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A one-flask synthesis and characterization of novel symmetrical pyridyl monoselenides and X-ray crystal structure of bis(5-bromo-2-pyridyl) selenide and bis(2-bromo-5-pyridyl) selenide

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ABSTRACT

The present work reports an efficient one-pot synthesis of symmetrical pyridyl monoselenides by the reaction of bromo-/iodopyridines with the isopropylmagnesium chloride, ^{i}PrMgCl followed by quenching with selenyl chloride, $SeCl_2$. The current methodology constitutes a convenient synthesis of bis(5-bromo-2-pyridyl) selenide **(I)**, bis(2-bromo-5-pyridyl) selenide **(II)** and bis(2,5-dibromo-3-pyridyl) selenide **(III)** under cryogenic conditions requiring shorter time duration to give satisfactory yields. The hitherto unknown compounds have been characterized by elemental analysis and various spectroscopic techniques i.e., ^{1}H NMR, ^{13}C NMR, FT-IR, mass spectrometry and X-ray crystallography.

1. Introduction

Organoselenium chemistry has been exploited to present an extensive range and high diversity of products that find an inevitable place in the area of synthetic [1,2] applications. In addition, organoselenium compounds are known to be suitable antioxidants because of their unique ability to imitate the enzymatic activities of glutathione peroxidase (Gpx) that catalyze the decomposition of hydroperoxides in various biochemical reactions [3,4]. Organoselenium compounds containing selenium in bivalent oxidation state play prominent role in coordination chemistry [5,6]. An extensive use of organoselenium compounds in semiconductors and MOCVD techniques consign these compounds a noticeable position in electronic chemistry [7,8].

A number of methods [9–13] have been developed to obtain an array of aryl alkyl monoselenides and symmetrical diselenides [14–16]. Symmetrical dialkyl/diaryl monoselenides have also been prepared by the cleavage of dialkyl/diaryl diselenides [17–19], while other methods use transition metal complexes [20–22]. However, the use of transition metal complexes not only increases the cost of these reactions but requires elevated temperature, high boiling solvents and longer time durations. In order to overcome these limitations, metal–halogen exchange route has been used to introduce electrophilic selenium into phenyl systems [23] that affords the symmetrical diphenyl monoselenides in good yields. Curiously, this methodology remained untouched for the pyridyl systems to synthesize the symmetrical pyridyl monoselenides.

Pyridyl monoselenides display a unique competitive coordination behavior [24,25] owing to the mixed donor characteristics of Se (soft donor) and N (hard donor) of the pyridine ring towards the same metal atom, in addition to their usefulness in biological systems [26]. The present procedure involves direct selenylation of the pyridine ring using selenyl chloride, $SeCl_2$ as compared to the existing procedures that employ multiple steps involving the preparation of diselenide, its cleavage to selenolate ion followed by arylation [20–22].

2. Results and discussion

2.1. Synthesis

The present write up reveals the synthesis of symmetrical pyridyl monoselenides (Scheme 1) wherein selenyl chloride has been used as an electrophilic reagent that introduces dicationic selenium on the pyridyl moieties conveniently. The generation of pyridylmagnesium chloride using ^{i}PrMgCl makes the introduction of –SeCl on the pyridine ring easier. This method of introduction of electrophilic selenium into pyridyl moieties has an advantage over the use of bromo-/iodopyridines as electrophiles into the pyridylselenomagnesium chlorides where poor electrophilicity of the halopyridines becomes a barrier for the synthesis of monoselenides.

