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Full Length Research Paper

Synthesis of series of macro compounds via alkylation and azotation reactions

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This paper involved synthesis of series from macro compounds through reaction between di carbonyl compounds like (cyclo hexane-1,3-dione., 1,3-diphenyl–propadione, acetyl acetone, maleic anhydride, maleic acid, malonic acid) with di amine compounds or thiophene compound to produce compounds [1-5 ,7, 8,11], which reacted with azo compound, benzaldehyde, via alkylation reaction and azotation reaction to yield compounds [6,9,10,12] .The structure of these compounds were characterized by (H.NMR, FT.IR, C.H.N–analysis) techniques and their melting points.

Key words: Macro compound, azotation, seven–membered, thiophene, diazepine, hydrazo.

INTRODUCTION

Since macro compounds have a variety of potential, biological activities and utilities as technologically useful materials, a number of methods for the preparation have been developed. In this literature, macro compounds are described under different chemical names because of the differences in chemical terminology like (macro compounds, supra compound..).

Since the discovery of the microbial activity of macro compounds, several studies have been carried out in order to synthesize many derivatives of these compounds and their importance were reported as well. The macro compounds which contain thiophene nucleus have been reported to posses pharmacological biological important such as insecticide, acaricide, fungicidal, antibacterial and antihypertensive (Sukhbir et al., 2011; Yadav and Senthilkumar, 2011; Murug et al., 2013; Tomachyn et al., 2012), for this, several different methods have been described for the synthesis of macro compounds including reaction of di carbonyl compounds such as (di ketone compounds, di carboxyl compounds, anhydrides) (Nagham, 2013) with amine compounds to yield derivatives which react with thiophene nucleus to produce macro compounds and hetero cyclic macro compounds; most of the macro compounds included azo groups and amine groups which increased important properties (Tai et al., 2003; Sohrab et al., 2009; Fusco et al., 1979; Reda et al., 2013) .

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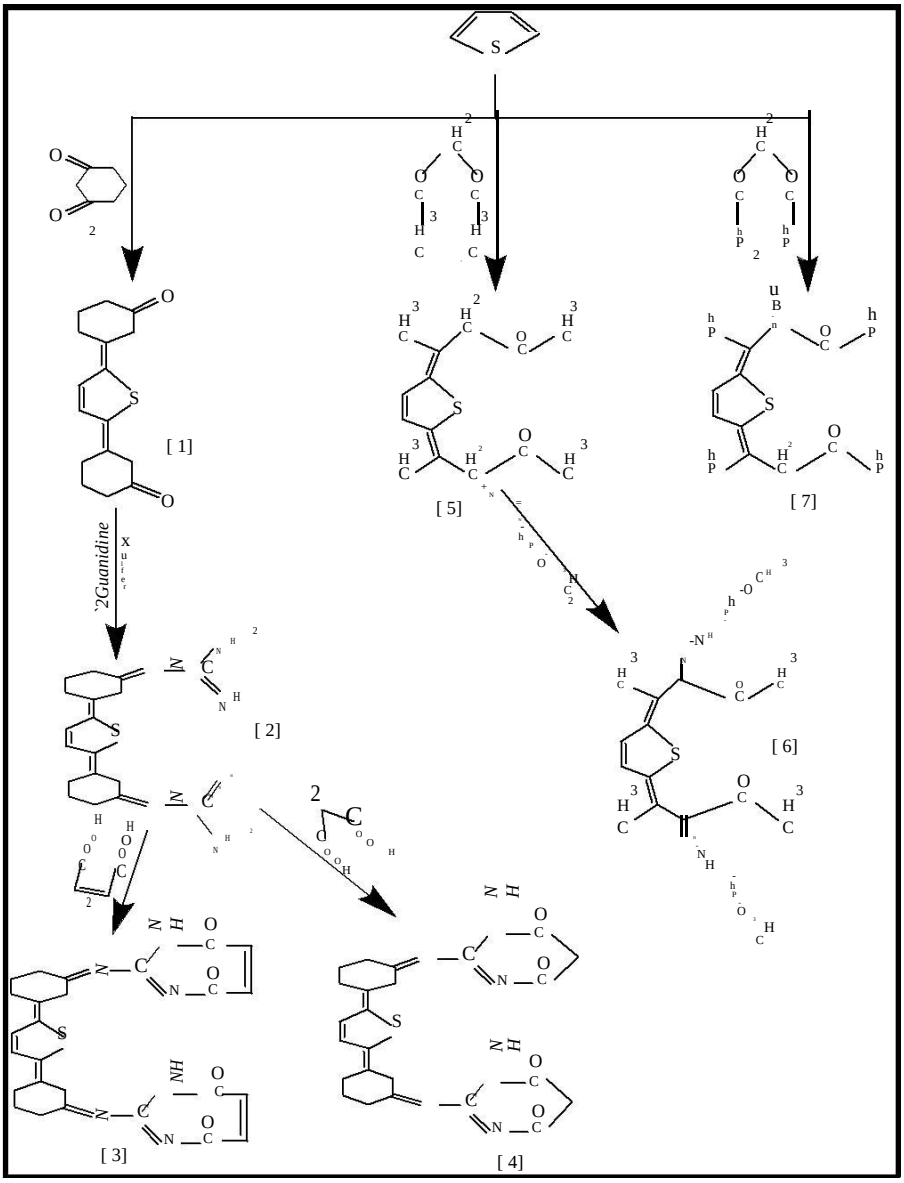
EXPERIMENTAL

Melting points were determined in open capillary tube and were uncorrected. The FT.IR–spectra were recorded in KBr–disc, shimadzu (8300)., (C.H.N)–elemental analysis and H.NMR–spectra in DMSO–solvent in Malaysia.

