



Article

Robust Supramolecular Dimers Derived from Benzylic-Substituted 1,2,4-Selenodiazolium Salts Featuring Selenium··· π Chalcogen Bonding

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Abstract: The series of benzylic-substituted 1,2,4-selenodiazolium salts were prepared via cyclization reaction between 2-pyridylselenenyl chlorides and nitriles and fully characterized. Substitution of the Cl anion by weakly binding anions promoted the formation supramolecular dimers featuring four center Se₂N₂ chalcogen bonding and two antiparallel selenium··· π interactions. Chalcogen bonding interactions were studied using density functional theory calculations, molecular electrostatic potential (MEP) surfaces, the quantum theory of atoms-in-molecules (QTAIM), and the noncovalent interaction (NCI) plot. The investigations revealed fundamental role of the selenium··· π contacts that are stronger than the Se···N interactions in supramolecular dimers. Importantly, described herein, the benzylic substitution approach can be utilized for reliable supramolecular dimerization of selenodiazolium cations in the solid state, which can be employed in supramolecular engineering.

Keywords: selenium··· π interactions; noncovalent interactions; chalcogen heterocycles; chalcogen bonding

1. Introduction

A bottom-up approach to the synthesis of functional materials with programmable structures and therefore properties is a long-standing challenge. In the past decades, coordination chemistry has been successfully employed as a tool to create such materials, which resulted in the emergence of metal-organic frameworks (MOFs) [1,2]. In analogous fashion, supramolecular organic frameworks (SOFs) [3,4] have recently emerged, which utilize noncovalent interactions as a tool for a programmable self-assembly. Among SOFs, hydrogen-bonded organic frameworks (HOFs) [4–8] represent a promising class of materials. However, halogen (XB) and chalcogen bonding (ChB) have recently appeared as powerful alternatives to the hydrogen bonding due to their directionality and tunability [9–30]. In spite of their potential advantages, XB and ChB have received a very limited attention for the creation of extended materials analogous to HOFs [31].

In this context, chalcogenodiazoles represent attractive objects for the creation of such materials [32–38]. They were shown to be capable of forming symmetrical antiparallel

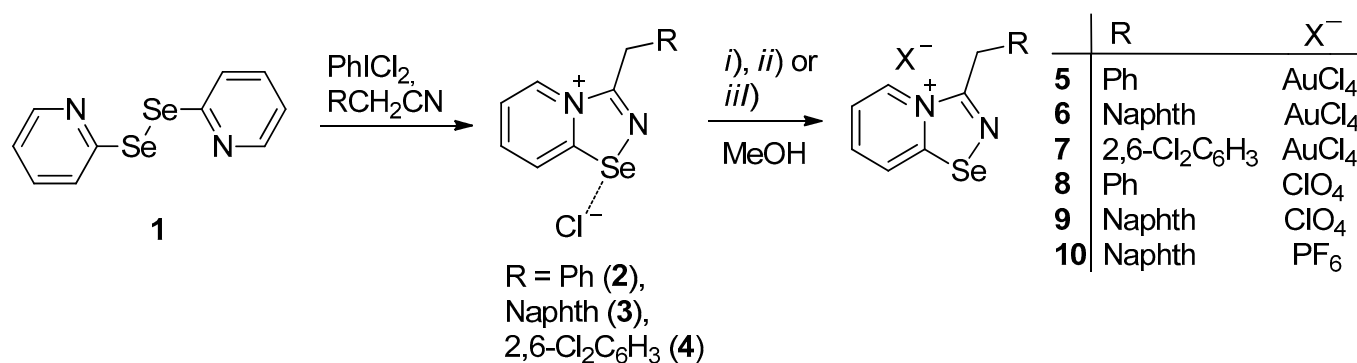
supramolecular dimers via two $\text{Se} \cdots \text{N}$ ChB interactions. These important supramolecular synthons were intensively studied in the last years [33–38].

Recently, we described the synthesis of cationic 1,2,4-selenodiazolium salts via unprecedented cyclization between bifunctional 2-pyridylselenyl reagents and nitriles [39–45]. The latter new heterocycles also showed a potency to form Se_2N_2 supramolecular dimers in some instances. However, for some of them, Se_2N_2 dimers formation was not observed when other weak noncovalent forces outcompeted the squares formation [41–43]. These stimulated us to search for the strategies to reliably form Se_2N_2 synthons.

Here, we describe the synthesis of benzylic-substituted 1,2,4-selenodiazolium salts. When halide anions were substituted by the weakly binding anions, we always observed the formation Se_2N_2 squares, supported by the pair of antiparallel selenium $\cdots$ arene ChB interactions. These interactions have been further studied and characterized using density functional theory (DFT) calculations, molecular electrostatic potential (MEP) surfaces, the quantum theory of atoms-in-molecules (QTAIM), and the noncovalent interaction (NCI) plot.

2. Results and Discussion

Benzylic-substituted 1,2,4-selenodiazolium chlorides **2–4** were prepared by the oxidation of diselenide **1** with PhICl_2 and sequential cyclization of in situ generated 2-pyridylselenyl chloride with corresponding aryl acetonitriles in 78–93% yields (Scheme 1). The NMR and mass spectrometry for data for **2–4** were in accord with the proposed structures.



Scheme 1. Synthesis of **2–10**. (i) NaAuCl_4 , (ii) LiClO_4 , (iii) NBu_4PF_6 .

Compounds **2–4** could be recrystallized from MeOH to give single crystals suitable for X-ray structural analysis, which confirmed their structures (Figure 1).

