Cyclization of (Chalcone- Aldole)-Compounds And Studying of (Identification ,Liquid Crystal , Solubility)-Behavior

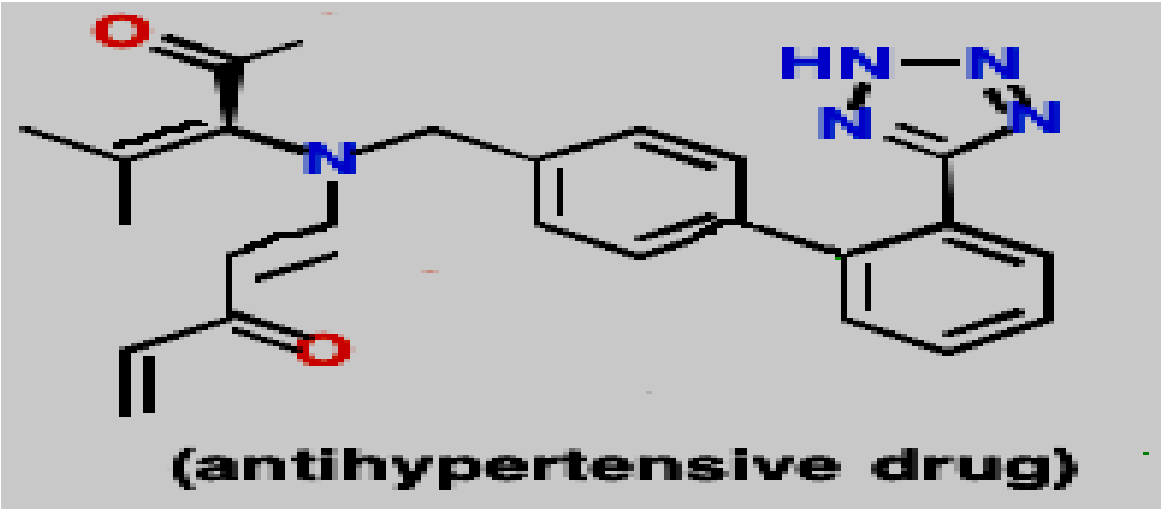
Dr. Nagham Mahmood Aljamali[1] , Rasha Neama H[2]*
[1]Department of Chemistry, Faculty of Education for Girls ,Kufa University, Iraq.
[2]M.Sc in chemistry , Ministry of Education ., Iraq[2].
**Corresponding Author E-mail: Dr.Nagham_mj@yahoo.com*

ABSTRACT
Series of cyclic compounds prepared via Aldole reaction , chalcone compounds reacted with several compounds (amine thiol , diamine , alkyl diamine , guanidine , urea , thiourea) to formation six – member ring which involved (di nitrogen atoms , nitrogen with sulfur atoms) , then identification of synthesized compounds via identification techniques (FT.IR , H.NMR , Mass) – spectrophotometric , studying of compounds behavior as a liquid crystals , their solubility in types of solvents , physical properties .

Keywords: Aldole , Chalcone , Liquid crystal , six member ring ,diamine, thiol , diazine , thiazine .

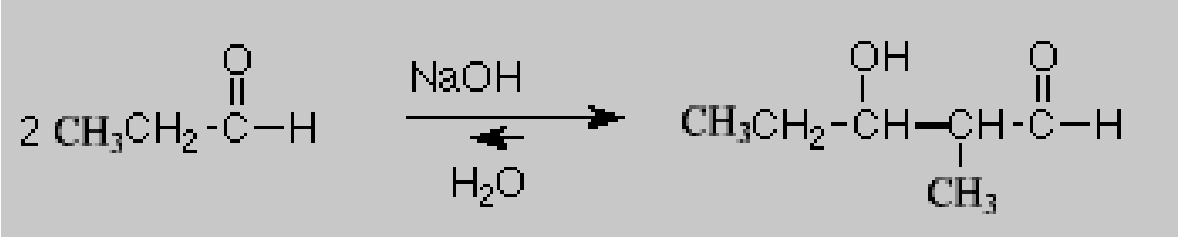
I.INTRODUCTION

Aldole reaction combines two carbonyl compounds (aldehydes and ketone) to form a new (β-hydroxy carbonyl) compound. These products are known as Chalcone . Aldol structural units are found in many important molecules, whether naturally occurring or synthetic [(1-3)] . Most of these structures have active properties in medicine field and drugs as: anti-tumor agent , antifungal agent amphotericin[(4-9)] or other .



