

# Topological properties of some PhSeX compounds

Nora Beatriz Okulik · Alicia H. Jubert ·  
Eduardo A. Castro

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**Abstract** A theoretical study on the series of compounds “PhSeX”, where Ph=phenyl, Se=selenium and X=Cl, Br, I, CN or SCN, is reported and compared with previously reported experimental data. The molecular geometry for these PhSeX compounds was studied at the DFT/B3LYP level of calculation by means of the 6-311G(d,p) basis set. The equilibrium structures of the molecules were dependent on the method employed to compare the known solid structures. A topological study of the calculated PhSeX species, based on the AIM theory, was carried out to gain a deeper insight into the bonding nature and to find an explanation for the structural diversity exhibited by these PhSeX compounds. The results reported herein illustrate the subtle differences in the solid-state structures of PhSeX compounds.

**Keywords** Topological study · DFT · Pseudohalogen · Selenium · PhSeX

## Introduction

Pseudohalogens are compounds that resemble the halogen elements,  $X_2$ , in their chemistry, e.g.,  $(CN)_2$ , cyanogen. Certain ions that have sufficient resemblance to halide ions are sometimes referred to as pseudohalide ions, e.g.,  $N_3^-$ ,  $SCN^-$ ,  $CN^-$ ,  $SeCN^-$  [1]. The pseudohalide concept [2] has been used extensively in nonmetal chemistry in both experimental and theoretical research [3].

Phenylselenenyl halides and pseudohalides (such as PhSeCN) are versatile electrophilic reagents used in a variety of organic transformations [4, 5]. Due to this behavior, a considerable body of recent work has documented the structural delineation of the nature of various phenylselenenyl compounds.

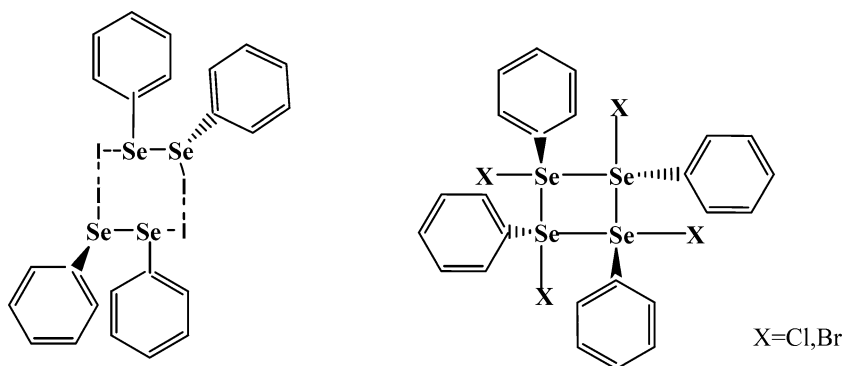
Crystallographic studies on phenylselenenyl halides, PhSeX (X=Cl, Br, I) have revealed a number of structural motifs. For example, PhSeI exists as a centrosymmetric dimer,  $(Ph_2Se_2I_2)_2$ , in the solid state [6]. Two diphenyldiselenane molecules are coupled with two  $I_2$  molecules in such a way that a slightly puckered eight-membered ring containing two Se-groups, and two  $I_2$ -groups are formed. Since the angles in this ring are alternately approximately  $90^\circ$  and  $180^\circ$ , an almost square geometry results. Diphenyldiselenane coordinates a diiodine molecule, with one selenium atom acting as donor towards an iodine atom. One selenium atom acts as a donor towards iodine (Se–I: 2.992 Å), whilst the other behaves as a weak acceptor (Se–I: 3.588 Å). This charge transfer system differs from the analogous PhSeCl and PhSeBr (see Scheme 1). Both these latter compounds consist of a tetrameric “square” structure,  $Ph_4Se_4Cl_4$  and  $Ph_4Se_4Br_4$ . The solid-state structures of PhSeCl [7] and PhSeBr [8] adopt a “square” motif where four PhSeX units are held together by weak selenium–selenium bonds to form  $Se_4$ . The Se–Se–Se angles are,

N. B. Okulik (✉)  
Universidad Nacional del Chaco Austral,  
Cte. Fernández 755,  
3700 Pcia. R. Sáenz Peña, Chaco, Argentina  
e-mail: nora@unca.edu.ar

A. H. Jubert  
CEQUINOR, Dpto. de Química, Facultad de Ciencias Exactas  
47 y 115 y Facultad de Ingeniería 1 y 47, Universidad Nacional  
de La Plata,  
1900 Buenos Aires, Argentina

