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Research Article

PREPARATION AND STUDY THE BEHAVIOR OF THE LIQUID CRYSTALLINE PHASES OF TWO SERIES OF SCHIFF'S BASE COMPOUNDS AND USING MIXTURE METHOD TO IDENTIFY THE SMECTIC PHASE

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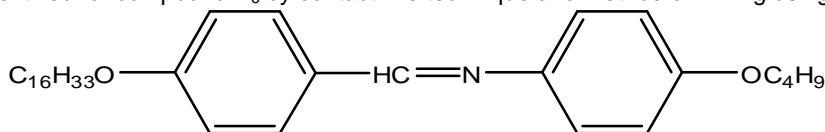
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Abstract

Two series were prepared 4-(alkoxy)-N-(4-(heptyloxybenzylidene) aniline (7BAn) and N-(4-alkoxybenzylidene)-4-(heptyloxy aniline) (nBA7) the compounds have been identified spectrally (FT-IR, HNMR), and(elemental analysis CHN) the mesomorphic phases were identified by polarized light microscope and measured transition temperatures for compounds in addition to the Differential Scanning Calorimeter (DSC) and when we draw transition temperatures against the number of Carbons atoms for each series it was found the odd-even effect of crystalline phase to smectic phase then to nematic phase then to isotropic phase , and when comparing the liquid crystal behavior for two series it was found that the series (7BAn) all compound exhibit smectic phase in addition to the nematic phase except compound (n = 4) did not show smectic phase, while the series (nBA7) only two compounds show smectic phase (n = 6,7) in addition to the nematic phase.

The smectic phase was identified for compound A₆ by contact line technique and method of mixing using the reference material:



4-butoxy-*N*-(4-(hexadecyloxy)benzylidene)aniline

Containing smectic C phase and it was found homogeneity when mixing the two compounds reference and unknowns by observing the mixture under the Polarizing Optical Microscope which indicates that the phase of the unknown is the smectic C phase and when we draw transition temperatures for the binary mixture it was reached Minimal point (Eutectic) at transitional 63C ° at 62% concentration For references substance

Keywords: 4-(alkoxy)-N-(4-(heptyloxybenzylidene) aniline, FT-IR, HNMR, smectic phase

Introduction

With development of liquid crystal science and technology, more mesogens have been prepared and studied. Thermotropic liquid crystal is one of type of mesogens currently extensively studied^(1, 2). 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. Schiff base, also known as imine (CH=N), is a linking group

used to connect between core groups. It provides a stepped core structure but still maintained the molecular linearity in order to exhibit higher stability and form mesophases⁽³⁾. Extensive studies on Schiff base core system had been conducted ever since discovery of MBBA showing nematic phase at room temperature⁽⁴⁾. In this continuation studies, Schiff base and alkoxy terminal moieties are incorporated into a new series of homologous compounds, 4-(alkoxy)-N-(4-(heptyloxy benzylidene) aniline N-(4-alkoxybenzylidene)-4-(heptyloxy aniline). 7BAn, nBA7. FT-IR, ¹H NMR, and

elemental analysis were employed to elucidate the molecular structure of the title compounds whereas the liquid crystal behaviors were determined by DSC, POM analysis. The mesomorphic behaviors of homologous compounds are rationalized based on the changing of alkyl length chain.

Experimental

Preparation of N- (4-hydroxyphenyl) actamide

In a beaker containing 500ml of distilled water, 18.3 mL of concentration hydrochloric acid and , (0.22mol, 23.98 gm) of pure para-amino phenol were introduced. 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) actamide was filtered with suction washed with a little distilled water ,and dried upon filter paper in air melting point was (169-170) C^{o(5,6)}.

Preparation of 4- N (actamide - alkyloxy phenyl)

To (3.75gm, 0.025mol) of 4- actamide phenol dissolved 15mL of ethanol in a conical flask was added potassium hydroxide solution (1.85gm, 0.033mol), in a least volume of (~ 1.5mL) by stirred magnetic stirrer then a solution of appropriate Alkyl bromide (0.025mol) in 12.5mL dissolved in added ethanol, the was heated mixture using appropriate condenser for more then one hour (then 6mL distilled water added and the product was washed recrystallize for ethanol, melting point (113-114C^o), ⁽⁷⁾.

Preparation of 4-alkyloxy aniline

In conical flask 4 N- (actamide - alkyloxy phenyl) (0.025mol), in (12.5ml) was added ethanol, (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 rotatory evaporator the product is liquid red color, ^(5,6).

Preparation 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 (~ 1.5 mL) 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 then one hour. 6mL of water was added to mixture and then the product was extracted by petroleum ether and then washed the extract with distilled water and the solvent was evaporated, the pure product was liquid yellow color ⁽⁷⁾.

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 . (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. ⁽⁸⁾.

Preparation of Schiff bases:-

(0.0004 mol) of 4-alkyloxy aniline dissolved in absolute ethanol with the equal moles number of 4-alkyloxy benzaldehyd dissolved in less of absolute ethanol with three drops of glacial acetic acid and heated the mixture was 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 as follows ⁽⁹⁾
A3 four times , A4 three times , A5 three times , A6 three times , A7-7 twice , B3 four times , B4 three times , B5 three times , B6 three times ., figures (1-4), Table(1).