Fig(1) :Chalcone compounds as drugs

Aldol reaction involved reaction of tow carbonyl compounds to form the α,β-unsaturated compound, then the reaction is termed the Aldol Condensation (loss of a molecule of water) , the reaction involved (keto – eno) form[(10-22)] , general mechanism[(23)] :



Fig(2) :General Mechanism of Aldole Reaction

Chalcone compounds have several applications in many fields , in (organic chemistry , medicinal chemistry , polymers ,…)[24-43] .

II.EXPERIMENTAL & MATERIALS

Chalcone compounds were characterized by : FT-IR spectra (FT-IR 8300 Shimadzu) in the range (400-4000) cm-1 as KBr discs ., 1H.NMR– Spectra in DMSO–solvent., Differential , Polarized Optical Microscope (POM) . physical with analytical studies carried out in chemistry Lab.

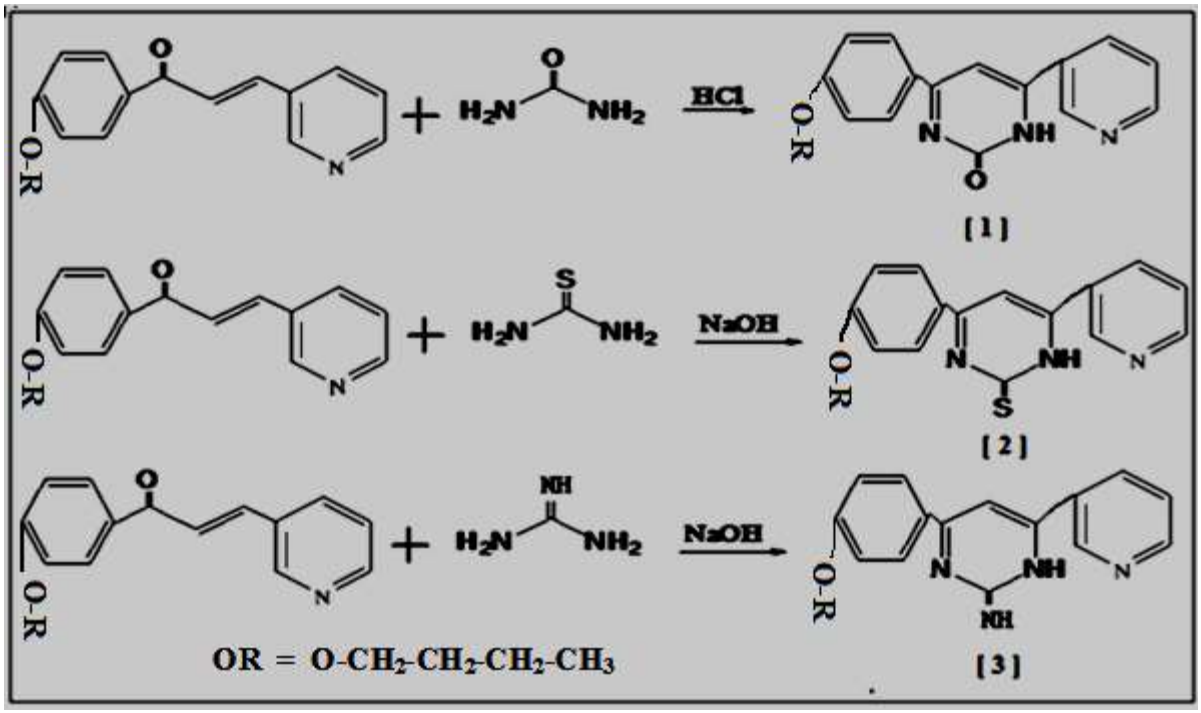
EXPERIMENTAL PART:

