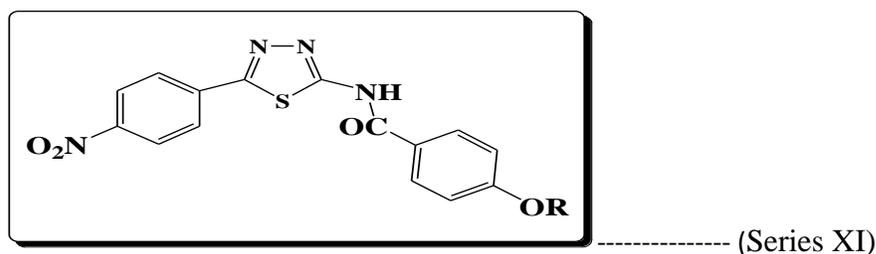
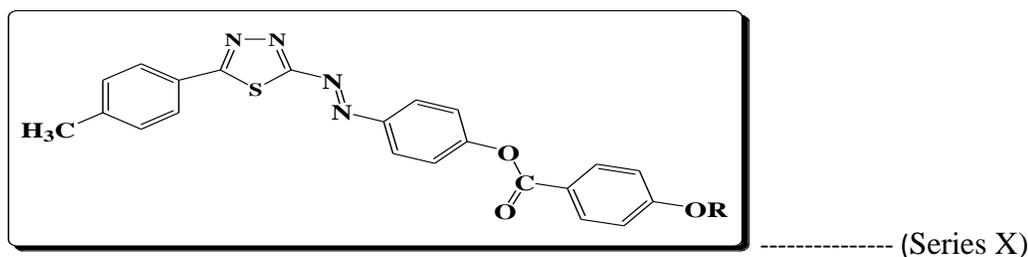


## 5.1 Introduction

Chemical structure has been understood to have the most significant effect in the mesophases formed by liquid crystal compounds [409]. A molecule which possesses a linear structure seems to have an advantage in the formation of mesophases; moreover, flexibility also has an important role in the packing of the molecules. However, quite a good number of novel compounds with non-linear structures have been investigated exhibiting liquid crystalline behavior are reported [455-458]. However some bent shaped compounds containing heterocyclic bent core are reported [459-466].

Synthesis of  $\pi$ -conjugated mesogenic molecules has shown great important research interest in the field of physics, chemistry, material science and engineering because these low molecular weight materials can be readily modified and exhibit interesting electronic, luminescent and liquid crystal properties, which favors the development of new functional materials in liquid crystal display, electronic and Optoelectronic applications [467-470]. Thus, in order to understand the co-relation between mesomorphic properties and structural variation of the mesogens, two new homologous series X and XI with common feature of bent core viz. 1, 3, 4-thiadiazole core has been synthesized. Series X composed of ester and azo central linkages as well as methyl group as terminal substituent and series XI composed of amide central linkage and nitro group as terminal substituent are synthesized. Both the series are compared with each other and with structurally related homologous series. The general molecular structure of these series is as follows:



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

## 5.2 Experimental

### 5.2.1 Materials

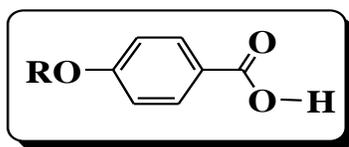
(1) 4-hydroxybenzoic acid, (2) *n*-alkyl halides, (3) phenol, (4) potassium hydroxide, (5) *n*, *n*-dimethylaminopyridine (DMAP), (6) *n*, *n*-dicyclohexylcarbodiimide (DCC), (7) Hydrazine monohydrate, (7) 4-methyl benzoic acid, (8) 4-nitro benzoic acid and all other chemicals are of Loba chemie or Merck used as received.

### 5.2.2 Synthesis

#### 5.2.2.1 Series X: 5-methylphenyl-2-(4''-*n*-alkoxybenzoyloxy)-phenylazo-1, 3, 4-thiadiazoles

##### 5.2.2.1a 4-*n*-alkoxybenzoic acids

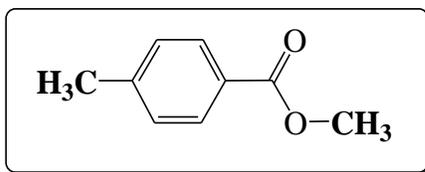
General molecular structure of 4-*n*-alkoxybenzoic acids



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

##### 5.2.2.1b Methyl-4-methylbenzoate

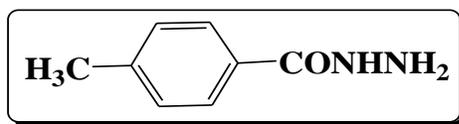
General molecular structure of Methyl-4-methylbenzoate



In a 250 ml R.B.F place a mixture of 0.123 moles of 4-methyl benzoic acid, 80 ml methanol and 2-3 drops of concentrated sulphuric acid. Add a few small chips of porous porcelain attach a reflux condenser and boil the mixture gently for 4 hours; distilled off the excess of methanol on a rotary evaporator and allow to cool, pour the residue into about 250 ml of water contained in a separatory funnel, add 10-15 ml of carbon tetrachloride and shake the mixture in the funnel vigorously; upon standing *p*-toluate with carbon tetrachloride separates in bottom part. Collect the lower layer and wash with sodium hydrogen carbonate to remove acid residue, check pH and no further evolution of carbon dioxide occurs then finally wash with water and dry the organic layer with sodium sulphate for half an hour and finally collect the *p*-toluate. Product confirmation done with the help of TLC and melting point found 35°C [472].

**5.2.2.1c 4-methylbenzohydrazide**

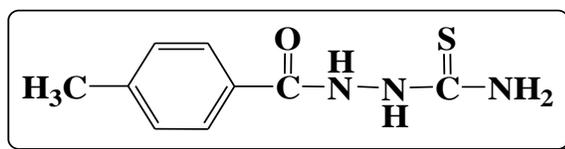
General molecular structure of 4-methylbenzohydrazide



A mixture of 0.0077 mole methyl-4-methylbenzoate and 0.0077 mole of hydrazine monohydrate were dissolved in methanol, and the solution heated under reflux for 24 h. After cooling, the reaction mixture was poured into water and the separated solid recrystallized from methanol and melting point found 138 °C [116, 465, 475].

**5.2.2.1d 4-methylphenyl carbonyl thiosemicarbazide**

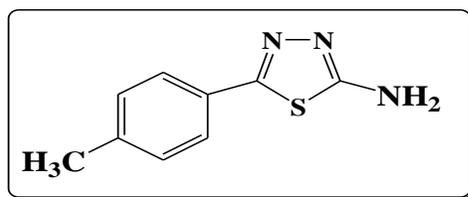
General molecular structure of 4-methylphenyl carbonyl thiosemicarbazide



4-methylbenzohydrazide 0.10 mole was suspended in 100 ml alcoholic hydrogen chloride (6.7 ml HCl 37% and 93.3 ml of ethanol) and mixture evaporated under reduced pressure. The residue dried by evaporation of small amounts of alcohol and heated under reflux for 18 hours with a solution of 0.15 mole dry ammonium thiocyanate in 50 ml of absolute ethanol. The solid was filtered, then suspended in water and neutralized with Concentrated NaOH, then filtered, washed several times with water and recrystallized from ethanol yielding white needles [466].

**5.2.2.1e 5-(4-methylphenyl)-2-amino-1, 3, 4-thiadiazole**

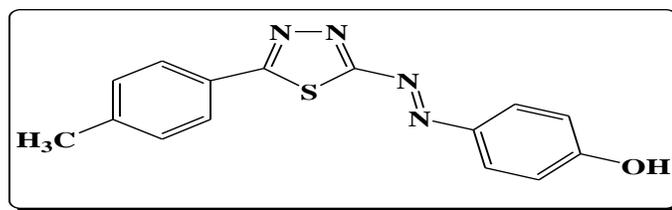
General molecular structure of 5-(4-methylphenyl)-2-amino-1, 3, 4-thiadiazole



Concentrated Sulphuric acid 15 ml was cooled to 0 °C and stirred while 4-methylphenyl carbonyl thiosemicarbazide 0.0045 moles was added portion wise. The reaction mixture was stirred for 3-5 hour in the cold and then allowed to warm to room temperature over a 1 hour period. The solution was poured onto crushed ice and adjusted to pH 12 with concentrated sodium hydroxide. The precipitated product was collected and recrystallized from methanol yielding white shining compound. Melting point 218 °C obtained [466].

**5.2.2.1f (E)-4''hydroxyphenyl -1-(5'-(4''-methylphenyl)-1', 3', 4'-thiadiazol-2-yl) diazene**

General molecular structure of (E)-4''hydroxyphenyl -1-(5'-(4''-methylphenyl)-1', 3', 4'-thiadiazol-2-yl) diazene.

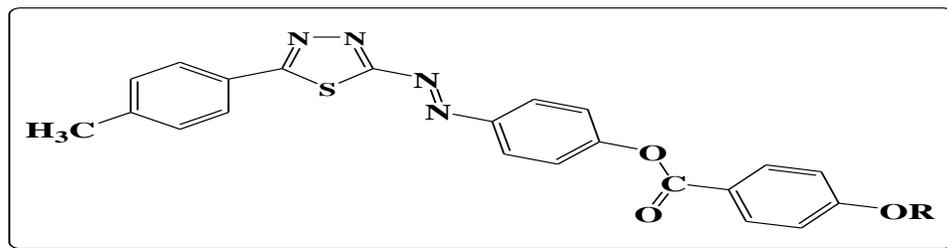


The diazo compound is prepared by the reported method. [434], in two steps.

- (i) Preparation of Diazonium salt of 5-(4-methylphenyl)-2-amino-1, 3, 4-thiadiazole, 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.

**5.2.2.1g 5-methylphenyl-2-(4''-n-alkoxybenzoyloxy)-phenylazo-1, 3, 4-thiadiazoles.**

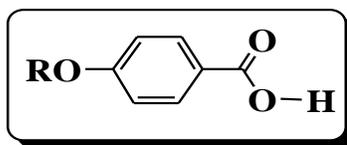
General molecular structure of 5-methylphenyl-2-(4''-n-alkoxybenzoyloxy)-phenylazo-1, 3, 4-thiadiazole.



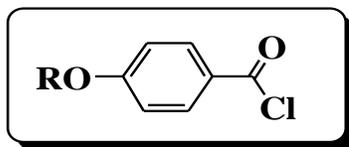
They are synthesized following the procedure reported in 3.2.2.4d [440].

**5.2.2.2 Series XI: 4-n-alkoxy-N-(5-(4''-nitrophenyl)-1', 3', 4'-thiadiazol-2-yl) benzamides****5.2.2.2a 4-n-alkoxybenzoic acids**

General molecular structure of 4-n-alkoxybenzoic acids



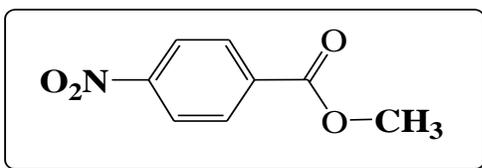
They are synthesized following the procedure reported in 3.2.2.1.a [433].