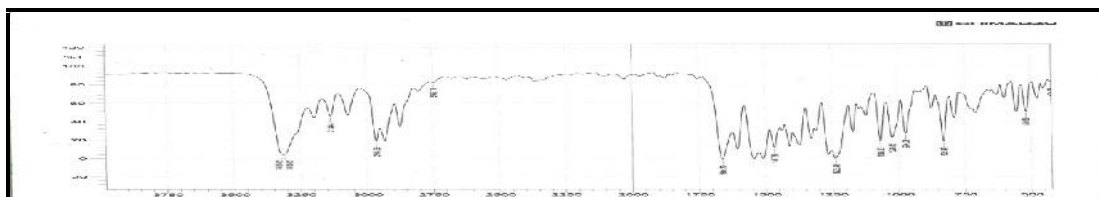


Figure (1) infrared spectrum of the compound 4-alkoxy actamide

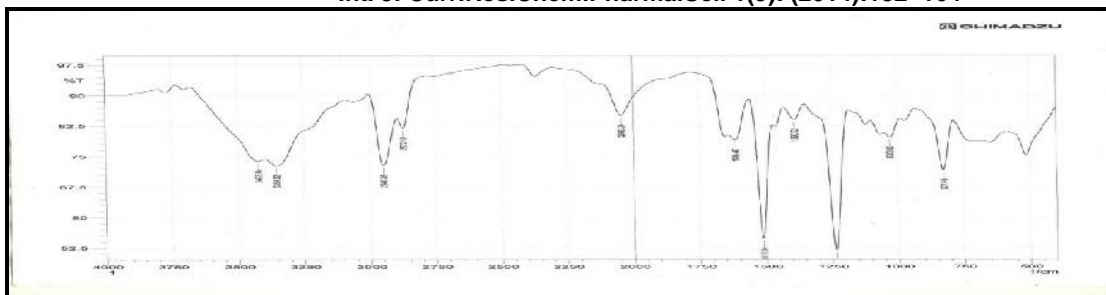


Figure (2) infrared spectrum of the compound 4-alkoxy aniline

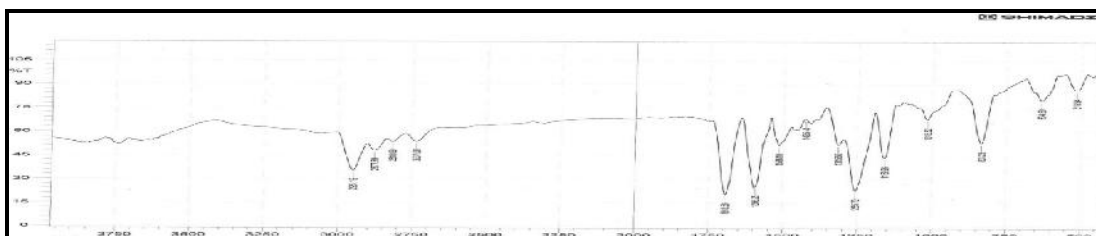


Figure (3) infrared spectrum of the compound 4-alkoxy benzaldehyde

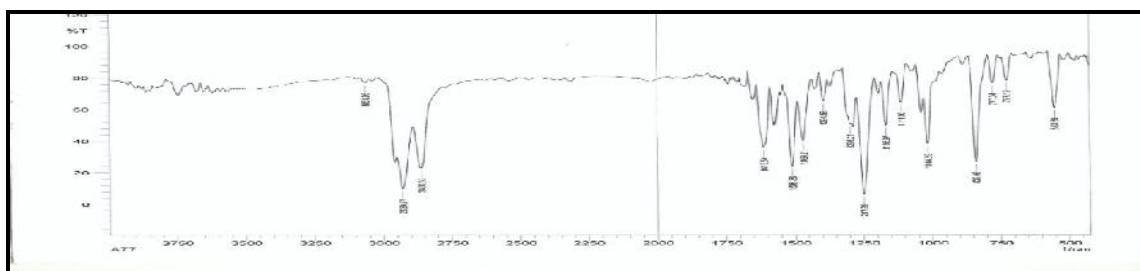
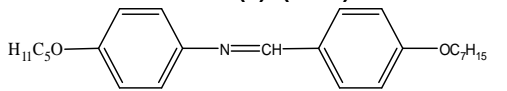
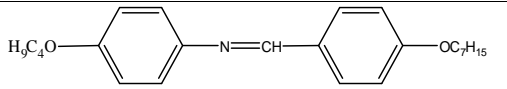
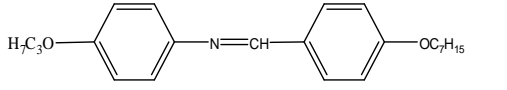
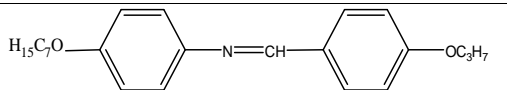
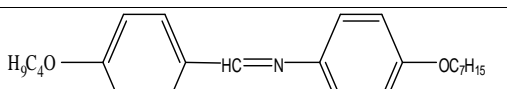
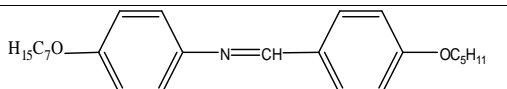
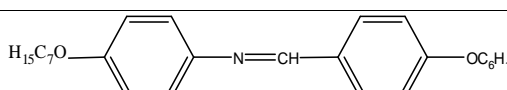


Figure (4) infrared spectrum of the compound A77

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 %
1	A ₇₇	yellow conqueror	107C°		77%
2	A ₆	Yellow conqueror	102C°		76%
3	A ₅	Blanch	83C°		74%

					
4	A ₄	Blanch	105C°		65%
5	A ₃	Blanch	94C°		52%
6	B ₃	Blanch	73C°		46%
7	B ₄	Blanch	102C°		62%
8	B ₅	Blanch	91C°		67%
9	B ₆	Yellow	103C°		71%

Results and Discussion

Identification of Prepared compounds:-
(C.H.N) -Analysis:-all data in table (2).

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

Compound Symbol	Positivism Formula	M.W	Calc./found		
			C%	H%	N%
A ₄	C ₂₄ H ₃₃ NO ₂	367.53	78.15 78.205	8.84 8.723	3.96 3.548
A ₆	C ₂₆ H ₃₇ NO ₂	395.58	78.94 78.677	9.43 9.214	3.54 3.326
A ₇₇	C ₂₇ H ₃₉ NO ₂	409.60	79.17 79.032	9.60 9.396	3.42 3.217
B ₆	C ₂₆ H ₃₇ NO ₂	395.58	78.94 78.693	9.43 9.244	3.54 3.301

FT-IR-spectra shown absorption bands in all compounds ($1600-1620\text{cm}^{-1}$) due to (C=C) belong to phenyl ring ,bands (9-11) at ($1500-1650\text{ cm}^{-1}$) belong to(C=N)group ,other bands (12-14) at ($1240-1250\text{ cm}^{-1}$) belong to(O-C-O) ,figures (5-11).