E. A. Castro  
INIFTA, Dpto. de Química, Facultad de Ciencias Exactas,  
Universidad Nacional de La Plata,  
1900 Buenos Aires, Argentina

**Scheme 1** Different structural motifs observed in phenylselenenyl halides (PhSeX) compounds



however, close to the anticipated  $90^\circ$  for a square (motif) structure, forming an essentially planar ring. The conformation of the  $\text{Se}_4$  square is such that the Se–X bonds lie in the  $\text{Se}_4$  plane with two phenyl rings lying above (the plane), and two below the plane. The selenium atom therefore lies in a pseudo-trigonal bipyramidal “see-saw”. The structure is further linked through long X–X contacts to form planar sheets of selenium and bromine or chlorine atoms.

In contrast, the pseudohalogen derivatives PhSeCN and PhSeSCN consist of essentially monomeric units. In the former, the two independent molecules in the unit cell are loosely linked by  $\text{Se}\cdots\text{N}$  contacts (see Fig. 2a) with  $\text{Se}\cdots\text{N}\text{C}$  contact angles close to linearity. Both  $\text{Se}\cdots\text{N}$  interactions are slightly shorter than the sum of the van der Waals radii for selenium and nitrogen. The Se–C bonds to the cyanide groups are considerably shorter than the Se–C bonds to the phenyl rings, reflecting the increased double bond character in the Se–C bond to the cyanide groups. In PhSeSCN, the thiocyanato group is coordinated to the selenium through the sulfur atom, and it would appear that the soft selenium center prefers to bind with sulfur, rather than with the harder nitrogen atom. The thiocyanate coordination mode was confirmed in solution by  $^{13}\text{C}\{^1\text{H}\}$  NMR studies [9]. The Se–S bond length (2.221 Å) is close to the reported mean for covalent Se–S bonds (2.193 Å) [10] and the geometry of the SCN group is near linear, with S–C and  $\text{C}\equiv\text{N}$  bond lengths similar to those observed for the free  $\text{SCN}^-$  ion in KSCN [11]. The bent geometry at both the selenium and sulfur atoms reflects the presence of lone pairs on both atoms, with angles S–Se–C close to  $100^\circ$  (see Fig. 1e). In the extended structure of PhSeSCN, individual molecules stack such that a weak interaction,  $\text{Se}\cdots\text{N}$  of 3.348 Å is set up, between a Se atom of one molecule interacting with the N atom of another.

The shortest  $\text{Se}\cdots\text{N}$  interaction between adjacent stacks (3.567 Å) is slightly longer than the sum of the van der Waals radii for selenium and nitrogen (3.45 Å). The  $\text{Se}\cdots\text{N}$  contacts appear to be the dominant packing force in PhSeCN and PhSeSCN compounds, and are strong enough to preclude any formation of the weak lattice of  $\text{Se}_4$  squares favored by  $\text{Ph}_4\text{Se}_4\text{Cl}_4$  and  $\text{Ph}_4\text{Se}_4\text{Br}_4$ .

We previously reported a detailed theoretical and topological study of some pseudohalogen compounds [12, 13]. As part of a more general study on pseudohalide compounds, we report here a topological analysis of the phenyl series of compounds, PhSeX (X=halides and pseudohalides) in an attempt to find an explanation for the structural diversity exhibited by these PhSeX compounds.

Due to the fact that spectroscopic studies suggest that all these compounds exist as monomers in solution, in this paper we presented theoretical calculations in the gas phase in order to compare the results with experimental data. Different conformers of some of these compounds can be analyzed, although herein we report results from the study performed only on the lowest energy conformers.

A notable point in the present study is the use of density charge analysis based on the atoms-in-molecules ((AIM) theory to better explain chemical bonding character, since this procedure has proven extremely useful for this purpose.

### Methods of calculation and computational details

Molecular geometries were optimized within the density functional theory (DFT) approach [14–16] at the B3LYP/6-311G(d,p) level. The B3LYP is a hybrid functional method based on the Becke’s three-parameter nonlocal exchange functional [17], with nonlocal correlation according to Lee et al. [18]. X-ray geometry was used as the starting input file. X-ray crystallographic data, with files in CIF format, for structures 1 and 2 were retrieved of the Cambridge Crystallographic Data Centre (CCDC 268776 and 268777) [19]. Densities used for topological analysis were obtained through single-point calculations on the above optimized geometries at the B3LYP/6-311++G(d,p) level. For iodine, we used the 6-311G(d) [20, 21] basis set, due to the fact that neither the 6-311G(d,p) nor 6-311++G(d,p) basis set are available for this atom. Frequency calculations were performed with the aim of assessing the nature of the stationary points. All calculations were carried out with the Gaussian 2003 package [22]. The analysis of the charge

electron density was performed using the PROAIM package [23].

