

Full Length Research Paper

Synthesis and Identification of Bis-(az-Compounds) via Alkylation of Dimethyl Malonate

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Abstract

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In this paper, dimethyl malonate has been used to the reaction with P-formal benzaldehyde forming the corresponding bis(Dimethyl malonate) which cyclize with di amine compounds to produce bis ((5,6,7) –membered of di aze cycles) and some of them reacts with different amino compounds to produce corresponding bis substituted. The structures of the synthesized compounds (1-10) have been confirmed by (FT.IR –spectra , H.NMR –spectra , C.H.N – analysis) and melting points .

Keyword: Synthesis, Alkylation, Malonate, di az, di cycle.

INTRODUCTION

Di alkyl malonate is an important class of compounds. It's several field of organic chemistry such as alkylation of carbonyl (Magherita et al., 2012; Nagham, 2012) compounds, incorporation with heterocyclic compounds to produce pharmaceutical compounds which have a wide range of pharmacological properties (Singh et al., 2011; Maher et al., 2012; Ashraf et al., 2011) in pharmaceutical chemistry field. Because of the number and the significance of these applications, many methods (Gowramma et al., 2009; Arshiya et al., 2011) have been reported for the preparation of these compounds in the last years (diazolidine, diazine, tir pam) (Wagnat et al., 2012; Nagham, 2010; Gernot and Wolfgang, 2008; Girija et al., 2013).

Di nitrogen (di az)-containing heterocyclic compounds (Kamal et al., 2006; Roshan et al., 1996) have received considerable attention due to their biological activity which represented as anti tumor, anti viral, anti fungal, anti cancer, analgesic, Anti –HIV, anti microbial ...etc .

In recent years, chemistry of di az compounds developed very fast due to the discovery of the diverse biologically active (diazolidine , diazine , tir pam) derivatives (Vijay et al., 2012).

Experimental

All chemical used from BDH and sigma-company, FT.IR -

spectra were recorded on shimadzu 8300, Kbr-disk., H.NMR -spectra and (C.H.N) -analysis were recorded in Maliesia, the melting points were determined by digital - electrothermal 9300 LTD, UK.

Synthesis of compounds (Magherita et al., 2012; Nagham, 2012)

A mixture of P -formal benzaldehyde (0.1 mole) reacted with di methyl malonate (0.2 mole) in basic medium of sodium hydroxide (10%) with mechanical stirr at room temperature for (4hrs) , the precipitate was filtered and recrystallized to yield 88% of compounds (Magherita et al., 2012), which (0.1 mole) reacts according to procedures(2,9) with (0.1 mole) of methylene di amine under reflux for (3hrs) in presence of absolute ethanol , the precipitate was filtered and recrystallized to give 89% of compounds (Nagham, 2012).

Synthesis of compounds (Singh et al., 2011; Maher et al., 2012; Ashraf et al., 2011; Gowramma et al., 2009)

The synthesis of these compounds was carried out according to literature (Nagham, 2012; Nagham, 2010), a mixture of compound (Nagham, 2012) (0.01 mole) with one of (0.01 mole) from (hydrazine, methylene di amine,

