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Lithiation of *N*,*N*,*N*′,*N*′-tetraisopropylpyridine-2,6-dicarboxamide: synthesis, characterization and single crystal X-ray studies of chalcogen (Se/Te) derivatives of *N*,*N*,*N*′,*N*′-tetraisopropylpyridine-2,6-dicarboxamide

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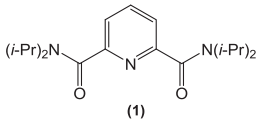
ABSTRACT

The lithiation of *N*,*N*,*N*′,*N*′-tetraisopropylpyridine-2,6-dicarboxamide (**1**) and its application in the synthesis of chalcogen (Se/Te) derivatives was investigated. It was found that the selectivity of the reaction changed with the change in the amount of *n*-BuLi used. The lithiation of **1** with 6.1 equiv of *n*-BuLi followed by subsequent reactions with selenium/tellurium and iodomethane exclusively afforded the monosubstituted chalcogen derivative (**2a**/**2b**) in excellent yield. However, the use of 2.1 or 4.2 equiv of *n*-BuLi gave two additional products along with **2a**/**2b**. One of the isolated products corresponded to the double lithiation of **1** and the other to the *ortho* lithiation followed by nucleophilic addition of *n*-BuLi to the one of the two carbonyl moieties. The prepared compounds have been characterized by single crystal X-ray crystallography, NMR (^{1}H, ^{13}C, ^{77}Se and ^{125}Te), IR, UV–Visible and Mass spectroscopy. Crystal structure of *N*,*N*,*N*′,*N*′-tetraisopropyl-3,5-bis(methyltelluryl)pyridine-2,6-dicarboxamide (**3b**) reveals a strong intramolecular C•O···Te secondary and intermolecular Te···π pyridyl interactions.

1. Introduction

Organoselenium and -tellurium compounds exhibiting Se/Te···heteroatom (N/O/halogen atoms) secondary interaction have shown immense potential as biological active agents,[1,2] chiral reagents for asymmetric synthesis[3] and precursor to semiconducting materials.[4–6] The presence of these secondary interactions often lead to the isolation of many hypervalent organochalcogen[7,8] and trichalcogen compounds.[9] Recently, we have reported the synthesis of internally chelated chalcogen derivatives of 2-pyridylcarboxamides through the lithiation of *N*,*N*-diisopropylpyridine-2-carboxamide.[10] While the lithiation of phenyl-[11,12] and pyridylcarboxamides[12–14] has been well investigated, the corresponding chemistry of dicarboxamides is unexplored. To the best of our knowledge, there is no report on the lithiation of *N*,*N*,*N*′,*N*′-tetraisopropylpyridine-2,6-dicarboxamide (**1**). The present work is an attempt to investigate the lithiation of **1** with the emphasis on the synthesis of the corresponding chalcogen derivatives. The crystal structures of some of the representative compounds have been determined by single crystal X-ray diffraction analysis in order to elucidate the Se/Te···heteroatom secondary interactions in these molecules.



(1)

2. Results and discussion

2.1. Synthesis of chalcogen derivatives of 1

The reaction of **1** with 2.1 equiv of *n*-BuLi in dry THF followed by treatment with selenium gave the corresponding selenolate anion, which on quenching with iodomethane afforded **2a** in 64% yield. Two more products, **3a** and **4a** were also obtained from the reaction in a 5% and 10% yield, respectively (Scheme 1). The use of tellurium

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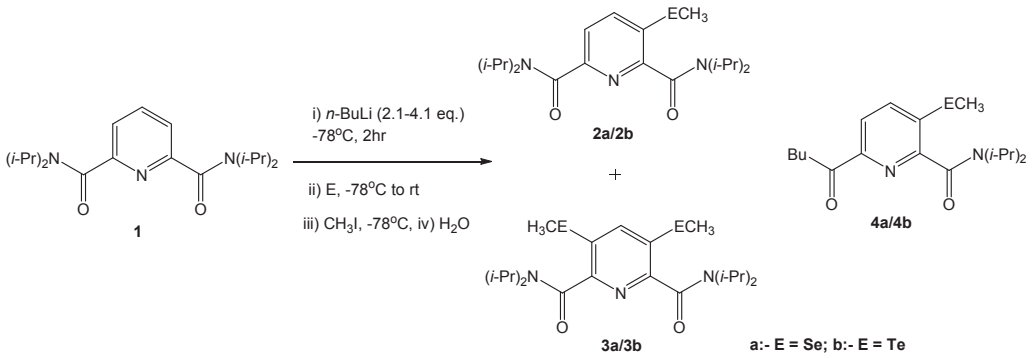


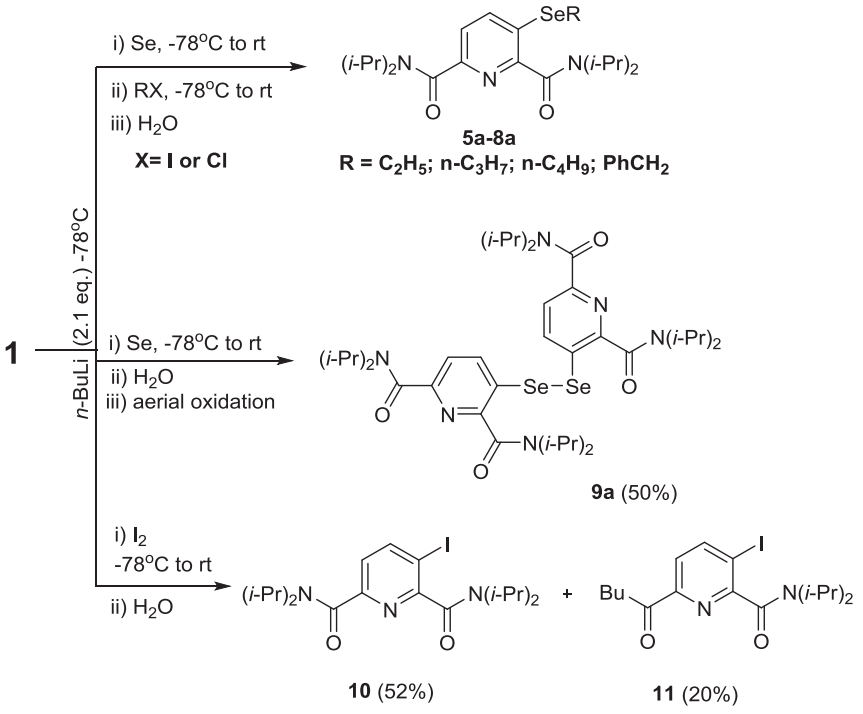
Scheme 1. Lithiation of **1** with 2.1 equiv of *n*-BuLi.

instead of selenium in the later reaction afforded **2b**, **3b**, and **4b** in 47%, 6% and 20% yield, respectively (Scheme 1). The compound **3a**/**3b** results from the double lithiation of **1** at the positions that are *ortho* to the two carboxamides moieties. The formation of **4a** and **4b** suggests *ortho* lithiation followed by nucleophilic addition of *n*-BuLi to the one of the two carbonyl moieties of **1**, which is surprising as *N*,*N*-diisopropylcarboxamides are known to resist the nucleophilic addition of *n*-BuLi.[15,16]

The reactions involving electrophiles other than iodomethane proceeded without the formation of any by-product. The treatment of the selenolate anion, with iodoethane, bromopropane, iodobutane and (chloromethyl)benzene afforded **5a**, **6a**, **7a**, and **8a**, respectively in moderate (54–58%) yields (Scheme 2, Table 1, entries 1–4). In another variation, the selenolate anion was directly hydrolyzed and subjected to aerial oxidation to afford the corresponding diselenide, **9a**, in 48% yield (Scheme 2). Since the products corresponding to **3a** and **4a** were not isolated from the later reactions, it can be inferred that the nature of the electrophile plays a detrimental role in the formation of the by-products. This was confirmed when we investigated the reaction with iodine as the electrophile. The treatment of **1** with 2.1 equiv of *n*-BuLi and subsequent trapping with iodine gave **10** and **11** in 52% and 20% yield, respectively (Scheme 2).

