Alkylation Reactions Via Organo Heteroatomes Halides

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Abstract: Series of heterocyclic compounds wer synthesized in this work through reaction of organo heteroatomes compounds or organo-(S,Se) halides with amino compounds to produce cyclic compounds which have two heteroatoms in content by using alkylation reactions. All prepared compounds [1-7] have been characterized by using several chemical techniques such as,(H.NMR–spectra,(C.H.N)–analysis), FT.IR–spectra and melting points.
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Key words: organo- (S,Se) compounds, alkylation reactions

1. Introduction

The chemistry of cyclic compounds has generated intensive scientific studies throughout the world, especially interest has been focused on the synthesis of macrobiomolecular,and variety of drugs such as: methyl seleno cystien, seleno cystien[1,2]. diazepam drugs[3],valium drugs.

These compounds have displayed a broad spectrum of pharmacological activities such as anti protozoal[4,5],anti fungal[6,7].

In the present study, synthesis of (diazonin, diazocane, selenthinin, selenthicine) cycles which are 8 – and 9 – membered rings with two heteroatoms (Se, S, N) as part of the portion in compounds [1-7].

These compounds are interesting structural motifs in medicinal chemistry, in recent times, their structures have been widely used, some of these hetero cycles have been indentified as antitumour a gents[8,9], antibiotics, anti – HIV a gents[10], in organic synthesis[11] and other applications[12-13].

Synthesis of these compounds via alkylation reaction give good yield by this methods in this paper.

2. Experimental:

- All chemical used were supplied from fluka and BDH – chemical company
- All measurements were 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.C. Iraq

– H.NMR-spectra and (C.H.N) – analysis: in center lab - Jordan.

2.1 Synthesis of compounds [1-3]:

To mixture of formaldehyde (15 ml, 40%) and sulphuric acid was added solution of 4- nitro aniline (0.2 mole, 27.6 g), the mixture was heated at 85C° for two hours, the precipitate was filtered off to give compound [1], then (0.01 mole, 2.8 g) of compound [1] was reacted with one of (0.01 mole, 0.9 g of 1,2 – di chloro ethane., 0.01 mole, 0.85 g of dichloromethane) respectively under heating for (8 hrs), the precipitate was filtered off and recrystallized to give 85% of 9 – membered cycles of compound [2] and 82% 8 – membered cycles of compound [3] respectively.

2.2 Synthesis of compounds [4-7]:

The compound [4] was synthesized by reaction between (0.2 mole, 27.8 g) of 4 – nitro phenol with (15 ml of formaldehyde 40% and 25 ml sulphuric acid 98%) under heating for four hours, the precipitate was formed and filtered off to give compound [4], which (0.01 mole, 2.9 g) of it was reacted with (0.02 mole, 3.8 g) of sodium seleno propoyl chloride under heating, the precipitate was formed and filtered off to give compound [5], (0.01 mole, 6.03 g) of compound [5] was reacted with one of (0.02 mole, 2.7 g of mercapto butoyl chloride., 0.02 mole, 2.4 g of mercapto propoyl chloride) respectively under heating for (8 hrs)[8,9], in alkali medium, the precipitate was formed and filtered off and recrystallized to yield 83% 9- membered cycle of compound [6] and 86% 8 – membered cycle of compound [7] respectively.

3. Results:

Mechanisim of this reaction involved polemerization of two mole from p-nitro aniline via alkylation of ortho-position then cyclization reaction of compounds to produce high yield from compounds[1-7] due to reaction of dimer, most of polymerization reaction give high products.

All formated compounds [1-7] have been characterized by their melting points & spectroscopic methods (FT.IR-spectra, (C.H.N)-analysis, & H-NMR-spectra):

FT.IR –Spectra:

In FT.IR –spectra,the reaction is followed by appearance amino group (- NH_2) absorption band at (3480)cm^{-1} in compound [1], which disappear and other bands are appear at (3290, 1537) cm^{-1} due to (- NH endo cyclic, C-N endo cyclic) respectively in compound [2]

and at (3240, 1540) cm^{-1} due to (- NH endo cyclic, C – N endo cyclic) [14-16], respectively in compound [3].
While FT. IR – spectra of compound [4] is appear absorption band at (3510) cm^{-1} due to hydroxyl[17] group (- OH) of phenol in compound [4], which also disappear and other bands are appear at (1710, 1520) cm^{-1} due to{ (O-C=O) [3], carbonyl of ester, protons[11] of (CH_2 -Se)} respectively in compound [5], at (1235, 1682, 670) cm^{-1} due to (C–O–C) of ether, (Se–C=O) carbonyl of selenide, (C–S) [18,19] endo cyclic) respectively in compound [6], and at (1240, 1680, 640) cm^{-1} due to (C-O–C) of ether,(Se – C=O) [1,2] carbonyl of selenide, (C – S) [19] endo cyclic) respectively in compound [7].
And other data of functional groups[19-21], shown in the following, table(1) and some figures (1-4).

