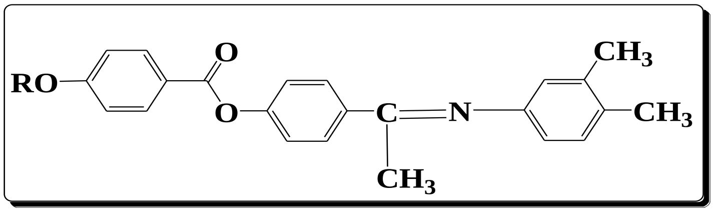
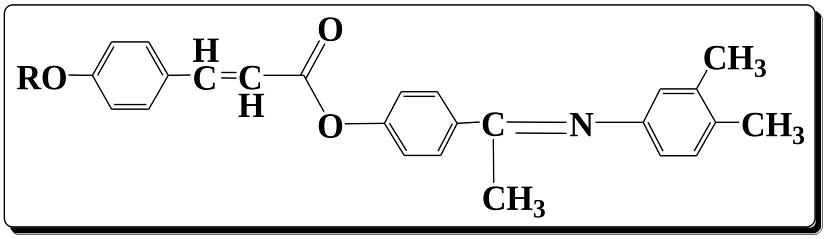
4.1 Introduction

Molecular structure of an organic compound is one of the most responsible factors for its mesomorphic behavior [409]. Liquid crystalline compounds with different central linkages; most of these central linkages are ester, chalcone, azo, or azomethine are known [412, 417-419, 442–448]. Central linkages in the molecular constitution of mesogenic compound play effective role in exhibition of their mesogenic properties. A survey of the literature indicates that mesogens having ethylideneamino central linkages are comparatively less explored [449–451]. Thus, in order to understand the co-relation between mesomorphic properties and structural variation of the mesogens, two new homologous series with ester and ethylideneamino central linkages having methyl group as terminal and lateral substituents are synthesized and their mesomorphic properties are studied. Both the series are compared with each other and with structurally related series. The general molecular structure is as follows:



…………….Series VIII



…………….Series IX

R = C_nH_{2n+1} n = 1 to 8, 10,12,14,16

4.2 Experimental

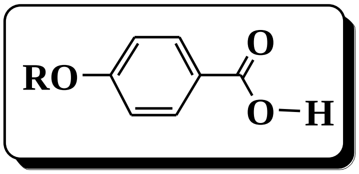
4.2.1 Materials

(1) 4-hydroxybenzoicacid, (2) 4-hydroxybenzaldehyde, (3) *n*-alkyl halides, (4) phenol, (5) 3,4-dimethyl aniline, (6) Glacial Acetic acid, (7) n,n–dimethylaminopyridine (DMAP), (8) n,n–dicyclohexylcarbodiimede (DCC) and all other chemicals are of Loba chemie or Merck used as received.

4.2.2 Synthesis

4.2.2.1 4-(4’-*n*-alkoxybenzoyloxy)-phenylethylidene-3”, 4”-dimethylanilines

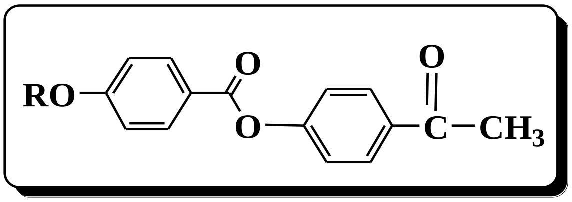
4.2.2.1a 4-*n*-alkoxybenzoic acids



They are synthesized following the procedure reported in 3.2.2.1a [433].

4.2.2.1b 4-(4’-*n*-alkoxybenzoyloxy)-acetophenones

General molecular structure of 4–(4’-*n*-alkoxybenzoyloxy)-acetophenones.

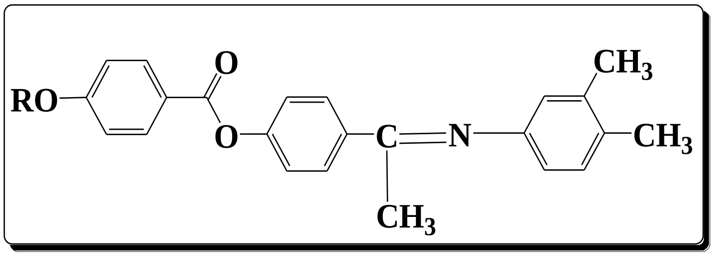


R = C_nH_{2n+1} n = 1 to 8, 10,12,14,16

They are prepared by esterification of the appropriate 4-n-alkoxybenzoic acids with p-hydroxyacetophenone following the similar method reported in step 3.2.2.4d**.** The compounds are recrystallized from methanol until constant transition temperatures are obtained [450, 452].

4.2.2.1c 4-(4’-*n*-alkoxybenzoyloxy)-phenylethylidene-3”, 4”-dimethylanilines

General molecular structure



R = C_nH_{2n+1} n = 1 to 8, 10,12,14,16.

They are synthesized by taking equimolar quantities of appropriate 4-(4’-*n*-alkoxybenzoyloxy)-acetophenone and 3,4-dimethylaniline in minimum quantity of ethanol with a few drops of glacial acetic acid and refluxing it on water bath for a period of 6 - 8 hours. The products are filtered, dried and recrystallized from acetone till constant transition temperatures are obtained. They are recorded in Table 4.1. The elemental analysis of some molecules is done and found is to be satisfactory and is recorded in Table 4.2.

4.2.2.2 *trans*-4-(4’-*n*-alkoxycinnamoyloxy)-phenylethylidene-3”, 4”-dimethylanilines

4.2.2.2a 4-*n*-alkoxybenzaldehydes

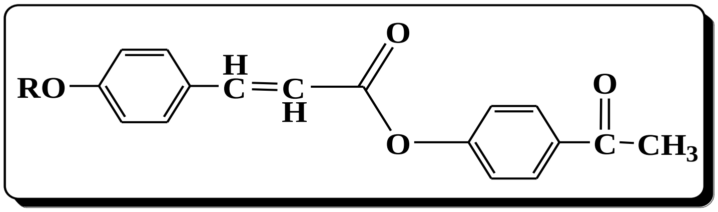
They are synthesized following the procedure reported in 3.2.2.4a [439].

4.2.2.2b *trans*-4-*n*-alkoxycinnamic acids

They are synthesized following the procedure reported in 3.2.2.4b [439].

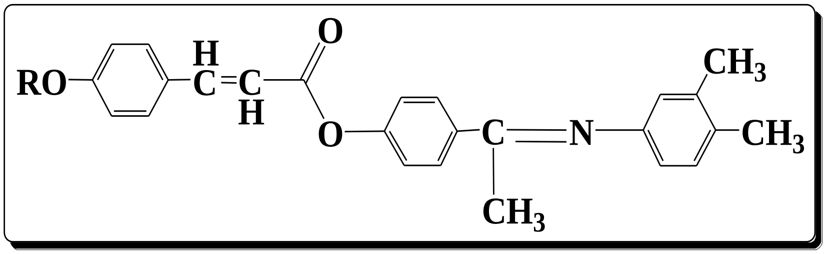
4.2.2.1c *trans*-4-(4’-*n*-alkoxycinnamoyloxy)-acetophenones

They are synthesized following the procedure reported in 3.2.2.4d [450, 452].



4.2.2.1d *trans*-4-(4'-*n*-alkoxycinnamoyloxy)-phenylethylidene-3", 4"-dimethylanilines

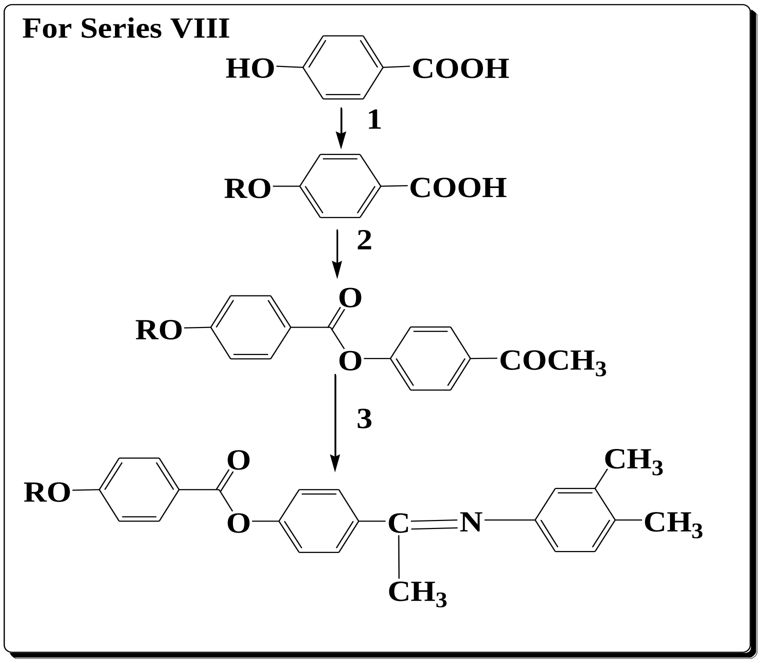
General molecular structure of the series VIII *trans*-4-(4'-*n*-alkoxycinnamoyloxy)-phenylethylidene-3", 4"-dimethylanilines



R = C_nH_{2n+1} n = 1 to 8, 10,12,14,16.

They are synthesized following the procedure reported in 4.2.2.1c [453]. The products are filtered, dried and recrystallized from acetone constant transition temperatures are obtained. They are recorded in Table 4.3. The elemental analysis of all compounds is found to be satisfactory and is recorded in Table 4.4.

