

## **Synthesis and Characterization of Some New Heterocyclic Selenium Compounds on 3, 5-Naphtho-1-Selenocyclohexane**

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### **Abstract:**

A new series of heterocyclic derivatives from 3, 5 – naphtho 1- selenocyclohexane have been prepared (i.e.:  $C_{12}H_{10}SeX$ ;  $X=Cl, Br, I$ ) and  $C_{12}H_{10}SeRX$ ;  $R=CH_3$ ;  $X=I$ )

The new compounds were characterized by elemental analysis, IR,  $H^1$ NMR and molar conductance. Conductivity measurements of these compounds in DMSO solution indicated that they behave as weak electrolytes

### **الخلاصة:**

حضرت سلسلة جديدة من مشتقات المركب 3, 5 – naphtho 1- selenocyclohexane وهي  $C_{12}H_{10}SeX$ ;  $X=Cl, Br, I$  وقد شخّصت هذه المركبات باستخدام التحليل العنصري الدقيق (CHN) واطياف تحت الحمراء (IR) واطياف الرنين النووي المغناطيسي ( $H^1$ -NMR). واثبتت التوصيلية المولارية في مذيب ثنائي مثيل سلفوكسايد (DMSO) بان المركبات الكتروليتات ضعيفة.

### **Introduction:**

The preparation, characterization and solution properties for heterocyclic tellurium and selenium had been described in previous paper [1-9].

3, 5- naphtho –1-tellurocyclohexane was studied firstly by Anderson *et al* [10] who studied the cyclic inversion that occurs in oxygen, sulphur, tellurium and selenium cyclic compounds.

Singh *et al* [11] was prepared 3, 5 - naphtho –1-tellurocyclohexane and 3, 5- naphtho –1-selenocyclohexane from 1, 8 - bis (bromo methyl) naphthalene.

Radhy [12] prepare charge transfer complexes with quinines. In the present work a new heterocyclic selenium compounds based on 3, 5 - naphtho –1-selenocyclohexane have been prepared and characterized by physical properties and spectroscopic methods.

### **Experimental:**

#### **A) Physical measurements**

All Physical measurements was achieved in university of basrah. Infra- red spectra were recorded as KBr pellets in a rang of  $4000-400\text{ cm}^{-1}$  [Pye-Unicam SP300s infrared spectrophotometer]. Elemental analysis were performed using EA-1108 Carlo-Erba elemental analyzer.  $H^1$  NMR spectra were recorded in  $CDCl_3$  or DMSO- $d_6$  solution containing TMS as interned standard using Joel EX-90 instrument 100MHz. Melting points were determined by Gallen Kamp apparatus and were uncorrected. Conductivity measurements were done with a WTW conductivity meter LBR using a standard conductivity cell with constant of  $0.8\text{ cm}^{-1}$ .

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#### **B) Synthesis**

1, 8- bis (bromo methyl) naphthalene  $C_{12}H_{12}Br_2$  (I)

A mixture of (2g, 50mmol) of 1,8-dimethylnaphthalene and (6.4gm, 25mmol) N-bromosuccinimide (NBS) with (0.25g ,1mmol) from benzoylchloride in 40ml  $CCl_4$  was heated to reflux for 5hrs. A small quantity of pale yellow crystal was deposited from this reaction on cooling. The precipitate was washed with a small amount of water and recrystallized from benzene m.p.  $165^\circ C$ .

3, 5- naphtho-1- selenocyclohexane  $C_{12}H_{10}Se$  (II)[11]

To a well- stirred suspension of selenium (0.12g) (1.59mmol) in water was added sodium borohydride (0.12gm, 1.59mmol) in water (25ml) at room temperature .The selenium was consumed with in 10 min. 1,8-bis (bromomethyl) naphthalene (0.59mmol) in toluene (25ml) was

there added through a dropping funnel. After addition of phase –transfer catalyst, tetrabutylammoniumhydrogensulphate(0.1g) the temperature was raised to 60 °C and kept at 60°C for 8 hrs. The organic layer was separated, washed with 5% aqueous sodium carbonate, then evaporated in vacuo to give an orange product. Recrystallisation from petroleum ether(40–60°C) yielded orange crystals mp. 82°C (lit. [9]). 83.5 – 84.5°C.

1, 1-Dibromo 3, 5–naphtha-1-selenocyclohexane  $C_{12}H_{10}Se Br_2$  (III).

A Solution of 3, 5–naphtha-1-selenocyclohexane (3mmol) in dry ether was treated dropwise a solution of bromine (3mmol) in ether a white precipitation was formed immediately. The solution was evaporated and the residue was recrystallized from methanol to give white crystals (m.p. 202 – 204°C)

1, 1-Dichloro-3, 5–naphtha-1-selenocyclohexane(IV).

