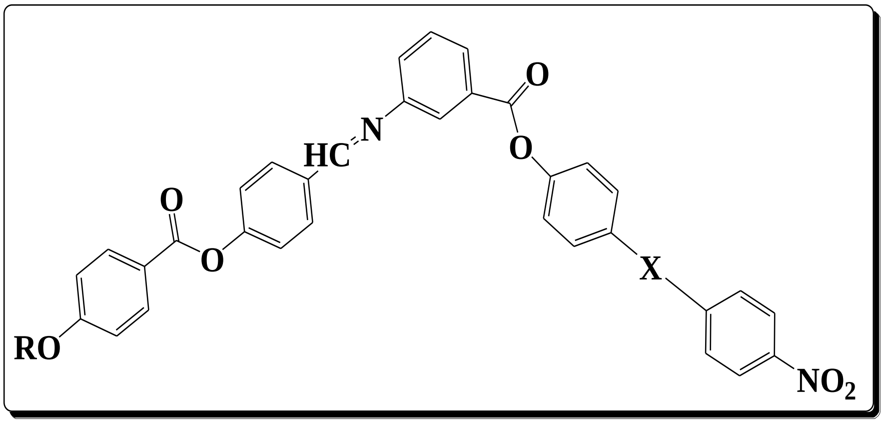
6.1 Introduction

Discovery of bent-shaped (banana, boomerang, bow) liquid crystals (LCs) opened a very promising area of new mesophases; the special properties of banana-shaped liquid crystals were discovered in 1996 [123]. Several mesogens with bent shape had already been synthesized in the early 20th century [123, 124,128,197,475,476]; by that time, however, their special properties were not recognized. Matsunaga & coworkers opened a new era in the field of bent core Liquid Crystals [126]. Most banana phases do not show similarities with conventional liquid crystalline phases shown by calamitic liquid crystalline mesophase. That is why according to recommendations of the workshop on Banana-shaped Liquid Crystals viz. "Chirality by Achiral Molecules" held in Berlin in 1997, these phases are simply designated as Bn. The subscript n corresponds to the sequence of discovery of the different phases. Number of Banana shaped molecules have been reported by variety of structural changes in bridging groups as well as lateral and terminal substituents to investigate effect of shape and substituents on mesomorphism [127-183]. Azo functionalized materials are of special interest due to their photo-sensitive nature, which can be exploited for optical and optoelectronic devices [488,489].



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

Series	Bridging Linkage
	X
Series 12	-N=N-
Series 13	-CH=N-

6.2 Experimental

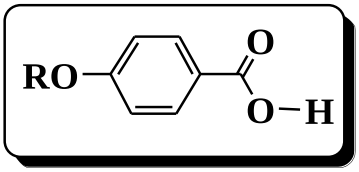
6.2.1 Materials

(1) 4-hydroxybenzoicacid, (2) 4-hydroxybenzaldehyde, (3) *n*-alkyl halides, (4) phenol, (5) 3-aminobenzoic acid, (6) 4-nitroaniline, (7) Glacial Acetic acid, (8) n, n-Dimethylaminopyridine (DMAP), (9) n, n-Dicyclohexylcabodiimide (DCC) and all other chemicals are of Loba chemie or Merck grade used as received.

6.2.2 Synthesis

6.2.2.1 3-[(4””-*n*-alkoxy benzoyloxy)-4’’’-benzilideneamino methyl]-4’’-nitrophenyl-4’-azophenyl benzoates.

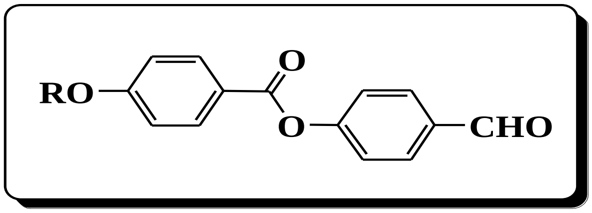
6.2.2.1a 4-*n*-alkoxybenzoic acids



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

6.2.2.1b 4-(4’-*n*-alkoxybenzoyloxy)-benzaldehydes.

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

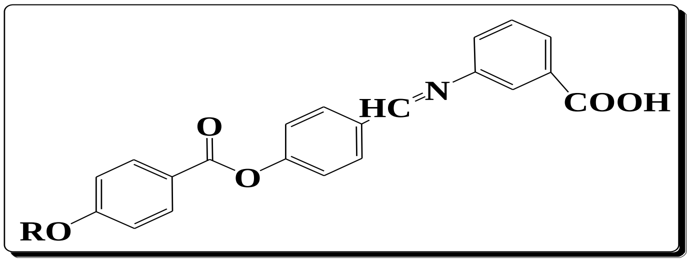


R = C_nH_{2n+1} n = 1 to 8, 10,12,14,16

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

6.2.2.1c 3-[(4"-*n*-alkyloxybenzoyloxy)-4'-benzilideneaminomethyl]-benzoicacids

General molecular structure 3-[(4"-*n*-alkyloxybenzoyloxy)-4'-benzilideneaminomethyl]-benzoicacids.

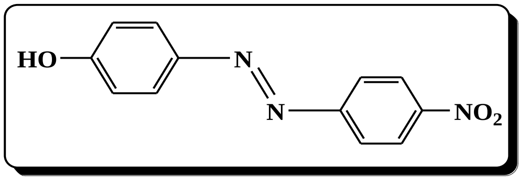


R = C_nH_{2n+1} n = 1 to 8, 10,12,14,16.

They are synthesized following the procedure reported in 5.2.2.1c [488].

6.2.2.1d 4-hydroxyphenylazo-4'-nitrobenzene

General molecular structure of 4-hydroxyphenylazo-4'-nitrobenzene.

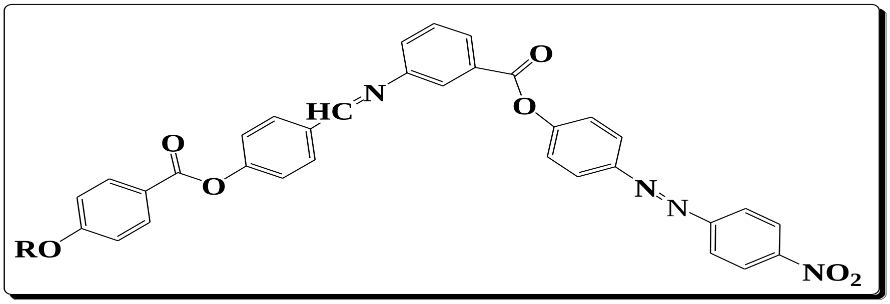


The diazo compound is prepared by the reported method [434], in two steps.

(i) Preparation of Diazonium salt of 4-nitrolaniline
The diazonium salt is prepared by the procedure described in 3.2.2.1.c
(ii) Coupling of 4-nitrobenzenediazoniumchloride with phenol.
The coupling is carried out by the procedure described in 3.2.2.1c

6.2.2.1e 3-[(4""-*n*-alkyloxybenzoyloxy)-4'''-benzilideneamino methyl]-4''-nitrophenyl-4'-azophenyl benzoates.

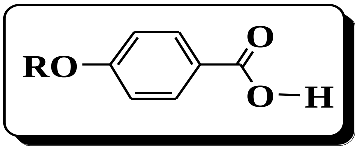
General molecular structure of 3-[(4""-*n*-alkyloxybenzoyloxy)-4'''-benzilideneamino methyl]-4''-nitrophenyl-4'-azophenyl benzoates.



They are synthesized following the procedure reported in 3.2.2.4d [440, 488].

6.2.2.2 3-[(4’’’’-*n*-alkyloxybenzoyloxy)-4’’’-benzilideneaminomethyl]-4’’-nitrophenylimino-4’-benzoates.

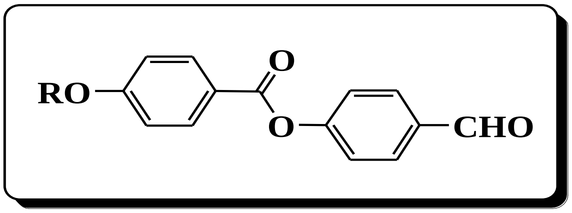
6.2.2.2a 4-*n*-alkoxybenzoic acids



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

6.2.2.2b 4-(4’-*n*-alkoxybenzoyloxy)-benzaldehydes.

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

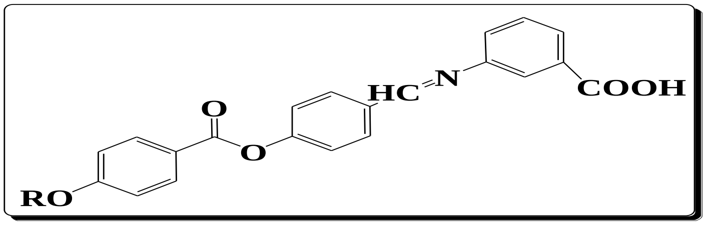


R = C_nH_{2n+1} n = 1 to 8, 10,12,14,16

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

6.2.2.2c 3-[(4"-*n*-alkyloxybenzoyloxy)-4'-benzilideneaminomethyl]-benzoicacids

General molecular structure 3-[(4"-*n*-alkyloxybenzoyloxy)-4'-benzilideneaminomethyl]-benzoicacids.

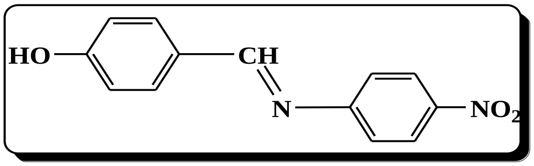


R = C_nH_{2n+1} n = 1 to 8, 10,12,14,16.

They are synthesized following the procedure reported in 5.2.2.1c [488]. The products are filtered, dried and recrystallized from acetone constant transition temperatures are obtained. They are recorded in table 6.3. The elemental analysis of all compounds is found to be satisfactory and is recorded in table 6.4.

6.2.2.2d 4-[(4'-nitrophenylimino) methyl]-phenol

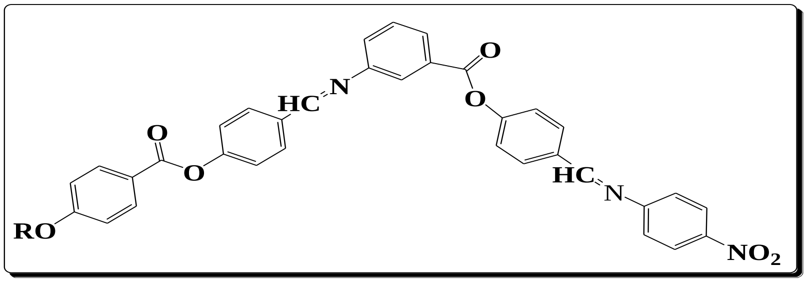
General molecular structure of 4-[(4'-nitrophenylimino) methyl] phenol.



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 6.3. The elemental analysis of all compounds is found to be satisfactory and is recorded in table 6.4.