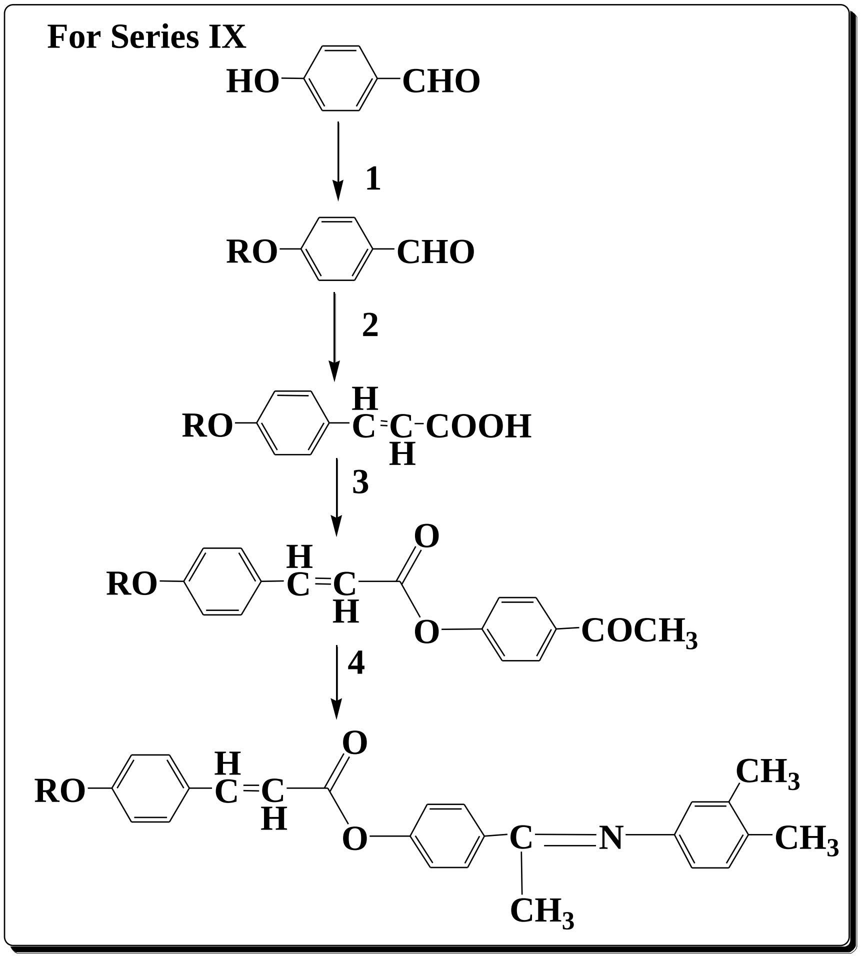
The synthetic route of series VIII and IX is shown in scheme 4.1.



Scheme 4.1: Synthetic route for series VIII

R = C_nH_{2n+1} n = 1to 8, 10,12,14,16.

(1) Alcohol, KOH, *n*-RBr, (2) DCC, DMAP, DCM, 4- Hydroxy acetophenone Stirred for Overnight Stirred for 12 hr, (3) Ethanol, 3, 4- dimethyl aniline, 1-2 drops Gla. Acetic acid.



Scheme 4.2: Synthetic route for series IX

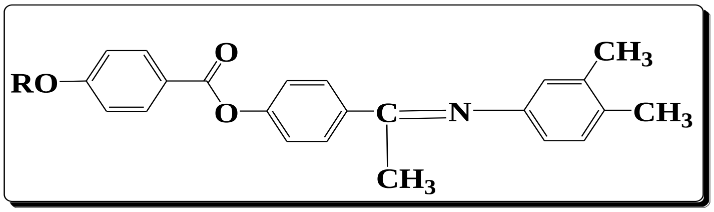
R = C_nH_{2n+1} n = 1to 8, 10,12,14,16.

(1) Anhyd. Potassium Carbonate, Dry Acetone, appropriate *n*-RBr, Reflux7-8 hr, (2) Malonic Acid,Dry Pyridine, Piperidine,Reflux 6-8 hr, (3) DCC, DMAP, DCM, 4- Hydroxy acetophenone , Stirred for Overnight Stirred for 12 hr, (4) Ethanol, 3,4- dimethyl aniline, 1-2 drops Gla. Acetic acid.

4.2.3 Characterization

Elemental analysis of some of the homologues are performed on Perkin Elmer Series II 2400-CHN analyzer, electronic spectra are recorded on a Shimadzu UV-2450 UV- visible spectrometer, IR spectra are recorded on a Perkin Elmer GX-FTIR, ^{1}H NMR spectra are measured on a Bruker Avance II- 400 spectrometer. Mass spectra are recorded on Thermo scientific DSQ II mass spectrometer. Transition temperatures and textures of the mesophases are studied using Leitz Laborlux 12 POL polarising microscope provided with a kofler heating stage. DSC are performed on a Mettler Toledo Star SW 7.01

Table 4.1: Transition Temperatures: Series VIII: 4-(4’-*n*-alkoxybenzoyloxy)-phenylethylidene-3”, 4”-dimethylanilines



R = *n*-Alkyl group	**Transition Temperature ºC**		
	Smectic A	**Nematic**	**Isotropic**
Methyl	--	--	163
Ethyl	--	--	138
Propyl	--	--	135
Butyl	--	--	109
Pentyl	--	--	98
Hexyl	--	--	95
Heptyl	--	(50)	89
Octyl	--	73	92
Decyl	--	71	89
Dodecyl	--	75	89
Tetradecyl	--	84	96
Hexadecyl	87	91	104

()* Value in parentheses indicates monotropic transitions

Table 4.2: Elemental Analysis

Series	Homologue	Theoretical			Practical		
		C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
VIII	C7	78.74	7.71	3.06	78.20	7.49	3.08
VIII	C16	80.23	9.15	2.40	80.15	9.02	2.49

FTIR (KBr pellets, cm^{-1})

Heptyl homologue : 2925 – 2858 (–C–H St, Alkyl $–CH_3$, SP^3 hybridization), 1734 (–C=O- St. of ester), 1606 (–C–H st of –C=N– St.), 1517 – 1479 (–C=C– St. of Aromatic ring), 1469 (–C–H bending of $–CH_2–$), 1262 (Aromatic ether St.),1172 (–C=N– St.), 1075(–C–O– St. of ester), 878 (strong –C–H– bending for 1:2:4 tri substituted benzene ring), 759 (weak –C–H– bending for – $(CH_2)_7$–).

Hexadecyl homologue: 2925 – 2858 (–C–H St, Alkyl CH_3, SP^3 hybridization), 1734 (–C=O– St. of ester), 1606 (–C–H st of –C=N– St.), 1517 – 1479 (–C=C– St. of Aromatic ring), 1469 (–C–H bending of $–CH_2–$), 1262 (Aromatic ether St.), 1172 (–C=N– St.), 1075(–C–O– St. of ester), 878 (strong –C–H– bending for 1:2:4 tri substituted benzene ring), 759 (weak –C–H– bending for – $(CH_2)_7$–).

^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm, standard TMS)

Heptyl homologue: δ = 0.90 (t, 3H, $–CH_3$), 1.29-1.57 (m, 8H, 4($–CH_2–$)), 1.78 (s, 6H, Ar–CH_3), 1.85 (Qunt, 2H, -$OCCH_2$), 2.61 (s, 3H, $–CH_3$ of ethylideneamino), 4.05 (t, 2H, $–OCH_2$), 6.95–8.15 (m, 10H, Ar–H)

Hexadecyl homologue: δ = 0.88 (t, 3H, $–CH_3$), 1.26–1.54 (m, 26H, 13($–CH_2–$)), 1.77 (s, 6H, Ar–CH_3), 1.82 (Qunt, 2H, -$OCCH_2$), 2.62 (s, 3H, $–CH_3$ of ethylideneamino), 4.04 (t, 2H, $–OCH_2$), 6.93–8.15 (m, 10H, Ar–H)

Mass Spectra: MS m/z:

Heptyl Homologue: Theoratical Mass value: 457.26 g/mol

Practical mass value: MS m/z: 457.60 (M^+)

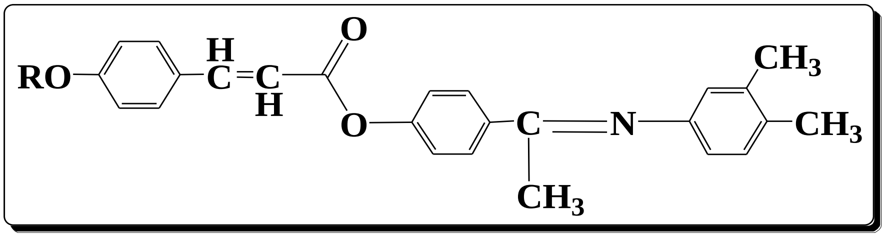
Table 4.3: DSC Data

Series	Member	Heating rate ºC/min	Transition Temperature ºC	ΔH=J/g	ΔS=J/g.K
VIII	C16	10	Cr – Sm 87.31 Sm – N 92.92 N – I 102.36	26.45 12.19 1.68	0.0734 0.0333 0.0044

Table 4.4: UV Data

Series	Homologue	UV λ max values nm (solvent – ethyl acetate)	
		π → π*	**n → π***
VIII	C7	265	315
	C12	265	315

Table 4.5: Transition Temperatures Series IX: 4-(4’-*n*-alkoxycinnamoyloxy)-phenylethylidene-3”, 4”-dimethylanilines



R = *n*-Alkyl group	Transition Temperature ºC		
	Smectic A	Nematic	Isotropic
Methyl	--	--	178
Ethyl	--	--	173
Propyl	--	--	164
Butyl	--	--	159
Pentyl	--	102	157
Hexyl	--	99	152
Heptyl	--	97	146
Octyl	--	95	140
Decyl	--	90	124
Dodecyl	--	88	116
Tetradecyl	83	90	109
Hexadecyl	81	93	102

Table 4.6: Elemental Analysis

Series	Homologue	Theoretical			Practical		
		C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
VIII	C8	79.57	7.83	2.81	79.65	7.85	2.89
VIII	C16	80.67	9.01	2.29	80.75	9.09	2.31

FTIR (KBr pellets, cm^{-1})

tetradecyl homologue : 2925 – 2858 (–C–H St, Alkyl CH_3, SP^3 hybridization), 1734 (–C=O– St. of ester), 1606 (–C–H st of –C=N– St.), 1517 – 1479 (–C=C– St. of Aromatic ring), 1469 (–C–H bending of –CH_2–), 1262 (Aromatic ether St.),1172 (–C=N– St.), 1075(–C–O– St. of ester), 897 (–C–H out of plane bending of –CH=CH–), 878 (strong –C–H– bending for 1:2:4 tri substituted benzene ring), 759 (weak –C–H– bending for –$(CH_2)_7$–).

Hexadecyl homologue: 2925 – 2858 (–C–H St, Alkyl CH_3, SP^3 hybridization), 1734 (–C=O– St. of ester), 1606 (–C–H st of –C=N– St.), 1517 – 1479 (–C=C– St. of Aromatic ring), 1469 (–C–H bending of $–CH_2–$), 1262 (Aromatic ether St.),1172 (–C=N– St.), 1075(–C–O– St. of ester), 897 (–C–H out of plane bending of –CH=CH–), 878 (strong –C–H– bending for 1:2:4 tri substituted benzene ring), 759 (weak –C–H– bending for $–(CH_2)_7–$).

