



Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis of Organic Compounds and Study its liquid Crystalline Behavior

Ridha SH* and Hanoush DA

Department of Chemistry, Faculty of Education for Women., Iraq

ABSTRACT

This research describes liquid-crystalline polymorphism of two series of Schiff bases differ in the type of terminal group, where one of them has a carboxyl as terminal group while the other contains methoxy as a terminal group 4-(-alkoxybenzylideneamino) benzoic acid and 4-methoxy-N-(4-alkoxybenzylidene) aniline. Based on the polarized optical microscopy (POM) and the differential scanning calorimetry (DSC); Influence of the alkyl chain length (and the type of terminal group) on the type of mesophases and entropic effects of phase transition are discussed. Extraordinary results have been found and not expected, where five of the ten synthesis compound has a liquid-crystalline properties and the other not.

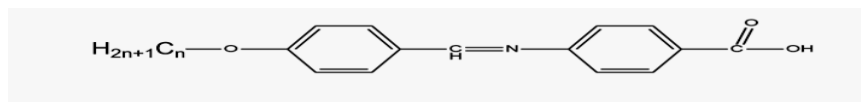
Keywords: Organic compounds; Schiff bases; Crystals

INTRODUCTION

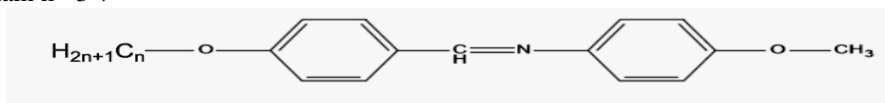
Schiff bases (azomethines) are one of the oldest groups of liquid crystals. Derivatives with the short alkyl chains (methyl and ethyl groups) were already synthesized at the beginning of the xx century. It is belong to the classic type of molecules with liquid-crystalline properties. This class of compounds is especially important, because many of them are acclaimed as the mesophase standards. Since the 1970s the series of 4-alkyloxybenzylidene-4-alkylanilines, showing very rich polymorphism, were extensively investigated, because many of them are acclaimed as the mesophase standards. Demus observed the presence of the six different mesophases in the 4-pentyloxybenzylidene-4-decylaniline (hexamorphism GBICAN type) [1] only derivatives with short alkyl chains were synthesized and mesophases were inaccurately assigned. In 2002 a preliminary article published describing a group of 11 homologous series (121 derivatives) of 4-alkyloxybenzylidene-4-alkyloxyanilines [2]. Solely on the basis on the observation of texture an influence of the length of both alkyloxy chains on the temperatures of phase transitions and the type of mesophase were discussed. In addition to the mentioned above Schiff bases, very interesting appear to be azomethines with both alkyloxy chains, but only compounds with short alkyloxy chain (until pentyloxy) were described in literature. We expect much more interesting liquid-crystalline polymorphism among molecules with longer alkyloxy chains.

The present paper reports data on two series of azomethines compounds, the first chain [C] 4-(-alkoxybenzylideneamino)benzoic acid, and the second chain [M] 4-methoxy-N-(4-alkoxybenzylidene) aniline (where alkoxy has a number of carbon atom from 3 to 7). 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. 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.

The first chain $n = 3-7$



The second chain $n = 3-7$



We Identification the compound by spectroscopy methods using infrared IR and nuclear magnetic resonance H NMR spectrum, besides elemental analysis that shows the exact chemical structure of the expected synthesized compounds. The liquid-crystalline behavior were study by POM and 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.

EXPERIMENTAL

Preparation of N- (4-hydroxyphenyl) actamide

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 H₂SO₄ acid concentration) 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]

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 H₂SO₄ acid 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 H₂SO₄ 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 % Na₂CO₃ solution and then with water, dried over anhydrous calcium chloride. it is used without further purification [6].

