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Synthesis and characterization of some α-naphthyl selenium/tellurium derivatives: X-ray crystal structure of benzyl-1-naphthyl selenide and diphenylmethyl-1-naphthyl selenide

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Abstract

A large number of α-naphthyl selenium and tellurium compounds (**1**–**14**) have been prepared through two different methods. The first method involves the alkylation of sodium 1-naphthylselenolate/tellurolate, generated in situ using hydrazine hydrate as reducing agent while the second method involves the reaction of in situ generated α-naphthylseleno/telluromagnesium bromide with an appropriate electrophile. The synthesized alkyl-1-naphthyl selenides/tellurides and some α,ω-bis(1-naphthylseleno)alkanes have been characterized with the help of elemental analysis and using various spectroscopic techniques viz., NMR (^{1}H, ^{13}C, ^{77}Se and ^{125}Te), IR, UV/vis spectroscopy and mass spectrometry (only in few representative cases). Interpretation of ^{1}H, ^{13}C NMR spectra and assignment of individual resonances for tris(1-naphthylseleno)methane have been done with the help of [^{1}H–^{1}H] and [^{1}H–^{13}C] correlation spectroscopy (COSY). X-ray crystallographic results and molecular geometry of benzyl-1-naphthyl selenide, **2** and diphenylmethyl-1-naphthyl selenide, **3** have also been illustrated.

Keywords: Naphthyl selenides/tellurides; Bis(1-naphthylseleno)alkanes; Hydrazine hydrate; ^{77}Se; ^{125}Te; X-ray crystal structure

1. Introduction

Aromatic selenides and tellurides have emerged as versatile synthons that find extensive applications in organic synthesis [1] biochemistry [2] organic superconductors [3] and semi-conducting materials [4]. α-Naphthyl chalcogenides have proved especially useful as chiral inducers and catalysts in asymmetric synthesis [5]. In addition substituted naphthalenes have been shown to possess interesting non-bonded interactions [6]. The presence of a naphthyl ring in selenoxides, bearing a coordinating amino group, enables the resolution of its enantiomers whereas the enantiomers of corresponding phenyl analogs undergo racemization and cannot be separated [7]. Chalcogen atoms at *peri* positions on the naphthalene result in stable compounds and their salts behave as organic metals [8]. These compounds have proved to be promising ligands in coordination chemistry [9].

Literature is inundated with several synthetic procedures involving the preparation of unsymmetrical aryl alkyl chalcogenides. Most existing methods, cited in literature for the synthesis of α- and β-naphthyl selenides, are based either on the reaction of naphthylselenenyl halides with organometallic reagents [10] or the reaction of naphthyl selenols or selenolates with various electrophiles [11,12]. Aryl selenolates/tellurolates can be readily generated by the reduction of diselenides/ditellurides [13] that in turn can be prepared via Grignard route [14]. Direct synthesis

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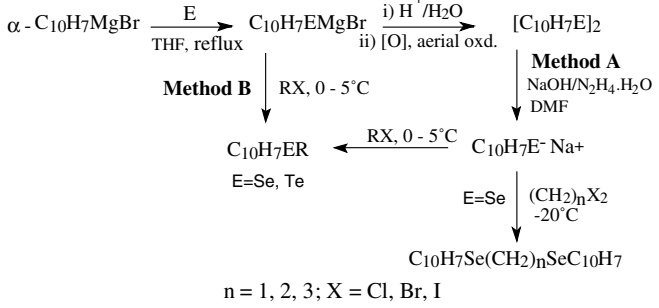
of symmetrical naphthyl tellurides has also been reported in the literature [15]. Organolithium route is relatively more popular due to its short synthetic procedure and high efficiency. Recently, we have reported a one-flask synthesis of some alkyl-1-naphthyl selenides and tellurides by the in situ alkylation of 1-naphthylseleno/telluromagnesium bromide [16].

We wish to report in this communication the preparation and characterization of some hitherto unknown alkyl-1-naphthyl selenides/tellurides and α,ω-bis(naphthylseleno) alkanes, along with the comparison of two different methodologies that have been employed for their synthesis.

2. Results and discussion

In continuation with the ongoing project, a number of alkyl-1-naphthyl selenides and tellurides have been synthesized by the alkylation of sodium 1-naphthylselenolate and tellurolate at 0–5 °C. The intermediate selenolate/tellurolate ions have been generated by the reductive cleavage of bis(1-naphthyl) diselenide/ditelluride using alkaline hydrazine hydrate in DMF at room temperature (Scheme 1, Method A). Alkaline hydrazine hydrate smoothly reduces dichalcogenide to generate nucleophilic chalcogenolate ion [17]. Grignard methodology involving alkylation of 1-naphthylseleno/telluromagnesium bromide (Method B), was also followed for comparison. The product yield obtained by adopting both methodologies was compared and it was found that Method A is superior (yield, 60–78%) over Method B (yield, 20–64%) for the synthesis of desired compounds. Latter method affords relatively poor experimental yield due to the concomitant formation of unwanted side products.

