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SYNTHESIS OF BI CYCLES CONTAINING HETERO (CYCLES AND ATOMS)

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ABSTRACT

The aim of this work, synthesis of new bicycles of (five, six, seven) - member hetero cyclic compounds which have more than one of heteroatom in bi cycles system via cyclization reactions and alkylation reaction. The formatted compounds [1-8] have been characterized using several chemical techniques (H.NMR-spectra, (C.H.N)-analysis, FT.IR-spectra) & melting points.

INTRODUCTION

Bi cycles system bearing nitrogen ,sulphur ,oxygen, constitute the core structure of a number of biologically interesting compounds ,some of them are pyrazoles, imidazoles, which are structural subunits of several biologically active compounds. In this work, the compounds have been synthesized from combination of two compounds by cyclocondensation or cyclization of same compound to produce hetero cycles including heteroatom from nitrogen & sulphur atoms for this reason their biological activity highly efficient & low poisonous. Since the discovery of the biological importance [1,2] of these compounds, the aim of many researches product was to synthesize many different substituted & various uses were a subject of many studies [3-12].

Experimental

-All chemicals used were supplied from Merck & BDH-chemical Company.

-All measurements were carried out by:1 – Melting points: electro thermal 9300, melting point engineering LTD, U.K 2 – FT.IR spectra: fourrier transform infrared shimadzu8300 – (FTIR), KBr disc was performed by CO.S.Q.C. Iraq 3 – H.NMR-spectra and (C.H.N) – analysis.

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Synthesis of 4-Ptopanoat -6-methyl-hydro pyridazinone [4]

The compound [4] was synthesized by reaction between (0.01 mole, 1.6 g) diethylmalonate& acetyl methyl chloride in refluxed for (2hrs) until the precipitate formed, after cooling, the precipitate was filtered off, then (0.01 mole, 2.1 g) of this precipitate was condensed with (0.01 mole, 0.32 g) of hydrazine in presence of absolute ethanol with reflux for (2hrs), after cooling, the precipitate was filtered off & recrystalized to yield 86% from compound [4].

Synthesis of: 3,4-pyrazolone-6-methyl hydro pyridazine [5]: and:3,4-thiazepanone -6-methyl –hydropyridazine [6]

Condensation reaction by refluxing mixture of (0.01 mole, 1.8 g) of compound [4] with one of [(0.01 mole, 0.32 g) of hydrazine, (0.01 mole, 0.7 g) of mercapto amino ethylene)] respectively, were react for (4hrs), after cooling, the precipitate was filtered off & recrystallized to give 84%, 87% of compounds [5,6] respectively.

Synthesis of 3-propanoate –hydro thiophen -2-one [7]

and 2, 3-thiazepinone –dihydrothiophen [8]

(0.01 mole, 1.6 g) of diethyl malonate was condensed with (0.01 mole, 0.9 g) of mercapto ethylene chloride in presence of ethanol with refluxing for (2hrs), the precipitate was filtered off, then (0.01 mole, 2.2 g) of this precipitate was cyclized upon heating in refluxing for (4hrs), after cooling, the precipitate was filtered off & recrystalized to yield 85% of compound [7]. The compound [8] was synthesized by refluxing between (0.01 mole 1.7 g) of compound [4] & (0.01 mole, 0.7 g) of mercapto amino ethylene for (4hrs), after cooling, the precipitate was filtered & recrystalized to yield 87 %.

RESULTS AND DISCUSSION

All synthesized compounds [1-8] have been characterized by their melting points & spectroscopic techniques (FT.IR-spectra, (C.H.N)-analysis, & H-NMR-spectra):

FT.IR-Spectra:

FT.IR-spectra of compounds [1-8] showed:

Compound [4]

Absorption band appeared at (1678) cm^{-1} due to carbonyl of amide (CO-NH-), other band appeared at (1588) cm^{-1} due to (C=N) endocyclic.

Compound [5]

Absorption band appeared at (1681) cm^{-1} due to carbonyl group of amide (CO-NH) appeared at (3345) cm^{-1} due to (-NH) of amide in cycle [13].

Compound [6]

Absorption band appeared at (1686) cm^{-1} due to carbonyl group of amide (CO-NH), two bands appeared at (651, 1438) cm^{-1} due to (C-S) & ($S-CH_2$) respectively of endocyclic, other bands appeared at (1595, 1460) cm^{-1} due to (C=N) endocyclic.

Compound [7]

Absorption band appeared at (1730) cm^{-1} due to carbonyl group of ester ($CO-OC_2H_5$), two bands appeared at (1436, 1629)cm^{-1} due to ($S-CH_2$) , (C=N) endocyclic respectively.