Finally, in order to get the best possible agreement between calculated and observed structures, the root mean square deviation (RMSD) between the coordinates were calculated using the Qmol program [24]. With the results obtained, we think that some of the patterns followed in the analysis and interpretation of charge density of PhSeX compounds could be useful for the theoretical study of other derivatives.

### AIM analysis

AIM theory [25], which is based on the critical points (CP) of the electronic density,  $\rho(\mathbf{r})$ , reveals insights into the nature of bonds. CPs are points where the gradient of the electronic density,  $\nabla\rho(\mathbf{r})$ , vanishes and are characterized by the three eigenvalues ( $\lambda_1, \lambda_2, \lambda_3$ ) of the Hessian matrix of  $\rho(\mathbf{r})$ . The CPs are labeled as  $(r,s)$  according to their rank,  $r$  (number of nonzero eigenvalues), and signature,  $s$  (the algebraic sum of the signs of the eigenvalues).

Four types of CP are of interest in molecules:  $(3, -3)$ ,  $(3, -1)$ ,  $(3, +1)$ , and  $(3, +3)$ . A  $(3, -3)$  point corresponds to a maximum in  $\rho(\mathbf{r})$  and appears generally at nuclear positions. A  $(3, +3)$  point indicates electronic charge depletion and is known as a cage CP.  $(3, +1)$  points, or ring CPs, are merely saddle points. Finally, a  $(3, -1)$  point, or bond critical point (BCP), is generally found between two neighboring nuclei indicating the existence of a bond between them.

Several properties that can be evaluated at the BCP constitute very powerful tools to classify the interactions between two fragments.

The two negative eigenvalues of the Hessian matrix ( $\lambda_1$  and  $\lambda_2$ ) at the BCP measure the degree of contraction of  $\rho(\mathbf{r})$  perpendicular to the bond towards the CP, while the positive eigenvalue ( $\lambda_3$ ) measures the degree of contraction parallel to the bond and from the BCP towards each of the neighboring nuclei. Different values of  $\lambda_1$  and  $\lambda_2$  at  $(3,-1)$  BCPs denote an anisotropic spread of electrons quantified through the concept of ellipticity:  $\varepsilon = \lambda_1/\lambda_2 - 1$ , (with  $\lambda_1 > \lambda_2$ ) where values of  $\varepsilon \gg 1$  can be indicative of  $\pi$  bonding. Calculated properties of electronic density at the BCP are labeled with the subscript 'b' throughout this work.

In AIM theory, atomic interactions are classified according to two limiting behaviors, namely, shared interactions and closed-shell interactions. Shared interactions are characteristic of covalent and polarized bonds and their main features are large values of  $\rho_b$ ,  $\nabla^2\rho_b < 0$  and  $E_b < 0$ ,  $E_b$  being the local electronic energy density of the system calculated at the BCP and defined as the sum of the local kinetic energy density and the local potential energy density, both computed at the BCP. In contrast, closed-shell interactions,

useful to describe ionic bonds, hydrogen bonds, and van der Waals interactions, are characterized by small values of  $\rho_b$ ,  $\nabla^2\rho_b > 0$  and  $E_b > 0$ .

## Results and discussion

### Geometric analysis

The optimized structures of single molecules of PhSeX (X = Cl, Br, I, CN and SCN) compounds in gas phase are shown in Fig. 1. Figure 2a shows the calculated structure of the two independent molecules in the unit cell of PhSeCN. The optimized structure of the square motif adopted by  $\text{Ph}_4\text{Se}_4\text{Cl}_4$  in the solid-state structure is displayed in Fig. 2b. Selected bond lengths and bond angles are shown in both figures.

Although the lowest energy conformers of the calculated structures are highly symmetric, small differences between the crystal data and theoretical values are observed. These differences can be assigned to the fact that the X-ray structures were measured in a compacted crystalline form, whereas the calculations were performed for free isolated molecules.