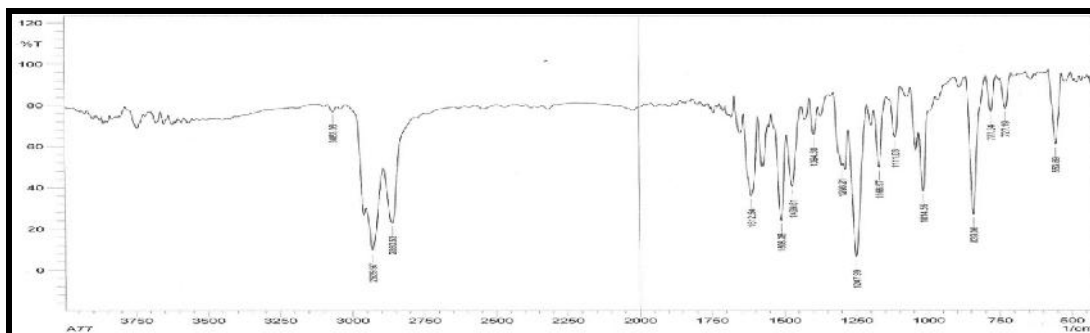


Figure (5) infrared spectrum of the compound A₇₇

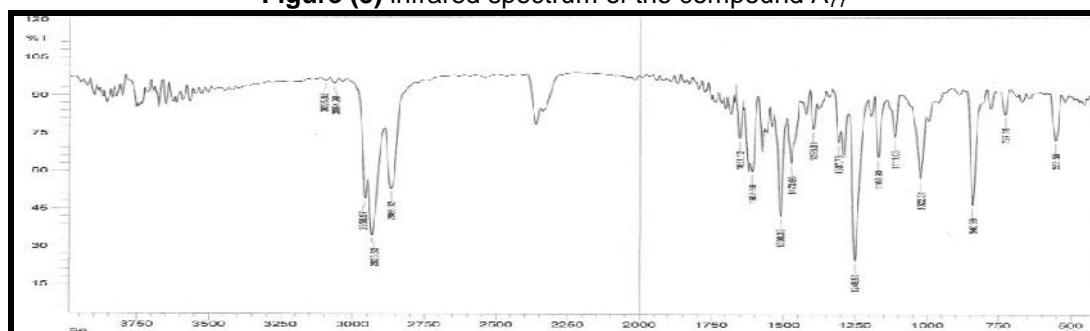


Figure (6) infrared spectrum of the compound B₆

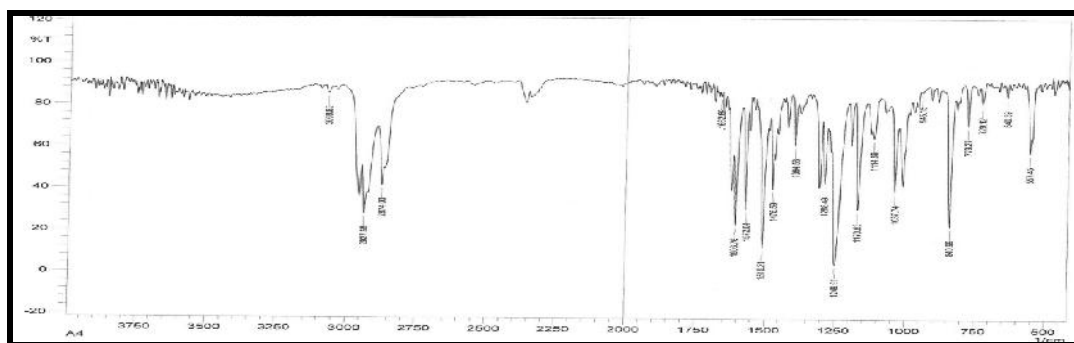


Figure (7) infrared spectrum of the compound A₄

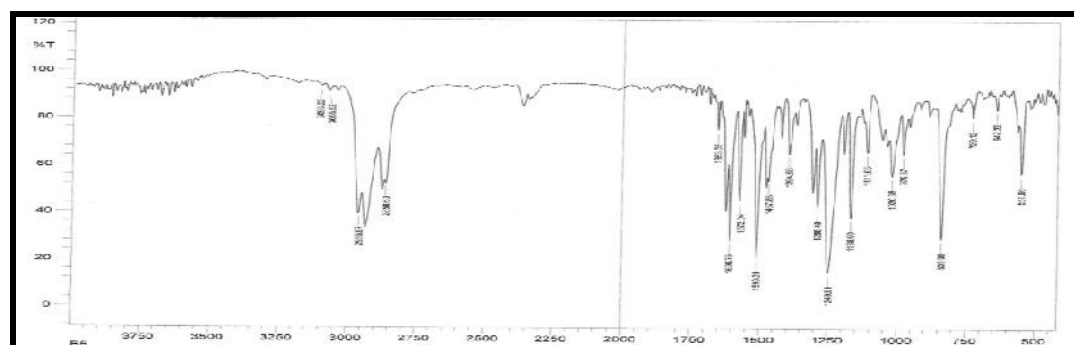


Figure (8) infrared spectrum of the compound B₅

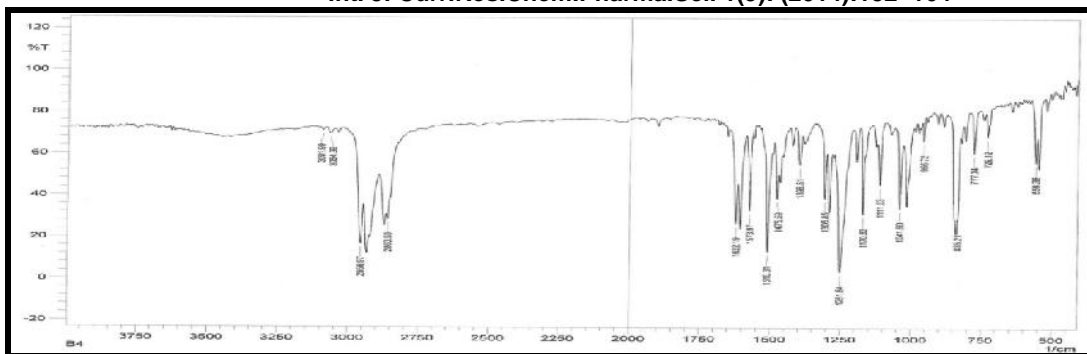


Figure (9) infrared spectrum of the compound B4

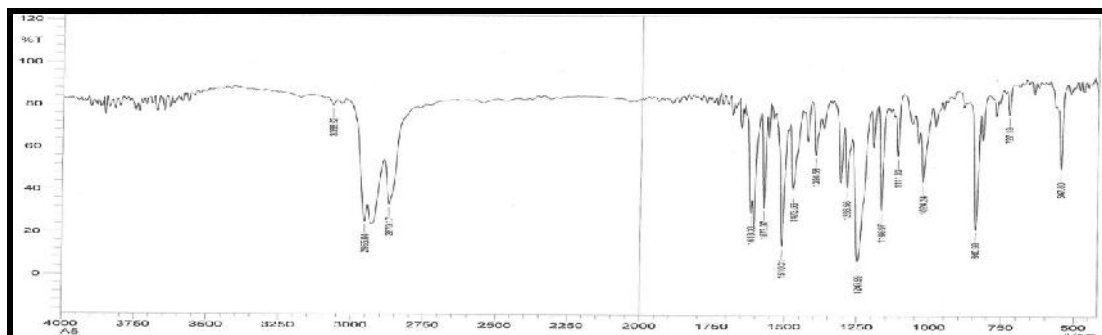