It has been noted that the conventional methods [14–19] for the synthesis of diaryl monoselenides suffer from the limitations like

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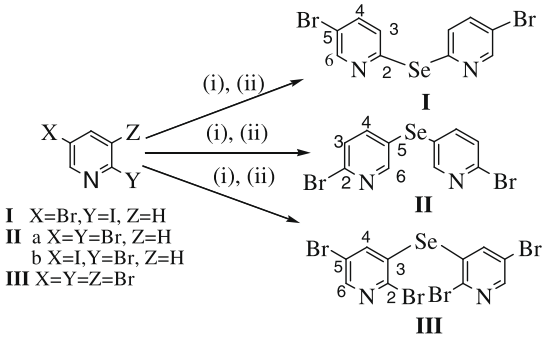


Product	T (°C)	Time (h)[a]	Yield (%)
I	-78	2	85
II a	-78	3	78
b	-78	2.5	80
III	-78	3	83

[a]Time recorded after the addition of $SeCl_2$

Reagents used: (i) ^{i}PrMgCl / THF, 0^{0}C, 2h (ii) $SeCl_2$

Scheme 1. Substrates, reagents and conditions used for the preparation of monoselenides **I**, **II** and **III**.

harsh refluxing conditions, use of high-boiling solvents, which are difficult to remove during work-up and require long time span for completion. However, the current methodology overcomes the above-mentioned limitations as the reaction can be carried out conveniently in one-flask under cryogenic conditions in shorter duration of time and the solvent can be easily removed during work-up. Moreover, selenyl chloride can be easily and freshly prepared at room temperature and is an effective electrophilic reagent [27].

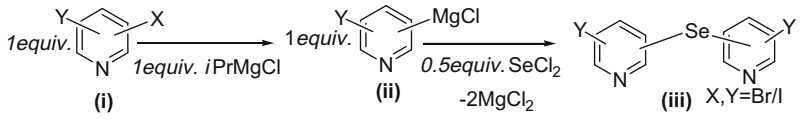
Attempted preparations of symmetrical monoselenides from 2-bromopyridine, 3-bromopyridine and 4-bromopyridine were not met with success in spite of the complete magnesium–halogen exchange of bromopyridines with iso-propylmagnesium chloride. It is probably because the carbon–magnesium bond in pyridylmagnesium chloride, formed from monobromopyridines, is strong enough to cause the electrophilic displacement of –MgCl with –SeCl of selenyl chloride. As a result, the reaction did not yield the corresponding monoselenide while the unused pyridylmagnesium chloride on hydrolysis gave pyridine that is soluble in water. However, the presence of additional electron-withdrawing halogen group in pyridylmagnesium chlorides prepared from polyhalopyridines facilitates the selenylation due to the weaker carbon–magnesium bond. In case of methyl substituted bromopyridines (2,5-dibromo-3-methylpyridine, 2,5-dibromo-4-methylpyridine, 2,5-dibromo-6-methylpyridine) the selenylation did not take place as the electron-releasing methyl group on the pyridylmagnesium chloride, makes the carbon–magnesium bond stronger enough to cause electrophilic displacement of –MgCl with –SeCl of selenyl chloride.

Using 2,5-dibromopyridine and 2-bromo-5-iodopyridine as substrates, we got the same product **II** in both cases because the metal–halogen exchange takes place efficiently at C-5 position of the pyridine ring giving 2-bromo-5-pyridylmagnesium chloride rather than 5-bromo-2-pyridylmagnesium chloride. This is because, in the later case, inter-electronic repulsions due to the coplanarity of lone pair on the nitrogen of pyridine ring with electrons of carbon–magnesium bond at C-2 position destabilizes the 2-magnesiated pyridine. The results obtained are in good agreement with the reactions carried by Queguiner et al. [28] for the functionalisation of 2,5-dibromopyridines. However, the yield was better in case of 2-bromo-5-iodopyridine because of the presence of good leaving group i.e., iodide at the C-5 position of the pyridyl ring. Similarly, in case of 2-iodo-5-bromopyridine the C-2 position is less electrophilic than C-5 position but the metal–halogen exchange occurs conveniently at this position because of the presence of iodide (a good leaving group) giving **I** in good yield. In case of 2,3,5-tribromopyridine, intramolecular coordination of bromine at C-2 with magnesium at C-3 position favors the Grignard formation at C-3 position and subsequently yielded monoselenide **III**. These results are also in agreement with previously obtained results of metal–halogen exchange reactions of 2,3,5-tribrompyridine with ^{i}PrMgCl in our laboratory [29]. It is seen that the C-5/C-3 halopyridines undergo efficient metal–halogen exchange reactions. The presence of additional halogen in halopyridines also facilitates the reaction. However, the methyl substituents on halopyridines have been found non-suitable for these reactions. As a result, the dependence of this methodology on the metal–halogen exchange route limits its scope and applicability.