Selenodiazolium cations expectedly interacted with the Cl anions via a pair of “chelating” $\text{Se} \cdots \text{Cl}$ and $\text{H} \cdots \text{Cl}$ non-covalent interactions. Such chelation was observed earlier for all structurally characterized selenodiazolium chlorides so far [40,42,43]. Compounds **2** and **3** did not feature Se_2N_2 dimers in the solid state. Instead, one of the Se σ -holes in **2** was involved in $\text{Se} \cdots \text{Cl}$ ChB interaction with co-crystallized CH_2Cl_2 molecule, while in **3** this position was found vacant (Figure 1). In contrast, compound **4** formed Se_2Cl_2 dimers featuring bridging Cl anions involved in two ChB interactions.

Further, we switched to salts with weakly coordinating anions, i.e., ClO_4^- , AuCl_4^- , and PF_6^- . The compounds **5–9** were simply prepared by the addition of saturated methanolic solutions of NaAuCl_4 , NBu_4PF_6 , or LiClO_4 to **2–4** in MeOH, which resulted in the precipitation of desired compounds in 48–67% yields (Scheme 1). Analytical data (see Experimental Part) suggested the formation of selenodiazolium salts **5–10**.

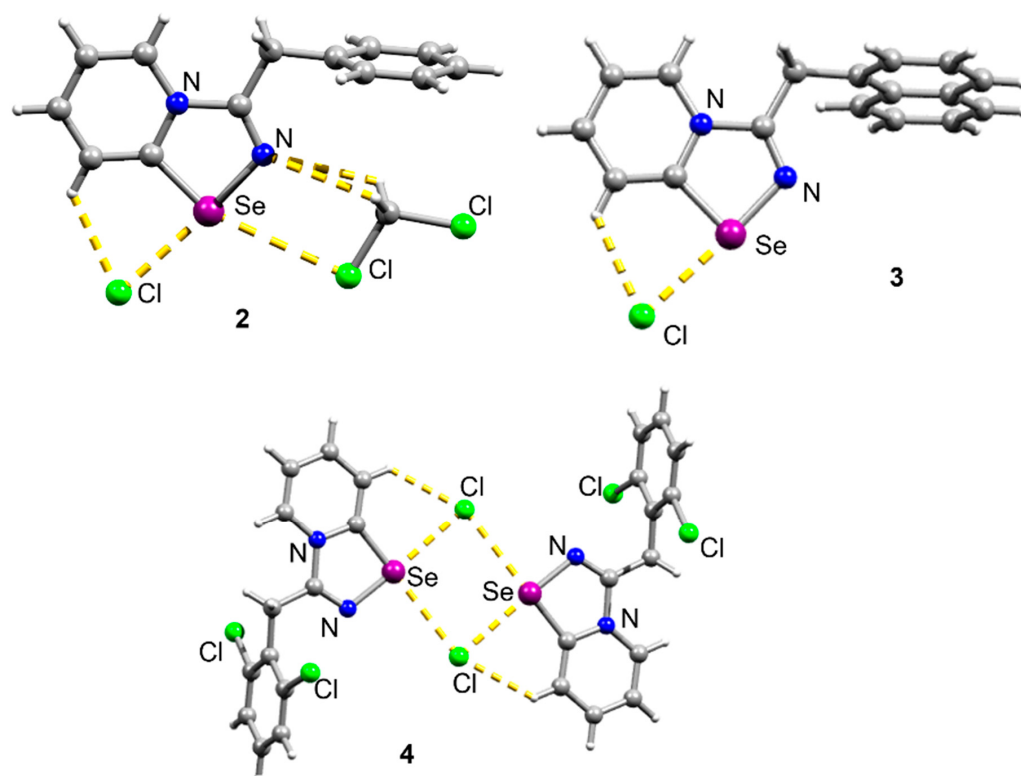


Figure 1. Ball-and-stick representations of crystal structures of 2–4. Grey and light-grey spheres represent carbon and hydrogen, respectively.

The structures were unambiguously established using single-crystal X-ray structural analysis (Figure 2). Bond lengths and angles are similar to what was observed earlier for selenodiazoles and other relevant heterocycles [46–52].

Importantly, 5, 6, 8, 9, and 10 formed supramolecular dimers in the solid state via two antiparallel $\text{Se} \cdots \text{N}$ and $\text{Se} \cdots \pi$ ChB interactions (Figure 2). The dimerization occurred for both benzyl and naphthylmethyl derivatives and did not depend on the nature of weakly coordinating anion.

The $\text{Se} \cdots \pi$ interactions resembled η^6 metal–arene coordination complexes in terms of their geometry. To obtain more insights into $\text{Se} \cdots \pi$ ChB in 5, 6, 8, 9, and 10, we performed theoretical studies starting from the calculations of the molecular electrostatic potential (MEP) surfaces using the salts to have neutral systems. The MEP surfaces are gathered in Figure 3. The values at both σ -holes (labeled a,c) and at the middle of both σ -holes (labeled as b) are indicated. In all cases, the σ -hole labeled as “c” is deeper (ranging 57 to 71 kcal/mol) than the other one (“a” ranging 35 to 49 kcal/mol) due to the overlap with the positive and adjacent H-atom of the pyridyl ring. The MEP values at the middle of both σ -holes are also positive (“b” ranging 29 to 43 kcal/mol), thus suggesting that the directionality of the $\text{Se} \cdots \pi$ interaction is not crucial. Regarding the aromatic rings, the MEP surfaces reveal that the values are negative, ranging from -8.5 in 5 to -21 kcal/mol in 10. The larger negative MEP values in the aromatic rings of 9 and 10 are due to the closer proximity of the counterion.