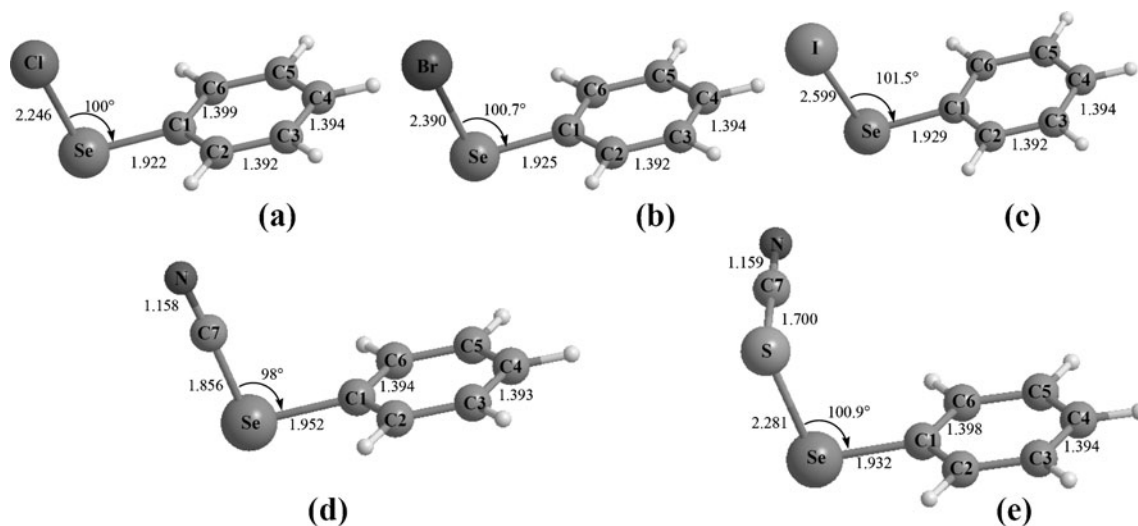
A common measure of conformational similarity in structural bioinformatics is the minimum RMSD between the coordinates of two macromolecules. Using this idea, we think that the close structural relationship between the calculated and crystallographic observed structures is best illustrated with the RMSD overlay error than by comparing the paired lengths bonds, bond angles and torsion angles.

In this paper, we shall consider a general framework for feature comparison based on the following:

1. In the isolated molecules, alignment is considered good if (a) the molecules have a similar shape, and (b) their aromatic atoms and Se atoms overlap.
2. In the dimeric structure observed for PhSeCN, and in the tetrameric structure of  $\text{Ph}_4\text{Se}_4\text{Cl}_4$ , an alignment is good if (a) the molecules have a similar shape, and (b) their Se atoms and the groups attached to Se atoms overlap.

These statements can be justified as follows: in the first case the solid state interactions are rather different because of the possibility of rotation of the side chain. So, benzene ring superposition becomes more important. On the contrary, in dimeric and tetrameric structures the interaction between Se atoms and the groups attached to Se atoms are more important than the benzene rings.

The calculated halogenated structures agree satisfactorily with the corresponding experimental structures. For example, RMS is 0.05 in PhSeCl while it is only 0.025 for PhSeBr and 0.020 for PhSeI. A good alignment is also observed for other calculated isolated structures. RMS



**Fig. 1** Optimized structures of **a** PhSeCl, **b** PhSeBr, **c** PhSeI, **d** PhSeCN and **e** PhSeSCN calculated at the B3LYP/6-311++G(d,p) level. For iodine, we used the 6-311G(d) the B3LYP/6-311++G\* level. The atomic labeling scheme and selected geometric parameters are indicated

overlay error is 0.025 for PhSeCN and only 0.017 for PhSeSCN. The optimized structures of the isolated molecules are superimposed on the crystallographic structures in

**Fig. 2** Optimized structures of **a** the two independent molecules in the unit cell of PhSeCN, and **b** the square motif adopted by Ph<sub>4</sub>Se<sub>4</sub>Cl<sub>4</sub> in the solid-state structure, calculated at B3LYP/6-311++G(d,p). The atomic labeling scheme and bond lengths are indicated