Synthesis of compounds [1-4]

A mixture of thiophene(0.01 mole) and 1,3-dione

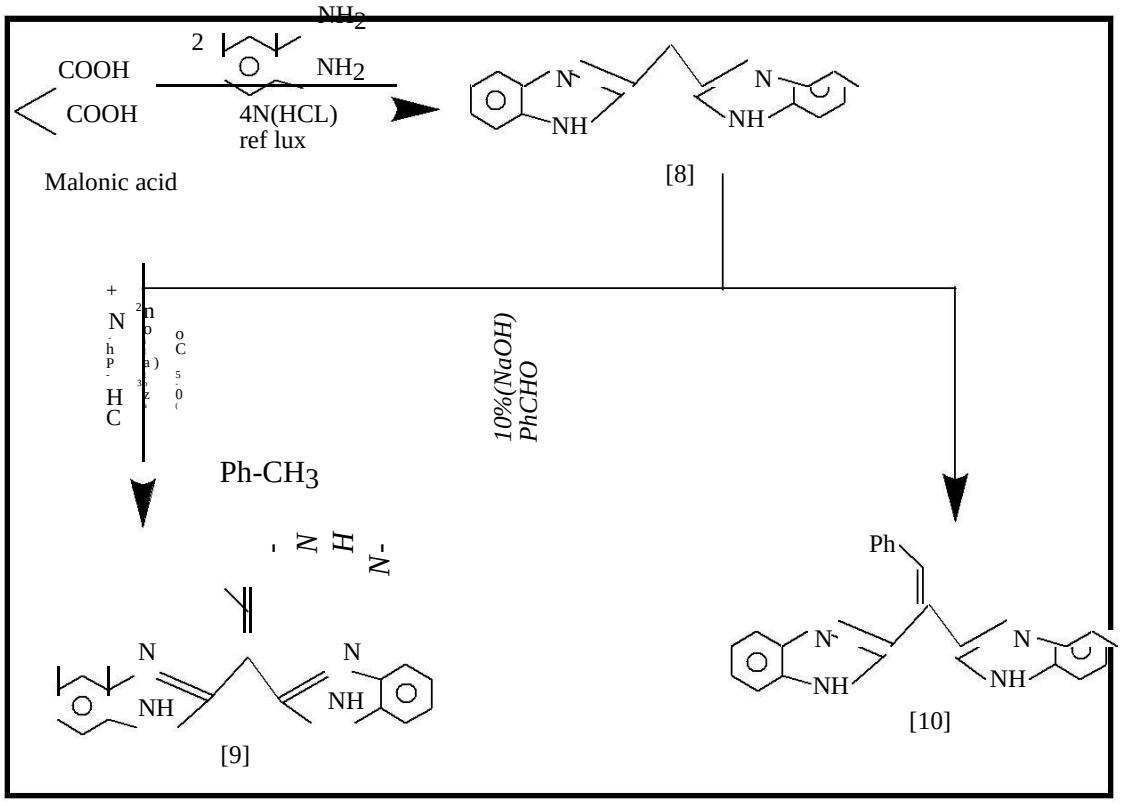


Scheme 1. Synthesis of compounds (1-7)

cyclohexan (0.01 mole) were reacted in the presence of acetic acid to produce 82% of compound [1], which (0.01 mole) reacted with guanidine (0.02 mole) in the presence of absolute ethanol with drops of glacial acetic acid and reflux for 4 h, the precipitate was filtered and dried with re crystallized to yield 84% of compound [2], which (0.01 mole) reacted with (0.02 mole) of maleic acid and malonic acid, respectively in presence of absolute ethanol with refluxing for 4 h, the precipitates filtered, re crystallized from ethanol to produce 86 and 83% of compound [3] and [4], respectively .

Synthesis of compounds [5-7]

(0.01 mole) of thiophene reacted with (0.02 mole) of acetyl acetone and benzoyl acetophenone, respectively in the presence of acetic acid for 2 h, the precipitates filtered, dried to yield 80 and 84% of compounds [5] and [7], respectively. Compounds [5] (0.01 mole) dissolved in ethanol in base medium (10%) of sodium hydroxide, then



Scheme 2. Synthesis of compounds (1-10)

the mixture added to solution of 4-methoxy phenyl azo to produce 89% of compound [6] .

Synthesis of compounds [8-10]

According to the procedure of Nagham (2013), malonic acid (0.01 mole) refluxed with o-phenylene di amine (0.02 mole) in the presence of (4N) of hydrochloric acid for (8 h), the precipitate filtered, dried to produce 81% of compound [8], which reacted in base medium with 4-methyl phenyl hydrazo at 0-5°C and benzaldehyde, respectively to give 88 and 84% of compounds [9] and [10], respectively.

