

Synthesis, spectral and structural properties of bis-imidazoline selones

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Abstract. New biphenyl derivatives of bis-imidazoline selones were synthesized in good yield and characterized by multinuclear (1D and 2D) NMR and UV-vis studies. The solid state structures of bis-imidazoline selones were further confirmed by single crystal X ray diffraction technique.

Keywords. Imidazole; selenium; selone; biphenyl.

1. Introduction

Organo selenium derivatives have been now established as essential trace element for thyroid functions.¹ The selenium analogue can show antioxidant activity by reducing H₂O₂ even in presence of Glutathione (GSH).^{1–6} Guziec *et al.* was the first to synthesize imidazole based thione ligand (MMI) and its selenium analogues.⁷ These types of selenium compounds can be biologically significant when coordinated with biologically important transition metals (Cu, Fe, Ni, Zn, Mn, Mo, etc.).^{8–10} Several such examples of bis-imidazoline selone compounds were synthesized for different applications. For instance, group-9 complexes of coordination 1,1'-methylenebis(3-methylimidazoline-2-selone) [**Mbis**], 1,1'-(1,2-ethanediyl)bis(3-methylimidazoline-2-selone) [**Ebis**], 1,1-(butane-1,4-diyl)bis(3-methylimidazoline-2-selone) [**Bbis**] and 1,1'-(pentane-1,5-diyl)bis(3-methylimidazoline-2-selone) [**Pbis**] ligands were reported by Lippolis *et al.*¹¹ and Mugesh *et al.*¹ in 2011 (chart 1). Later in 2008, **Mbis** and **Ebis** ligands were synthesized by Jin *et al.* and introduced to cyclopentadienyl group (Cp*) which resulted in the first half-sandwich iridium and rhodium complexes.¹² Recently, a method for synthesis of 1,1'-methylene-bis(3-aryl-imidazole-2-ylidene) ligands and derivatisation with chalcogenides was reported by Danopoulos *et al.* in 2013 (chart 1).¹³ The known bis imidazoline selones were isolated with alkyl bridging groups, where the two biologically active selones are expected to function

at the same site. On the other hand, separation of selone active centres by long range rigid spacers can provide enough room to show the independent activities. Similar such examples are not synthesized yet. Thus, we report the first aryl bridged bis-imidazoline selones from a straight forward route. The imidazolone compounds were prepared by treating imidazolium salt having biphenyl spacer with selenium powder in the presence of potassium carbonate.

2. Experimental

2.1 General remarks

All manipulations were carried out under argon using Schlenk line techniques. The solvents were purchased from commercial sources and purified according to standard procedures.¹⁴ Methyl imidazole, allyl imidazole, acetonitrile, methanol, potassium carbonate, selenium powder and 4,4'-bis(chloromethyl)-1,1'-biphenyl (**1**) were purchased from commercial sources. FT-IR measurements were carried out on a Bruker Alpha-P Fourier transform spectrometer. The UV- vis spectra were measured on a T90+ UV-visible spectrophotometer. NMR spectra were recorded on Bruker Ultrashield 400 spectrometer at 25°C, unless otherwise stated. Chemical shifts are given relative to Me₄Si and were referenced to the solvent resonances as internal standards. The crystal structure of **3a** and **3b** were measured on an Oxford Supernova diffractometer. Single crystals were mounted on a Goniometer KM4/Xcalibur equipped with Sapphire2 (large Be window) detector (CuK_α radiation source, λ = 1.5418 Å). Crystals of **3a** and **3b** were obtained from mixture of dichloromethane

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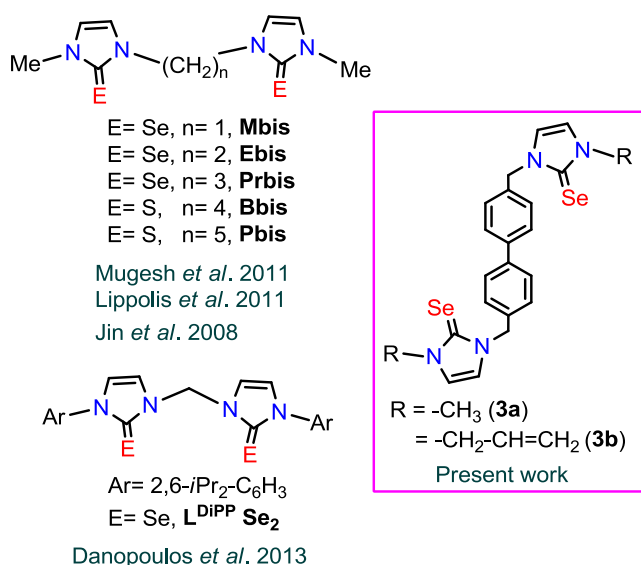