^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm, standard TMS)

Octyl homologue: δ = 0.88 (t, 3H, $–CH_3$), 1.29–1.54 (m, 10H, 5($–CH_2–$)), 1.78 (s, 6H, Ar–CH_3), 1.82 (Qunt, 2H, -$OCCH_2$), 2.61 (t, 3H, $–CH_3$ of ethylideneamino), 4.00 (t, 2H, –OCH_2), 6.45 (d, J = 21.2, 1H,=CH–COO), 7.86 (d, J = 21.2, 1H, Ar–CH=), 6.91-8.03 (m, 11H, Ar–H)

Tetradecyl homologue: δ = 0.88 (t, 3H, $–CH_3$), 1.29–1.67 (m, 22H, 11($–CH_2–$)), 1.78 (s, 6H, Ar–CH_3), 1.79 (Qunt, 2H, -$OCCH_2$), 2.60 (t, 3H, $–CH_3$ of ethylideneamino), 4.00 (t, 2H, -OCH_2), 6.35 (d, J = 20.4, 1H,=CH–COO), 7.66 (d, J = 20.4, 1H, Ar-CH=), 6.87-7.71 (m, 11H, Ar–H)

Mass Spectra: MS m/z:

Octyl Homologue: Theoratical Mass value: 497.29 g/mol

Practical mass value: MS m/z: 497.67 (M^+)

Table 4.7: DSC Data

Series	Member	Heating rate °C/min	Transition Temperature °C	ΔH=J/g	ΔS=J/g.K
IX	C8	10	Cr – N 96.05 N – I 139.33	13.78 1.49	0.0373 0.0036

Table 4.8: UV Data

Series	Homologue	UV λ max values nm (solvent – ethyl acetate)	
		π → π*	n → π*
IX	C8	266	314
	C14	266	314

