Synthesis of Organic Compounds And Study its liquid Crystalline Behavior

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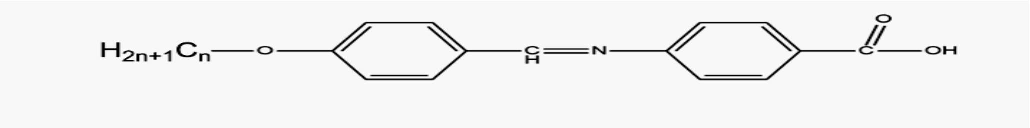
ABSTRACT :
These research includes synthesis of two series of Schiff bases differ in the type of terminal group, where one of them has a terminal carboxyl group COOH while the other contains methoxy OCH_3 as a terminal group. In the first part of this research it was Identification by spectroscopy methods using infrared IR and nuclear magnetic resonance H NMR spectrum, besides elemental analysis shows the exact chemical structure of the expected synthesized compounds. In the second part was the study of liquid-crystalline behavior by polarized optical microscopy POM and differential scanning calorimetry DSC that showed a liquid crystal phase in the compounds that has odd number of carbon atoms in the terminal chain compounds in the first series, while the second series compounds showed liquid crystal phase in the compounds that containing even number of atoms of carbon in the terminal chain.

I.INTRODUCTION

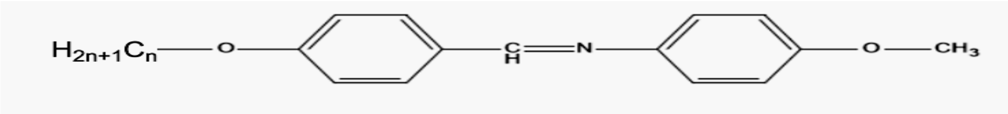
Liquid crystals are a new phases of mater add to the three well-known phases (solid, liquid and gas)[1]. The differences between these three well-known states can be attributed to the temperature of the substance. Temperature is a measure of the randomness of the molecules and therefore the higher of temperature is the less order they exist. Increasing temperature will cause the transition from a solid to a liquid and then to a gas. However, Many materials exhibit more than a single transition when passing from solid to liquid, which proves the presence of one or more intermediate phases[2]. The new phases have mechanical, optical and structural properties between those of crystalline solid and the corresponding isotropic liquid. These phases are referred to as liquid crystalline phases[3,4]. Thermotropic liquid crystals is one of two types of liquid crystals (and the second is called lyotropic) , Most thermotropic liquid crystals are rod-like molecules having a rigid core composed of two or more aromatic rings and one or more flexible terminal chains. The liquid crystal mesogen must contain a side-chain to give a linear that required to the liquid crystalline behavior. Schiff base (also known as imine CH=N) is a linking group used to connect between core groups. It has been received overwhelming response in liquid crystals research ever since in 1970 where Kelker discovered the 4-methoxylbenzylidene-4’-butylaniline (MBBA) which exhibit nematic phase at room temperature .

The first chain



n= 3-7

The second chain n= 3-7



In this our studies, Schiff base and alkyloxy terminal moieties are incorporated into a new series of homologous compounds with two different group in the other side of chain , 4-(-alkoxybenzylideneamino)benzoic acid and 4-methoxy-N-(4-alkoxybenzylidene)aniline. This two chain where prepared and then make a study about it is liquid crystallain behavior , Transition temperatures and phase characterization were studied by differential scanning calorimetry (DSC) and polarizing optical microscope (POM) techniques.

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II. EXPERIMENTAL WORK

The melting range of the synthesized compounds was performed by melting point apparatus and is uncorrected.

STEP-1: Preparation of N- (4-hydroxyphenyl) acetamide

(18.3 mL of concentration hydrochloric acid and , (0.22mol, 23.98 gm) of para-amino phenol were introduced in a beaker containing 500ml of distilled water. The mixture was stirred until the amine completely passes in to solution .To the resulting solution 25.6mL of acetic anhydride with (three drops of H_2SO_4acidconcentration) were added and stirred and then immediately was poured in a solution of (33gm, 0.402mol) of crystallized sodium acetate in 100mL of water. The solution was stirred vigorously and cooled in ice. The N- (4-hydroxyphenyl) acetamide was filtered with suction washed with a little distilled water ,and dried upon filter paper in air melting point was (169-170) C° . [5,6].

STEP-2: Preparation of N-Alkali bromides

In a round bottomed flask equipped with a separation funnel and a condenser set downward for distillation, (71ml) of HBr acid (48%) and (16.5ml) of concentration H_2SO_4acid drop wise was added with stirring. After cooling(0.5mol) of appropriate alcohol was added in portions (the end of the condenser was connected to an adapter dipping in to water contained in a 250ml flask, the later was surrounded by ice) then (2.5ml) of concentration H_2SO_4 acid was introduced gradually through the separation funnel and the mixture was distilled slowly until no more oily drops pass over ,the organic layer was separated ,washed successively with water ,10 % Na_2CO_3solution and then with water ,dried over anhydrous calcium chloride .it is used without further purification.[6].

STEP-3: Preparation of N-(4-methoxyphenyl) acetamide

(3.75gm, 0.025mol)of 4-actemido phenol were dissolved in 15mL of ethanol in a conical flask and with added potassium hydroxide solution (1.85gm, 0.033mol),in a lest volume of (~ 1.5mL)by stirred magnetic stirrer . A solution of appropriate methane bromide (0.025mol) in 12.5mLdissolved in added ethanol, the mixture heated by using appropriate condenser for more then one hour(then6mL distilled water added and the product was washed re crystallize for ethanol, melting point (129C°), [7].

STEP-4 : Preparation of 4-methoxy aniline

In conical flask4 N- (acetamide – methoxy phenyl)(0.025mol) is dissolved in (12.5ml) ethanol and heated .Add to the mixture (3.75ml) potassium hydroxide solution (20M) ,the mixture was heated for three hours ,the solvent was distillation by using evaporator rotator. The product was extract of benzene then dried by anhydrous magnesium sulfate. The benzene was evaporated by rotary evaporator , the product has a melting point $58C^0$ [5.6].

STEP-5: Preparation of 4-alkyloxy banzaldehayde

(3.77gm)(0.025mol,) of 4-hydroxy banzaldehayde dissolved in 15 mL of ethanol in a conical flask to the stirred solution and slowly was added solution of (0.033 mol) for KOH (1.85gm dissolved in less volume of water a (~ 1.5mL) .Then it was added of a solution of appropriate Alkyl bromide (0.025mol) in 12.5mL ethanol. The mixture was heated with stirring continued stir for more than one hour.6mL of water was added to mixture and then the product was extracted by petroleum ether and

4- Then washed the extract with distillated water and the solvent was evaporated, the pure product was liquid yellow color , [7].

STEP-6: The first chain :4-(4-alkoxybenzylideneamino)benzoic acid – Schiff Base

Equal moles number of 4- amino benzoic acid and 4-alkyloxy banzaldehayde dissolved in absolute ethanol with three drops of glacial acetic acid , the mixture was heated reflux for three hours, the mixture was cooled and washed with a small amount of ethanol and then dried the resulting, the compound was purified by ethanol about three once .

STEP-7 : The second chain4-methoxy-N-(4-alkoxybenzylidene)aniline – Schiff Base
Equal moles number of 4- methoxy aniline and 4-alkyloxy banzaldehayde dissolved in absolute ethanol with three drops of glacial acetic acid ,the mixture was heated reflux for less than hours, the mixture was cooled and washed with a small amount of ethanol and then dried the resulting, the compound was purified by ethanol about three once .[8]

The IR spectrum studies of the synthesized compound were recorded by pressed-pellet technique. IR spectra were recorded in KBr press (Shimadzu). H-NMR-Bruker avance 300MHz using TMS as internal standard.