2.2. Proposed mechanism

In order to justify the pathway of the reaction, a tentative mechanism has been proposed for the method employed to synthesize the symmetrical pyridyl monoselenides by schematic representation (Scheme 2). It has been suggested that bromo-/iodopyridines (i) undergo complete metal–halogen exchange reaction with one equivalent of ^{i}PrMgCl as indicated by initial color change from light yellow to deep red colored solution and finally giving the reddish-brown suspension of corresponding pyridylmagnesium chloride (ii) in the reaction mixture. Pyridylmagnesium chloride formed reacts with half (0.5) equivalent of selenyl chloride ($SeCl_2$) followed by elimination of magnesium dichloride ($MgCl_2$) utilizing the two chlorides of $SeCl_2$ simultaneously to give the corresponding symmetrical monoselenide (iii) in satisfactory yields as depicted in the table included in Scheme 1. During the work-up of the reaction, unreacted selenium in colloidal (red coloured) form was separated by filtration.

A number of reactions were carried out with an objective to explore the utility of the present methodology to prepare the unsymmetrical pyridyl monoselenides by treating the separately prepared Grignard (1) of 2-iodo-5-bromopyridine with one equivalent amount of $SeCl_2$ at −78 °C followed by the addition of Grig-



Scheme 2. General reaction pathway for the halopyridines.

Table 1
Crystallographic data and structural refinement **I** and **II**.

	I	II
Empirical formula	$C_{10}H_6Br_2N_2Se$	$C_{10}H_6Br_2N_2Se$
Formula weight (g mol)	392.95	392.95
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/c$
Unit cell dimensions		
a (Å)	7.645(5)	9.3322(5)
b (Å)	13.180(5)	16.1847(8)
c (Å)	11.310(5)	7.7901(4)
Cell volume (Å^3)	1080.2(9)	1127.46(10)
Z	4	4
Calculated density (g/cm^3)	2.40651	2.315
R indices (all data)	0.0228	0.1003
Absorbed coefficients (mm^{-1})	10.838	10.384
Number of observed reflections [$I > 2\sigma(I)$]	3340	45241
Final $R(F)$[$I > 2\sigma(I)$]	0.0865	0.0640
$\omega R(F^2)$ [$I > 2\sigma(I)$]	0.1076	0.1579
Number of data/restraints/parameters	1324/0/69	4162/6/137
Goodness-of-fit	1.329	1.020

nard (2) of 2,5-dibromopyridine. Curiously, the expected unsymmetrical product was not obtained in any of the cases. Instead, a trace amount of the corresponding symmetrical monoselenides along with diselenide corresponding to Grignard (1) i.e., bis(5,5′-dibromo pyridyl) diselenide was obtained. The unexpected diselenide might have formed due to the insertion of the elemental selenium, left unreacted during the preparation of $SeCl_2$, into the Grignard (1) to afford the corresponding pyridyl selenomagnesium chloride followed by hydrolysis and aerial oxidation and is well supported by methodology practiced in our laboratory for the preparation of diselenides [29]. The diselenide formed was characterized by m.p. 110–112 °C, ^{1}H NMR (δ ppm) 8.414–8.425 (d, 2H, J = 3.3 Hz), 7.563–7.591 (m, 4H, J = 8.4 Hz) and ^{13}C NMR (δ ppm) 152.66 (C-6), 150.49 (C-2), 139.81 (C-4), 125.01 (C-3), 118.74 (C-5). The formation of the diselenide was avoidable under rigorously dried conditions during the preparation of the $SeCl_2$.