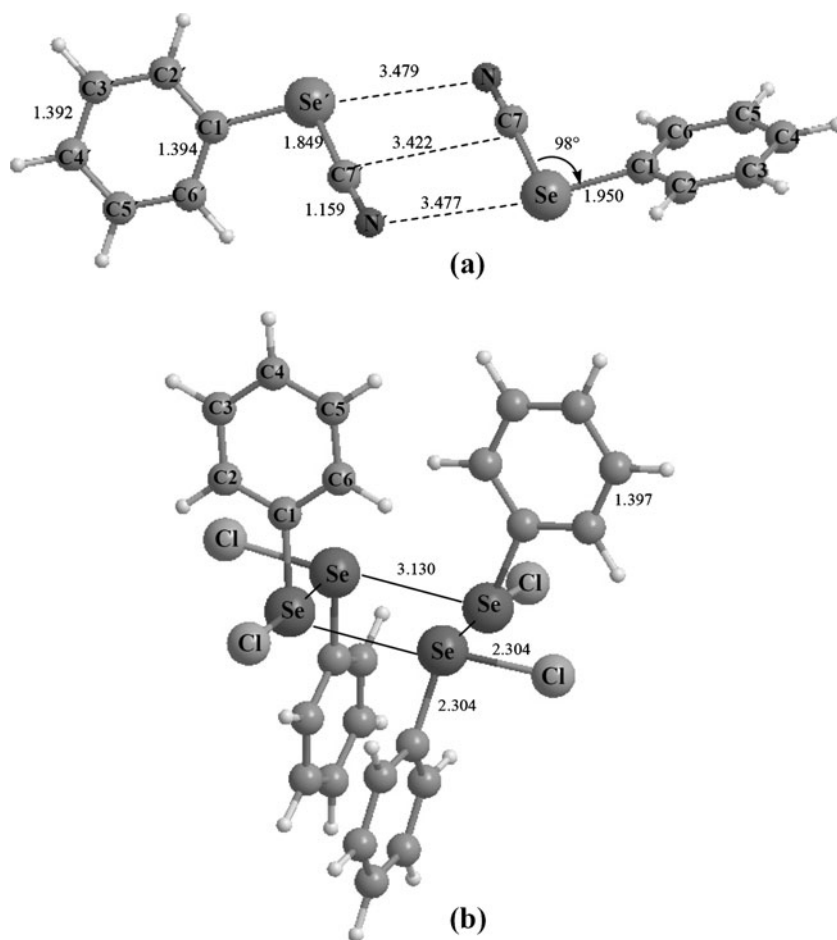
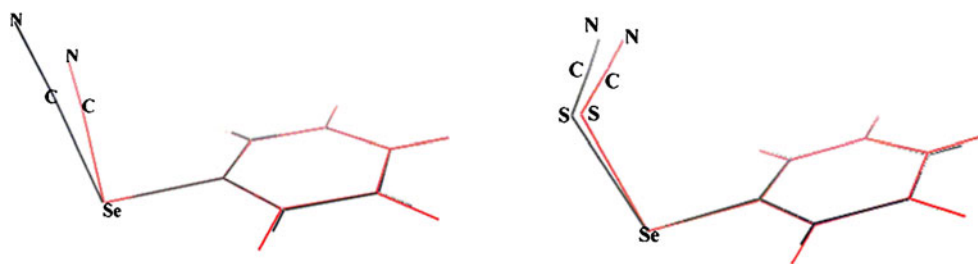


Fig. 3. It can be seen that the molecules have a similar shape and the benzene rings and Se atoms overlap completely.

**Fig. 3** Overlaid structures of the calculated (*grey*) and solid state (*red*) structures of PhSeCN (*left*) and PhSeSCN (*right*)



The  $\text{Se}\cdots\text{N}$  bonds between the two molecules of PhSeCN optimized as a dimer are somewhat longer (3.477 Å and 3.479 Å) than that in the crystal (3.329 or 3.444 Å). A RMSD value of 0.119 is obtained in the alignment of the dimeric structures. This low RMSD value reveals a good alignment due to the similar shape of the molecules and the fact that the Se, C and N atoms overlap (Fig. 4, left).

The increased RMS overlay error of the tetrameric structure of  $\text{Ph}_4\text{Se}_4\text{Cl}_4$  (0.414) is most probably due to the increased number of atoms that must overlap; many of them belong to non-rigid structures but have four benzene rings with side chains with free rotation. According to the conventions adopted for comparison, in this case, Se atoms and the groups attached to Se atoms overlap each other but do not overlap benzene rings because preference was given to overlap of the side chains rather than rings, as illustrated in Fig. 4 (right). However, the RMSD value is acceptable for the alignment of both structures.

In summary, the results of these quantum chemical calculations overall correctly describe, to a good approximation, the experimentally observed peculiarities in molecular structures of the different species studied.