Compounds which have been prepared and characterized include some unsymmetrical alkyl-1-naphthyl selenides and tellurides viz. $C_{10}H_7SeCH_3$ (**1**), $C_{10}H_7SeCH_2C_6H_5$ (**2**), $C_{10}H_7SeCH(C_6H_5)_2$ (**3**), $(C_{10}H_7Se)_3CH$ (**4**), $C_{10}H_7SeCH_2CH_2N(C_2H_5)_2$ (**5**), $C_{10}H_7SeCH_2CH=CH_2$ (**6**), $C_{10}H_7SeC_6H_9$ (**7**), $C_{10}H_7TeCH_2CH=CH_2$ (**8**), $C_{10}H_7TeCH_2C_6H_5$ (**9**) and α,ω-bis(naphthylseleno) alkanes viz., $C_{10}H_7SeCH_2SeC_{10}H_7$ (**10**), $C_{10}H_7Se(CH_2)_2SeC_{10}H_7$ (**11**), $C_{10}H_7Se(CH_2)_3SeC_{10}H_7$ (**12**). The methylene bridged diseleno-ethers [18] can display interesting chelating properties as they possess two donor atoms which can undergo complexation with soft transition metal ions. Diselenoethers, particularly compound **12**, gave poor or no yield unless alkylation was performed at low temperatures (−20 to −25 °C). This can be attributed to the formation of an unstable episelenonium ion [19] intermediate, which eliminates a molecule of ethylene to regenerate the starting diselenide. Only moderate yields were obtained for unsymmetrical tellurides. McWhinnie et al. [20a] have successfully attempted the synthesis of ditelluroethers $RTe(CH_2)_nTeR$ (where $R = C_6H_4$-(*p*-OEt) and $n = 1$, 6, 7, 9 or 10) by the reaction of RTeNa with $Br(CH_2)_nBr$. In contrast to the clean reactions of RS^- and RSe^-, the reaction of RTe^-, with dihaloalkanes is known to be difficult and depends both on reaction conditions and type of reagent used. It is observed that when $n = 2$ (where n is the number of intervening methylene groups), rapid elimination of ethylene occurs and ditelluride is recovered back [20]. However, with $n = 3$, 4 or 5, the product is mainly a telluronium compound. Unfortunately, our efforts to isolate and characterize the corresponding α,ω-bis(1-naphthyltelluro)alkanes could not be met with success.



Scheme 1. Reaction methodology for the synthesis of alkyl-1-naphthyl selenides/tellurides and some α,ω-bis(1-naphthylseleno)alkanes.

Characterization of compounds was done using elemental analysis and various spectroscopic techniques viz., NMR (^1H, ^{13}C, ^{77}Se, ^{125}Te, etc.), IR, UV/vis spectroscopy and mass spectrometry (only in few representative cases). Single crystal X-ray analysis of two compounds, i.e. **2** and **3** was done and their molecular structure was established. Compounds **1**, **5**, **6**, **7** and **10** exist as viscous high boiling liquids, which decompose prior to distillation whereas **2**, **3**, **4**, **11**, **12**, **13** and **14** are sharp melting colorless or yellow to red colored crystalline solids. Monotellurides are unstable in solution and a quick isolation of these compounds is necessary. As a result, detailed spectroscopic characterization of such compounds has scarcely been reported in the literature. Menon et al. [21] have reported a number of stable low valent 1-naphthyl tellurides which incorporate dimethylamino group at C-8 position in the naphthyl ring. Intramolecular Te···N coordination is found to be responsible for the greater stability of these derivatives. The tellurides prepared by us have been thoroughly characterized through various spectroscopic techniques. However, ^{125}Te NMR of monotellurides prepared could not be obtained as these compounds were unstable in solution and decomposed before multinuclear NMR studies could be performed.

2.1. Spectroscopic studies

^1H NMR characterization of **1**–**14** shows that alkyl hydrogens resonate at a higher field than the corresponding alkyl halides employed for alkylation in the preparation of compounds. As compared to the ring protons of selenides, those of tellurides are shifted upfield due to a greater shielding of protons by tellurium metal. Two-dimensional [^1H–^1H] and [^1H–^{13}C] correlation spectroscopy (COSY) is a potential technique in understanding the spin–spin coupling interactions between nuclei and assignment of ^1H

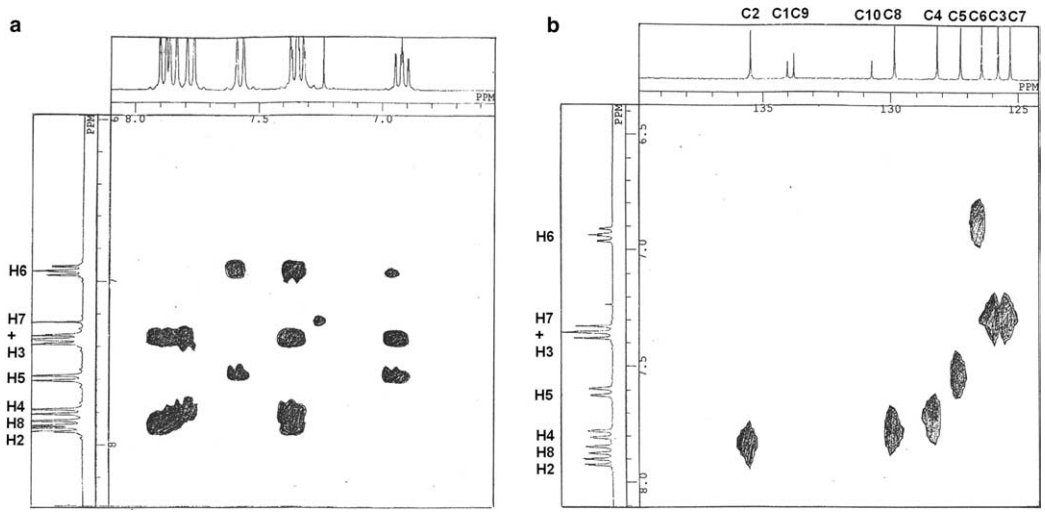


Fig. 1. (a) [^{1}H–^{1}H] and (b) [^{1}H–^{13}C] COSY spectra of tris(1-naphthylseleno) methane (**4**).