STEP . 1: Synthesis of Compounds (1 , 2 , 3):

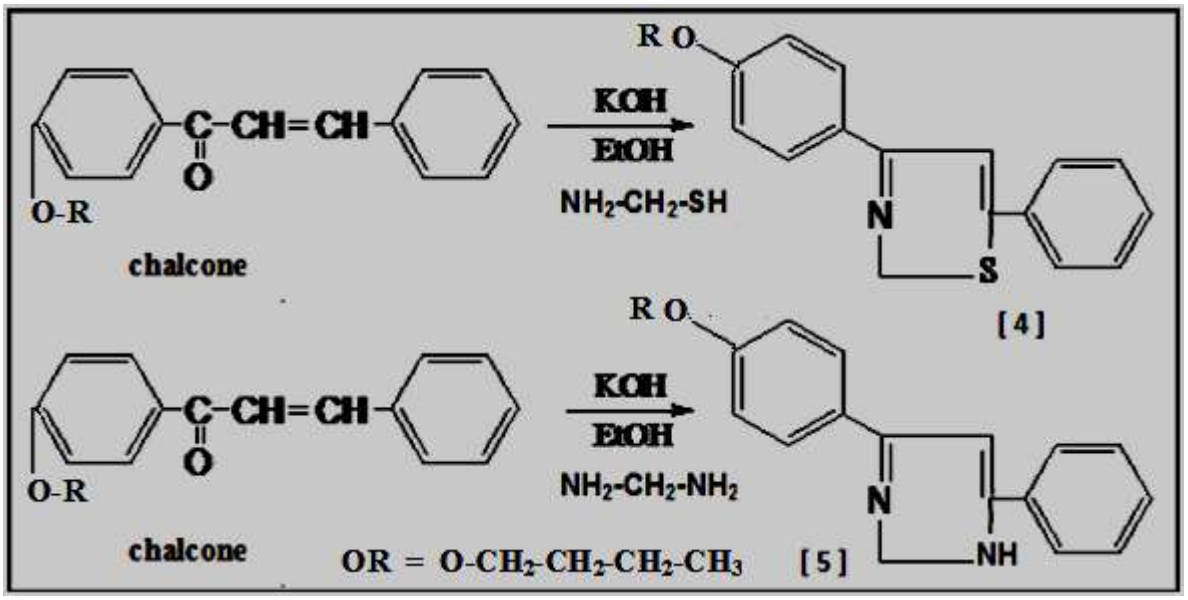
P-Alkoxy benzaldehyde (0.01 mole) reacted with (0.01mole) of 3-aceto pyridine for (8 hrs) in ethanol as a solvent of aldole reaction in basic medium with rotation according to literature[21] , to yield precipitation which filtered and dried then re crystallized to yield chalcone compounds , which (0.01 mole) refluxed for (6 hrs) with (0.01 mole) of (urea in HCl ., thiourea in basic medium ., guanidine in basic medium) respectively to gave compounds (1 , 2 , 3).

STEP .2 : Synthesis of Compounds (4 , 5):

Benzaldehyde (0.01 mole) reacted with (0.01mole) of p-alkoxy -acetophenone for (10 hrs) in ethanol as a solvent of aldole reaction in basic medium with rotation according to literature[21] , to yield precipitation which filtered and dried then re crystallized to yield chalcone compounds , which (0.01 mole) refluxed for (7 hrs) with (0.01 mole) of (NH_2-CH_2-SH in basic medium ., NH_2-CH_2-NH_2 in basic medium) respectively to gave compounds (4 , 5)



Scheme(1): Synthesis of Cycles from Aldol - Chalcone Reaction



Scheme (2): Formation of Six membered ring from Chalcones

II.RESULTS AND DISCUSSION

Our work involved ,preparation of new six – membered ring (1-5) will identified them by spectral methods like

(FT.IR , H.NMR , Mass) spectra and physical studying with chemical applications (liquid crystal ,POM).