Preparation of N-(4-methoxyphenyl) actamide

(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 less volume of (~ 1.5mL) by stirred magnetic stirrer. A solution of appropriate methane bromide (0.025mol) in 12.5mL dissolved in added ethanol, The mixture heated by using appropriate condenser for more than one hour (then 6mL distilled water added and the product was washed recrystallize for ethanol, melting point (129C°) [7].

Prepare of 4-methoxy aniline

In conical flask 4 N- (actamide – 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 and the benzene was evaporated by rotary evaporator, the product has a melting point 58C° [5,6].

Prepare of 4-alkyloxy benzaldehyd

(3.77gm)(0.025mol,) of 4-hydroxy benzaldehyd 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 after that washed the extract with distilled water and the solvent was evaporated, the pure product was liquid yellow color [7].

Prepare of Schiff bases

We prepared two chain schiff bases

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

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

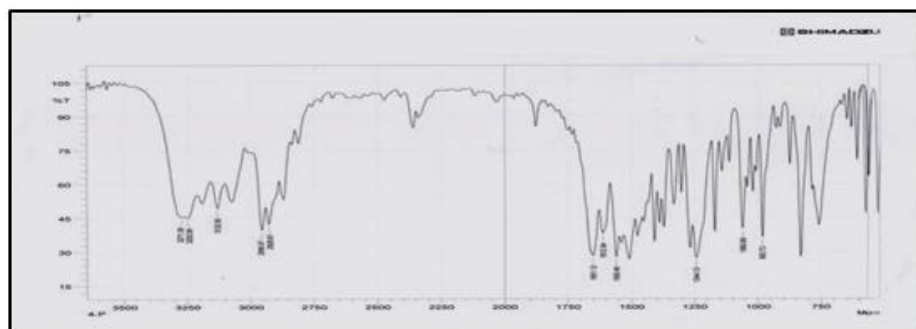


Figure 1: Infrared spectrum of the compound4-mehoxy actamide

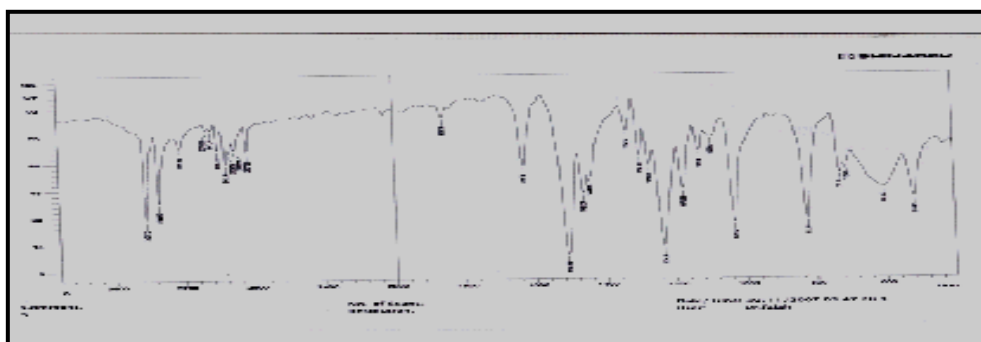


Figure 2: Infrared spectrum of the compound 4-alkoxy aniline

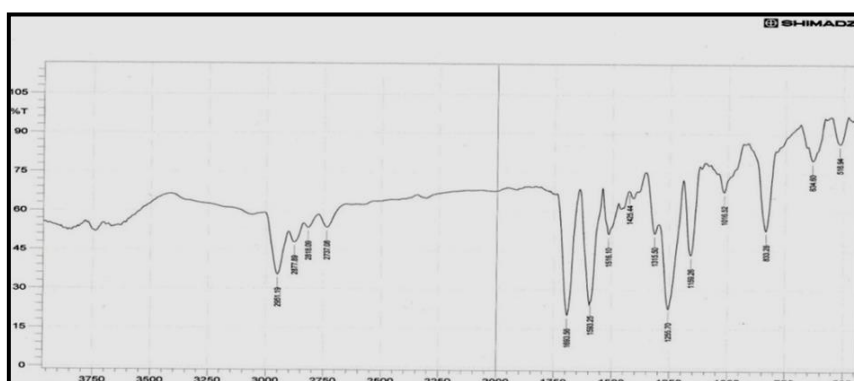


Figure 3: Infrared spectrum of the compound4-alkoxy banzaldehyd

Table 1: Chemical structures and melting point, color and yield of the prepared compounds

Seq.	Symbol of compound	color	m.p C°	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

RESULTS AND DISCUSSION

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.