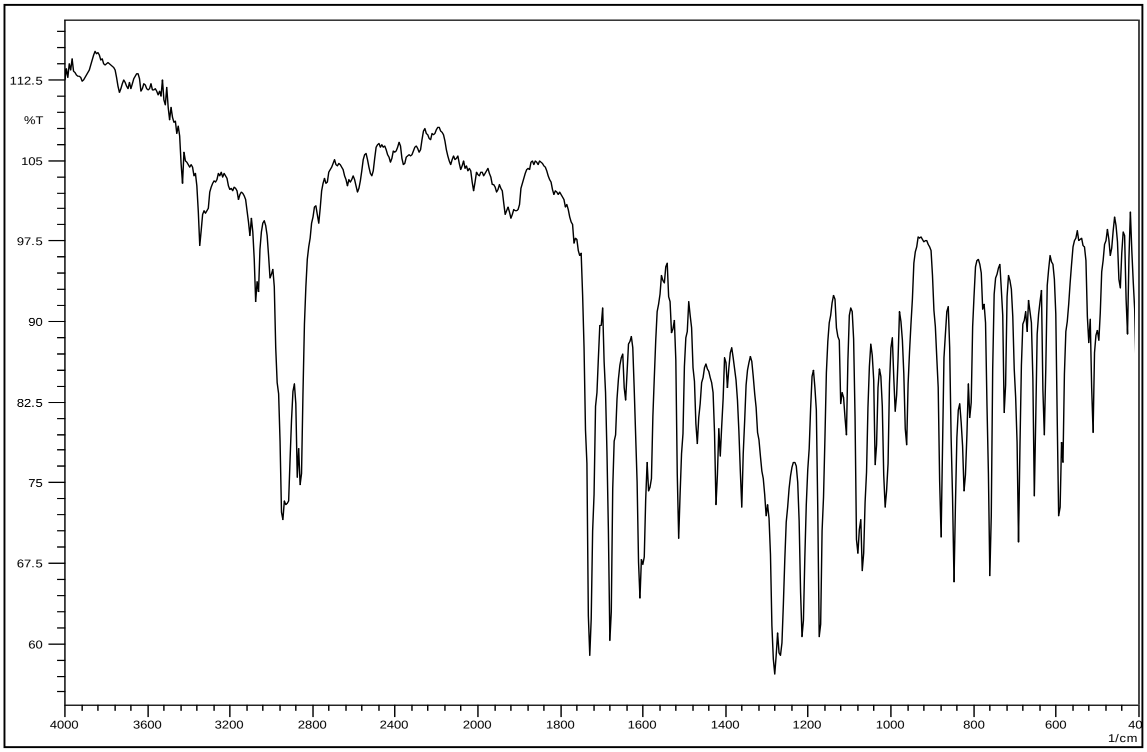


Figure 4.1 (a): IR spectra of C7 homologue of series VIII

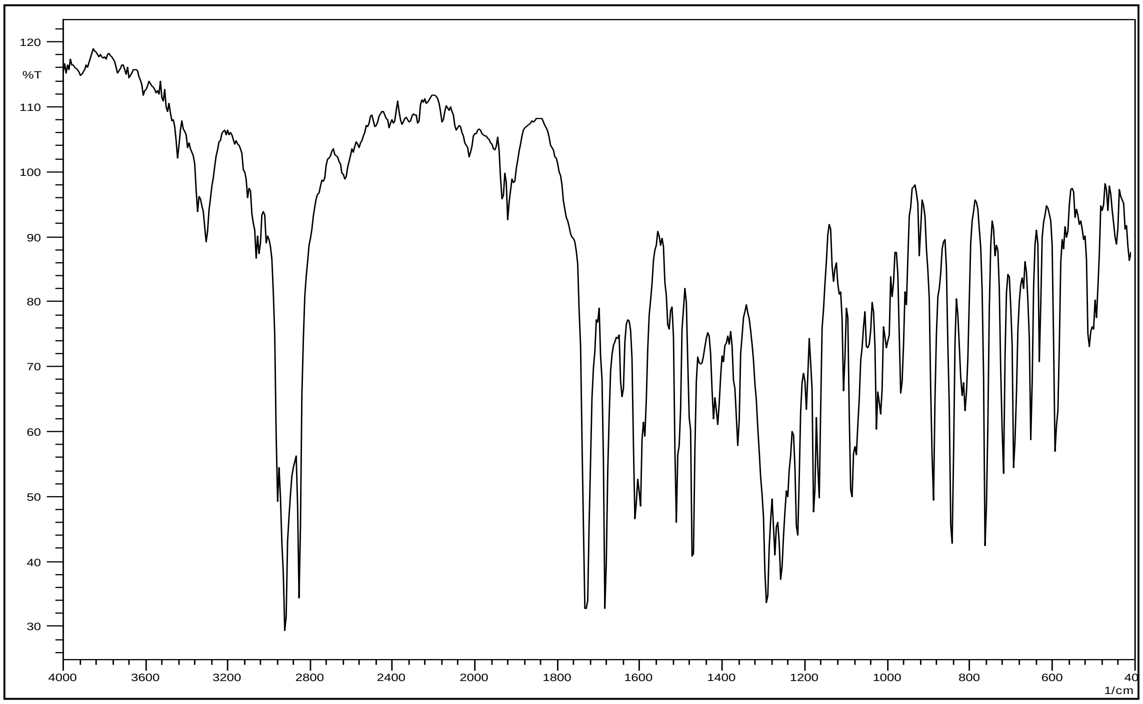


Figure 4.1 (b): IR spectra of C16 homologue of series VIII

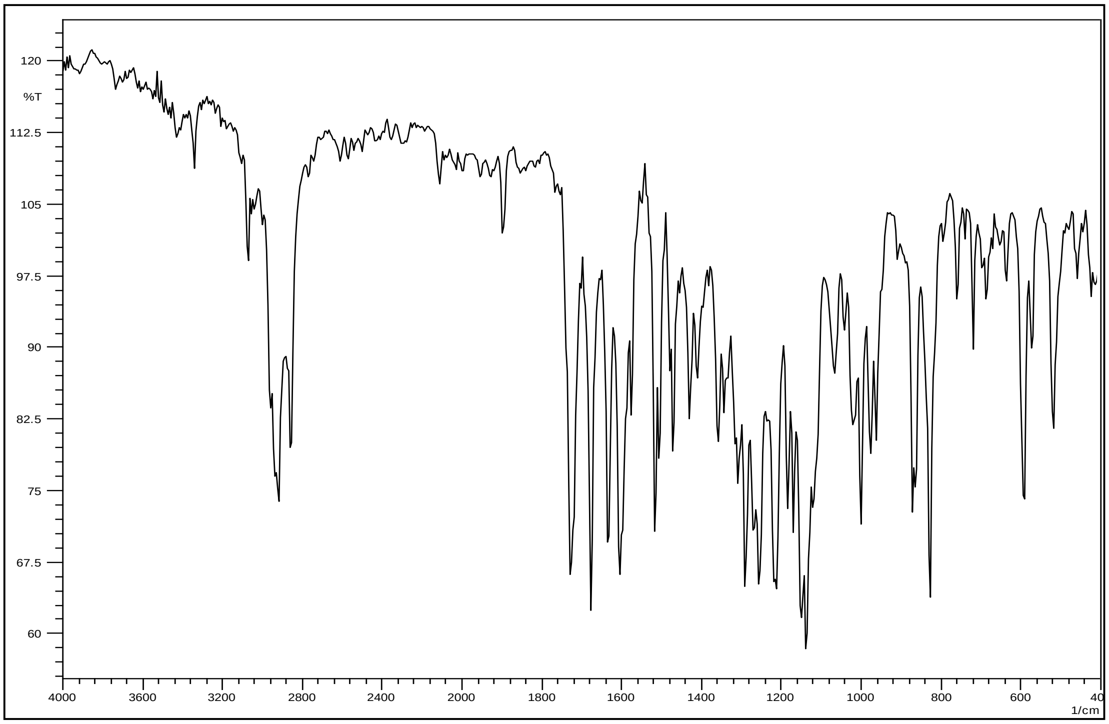


Figure 4.1 (c): IR spectra of C14 homologue of series IX

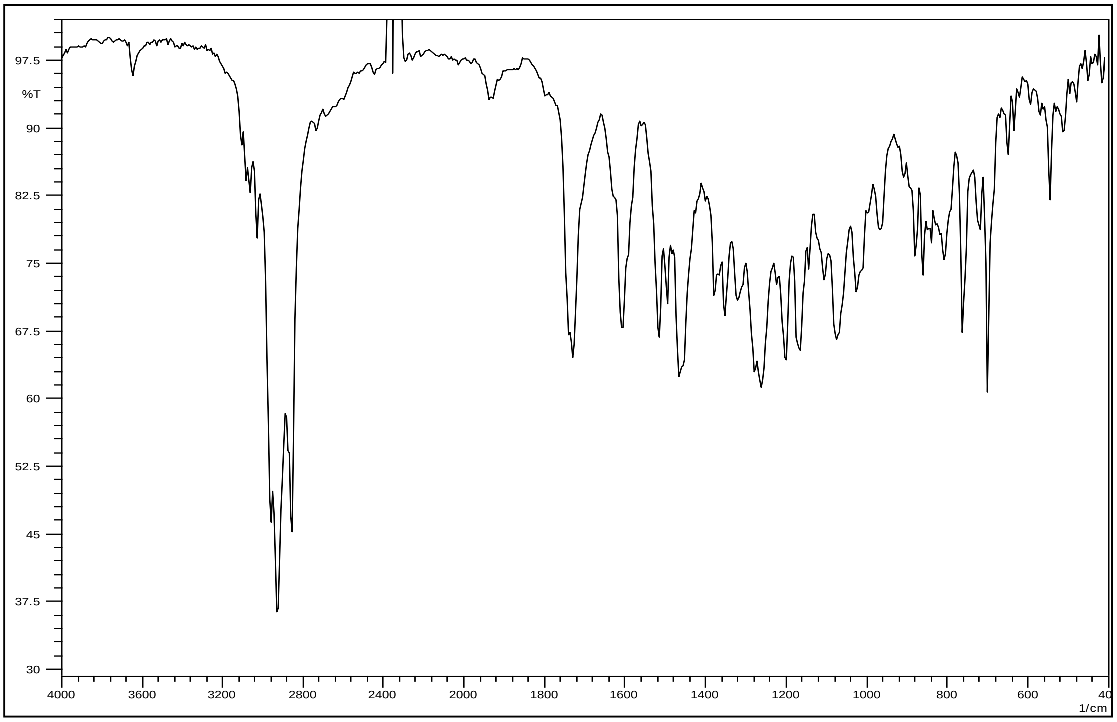


Figure 4.1 (d): IR spectra of C16 homologue of series IX

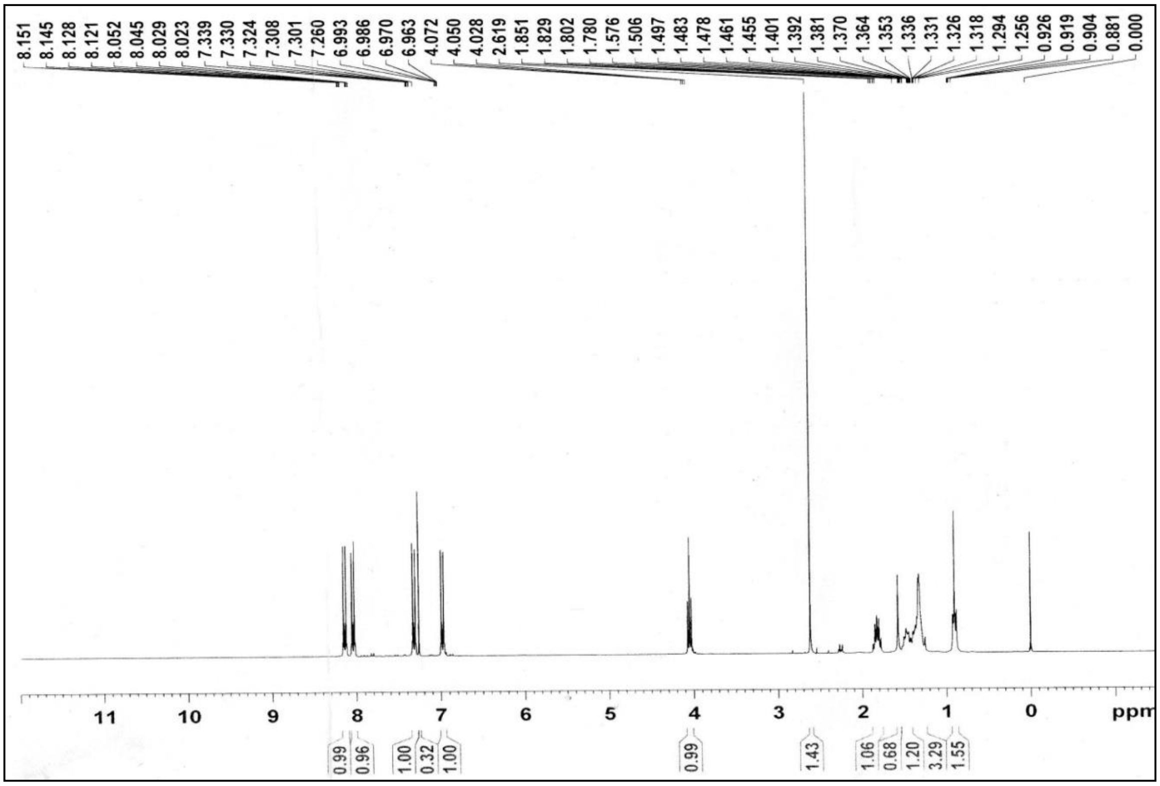


Figure 4.2 (a): ^{1}H NMR spectra of C7 homologue of series VIII

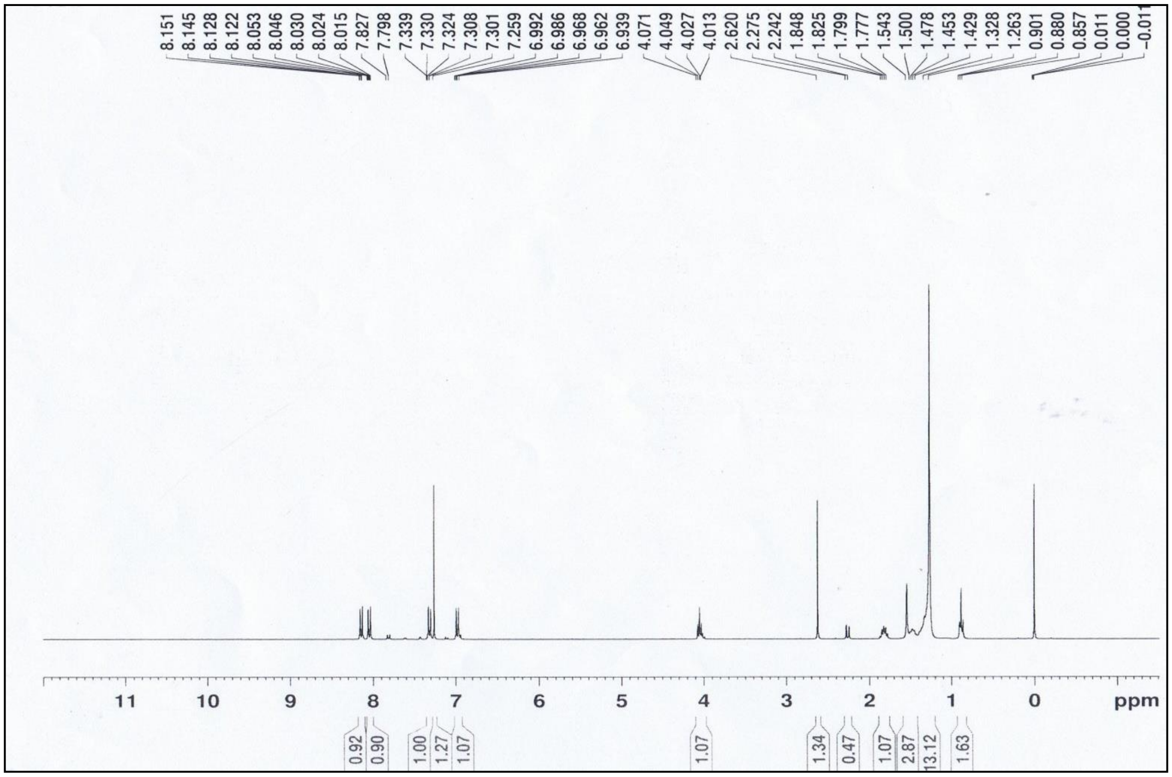


Figure 4.2 (b): ^{1}H NMR spectra of C16 homologue of series VIII

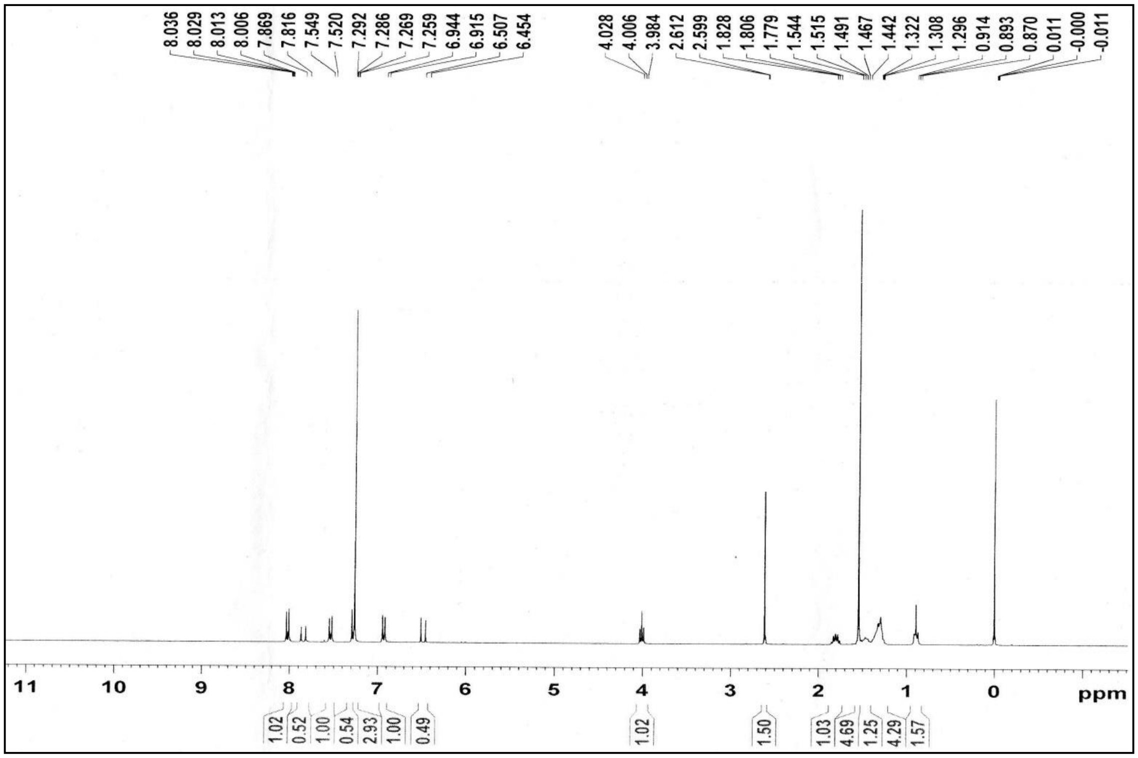


Figure 4.2 (c): ^{1}H NMR spectra of C8 homologue of series IX

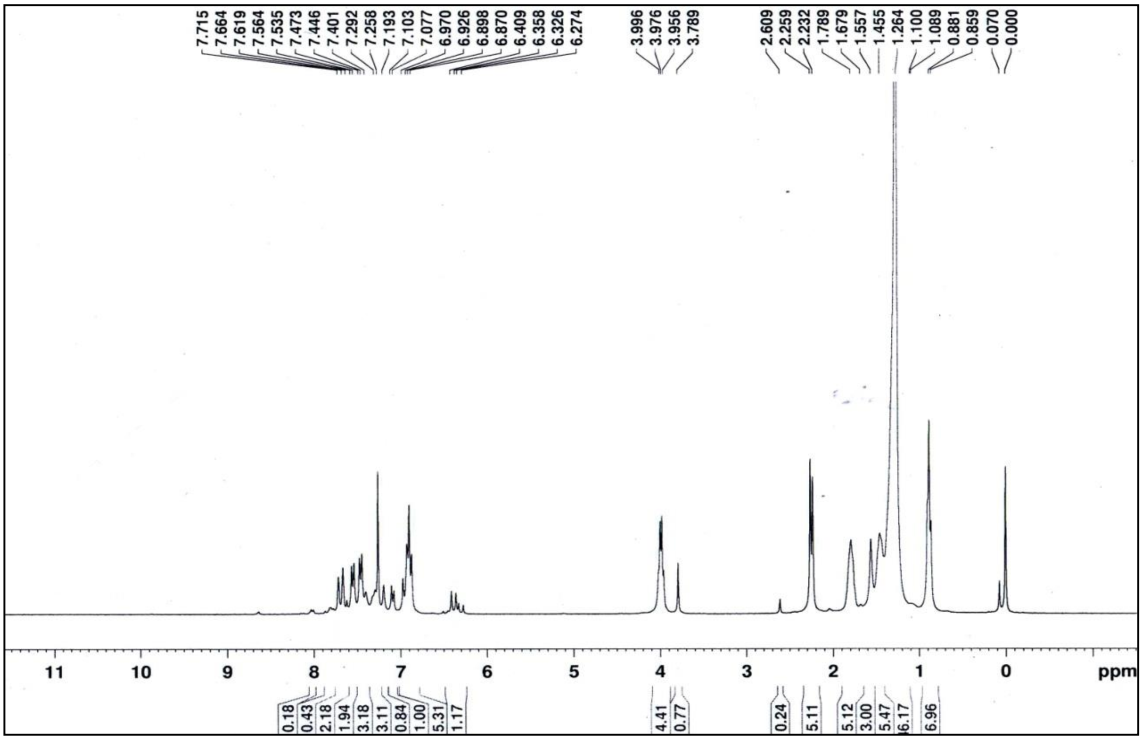


Figure 4.2 (d): ^{1}H NMR spectra of C14 homologue of series IX

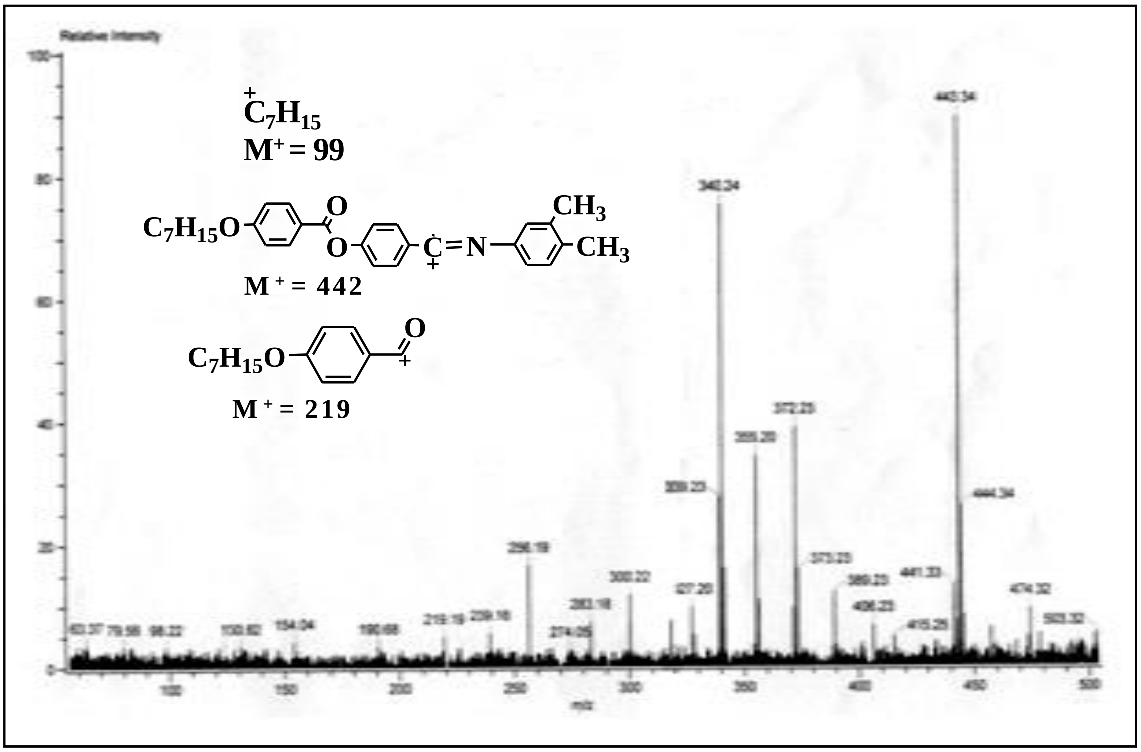


Figure 4.3 (a): Mass spectra of C7 homologue of series VIII

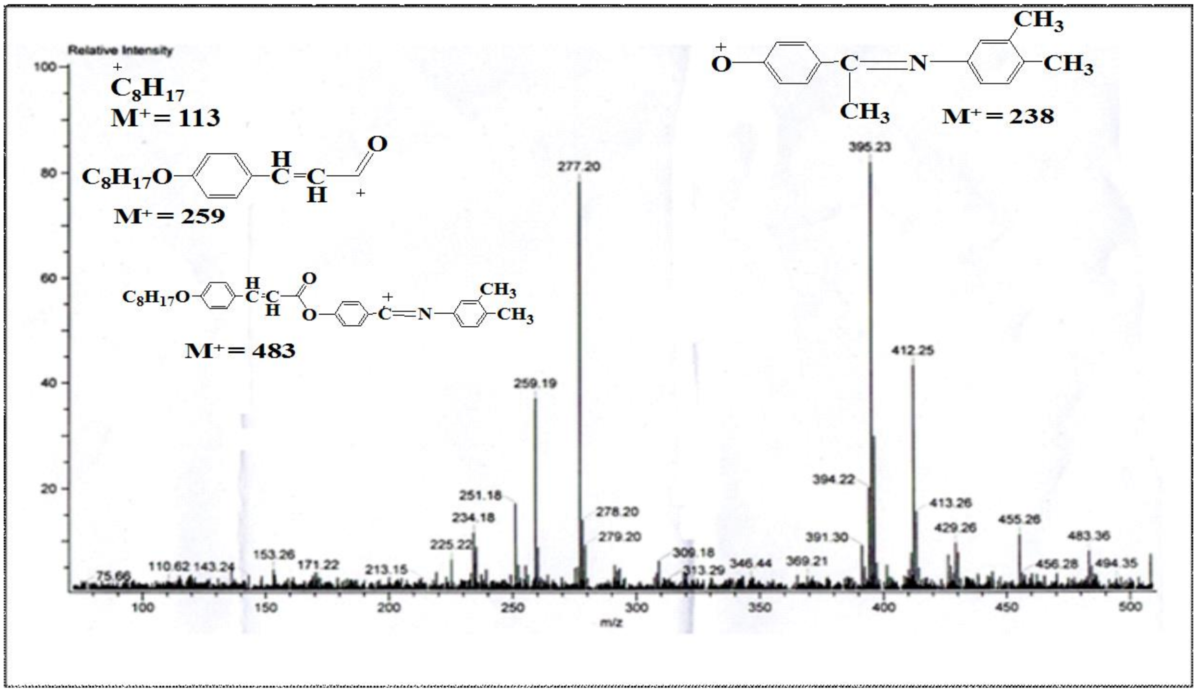


Figure 4.3 (b): Mass spectra of C8 homologue of series IX

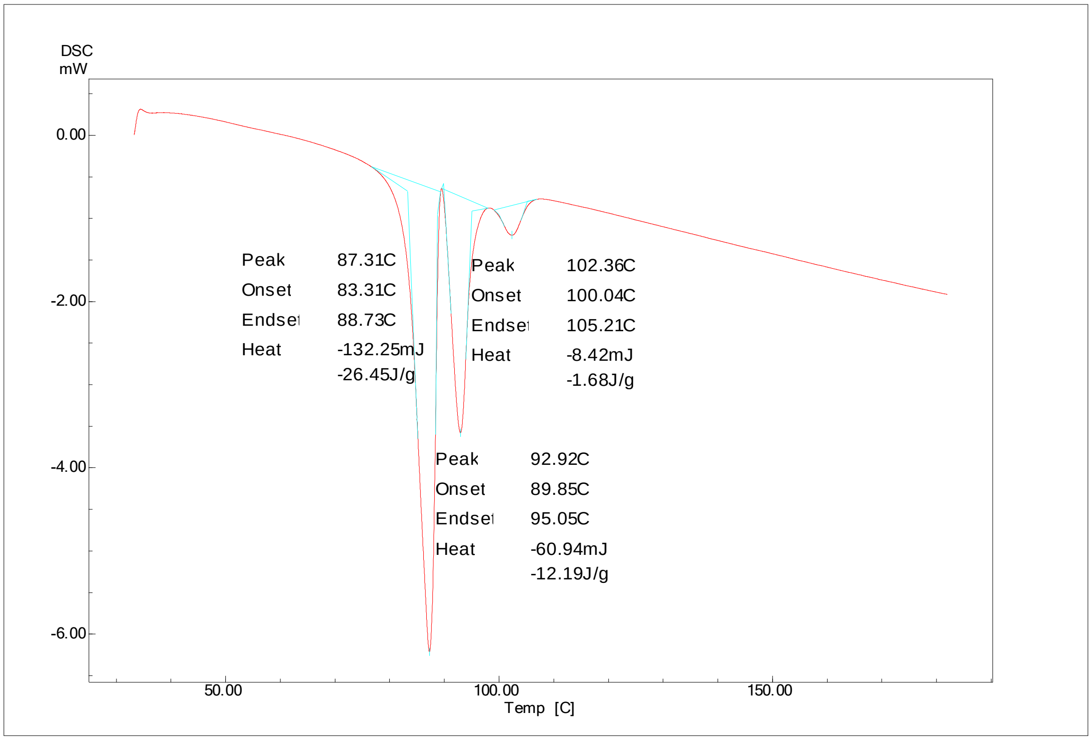


Figure 4.4 (a): DSC Thermogram of C16 homologue of series VIII

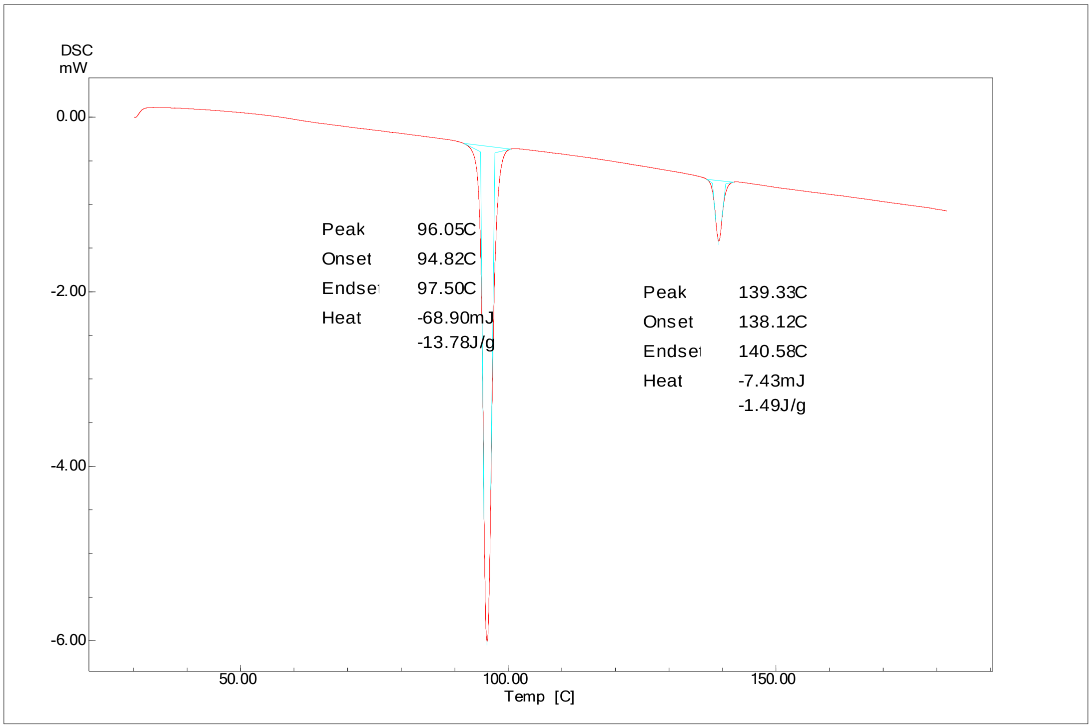


Figure 4.4 (b): DSC Thermogram of C8 homologue of series IX

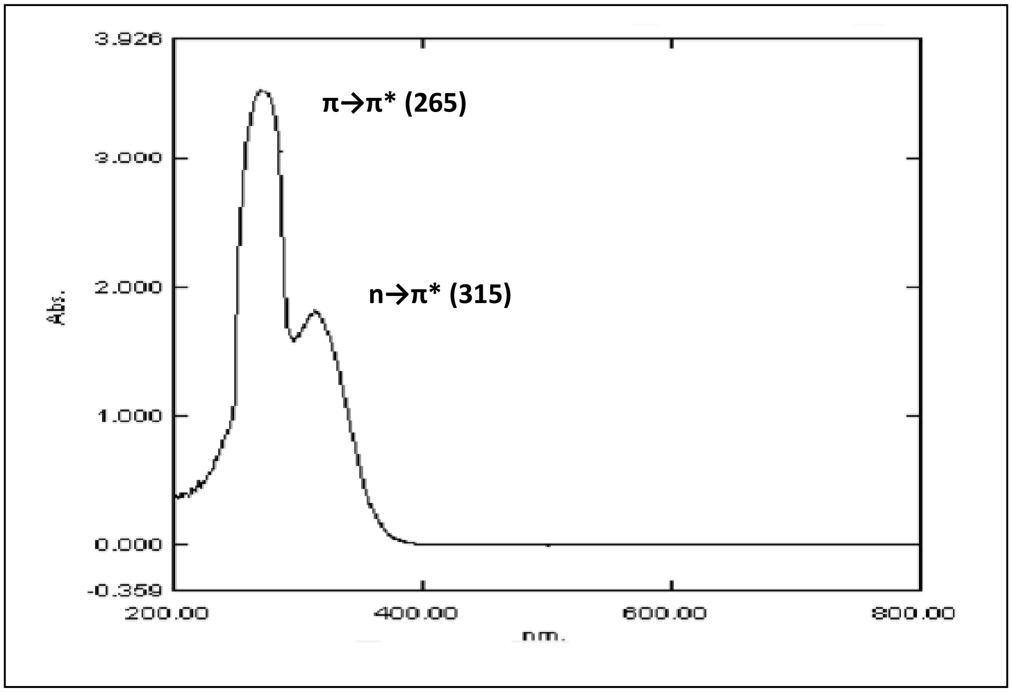


Figure 4.5 (a): UV Spectra of C7 homologue of series VIII