5.2.2.2b 4-*n*-alkoxybenzoylchlorides

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

## 5.2.2.2c Methyl-4-nitrobenzoate

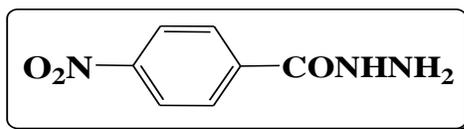
General molecular structure of Methyl-4-nitrobenzoate



They are synthesized following the procedure reported in 5.2.2.1.b [471] Melting point found 96 °C.

## 5.2.2.2d 4-nitrobenzohydrazide

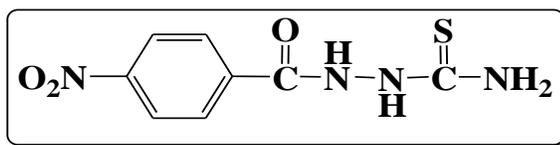
General molecular structure of 4-nitrobenzohydrazide



They are synthesized following the procedure reported in 5.2.2.1.c [116, 465, 475] M. P 218 °C.

## 5.2.2.2e 4-nitrophenyl carbonyl thiosemicarbazide

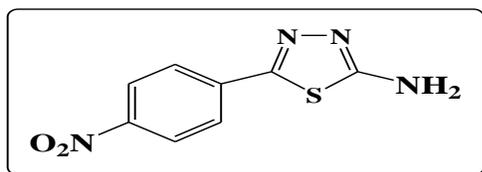
General molecular structure of 4-nitrophenyl carbonyl thiosemicarbazide



They are synthesized following the procedure reported in 5.2.2.1.d [466].

## 5.2.2.2f 5-(4'-nitrophenyl)-2-amino-1,3,4-thiadiazole

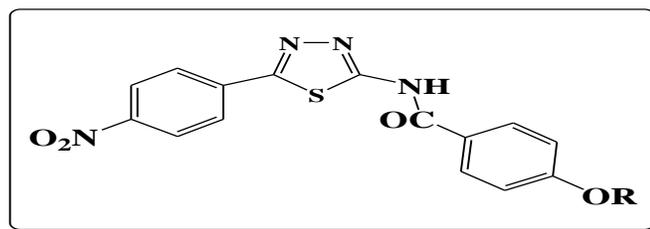
General molecular structure of 5-(4-methylphenyl)-2-amino-1,3,4-thiadiazole



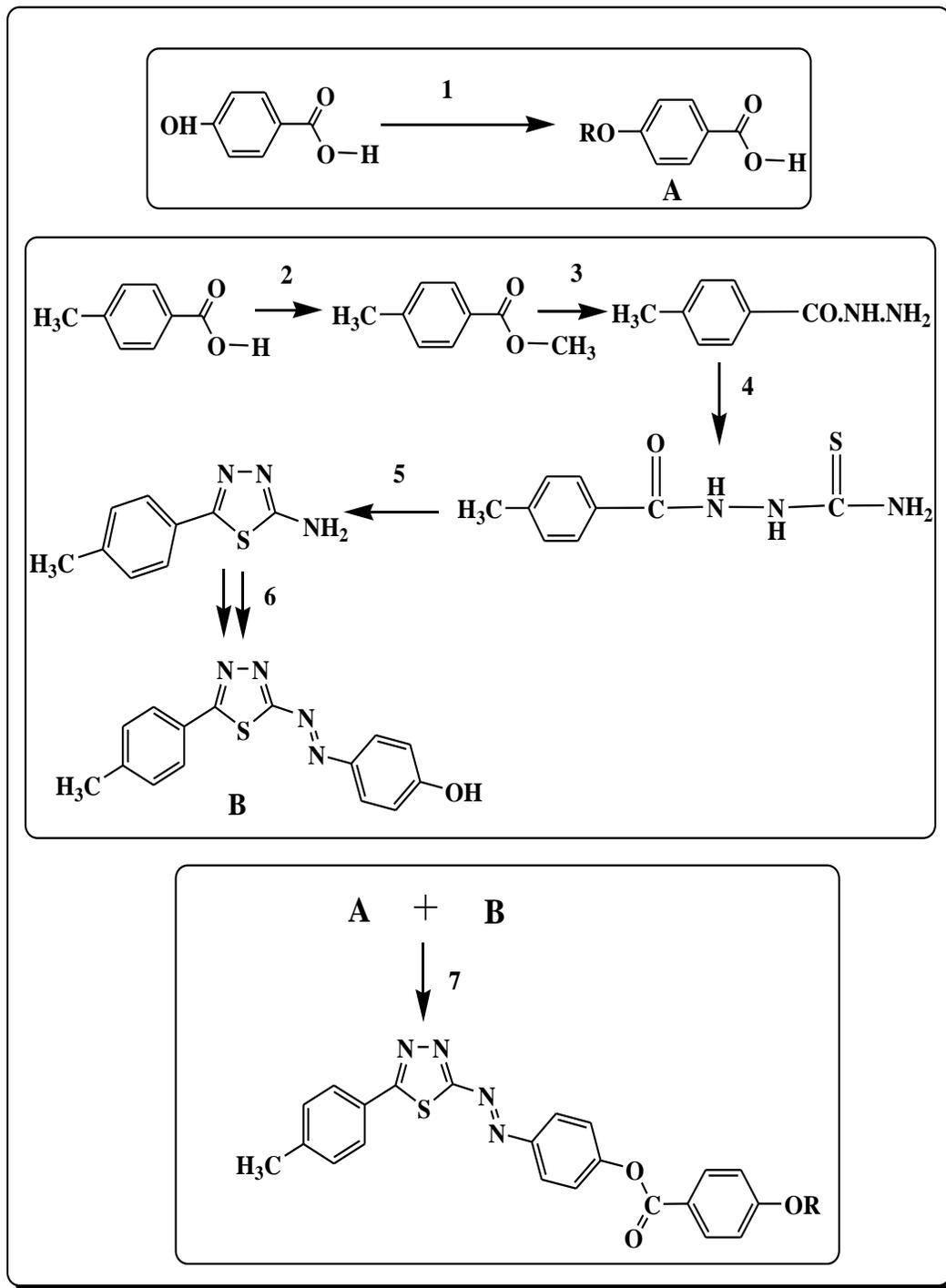
They are synthesized following the procedure reported in 5.2.2.1.e [466].

**5.2.2.2g 4-*n*-alkoxy-N-(5-(4''-nitrophenyl)-1', 3', 4'-thiadiazol-2-yl) benzamides**

General molecular structure of 4-*n*-butoxy-N-(5-(4''-nitrophenyl)-1', 3', 4'-thiadiazol-2-yl) benzamide



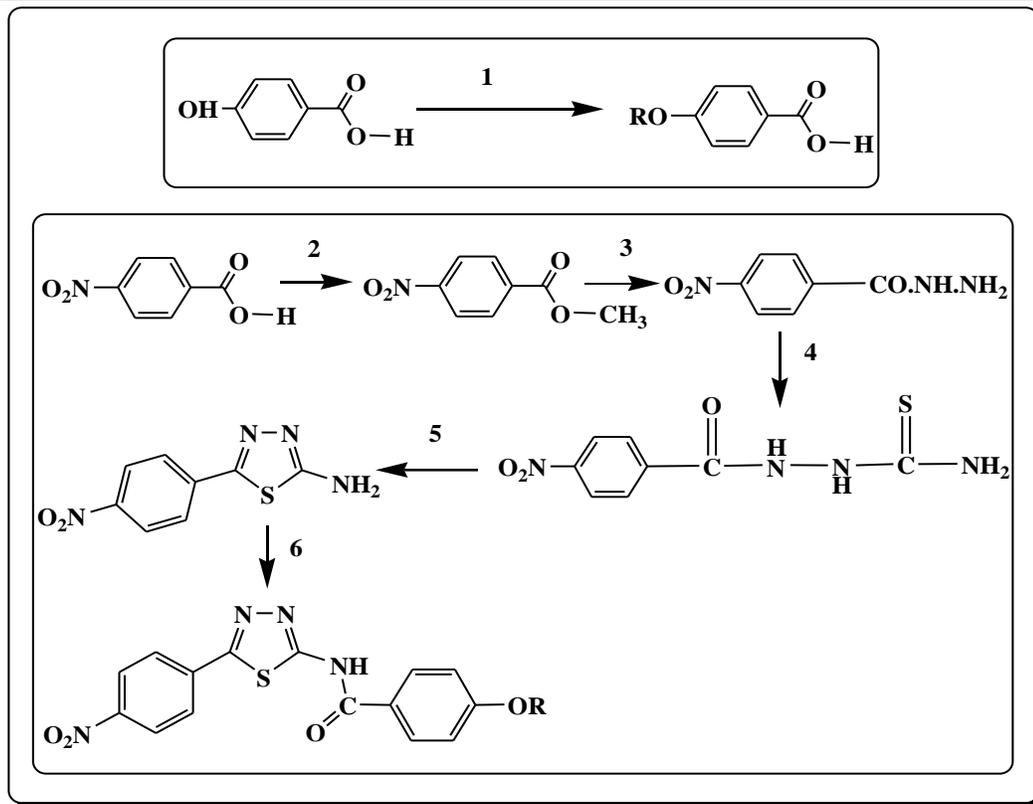
In this reaction we do not need to required to add DMAP as catalyst, all homologues of the series are synthesized following the procedure reported in 3.2.2.1d [461]



Scheme 5.1: Synthetic route for series X

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

(1) Alcohol, KOH,  $n$ -RBr, Reflux 8-10 hrs (2) Conc.  $H_2SO_4$ , methanol, Reflux 4-6 hrs, (3) methanol, Hydrazine monohydrate, reflux for 24 hrs, (4) Alcohol, dry ammonium thiocyanate ( $NH_4SCN$ ), reflux 18 hrs, (5) Conc.  $H_2SO_4$ , stirred for 3-5 hrs,  $0^\circ C$  temperature, (6) (i) Conc. HCl,  $NaNO_2$ , (ii) phenol aq. NaOH, at  $0-10^\circ C$ , pH 8-12, (7) DCC, DMAP, DCM, Stirred for 12 – 16 hrs,



**Scheme 5.2: Synthetic route for series XI**

(1) Alcohol, KOH, *n*-RBr, Reflux 8-10 hrs (2) Conc. H<sub>2</sub>SO<sub>4</sub>, methanol, Reflux 4-6 hrs, (3) methanol, Hydrazine monohydrate, reflux for 24 hrs, (4) Alcohol, dry ammonium thiocyanate (NH<sub>4</sub>SCN), reflux 18 hrs, (5) Conc. H<sub>2</sub>SO<sub>4</sub>, stirred for 3-5 hrs, 0°C temperature, (6) DCC, DCM, Stirred for 12 – 16 hrs.