III.RESULTS AND DISCUSSION

The identification of Prepared compound (IR-spectra): all data of analysis of compounds in this table (2):

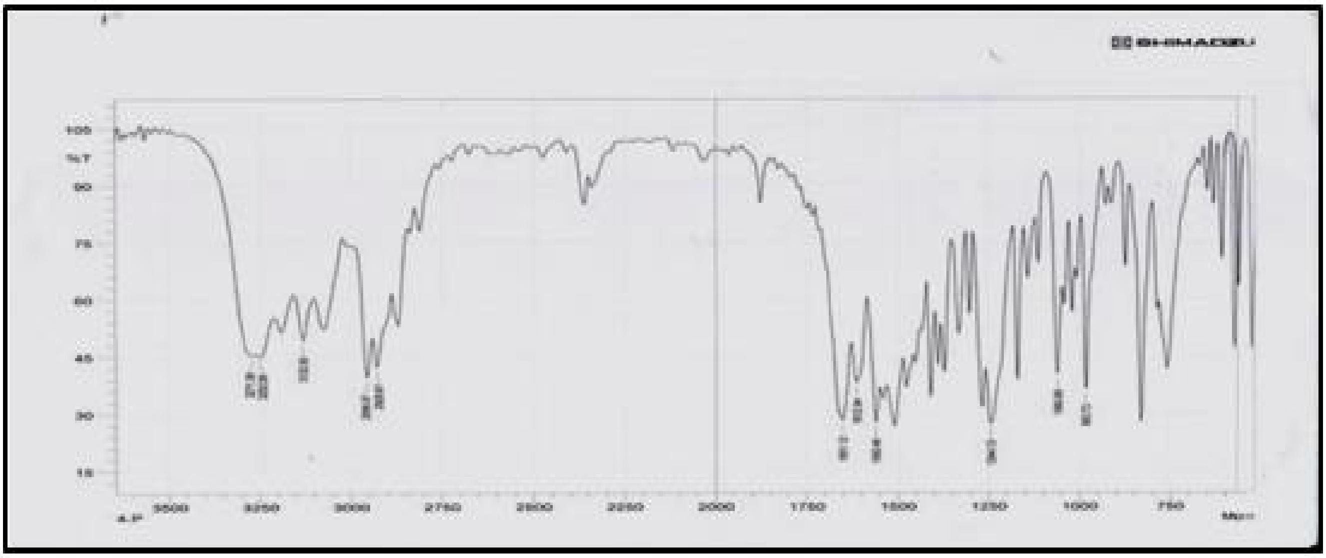


Figure.1: infrared spectrum of the compound4-mehoxy acetamide

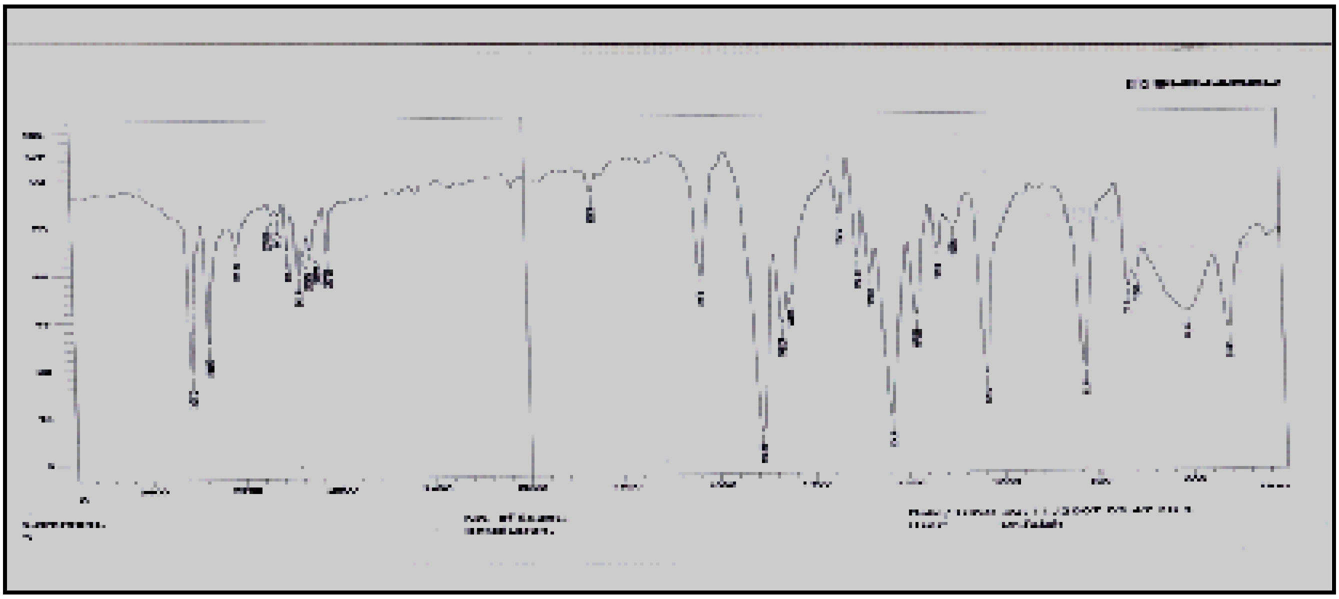


Figure.2: infrared spectrum of the compound 4-alkoxy aniline

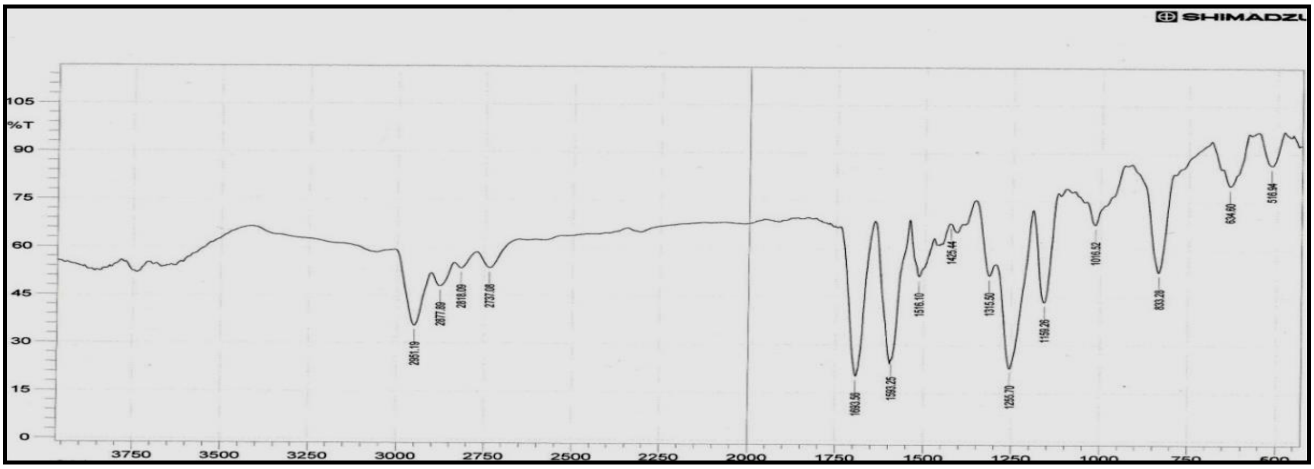
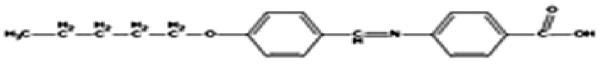
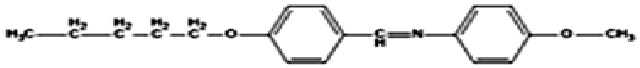


Figure.3: infrared spectrum of the compound 4-alkoxy banzaldehayde

All physical properties are listed in table (1) :

Table (1) chemical structures and melting point , color and yield of the prepared compound s

Seq.	Symbol of compound	color	m.p C⁰	Chemical structure	Product	M.w
1	C3	Yellow	194 C°		51%	283
2	C4	Yellow	183 C°		72%	297
3	C5	Yellow	158 C°		63%	311
4	C6	Yellow	169 C°		66%	325
5	C7	Yellow	158 C°		%69	339
6	M3	Silver	118 C°		85%	269
7	M4	Silver	112 C°		87%	283
8	M5	Silver	90 C°		81%	297
9	M6	Silver	104 C°		86%	311
10	M7	Silver	108 C°		79%	325

While the identification of Prepared compound (CHN analysis): all data of analysis of compounds in this table (2):

Table (2): physical properties of compounds & Elemental analysis

Compound Symbol	Positivism Formula	M.wt g/mol	C%		H%		N%	
			Calc	found	Calc	found	Calc	found
M4	$C_{17}H_{19}NO_2$	269.34	75.81	75.885	7.11	7.113	5.20	4.227
M6	$C_{20}H_{25}NO_2$	311.42	77.14	76.774	8.09	7.635	4.50	4.137
C5	$C_{19}H_{21}NO_3$	311.37	73.29	72.920	6.80	6.045	4.50	4.095
C7	$C_{21}H_{25}NO_3$	339.34	74.31	73.872	7.42	7.014	14.31	3.878

FT.IR-spectra : which gave good indicators about all data of functional groups in prepared compounds