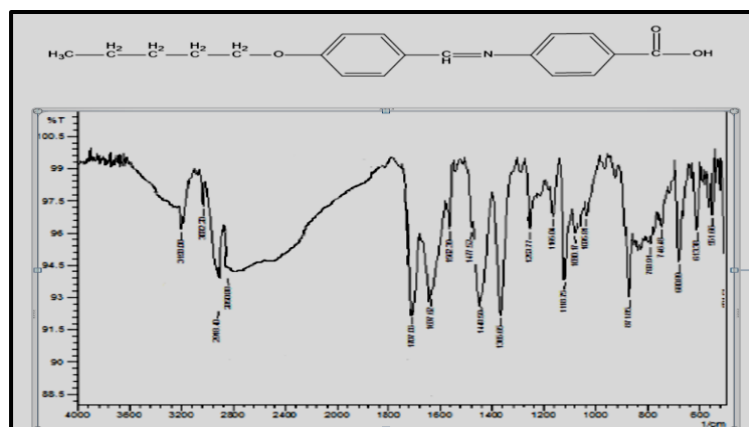


Figure 4 : Infrared spectrum of the compound C5

- absorption bands at 1118 due to a group -O-CH₂-CH₂
- absorption bands at 1618 due to imine group CH = N
- absorption bands at 1737 due to the carbonyl group carboxylic
- absorption bands at 2918 due to aliphatic CH
- absorption bands at 2600-3198 due to OH of the carbonyl
- absorption bands at 3032 due to aromatic CH

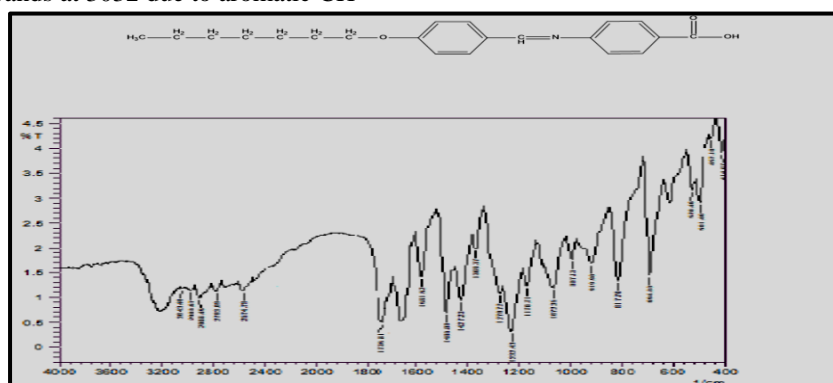


Figure 5 : Infrared spectrum of the compound C7

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

- absorption band at 1170 due to a group -O-CH₂-CH₂
- absorption band at 1630 belonged due to imine group CH = N
- absorption band at 1735 due to the carbonyl of carboxylic group
- absorption band at 2983 due to aliphatic CH
- Broadband absorption at 2574-3200 due to OH of Carbonyl group.
- absorption band at 3034 due to aromatic CH