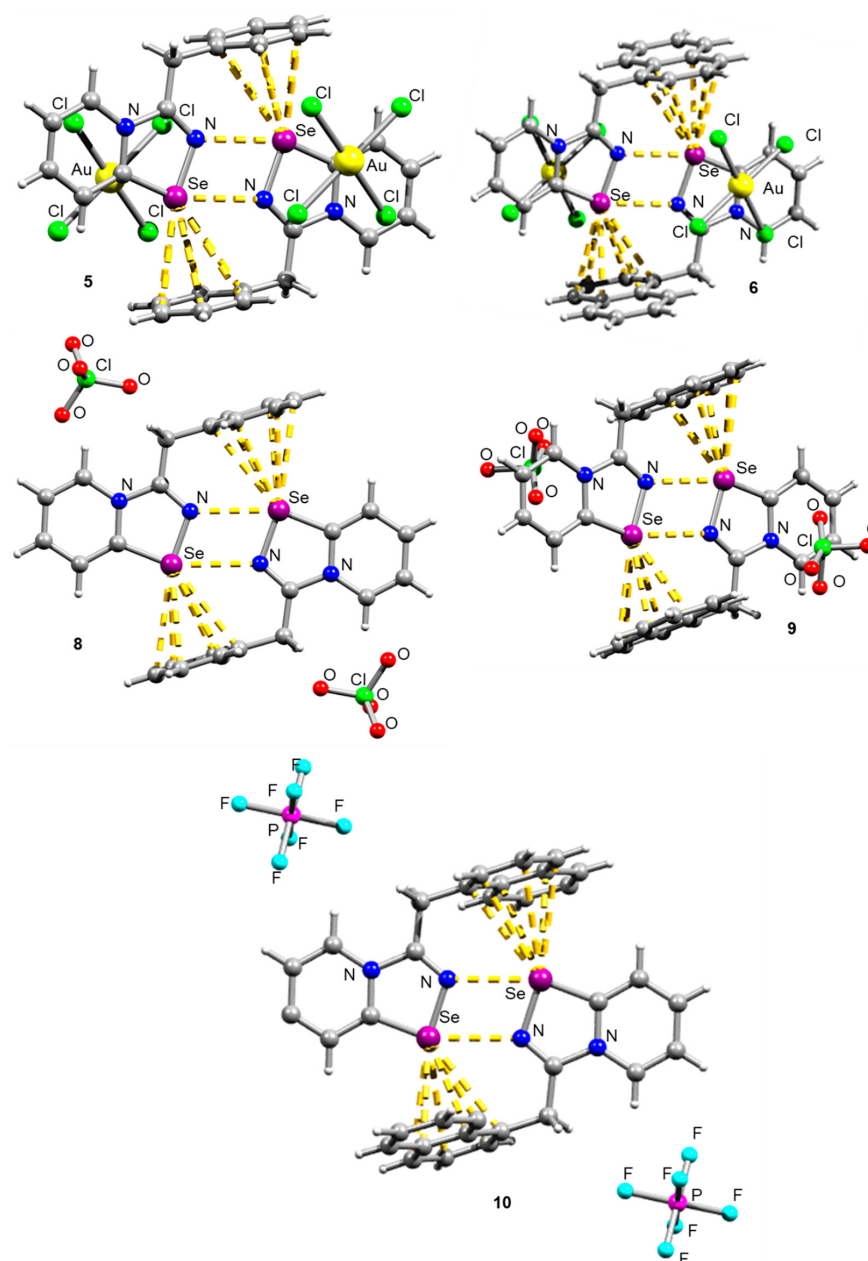


Figure 2. Ball-and-stick representations of crystal structures of **5**, **6**, **8**, **9**, and **10**, demonstrating supramolecular dimerization via two $\text{Se} \cdots \text{N}$ and $\text{Se} \cdots \pi$ ChB interactions. Grey and light-grey spheres represent carbon and hydrogen, respectively.

The combined QTAIM/NCIplot analyses of the self-assembled dimers of the compounds shown in Figure 3 were computed and are represented in Figure 4 along with the dimerization energies. These dimerization energies were computed considering the salt as the monomer. Moreover, only intermolecular interactions were represented in the plots. It can be observed that in all cases the $\text{Se} \cdots \text{N}$ ChBs are characterized by a bond critical point (CP) and bond path connecting the N to the Se atoms. The bond CPs are represented as red spheres and bond paths as orange lines in Figure 4. Moreover, the reduced density gradient (RDG) isosurfaces were represented overlapped with the QTAIM analysis. The NCIplot analysis shows the existence of blue disk-shaped RDG isosurfaces that further characterize the $\text{Se} \cdots \text{N}$ contacts, thus confirming the attractive nature of the interaction. Interestingly, a yellow RDG isosurface is also observed connecting the blue disks that characterize the $\text{Se} \cdots \text{N}$ bonds, as is detailed in the enlargement given in Figure 4f, thus revealing a $\text{N} \cdots \text{N}$ repulsion (blue and green colors are used for attractive interactions and yellow and red for repulsive). In fact, in

compound **8**, where the N $\cdots$ N distance is shorter, a bond CP and bond path interconnect both nitrogen atoms, further confirming the existence of a N $\cdots$ N interaction. The yellow color of the isosurface evidences the repulsive contribution of this contact that is obviously compensated by the Se $\cdots$ N attraction. Interestingly, the existence of the Se $\cdots$ π ChBs is also confirmed by both the QTAIM and NCIPLOT analyses. The shape and extension of the RDG isosurfaces in all compounds reveal that most of the π -cloud of the aromatic ring participates in the ChB. The dimerization energies range from -15.6 kcal/mol in **5** to -22.6 kcal/mol in compound **10**, which confirms the importance of these interactions in the solid state of the 1,2,4-selenodiazolium salts reported herein. In an effort to estimate the relative contribution of the Se $\cdots$ π interaction, we also computed the dimerization energies using mutated dimers. The mutation consists of the replacement of the aromatic ring (either phenyl or naphthyl) by a hydrogen atom. As a consequence, the symmetrically equivalent Se $\cdots$ π interactions in the dimers are not established, and the binding energy is drastically reduced (see values in red in Figure 4). The values range from -4.8 kcal/mol in **5** to -9.3 kcal/mol in compound **10**, thus revealing that the contribution of the Se $\cdots$ π is indeed dominant in these complexes, in line with the participation of the deeper σ -hole of selenium.