and ^{13}C signals. The ^{1}H NMR spectrum of compound **4** shows a clear resolution and well-defined splitting of aromatic protons. A careful examination of COSY spectra (Fig. 1) reveals that C-2 signal appears most downfield, whereas remaining naphthyl ring carbon nuclei fall in the region 125–135 ppm. The carbon bearing selenium is recognizable from its low intensity and small satellites flanking the ^{13}C NMR signal. Maximum shielding in aromatic ring was observed in case of H-6 proton and C-7 carbon. The chemical shift (δ) of ring protons in this compound follows the order H-2 > H-8 > H-4 > H-5 > H-3 ≈ H-7 > H-6 > H-11 and carbon nuclei chemical shift values were found to decrease in the sequence C-2 > C-1 > C-9 > C-10 > C-8 > C-4 > C-5 > C-6 > C-3 > C-7 > C-11.[1]

^{77}Se resonance signals in case of monoselenides appear to be very sensitive to even small variations of substituents in the structure. As the substituent moves away from α-carbon, the impact becomes less or negligible. ^{77}Se and ^{125}Te NMR results for most of the compounds characterized have been listed in Table 1. The magnitude of ^{77}Se NMR chemical shift ranges from 154 to 407 ppm in selenides. Successive phenylation of methyl carbon in **1**–**3**, leads to a steady increase in ^{77}Se chemical shift. As the number of intervening methylene groups in α,ω-bis(naphthylseleno) alkanes increase, there is an observed decrease in the ^{77}Se chemical shift. These observations are consistent with the NMR results of corresponding bis(phenylseleno)ethers, $PhSe(CH_2)_nSePh$, reported by Levason et al. [18d].

[1] The numbering of the naphthyl ring carbon atoms has been done according to the following scheme.

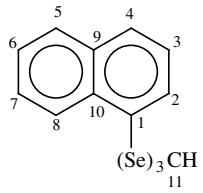


Table 1
^{77}Se and ^{125}Te NMR of some compounds

Entry	Compound	δ ^{77}Se/^{125}Te NMR
1	1-$C_{10}H_7SeCH_3$	154.5
2	1-$C_{10}H_7SeCH_2C_6H_5$	311.7
3	1-$C_{10}H_7SeCH(C_6H_5)_2$	407.2
4	$(1\text{-}C_{10}H_7Se)_3CH$	401.8
5	1-$C_{10}H_7SeCH_2CH_2N(CH_2CH_3)_2$	223.8
10	1-$C_{10}H_7SeCH_2Se(1\text{-}C_{10}H_7)$	285.0
11	1-$C_{10}H_7Se(CH_2)_2Se(1\text{-}C_{10}H_7)$	276.0
12	1-$C_{10}H_7Se(CH_2)_3Se(1\text{-}C_{10}H_7)$	227.4
13	$(1\text{-}C_{10}H_7Se)_2$	429.7
14	$(1\text{-}C_{10}H_7Te)_2$	357.0

The UV absorption maxima of most acyclic selenides and diselenides, depend mainly on three effects: inductive, hyperconjugative and torsional (steric) [22]. The value of λ_{max} in most selenides, synthesized by us fall in the range of 284–336 nm. In some compounds, an additional weak band at ca. 240–245 nm is also seen. The band at ~250 nm is presumed to arise due to a perturbed transition state of the aromatic ring whereas the one around higher wavelength (~300 nm) is due to the Se–$C_{10}H_7$ chromophore, which involves 4*p* electrons of selenium atom in conjugation with 10π electrons of naphthyl ring. These assumptions can be supported by the interpretation of UV/vis spectra of related compounds cited in the literature [23].

A comparison of ν_{E-C} (where E = Se, Te) stretching bands in naphthyl chalcogenides reveals a regular trend in the variation of ν_{E-C} absorption frequencies. Most selenides show a weak band at ~530 cm^{-1} whereas the tellurides absorb nearly at 520 cm^{-1}. These values are consistent with the reported value of selenides [1a] and tellurides [1b].

2.2. Solid state structural features of **2** and **3**

In order to understand the structural details and packing of molecules, diffraction quality crystals of benzyl-1-naphthyl selenide, **2** and diphenylmethyl-1-naphthyl selenide, **3**

were grown in pure hexane and subjected to X- ray crystallography. A perspective view of the molecular structure with atom numbering scheme has been given in Fig. 2 and selected bond parameters have been listed in Table 2. All other relevant information about data collection and refinement parameters has been listed in Table 3.

Naphthyl moiety is well known to give rise to various conformational forms with different cell packing, leading to various steric and electronic effects. As expected, the naphthyl ring is found to be substituted at 1 position, with average C–Se bond length of 1.913(3) Å in compound **2**. The C–Se bond length between benzylic carbon and Se is 1.949(3) Å. Both C–Se bond distances lie within the range (1.90–1.95 Å), reported for several related derivatives [24]. Both **2** and **3**, adopt an angular 'V' shaped geometry about C–Se–C bond, indicating distortion of sp^3 carbon from its regular tetrahedral geometry.

As evident from the torsional angles, both phenyl and naphthyl rings are approximately planar and are disposed almost normal to one another. However, the two rings lie trans with respect to each other across the C(11)–Se(1) bond. The possibility of intermolecular Se···H non-bonded interaction has been ruled out. There is an observed deviation in the C(10)–C(1)–Se(1) and C(10)–C(9)–H(9) bond angles from regular trigonal planar (120°) to distorted trigonal, i.e. 116.95(18)° and 117.3(16)°, respectively.

The molecular structure of compound **3** (theoretically speaking, whose one more α-H has been replaced by a phenyl group) can be compared with **2**. The C–C bond distances adjacent to fused ring positions are relatively longer in the naphthyl ring (1.409–1.435 Å) of **3** than other bonds (1.37–1.39 Å). Steric repulsion places the two phenyl rings at 120° with respect to each other. The inter-electronic repulsion between aromatic rings distorts the geometry of tetrahedral carbon. Incorporation of second phenyl group on sp^3 carbon leads to the reduction in C–Se–C bond angle from 101.21(11)° in **2** to 95.19(11)° in **3**. The bond distance between substituted methyl carbon and selenium, increases from 1.949(3) to 1.997(3) Å in **3**, indicating the weakening of C–Se bond as a result of phenyl substitution. Nevertheless, both average C–Se bond lengths in **3** are well within the reported range.