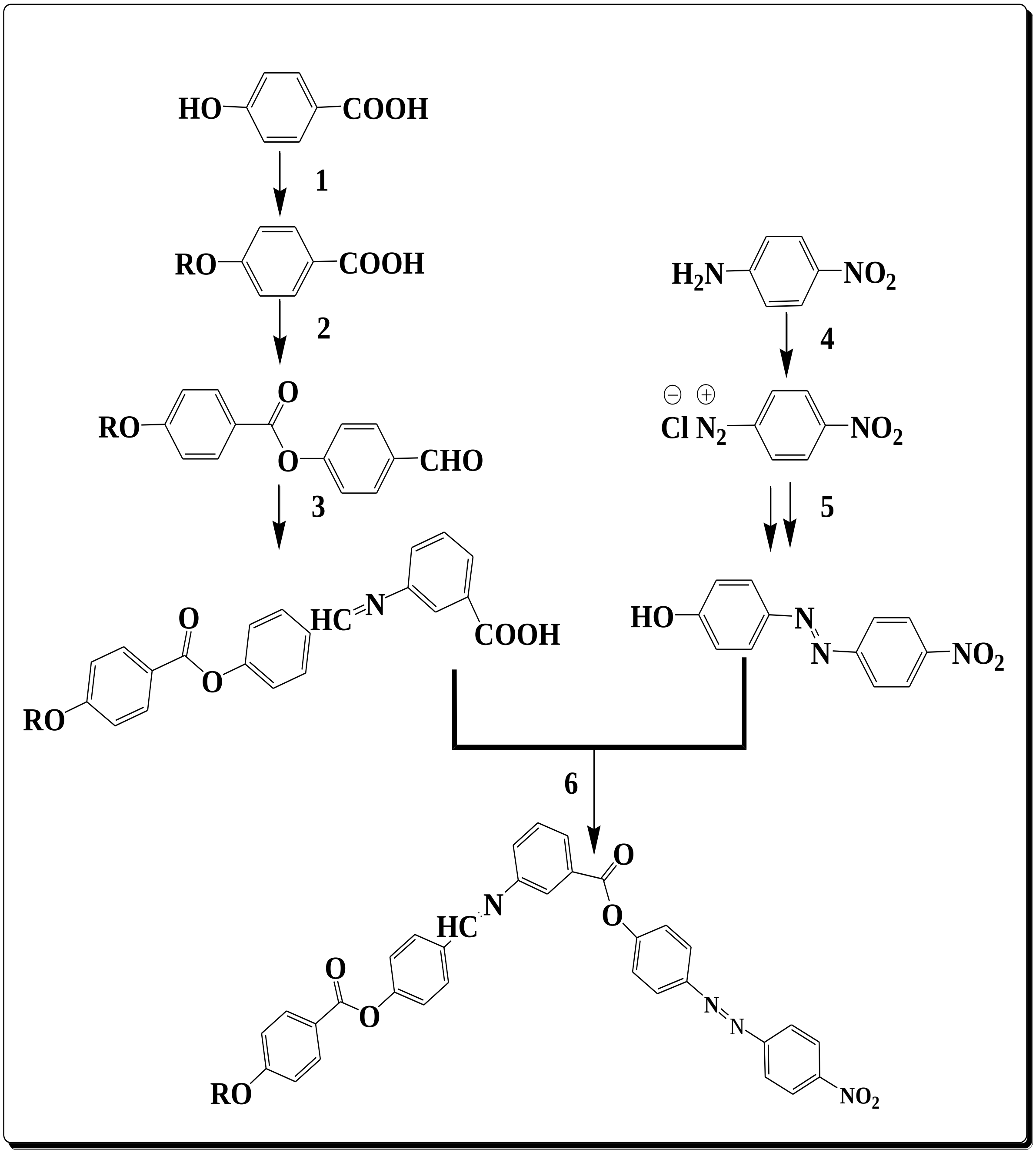
6.2.2.2e 3-[(4""-*n*-alkyloxybenzoyloxy)-4'''-benzilideneaminomethyl]-4''-nitrophenylimino-4'-benzoates.

General molecular structure of 3-[(4""-*n*-alkyloxybenzoyloxy)-4'''-benzilideneaminomethyl]-4''-nitrophenylimino-4'-benzoates.



They are synthesized following the procedure reported in 3.2.2.4d [440, 488].

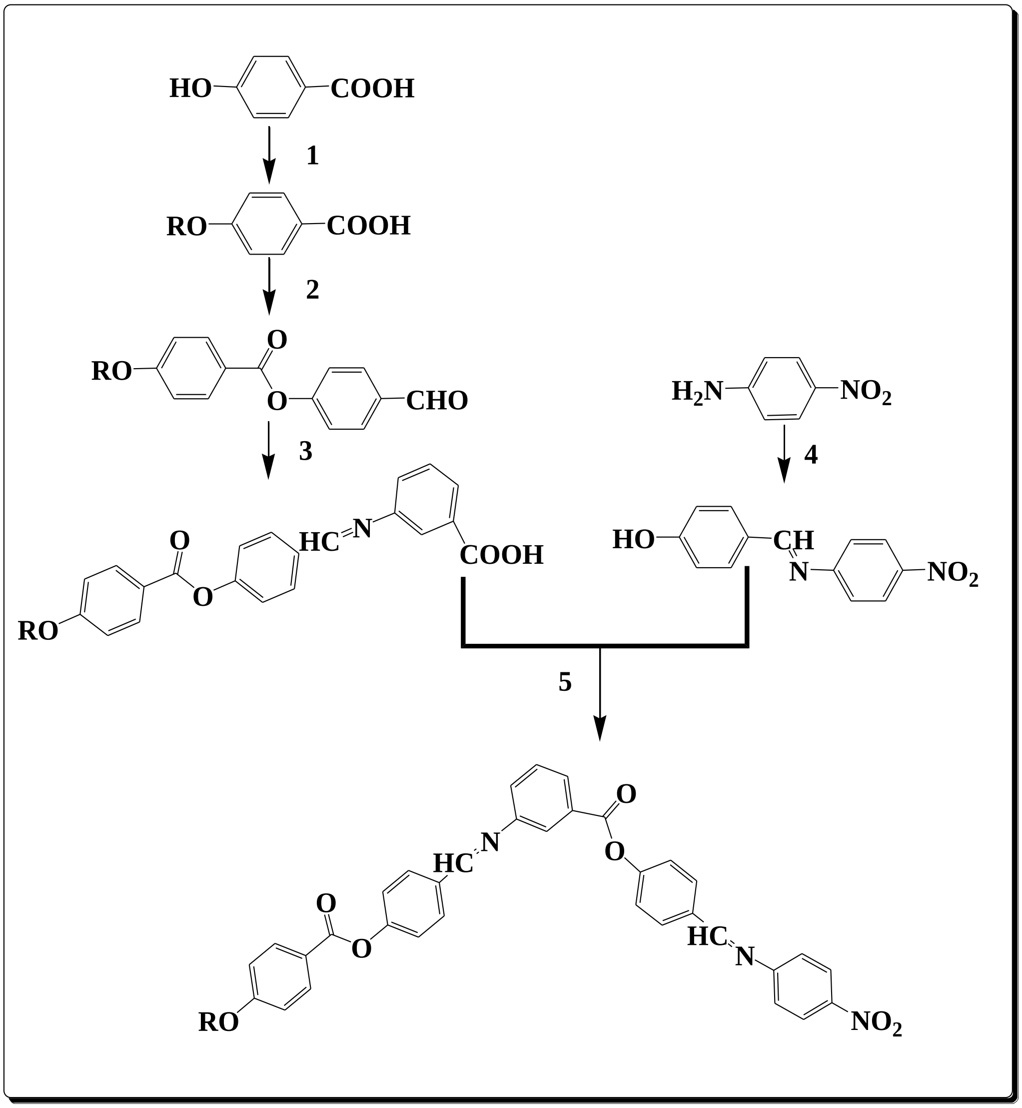
The synthetic route of series XII and XIII is shown in scheme 6.1.



Scheme 6.1: Synthetic route for series XII

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

(1) Alcohol, KOH, *n*-RBr, (2) DCC, DMAP, DCM, p- Hydroxy benzaldehyde Stirred for Overnight Stirred for 12 hr, (3) Ethanol, 4- amino benzoic acid, 1-2 drops Gla. Acetic Acid, (4) HCl, $NaNO_2$, H_2O/0-5 ^{o} C, (5) (i) Conc. HCl, $NaNO_2$, (ii) phenol aq.NaOH, at 0-10 ^{o}C, pH 8-12, (6) DCC, DMAP, DCM, Stirred for Overnight Stirred for 12 hrs.



Scheme 6.2: Synthetic route for series XIII

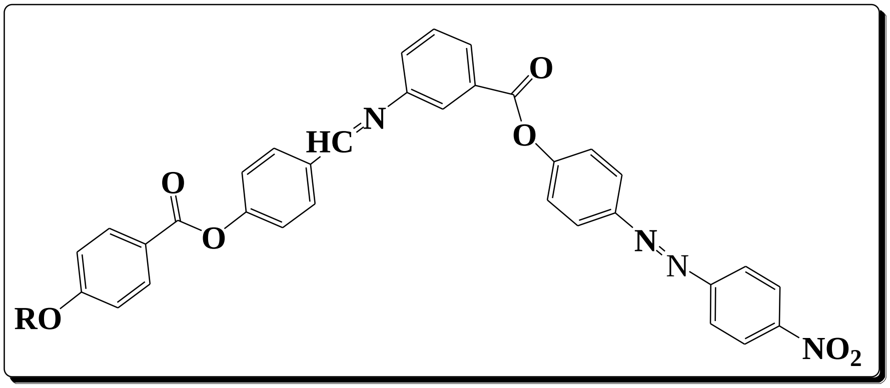
R = C_nH_{2n+1} n = 1to 8, 10,12,14,16.

(1) Alcohol, KOH, n-RBr, (2) DCC, DMAP, DCM, p- Hydroxy benzaldehyde Stirred for Overnight Stirred for 12 hr, (3) Ethanol, 4- amino benzoic acid, 1-2 drops Gla. Acetic Acid, (4) Ethanol, 4-nitroaniline, 1-2 drops Gla. Acetic Acid (5) DCC, DMAP, DCM, Stirred for 12 hr.

6.2.3 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 is performed on a Mettler Toledo Star SW 7.01.

Table 6.1: Transition Temperatures Series XII: 3-[(4’’’’-*n*-alkyloxybenzoyloxy)-4’’’-benzilideneamino methyl]-4’’-nitrophenyl-4’-azophenyl benzoates.



R = *n*-Alkyl group	Transition Temperature °C		
	B7	**Nematic**	**Isotropic**
Methyl	--	194	264
Ethyl	--	181	275
Propyl	--	133	279
Butyl	--	135	270
Pentyl	--	126	264
Hexyl	--	107	245
Heptyl	109	185	228
Octyl	90	192	219
Decyl	92	202	208
Dodecyl	87	--	186
Tetradecyl	83	--	172
Hexadecyl	78	--	163

Table 6.2: Elemental Analysis

Series	Homologue	Theoretical			Practical		
		C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
XII	C7	70.09	5.25	8.17	70.12	5.24	8.16
XII	C10	70.99	5.77	7.70	70.97	5.72	7.69

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

Propyl homologue : 2925 – 2858 (–C–H St, Alkyl –CH_3, SP^3 hybridization), 1734 (–C=O– St. of ester), 1604 (–N=N– St., -C-H St. of –C=N–), 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 –$(CH_2)_7$–).

Dodecyl homologue : 2925 – 2858 (–C–H St, Alkyl –CH_3, SP^3 hybridization), 1734 (–C=O– St. of ester), 1604 (–N=N– St., –C–H St. of –C=N-), 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), 1.25–1.68 (m, 8H, 4(–CH_2–)), 1.83 (Qunt, 2H, –$OCCH_2$), 4.06 (t, 2H, –OCH_2), 8.40 (s, 1H, –CH=N–) 6.97-8.38 (m, 20H, Ar–H)

Octyl homologue: δ = 0.90 (t, 3H, –CH_3), 1.25-1.54 (m, 10H, 5(–CH_2–)), 1.83 (Qunt, 2H, –$OCCH_2$), 4.06 (t, 2H, –OCH_2), 8.41 (s, 1H, –CH=N–) 6.98-8.38 (m, 20H, Ar–H)

Mass Spectra: MS m/z:

Heptyl Homologue: Theoratical Mass value: 684.26 g/mol

Practical mass value: MS m/z: 683.98 (M^+)

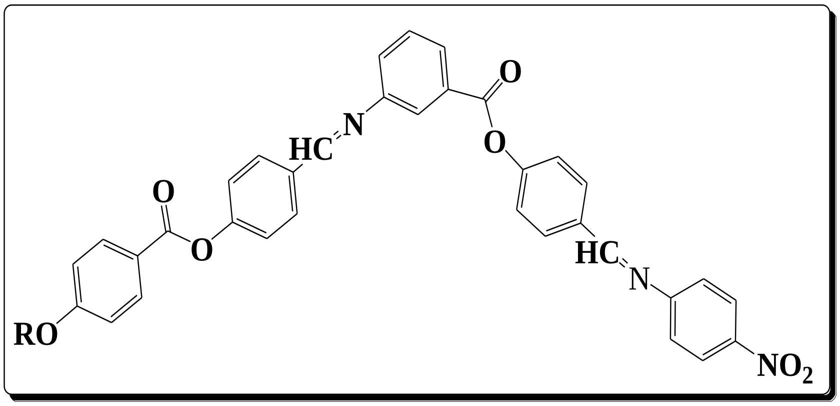
Table 6.3: DSC Data

Series	**Member**	**Heating rate ºC/min**	**Transition Temperature ºC**	**ΔH=J/g**	**ΔS=J/g.K**
XII	C3	10	Cr-M 154.20 N-I 291.70	19.63 0.25	0.04595 0.00045
XII	C7	10	Cr-M 109.49 S-N 185.65 N-I 228.80	29.35 2.66 0.76	0.0768 0.0058 0.0015

Table 6.4: UV Data

Series	**Homologue**	**UV λ max values nm (solvent – ethyl acetate)**	
		π → π*	**n → π***
XI1	C4	340	453
	C10	342	458

Table 6.5: Transition Temperatures Series XIII: 3-[(4’”’-*n*-alkyloxybenzoyloxy)4’’’benzilideneamino methyl]-4’’-nitrophenylimino-4’-benzoates.



