Synthesis and Characterization of New Cycles of Selenazane and Thiazane

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Abstract

The aim of this paper ,cyclic compounds from selenium and sulphur were prepared via condensation reaction of 4-methyl benzaldehyde with 4-toluidine or p-phenylene diamine to produce anil compound ,which reacts with seleno or thio-organic compounds to yield selenazane and thiazine [1-6].The synthesized compounds [1-6] have been investigated using several chemical techniques ,such as (H.NMR-spectra , FT.IR –spectra , (C.H.N) –analysis and melting points).

Keyword: condensation of anil compounds, seleno cycles, sulphur cycles.

الخلاصة

أشار البحث لتحضير مركبات حلقية للسلينيوم والكبريت عن طريق تفاعل التكاثف بين 4–مثيل بنزالديهايد مع 4–تولودين أو p–فنيلين ثنائي الأمين لينتج مركب أنيل والذي بدوره تفاعل مع مركبات السلينيوم أو مركبات الكبريت العضوية ليعطي مركبات السلينازان والثيازان الحلقية [1–6] .شُخصت المركبات المحضرة في البحث بعدة تقنيات كيميائية منها (طيف الرنين النووي المغناطيسي ,طيف الأشعة تحت الحمراء ,التحليل الكمي الدقيق للكاربون.الهيدروجين.النيتروجين و درجات الأنصهار).

Introduction

Organosulphur and selenium chemistry has played a prominent role in our laboratory,both in the develop-ment of new synthetic methodology and in the design of biologically intersting compounds containing these elements[1-5].They are class of compounds well known for along time,and still continue the object of considerable interest , mainly due[6-14] to their applications in different fields such as:

Ph-Se-Cl , Ph-CO-Se Na ,Ph-S-CH_3

In this paper set out to synthesize a new group of seleno and sulphur –hetero cycles namely selenazane and thiazane compounds [1-6] through a cyclo addition between the anile group and selenium compounds or sulphur compounds in the following ,scheme(1).

Experimental

- All chemical used where supplied from Merck & BDH-chemical company. And all measurement where carried out by :

- Melting points :Electro thermal 9300 , melting point Engineering LTD ,U.K .

-FT.IR-spectra: fourrier transform infrared shimadzu (8300) , (FT.IR) , KBr-disc was performed by CO.S.Q. Iraq .

- H.NMR-Spectra &(C.H.N)-Analysis : in centre lab-Institute of earth & environmental science , Al-Bayt University ,Jordan .

Synthesis of bis (4-methyl phen yl) imine[1] :

Condensation reaction[23,24] by refluxing ethanolic mixture of equimolar amounts (0.01 mole,1.2g) of 4-methyl benzaldehyde and (0.01 mole ,1.07g) of 4-toluidine were reacts for (2 hrs) , the precipitate was filtered and recrystallized to give %85 of compound [1] .

2-(4-methyl phenyl)-3-(4-methyl phenyl)-1,3-selenazane-4-one[2]:

Refluxing mixture of bis (4-methyl phenyl) imine[1] (0.01 mole ,2.09g) with (0.01 mole,1.9g of sodium selenide ethyl chloride) , was refluxed for (4 hrs) , the precipitate was filtered and recrystallized to puduce 87% of compound [2] .

2-(4-methyl phenyl)-3-(4-methyl phenyl)-1,3-thiazane-4-one [3] :

Refluxing mixture of bis(4-methyl phenyl) imine[1] (0.01 mole ,2.09g) with (0.01mole ,1.24g of 3-mercapto propoyl chloride) , was refluxed for (4 hrs) , the precipitate was filtered and recrystallized to puduce 84% of compound [3].

Synthesis of bis (4-methyl phenyl) -4-phenylene di imine [4] :

(0.01mole ,1.08g)of P-phenylene diamine was condensed with (0.02 mole,2.4g)of P-methyl benzaldehyde in presence of absolute ethanol(100 ml),the precipitate was filtered and recrystallized to give 85% of compound [4] .