#### Topological analysis of electron density

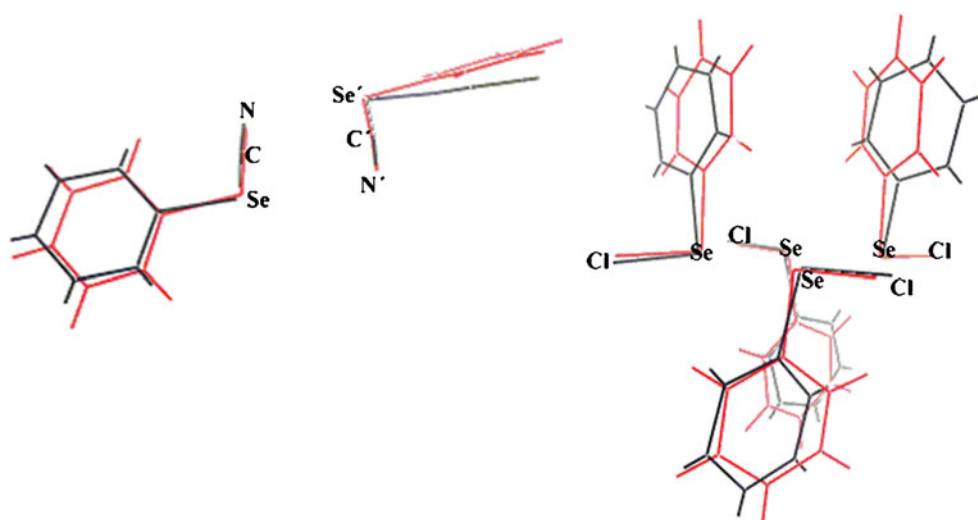
Table 1 presents characteristics of the BCPs obtained from topological analysis of the electron density distributions of

the PhSeX (X=Cl, Br, I, CN and SCN) species studied. As mentioned in the section above on [Methods of calculation and computational details](#), the basis set employed for iodine [6-311G(d)] is different from that used for the rest of the atoms [6-311G(d,p)]. In order to check the sensibility of AIM results to the different basis set employed for iodine, for bromine compound, we performed AIM calculations with both basis sets, with similar results (Table 1). We consider, therefore, that we can safely analyze the trend of AIM results along the series, even when using a slightly different basis set for the iodine atom.

Topological analysis of BCPs in  $\rho$  of PhSeX (X=Cl, Br, I, CN, SCN) reveals that all bonds forming the phenyl ring correspond to covalent interactions, namely, a relatively large value for  $\rho_b$  and a negative value for  $\nabla^2\rho_b$ . The ellipticities of bonds forming the ring have relatively large numerical values, revealing their partial double bond character due electronic charge delocalization over the ring surface. The  $E_b$  values are negative as expected for covalent bonds. The topologic properties computed on C–C BCPs of the benzene ring are only slightly affected by the halogen atom, CN group or SCN group attached to selenium atom (at the same level of calculation in a C–C bond of benzene, they are:  $\rho_b=0.3092$  a.u.,  $\nabla^2\rho_b=-0.8640$  a.u.,  $\epsilon=0.1999$  and  $E_b=-0.3162$  a.u.).

Details of the electron density topology at the CP can provide more insight into the nature of a particular bond.

**Fig. 4** Overlaid structures of the calculated (*grey*) and solid state (*red*) structures of dimer  $(\text{PhSeCN})_2$  (*left*) and tetramer  $\text{Ph}_4\text{Se}_4\text{Cl}_4$  (*right*)





**Table 1** Topological properties of charge density<sup>a,b</sup> calculated at some bond critical points (BCPs) of phenylselenenyl halides (PhSeX; X=Cl, Br, I, CN, SCN)

Compound	Bond <sup>c</sup>	$\rho_b$	$\nabla^2\rho_b$	$\varepsilon$	$E_b$
PhSeCl	C1-C2	0.3061	-0.8422	0.1943	-0.3094
	C1-Se	0.1527	-0.1061	0.0696	-0.0871
	Se-Cl	0.0981	0.0490	0.1408	-0.0350
PhSeBr	C1-C2	0.3061 (0.3063)	-0.8415 (-0.8427)	0.1952 (0.1950)	-0.3092 (-0.3096)
	C1-Se	0.1511 (0.1513)	-0.1020 (-0.1023)	0.0620 (0.0618)	-0.0854 (-0.0857)
	Se-Br	0.0887 (0.0876)	0.0119 (0.0120)	0.1326 (0.1328)	-0.0315 (-0.0314)
PhSeI	C1-C2	0.3062	-0.8419	0.1970	-0.3096
	C1-Se	0.1495	-0.0976	0.0501	-0.0837
	Se-I	0.0744	-0.0040	0.1143	-0.0240
PhSeCN	C1-C2	0.3082	-0.8511	0.2097	-0.3145
	C1-Se	0.1448	-0.1071	0.0572	-0.0782
	Se-C7	0.1595	-0.0265	0.1919	-0.1035
	C7-N	0.4724	-0.2263	0.0116	-0.8536
PhSeSCN	C1-C2	0.3063	-0.8419	0.1988	-0.3101
	C1-Se	0.1499	-0.1032	0.0456	-0.0840
	Se-S	0.0999	0.0090	0.0649	-0.0369
	S-C7	0.2090	-0.3845	0.3608	-0.2396
	C7-N	0.4715	-0.2848	0.0085	-0.8492