Next, the role of the amount of *n*-BuLi on the selectivity of the reactions depicted in Scheme 1 was examined. Our thought was that an increase in the amount of *n*-BuLi would lead to increase in the proportion of **3a**/**3b** and **4a**/**4b**. This to some extent was the case when 4.1 equiv of *n*-BuLi was used. There was 10% increase in the yield of **4a** and a corresponding decrease in the yield of **2a** (Table 1, entry 6). This suggested nucleophilic addition of *n*-BuLi on the carbonyl moiety of **2a**. However, the reaction of **1** with 6.1 equiv of *n*-BuLi gave result that was contrary to the expectation. **2a**/**2b** was the sole product obtained and there was no indication of the formation of **3a**/**3b** or **4a**/**4b** (Table 1, entries 7 and 8). Similarly, the monosubstituted product, **10**, was the only product obtained when iodine was used as the electrophile (Table 1, entry 9). In case of the reactions where no by-products were formed (Table 1, entries 3 and 5), a substantial improvement in the yield of the product was noticed (Table 1, entries 10 and 11).

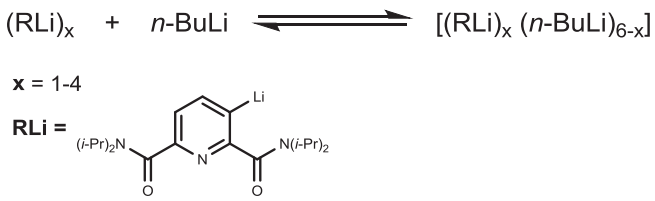
In light of the above results, it appears that a pure organolithium species $(RLi)_x$ exists in equilibrium with a lithium hetero-aggregate, $[(RLi)_x\ (n\text{-BuLi})_{6-x}]$, (Scheme 3). At a lower *n*-BuLi concentration,



Scheme 2. Synthesis of selenium and iodo derivative of **1**.

Table 1
Lithiation of **1** with *n*-BuLi or LDA

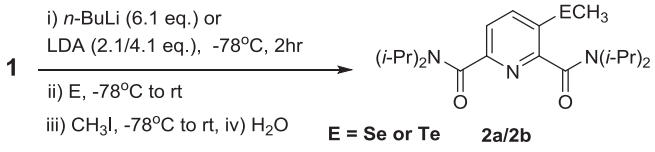
Entry	Base (equiv)	Electrophile	Product (yield)
1.	*n*-BuLi (2.1)	Se+C_2H_5I	**5a** (58%)
2.	*n*-BuLi (2.1)	Se+*n*-C_3H_9Br	**6a** (58%)
3.	*n*-BuLi (2.1)	Se+*n*-$C_4H_{11}I$	**7a** (58%)
4.	*n*-BuLi (2.1)	Se+$PhCH_2Cl$	**8a** (54%)
5.	*n*-BuLi (2.1)	Se and aerial oxidation	**9a** (48%)
6.	*n*-BuLi (4.1)	Se+CH_3I	**2a** (54%), **3a** (5%), **4a** (25%)
7.	*n*-BuLi (6.1)	Se+CH_3I	**2a** (90%)
8.	*n*-BuLi (6.1)	Te+CH_3I	**2b** (77%)
9	*n*-BuLi (6.1)	I_2	**10** (67%)
10.	*n*-BuLi (6.1)	Se+*n*-$C_4H_{11}I$	**7a** (74%)
11.	*n*-BuLi (6.1)	Se and aerial oxidation	**9a** (62%)
12.	LDA (2.1)	Se+CH_3I	**2a** (86%)
13.	LDA (4.1)	Se+CH_3I	**2a** (88%)
14.	LDA (4.1)	Te+CH_3I	**2b** (75%)



Scheme 3. Formation of lithium aggregate of **1**.

the equilibrium lies more towards the left side that makes *n*-BuLi available for the nucleophilic addition reaction. At a higher *n*-BuLi concentration (6.1 equiv), the equilibrium shifts towards the thermodynamically more stable lithium hetero-aggregate so that *n*-BuLi is not available for the addition reaction. This partly explains the non-isolation of the bimetallated species in the later reactions. The product yield of ~50% in the reactions involving 2.1 equiv of *n*-BuLi (Table 1, entries 1–5) also indicates towards the formation of lithium aggregate in the reaction mixture. The formation of lithium hetero-aggregates and its influence on the selectivity of the reaction has been reported by other research groups also.[17,18]

We next investigated the reaction of **1** with lithium diisopropylamide (LDA), which is a hindered and non-nucleophilic base. The reaction of **1** with 2.1 equiv of LDA followed by selenium insertion and trapping with iodomethane exclusively gave **2a** in excellent yield (Scheme 4, Table 1, entry 12). The effect of the amount of LDA on the selectivity of the reaction was examined in this case also. Interestingly, there was no indication of any bimetallated species when the amount of LDA was increased from 2.1 to 4.1 equiv (Table 1, entries 13 and 14).



Scheme 4. Treatment of **1** with 6.1 equiv of *n*-BuLi or 2.1/4.1 equiv of LDA.

2.2. Spectroscopic studies

The ^{1}H NMR spectra of **2a**, **2b**, **4a**, **4b**, **5a**–**9a**, **10**, and **11** show two doublets in the aromatic region. On the other hand, the ^{1}H NMR spectra of **3a** and **3b** showed only one singlet in the aromatic region indicating double lithiation of the pyridine ring. The [^{1}H–^{1}H] COSY NMR technique was used to determine the position of –$TeCH_3$ in **4b** as ^{1}H NMR data was inconclusive. A horizontal line (Fig. 1) from the spot at δ 2.28 ppm (labeled **A**, corresponding to –Te**CH_3** protons) that meets the two low intensity off-diagonal spots (labeled **B** and **C**,