Compound [8]

Absorption band appeared at (1660)cm^{-1} due to carbonyl group of amide (CO-NH-), & two bands appeared at (663 , 1486)cm^{-1} due to (C-S) & ($S-CH_2$) endocylic , respectively , & other data of functional groups shown in the following in table (1) , fig. (1-5).

Table 1. FT.IR data (cm^{-1}) of compounds [4-8]

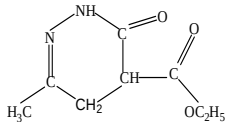
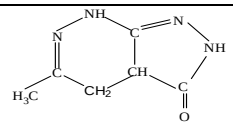
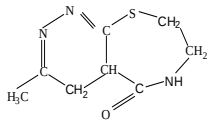
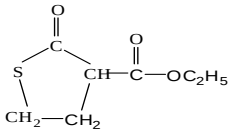
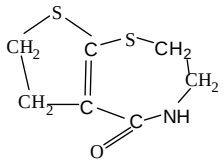
Comp. No.	Structural formula	υ(-CO)-carbonyl of amide	υ (NH)str. (NH)bend	(C-S) ($S-CH_2$) Endo cyclic	(C=N) Endo cyclic	υ (-CO-) carbonyl of ester	(-CO-) carbonyl of sulphide
[4]		1678	3388 1537	----	1588	1735	----
[5]		1681	3345 1537	----	1577 , 1488	----	----
[6]		1686	3340 1569	651 1438	1595 , 1460	----	----
[7]		----	----	---- 1436	----	1730	1629
[8]		1660	3365 1580	663 1486	----	-----	----

Table 2. Melting points, M.F, & Elemental Analysis of compounds [4-8]

Comp. No.	M.F	M.P C%	Calc /Found. C%	H%	N%
[4]	$C_8H_{12}N_2O_3$	169	52.173 52.058	6.521 6.387	15.217 15.106
[5]	$C_6H_8N_4O$	182	47.368 47.205	5.263 5.094	36.842 36.617
[6]	$C_8H_{11}N_3OS$	218	48.730 48.583	5.583 5.402	21.319 21.182
[7]	$C_7H_{10}O_3S$	197	48.173 48.045	5.747 5.614	-------
[8]	$C_7H_9NOS_2$	236	44.919 44.778	4.812 4.653	7.486 7.317

Fig 1. FT.IR – spectrum of compound [1]

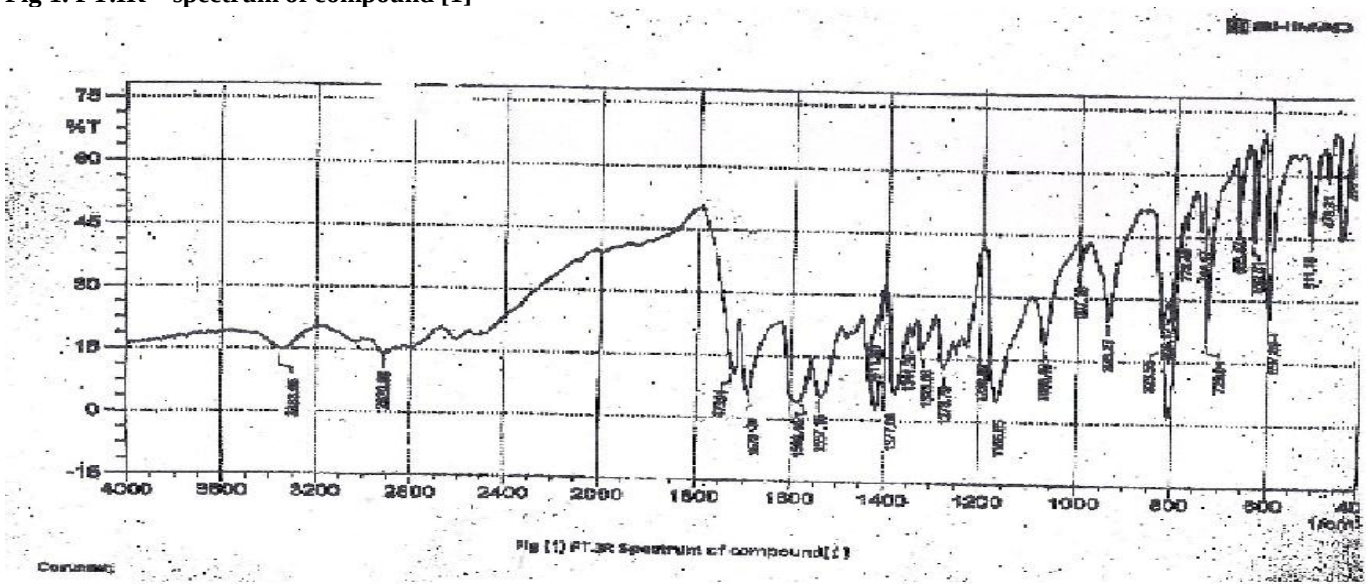


Fig 2..FT.IR – spectrum of compound [2]