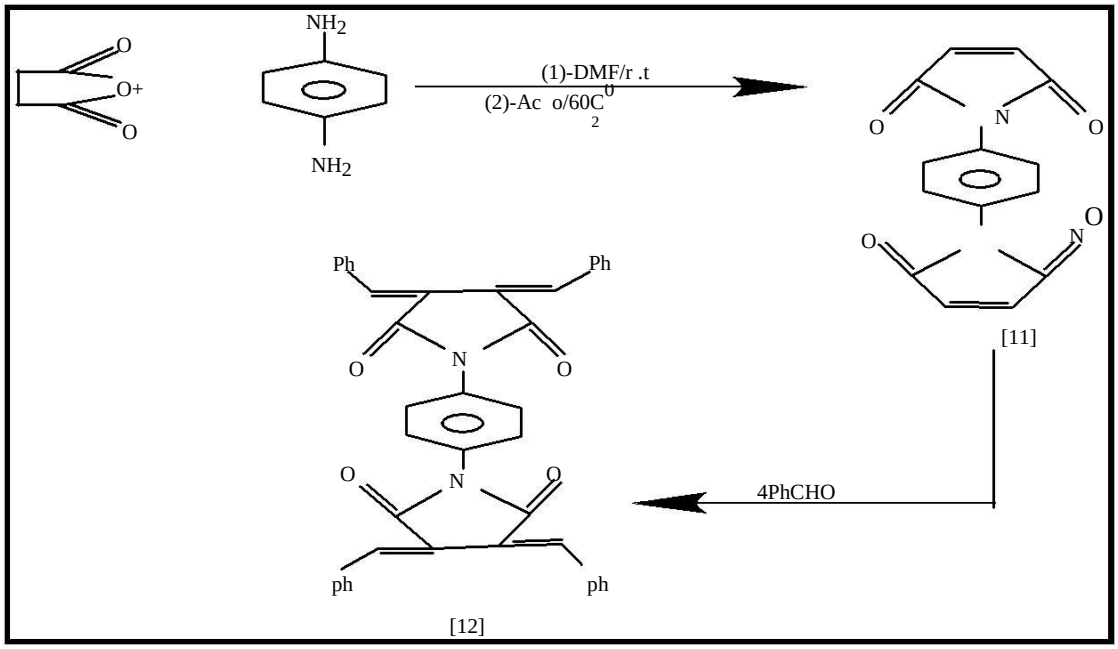
Synthesis of compounds [11,12]

Maleic anhydride (0.02 mole) reacted with 4- amino aniline (0.01 mole) in the presence of di methyl formamide at room temperature, then heated at 60°C, the precipitate filtered and dried to yield 84% of compound [11], which (0.01 mole) reacted with benzaldehyde (0.04 mole) in base medium, the precipitate filtered, dried and recrystallized from ethanol to give 86% of compound [12].

RESULTS AND DISCUSSION

This paper involved the synthesis of different compounds, some of them started from thiophene compound via alkylation of thiophene, then formation of six and seven–membered ring and azotation with coupling reaction to yield macro compounds. All synthesized compounds [1-12] were characterized by FT.IR–spectra, (C.H.N)-analysis, melting points and some of them by H.NMR–spectra .

FT.IR –spectra showed appearance absorption bands at 1720 cm^{-1} due to (-CO-) carbonyl of ketone in compound [1], which disappeared and other bands appeared such as [(1683) and (3479, 3312)cm^{-1} due to [(C=N) (Manish et al., 2010; Sulekh and Avdhesh, 2011; Vishnuv et al., 2013) and (NH_2)], respectively in compound [2] , bands at [(1690-1694), (3320-3345)]cm^{-1} due to [(CO-NH) carbonyl of amide (Nagham, 2014, 2013) and (NH) of amide] in compounds [3] and [4] respectively, bands at (1724-1718)cm^{-1} due to (-CO-CH_3) carbonyl of ketone in compounds [5] and [7], respectively, bands at (3479)cm^{-1}due to (-NH-N-) amine of hydrazo in compound [6], band at (3317-3428)cm^{-1} due to (-NH)



Scheme 3. Synthesis of compounds (1-12)

Table 1. FT.IR- data (cm^{-1}) of compounds [1-12] .

Comp. No.	(-CO-) ketone	(-CO-NH) amide	(C=N)	(-NH-) amine	Name of compounds
[1]	1720	--	--	--	2,5-bis(3-cyclo hexanone)thiophene .
[2]	--	--	1683	3479 3312	2,5-bis(3-guanidinecyclohexyl amine)thiophene.
[3]	--	1694	1623	3320	2,5-bis[3-(1,3-diazepine-4,7-dione)-2-cyclohexylamine]thiophene.
[4]	--	1690	1627	3345	2,5-bis[3-(1,3-diazine-4,6-dione)-2-cyclohexyl amine]thiophene .
[5]	1724	--	--	--	2,5-bis(2-pentyl -4-one)thiophene.
[6]	1728	--	1622	3479	2,5-bis[3-(4-methoxy phenyl hydraazo)-2-pentyl-4-one]thiophene.
[7]	1718	--	--	--	2,5-bis[1,3-(diphenyl)propyl-3-one] thiophene .
[8]	--	--	1624	3358	Methylene-bis(2-benzo imidazole) .
[9]	--	--	1631	3317	Bis(2-benzoimidazole)-(4-methyl phenyl hydrazo) methylene .
[10]	--	--	1660	3428	Bis(2-benzoimidazole)styrene
[11]	--	1698	--	--	1,4-bis(male amide)benzene.
[12]	--	1692	--	--	1,4-bis[3,4-bis(styrene)succin amide]benzene .