Scheme of Reaction:

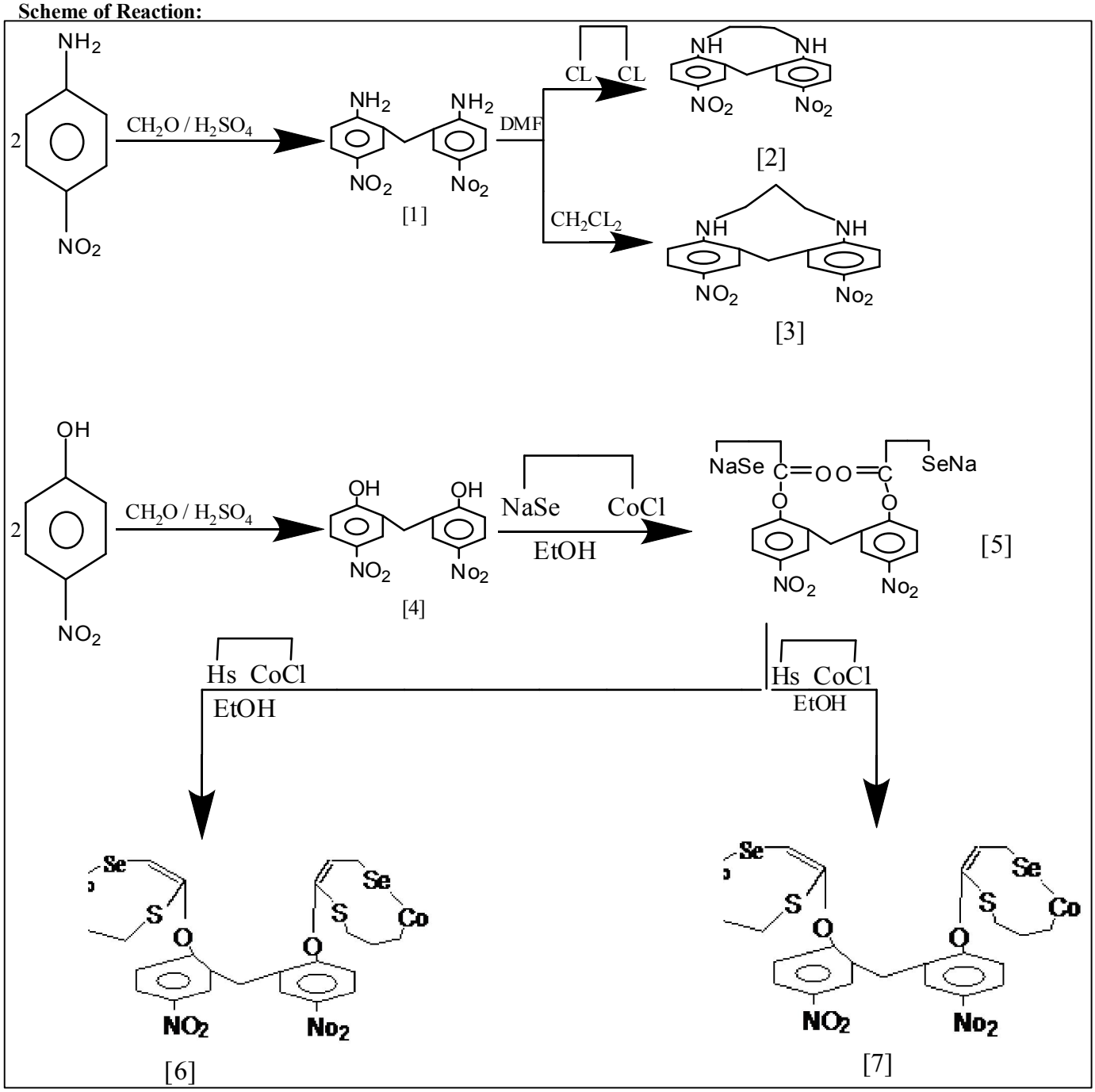
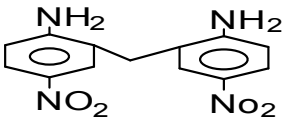
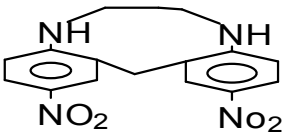
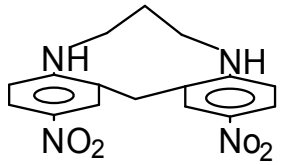
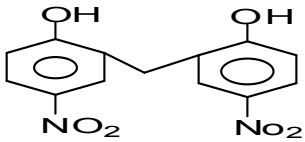
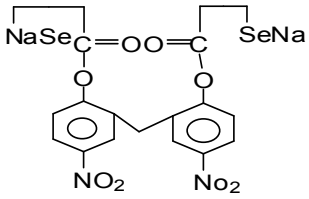
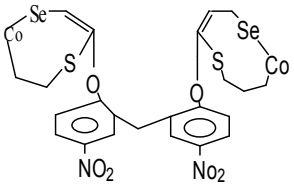
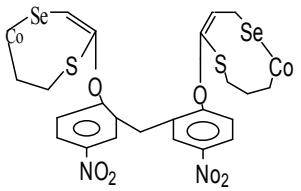