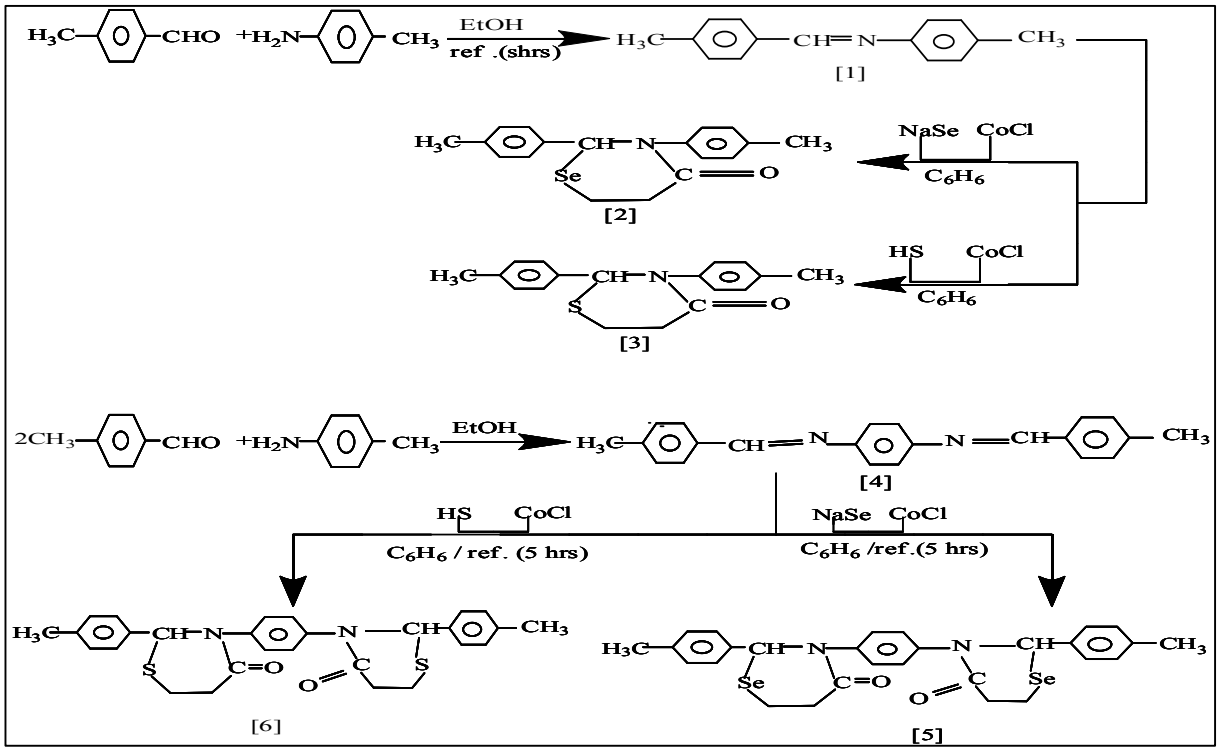
1,4–bis(2-(4-methyl phenyl)-1,3-selenazane-4-one benzene [5] :

Refluxing mixture of bis (4-toluilidine) -4-phenylene diamine [4] (0.01 mole,3.1g) with (0.02 mole,3.8g of sodium selenide propoyl chloride) were refluxed for (5 hrs) ,after cooling , the precipitate was filtered and recrystallized to yield 86% of compounds [5].

1,4–bis(2-(4-methyl phenyl)-1,3-thiazane-4-one)-benzene [6]:

Refluxing mixture of bis(4-methyl phenyl)-4-phenylene di imine [4] (0.01 mole,3.1g) with (0.02 mole ,2.4 g of 3-mercapto propoyl chloride) were refluxed for (5 hrs) ,after cooling , the precipitate was filtered and recrystallized to yield 84% of compounds [6].

Synthesis scheme (1):



Results and Discussion

These compounds [1-6] are saturated six–membered cycles which are important building blocks in various biologically active compounds , compose the core structures of some pharmaceutical drugs and in other fields[15-22].for this reason ,several synthetic methods for selenium and sulphur cyclic compounds have been developed which will also open new ways in organic synthesis chemistry.All the synthesized compounds[1-6] have been characterized by their melting points and spectroscopic methods (FT.IR –spectra ,(C.H.N) –analysis , and H.NMR –spectra) :

In FT.IR spectra , the reaction is followed by appearance (CH=N) absorption band of anil group[23,24] at (1620)cm^{-1} in compound [1] ,while this band disappears and other bands are appear at (1710,1655) cm^{-1} due to carbonyl group of amide ($-\overset{O}{\overset{\|}{C}}-NH$) and (CH-Se) respectively in compound [2] and at (1708,1660)cm^{-1} due to carbonyl group of amide ($-\overset{O}{\overset{\|}{C}}-NH$) and (CH-S) respectively in compound [3] .

FT.IR –showed appearance of broad band at (1618)cm^{-1} due to anil group (CH=N) of compound [4] ,while this band disappears and other bands are appear at (1696,1686)cm^{-1} due to carbonyl group of amide ($-\overset{O}{\overset{\|}{C}}-NH$) and(CH-Se) respectively in compound [5] ,and at (1705,1645) cm^{-1} due to carbonyl group of amide ($-\overset{O}{\overset{\|}{C}}-NH$) and (CH-S)endo cyclic , respectively in compound [6] .

Appearance of these bands strong evidence to formation of compounds [1-6] , other data of functional groups shown in the following , table(1) and figures (1-6)

H.NMR-spectrum of compounds [1-6] showed :

-Singlet signal at δ9.94 for one proton of anil groups (-CH=N) , singlet signal at δ 1.5 of proton of methyl group (- CH3) and doublet of doublet signals[18] at δ 6.55 for protons of phenyl group in compound [1] .

-Singlet signal at δ 4.25 for one proton of (Se-CH-N) endo cyclic ,signal at δ 3.97 for protons of (Se-CH_2-CH_2) end o cyclic ,singlet signal at δ 1.69 for protons of methyl group (- CH_3) and doublet of doublet signals at δ 6.54 in compound [2].

-Singlet signal at δ 3.43 for one proton of (S-CH-N) endo cyclic , signal at δ 3.06 for protons of (S-CH_2CH_2) endo cyclic in compound [3].

-Singlet of two signals at δ 9.72 , δ 9.26 for proton of two anil groups (CH=N) in compound [4].

-Singlet of two signals at δ 4.36, δ 4.12 for proton of two groups of (Se-CH-N) endo cyclic and signals at δ 3.85 , δ 3.76 for protons of two groups of (Se-CH_2CH_2) endo cyclic in compound [5] .

-Singlet of two signals at δ 3.41 , 3.34 for proton of two groups of (S-CH-N) endo cyclic and signals at δ 3.06 for protons of two groups of (S-CH_2CH_2) endo cyclic in compound [6].