(Suresh et al., 2011; Dusan et al., 2011) of imidazole ring in compounds [8-10], bands at [(1631) and (3091)]cm^{-1} respectively due to [(C=N) and (CH=C)]in compounds [9] and [10] respectively, bands at (1692) and (1698)cm^{-1} due to (-CO-NH) carbonyl of amide in compounds [11] and [12] respectively, and bands are summarized in Table 1 and Figures 1 to 5.

The H.NMR-spectra showed peaks at ɓ (5.90-7.5) due to protons of thiophene ring (-CH=CH-) in compounds [2,3,6], respectively, peaks at ɓ (4.8-5.0) due to proton of amine (-NH) in compounds [2,6, 9] respectively, peaks at ɓ (10.05) due to (NH-CO) proton of amide in compound [3], peaks at ɓ (3.6 and 3.70) due to (CO-CH=CH-CO) proton in diazepine cycle in compound [3], peaks at ɓ

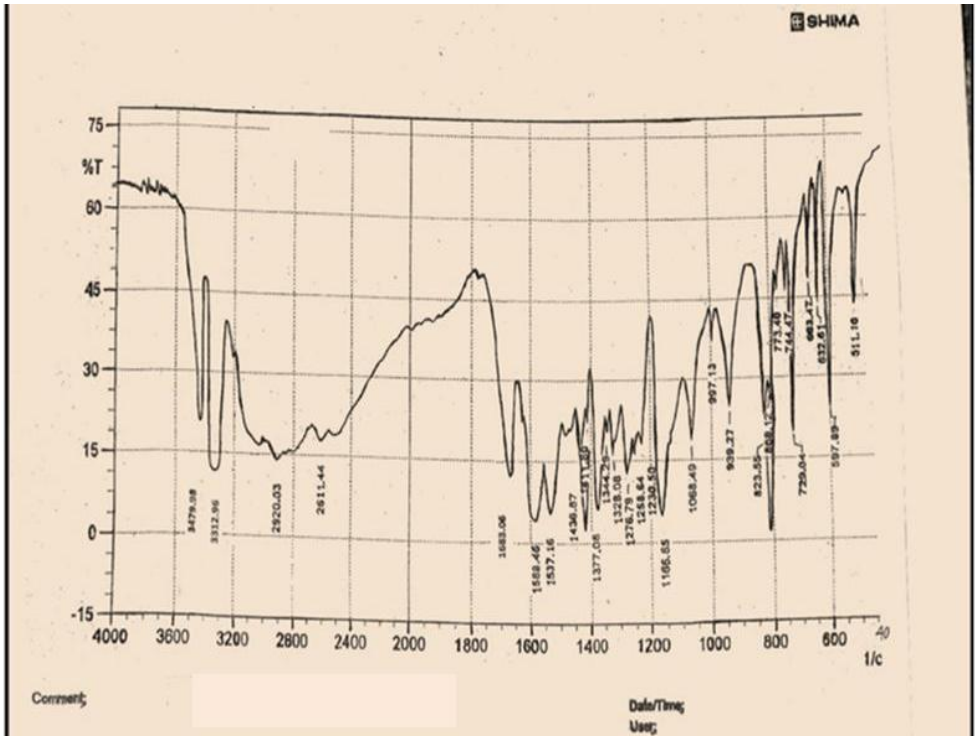


Figure 1. FT.IR spectrum of compound [2].