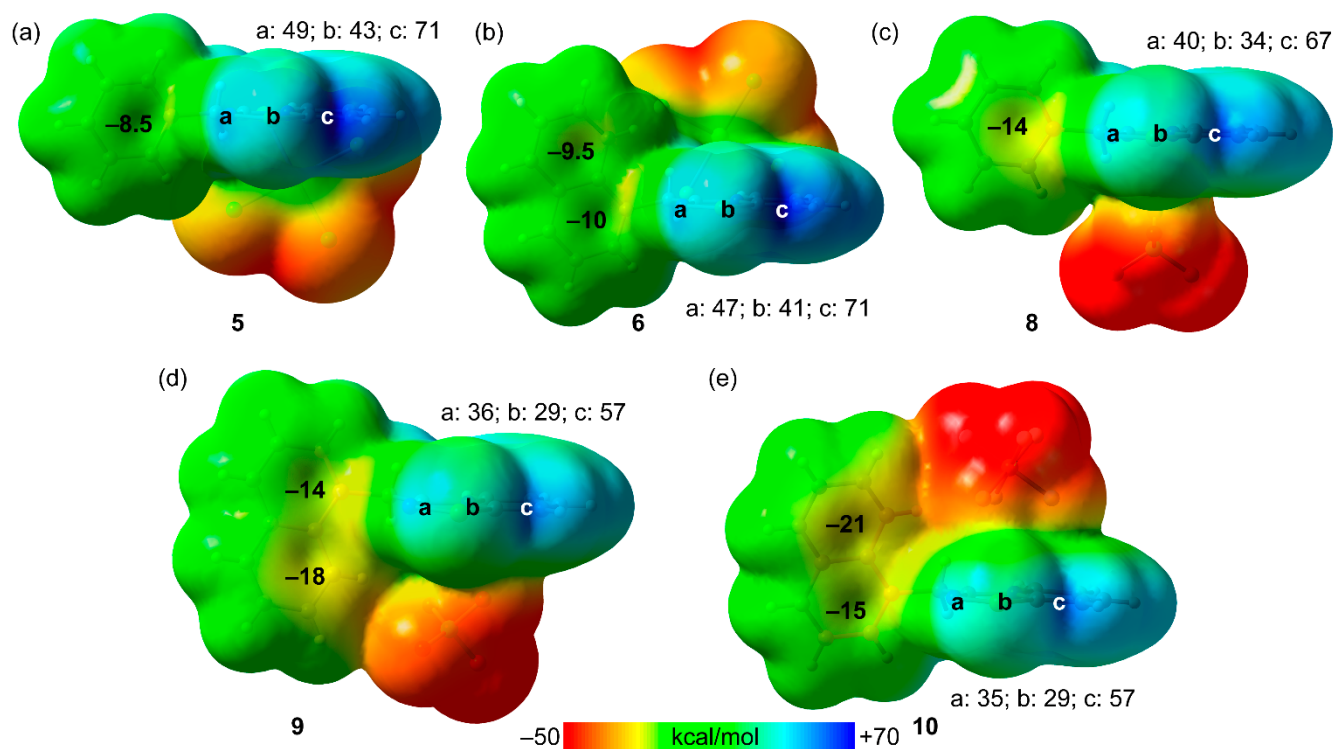


Figure 3. MEP surfaces of compounds **5** (a), **6** (b), **8** (c), **9** (d), and **10** (e) at the PBE0-D3/def2-TZVP level of theory. The values at selected points of the surfaces are given in kcal/mol.

Further, we were interested how introduction of electron deficient aryl substituent would affect the self-assembly of the corresponding selenodiazolium salts with weakly coordinating anion. Electron-deficient arenes are very weak Lewis bases, and their η^6 metal complexes are very scarce. Thus, we expected that selenodiazolium cations carrying electron deficient aryls would not undergo supramolecular dimerization via two Se $\cdots$ N and Se $\cdots$ π ChB interactions. In order to verify this hypothesis, we prepared compound **7**, whose structure in the solid state was established by means of single-crystal X-ray crystallography (Figure 5).