<sup>a</sup>  $\rho_b$ ,  $\nabla^2\rho_b$  y  $E_b$  in au<sup>b</sup> Calculated at the B3LYP/6-311G(d,p) level. Values in parentheses were obtained using the 6-311G(d) basis sets for the halogen atom<sup>c</sup> For atom labels, see Fig. 1

Large positive values of  $\rho_b$  and large negative values of the Laplacian are indicators of strong covalent bonds (see, for example, values for the C–C and C–N single bonds in Table 1). In case of a pure ionic bond (close shell interaction) one would expect a small value of  $\rho_b$ , indicating depletion of the electron density and positive values of the Laplacian. In our case we have considerable  $\rho_b$  values and positive Laplacian values for the Se–Cl (0.0981 a.u. and 0.0490 a.u.), Se–Br (0.0887 a.u. and 0.0119 a.u.) and Se–S (0.099 a.u. and 0.0090 a.u.), but (is)  $E_b < 0$  in all cases. Clearly, here we have a superposition of two extreme cases that allows us to conclude that these bonds should be classified as strong, highly polarized covalent bonds.

When the C–X bonds are compared, a decrease in the electron density (0.0981 a.u., 0.0887 a.u. and 0.0744 a.u.) and a corresponding decrease of the electronic energy density (0.0350 a.u., 0.0310 a.u. and 0.0240 a.u.) can be seen. These findings can be interpreted as a decrease in covalent character of the bonds when going from Se–Cl to Se–I. Moreover, the features of the C–N bond are not affected by inclusion of the S atom in the group attached to selenium atom, those being strong covalent bonds (see Table 1). The electron density of the Se–C bond to the cyanide group (0.1591 a.u.) is slightly higher than the

electron density of the Se–C bonds to the phenyl rings (0.1445 a.u.). Accordingly, the ellipticity is 0.1919 against 0.0572, respectively, reflecting the double bond character in the Se–C bond to the sp hybridized cyanide carbon, compared with the sp<sup>2</sup> hybridized ring carbon.

**Table 2** Topological properties of charge density<sup>a,b</sup> calculated at selected BCPs of the PhSeCN dimer and Ph<sub>4</sub>Se<sub>4</sub>CN<sub>4</sub>

Compound	Bond <sup>c</sup>	$\rho_b$	$\nabla^2\rho_b$	$\varepsilon$	$E_b$
(PhSeCN) <sub>2</sub>	C1-C2	0.3070	-0.8410	0.2116	-0.3130
	C1-Se	0.1454	-0.1077	0.1715	-0.0790
	Se-C7	0.1618	-0.0263	0.1964	-0.1066
	C7-N	0.4725	-0.2550	0.0105	-0.8532
	Se'-N	0.0051	0.0169	0.1654	0.0008
	C7'-C7	0.0051	0.0157	1.6579	0.0008
	Se-N'	0.0051	0.0169	0.1663	0.0008
Ph <sub>4</sub> Se <sub>4</sub> Cl <sub>4</sub>	C1-C2	0.3065	-0.8416	0.2030	-0.3107
	Cl-Se	0.1500	-0.1145	0.0402	-0.0835
	Se-Cl	0.0888	0.0574	0.1102	-0.0285
	Se-Se	0.0244	0.0401	0.1279	-0.0010

<sup>a</sup>  $\rho_b$ ,  $\nabla^2\rho_b$  y  $E_b$  in au<sup>b</sup> Calculated at the B3LYP/6-311G(d,p) level<sup>c</sup> For atom labels, see Fig. 2

The atom bonding network that connects both PhSeCN units is an important feature of the dimeric structure of this compound, which seems to be aiding the crystallization. The dimeric structure shows three intermolecular interactions. The Se $\cdots$ N distances are 3.48 Å and the C $\cdots$ C distance is 3.42 Å, which are almost equal to the sum of the van der Waals radii of the selenium and nitrogen atoms (3.45 Å) and of the carbon atoms (3.40 Å). However, the experimental distances are shorter than the sum of the van der Waals radii, suggesting that there is appreciable interaction at the long Se $\cdots$ N contact distance (3.33 Å and 3.44 Å, respectively).

