Synthesis, Characterization and mesomorphic properties of amide-linked Rod-Shaped Liquid Crystals

Synthesis, Spectroscopic Characterization, and Phase Transition Analysis

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***Abstract*—Rod shaped liquid crystalline compounds were synthesized with the aim to explore the impact of amide linkage on mesophase behaviour. The conventional condensation methods were employed to prepare chromane and (S)-naproxen cores substituted with fluorine. Various spectroscopic methods and mass spectrometry was employed for structural elucidation. Polarised optical microscopy suggested the formation of enantiotropic Smectic-A phases and chiral Smectic-C* phases from chromane-based and naproxen-based moieties, respectively. Results unveil that mesophase architecture can be finely tuned altering the molecular core and amide linkage. It offers new routes for the development of advanced functional liquid crystalline compounds.**

***Index Terms*—Amide-linked liquid crystals, Rod-shaped mesogens, Mesophase characterization, Smectic-A phase, Chiral Smectic-C phase**

I. INTRODUCTION

A very large number of chemical compounds are known to exhibit one or several liquid crystalline phases. Despite significant differences in chemical compositions, these molecules have some common features in chemical and physical properties. These are two types of thermotropic LCS: discotic and rod-shaped molecules. Discotic are flat disc-like molecules consisting of a core of adjacent aromatic rings. This allows for two-dimensional columnar ordering. Road shaped molecules have an elongated, anisotropic geometry which allows for preferential alignment along one spatial direction. The structure/ mesomorphic property relationship is a most attractive study area of the chemist devoted to liquid crystal research. Within the classical calamitic structure some functional groups have proven to be very useful to promote mesomorphic properties. For example, the 'ester' group is one of the most used as a central bringing units and is incorporated in many temperatures system [1]. The mesomorphic behavior of an organic compound is basically dependent on its molecular architecture in which a slight change in the molecular geometry bring about considerable change in its mesomorphic properties. Nevertheless, the vast range of synthetic possibilities in organic chemistry means a verity of structure remain relatively unstudied. The number of mesogenic homologous series have been reported that have –COO-(ester), -CH=N- (azomethine), -N=N-(azo), -CH=CH- (ethylinic), -CH=CH-COO-(cinnamatic) –C≡C – (acetylinic) etc. as their central linkages.

Liquid crystalline behavior has been observed mainly in two types of molecules: linear or road like molecules that form calamitic phases and disc like molecules that form discotic phases. The structure of liquid crystalline phase is characterized by the arrangement of the molecules, the conformation of the molecules and the inter-molecular interactions. The transition between the various liquid crystal mesophase from crystalline to smectic to nematic occurs at definite temperatures which can be detected using differential scanning calorimeter (DSC), while the nature and texture of the mesophase is normally investigated using polarized optical microscopy. The scenario involving phase transitions requires, as the first step, the breakdown of the molecules packing order under influence of an external heating source causing oscillation or rapid rotation about the long axis of the molecules to give a smectic –like crystal phase. Next the long-range positional order is lost resulting in a smectic liquid crystal mesophase. Next the local packing order is destroyed but the orientational order remains with the molecules reorganizing so that their long axis lie in the same direction producing the nematic phase. Finally, all order is lost forming an isotropic liquid [2].

Calamitic liquid crystal are characterized by their elongated rod-like shape, and composed of three main structural elements, rigid ring systems, connective linking groups, and flexible terminal groups, many times lateral substituents are also present.

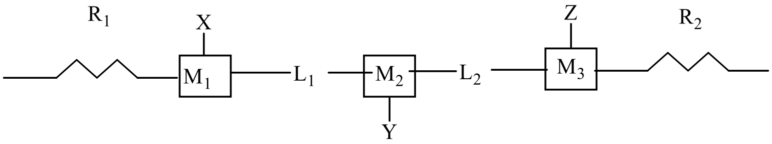


Figure (1)

Figure (1) Model represents typical features of calamitic liquid crystals, where M_1, M_2, M_3 are rigid ring system, L_1 and L_2 are linking group as shown earlier R_1 and R_2 are terminal groups and X, Y and Z are laterally substituted groups. Here, R_1 and R_2 are terminal group generally they are alkyl or alkoxy long chain, M_1, M_2 and M_3 are ring systems and usually two to four of these units are present, they could be identical or different groups and finally, L representing linking group [3]. A wide range of lateral substituent (e.g. F, CI, CN, NO_2, CH_3, CF_3) have been incorporated in to many liquid crystal's structure, a lateral substituent is one that is attached to the linear axis of the molecules, usually on the side of an aromatic core or even alicyclic moieties. The presence of the lateral substituent leads to disruption of molecules packing and therefore, reduces liquid crystalline phase stability. This disruption of molecules packing is particularly advantageous for the mesomorphic and physical properties required for specific applications. In general dimension of the cleaning point expressed as TM-I by a lateral substituent is directly proportional to the substituent size, irrespective of its polarity [3].