R = *n*-Alkyl group	Transition Temperature ºC		
	Smectic A	Nematic	Isotropic
Methyl	--	--	278
Ethyl	--	--	267
Propyl	--	--	254
Butyl	--	229	258
Pentyl	--	225	243
Hexyl	135	213	238
Heptyl	126	--	216
Octyl	128	--	186
Decyl	105	--	165
Dodecyl	61	--	126
Tetradecyl	58	--	125
Hexadecyl	55	--	109

Table 6.6: Elemental Analysis

Series	Homologue	Theoretical			Practical		
		C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
XIII	C6	71.67	5.22	6.27	71.64	5.23	6.32
XIII	C16	74.07	6.79	5.18	74.10	6.68	5.10

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

Heptyl homologue : 2925 – 2858 (–C–H St, Alkyl –CH_3, SP^3 hybridization), 1734 (–C=O– St. of ester), 1604 (–C–H St. of –C=N–), 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 –$(CH_2)_7$–).

Decyl homologue : 2925 – 2858 (C–H St, Alkyl –CH_3, SP^3 hybridization), 1734 (–C=O– St. of ester), 1604 (–C–H St. of –C=N–), 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 – $(CH_2)_7$–).

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

Hexyl homologue: δ = 0.92 (t, 3H, –CH_3), 1.25-1.53 (m, 6H, 3(–CH_2–)), 1.85 (Qunt, 2H, –$COCH_2$), 4.05 (t, 2H, –OCH_2), 8.43 (s, 2H, –CH=N–) 6.59-8.29 (m, 20H, Ar–H)

Mass Spectra: MS m/z:

Heptyl Homologue: Theoratical Mass value: 683.26 g/mol

Practical mass value: MS m/z: 685 (M^{+1})

Table 6.7: DSC Data

Series	Member	Heating rate °C/min	Transition Temperature °C	ΔH=J/g	ΔS=J/g.K
XII	C12	10	Cr-M 60.21 N-I 126.50	93.28 14.25	0.2799 0.0356
XII	C16	10	Cr-M 53.91 N-I 108.61	91.25 5.28	0.2791 0.0138

Table 6.8: UV Data

Series	Homologue	UV λ max values nm (solvent – ethyl acetate)	
		π → π*	**n → π***
XI1	C5	275	327
	C16	278	328.50