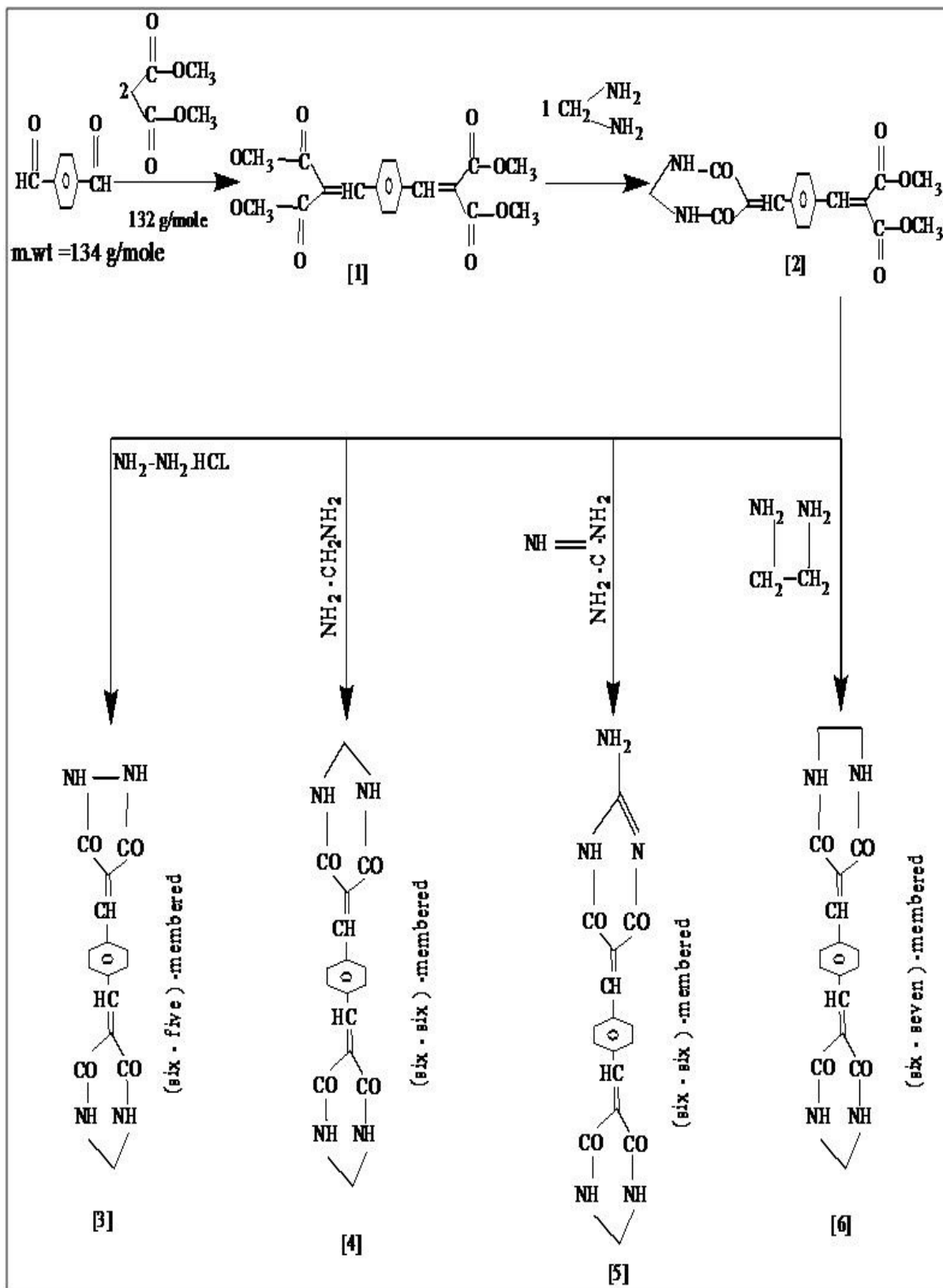


Figure 1. Scheme of preparation

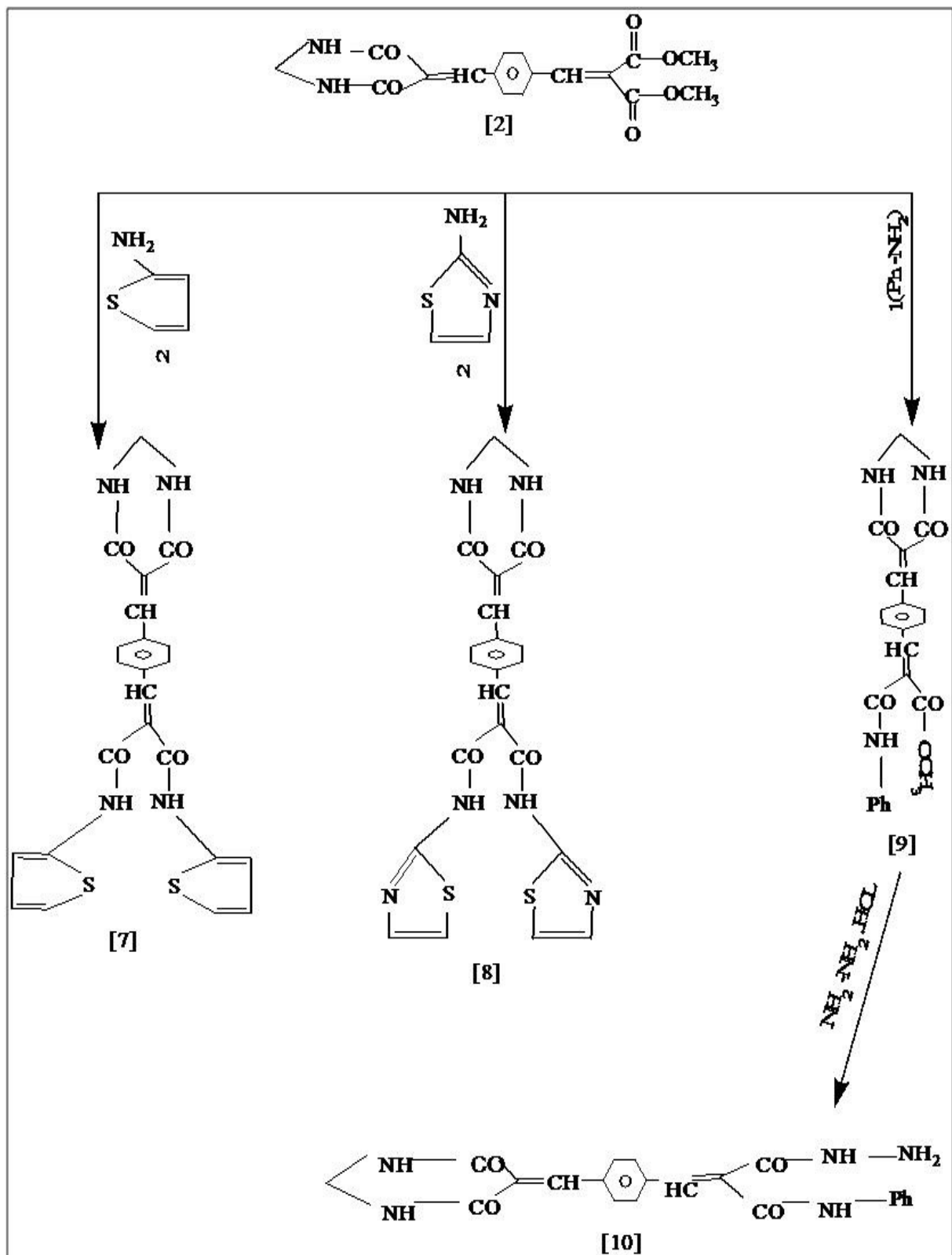


Figure 2. Scheme of synthesis of compounds

Table 1. (FT.IR) -data (cm⁻¹) of compounds (1-10)