Polarized light microscopy is commonly used to identify the texture of liquid crystalline mesophases. The textures are pictures that are observed microscopically under polarized light and characterized by detecting the phase structure by the surrounding glass slides and cover slip (surface phenomena). Therefore, several different textures can be observed for a given structure depending on the conditions of sample preparation [4]. For example, an isotropic liquid will be dark under crossed polarizers, while birefrigent liquid crystal exhibit interference colors. A thin sample of the nematic phase when viewed under polarizing microscopy, is often seen optically extinct and appears dark. However, there may be small areas of a birefringent texture with dark (optically extinct) thread like defects, if the samples is thick. Displacement of cover ship (shearing) includes homogeneous (planar) alignment, producing a temporary birefrigent flash. On heating the sample homogeneous alignment is often induced close to the clearing point. It is at this point that the phase appears most colourful (schlieren textures) and a thin sample looks particularly sharp and is readily imaged [3,5]. When cooling an isotropic liquid, birefringent droplets appear against a dark back ground as the nematic phase is generated. In thick samples, these droplets coalesce to give a schlieren texture that may contain the thread-like defects. On cooling, the nematic phase appears from the isotropic liquid and so the texture that results are called a natural texture.

Calamatic liquid crystal based on p-alkoxy benzoic acid were investigated earlier for their liquid crystalline properties [6,7], and recently gained increased interest for the design of many liquid crystalline compounds. Demus et al. were among the first researchers to use calamitic liquid crystal for practical applications in the LCD industry [8,11]. However, the terminal end of the compounds was unfunctionalized linear aliphatic chains. On the other hand, alkoxy benzoate monomers are a functionalized version of alkoxy benzoate, a construct that also gained special attention in the design of functionalized liquid crystalline materials [12-16]. Sledzinska et al. [17] reported the evidence of the smectic antiphase Č in 4-decyloxy biphenyl ester imide derivatives. The series of liquid crystalline 4-[(4'-decyloxybiphenyl-4-yl] oxycarbonyl] phthalimide alkane acid methyl ester has been synthesized and studied by DSC, Polorised optical microscopy and X-ray diffraction methods. All compounds form a monolayer smectic A phase. It was also found that two compounds of the series form a ribbon Sc phase.

II. EXPERIMENTAL SECTION

Materials: 2-Naphthol, liquid bromine, dichloromethane (DCM), sodium bisulfite, methyl chloride, acrylic acid, bromochloromagnesium, N-octyl-glucamine, isopropanol, *p*-fluorophenol, anhydrous $AlClO_3$, acetyl chloride, diethyl oxalate, sodium methoxide. All the reagents and chemicals used in this study were of reagent grade and purchase from Merk, Acros Organic, Sigma Aldrich. Solvents were dried by standard techniques and distilled prior to use other chemicals were used as received.

Measurements

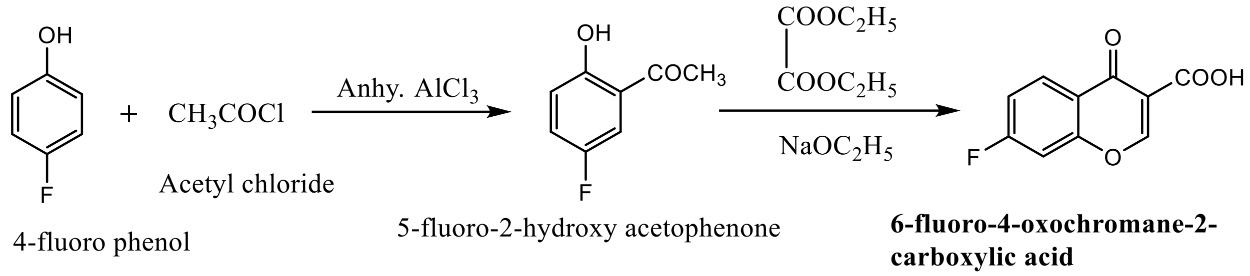
The C,H, and N contents of selected mesogenic samples was estimated by G.N.F.C. (Gujarat Narmda Valley Fertilizer Company Ltd., Bharuch). Infrared spectra were recorded with a THERMO SCIENTIFIC NICOLET iSO-10 spectrophotometer in the frequency range 4000–400 cm−1 with samples embedded in KBr discs at our department. High resolution (400 MHz) NMR spectra of the mesogenic compounds were recorded at room temperature as 15%–20% solution in CDCl3 using TMS as internal standard on a BRUKER AVANCE II 400 NMR spectrometer at SAIF (Sophisticated Analytical Instrument Facilities), Panjab University, Chandigarh. Mass spectra (TOFMSES+) of the compounds were recorded using Finnegan MAT-8230 Mass Spectrometer at SAIF (Sophisticated Analytical Instrument Facilities), Panjab University, Chandigarh. Thin-layer chromatography (TLC) analyses were performed using aluminium-backed silica-gel plates (Merck60 F524) and examined under shortwave UV light. Thermal (DSC) analyses of the liquid crystalline compounds were carried out from Atul Industries Ltd. P-P site Atul. DSC analyses were performed on METTELER M-3 thermo balance (Switzerland) with microprocessor TA-300 instrument at a heating rate of 10◦C/min in N2 atmosphere. The optical microscopy studies were determined by using polarizing microscope NICON ECLIPSE 50i POL (Japan) equipped with Linkam Analysa-LTS420 hot stage (London) at our department. The textures of the compounds were observed using polarized light with crossed polarizers with the sample in a thin film sandwiched between a glass slide and cover slip.