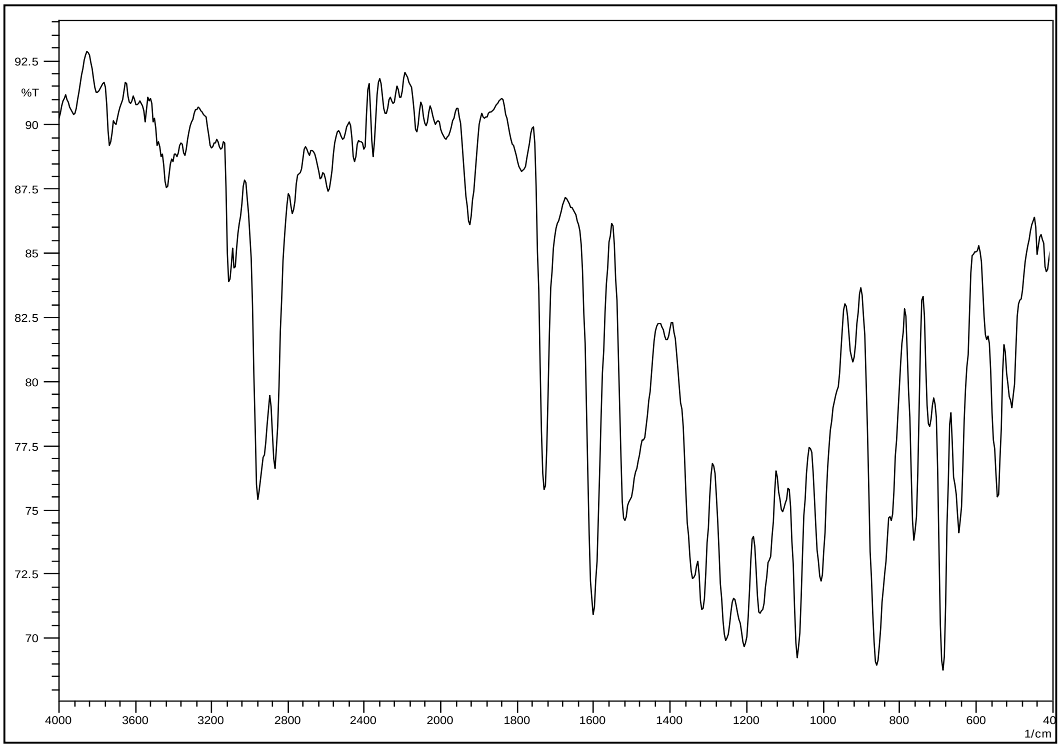


Figure 6.1 (a): IR spectra of C7 homologue of series XII

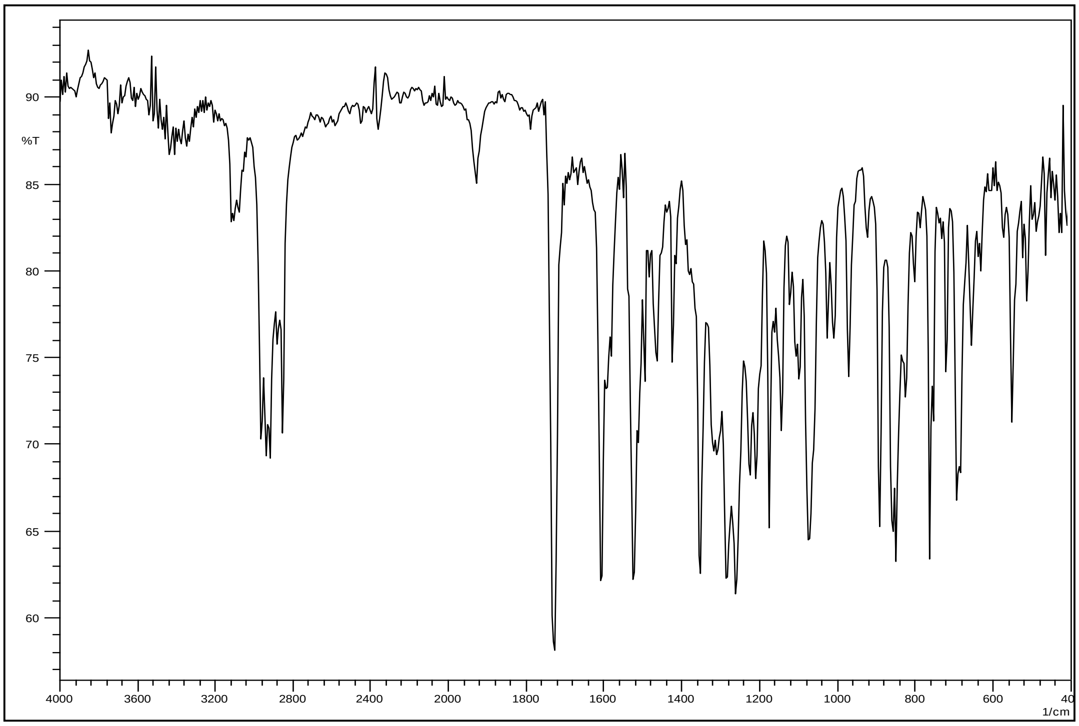


Figure 6.1 (b): IR spectra of C10 homologue of series XII

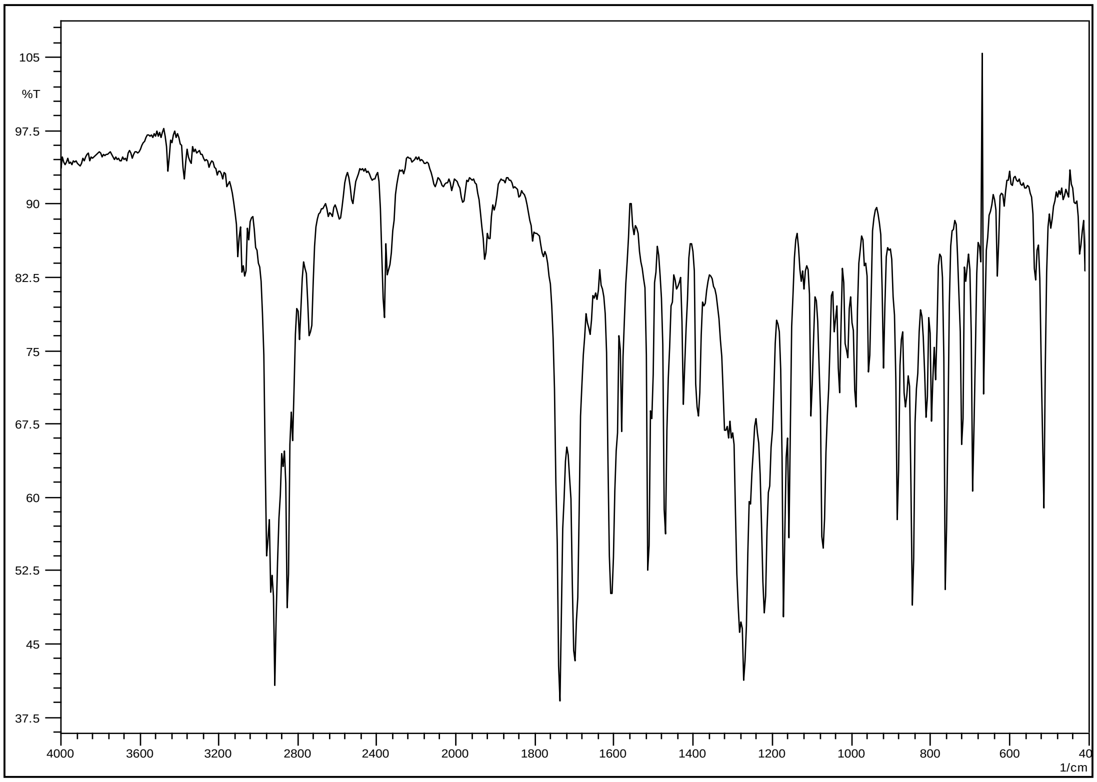


Figure 6.1 (c): IR spectra of C12 homologue of series XIII

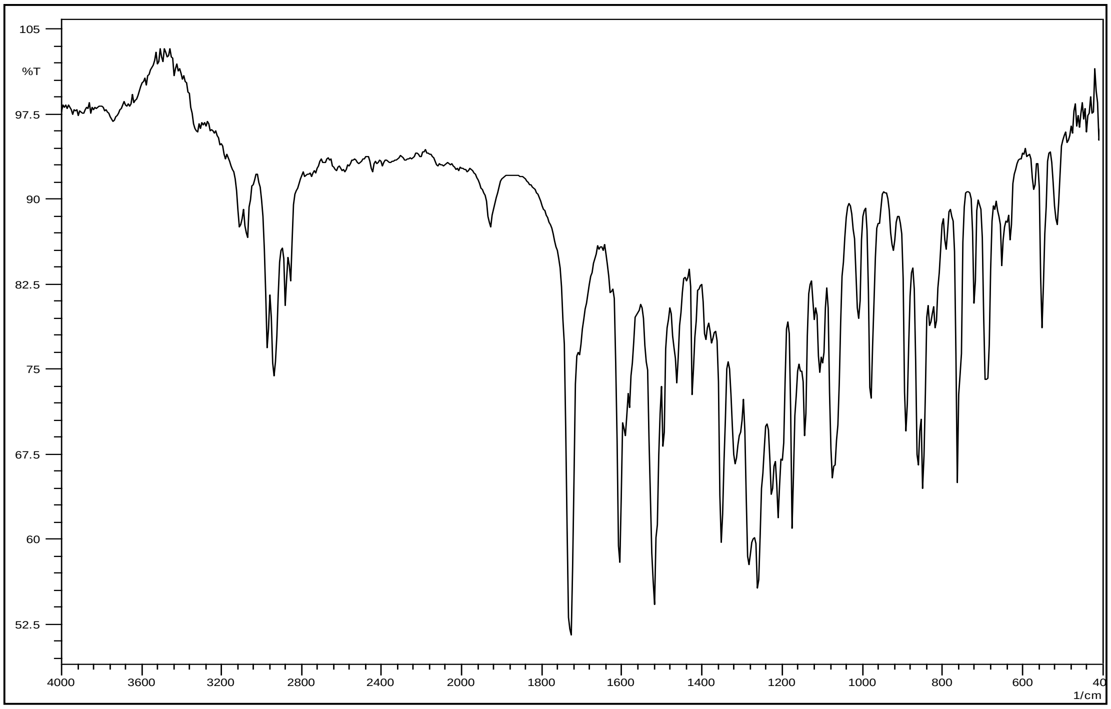


Figure 6.1 (d): IR spectra of C3 homologue of series XIII

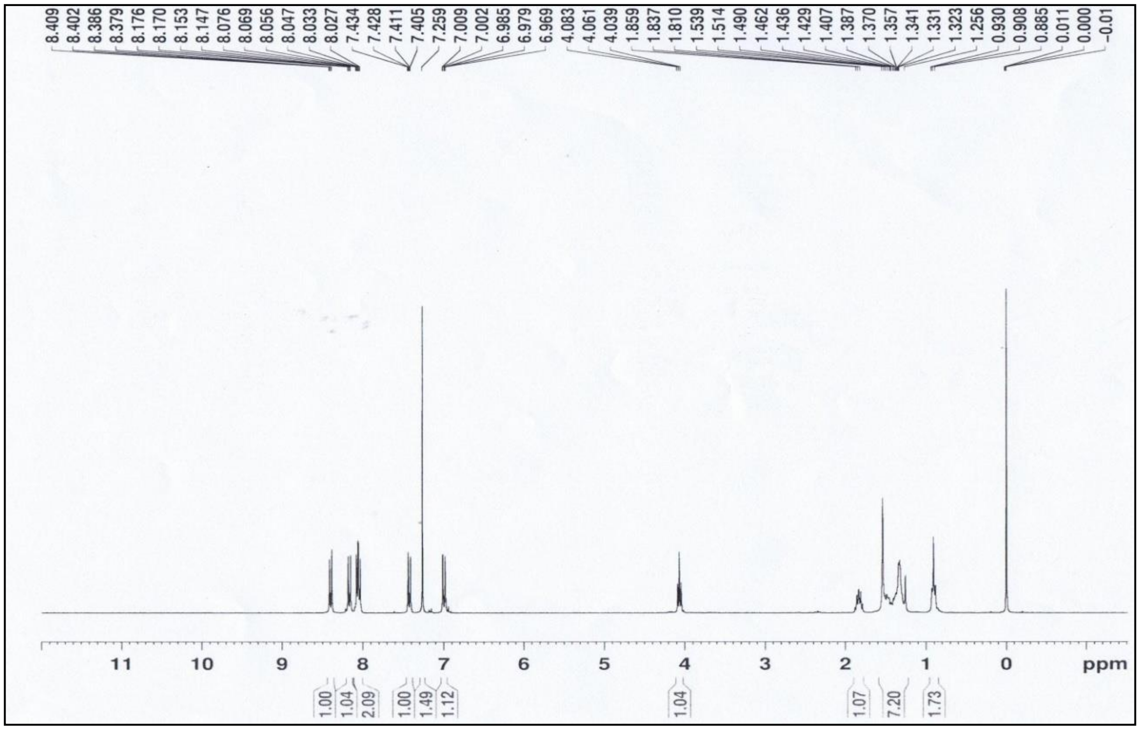


Figure 6.2 (a): ^{1}H NMR spectra of C7 homologue of series XII

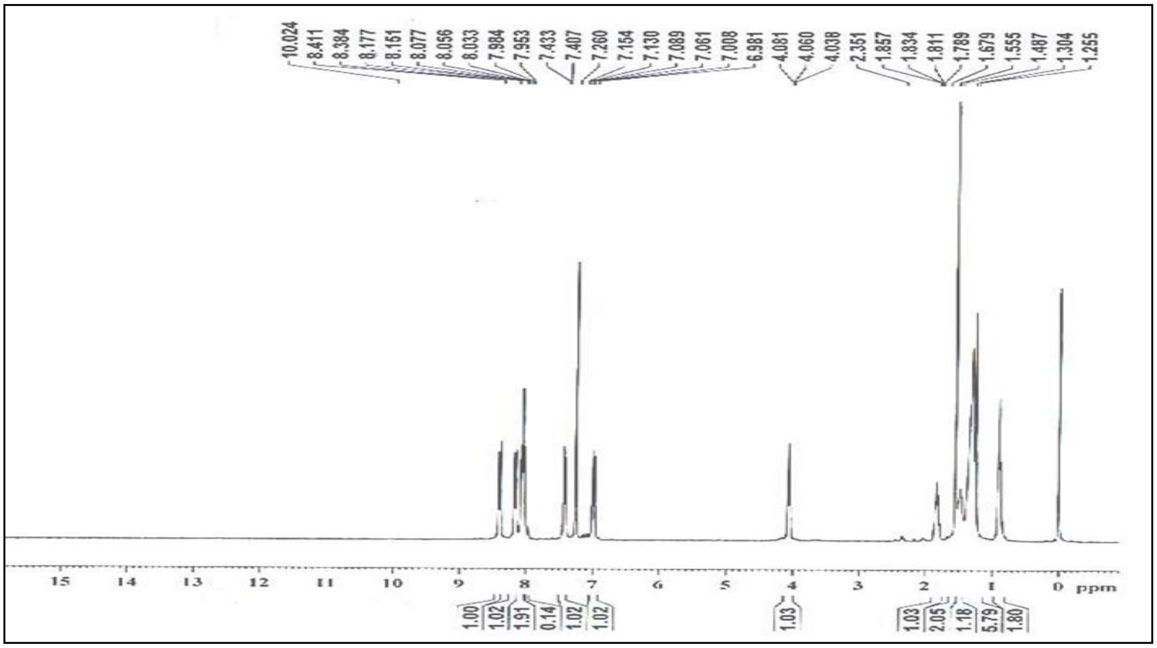


Figure 6.2 (b): ^{1}H NMR spectra of C8 homologue of series XII

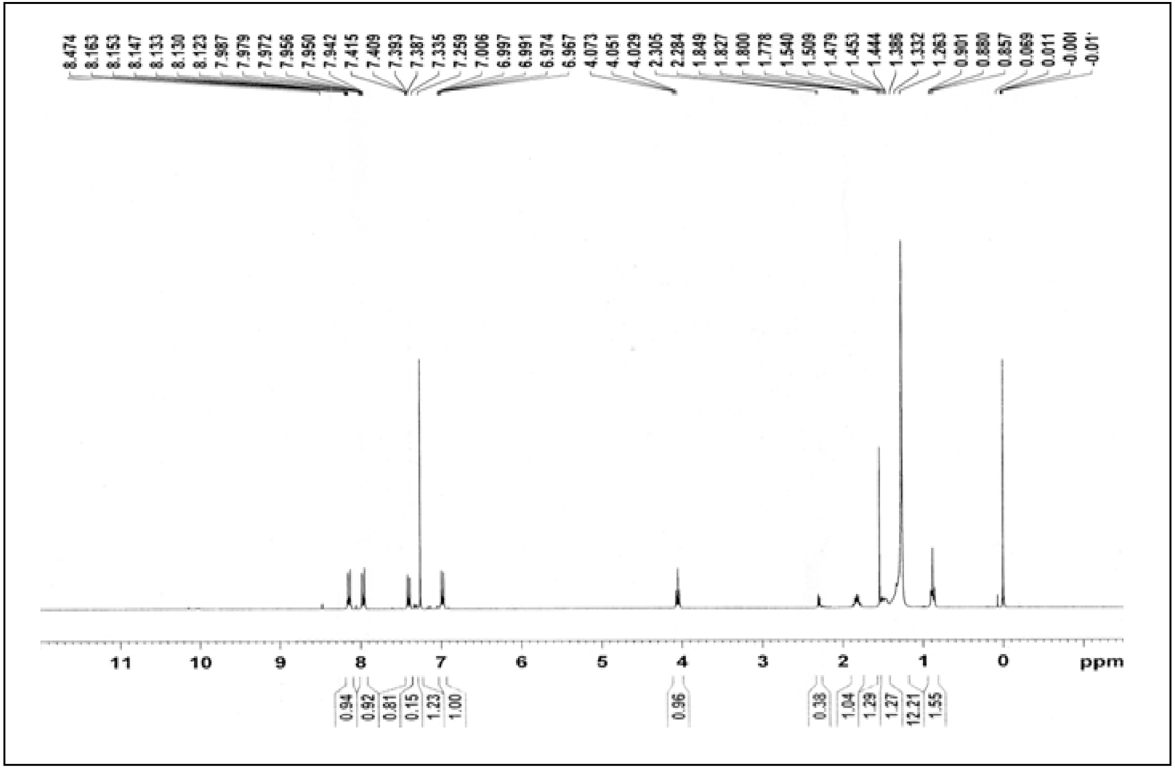