Comp. No.	(Only important frequency)			Other groups
	(CO) carbonyl of amide	(NH) of amide	(CH=C)	
[1]	----	----	3048	(CO-O-)carbonyl of ester :1728
[2]	1660	3482	3046	(CO-O)carbonyl of ester: 1714
[3]	1695	3299	3091	-----
[4]	1696	3290	3070	-----
[5]	1688	3312	3080	(C=N) :endocycle : 1537 , (NH ₂) :3478 .
[6]	1691	3492	3091	-----
[7]	1696	3317	3091	(C-S) in thiophene ring :676 ,1271
[8]	1686	3278	3081	(C-S) in thiophene ring :675 , 1211 , (C-N) in thiophene ring :1168
[9]	1682	3478	3026	(CO-O-) carbonyl of ester :1728
[10]	1688	3278	3095	(NH ₂) : 3300 .

Table 2. H.NMR (δ ppm) of some Compounds.

Comp. No.	H.NMR _(DMSO) ((Only important peaks))			
	(NH) of amide	(CH=C)	methylene of (NH-CH ₂ -NH)	Other peaks
[2]	10.04	6.60	3.62	4.30(COOCH ₃)methyl of ester .
[3]	10.10 , 10.28	6.40 , 6.66	3.50	----
[8]	10.08 , 10.22	6.45	3.55	7.35 (proton of thiazol ring)
[9]	10.24 , 10.03	6.50	3.35	3.85 (COOCH ₃)methyl of ester

Table 3. Physical properties & (C.H.N) -analysis of Compounds (1-10).

Comp. No.	M.F	M.p (+2)C°	Name of compounds	Calc. /Found.		
				%C	%H	%N
[1]	C ₁₈ H ₁₈ O ₈	162	1-{{(1',4'-phenyl)-tetra methyl -bis (2 -ene - propanoate)}} .	59.668 59.421	4.972 4.763	--- ---
[2]	C ₁₇ H ₁₆ O ₆ N ₂	189	1-{2-(diazane-4,6-dione)styrene}-3-dimethyl-2-ene-propanoate	59.302 59.188	4.651 4.44	8.139 8.09
[3]	C ₁₅ H ₁₂ O ₄ N ₄	194	2-(diazane-4,6-dione)-2-(diazolidine-3,5-dione)-4- ethene-1-styrene .	57.692 57.38	3.846 3.67	17.948 17.71
[4]	C ₁₆ H ₁₄ O ₄ N ₄	198	2,2-bis(diazane-4,6-dione)-4-ethene -styrene .	58.895 58.625	4.294 4.13	17.177 17.05
[5]	C ₁₆ H ₁₃ O ₄ N ₅	220	2-(diazine-4,6-dione-2-amino)-2-(diazane-4,6-dione)-4- ethene styrene .	56.637 56.37	3.384 3.601	20.64 20.41
[6]	C ₁₇ H ₁₆ O ₄ N ₄	208	2-(diazepane-5,7-dione)-2-(diazane-4,6-dione)-4-ethene-styrene .	60.00 59.93	4.705 4.44	16.470 16.25
[7]	C ₂₃ H ₁₈ O ₄ N ₄ S ₂	241	(1,4-phenyl)-2-(diazane -4,6-dione)-ethene-2-bis (thiophene amide) ethene .	57.740 57.51	3.765 3.56	11.715 11.54
[8]	C ₂₁ H ₁₆ O ₄ N ₆ S ₂	284	(1,4-phenyl)-2-(diazane -4,6-dione)-ethene-bis (thiazole amide) ethene .	52.5 52.31	3.33 3.20	17.50 17.27

Table 3. Continue

[9]	$C_{22}H_{19}O_5N_3$	273	(1,4-phenyl)-2-(diazane-4,6-dione)-ethene-2-(phenyl amide)-3-methyl-1-ene-propanoate .	65.18 65.04	4.69 4.43	10.37 10.27
[10]	$C_{21}H_{19}O_4N_5$	259	(1,4-phenyl)-2-(diazane-4,6-dione)-ethene-2-(phenyl amide)-3-hydrazo-3-one-1-propane .	62.22 62.10	4.69 4.29	17.28 17.15