And other peaks shown in the following ,figures (7-12).

(C.H.N)-analysis :It was found from compared the calculated data with found data of these compounds . the results were compactable , the data of analysis , M.F , and melting points are listed in table (2)

Acknowledgment :

I would like to express my thanks to ((Zaidan-company of chemical)) for supplied materials in Jordan , and express thanks to Mr.Muhanned –Hussain in center –lab-institute of earth and Environmental science –Al-bayt University H.J.K in Jordan for providing (C.H.N) element analytical , H.NMR and melting points .

Table (1) : FT.IR data(cm^{-1}) of compounds [1-6]

Comp. No.	(CH=N) of anile group	carbonyl of amide	(CH-Se) Endocycle	(CH-S) Endocycle
[1]	1620 S	-----	-----	-----
[2]	-----	1710 S	1655 S	-----
[3]	-----	1708 S	-----	1660 S
[4]	1618 b	-----	-----	-----
[5]	-----	1696 S	1686 S	-----
[6]	-----	1705 S	-----	1645 S

Table (2): Melting points , MF , & Elemental analysis of compound [1-6]

Comp. No.	M.F	m.p C°	Calc./ Found. C%	H %	N %
[1]	$C_{15}H_{15}N$	105	86.124 86.006	7.177 7.024	6.698 6.437
[2]	$C_{18}H_{19}NOSe$	158	62.797 62.544	5.523 5.308	4.070 3.910
[3]	$C_{18}H_{19}NOS$	164	72.727 72.677	6.397 6.206	4.713 4.587
[4]	$C_{22}H_{20}N_2$	122	84.615 84.465	6.410 6.278	8.974 8.815
[5]	$C_{28}H_{28}N_2O_2Se_2$	188	57.739 57.507	4.811 4.645	4.811 4.734
[6]	$C_{28}H_{28}N_2O_2S_2$	176	68.852 68.764	5.737 5.617	5.737 5.568

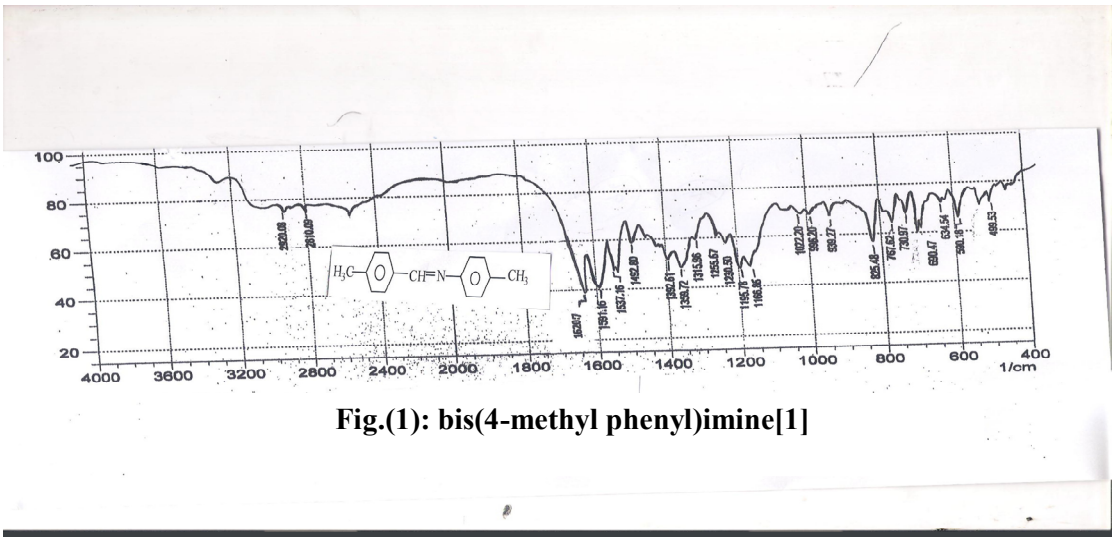


Fig.(1): bis(4-methyl phenyl)imine[1]