Organic Investigation:

The FT.IR- Investigation : absorption bands appeared at (NH-) Amine : 3204 ., (C=N) Endocycle: 1645 ., (CO-N) Amide: 1687 in compound(1) , bands are appeared at (NH-) Amine : 3290 ., (C=N) Endocycle: 1640 ., (S=O) : 1233 in compounds (2) ,while other bands appeared at (NH-) Amine : 3272 ., (C=N) Endocycle: 1651 in compound (3) ., bands at (C=N) Endocycle: 1637 .,(CH_2 -S): 1204 in compound (4) , bands at (NH-) Amine : 3216 .,(C=N) Endocycle: 1643 in compound (5) ., all bands summarized in Table (1) .

Table (1): FT.IR- data (cm^{-1}) of Compounds (1-5).

Comp	Other Groups
(1)	(NH-) Amine : 3204 ., (C=N) Endocycle: 1645 ., (CO-N) Amide: 1687
(2)	(NH-) Amine : 3290 ., (C=N) Endocycle: 1640 ., (S=O) : 1233
(3)	(NH-) Amine : 3272 ., (C=N) Endocycle: 1651
(4)	(C=N) Endocycle: 1637 ., (CH_2 -S): 1204 .
(5)	(NH-) Amine : 3216 ., (C=N) Endocycle: 1643

The ^{1}H.NMR- Spectra: showed peaks at ɓ (NH-CO) Proton of amide: 9.17 .,Protons of Phenyl ring and pyridine:(6.86-7.91) in compound (1) .While compound (2) showed signals at (NH-S=O) Proton of Thioamide: 9.63 .,Protons of Phenyl ring and pyridine : (6.74-7.95)., compound(3) appeared peak at (NH-) Proton of amine: (5.28 , 5.11) .,Protons of Phenyl ring and pyridine : (6.86-7.91) . But compounds (4) showed signals at Protons of Phenyl ring : (6.86-7.63) .,

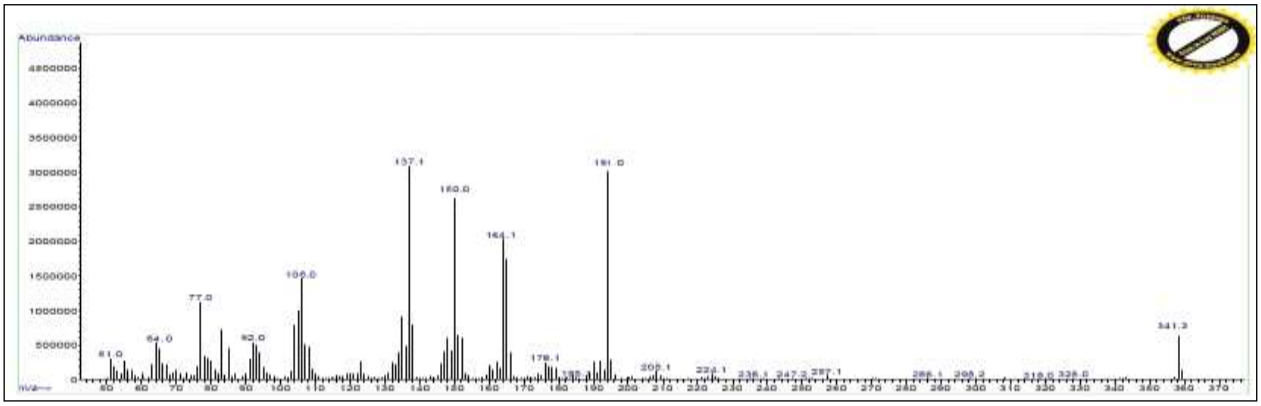
(CH_2-) methylene : 1.26 ., While compound (5) showed signals at (NH-) Proton of amine: 5.22 .,Protons of Phenyl ring : (6.97 -7.71) ., (CH_2-) methylene : 1.34 , and other signals in table (2) .