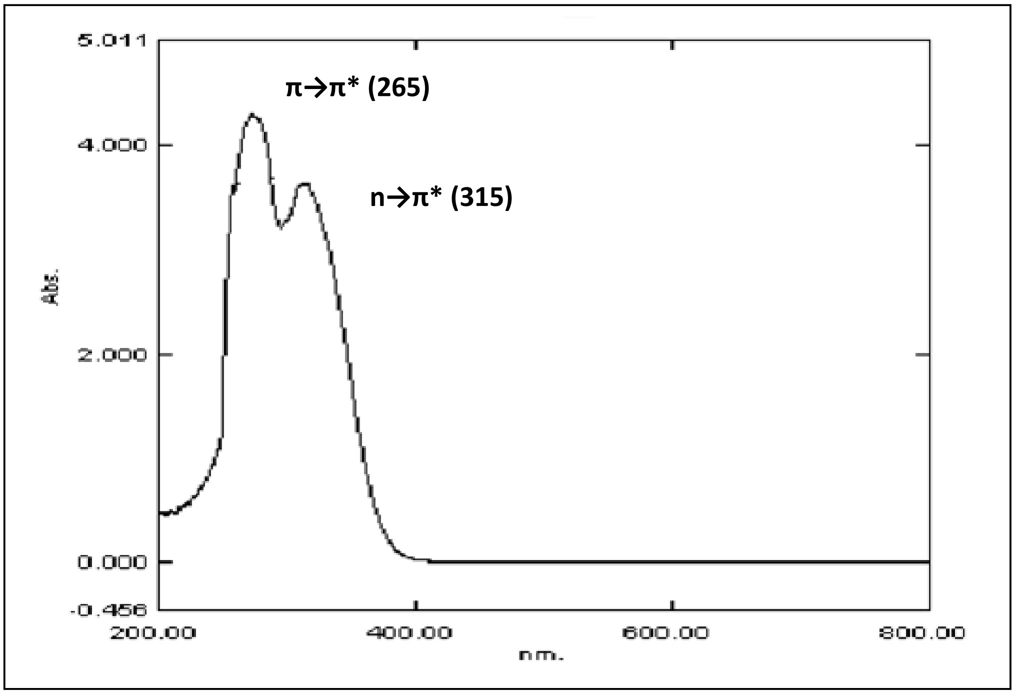


Figure 4.5 (b): UV Spectra of C12 homologue of series VIII

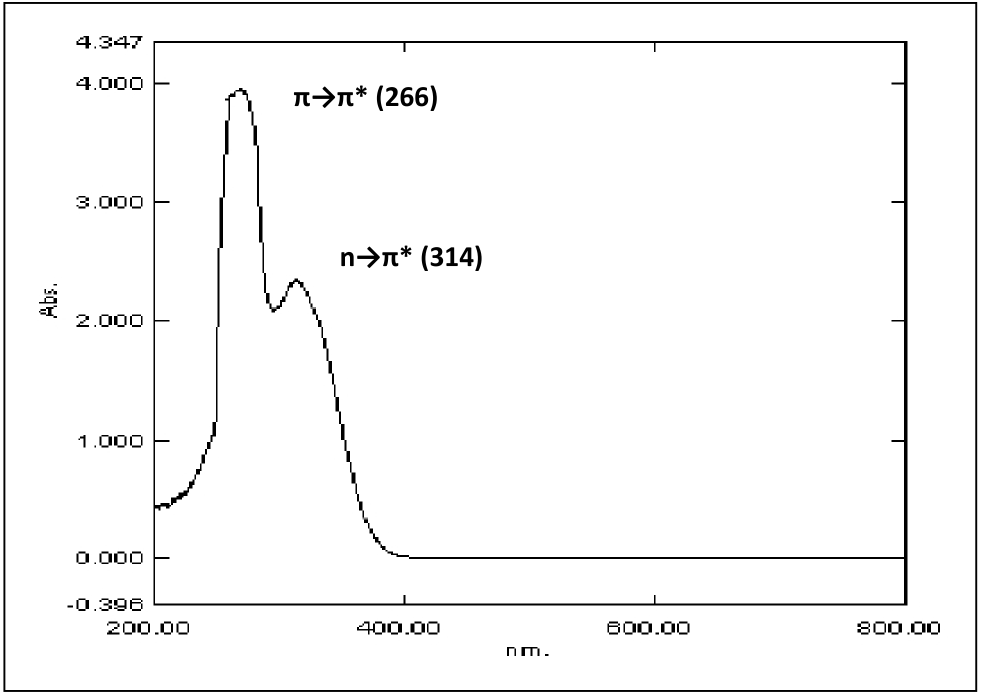


Figure 4.5 (c): UV Spectra of C8 homologue of series IX

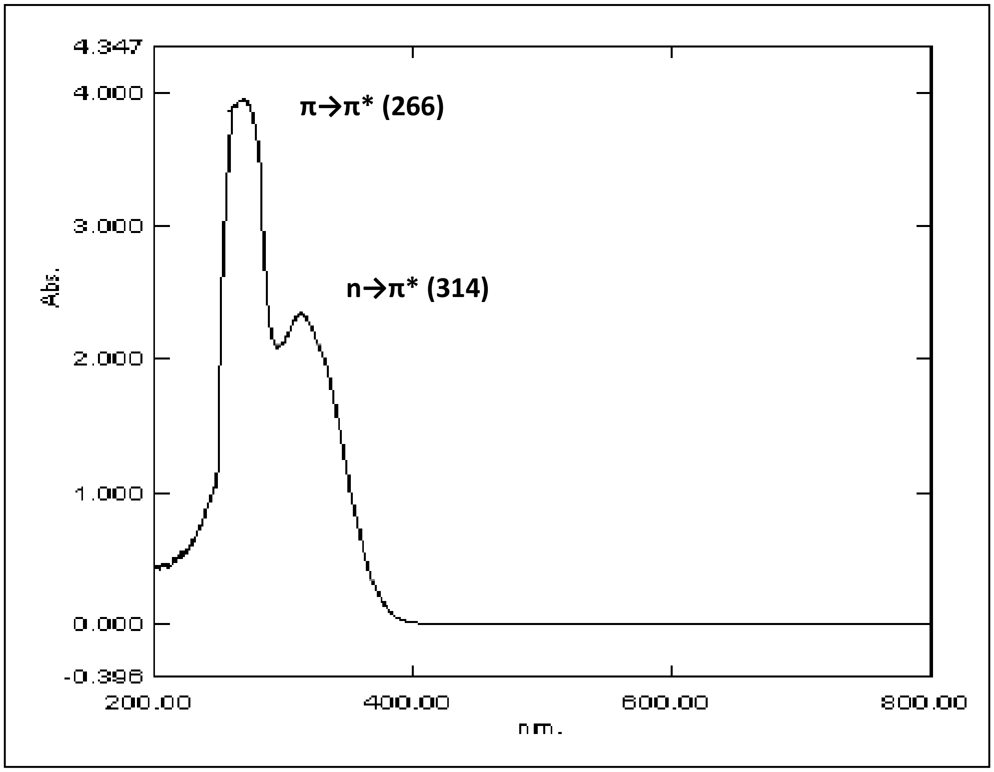
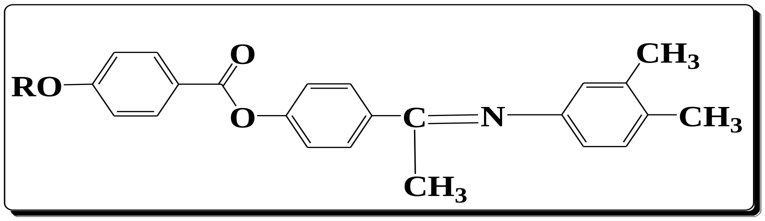


Figure 4.5 (d): UV Spectra of C14 homologue of series IX

4.3 Results and Discussion

4.3.1 Series VIII: 4-(4’-*n*-alkoxybenzoyloxy)-phenylethylidene-3”, 4”-dimethylanilines

General molecular structure of the series VIII: 4-(4’-*n*-alkoxybenzoyloxy)-phenylethylidene-3”, 4”-dimethylanilines



Where, R is C_nH_{2n+1} *n* = 1 to 8,10,12,14 and 16

In this homologous series mesogenic behavior appears in the form of nematic mesophase from the C7 derivative in monotropic form (Table: 4.1, Figure: 4.5) which becomes enantiotropic at C8 homologue and continues till the last C16 derivative synthesized. All the mesogenic homologues of the series show nematic mesophase expect C16 homologue which shows smectic A mesophase alongwith nematic phase. Figure 4.5, shows plot of transition temperatures against number of carbon atoms in the n-alkoxy chain; it indicates that Cr – I curve shows an overall steep fall from C1 to C6 derivative and then merges with falling Cr – M curve till C10 derivative then it rises gradually till the last C16 derivative synthesized. The N – I curve shows falling tendency from C8 to C12 derivative and then it shows gradual rise till C16 derivative. The smectic phase of the series show the focal conic fan shaped texture whereas the nematic mesophase exhibits marble/schlieren texture.

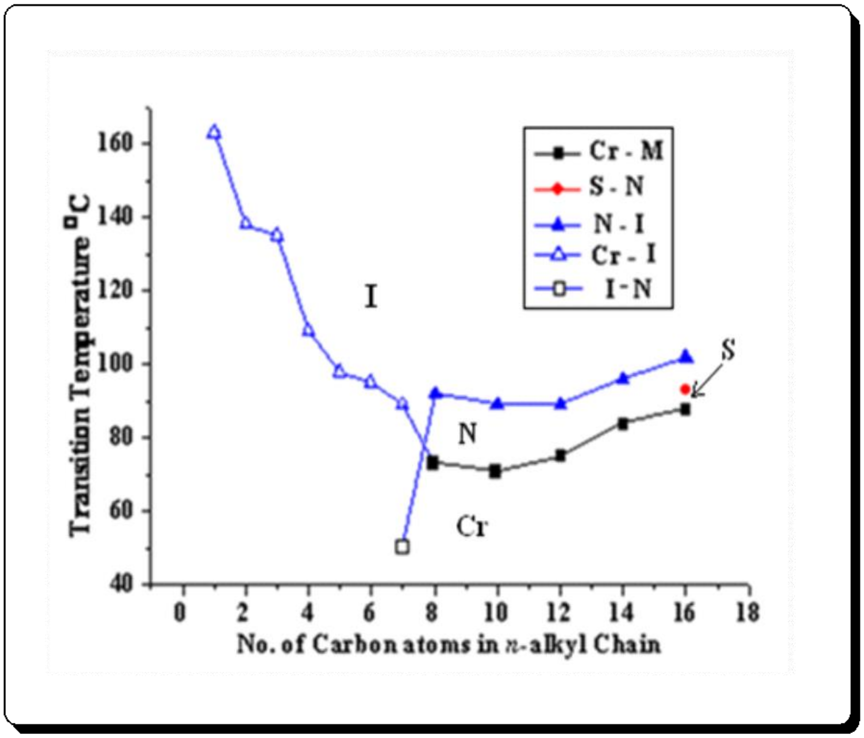


Figure 4.5: 4-(4’-*n*-alkoxybenzoyloxy)-phenylethylidene-3”, 4”-dimethylanilines (Series VIII)

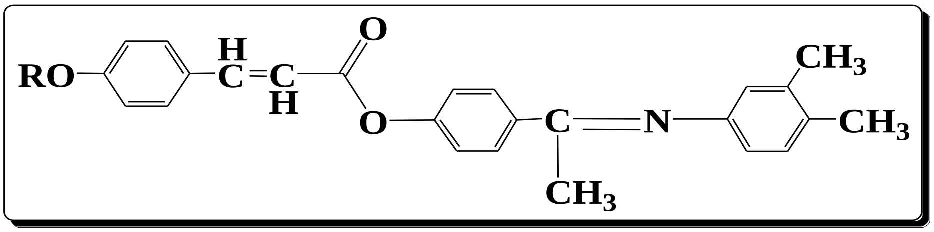
Table 4.1: Transition Temperatures: Series VIII: 4-(4’-*n*-alkoxybenzoyloxy)-phenylethylidene-3”, 4”-dimethylanilines

R = *n*-Alkyl group	**Transition Temperature °C**		
	Smectic A	**Nematic**	**Isotropic**
Methyl	--	--	163
Ethyl	--	--	138
Propyl	--	--	135
Butyl	--	--	109
Pentyl	--	--	98
Hexyl	--	--	95
Heptyl	--	(50)*	89
Octyl	--	73	92
Decyl	--	71	89
Dodecyl	--	75	89
Tetradecyl	--	84	96
Hexadecyl	87	91	104

()* Value in parentheses indicates monotropic transitions.

4.3.2 Series IX: 4-(4’-*n*-alkoxyCinnamoyloxy)-phenylethylidene-3”, 4”-dimethylanilines

General molecular structure of the series IX: 4-(4’-*n*-alkoxyCinnamoyloxy)-phenylethylidene-3”, 4”-dimethylanilines



Where, R is C_nH_{2n+1} n = 1 to 8,10,12,14 and 16