### 5.2.3 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,  $^1\text{H}$  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 5.1:** Transition Temperatures: Series X

| R = <i>n</i> -Alkyl group | Transition Temperature °C |         |           |
|---------------------------|---------------------------|---------|-----------|
|                           | Smectic C                 | Nematic | Isotropic |
| Methyl                    | --                        | --      | 243       |
| Ethyl                     | --                        | --      | 230       |
| Propyl                    | --                        | 159     | 233       |
| Butyl                     | --                        | 154     | 199       |
| Pentyl                    | --                        | 155     | 193       |
| Hexyl                     | --                        | 148     | 196       |
| Heptyl                    | --                        | 151     | 182       |
| Octyl                     | --                        | 149     | 181       |
| Decyl                     | 143                       | 156     | 184       |
| Dodecyl                   | 131                       | 168     | 173       |
| Tetradecyl                | 124                       | 160     | 175       |
| Hexadecyl                 | 118                       | 164     | 172       |

**Table 5.2:** Elemental Analysis

| Series | Homologue | Theoretical |       |       | Practical |       |       |
|--------|-----------|-------------|-------|-------|-----------|-------|-------|
|        |           | C (%)       | H (%) | N (%) | C (%)     | H (%) | N (%) |
| X      | C5        | 66.58       | 5.34  | 11.50 | 66.54     | 5.30  | 11.26 |
| X      | C14       | 70.55       | 7.18  | 9.14  | 70.51     | 7.26  | 9.17  |

#### FTIR (KBr pellets, $\text{cm}^{-1}$ )

**Pentyl homologue :** 2925 – 2858 (–C–H St, Alkyl  $\text{CH}_3$ ,  $\text{SP}^3$  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 – $\text{CH}_2$ –), 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 –  $(\text{CH}_2)_7$ –).

**Tetradecyl homologue** : 2925 – 2858 (–C–H St, Alkyl CH<sub>3</sub>, SP<sup>3</sup> 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<sub>2</sub>–), 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<sub>2</sub>)<sub>7</sub>–).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, δ ppm, standard TMS)

**Pentyl homologue:** δ = 0.92 (t, 3H, –CH<sub>3</sub>), 1.25-1.55 (m, 6H, 3(–CH<sub>2</sub>–)), 1.83 (Qunt, 2H, –OCCH<sub>2</sub>), 2.42 (s, 3H, Ar–CH<sub>3</sub>), 4.06 (t, 2H, –OCH<sub>2</sub>), 6.97-8.18 (m, 11H, Ar–H).

**Tetradecyl homologue:** δ = 0.88 (t, 3H, –CH<sub>3</sub>), 1.25-1.54 (m, 22H, 11(–CH<sub>2</sub>–)), 1.82 (Qunt, 2H, –OCCH<sub>2</sub>), 2.43 (s, 3H, Ar–CH<sub>3</sub>), 4.07 (t, 2H, –OCH<sub>2</sub>), 6.98-8.17 (m, 11H, Ar–H).

**Mass Spectra: MS m/z:**

**Tetradecyl Homologue: Theoretical Mass value: 612.30 g/mol**

**Practical mass value: MS m/z: 612.31 (M<sup>+</sup>)**

**Table 5.3: DSC Data**

| Series | Member | Heating rate °C/min | Transition Temperature °C | ΔH=J/g | ΔS=J/g.K |
|--------|--------|---------------------|---------------------------|--------|----------|
| X      | C5     | 10                  | Cr – SmC 289.20           | 32.86  | 0.0584   |
|        |        |                     | SmC – I 323.03            | 11.53  | 0.0193   |

**Table 5.4: UV Data**

| Series | Homologue | UV λ max values nm (solvent – ethyl acetate ) |        |
|--------|-----------|---|--------|
|        |           | π → π*  | n → π* |
| X      | C5        | 327   | 426.50 |
|        | C14       | 326   | 430.50 |

**Table 5.5:** Transition Temperatures: Series XI

| R = <i>n</i> -Alkyl group | Transition Temperature °C |           |
|---------------------------|---------------------------|-----------|
|                           | Smectic C                 | Isotropic |
| <b>Methyl</b>             | --                        | 334       |
| <b>Ethyl</b>              | --                        | 330       |
| <b>Propyl</b>             | --                        | 332       |
| <b>Butyl</b>              | 288                       | 325       |
| <b>Pentyl</b>             | 290                       | 325       |
| <b>Hexyl</b>              | 288                       | 320       |
| <b>Heptyl</b>             | 275                       | 324       |
| <b>Octyl</b>              | 268                       | 315       |
| <b>Decyl</b>              | 257                       | 307       |
| <b>Dodecyl</b>            | 249                       | 303       |
| <b>Tetradecyl</b>         | 244                       | 298       |
| <b>Hexadecyl</b>          | 246                       | 286       |

**Table 5.6: Elemental Analysis**

| Series    | Homologue | Theoretical |       |       | Practical |       |       |
|-----------|-----------|-------------|-------|-------|-----------|-------|-------|
|           |           | C (%)       | H (%) | N (%) | C (%)     | H (%) | N (%) |
| <b>XI</b> | C4        | 57.22       | 4.51  | 14.05 | 57.32     | 4.53  | 14.06 |
| <b>XI</b> | C16       | 65.63       | 7.41  | 9.88  | 65.44     | 7.45  | 7.39  |

**FTIR (KBr pellets, cm<sup>-1</sup>)**

**Tetradecyl homologue :** 2925 – 2858 (–C–H St, Alkyl CH<sub>3</sub>, SP<sup>3</sup> hybridization), 3170 (–N–H St. of amide), 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<sub>2</sub>–), 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<sub>2</sub>)<sub>7</sub>–).

**Hexadecyl homologue :** 2925 – 2858 (–C–H St, Alkyl CH<sub>3</sub>, SP<sup>3</sup> hybridization), 3170 (–N–H St. of amide) 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<sub>2</sub>–), 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<sub>2</sub>)<sub>7</sub>–).

**$^1\text{H}$  NMR (DMSO, 300 MHz,  $\delta$  ppm, standard TMS)**

**Butyl homologue:**  $\delta = 0.92$  (t, 3H,  $-\text{CH}_3$ ), 12.80 (s, 1H,  $-\text{NH}$ ), 1.41-1.48 (sextet, 4H, 2( $-\text{CH}_2-$ )), 1.70 (Qunt, 2H,  $-\text{OCCH}_2$ ), 4.10 (t, 2H,  $-\text{OCH}_2$ ), 7.07–8.37 (m, 8H, Ar-H).

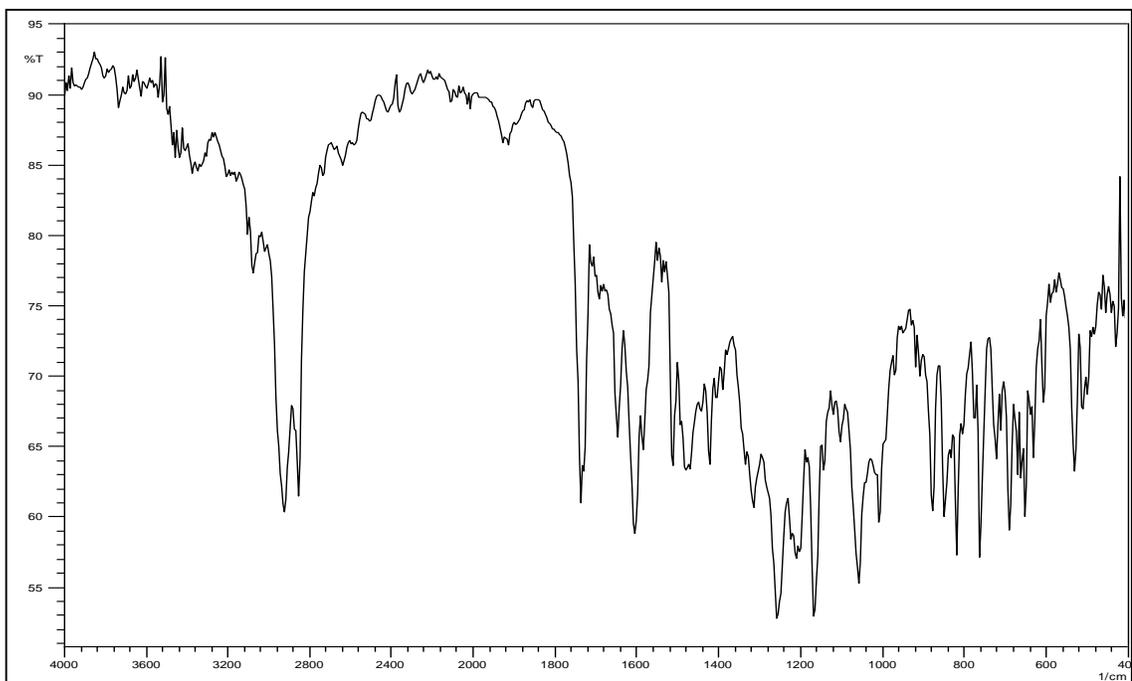
**Mass Spectra: MS m/z:**

**Dodecyl Homologue: Theoretical Mass value: 510.23 g/mol**

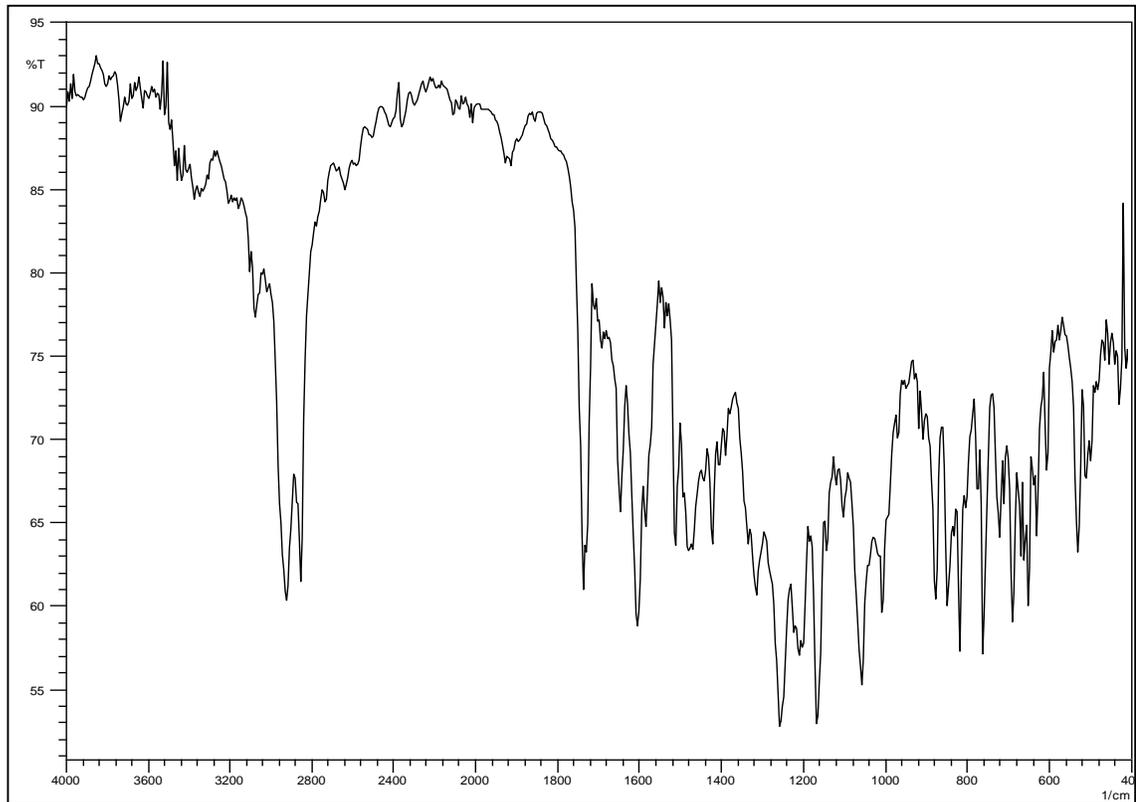
**Practical mass value: MS m/z: 510.23 ( $\text{M}^+$ )**