Chart 1. Known bis-imidazoline selones.

and ethanol solution of **3a** and **3b** at room temperature over a period of 12 hours. Data were collected at 150 K. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss-Newton minimisation.¹⁵

2.2 Synthesis of **2a**

Acetonitrile (35 mL) was added to **1** (5 g, 19.9 mmol) under argon atmosphere then N-methyl imidazole (4.7 mL, 59.7 mmol) was added to it at 90°C temperature and stirred for 46 h. The reaction progress was monitored by TLC. After completion of the reaction, the product, **2a** was formed as white precipitate. Yield: 98% (based on **1**). M.p. 102 – 104°C (melted to transparent liquid). ¹H NMR (D₂O, 400 MHz): δ 8.75 (s, 1H, ImH), 7.67–7.65 (d, ²J_{HH} = 6.8 Hz, 4H, ImH), 7.46–7.44 (d, ²J_{HH} = 8 Hz, 4H, ArH), 7.41–7.40 (d, ²J_{HH} = 4 Hz, 6.6 Hz, 4H, ArH), 5.37 (s, 4H, NCH₂), 3.84 (s, 6H, CH₃) ppm. ¹³C NMR (D₂O, 100 MHz): δ 122.09, 123.83 (Im-CH), 133.23, 140.27 (Ph-C), 35.72 (CH₃), 129.21, 127.61 (Ph-C), 52.34 (N-CH₂-) ppm. FT-IR (neat, ν): 3367(s), 3296(m), 3138(m), 3118(m), 3077(m), 2984(m), 2845(w), 1652(w), 1569(s), 1560(s), 1501(m), 1453(m), 1186(m), 1159(s), 801(m), 753(s) cm⁻¹.

2.3 Synthesis of **2b**

Acetonitrile (25 mL) was added to **1** (5 g, 19.9 mmol) under argon atmosphere with stirring. Then allyl

imidazole (6.43 mL, 59.6 mmol) was added to the reaction mixture and stirred for 16 h at 90°C. The reaction progress was monitored by TLC. The volatiles were removed under reduced pressure, then the crude product was washed with diethyl ether (5 mL × 3) and dried under high vacuum to obtain off-white solid, **2b**. Yield: 95% (based on **1**). M.p. 74–76°C (melted to transparent liquid). ¹H NMR (D₂O, 400 MHz): δ 7.50 (s, 4H, ImH), 7.42–7.40 (m, 8H, ArH), 5.93–5.87 (m, 2H, CH₂=CH-), 5.37–5.34 (m, 6H, CH₂=CH-, merged with NCH₂), 5.30–5.26 (d, ²J_{HH}=16 Hz, 2H, CH₂=CH-), 4.70 (s, 4H, NCH₂) ppm. The imidazolium proton (N-CH-N) peak is not obtained as it has been exchanged with D₂O. ¹³C NMR (D₂O, 100 MHz): δ 122.74, 122.33 (Im-CH), 130.18, 140.31 (Ph-C) 121.23 (CH₂=CH), 133.23 (CH₂=CH-), 51.61 (CH₂=CH-CH₂-), 129.23, 127.66 (Ph-C), 52.48 (N-CH₂-) ppm. FT-IR (neat, ν): 3358(s), 3242(w), 3121(m), 3058(m), 2845(w), 1643(w), 1621(w), 1555(s), 1397(m), 1207(w), 1192(w), 1141(s), 995(m), 961(s), 849(s), 804(s), 754(s) cm⁻¹.