In ether was added slowly to a stirred solution of (3mmol) from 3,5-naphtho-1-selenocyclohexane in the same solvent at room temperature. A white precipitation was formed immediately. The precipitate was washed with water and recrystallized from ethanol to give a white crystal (m.p. 200—201°C)

1, 1-diodo-3, 5-naphthol-selenocyclohexane  $C_{12}H_{10}SeI_2$ (V).

A solution of 3,5 naptho-1-selenocyclohexane (1.mmol) in dry ether (10ml) was treated drop wise with a solution of iodine (0.39g,1.5mmol) in ether. A white precipitation was formed. The solution was evaporated and the residue was recrystallized from ethanol to give white crystal (m.p. 188-200°C).

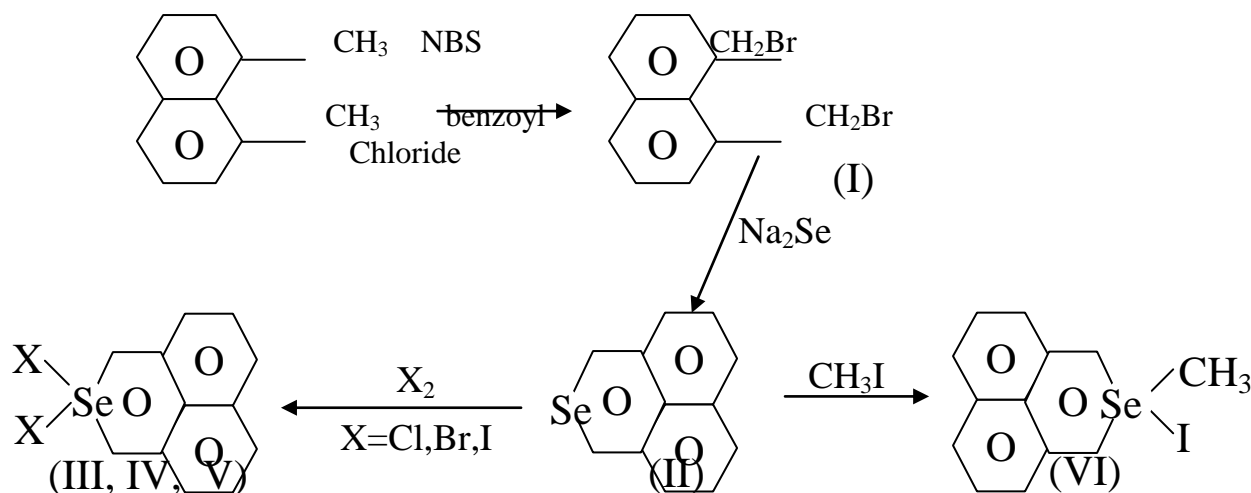
Iodo-1-methyl–3, 5-naphho-1-selenocyclohexane  $C_{13}H_{13}SeI$  (VI).

(3mmol) of freshly distilled iodo methane was introduced with cyclic selenide (3mmol). Recrystallized from ethanol/water (3/1) give white crystals of m.p. 170-173°C.

## Result and discussion

This paper deals with the synthesis of 3, 5-naphtho-1-selenocyclo hexane (II) which was then converted to dihalo derivatives through the reaction with halogen in 70% yield. Its treatment with methyl iodide to form compound  $C_{12}H_{10}SeCH_3I$ (VI).

The synthesized compounds and their synthesis modes are show in Scheme (1).



[Scheme-1]

All compounds are soluble in DMSO, their physical properties and elemental analysis are listed in table (1).

The infrared spectra (KBr disk) of all compounds show a weak to moderate band near 585 - 600  $cm^{-1}$  which characteristic of the C-Se stretching [7].

Two strong absorption, this first at 770- 780  $\text{cm}^{-1}$  owing to bending stretching of C-H and the second at 1620 – 1590  $\text{cm}^{-1}$  owing to aromatic stretching C=C Table (2).

In addition to these absorption bands, there are a number of characterization absorption such Se-Br, Se-Cl and Se-I stretching at 620, 610 and 605  $\text{cm}^{-1}$  respectively.

**Table 1. Analytical and physical properties for (II- VI) Compounds.**

No.	Chemical formula	Colour	M.P. °C	Yield %	Anal. Found (cal.) %	
					C	H
II	$\text{C}_{12}\text{H}_{10}\text{Se}$	Orange	82	70	<del>61.20</del> (61.81)	<del>4.34</del> (4.32)
III	$\text{C}_{12}\text{H}_{10}\text{SeBr}_2$	White	202 – 204	75	36.10 (36.67)	2.51 (2.56)
IV	$\text{C}_{12}\text{H}_{10}\text{SeCl}_2$	White	200 – 201	70	47.47 (47.41)	2.29 (3.31)
V	$\text{C}_{12}\text{H}_{10}\text{SeI}_2$	White	188 – 200	70	29.58 (29.59)	2.40 (2.06)
VI	$\text{C}_{12}\text{H}_{10}\text{SeCH}_3\text{I}$	White	170 - 173	75	41.60 (41.62)	3.42 (3.49)