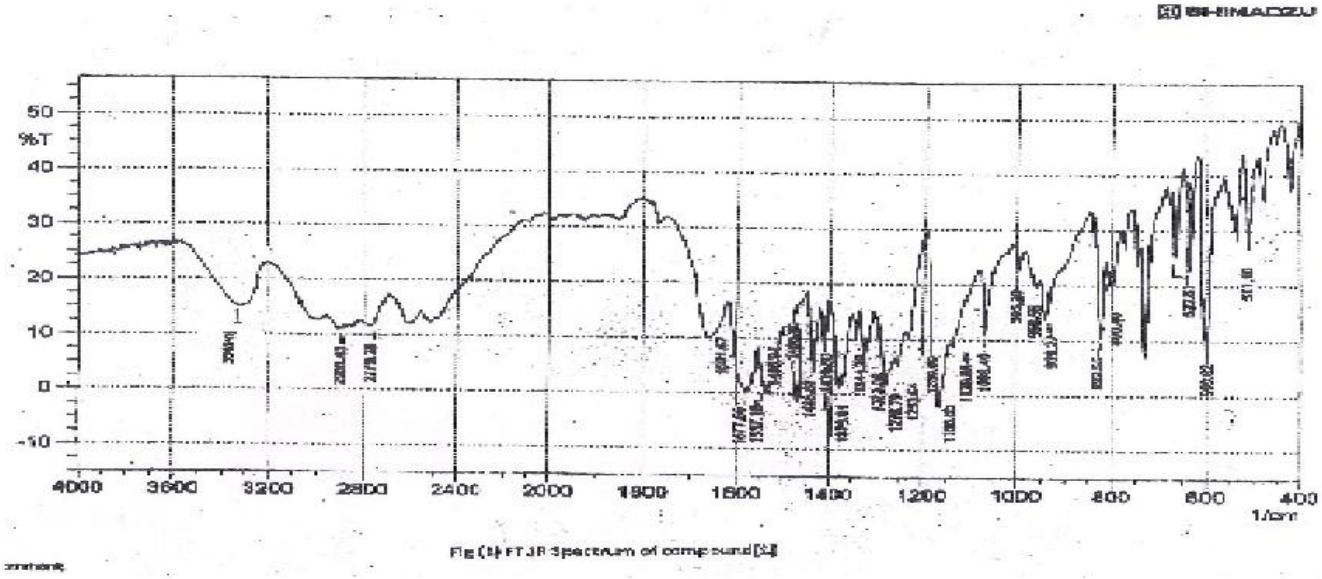


Fig 3 & 4. FT.IR – spectrum of compounds [3 ,4]