2.4 Synthesis of **3a**

In a schlenk tube, **2a** (4 g, 9.63 mmol) was added to activated potassium carbonate (2.6 g, 19.26 mmol). To which, MeOH (10 mL) was added then Se powder (1.5 g, 19.26 mmol) was added under argon atmosphere. The temperature was set at 70°C and the reaction mixture was stirred for 24 h. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was transferred to a flask and the solvent was evaporated. Then water was added to it and extracted with dichloromethane (3 × 15 mL). The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄. Organic solvent was evaporated under reduced pressure to result crude amorphous off-white product, **3a**. Yield: 55% (based on **2a**). M.p., 168–170°C (became brown), 260–262°C ¹H NMR (CDCl₃, 400 MHz): δ 7.54–7.52 (d, ²J_{HH} = 8 Hz, 4H, ArH), 7.40–7.38 (d, ²J_{HH} = 4 Hz, 4H, ArH), 6.86–6.85 (d, ²J_{HH} = 4 Hz, 2H, ImH), 6.78–6.77 (d, ²J_{HH} = 4 Hz, 2H, ImH), 5.38 (s, 4H, CH₂) 3.75 (s, 6H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ 155.40 (C=Se), 139.06 (Ph-C), 135.95 (CH₂-C), 128.31 (Im-CH), 126.68 (Ph-CH), 120.95 (Im-CH), 119.29 (Im-CH), 51.1 (N-CH₂), 36.53 (N-CH₃) ppm. FT-IR (neat, ν): 3130(w), 2958(w), 2921(m), 2851(m), 2349(w), 2149(w), 1665(m), 1564(w), 1496(w), 1459(s), 1392(s), 1360(s), 1260(m), 1228(s), 1186(m), 1116(m), 1083(m), 1018(m), 940(w), 845(m), 801(s), 760(s), 706(s), 669(s) cm⁻¹.

2.5 Synthesis of **3b**

Potassium carbonate (2.1 g, 8.03 mmol) was heated for about 10 min. by hot airgun and after cooling it for sometimes, **2b** (2 g, 4.02 mmol) and Se powder (0.634 g, 8.04 mmol) were added under argon atmosphere and then methanol (25 mL) was added to the reaction mixture. Then the reaction mixture was stirred for 36 h at 70°C. The progress of the reaction was monitored by TLC. After completion of the reaction, water was added to the reaction mixture and extracted with dichloromethane (3 × 15 mL). The organic extract was washed with brine solution, dried over anhydrous Na₂SO₄. Organic solvent was evaporated under reduced pressure. As a result crude amorphous yellowish product was obtained. Yield: 70% (based on **2b**). M.p. 214–218°C (melted to black). ¹H NMR (CDCl₃, 400 MHz): δ 7.53–7.51 (d, ²J_{HH} = 8 Hz, 4H, ArH), 7.39–7.37 (d, ²J_{HH} = 8 Hz, 4H, ArH), 6.85–6.84 (d, ²J_{HH} = 4 Hz, 2H, ImH), 6.79–6.78 (d, ²J_{HH} = 4 Hz, 2H, ImH), 6.0–5.90 (m, 2H, CH₂=CH-), 5.40 (s, 4H, Ar-CH₂-Im), 5.32–5.29 (d, ²J_{HH} = 12 Hz, 2H, CH₂=CH-), 4.82–4.80 (d, ²J_{HH} = 4 Hz, 4H, Im-CH₂-CH=) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ 156.64 (C=Se), 140.38 (Ph-C), 134.70 (CH₂-C), 139.59 (Im-CH), 128.77 (Ph-CH), 127.46 (CH₂-Ph-C), 119.57 (CH₂=CH), 118.73 (CH₂=CH), 118.62 (Im-CH), 52.75 (=CH-CH₂), 52.24 (N-CH) ppm. FT-IR (neat, ν): 2922(w), 2850(w), 2342(w), 2148(w), 1665(m), 1566(m), 1496(m), 1447(m), 1397(s), 1220(m), 1170(m), 1103(w), 1044(w), 990(m), 935(m), 730(s), 619(m) cm⁻¹.

