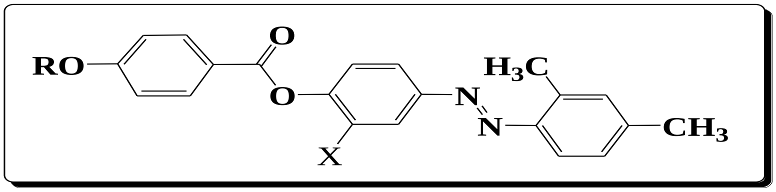
3.1 Introduction

The properties of liquid crystals depend on the molecular structure of liquid crystal molecules [409].A number of homologous series with ester and azo central linkages have been synthesized having different terminal groups [410]; terminal substituents play a significant role in imparting liquid crystalline properties to compounds. Introduction of lateral substitution makes molecules broad and plays an effective role in mesogenic properties of liquid crystalline compounds [411]. The variations in structural characteristics of compounds play a very vital role in exhibition of different types of mesophases, their transition temperatures and thermal stabilities of these mesophases [412]. In this connection, systematic studies have been carried out by various researchers [413-430]. In order to investigate the effect of terminal and lateral substituents and adding flexibility in ester central bridging linkage. Seven homologous series having ester and azo central linkages and different lateral groups in the terminal and central benzene ring are synthesized and their mesomorphic properties are studied.

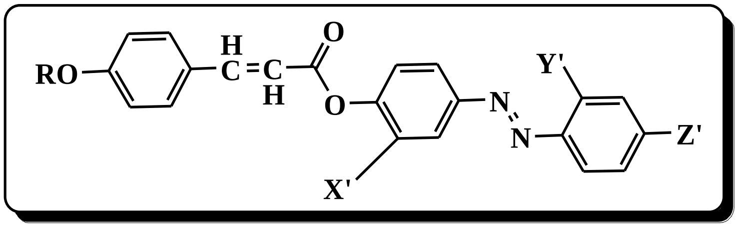
Part I of the chapter consisting of three homologous series having benzoyloxy and azo central linkages whereas, part II of the chapter consisting of the rest four homologous series having cinnamoyloxy and azo central linkages.

General molecular structure of the series of part I



Series	I	II	III
Lateral Substituent = X	-H	$-CH_3$	-Cl

General molecular structure of the series of part II



Series	IV	V	VI	VII
Lateral Substituent =X’	-H	$-CH_3$	-H	-H
Lateral substituent =Y’	$-CH_3$	-H	-H	-H
Terminal Substituent =Z’	$-CH_3$	$-CH_3$	$-CH_3$	$-NO_2$

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

3.2 Experimental

3.2.1 Material

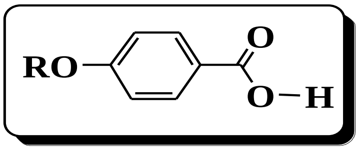
(1) 4-hydroxybenzoicacid, (2) *n*-alkyl halides, (3) phenol, (4) 2-methyl phenol, (5) 2-chloro phenol, (6) 2, 4-dimethyl aniline, (7) potassium hydroxide, (8) n,n-dimethylaminopyridine (DMAP), (9) n,n-dicyclohexylcarbodiimede (DCC) and all other chemicals are of Merck or Loba chemie and used as received.

3.2.2 Synthesis

3.2.2.1 Series I: Series I: 4-(4’-*n*-alkyloxybenzoyloxy)-phenylazo-2”, 4”-dimethylbenzenes

3.2.2.1a 4-*n*-alkoxybenzoic acids

General molecular structure of 4-*n*-alkoxybenzoicacids



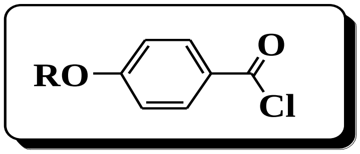
Where, R is C_nH_{2n+1} n = 1 to 8,10,12,14 and 16

Commercially available 4-methoxybenzoicacid (anisicacid, Loba) is used. Number of methods are known for the alkylation of 4-hydroxybenzoicacid [431-433]. In the present study, following modified method is used [433].

0.1 mole of 4-hydroxybenzoic acid and 0.25 moles of KOH pellets are dissolved in the 100ml ethanol. 0.12 mole of respective n-alkyl halide is added and the solution is refluxed for 8 – 10 hours. 10% of 25ml aq. KOH solution is added after the reflux period, and the reflux is continued for two more hours to hydrolyze any ester formed. The solution is cooled to room temperature and acidified with 1:1 HCl to precipitate the desired acid product. They are recrystallized several times from ethanol until constant transition temperatures are obtained. The transition temperatures are in good accordance with the reported values [433].

3.2.2.1b 4-*n*- alkoxybenzoylchlorides [433]

General molecular structure of 4-*n*-alkoxybenzoylchlorides

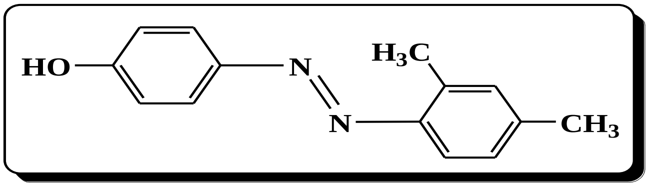


Where, R is C_nH_{2n+1} $n = 1$ to 8,10,12,14 and 16

4-*n*-alkoxybenzoylchlorides are prepared by refluxing the corresponding 0.01 mole 4-n-alkoxybenzoicacids with an excess of Thionyl chloride (10-12ml) under moisture free condition in a water bath, till the evaluation of hydrogen chloride gas ceased. Excess of thionylchloride is distilled off under reduced pressure and the acid chloride left behind as a residue, which is used in the next reaction without further purification.

3.2.2.1c 4-hydroxyphenylazo-2', 4'-dimethylbenzene

General molecular structure of 4-hydroxyphenylazo-2', 4'-dimethylbenzene



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

(i) Preparation of Diazonium salt of 2,4-dimethylaniline

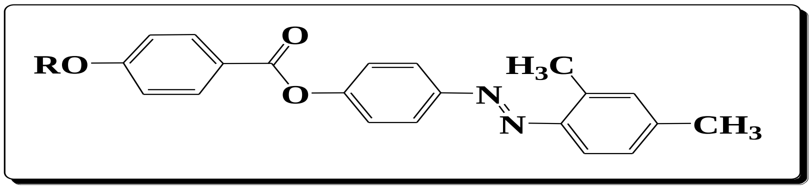
0.036 moles of 2, 4-dimethylaniline is dissolved in a mixture of 13 ml of conc. HCl and 13 ml of water and cooled to 0-5°C in a bath of ice and salt mixture. A cold solution of 0.054 mole of $NaNO_2$ in 8 ml of water is added in small portions at 5°C. During addition the mixture is stirred vigorously. The completion of diazotization is checked by using KI-starch paper. The diazonium salt is used immediately in next step.

(ii) Coupling of 2-4-dimethylbenzenediazoniumchloride with phenol

0.036 mole of phenol is dissolved in 30 ml of 20% NaOH solution; While maintain temperature below 5°C. The mixture is stirred continuously and the cold diazonium salt is added slowly, maintaining the pH 8 to 9. Crystals of the sodium salt of the dye separated out; its mixture is allowed to stand for half an hour; after which it is acidified with 1:1 HCl. The diazo compound obtained is filtered and washed with hot water to remove any decomposed diazoniumsalt; it is recrystallized twice from methanol.

3.2.2.1d 4-(4'-*n*-alkyloxybenzoyloxy)-phenylazo-2", 4"-dimethylbenzenes

General Molecular structure of 4-(4'-*n*-alkyloxybenzoyloxy)-phenylazo-2", 4"-dimethylbenzenes



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

0.01 moles 4-hydroxyphenylazo-2’, 4’-dimethylbenzene is dissolved in 10 ml of dry pyridine and is added slowly to a cold solution of respective 0.01 mole 4-*n*-alkoxybenzoylchlorides in pyridine. The mixture is refluxed in a water bath for an hour and is allowed to stand overnight at room temperature. It is acidified with 1:1 cold HCl and the separated solid was filtered, and successively washed with water, $NaHCO_3$ and NaOH solutions to remove any unreacted acid and phenol. The precipitates were again washed with water till filtrate neutralized solid was dried and column chromatographed on silica gel (60–120 mesh) with 1% ethyl acetate – petroleum ether (60–80°C) (1:99) mixture as eluent. Removal of solvent from the eluate afforded a solid material, which was crystallized repeatedly from ethyl acetate – petroleum ether solvent mixture or methanol until constant transition temperatures were obtained. They are recorded in Table 3.1. The elemental analysis of some of the representative compounds are found to be satisfactory and are recorded in Table 3.2.

3.2.2.2 Series II: 4-(4’-*n*-alkyloxybenzoyloxy)-3-methylphenylazo-2”, 4”-dimethylbenzenes

3.2.2.2a 4-*n*-alkoxybenzoic acids

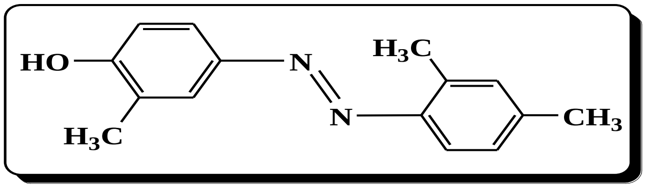
They are synthesized following the procedure reported in 3.2.2.1a [433].

3.2.2.2b 4-*n*-alkoxybenzoylchlorides

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

3.2.2.2c 3-methyl-4-hydroxyphenylazo-2’, 4’-dimethylbenzene

General molecular structure of 3-chloro-4-hydroxyphenylazo-2’, 4’-dimethylbenzene



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

(i) Preparation of Diazonium salt of 2,4-dimethylaniline

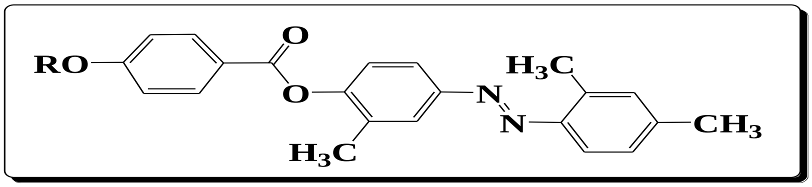
The diazonium salt is prepared by the procedure described in 3.2.2.1.c

(ii) Coupling of 2,4 dimethylbenzenediazoniumchloride with 2-chlorophenol

The coupling is carried out by the procedure described in 3.2.2.1c

3.2.2.2d 4-(4’-*n*-alkyloxybenzoyloxy)-3-methylphenylazo-2”, 4”-dimethylbenzenes

General Molecular structure of 4-(4’-*n*-alkyloxybenzoyloxy)-phenylazo-2”, 4”-dimethylbenzenes



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

0.01 moles 3-methyl-4-hydroxyphenylazo-2’, 4’-dimethylbenzene is dissolved in 10 ml of dry pyridine and is added slowly to 1 cold solution of respective 4-n-alkoxybenzoylchloride in pyridine. The mixture is refluxed in a water bath for an hour and is allowed to stand overnight at room temperature. It is acidified with 1:1 cold HCl and the separated solid was filtered, and successively washed with water, $NaHCO_3$ and NaOH solutions to remove any unreacted acid and phenol. The precipitates were again washed with water till filtrate neutralized solid was dried and column chromatographed on silica gel (60–120 mesh) with 1% ethyl acetate – petroleum ether (60–80°C) (1:99) mixture as eluent. Removal of solvent from the eluate afforded a solid material, which was crystallized repeatedly from ethyl acetate – petroleum ether solvent mixture or methanol until constant transition temperatures were obtained. They are recorded in Table 3.5. The elemental analysis of some of the representative compounds are found to be satisfactory and are recorded in Table 3.6.

3.2.2.3 Series III: 4-(4’-*n*-alkyloxybenzoyloxy)-3chlorophenylazo-2”, 4”-dimethylbenzenes

3.2.2.3a 4-*n*-alkoxybenzoic acids

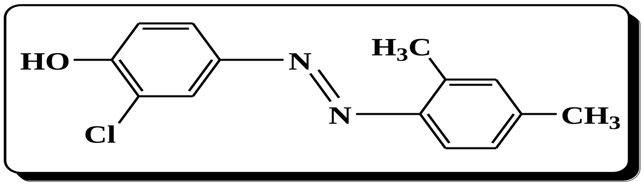
They are synthesized following the procedure reported in 3.2.2.1.a [433].

3.2.2.3b 4-*n*-alkoxybenzoylchlorides

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

3.2.2.3c 3-chloro-4-hydroxyphenylazo-2’, 4’-dimethylbenzene

General molecular structure of 3-chloro-4-hydroxyphenylazo-2’, 4’-dimethylbenzene



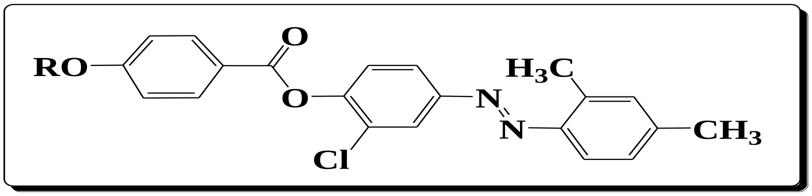
The diazo compound is prepared by the reported method [434], in two steps.

(i) Preparation of Diazonium salt of 2,4-dimethylaniline
The diazonium salt is prepared by the procedure described in 3.2.2.1.c

(ii) Coupling of 2,4-dimethylbenzenediazoniumchloride with 2-chlorophenol
The coupling is carried out by the procedure described in 3.2.2.1c

3.2.2.3d 4-(4’-*n*-alkyloxybenzoyloxy)-3-chlorophenylazo-2”, 4”-dimethylbenzenes

General Molecular structure of 4-(4’-*n*-alkyloxybenzoyloxy)-3-chlorophenylazo-2”, 4”-dimethylbenzenes



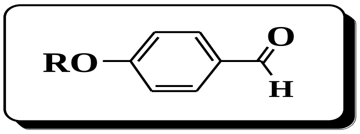
Where, R is C_nH_{2n+1} *n* = 1 to 8,10,12,14 and 16

0.01 mole 3-methyl-4-hydroxyphenylazo-2’, 4’-dimethylbenzene is dissolved in 10 ml of dry pyridine and is added slowly to 1 cold solution of respective 4-*n*-alkoxybenzoylchloride in pyridine. The mixture is refluxed in a water bath for an hour and is allowed to stand overnight at room temperature. It is acidified with 1:1 cold HCl and the separated solid was filtered, and successively washed with water, $NaHCO_3$ and NaOH solutions to remove any unreacted acid and phenol. The precipitates were again washed with water till filtrate neutralized solid was dried and column chromatographed on silica gel (60–120 mesh) with 1% ethyl acetate – petroleum ether (60–80°C) (1:99) mixture as eluent. Removal of solvent from the eluate afforded a solid material, which was crystallized repeatedly from ethyl acetate – petroleum ether solvent mixture or methanol until constant transition temperatures were obtained. They are recorded in Table 3.9. The elemental analysis of some of the representative compounds are found to be satisfactory and are recorded in Table 3.10.

3.2.2.4 Series IV: *trans*-4-(4’-*n*-alkyloxycinnamoyloxy)-phenylazo-2”, 4”-dimethylbenzene

3.2.2.4a 4-*n*-alkoxybenzaldehydes

General molecular structure of 4-*n*-alkoxybenzaldehydes

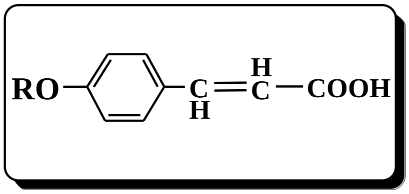


Preparation of 4-*n*-alkoxybenzaldehydes where alkoxy group varies from $-OCH_3$ to $-OC_{16}H_{33}$ has been variously described by Hildesheimer [435], Stoemer and Wodarg [436], Weygard and Gabler [437], Gray and Jones [431]. In this investigation, however, the following procedure has been adopted with better results. The first member viz. 4-methoxybenzaldehyde, also known as p-anisaldehyde has been bought of Loba grade and used by checking with thin layer chromatography (TLC) as received.

0.1 mole 4-*n*-hydroxybenzaldehyde, 0.15 mole of anhydrous potassium carbonate and 0.15 mole of the corresponding n-alkyl bromide or iodide were added to dry acetone (60 ml). The mixture was refluxed in water bath for three to four hours. In the case of higher members the refluxing period was extended upto six to eight hours. The whole mass was then added to water and aldehyde thus separated was extracted with ether. Ether extracted was washed with dilute sodium hydroxide to remove any unreacted 4-*n*-hydroxybenzaldehydes followed by water and dried. Ether was evaporated and the 4-*n*-alkoxybenzaldehydes thus obtained were purified by distilling under reduced pressure. Boiling points almost agreed with those reported in literature [438-439]

3.2.2.4b *trans*-4-*n*-alkoxycinnamic acids

General molecular structure of trans-4-*n*-alkoxycinnamic acids

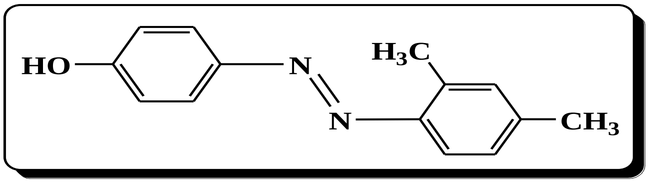


trans-4-*n*-alkoxycinnamic acids were prepared by Knoevenagel reaction.

The appropriate 0.02 mole trans-4-*n*-alkoxybenzaldehydes, 0.04 mole malonic acid, 8 ml pyridine and three drops of piperidine were mixed and heated at 100 °C on a steam bath for three to four hours. In the higher homologues the refluxing period was extended to five to six hours. The mixture was poured in ice (25 g) containing hydrochloric acid (25 ml). The precipitates were filtered and washed with dilute hydrochloric acid followed by water. Compounds were crystallized from 98% acetic acid. Yield of colorless product was 85 to 90 %. Higher homologous were crystallized twice from benzene and and then acetic acid till constant transition temperatures (139) were obtained. [431, 439]

3.2.2.4c 4-hydroxyphenylazo-2’, 4’-dimethylbenzene

General molecular structure of 4-hydroxyphenylazo-2’, 4’-dimethylbenzene



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

(i) Preparation of Diazonium salt of 2,4-dimethylaniline

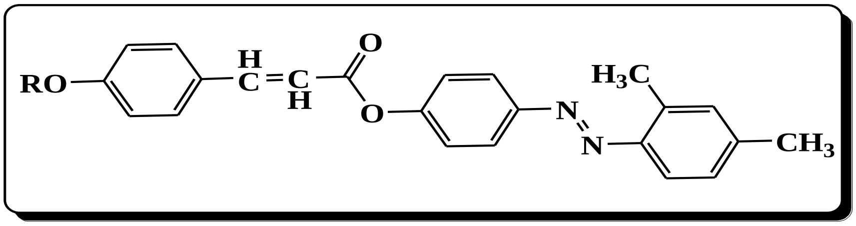
The diazonium salt is prepared by the procedure described in 3.2.2.1.c

(ii) Coupling of 2,4 dimethylbenzenediazoniumchloride with phenol

The coupling is carried out by the procedure described in 3.2.2.1c

3.2.2.4d *trans*-4-(4’-*n*-alkyloxycinnamoyloxy)-phenylazo-2”, 4”-dimethylbenzenes

General Molecular structure of 4-(4’-*n*-alkyloxycinnamoyloxy)-phenylazo-2”, 4”-dimethylbenzene



N,N’-Dicyclohexylcabodiimide (DCC, 0.0055 mole) was dissolved in a solution of 4-*n*-Alkoxy cinnamic acid (0.005 mole) and Diazo compound (4-Hydroxyphenylazo-2’, 4’- dimethylbenzene (0.005 mole) and N, N- 4-(dimethylamino)-pyridine (DMAP, 0.0005 mole) dry dichloromethane (DCM, 25 ml) and the solution stirred at room temperature for 12 h under a condenser fitted with a silica gel guard tube. The precipitated material was filtered and the filtrate concentrated [440].

The solid residue obtained, was purified by column chromatography on silica gel (60-120 mesh) with 3% ethyl acetate - petroleum ether (60-80ºC) (3:97) mixture as eluent. Removal of solvent from the eluate afforded a solid material, which was crystallized repeatedly using methanol until constant transition temperatures were obtained.

3.2.2.5 Series V: *trans*-4-(4’-*n*-alkyloxycinnamoyloxy)-3-methylphenylazo-4”-methylbenzenes

3.2.2.5a 4-*n*-alkoxybenzaldehydes

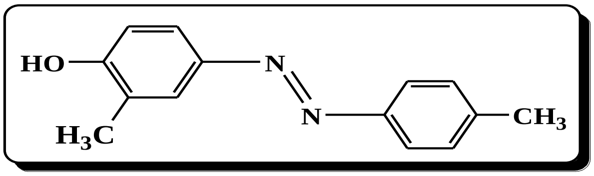
They are synthesized following the procedure reported in 3.2.2.4a [439].

3.2.2.5b *trans*- 4-*n*-alkoxycinnamic acids

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

3.2.2.5c 3-methyl-4-hydroxyphenylazo- 4’-methylbenzene

General molecular structure of 3-methyl-4-hydroxyphenylazo-4’-methylbenzene.



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

(i) Preparation of Diazonium salt of 4 methyl aniline

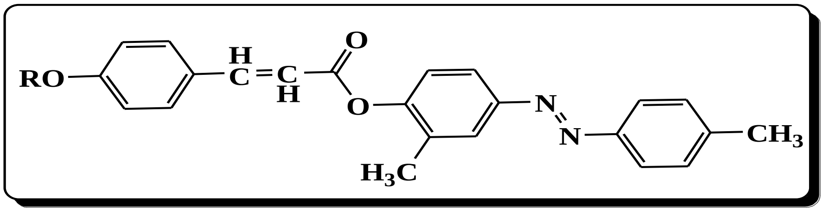
The diazonium salt is prepared by the procedure described in 3.2.2.1.c

(ii) Coupling of 4 methylbenzenediazoniumchloride with 2-methylphenol

The coupling is carried out by the procedure described in 3.2.2.1c

3.2.2.5d *trans* -4-(4’-*n*-alkyloxycinnamoyloxy)-3-methylphenylazo-4”-methylbenzene

General molecular structure of 4-(4’-*n*-alkyloxycinnamoyloxy)-3-methylphenylazo-4”- methylbenzene



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

3.2.2.6 *trans* -4-(4’-*n*-alkyloxycinnamoyloxy)-phenylazo-4”-methylbenzene

3.2.2.6a 4-*n*-alkoxybenzaldehydes

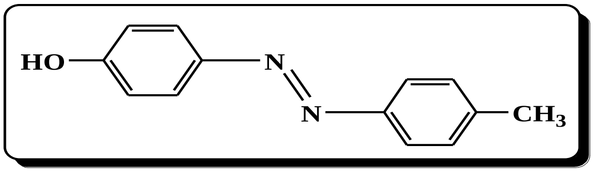
They are synthesized following the procedure reported in 3.2.2.4a [439].

3.2.2.6b *trans*- 4-*n*-alkoxycinnamic acids

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

3.2.2.6c 4-hydroxyphenylazo- 4’-methylbenzene

General molecular structure of 4-hydroxyphenylazo- 4’-methylbenzene.



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

(i) Preparation of Diazonium salt of 4 methyl aniline

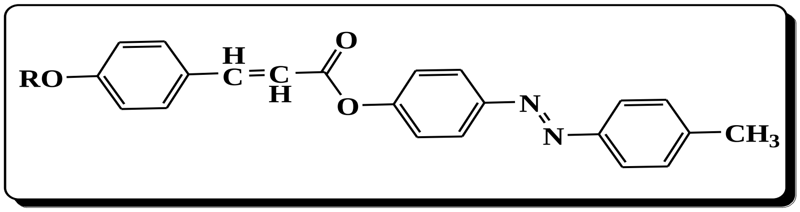
The diazonium salt is prepared by the procedure described in 3.2.2.1.c

(ii) Coupling of 4 methylbenzenediazoniumchloride with phenol

The coupling is carried out by the procedure described in 3.2.2.1c

3.2.2.6d *trans* -4-(4’-*n*-alkyloxycinnamoyloxy)-phenylazo-4”-methylbenzenes

General molecular structure of 4-(4’-*n*-alkyloxycinnamoyloxy)-phenylazo-4”- methylbenzene



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

3.2.2.7 *trans* -4-(4’-*n*-alkyloxycinnamoyloxy)-phenylazo-4”-nitrobenzenes

3.2.2.7a 4-*n*-alkoxybenzaldehydes

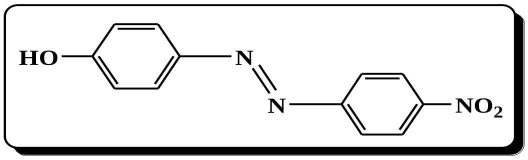
They are synthesized following the procedure reported in 3.2.2.4a [439].

3.2.2.7b *trans*-4-*n*-alkoxycinnamic acids

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

3.2.2.7c 4-hydroxyphenylazo- 4’-nitrobenzene

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



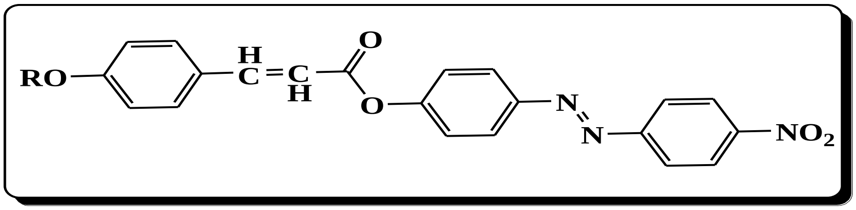
The diazo compound is prepared by the reported method [434], in two steps.

(i) Preparation of Diazonium salt of 4-nitroaniline
The diazonium salt is prepared by the procedure described in 3.2.2.1.c

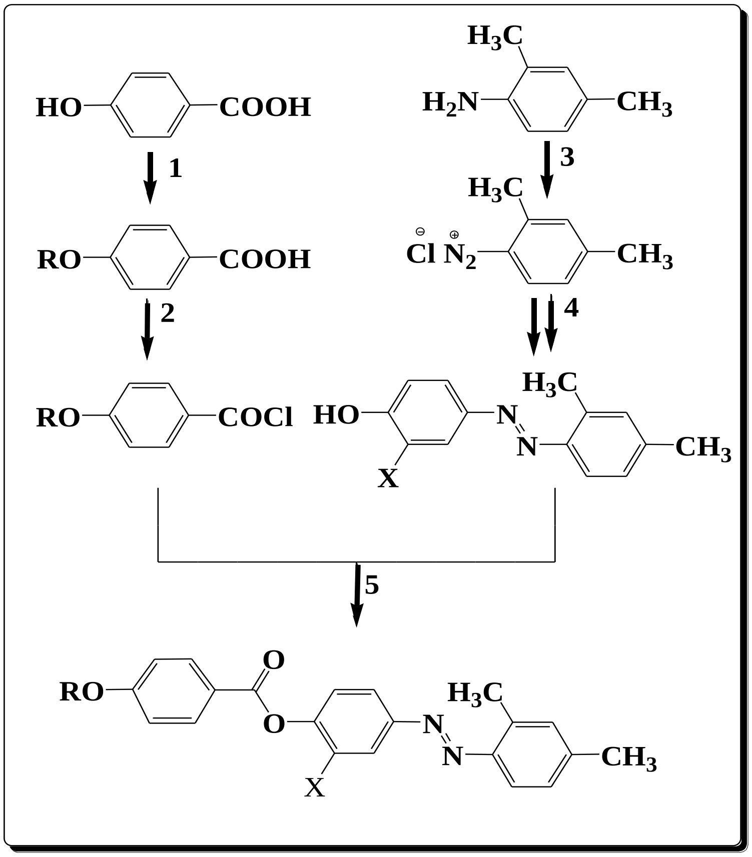
(ii) Coupling of 4-nitrobenzenediazoniumchloride with phenol
The coupling is carried out by the procedure described in 3.2.2.1c

3.2.2.7d *trans*-4-(4'-*n*-alkyloxycinnamoyloxy)-phenylazo-4"-nitrobenzenes

General molecular structure of *trans*-4-(4'-*n*-alkyloxycinnamoyloxy)-phenylazo-4"- nitrobenzene



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



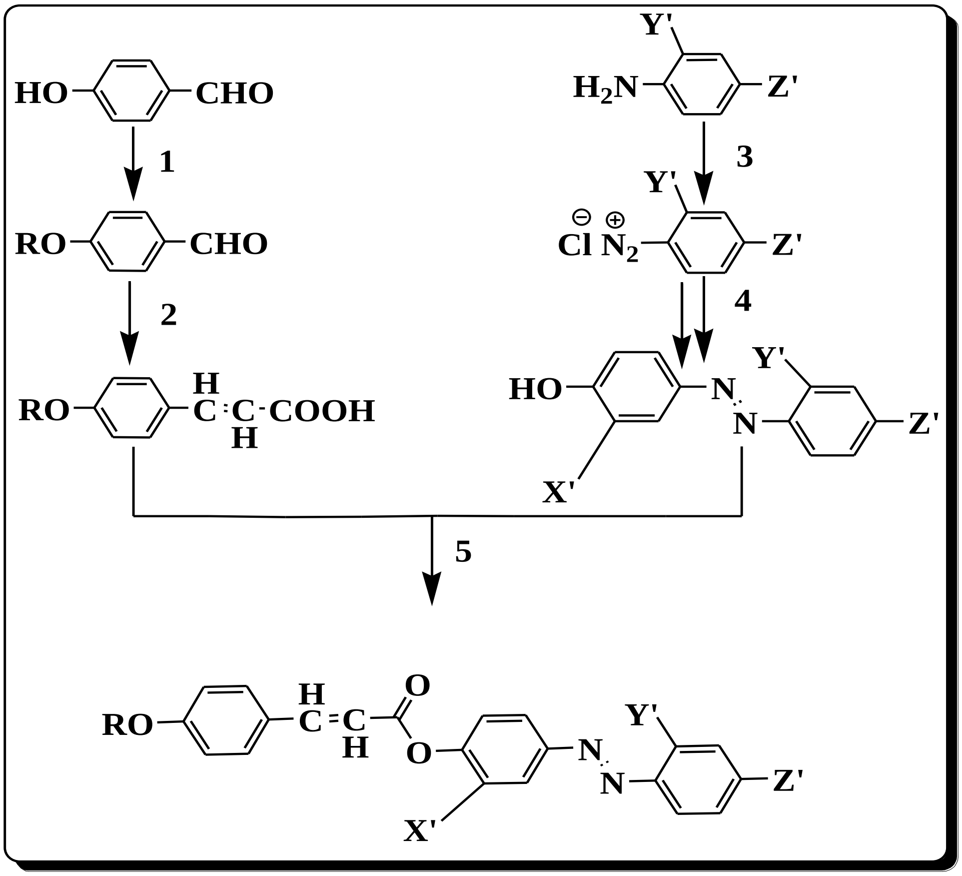
Scheme 3.1: Synthetic route for series I to III (Part I)

X = -H (for Series I), $-CH_3$ (for Series II), -Cl (for series III)

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

(1) Alcohol, KOH, n-RBr, Reflux for 8-10 hrs, (2) $SOCl_2$, (3) HCl, $NaNO_2$, H_2O/0-5 ^oC,

(4) (i) Conc. HCl, $NaNO_2$, (ii) Phenol (series I) or 2-methyl phenol (series II) or 2- Chloro phenol (Series III) aq.NaOH, at 0-10^o C, pH 8-12, (5) Dry Pyridine, 1:1 cold HCl.



Scheme 3.1a: Synthetic route for series IV to VII (Part II)

X’ = –H, Y’ = $-CH_3$, Z’ = $-CH_3$ ……...For series IV

X’ = $-CH_3$, Y’ = –H , Z’ = $-CH_3$ ………For series V

X’ = –H , Y’ = –H , Z’ = $-CH_3$ ……… For series VI

X’ = –H , Y’ = –H , Z’ = $-NO_2$ ……… For series VII

R = C_nH_{2n+1} n = 1 to 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) Conc. HCl, $NaNO_2$, H_2O/0-5 ^oC, (4) (i) Conc. HCl, $NaNO_2$, (ii) phenol (for Series IV, VI, VII) or 2-methyl phenol (for Series V), aq.NaOH, at 0-10^o C, pH 8-12, (5) DCC, DMAP, DCM, Stirred for Overnight Stirred for 12 hrs.

3.2.3 Characterization

Elemental analysis of some of the homologues are performed on Perkin Elmer Series II 2400-CHN analyzer, electronic spectra are recorded on Shimadzu UV-2450 UV- visible spectrometer, IR spectra are recorded on Perkin Elmer GX-FTIR, ^{1}H NMR spectra are measured on 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 Mettler Toledo Star SW 7.01.

Polarizing Optical Microscopy

The transition temperatures are determined by using a “ Leitz Labourlux 12POL Microscope”, polarizing microscope provide with kofler heating stage.

The figure below is a schematic representation of polarizing optical microscope.

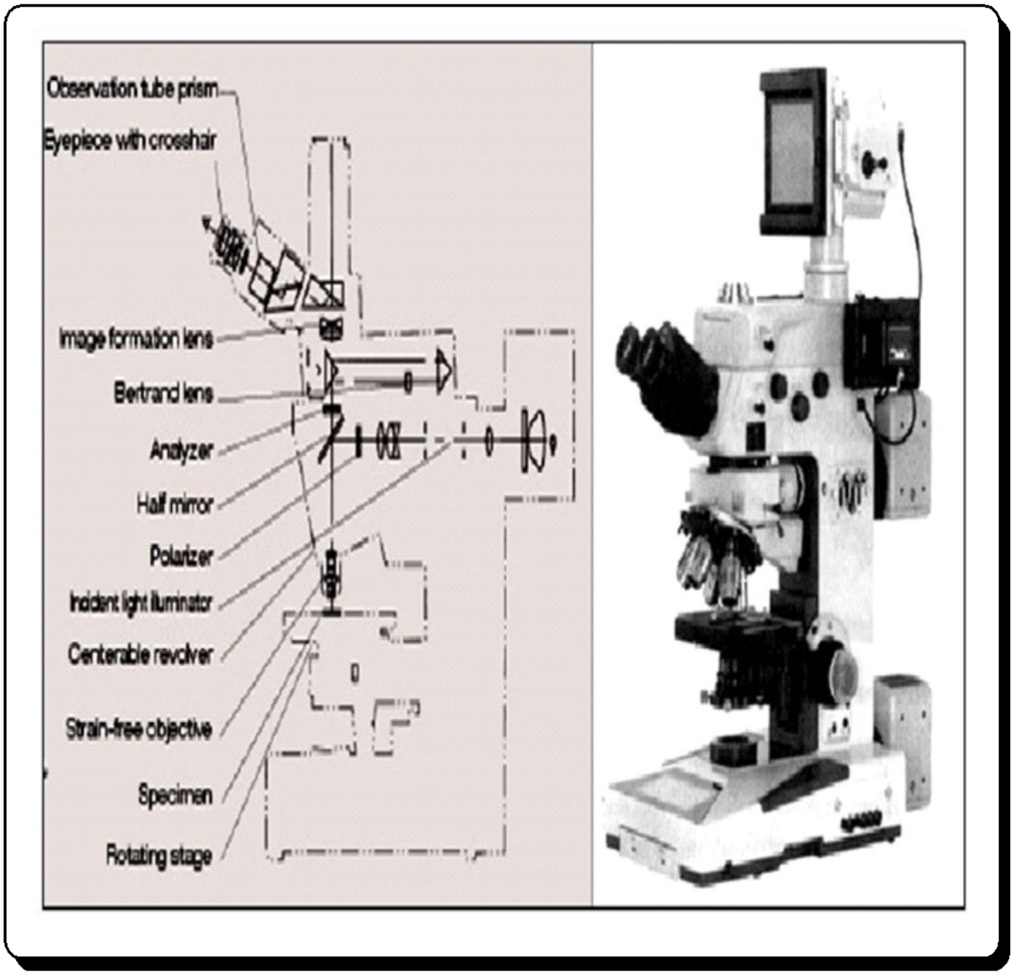


Figure 3.1: Polarizing optical microscope provided with heating stage.

The microscope is standardized by taking melting points and transition temperatures of very pure and known substances like benzoicacid, succinicacid, p-azoxyanisole, vanillin, p-anisaldehyde.

To determine the various transitions, a glass slide carrying a thin section of the material with coverslip on it is heated and observed under the microscope. The slide is insterted into the specimen chamber and the temperature is raised 5°C/min to find the approximate transition temperatures. The measurement are repeated and the rate of heating is regulated to about 1°C/min , near the transition to be observed. The changing texture over the temperature ranges are carefullyu observed and recorded as focal-conic, plane, homeotropic and threaded texture of smectic and nematic phases as they appeared under the polarized light. All observations are repeated several times. In case of any doubt the compounds are purified again and are subjected to study uder the microscopr a fresh.

In this study, I have used L10 magnification as well as all the liquid crystalline micrographs have been taken with 5.0 mega pixel mobile camera.