Table (2): H.NMR-data (ɓ - ppm) of Compounds (1-5)

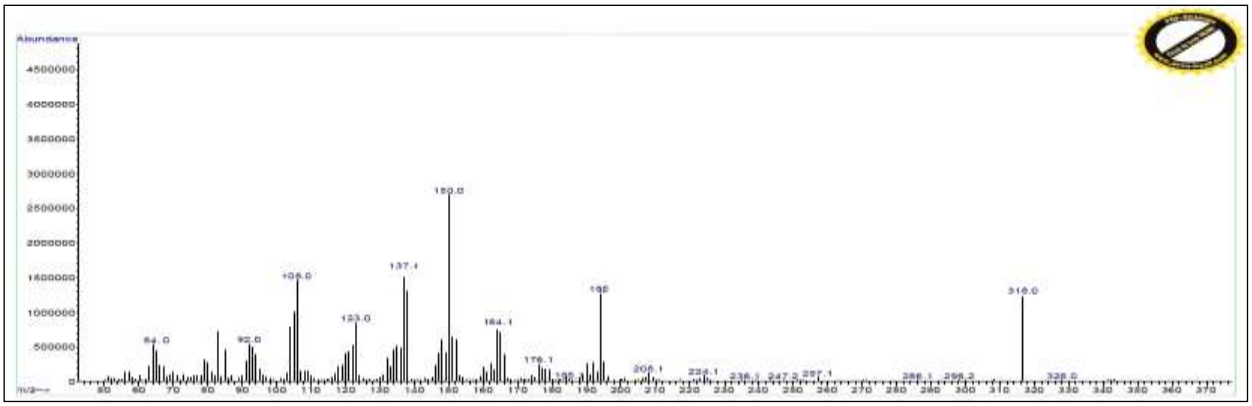
Comp	Other groups
(1)	DMSO-d6(solvent): 2.50 ., (NH-CO) Proton of amide: 9.17 .,Protons of Phenyl ring and pyridine : (6.86-7.91).

(2)	DMSO-d6(solvent): 2.50 ., (NH-S=O) Proton of Thioamide: 9.63 .,Protons of Phenyl ring and pyridine : (6.74-7.95).
(3)	DMSO-d6(solvent): 2.50 ., (NH-) Proton of amine: (5.28 , 5.11) .,Protons of Phenyl ring and pyridine : (6.86-7.91).
(4)	DMSO-d6(solvent): 2.50 .,Protons of Phenyl ring : (6.86-7.63) ., (CH_2-)methylene in cycle : 1.26 .
(5)	DMSO-d6(solvent): 2.50 ., (NH-) Proton of amine: 5.22 .,Protons of Phenyl ring : (6.97 -7.71) ., (CH_2-)methylene in cycle: 1.34 .

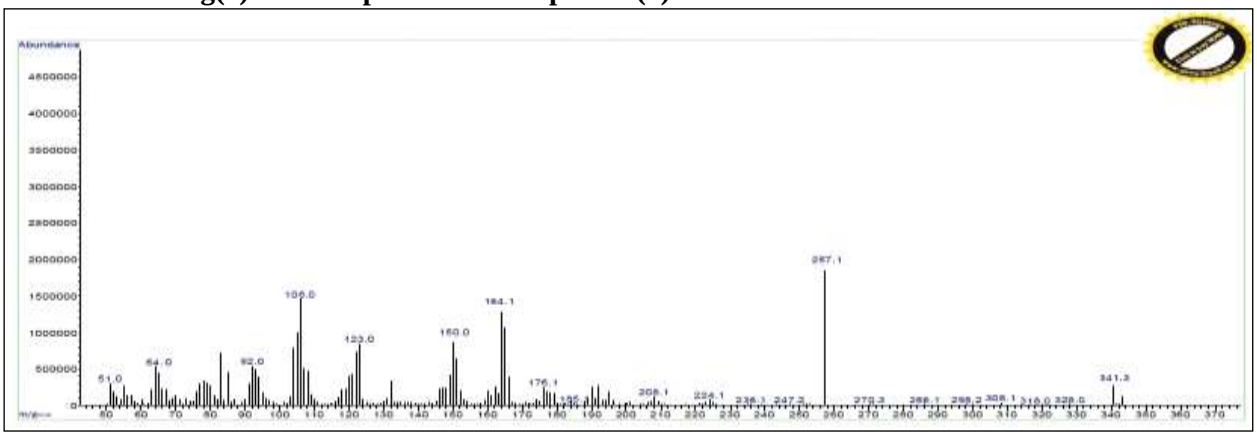
The Mass Spectra : Showed all fragments about parts of our formatted compounds in figures(1-3):