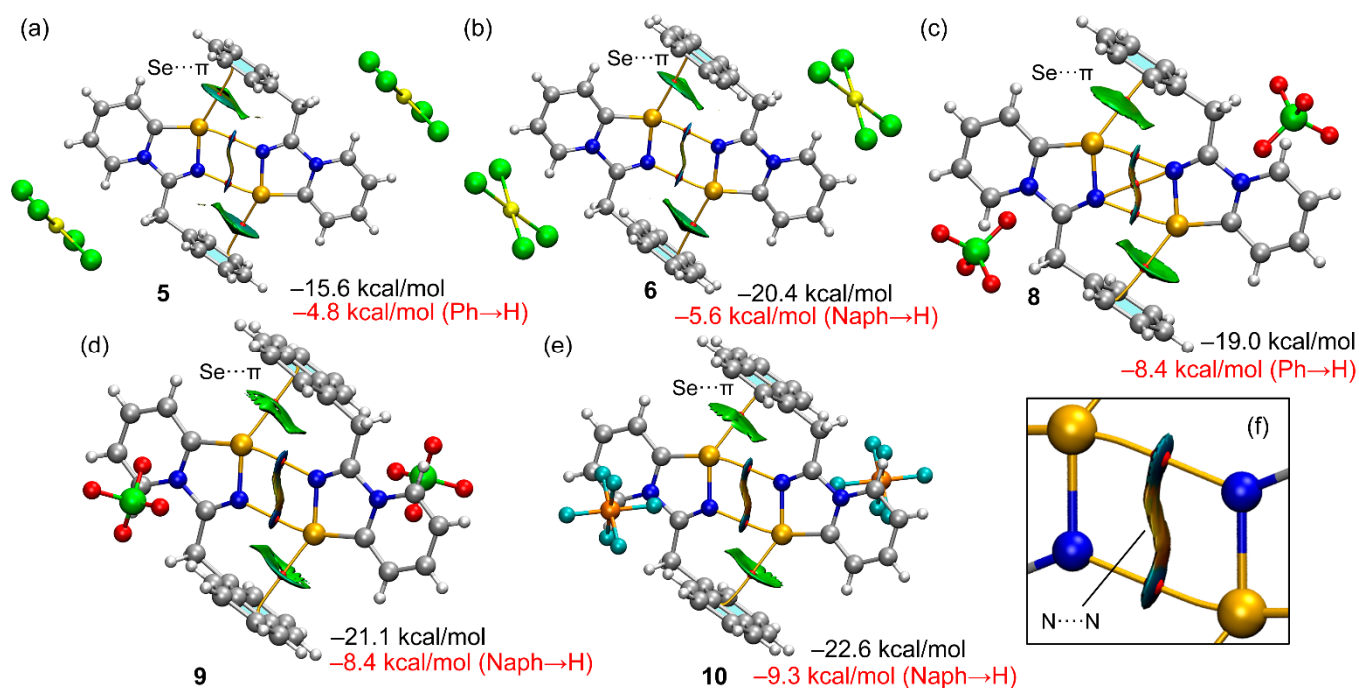


Figure 4. Combined QTAIM (CPs in red and bond paths as orange lines) and NCIPlot analyses of the dimers of 5 (a), 6 (b), 8 (c), 9 (d), and 10 (e) and an amplification of the Se...N interaction (f). The dimerization energies using the X-ray geometries and the mutated dimers are indicated using black and red font, respectively. Isovalue for the RDG isosurface 0.45.

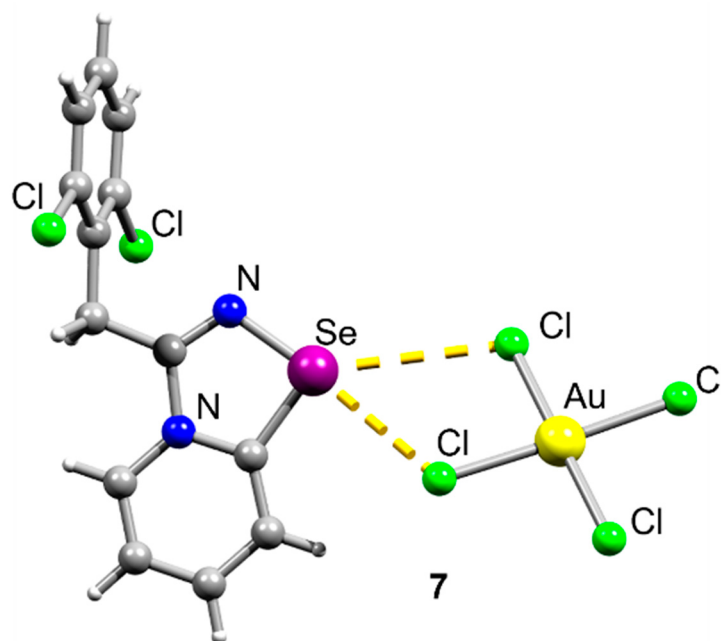


Figure 5. Ball-and-stick representation of crystal structure of 7, demonstrating Se...Cl ChB interactions. Grey and light-grey spheres represent carbon and hydrogen, respectively.

As we expected, 7 did not feature Se... π ChB. This further demonstrates the predictable behavior of benzylic-substituted selenodiazolium salts towards self-aggregation via two Se...N and Se... π ChB interactions in the solid state and supports the theoretical analysis above that demonstrates the dominant role of the Se... π ChB in the self-assembled dimers.

3. Materials and Methods

3.1. General Remarks

All manipulations were carried out in air unless specified. All the reagents used in this study were obtained from the commercial sources (Aldrich, TCI-Europe, Strem, ABCR). Commercially available solvents were purified by conventional methods and distilled immediately prior to use. NMR spectra were recorded on a Bruker Avance neo-700; chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. C, H, and N elemental analyses were carried out on a Euro EA 3028HT CHNS/O analyzer. Di(2-pyridyl)diselenide was prepared as reported earlier [39,40].

3.2. X-ray Crystal Structure Determination

The single-crystal X-ray diffraction data were collected on three-circle Bruker Smart APEX-II (2, 3), Bruker D8 QUEST (4, 6, 8), and Bruker D8 Venture (9) diffractometers (graphite monochromator, ω and θ scanning mode) and on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (graphite monochromator, shutterless ω -scan mode) (5, 7, 10). For 2–4, 6, 8, and 9, the data were indexed and integrated using the SAINT program [53] and then scaled and corrected for absorption using the SADABS program [54]. For 5, 7, and 10, the data were integrated and corrected for absorption by the *CrysAlisPro* program. For details, see Table S1 (Electronic Supporting Information). The structures were determined by direct methods and refined by full-matrix least-squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms in all compounds were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters ($U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the CH_3 -groups and $1.2U_{\text{eq}}(\text{C})$ for the other groups). All calculations were carried out using the SHELXTL program [55].