Differential Scanning Calorimetry

The technique maintained the sample and reference materials isothermal to each other by proper application of electrical energy, as they are heated or cooled at a linear rate. The curve obtained is a recording of heat flow dH/dt, in m.cal/sec. as a function of temperature.

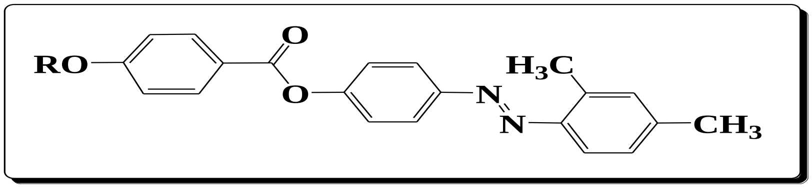
In the true thermodynamic sense, an endotherm curve peak is indicated by a peak in the upward direction (increase in enthalpy) while an exotherm curve peak is recorded by a peak in the oppsite direction. In all appearance a DSC curve looks very similar to that of a DTA curve, expect for the ordinate axis units. As in DAT, the area enclosed by the DSC curve peak is directly proportional to enthalpy change.

Area = K x ΔHm

Expect that K is independent of temperature

In the present work, calorimetry study is carried out for number of compounds on Mettler Toledo Star SW 7.01 in nitrogen enviroment.

Table 3.1: Transition Temperatures: Series I: 4-(4'-*n*-alkyloxybenzoyloxy)-phenylazo-2", 4"-dimethylbenzenes



R = *n*-Alkyl group	Transition Temperature °C		
	Smectic C	**Nematic**	**Isotropic**
Methyl	-	136	234
Ethyl	-	127	214
Propyl	-	125	202
Butyl	-	111	167
Pentyl	-	91	161
Hexyl	-	92	143
Heptyl	-	94	144
Octyl	-	80	164
Decyl	-	93	152
Dodecyl	-	73	128
Tetradecyl	-	55	83
Hexadecyl	54	62	75

Table 3.2: Elemental Analysis

Series	Homologue	Theoretical			Practical		
		C (%)	**H (%)**	**N (%)**	**C (%)**	**H (%)**	**N (%)**
I	C4	74.60	6.51	6.96	74.65	6.52	6.94
I	C8	75.92	7.40	6.10	75.51	7.67	6.27

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

Octyl homologue : 2925 – 2858 (C-H St, Alkyl CH_3, SP^3 hybridization), 1734 (-C=O- St. of ester), 1606 (-N=N- St.), 1517 – 1479 (-C=C- St. of Aromatic ring), 1469 (-C-H bending of $-CH_2-$), 1262 (Aromatic ether 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 : 2929 – 2859(C-H St, Alkyl CH_3, SP^3 hybridization), 1735 (-C=O- St. of ester), 1604 (-N=N- St.), 1516 – 1480 (-C=C- St. of Aromatic ring), 1472 (-C-H bending of $-CH_2-$), 1260 (Aromatic ether St.), 1078 (-C-O- St. of ester), 882 (strong –C-H- bending for 1:2:4 tri substituted benzene ring), 760 (weak –C-H- bending for $-(CH_2)_7-$) .

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

Butyl homologue: δ = 0.90 (t, 3H, $–CH_3$), 1.49-1.56 (m, 4H, $2(-CH_2-)$), 1.83 (Qunt, 2H, $-OCCH_2$), 2.38 (s, 3H, Ar-CH_3), 2.69 (s, 3H, Ar-CH_3), 4.06 (t, 2H, $-OCH_2$), 6.92-8.18 (m, 11H, Ar-H)

Octyl homologue: δ = 0.89 (t, 3H, $–CH_3$), 1.29-1.82 (m, 12H, $6(-CH_2-)$), 1.85 (Qunt, 2H, $-OCCH_2$), 2.38 (s, 3H, Ar-CH_3), 2.69 (s, 3H, Ar-CH_3), 4.04 (t, 2H, $-OCH_2$), 6.95-8.15 (m, 11H, Ar-H)

Mass Spectra: MS m/z:

Octyl Homologue: Theoratical Mass value: 458.26 g/mol

Practical mass value: MS m/z: 459.4 $[(M+1)]^+$

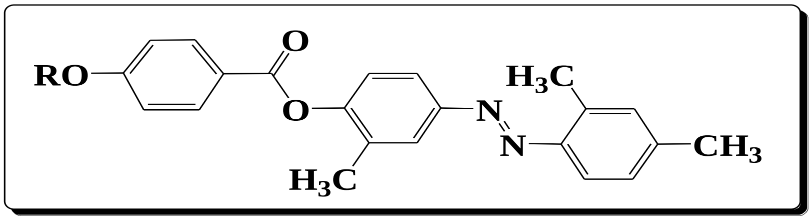
Table 3.3: DSC Data

Series	Member	Heating rate °C/min	Transition Temperature °C	ΔH=J/g	ΔS=J/g.K
I	C8	10	Cr-M 79.50 N-I 164.29	77.42 2.72	0.2195 0.0062
I	C16	10	Cr-M 52.74 S-N 60.38 N-I 74.54	1.00 17.88 0.37	0.0031 0.0536 0.0011

Table 3.4: UV Data

Series	Homologue	UV λ max values nm (solvent – ethyl acetate)	
		π → π*	**n → π***
I	C8	340	445.50
	C10	341	445

Table 3.5: Transition temperatures Series II: 4-(4’-*n*-alkyloxybenzoyloxy)-3-methylphenylazo-2”, 4”-dimethylbenzenes



R = *n*-Alkyl group	Transition Temperature ºC	
	Nematic	Isotropic
Methyl	135	162
Ethyl	115	188
Propyl	92	138
Butyl	90	155
Pentyl	93	134
Hexyl	95	145
Heptyl	78	94
Octyl	56	93
Decyl	44	84
Dodecyl	45	68
Tetradecyl	52	70
Hexadecyl	55	76

Table 3.6: Elemental Analysis

Series	Homologue	Theoretical			Practical		
		C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
II	C6	75.65	7.26	6.30	75.62	7.30	6.28
II	C10	76.77	8.05	5.60	76.78	8.06	5.58

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

Pentyl homologue : 2930 – 2858 (–C–H St, Alkyl CH_3, SP^3 hybridization), 1732 (–C=O– St. of ester), 1602 (–N=N– St.), 1518 – 1477 (-C=C- St. of Aromatic ring), 1465 (-C-H bending of $–CH_2–$), 1265 (Aromatic ether St.), 1069 (-C-O- St. of ester), 875 (strong –C–H– bending for 1:2:4 tri substituted benzene ring), 755 (weak –C–H– bending for $-(CH_2)_7-$) .

Decyl homologue : 2926 – 2862 (–C–H St, Alkyl CH_3, SP^3 hybridization), 1730 (–C=O– St. of ester), 1604 (–N=N– St.), 1520 – 1477 (–C=C– St. of Aromatic ring), 1465 (–C–H bending of $–CH_2–$), 1270 (Aromatic ether St.), 1072 (-C-O- St. of ester), 871 (strong –C–H– bending for 1:2:4 tri substituted benzene ring), 758 (weak –C–H– bending for $–(CH_2)_7–$) .

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

Butyl homologue: δ = 0.90 (t, 3H, aliphatic $–CH_3$), 1.35–1.82 (m, 4H, $2(–CH_2–)$), 1.85 (Qunt, 2H, $-OCCH_2$), 2.32 (s, 3H, $Ar–CH_3$), 2.37 (s, 3H, $Ar–CH_3$) 2.68 (s, 3H, $Ar–CH_3$), 4.04 (t, 2H, $–OCH_2$), 6.95–8.15 (m, 11H, Ar–H).

Hexyl homologue: δ = 0.99 (t, 3H, aliphatic $–CH_3$), 1.46–1.58 (m, 8H, $4(–CH_2–)$), 1.83 (Qunt, 2H, $-OCCH_2$), 2.35 (s, 3H, $Ar–CH_3$), 2.37 (s, 3H, $Ar–CH_3$) 2.71 (s, 3H, $Ar–CH_3$), 4.08 (t, 2H, $–OCH_2$), 6.95–8.24 (m, 11H, Ar–H).

Mass Spectra: MS m/z:

Hexyl Homologue: Theoratical Mass value: 444.24 g/mol

Practical mass value: MS m/z: 445.30 $[(M+1)]^+$

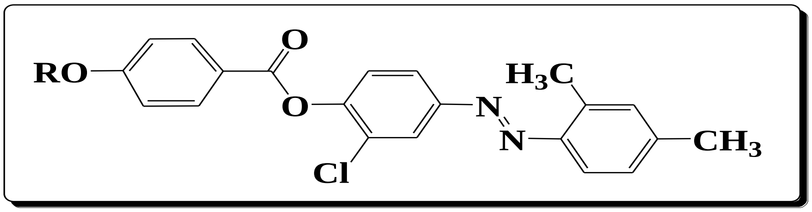
Table 3.7: DSC Data

Series	**Homologue**	**Heating rate °C/min**	**Transition Temperature °C**	**ΔH=J/g**	**ΔS=J/g.K**
II	C5	10	Cr-M 94.28 N-I 135.14	118.23 4.38	0.3219 0.0066
II	C6	10	Cr-M 93.10 N-I 139.02	107.55 2.70	0.2936 0.0065

Table 3.8: UV Data

Series	**Homologue**	**UV λ max values nm (solvent – ethyl acetate)**	
		π → π*	**n → π***
I1	C4	340	444
	C8	336	445

Table 3.9: Transition temperatures Series III: 4-(4'-*n*-alkyloxybenzoyloxy)-3-chlorophenylazo-2", 4"-dimethylbenzenes



R = *n*-Alkyl group	Transition Temperature °C	
	Nematic	**Isotropic**
Methyl	121	163
Ethyl	118	160
Propyl	109	153
Butyl	98	141
Pentyl	92	139
Hexyl	80	133
Heptyl	79	126
Octyl	84	129
Decyl	72	124
Dodecyl	75	102
Tetradecyl	72	93
Hexadecyl	63	85

Table 3.10: Elemental Analysis

Series	Homologue	Theoretical			Practical		
		C (%)	**H (%)**	**N (%)**	**C (%)**	**H (%)**	**N (%)**
III	C8	70.65	6.75	5.68	70.66	6.81	5.69
	C14	72.83	7.86	4.85	72.84	7.85	4.89

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

Heptyl homologue : 2952 – 2858 (–C–H St, Alkyl CH_3, SP^3 hybridization), 1730 (–C=O– St. of ester), 1602 (–N=N– St.), 1570 – 1500 (–C=C– St. of Aromatic ring), 1477(–C–H bending of $-CH_2-$), 1250(Aromatic ether St.), 1061(-C-O- St. of ester), 893(strong –C–H– bending for 1:2:4 tri substituted benzene ring), 725 (weak –C–H– bending for $-(CH_2)_6-$) .

Dodecyl homologue : 2954 – 2858 (–C–H St, Alkyl CH_3, SP^3 hybridization), 1733 (–C=O– St. of ester), 1604 (–N=N– St.), 1574 – 1505 (–C=C– St. of Aromatic ring), 1482(–C–H bending of $–CH_2–$), 1248(Aromatic ether St.), 1067(–C–O–St. of ester), 895(strong –C–H– bending for 1:2:4 tri substituted benzene ring), 725 (weak –C–H– bending for $–CH_2)_{11}–$) .

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

Octyl homologue: δ = 0.89 (t, 3H, $–CH_3$), 1.25–1.54 (m, 12H, 6($–CH_2–$)), 1.83 (Qunt, 2H, $-OCCH_2$), 2.39 (s, 3H, $Ar–CH_3$), 2.70 (s, 3H, $Ar–CH_3$), 4.06 (t, 2H, $–OCH_2$), 6.69–8.22 (m, 11H, Ar–H)

Decyl homologue: δ = 0.88 (t, 3H, aliphatic $–CH_3$), 1.25-1.83 (m, 16H, 8($–CH_2–$)), 1.85 (Qunt, 2H, $-OCCH_2$), 2.39 (s, 3H, $Ar–CH_3$) 2.70 (s, 3H, $Ar–CH_3$), 4.04 (t, 2H, $–OCH_2$), 6.98–8.21 (m, 11H, Ar–H)

Mass Spectra: MS m/z:

Heptyl Homologue: Theoratical Mass value: 478.20 g/mol

Practical mass value: MS m/z: 479.00 $[(M+1)]^+$

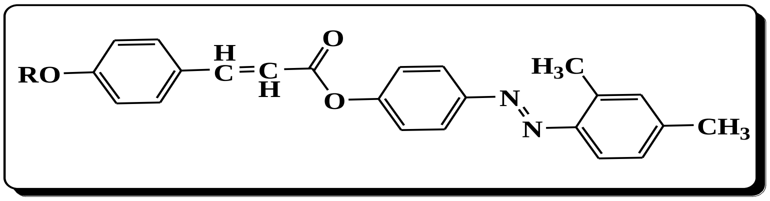
Table 3.11: DSC Data

Series	Homologue	Heating rate ºC/min	Transition Temperature ºC	ΔH=J/g	ΔS=J/g.K
III	C10	10	Cr – N 70 N – I 123	74.97 1.21	0.2120 0.0028

Table 3.12: UV Data

Series	Homologue	UV λ max values nm (solvent – ethyl acetate)	
		π → π*	n → π*
III	C7	341	444.50
	C12	341	442

Table 3.13: Transition temperatures Series IV: *trans*-4-(4'-*n*-alkyloxycinnamoyloxy)-phenylazo-2", 4"-dimethylbenzenes



R = *n*-Alkyl group	Transition Temperature °C		
	Smectic A	**Nematic**	**Isotropic**
Methyl	-	138	258
Ethyl	-	132	184
Propyl	-	105	196
Butyl	-	88	175
Pentyl	-	93	197
Hexyl	-	91	183
Heptyl	-	96	187
Octyl	-	92	199
Decyl	(65)*	74	164
Dodecyl	74	86	158
Tetradecyl	73	89	159
Hexadecyl	76	94	161

()* Value in the parentheses indicates monotropic transition.

Table 3.14: Elemental Analysis

Series	Homologue	Theoretical			Practical		
		C (%)	**H (%)**	**N (%)**	**C (%)**	**H (%)**	**N (%)**
IV	C5	75.99	6.83	6.33	75.86	6.85	6.45
IV	C10	77.31	7.86	5.46	77.39	7.94	5.62

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

Decyl homologue : 2917 – 2850 (C-H St, Alkyl–CH_3, SP^3 hybridization), 1731 (– C=O– St. of ester), 1607 (–N=N– St.), 1510–1462 (–C=C– St. of Aromatic ring), 1462 (–C–H bending of –CH_2–), 1251 (Aromatic ether St.), 1080(–C–O St. of ester), 802 (strong –C–H– bending for 1:2:4 tri substituted benzene ring), 849 (–C–H out of plane bending of –CH=CH–), 762 (weak –C–H– bending – $(CH_2)_{15}$–).

Hexadecyl Homologue : 2927 – 2850 (–C-H St, Alkyl–CH_3, SP^3 hybridization), 1740 (-–C=O– St. of ester), 1597 (–N=N– St.), 1511 – 1462 (–C=C– St. of Aromatic ring), 1462 (–C–H bending of –CH_2–), 1262 (Aromatic ether St.), 1089(–C–O– St. of ester), 802 (–C–H– bending for 1:2:4 tri substituted benzene ring), 850 (–C-H out of plane bending of –CH=CH–), 764 (weak –C–H– bending– $(CH_2)_{15}$–) .

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

Octyl homologue: δ = 0.91 (t, 3H, $–CH_3$), 1.31-1.61 (m, 10H, 5($–CH_2–$)), 1.84 (Qunt, 2H, $-OCCH_2$), 2.40 (s, 3H, $Ar–CH_3$), 2.71 (s, 3H, $Ar–CH_3$), 4.02 (t, 2H, $–OCH_2$), 6.94–7.99 (m, 11H, Ar–H),6.40 (d,J = 20.4, 1H,=CH-COO), 7.71 (d, J = 20.4, 1H, Ar–CH=)

Tetradecyl homologue: δ = 0.88 (t, 3H. $–CH_3$), 1.26–1.53 (m, 22H, 11($–CH_2–$)), 1.80 (Qunt, 2H, $-OCCH_2$), 2.38 (s, 3H, $Ar–CH_3$), 2.69 (s, 3H, $Ar–CH_3$), 4.03 (t, 2H, $–OCH_2$), 6.47–7.97 (m, 11H, Ar–H), 6.53 (d, J = 20.4, 1H,=CH–COO), 7.58 (d, J=20.4, 1H, Ar-CH=).

Mass Spectra:

Octyl Homologue: Theoratical Mass value: 484.27 g/mol

Practical mass value: MS m/z: 484.90 (M^+)

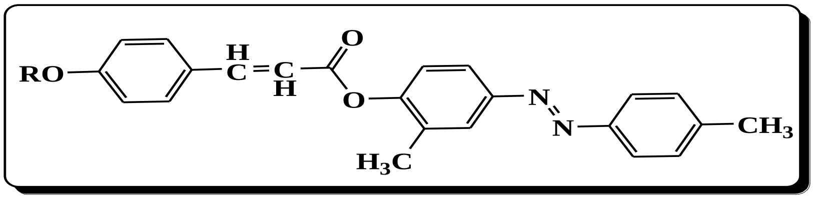
Table 3.15: DSC Data

Series	Member	Heating rate ºC/min	Transition Temperature ºC	ΔH=J/g	ΔS=J/g.K
IV	C8	10	Cr – N 91.65 N – I 198.93	74.20 3.55	0.2034 0.0075
IV	C16	10	Cr – Sm 77.37 Sm – N 93.50 N – I 161.31	114.33 34.94 2.80	0.3263 0.0953 0.0064

Table 3.16: UV Data

Series	Homologue	UV λ max values nm (solvent – ethyl acetate)	
		π → π*	n → π*
IV	C2	333	491
	C8	331	488

Table 3.17: Transition temperatures Series V: *trans*-4-(4'-*n*-alkyloxycinnamoyloxy)-3-methylphenylazo-4"-methylbenzenes



R = *n*-Alkyl group	Transition Temperature °C		
	Smectic C	Nematic	Isotropic
Methyl	-	172	244
Ethyl	-	171	232
Propyl	-	123	243
Butyl	-	121	232
Pentyl	-	109	220
Hexyl	-	115	220
Heptyl	-	110	214
Octyl	-	107	199
Decyl	-	93	190
Dodecyl	-	93	157
Tetradecyl	(67)*	93	156
Hexadecyl	82	105	158

()* Value in the parentheses indicates monotropic transition.

Table 3.18: Elemental Analysis

Series	Homologue	Theoretical			Practical		
		C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
V	C12	77.74	8.20	5.18	77.49	8.35	5.26
V	C14	78.13	8.51	4.93	78.25	8.75	5.05

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

Tetradecyl homologue : 2917 – 2846 (–C–H St, Alkyl –CH_3, SP^3 hybridization), 1730 (–C=O– St. of ester), 1596 (–N=N– St.), 1577 – 1510 (–C=C– St. of Aromatic ring), 1479 (–C–H bending of –CH_2–), 1256 (Aromatic ether St.), 1014(-C-O- St. of ester), 821 (strong –C-H- bending for 1:2:4 tri substituted benzene ring), 897 (–C–H out of plane bending of –CH=CH–), 716 (weak –C–H– bending for –$(CH_2)_{15}$–) .

Hexadecyl homologue : 2921 – 2856 (C–H St, Alkyl CH_3, SP^3 hybridization), 1730 (–C=O– St. of ester), 1600 (–N=N– St.), 1573 – 1507 (–C=C– St. of Aromatic ring), 1470 (–C–H bending of –CH_2–), 1256 (Aromatic ether St.), 1023(–C–O– St. of ester), 830 (strong –C–H– bending for 1:2:4 tri substituted benzene ring), 889 (–C–H out of plane bending of –CH=CH–) 726 (weak –C–H– bending for –$(CH_2)_{15}$–)

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

Decyl homologue: δ = 0.90 (t, 3H. $–CH_3$), 1.29–1.59 (m, 16H, 8($–CH_2–$)), 1.82 (Qunt, 2H, $-OCCH_2$), 2.34 (s, 3H, $Ar–CH_3$), 2.46 (s, 3H, $Ar–CH_3$), 4.02 (t, 2H, $–OCH_2$), 6.54–7.85 (m, 11H, Ar–H),6.58 (d, J = 16, 1H,=CH–COO), 7.87 (d, J=16, 1H, Ar–CH=).

Dodecyl homologue: δ = 0.88 (t, 3H. $–CH_3$), 1.28–1.54 (m, 18H, 9($–CH_2–$)), 1.82 (Qunt, 2H, $-OCCH_2$), 2. 31 (s, 3H, $Ar–CH_3$), 2.43 (s, 3H, $Ar–CH_3$), 4.01 (t, 2H, $–OCH_2$), 6.49–7.89 (m, 11H, Ar–H),6.56 (d, J =16, 1H,=CH-COO), 7.56 (d, J=16, 1H, Ar-CH=).

Mass Spectra: MS m/z:

Octyl Homologue: Theoratical Mass value: 484.27 g/mol

Practical mass value: MS m/z: 485.10 (M^+)

Butyl Homologue: Theoratical Mass value: 428.21 g/mol

Practical mass value: MS m/z: 428.90 (M^+)

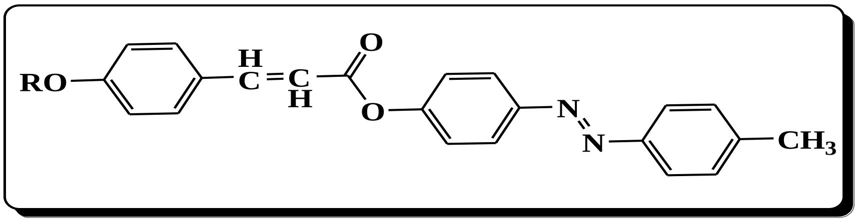
Table 3.19: DSC Data

Series	Member	Heating rate °C/min	Transition Temperature °C	ΔH=J/g	ΔS=J/g.K
V	C12	10	Cr - N 92.22 N – I 156.49	67.79 2.03	0.1856 0.0047
V	C14	10	Cr - N 84.20 N – I 147.87 I – N 146.75 N – Sm 101.12 Sm – Cr 68.12	94.852 2.455 2.319 3.688 94.579	0.2646 0.0058 0.0055 0.0098 0.2772
V	C16	10	Cr – Sm 87.22 Sm – N 105.71 N – I 151.75	94.701 3.083 1.013	0.2628 0.0081 0.0023

Table 3.20: UV Data

Series	Homologue	UV λ max values nm (solvent – ethyl acetate)	
		$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
V	C4	329.50	491.50
	C6	330.50	491.50

Table 3.21: Transition temperatures Series VI: *trans*-4-(4'-*n*-alkyloxycinnamoyloxy)-phenylazo-4"-methylbenzenes



R = *n*-Alkyl group	Transition Temperature ºC		
	Smectic C	**Nematic**	**Isotropic**
Methyl	-	172	313
Ethyl	-	145	291
Propyl	-	171	293
Butyl	-	148	286
Pentyl	-	110	262
Hexyl	-	122	273
Heptyl	-	133	282
Octyl	-	127	252
Decyl	101	131	235
Dodecyl	100	152	194
Tetradecyl	95	146	213
Hexadecyl	83	150	184

Table 3.22: Elemental Analysis

Series	Homologue	Theoretical			Practical		
		C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
VI	C7	76.21	7.00	6.13	76.48	6.88	6.15
VI	C5	75.60	6.53	6.53	75.72	6.48	6.55

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

Butyl homologue : 2935–2860 (–C–H, stretching, alkyl –$CH_{3,}$ sp^3 hybridization), 1735cm^{-1}(–C=O stretching of ester), 1630(–C=C–,stretching, Vinyl group of cinnamate),1606 (–N=N– st.), 1515–1475 (–C=C– st. of aromatic ring), 1450 (–C–H bending of –CH_2), 1180 (–C–O st. of ester,sp^2 hybridization), 840 (–C–H bending of 1,4-disustituted benzene ring), 720 (weak –C–H bending for –$(CH_2)_n$–).

Hexyl homologue : 2970–2860 (-C-H, st., alkyl CH_3, sp^3 hybridization), 1730 (-C=O st. of ester), 1627 (–C=C–,st., Vinyl group of cinnamate),1606 (–N=N– st.), 1515–1470 (–C=C st. of aromatic ring), 1460 (–C–H bending of $–CH_2$), , 1170 (–C–O st. of ester,sp^2 hybridization), 830 (–C–H bending of 1,4-disustituted benzene ring), 730 (weak –C–H bending for $–(CH_2)_n–$).

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

Butyl homologue: δ = 0.90 (t, 3H. $–CH_3$), 1.50-1.59 (m, 4H, 2($–CH_2–$)), 1.82 (Qunt, 2H, $-OCCH_2$), 2.46 (s, 3H, $Ar–CH_3$), 4.03 (t, 2H, $–OCH_2$), 6.50-7.98 (m, 11H, Ar–H),6.58 (d, 1H,=CH–COO), 7.57 (d, 1H, Ar–CH=).

Hexyl homologue: δ = 0.89 (t, 3H. $–CH_3$), 1.25-2.44 (m, 10H, 5($–CH_2–$)), 1.80 (Qunt, 2H, $-OCCH_2$), 2.44 (s, 3H, $Ar–CH_3$), 4.00 (t, 2H, $–OCH_2$), 6.47-7.97 (m, 11H, Ar–H),6.52 (d, J = 16, 1H,=CH–COO), 7.52 (d, J = 16, 1H, Ar–CH=).

Mass Spectra: MS m/z:

Octyl Homologue: Theoratical Mass value: 470.26 g/mol

Practical mass value: MS m/z: 470.01 (M^+)

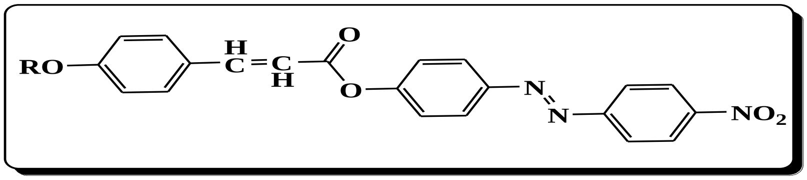
Table 3.23: DSC Data

Series	**Member**	**Heating rate °C/min**	**Transition Temperature °C**	**ΔH=J/g**	**ΔS=J/g.K**
VI	C16	10	Cr-Sm 86.38 Sm-N 148.79 N-I 183.62	92.15 3.01 1.40	0.256 0.0071 0.0030

Table 3.24: UV Data

Series	**Homologue**	**UV λ max values nm (solvent – ethyl acetate)**	
		π → π*	**n → π***
V1	C6	327.50	440
	C16	328.50	438.50

Table 3.25: Transition temperatures Series VII: *trans*-4-(4'-*n*-alkyloxycinnamoyloxy)-phenylazo-4"-nitrobenzenes



R = *n*-Alkyl group	Transition Temperature °C		
	Smectic C	Nematic	Isotropic
Methyl	-	182	276
Ethyl	-	161	293
Propyl	-	135	262
Butyl	-	162	271
Pentyl	-	136	243
Hexyl	-	155	257
Heptyl	147	200	262
Octyl	135	206	255
Decyl	104	-	232
Dodecyl	89	-	222
Tetradecyl	95	-	228
Hexadecyl	92	-	230

Table 3.26: Elemental Analysis

Series	Homologue	Theoretical			Practical		
		C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
VII	C8	69.42	6.18	8.37	69.49	6.25	6.18
VII	C16	72.33	7.65	6.84	72.65	7.50	6.53

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

Decyl homologue : 2952–2858(–C–H st., Alkyl –CH_3, sp^3 hybridization), 1750(–C=O ester), 1604(–N=N– st.), 1579–1508(–C=C– st. aromatic ring), 1480(–CH bending of –CH_2–), 860(–CH=CH st.), 1069(–C–O st. of ester), 860-850(Para–substituted phenyl ring), 1520(Asymmetric st. aromatic –NO_2), 1345(Symmetric st. aromatic –NO_2).

Hexadecyl homologue : 2950–2856(–C–H st, Alkyl–CH_3, sp^3 hybridization), 1742(–C=O ester), 1606(–N=N– st.), 1580–1508(–C=C– st. aromatic ring), 1478(–CH bending of CH_2), 860(–CH=CH st.), 1069(–

C–O st. of ester), 860–850(Para–substituted phenyl ring), 1520(Asymmetric st. aromatic $–NO_2$), 1345(Symmetric st. aromatic $–NO_2$).

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

Butyl homologue: δ = 0.98 (t, 3H. $–CH_3$), 1.25–1.57 (m, 4H, 2($–CH_2–$)), 1.81 (Qunt, 2H, $-OCCH_2$), 4.02 (t, 2H, $–OCH_2$), 6.44-8.03 (m, 11H, Ar–H),6.50 (d, 1H,=CH–COO), 7.52 (d, 1H, Ar–CH=).

Pentyl homologue: δ = 0.99 (t, 3H. $–CH_3$), 1.50-1.57 (m, 6H, 3($-CH_2-$)), 1.83 (Qunt, 2H, $-OCCH_2$), 4.03 (t, 2H, $–OCH_2$), 6.94–8.16 (m, 11H, Ar–H),6.50 (d, J = 21.2, 1H,=CH-COO), 7.50 (d, J = 21.2, 1H, Ar–CH=).

Mass Spectra: MS m/z:

Heptyl Homologue: Theoratical Mass value: 487.21 g/mol

Practical mass value: MS m/z: 487.21 (M^+)

Table 3.27: DSC Data

Series	Member	Heating rate °C/min	Transition Temperature °C	ΔH=J/g	ΔS=J/g.K
VII	C16	10	Cr – Sm 91.14 Sm – I 122.58	31.26 8.26	0.085 0.021

Table 3.28: UV Data

Series	Homologue	UV λ max values nm (solvent – ethyl acetate)	
		π → π*	**n → π***
VII	C12	335	442
	C16	342	438.50