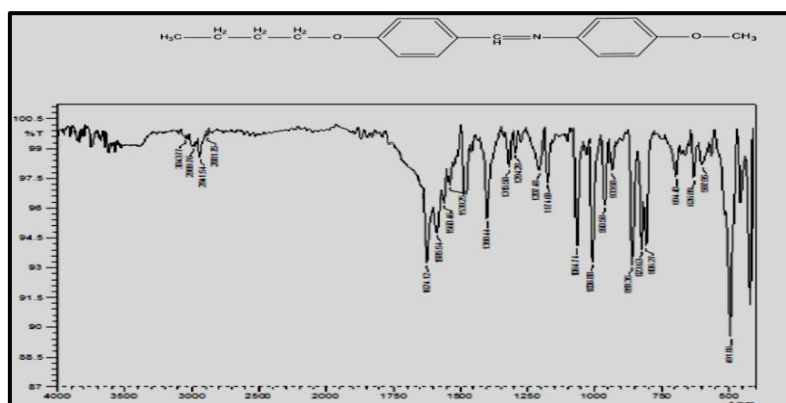


Figure 6 : Infrared spectrum of the compound M4

- absorption band at 1116 due to ether -O-CH₂-CH₂
- absorption band at 1154 due to ether -O- CH₃
- absorption band at 1624 due to imine group CH = N
- absorption band at 2968 due to aliphatic CH
- 5- absorption band at 3043 due to aromatic CH

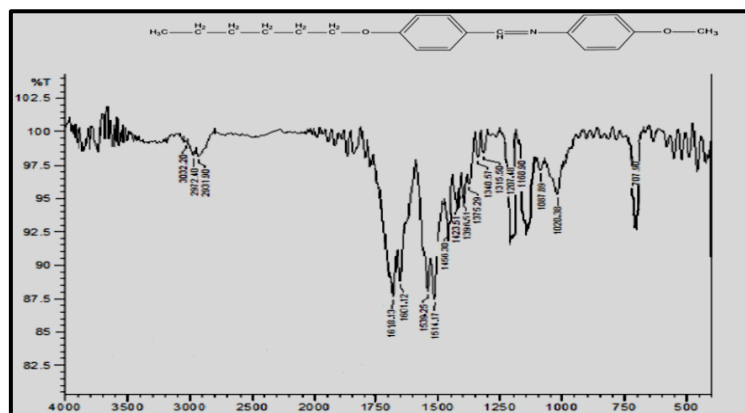


Figure 7: Infrared spectrum of the compound M6

- absorption band at 1168 due to ether -O-CH₂-CH₂
- absorption band at 1618 due to imine group CH = N
- absorption band at 1207 due to ether -O- CH₃
- absorption band at 2912 due to aliphatic CH
- 5- absorption band at 3032 due to aromatic CH

HNMR spectra

All peaks appeared in figures

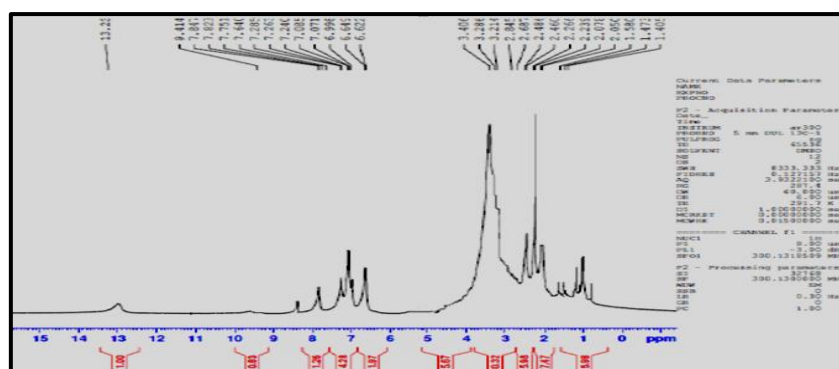


Figure 8: Nuclear magnetic resonance spectrum of the compound C5

- peaks at (0.90-1.80)ppm due to alkyl groups (CH₃CH₂ CH₂ CH₂)
- peaks at (6.2-5) ppm solvent due to DMSO-d
- peaks at (3-4) ppm solvent due to O-CH₂
- 4. peaks at (6.62-7.84)ppm due to phenyl ring
- peaks at (8.41)ppm due to (CH = N)