3. Results and Discussion

3.1 Synthesis and characterization of **2a** and **2b**

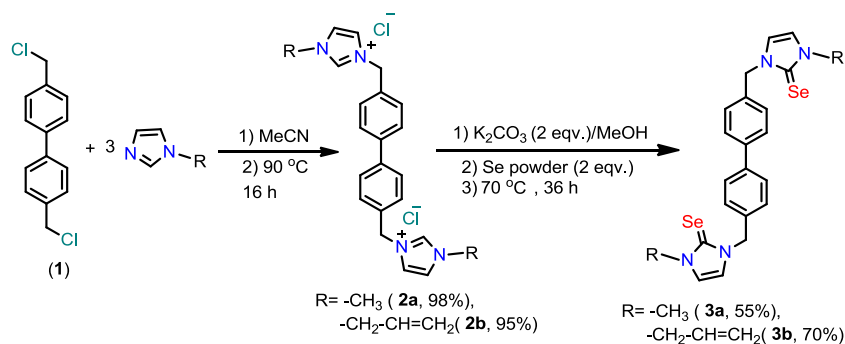
As outlined in scheme 1, compounds **2a** and **2b** were obtained in excellent yield by combining N-methyl

or allyl imidazole with 4,4'-bis(chloromethyl)-1,1'-biphenyl (**1**) in acetonitrile at 90°C under argon atmosphere. Compounds **2a** and **2b** were soluble in water and hygroscopic in nature. **2a** and **2b** were characterized by FT-IR, UV-vis, ¹H NMR and ¹³C NMR techniques. In **2a**, the N₂CH peak appeared at δ 8.75 ppm, while it is absent for **2b** due to fast proton exchange of N₂CH by deuterium. The N-CH₂ peak appeared at δ 5.37 ppm for **3a**, while it is upfield shifted (δ 4.70 ppm) for **3b**.

3.2 Synthesis and characterization of **3a** and **3b**

In a schlenk tube **2a** or **2b** were further heated with 2 equivalent of activated potassium carbonate and 2 equivalent of Se powder in methanol at 70°C to result **3a** and **3b**, respectively (scheme 1). Compound **3a** is soluble in methanol-dichloromethane mixture, while **3b** is soluble only in dichloromethane. **3a** is off-white solid whereas the colour of **3b** is yellowish. The compounds **3a** and **3b** were characterized by FT-IR, ¹H NMR, ¹³C NMR, UV-vis and single crystal X-ray diffraction techniques. The selected characterization parameters for **2a**, **2b**, **3a** and **3b** are listed in table 1. In **3a**, C=Se stretching frequency appeared at 1116 cm⁻¹ while in **3b** it appeared at 1103 cm⁻¹.¹² The N-C-N stretching frequency for **3a** and **3b** are comparable.¹² In ¹H NMR, the chemical shift values for Im-CH, Im-CH₂ and aryl protons are comparable in **3a** and **3b**. In ¹³C NMR, the C=Se chemical shift value for **3a** and **3b** are comparable (δ 155.4 ppm for **3a** and δ 156.6 ppm for **3b**). Similarly, the ¹³C NMR chemical shift values of Im-CH₂ for **3a** (δ 51.1 ppm) and **3b** (δ 52.75 ppm) are comparable.

The formation of **3a** and **3b** were further characterized by 2D NMR spectroscopy (DEPT, HMBC and HSQC). Notably the structural exploration for the imidazole selone using 2D NMR is rare. The structures of **3a** and **3b** are confirmed by 2D NMR studies, which are further verified by single crystal X-ray diffraction study (*vide infra*). Therefore the present investigation



Scheme 1. Synthesis of **2a**, **2b**, **3a** and **3b**.

Table 1. Analytical and spectral data of **2a**, **2b**, **3a** and **3b**.

Compound	M.p. (°C)	Yield (%)	¹ H NMR δ Im-CH (ppm)	¹³ C NMR δ N-C-N (ppm)	Solution UV-vis abs. (nm)	Solid state UV-vis abs. (nm)
2a	102–104	98	7.67		263	286
2b	74–76	95	7.5		262	267
3a	260–262	55	6.86–6.85 6.78–6.77	155.40	272	341
3b	214–218	70	6.85–6.84 6.79–6.78	156.64	273	322

can help to assign the unknown structures of similar class of compounds in biological system. In DEPT spectrum, **3a** showed the existence of one CH₂ group, one CH₃ group and four CH groups, while **3b** displayed three CH₂ groups and five CH groups which are in accordance with the structures of **3a** and **3b** (*vide infra*).