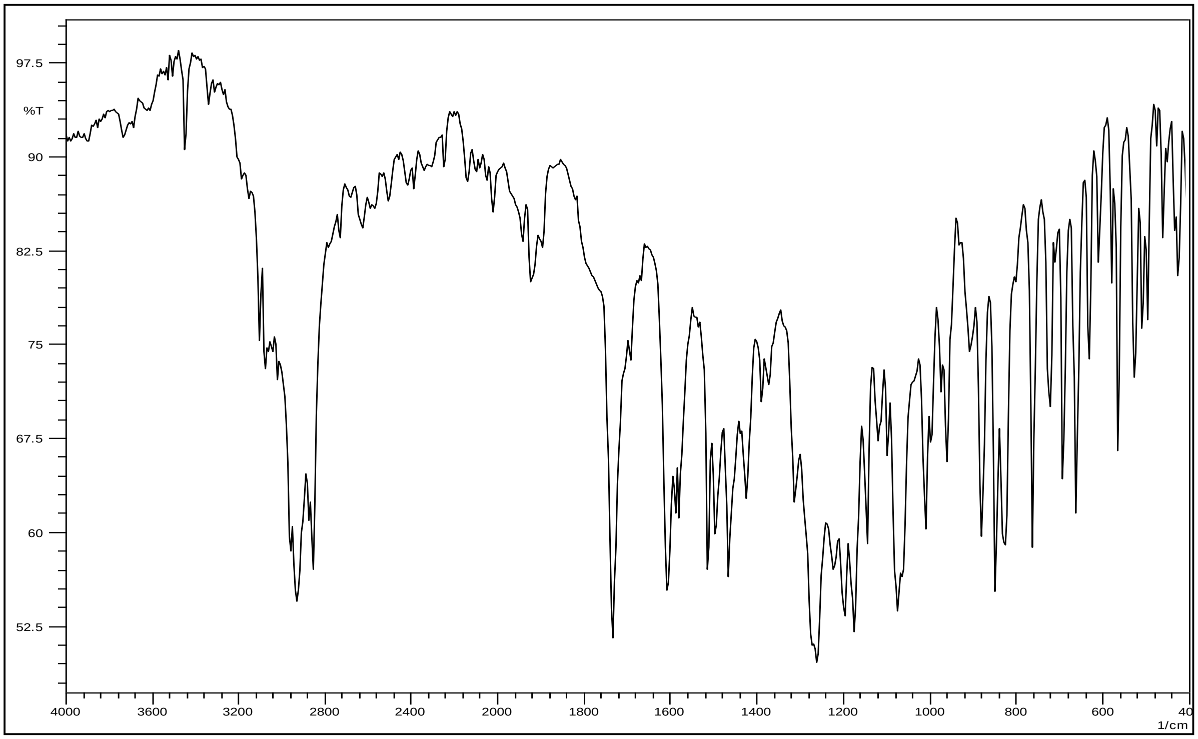


Figure 3.1 (a): IR spectra of C8 homologue of series I

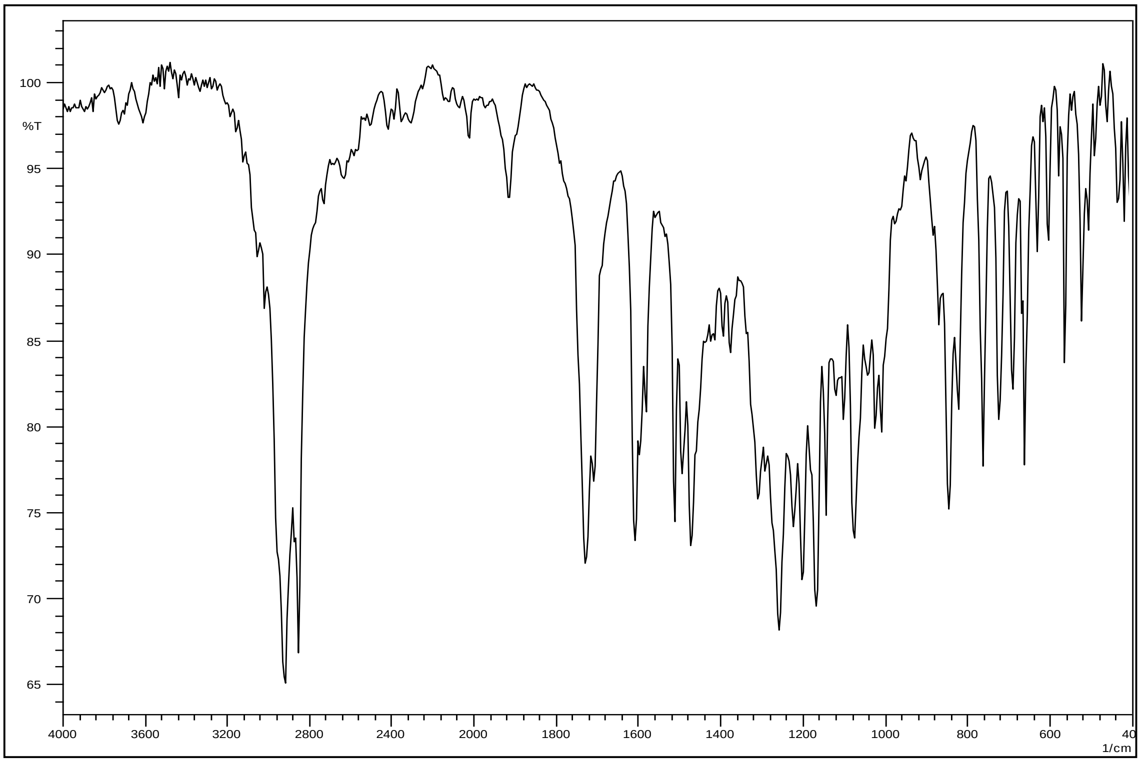


Figure 3.1 (b): IR spectra of C16 homologue of series I

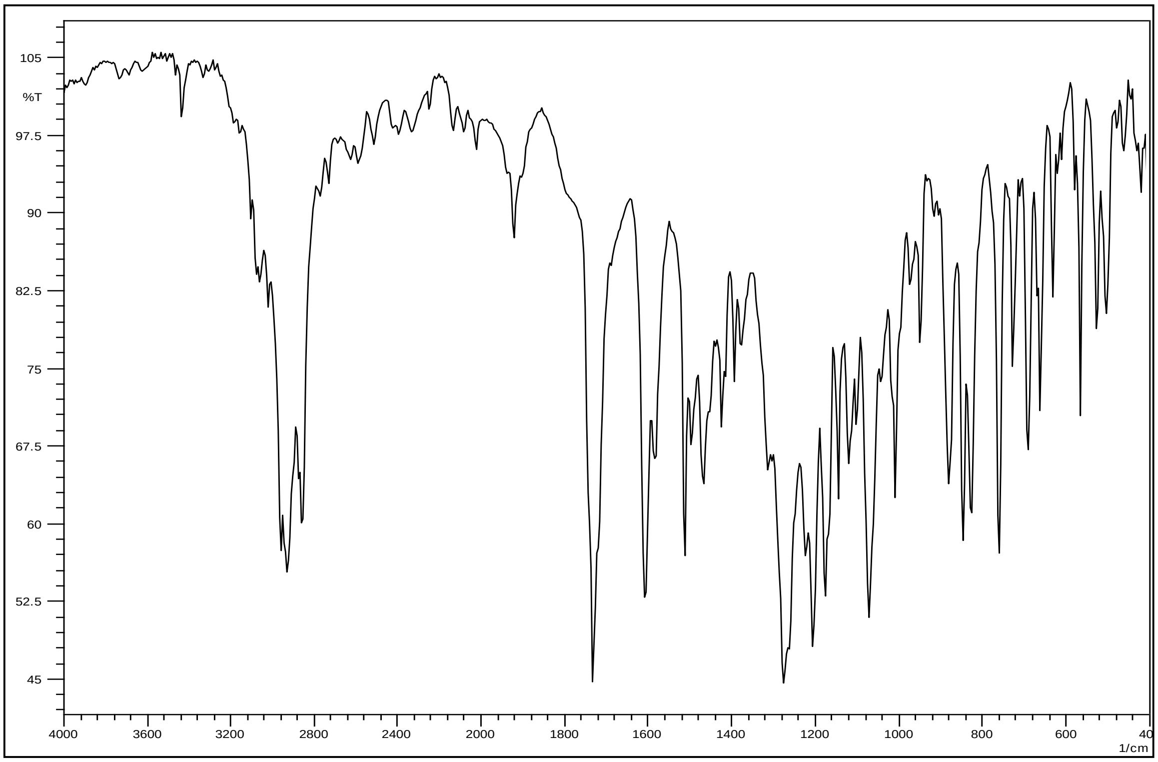


Figure 3.1 (c): IR spectra of C5 homologue of series II

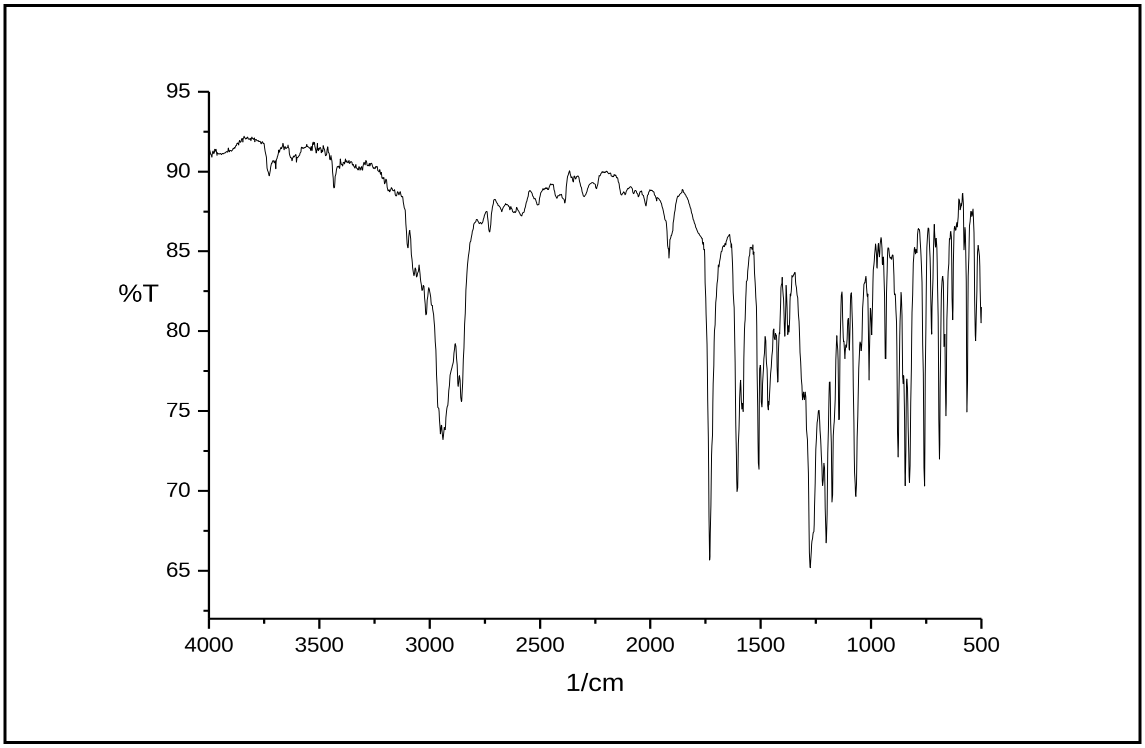


Figure 3.1 (d): IR spectra of C10 homologue of series II

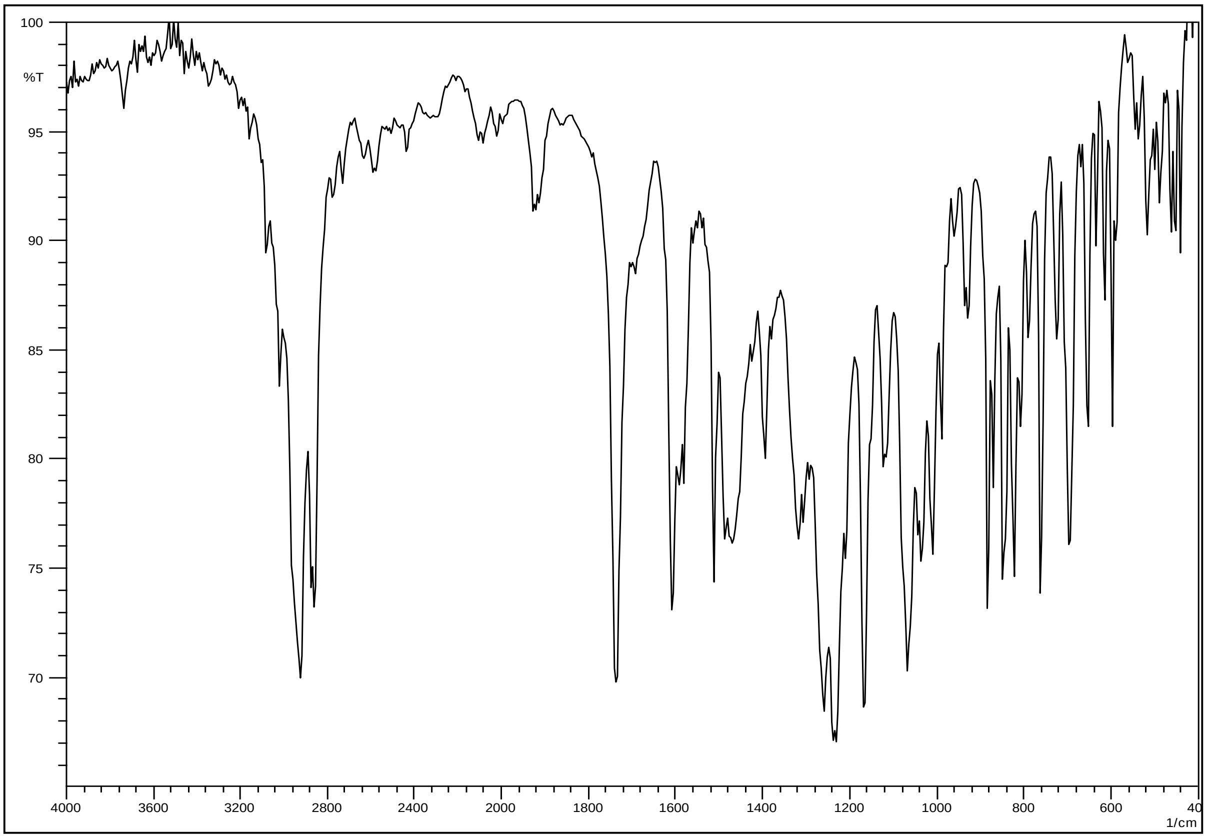


Figure 3.1 (e): IR spectra of C7 homologue of series III

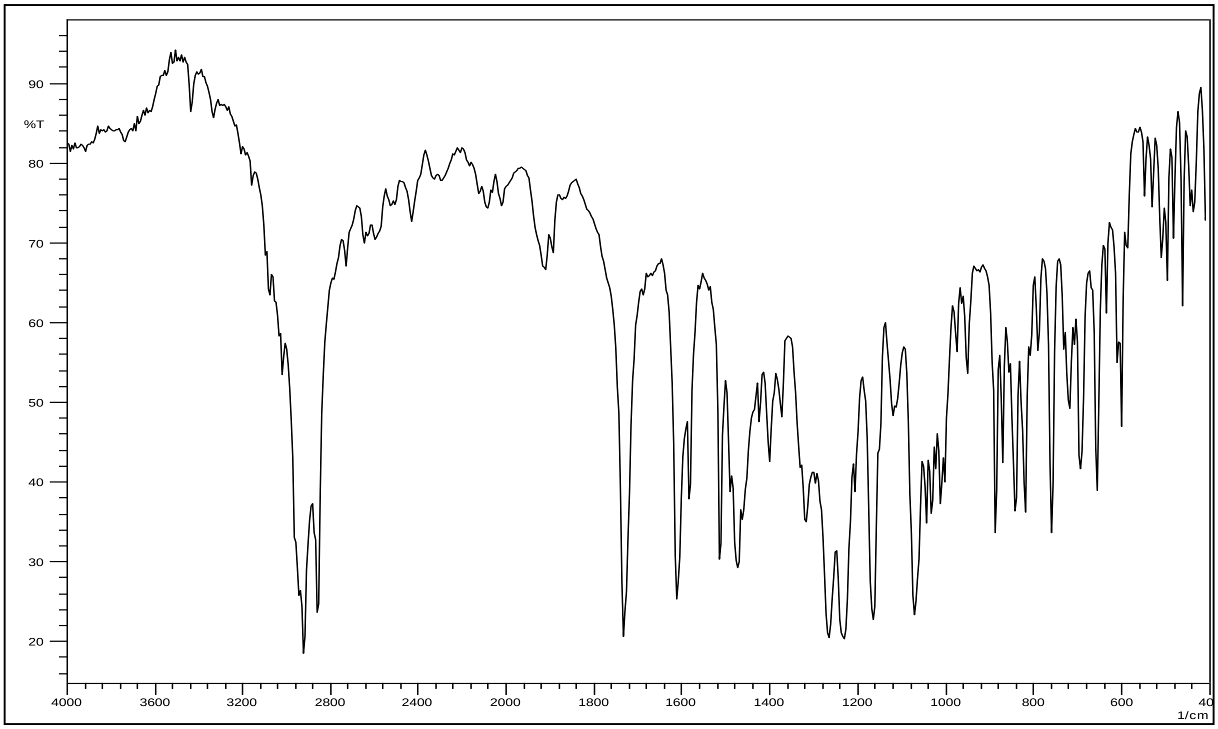


Figure 3.1 (f): IR spectra of C12 homologue of series III

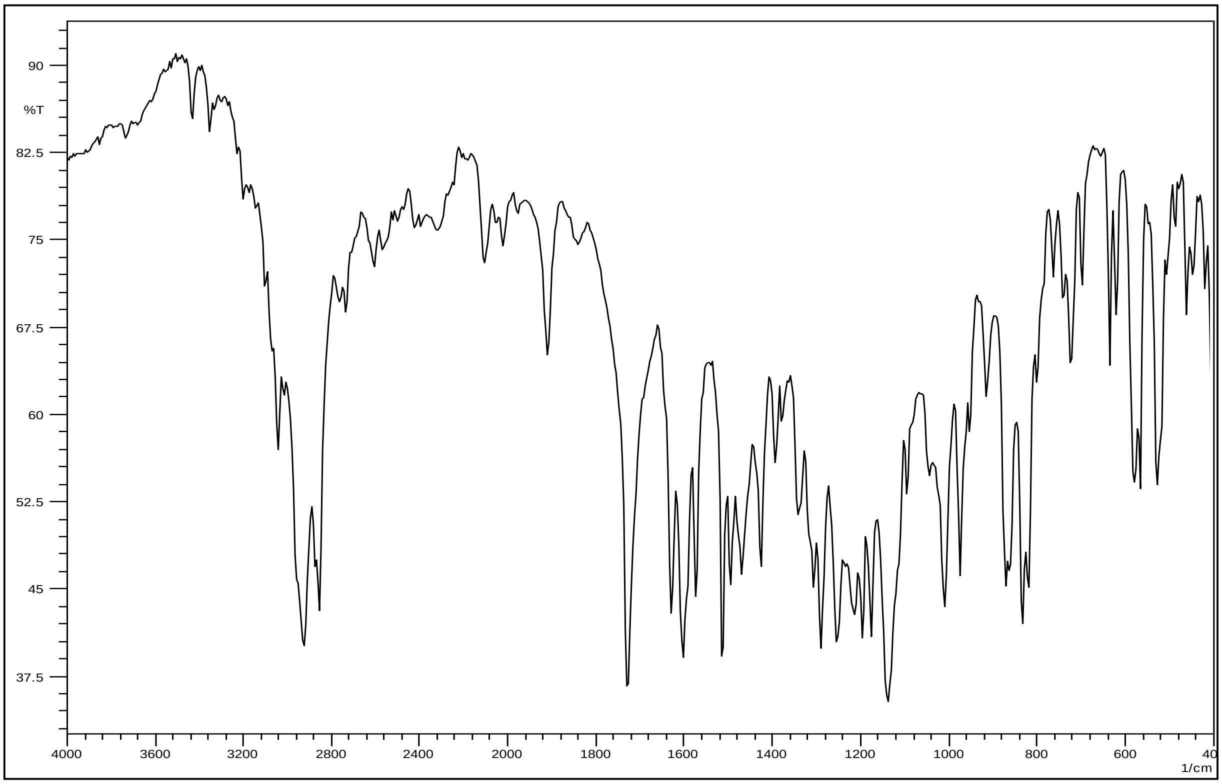


Figure 3.1 (g): IR spectra of C10 homologue of series IV

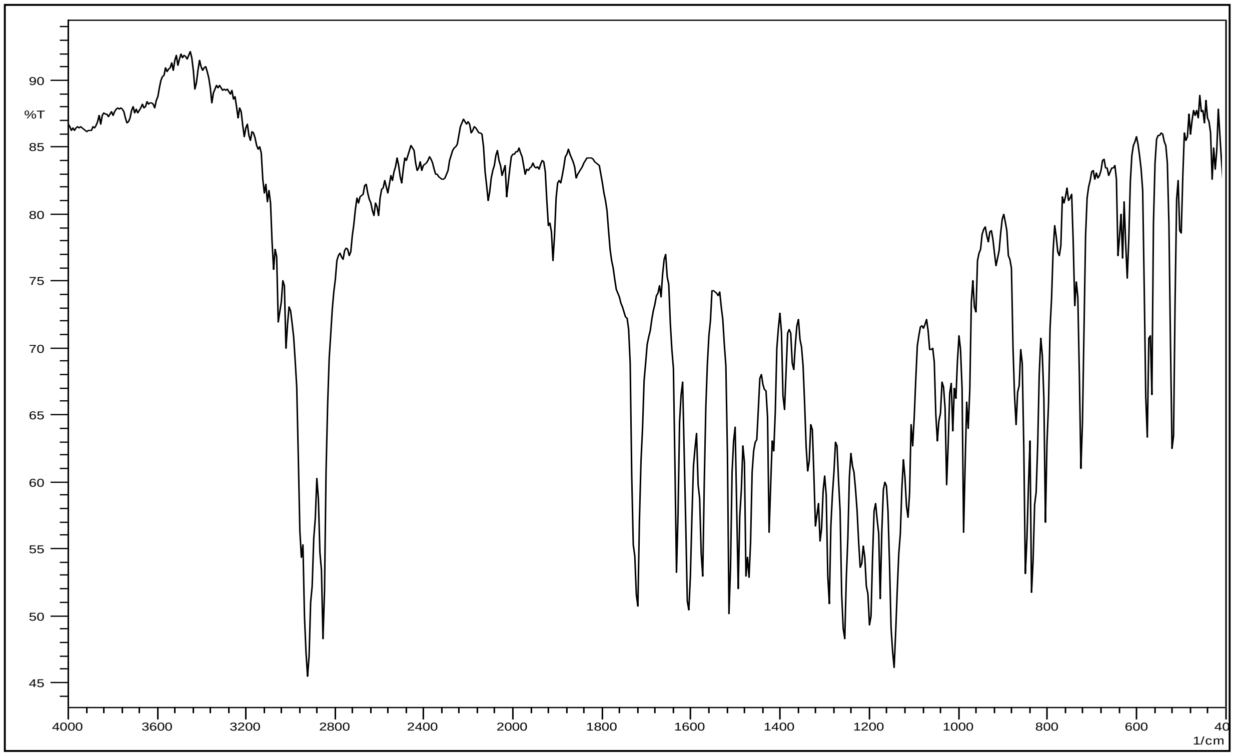


Figure 3.1 (h): IR spectra of C16 homologue of series IV

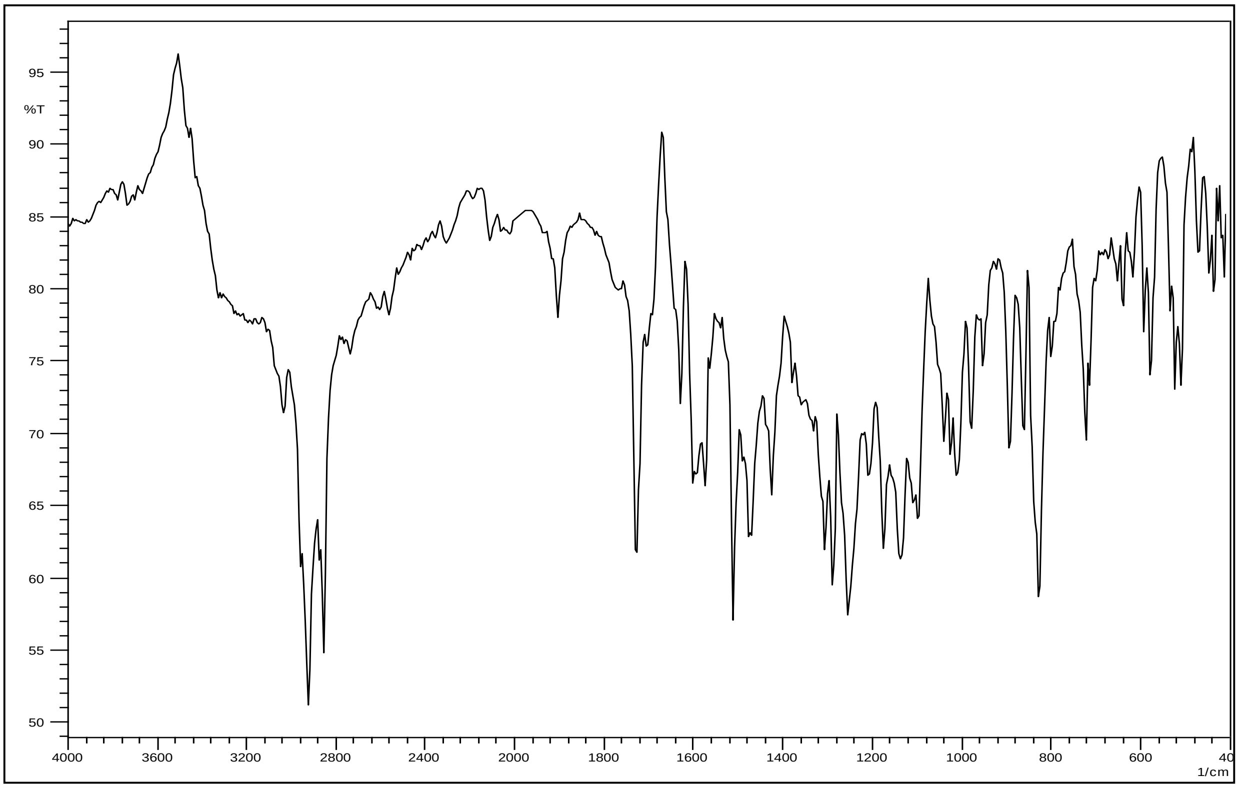


Figure 3.1 (i): IR spectra of C14 homologue of series V

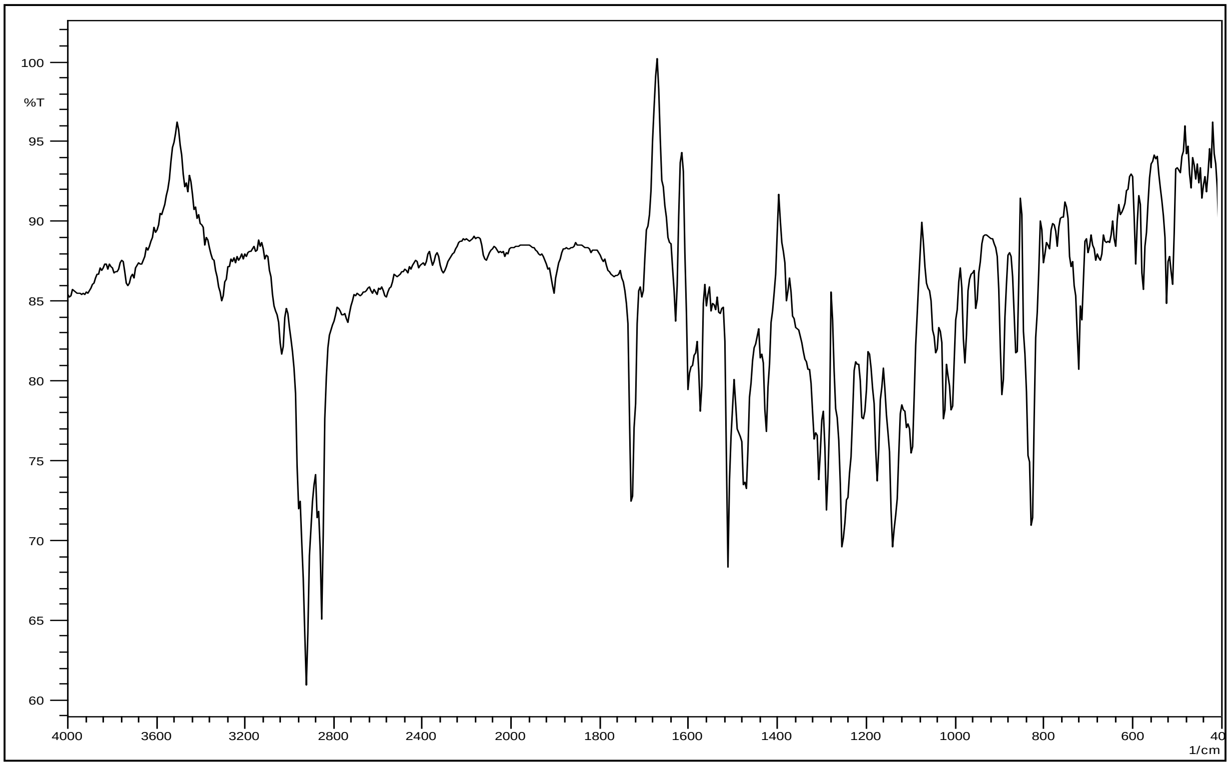


Figure 3.1 (j): IR spectra of C16 homologue of series V

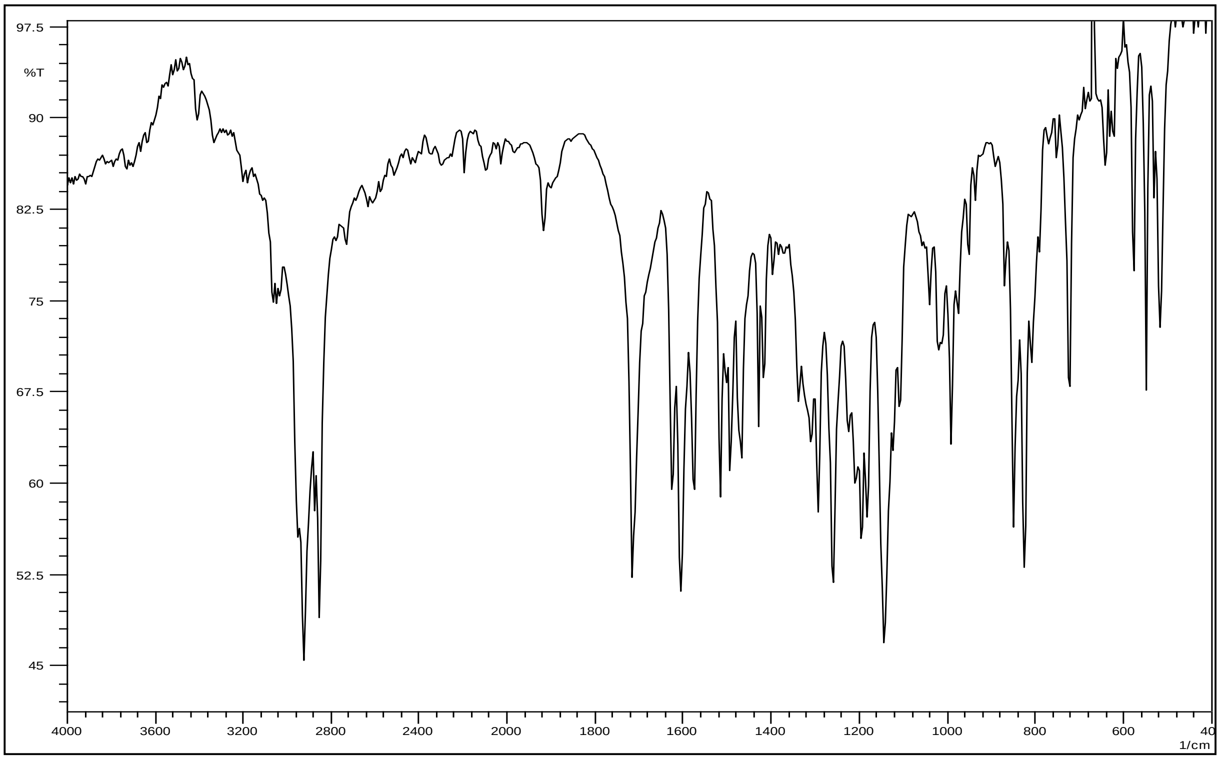


Figure 3.1 (k): IR spectra of C4 homologue of series VI

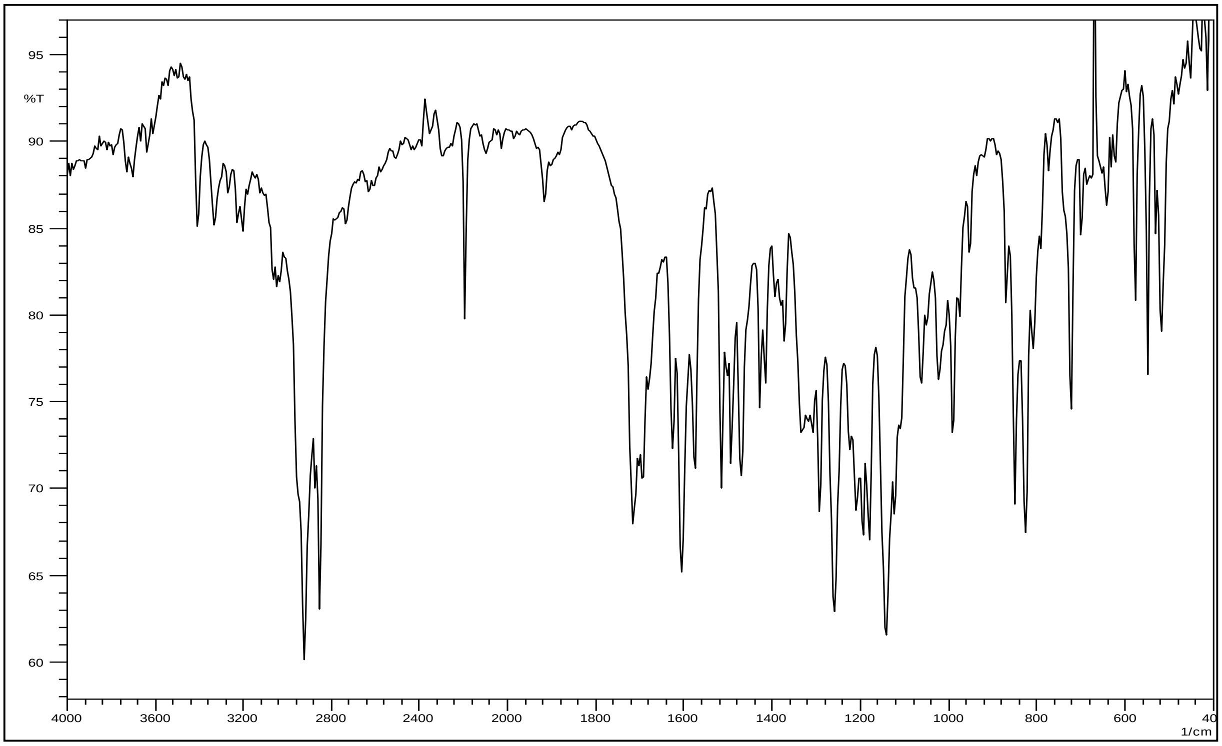


Figure 3.1 (l): IR spectra of C6 homologue of series VI

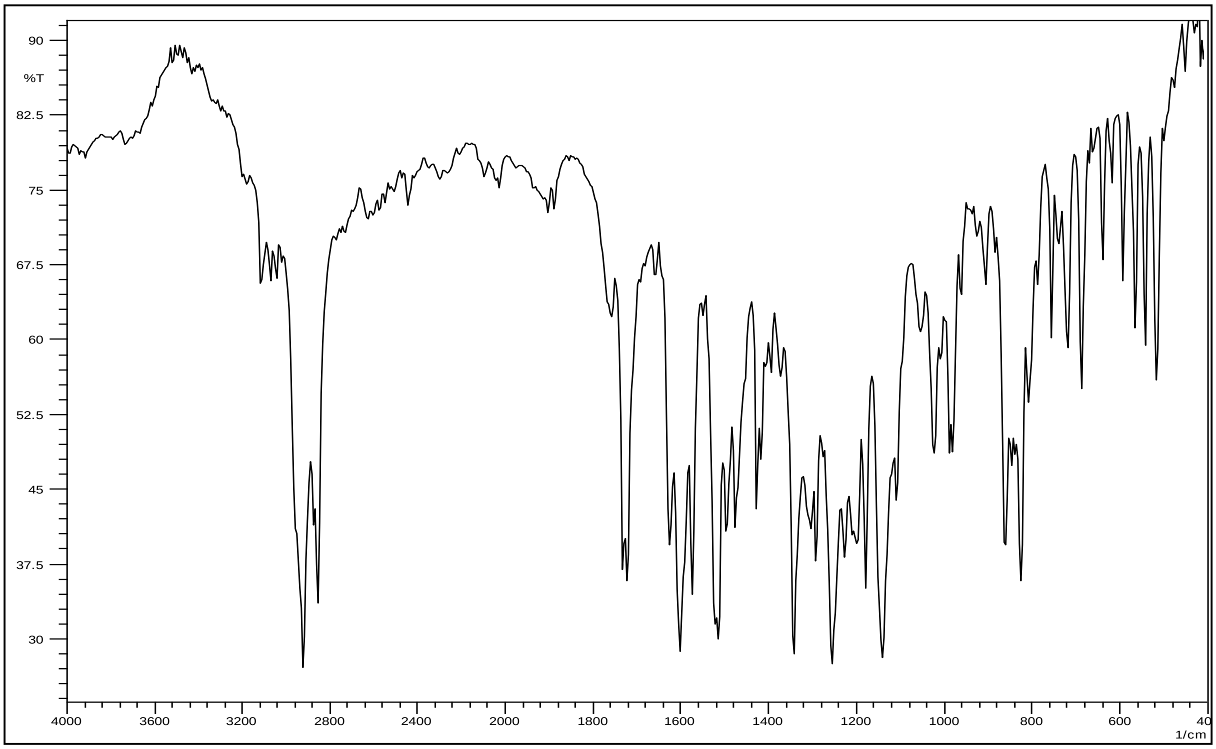