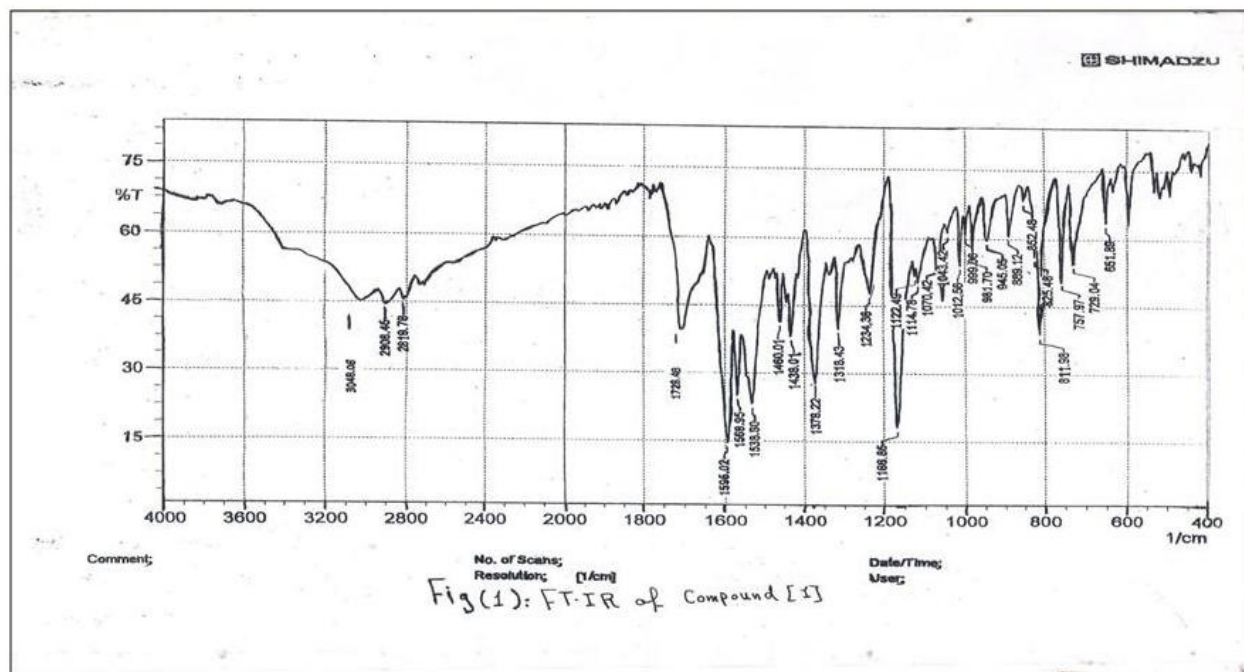


Figure 3. FT-IR of compound [1]

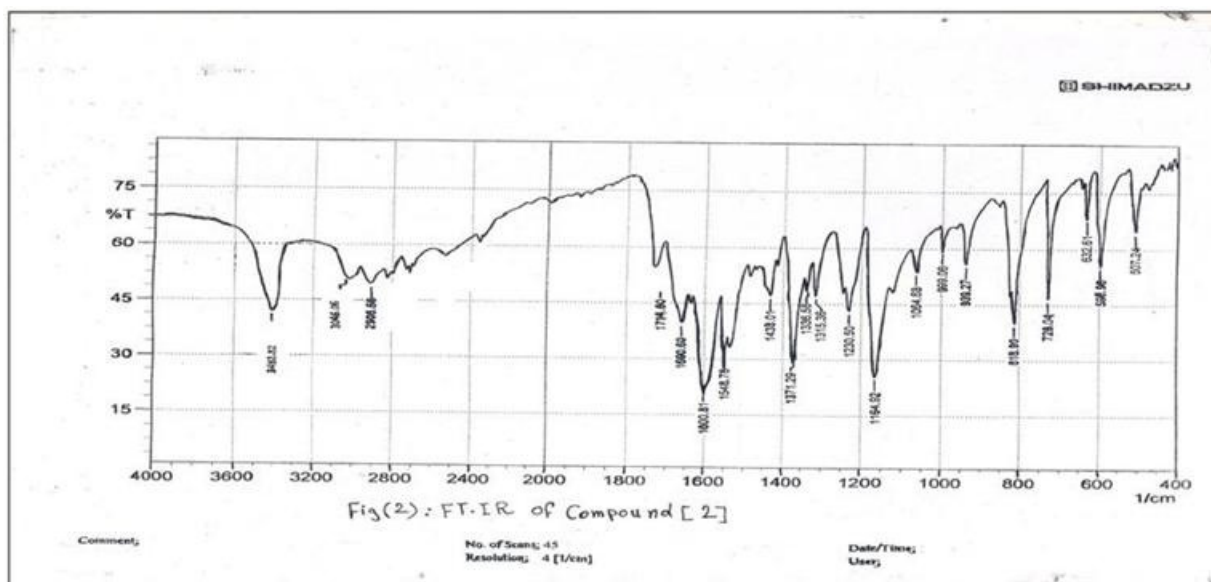


Figure 4. FT-IR of compound [2]