HSQC spectrum of **3a** and **3b** both showed CH correlations as follows, the imidazolium CH group showed strong correlation between the carbons and hydrogen attached to corresponding moieties. The CH group of benzene ring also showed a strong correlation between CH carbon and hydrogen atom attached and in CH₂ group, the CH correlation is also observed. In **3a**, the CH correlation of CH₃ group is observed whereas in **3b**, the CH correlation of allyl group is also observed. From this, the complete CH correlations are confirmed.

The structures of **3a** and **3b** are further confirmed by HMBC spectrum that showed the mapping of carbon coupling with neighbouring protons. In **3a**, the CH₂ proton couples strongly with the nearest imidazolium carbons (³J), it also couples with the nearest carbon atom (³J) of CH group in benzene ring but does not couple with the farthest one. Coupling between the mentioned CH₂ carbon and the quaternary carbon of benzene ring is quite strong (²J). The proton of CH₃ group strongly couples with the nearest Imidazolium carbons (³J). The CH₃ carbon couples with the nearest Imidazolium proton (³J). Another strong correlation is observed between CH₂ carbon and nearest aromatic proton (³J). Whereas in **3b**, the CH₂ carbon couples with the nearest proton of the benzene ring (³J). CH₂ carbon of the allyl group attached to nitrogen atom couples with the CH-proton (²J) of allyl moiety and CH₂-proton (³J) of allyl moiety. CH carbon of allyl moiety shows correlation with the imidazole proton (⁴J, ³J). CH₂ proton of allyl moiety attached to nitrogen shows correlation with nearest CH-carbon (³J) of imidazolium moiety. Protons of the CH₂ group, nearest to the benzene ring show correlation to the neighbouring carbon atom (⁴J) of that benzene ring. Imidazolium CH-carbon couples with the CH₂-proton (⁴J) of the allyl moiety. Quaternary carbon of

benzene ring shows correlation with the neighbouring CH₂ proton (²J). The carbon containing selenium correlates with the imidazolium protons (³J, ³J) and it also correlates with protons of both the neighbouring CH₂ moieties (³J, ³J).

3.3 UV-vis solid and solution state absorption spectra of **2a**, **2b**, **3a** and **3b**

Solution state UV-vis absorption spectrum of **2a**, **2b**, **3a** and **3b** were measured in DMSO (figure 1). The solution state UV-vis absorption patterns of **2a**, **2b**, **3a** and **3b** are comparable. The absorption properties of **2a** and **2b** are much stronger than **3a** and **3b**. **2a** and **2b** both shows an absorption band at 262 and 263 nm due to π - π^* transition, in which absorption of **2b** ($\epsilon = 84623 \text{ L mol}^{-1} \text{ cm}^{-1}$) is stronger than **2a** ($\epsilon = 65427 \text{ L mol}^{-1} \text{ cm}^{-1}$). Similarly, **3a** shows an absorption band at 270 nm with higher molar extinction coefficient ($\epsilon = 50552 \text{ L mol}^{-1} \text{ cm}^{-1}$) compared to **3b** (274 nm, $\epsilon = 43015 \text{ L mol}^{-1} \text{ cm}^{-1}$) due to π - π^* transition. The solid state UV-vis absorption spectra of **2a**, **2b**, **3a** and **3b** are different from respective solution state spectra (figure 2).

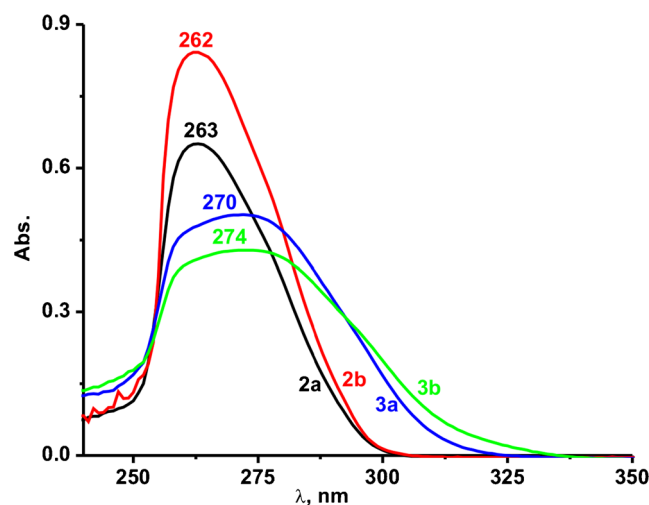


Figure 1. The solution state UV-vis spectra of **2a**, **2b**, **3a** and **3b** in DMSO at RT (9.95×10^{-6} M).