Figure 3.1 (m): IR spectra of C10 homologue of series VII

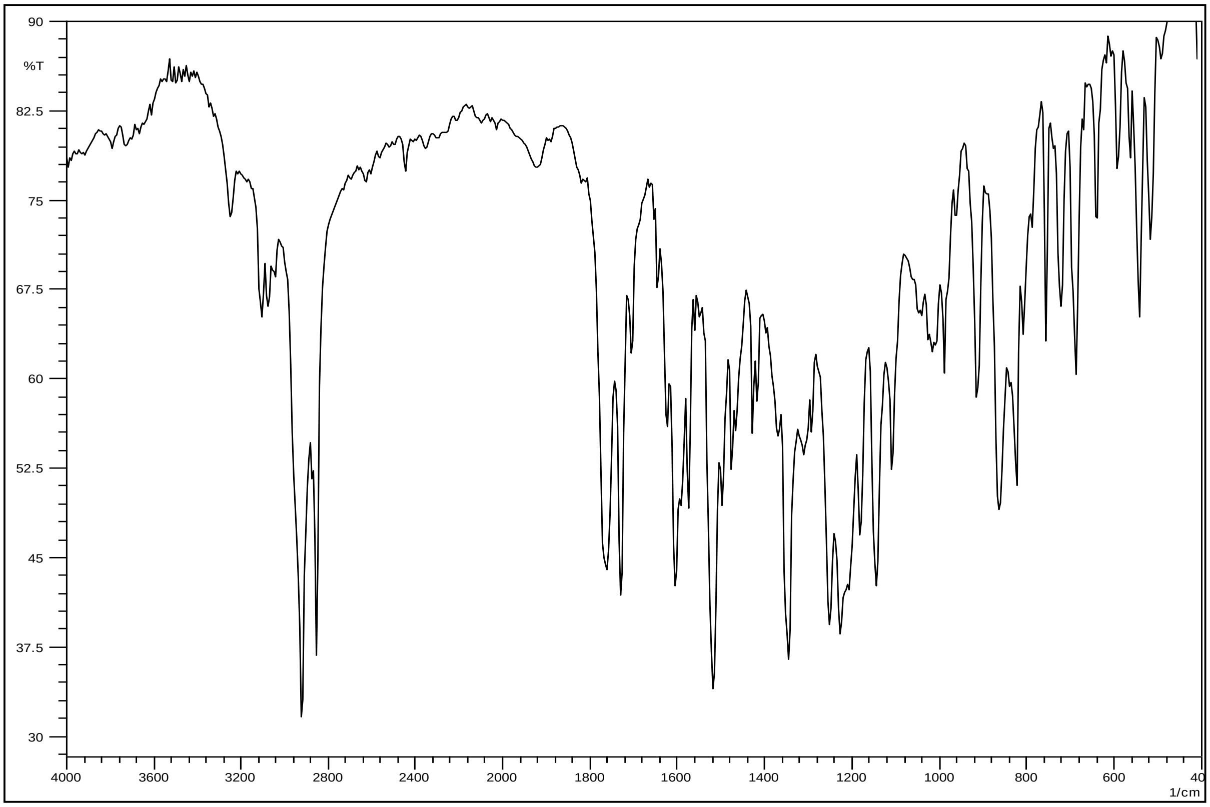


Figure 3.1 (n): IR spectra of C16 homologue of series VII

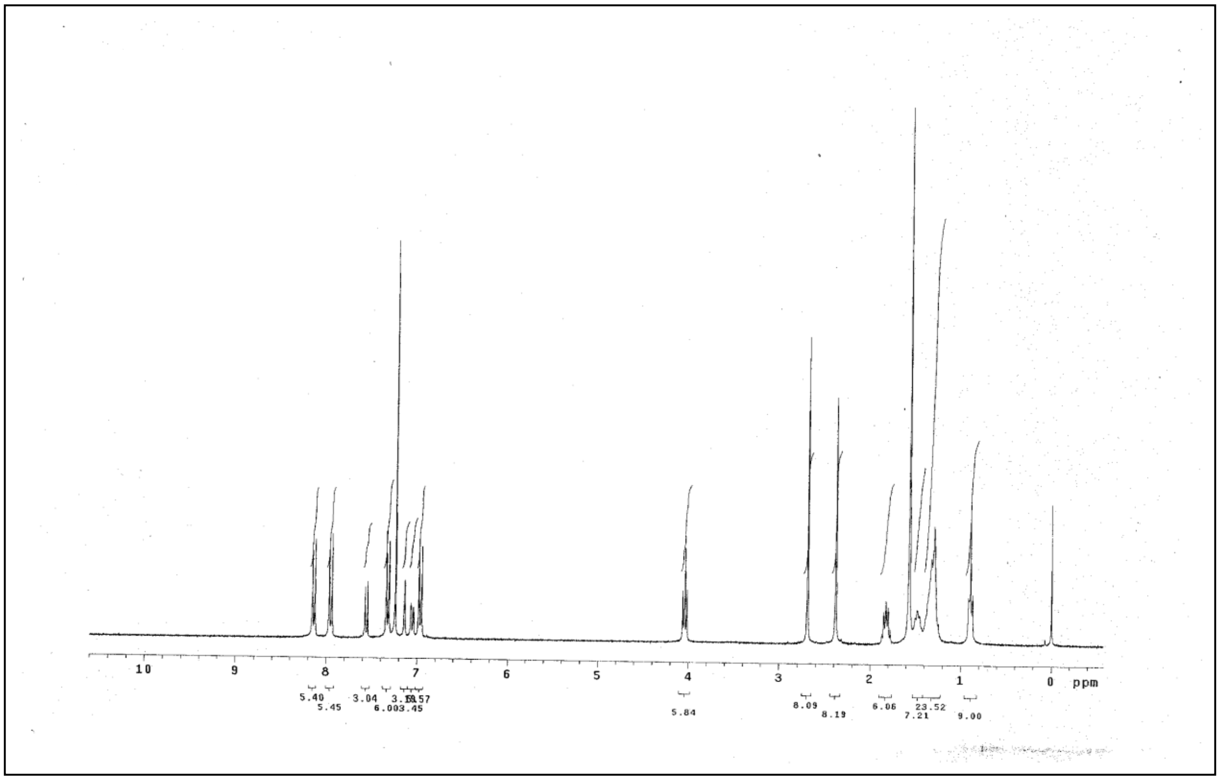


Figure 3.2 (a): ^{1}H NMR spectra of C8 homologue of series I

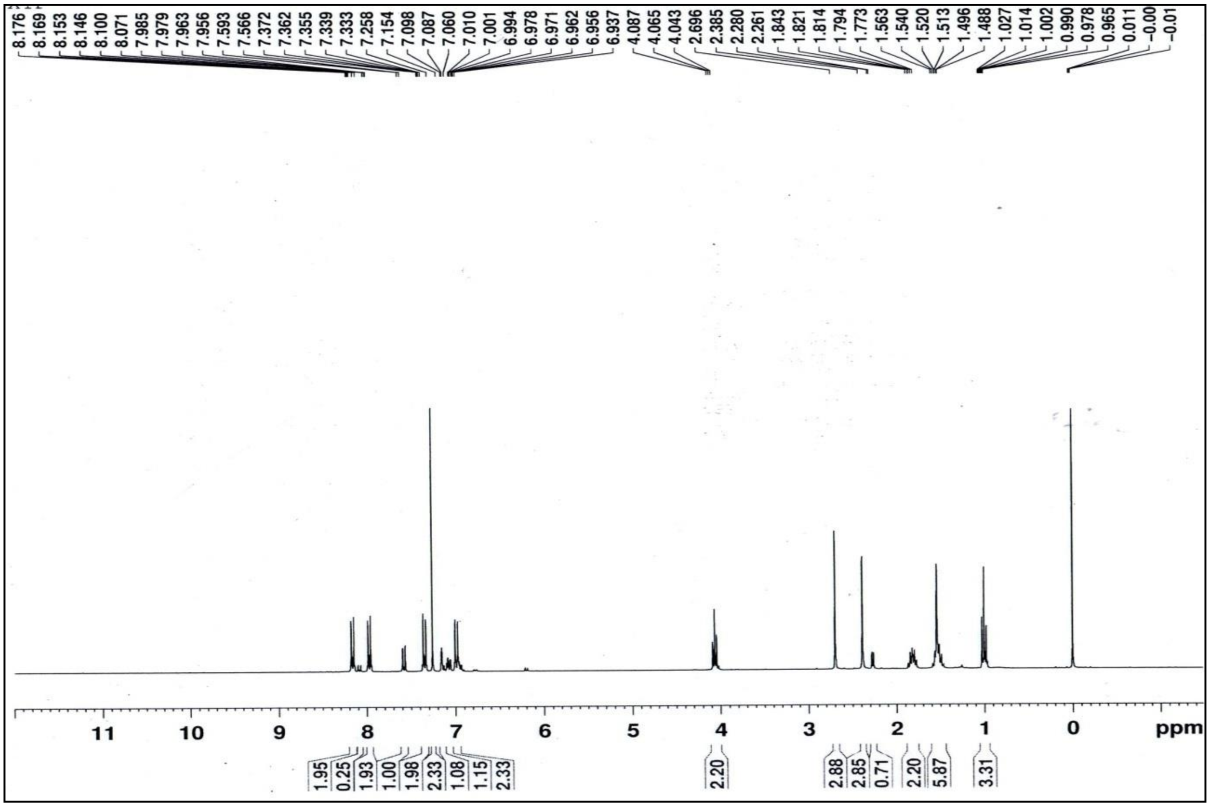


Figure 3.2 (b): ^{1}H NMR spectra of C4 homologue of series I

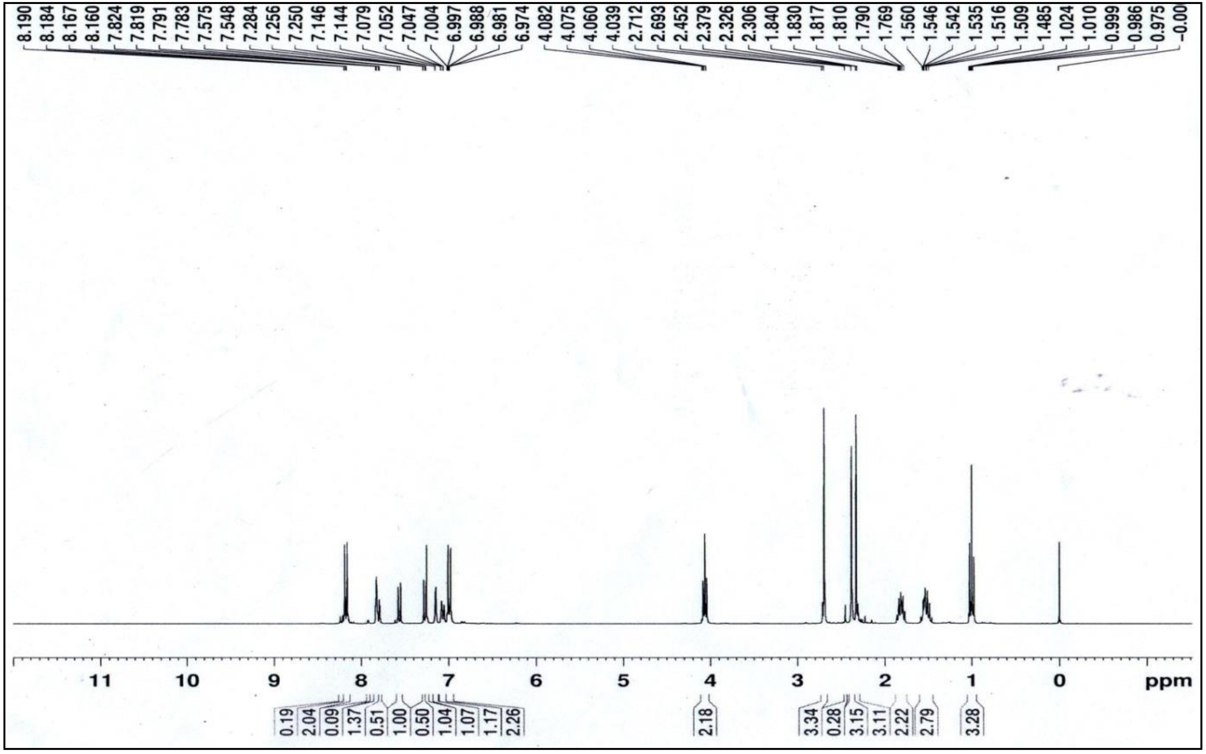


Figure 3.2 (c): ^{1}H NMR spectra of C4 homologue of series II

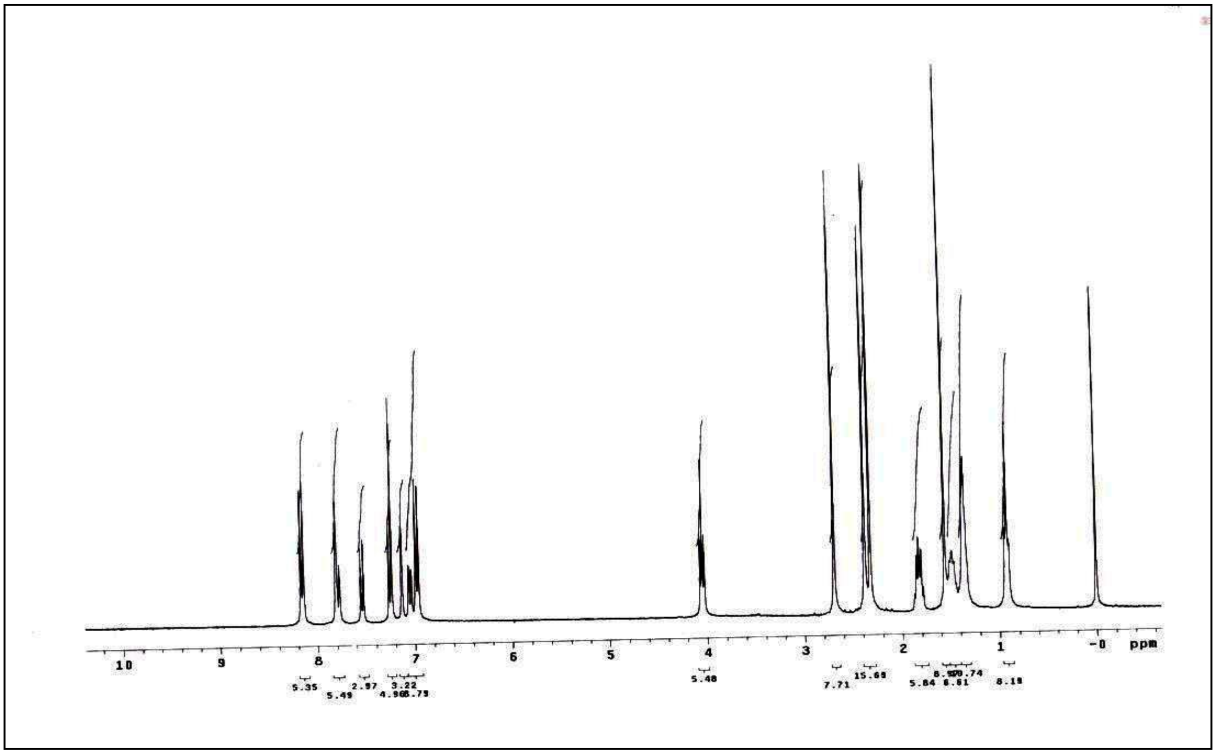


Figure 3.2 (d): ^{1}H NMR spectra of C6 homologue of series II

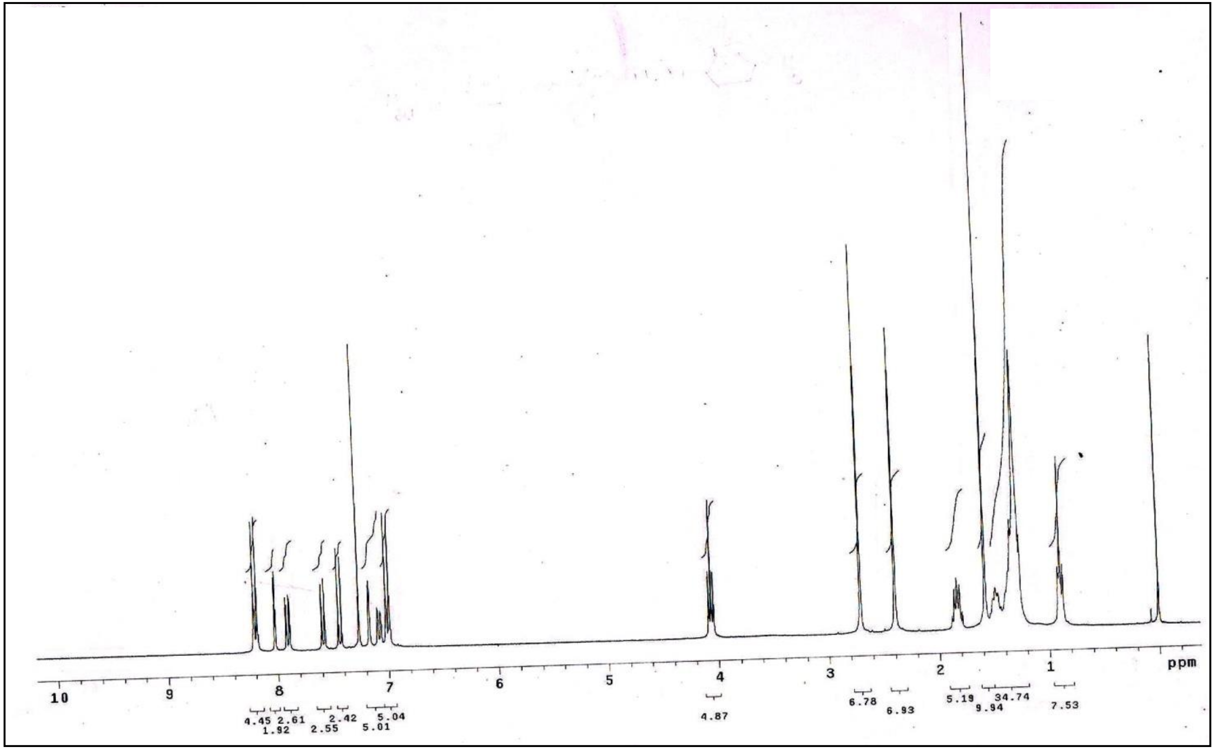


Figure 3.2 (e): ^{1}H NMR spectra of C8 homologue of series III

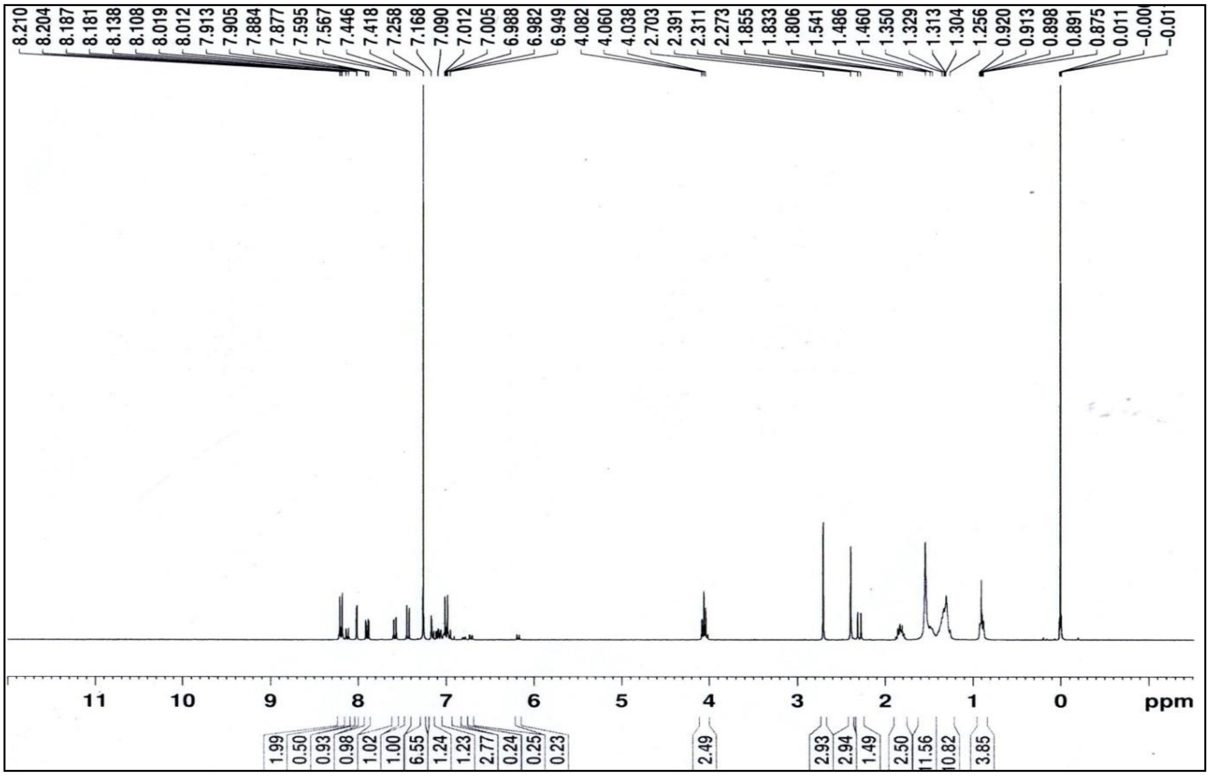


Figure 3.2 (f): ^{1}H NMR spectra of C10 homologue of series III

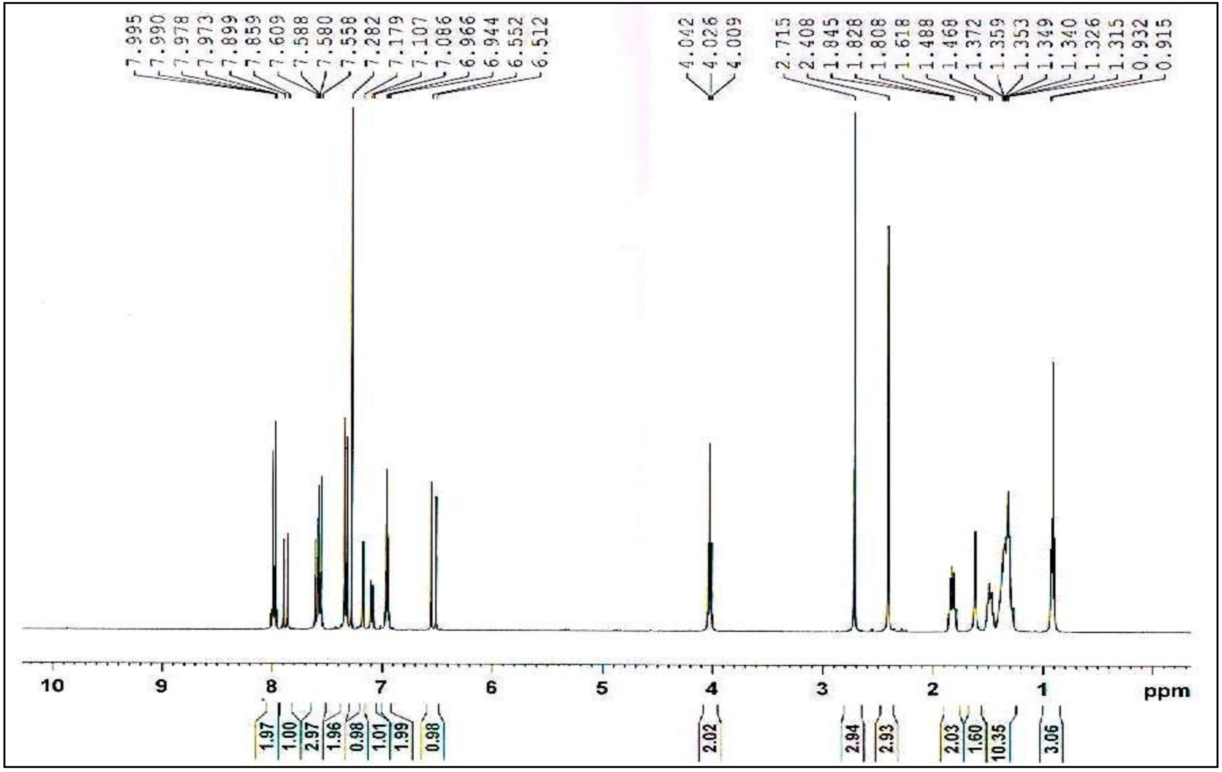


Figure 3.2 (g): ^{1}H NMR spectra of C8 homologue of series IV

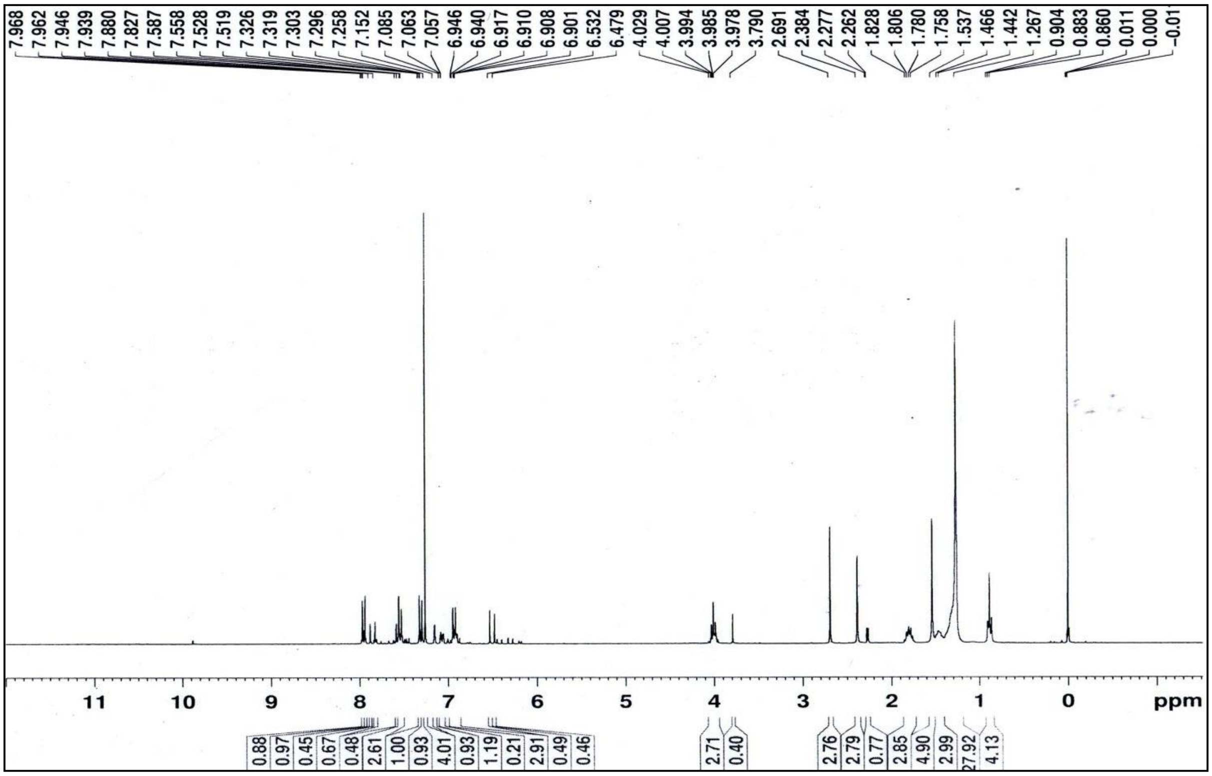


Figure 3.2 (h): ^{1}H NMR spectra of C14 homologue of series IV

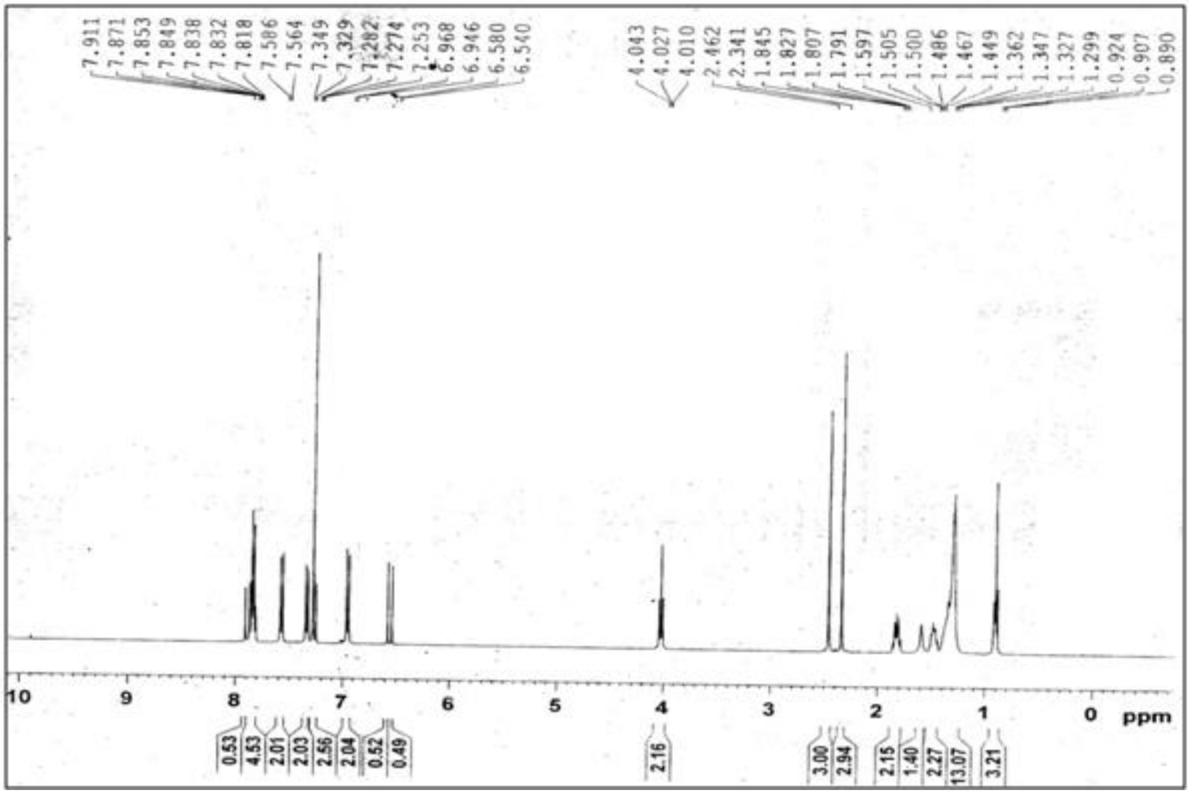


Figure 3.2 (i): ^{1}H NMR spectra of C10 homologue of series V

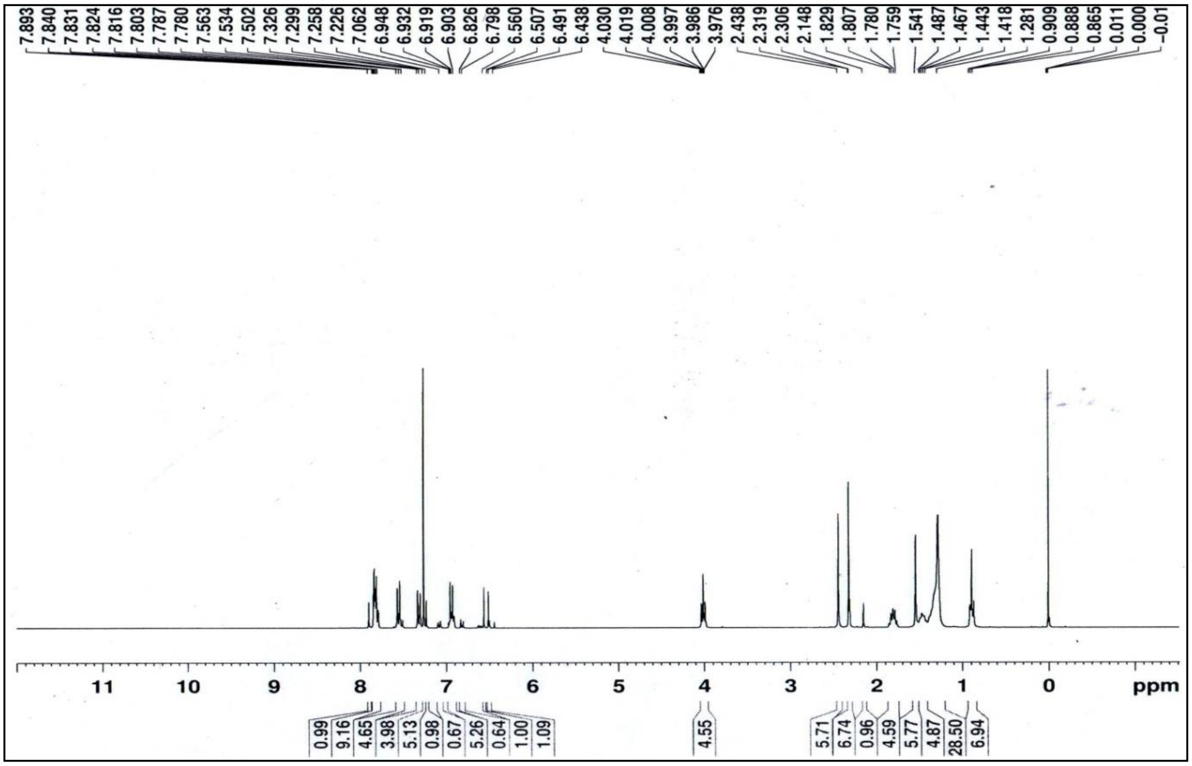


Figure 3.2 (j): ^{1}H NMR spectra of C12 homologue of series V