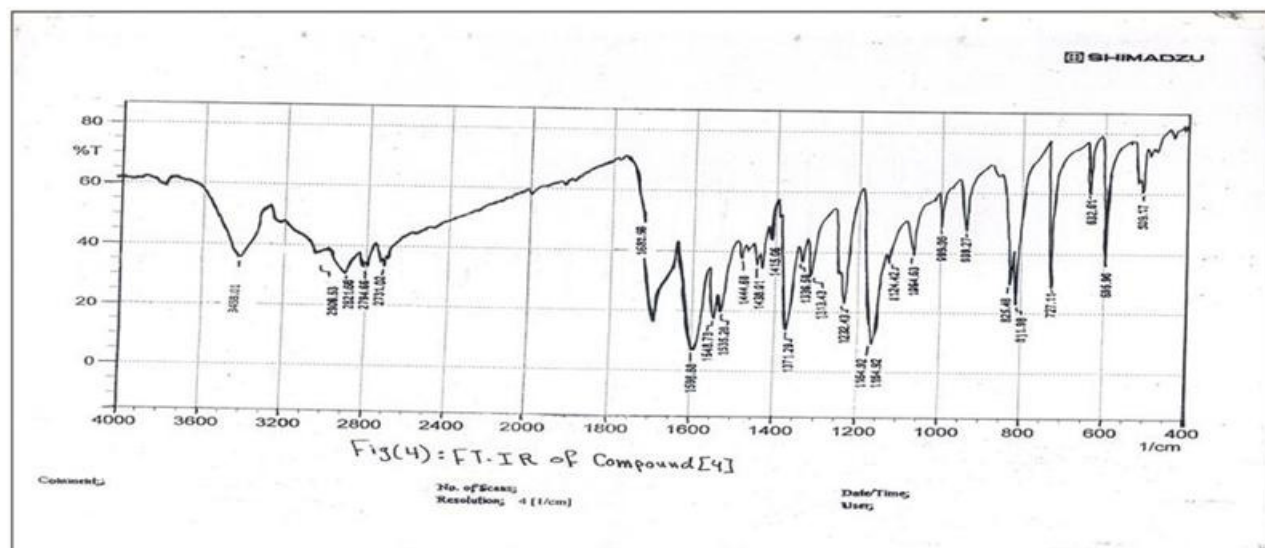
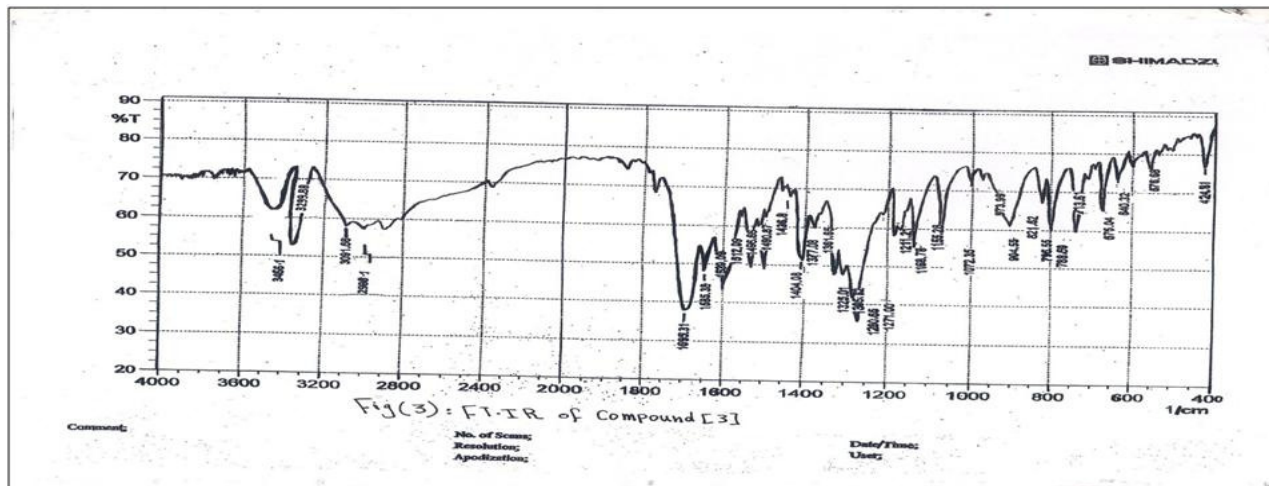


Figure 5, 6. FT-IR of compound [3, 4]

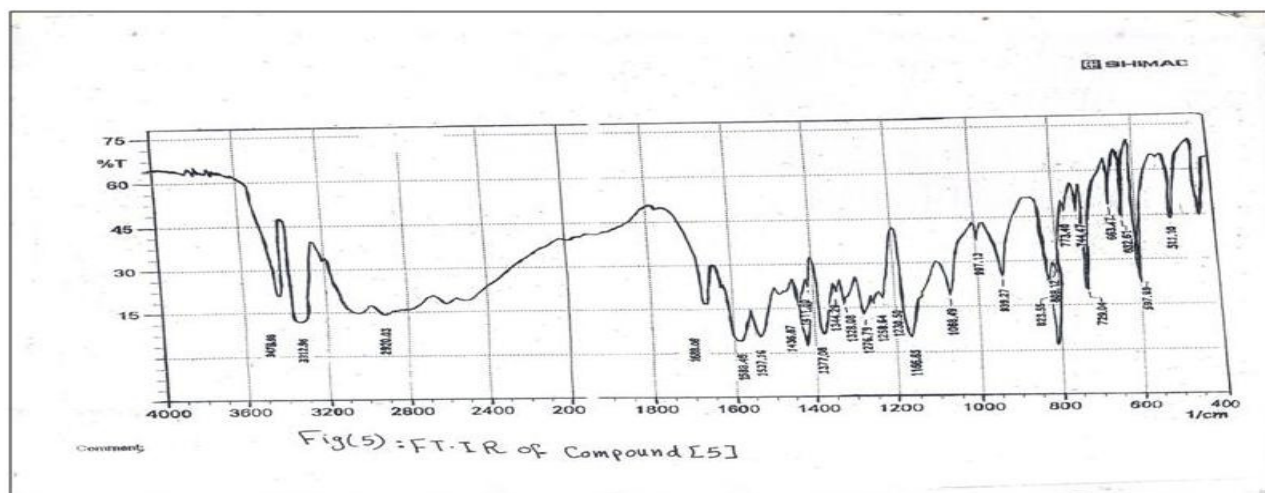


Figure 7. FT-IR of compound [5]