**Table 5.7: DSC Data**

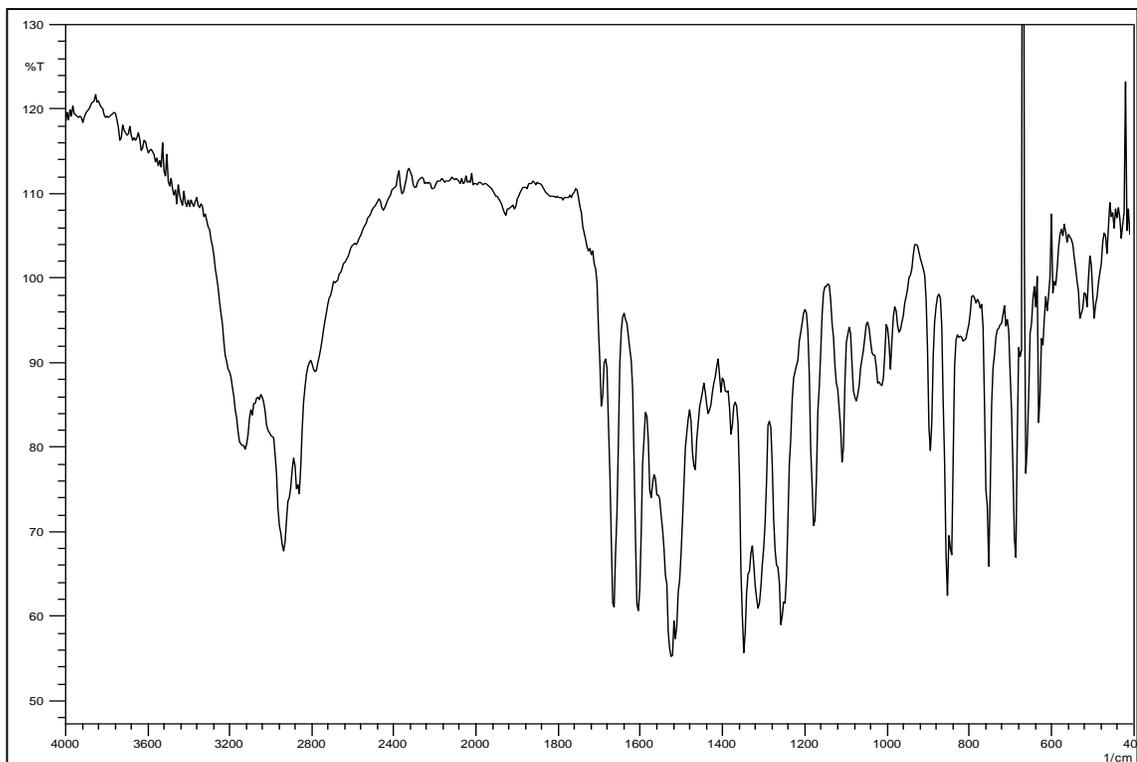
| Series | Member | Heating rate<br>$^{\circ}\text{C}/\text{min}$ | Transition Temperature $^{\circ}\text{C}$ | $\Delta\text{H}=\text{J}/\text{g}$ | $\Delta\text{S}=\text{J}/\text{g}\cdot\text{K}$ |
|--------|--------|---|---|------------------------------------|---|
| XI     | C4     | 10  | Cr – SmC 289.20                           | 32.86                              | 0.0584  |
|        |        |   | SmC – I 323.03                            | 11.53                              | 0.0193  |



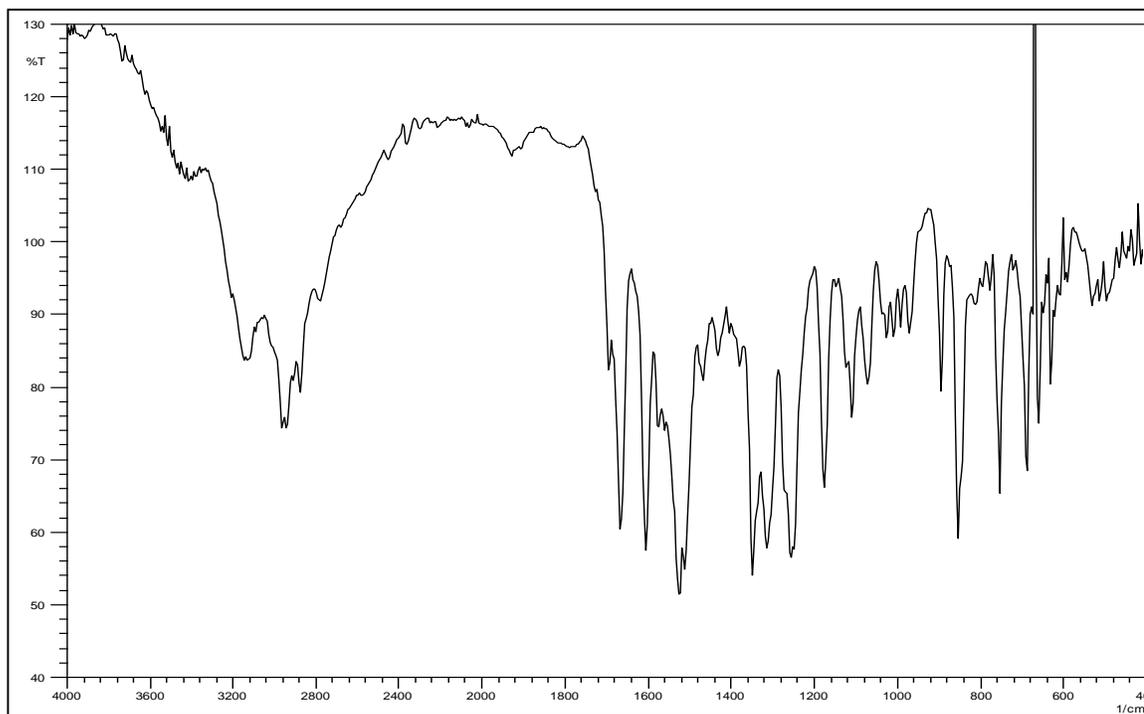
**Figure 5.1 (a): IR spectra of C5 homologue of series X**