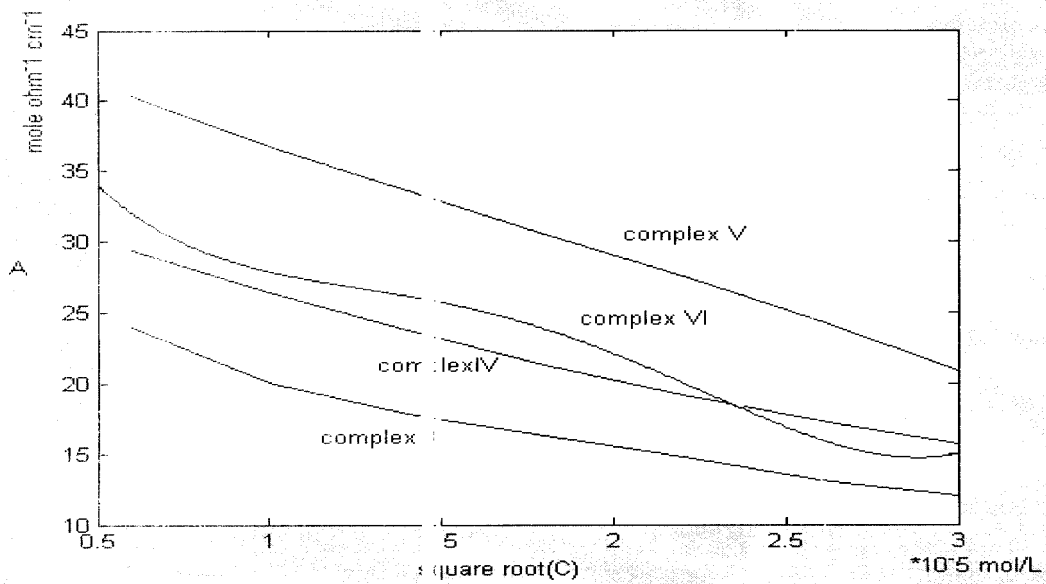
**Table 2. IR and  $^1\text{H}$ NMR for (II – VI) Compounds.**

No.	Se – C $\text{cm}^{-1}$	C = C $\text{cm}^{-1}$	C - H <sub>ben</sub> $\text{cm}^{-1}$	$\delta$ (ppm)	Solvent
II	585	1580	780	4.30 s (H <sub>2,6</sub> ) 7.70 – 8.00 (H <sub>aromatic</sub> )	DMSO-d <sub>6</sub> 2.15
III	585	1590	775	4.60 s (H <sub>2,6</sub> ) 7.20– 8.10m(H <sub>aromatic</sub> )	$\text{CDCl}_3$
IV	590	1580	770	4.80 s (H <sub>2,6</sub> ) 7.20–8.20m(H <sub>aromatic</sub> )	$\text{CDCl}_3$
V	590	1620	770	4.50 {S , H (2,6)} 7.20–8.00m (H <sub>aromatic</sub> )	$\text{CDCl}_3$
VI	600	1608	780	1.20 {S , CH <sub>3</sub> } 5.23 {M , H (2,6) } 7.20–8.20m (H <sub>aromatic</sub> )	DMSO-d <sub>6</sub>

$^1\text{H}$  NMR spectra for compounds (II-VI) were measured in  $\text{CDCl}_3$  and DMSO-d<sub>6</sub>. These compounds  $\text{C}_{12}\text{H}_{10}\text{SeX}_2$  in  $\text{CDCl}_3$  solvent gave two types of bands: the first, a singlet signal related to methylene protons (2,6) and the second, a multiple signal at 7-8.2 ppm for aromatic protons. Table (2), figure(2).

$^1\text{H}$  NMR for  $\text{C}_{12}\text{H}_{10}\text{SeCHI}$  (VI) shows a quartet signal for methylene proton (2,6) at 5.23 ppm which are not equivalent as compared with  $\text{C}_{12}\text{H}_{10}\text{Se}$  and  $\text{C}_{12}\text{H}_{10}\text{SeX}_2$  compounds. This results in agreement with  $\text{C}_{12}\text{H}_{10}\text{TeRX}$ . [13] And  $\text{C}_{12}\text{H}_{10}\text{SeRX}$  [14].

The molar conductivity for these compounds in DMSO as solvent with concentration between  $10^{-4}$  –  $10^{-5}$  molar were measured. When plots molar conductance ( $\text{ohm}^{-1} \text{cm}^{-1} \text{mole}$ ) against square root of concentration for compounds, showed a typical behavior of weak electrolyte in DMSO solvent Fig.1 and this result agrees with previous studies [12-15].



Fig(1).Molar Conductance versus Square Root of Concentration.



Figure(2):  
proton NMR to complexes(CH<sub>12</sub>H<sub>10</sub>SeI<sub>2</sub>).

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