Figure (9) infrared spectrum of the compound A5

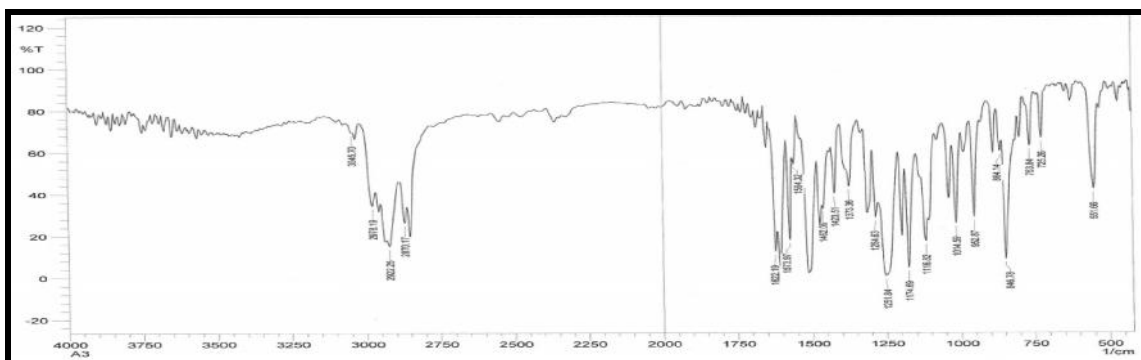


Figure (10) infrared spectrum of the compound A3

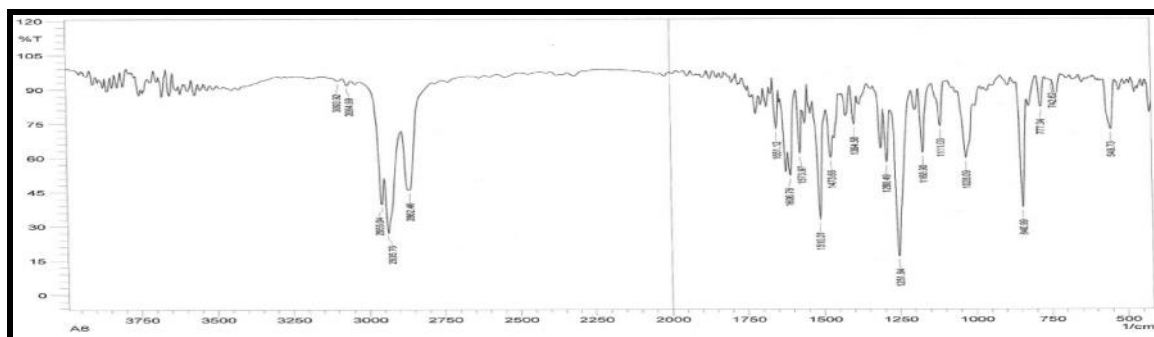


Figure (11) infrared spectrum of the compound A6

¹HNMR spectra of five compounds show peaks at (8.505) ppm for all compounds due to (-CH=N-) (11-14) peaks at (0.85-1.71) ppm due to methyl and methylene., peaks at (3.9-4.01) ppm due to (-OCH₂) , and other peaks (12-14) are shown in figures (12-15) .