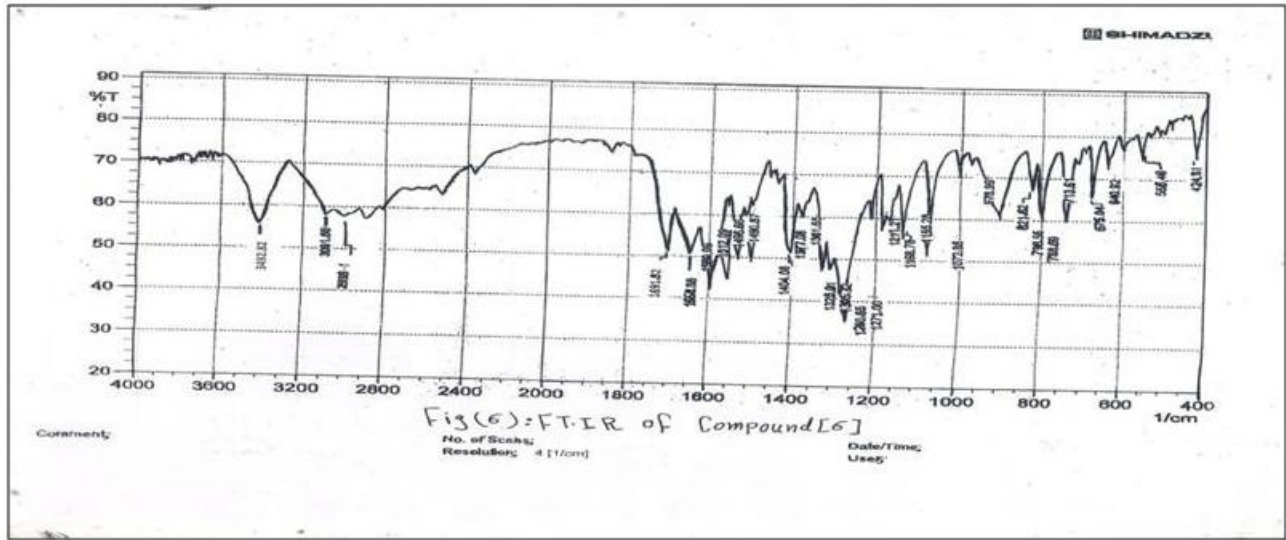


Figure 8. FT-IR of compound [6]

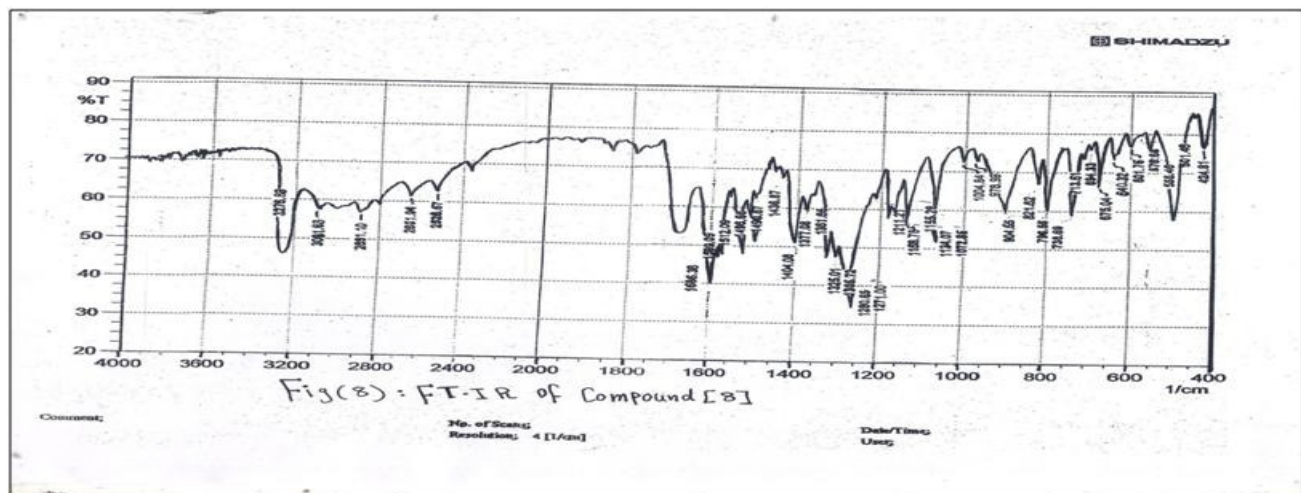
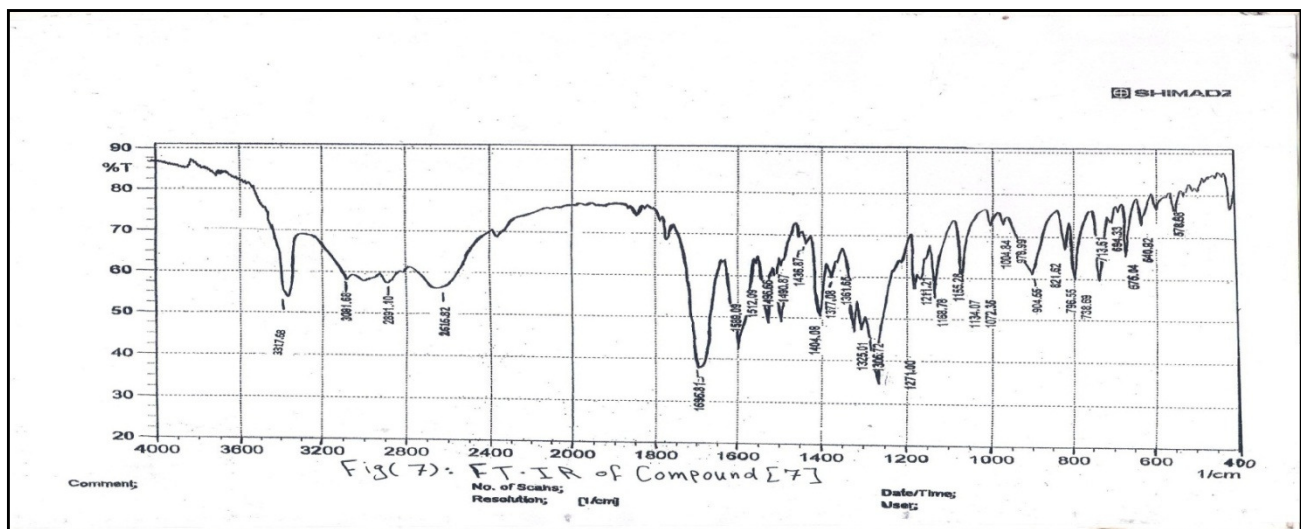