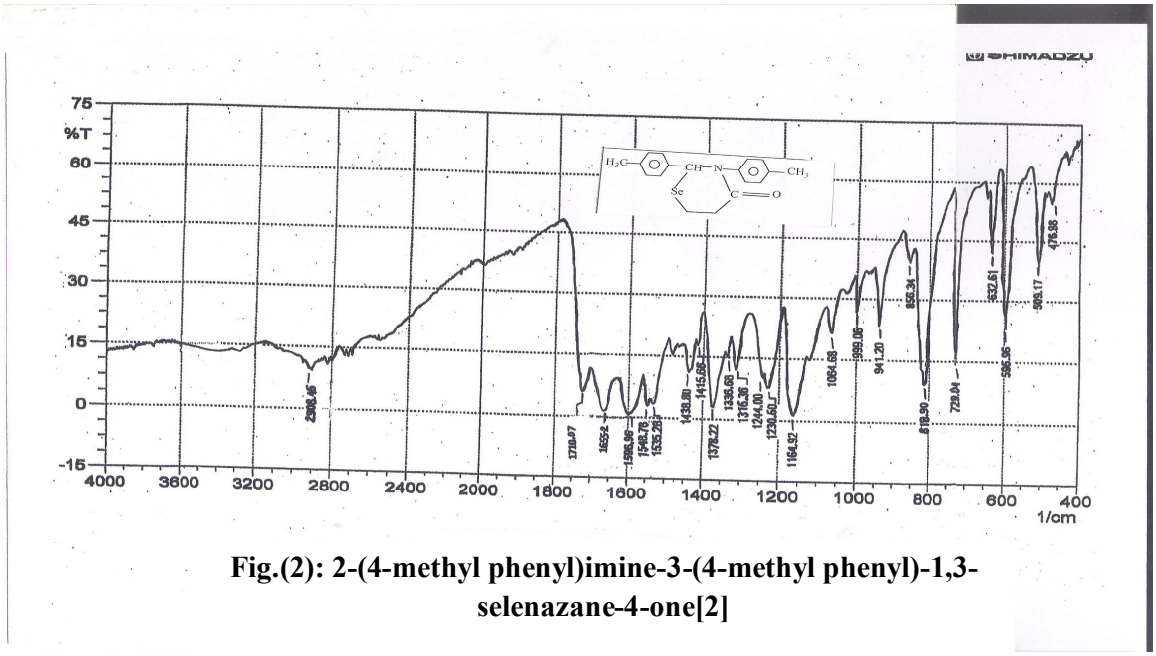


Fig.(2): 2-(4-methyl phenyl)imine-3-(4-methyl phenyl)-1,3-selenazane-4-one[2]

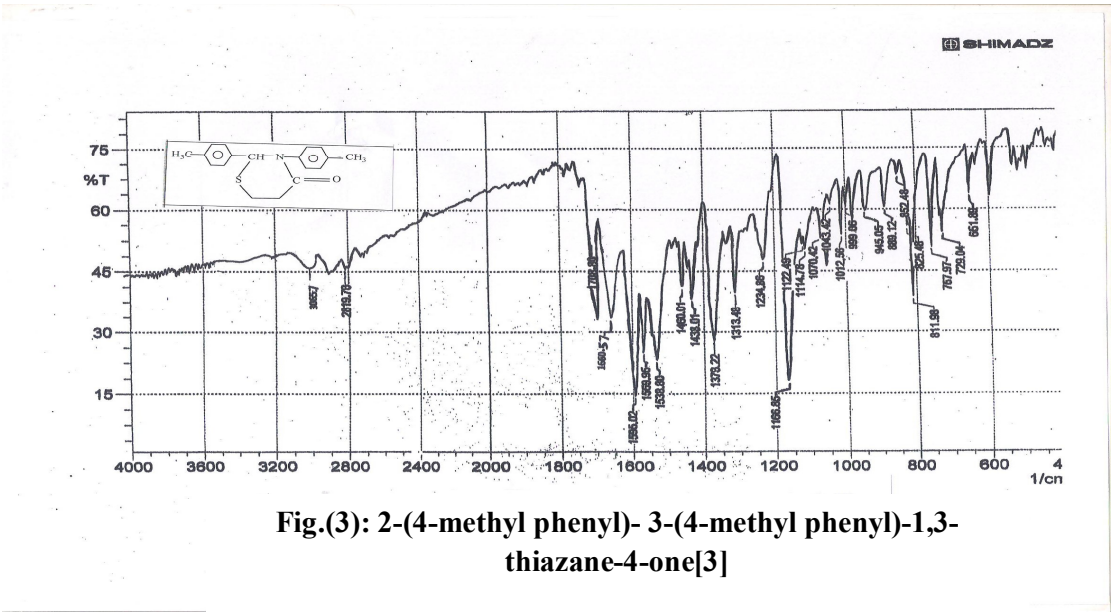


Fig.(3): 2-(4-methyl phenyl)- 3-(4-methyl phenyl)-1,3-thiazane-4-one[3]

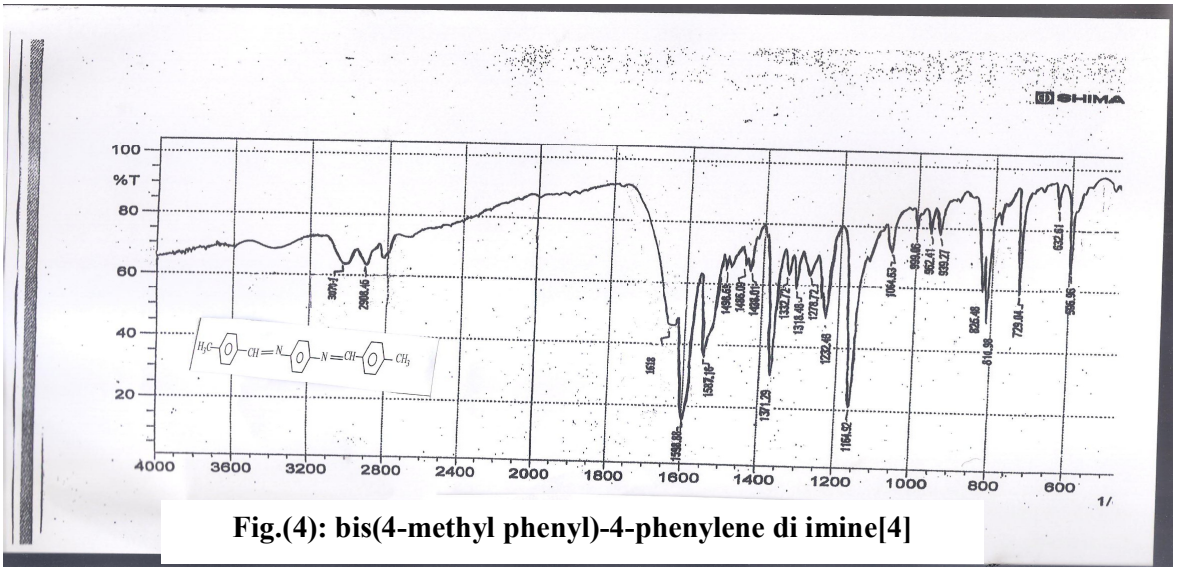


Fig.(4): bis(4-methyl phenyl)-4-phenylene di imine[4]