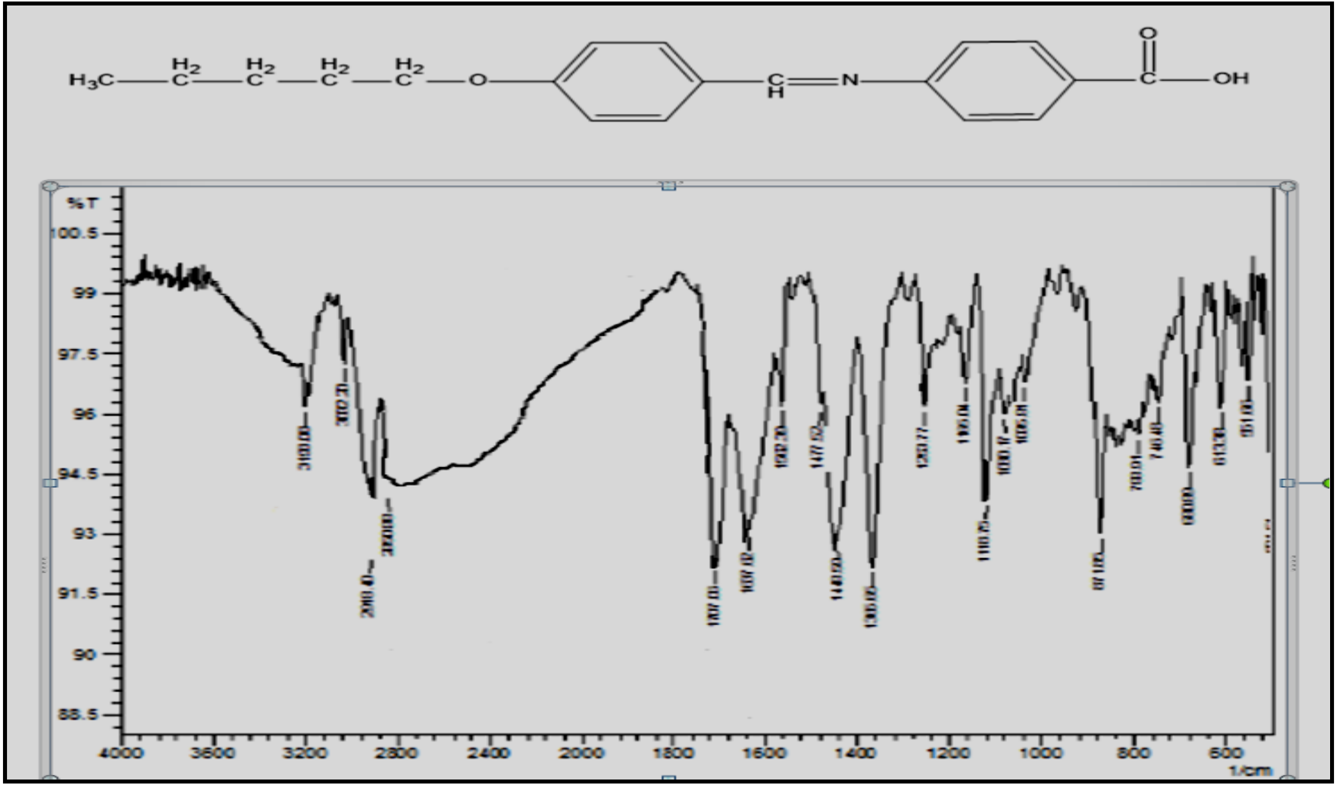


Figure.4: infrared spectrum of the compound C5

1. absorption bands at 1118 due to a group -O-CH_2-CH_2
2. absorption bands at 1618 due to imine group CH = N
3. absorption bands at 1737 due to the carbonyl group carboxylic
4. absorption bands at 2918 due to aliphatic CH
5. absorption bands at 2600-3198 due to OH of the carbonyl
6. absorption bands at 3032 due to aromatic CH

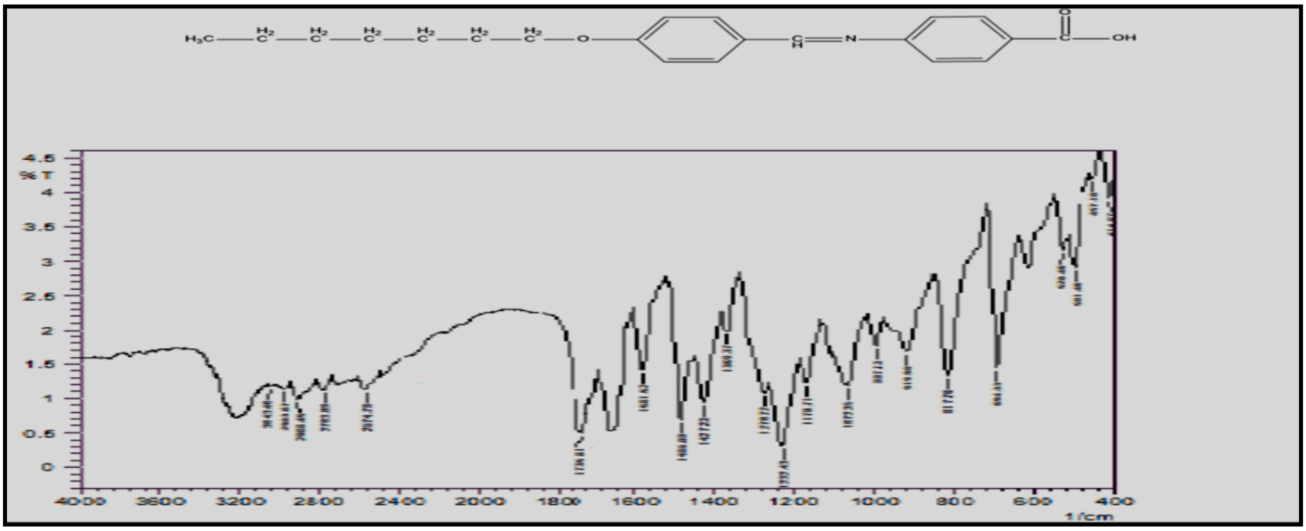


Figure .5: infrared spectrum of the compound C7

From IR spectrum of a compound most important absorption bands represent functional groups are:

1. absorption band at 1170 due to a group -O-CH_2-CH_2
2. absorption band at 1630 belonged due to imine group CH = N
3. absorption band at 1735 due to the carbonyl of carboxylic group
4. absorption band at 2983 due to aliphatic CH
5. Broadband absorption at 2574-3200 due to OH of Carbonyl group .
6. absorption band at 3034 due to aromatic CH

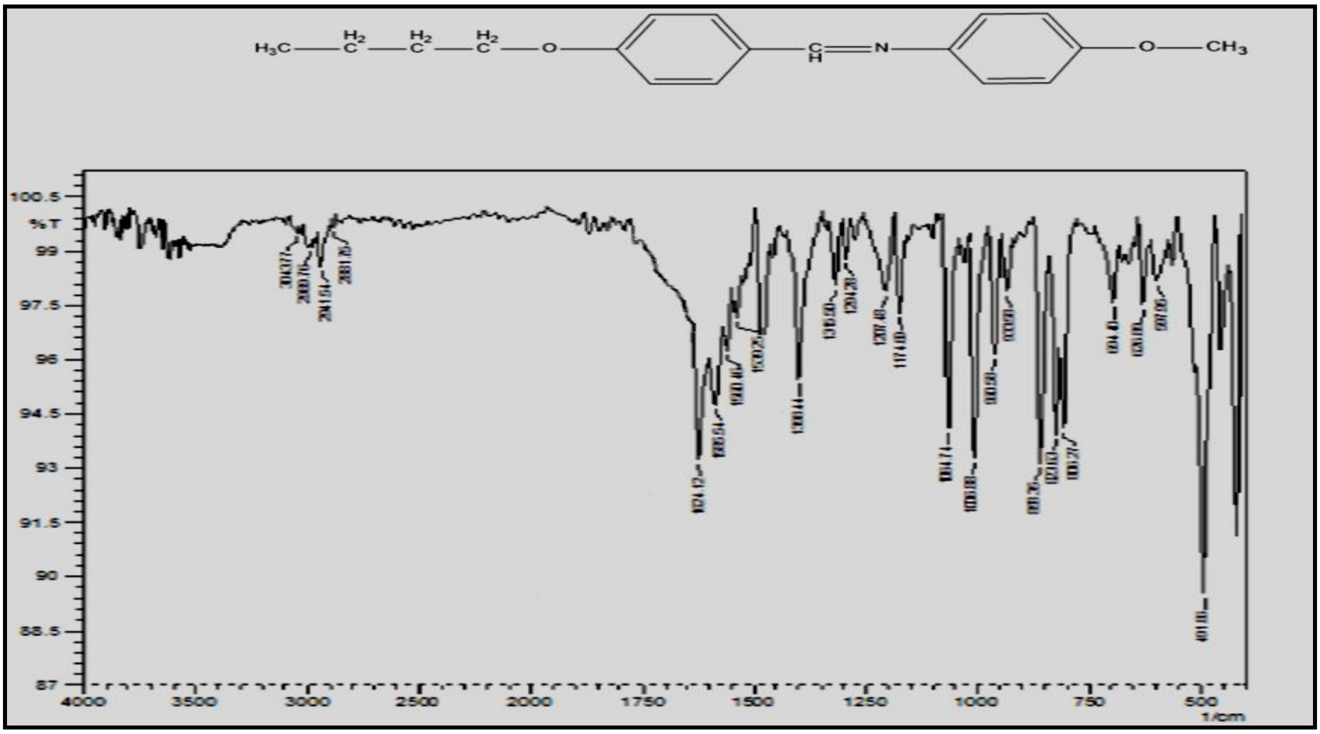


Figure.6: infrared spectrum of the compound M4

1. absorption band at 1116 due to ether -O-CH_2-CH_2
2. absorption band at 1154 due to ether -O- CH_3
3. absorption band at 1624 due to imine group CH = N
4. absorption band at 2968 due to aliphatic CH
5- absorption band at 3043 due to aromatic CH