Figure 6.2 (c): ^{1}H NMR spectra of C6 homologue of series XIII

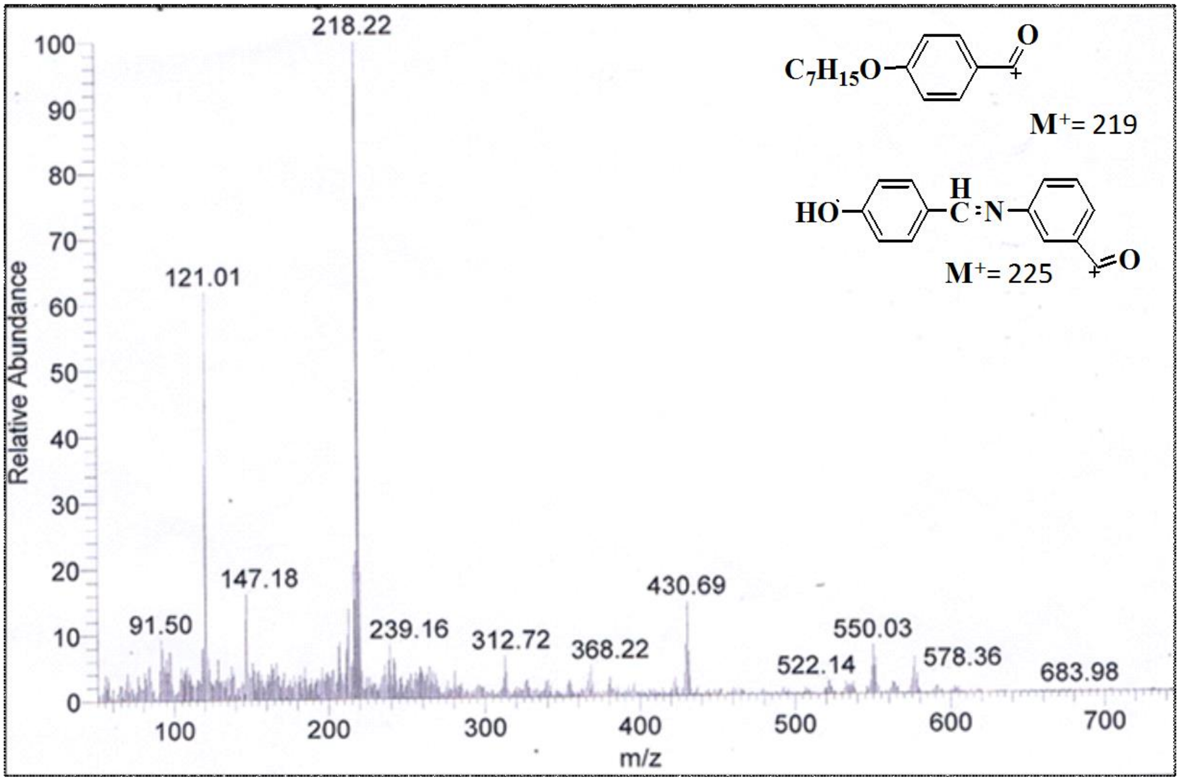


Figure 6.3 (a): Mass spectra of C7 homologue of series XII

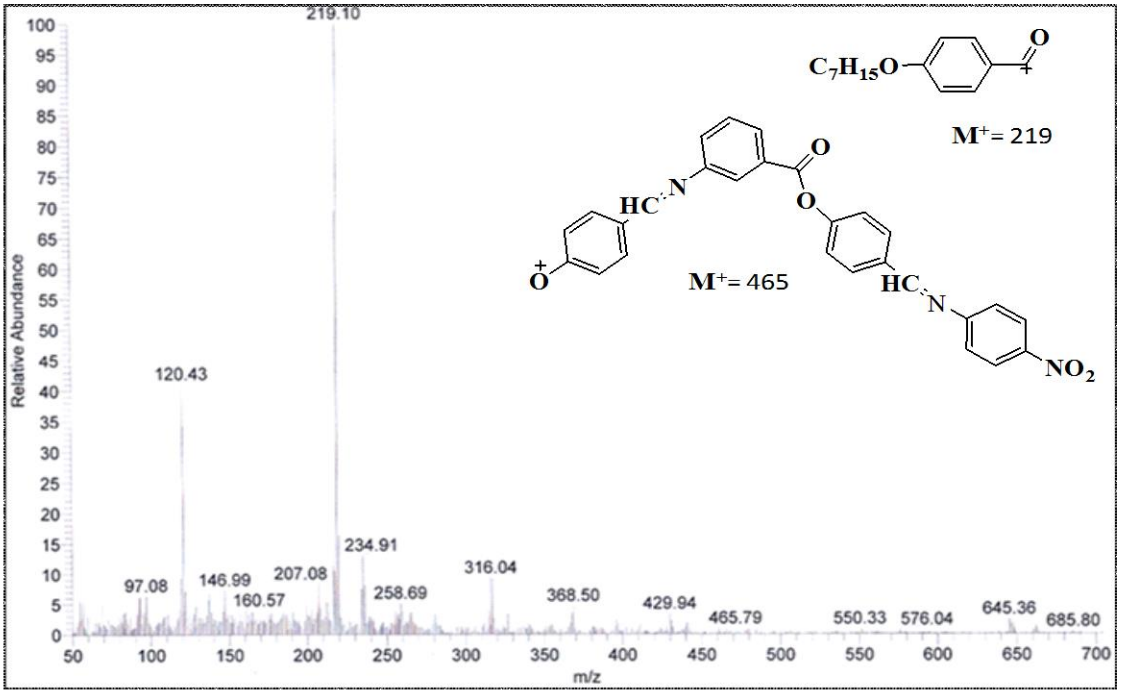


Figure 6.3 (b): Mass spectra of C16 homologue of series XIII

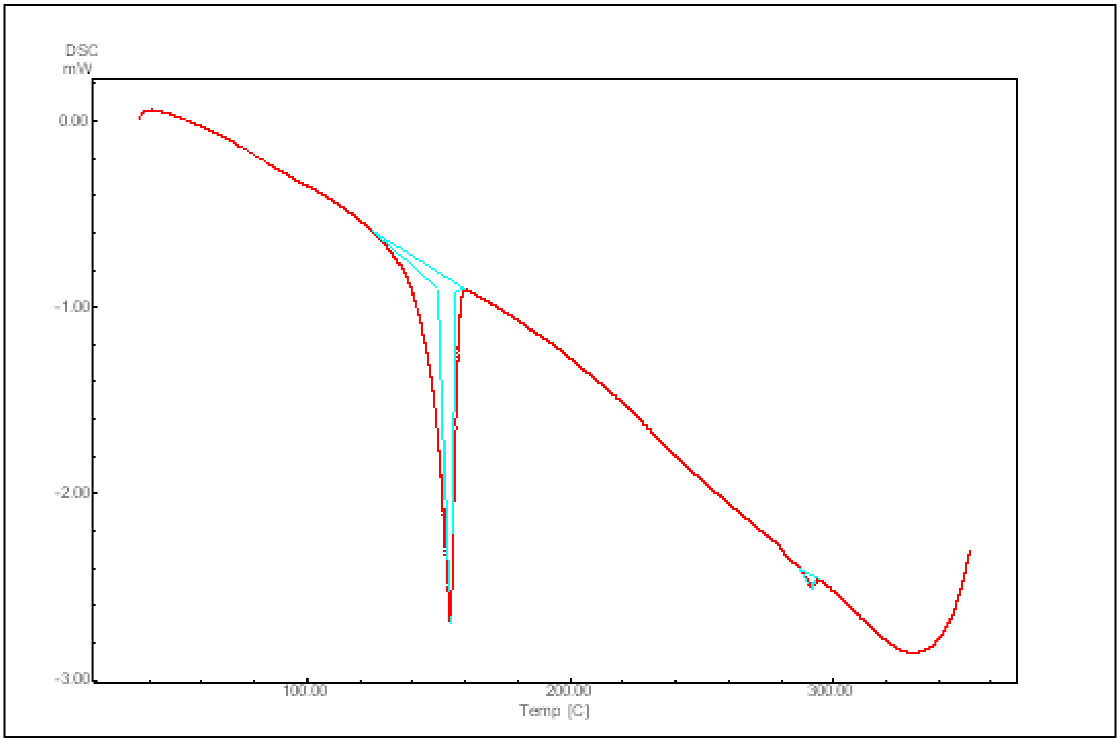


Figure 6.4 (a): DSC Thermogram of C3 homologue of series XII

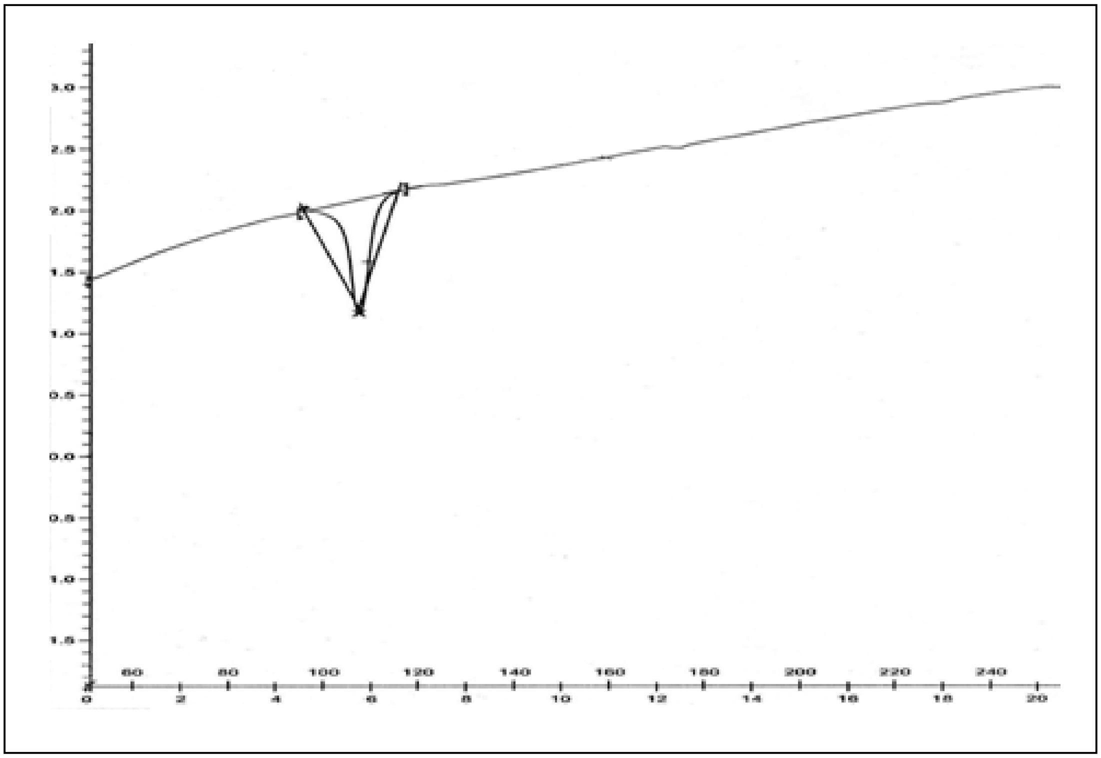


Figure 6.4 (b): DSC Thermogram of C7 homologue of series XII

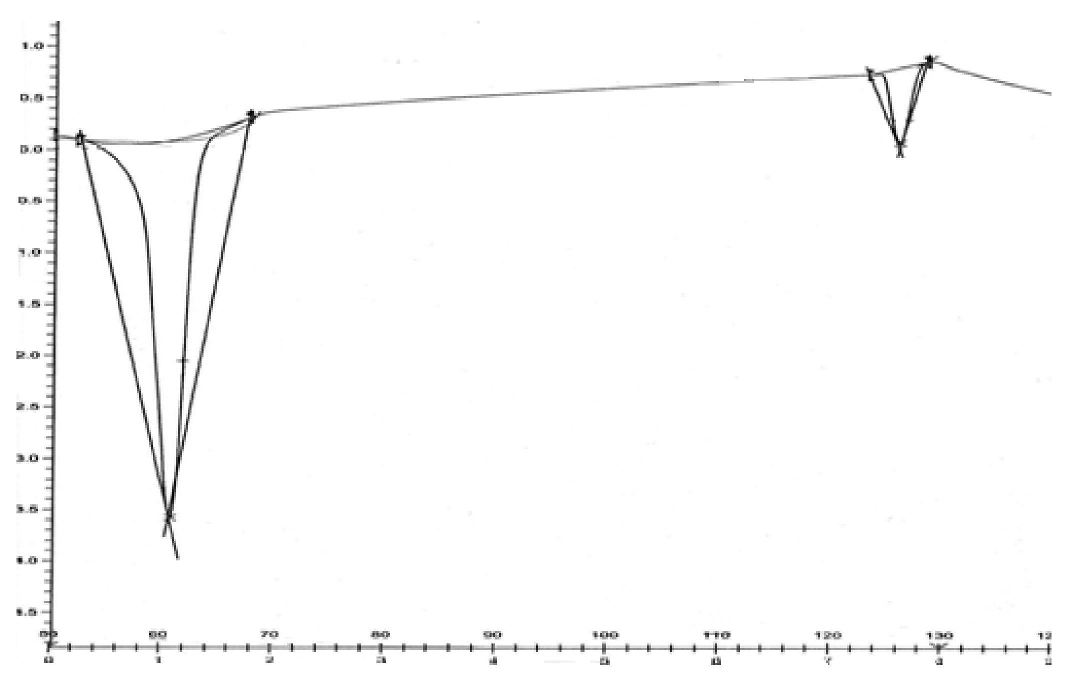


Figure 6.4 (c): DSC Thermogram of C12 homologue of series XIII

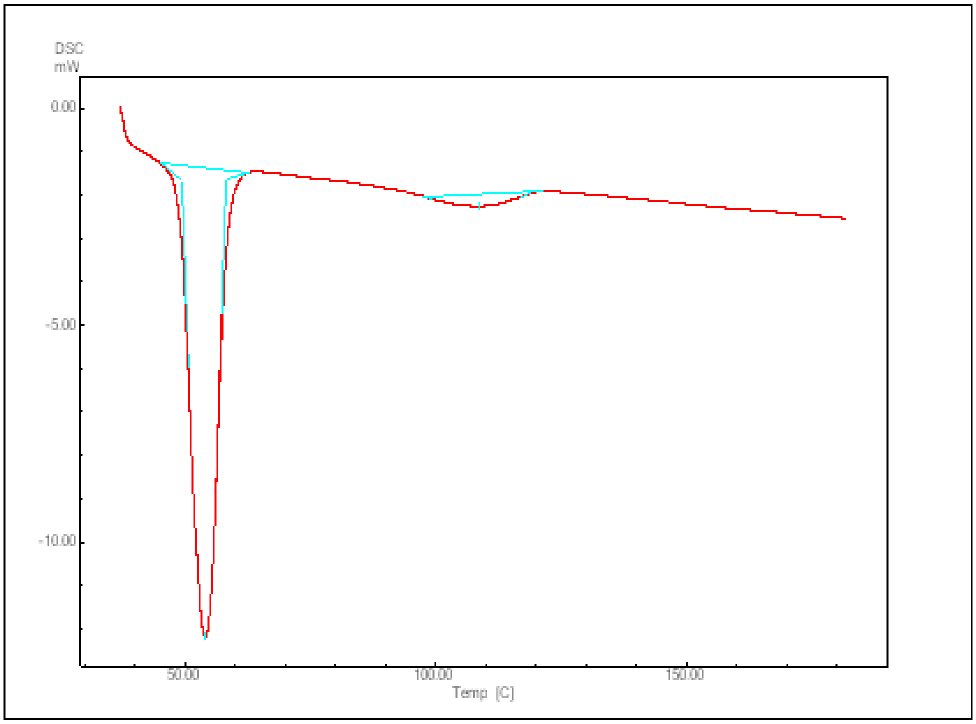