In series IX mesogenic behavior commences from the C5 homologue (Table: 4.5, Figure: 4.6) in the form of nematic mesophase and remains upto the last C16 derivative synthesized. The smectic mesophase commences from C14 derivative and remains till the last C16 derivative synthesized alongwith nematic mesophase; Figure 4.6 shows the plot of transition temperatures against number of carbon atoms in the *n*-alkoxy chain; the Cr – I curve shows gradual falling till C4 derivative, the Cr – M curve shows gradual falling tendency from C5 till the last C16 derivative synthesized. The N-I curve shows steady fall from C5 to C16 derivative. The S – N curve shows rising tendency between C14 and C16 homologues. The smectic phase of the series shows focal conic fan shaped texture whereas the nematic mesophase shows marble/schlieren texture.

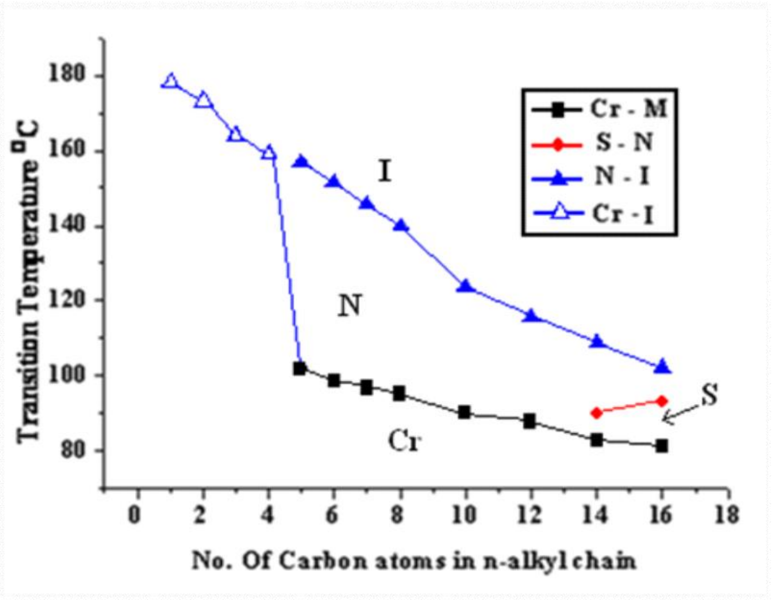


Figure 4.6: 4-(4’-*n*-alkoxybenzoyloxy)-phenylethylidene-3”, 4”-dimethylanilines (Series IX)

Table 4.5: Transition Temperatures: Series IX: 4-(4’-*n*-alkoxycinnamoyloxy)-phenylethylidene-3”, 4”-dimethylanilines

R = *n*-Alkyl group	**Transition Temperature ºC**		
	Smectic A	**Nematic**	**Isotropic**
Methyl	--	--	178
Ethyl	--	--	173
Propyl	--	--	164
Butyl	--	--	159
Pentyl	--	102	157
Hexyl	--	99	152
Heptyl	--	97	146
Octyl	--	95	140
Decyl	--	90	124
Dodecyl	--	88	116
Tetradecyl	83	90	109
Hexadecyl	81	93	102

Table 4.9: Average thermal stability °C

Series	**N –I**	**Commencement of Smectic mesophase**
VIII	76.2 (C8-C16)	C16
IX	130.75 (C5-C16)	C14
A	130.50 (C1-C16)	-