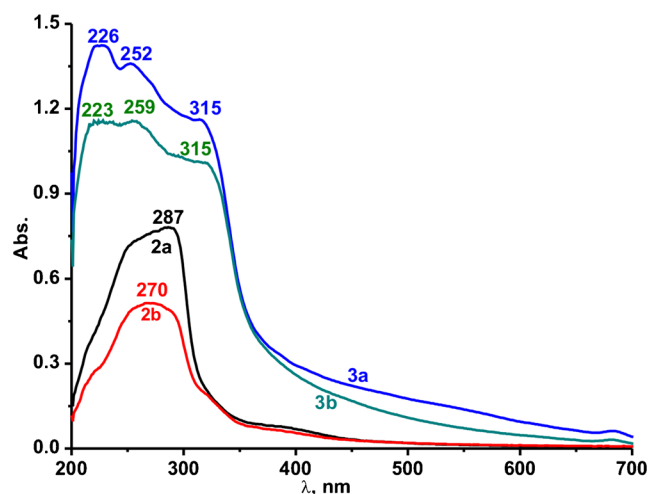


Figure 2. The solid state UV-vis spectra of **2a**, **2b**, **3a** and **3b**.

In solid state, the strong absorption was observed with bathochromic shift from **2** to **3**. In **2a** and **2b**, an

absorption band arises at 287 and 270 nm respectively, while in **3a**, the absorption arises at 226, 252 and 315 nm, while **3b** shows absorption bands at 223, 259 and 315 nm. The absorption in solid state is red shifted compared to solution spectra due to inter molecular stabilization of the molecules in the solid phase.

3.4 Single crystal X-ray structure of **3a** and **3b**

The solid state structures of **3a** and **3b** were unambiguously determined by single crystal X-ray diffraction techniques. The structural parameters are listed in table 2. The selected bond distance and bond angles are accumulated in table 3. Molecules **3a** and **3b** were crystallized in monoclinic space group, $P2_1/c$ and $C2/c$ respectively. Molecular structures of **3a** and **3b** are isostructural (figures 3–6). Thus, the structural feature of **3a** is discussed in detail. Interestingly the biphenyl rings are on the same plane. The reason for being biphenyl rings on the same plane

Table 2. Crystallographic data, details of data collection and structure refinement parameters for **3a** and **3b**.

	3a	3b
Empirical formula	$C_{18}H_{20}N_4SeBr$	$C_{6.5}H_{6.5}NSe0.5$
Formula weight	500.37	552.44
Temperature (K)	150	150
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a , Å	13.3310(5)	24.2299(17)
b , Å	10.0589(3)	8.6581(5)
c , Å	7.7456(3)	13.6583(7)
α , °	90	90
β , °	96.485(3)	119.926(9)
γ , °	90	90
Volume, Å ³	1031.99(6)	2483.3(3)
Z	2	4
ρ_{calc} , mg mm ⁻³	1.6101	1.4775
μ , mm ⁻¹	4.590	3.873
$F(000)$	497.8	1108.0
Data collected	6.68 to 141.48°	7.46 to 141.58°
Unique data	1859	2362
R_{int}	0.0151	0.0279
GOF on F^2	1.040	1.036
R_1 values (all data)	0.0300	0.0554
wR_2 values (all data)	0.0772	0.1323

Table 3. Selected bond lengths [Å] and angles [°] of **3a** and **3b**.

	Bond lengths [Å]		Bond angles [°]		
	3a	3b	3a	3b	
C–Se	1.874	1.850	N–C(Se)–N	105.7	105.3
C(Se)–N	1.355	1.357	N–C–C(Ph)	112.96	