Table (1): FT.IR data (cm^{-1}) of compounds [1-7]

Comp. No.	Structural formula	Name of compound	Functional group in every compound
[1]		2.2`-methylene bis(4-nitro aniline)	ν ($-NH_2$):3480 S
[2]		2,11-dinitro-6,7-dihydro -13H-dibenzo –diazonin	ν ($-NH_2$) endo cyclic: 3290 M (C-N)endo cyclic: 1537S
[3]		2,11-dinitro-6,7-dihydro -12H-dibenzo –diazonin	ν ($-NH_2$)endo cyclic: 3240 M (C-N)endo cyclic: 1540 S
[4]		2.2`-methylene bis(4-nitro phenol)	ν (-OH): 3510 S
[5]		2.2`-methylene- bis(4-nitro phenol sodium seleno propanoate).	ν ($-\overset{O}{\overset{\|}{C}}-$) of ester: 1710 ($CH_2$-Se): 1520
[6]		2.2`-methylene-bis{2-(4-nitro phenoxy)-1,5-selen thinin -6-one}.	(C-O-C) of ether: 1235 ($Se-\overset{O}{\overset{\|}{C}}-$) carbonyl of selenide: 1682 (C-S)endo cyclic:670
[7]		2.2`-methylene-bis{2-(4-nitro phenoxy)-1,5-selen thicine -6-one}.	(C-O-C) of ether: 1240 ($Se-\overset{O}{\overset{\|}{C}}-$) carbonyl of selenide: 1680 (C-S)endo cyclic:640

S=strong, M=medium, VS = very strong

Table (2):Melting points, M.F, & (C.H.N)- analysis of compounds [1-7]

Comp. No.	M.F	M.P C° (+2)	Calc./ Found C%	H %	N %
[1]	$C_{13}H_{12}N_4O_4$	131	54.166 54.064	4.166 4.076	19.444 19.328
[2]	$C_{15}H_{14}N_4O_4$	162	57.324 57.207	4.458 4.319	17.834 17.681
[3]	$C_{14}H_{12}N_4O_4$	169	56.000 55.891	4.00 3.864	18.666 18.417
[4]	$C_{13}H_{10}N_2O_6$	139	53.793 53.581	3.448 3.237	9.655 9.518
[5]	$C_{19}H_{16}N_2O_8Se_2Na_2$	167	37.755 37.678	2.649 2.574	4.636 4.484
[6]	$C_{27}H_{26}N_2O_8S_2Se_2$	192	44.510 44.387	3.571 3.409	3.846 3.702
[7]	$C_{25}H_{22}N_2O_8S_2Se_2$	205	42.862 42.729	3.143 3.038	4.000 3.967