2.3. ^{1}H NMR and ^{13}C NMR spectroscopy

From the spectroscopic data given in Section 3.3, the replacement of halogen with selenium can be justified by noticeable variation in the chemical shift (δ ppm) of the aromatic protons of the prepared compounds (**I**, **II** and **III**) in comparison to those of the starting materials [30,31]. In ^{13}C NMR spectroscopic data obtained for the three compounds, the order of chemical shifts observed for substituted and unsubstituted carbons of pyridyl ring is in fair agreement with those assigned for the substituted pyridines in literature [32,33]. The assignment of the peaks to each carbon of the prepared molecules is based on the numbering followed for the compounds in Scheme 1.

2.4. Infrared spectroscopy and mass spectrometry

IR data confirms the formation of the titled compounds as the C–H stretching band appears in the region 3100–2900 cm^{-1} while the strong bands corresponding C=C and C=N appear in the region 1630–1430 cm^{-1}. The absorption peaks due to C–Br bonds for both the compounds **I**, **II** and **III** appear at 622 cm^{-1}, 620 cm^{-1} and 673 cm^{-1}, respectively and are in agreement with the recorded values in the literature that are generally in the region 600–800 cm^{-1} [34]. Similarly, the peaks corresponding to the C–Se bonds appear at 466 cm^{-1} for compound **I**, 477 cm^{-1} for compound **II** and 467 cm^{-1} for compound **III**, thus are in the expected range (400–500 cm^{-1}) [35].

Mass spectrometry studies of both monoselenides **I** and **II** showed the appearance of molecular ion peak $[C_{10}H_6N_2Br_2{}^{80}Se]^+$, ($M^+$) at *m*/*z*; 394. The peaks corresponding to other isotopes of selenium were observed at 396 $[C_{10}H_6N_2Br_2{}^{82}Se]^+$, 392 $[C_{10}H_6N_2Br_2{}^{78}Se]^+$, 391 $[C_{10}H_6N_2Br_2{}^{77}Se]^+$, 390 $[C_{10}H_6N_2Br_2{}^{76}Se]^+$, 388 $[C_{10}H_6N_2Br_2{}^{74}Se]^+$, respectively. In the mass spectrum of monoselenide **III** the molecular ion peak at *m*/*z*; 552 $[C_{10}H_4N_2Br_4{}^{80}Se]^+$ was not observed. However, the fragmented peaks at *m*/*z*; 391 $[C_{10}H_4N_2Br_2{}^{80}Se]^+-1$ and at *m*/*z* 231 $[C_{10}H_4N_2{}^{80}Se]^+-1$ were observed by the subsequent loss of two and four bromines respectively from the molecular ion.

2.5. X-ray crystallography

Perspective view of the compounds **I** and **II** is shown in Fig. 1 and X-ray data of the prepared monoselenides is presented in Table 1. It was found that compounds **I** and **II** were monoclinic crystals with C_2/c and $P2_1/c$ space group, respectively. The perspective view of crystals structures (**I**, **II**) also exhibits some secondary Se···Br [36,37], Br···N and interactions as shown in Fig. 1. The C–Se bond distances are depicted in Table 2. In case of compound **I**, the C1–Se1 and C1a–Se1 bond distances are same i.e., 1.927 Å. However, C3–Se1 and C6–Se1 bond distances for compound **II** are 1.906 Å and 1.910 Å, respectively.

The bond angles as depicted in Table 2 for the compounds **I** and **II** showed that angle C1Se1C1a (97.4°) for compound **I** is smaller than angle C3Se1C6 (100.8°) for compound **II**. In structure **II**, C–Se carbon is in contact with the adjacent carbon atoms bearing hydrogen atoms on both the sides. Thus the steric repulsion caused due to the presence of substituents on the pyridyl rings increases the C–Se–C bond angle. On the other hand, in case of compound **I** the carbon atoms of the two pyridine rings; C1 and C1a have one adjacent naked nitrogen atom and one adjacent carbon atom bearing hydrogen atom only, thus causing lesser steric crowding responsible for decreased bond angle in case of **I** as compared to that in structure **II**. The steric crowding and the bond angles are also responsible for the variation in the orientation of the molecules and their arrangement in the cubic lattice.