**Figure 5.1 (b): IR spectra of C14 homologue of series X**



**Figure 5.1 (b): IR spectra of C14 homologue of series XI**



**Figure 5.1 (b): IR spectra of C16 homologue of series XI**

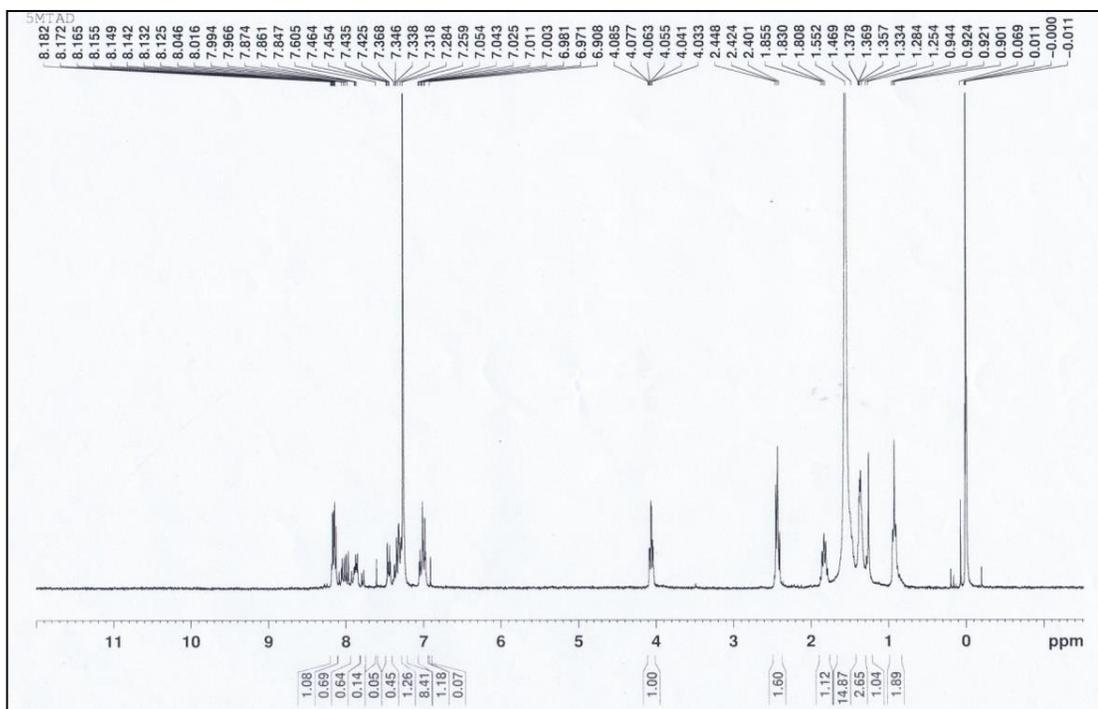


Figure 5.2 (a):  $^1\text{H}$  NMR spectra of C5 homologue of series X

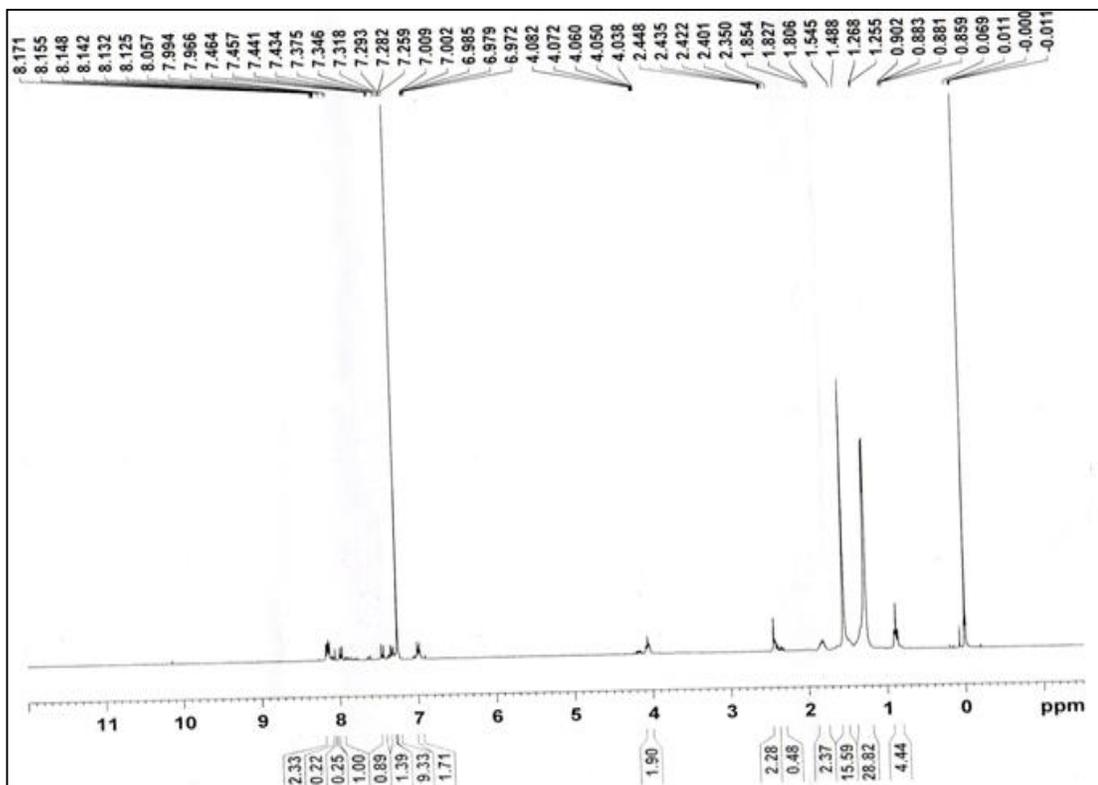


Figure 5.2 (b):  $^1\text{H}$  NMR spectra of C14 homologue of series X

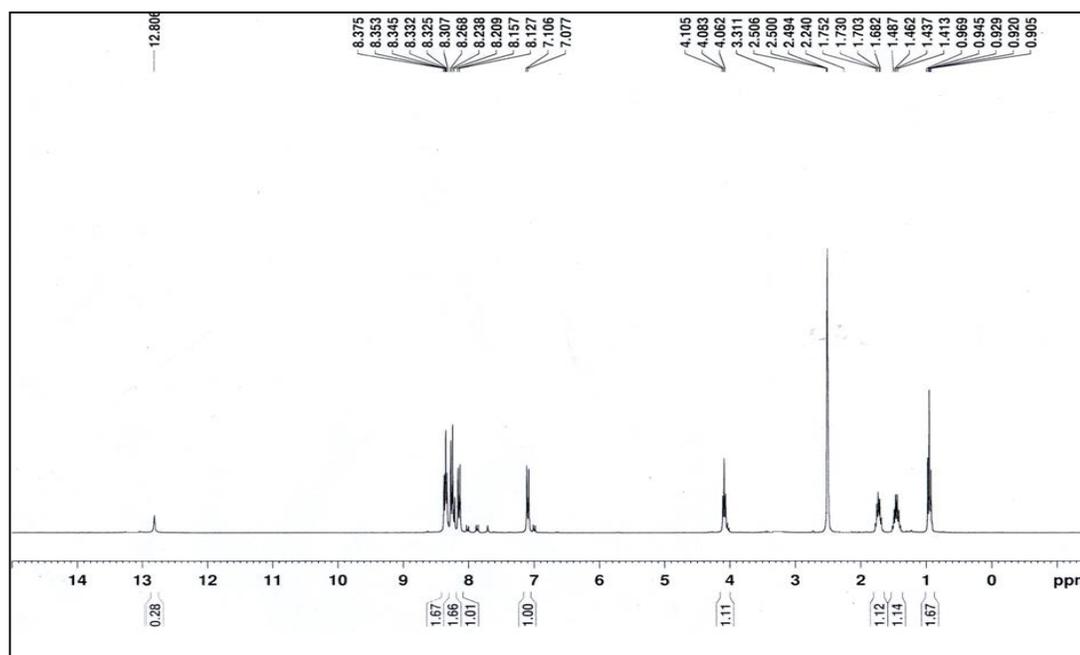


Figure 5.2 (c):  $^1\text{H}$  NMR spectra of C4 homologue of series XI

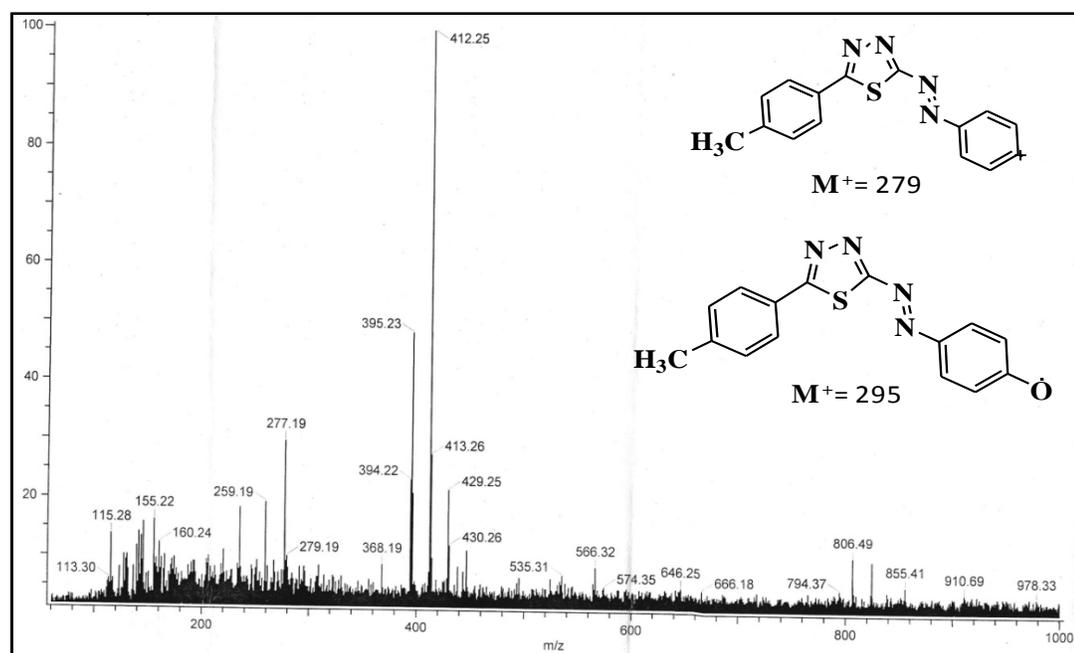


Figure 5.3 (a): Mass spectra of C14 homologue of series X

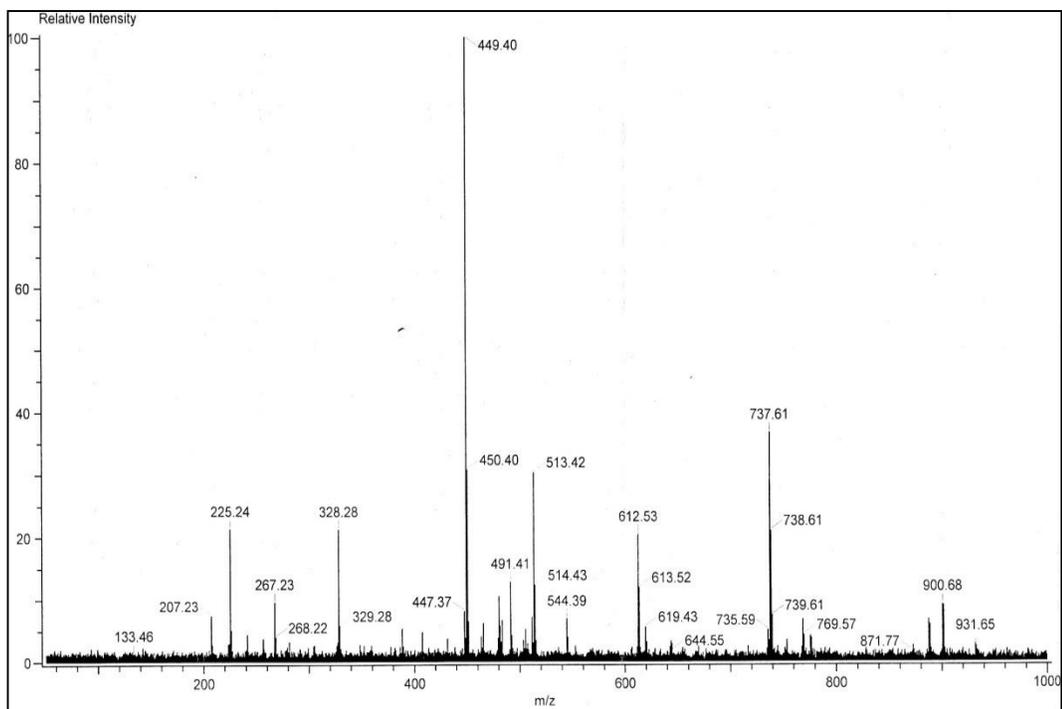