Figure 6.4 (d): DSC Thermogram of C16 homologue of series XIII

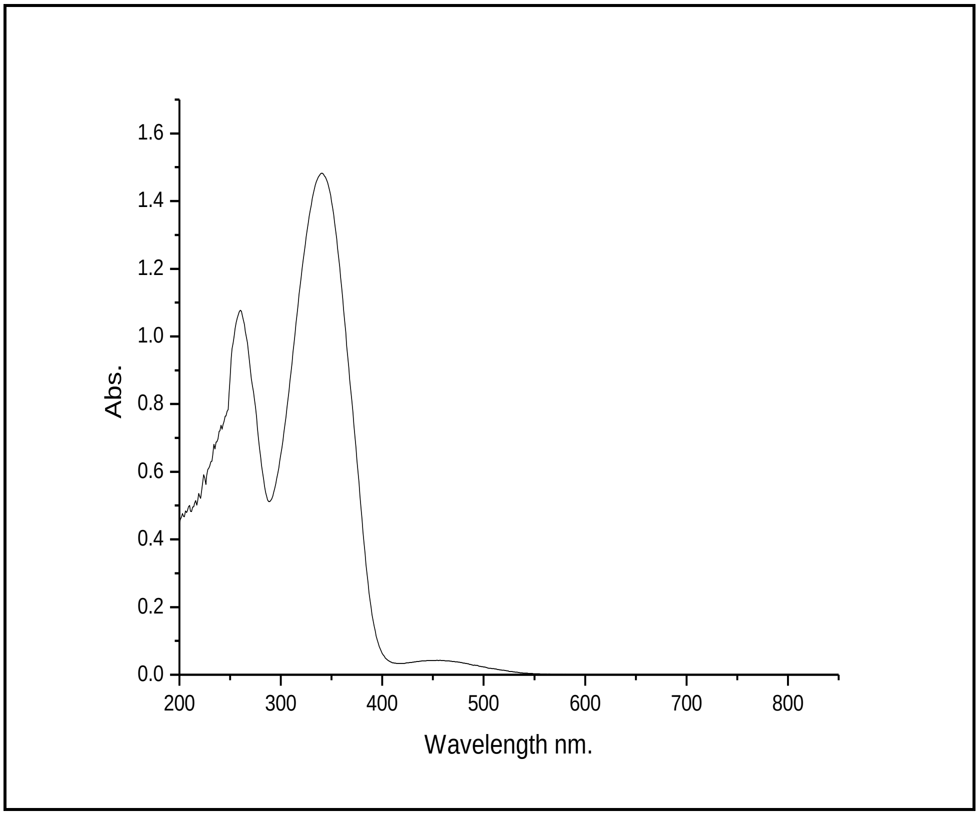


Figure 6.5 (a): UV spectra of C4 homologue of series XII

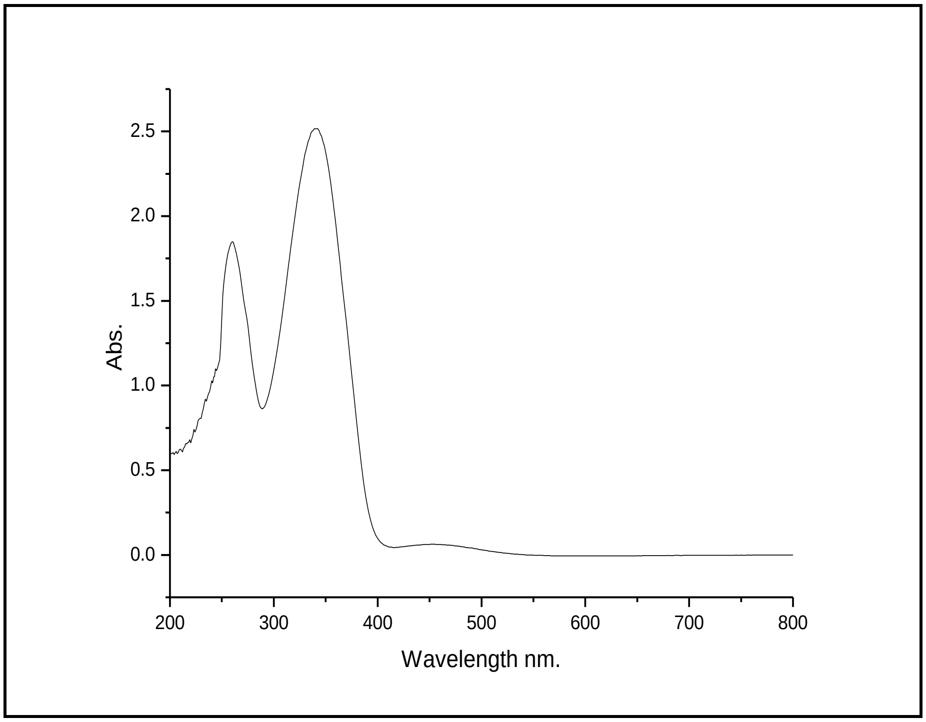


Figure 6.5 (b): UV spectra of C10 homologue of series XII

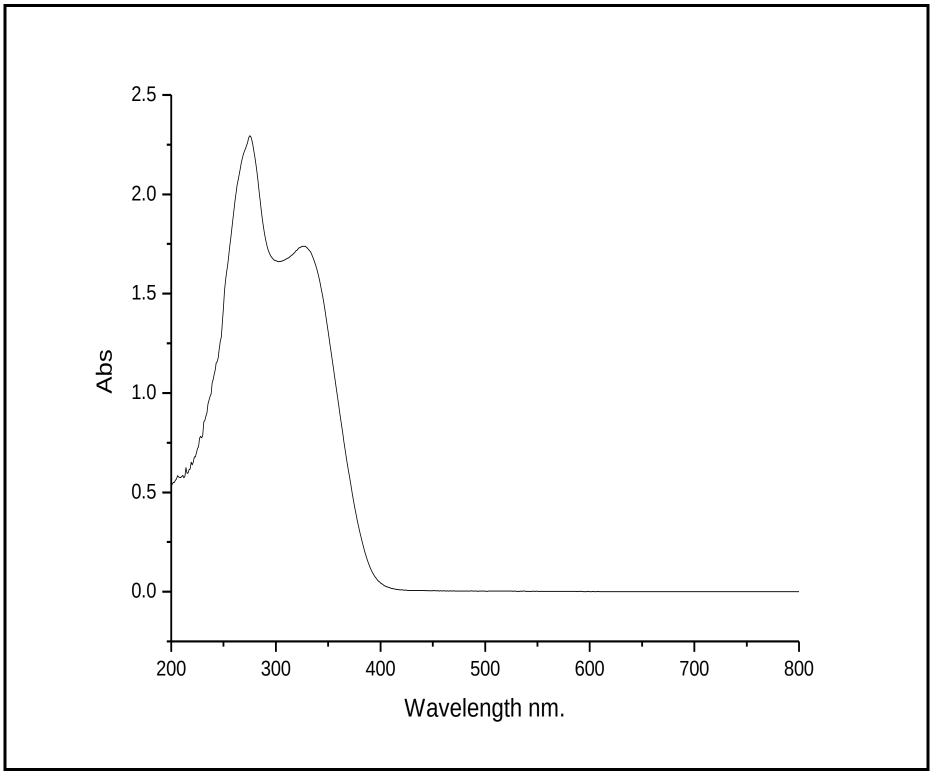


Figure 6.5 (c): UV spectra of C5 homologue of series XIII

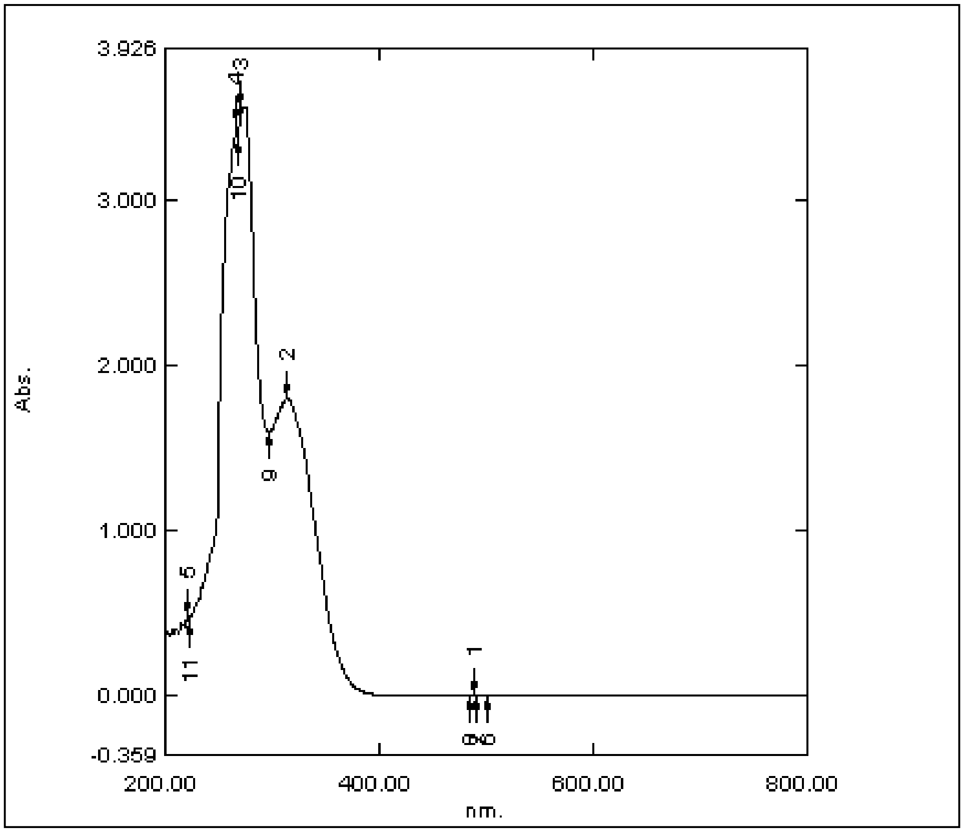
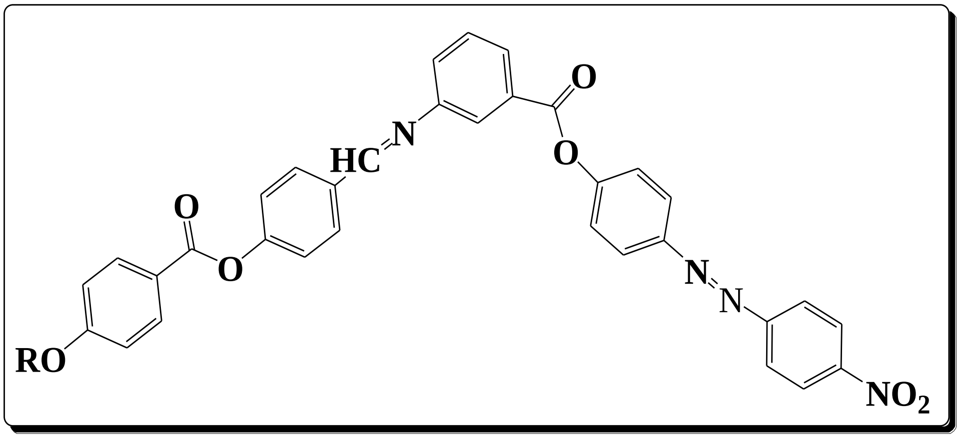


Figure 6.5 (d): UV spectra of C16 homologue of series XIII

6.3 Results and Discussion

6.3.1 Series XII: 3-[(4’’’’-*n*-alkyloxybenzoyloxy)-4’’’-benzilideneamino methyl]-4’’-nitrophenyl-4’-azophenyl benzoates.