3. Materials and methods

All the experimental manipulations were carried out in dry and deoxygenated nitrogen atmosphere. Tetrahydrofuran (THF) was dried over sodium–benzophenone and distilled. All the starting materials were prepared according to the methods reported in literature [30,31]. Selenyl chloride ($SeCl_2$) was freshly prepared by reacting elemental selenium (Loba) with sulfuryl chloride (Aldrich) [27]. All the compounds prepared were fully characterized using elemental analysis on a Perkin–Elmer 2400 CHN analyzer. ^{1}H, ^{13}C NMR spectra were recorded on a Jeol AL 300 MHz spectrometer in $CDCl_3/CCl_4$. Tetramethylsilane (TMS) was used as an internal standard for ^{1}H NMR and ^{13}C NMR. Infrared spectra were obtained between KBr plates using CCl_4 as mulling agent on a Perkin–Elmer model 1430 spectrophotometer. Mass spectrometry was carried out on ES-MS Q-TOF while X-ray crystallography was carried out on Bruker Smart Apex.

3.1. General procedure for the synthesis of symmetrical pyridyl monoselenides (Scheme 1)

A 2 M solution of ^{i}PrMgCl (20 mmol) in THF was added drop wise to the well stirred solution of (20 mmol) 5-bromo-2-iodopyridine/2,5-dibromopyridine/2-bromo-5-iodopyridine/2,3,5-tribromopyridine in THF at room temperature leading to a perceptible change in color from orange to reddish brown at room temperature. After two hours of continuous stirring at room temperature, a freshly prepared selenyl chloride ($SeCl_2$) solution (10 mmol)