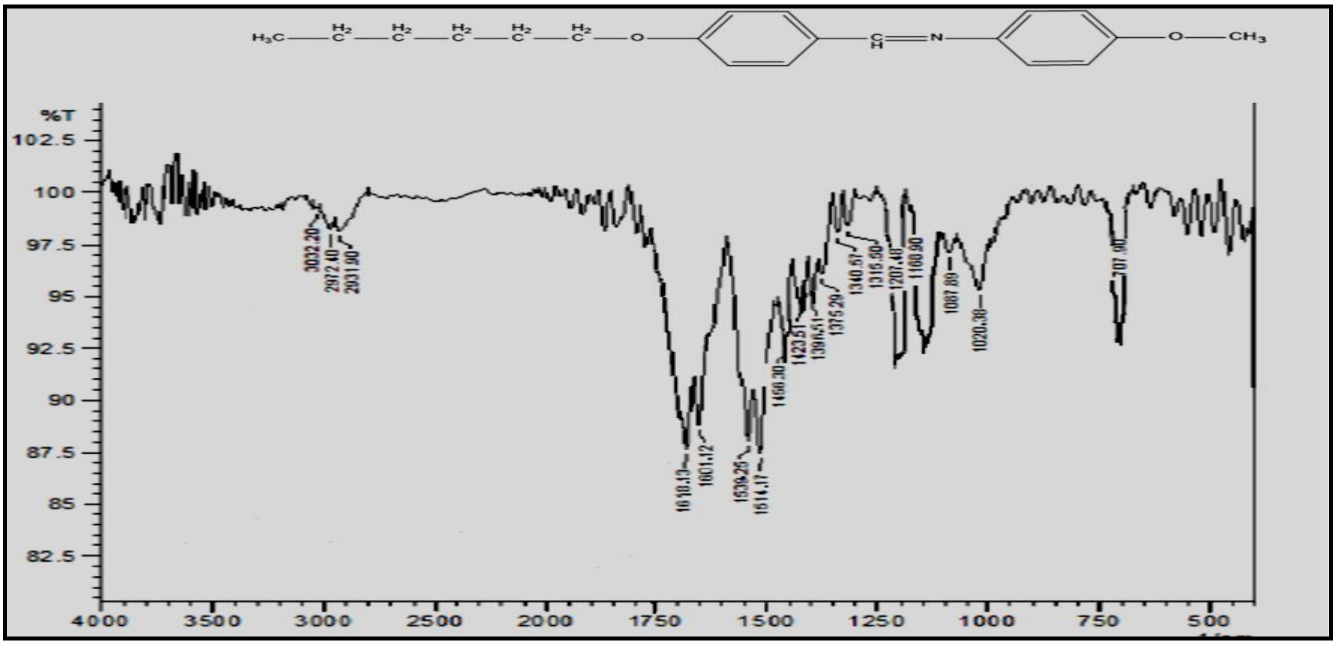


Figure .7: infrared spectrum of the compound M6

1. absorption band at 1168 due to ether -O-CH_2-CH_2
2. absorption band at 1618 due to imine group CH = N
3. absorption band at 1207 due to ether -O- CH_3
4. absorption band at 2912 due to aliphatic CH
5- absorption band at 3032 due to aromatic CH

The HNMR spectra : all peaks appeared in figures

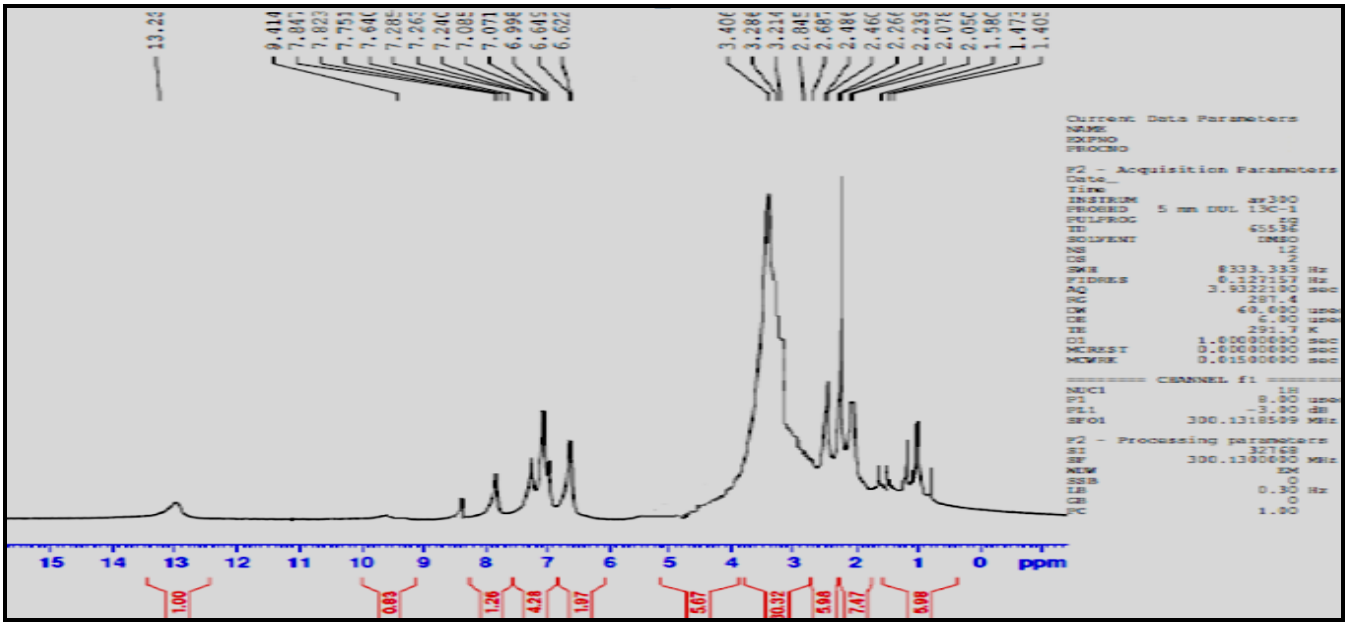


Figure .8: nuclear magnetic resonance spectrum of the compound C5

1. peaks at (0.90-1.80)ppm due to alkyl groups (CH_3CH_2 CH_2 CH_2)
2. peaks at (6 2.5) ppm solvent due to DMSO-d
3. peaks at (3:41) ppm solvent due to O-CH_2
4.peaks at (6.62-7.84)ppm due to phenyl ring
5. peaks at (8.41))ppm due to (CH = N)
6. peaks at (13:28) ppm due to Carboxyl group

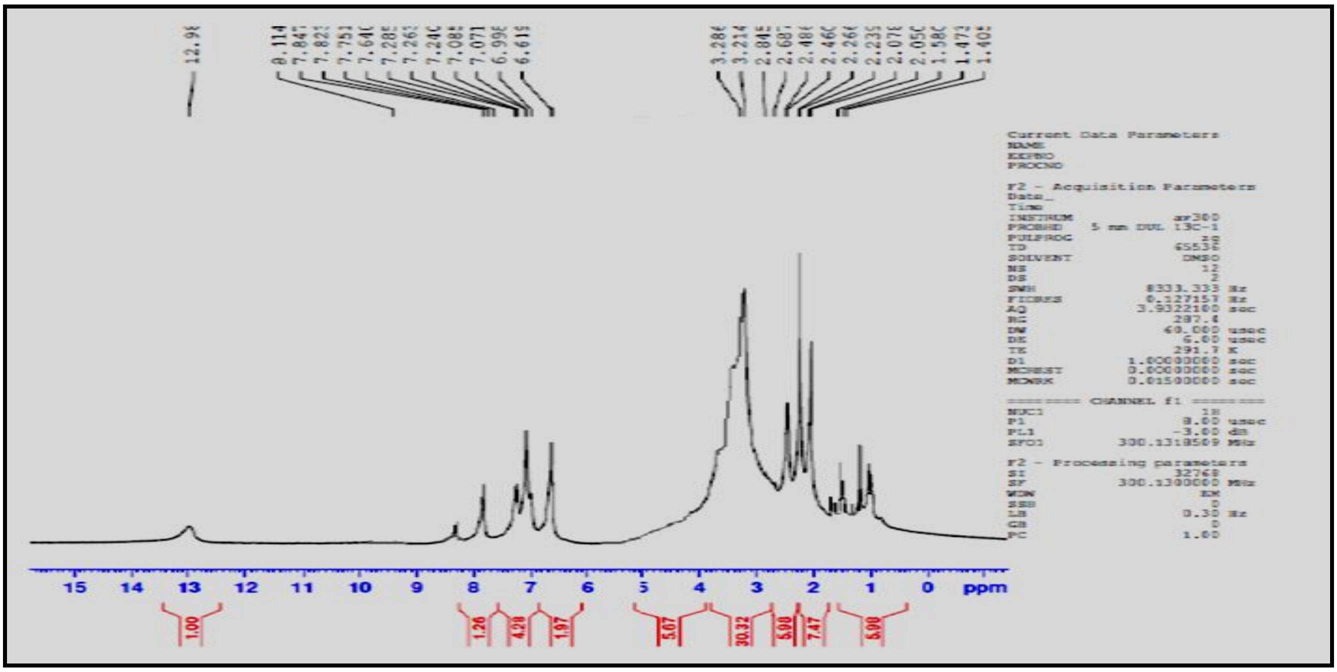


Figure .9: HNMR spectrum of the compound C7

1. peaks at (0.90-1.50)ppm due to alkyl groups (CH_3CH_2 CH_2 CH_2)
2. peaks at (2.5) ppm solvent due to DMSO-d
3. peaks at (3:5) ppm solvent due to O-CH2
4.peaks at (6.61-7.42)ppm due to phenyl ring
5. peaks at (8. 11))ppm due to (CH = N)
6. peaks at(12.98) ppm due to Carboxyl group