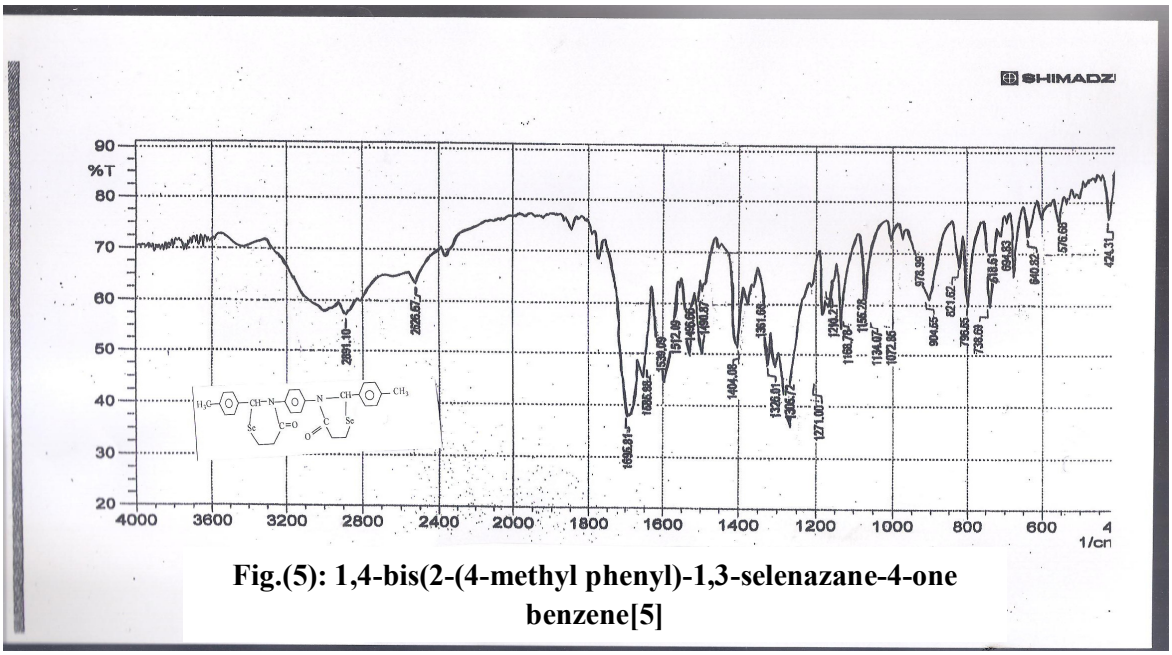


Fig.(5): 1,4-bis(2-(4-methyl phenyl)-1,3-selenazane-4-one benzene[5]

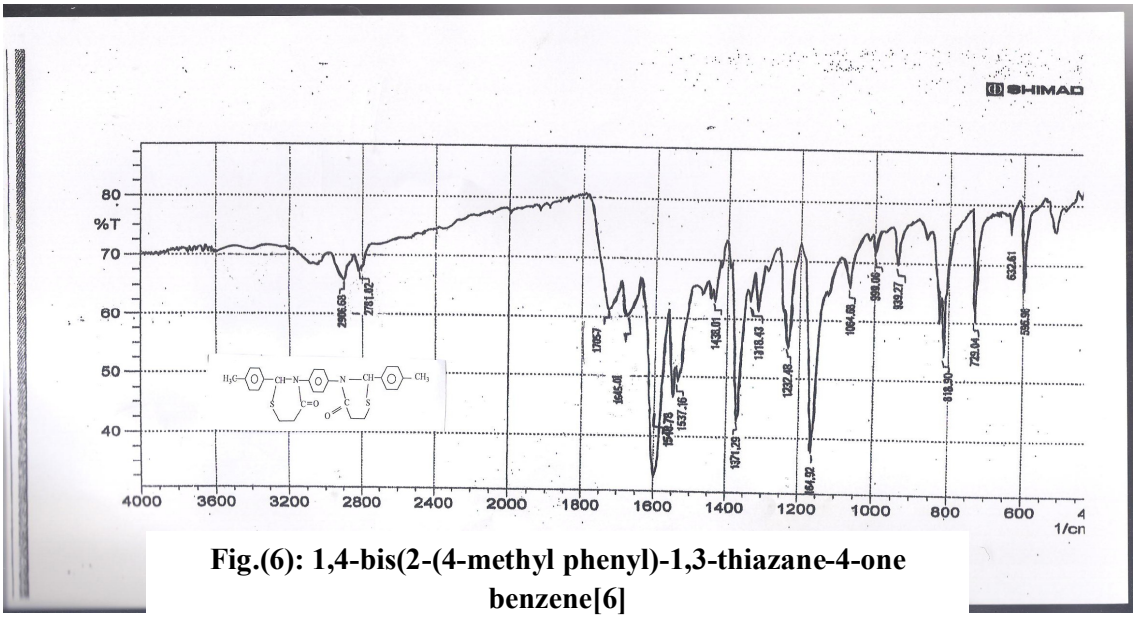


Fig.(6): 1,4-bis(2-(4-methyl phenyl)-1,3-thiazane-4-one benzene[6]