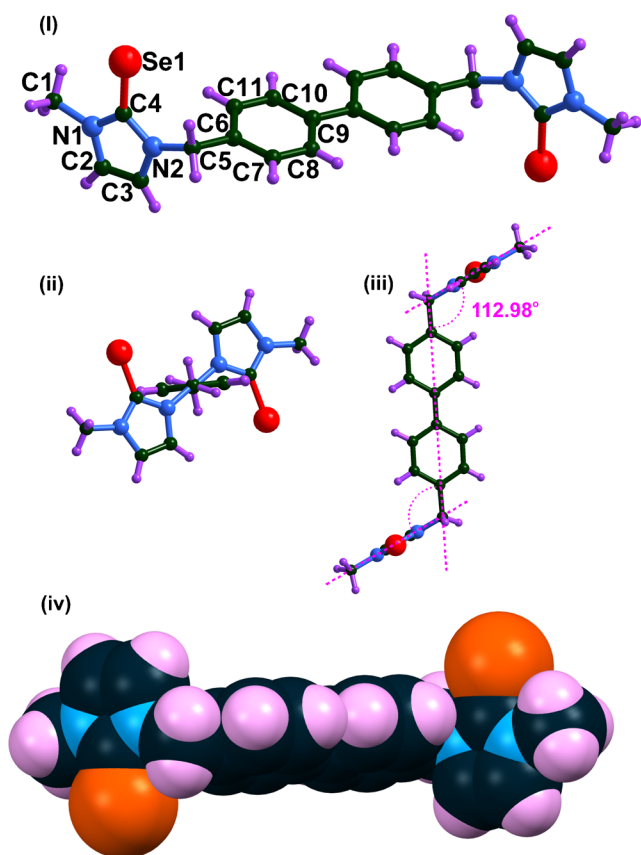


Figure 3. (i) Molecular structure of **3a**; (ii) Non-planar orientation of selone with respect to biphenyl planes; (iii) Trans orientation of selone with respect to biphenyl planes; (iv) Space filling model of **3a**.

is unclear because the aryl-aryl pi-pi interaction is absent. However, this can be due to the crystal packing effect. The $[(\text{HCN})_2\text{C}(\text{Se})]$ heterocyclic rings are oriented in the trans position with respect to biphenyl plane. The $(\text{Ph})\text{CC}(\text{H}_2)\text{N}(\text{Imidazole})$ angle is close to 112° (112.96° for **3a** and 111.86° for **3b**). The $\text{NC}(\text{Se})\text{N}$ angle observed in **3a** (105.7°) and **3b** (105.3°) are comparable with that of reported selone, $\text{C}_{11}\text{H}_{16}\text{N}_4\text{Se}_2$ (105.3°).¹ The $\text{C}=\text{Se}$ bond length in **3a** (1.874 \AA) and **3b** (1.850 \AA) are also comparable with that of $[\text{MeN}(\text{HC})_2\text{N}(\text{CH}_2)_2\text{C}(\text{Se})]_2$ (1.846 \AA).¹ Thus, the $\text{C}=\text{Se}$ bond distance can be described as double bond in nature. The $\text{N}-\text{C}(\text{Se})$ bond distance in **3a** are same (1.355 \AA and 1.356 \AA), which are comparable to that of **3b** (1.357 \AA and 1.342 \AA).

Notably the molecular packing of **3a** and **3b** are nearly comparable. Molecules **3a** and **3b** are arranged in a zigzag one dimensional polymeric structure without any interaction (figures 4 and 5). As shown in figures 4 (right) and 5b the similar such one-dimensional polymeric arrangements are packed as close as possible through *a* axis for **3a** and *b* axis for **3b**.

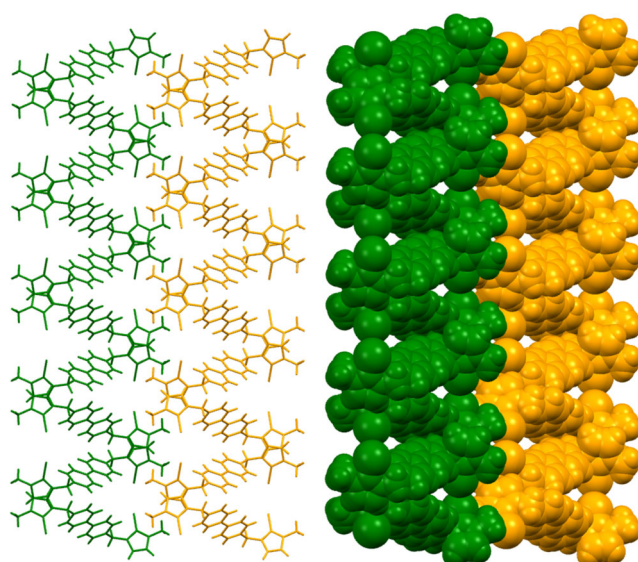


Figure 4. Left: Molecular packing of **3a** view along a axis; Right: Space filling model of molecular packing of **3a**.