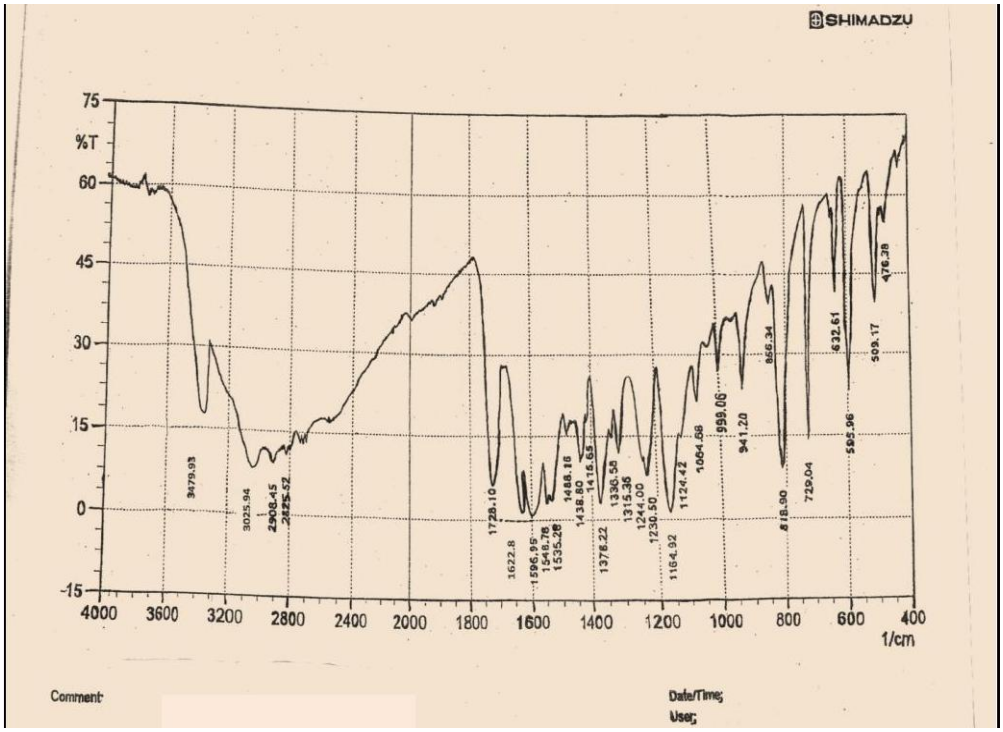


Figure 2. FT.IR spectrum of compound [6].

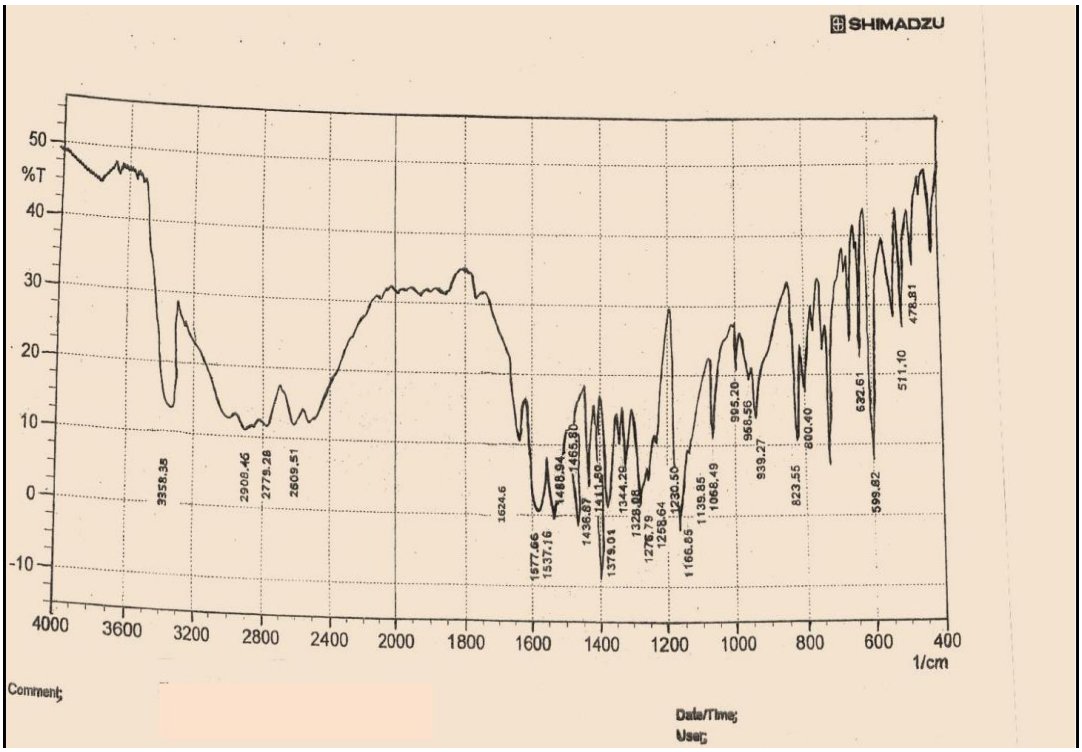


Figure 3. FT.IR spectrum of compound [8].