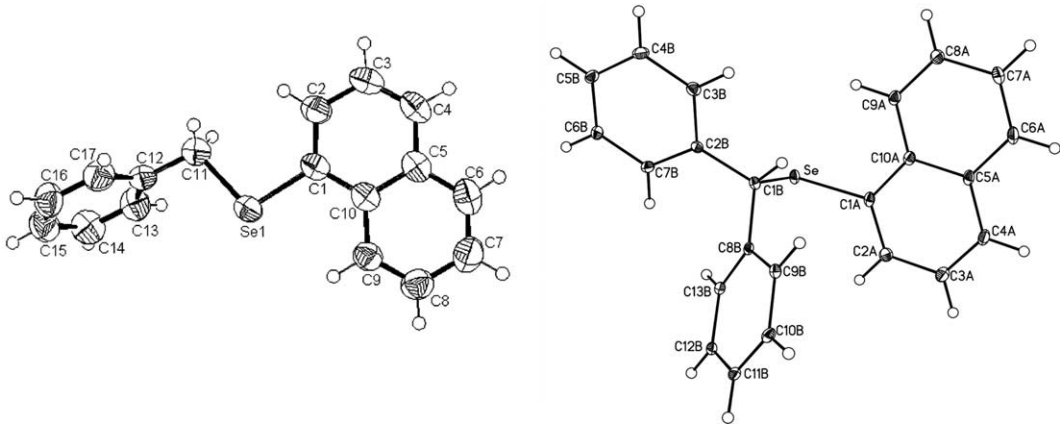


Fig. 2. ORTEP diagram of benzyl-1-naphthyl selenide (**2**) and diphenylmethyl-1-naphthyl selenide (**3**) molecules showing the atom numbering scheme.

Table 2
Selected bond parameters of **2** and **3**

Bond length (Å)		Bond angle (°)		Torsional angle (°)	
Compound **2**					
Se(1)–C(1)	1.913(2)	C(1)–Se(1)–C(11)	101.21(11)	C(11)–Se(1)–C(1)–C(2)	7.2(3)
Se(1)–C(11)	1.949(3)	C(10)–C(1)–Se(1)	116.95(18)	C(1)–Se(1)–C(11)–C(12)	175.9(2)
C(11)–C(12)	1.497(4)	C(2)–C(1)–Se(1)	122.7(2)	Se(1)–C(11)–C(12)–C(13)	−79.0(3)
C(12)–C(13)	1.377(4)	Se(1)–C(11)–C(12)	108.67(18)	C(2)–C(1)–C(10)–C(5)	1.3(4)
C(1)–C(2)	1.374(4)			C(7)–C(6)–C(11)–C(2)	0.6(4)
				C(12)–C(13)–C(14)–C(15)	−0.2(5)
Compound **3**					
C(1B)–H(1BA)	1.0000	C(1A)–Se–C(1B)	95.19(11)	C(1B)–Se–C(1A)–C(2A)	97.6(3)
Se–C(1A)	1.916(3)	C(2A)–C(1A)–C(10A)	120.2(3)	C(1B)–Se–C(1A)–C(10A)	−81.5(2)
Se–C(1B)	1.997(3)	C(2A)–C(1A)–Se	119.3(2)	C(1A)–Se–C(1B)–C(8B)	−70.6(2)
C(1B)–C(8B)	1.508(4)	C(10A)–C(1A)–Se	120.5(2)	C(1A)–Se–C(1B)–C(2B)	160.59(19)
C(1B)–C(2B)	1.517(4)	C(8B)–C(1B)–Se	110.57(17)	Se–C(1B)–C(2B)–C(3B)	−103.1(2)
		C(2B)–C(1B)–Se	108.35(18)	Se–C(1B)–C(8B)–C(9B)	121.3(2)
		C(8B)–C(1B)–C(2B)	116.5(2)	Se–C(1A)–C(10A)–C(9A)	0.8(4)
		Se–C(1B)–H(1BA)	107.0		

Table 3
Crystallographic data and measurements of **2** and **3**

	Compound **2**	Compound **3**
Empirical formula	$C_{17}H_{14}Se$	$C_{23}H_{18}Se$
Formula weight (g/mol)	297.24	373.33
Temperature (K)	293(2)	93(2)
Diffractometer used	Nonius MACH3	Bruker Smart CCD
Radiation used, λ Mo Kα (Å)	0.70930	0.71073
Crystal system/space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1$
Unit cell dimensions		
a (Å)	5.9280(5)	12.2784(13)
b (Å)	9.4210(10)	5.5886(6)
c (Å)	12.2470(8)	12.4428(13)
α (°)	92.683(7)	90
β (°)	91.978(6)	92.567(2)
γ (°)	102.885(7)	90
V (Å^3)	665.30(10)	852.96(16)
Z, calculated density (Mg/m^3)	2, 1.484	2, 1.454
Absorption coefficient (mm^{-1})	2.800	2.201
F(000)	300	380
Crystal size (mm^3)	$0.40 \times 0.20 \times 0.15$	$0.30 \times 0.30 \times 0.56$
Index ranges	$-6 <= h <= 7$	$-16 <= h <= 16$
	$11 <= k <= 0$	$-6 <= k <= 7$
	$-14 <= l <= 14$	$-16 <= l <= 16$
Reflection collected/unique	2477/2322	2967
R_{int}	0.0104	0.0566
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Final R indices, [$I > 2\sigma(I)$]	$R_1 = 0.0289$, $wR_2 = 0.0729$	$R_1 = 0.0324$, $wR_2 = 0.0784$
R indices [all data]	$R_1 = 0.0425$, $wR_2 = 0.0787$	$R_1 = 0.0340$, $wR_2 = 0.0800$
Largest difference in peak and hole (e Å^{-3})	0.572 and −0.339	0.675 and −0.604