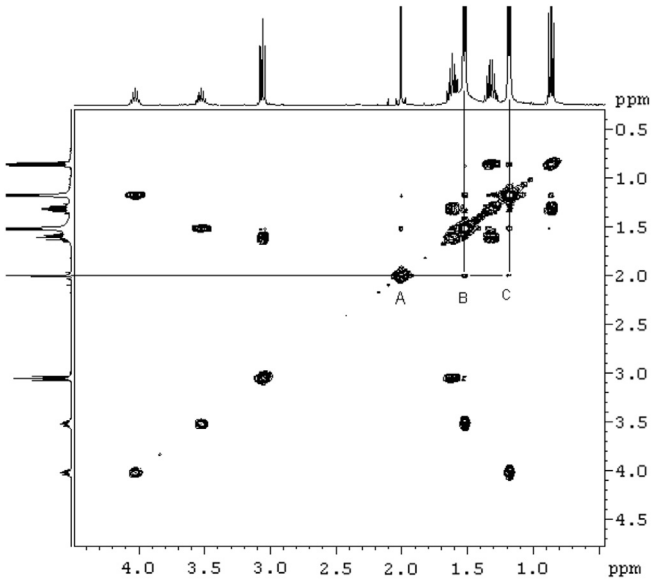


Fig. 1. COSY NMR spectrum of **4b**.

corresponding to –CH(**CH_3**)$_2$ protons) represents long range coupling between these hydrogen nuclei. This suggests that –$TeCH_3$ is *ortho* to the carboxamide moiety rather to the *keto* group. The IR C•O stretching band in **2a**, **3a** and **4a** (1632, 1634 and 1628 cm^{-1}, respectively) is very close to the corresponding band in **1** (1629 cm^{-1}). Conversely, this band appeared at a lower frequency (~1617 cm^{-1}) in the corresponding tellurium derivatives (**2b**, **3b**, and **4b**). The C•O stretching band in the selenium derivatives, **5a**–**9a**, is also observed at lower frequency than **1**. All these observations are indicative of the absence of C•O···Se interaction in **2a**–**4a** and the presence of C•O···Te interaction in the corresponding tellurium derivatives. The later inference has been validated by X-ray structure of **2a**, **3b**, and **4b**. A direct correlation between the ^{125}Te NMR chemical shifts and the strength of C•O···Te intramolecular interactions has also been observed. The ^{125}Te NMR signal in **2b** and **3b** appears at δ 315.0 and 327.2 ppm, respectively. The shortest C•O···Te intramolecular distance in **3b** is found to be 3.1992 Å, whereas it is 2.825 Å in **4b**.

The UV–Visible spectra of **2a** and **5a**–**8a** show three intense absorption bands (one $\pi\rightarrow\pi^*$ and two $n\rightarrow\pi^*$). Contrary to the expectation, the $n^1\rightarrow\pi^*$ transition band in **2a**, **5a** and **6a** is more intense than the $\pi\rightarrow\pi^*$ transition band. Selenium atom is responsible for this hyperchromic effect as the corresponding band in the tellurium derivatives and starting material is less intense than the $\pi\rightarrow\pi^*$ transition band. Interestingly, the compound **3a** and **3b** shows only two absorption bands. While there is no change in the position of $\pi\rightarrow\pi^*$ transition band relative to **2a**/**2b**, the $n\rightarrow\pi^*$ band shows large bathochromic shift, and is sensitive to the nature of the chalcogen atom (Fig. 2). The later band in **4b** is broader and 37 nm to the red of the corresponding selenium derivative.

2.3. Solid state structural features of 2a, 3b, and 4b

The single crystal X-ray studies were carried out in order to determine structural features of **2a**, **3b** and **4b**. The crystals were grown in a solution of hexane and ethyl acetate. Fig. 3a depicts the molecular structure of **2a** and Table 2 shows its selected bond lengths and angles. The two carbonyls of the amide groups adopt a *syn*-spatial disposition relatively to the pyridine ring with the *ortho* and *para* amide units intercepting the pyridine ring at 49.47(7)° and 86.22 (8)°, respectively. The C(25)–Se–C(1)–C(2) torsion angle of 173.1°(1) indicates that the –$SeCH_3$ is planar to the pyridine ring. The C(sp^2)–Se bond length (1.908(1) Å) in **2a** is much

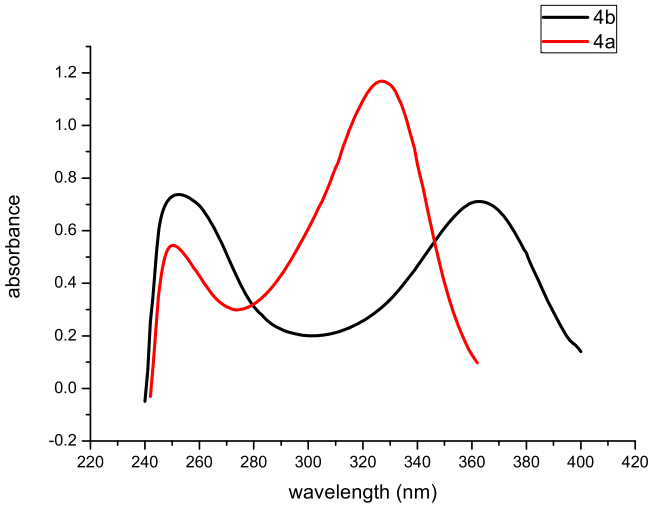


Fig. 2. UV-Visible spectra of **4a** and **4b**.

37.5(2)°, which is mainly due to the presence of the sterically demanding *ortho* carboxamide group.

The crystal structure of **4b** is built from an asymmetric unit composed of two independent molecules (A and B) shown in Fig. 4a. These molecules have identical structures as indicated by the selected bond distances and angles listed in Table 3. Indeed, the rms between two molecules, excluding the hydrogen atoms, is only 0.142 Å. As observed for **3b**, the two carbonyls of the amide groups adopt an *anti*-configuration in each molecule relatively to the corresponding pyridine ring. These two molecules exhibit similar Te–C bond lengths and C–Te–C and C–C–Te angles, which are consistent with a 'V' shaped geometry around each tellurium atom. Interestingly, the two $-TeCH_3$ substituents in both the independent molecules are almost coplanar with the pyridine ring while it is out of the plane of the pyridine ring in **3b**. In the crystal structure of **4b**, the molecules A and B adopt an almost parallel disposition establishing two independent Te···π pyridyl interactions with distances of 3.852 and 3.662 Å between Te and the centroid of the pyridine rings (see Fig. 4b). In addition, the structure of **4b** also exhibits

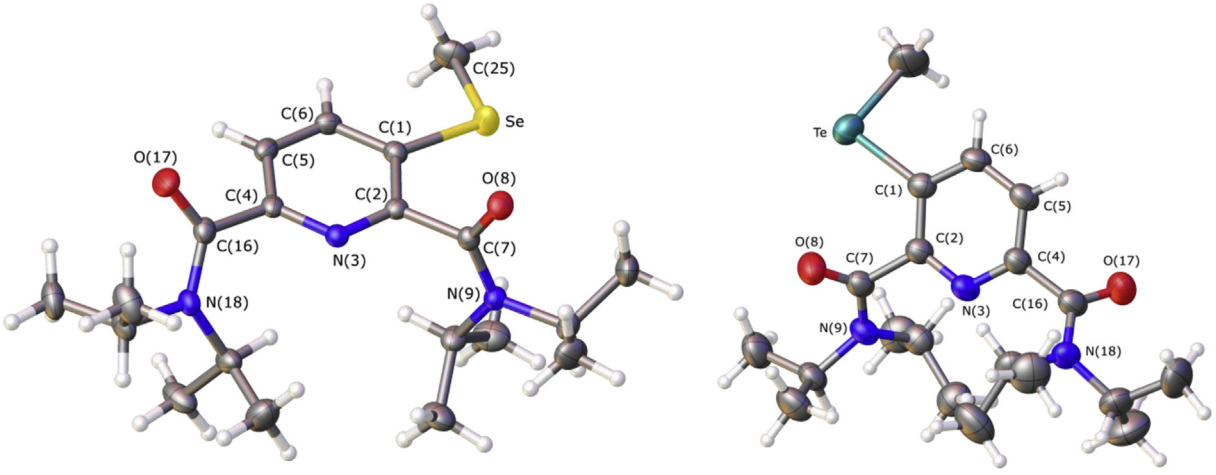


Fig. 3. ORTEP diagram of **2a** (left) and **3b** (right) with the thermal ellipsoids drawn at the 50% probability level and labeling scheme used for selected atoms.