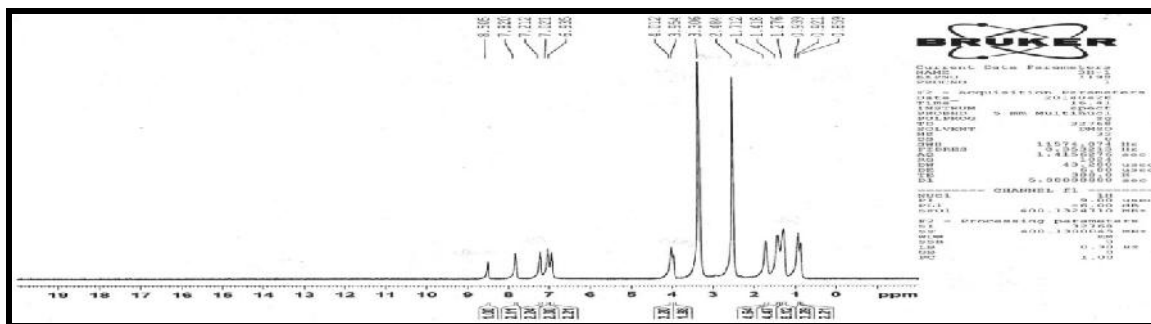


Figure (12), nuclear magnetic resonance spectrum of the compound A4

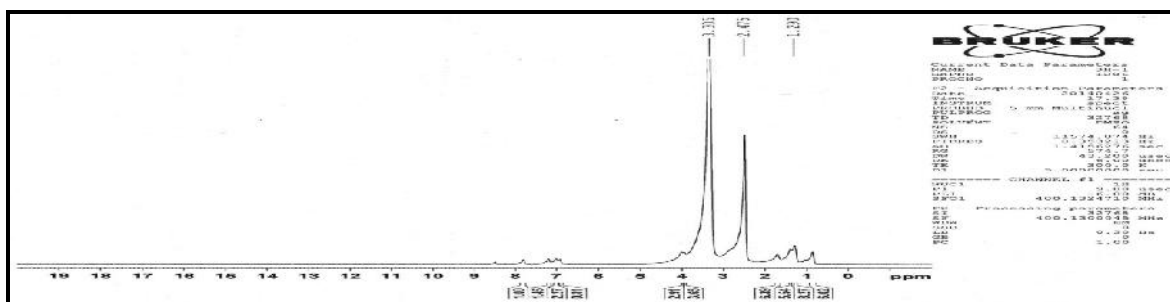


Figure (13) HNMR spectrum of the compound A6

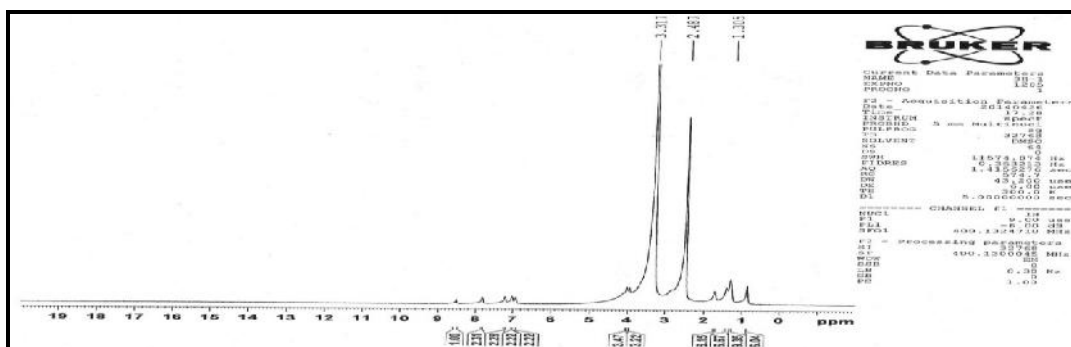


Figure (14) HNMR spectrum of the compound B6

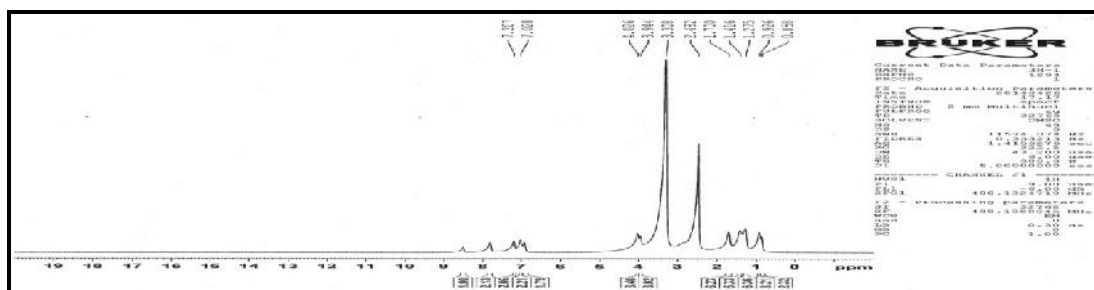


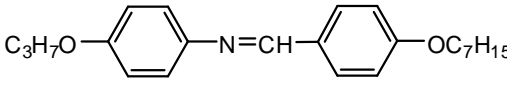
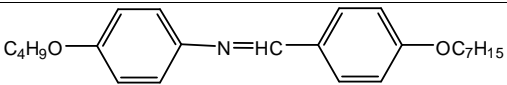
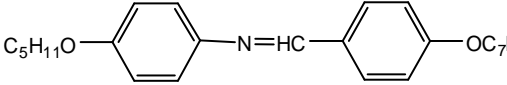
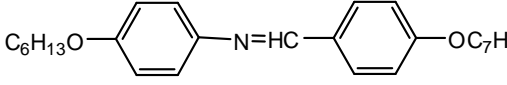
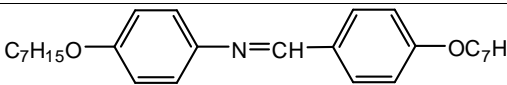
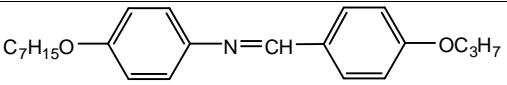
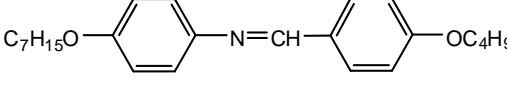
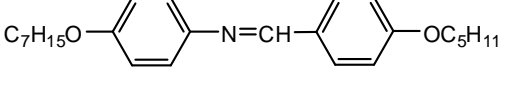
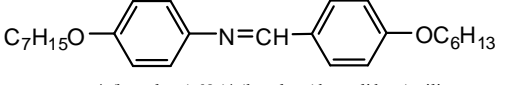
Figure (15) HNMR spectrum of the compound B4

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).

The compounds (A_{77} , B_3 , A_3) transition from crystalline phase to nematic liquid crystalline phase then to isotropic phase, (B_6 , A_6) showed transition of the crystalline phase to smectic liquid crystalline phase and then to isotropic phase, and the compounds (A_4 , B_4 , B_5) showed transition of the crystalline phase to nematic liquid crystalline phase only then to isotropic phase, and finally compound (A_5) showed transition to the unknown smectic liquid crystalline phase then to nematic liquid crystalline phase and then to the isotropic phase.