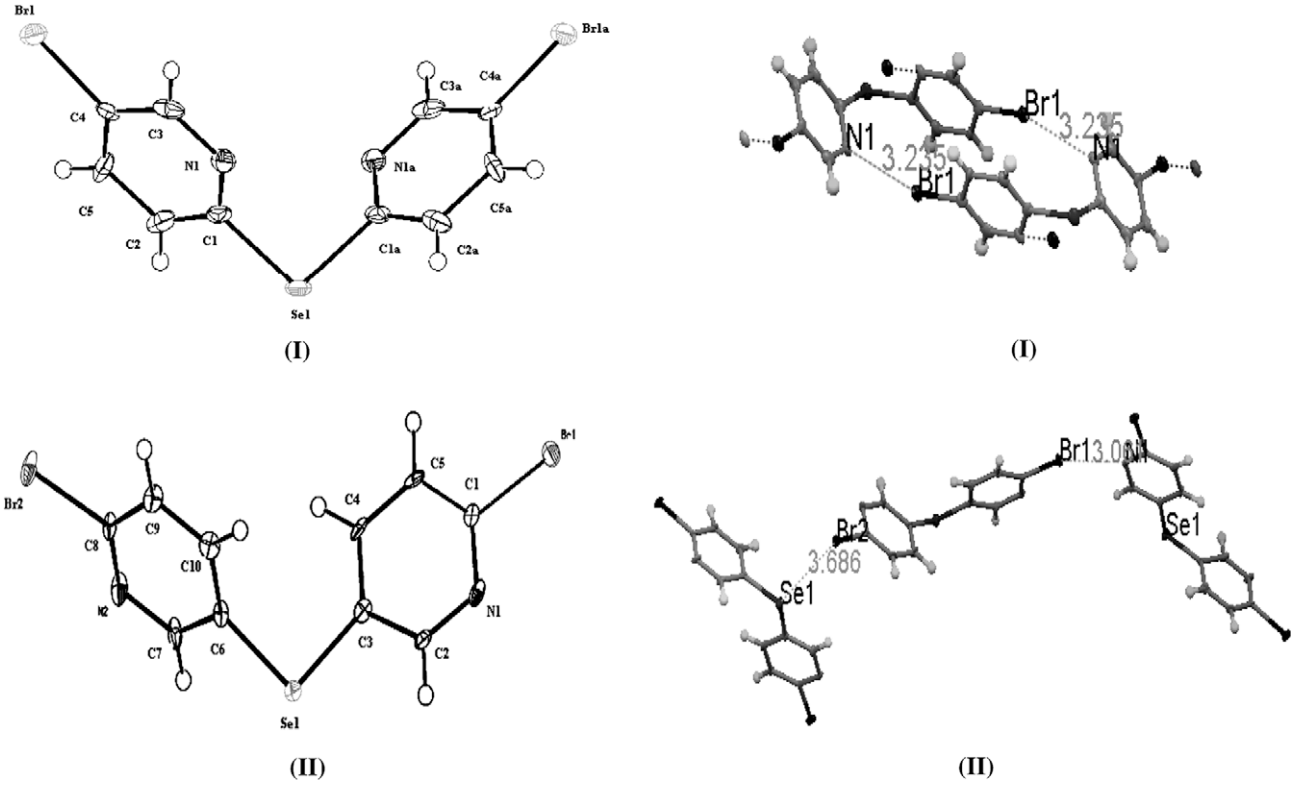


Fig. 1. ORTEP representations and perspective view of bis(5-bromo-2-pyridyl) selenide (**I**) showing Br···N secondary interactions, and bis(2-bromo-5-pyridyl) selenide (**II**) showing the Se···Br and N···Br secondary interactions.

Table 2
Structural comparison of selenides **I** and **II** on the basis of selected C–Se and C–Br bond distances in terms of [Å] and bond angles in terms of [°].

I				II			
Atoms 1,2	d 1,2 [Å]	Atoms 1,2,3	Angle 1,2,3 [°]	Atoms 1,2	d 1,2 [Å]	Atoms 1,2,3	Angle 1,2,3 [°]
C1–Se1	1.927(9)	C1–Se1–C1a	97.4(5)	C1–Br1	1.895(5)	C3–Se1–C6	100.8(2)
C1a–Se1	1.927(8)	N1–C1–Se1	117.0(9)	C8–Br2	1.903(5)	C10–C6–Se1	123.3(3)
C4–Br1	1.896(9)	C2–C1–Se1	118.1(7)	C3–Se1	1.906(5)	C7–C6–Se1	117.7(4)
–	–	C5–C4–Br1	120.4(7)	C6–Se1	1.910(5)	C2–C3–Se1	116.3(4)
–	–	C3–C4–Br1	119.5(6)	–	–	C4–C3–Se1	125.3(4)

was added *in situ* at −78 °C *via* cannulation ensuing a red colored suspension and was then left for stirring at room temperature. The progress of the reaction was monitored by thin layer chromatography. After completion of the reaction, the resulting solution was poured into water and extracted with dichloromethane (3×50 mL). The organic layer was then filtered through celite and dried over anhydrous sodium sulfate. Evaporation of the solvent afforded the reddish brown colored solid that was purified in silica 60–120 (hexane:ethyl acetate; 5:1).

3.2. Single crystal X-ray analysis

Compounds **I** and **II** were recrystallised in dichloromethane/hexane (1/4) mixture at room temperature and fine diffraction quality crystals of the respective compounds were obtained. A suitable crystal was mounted on glass capillaries of Bruker Smart Apex. The structures were solved by the direct methods (SHELXL-97) [38] and refined by full-matrix least squares method. The final cycle of full-matrix least squares refinement for structure **I** and **II** was based on 1324 (diffraction temperature 100 K) and 4162 (diffraction temperature 150 K) observed reflections, at 69 and 137 variable parameters respectively for $[I > 2\sigma(I)]$ converged with unweighted and weighted agreement factors of $R = 0.0228$ and $\omega R = 0.1076$ for structure **I** and $R = 0.1003$ and $\omega R = 0.1579$ for structure **II**. Anisotropic thermal parameters were employed for non-hydrogen atoms and all the hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