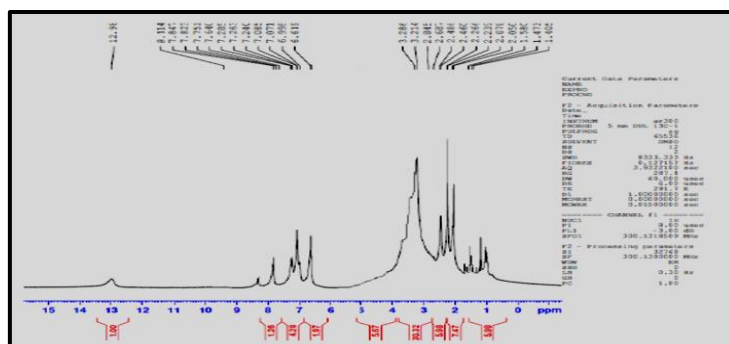


Figure 9: HNMR spectrum of the compound C7

- peaks at (0.90-1.50)ppm due to alkyl groups (CH₃CH₂ CH₂ CH₂)
- peaks at (2.5) ppm solvent due to DMSO-d
- peaks at (3:5) ppm solvent due to O-CH₂
- 4. peaks at (6.61-7.42)ppm due to phenyl ring
- peaks at (8. 11))ppm due to (CH = N)
- peaks at(12.98) ppm due to Carboxyl group

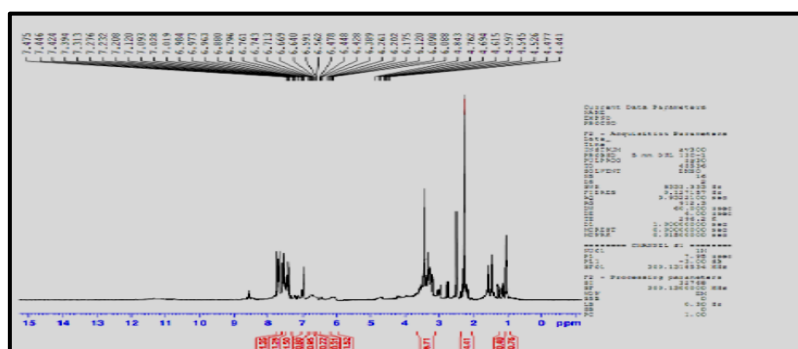


Figure 10: HNMR spectrum of the compound M4

- peaks at (0.90-1.70)ppm due to alkyl groups (CH₃ CH₂ CH₂)
- peaks at (2.5) ppm due to solvent DMSO-d
- peaks at (3:10) ppm due to O-CH₃
- 4-. peaks at (3.30-3.60) ppm due to OCH₂CH₂
- 5. peaks at (6.97-7.47)ppm due to phenyl ring
- 6. peaks at (8.55))ppm due to (CH = N)

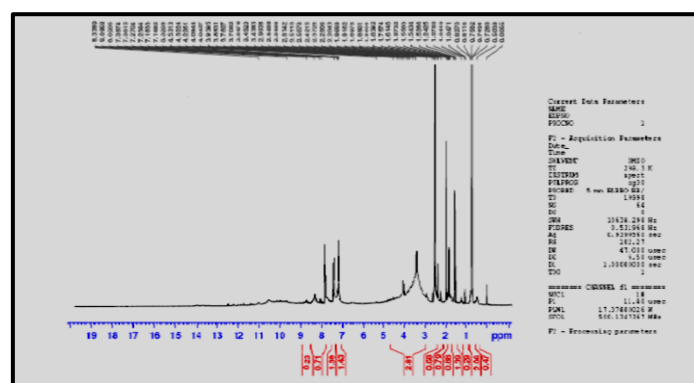


Figure 11: HNMR spectrum of the compound M6

- peaks at (0.74-2.42)ppm due to alkyl groups (CH₃CH₂CH₂CH₂CH₂-)
- peaks at (2.5) ppm due to solvent DMSO-d