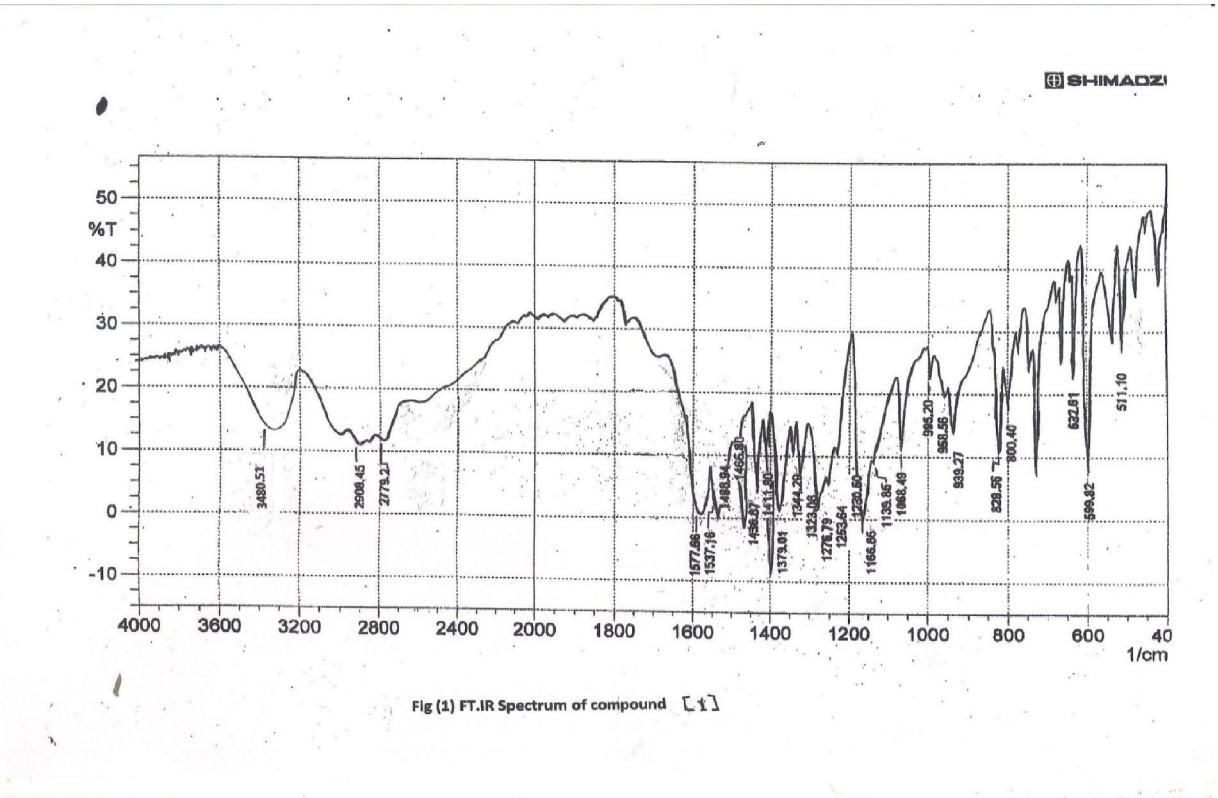


Fig (1) FT.IR Spectrum of compound [1]