Fig(1): Mass Spectra of Compound (1)



Fig(2): Mass Spectra of Compound (3)



Fig(3): Mass Spectra of Compound (5)

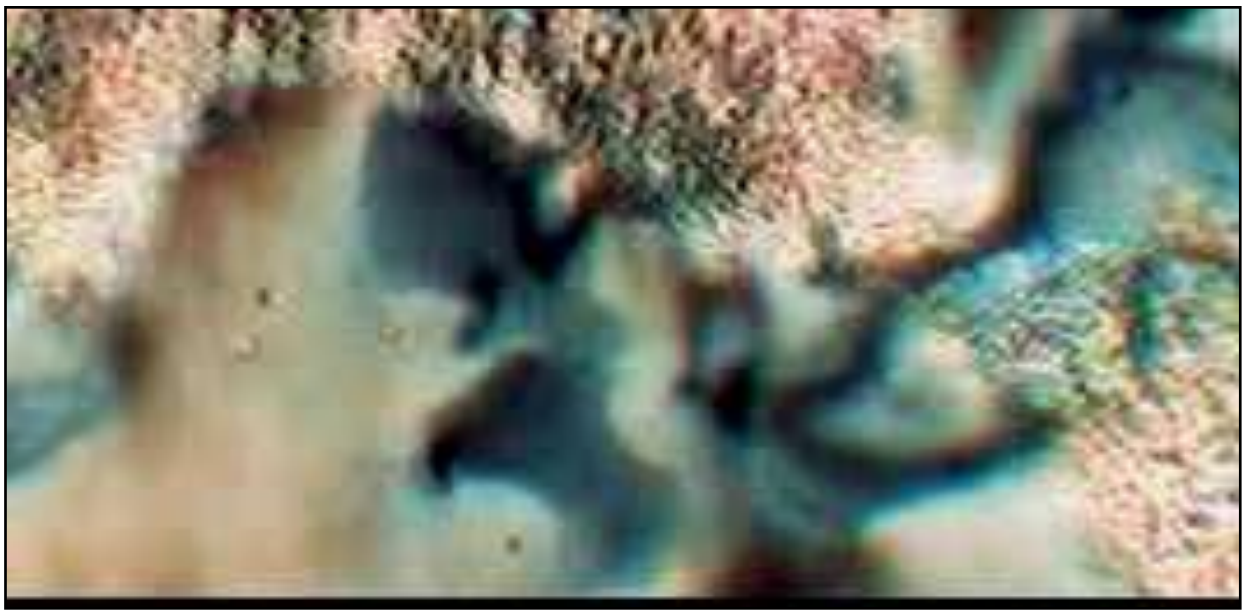
Studying of Compounds Behavior Via Polarized Optical Microscope :

Through optical microscope ,we studied optical behavior for our compounds by using high temperatures with following their behavior toward different temperatures.