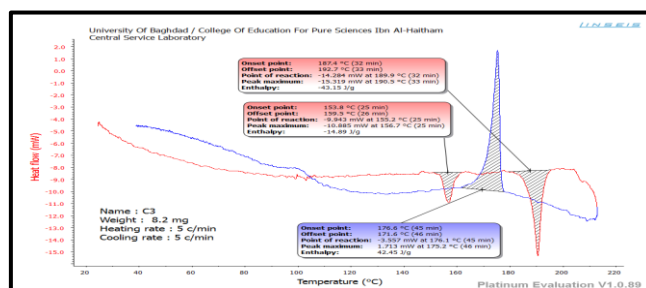
- peaks at (3:43) ppm due to O-CH₃
- peaks at 3.93 ppm due to OCH₂CH₂
- peaks at (7.16-7.39)ppm due to phenyl ring
- peaks at (8.30)ppm due to (CH = N)

RESULTS AND DISCUSSION

Determination of the transition temperatures of the two series prepared compounds:

All phase transition parameters were obtained from the the Polarization microscopy POM and Differential scanning calorimetry DSC. Both methods showed the same phase transition temperatures in the heating and cooling modes. The temperatures of melting point in both methods was approximate like the value of what has been measured by melting point device in the laboratory, and us below:

The compound C3 4-((4-propoxybenzylidene) amino) benzoic acid: The melting point to this compound was (190-193C⁰). In DSC it has 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 monotropic liquid crystalline properties at (160- 187 C⁰), as it is clear in the curve.

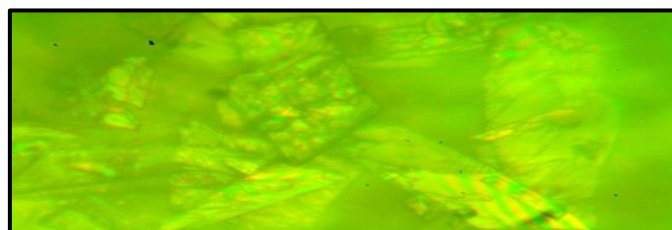
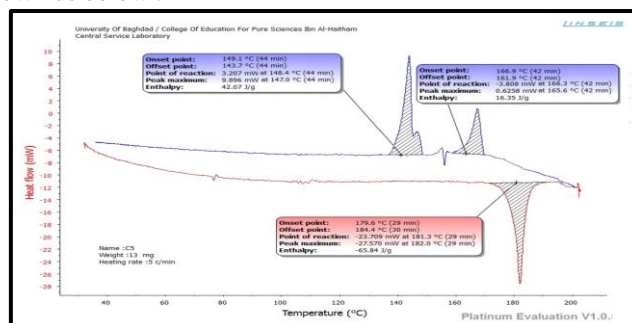


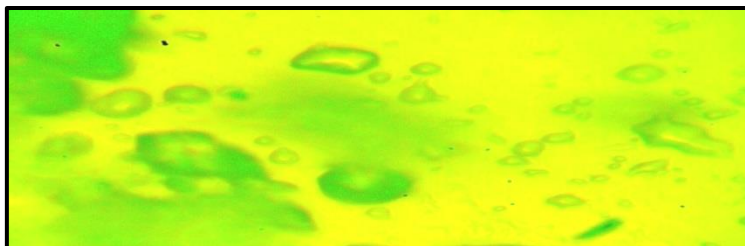
Image 1: POM of the compound C3 at 169 C⁰ at heating

The compound C54-((4-pentyloxy)benzylidene)aminobenzoic acid The melting point to this compound was (180-183C⁰). In DSC it shown us below :