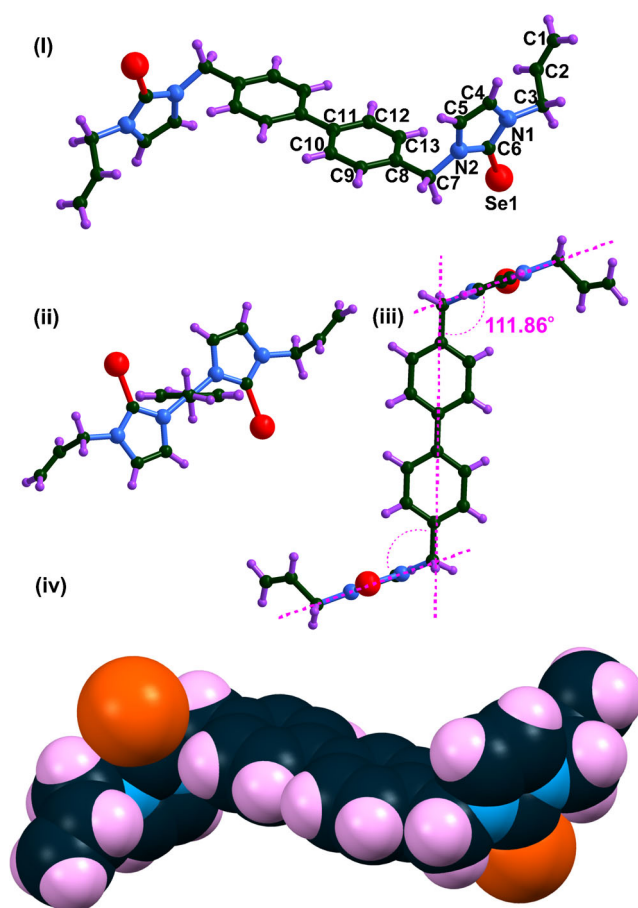


Figure 5. (i) Molecular structure of **3b**; (ii) Non-planar orientation of selone with respect to biphenyl plane; (iii) Trans orientation of selone with respect to biphenyl plane; (iv) Space filling model of **3b**.

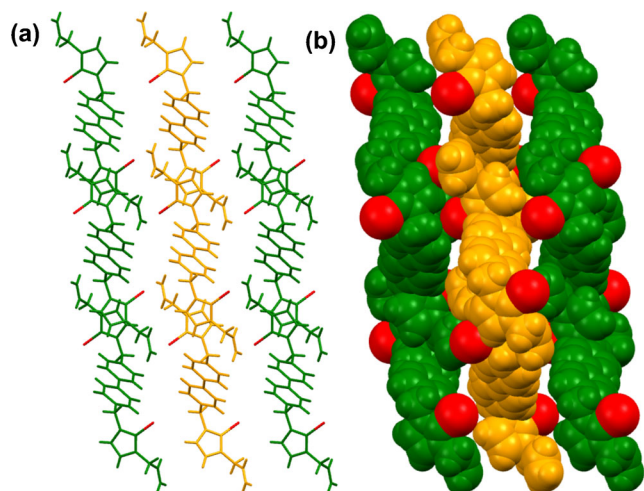


Figure 6. (a) Molecular packing of **3b**; view along b axis; (b) Space filling model of molecular packing of **3b**.

4. Conclusions

In summary, the new allyl and methyl imidazolium salts, **2a** and **2b**, and their corresponding diselenated compounds, **3a** and **3b** separated by aromatic spacer were synthesized. The smooth formation of compounds **2a**, **2b**, **3a** and **3b** were proved by multinuclear NMR (1D and 2D), UV-vis (solid and solution state), FT-IR and single crystal X-ray diffraction techniques. The long biphenyl spacer in **3a** and **3b** is expected to keep the reactive centres (C=Se bond mainly) far apart from each other. As reported for monoselone, the diselone compounds are expected to be more efficient in biological activities as more than one C=Se moieties are there, in which the Se center acts as nucleophile towards some harmful moieties, which are generated in biological systems.

Supplementary Information

CCDC 994138-994139 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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