Figure 5.3 (b): Mass spectra of C12 homologue of series XI

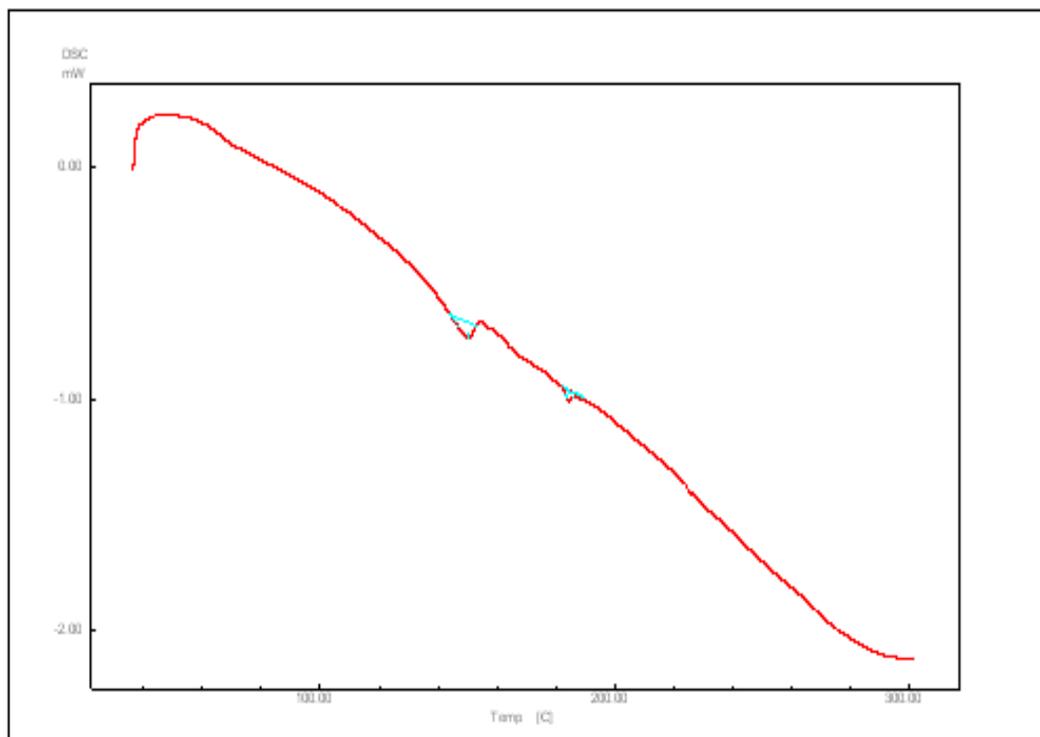


Figure 5.4 (a): DSC Thermogram of C5 homologue of series X

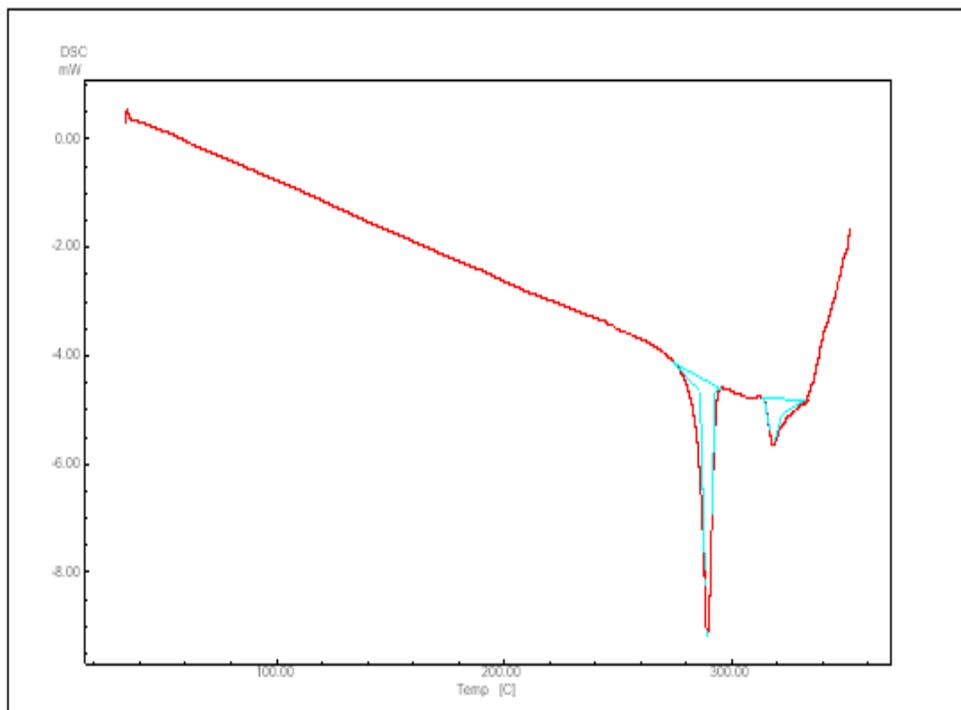


Figure 5.4 (b): DSC Thermogram of C4 homologue of series XI

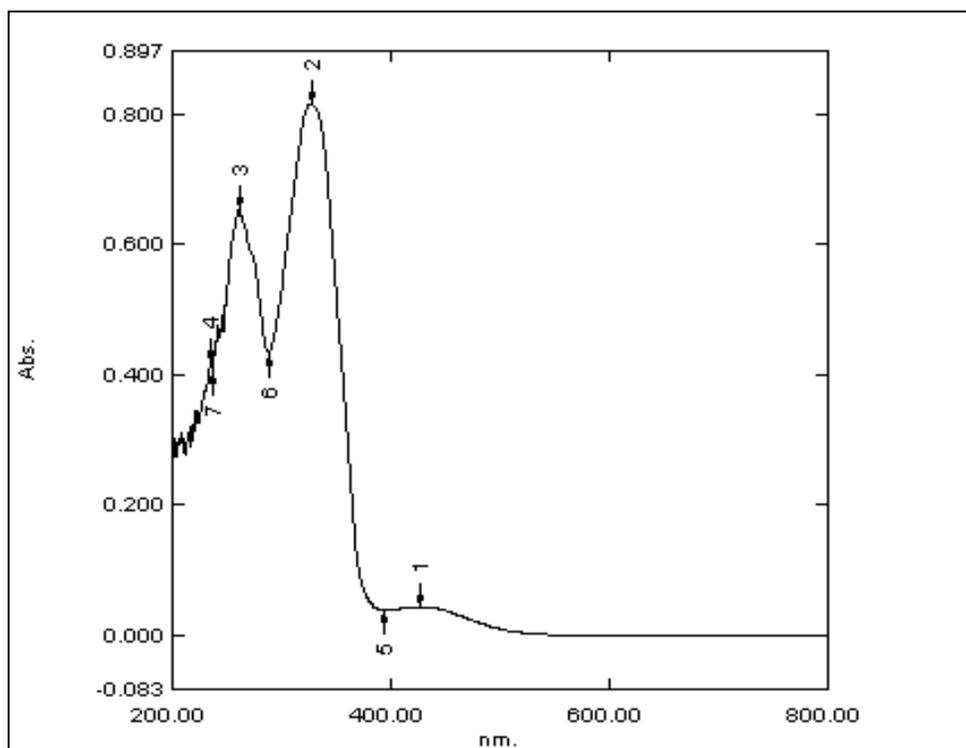


Figure 5.5 (a): UV spectra of C5 homologue of series X

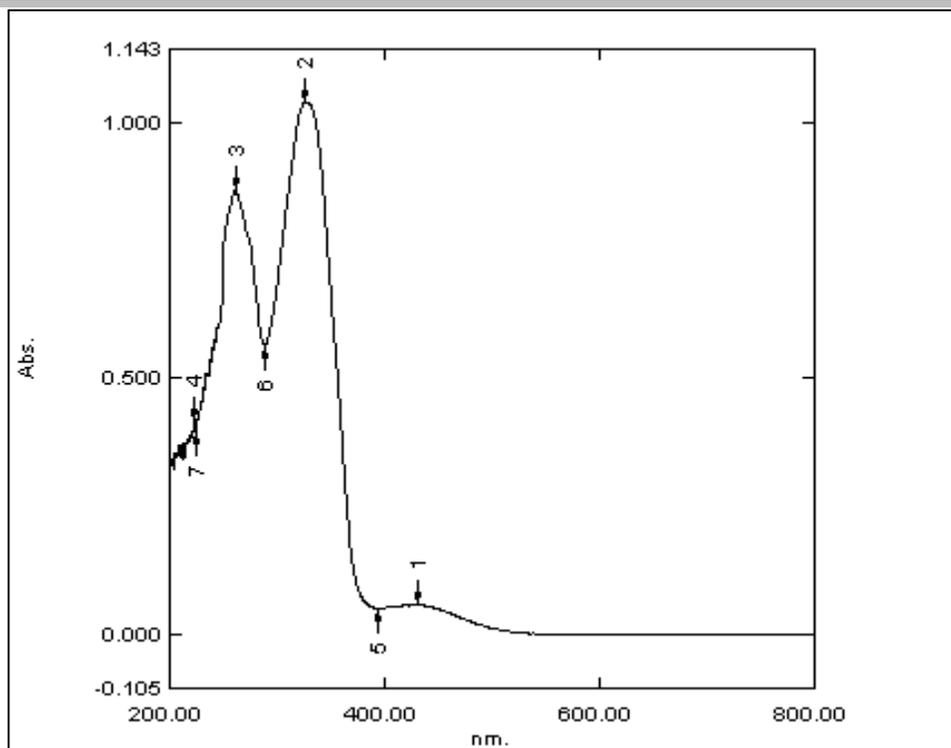


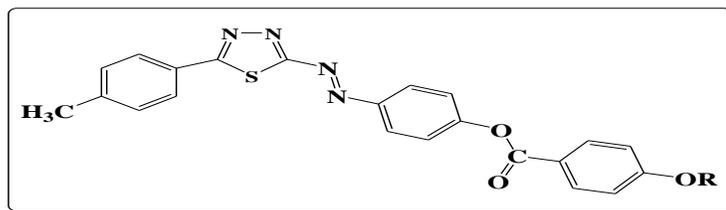
Figure 5.5 (a): UV spectra of C14 homologue of series X

### 5.3 Results and Discussion

In the present chapter, twelve homologues from each of the two series; viz. Series X and series XI, were synthesized and their mesomorphic properties were studied.