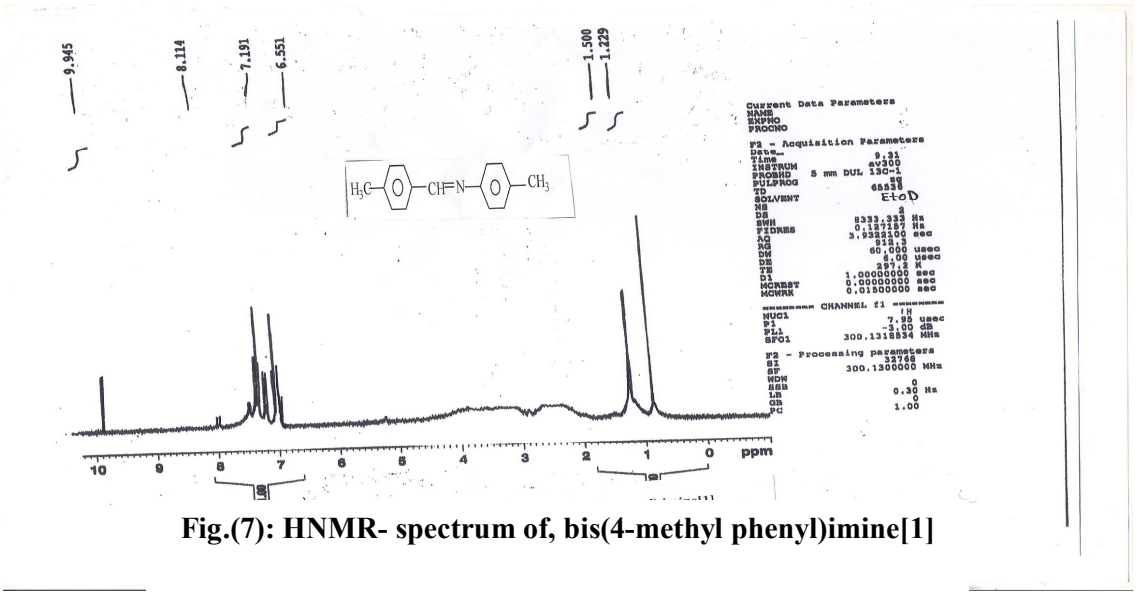


Fig.(7): HNMR- spectrum of, bis(4-methyl phenyl)imine[1]

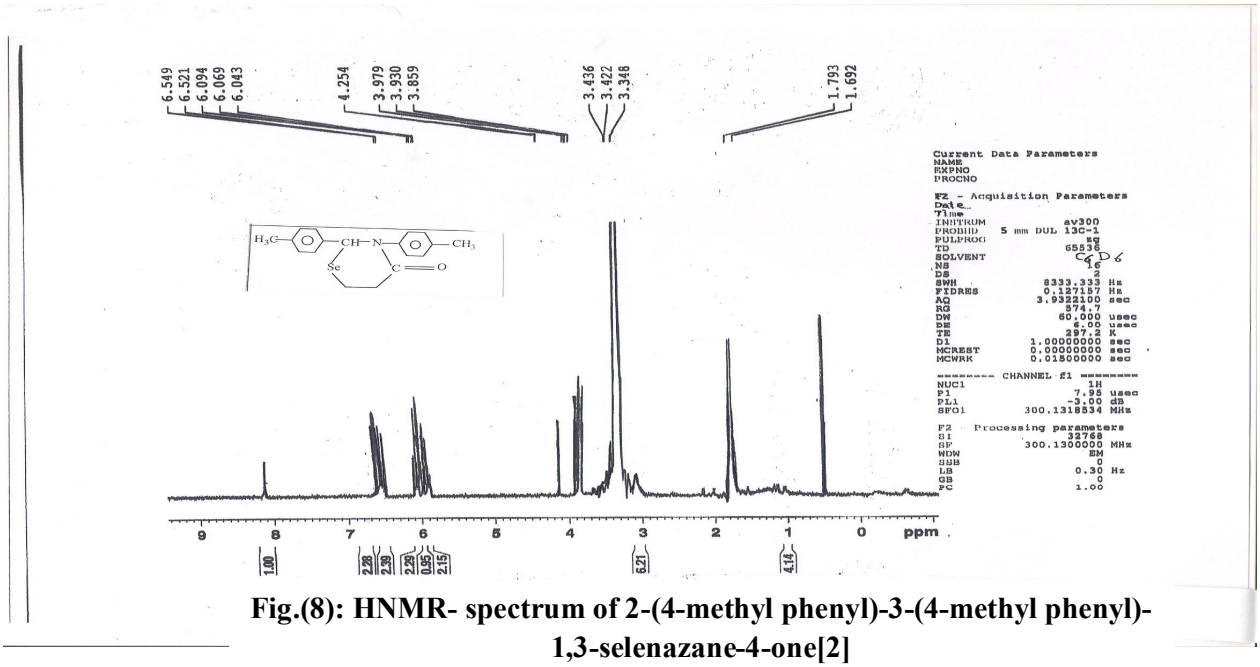


Fig.(8): HNMR- spectrum of 2-(4-methyl phenyl)-3-(4-methyl phenyl)-1,3-selenazane-4-one[2]