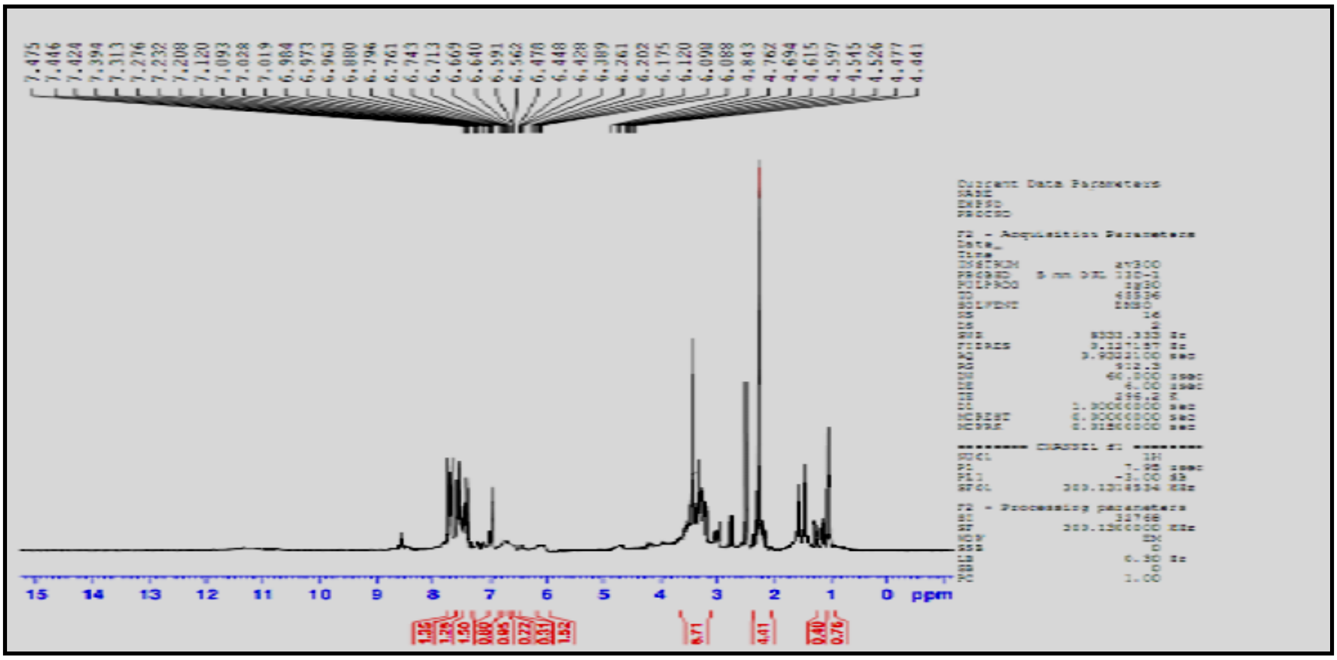


Figure .10: HNMR spectrum of the compound M4

1. peaks at (0.90-1.70)ppm due to alkyl groups (CH_3 CH_2 CH_2)
2. peaks at (2.5) ppm due to solvent DMSO-d
3. peaks at (3:10) ppm due to O-CH_3
4- . peaks at (3.30-3.60) ppm due to OCH_2CH_2
5.peaks at (6.97-7.47)ppm due to phenyl ring
6. peaks at (8.55))ppm due to (CH = N)

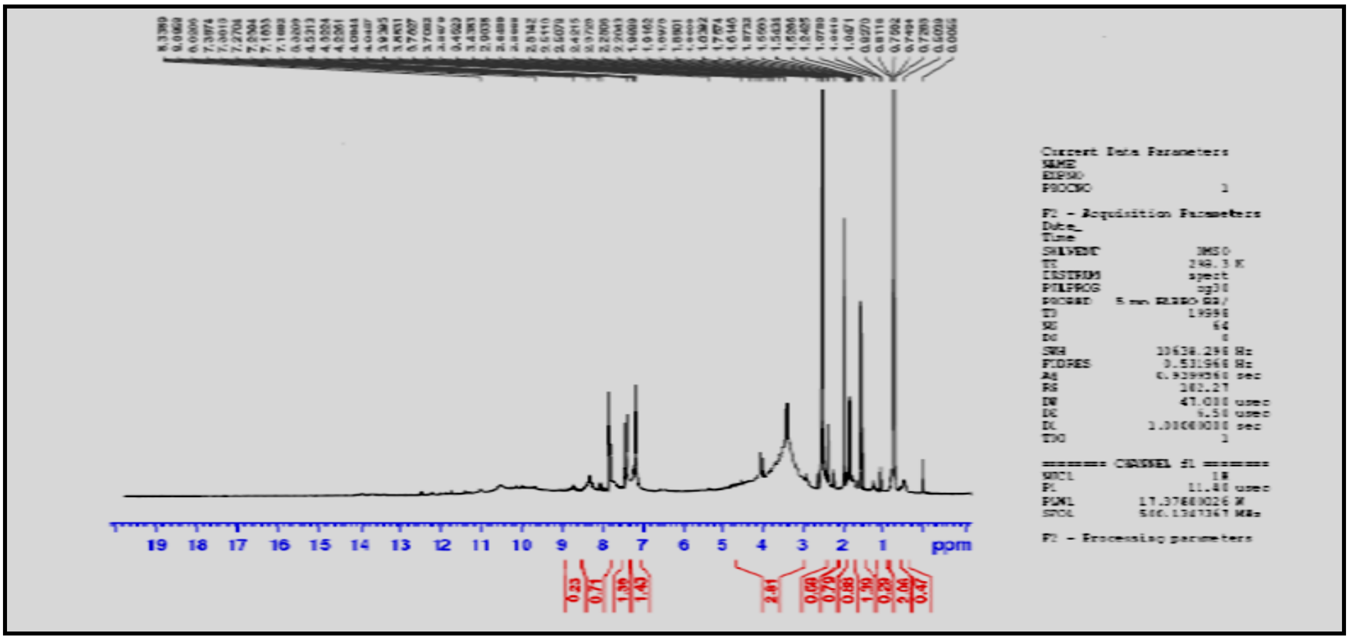
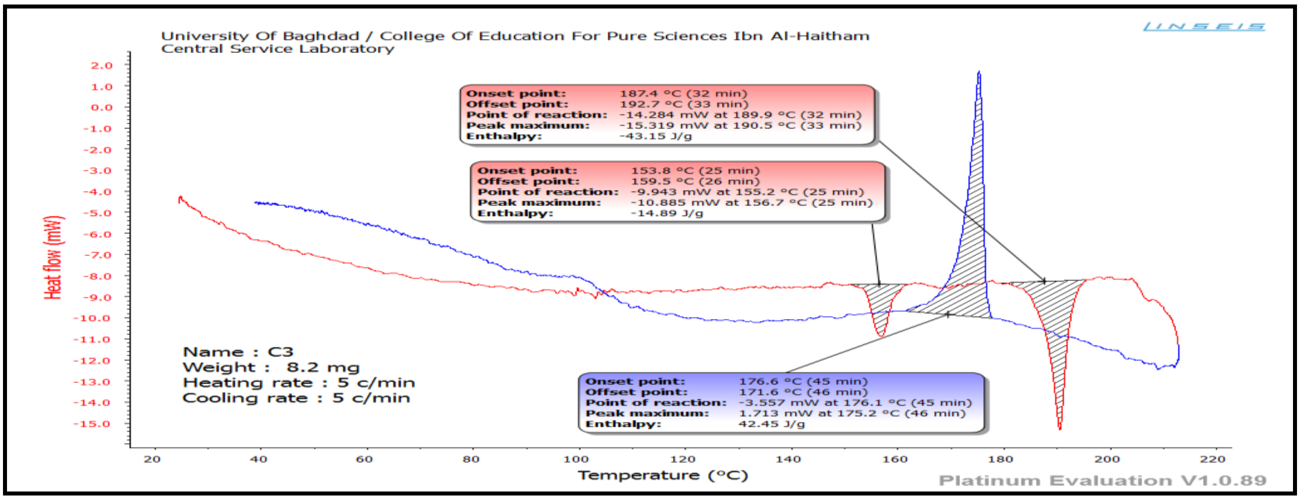


Figure .11: HNMR spectrum of the compound M6

1. peaks at (0.74-2.42)ppm due to alkyl groups ($CH_3CH_2CH_2CH_2CH_2$-)
2. peaks at (2.5) ppm due to solvent DMSO-d
3. peaks at (3:43) ppm due to O-CH_3
4- . peaks at 3.93 ppm due to OCH_2CH_2
5.peaks at (7.16-7.39)ppm due to phenyl ring
6. peaks at (8. 30))ppm due to (CH = N)

Determination of the transition temperatures of the two series prepared compounds: -
The transition temperatures for the compounds of the two of series using a polarized optical microscope (POM) and differential scanning calorimeter with increasing the temperature transform from crystal phase to liquid crystal phase then to the liquid phase (Isotropic).