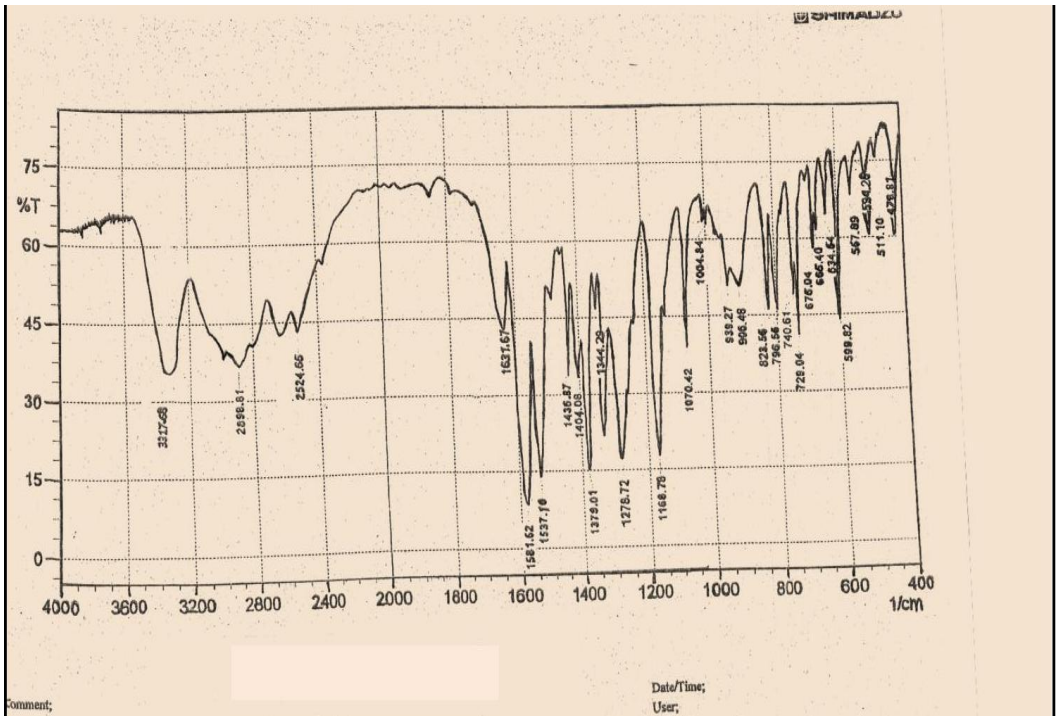


Figure 4. FT.IR spectrum of compound [9].

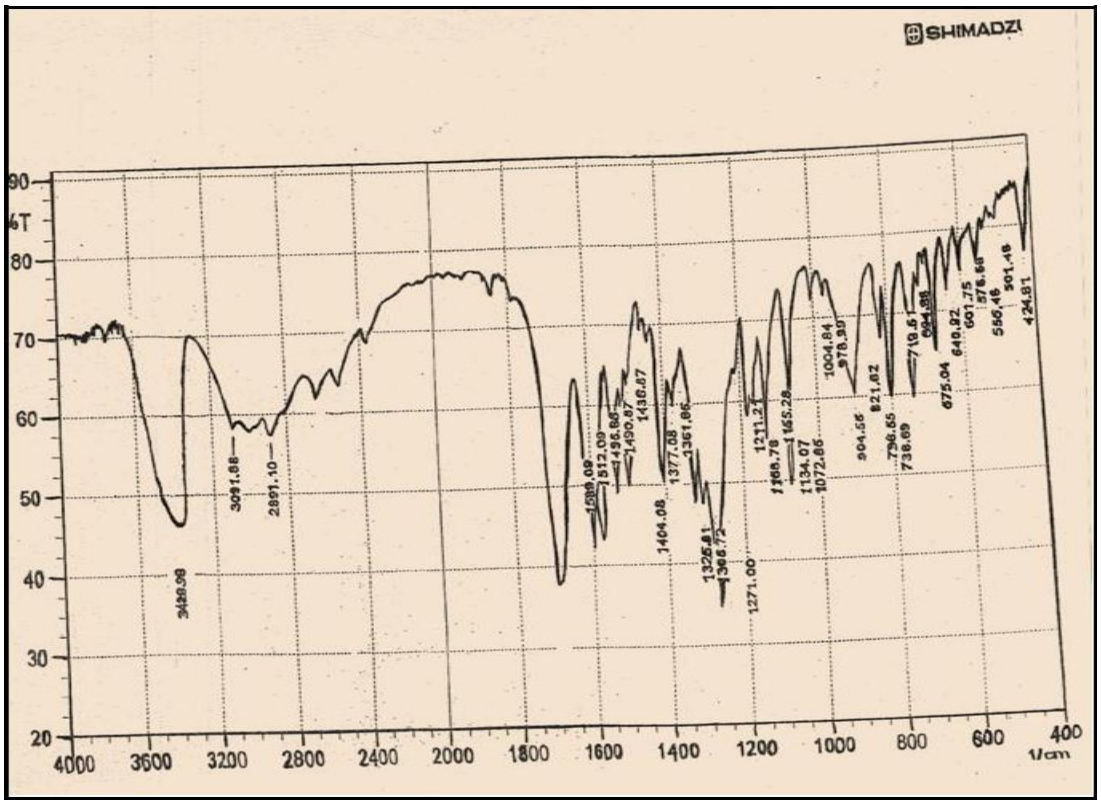


Figure 5. FT.IR spectrum of compound [10].

Table 2. H.NMR (ɓ ppm) of some compounds.

Comp. No.	H.NMR(DMSO).(only important peaks)			
	(CH=CH) of thiophene	(NH) amine	(NH) amide	Other peaks
[2]	7.5, 7.4	4.9, 5.0	-	(1.3, 1.45, 1.60)protons of cyclohexane .
[3]	5.90, 6.0	--	10.5	(1.4, 1.65)protons of cyclohexane ., (3.6,3.70)protons of diazepine cycle(CO-CH=CH-CO).
[6]	6.0, 6.05	5.0	--	(3.80)protons of ketone(-CO-CH_3)., (4.0)protons of (OCH_3).,(1.25)protons of (-CH_3).
[9]	--	4.8	--	(1.10)protons of(CH_3).,(5.95)proton of (NH) imidazole .,(7.20-7.50)protons of phenyl rings .
[11]	--	--	--	(4.70,4.85)protons of (-CH=CH-) cycle., (7.30-7.50)protons of phenyl ring .
[12]	--	--	--	(5.0)proton of (-CH=C-) of styrene .