General molecular structure of the series XII: 3-[(4’’’’-*n*-alkyloxybenzoyloxy)-4’’’-benzilideneamino methyl]-4’’-nitrophenyl-4’-azophenyl benzoates.



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

All the twelve homologues of the series XII are mesogens (Table:6.1, Figure: 6.5); the nematic phase commences from the very first derivative and remains upto the C10 derivative, whereas the B7 phase is commences from the C7 derivative and is exhibited along with nematic mesophase till the C10 derivative, C12 to C16 homologues show B7 mesophase only. Figure: 6.5 show the plot of transition temperatures against number of carbon atoms in the *n*-alkoxy chain; it indicates that the N-I curve shows slight rising tendency in the initial members from C2 to C3 of the series and then from C4 to C16 derivatives it shows falling tendency as series is ascended. The Cr – M transitions show steep fall from the C1 to C3 derivative and then gradually falls with a slight rise at C7 homologue synthesized. The nematic phase of the series shows marble/schlieren texture whereas the B7 phase shows spiral filament texture which is the hallmark [490-492] of the B7 banana mesophase.

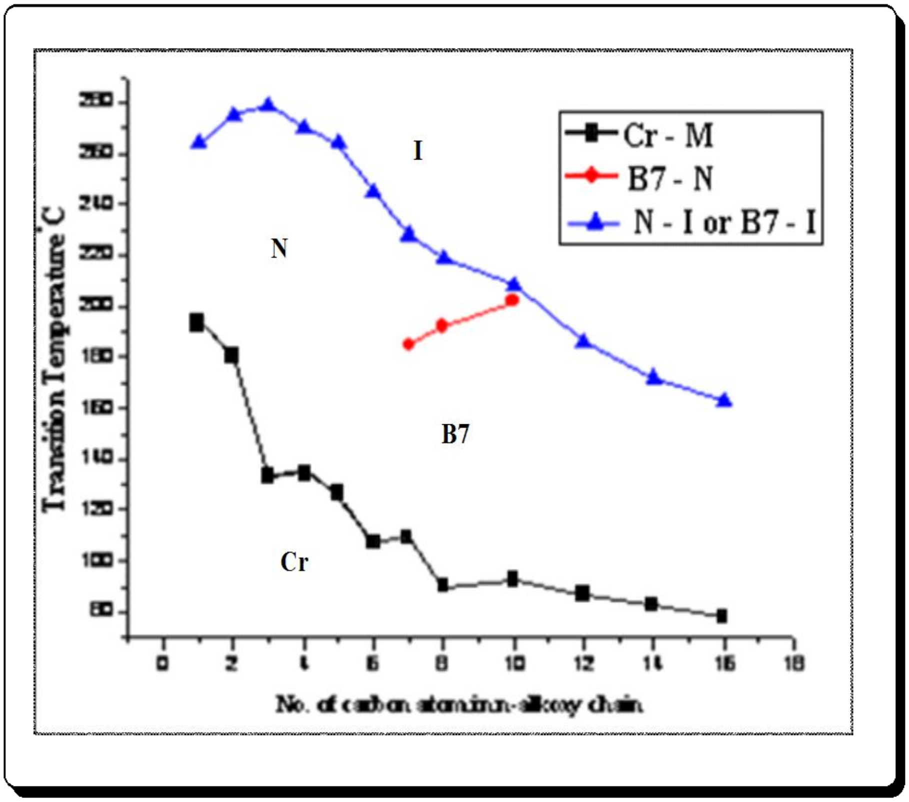


Figure 6.5: 3-[(4””-*n*-alkyloxybenzoyloxy)-4’’’-benzilideneamino methyl]-4’’-nitrophenyl-4’-azophenyl benzoates. (Series XII)

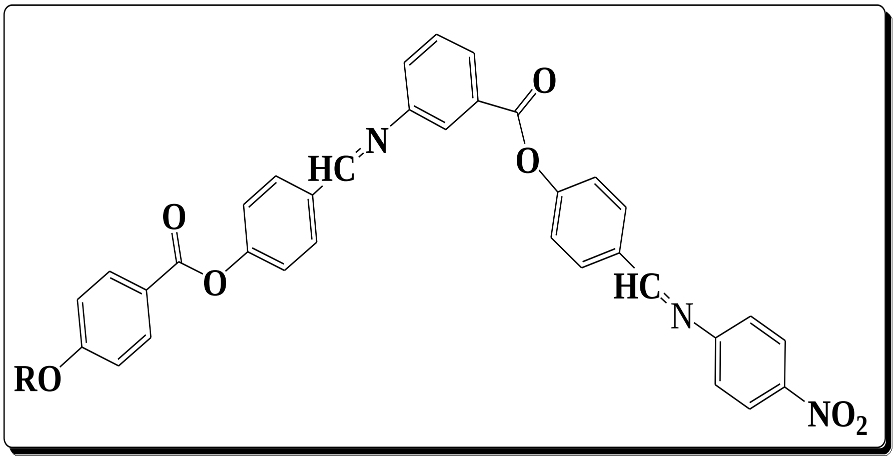
Table 6.1: Transition Temperatures: Series XII

R = *n*-Alkyl group	Transition Temperature ºC		
	B7	**Nematic**	**Isotropic**
Methyl	--	194	264
Ethyl	--	181	275
Propyl	--	133	279
Butyl	--	135	270
Pentyl	--	126	264
Hexyl	--	107	245
Heptyl	109	185	228
Octyl	90	192	219
Decyl	92	202	208
Dodecyl	87	--	186
Tetradecyl	83	--	172

Hexadecyl	78	--	163

6.3.2 Series XIII: 3-[(4'''''-*n*-alkyloxybenzoyloxy)-4'''-benzilideneaminomethyl]-4''-nitrophenylimino-4'-benzoates

General molecular structure of the series XIII: 3-[(4''''-*n*-alkyloxybenzoyloxy)4'''benzilideneamino methyl]-4''-nitrophenylimino-4'-benzoates.



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

In this homologous series the first three members are non-mesogenic in nature (Table: 6.2, Figure: 6.6); the mesogenic behavior commences from C4 homologue in the form of nematic phase & continue to be exhibited upto C6 homologue. The smectic phase commences from C6 homologue alongwith nematic phase; the C7 to C16 derivatives show only smectic mesophase. The Cr – S curve slight falls initially C6 to C7 derivative and then a slight rise at C8 derivative & then more or less steep fall upto the last C16 derivative. The Cr – N curve shows a slight fall from C4 to C5 derivative. The N – I curve shows gradual falling tendency from C4 to C6 derivative and then merges with falling S – I curve at C7 derivative which then show more or less a steep falling tendency with a very steep fall at the last C16 derivative. The nematic phase of the series shows marble/schlieren texture whereas the smectic phase of the series shows broken focal conic fan shaped texture of smectic A variety.

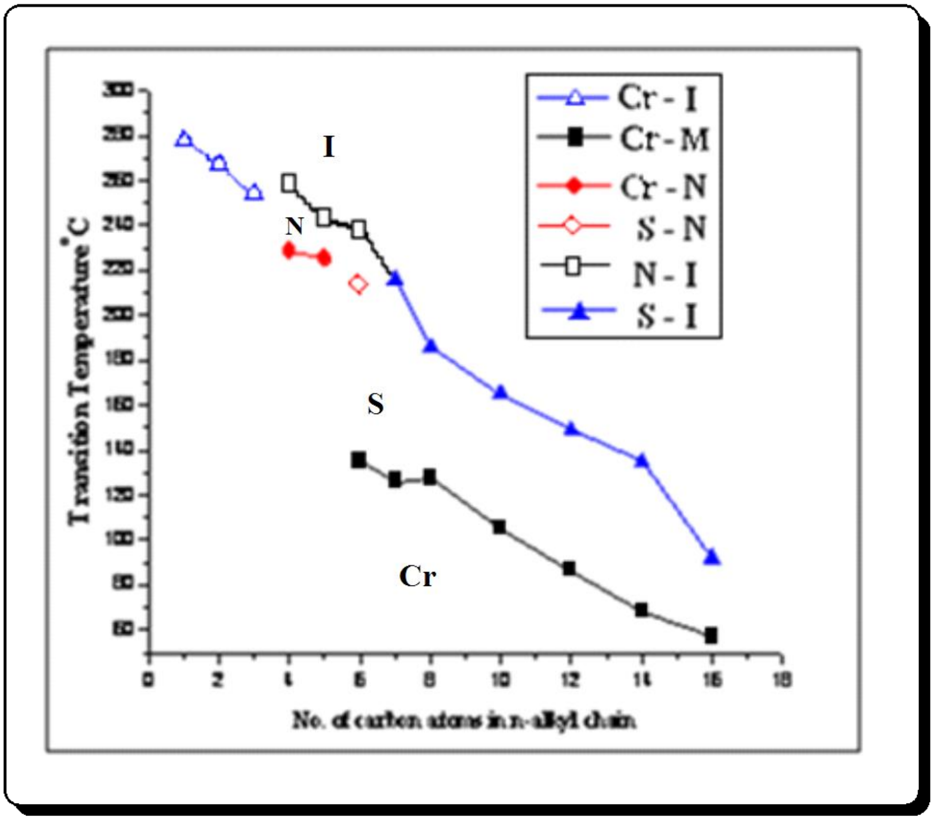


Figure 6.6: 3-[(4””-*n*-alkyloxybenzoyloxy)-4’’’-benzilideneaminomethyl]-4’’-nitrophenylimino-4’-benzoates (Series XIII).