1- The compound C3 : 4-((4-propoxybenzylidene)amino)benzoic acid
The melting point to this compound was (190-193C^0) .In DSC it shown us below :



Form .1: curve differential scanning Calorimeter to compound C3

The amount of the sample used in the DSC has been very little 8.2mg , so there was interference between curves in the cooling and heating , in addition to the fact that the amount of heat absorbed in the transition (solid - liquid crystalline) more than (liquid crystal - isotropic). It showed that the compound is a mono tropic liquid crystalline properties at (160- 187 C^0), as it is clear in the curve.

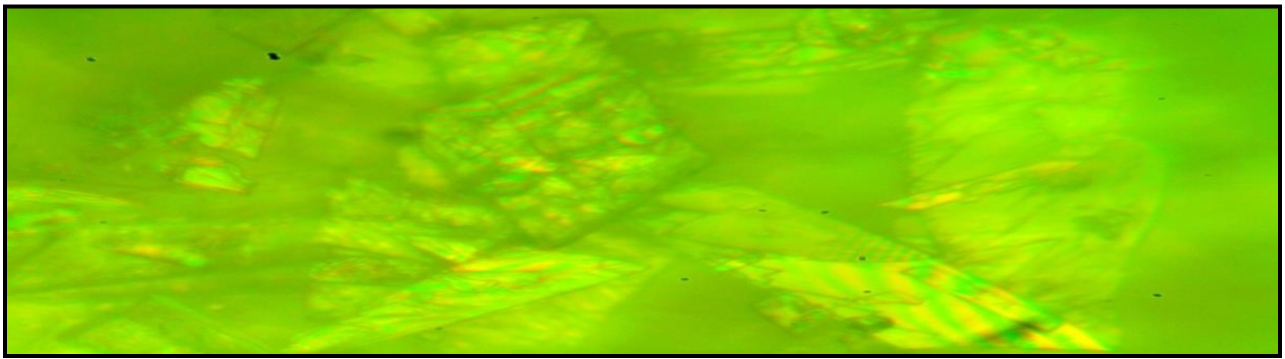
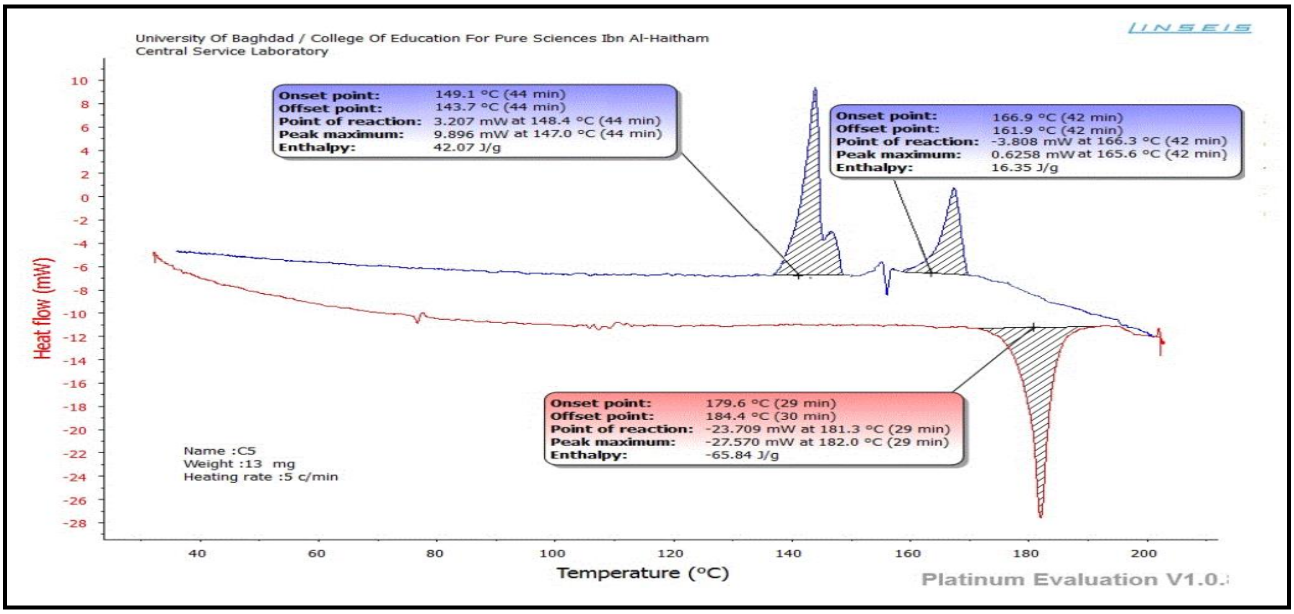


Image .1: POM of the compound C3 at 169 C^0 at heating

2- The compound C54-((4-pentyloxy)benzylidene)aminobenzoic acid
The melting point to this compound was (180-183C^0) .In DSC it shown us below :



Form .2: curve differential scanning Calorimeter to compound C5

We note also the properties of mono tropic liquid crystalline phase at cooling between (161-149C^0) . and in POM below we note a Nematic phase

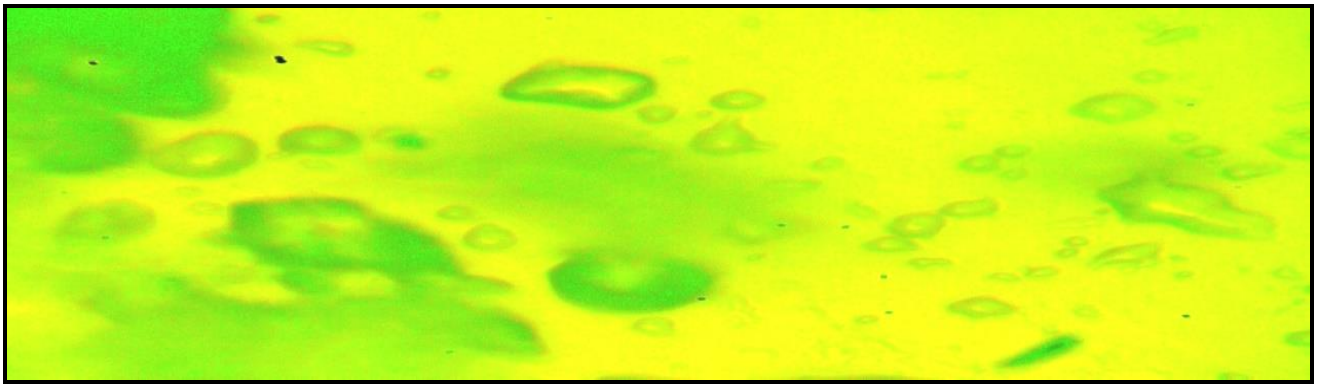
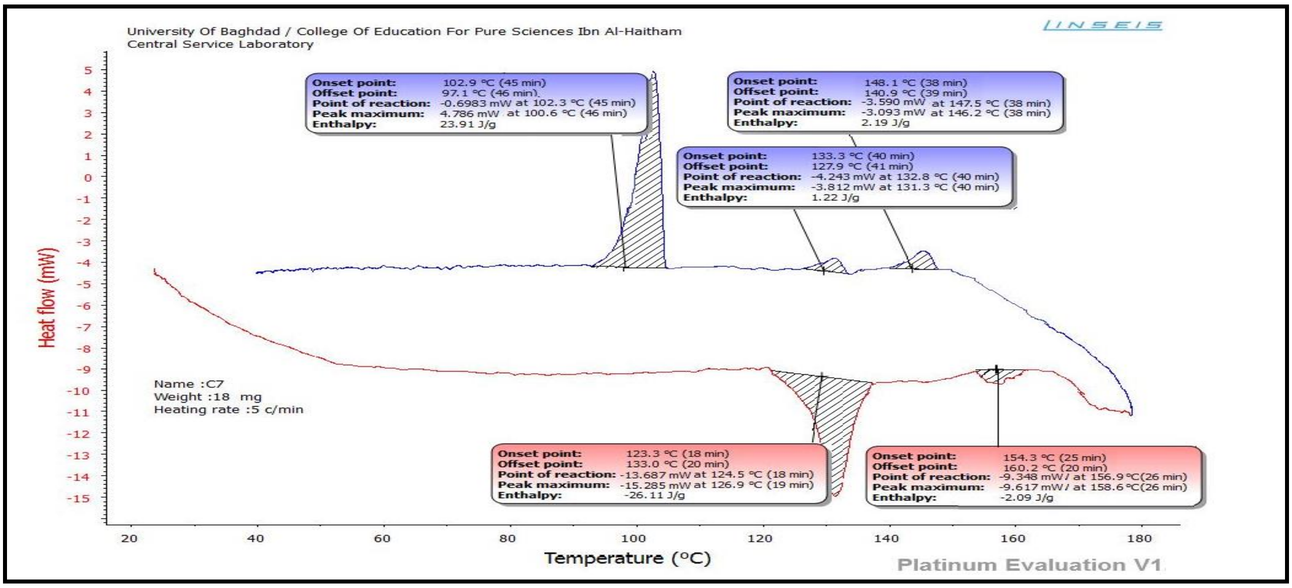