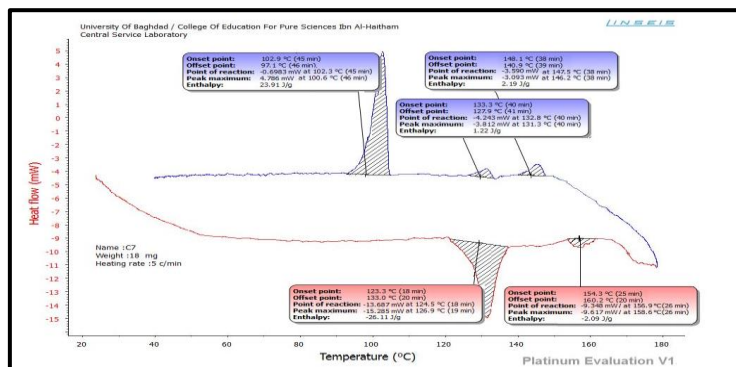


Form 2: curve differential scanning Calorimeter to compound C5

We note also the properties of monotropic liquid crystalline phase at cooling between (161-149C⁰), and in POM below we note a Nematic phase.

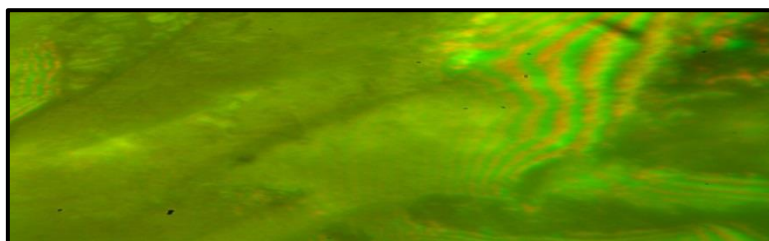
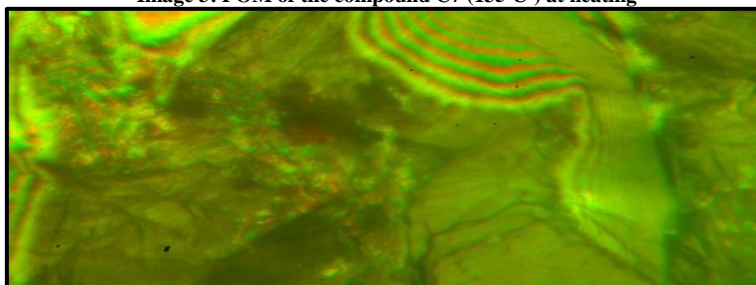
Image 2 : POM of the compound C5 154 C⁰ at cooling

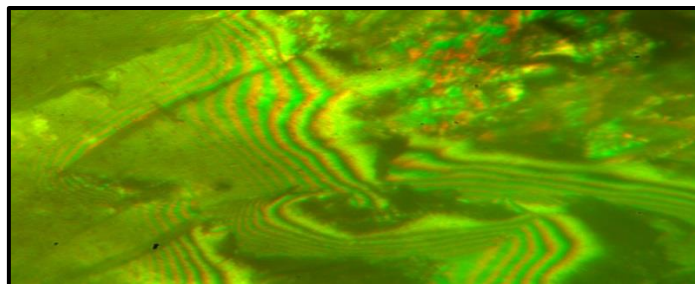
Compound C7 4-((4-heptyloxy)benzylidene)amino) benzoic acid: The melting point to this compound was (158-156C⁰). In DSC it shown us below



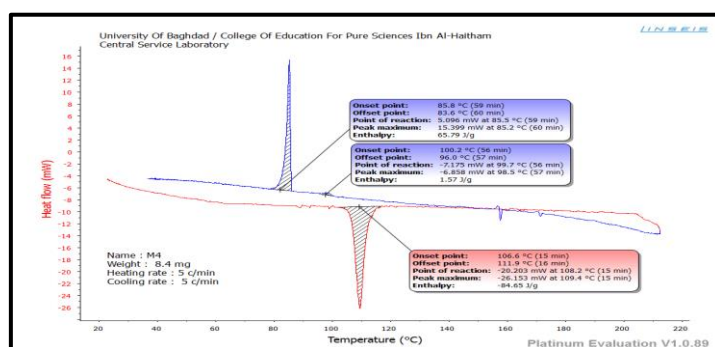
Form 3: curve differential scanning Calorimeter to compound C7