3. Experimental

All the manipulations were carried under dry and deoxygenated nitrogen atmosphere. THF was distilled under N_2 from sodium–benzophenone immediately before use. Hydrazine hydrate (Aldrich), selenium (Fluka), tellurium (Fluka) and 1-bromonaphthalene (CDH) were of analytical grade and used as such. Dinaphthyl diselenides and ditelluride were prepared by literature method [16]. Melting points were uncorrected. ^{1}H, ^{13}C, ^{77}Se and ^{125}Te NMR spectra were recorded on a Jeol AL 300Mz spectrometer in $CDCl_3$ using Me_4Si as an internal standard for ^{1}H, ^{13}C NMR. Me_2Se and Me_2Te were used as external reference for ^{77}Se NMR and ^{125}Te NMR, respectively. UV spectra were recorded on JASCO V-530 UV/vis spectrophotometer in acetonitrile. Infrared spectra were obtained between KBr plates on a Perkin–Elmer model 1430 spectrometer. C, H and N analysis were performed on a Perkin–Elmer 2400 CHN analyzer. Selenium was estimated by standard method [25]. Mass spectra were obtained on a VG-70S 11-250J mass spectrometer.

Separation and purification of compounds was done by column chromatography performed on activated silica gel (230–400) using hexane as eluant.

3.1. Crystal structure analysis

Suitable crystals of **2** and **3** were chosen from a crop of crystals and mounted on glass fiber and data sets were collected for cell determination and intensity data collection. Crystal structure of both compounds were solved by direct method (SHELX-97) [26] and refined by full-matrix least-squares method. Anisotropic thermal parameters were employed for non-hydrogen atoms. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding model. The absorption corrections for compound **3** were performed using SADABS program [27]. Recollection of initial 50 frames and analysis of these frames showed that no decay correction was needed in this case.

3.2. Two-step synthesis of unsymmetrical 1-naphthyl selenides/tellurides

3.2.1. Method A

To a vigorously stirred mixture of 1,1′-dinaphthyl diselenide (2.07 g, 5 mmol) or ditelluride (2.54 g, 5 mmol) and powdered sodium hydroxide (1.0 g, 25 mmol) in 30 ml dimethyl formamide (DMF) was added a solution of hydrazine monohydrate (0.3 ml, 6 mmol) in the solvent under nitrogen atmosphere at room temperature. After 2–3 h of stirring, the color of reaction mixture turned pale yellow from orange or red. The reaction mixture was then cooled to 0–5 °C (−20 to −25 °C in case of diselenoethers) and a solution of alkyl halide (10 mmol) or dihaloalkanes (5 mmol)/trihaloalkane (3.4 mmol) diluted with an equal volume of the solvent, was added dropwise. Stirring was continued until the reaction was complete and temperature was allowed to rise slowly. The reaction mixture was diluted with 50–60 ml water and extracted in dichloromethane (3×30 ml). The organic layer was washed with acidified

water (6 N hydrochloric acid) twice (2 × 30 ml) followed by distilled water (3 × 40 ml) and then dried over anhydrous sodium sulfate. Solvent was evaporated on rota-evaporator and product purified over silica column using hexane as eluant.

3.3. One-flask synthesis of unsymmetrical 1-naphthyl selenides/tellurides

3.3.1. Method B

In a 100 ml three-necked round-bottomed flask, 1 g of magnesium (40 mmol) was taken in 25 ml anhydrous THF. A small crystal of iodine and 0.1 ml of 1,2-dibromoethane were added for entrainment before starting the drop wise addition of 1-bromonaphthalene (5.56 ml, 40 mmol). Stirring and refluxing was continued until the completion of reaction, which is indicated by the disappearance of magnesium. Dry elemental selenium (3.2 g, 40 mmol) or tellurium (5.08 g, 40 mmol) was added in small portions to the reaction mixture over a period of 20–30 min so as to maintain a gentle reflux as the reaction is exothermic. The color of reaction mixture turns deep red due to the formation of 1-naphthylseleno/telluromagnesium bromide. To 10 mmol of this intermediate, a solution of alkylating agent RX (10 mmol) or $(CH_2)_nX_2$, (5 mmol), diluted with an equal volume of dry deoxygenated THF, was added drop wise. Temperature was maintained between 0 and 5 °C in former case and ~−20 °C in latter. Stirring was continued for 3–4 h till the color of reaction mixture became pale yellow. The solvent was then removed on rota-evaporator and dark yellow residue obtained was dissolved in diethyl ether (100 ml). Ionic impurities were removed by washing the organic extract repeatedly with chilled distilled water. The organic fraction was dried over anhydrous sodium sulfate for 1 h and solvent was evaporated. The crude product so obtained was purified as in Section 3.2.

3.3.2. Unsymmetrical 1-naphthylselenomethanes

*Methyl-1-naphthyl selenide, [1-$C_{10}H_7SeCH_3$] (**1**).* Yellow oil; ^{1}H NMR: δ 8.17–8.20 (d, 1H, 8.4 Hz), 7.65–7.68 (d, 1H, 8.1 Hz), 7.56–7.58 (d, 1H, 8.1 Hz), 7.47–7.50 (d, 1H, 7.2 Hz), 7.31–7.40 (m, 2H), 7.18–7.23 (t, 1H, 7.2 Hz), 2.25 (s, 3H); ^{13}C NMR: δ 133.81, 133.4, 131.22, 128.84, 128.51, 127.18, 126.83, 126.26, 126.00, 125.69, 7.46; ^{77}Se NMR: δ 154.5; IR (KBr, ν cm^{-1}): 3051.8, 3004.0, 2926.6, 1560.7, 1502.3, 1379.2, 1332.5, 1059.9, 1022.1, 620.2, 533.3, 474.2, 407.3; UV/vis (λ_{max} nm, CH_3CN): 306, 242. Anal. calcd. for $C_{11}H_{10}Se$: C, 59.45; H, 4.50, Se, 36.03. Found: C, 59.20; H, 4.25; Se, 35.98%.