Within the tetramer, the solid-state structures of Ph<sub>4</sub>Se<sub>4</sub>Cl<sub>4</sub>, four PhSeCl units are held together by weak Se $\cdots$ Se bonds forming an essentially planar ring of Se<sub>4</sub> and the Se–Cl bonds lie in the Se<sub>4</sub> plane, with two phenyl rings lying above the plane, and two below it.

The calculated Se $\cdots$ Se distance (3.13 Å) is significantly smaller than the sum of van der Waals radii of the selenium atoms (3.80 Å) but longer than the covalent radii (3.80 Å), revealing the existence of the non-covalent interactions.

No significant changes in the topological properties of the bonds are observed when the dimeric structure of (PhSeCN)<sub>2</sub> is formed (Table 2). Indeed, when the corresponding bonds are compared, similar characteristics appear. For example, in the Se–C7 bond, the electronic density is 0.1595 a.u. and 0.1618 a.u. in the monomer and dimer, respectively. In the same direction, the Laplacian of the density is –0.0265 a.u. and –0.0263 a.u., respectively, in this bond. It is interesting to note that the three bonds that hold the two molecules together have similar topological properties. The low value of the electron density (0.0051 a.u.) and positive and low values of the Laplacian of the density (between 0.0157 a.u. and 0.0169 a.u.) at the CPs of the Se $\cdots$ N and C $\cdots$ C bonds indicates a weak interaction between the two molecules. The high value of the ellipticity at the BCP in the C–C bond linking the two molecules can be explained by the strong  $\pi$  character of this bond.

The topological properties of the bonds in the monomer were similar in the corresponding tetrameric structure. A topological analysis of BCPs in  $\rho$  of Ph<sub>4</sub>Se<sub>4</sub>CN<sub>4</sub> revealed that all bonds forming the phenyl ring correspond to covalent interactions ( $\rho_b=0.3070$  a.u.,  $\nabla^2\rho_b=-0.8410$  a.u. and  $E_b=-0.3130$  a.u.), and the ellipticities values ( $\epsilon=0.2116$ ) reveal the partial double bond character, as in the PhSeCN monomeric structure.

As seen previously, weak interactions are observed taking into account the calculated and experimental Se $\cdots$ Se distances. Accordingly, topological properties at the BCPs in  $\rho$  of Se–Se bonds correspond to weak interactions: low values of electron densities ( $\rho_b=0.0244$  a.u.), positive and low values of the Laplacian of the density ( $\nabla^2\rho_b=0.0401$  a.u.) and  $E_b$  values near to zero (–0.010 a.u.).

## Conclusions

This paper reports a theoretical study of a “PhSeX” series of compounds, where Ph=phenyl, Se=selenium and X=Cl, Br, I, CN or SCN. The molecular geometry was calculated at DFT/B3LYP level of calculation by means of the 6-311 G(d,p) basis sets. The equilibrium structures of the molecules were found to depend on the method employed for comparison with previously reported experimental data. A topological study of the calculated PhSeX species, based on the AIM theory, illustrates the subtle differences in the solid-state structures of PhSeX compounds.

A decrease in the electron density and a corresponding decrease in the electronic energy density was observed when going from PhSeCl to PhSeI, which can be interpreted as a decrease in the covalent character of the C–X bonds. In PhSeCN, the ellipticity of the Se–C attached to the cyanide group is slightly higher than the ellipticity of the Se–C bonds to the phenyl rings, reflecting the double bond character of the former bond in the cyanide group. In PhSeSCN, the features of the C–N bond are not affected by the inclusion of the S atom in the group attached to the selenium atom.

The atom bonding network connecting two units seems to aid the crystallization process in the dimeric structure of (PhSeCN)<sub>2</sub>, showing three intermolecular interactions.

In the structure of Ph<sub>4</sub>Se<sub>4</sub>Cl<sub>4</sub>, four PhSeCl units are held together by weak Se $\cdots$ Se bonds forming an essentially planar ring of Se<sub>4</sub> with non-covalent Se $\cdots$ Se interactions.

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