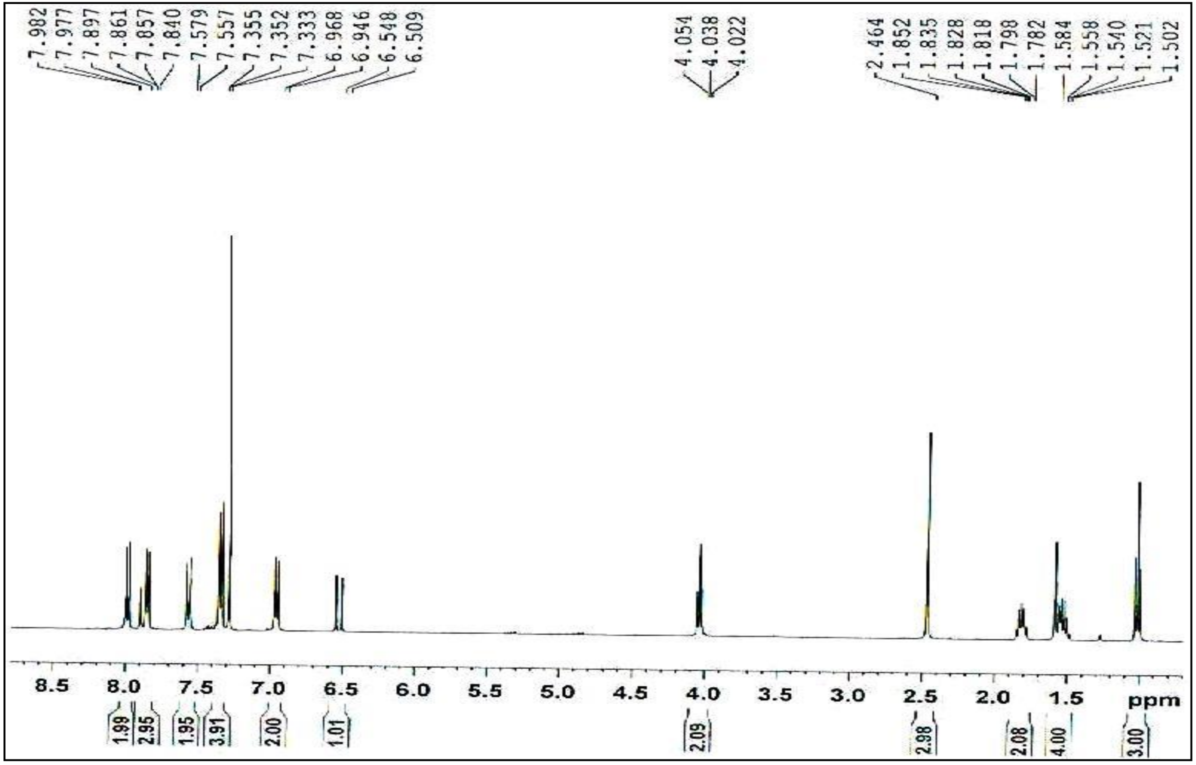


Figure 3.2 (k): ^{1}H NMR spectra of C4 homologue of series VI

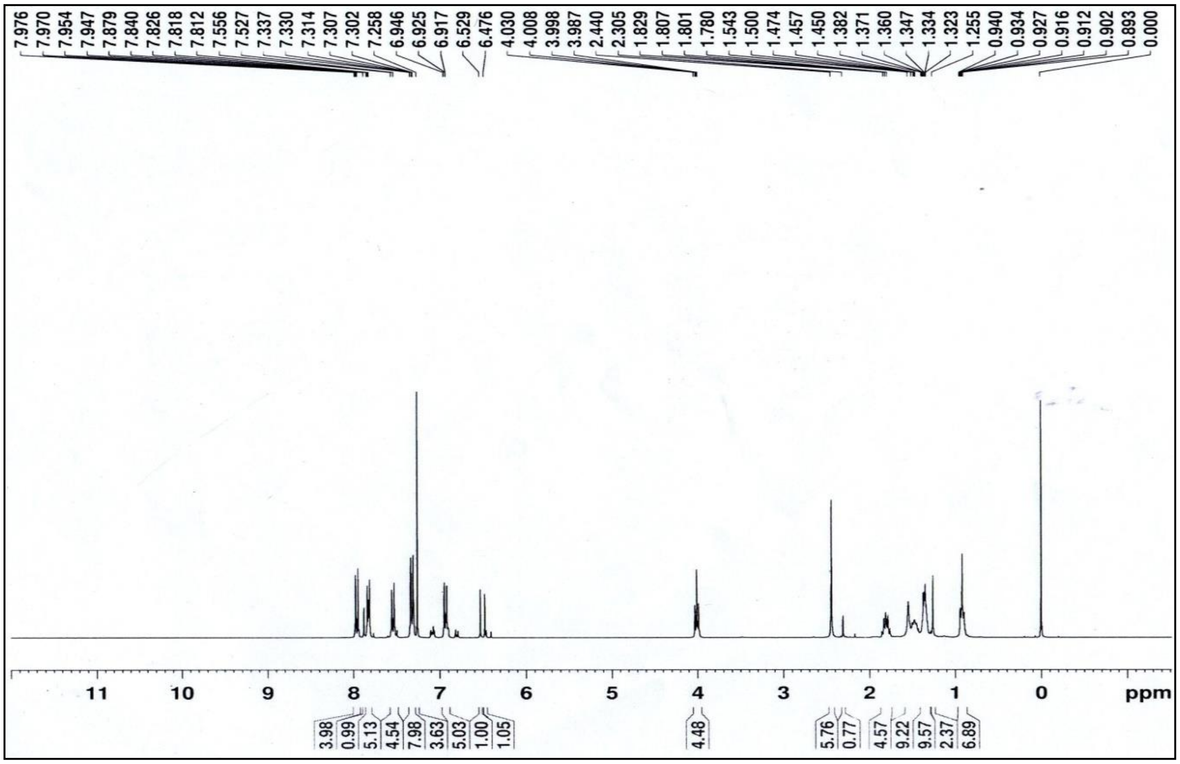


Figure 3.2 (l): ^{1}H NMR spectra of C6 homologue of series VI

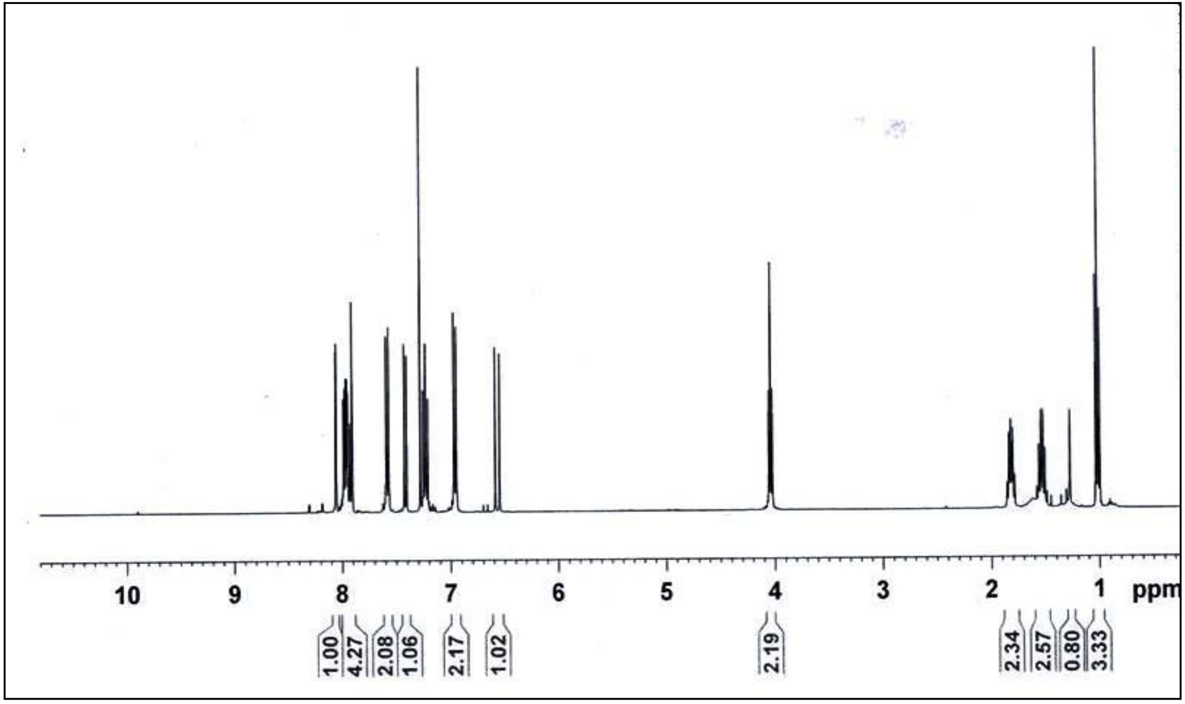


Figure 3.2 (m): ^{1}H NMR spectra of C4 homologue of series VII

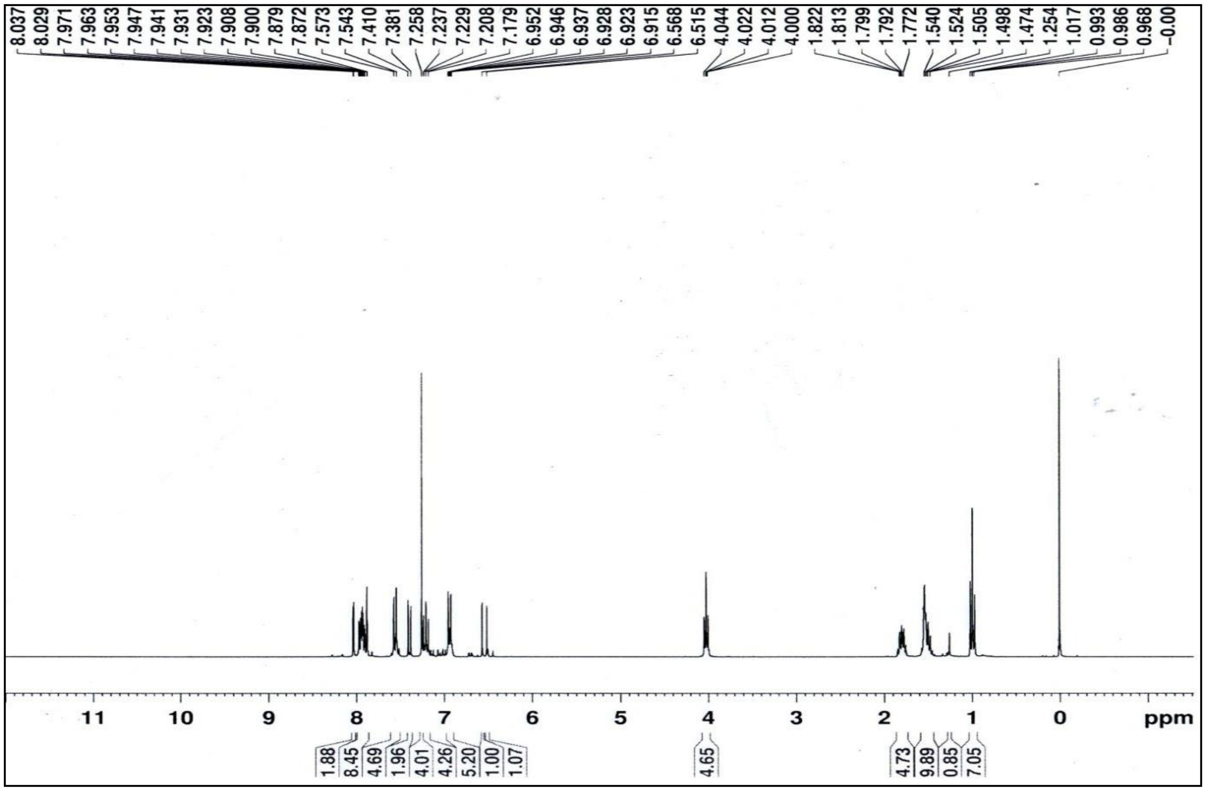


Figure 3.2 (n): ^{1}H NMR spectra of C5 homologue of series VII

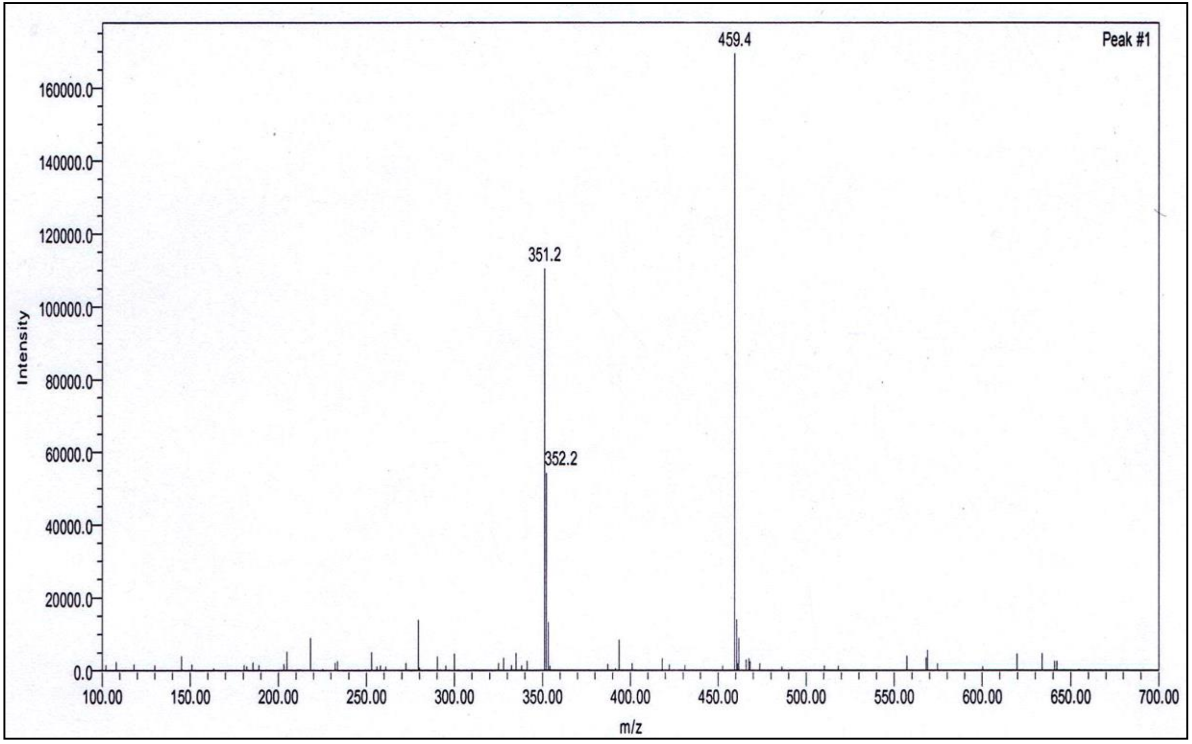


Figure 3.3 (a): Mass spectra of C8 homologue of series I

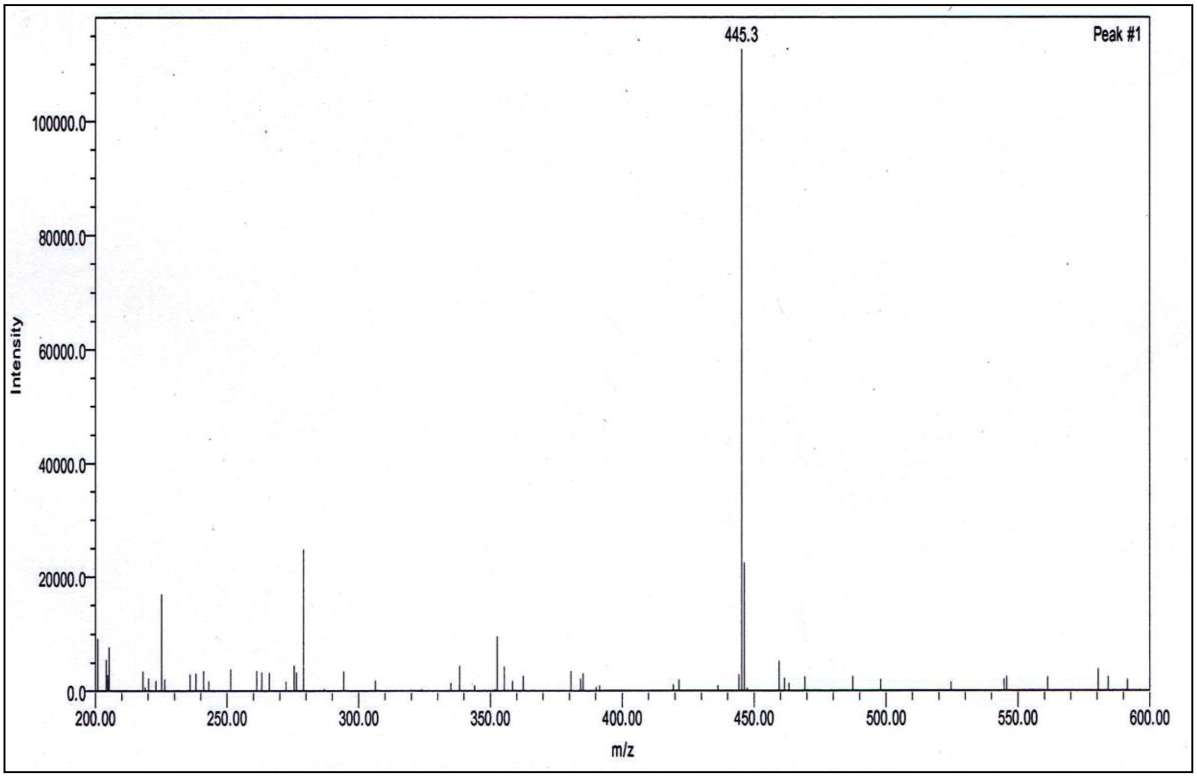


Figure 3.3 (b): Mass spectra of C6 homologue of series II

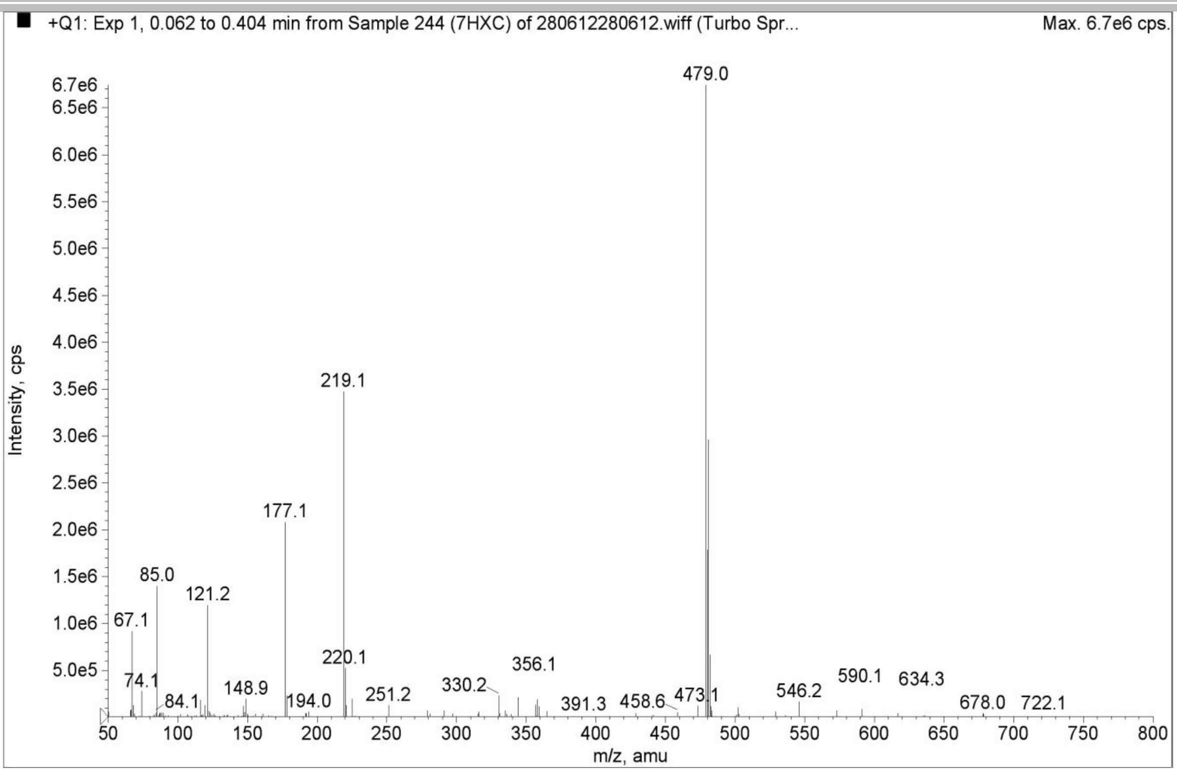


Figure 3.3 (c): Mass spectra of C7 homologue of series III

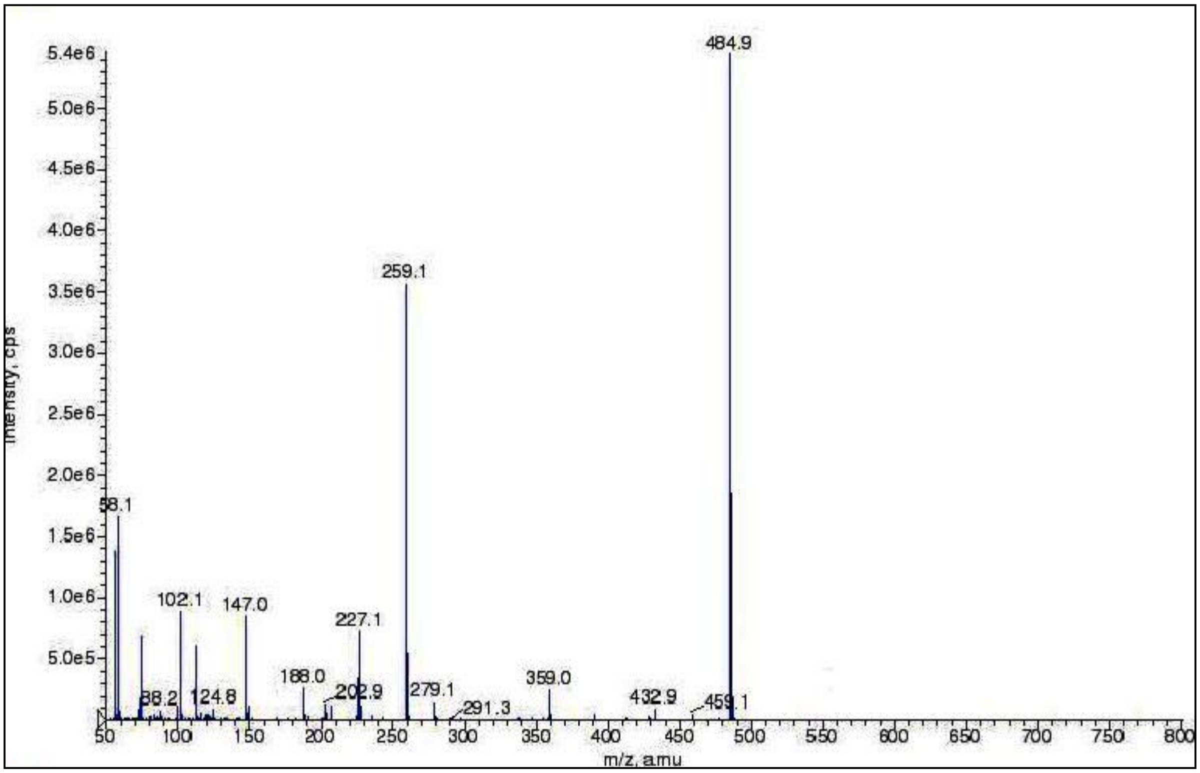


Figure 3.3 (d): Mass spectra of C8 homologue of series IV

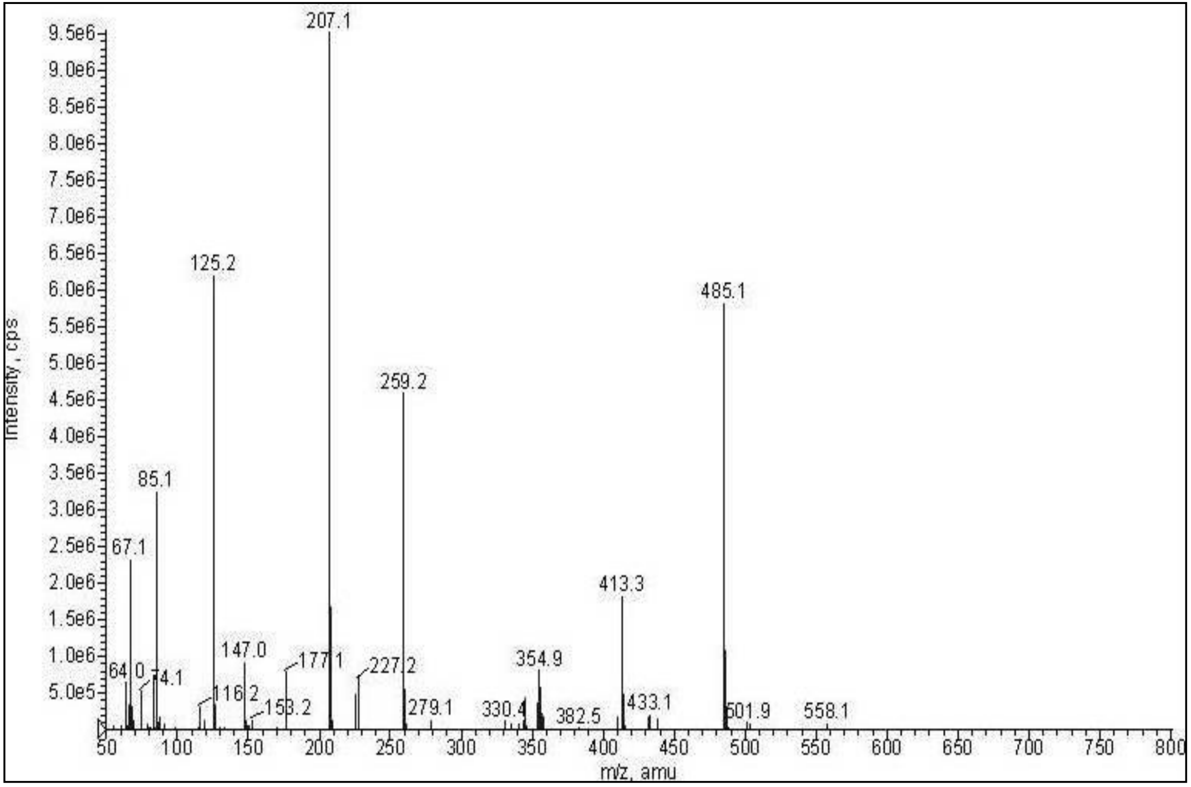
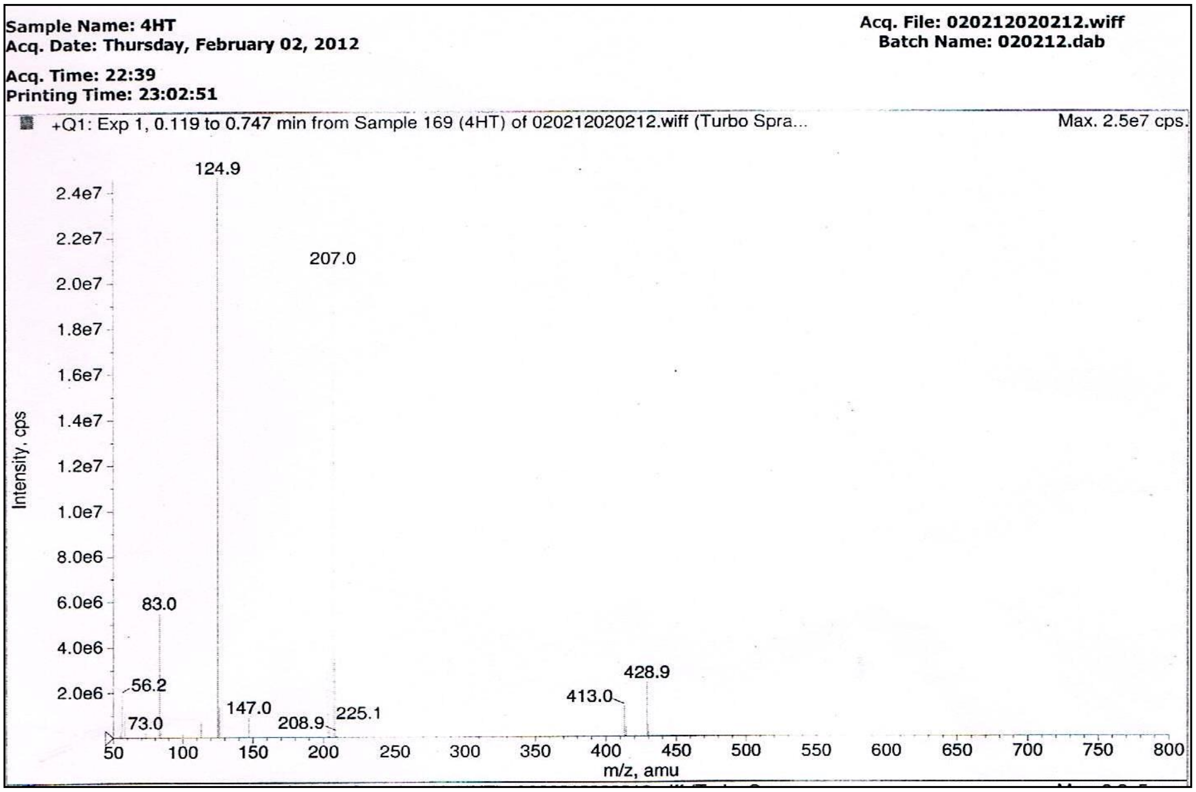


Figure 3.3 (e): Mass spectra of C8 homologue of series V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Acq. Date: Thursday, February 02, 2012
Acq. Time: 22:39
Printing Time: 23:02:51

Acq. File: 020212020212.wiff
Batch Name: 020212.dab

+Q1: Exp 1, 0.119 to 0.747 min from Sample 169 (4HT) of 020212020212.wiff (Turbo Spra...

Max. 2.5e7 cps.