#### 5.3.1 Series X: 5-methylphenyl-2-(4''-*n*-alkoxybenzoyloxy)-phenylazo-1, 3, 4-thiadiazoles

General molecular structure of the series X: 5-methylphenyl-2-(4''-*n*-alkoxybenzoyloxy)-phenylazo-1, 3, 4-thiadiazoles



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

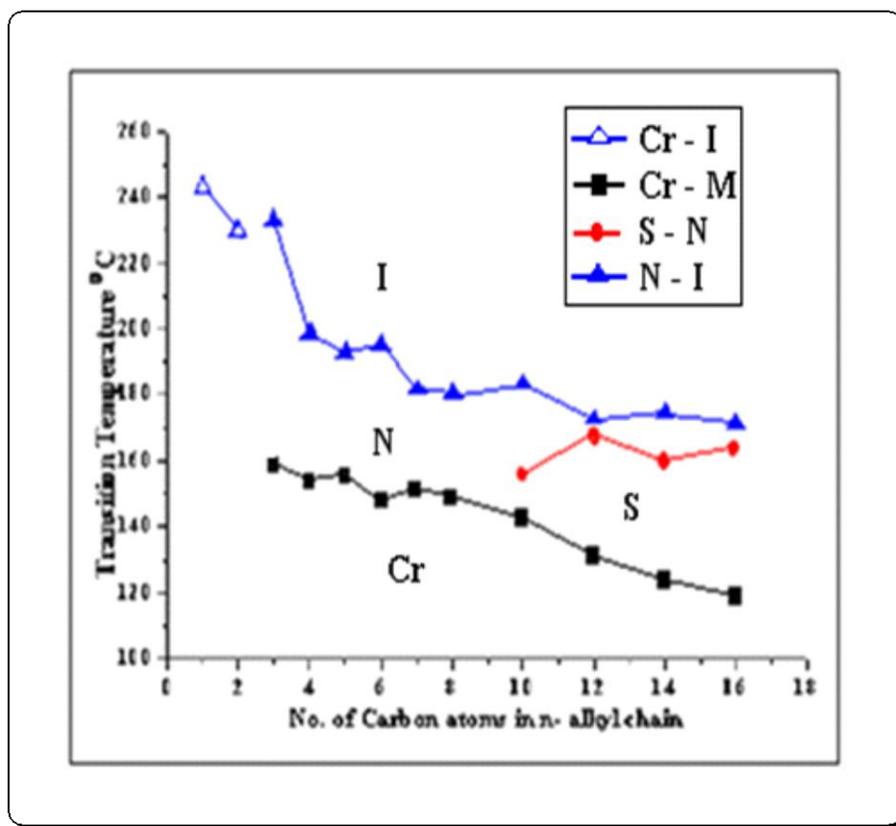


Figure 5.6: 5-methylphenyl-2-(4''-*n*-alkoxybenzoyloxy)-phenylazo-1, 3, 4-thiadiazoles (Series X)

In the homologous Series X mesogenic behavior commences from the C3 homologue (Table: 5.1, Figure: 5.6) in the form of nematic mesophase and remains upto the last C16 derivative synthesized; smectic C mesophase commences from C10 derivative and continues upto the last C16 derivative alongwith nematic mesophase. Figure 5.6 shows the plot of transition temperatures against number of carbon atoms in the *n*-

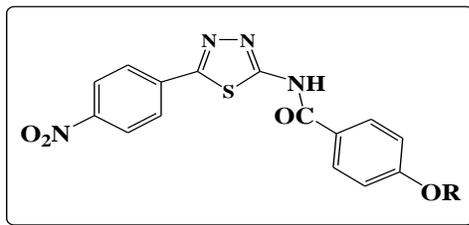
alkoxy chain; it indicates that Cr – I transition curve falls between C1 & C2 homologue. The N – I curve falls steeply from C3 to C4 homologue and then, with a slight rise at C6 homologue, again falls till C8 derivative; the curve again rises at C10 derivative & then falls from C12 derivative to C16 derivative with a slight rise at C14 homologue. The Cr – M curve shows gradual falling tendency from C3 derivative till the last C16 derivative with a slight rise at C5 and C7 homologues as the series is ascended. The S – N curve shows rising tendency from C10 derivative to C12 derivative & then falls at C14 derivative and then again rises till C16 homologue studied. The nematic phase of the series shows marble/Schileren texture whereas the smectic phase shows schileren texture of the smectic C variety.

**Table 5.1:** Transition Temperatures: Series X: 5-methylphenyl-2-(4''-*n*-alkoxybenzoyloxy)-phenylazo-1, 3, 4-thiadiazoles

| <b>R = <i>n</i>-Alkyl group</b> | <b>Transition Temperature °C</b> |                |                  |
|---------------------------------|----------------------------------|----------------|------------------|
|                                 | <b>Smectic C</b>                 | <b>Nematic</b> | <b>Isotropic</b> |
| <b>Methyl</b>                   | --                               | --             | 243              |
| <b>Ethyl</b>                    | --                               | --             | 230              |
| <b>Propyl</b>                   | --                               | 159            | 233              |
| <b>Butyl</b>                    | --                               | 154            | 199              |
| <b>Pentyl</b>                   | --                               | 155            | 193              |
| <b>Hexyl</b>                    | --                               | 148            | 196              |
| <b>Heptyl</b>                   | --                               | 151            | 182              |
| <b>Octyl</b>                    | --                               | 149            | 181              |
| <b>Decyl</b>                    | 143                              | 156            | 184              |
| <b>Dodecyl</b>                  | 131                              | 168            | 173              |
| <b>Tetradecyl</b>               | 124                              | 160            | 175              |
| <b>Hexadecyl</b>                | 118                              | 164            | 172              |

### 5.3.2 Series XI: 4-*n*-alkoxy-N-(5-(4''-nitrophenyl)-1', 3', 4'-thiadiazol-2-yl)-benzamides

General molecular structure of the series XI: 4-*n*-alkoxy-N-(5-(4''-nitrophenyl)-1', 3', 4'-thiadiazol-2-yl) benzamides



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

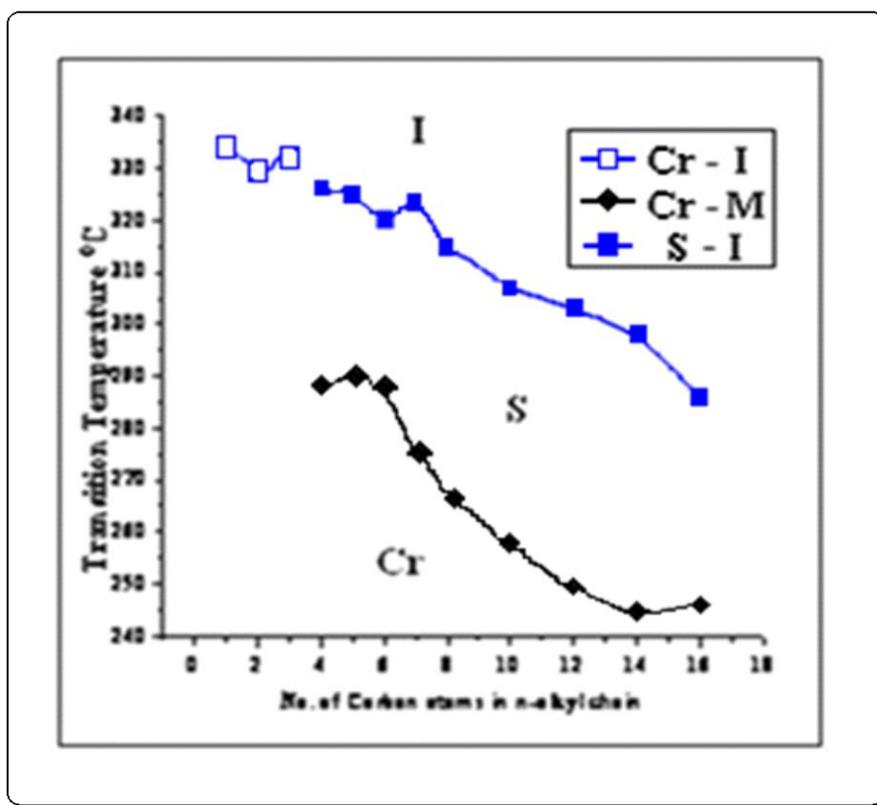


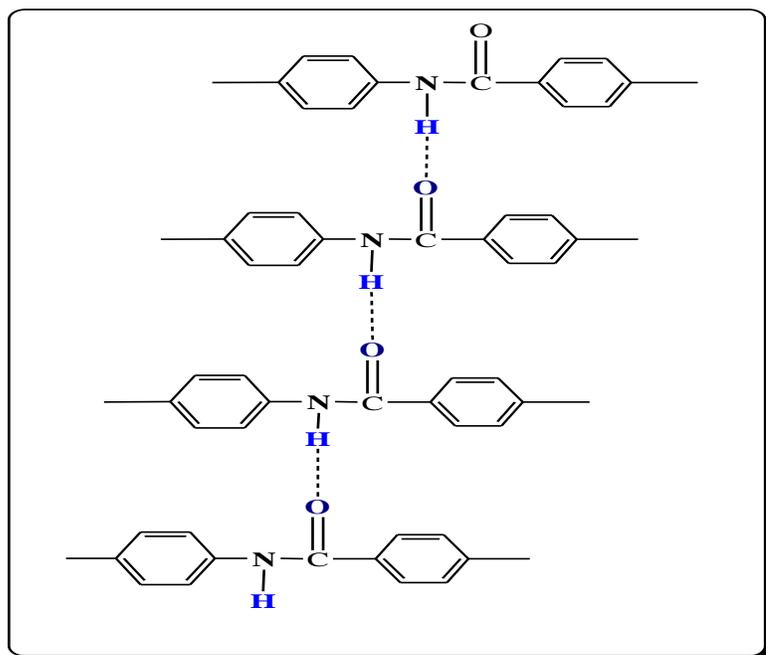
Figure 5.7: 4-*n*-alkoxy-N-(5-(4''-nitrophenyl)-1', 3', 4'-thiadiazol-2-yl) benzamide (Series XI)

In series XI mesogenic behavior commences in the form of smectic mesophase (Table: 5.5, Figure: 5.7); from the C4 homologue without exhibition of nematic mesophase in any homologue and remains upto the last C16 derivative synthesized, Figure 5.7 shows the plot of transition temperatures against number of carbon atoms in the *n*-alkoxy chain; it indicates that Cr-I curve shows zig-zag tendency between C1 & C3 homologue. The Cr – M curve shows initial rising tendency from C4 to C5 homologue and then a steep fall from C5 till C14 derivative and then rising by 2°C temperature at the last C16 derivative. The S – I curve remains parallel between C4 & C5 homologue then falls steadily from C5 homologue till the last C16 homologue

with a slight rise at C7 derivative. The smectic mesophase of the series shows Schlieren texture of smectic C variety.