One molecule of MeOH in the unit cell ($V = 232 \text{ \AA}^3$ in one void) of 9 was found to be disordered over multiple positions and could therefore not be modelled satisfactorily. It was removed from the electron density map using the OLEX solvent mask command.

Crystallographic data for all investigated compounds were deposited with the Cambridge Crystallographic Data Center, CCDC 2220382–2220390. 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 www.ccdc.cam.ac.uk, accessed on 18 November 2022).

3.3. Computational Details

The single-point calculations of the self-assembled dimers of compounds 5, 6, 8, 9, and 10 were performed using the Turbomole 7.2 program [56]. The level of theory used was PBE0-D3/def2-TZVP [57–60] since it has been recently used for similar interactions [61]. The MEP surfaces were generated at the same level of theory and the 0.001 a.u. isosurface. The QTAIM [62] distribution of CPs and bond paths and NCIPLOT RDG isosurfaces [63] were plotted using the VMD program [63]. The following settings were used for the RDG plots: $s = 0.45 \text{ a.u.}$; cut-off $\rho = 0.04 \text{ a.u.}$; and color scale $-0.025 \text{ a.u.} \leq \text{sign}(\lambda_2)\rho \leq 0.025 \text{ a.u.}$

3.4. Synthetic Procedures

Synthesis of 2. The solution of PhICl_2 (21.6 mg, 0.08 mmol) and phenylacetone nitrile (500 μL) in CH_2Cl_2 (3 mL) was added to 2,2'-dipyridyldiselenide (24.9 mg, 0.08 mmol) in CH_2Cl_2 (1 mL), and the reaction mixture was left without stirring for 5 h. After that, a solution was decanted from colorless crystalline precipitate, which was washed with Et_2O ($3 \times 1 \text{ mL}$) and dried under vacuum. Yield: 45.6 mg (93%). ^1H NMR (600 MHz, CD_3OD) δ 9.46 (d, $J = 6.8 \text{ Hz}$, 1H, H5), 8.98 (d, $J = 8.7 \text{ Hz}$, 1H, H8), 8.39 (t, $J = 8.4 \text{ Hz}$, 1H, H7), 7.98 (t, $J = 7.0 \text{ Hz}$, 1H, H6), 7.42–7.24 (m, 5H, from Ph's), 4.74 (s, 2H, CH_2). ^{13}C NMR (151 MHz, CD_3OD) δ 170.6 (C3), 158.2 (C9), 140.3 (C5), 137.7 (C8), 127.9 (C7), 124.2 (C6), 134.1 (C from Ph's), CH from Ph's: 130.6, 130.2, 129.0; 38.4 (CH_2). MS (ESI⁺), found: 275.0082 [M–Cl]⁺; calcd for $\text{C}_{13}\text{H}_{11}\text{N}_2\text{Se}$: 275.0082.

Synthesis of 3. The solution of PhICl_2 (15.6 mg, 0.06 mmol) and 2-(naphthalen-1-yl)acetonitrile (50 mg) in CH_2Cl_2 (3 mL) was added to 2,2'-dipyridyldiselenide (17.8 mg, 0.06 mmol) in CH_2Cl_2 (1 mL), and the reaction mixture was left without stirring for 5 h. After that, a solution was decanted from colorless crystalline precipitate, which was washed with Et_2O (3×1 mL) and dried under vacuum. Yield: 39 mg (90%). ^1H NMR (600 MHz, CD_3OD) δ 9.62 (d, $J = 6.7$ Hz, 1H, H5), 8.98 (d, $J = 8.7$ Hz, 1H, H8), 8.49–8.42 (m, 1H, H7), 8.11–8.03 (m, 2H), 7.97–7.88 (m, 2H), 7.56–7.43 (m, 4H), 5.18 (s, 2H, CH_2). ^{13}C NMR (151 MHz, CD_3OD) δ 170.3 (C3), 157.8 (C9), 140.2 (C5), 137.7 (C8), 135.5, 133.6, 130.9, 130.5, 129.8, 129.0, 127.7, 127.6, 127.1, 126.5, 124.9 (C7), 124.0 (C6), 36.4 (CH_2). MS (ESI^+), found: 325.0239 $[\text{M}-\text{Cl}]^+$; calcd for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{Se}$: 325.0238.

Synthesis of 4. The solution of PhICl_2 (22 mg, 0.08 mmol) and 2-(2,6-dichlorophenyl)acetonitrile (50 mg) in CH_2Cl_2 (3 mL) was added to 2,2'-dipyridyldiselenide (25 mg, 0.08 mmol) in CH_2Cl_2 (1 mL), and the reaction mixture was left without stirring for 5 h. After that, a solution was decanted from yellow crystalline precipitate, which was washed with Et_2O (3×1 mL) and dried under vacuum. Yield: 47 mg (78%). ^1H NMR (600 MHz, D_2O) δ 9.59 (d, $J = 6.9$ Hz, 1H, H5), 8.85 (d, $J = 8.6$ Hz, 1H, H8), 8.47 (t, $J = 8.3$ Hz, 1H), 8.56–8.41 (m, 1H, H7), 8.19–8.05 (m, 1H, H6), 7.55 (d, $J = 8.1$ Hz, 2H), 7.42 (dd, $J = 8.5, 7.8$ Hz, 1H), 5.01 (s, 2H, CH_2). ^{13}C NMR (151 MHz, D_2O) δ 168.3, 155.0, 134.0, 136.2, 135.9, 130.6, 129.4, 128.6, 126.1, 123.3, 33.7 (CH_2).