Table (3) shows the transition temperatures of the prepared compounds

Transition temperature C° M.p Sx N I	Name and structure	Compound
61.42 / 72.56	 <i>N</i> -(4-(heptyloxy)benzylidene)-4-propoxyaniline	A_3
93.24 / 102.8 /	 4-butoxy- <i>N</i> -(4-(heptyloxy)benzylidene)aniline	A_4
87.32 / 78.44	 <i>N</i> -(4-(heptyloxy)benzylidene)-4-(pentyloxy)aniline	A_5
93.9S / 110.34	 <i>N</i> -(4-(heptyloxy)benzylidene)-4-(hexyloxy)aniline	A_6
93.4 / 99.9	 4-(heptyloxy)- <i>N</i> -(4-(heptyloxy)benzylidene)aniline	A_{77}
65.12 / 73.52	 4-(heptyloxy)- <i>N</i> -(4-propoxybenzylidene)aniline	B_3
102.86 / 87.32	 <i>N</i> -(4-butoxybenzylidene)-4-(heptyloxy)aniline	B_4
78.4 / 83.62	 4-(heptyloxy)- <i>N</i> -(4-(pentyloxy)benzylidene)aniline	B_5
93.98 S → I	 4-(heptyloxy)- <i>N</i> -(4-(hexyloxy)benzylidene)aniline	B_6

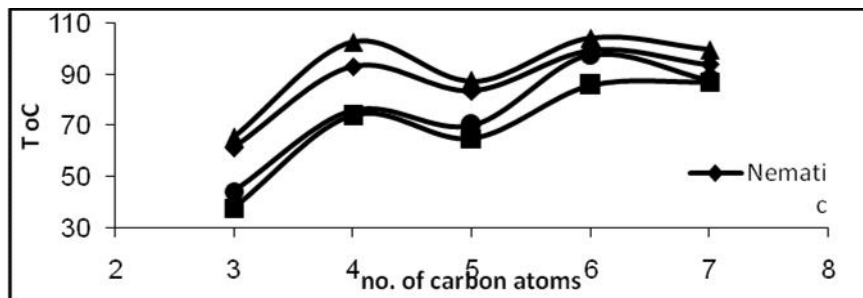


Figure (16) the relationship between temperature and the number of carbon atoms of the series N-(4-heptyloxybenzylidene)-4-(alkoxy)aniline (7B An) I

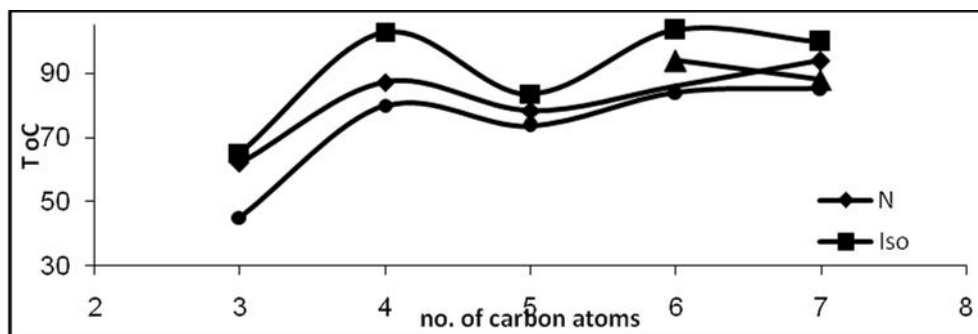


Figure (18) the relationship between temperature and the number of carbon atoms of the series. (4-(alkoxy)-N-(4-(heptyloxybenzylidene)aniline) (nB7A) II

From (Figure 17) for the series (I) the odd-even effect with transitional temperatures from crystalline phase to smectic liquid crystalline phase then to nematic liquid crystalline phase and then to isotropic phase, the compound with number $n = \text{even}$ of carbon atoms the transition temperature is higher than the compound with number $n = \text{odd}$ of carbon atoms,

figure (18) for the series II. Note that the transition temperature from the crystalline phase to nematic liquid crystalline phase then to the isotropic phase is also shows the odd-even effect, it was found the compound $n = \text{odd}$ number of carbon atoms is a temperature less than the compound with $n = \text{even}$ number of carbon atoms.



Image (1) cooling transformation from I to N (homotropic) of the compound A_3 at 56.24°C

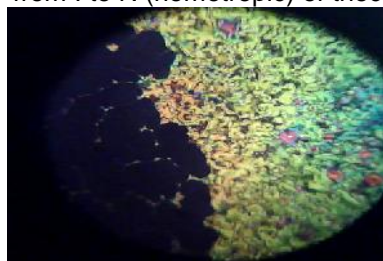


Image (2) phase transition N to N (homotropic) for compound A_4 at 93.24°C

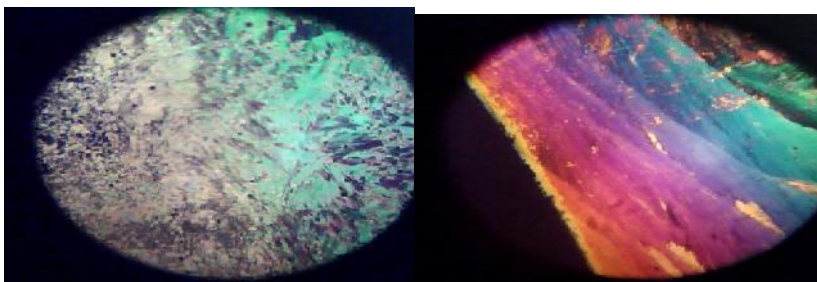


Image (3) compound A₅ Image (4) for compound A₇₇
 Transition of Sxat transition phase I to the N
 N-phase 74C ° at 99.9C °