Figure 3.3 (f): Mass spectra of C4 homologue of series V

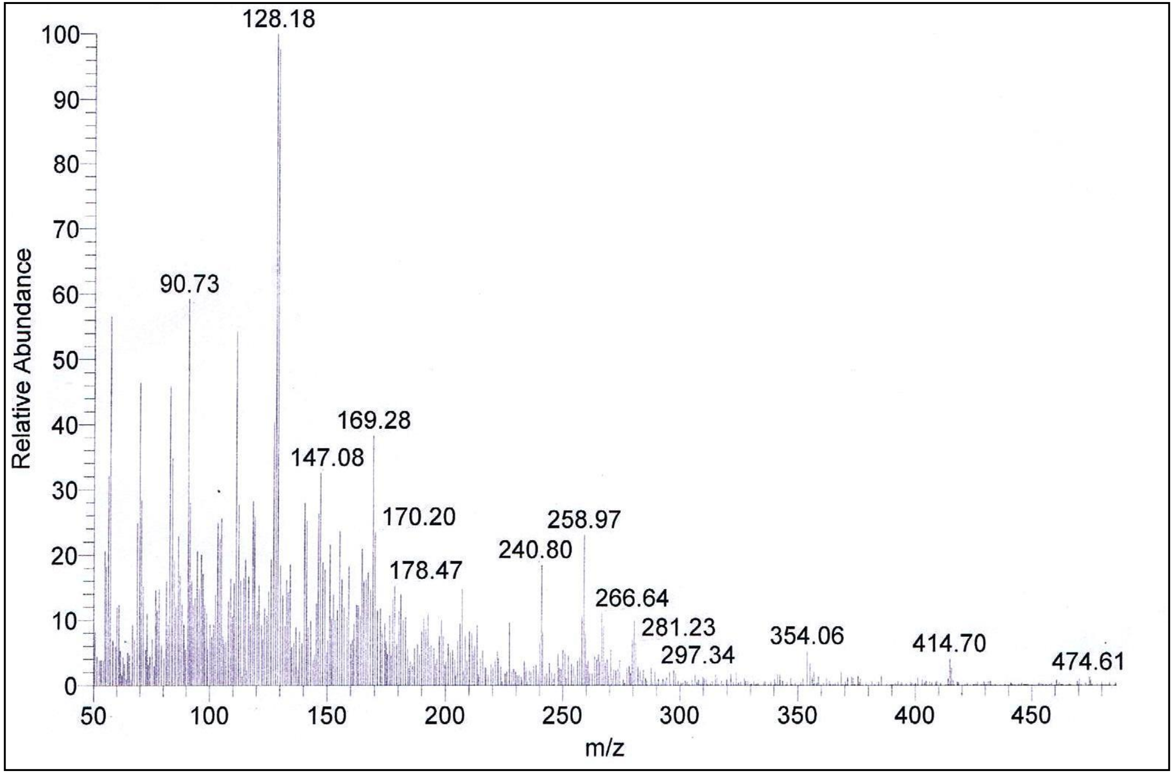


Figure 3.3 (h): Mass spectra of C8 homologue of series VI

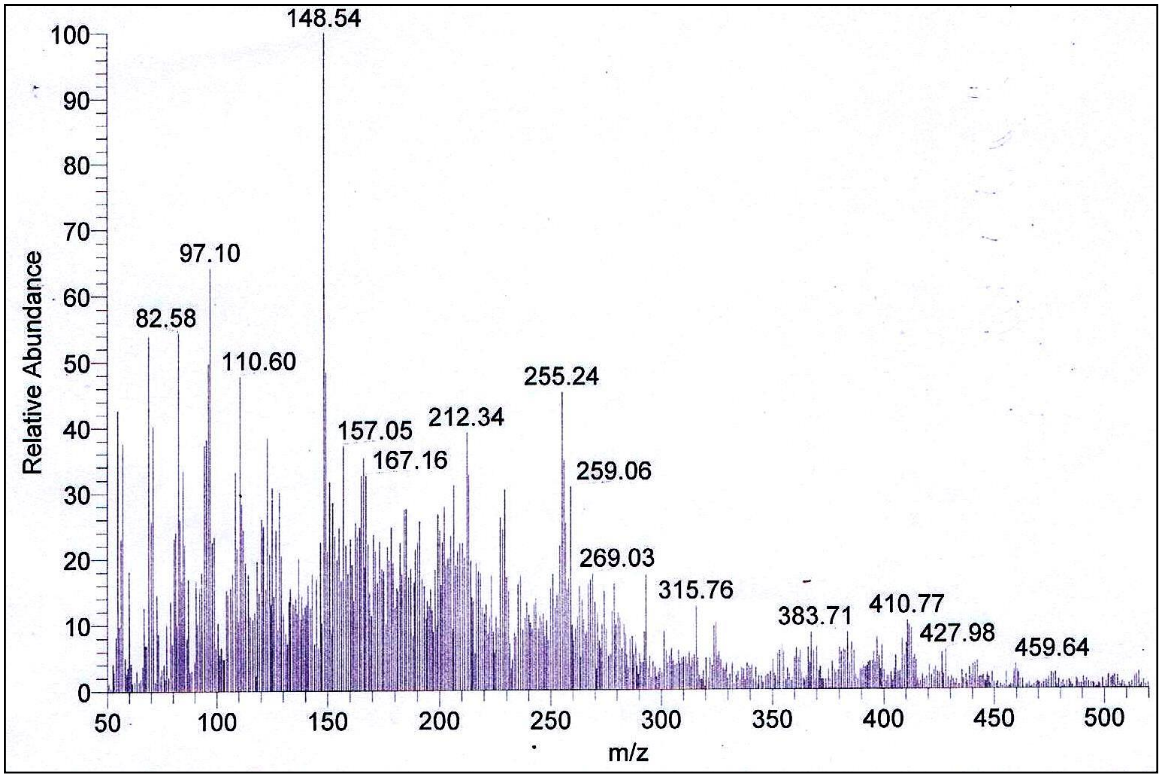


Figure 3.3 (i): Mass spectra of C7 homologue of series VII

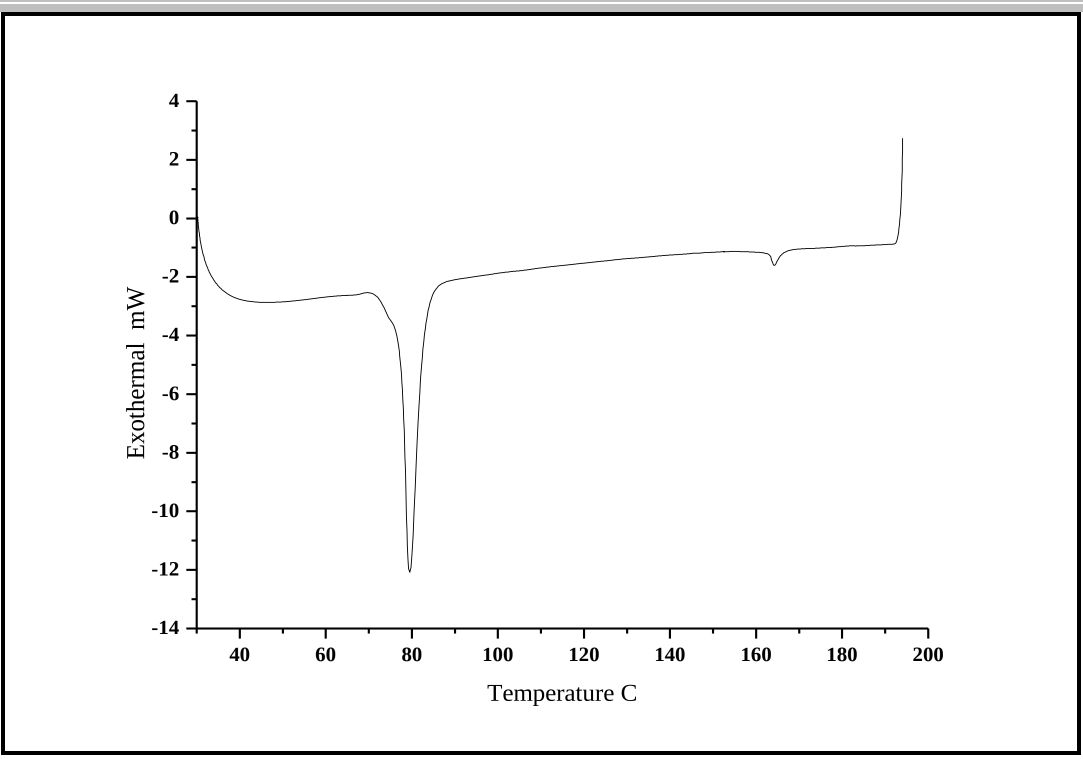


Figure 3.4 (a): DSC Thermogram of C8 homologue of series I

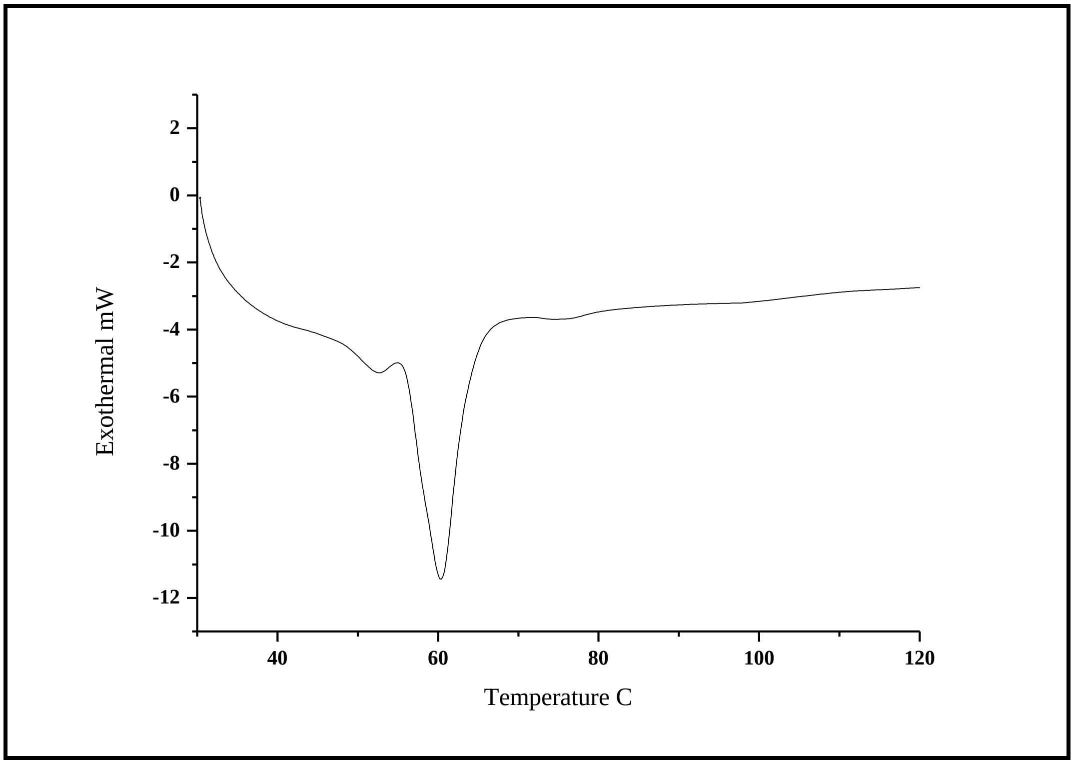


Figure 3.4 (b): DSC Thermogram of C16 homologue of series I

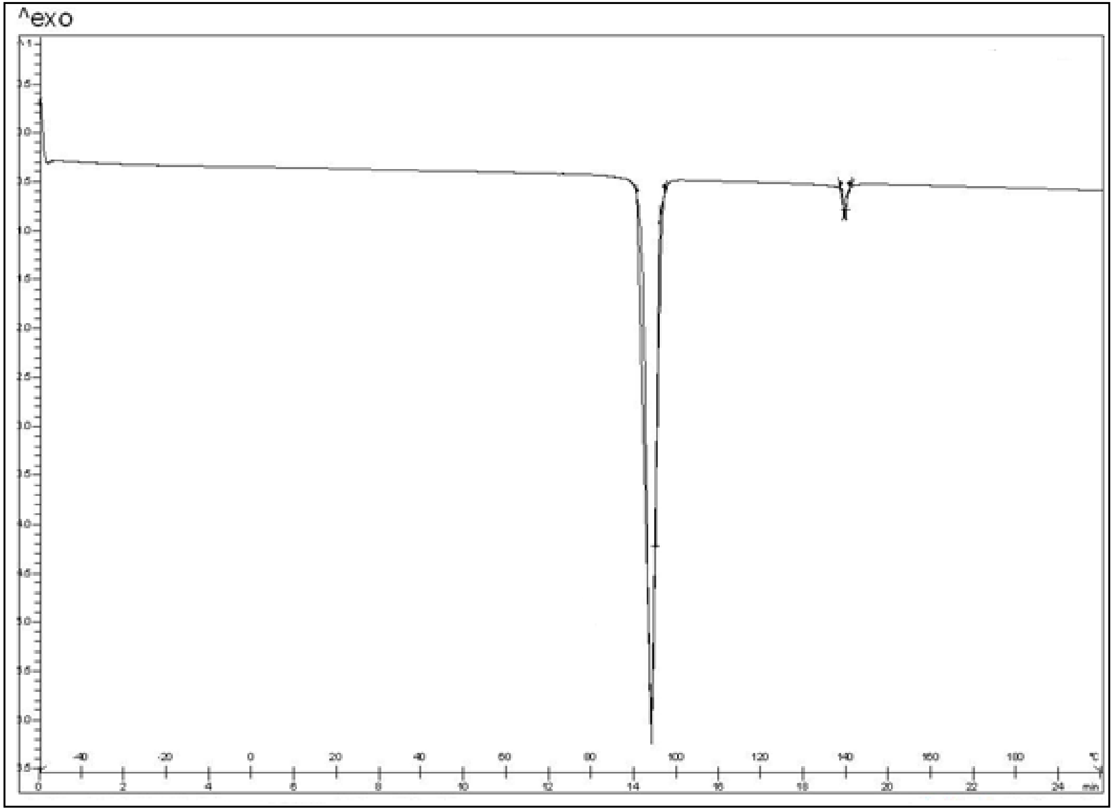


Figure 3.4 (c): DSC Thermogram of C5 homologue of series II

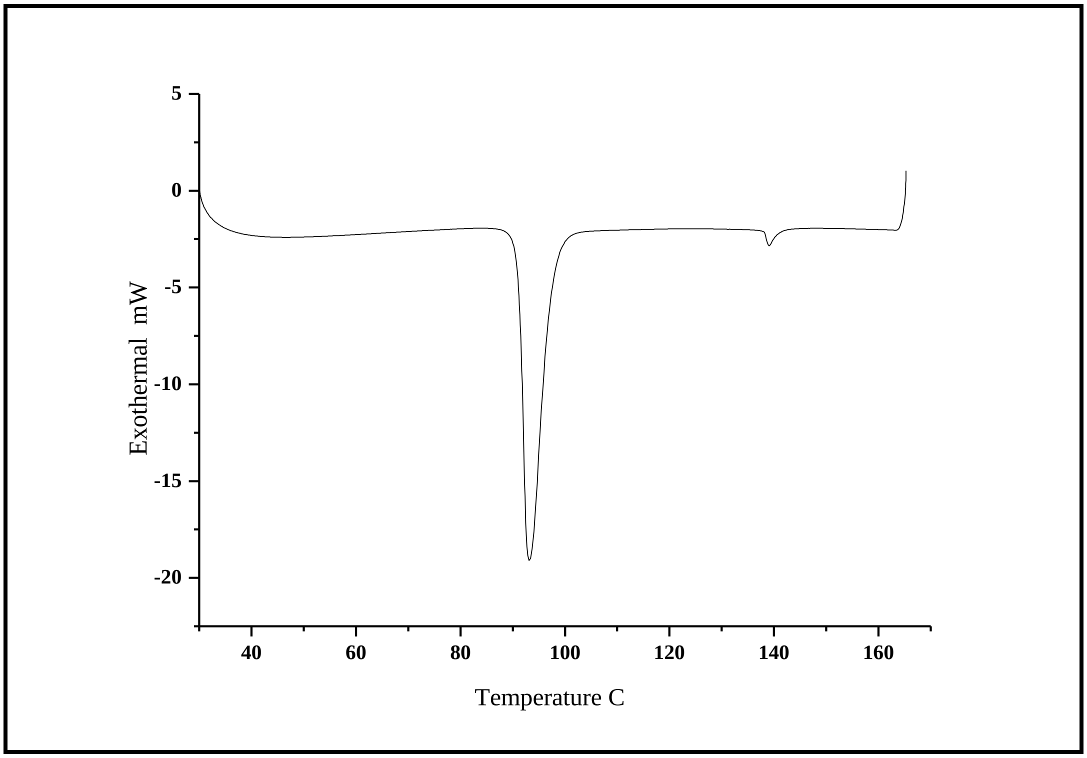


Figure 3.4 (d): DSC Thermogram of C6 homologue of series II

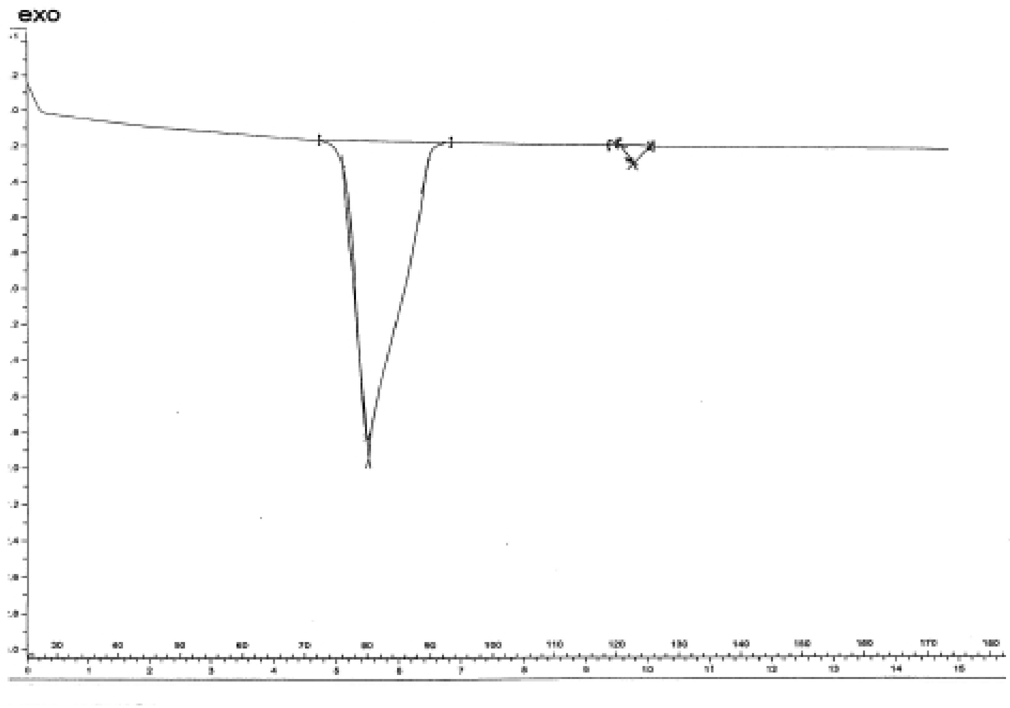


Figure 3.4 (e): DSC Thermogram of C10 homologue of series III

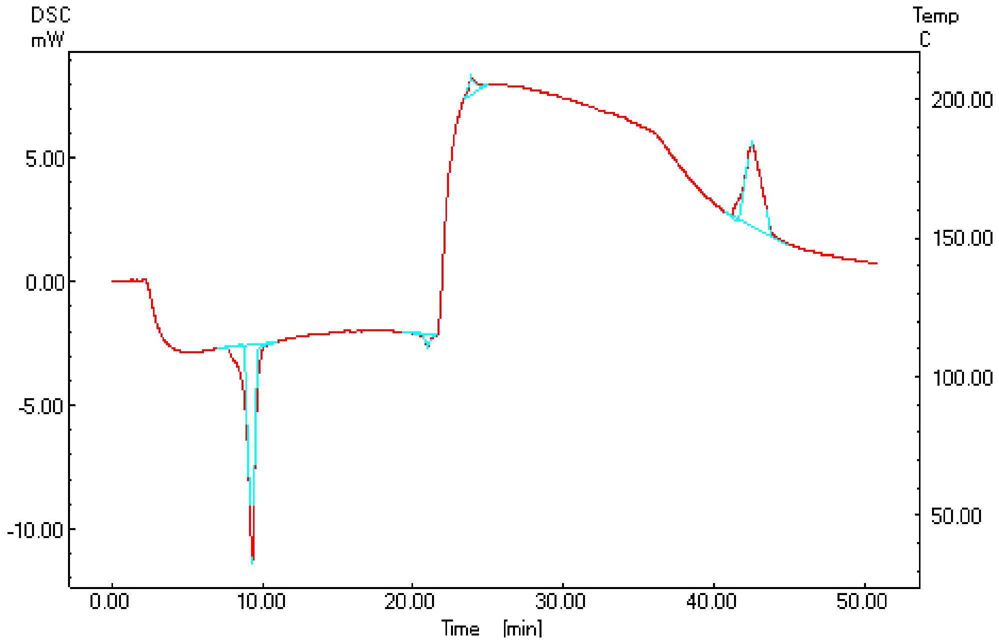


Figure 3.4 (f): DSC Thermogram of C8 homologue of series IV

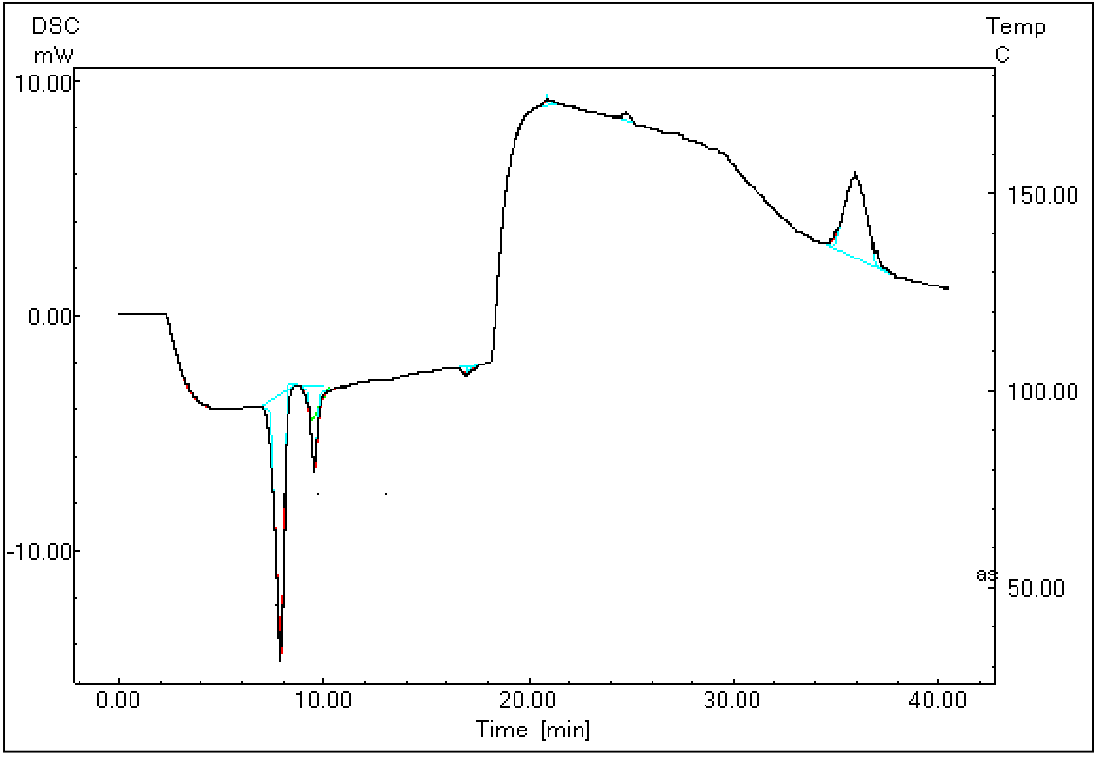


Figure 3.4 (g): DSC Thermogram of C16 homologue of series IV

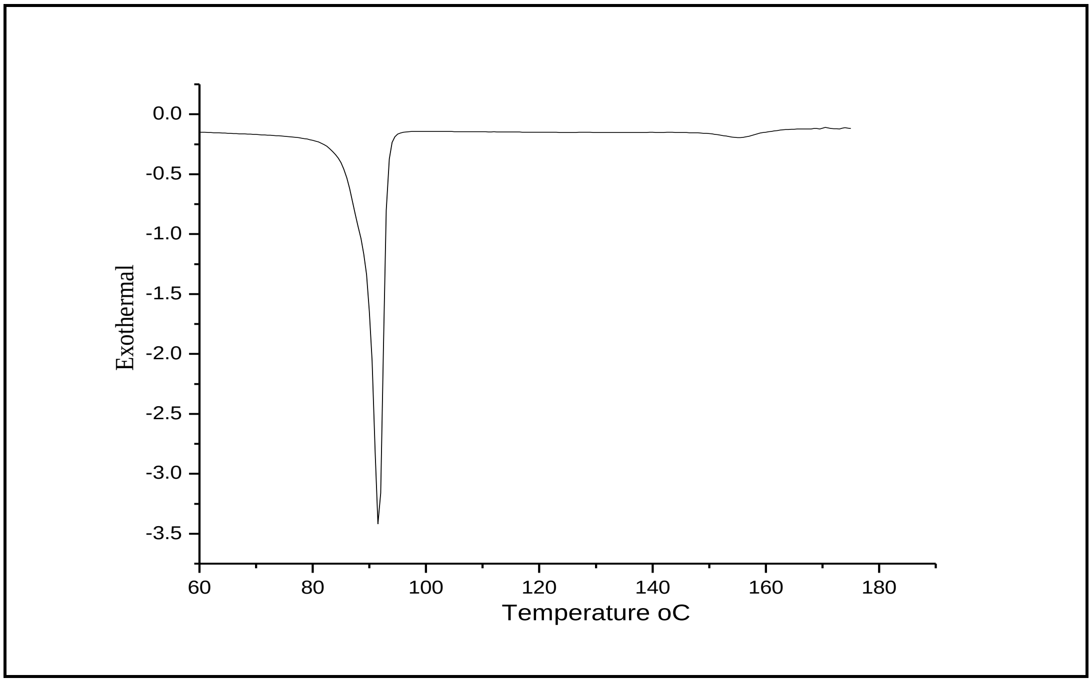


Figure 3.4 (h): DSC Thermogram of C12 homologue of series V

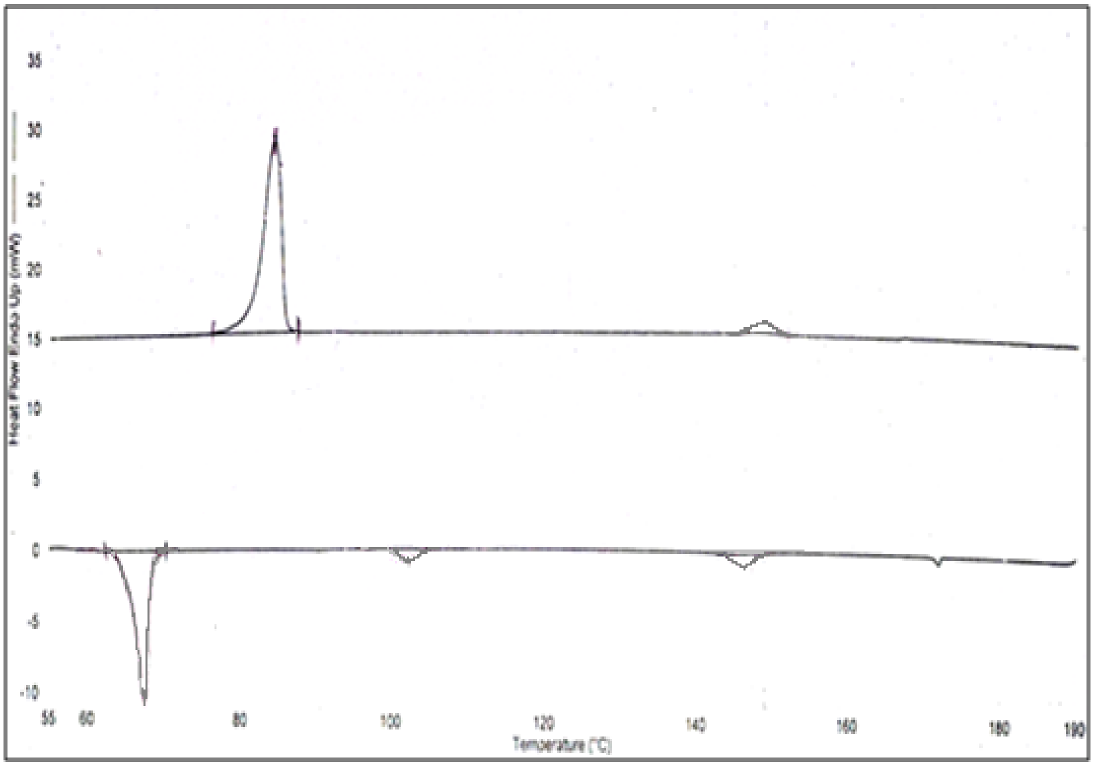


Figure 3.4 (i): DSC Thermogram of C14 homologue of series V

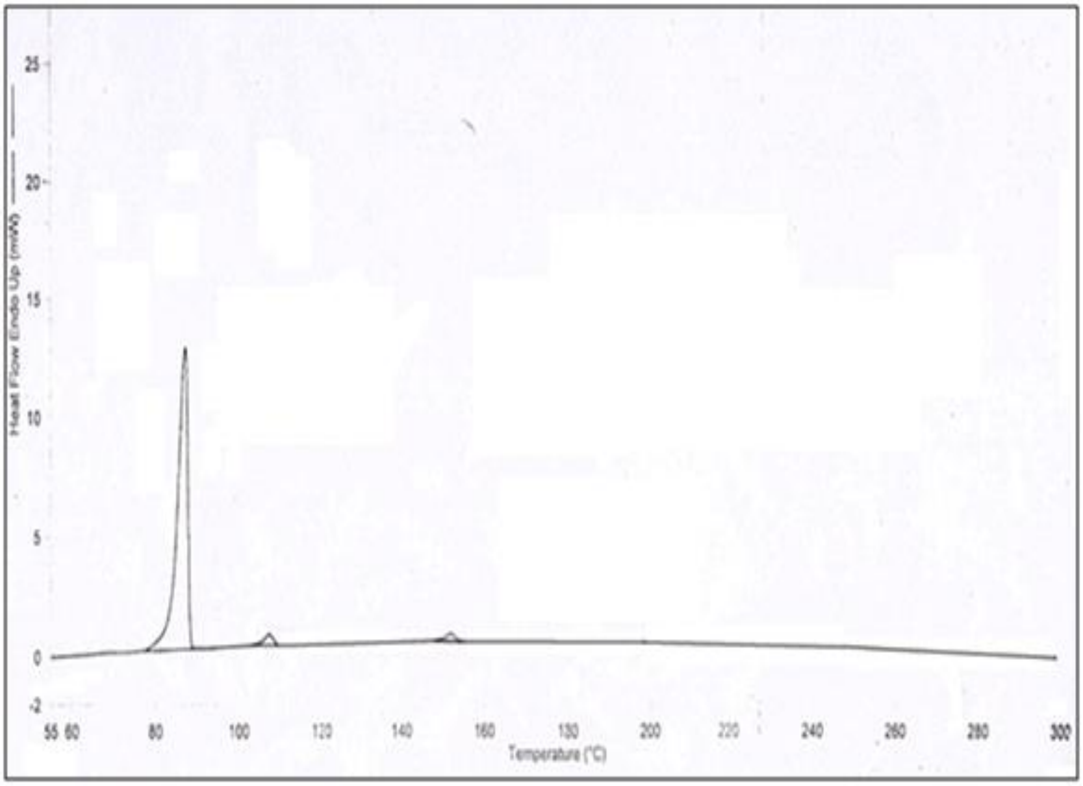


Figure 3.4 (j): DSC Thermogram of C16 homologue of series V

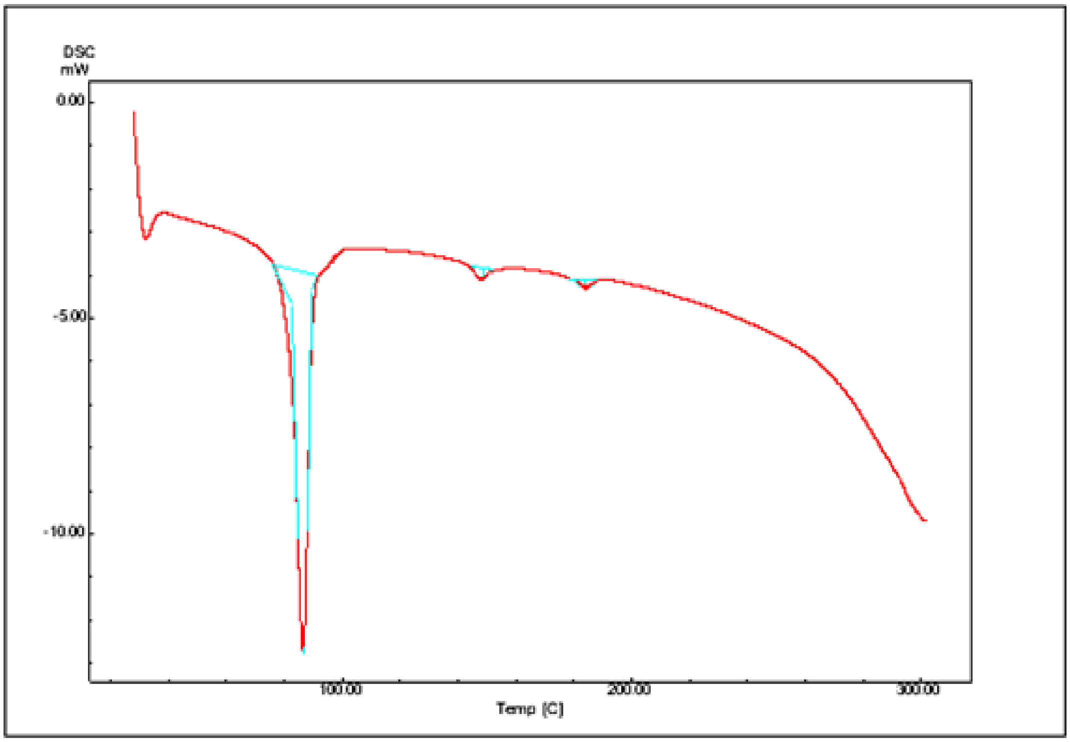


Figure 3.4 (k): DSC Thermogram of C16 homologue of series VI

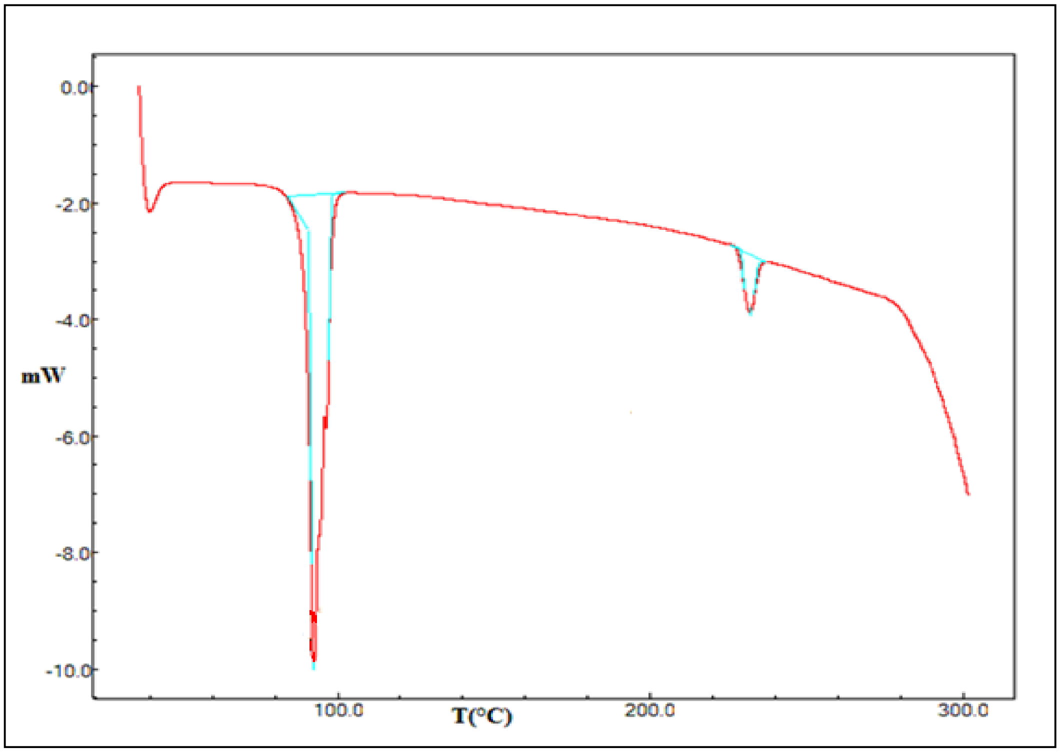


Figure 3.4 (l): DSC Thermogram of C16 homologue of series VII

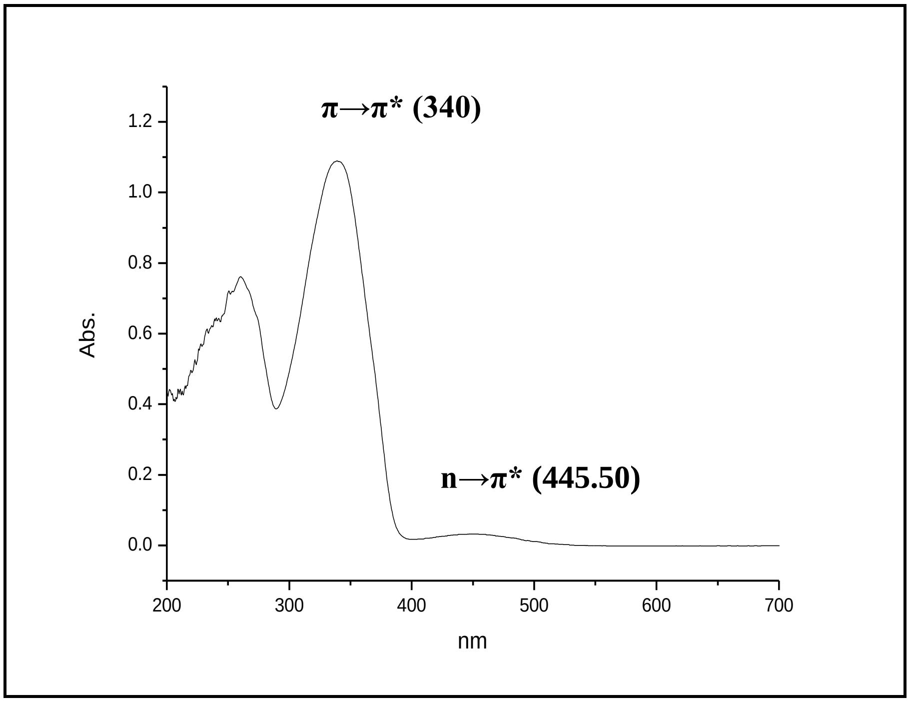


Figure 3.5 (a): UV Spectra of C8 homologue of series I

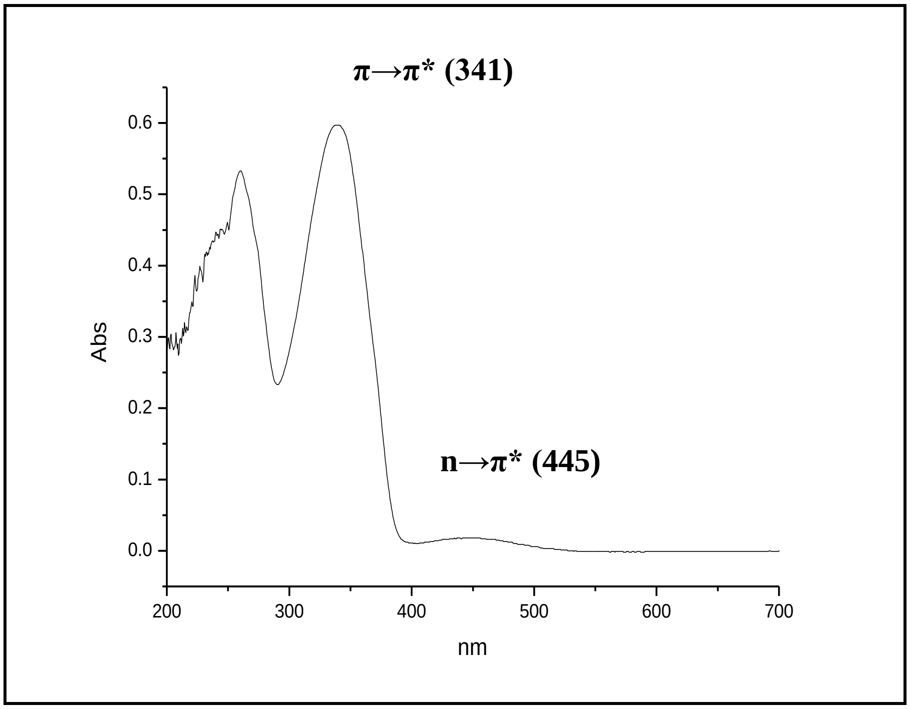


Figure 3.5 (b): UV Spectra of C10 homologue of series I

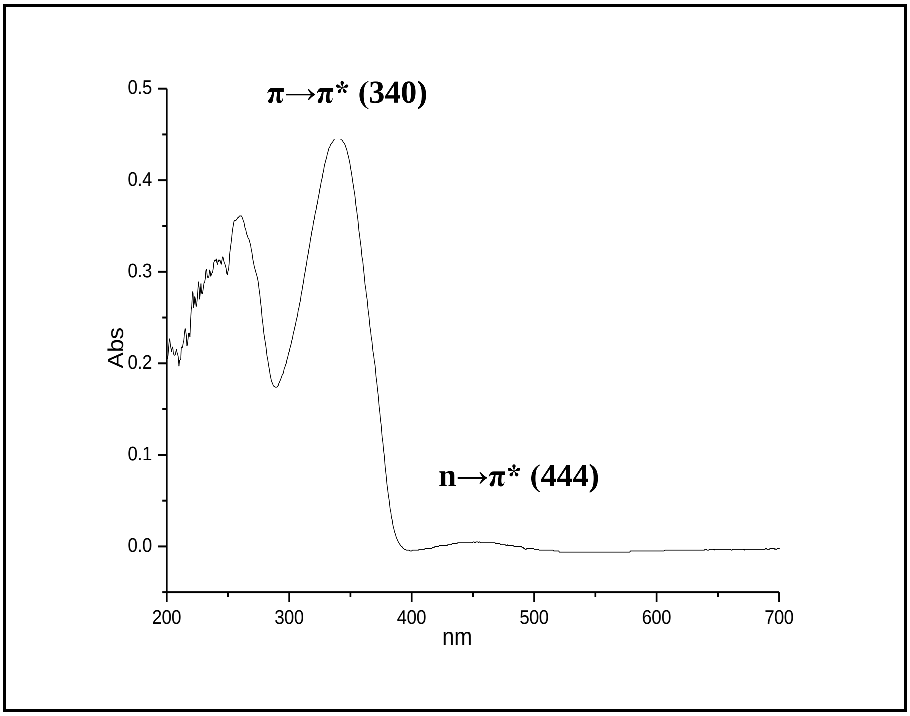


Figure 3.5 (c): UV Spectra of C4 homologue of series II

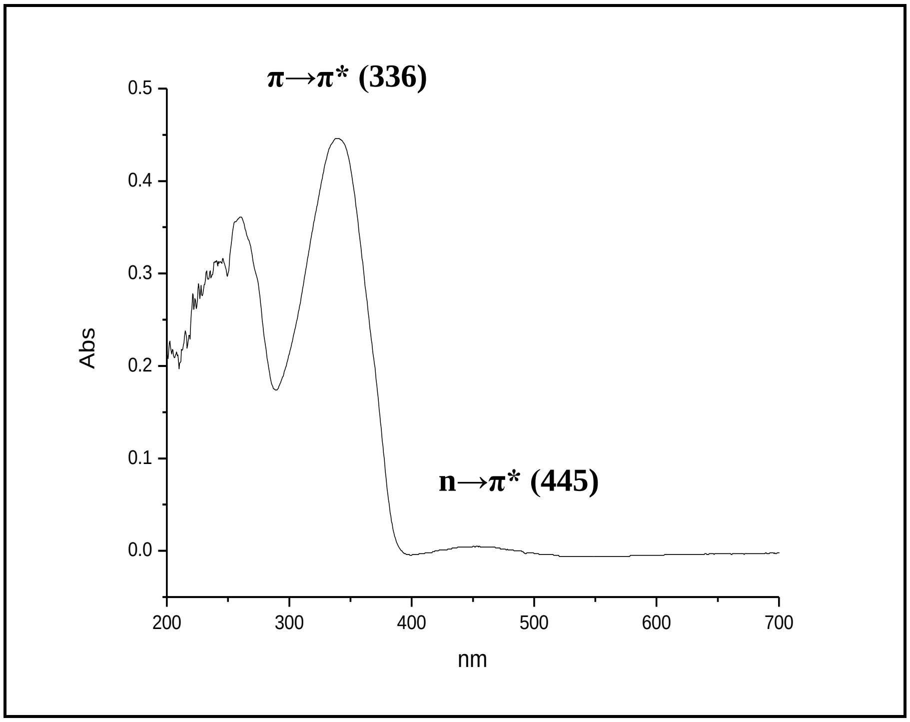


Figure 3.5 (d): UV Spectra of C8 homologue of series II

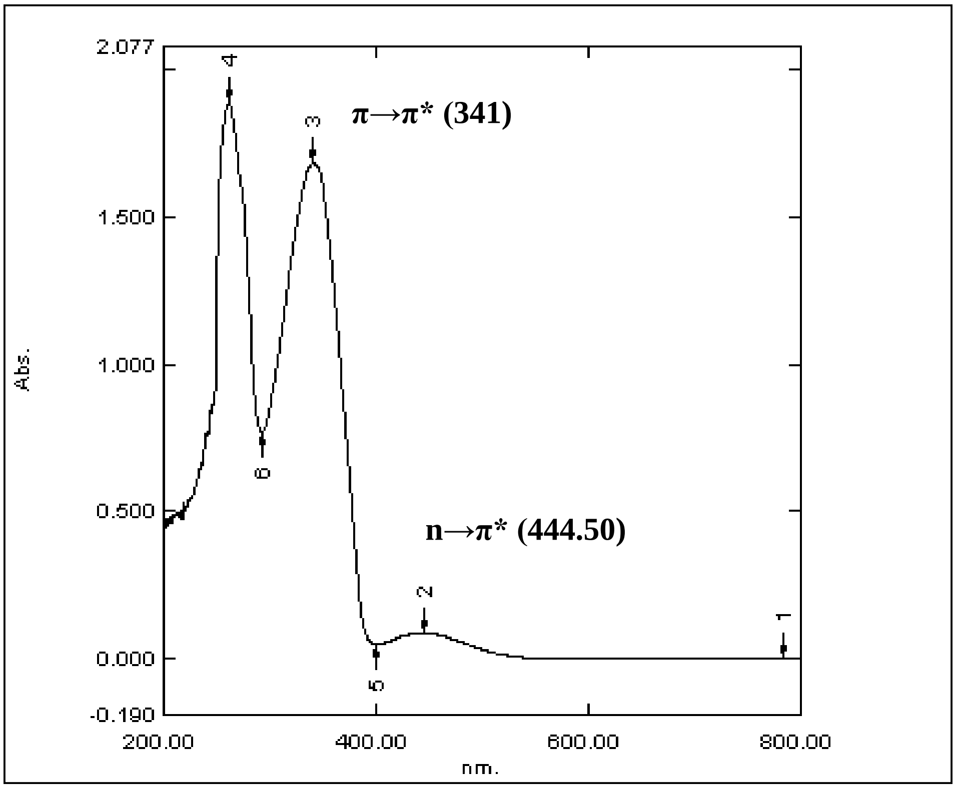


Figure 3.5 (e): UV Spectra of C7 homologue of series III

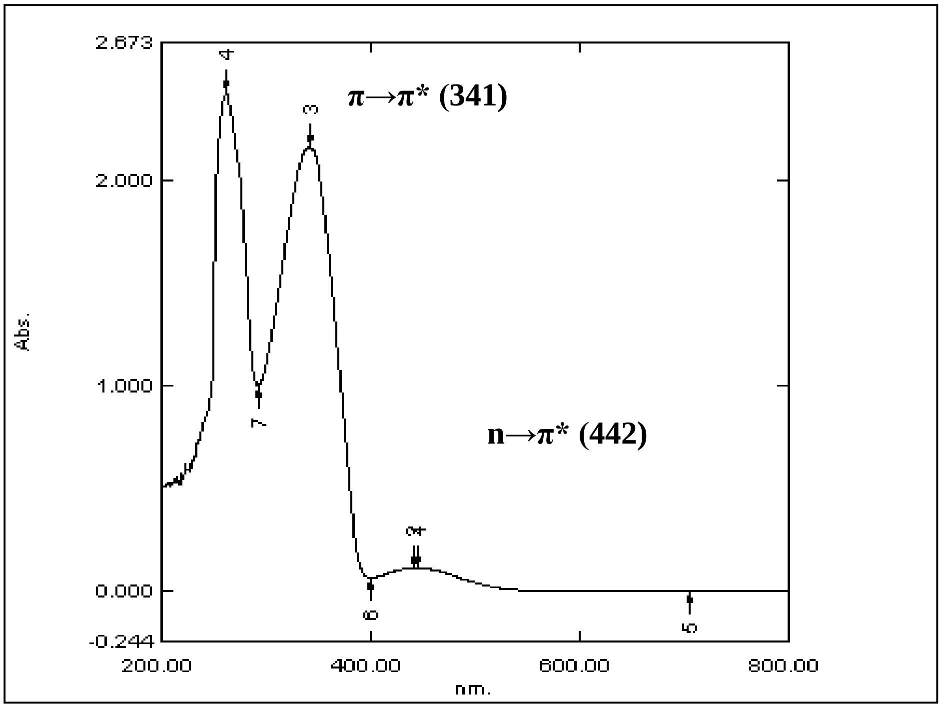


Figure 3.5 (f): UV Spectra of C12 homologue of series III

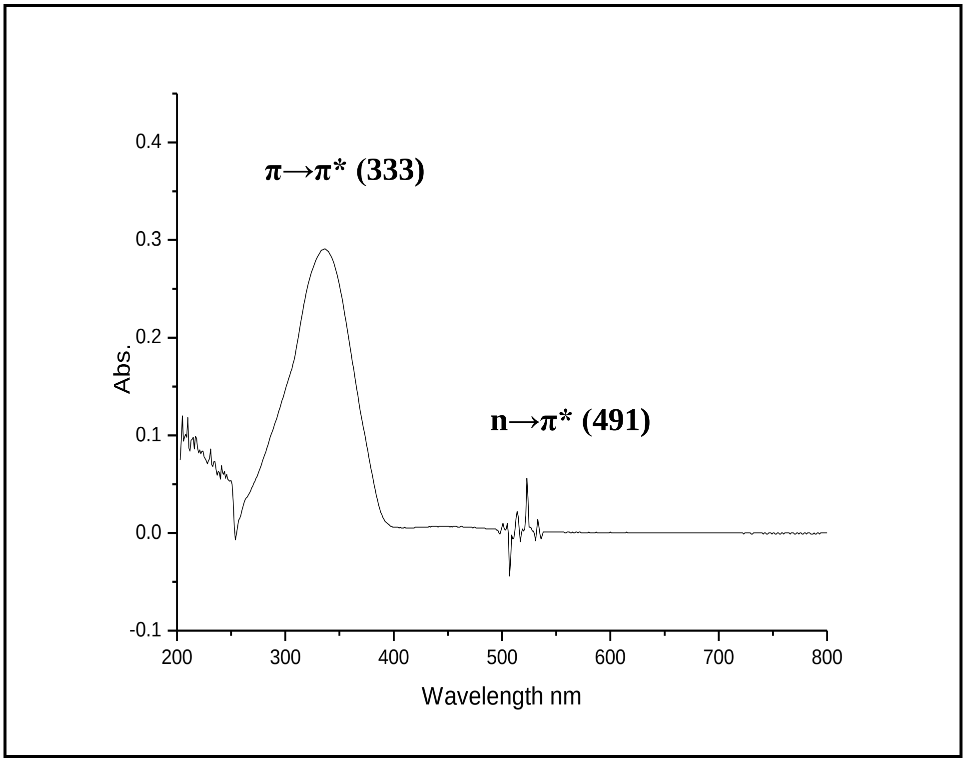


Figure 3.5 (g): UV Spectra of C2 homologue of series IV

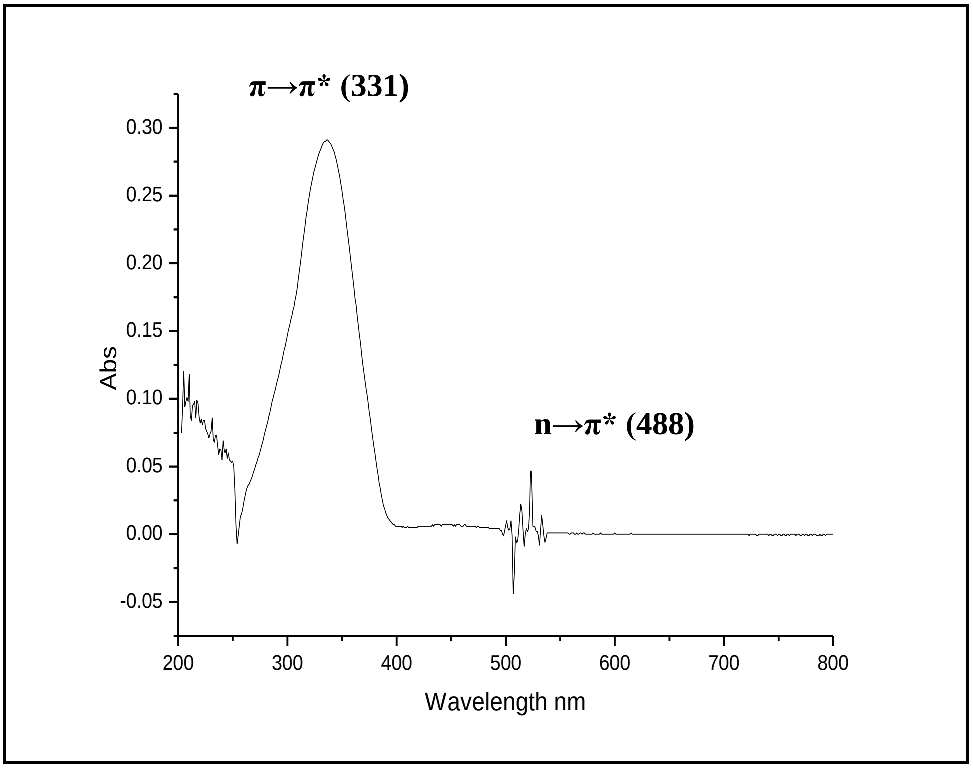


Figure 3.5 (h): UV Spectra of C8 homologue of series IV

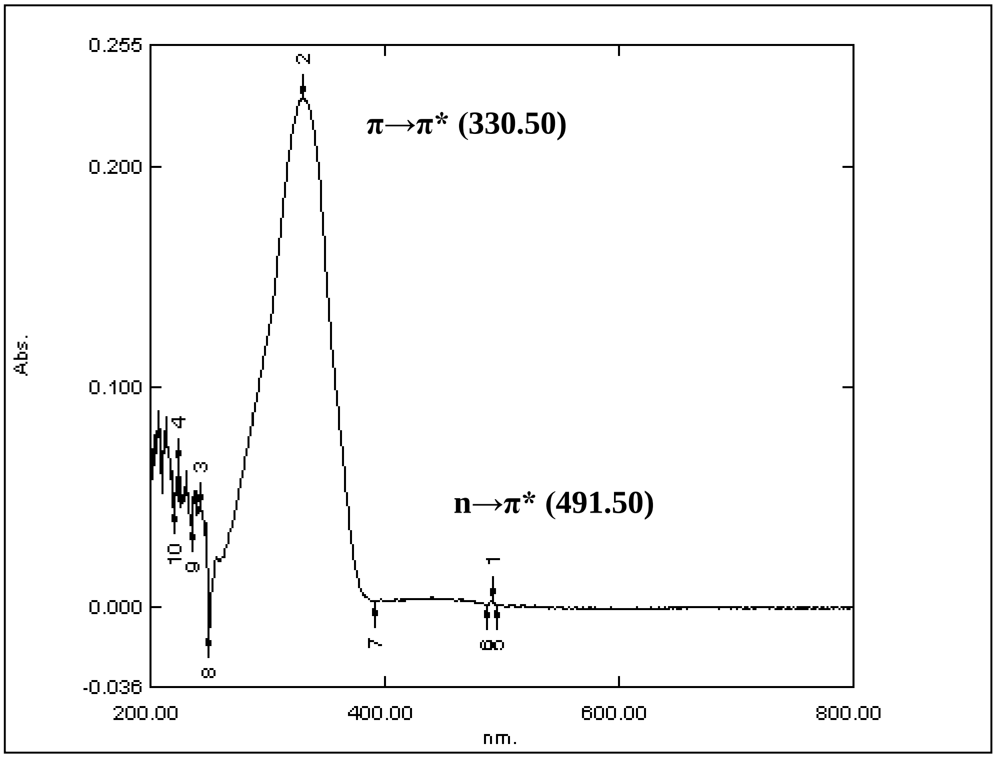


Figure 3.5 (i): UV Spectra of C4 homologue of series V

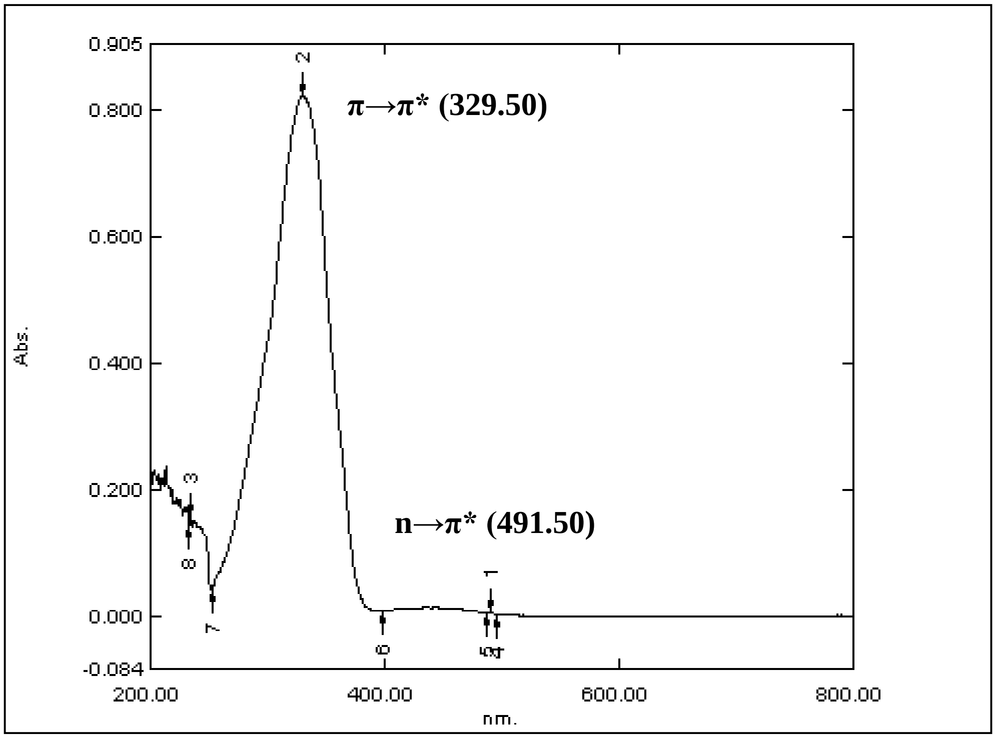


Figure 3.5 (j): UV Spectra of C6 homologue of series V

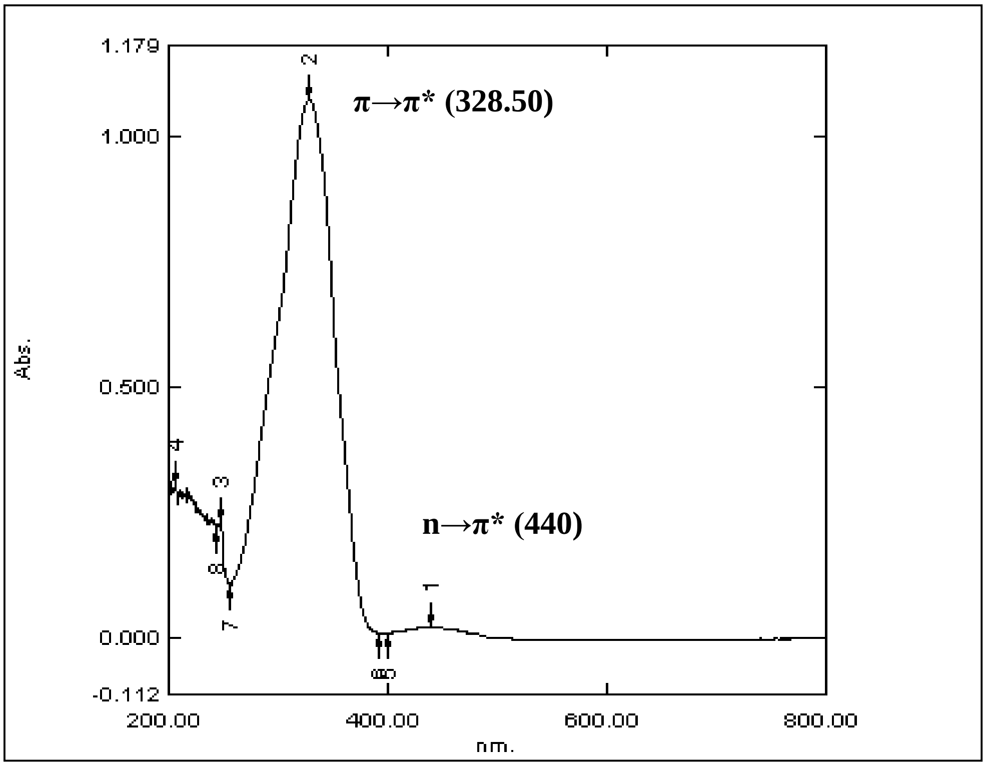


Figure 3.5 (k): UV Spectra of C6 homologue of series VI

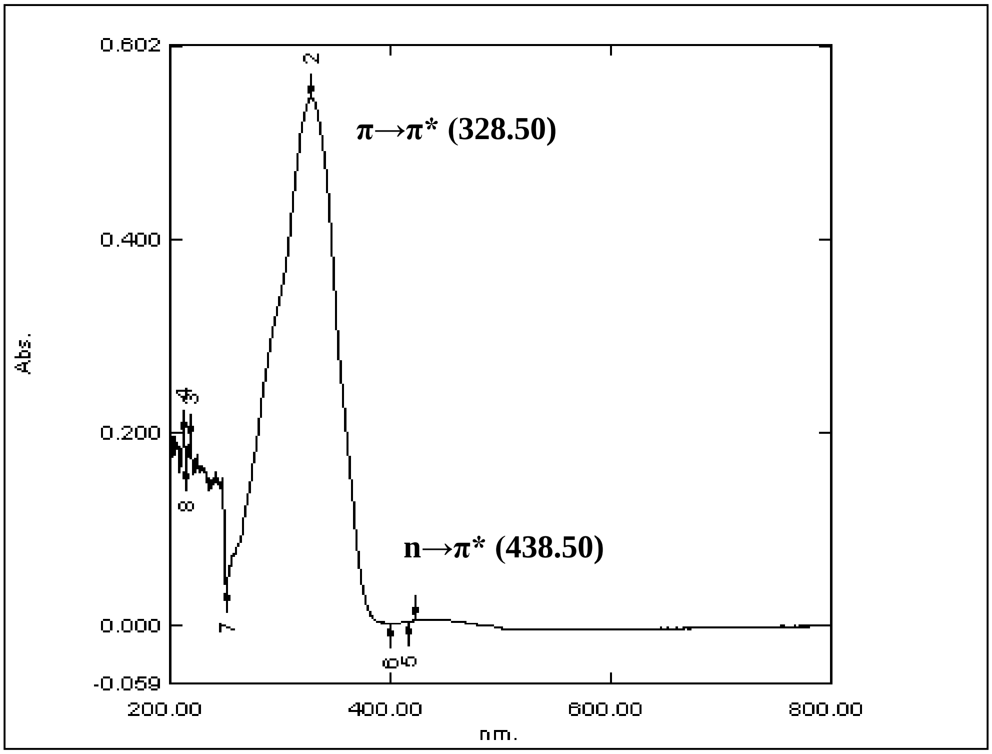


Figure 3.5 (l): UV Spectra of C16 homologue of series VI

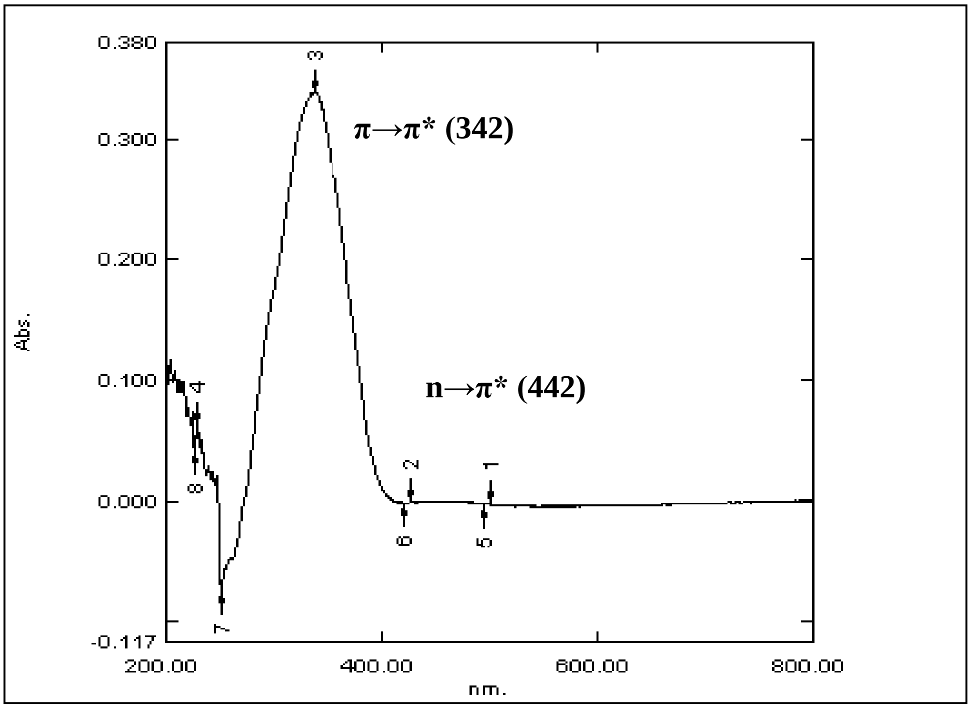


Figure 3.5 (m): UV Spectra of C12 homologue of series VII

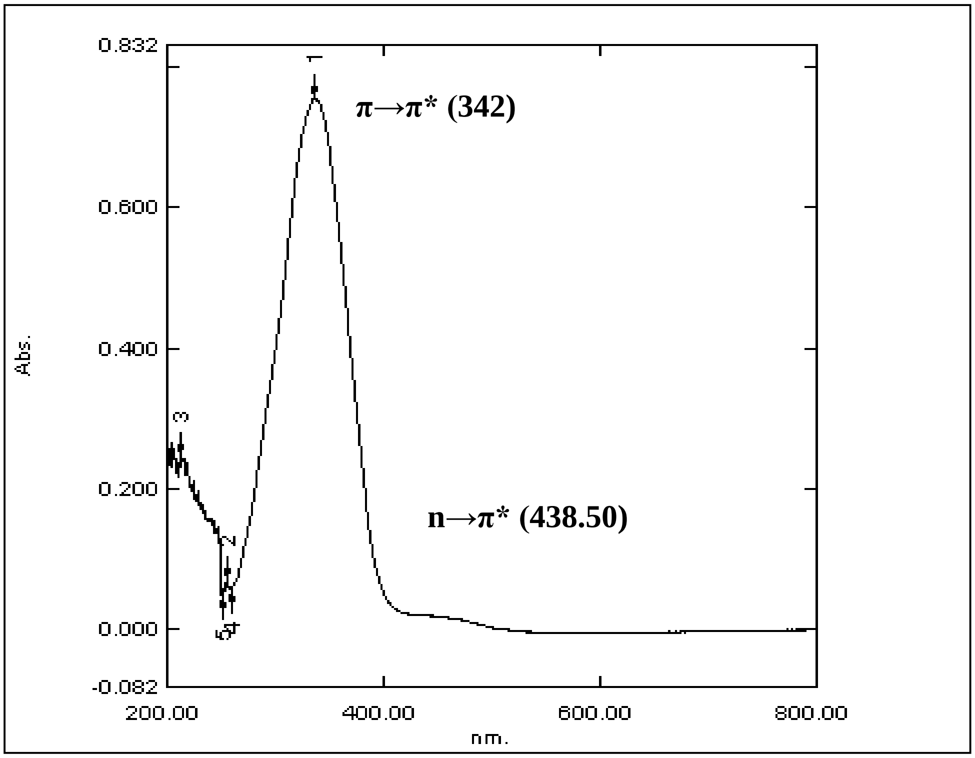
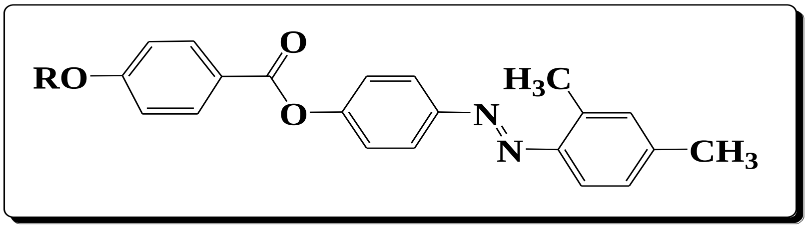


Figure 3.5 (n): UV Spectra of C16 homologue of series VII

3.3 Results and Discussion

3.3.1 Series I: 4-(4’-*n*-alkyloxybenzoyloxy)-phenylazo-2”, 4”-dimethylbenzenes

General molecular structure of the series I: 4-(4’-*n*-alkyloxybenzoyloxy)-phenylazo-2”, 4”-dimethylbenzenes



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

All the twelve homologues of series I are mesogens (Table 3.1, Figure 3.6); the nematic phase commences from the very first derivative and remains upto the tetradecyl derivative, whereas the smectic C phase is observed only in the hexadecyl derivative. Figure 3.6 shows the plot of transition temperatures against number of carbon atoms in the n-alkoxy chain; it indicates that Cr – M transitions show overall falling tendency from the methyl to octyl derivative and then a slight rising tendency at the 10th homologue and then the curve shows falling tendency upto hexadecyl derivative. The N – I curve shows overall falling tendency with a jump at the C8 derivative as the series is ascended. The nematic phase of the series shows marble/schlieren texture whereas the smectic phase shows schlieren texture of the smectic C variety. No odd-even effect is observed in N – I transition temperature curve.

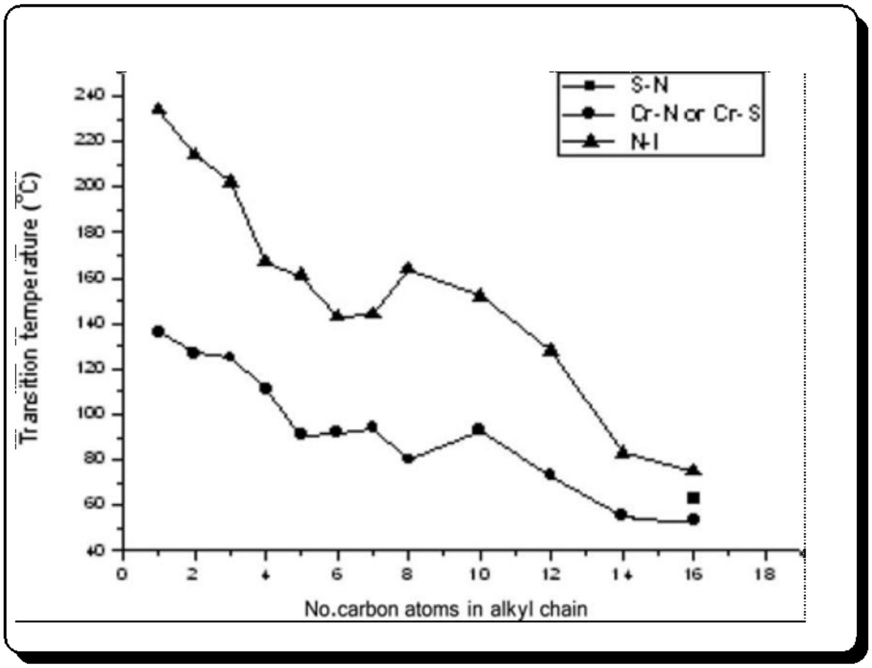


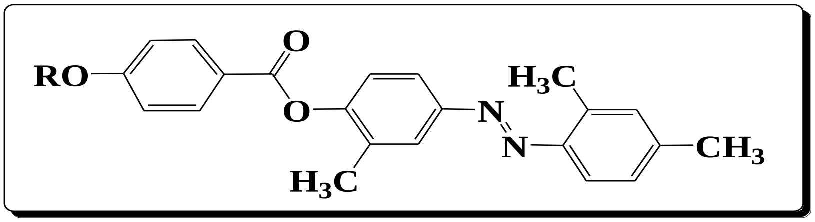
Figure 3.6: 4-(4’-*n*-alkyloxybenzoyloxy)-phenylazo-2”, 4”-dimethylbenzenes (Series I)

Table 3.1: Transition Temperatures: Series I: 4-(4’-*n*-alkyloxybenzoyloxy)-phenylazo-2”, 4”-dimethylbenzenes

R = *n*-Alkyl group	**Transition Temperature ºC**		
	Smectic C	**Nematic**	**Isotropic**
Methyl	-	136	234
Ethyl	-	127	214
Propyl	-	125	202
Butyl	-	111	167
Pentyl	-	91	161
Hexyl	-	92	143
Heptyl	-	94	144
Octyl	-	80	164
Decyl	-	93	152
Dodecyl	-	73	128
Tetradecyl	-	55	83
Hexadecyl	54	62	75

3.3.2 Series II: 4-(4’-*n*-alkyloxybenzoyloxy)-3methylphenylazo-2”, 4”-dimethylbenzenes

General molecular structure of the series II: 4-(4’-*n*-alkyloxybenzoyloxy)-3methylphenylazo-2”, 4”-dimethylbenzenes



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

All the twelve homologues of series II are mesogens (Table 3.5, Figure 3.7); the nematic phase commences from the very first derivative and remains upto the last hexadecyl derivative. Smectic phase is absent in the entire series; thus, all homologues are nematogens. Figure 3.7, shows plot of transition temperatures against number of carbon atoms in the n-alkoxy chain; it indicates that the N I curve shows an odd–even effect in the initial members upto C6 derivative, with even members show upper curve and odd members show lower curve and then after the N – I curve merge with each other & show a steep fall at C7 homologue and then overall steady fall upto C12 homologue afterwards the N – I curve shows slight rising tendency upto C16 homologue studied. The Cr – M transitions show initially falling tendency upto C3 derivative and then rising tendency upto C6 derivative, then the Cr – M curve shows overall falling tendency with slight increase from C12 to the last C16 derivative studied. The nematic phase of the series shows the same Marble/Schlieren texture.