Synthesis of 5. The solution of PhICl_2 (28.6 mg, 0.08 mmol) and phenylacetonitrile (500 μL) in CH_2Cl_2 (3 mL) was added to 2,2'-dipyridyldiselenide (24.9 mg, 0.09 mmol) in CH_2Cl_2 (1 mL), and the reaction mixture was left without stirring for 5 h. After that, a solution was decanted from colorless crystalline precipitate, which was washed with Et_2O (3×1 mL) and dried under vacuum. Addition of the MeOH solution (100 μL) of NaAuCl_4 (50 mg) to MeOH solution of **2** (1 mL) resulted in the formation of yellow microcrystalline precipitate. Yield: 64 mg (65%). ^1H NMR (600 MHz, $\text{Me}_2\text{CO}-d_6$) δ 9.74 (d, $J = 6.8$, 1H, H5), 9.16 (d, $J = 8.6$, 1H, H8), 8.61 (ddd, $J = 8.5, 7.2, 1.1$ Hz, 1H, H7), 8.23 (t, $J = 7.0$, 1H, H6), 7.52–7.36 (m, 5H), 4.94 (s, 2H, CH_2). ^{13}C NMR (151 MHz, $\text{Me}_2\text{CO}-d_6$) δ 169.7 (C3), 158.1 (C9), 140.6 (C5), 137.5 (C8), 130.5, 129.7, 128.6, 127.4 (C7), 124.2 (C6), 133.7 (C from Ph), 38.1 (CH_2).

Synthesis of 6. The solution of PhICl_2 (16.5 mg, 0.06 mmol) and 2-(naphthalen-1-yl)acetonitrile (50 mg) in CH_2Cl_2 (3 mL) was added to 2,2'-dipyridyldiselenide (19 mg, 0.06 mmol) in CH_2Cl_2 (1 mL), and the reaction mixture was left without stirring for 5 h. After that, a solution was decanted from colorless crystalline precipitate, which was washed with Et_2O (3×1 mL) and dried under vacuum. Addition of the MeOH solution (100 μL) of NaAuCl_4 (50 mg) to MeOH solution of **3** (1 mL) resulted in the formation of orange microcrystalline precipitate. Yield: 46 mg (58%). ^1H NMR (600 MHz, $\text{Me}_2\text{CO}-d_6$) δ 9.95 (d, $J = 6.8$ Hz, 1H, H5), 9.18 (d, $J = 8.7$ Hz, 1H, H8), 8.66 (ddd, $J = 8.4, 7.3, 0.9$ Hz, 1H, H7), 8.31 (td, $J = 7.0, 1.1$ Hz, 1H, H6), 8.13 (d, $J = 8.4$ Hz, 1H), 8.01 (dd, $J = 17.6, 8.2$ Hz, 2H), 7.59–7.50 (m, 4H), 5.38 (s, 2H, CH_2). ^{13}C NMR (151 MHz, $\text{Me}_2\text{CO}-d_6$) δ 169.6 (C3), 157.8 (C9), 145.6, 140.6 (C5), 138.0 (C8), 135.0, 133.3, 130.4, 129.5, 129.1, 127.3, 126.9, 126.4, 125.3, 125.18 (C7), 124.1 (C7), 36.2 (CH_2).

Synthesis of 7. The solution of PhICl_2 (16.1 mg, 0.06 mmol) and 2-(2,6-dichlorophenyl)acetonitrile (50 mg) in CH_2Cl_2 (3 mL) was added to 2,2'-dipyridyldiselenide (18.5 mg, 0.06 mmol) in CH_2Cl_2 (1 mL), and the reaction mixture was left without stirring for 5 h. After that, a solution was decanted from yellow crystalline precipitate, which was washed with Et_2O (3×1 mL) and dried under vacuum. Addition of the MeOH solution (100 μL) of NaAuCl_4 (50 mg) to MeOH solution of **4** (1 mL) resulted in the formation of orange microcrystalline precipitate. Yield: 39 mg (48%). ^1H NMR (600 MHz, $\text{Me}_2\text{CO}-d_6$) δ 10.01 (d, $J = 6.8$ Hz, 1H, H5), 9.21 (d, $J = 8.6$ Hz, 1H, H8), 8.67 (ddd, $J = 8.4, 7.2, 1.0$ Hz, 1H, H7), 8.38–8.32 (m, 1H, H6), 7.63–7.58 (m, 2H), 7.46 (dd, $J = 8.6, 7.5$ Hz, 1H), 5.19 (s, 2H, CH_2). ^{13}C NMR (151 MHz, $\text{Me}_2\text{CO}-d_6$) δ 155.2, 140.9, 137.8, 137.0, 131.7, 131.4, 129.7, 129.5, 127.6, 124.3, 34.6 (CH_2).