Table 6.2: Transition Temperatures: Series XIII

R = *n*-Alkyl group	Transition Temperature ºC		
	Smectic A	**Nematic**	**Isotropic**
Methyl	--	--	278
Ethyl	--	--	267
Propyl	--	--	254
Butyl	--	229	258
Pentyl	--	225	243
Hexyl	135	213	238
Heptyl	126	--	216
Octyl	128	--	186
Decyl	105	--	165
Dodecyl	61	--	126
Tetradecyl	58	--	125
Hexadecyl	55	--	109

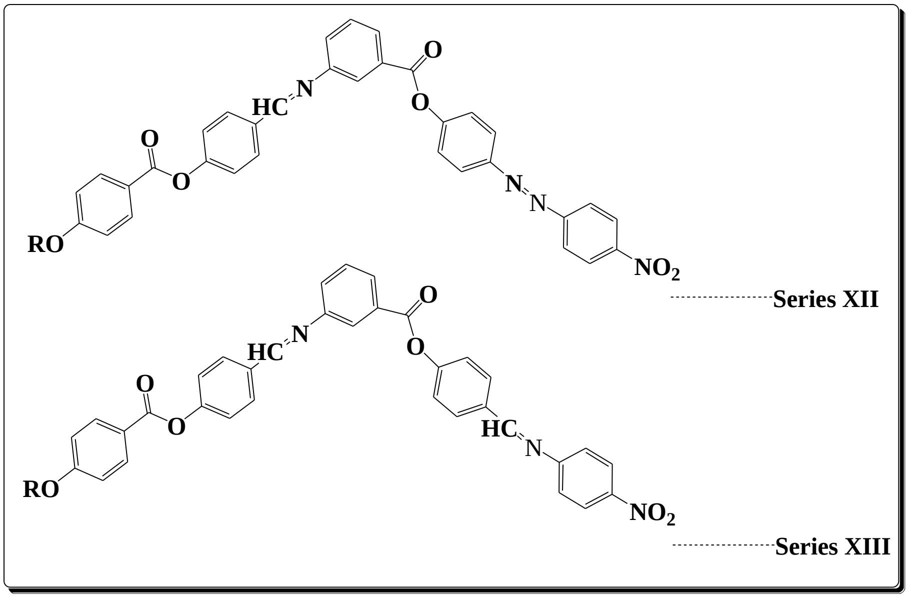


Figure 6.7: Molecular geometry of the homologous series under comparison

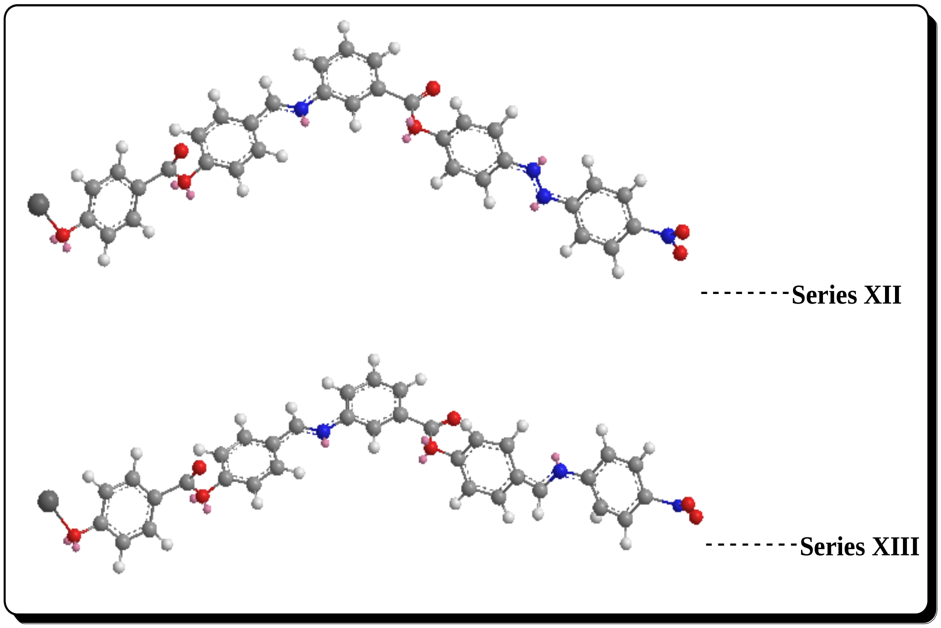


Figure 6.8: Energy minimized 3D Molecular geometry of the homologous series under comparison from ChemDraw Ultra 8.0 software.

Table 6.5: Average thermal stabilities °C

Series	N-I	B7 – I / Cr – M	Commencement of B7 or Smectic mesophase
XII	250.22 (C1-C10)	183.33 (C7-C16)	C7
XIII	246.33 (C4-C6)	162.85 (C4-C16)	C6

The average thermal stabilities of the two homologous series are compared with each other (Table: 6.5, Figure 6.7, 6.8 and 6.9), molecular geometry of both of the series is similar except that series XIII has azomethine. Figure 6.7 and 6.8 show general molecular geometry and energy minimized 3D molecular structures of the homologous series under comparison from ChemDraw ultra 8.0 software.

–CH=N– bridging linkage in place of azo, –N=N– bridging linkage in series XII. The observation of banana phases in azo compounds assumes significance from the fact that the introduction of azo linkage bring in a new dimension to this field, namely photochromism [488, 489]. Keeping this idea in view, the synthesis of bent shaped molecules with azo bridging linkage is carried out; another series replacing azo –N=N– bridging linkage by azomethine –CH=N– is synthesized to study the effect of this structural modification on mesomorphic properties of homologues.

The N–I thermal stability of series XII is higher than series XIII due to presence of –N=N– (azo) bridging linkage in place of –CH=N– azomethine [409] bridging linkage in bridging linkage in series XIII; series XII exhibits B7 mesophase which may also be due to azo –N=N– linkage which can show photochromism; series XIII with –CH=N– azomethine bridging linkage in place of azo –N=N– bridging linkage in series XII.

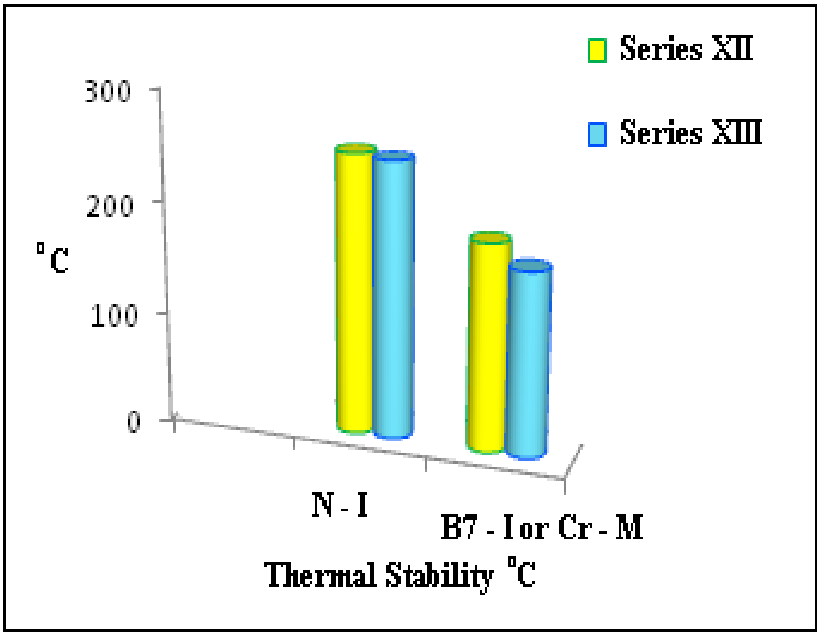
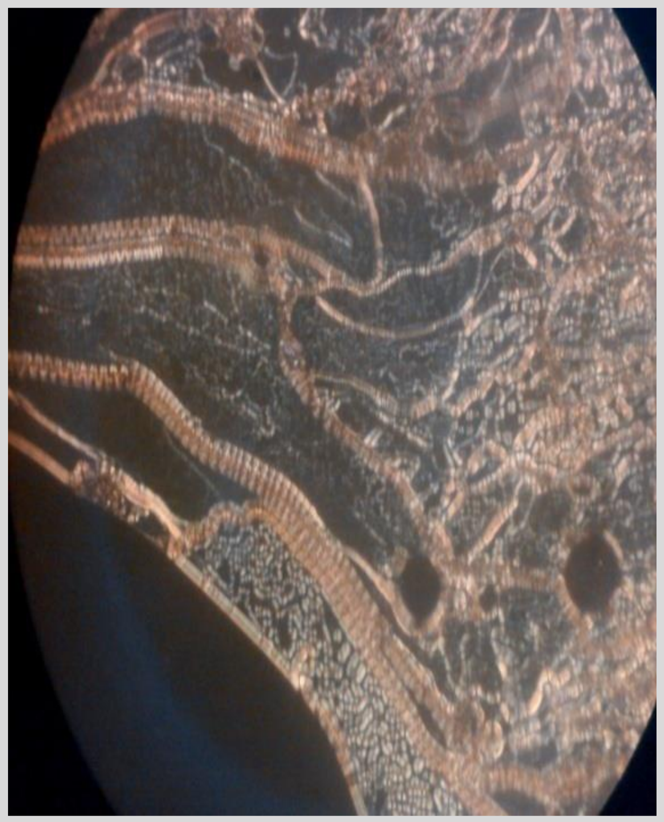
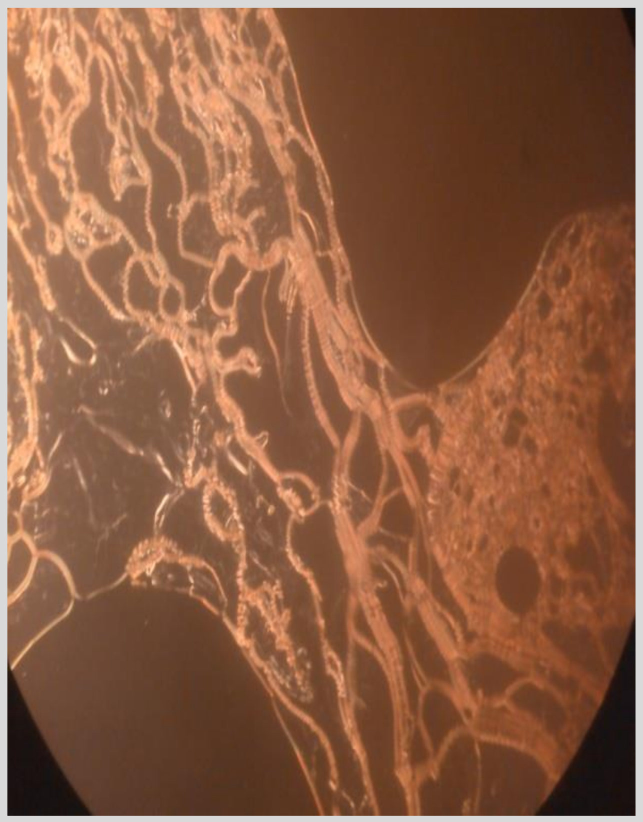


Figure 6.9: Average thermal stability (TS) for the homologous series under comparison

Polarizing optical microscopic images of Liquid Crystals



(a)



(b)

(a) Helical Spiral texture of B7 phase of C7 homologue of Series XII at 147 °C on cooling.

(b) Helical Spiral texture of B7 phase of C8 homologue of Series XII at 116 °C on cooling.

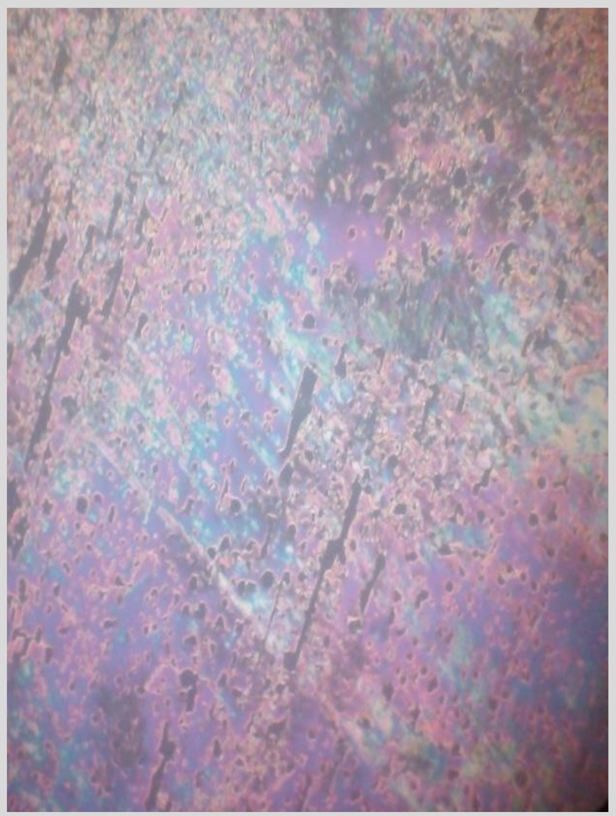
(c)

(d)

(c) Helical Spiral texture of B7 phase of reported compounds [503]

(d) Magnified image of C7 homologue of Series XII at 116 °C on cooling.

(e)



(f)

(e) Focal conic fan shaped texture of smectic phase of C6 homologue of Series XIII at 189 °C on cooling.

(f) Marble texture of nematic phase of C6 homologue of Series XIII at 227 °C on cooling.