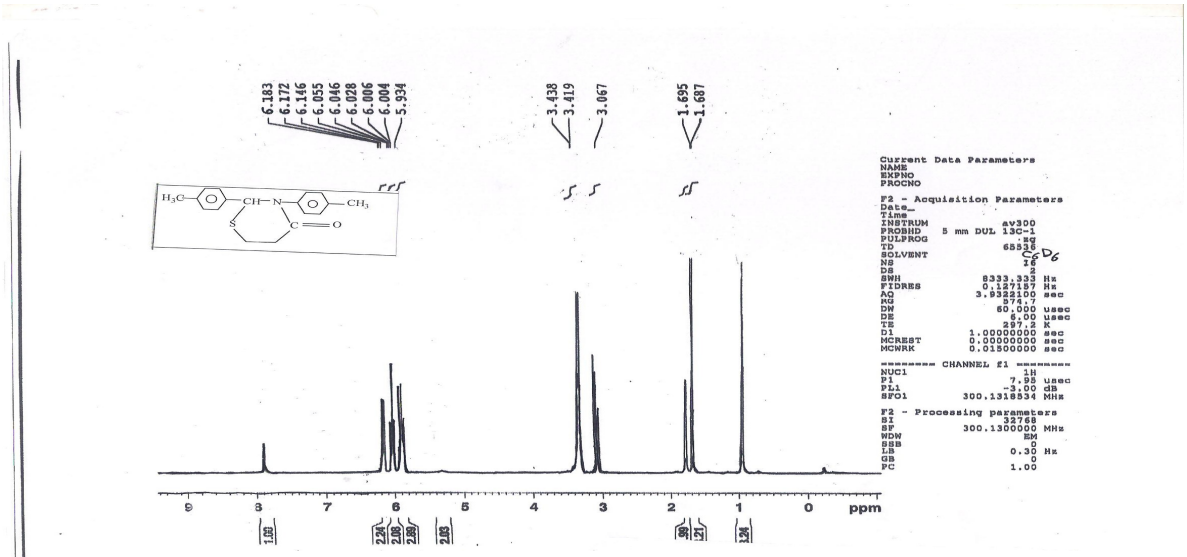


Fig.(9): HNMR- spectrum of 2-(4-methyl phenyl)-3-(4-methyl phenyl)-1,3-thiazane-4-one[3]

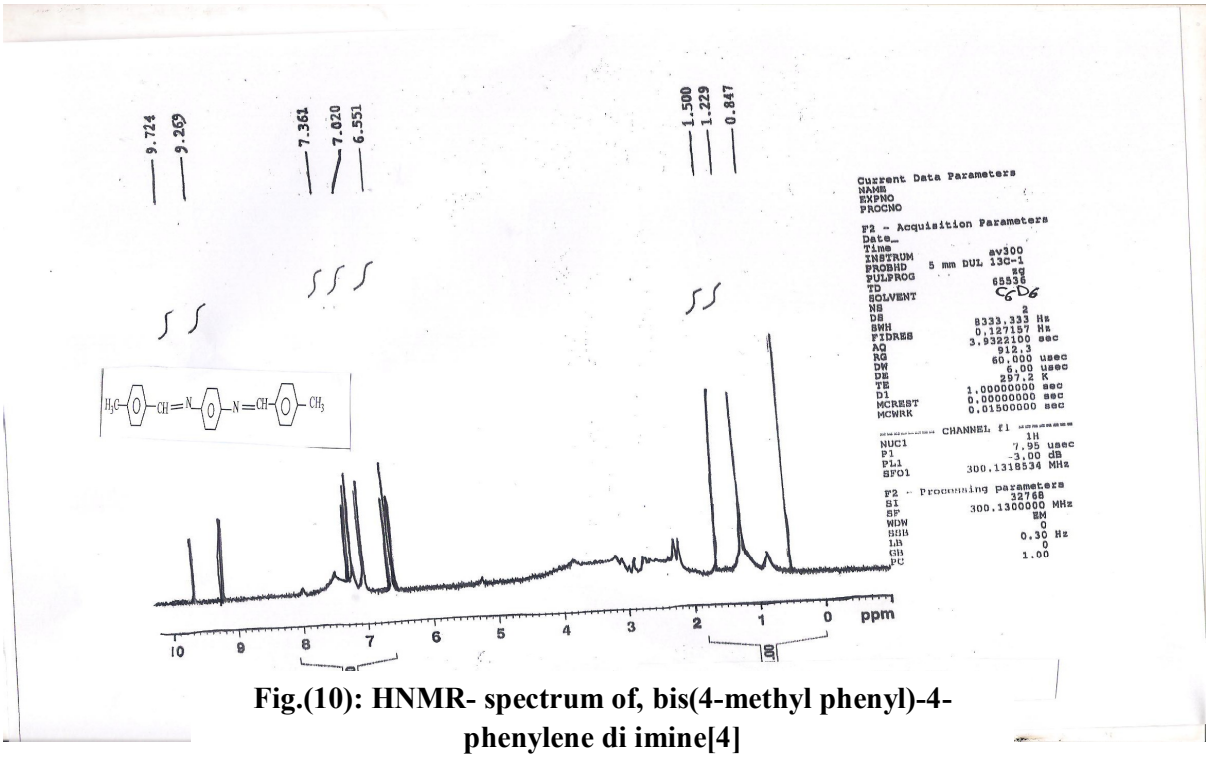


Fig.(10): HNMR- spectrum of, bis(4-methyl phenyl)-4-phenylene di imine[4]