*Benzyl-1-naphthyl selenide, [1-$C_{10}H_7SeCH_2C_6H_5$] (**2**).* Colourless crystalline solid; m.p. 60–62 °C; ^{1}H NMR: δ 8.32–8.35 (dd, 1H, 8.4 Hz), 7.69–7.75 (m, 2H), 7.58–7.60 (d, 1H, 7.2 Hz), 7.39–7.48 (quintet, 2H, 7.9 Hz), 7.20–7.25 (t, 1H, 7.2 Hz), 7.06–7.13 (m, 3H), 6.99–7.04 (m, 2H), 4.02 (s, 2H); ^{13}C NMR: δ 138.59, 134.75, 134.07, 133.93, 129.84, 128.93, 128.84, 128.61, 128.32, 128.11, 126.79, 126.62, 126.10, 125.64, 32.33; ^{77}Se NMR: δ 311.7; IR (KBr, ν cm^{-1}): 3046.9, 2930.6, 1550.7, 1493.2, 1452.9, 1374.0, 1329.0, 1061.9, 1021.6, 954.6, 759.8, 690.0, 636.6, 527.5, 462.7; UV/vis (λ_{max} nm, CH_3CN): 336. Anal. calcd. for $C_{17}H_{14}Se$: C, 68.45; H, 4.90, Se, 26.84. Found C, 68.35; H, 4.85; Se, 26.98%.

*Diphenylmethyl-1-naphthyl selenide, [1-$C_{10}H_7SeCH(C_6H_5)_2$] (**3**).* Colourless crystalline solid; m.p. 77–79 °C; ^{1}H NMR: δ 8.39–8.41 (d, 1H, 8.4 Hz), 7.72–7.75 (m, 1H), 7.69–7.66 (d, 1H, 8.1 Hz), 7.39–7.50 (m, 3H), 7.23–7.29 (m, 4H), 7.08–7.20 (m, 7H), 5.54 (s, 1H); ^{13}C NMR: δ 141.52, 134.91, 134.60, 134.04, 129.00, 128.85, 128.65, 128.24, 128.40, 128.11, 127.03, 126.68, 126.06, 125.64, 52.69; ^{77}Se NMR: δ 407.2; IR (KBr, ν cm^{-1}): 3058.4, 3028.7, 2926.0, 2854.4, 1560.7, 1494.1, 1449.1, 1378.4, 1076.0, 1031.3, 1021.6, 1002.2, 962.1, 624.6, 616.4, 581.1, 533.0, 473.9, 411.6; UV/vis (λ_{max} nm, CH_3CN): 327; MS–EI, *m/e* (RI, assignment): 374 (0.5, $[M]^+$), 167 (100, $[(C_6H_5)_2CH]^+$), 207(12.6, $[C_{10}H_7Se]^+$), 128 (89.4, $[C_{10}H_8]^+$). Anal. calcd. for $C_{23}H_{18}Se$: C, 73.79; H, 4.81, Se, 21.39. Found C, 73.56; H, 4.62; Se, 21.68%.

*Tris-(1-naphthylseleno)methane, [(1-$C_{10}H_7Se)_3CH$] (**4**).* Yellow crystalline solid; m.p. 137–138 °C; ^{1}H NMR: δ 7.84–7.86 (d, 3H, 7.2 Hz), 7.78–7.81 (d, 3H, 8.1 Hz), 7.71–7.74 (d, 3H, 8.1 Hz), 7.49–7.52(d, 3H, 8.7 Hz), 7.26–7.34 (m, 6H), 6.20–6.87 (t, 3H, 7.8 Hz), 5.29 (s, 1H); ^{13}C NMR: δ 135.63, 134.18, 133.93, 130.91, 130.06, 128.43, 127.52, 126.67, 126.05, 125.57, 33.52 ^{77}Se NMR: δ 401.8; IR (KBr, ν cm^{-1}): 3042.7, 1583.2, 1555.8, 1494.6, 1455.1, 1194.0, 1053.1, 1015.9, 955.5, 793.2, 766.7, 734.0, 645.2, 571.1, 410.4; UV/vis (λ_{max} nm, CH_3CN): 290, 240; MS–EI, *m/e* (RI, assignment): 427(13.1, $[(C_{10}H_7Se)_2CH]^+$), 267 (47, $[(C_{10}H_7)_2CH^+]$), 207(26.6, $[C_{10}H_7Se]^+$), 128 (100, $[C_{10}H_8]^+$). Anal. calcd. for $C_{31}H_{22}Se_3$: C, 58.67; H, 3.47, Se, 37.85. Found C, 58.95; H, 3.43; Se, 37.22%.

*2-(N,N-diethylamino)ethyl-1-naphthyl selenide, [1-$C_{10}H_7SeCH_2CH_2N(C_2H_5)_2$] (**5**).* Dark yellow viscous oil; ^{1}H NMR: δ 8.18–8.21 (d, 1H, 8.4 Hz), 7.43–7.52 (m, 3H), 7.30–7.17 (m, 2H), 7.03–7.07 (t, 1H, 7.5 Hz), 2.73–2.78 (m, 2H), 2.48–2.53 (m, 2H), 2.19–2.26 (q, 4H, 7.2 Hz), 0.71–0.76 (t, 6H, 7.2 Hz); ^{13}C NMR: δ 134.35, 133.87, 131.69, 129.92, 128.38, 127.85, 127.61, 126.22, 125.86, 125.42, 52.74, 46.67, 25.73, 11.89; ^{77}Se NMR: δ 223.8; IR (KBr, ν cm^{-1}): 3051.9, 2967.6, 2927.4, 2851.8, 1560.6, 1501.4, 1463.7, 1379.2, 1332.4, 1463.7, 1379.0, 1067.9, 1021.9, 961.4, 770.3, 732.2, 650.3, 535.0, 409.7. Anal. calcd. for $C_{16}H_{21}SeN$: C, 62.54; H, 6.84; Se, 26.05; N, 4.56. Found: C, 62.70; H, 6.38; Se, 25.88; N, 4.21%.