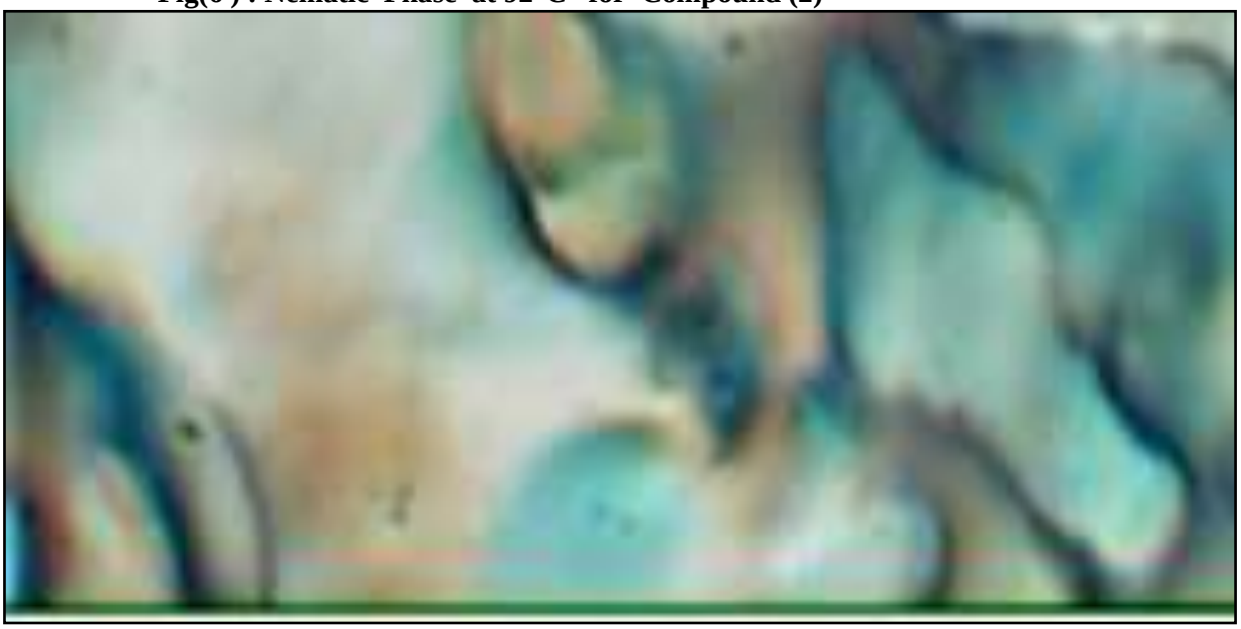
Fig (4): Optical Microscope

From results ,we found compounds (1- 5) are liquid crystals, some figures for compounds by optical microscope measurements are shown :

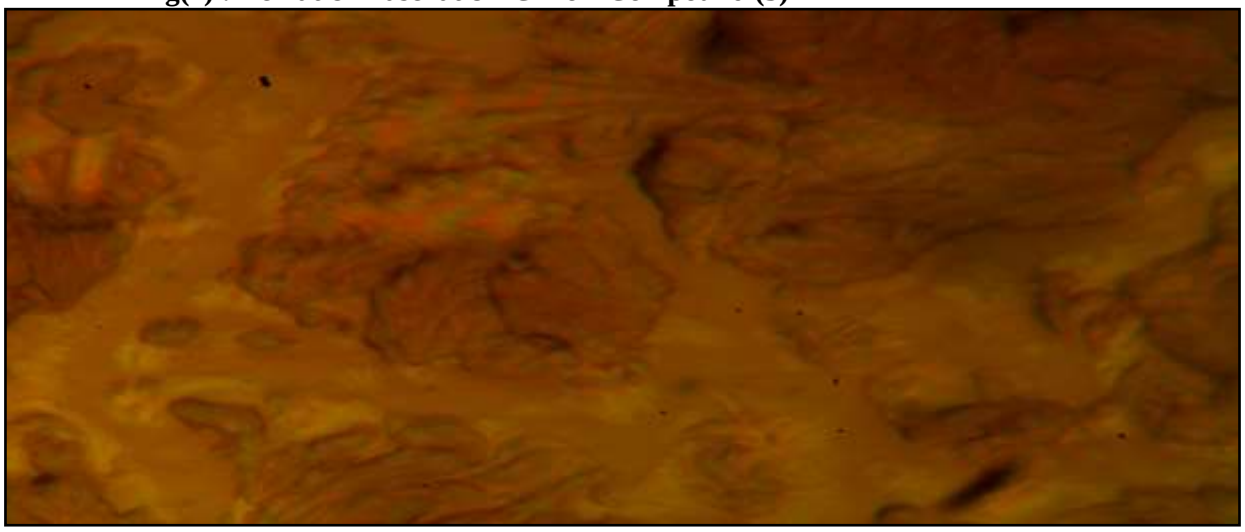
Fig(5): Nematic Phase at 78 °C for Compound (1)