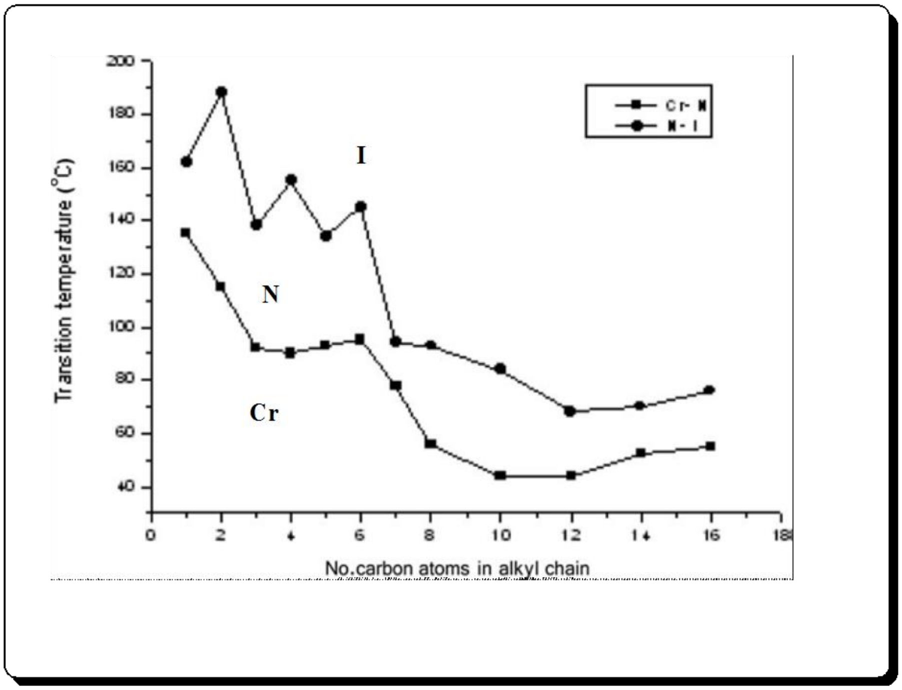


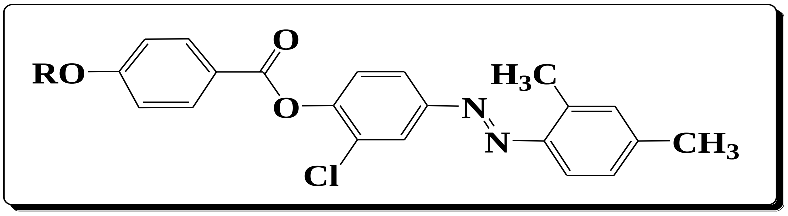
Figure 3.7: 4-(4’-*n*-alkyloxybenzoyloxy)-3-phenylazo-2”, 4”-dimethylbenzenes (Series II)

Table 3.5: Transition temperatures Series II: 4-(4’-*n*-alkyloxybenzoyloxy)-3-methylphenylazo-2”, 4”-dimethylbenzenes

R = *n*-Alkyl group	**Transition Temperature ºC**	
	Nematic	**Isotropic**
Methyl	135	162
Ethyl	115	188
Propyl	92	138
Butyl	90	155
Pentyl	93	134
Hexyl	95	145
Heptyl	78	94
Octyl	56	93
Decyl	44	84
Dodecyl	45	68
Tetradecyl	52	70
Hexadecyl	55	76

3.3.3 Series III: 4-(4’-*n*-alkyloxybenzoyloxy)-3-chlorophenylazo-2”, 4”-dimethylbenzenes

General molecular structure of the series III: 4-(4’-*n*-alkyloxybenzoyloxy)-3-chlorophenylazo-2”, 4”-dimethylbenzenes



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

All the 12 homologues of the series are mesogens (Table 3.9, Figure 3.8); the nematic phase commences from the very first derivative and remains up to the last hexadecyl derivative synthesized. Figure 3.8 shows the plot of transition temperatures against number of carbon atoms in the n-alkoxy chain; it indicates that Cr-M transitions show overall falling tendency with a jump at the C8 derivative. The N-I curve shows overall falling tendency with a rising tendency at C8 and C10 homologues as the series is ascended. The nematic phase of the series shows marble texture. No odd-even effect is observed in N – I T.T curve.

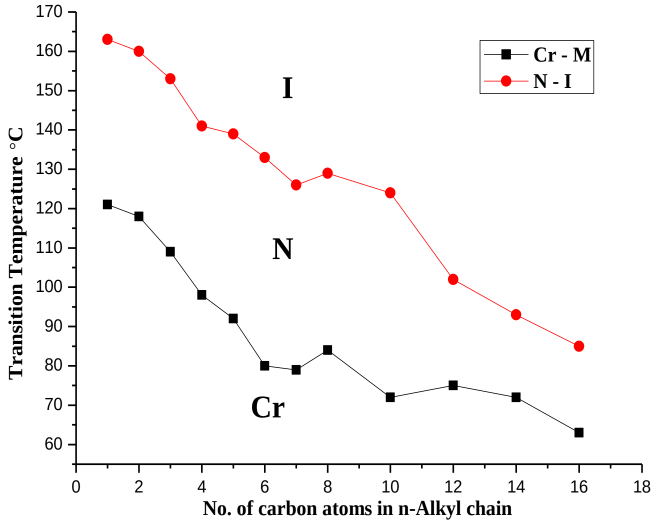


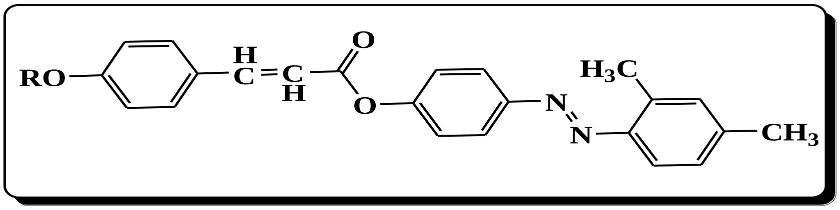
Figure 3.8: 4-(4’-*n*-alkyloxybenzoyloxy)-3-chlorophenylazo-2”, 4”-dimethylbenzenes (Series III)

Table 3.9: Transition temperatures Series III: 4-(4'-*n*-alkyloxybenzoyloxy)-3-chlorophenylazo-2", 4"-dimethylbenzenes

R = *n*-Alkyl group	Transition Temperature ºC	
	Nematic	**Isotropic**
Methyl	121	163
Ethyl	118	160
Propyl	109	153
Butyl	98	141
Pentyl	92	139
Hexyl	80	133
Heptyl	79	126
Octyl	84	129
Decyl	72	124
Dodecyl	75	102
Tetradecyl	72	93
Hexadecyl	63	85

3.3.4 Series IV: *trans*-4-(4’-*n*-alkyloxycinnamoyloxy)-phenylazo-2”, 4”-dimethylbenzenes

General molecular structure of the series IV: *trans*-4-(4’-*n*-alkyloxycinnamoyloxy)-phenylazo-2”, 4”-dimethylbenzenes



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

All the twelve homologues of series IV are mesogens (Table 3.13, Figure 3.9); the nematic phase commences from the very first derivative and remains upto the octyl derivative, whereas the smectic A phase is observed in monotropic form in decyl derivative and then continues as an enantiotropic phase till hexadecyl derivative synthesized. Figure 3.9 shows the plot of transition temperatures against number of carbon atoms in the n-alkoxy chain; it indicates that Cr – M transitions show overall falling tendency from the methyl to butyl derivative and then a slight rising tendency from the butyl to decyl homologue studied. The S – N transition curve shows rising tendency from C12 to C16 homologue and merge with N –S curve at C10 homologue by an extrapolation. The N – I curve shows odd-even effect for the first 7 derivatives and then overall falling tendency with a jump at the C8 derivative as the series is ascended. The nematic phase of the series shows marble texture whereas the smectic phase shows schlieren texture of the smectic A variety.

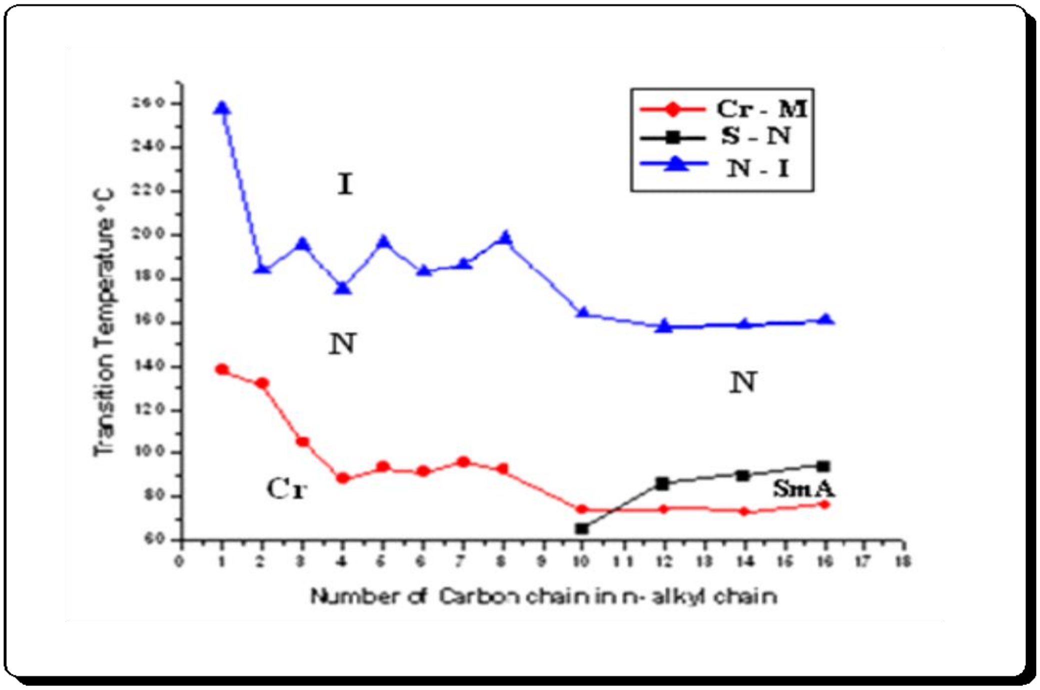


Figure 3.9: ***trans*-4-(4’-*n*-alkyloxycinnamoyloxy)-phenylazo-2”, 4”-dimethylbenzenes (Series IV)**

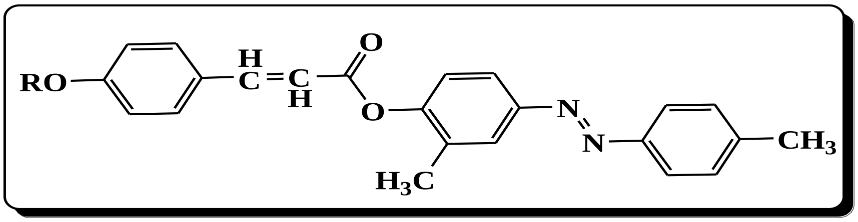
Table 3.13: Transition temperatures Series IV: 4-(4'-*n*-alkyloxycinnamoyloxy)-phenylazo-2", 4"-dimethylbenzenes

R = *n*-Alkyl group	**Transition Temperature ºC**		
	Smectic A	**Nematic**	**Isotropic**
Methyl	-	138	258
Ethyl	-	132	184
Propyl	-	105	196
Butyl	-	88	175
Pentyl	-	93	197
Hexyl	-	91	183
Heptyl	-	96	187
Octyl	-	92	199
Decyl	(65) *	74	164
Dodecyl	74	86	158
Tetradecyl	73	89	159
Hexadecyl	76	94	161

()* Value in the parentheses indicates monotropic transition.

3.3.5 Series V: *trans*-4-(4'-*n*-alkyloxycinnamoyloxy)-3-methylphenylazo-4"-methylbenzenes

General molecular structure of the series V: *Trans*-4-(4'-*n*-alkyloxycinnamoyloxy)-3-methylphenylazo-4"-methylbenzenes



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

All the twelve homologues of series II are mesogens (Table 3.17, Figure 3.10); the nematic phase commences from the very first derivative and remains upto the tetradecyl derivative. Smectic phase C commences in the form of monotropic phase at C14 derivative and then in hexadecyl derivative it is observed in enantiotropic form in the series. Figure 3.10, shows plot of transition temperatures against number of carbon atoms in the n-alkoxy chain; it indicates that the Cr – M curve shows overall falling tendency upto C16 homologue as the series is ascended. The Cr-Sm transition curve shows rising tendency and Cr - N curve shows overall falling tendency with slight increase from sixth derivative. The N – S transition curve at C14 derivative merge with S – N curve at C16 derivative. The N – I transition curve shows overall falling tendency upto C16 derivative as the series is ascended. The nematic phase of the series shows the same Marble texture as that of the series I and Smectic Mesophase of the series II shows Schileren texture of Smectic C variety.