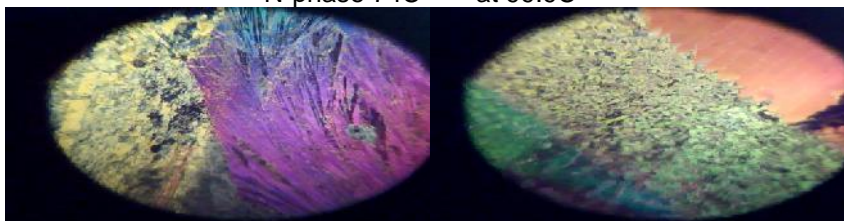
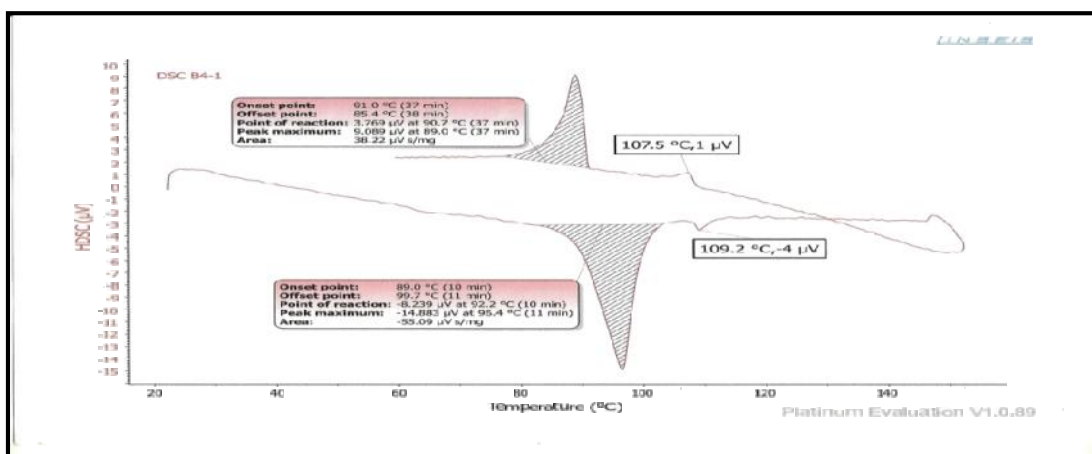
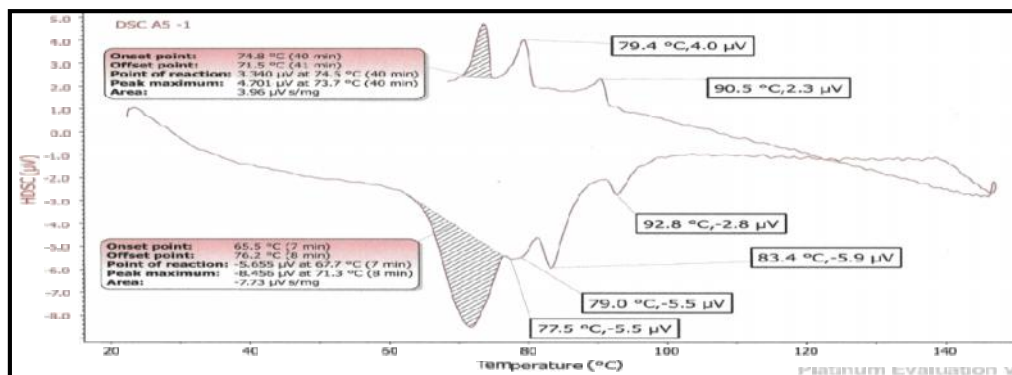


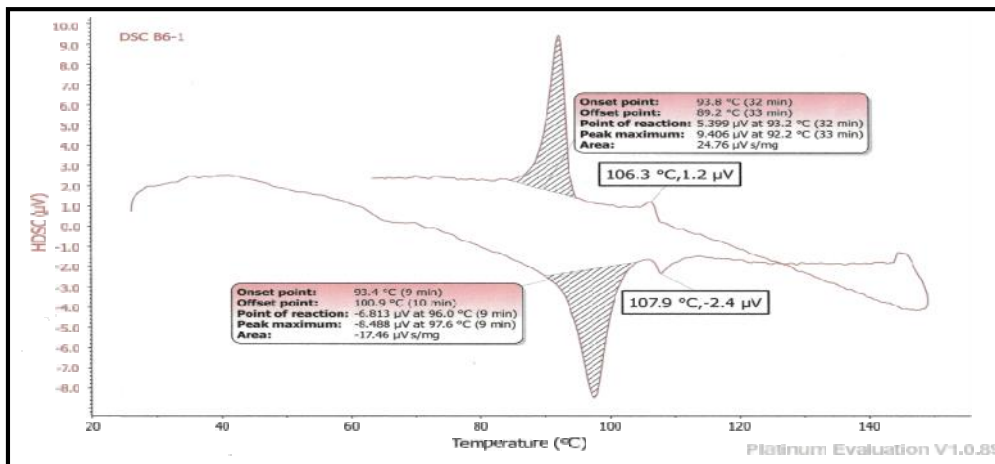
Image (5) of the compound A₆ Image (6) cooling transition from Sx to Scat 94.96 C° from N to Sx to Cr at 87.3C °



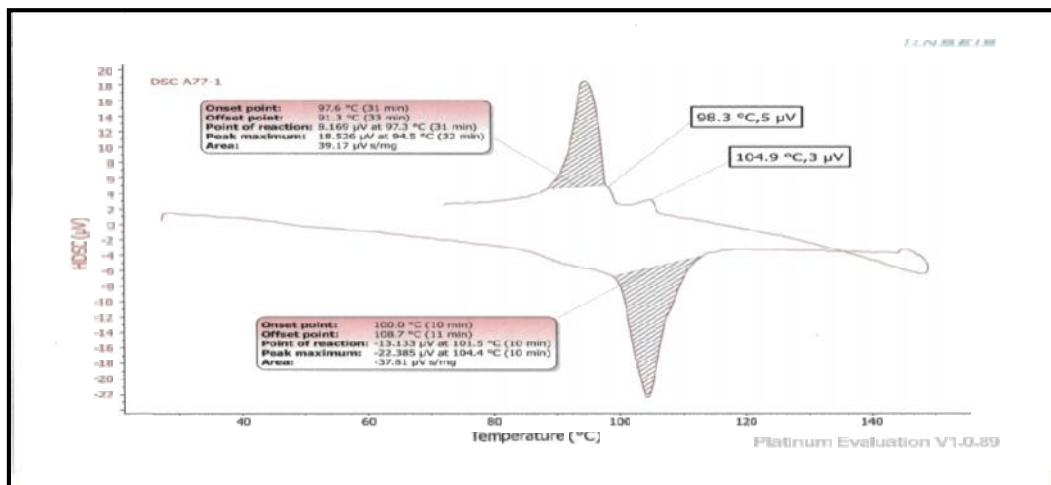
Form (1) curve differential scanning Calorimeter compound A₅