(4.7-5.0) due to [(-CH=CH-) and (-CH=C-)] in compounds [11] and [12], respectively. Other peaks of functional groups which demonstrate inflowing are shown in Table 2 and Figures 6 to 11. Other data of (C.H.N)–analysis and

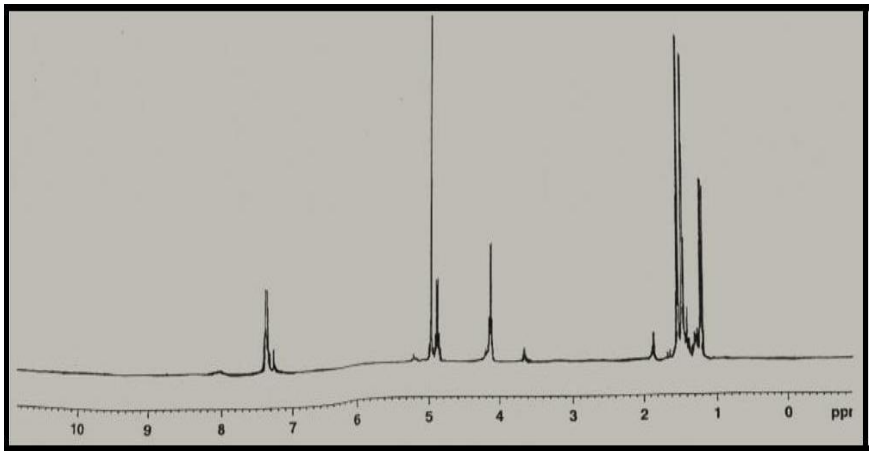


Figure 6. HNMR- spectrum of compound [2].

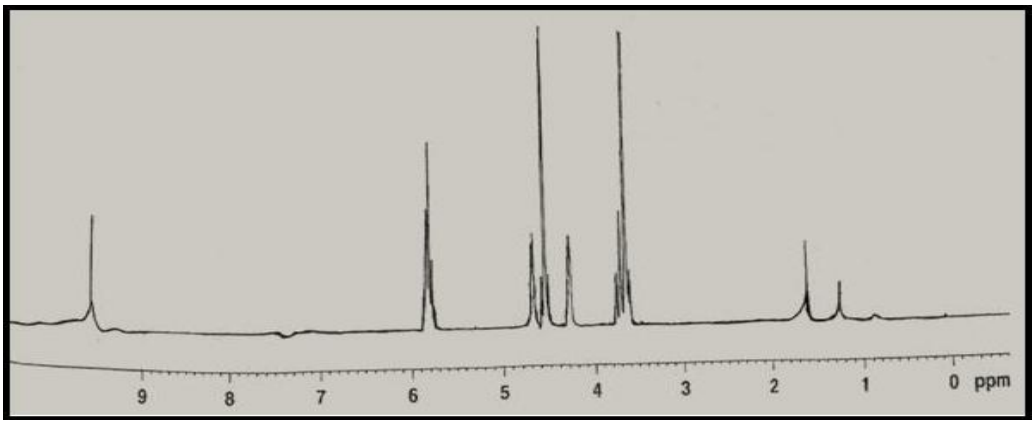


Figure 7. HNMR- spectrum of compound [3].

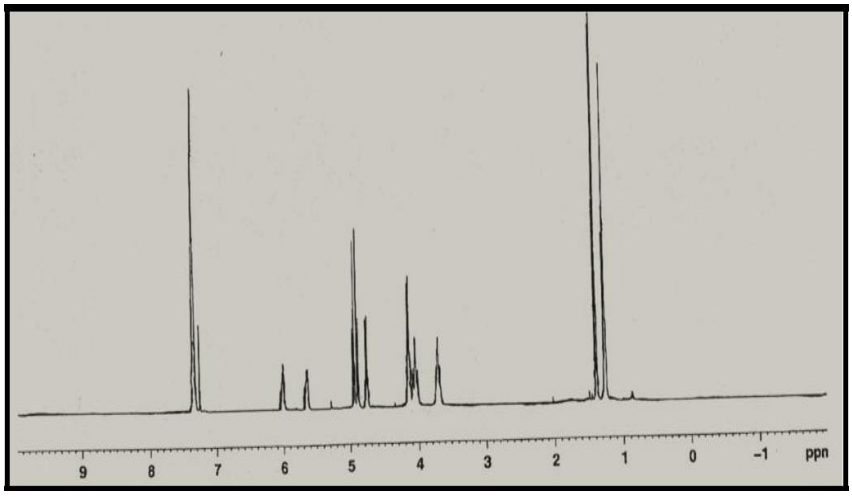


Figure 8. HNMR- spectrum of compound [6].

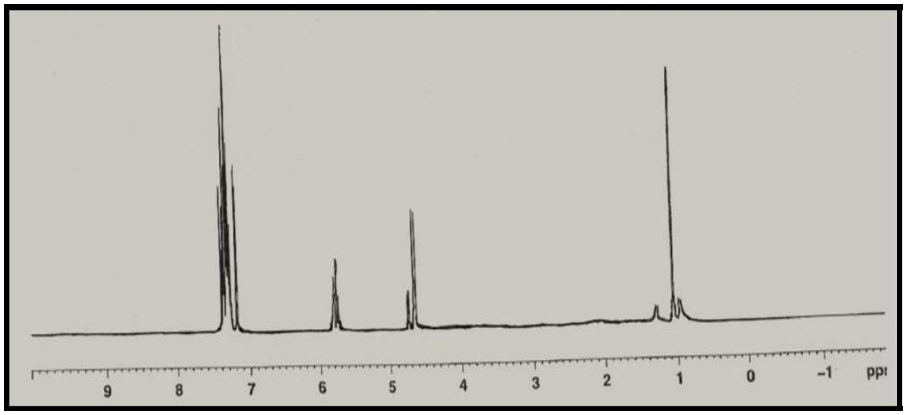


Figure 9. HNMR- spectrum of compound [9].