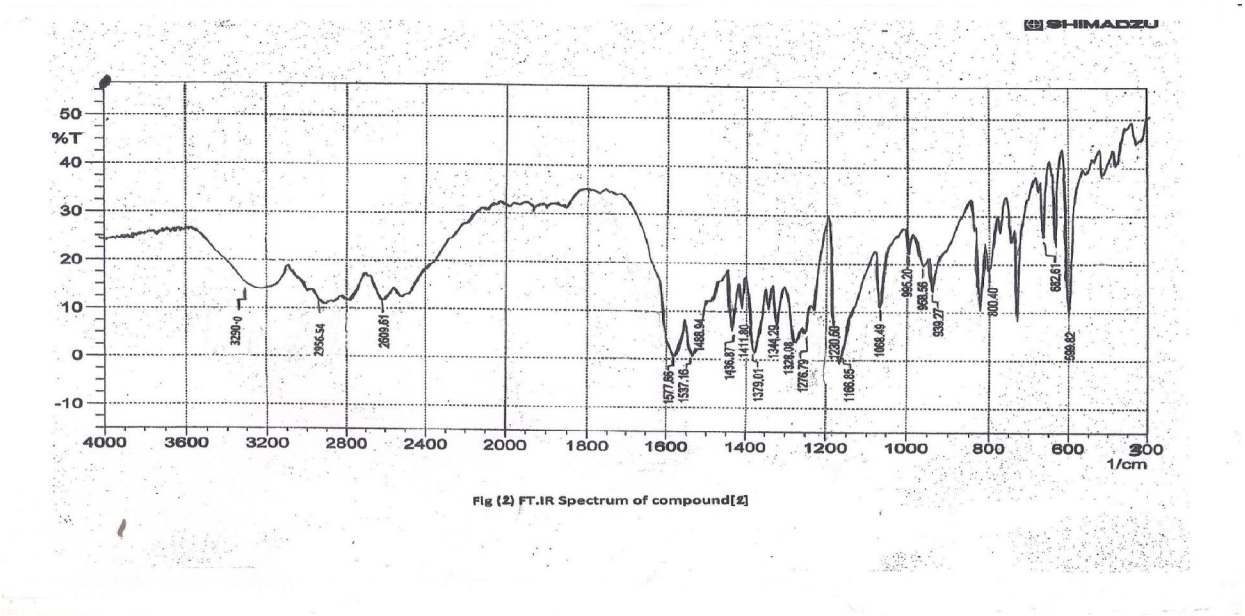


Fig (2) FT.IR Spectrum of compound[2]

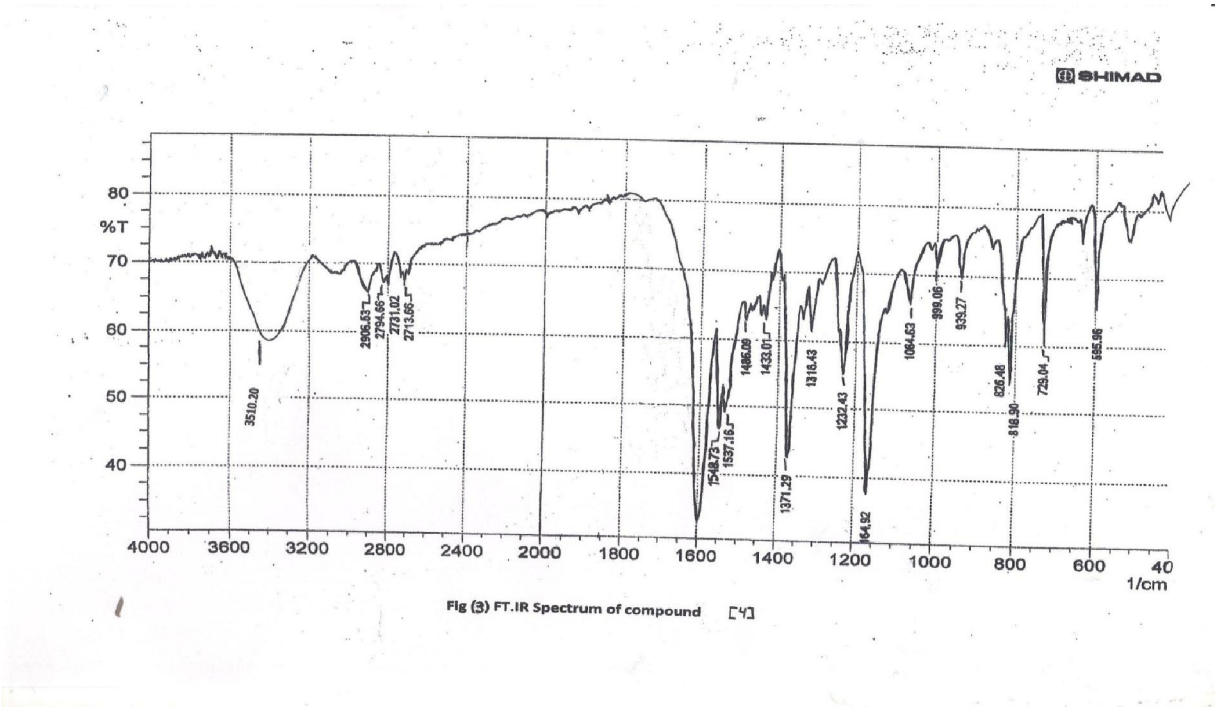


Fig (3) FT.IR Spectrum of compound [4]