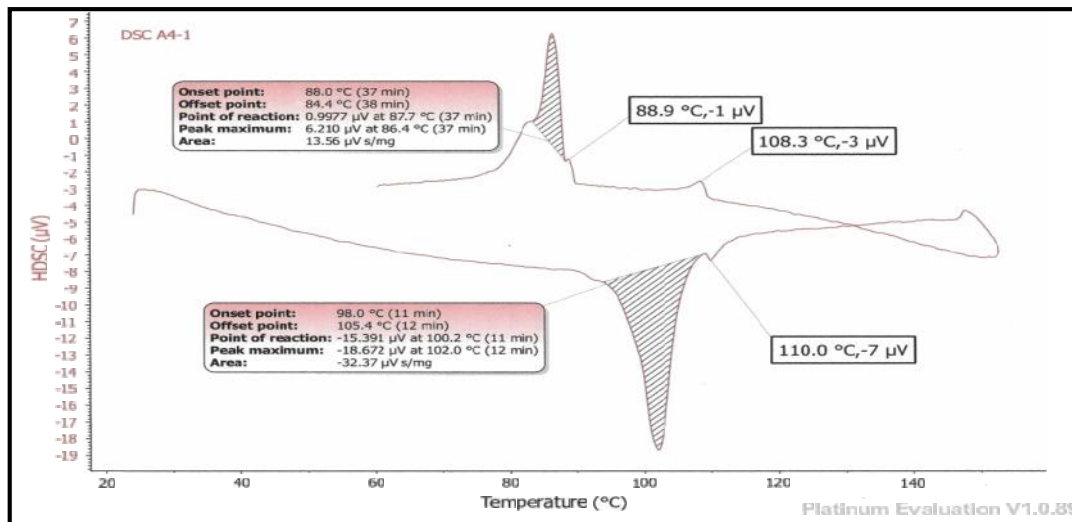
Form (2) curve differential scanning Calorimeter compound B6



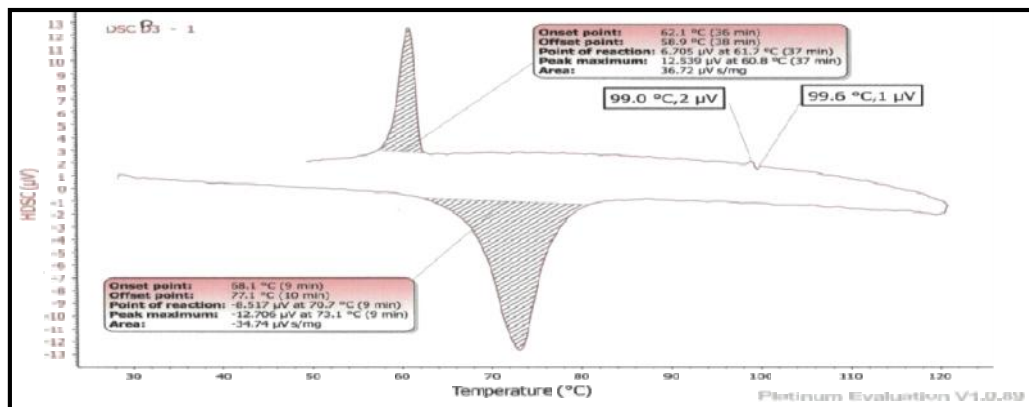
Form (3) curve differential scanning Calorimeter compound B6



Form (4) curve differential scanning Calorimeter compound B₄



Form (5) curve differential scanning Calorimeter compound A₄

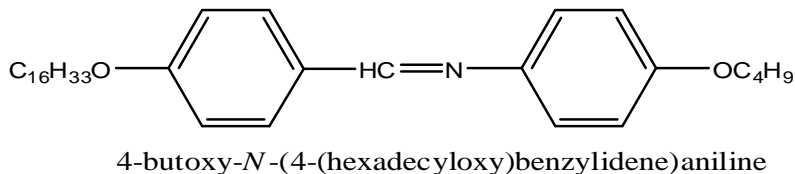


Form (6) curve differential scanning Calorimeter compound B₃

Identification of smectic phase

Using mixture method to identify the smectic phase that showed in compound (A₆) N-(4-heptyloxy benzylidene)-4-(hexyloxy) aniline (B) with reference compound 4-butoxy-N-(4-(hexadecyloxy) benzylidene)aniline (A), taking mol fractions of different values of noting the phases (Cr, Sc, N, I), mixture A:

with compound (B), it was content of phases (Cr, Sx, N, I), using binary system method between compounds A and B, the mixture showed homogeneous in all phases between two compounds A and B, which mean the compound B contain the smectic C (Sx) in different texture, the Eutectic point appeared of 62-63 °C at 63% concentration of compound A, shown in figure (19)



B:

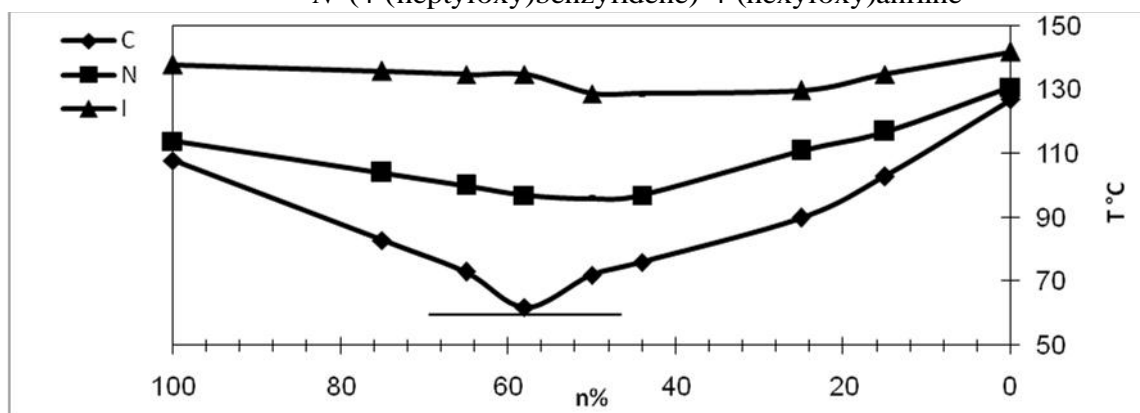
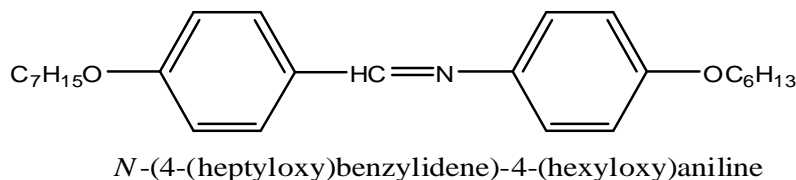


Figure (19) transition temperature of mixture A and B.

4-butoxy-N-(4-(hexadecyloxy)benzylidene)aniline A:
 N-(4-(heptyloxy)benzylidene)-4-(hexyloxy)aniline : B

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