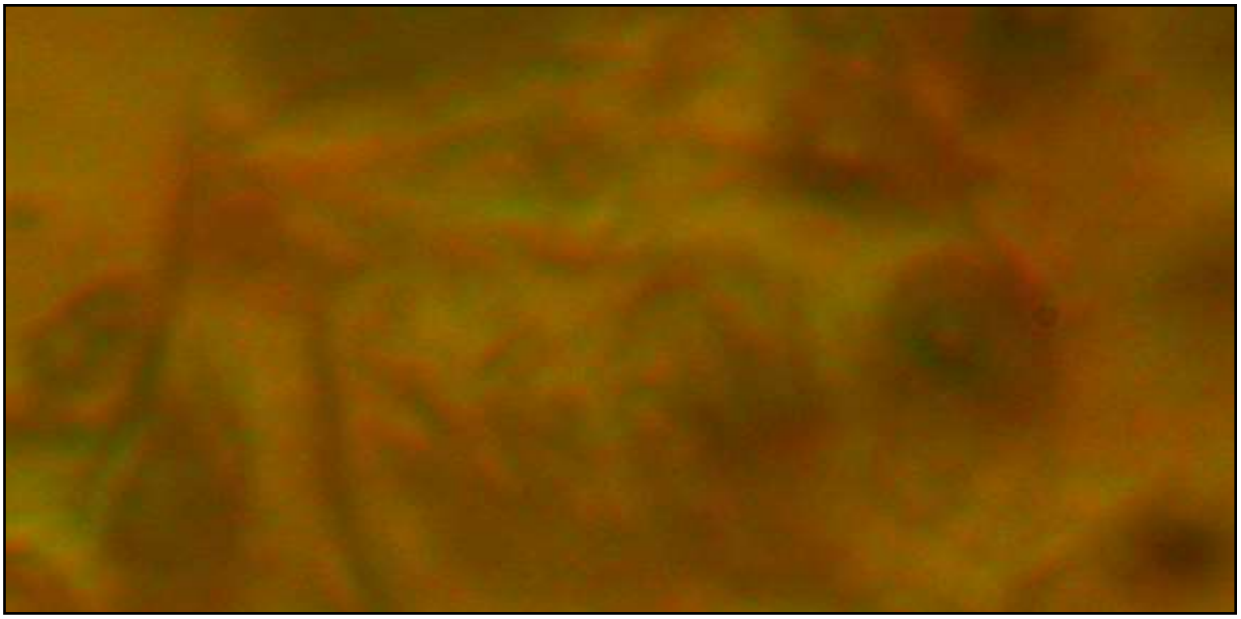
Fig(6) : Nematic Phase at 92 °C for Compound (2)



Fig(7) : Nematic Phase at 84 °C for Compound (3)



Fig(8) : Nematic Phase at 112 °C for Compound (4)



Fig(9) :Nematic Phase at 100 ^{o}C for Compound (5)

Solvation in Organic Solvents :

The six – membered ring (compounds) were tested in many types of solvents according to polarity of solvents with activity of functional groups in our compounds in this paper , all results are summarized in Table (3).

Table (3) : Solvaton of compounds in organic Solvents.

Compounds	Solvents					
	C_2H_5OH	DMSO	Hexane	Benzene	Acetone	Dioxan
(1)	+	+	-	-	-	-
(2)	+	+	-	-	-	-
(3)	+	+	-	-	-	-
(4)	+	+	-	-	-	-
(5)	+	+	-	-	-	-

The solvation of prepared compounds depends on type of functional group and terminal of compounds ((activity and polarity of groups)) in compounds which cause interaction[23] which represented in :(NH – group of amine , carbonyl group) or any other active functional groups in compounds.

Conclusions

The synthesized cyclic compounds gave good solubility in dimethyl sulphoxide and ethanol according to interactions with polarity of terminal cyclic compounds and appeared that these cyclic compounds are liquid crystals.

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