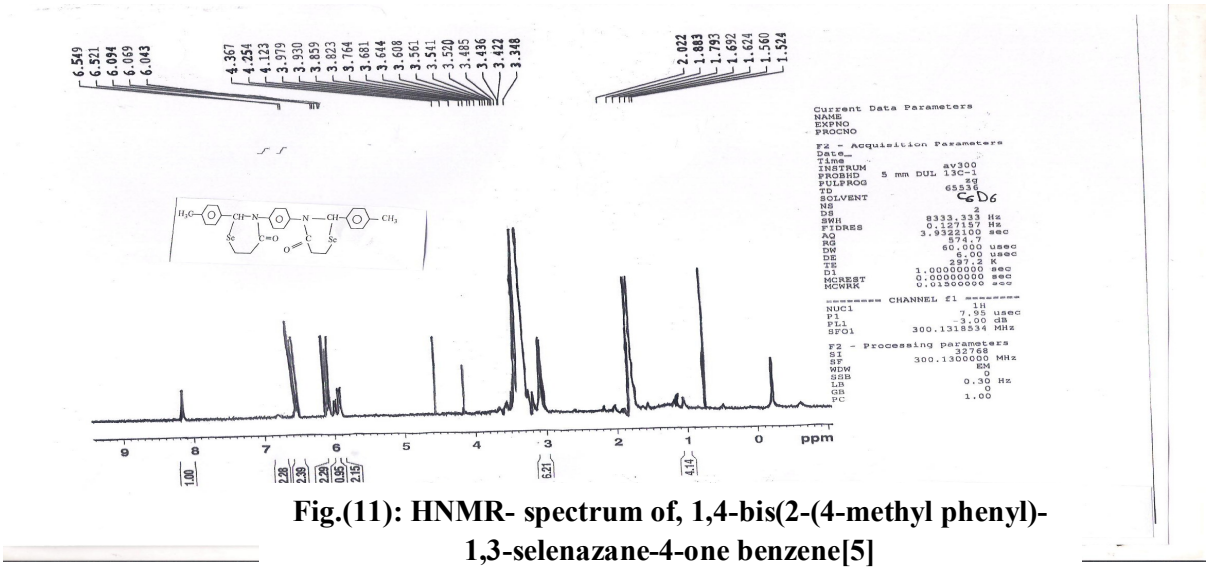


Fig.(11): HNMR- spectrum of, 1,4-bis(2-(4-methyl phenyl)-1,3-selenazane-4-one benzene[5]

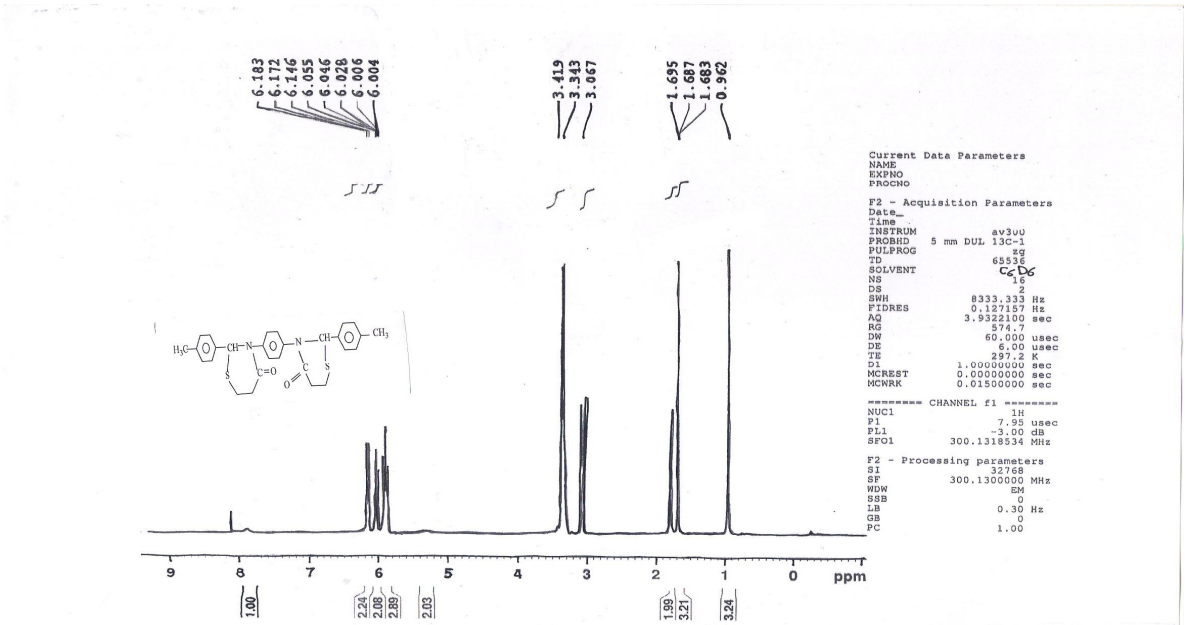


Fig.(12): HNMR- spectrum of, 1,4-bis(2-(4-methyl phenyl)-1,3-thiazane-4-one)- benzene[6]

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