Table 2
Selected bond lengths (Å) and bond angles (°) of **2a**

Se–C(1)	1.908(1)	Se–C(25)	1.934(2)
C(7)–O(8)	1.231(2)	C(7)–N(9)	1.344(2)
C(16)–O(17)	1.230(2)	C(16)–N(18)	1.353(2)
C(1)–Se–C(25)	99.99(7)	Se–C(1)–C(2)	118.0(1)

smaller than that found in substituted bis(2-pyridyl) diselenides (1.920–1.934 Å)[19–23] and bis(methylselenenyl)pyridines (1.914–1.929 Å).[21,22] In contrast, the C(sp^3)–Se bond length (1.935(2) Å) is similar to that in bis(methylselenenyl)pyridines.[21,22] The shortest Se···O distance of 3.439(1) Å, slightly more than the sum of oxygen and selenium atoms van der Waals radii (3.42 Å),[24] indicates the absence of a Se···O (carbonyl) secondary interaction.

The asymmetric unit of **3b** presented in Fig. 3b shows that the two carbonyl groups are positioned above and below the pyridine ring with a torsion angle between them of −139.2(3)°, which is consistent with the *anti*-configuration. The amide groups *ortho* and *para* to the $-TeCH_3$ substituent are rotated relatively to the pyridine ring by a dihedral angle of 52.11(1)° and 50.47(3)°, respectively. The O atom belonging to the *ortho* carboxamides moiety points towards the Te atom, and is responsible for a very strong Te···O secondary interaction at an intramolecular distance of 3.199(2) Å. This distance is significantly shorter than the sum of their van der Waals radii of 3.62 Å.[24] The $-TeCH_3$ unit is oriented out of the plane of the pyridine ring with the C(6)–C(1)–Te–C(25) torsion angle of

intramolecular secondary interactions between the Te and O atoms of the carboxamide groups. The Te(2A)···O(17A) distance is 2.825(2) Å, whereas Te(1A)···O(8A) distance is 3.164(2) Å. The Te···O distance of 2.825(2) Å is one of the smallest distances known among the organotellurium compounds.[25]

3. Conclusions

In conclusion, we have provided an efficient methodology for the lithiation of *N*,*N*,*N*′,*N*′-tetraisopropylpyridine-2,6-dicarboxamide, which is useful for the synthesis of the corresponding *ortho* substituted chalcogen derivatives. In addition, we have demonstrated change in the selectivity of the reaction with the change in the amount of *n*-BuLi used. Strong intramolecular C•O···Te secondary and intermolecular Te···π pyridyl interactions has been identified in *N*,*N*,*N*′,*N*′-tetraisopropyl-3,5-bis(methyltelluryl)pyridine-2,6-dicarboxamide.

4. Experimental section

4.1. General

All the reactions were carried out under nitrogen atmosphere. Solvents were dried by standard procedures and were freshly distilled prior to use.[26] The ^{1}H NMR and ^{13}C NMR spectra were obtained at Bruker 400 MHz spectrophotometer in $CDCl_3$. The ^{1}H

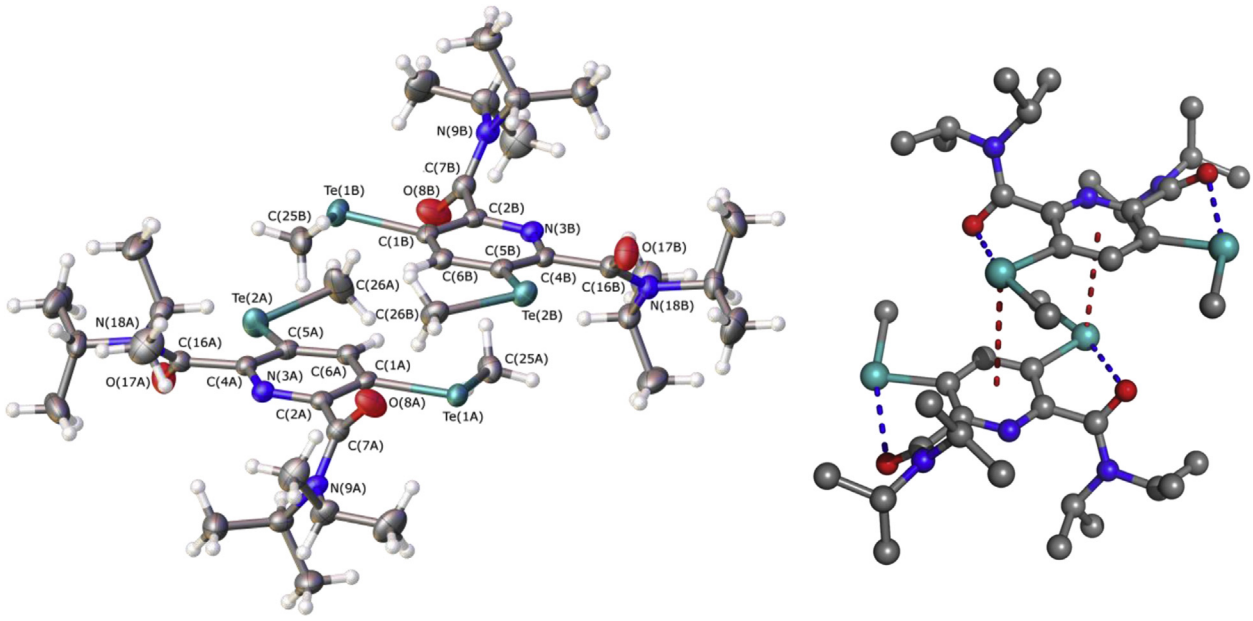


Fig. 4. Different structural features of the Crystal structure of **4b**: ORTEP diagram of asymmetric unit of **4b** showing the two independent crystallographic molecules with thermal ellipsoids drawn at the 60% probability level (left); molecular diagram showing the Te···π and Te···O intermolecular interactions drawn as red and blue dashed lines (right), respectively.