It gave the properties of liquid crystalline phases at heating and cooling (enantiotropic properties), it showed liquid crystalline phase at heating (130-154C⁰)

Image 3: POM of the compound C7 (135 C⁰) at heatingImage 4: POM of the compound C7 (131 C⁰) at cooling

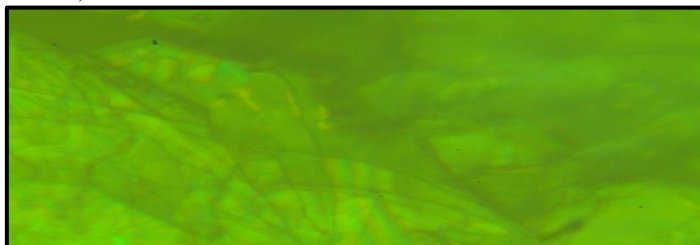
Image 5: POM of the compound C7(100 C⁰) at cooling

The compound M4 N-(4-butoxybenzylidene)-4-methoxyaniline: The melting point to this compound was (112 C⁰). In DSC it has shown us below:

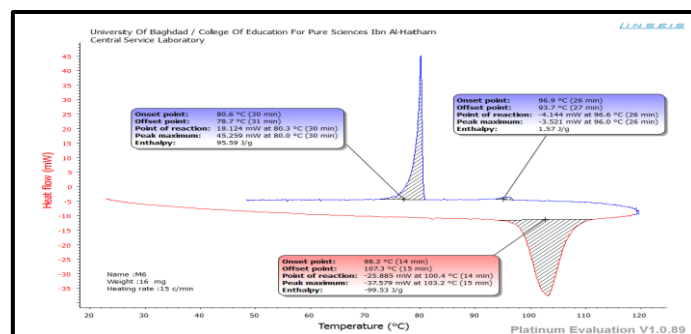


Form 4: curve differential scanning Calorimeter compound M4

According to the DSC compound M4 gave monotropic properties at cooling only. gave the liquid crystalline phase between the (100-83 C⁰)

Image 6: POM of the compound M4 (94 C⁰) at cooling

The compound M6 N-(4-(hexyloxy)benzylidene)-4-methoxyaniline: The melting point to this compound was (103-104 C⁰). In DSC it shown us below:



Form 5: curve differential scanning Calorimeter compound M6

It showed a monotropic properties according to the DSC where we see liquid crystal phase between (80-93C⁰)

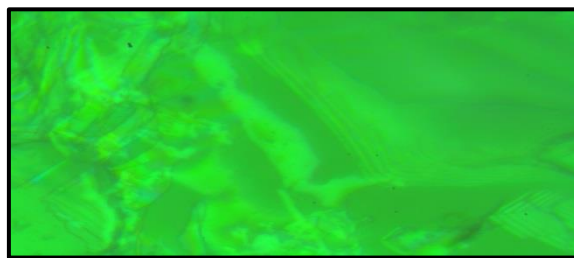


Image 7: POM of the compound M4 (83 C⁰) at cooling

REFERENCES

- [1] O Lehmann. *Ber* **1908**, 41, 3774
- [2] W Maier; A Saupe. *Z Naturforsch A (in German)* **1958**, 13, 564-566
- [3] GW Gray. *The Chemistry of Liquid Crystal*, Philosophical transaction of the society of London, **1983**, series A, Ch.1:77.
- [4] STLK Ong; ST Ong; GY Yeapand; JPW Wong. *Chin Chem Lett*, **2009**, 20, 767-770
- [5] AS Travis. *Chemistry of Anilines*, **2007**.
- [6] AI Vogel, *Practical Organic Chem*. Longman, 5th Edition, London, **1989**.
- [7] GW Gray; M Hird; DL Acq; KI Toyne. *Mol Cryst Liq Cryst*, **1989**, 172, 165
- [8] GG Mohamed; MM Omar; AM Hindy . *Turk J Chem* **2006**, 30, 361- 382