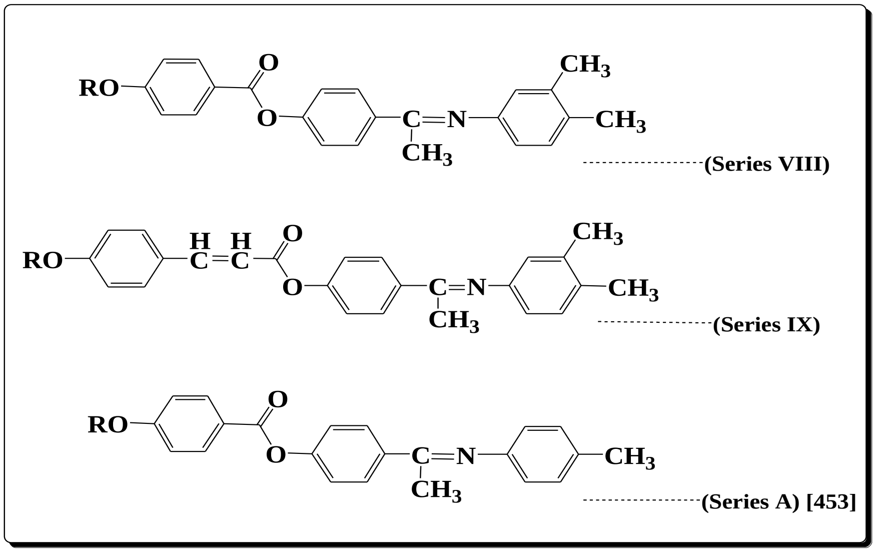


Figure 4.7: Molecular geometry of the homologous series under comparison

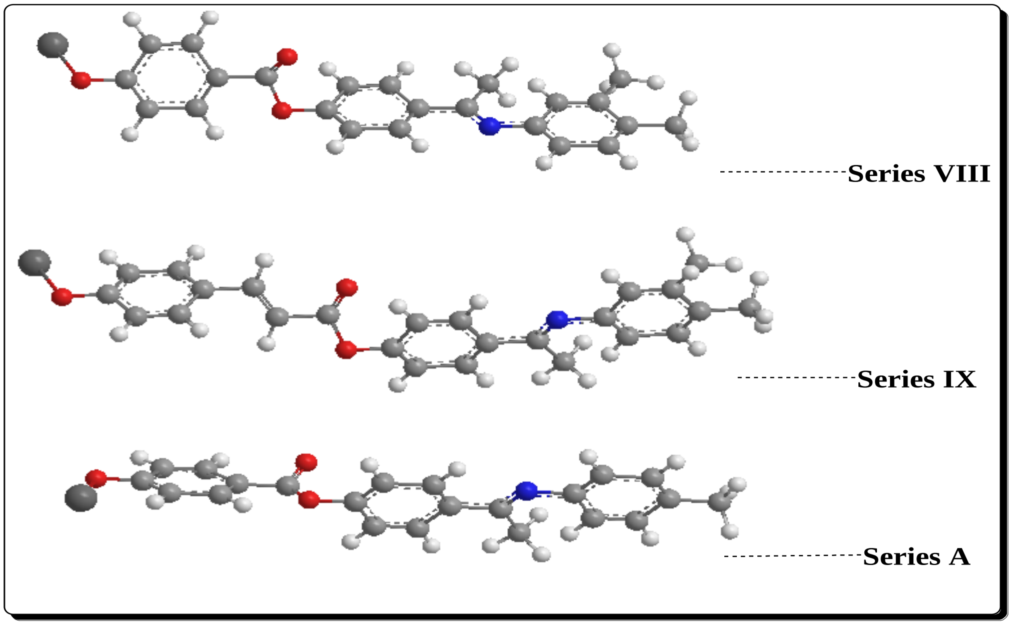


Figure 4.8: Energy minimized 3D Molecular geometry of the homologous series under comparison from ChemDraw Ultra 8.0 software.

While comparing these presently synthesized homologous series VIII and IX with each other (Figure 4.7, 4.8 and 4.9), it is seen that most of the structural features of these series in comparison are same except one of the central bridges viz. series VIII has –COO– (benzoyloxy) and series IX has -CH=CH–COO– (cinnamoyloxy) central bridge. Figure 4.7 and 4.8 show general molecular geometry and energy minimized 3D molecular structures of the homologous series under comparison from ChemDraw ultra 8.0 software.

Series IX has higher thermal stability than series VIII; this may be due to the longer –CH=CH–COO– central linkage in series IX as compared to –COO– central linkage in series VIII which is responsible for higher polarizability of series IX. It is in seen that in series IX central benzene ring is attached with two conjugated central group (vinyl carboxy) viz. –CH=CH–and –COO– which is responsible for higher thermal stability in series IX as compared to series VIII (454). Series VIII compared with structurally related homologous series A [453], which clearly shows lateral substitution at terminal benzene ring lower down thermal stability. The introduction of the lateral group in homologous series changes the molecular conformation and broadens the molecules, which decreases, the transition temperatures and thermal stabilities of nematic mesophase [410, 422, 423].

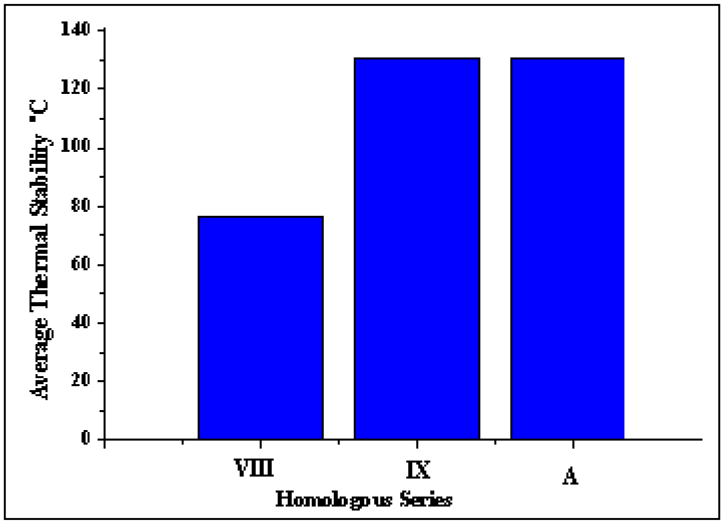
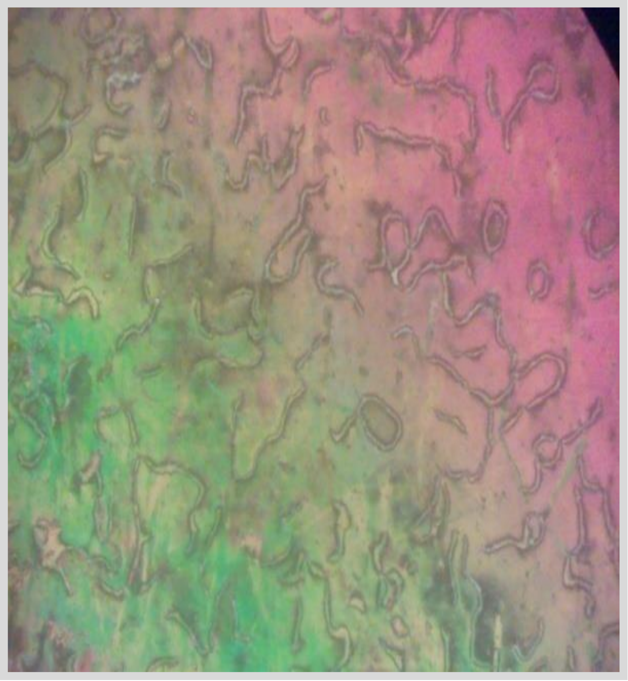
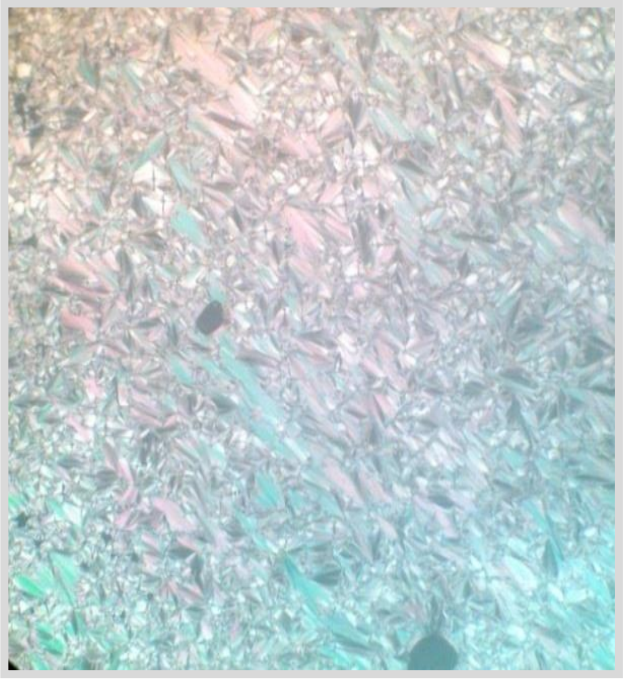


Figure 4.9: Average thermal stability (TS) for the homologous series under comparison

Polarizing optical microscopic images of Liquid Crystals



(a)

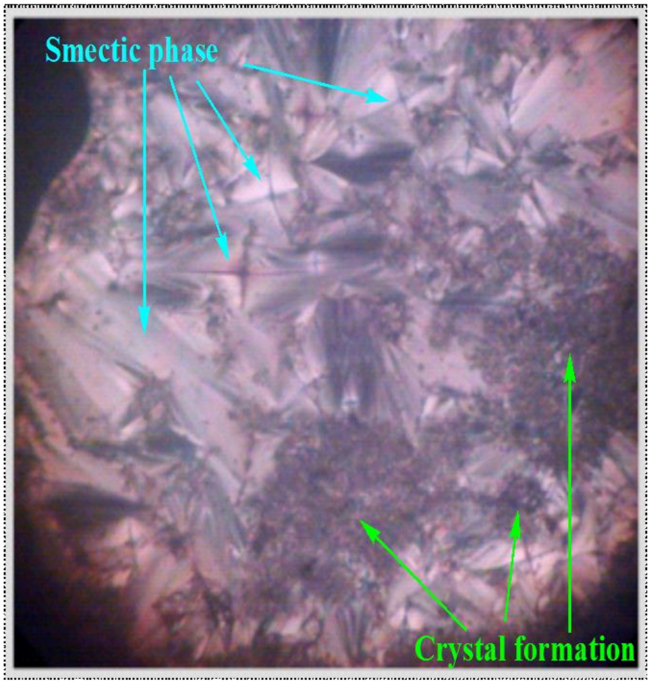


(b)

(a) Marble texture of nematic phase of C10 homologue of Series VIII at 78 °C on cooling.

(b) Focal conic fan shaped texture of the Smectic A phase of C16 homologue of Series VIII at 88 °C on cooling.

(c)



(d)

(c) Marble texture of nematic phase of C8 homologue of Series IX at 126 °C on cooling.

(d) Focal conic fan shaped texture of the Smectic A phase of C16 homologue of Series IX at 84 °C on cooling.