*Allyl-1-naphthyl selenide, [1-$C_{10}H_7SeCH_2CH{=}CH_2$] (**6**).* Yellow oil; ^{1}H NMR: δ 8.37–8.40 (d, 1H, 8.4 Hz), 7.55–7.67 (m, 3H), 7.38–7.43 (m, 1H), 7.28–7.34 (m, 1H), 7.15–7.20 (t, 1H), 5.75–5.89 (m, 1H), 4.73–4.78 (m, 2H), 3.35–3.42 (d, 2H, 7.2 Hz); ^{13}C NMR: δ 134.30, 134.10, 133.80, 132.89, 129.30, 128.42, 128.29, 127.56, 126.39, 125.92, 125.48, 116.68, 30.54; IR (KBr, ν cm^{-1}): 3051.9, 3006.4, 2976.4, 2925.9, 2853.0, 1632.2, 1560.6, 1501.0, 1428.1, 1378.1, 1333.6, 985.6, 914.0, 651.4, 577.3, 533.8,

475.8. Anal. calcd. for $C_{13}H_{12}Se$: C, 62.90; H, 4.83, Se, 32.25. Found C, 62.28; H, 4.75; Se, 32.66%.

*2-cyclohexenyl-1-naphthyl selenide, [1-$C_{10}H_7SeC_6H_9$] (**7**)*. Yellow oil; ^{1}H NMR: δ 8.35–8.38 (d, 1H, 8.4 Hz), 7.56–7.71 (m, 3H), 7.27–7.38 (m, 2H), 7.15–7.20 (m, 1H), 5.72–5.77 (m, 1H), 5.57–5.61 (m, 1H), 3.80(d, 1H, 1.8 Hz), 1.85–1.96 (m, 4H), 1.71–1.77(m, 2H); ^{13}C NMR: δ 134.90, 134.00,133.76,130.24, 129.60, 128.63, 128.50, 128.16, 127.72, 126.53, 126.05, 125.66, 41.36, 29.27, 24.94, 19.58; IR (KBr, ν cm^{-1}): 3051.4, 3024.9, 2926.9, 2856.3, 2831.7, 1587.9, 1560.2, 1534.0, 1500.3, 1438.5, 1021.1, 770.3, 732.5, 588.2, 534.3, 453.7. Anal. calcd. for $C_{16}H_{18}Se$: C, 66.6; H, 5.55, Se, 27.7. Found C, 66.0; H, 5.2; Se, 26.9%.

*Allyl-1-naphthyl telluride, [1-$C_{10}H_7TeCH_2CH{=}CH_2$] (**8**)*. Yellow viscous oil, ^{1}H NMR: δ 8.09–8.12 (d, 1H, 8.7 Hz), 7.86–7.88 (dd, 1H, 6.9, 1.2 Hz), 7.50–7.58 (m, 2H), 7.25–7.34 (m, 2H), 7.05–7.13 (m, 1H), 5.72–5.87 (m, 1H), 4.45–4.46 (m, 2H), 3.34–3.41 (d, 2H, 9 Hz); ^{13}C NMR: δ 139.7, 136.5, 135.8, 133.5, 132.7, 129.4, 128.7, 126.7, 126.1, 126.0, 116.4, 115.3, 25.0; IR (KBr, ν cm^{-1}) 3049.9, 2955.0, 2925.5, 2869.0, 1585.9, 1556.0, 1499.6, 1454.1, 1376.3, 1330.0, 1041.1, 1020.8, 769.0, 672.7, 522.7, 403.9. Anal. calcd. for C, 53.24; H, 4.09. Found C, 53.07; H, 3.92%.

*Benzyl-1-naphthyl telluride, [1-$C_{10}H_7TeCH_2C_6H_5$] (**9**)*. Pale yellow waxy solid; ^{1}H NMR: δ 8.10–8.19 (m, 1H), 7.89–7.91 (d, 1H, 6.9 Hz), 7.62–7.71 (m, 2H), 7.34–7.43 (m, 2H), 7.10–7.15 (m, 1H), 6.90–7.05(m, 5H), 4.11(s, 2H); ^{13}C NMR: δ 140.27, 136.56, 133.49, 132.92, 129.67, 128.88, 128.77, 128.39, 128.25, 126.81, 126.16, 126.12, 126.07, 117.06, 12.07; IR (KBr, ν cm^{-1}): 3050.3, 2924.6, 2852.2, 1598.1, 1555.3, 1492.1, 1383.3, 1329.9, 1056.8, 1020.4, 951.2, 769.0, 694.7, 521.5, 441.7. Anal. calcd. for C, 60.17; H, 4.12. Found C, 59.67; H, 4.02%.

3.3.3. α,ω-Bis(1-naphthylseleno)alkanes

*Bis(1-naphthylseleno) methane, [(1-$C_{10}H_7Se)_2CH_2$] (**10**)*. Colourless viscous oil; ^{1}H NMR: δ 8.12–8.06 (d, 2H), 7.63–7.56 (m, 6H), 7.31–7.25 (m, 4H), 7.10–7.13 (t, 2H), 4.06 (s, 2H); ^{13}C NMR: δ 134.24, 134.05, 133.20, 130.11, 128.98, 128.61, 127.66, 126.70, 126.15, 125.65, 21.36; ^{77}Se NMR: δ 285.08; IR (KBr, ν cm^{-1}): 3051.3, 2924.6, 2853.0, 1561.0, 1501.3, 1454.1, 1377.4, 1333.7, 1021.3, 960.3, 769.0, 735.8, 621.6, 530.2, 410.4; UV/vis (λ_{max} nm, CH_3CN): 310, 286. Anal. calcd. for $C_{21}H_{16}Se_2$: C, 58.87; H, 3.73, Se, 37.38. Found: C, 59.01; H, 3.65; Se, 37.18%.