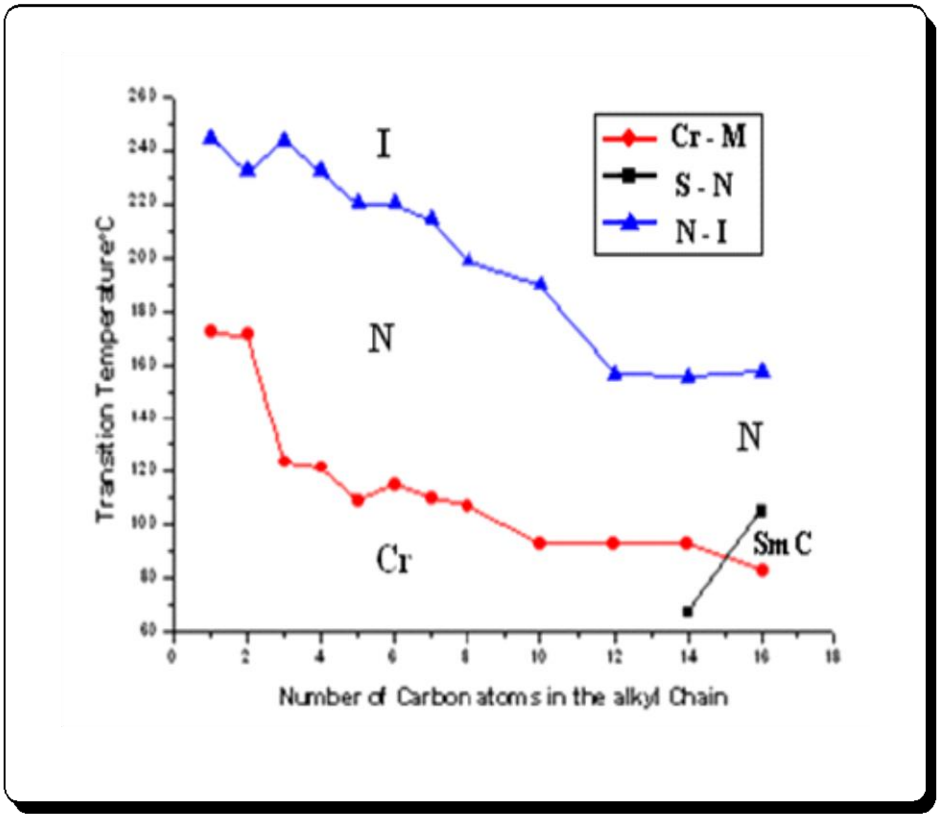


Figure 3.10: *trans*-4-(4'-*n*-alkyloxycinnamoyloxy)-3-methylphenylazo-4"-methylbenzenes

(Series V)

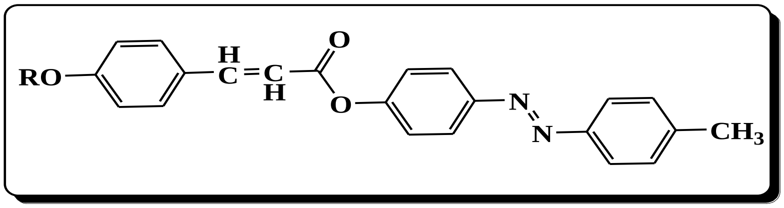
Table 3.17: Transition temperatures Series V: 4-(4'-*n*-alkyloxycinnamoyloxy)-3-methylphenylazo-4"-methylbenzenes

R = n-Alkyl group	Transition Temperature °C		
	Smectic C	Nematic	Isotropic
Methyl	-	172	244
Ethyl	-	171	232
Propyl	-	123	243
Butyl	-	121	232
Pentyl	-	109	220
Hexyl	-	115	220
Heptyl	-	110	214
Octyl	-	107	199
Decyl	-	93	190
Dodecyl	-	93	157
Tetradecyl	(67)*	93	156
Hexadecyl	82	105	158

()* Value in the parentheses indicates monotropic transition.

3.3.6 Series VI: *trans*-4-(4'-*n*-alkoxycinnamoyloxy)-phenylazo-4''-methylbenzenes

General molecular structure of the series VI: *trans*-4-(4'-*n*-alkoxycinnamoyloxy)-phenylazo-4"-methylbenzenes



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

All the homologues of the series VI are mesogens; (Table: 3.21, Figure: 3.11) mesomorphism commences from the first homologue of the series in the form of nematic phase and continues upto eight and continues upto the C8 homologue, smectic mesophase (SmC) appears from the C10 homologue of the series and continues upto the last C16 homologue synthesized. N – I curve shows overall falling tendency with rises at C6, C7 and C14 homologue as the series is ascended. Cr – M curve show overall falling tendency with a steep fall between C3 to C5 homologue. S – N curve shows rising tendency as the series is ascended from C10 to C16 homologue. The nematic phase of the series shows marble/schlieren texture whereas the smectic phase shows schlieren texture of the smectic C variety observed.

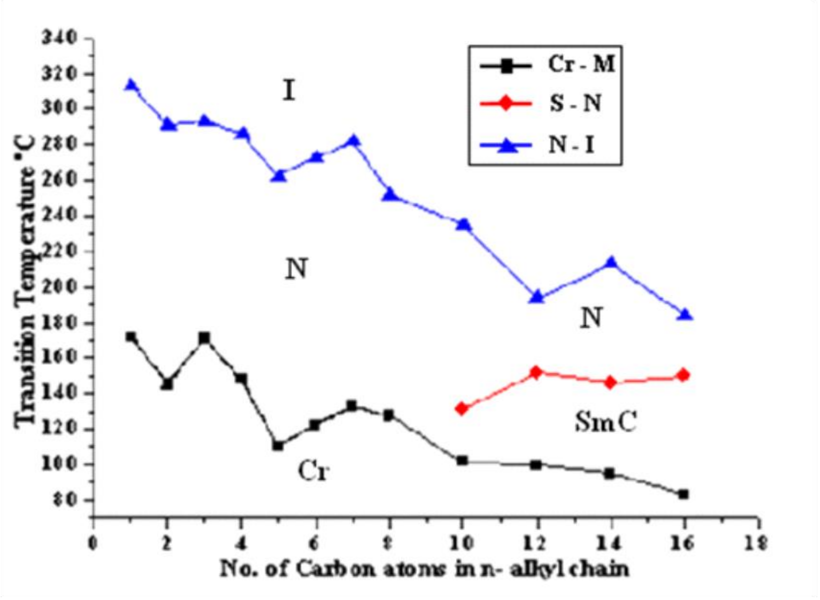


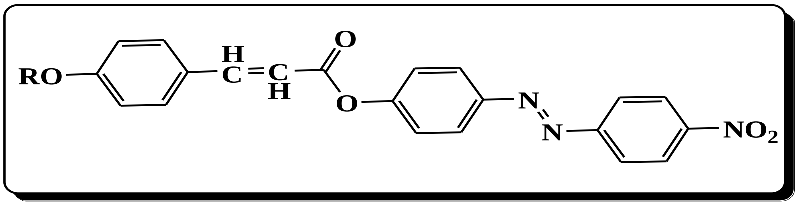
Figure 3.11: ***trans*** **-4-(4'-*n*-alkoxycinnamoyloxy)-phenylazo-4''-methylbenzenes (Series VI)**

Table 3.21: Transition temperatures Series VI: 4-(4'-*n*-alkyloxycinnamoyloxy)-phenylazo-4"-methylbenzenes

R = *n*-Alkyl group	Transition Temperature ºC		
	Smectic C	**Nematic**	**Isotropic**
Methyl	**-**	172	313
Ethyl	**-**	145	291
Propyl	**-**	171	293
Butyl	**-**	148	286
Pentyl	**-**	110	262
Hexyl	**-**	122	273
Heptyl	-	133	282
Octyl	-	127	252
Decyl	101	131	235
Dodecyl	100	152	194
Tetradecyl	95	146	213
Hexadecyl	83	150	184

3.3.7 Series VII: *trans*-4-(4'-*n*-alkoxycinnamoyloxy)-phenylazo-4''-nitrobenzenes

General molecular structure of the series VII: *trans*–4–(4'–*n*–alkoxycinnamoyloxy)-phenylazo-4"-nitrobenzenes



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

All the homologues of the series VII are mesogens; (Table: 3.25, Figure: 3.12), synthesized and their mesogenic properties were evaluated. C1 to C6 homologue exhibit nematic mesophase, C7 and C8 exhibit both smectic and nematic mesophases and C10 to C16 exhibit smectic mesophase. The N – I curve shows odd–even effect initial for first six homologues and then rising tendency upto C8 homologue and then exhibits falling tendency. The N – I curve merges with S – I curve at C8 homologue and shows falling tendency upto C16 homologue synthesized. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain (Figure: 3.12) shows that the Cr – M curve shows overall falling tendency with a slight increase at C4 and C6 homologues. The nematic phase of the series shows marble/schlieren texture whereas the smectic phase shows schlieren texture of the smectic C variety.

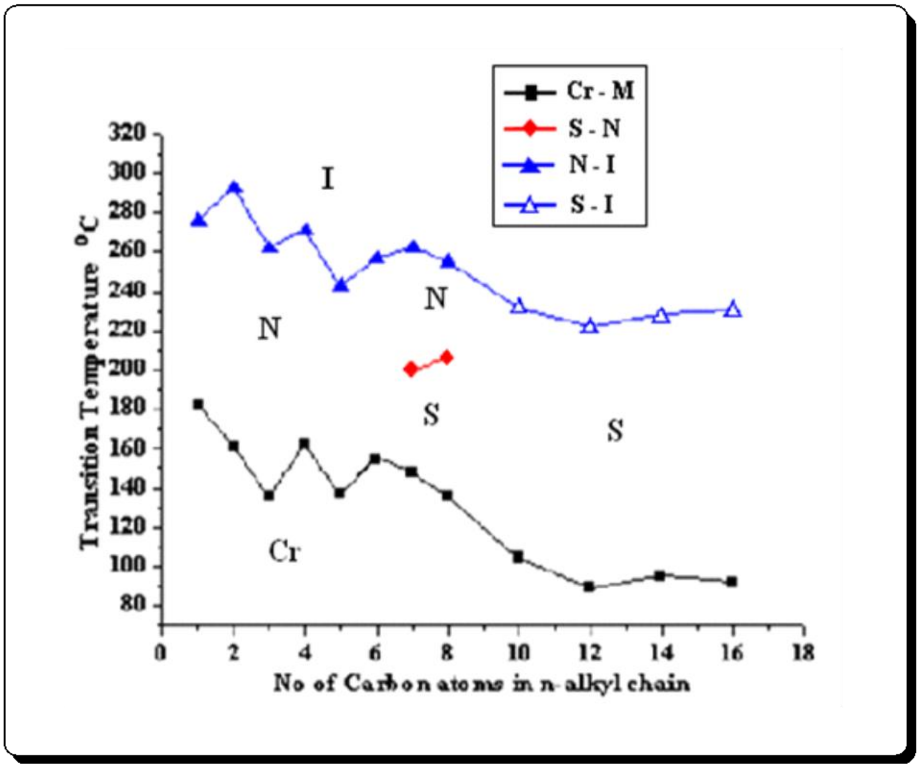


Figure 3.12: ***trans*-4-(4'-*n*-alkoxycinnamoyloxy)-phenylazo-4''-nitrobenzenes (Series VII)**

Table 3.25: Transition temperatures Series VII: **4-(4'-*n*-alkyloxycinnamoyloxy)-phenylazo-4"-nitrobenzenes**

R = *n*-Alkyl group	Transition Temperature ºC		
	Smectic C	**Nematic**	**Isotropic**
Methyl	-	182	276
Ethyl	-	161	293
Propyl	-	135	262
Butyl	-	162	271
Pentyl	-	136	243
Hexyl	-	155	257
Heptyl	147	200	262
Octyl	135	206	255
Decyl	104	-	232
Dodecyl	89	-	222
Tetradecyl	95	-	228
Hexadecyl	92	-	230

The molecular geometry of the homologous series (Figure: 3.13) shows that all the series in comparison are structurally similar, consisting of three aromatic cores, ester and azo central linkages and *n*-alkoxy as one of its terminal groups. In Part I of the chapter all the three series having difference in lateral substituents only viz. –H, $–CH_3$ and –Cl at ortho position of –COO– linkages on central benzene ring. Whereas in part II of the chapter consists of four homologous series composed of rod shaped liquid crystalline molecules consisting of three aromatic cores as benzene, cinnamoyloxy and azo central linkages Series IV and V compared with each other to evaluate the effect of methyl group as lateral substituent at ortho position of azo and ester central linkages respectively. Series IV having methyl group as lateral substituent on terminal benzene ring whereas series V having methyl group as lateral substituent at central benzene ring hence molecules of series IV and V are positional isomers. Series VI and VII differ only in one of their terminal substituent, series VI having methyl group and Series VII having nitro group as terminal substituent to study the effect terminal substituent on mesomorphism.

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 smectic and nematic mesophase [410, 422, 423]. This factor is a direct result of an increase in the thickness of the molecule [441]. The increased dissymmetry resulting from the lateral substituent leads to less effective molecular packing in the crystal lattice, and therefore, lowers the crystal to mesophase transition temperature as shown in Tables 3.1 and 3.5 [423]. Thus, the effect of substitution, which leads to an increase in molecular breadth, is that the long narrow molecules will be forced further apart so reducing the strength of the intermolecular lateral attractions. Both smectic and nematic mesophases depend to a greater or lesser extent on these cohesive forces to maintain the parallel orientation of the molecules. Therefore, substitution leading to an increase in molecular breadth will decrease the smectic and nematic thermal stabilities, which is actually found in the present series I, II and III under comparison [410].

Comparison of average thermal stabilities of all seven series (Table: 3.29) shows that both the N-I/ S-I and S-N average thermal stabilities of series I are higher than series II and III. Series II and III show only nematic mesophase and the average N-I thermal stabilities of both the series are lower than that of series I. This may be due to the presence of lateral substituent in central benzene ring in series II and III (Figure 3.13). The lateral group order for nematic phase can be derived from the comparison of average thermal stabilities of the current series I, II and III is, Nematic order:
Increasing sequence: -H > -Cl > $-CH_3$.which is in agreement with Gray [409].

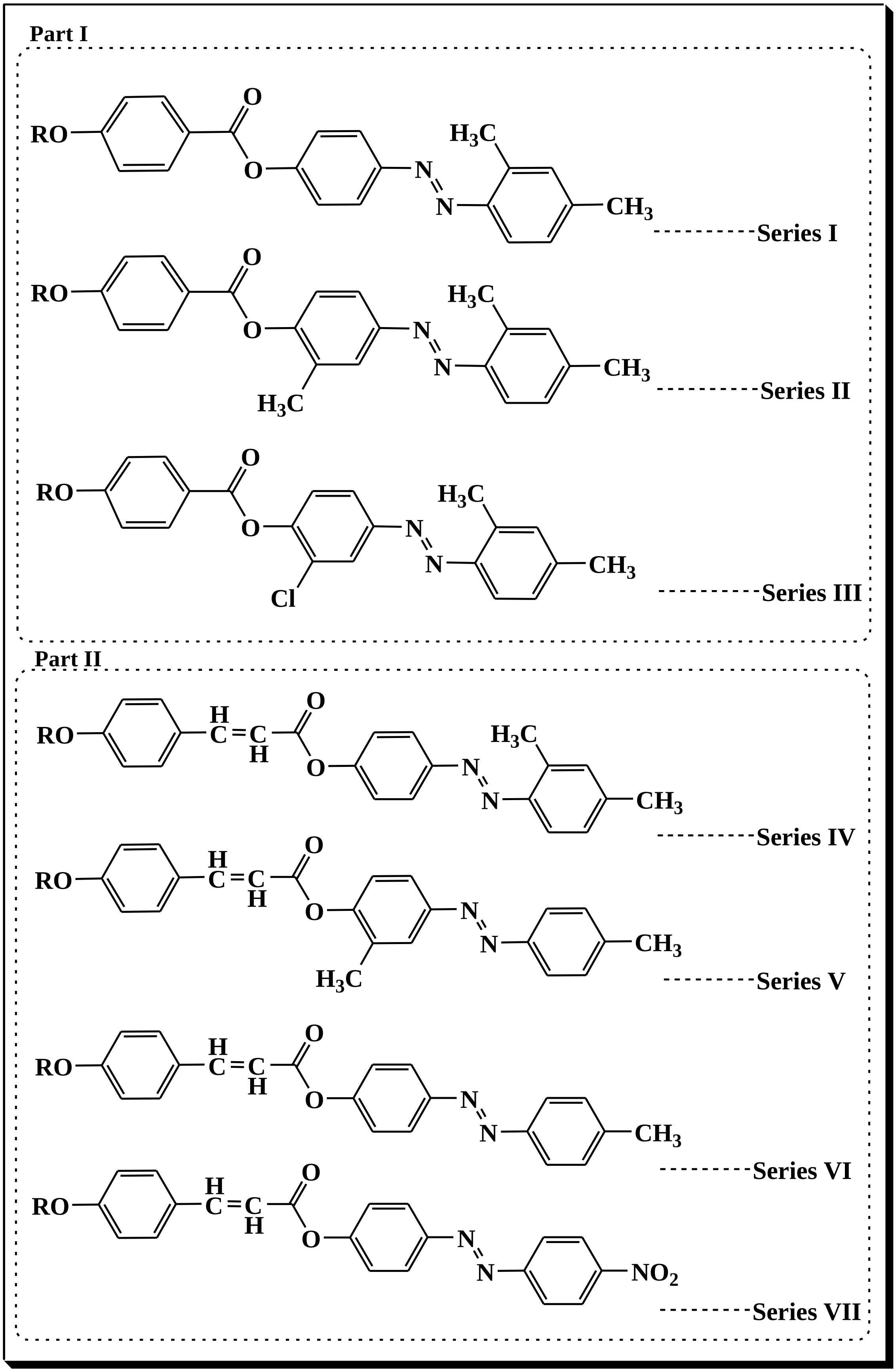


Figure 3.13: Molecular geometry of the homologous series under comparison

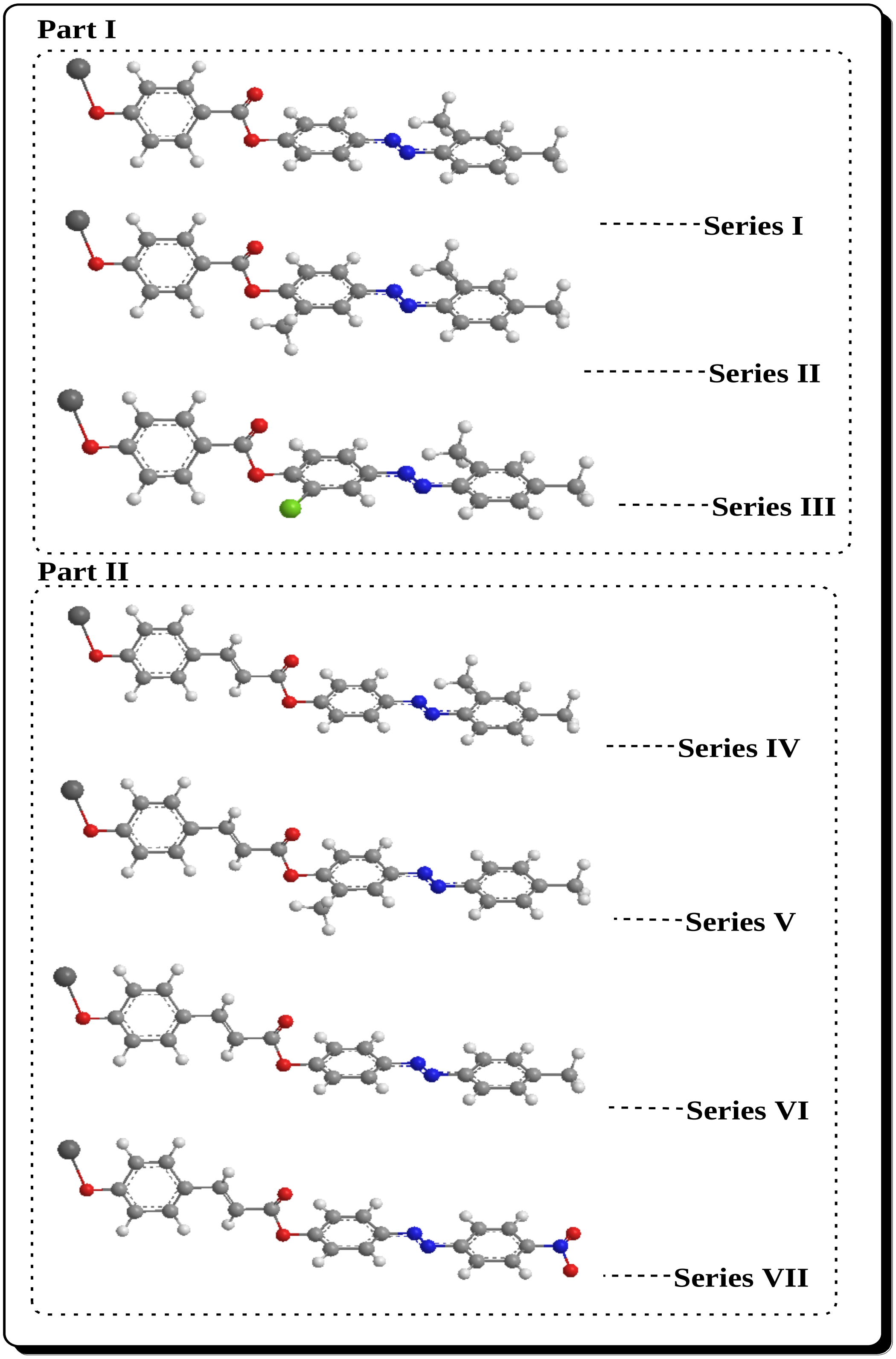


Figure 3.14: Energy minimized 3D Molecular geometry of the homologous series under comparison from ChemDraw Ultra 8.0 software

The average thermal stabilities of all the six series are compared internally with each other. Table 3.29 and Figure 3.15 show the average thermal stability for the homologous series, Figure 3.13 and 3.14 show general molecular geometry and energy minimized 3D molecular structure of the homologous series under comparison from ChemDraw ultra 8.0 software.

Table 3.29: Average thermal stability °C

Series		N –I / S – I	S-N	Commencement of Smectic mesophase
Part I	**I**	155.58 (C1-C16)	62 (C16)	16
	II	117.25 (C1-C16)	--	--
	III	129.00 (C1-C16)	--	--
Part II	**IV**	185.08 (C1-C16)	87.5 (C10-C14)	10
	V	205.41 (C1-C16)	105.00 (C14-C16)	14
	VI	256.50 (C1-C16)	144.75 (C10-C14)	10
	VII	264.87 (C1-C8)	219.66 (C7-C16)	07

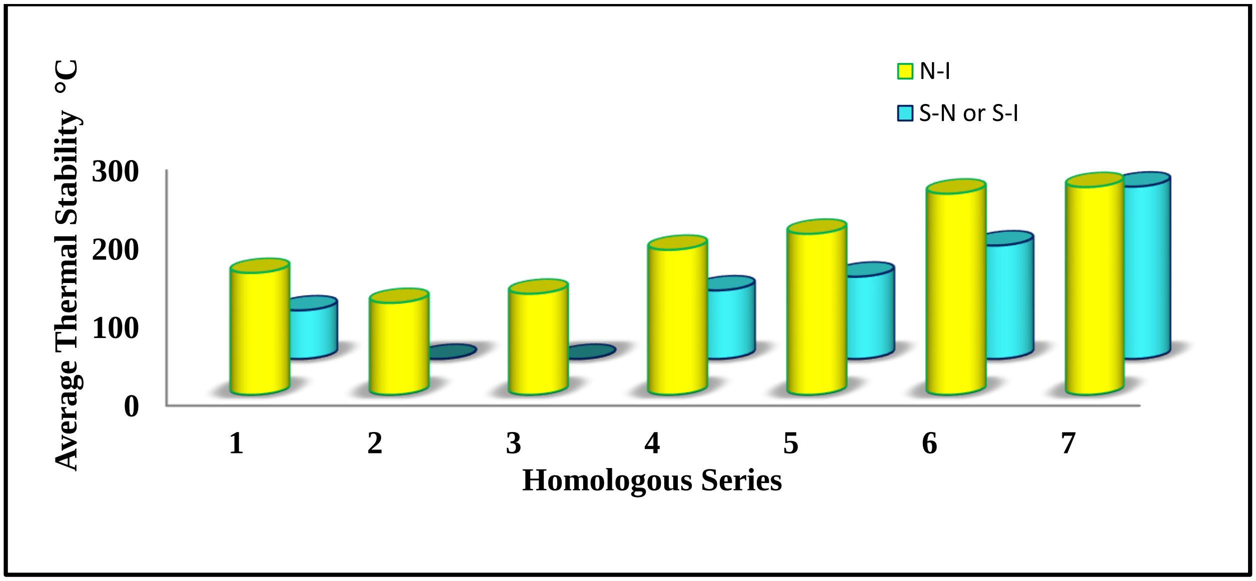


Figure 3.15: Average thermal stability (TS) for the homologous series

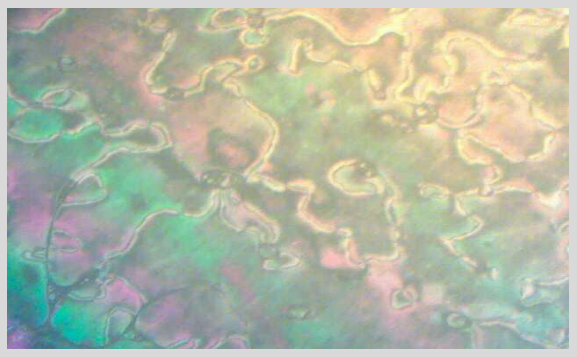
Series IV and V can also be compared with each other as both the series can be considered a positional isomers as their molecular geometry possesses same molecular formula but difference in position of lateral substitution only. The average N-I thermal stability of series IV is 185.08 °C and series V is 205.41 °C. From the average thermal stability data it is seen that the methyl group at terminal benzene ring in ortho position to azo central linkage exhibits lower stability as compared to methyl group in central benzene ring in ortho position to ester central linkage at central benzene ring; the methyl group in central benzene ring has more thermally stable molecules than those of the methyl group at terminal benzene ring.

In contrast, to this on the basis of mass spectroscopy [Figure 3.3 (d), 3.3 (e), 3.3 (f)] it is observed that series IV exhibits the molecular ion peak and the base peak of the same value whereas in series V has different molecular ion peak and base peak values obtained which can clearly says that the series IV is less thermally stable but more electronically stable whereas series V is more thermally stable but less electronically stable. Similarly the S-N thermal stability of series IV is lower than series V as series IV is less thermally stable than series V.

Series VI and series VII differ only in their terminal Substituents i.e. $-CH_3$ and $-NO_2$ group respectively. The average N-I as well as thermal stability of series VII is higher than series VI this may be due to the presence of nitro group in series VII and methyl group in Series VI . the nitro group with its strong dipole acting along the long axis of the molecule yields a smectic mesophase which is more thermally stable than for $-CH_3$, for which the dipole acts at an angle across the long axes of the molecule; this fact also suggests that terminal dipoles contribute to the terminal intermolecular interactions, either by polarization or dipole-dipole interactions (409).

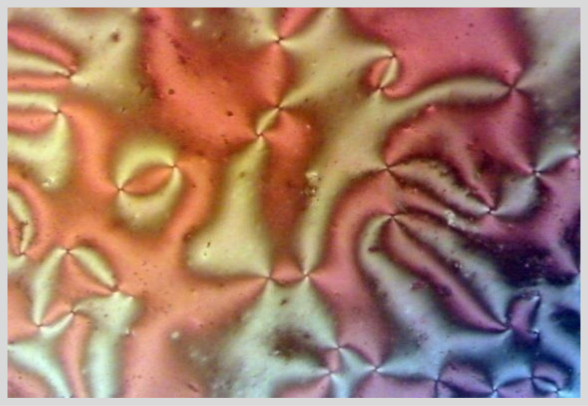
Polarizing Optical microscopic images of Liquid Crystals

(a)



(b)

(a) Marble texture of nematic phase of C8 homologue of Series I at 114 °C on cooling.
(b) Schlieren texture of the nematic phase of C12 homologue of Series I at 116 °C on cooling.



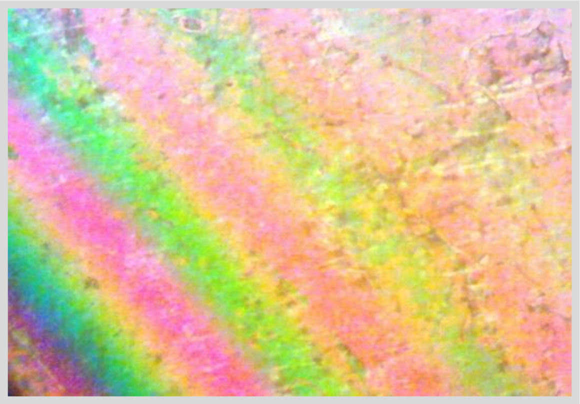
(c)

(d)

(c) Schlieren texture of the nematic phase of C6 homologue of Series II at 121 °C on cooling.

(d) Schlieren texture of the nematic phase of C12 homologue of Series II at 56 °C on cooling.

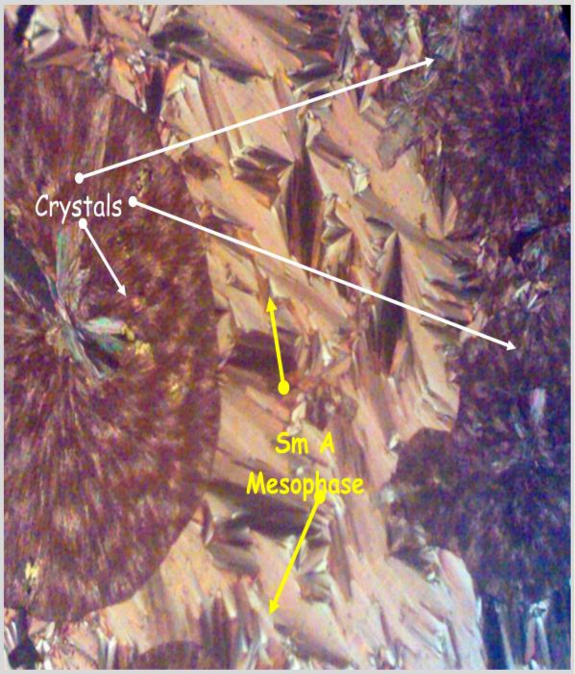
(e)



(f)

(e) Marble texture of nematic phase of C7 homologue of Series III at 92˚C on cooling.
(f) Marble texture of the nematic phase of C10 homologue of Series III at 98˚C on cooling.

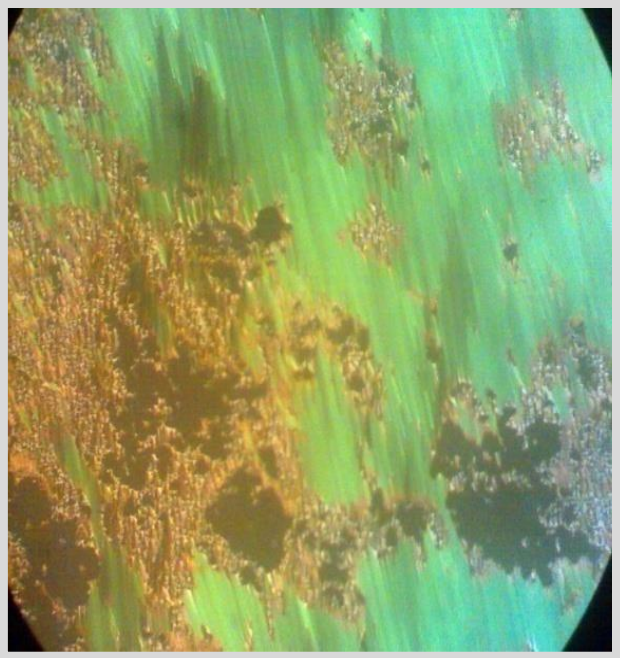
(g)



(h)

(g) Fan shaped texture of Smectic A phase of C12 homologue of Series IV at 78◦C on cooling.

(h) Fan shaped texture of Smectic A phase of C14 homologue of Series IV at 74◦C on cooling.

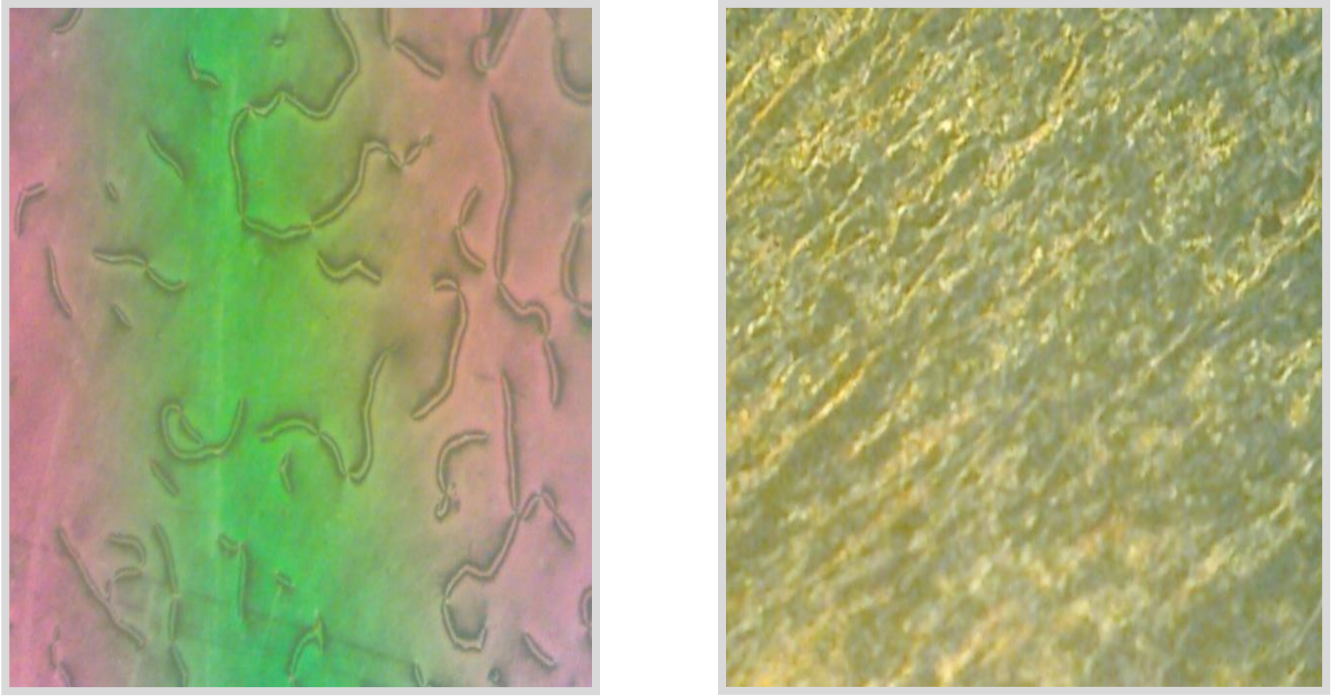


(i)

(j)

(i) Schlieren texture of Smectic C phase of C14 homologue of Series V at 89 ^{o}C on cooling.

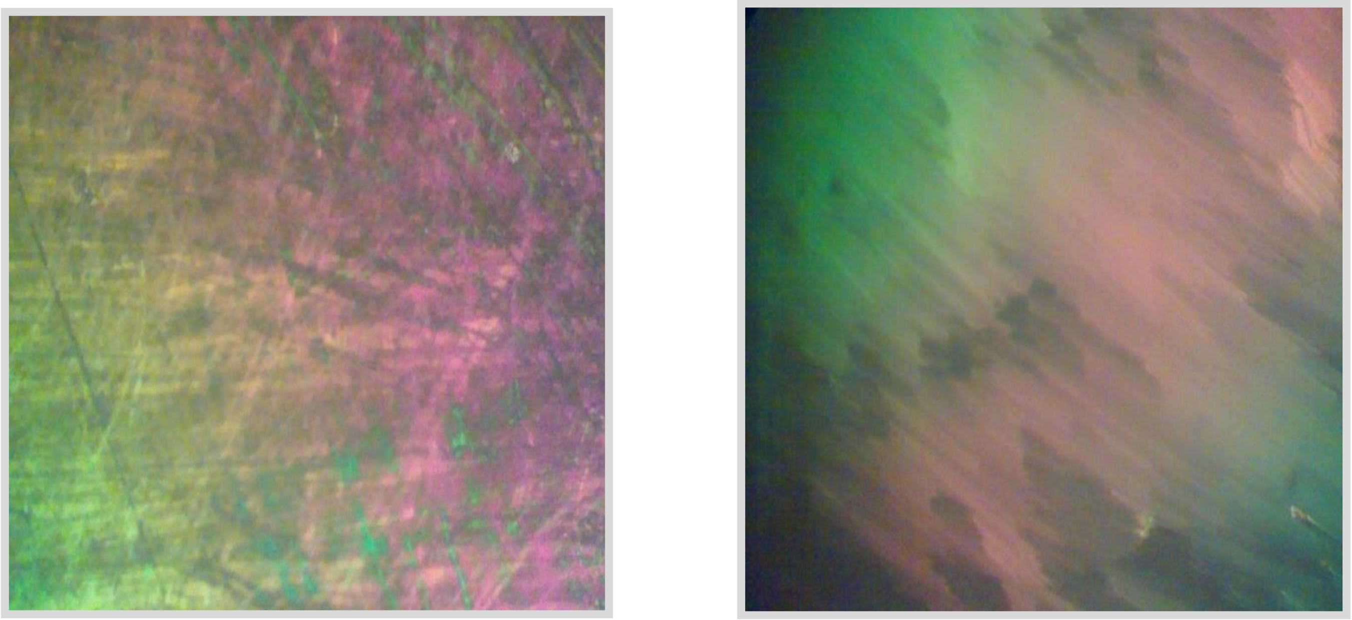
(j) Schlieren texture of Smectic C phase of C16 homologue of Series V at 93 ^{o}C on cooling.



(k) (l)

(k) Marble texture of nematic phase of C10 homologue of Series VI at 152 ^{o}C on cooling.

(l) Schlieren texture of Smectic C phase of C10 homologue of Series VI at 120 ^{o}C on cooling.



(m) (n)

(m) Marble texture of nematic phase of C7 homologue of Series VII at 215 ^{o}C on cooling.

(n) Schlieren texture of smectic C phase of C7 homologue of Series VII at 196 ^{o}C on cooling.