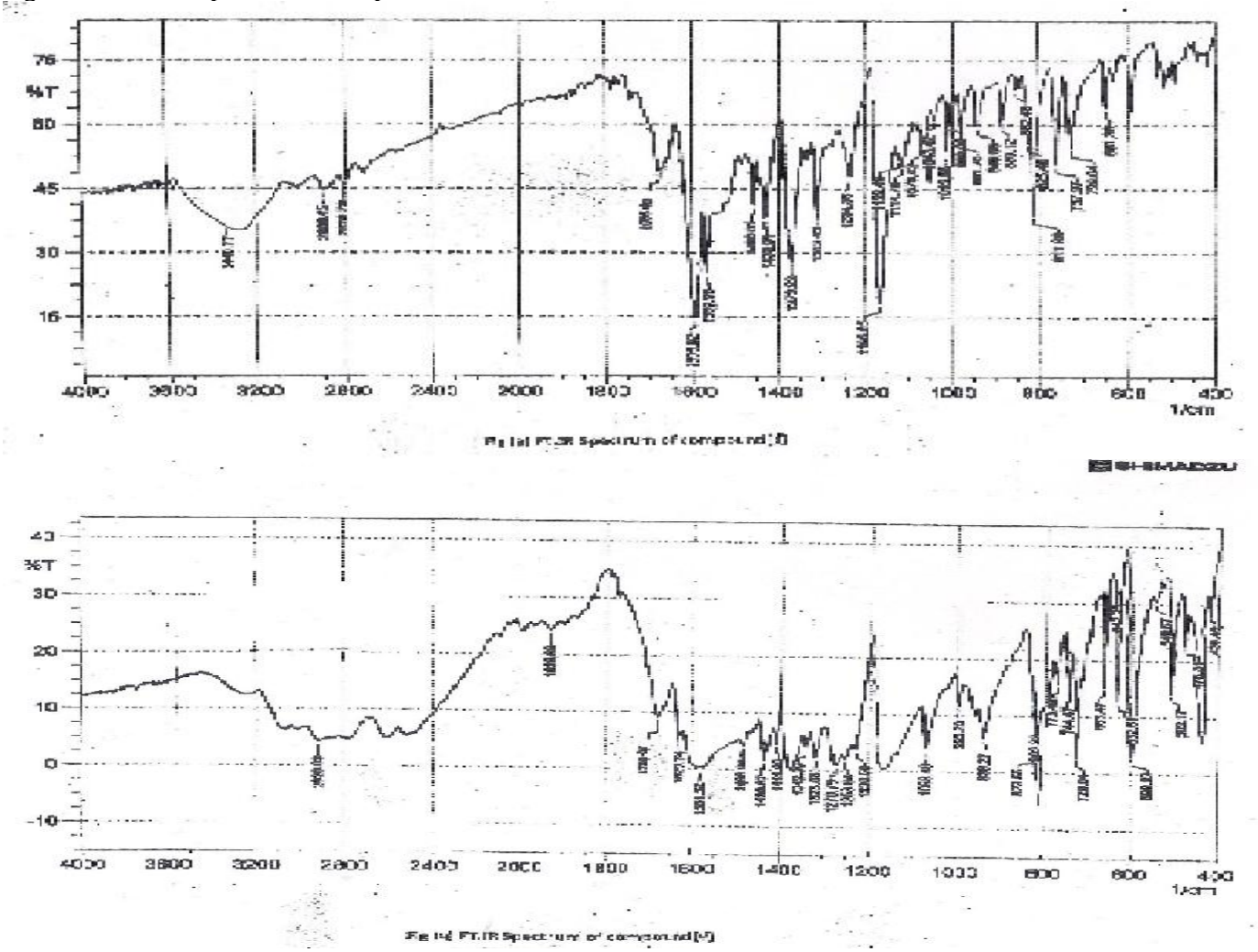
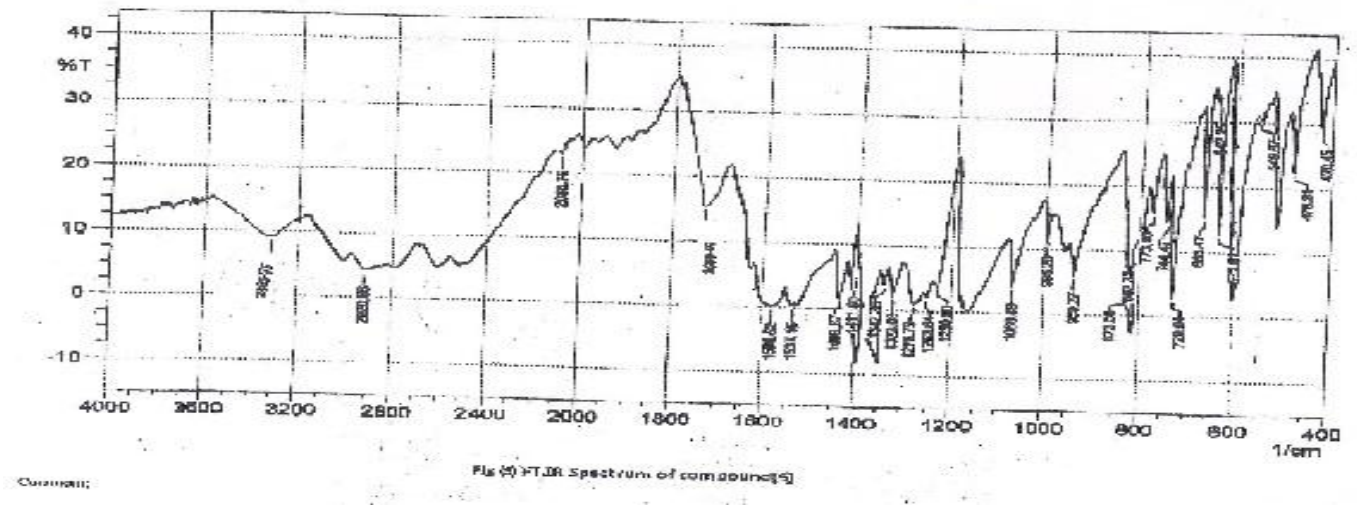


Fig 5. FT.IR – spectrum of compound [5]



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