Table 3
Selected bond lengths (Å) and bond angles (°) of **3b** and **4b**

Compound	**3b**	**4b**	
		A	**B**
Te(1)–C(1)	2.116(2)	2.115(3)	2.114(3)
Te(1)–C(25)	2.133(3)	2.142(3)	2.133 (3)
Te(2)–C(5)	—	2.110(2)	2.102(2)
Te(2)–C(26)	—	2.134(3)	2.135(3)
C(7)–O(8)	1.229(3)	1.233(3)	1.235(3)
C(16)–O(17)	1.227(3)	1.238(3)	1.235(3)
C(1)–Te(1)–C(25)	93.8(1)	95.2(1)	95.3(1)
C(5)–Te(2)–C(26)	—	95.4(1)	94.6(1)
Te(1)–C(1)–C(2)	122.3(2)	120.0(2)	121.1(2)
Te(1)–C(1)–C(6)	121.2(2)	122.1(2)	121.6(2)
Te(2)–C(4)–C(5)	—	120.1(2)	122.1(2)
Te(2)–C(5)–C(6)	—	122.1(2)	120.8(2)

NMR and ^{13}C NMR chemical shifts were cited with respect to tetramethylsilane as an internal standard. The ^{77}Se and ^{125}Te NMR spectra were recorded in $CDCl_3$ using 4-dimethylamino-2,6-bis(methylselenenyl)pyridine and 4-dimethylamino-2,6-bis(methyltelluryl)pyridine, respectively, as external standards on Bruker Avance 400 MHz spectrometer. The ESI mass spectra were taken on Water Q-TOF Micro spectrometer. The EI mass spectra were taken by using GC-Mass Spectrometer [GC–MS QP-2010 plus] with Rtx-1MS (30m×0.25 mm ID×0.25 μm) capillary column. The UV-Visible spectra were taken in chloroform on Shimadzu PharmaSpec UV-1700 spectrophotometer. Microanalysis was carried out on Vario MICRO Elemantar analyzer at Department of Chemistry, Punjabi University, Patiala.

4.2. General procedure

n-BuLi (2.52 mL, 6.3 mmol, 2.5 N) was added to a solution of **1** (0.999 g, 3.0 mmol) in dry THF (30 mL) at −78 °C. The reaction mixture was stirred for 2 h at the same temperature and selenium (0.497 g, 6.3 mmol) or tellurium (0.812 g, 6.3 mmol) powder was added to it. The reaction mixture was slowly brought to room temperature and stirred till most of the selenium/tellurium got dissolved. The selenolate or tellurolate anion thus obtained was labeled as **1-Se** and **1-Te**, respectively.

4.3. Preparation of (methylselenenyl) derivatives of 1

Treatment of **1-Se** with iodomethane (0.894 g, 0.38 mL, 6.3 mmol) followed by hydrolysis and purification by column chromatography (silica gel 100–120 mesh, hexane/EtOAc 10:1) yielded three products, **2a** (0.83 g, 64%), **3a** (0.05 g, 5%) and **4a** (0.11 g, 10%). However, the use of 6.1 equiv of *n*-BuLi (7.32 mL, 18.3 mmol, 2.5 N), 2.1 or 4.1 equiv of LDA (6.3 or 12.3 mmol) in the later reaction exclusively gave **2a** in 90% (1.53 g), 86% (1.09 g) and 88% (1.13 g) yield, respectively.

*4.3.1. N,N,N′,N′-Tetraisopropyl-3-(methylselenenyl)pyridine-2,6-dicarboxamide (**2a**).* Brown crystalline solid; Mp 120–121 °C; [Found: C, 56.49; H, 7.96; N, 9.91. $C_{20}H_{33}N_3O_2Se$ requires C, 56.32; H, 7.79; N, 9.85%]; R_f (30% EtOAc/hexane) 0.65; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.73–7.71 (d, 1H, ^3J=8.0 Hz, CH_{Ar}(4)), 7.43–7.41 (d, 1H, d, ^3J=8.0 Hz, CH_{Ar}(3)), 4.08–4.03 (m, 1H, CH), 3.58–3.51 (m, 1H, CH), 3.49–3.42 (m, 2H, CH), 2.25 (s, 3H, $SeCH_3$), 1.50–1.48 (d, 6H, ^3J=6.8 Hz, CH_3), 1.45–1.44 (d, 6H, ^3J=6.8 Hz, CH_3), 1.11–1.10 (d, 6H, ^3J=6.6 Hz, CH_3), 1.08–1.07 (d, 6H, ^3J=6.6 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.8, 167.4, 153.9, 152.2, 138.7, 128.2, 123.4, 50.9, 50.9, 46.2, 46.0, 20.7, 20.6, 20.4, 20.3, 7.0 ppm; ^{77}Se NMR (400 MHz, $CDCl_3$): δ=188.3 ppm; IR (KBr) ν=3061, 2965, 2873, 1632, 1552, 1458, 1443, 1413, 1206, 1039 cm^{-1}; UV–vis ($CHCl_3$): λ_{max} (log ε)=306 (3.9), 286 (4.0), 253 (3.9) nm; MS (ESI) m/z=450 [M+Na (^{80}Se)]$^+$.

*4.3.2. N,N,N′,N′-Tetraisopropyl-3,5-bis(methylselenenyl)pyridine-2,6-dicarboxamide (**3a**).* Light yellow crystalline solid, Mp 162–164 °C; [Found: C, 48.68; H, 6.84; N, 8.11. $C_{21}H_{35}N_3O_2Se_2$ requires C, 48.55; H, 6.79; N, 8.08%]; R_f (30% EtOAc/hexane) 0.8; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.75 (s, 1H, CH_{Ar}(4)), 3.77–3.73 (m, 2H, CH), 3.54–3.50 (m, 2H, CH), 2.32 (s, 6H, $SeCH_3$), 1.55–1.54 (d, 12H, ^3J=6.8 Hz, CH_3), 1.16–1.15 (d, 12H, ^3J=6.7 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.1, 151.9, 139.8, 128.0, 50.9, 46.1, 20.7, 20.3, 7.2 ppm; IR (KBr) ν=3060, 2959, 2871, 1630, 1540, 1446, 1405, 1205, 1038 cm^{-1}; MS (ESI): m/z=544 [M+Na (^{80}Se)]$^+$

*4.3.3. N,N-Diisopropyl-3-(methylselenenyl)-6-pentanoylpicolinamide (**4a**).* Light yellow crystalline solid Mp 98–99 °C;

[Found: C, 56.27; H, 7.30; N, 7.49. $C_{18}H_{28}N_2O_2Se$ requires C, 56.38; H, 7.36; N, 7.30%]; R_f (30% EtOAc/hexane) 0.90; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83–7.81 (d, 1H, ^3J=8.2 Hz, $CH_{Ar}(4)$), 7.74–7.72 (d, 1H, d, ^3J=8.2 Hz, $CH_{Ar}(3)$), 3.61–3.50 (m, 2H, CH), 3.08–3.05 (t, 2H, CH_2), 2.28 (s, 3H, $SeCH_3$), 1.62–1.61 (m, 2H, CH_2), 1.54–1.53 (d, 6H, ^3J=6.8 Hz, CH_3), 1.34–1.32 (m, 2H, CH_2), 1.14–1.12 (d, 6H, ^3J=6.7 Hz, CH_3), 0.87–0.83 (t, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=200.7, 166.1, 153.2, 148.3, 136.3, 132.7, 120.5 49.8, 45.2, 36.2, 25.2, 21.4, 19.7, 19.3, 12.9, 5.6 ppm; IR (KBr) ν=3060, 2960, 2871, 1701, 1628, 1551, 1464, 1411, 1207 cm^{-1}; UV–vis ($CHCl_3$): λ_{max} (log ε)=327 (3.8), 250 (3.5) nm; MS (ESI) m/z=385 [M+1(^{80}Se)]$^+$.

