635 / -0.922	0.707 / -1.348	0.710 / -2.595	0.802 / -0.897
CCDC number	941919	941220	941221	941222

Table 6. cont.

	3a	3b · 1/2 hexane	4a	4b
Formula	C ₂₂ H ₁₆ BrOP	C ₂₇ H ₂₅ BrOP	C ₂₂ H ₁₆ BrPS	C ₂₄ H ₁₈ BrPS
Formula weight, g mol ⁻¹	407.23	476.35	423.29	449.32
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Crystal size, mm	0.4×0.3×0.2	0.4×0.3×0.2	0.5×0.4×0.3	0.9×0.6×0.6
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	Pna2 ₁
<i>a</i> , Å	8.6407(17)	18.085(3)	18.539(4)	7.8916(9)
<i>b</i> , Å	17.282(4)	10.2819(19)	12.063(2)	14.148(5)
<i>c</i> , Å	12.599(3)	12.056(4)	17.930(4)	17.6186(18)
α , °	90	90	90	90
β , °	110.04(3)	98.293(17)	108.63(3)	90
γ , °	90	90	90	90
<i>V</i> , Å ³	1767.4(6)	2218.4(9)	3799.8(13)	1967.1(8)
<i>Z</i>	4	4	8	4
ρ_{calcd} , Mg m ⁻³	1.530	1.426	1.480	1.517
μ (Mo <i>K</i> α), mm ⁻¹	2.423	1.942	2.359	2.283
<i>F</i> (000)	824	980	1712	912
θ range, deg	0.94 to 25.96	0.98 to 25.99	2.05 to 26.01	2.88 to 27.51
Index ranges	-10 ≤ <i>h</i> ≤ 15	-22 ≤ <i>h</i> ≤ 22	-21 ≤ <i>h</i> ≤ 22	0 ≤ <i>h</i> ≤ 10
	-21 ≤ <i>h</i> ≤ 21	-12 ≤ <i>h</i> ≤ 12	-14 ≤ <i>h</i> ≤ 14	0 ≤ <i>h</i> ≤ 18
	-15 ≤ <i>h</i> ≤ 15	-14 ≤ <i>h</i> ≤ 14	-20 ≤ <i>h</i> ≤ 21	-22 ≤ <i>h</i> ≤ 22
No. of reflns collected	14718	15717	28478	4517
Completeness to θ_{max}	94.0%	97.9%	92.7%	99.8%
No. indep. Reflns	3257	4281	6930	4517
No. obsd reflns with (<i>I</i> > 2 σ (<i>I</i>))	2475	3240	4332	3888
No. refined params	226	272	451	244
GooF (<i>F</i> ²)	0.965	1.002	0.886	1.005
<i>R</i> ₁ (<i>F</i>) (<i>I</i> > 2 σ (<i>I</i>))	0.0354	0.0388	0.0458	0.0345
<i>wR</i> ₂ (<i>F</i> ²) (all data)	0.0987	0.0966	0.1116	0.0806
Largest diff peak/hole, e Å ⁻³	0.407 / -0.704	1.311 / -0.559	0.662 / -0.339	0.298 / -0.586
CCDC number	941223	941224	941225	941226

Table 6. cont.

	5a	5b
Formula	C ₂₂ H ₁₆ BrPSe	C ₂₄ H ₁₈ BrPSe
Formula weight, g mol ⁻¹	470.19	496.22
Crystal system	monoclinic	triclinic
Crystal size, mm	0.5×0.4×0.3	0.9×0.6×0.4
Space group	P2 ₁ /n	P-1
<i>a</i> , Å	9.5117(19)	9.076(2)
<i>b</i> , Å	11.662(2)	10.387(3)
<i>c</i> , Å	16.926(3)	11.791(4)
α , °	90	70.100(10)
β , °	98.46(3)	72.480(10)
γ , °	90	78.880(10)
<i>V</i> , Å ³	1857.1(6)	991.6(5)
<i>Z</i>	4	2
ρ_{calcd} , Mg m ⁻³	1.682	1.662
μ (Mo <i>K</i> α), mm ⁻¹	4.261	3.995
<i>F</i> (000)	928	492
θ range, deg	2.13 to 26.00	2.13 to 26.00
Index ranges	-11 ≤ <i>h</i> ≤ 11 -14 ≤ <i>h</i> ≤ 14 -20 ≤ <i>h</i> ≤ 20	-11 ≤ <i>h</i> ≤ 11 -12 ≤ <i>h</i> ≤ 12 0 ≤ <i>h</i> ≤ 15
No. of reflns collected	17491	4446
Completeness to θ_{max}	98.0%	97.5%
No. indep. Reflns	3579	4446
No. obsd reflns with (<i>I</i> > 2 σ (<i>I</i>))	2708	3487
No. refined params	226	244
GooF (<i>F</i> ²)	0.794	1.022
<i>R</i> ₁ (<i>F</i>) (<i>I</i> > 2 σ (<i>I</i>))	0.0354	0.0644
<i>wR</i> ₂ (<i>F</i> ²) (all data)	0.1110	0.1735
Largest diff peak/hole, e Å ⁻³	0.560 / -0.469	1.916 / -1.554
CCDC number	941227	941228