Image .2: POM of the compound C5 154 C^0 at cooling

3- the compound C7 4-((4-heptyloxy)benzylidene)amino)benzoic acid
The melting point to this compound was (158-156C^0) In DSC it shown us below



Form .3: curve differential scanning Calorimeter to compound C7

It gave the properties of liquid crystalline phases at heating and cooling (enantiotropic properties) , it showed liquid crystalline phase at heating (130-154C^0)

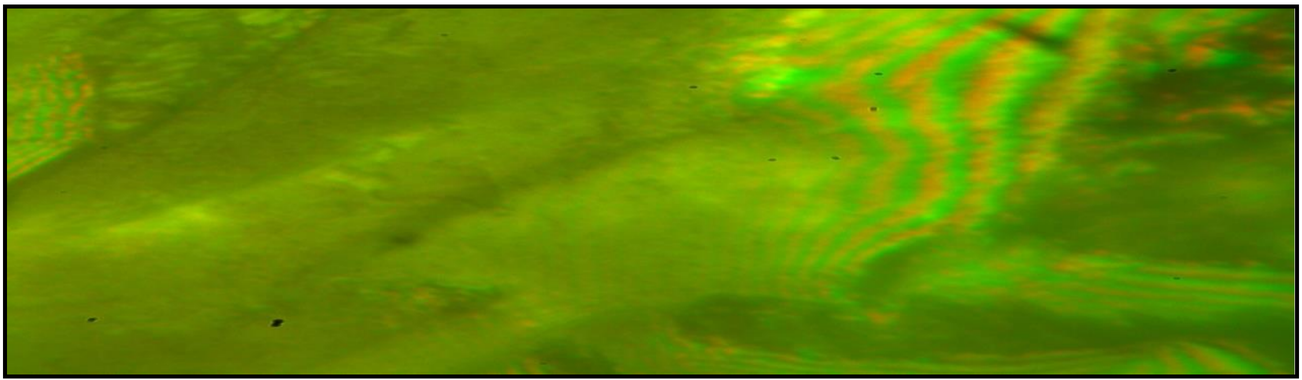


Image .3: POM of the compound C7 (135 C^0) at heating

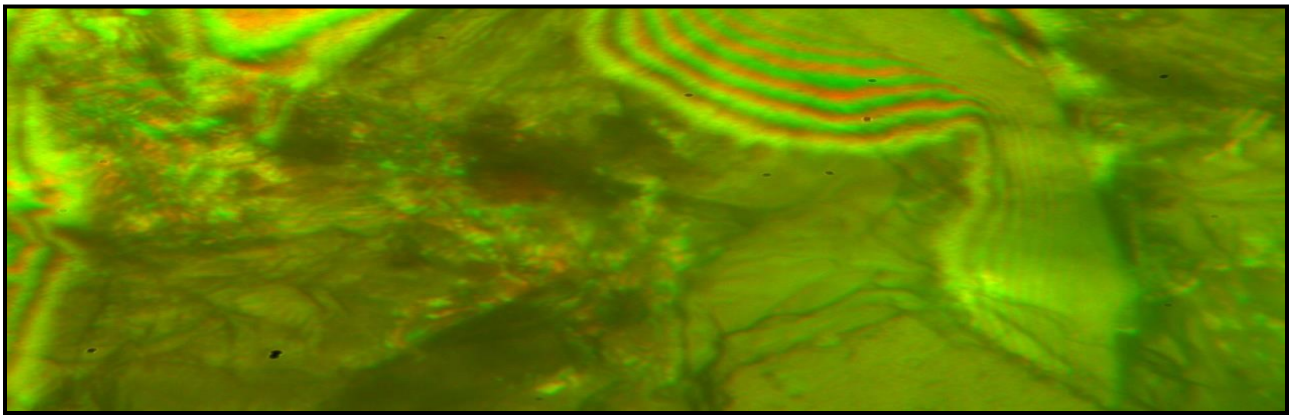


Image .4: POM of the compound C7 (131 C^0) at cooling

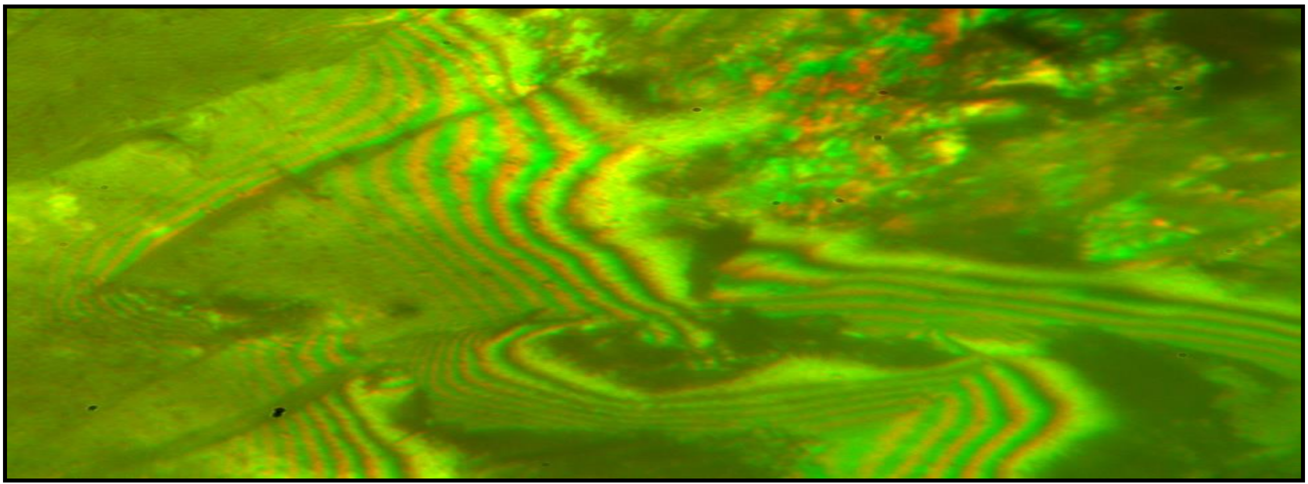
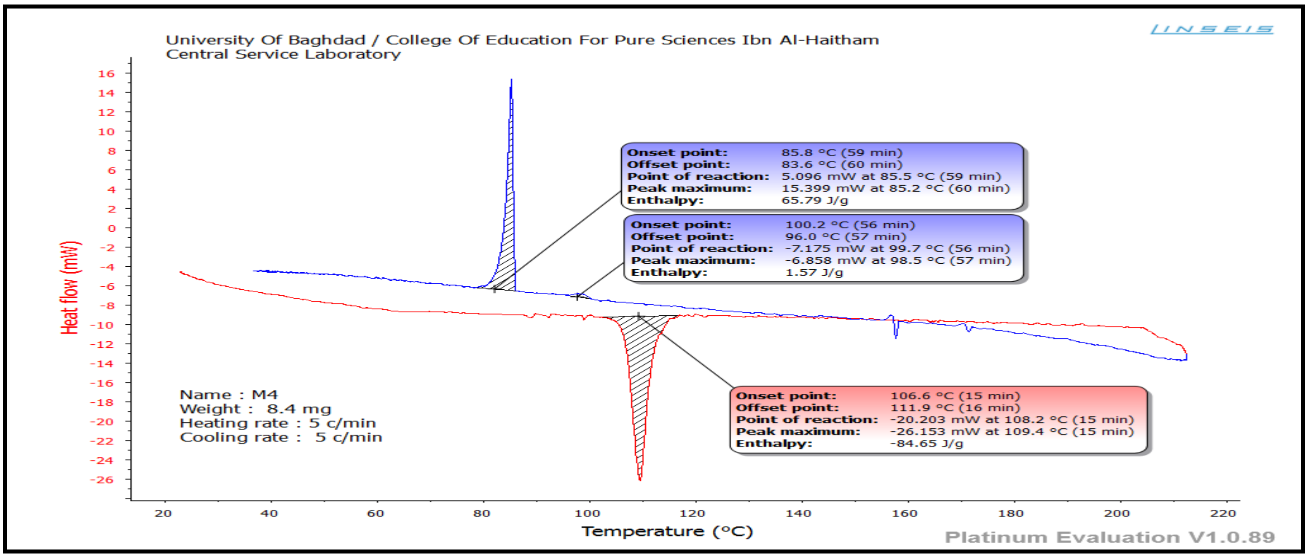