4.4. Preparation of (methyltelluryl) derivatives of 1

Treatment of **1-Te** with 6.3 mmol of iodomethane (0.894 g, 0.38 mL) yielded three different products, 0.67 g (47%) **2b**, 0.11 g (6%) **3b** and 0.26 g (20%) **4b**. However, the use of 6.1 equiv of *n*-BuLi (7.56 mL, 18.9 mmol, 2.5 N) or 4.1 equiv of LDA (12.3 mmol) exclusively gave **2b** in 77% (1.10 g) and 75% (1.06 g) yield, respectively.

*4.4.1. N,N,N′,N′-Tetraisopropyl-3-(methyltelluryl)pyridine-2,6-dicarboxamide (**2b**).* Yellow crystalline solid, Mp 135–137 °C; [Found: C, 56.63; H, 7.05; N, 8.80. $C_{20}H_{33}N_3O_2Te$ requires C, 56.56; H, 7.00; N, 8.84%]; Rf (30% EtOAc/hexane) 0.60; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.86–7.84 (d, 1H, ^3J=8.0 Hz, $CH_{Ar}(4)$), 7.32–7.30 (d, 1H, d, ^3J=8.0 Hz, $CH_{Ar}(3)$), 3.91–3.83 (m, 2H, CH), 3.48–3.43 (m, 2H, CH), 1.99 (s, 3H, $TeCH_3$), 1.48–1.46 (d, 6H, ^3J=6.8 Hz, CH_3), 1.46–1.44 (d, 6H, ^3J=6.8 Hz, CH_3), 1.11–1.09 (d, 6H, ^3J=6.4 Hz, CH_3), 1.09–1.08 (d, 6H, ^3J=6.4 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.8, 167.1, 154.4, 151.2, 141.9, 122.2, 112.3 49.9, 45.2, 45.1, 19.7, 19.6, 19.4, 19.3, −17.1 ppm; ^{125}Te NMR (400 MHz, $CDCl_3$): δ=315.0 ppm; IR (KBr) ν=3061, 2971, 2871, 1616, 1556, 1460, 1417, 1208, 1035 cm^{-1}; UV–vis ($CHCl_3$): λ_{max} (log ε)=332 (3.7), 291 (3.8), 252 (4.0) nm; MS (ESI) m/z=500 [M+Na (^{130}Te)]$^+$.

*4.4.2. N,N,N′,N′-Tetraisopropyl-3,5-bis(methyltelluryl)pyridine-2,6-dicarboxamide (**3b**).* Yellow crystalline solid, Mp 158–159 °C; [Found: C, 40.83; H, 5.70; N, 6.83. $C_{21}H_{35}N_3O_2Te_2$ requires C, 40.89; H, 5.72; N, 6.81%]; R_f (30% EtOAc/hexane) 0.75; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.98 (s, 1H, $CH_{Ar}(4)$), 4.00–3.97 (m, 2H, CH), 3.53–3.50 (m, 2H, CH), 2.06 (s, 6H, $SeCH_3$), 1.54–1.52 (d, 12H, ^3J=6.8 Hz, CH_3), 1.18–1.16 (d, 12H, ^3J=6.7 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=168.6, 153.0, 146.9, 114.1, 51.0, 46.3, 20.8, 20.4, −16.0 ppm; ^{125}Te NMR (400 MHz, $CDCl_3$): δ=327.2 ppm; IR (KBr) ν=3058, 2964, 2870, 1691, 1617, 1542, 1446, 1409, 1208 cm^{-1}; UV–vis ($CHCl_3$): λ_{max} (log ε)=321 (3.8), 295 (3.7), 253 (3.9) nm; MS (ESI) m/z=644 [M+Na (^{130}Te)]$^+$.

*4.4.3. N,N-Diisopropyl-3-(methyltelluryl)-6-pentanoylpicolinamide (**4b**).* Yellow crystalline solid Mp 92–94 °C; [Found: C, 50.17; H, 6.60; N, 6.45. $C_{18}H_{28}N_2O_2Te$ requires C, 50.04; H, 6.53; N, 6.48%]; R_f (30% EtOAc/hexane) 0.87; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.92–7.90 (d, 1H, ^3J=8.1 Hz, $CH_{Ar}(4)$), 7.75–7.73 (d, 1H, d, ^3J=8.1 Hz, $CH_{Ar}(3)$), 4.04–4.01 (m, 1H, CH), 3.54–3.51 (m, 1H, CH), 3.07–3.04 (t, 2H, CH_2), 2.00 (s, 3H, $TeCH_3$), 1.65–1.57 (m, 2H, CH_2), 1.55–1.51 (d, 6H, ^3J=6.8 Hz, CH_3), 1.35–1.27 (m, 2H, CH_2), 1.19–1.17 (d, 6H, ^3J=6.6 Hz, CH_3), 0.88–0.87 (t, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=201.8, 168.3, 157.8, 149.4, 142.3, 121.5, 120.6, 50.8, 46.5, 37.2, 26.1, 22.5, 20.9, 20.4, 13.9, −15.6 ppm; IR (KBr) ν=3058, 2964, 2870, 1691, 1617, 1542, 1446, 1409, 1208 cm^{-1}; UV–vis ($CHCl_3$): λ_{max} (log ε)=364 (3.6), 253 (3.8) nm; MS (ESI) m/z=457 [M+Na (^{130}Te)]$^+$.

4.5. 3-(Ethylselenenyl)-*N,N,N′,N′*-tetraisopropylpyridine-2,6-dicarboxamide (5a)

According to general procedure, the use of **1** (0.999 g, 3.0 mmol), *n*-BuLi (2.52 mL, 6.3 mmol, 2.5 N), selenium (0.497 g, 6.3 mmol), iodoethane (0.983 g, 0.51 mL, 6.3 mmol), and hydrolysis gave **5a** as a brown crystalline solid (0.78 g, 58%); Mp 40–42 °C; [Found: C, 57.37; H, 7.96; N, 9.55. $C_{21}H_{35}N_3O_2Se$ requires C, 57.26; H, 8.00; N, 9.53%]; Rf (30% EtOAc/hexane) 0.66; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.86–7.84 (d, 1H, ^3J=8.1 Hz, $CH_{Ar}(4)$), 7.49–7.47 (d, 1H, d, ^3J=8.1 Hz, $CH_{Ar}(3)$), 4.016–4.13 (m, 1H, CH), 3.60–3.49 (m, 3H, CH), 2.98–2.93 (q, 2H, $SeCH_2$), 1.57–1.55 (d, 6H, ^3J=6.8 Hz, CH_3), 1.52–1.50 (d, 6H, ^3J=6.8 Hz, CH_3), 1.45–1.40 (t, 3H, CH_3), 1.19–1.17 (d, 6H, ^3J=6.6 Hz, CH_3), 1.15–1.13 (d, 6H, ^3J=6.6 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.8, 167.5, 155.3, 152.7, 140.5, 126.1, 123.2, 51.0, 50.9, 46.2, 45.9, 20.9, 20.7, 20.5, 20.4, 20.2, 15.0 ppm; IR (KBr) ν=3057, 2963, 2867, 1621, 1559, 1461, 1445, 1417, 1210, 1038 cm^{-1}; UV–vis ($CHCl_3$): λ_{max} (log ε)=311 (4.0), 287 (4.1), 253 (4.0) nm; MS (ESI) m/z=464 [M+Na (^{80}Se)]$^+$.