**Table 5.5:** Transition Temperatures: Series XI: 4-*n*-alkoxy-N-(5-(4''-nitrophenyl)-1', 3', 4'-thiadiazol-2-yl) benzamides

| R = <i>n</i> -Alkyl group | Transition Temperature °C |           |
|---------------------------|---------------------------|-----------|
|                           | Smectic C                 | Isotropic |
| Methyl                    | --                        | 334       |
| Ethyl                     | --                        | 330       |
| Propyl                    | --                        | 332       |
| Butyl                     | 288                       | 325       |
| Pentyl                    | 290                       | 325       |
| Hexyl                     | 288                       | 320       |
| Heptyl                    | 275                       | 324       |
| Octyl                     | 268                       | 315       |
| Decyl                     | 257                       | 307       |
| Dodecyl                   | 249                       | 303       |
| Tetradecyl                | 244                       | 298       |
| Hexadecyl                 | 246                       | 286       |



**Figure 5.8:** Schematic representation of inter molecular Hydrogen bonding.

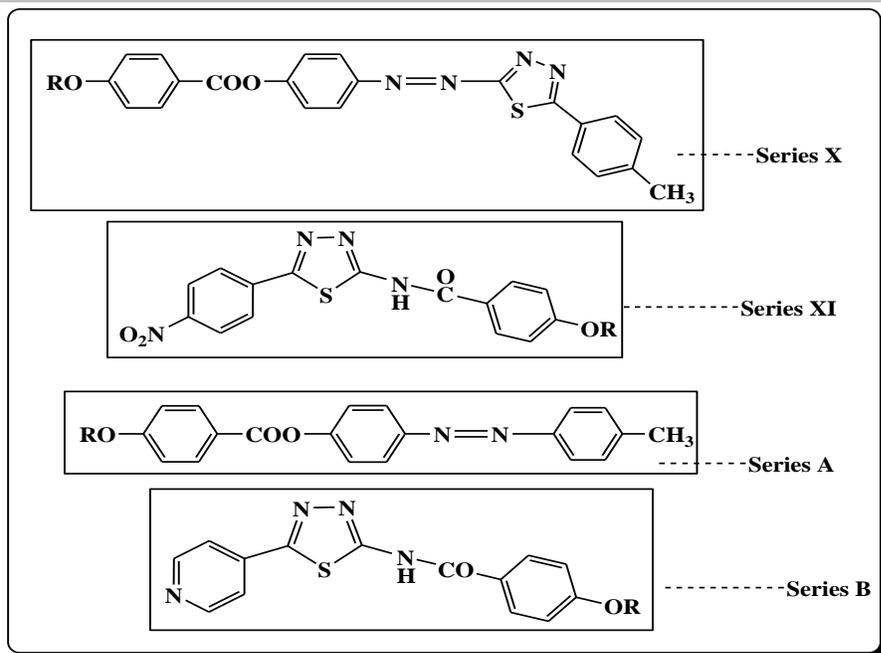


Figure 5.9: Molecular geometry of the homologous series under comparison

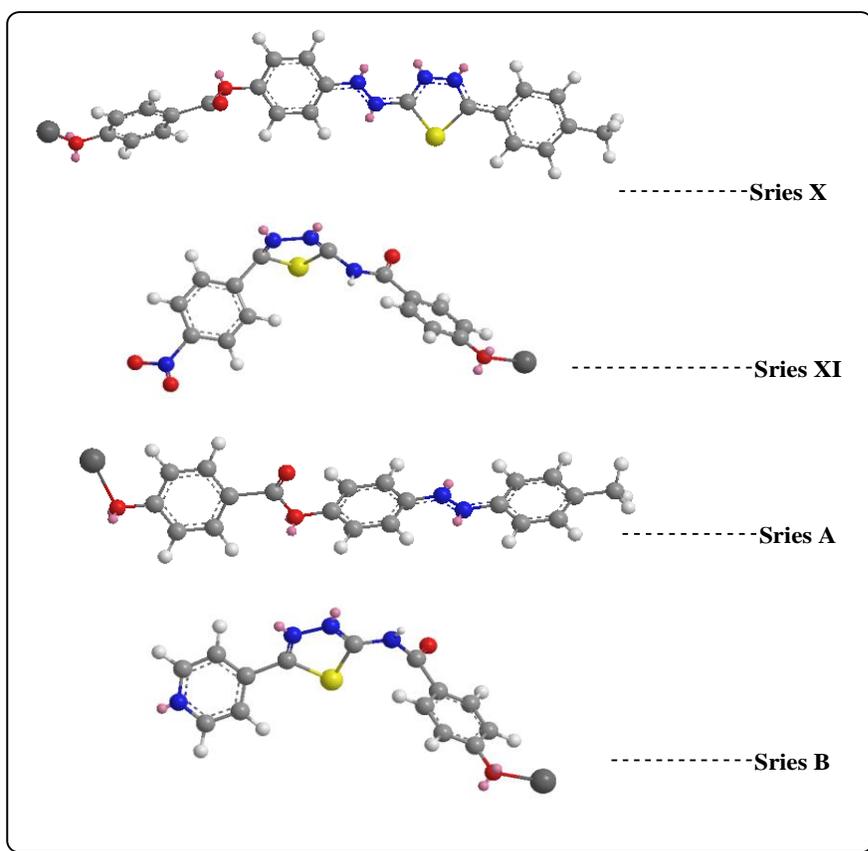


Figure 5.10: Energy minimized 3D Molecular geometry of the homologous series under comparison from ChemDraw Ultra 8.0 software.

The average thermal stabilities of the series are compared with structurally related homologous series (Table: 5.9, Figure: 5.9, 5.10 and 5.11) show the average thermal stabilities for the homologous series. Figure 5.8 shows inter molecular Hydrogen bonding of -CONH- bridging linkage. Figure 5.9 and 5.10 show general molecular geometry and energy minimized 3D molecular structures of the homologous series under comparison from ChemDraw ultra 8.0 software.

Table 5.9: Average thermal stabilities °C

| Series    | N-I               | S- N or S-I        | Commencement of Smectic mesophase |
|-----------|-------------------|--------------------|-----------------------------------|
| <b>X</b>  | 197.33<br>(C3-C8) | 162<br>(C10-C16)   | C10                               |
| <b>XI</b> | --                | 311.44<br>(C4-C16) | C4                                |
| <b>A</b>  | 242<br>(C1-C8)    | 106.5<br>(C10-C16) | C10                               |
| <b>B</b>  | --                | 252<br>(C5-C8)     | C6                                |

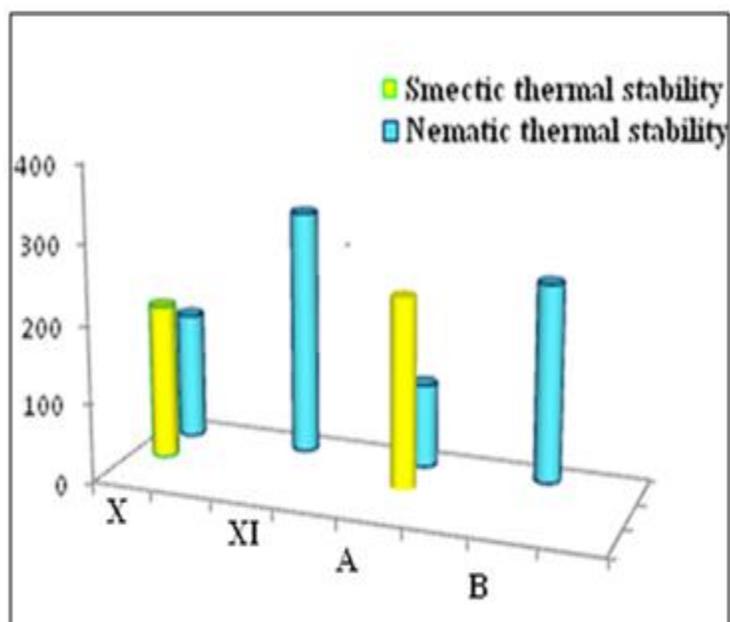


Figure 5.11: Average thermal stability (TS) for the homologous series under comparison

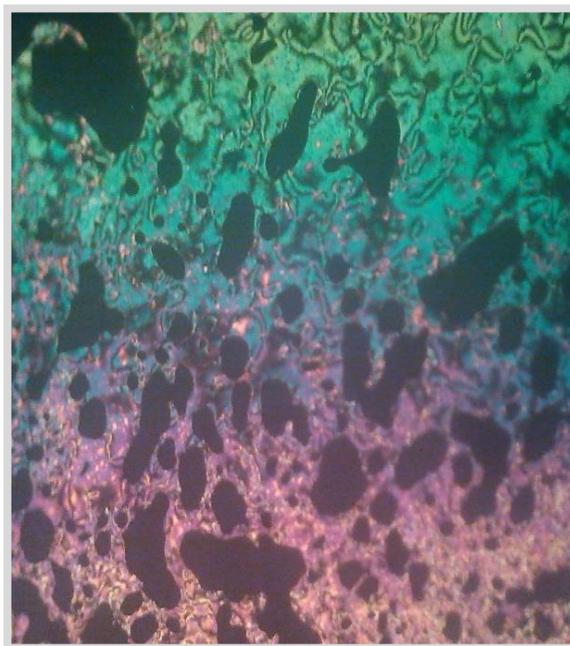
It is seen that the N – I thermal stability of the series A is higher than the series X however, S – N thermal stability of series X is higher than series A which may be due to bent shaped molecules of series X which shows rod shaped molecules have higher N – I thermal stability whereas bent shaped molecules, imparts more smectic thermal stability which corresponds to form more layers structures due to its bent shape. Bent molecules forces apart the long molecular axes of the molecules, thereby lowering the N-I stability. Addition of 1, 3, 4-thiadiazole core changes the molecular conformation and broadens the molecules which decreases the thermal stabilities. Hence, bent shaped molecules possesses more S-I thermal stabilities than

the N-I. The introduction of 1, 3, 4-thiadiazole ring makes the molecule bent by an angle of  $157^\circ$  which confirms the formation of bent core molecules.

Series XI compared with other structurally related series B, which could derive the important information about mesogenic behavior of the series. The absence of nematic phase in the entire series may be due to more lateral attraction caused by bent shaped molecules of series XI. The S – I thermal stability of series XI is also higher than structurally related series B; this may be due to the presence of nitro group as terminal substituent in series XI (409). Here in the series XI presence of nitro group possesses strong dipole acting along the long axes of the molecules yields the more smectogenic behavior [472] as well as amide linkage present in the molecule which forms inter molecular Hydrogen bonding (Figure 5.9) which results in to higher the clearing points and more S-I thermal stability for the Series XI [473, 474].

**Polarizing optical microscopic images of Liquid Crystals**

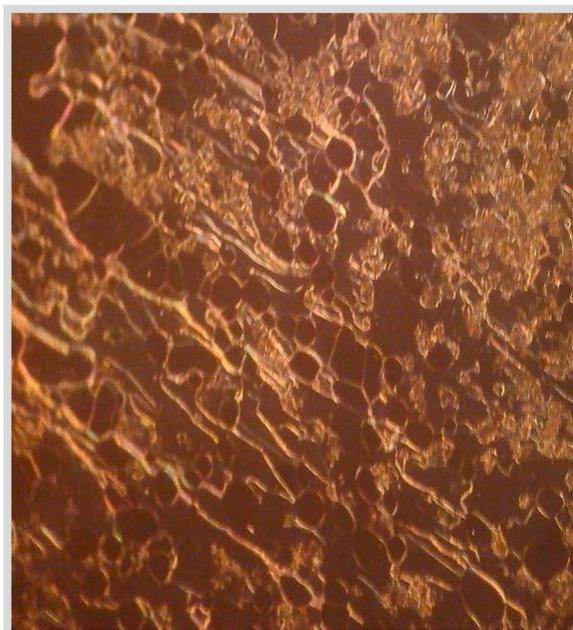
(a)



(b)

(a) Marble texture of nematic phase of C4 homologue of Series X at 168 °C on cooling.

(b) Schlieren texture of Smectic C phase of C14 homologue of Series X at 152 °C on cooling.



(a)



(b)

(a) Schlieren texture of Smectic C phase of C4 homologue of Series XI at 302 °C on cooling.

(b) Schlieren texture of Smectic C phase of C14 homologue of Series XI at 276 °C on cooling.