3.3. Spectroscopic data of the titled compounds

3.3.1. Bis(5-bromo-2-pyridyl) selenide (*I*)

Orange-yellow colored crystalline, m.p. 94–95 °C, Yield: 85%, *Anal.* Calc. (%) for $C_{10}H_6Br_2N_2Se$: C, 30.64; H, 1.52; N, 7.10. Found: C, 30.64; H, 1.48; N, 6.71%. ^{1}H NMR: (300 MHz, $CDCl_3/CCl_4$, δ ppm) 8.53–8.55 (d, 2H, $J = 6$ Hz), 7.63–7.67 (dd, 2H, $J = 12$ Hz), 7.40–7.48 (d, 2H, $J = 24$ Hz); ^{13}C NMR: (75 MHz, $CDCl_3/CCl_4$, δ ppm) 152.90 (C-6), 151.35 (C-2), 139.40 (C-4), 129.06 (C-5), 119.53 (C-3); IR(KBr/CCl_4, ν cm^{-1}) 2922, 1591, 1436, 1249, 1091, 999, 836, 794, 705, 622, 466 cm^{-1}; ES-MS: m/z (R.I.) 394 (M^+, 100), 396 (46), 392 (85), 390 (36), 388 (9), 155 (3), 120 (16).

3.3.2. Bis(2-bromo-5-pyridyl) selenide (*II*)

White crystalline, m.p. 108–110 °C, Yield: 80%, *Anal.* Calc. (%) for $C_{10}H_6Br_2N_2Se$: C, 30.64; H, 1.52; N, 7.10. Found: C, 30.66; H, 0.71;

N, 6.66%. ^{1}H NMR: (300 MHz, $CDCl_3/CCl_4$, δ ppm) 8.45–8.46 (d, 2H, J = 3 Hz), 7.59–7.62 (dd, 2H, J = 9 Hz), 7.42–7.44 (d, 2H, J = 6 Hz); ^{13}C NMR: (75 MHz $CDCl_3/CCl_4$, δ ppm) 153.44 (C-6), 153.22 (C-2); 142.89 (C-4), 129.21 (C-5), 126.11 (C-3), IR(KBr/CCl_4, ν cm^{-1}) 2924, 1551, 1444, 1350, 1260, 1091, 1002, 791, 705, 620, 477; ES-MS: m/z (R.I.) 394 (M^+, 100), 396 (52), 392 (83), 390 (35), 388 (10), 155 (27), 120 (90).

*3.3.3. Bis(2,5-bromo-3-pyridyl) selenide (**III**)*

Off-white crystalline, m.p. 120–122 °C, Yield: 83%, *Anal.* Calc. (%) for $C_{10}H_4Br_4N_2Se$: C, 21.74; H, 1.01; N, 5.07. Found: C, 21.97; H, 0.97; N, 4.55%. ^{1}H NMR: (300 MHz, $CDCl_3/CCl_4$, δ ppm) 8.33–8.35 (d, 2H, J = 6 Hz), 7.50–7.57 (d, 2H, J = 21 Hz); ^{13}C NMR: (75 MHz, $CDCl_3/CCl_4$, δ ppm) 150.30 (C-6), 143.77 (C-2), 140.38 (C-4), 132.09 (C-3), 120.45 (C-5); IR(KBr/CCl_4, ν cm^{-1}) 2913, 1591, 1384, 1249, 1110, 1063, 1015, 840, 794, 705, 673, 467; ES-MS: m/z (R.I.) 231 (11), 391 (5).

4. Conclusions

In this paper the authors have developed a convenient methodology for the synthesis of hitherto unknown symmetrical pyridyl monoselenides. The crystal structures of the synthesized compounds display, Se···Br and Br···N non-bonding interactions that are usually known to impart supramolecular [39] characteristics to these compounds.

5. Supplementary material

CCDC 736024 and 736025 contain the supplementary crystallographic data for compounds **I** and **II**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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