4.6. *N,N,N′,N′*-Tetraisopropyl-3-(propylselenenyl)pyridine-2,6-dicarboxamide (6a)

The use of bromopropane (0.775 g, 0.57 mL, 6.3 mmol) instead of iodomethane in the above reaction gave **6a** as a yellow crystalline solid (0.79 g, 58%). Mp 104–105 °C; [Found: C, 58.26; H, 8.23; N, 9.23. $C_{22}H_{37}N_3O_2Se$ requires C, 58.13; H, 8.20; N, 9.24%]; R_f (30% EtOAc/hexane) 0.67; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.79–7.77 (d, 1H, ^3J=8.1 Hz, $CH_{Ar}(4)$), 7.41–7.39 (d, 1H, d, ^3J=8.1 Hz, $CH_{Ar}(3)$), 4.10–4.07 (m, 1H, CH), 3.52–3.42 (m, 3H, CH), 2.87–2.83 (t, 2H, $SeCH_2$), 1.69–1.60(m, 2H, CH_2), 1.50–1.48 (d, 6H, ^3J=6.8 Hz, CH_3), 1.46–1.44 (d, 6H, ^3J=6.8 Hz, CH_3), 1.12–1.10 (d, 6H, ^3J=6.6 Hz, CH_3), 1.08–1.06 (d, 6H, ^3J=6.6 Hz, CH_3), 0.95–0.91 (t, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.8, 167.5, 155.3, 152.7, 140.6, 126.5, 123.3, 51.0, 50.9, 46.2, 45.9, 29.5, 23.1, 20.7, 20.5, 20.4, 20.3, 14.4 ppm; IR (KBr) ν=2965, 2930, 2872, 1624, 1457, 1441, 1205, 1150, 1132, 1104, 1040, 1028 cm^{-1}; UV–vis ($CHCl_3$): λ_{max} (log ε)=312 (4.0), 286 (4.0), 252 (4.0) nm; MS (EI): m/z=455 [M (^{80}Se)]$^+$.

4.7. 3-(Butylselenenyl)-*N,N,N′,N′*-tetraisopropylpyridine-2,6-dicarboxamide (7a)

The use of **1** (0.999 g, 3.0 mmol), *n*-BuLi (7.32 mL, 18.3 mmol, 2.5 N), selenium (1.445 g, 18.3 mmol), iodobutane (3.477 g, 2.16 mL, 18.3 mmol), and hydrolysis gave **7a** as a yellow crystalline solid (1.04 g, 74%). Mp 84–85 °C; [Found: C, 59.09; H, 8.30; N, 8.99. $C_{23}H_{39}N_3O_2Se$ requires C, 58.95; H, 8.38; N, 8.96%]; R_f (30% EtOAc/hexane) 0.70; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.79–7.77 (d, 1H, ^3J=8.1 Hz, $CH_{Ar}(4)$), 7.42–7.40 (d, 1H, d, ^3J=8.1 Hz, $CH_{Ar}(3)$), 4.10–4.07 (m, 1H, CH), 3.51–3.42 (m, 3H, CH), 2.89–2.85 (t, 2H, $SeCH_2$), 1.63–1.56 (m, 2H, CH_2), 1.50–1.48 (d, 6H, ^3J=6.8 Hz, CH_3), 1.45–1.43 (d, 6H, ^3J=6.8 Hz, CH_3), 1.38–1.32 (m, 2H, CH_2), 1.12–1.10 (d, 6H, ^3J=6.6 Hz, CH_3), 1.08–1.06 (d, 6H, ^3J=6.6 Hz, CH_3), 0.85–0.82 (t, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.8, 167.5, 155.2, 152.6, 140.4, 126.6, 123.3, 51.0, 50.9, 46.2, 45.9, 31.8, 27.1, 22.9, 20.7, 20.5, 20.4, 20.3, 13.5 ppm; IR (KBr) ν=2962, 2929, 2871, 1628, 1457, 1441, 1418, 1258, 1207, 1153, 1134, 1105, 1036 cm^{-1}; UV–vis (CH_3OH): λ_{max} (log ε)=315 (3.8), 286 (3.9), 249 (3.9) nm; MS (EI): m/z=469 [M (^{80}Se)]$^+$.

4.8. 3-(Benzylselenenyl)-*N,N,N′,N′*-tetraisopropylpyridine-2,6-dicarboxamide (8a)

According to general procedure, the use of **1** (0.999 g, 3.0 mmol), *n*-BuLi (2.52 mL, 6.3 mmol, 2.5 N), selenium (0.497 g, 6.3 mmol), (chloromethyl)benzene (0.797 g, 0.72 mL, 6.3 mmol) and hydrolysis gave **8a** as a yellow crystalline solid (0.81 g, 54%). Mp 92–96 °C; [Found: C, 62.11; H, 7.47; N, 8.43. $C_{26}H_{37}N_3O_2Se$ requires C, 62.13; H, 7.42; N, 8.36%]; Rf (30% EtOAc/hexane) 0.72; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.73–7.71 (d, 1H, ^3J=8.0 Hz, Ar), 7.38–7.36 (d, 1H, d, ^3J=8.0 Hz, Ar), 7.27–7.17 (5H, m, Ar), 4.09–4.06 (m, 1H, CH), 4.18 (s, 2H, $SeCH_2$), 3.54–3.48 (m, 3H, CH), 1.58–1.56 (d, 6H, ^3J=6.7 Hz,

CH_3), 1.52–1.51 (d, 6H, ^3J=6.7 Hz, CH_3), 1.19–1.17 (d, 6H, ^3J=6.6 Hz, CH_3), 1.11–1.09 (d, 6H, ^3J=6.6 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.7, 167.5, 156.5, 153.6, 142.6, 137.7, 129.8, 128.4, 127.0, 125.1, 122.9, 50.9, 46.2, 45.9, 32.0, 20.7, 20.5, 20.4, 20.3 ppm; ^{77}Se NMR (400 MHz, $CDCl_3$): δ=338.2 ppm; IR (KBr)=3058, 2973, 2872, 1637, 1556, 1464, 1420, 1209, 1029 cm^{-1}; UV–vis (CH_3OH): λ_{max} (log ε)=309 (3.7), 288 (3.9) 249 (4.1) nm; MS (ESI): m/z=503 [M (^{80}Se)]$^+$.