Synthesis of 8. The solution of PhICl_2 (22 mg, 0.08 mmol) and phenylacetonitrile (500 μL) in CH_2Cl_2 (3 mL) was added to 2,2'-dipyridyldiselenide (25 mg, 0.08 mmol) in CH_2Cl_2 (1 mL), and the reaction mixture was left without stirring for 5 h. After that, a solution was decanted from colorless crystalline precipitate, which was washed with Et_2O ($3 \times 1 \text{ mL}$) and dried under vacuum. Addition of the MeOH solution (100 μL) of NaClO_4 resulted in the formation of colorless microcrystalline precipitate. Addition of the MeOH solution (100 μL) of LiClO_4 to MeOH solution of **2** (1 mL) resulted in the formation of colorless microcrystalline precipitate. Yield: 40 mg (67%). ^1H NMR (600 MHz, $\text{Me}_2\text{CO}-d_6$) δ 9.73 (d, $J = 6.8 \text{ Hz}$, 1H, H5), 9.14 (d, $J = 8.6 \text{ Hz}$, 1H, H8), 8.59 (ddt, $J = 8.5, 7.2, 1.0 \text{ Hz}$, 1H, H7), 8.20 (t, $J = 6.9 \text{ Hz}$, 1H, H6), 7.49–7.38 (m, 5H), 4.92 (s, 2H, CH_2). ^{13}C NMR (151 MHz, $\text{Me}_2\text{CO}-d_6$) δ 158.2, 140.5, 137.7, 133.9, 130.5, 129.7, 128.9, 128.5, 127.4, 124.1, 38.1 (CH_2).

Synthesis of 9. The solution of PhICl_2 (20.3 mg, 0.06 mmol) and 2-(naphthalen-1-yl)acetonitrile (50 mg) in CH_2Cl_2 (3 mL) was added to 2,2'-dipyridyldiselenide (17.8 mg, 0.06 mmol) in CH_2Cl_2 (1 mL), and the reaction mixture was left without stirring for 5 h. After that, a solution was decanted from colorless crystalline precipitate, which was washed with Et_2O ($3 \times 1 \text{ mL}$) and dried under vacuum. Addition of the MeOH solution (100 μL) of LiClO_4 to MeOH solution of **3** (1 mL) resulted in the formation of colorless microcrystalline precipitate. Yield: 32 mg (61%). ^1H NMR (600 MHz, $\text{Me}_2\text{CO}-d_6$) δ 9.86 (d, $J = 6.8 \text{ Hz}$, 1H, H5), 9.07 (d, $J = 8.7 \text{ Hz}$, 1H, H8), 8.62–8.55 (m, 1H, H7), 8.22 (td, $J = 7.0 \text{ Hz}$, 1H, H6), 8.10 (d, $J = 8.5 \text{ Hz}$, 1H), 8.01–7.92 (m, 2H), 7.57–7.44 (m, 4H), 5.30 (s, 2H, CH_2). ^{13}C NMR (151 MHz, $\text{Me}_2\text{CO}-d_6$) δ 157.7, 140.4, 137.8, 134.9, 133.4, 130.4, 129.6, 129.4, 129.0, 127.1, 127.0, 126.9, 126.48, 125.1, 123.9, 100.9, 35.2 (CH_2).

Synthesis of 10. The solution of PhICl_2 (18 mg, 0.07 mmol) and 2-(naphthalen-1-yl)acetonitrile (50 mg) in CH_2Cl_2 (3 mL) was added to 2,2'-dipyridyldiselenide (22 mg, 0.07 mmol) in CH_2Cl_2 (1 mL), and the reaction mixture was left without stirring for 5 h. After that, a solution was decanted from colorless crystalline precipitate, which was washed with Et_2O ($3 \times 1 \text{ mL}$) and dried under vacuum. Addition of the saturated MeOH solution of tetrabutylammonium hexafluorophosphate (100 μL) to MeOH solution of **3** (1 mL) resulted in the formation of microcrystalline precipitate. Yield: 35 mg (53%). ^1H NMR (600 MHz, $\text{Me}_2\text{CO}-d_6$) δ 9.92 (d, $J = 6.9 \text{ Hz}$, 1H, H5), 9.15 (d, $J = 8.7 \text{ Hz}$, 1H, H8), 8.67–8.60 (m, 1H, H7), 8.30–8.25 (m, 1H, H6), 8.13 (d, $J = 8.6, 1.0 \text{ Hz}$, 1H), 8.03–7.98 (m, 2H), 7.59–7.49 (m, 4H), 5.36 (s, 2H, CH_2). ^{13}C NMR (151 MHz, $\text{Me}_2\text{CO}-d_6$) δ 169.5, 157.9, 140.7, 138.0, 135.0, 133.4, 130.5, 129.6, 129.2, 127.7, 127.3, 127.2, 126.9, 126.5, 125.2, 124.1, 36.2 (CH_2).

4. Conclusions

We have synthesized a series of benzylic-substituted 1,2,4-selenodiazolium salts with weakly binding anions that promote the formation self-assembled dimers with the recurrent Se_2N_2 supramolecular motif. The dimers are further supported by two symmetrically equivalent selenium $\cdots$ arene ChB interactions. The $\text{Se} \cdots \text{N}$ and $\text{Se} \cdots \pi$ ChB interactions have been studied theoretically, and we disclosed the fundamental role of the $\text{Se} \cdots \pi$ interactions, which are stronger than the $\text{Se} \cdots \text{N}$ interactions observed in the Se_2N_2 motifs. The DFT analysis demonstrates that the stronger nature of the $\text{Se}-\pi$ interactions is due to the participation of the more positive σ -hole and to the existence of a repulsive $\text{N} \cdots \text{N}$ interaction in the Se_2N_2 motif. The relevance of the $\text{Se} \cdots \pi$ interaction is further supported by the fact that compound **7** does not exhibit the $\text{Se} \cdots \pi$ interaction in the solid state due to the presence of electron withdrawing groups in the phenyl ring.

Importantly, the herein-described strategy can be employed for reliable supramolecular dimerization of 1,2,4-selenodiazolium cations in the solid state. This supramolecular synthon can be employed in supramolecular engineering for the creation of SOFs with programmable structures and properties.

Supplementary Materials: The supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ijms232314973/s1>.

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