Figure 9, 10. FT-IR of compound [7, 8]

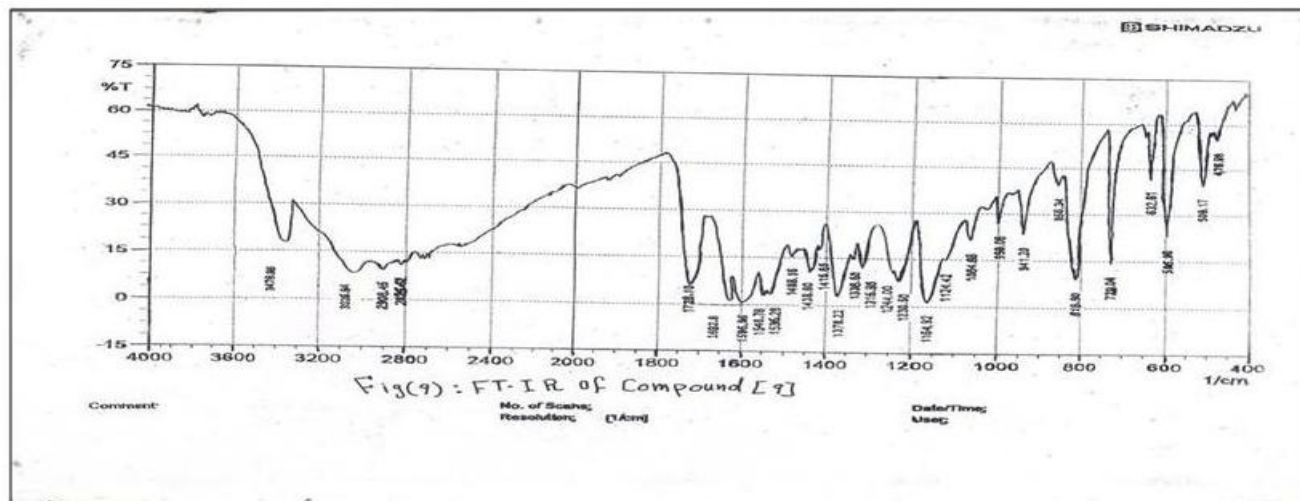


Figure 11. FT.IR of compound 9

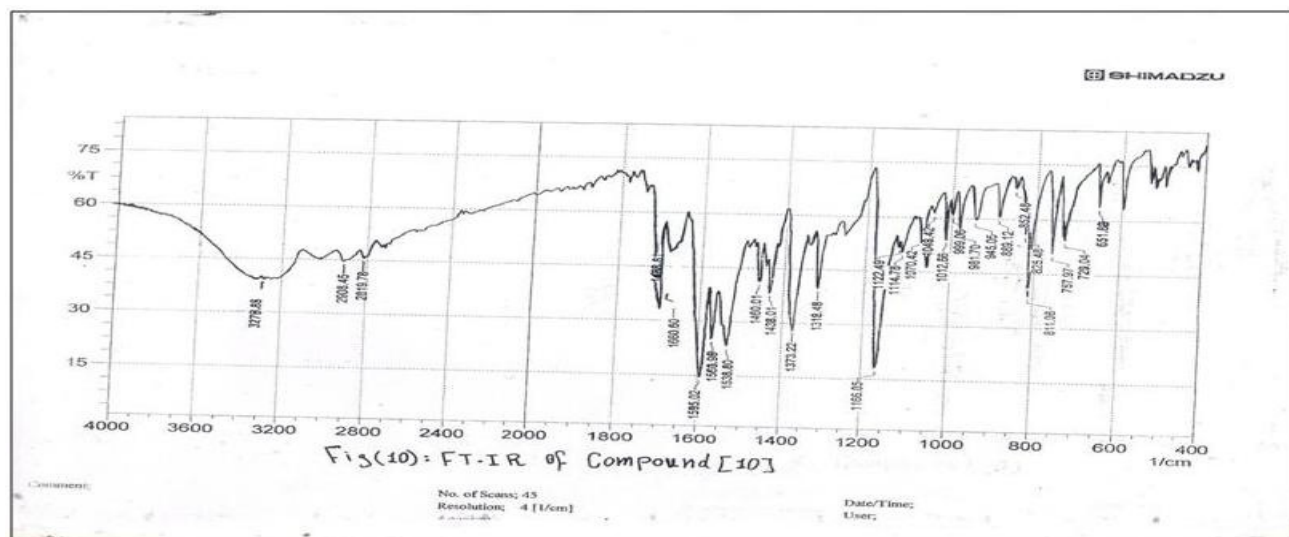


Figure 12. FT.IR of compound [10]

quandine, ethylene di amine) respectively were heated under reflux for (5hrs) in presence of absolute ethanol, the precipitate was filtered and recrystallized to yield (87, 85, 87, 89) % of compounds (Singh et al., 2011; Maher et al., 2012; Ashraf et al., 2011; Gowramma et al., 2009) respectively.