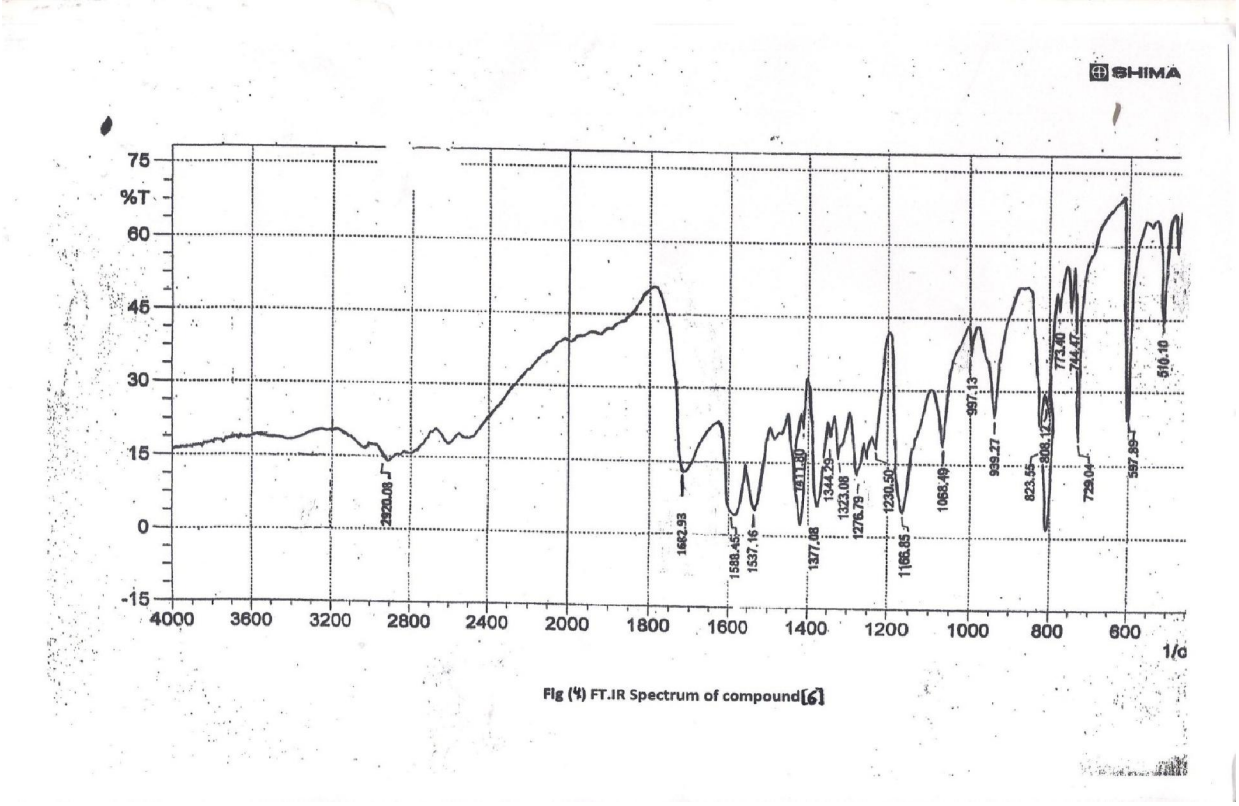


Fig (4) FT.IR Spectrum of compound[6]

4. Discussion:

H.NMR – Spectra:

H.NMR – spectrum of compounds [1-7] showed:Singlet signal at б8.62 for protons of amine group ($-NH_2$) in compound [1], which disappear and other signals are appear: signals at б (3.8, 4.28) for protons of (NH / NH)[3], endo cycle is compound [2] & at б (3.9,4.4) for protons of (NH / NH) endo cycle in compounds [3].

While the spectrum of compound [4] showed:Singlet signal at б 10.43 for protons of hydroxyl group (-OH) in compound [4], which also disappear & other signals are appear: signals[11] at б (3.6, 3.9) for protons of ($-CH_2CH_2$-Se) in compound [5], signals at б (3.83, 4.38, 4.62) for protons of { (Se) endo cycle, (S) endo cycle[19] } respectively in compound[6], and signals at б (4.10, 4.40, 4.70) for protons of{(Se) endo cyclic[11],(S) endo cyclic[19] } respectively in compound[7].

(C.H.N) – Analysis:

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

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