Image .5: POM of the compound C7(100 C^0) at cooling

4- the compound M4 N-(4-butoxybenzylidene)-4-methoxyaniline
The melting point to this compound was (112 C^0) .In DSC it shown us below :



Form .4: curve differential scanning Calorimeter compound M4

According to the DSC compound M4 gave mono tropic properties at cooling only, gave the liquid crystalline phase between the (100-83 C^0)

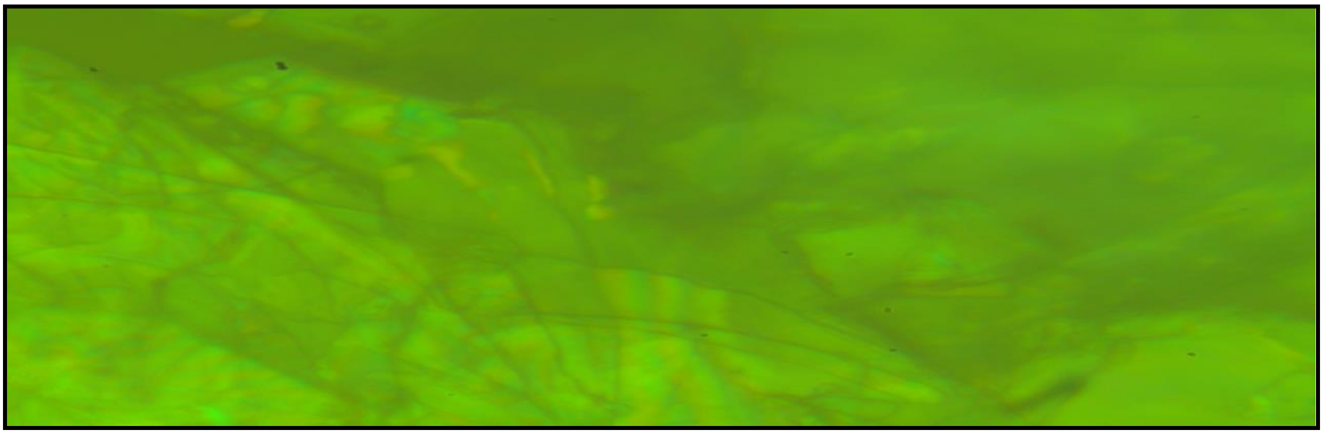
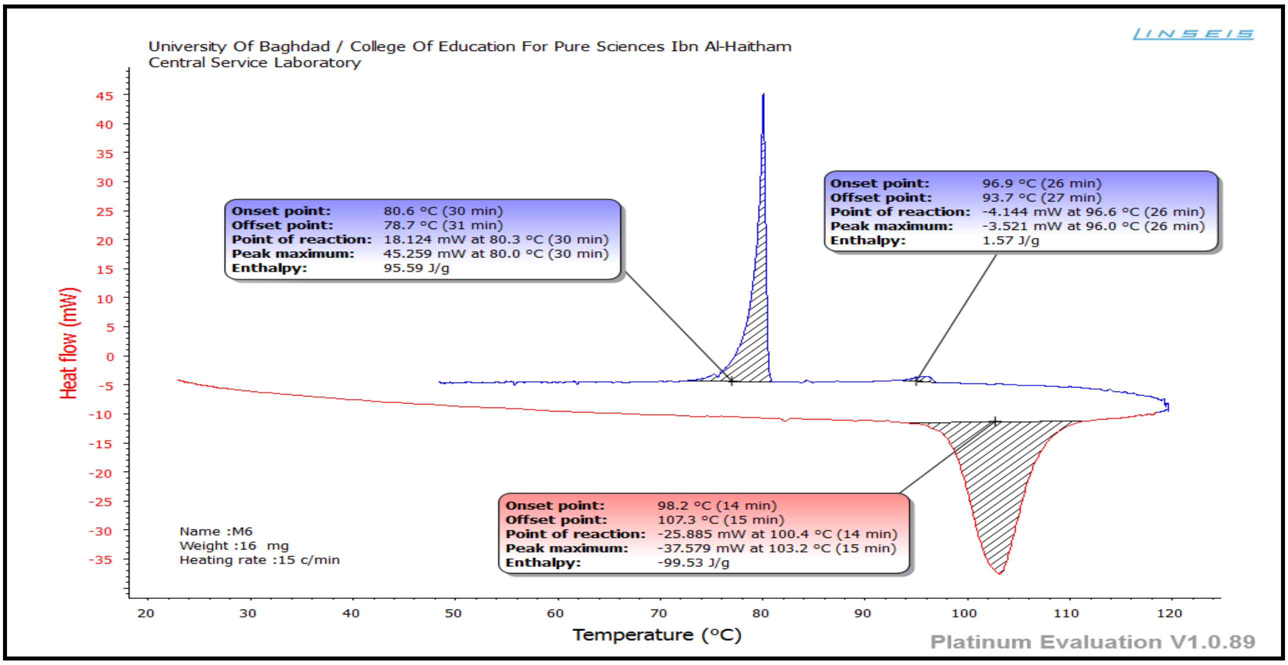


Image .6: POM of the compound M4(94 C^0) at cooling

5- the compound M6 N-(4-(hexyloxy)benzylidene)-4-methoxyaniline
The melting point to this compound was (103-104 C^0) .In DSC it shown us below :



Form .5: curve differential scanning Calorimeter compound M6

It showed a mono tropic properties according to the DSC where we see liquid crystal phase between (80-93C^0)

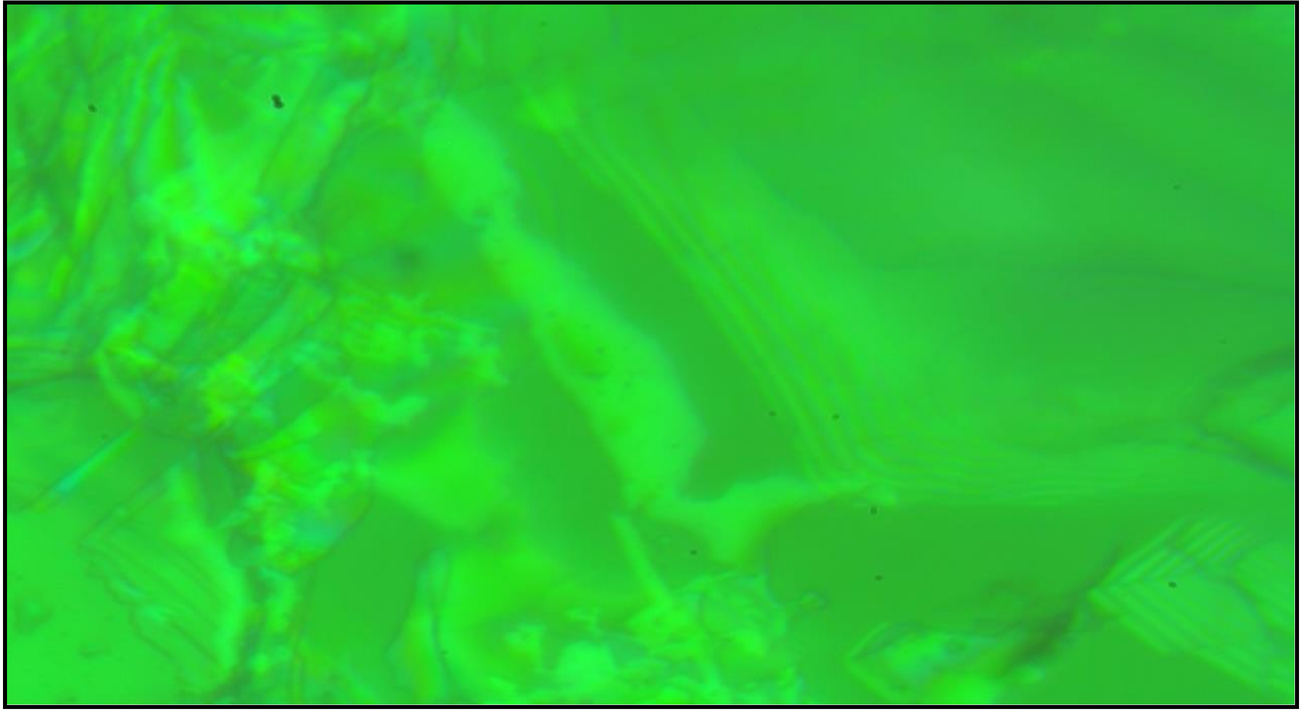


Image .7: POM of the compound M4 (83 C^0) at cooling

CONCLUSION

Polarized optical microscopy POM and differential scanning calorimetry DSC that showed a liquid crystal phase in the compounds that has odd number of carbon atoms in the terminal chain compounds in the first series.

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