Synthesis of compounds (Arshiya et al., 2011; Wagnat et al., 2012; Nagham, 2010)

According to procedure(9) , a mixture of compounds [2] (0.01 mole) with one of ((0.02 mole) from (2 -amino thiophene, 2 -aminothiazole) (0.01 of aniline)) respectively were refluxed for (5-6 hrs) in presence of absolute ethanol, the precipitate filtered recrystallized to

yield (85, 87, 88) % of compounds (Arshiya et al., 2011; Wagnat et al., 2012; Nagham, 2010) respectively.

Synthesis of compound (Gernot and Wolfgang, 2008)

A mixture of equimolar (0.01 mole) of compound (Nagham, 2010) with hydrazine were reacted under reflux for (4hrs) and stirred, precipitate was filtered and dried, recrystallized to yield 86 % of compound (Gernot and Wolfgang, 2008).

RESULTS AND DISCUSSION

The formation of compound [1] as starting compound

proceed via reaction between dimethyl malonate with di aldehyde compound such as P -formal benzaldehyde, then compound (Magherita et al., 2012) reacts with diamine compounds such as (methylene diamine, hydrazine, guanidine, ethylene diamine to yield cyclic compounds (Nagham, 2012; Singh et al., 2011; Maher et al., 2012; Ashraf et al., 2011; Gowramma et al., 2009) and compound (Nagham, 2012) reacts with primary amine compounds in one side or two side from compound (Nagham, 2012) to yield compounds (Arshiya et al., 2011; Wagnat et al., 2012; Nagham, 2010; Gernot and Wolfgang, 2008).

All these compounds characterized by I.R -spectra, (C.H.N) -analysis, melting points and some of them by H.NMR-spectra.

The I.R -spectra, showed an absorption band at (3026-3095) cm^{-1} due to (CH=C) of alkene in all compounds [1-10] for formation of double bond of alkene, absorption band at (1728) cm^{-1} due to carbonyl of ester group (2) (CO-O-) in compounds [1,2] which disappeared one of them and appeared other bands such as ((1660 - 1696) , (3278 - 3478)) due to ((carbonyl of amide CO-NH), (amine of amide NH -CO)) (2) respectively in compounds [3-10], and other bands are summarized in table (1) and figures (1-10) .

The H.NMR -spectra showed important peaks at δ (6.40-6.60) due to proton of (CH=C) alkene in all compounds , peaks at δ (10.03-10.28) due to (NH-CO) proton of amide(2) in compounds [2,3,8,9] , peaks at δ (3.85, 4.30) due to protons of methyl group in ester

(-COOCH₃) in compounds [2,9] respectively, peaks at δ (3.35-3.62) due to protons of methylene (15) in cycle (NH-CH₂-NH) in compounds [2,3,8,9] and other signals of functional groups show in the following, table (2).

The (C.H.N)-analysis and melting points, the experimental data were good results with calculated data, all these data and physical properties in table (3).

REFERENCES

- Arshiya F, Sayaji R, Venkateshwarlu G (2011). *Int . J. Chem Tech . Res* .,3,4,1769-1780 .
- Ashraf M, Abelgalil A, Musaed A, Husam R, Mosa O, Mohammed A (2011). *American . J . Biochem. and Biotech .*, 7,2,43-54., Cited by Ivsl of Iraq .
- Gernot A, Wolfgang H (2008). *Molbank . J.*, M569 , 1-4 .
- Girija S, Tarjeet S, Ram L (2013). *Arkivoc* , ii , 213-219 .
- Gowramma B, Jubie S, Kalirajan R, Gomathy S, Elango K (2009). *Int .J. Pharmtech . Res .*,1,2,347-352 .
- Kamal M, Ahmed M, Hatem A (2006). *J . Chinese .Chem . Soci .* , 53 , 873 - 880 .
- Magherita B, Silvano C, Stefano D (2012). *Arkivoc* , ix , 262-279 .
- Maher A, Sameh A, Fakhry A (2012). *Global .J . Health .Sci.* , 4,1,174-183 .,Cited by Ivsl of Iraq.
- Nagham M (2010). *J.Babylone .Sci .*,18,3,925-942 .
- Nagham M, Aljamali (2012). *As . J . ExpChem.*,7,1,52-56.
- Nagham MA (2013). *J . Chem and Cheml .* , 3,1,37-47.
- Roshan A, Zia M, Rukhsana J (1996). *Tr . J . Chem .* , 20 , 186 - 193 .
- Singh V, Yashovardhan S, Sudhir K (2011). *Int. J . Chem Tech .Res .* , 3,2,892-900 .
- Vijay V, Gandhale S, Shinde N (2012). *Der . Pharma. Chemica* , 4,1, 320-328 .
- Wagnat W, Sherif M, Rafat M, Amr S (2012). *Int. J . Org Chem .*,2, 321-331