4.9. Bis[*N,N,N′,N′*-tetraisopropylpyridine-2,6-dicarboxamide]-3,3′-diselenide (9a)

The use of **1** (0.999 g, 3.0 mmol), *n*-BuLi (7.32 mL, 18.3 mmol, 2.5 N), selenium (1.445 g, 18.3 mmol) gave the selenolate anion. The selenolate anion on hydrolysis and aerial oxidation yielded **9a** as a yellow solid (0.78 g, 62%). Mp 120–121 °C; [Found: C, 55.57; H, 7.31; N, 10.29. $C_{38}H_{60}N_6O_4Se_2$ requires C, 55.46; H, 7.34; N, 10.21%]; R_f (30% EtOAc/hexane) 0.43; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.12–8.10 (d, 1H, ^3J=8.0 Hz, CH_{Ar}(4)), 7.39–7.37 (d, 1H, d, ^3J=8.0 Hz, CH_{Ar}(3)), 4.04–3.97 (m, 1H, CH), 3.90–3.84 (m, 1H, CH), 3.62–3.48 (m, 2H, CH), 1.58–1.56 (d, 6H, ^3J=6.7 Hz, CH_3), 1.52–1.50 (d, 6H, ^3J=6.7 Hz, CH_3), 1.21–1.19 (d, 6H, ^3J=6.6 Hz, CH_3), 1.16–1.14 (d, 6H, ^3J=6.6 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.8, 167.4, 152.7, 151.5, 139.9, 128.4, 123.9, 51.1, 51.0, 46.5, 46.2, 20.8, 20.6, 20.4, 20.3 ppm; ^{77}Se NMR (400 MHz, $CDCl_3$): δ=408.7 ppm; IR (KBr)=3057, 2970, 2873, 1618, 1561, 1446, 1417, 1209, 1039 cm^{-1}; UV–vis ($CHCl_3$): λ_{max} (log ε)=308 (3.9), 278 (4.2), 260 (4.2) nm; MS (ESI): m/z=825 [M+1 (^{80}Se)]$^+$.

4.10. Preparation of iodo derivatives of 1

The use of **1** (0.999 g, 3.0 mmol), *n*-BuLi (2.52 mL, 6.3 mmol, 2.5 N) and iodine (0.80 g, 6.3 mmol) gave **10** (0.71 g, 52%) and **11** (0.25 g, 20%). However, the use of 6.1 equiv of *n*-BuLi (7.32 mL, 18.3 mmol, 2.5 N) in the later reaction gave **10** in 67% (0.92 g) yield.

*4.10.1. 3-Iodo-N,N,N′,N′-tetraisopropylpyridine-2,6-dicarboxamide (**10**).* Light yellow solid, Mp 136–138 °C; [Found: C, 49.58; H, 6.57; N, 9.21. $C_{19}H_{30}N_3O_2I$ requires C, 49.67; H, 6.58; N, 9.14%]; R_f (30% EtOAc/hexane) 0.67; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.12–8.10 (d, 1H, ^3J=8.2 Hz, CH_{Ar}(4)), 7.23–7.21 (d, 1H, d, ^3J=8.0 Hz, CH_{Ar}(3)), 4.05–3.98 (m, 1H, CH), 3.50–3.36 (m, 3H, CH), 1.51–1.49 (d, 6H, ^3J=6.8 Hz, CH_3), 1.45–1.43 (d, 6H, ^3J=6.8 Hz, CH_3), 1.12–1.11 (d, 6H, ^3J=2.8 Hz, CH_3), 1.10–1.09 (d, 6H, ^3J=2.8 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.4, 167.1, 157.3, 154.7, 147.7, 124.0, 89.9, 51.1, 51.0, 46.3, 46.0, 20.7, 20.6, 20.4, 20.1 ppm; IR (KBr) ν=2967, 2927, 2872, 1628, 1458, 1442, 1205, 1155, 1136, 1106, 1039 cm^{-1};.UV–vis ($CHCl_3$): λ_{max} (log ε)=285 (3.7), 250 (3.7) nm; MS (EI): m/z=459 [M]$^+$.

*4.10.2. 3-Iodo-N,N-diisopropylcarboxamide-6-pentanoylpyridine (**11**).* White solid, Mp 90–92 °C; [Found: C, 49.18; H, 6.11; N, 6.63. $C_{17}H_{25}N_2O_2I$ requires C, 49.04; H, 6.05; N, 6.72%]; Rf (30% EtOAc/hexane) 0.85; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.21–8.19 (d, 1H, ^3J=8.3 Hz, CH_{Ar}(4)), 7.62–7.60 (d, 1H, d, ^3J=8.2 Hz, CH_{Ar}(3)), 3.56–3.49 (m, 1H, CH), 3.08–3.04 (m, 1H, CH), 3.08–3.04 (t, 2H, CH_2), 1.64–1.56 (m, 2H, CH_2), 1.54–1.52 (d, 6H, ^3J=7.8 Hz, CH_3), 1.36–1.27 (m, 2H, CH_2), 1.14–1.12 (d, 6H, ^3J=7.3 Hz, CH_3), 0.88–0.83 (t, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=201.5, 167.4, 158.3, 151.8, 147.9, 122.1, 94.7, 51.2, 46.2, 37.3, 26.1, 22.4, 20.6, 20.2, 13.9 ppm; UV–vis ($CHCl_3$): λ_{max} (log ε)=307 (3.0), 279 (3.5), 254 (3.7) nm; MS (EI): m/z=416 [M]$^+$.

4.11. Crystallography

The single crystal X-ray data of compounds **2a**, **3b** and **4b** were collected on a Bruker SMART Apex II CCD-based diffractometer at 150(2) K using graphite monochromatized Mo-Kα radiation (λ=0.71073 Å). The data reduction of each compound was carried out using the SAINT-NT software package from Bruker AXS.[27] The raw intensities were corrected for absorption effects through the multi-scan method with the SADABS.[28] The structures were solved by a combination of direct methods and subsequent difference Fourier syntheses and refined by full matrix least squares on F^2 using the SHELX-2013 suite.[29] Anisotropic thermal parameters were used for all non-hydrogen atoms. The hydrogen atoms were inserted at geometrical positions and refined with isotropic parameters equivalent 1.2 times those of the atom to which they are bounded. The molecular diagrams were drawn with the Olex2[30] and PyMOL.[31] The crystal data and refinement details for the three compounds are gathered in Table 4.

Table 4
Crystal data and relevant refinement details of **2a**, **3b**, and **4b**

Compound	**2a**	**3b**	**4b**
Empirical formula	$C_{20}H_{33}N_3O_2Se$	$C_{20}H_{33}N_3O_2Te$	$C_{21}H_{35}N_3O_2Te_2$
M_w	426.45	475.09	616.72
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	$Pbca$	$p\bar{1}$
a/[Å]	7.7819(6)	23.2324(10)	7.7951(3)
b/[Å]	12.5851(9)	10.1166(5)	14.9764(6)
c/[Å]	23.247(2)	12.6511(6)	22.4767(9)
α/[°]	(90)	(90)	77.662(1)
β/[°]	99.434(4)	(90)	83.419(1)
γ/[°]	(90)	(90)	86.647(1)
V [Å^3]	2245.9(3)	4595.8(7)	2544.93(2)
Z	4	8	4
D_c [Mg m^{-3}]	1.261	1.373	1.610
μ/[mm^{-1}]	1.689	1.312	2.312
Reflections collected	25,420	23,731	46,002
Unique reflections, [R_{int}]	5373 [0.0285]	5509 [0.0498]	13,566 [0.0220]
Final R indices			
R_1, wR_2 [$I>2\sigma I$]	0.0289, 0.0683 [4626]	0.0384, 0.1004 [4017]	0.0299,0.0610 [11,715]
R_1, wR_2 (all data)	0.0364, 0.1439	0.0553, 0.1087	0.0389, 0.0652

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Supplementary data

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, with numbers CCDC 978863, 978864, and 978865, for compounds **2a**, **3b**, and **4b**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44(01223)336033, e-mail: deposit@ccdc.cam.ac.uk, or http://www.ccdc.cam.ac.uk).

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