*1,2-Bis(1-naphthylseleno)ethane, [1-$C_{10}H_7Se(CH_2)_2Se$-(1-$C_{10}H_7$1)] (**11**)*. Colourless crystalline solid; m.p. 112–114 °C; ^{1}H NMR: δ 8.23–8.26 (m, 2H), 7.67–7.77 (m, 4H), 7.50–7.53 (d, 2H, 7.2 Hz), 7.38–7.47 (m, 4H), 7.13–7.16 (m, 2H), 3.07 (s, 4H); ^{13}C NMR: δ 134.65,134.16, 132.73, 129.15, 128.65, 128.56, 127.82, 126.72, 126.24, 125.65, 27.44; ^{77}Se NMR: δ 276.02; IR (KBr, ν cm^{-1}): 2925.0, 2853.9, 1585.5, 1548.1, 1498.7, 1467.5, 1415.6, 1020.3, 651.4, 573.4, 531.9, 408.3; UV/vis (λ_{max} nm, CH_3CN): 306, 285 nm. Anal. calcd. for $C_{22}H_{18}Se_2$: C, 59.72; H, 4.07, Se, 32.25. Found C, 59.24; H, 4.05; Se, 32.51%.

*1,3-Bis(1-naphthylseleno)propane, [1-$C_{10}H_7Se(CH_2)_3$-Se(1-$C_{10}H_7$)] (**12**)*. Colorless crystalline solid; m.p. 73–75 °C; ^{1}H NMR: δ 8.31–8.33 (d, 1H, 7.5 Hz), 7.76–7.79 (d, 1H, 7.5 Hz), 7.69–7.72 (d, 1H, 8.1 Hz), 7.61–7.63 (d, 1H, 7.5 Hz), 7.15–7.20 (t, 1H), 7.42–7.52 (doublet of quintet, 2H), 7.21–7.26 (t, 1H, 7.8 Hz), 2.93–2.98 (t, 2H, 6.9 Hz), 1.87–1.97 (m, 1H, 7.2, 3.9 Hz); ^{13}C NMR: δ 134.28, 133.95, 132.35, 129.08, 128.64, 128.30, 127.2, 126.64, 126.20, 125.73, 30.15, 27.69; ^{77}Se NMR: δ 227.4; IR (KBr, ν cm^{-1}): 3042.0, 2918.5, 2854 560.1, 1508.1, 1448.4, 1438.1, 1420.1, 1021.0, 961.9, 541.0, 532.1, 420.5; UV/vis (λ_{max} nm, CH_3CN): 308, 284, 245. Anal. calcd. for $C_{23}H_{20}Se_2$: C, 60.52; H, 4.38, Se, 35.08. Found C, 59.93; H, 4.04; Se, 35.02%.

3.3.4. Symmetrical 1,1'-dinaphthyl diselenides/ditellurides

*Bis(1-naphthyl) diselenide, [1-$C_{10}H_7Se]_2$ (**13**)*. Yellow crystalline solid; m.p. 85–87 °C; ^{1}H NMR: δ 7.90–7.98 (d, 2H, 8.1 Hz), 7.45–7.50 (t, 6H, 7.5 Hz), 7.08–7.22 (m, 4H), 6.91–6.96 (t, 2H); ^{13}C NMR: δ 134.13, 130.27, 129.78, 128.54, 128.22, 127.99, 126.62, 126.26, 125.81, 125.57; ^{77}Se NMR: δ 429.7; IR (KBr, ν cm^{-1}): 3053.8, 2925.8, 2854.2, 1588.3, 1560.2,1504.0, 1384.1, 1334.6, 1198.0, 782.4, 650.1, 530.5, 409.0; UV/vis (λ_{max} nm, CH_3CN): 300. Anal. calcd. for $C_{20}H_{14}Se_2$: C, 59.45; H, 4.50, Se, 36.03. Found C, 59.20; H, 4.25; Se, 35.98%.

*Bis (1-naphthyl)ditelluride, [1-$C_{10}H_7Te]_2$ (**14**)*. Red crystalline solid; m.p. 119–120 °C; ^{1}H NMR: δ 8.13–8.15 (d, 2H, 7.2 Hz), 8.00–8.03 (d, 2H, 8.4 Hz), 7.75–7.80 (dd, 4H, 14.4, 8.4 Hz), 7.43–7.47 (m, 2H), 7.30–7.34(t, 2H, 7.2 Hz), 7.19–7.23 (t, 2H, 7.6 Hz); ^{13}C NMR: δ 140.8, 136.4, 133.6, 133.1, 130.2, 128.7, 126.7, 126.2, 126.1, 111.5; ^{77}Se NMR: δ 429.7; IR (KBr, ν cm^{-1}): 3054.2, 2926.7, 2854.7, 1584.4, 1562.6, 1548.1, 1493.2, 1467.8, 1426.0, 1008.1, 793.5, 530.1, 522.4, 464.1, 428.3; ^{125}Te NMR: δ 357.0; UV/vis (λ_{max} nm, CH_3CN): 291, 289. Anal. calcd. for $C_{20}H_{14}Te_2$: C,47.61; H, 2.77. Found C, 47.22, H, 2.32%.

4. Supplementary material

Crystallographic information (excluding structure factors) has been deposited in the crystallographic information file (CIF) format with the Cambridge Crystallographic Data Center as supplementary Publication No. CCDC Nos. 221480 and 246467 for compound **2** and **3**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12-Union Road, Cambridge CB21E2, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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