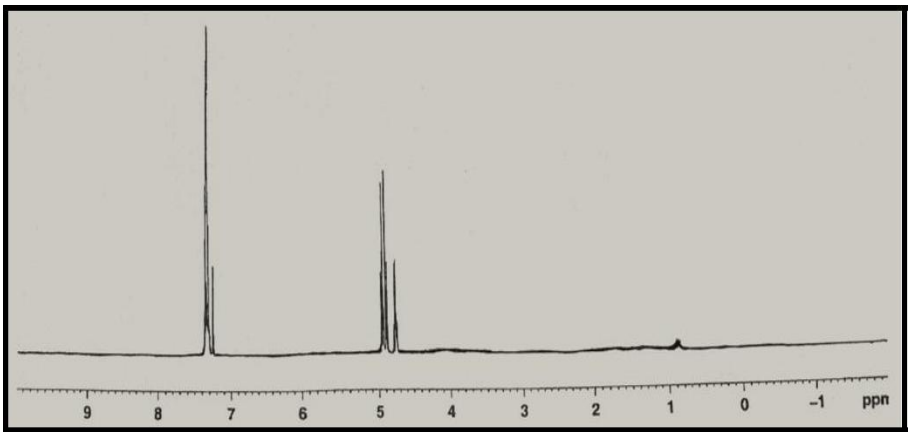


Figure 10. HNMR- spectrum of compound [11].

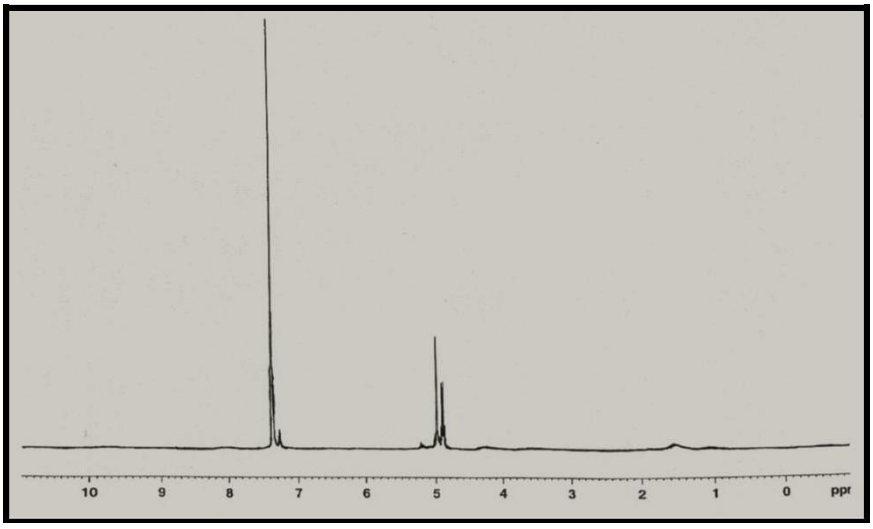


Figure 11. HNMR- spectrum of compound [12].

Table 3. physical properties and (C.H.N).analysis of compounds [1-12].

Comp. No.	M.F	M.P (+2)C^0	Calc./Found		
			C%	H%	N%
[1]	$C_{16}H_{18}O_2S$	196	70.07 69.83	6.56 6.31	-- --
[2]	$C_{18}H_{24}N_6S$	208	60.67 60.43	6.74 6.50	23.59 23.30
[3]	$C_{26}H_{26}N_6O_4S$	235	60.23 60.06	5.01 4.80	16.21 16.05
[4]	$C_{25}H_{26}N_6O_4S$	222	59.28 59.11	5.13 5.02	16.60 16.38
[5]	$C_{14}H_{18}O_2S$	194	67.20 67.03	7.20 6.07	-- --
[6]	$C_{28}H_{30}N_4O_4S$	215	64.86 64.61	5.79 5.48	10.81 10.63
[7]	$C_{34}H_{26}O_2S$	204	81.92 81.74	5.22 5.08	-- --
[8]	$C_{15}H_{12}N_4$	198	72.58 72.36	4.83 4.58	22.58 22.32
[9]	$C_{22}H_{18}N_6$	220	72.13 72.05	4.91 4.75	22.95 22.71
[10]	$C_{22}H_{16}N_4$	216	78.57 78.36	4.76 4.58	16.66 16.51
[11]	$C_{14}H_8N_2O_4$	188	62.68 62.43	2.98 2.83	10.44 10.31
[12]	$C_{42}H_{28}N_2O_4$	245	80.76 80.58	4.48 4.32	4.48 4.36

physical properties are shown in Table 3.

Conclusion

The results of all measurements gave good evidence for synthesized compounds [1-12].

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