Synthesis

Synthesis of 6-fluoro-4-oxochromane-2-carboxylic acid:

6-fluoro-4-oxochromane-2-carboxylic acid was synthesized as reported method [18]. In a round bottom flask, fitted with stirrer 4-fluoro phenol (50 g, 0.446 mole) was added to acetyl chloride (52.58 g, 0.669 mol) with stirring at 25-30 °C. The reaction mass was heated to 60 °C and add $AlCl_3$ (114.1g, 0.893mol) in portion wise in about 1 h. The resulting mixture was heated to 130 °C for 2 h. After monitoring by TLC. The thick syrupy mass added to precooled water (250 mL), white solid precipitates to 5-fluoro-2-hydroxy-acetophenone (61.9 g, 90%) obtained now prepared solution of sodium ethoxide (127.59g, 1.88 mol) in ethanol (800 mL) were added above acetophenone (60 g, 0.389 mol) and diethyloxalate (147.9 g, 1.013 mol) at 25 to 30 °C. The resulting mix was refluxed for 2hrs and monitored reaction with TLC. Then Reaction mixture was concentrated under vacuum at below 50°C resulted mass diluted with methylene dichloride (300 mL) and DM water (900 mL) then acidified with HCl. Layers were separated out, aqueous phase extracted with MDC (2x300 mL) combined organic layer washed with DM water (250 mL) the Methylene dichloride was recovered from organic layer by vacuum distillation resulted residue was dissolved in ethanol (400 mL) added HCl (210 mL) stirred for 15 h, monitored reaction with TLC, for complete consumed starting materiel. Then reaction mixture completely concentrated under vacuum distillation below (35 °C). Then resulted residue was mixed with water 300 mL and Methylene dichloride (150mL below 35°C). The organic layer was separated and washed with aq. $NaHCO_3$ solution followed by water (120 mL). The organic phase was concentrated at below 35 °C to afford a white solid (68.61g, 74%) i.e 6-fluoro-4-oxo-chromane-2-carboxylic acid. This ester was hydrolysed by (1:10) NaOH solution to get title compound.

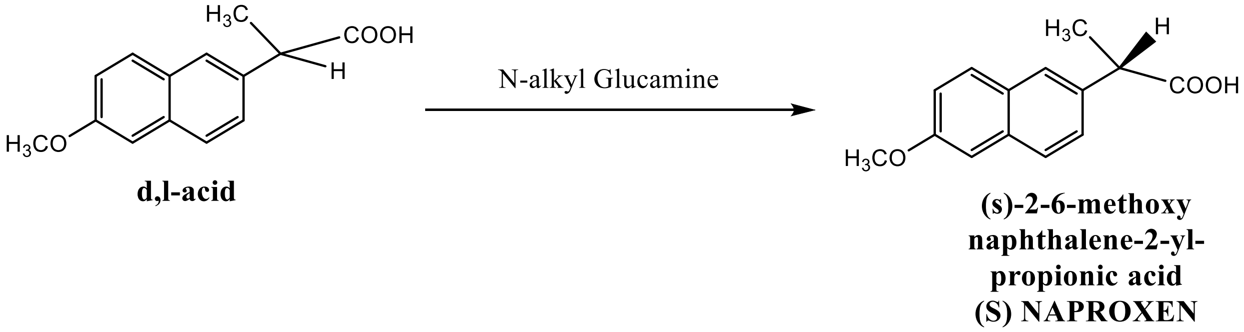
Preparation of 6-fluoro-3-4dihydro 2H-cromene-2-carboxylic acid



Synthesis of s-naproxen

S-naproxen has been prepared as described by Holton & Amold Meth. As per scheme shown above β-naphthol was brominated in methylene chloride to produce 1,6-dibromonaphthol. The labile bromine at the 1st position was removed with bisulfite. The resulting 2-bromo -6-hydroxy naphthalene (BHN) was methylated with methyl chloride in water-propanol mixed solvent. The yield of 2-bromo-6-methoxy naphthalene (BMN) was 85.90% from B-naphthol. BMN was converted to a Grignard reagent which was trans metalated with zinc chloride and then the naphthyl zinc chloride and then naphthyl zinc coupled with ethyl bromo propionate. Hydrolysis of the ester yielded d,l-acid. The yield from BMN to d,l-acid was 50-60%. Again, resolution with N-alkyl glucamine was highly efficient up to >95%. In a round bottom flask (0.01 mol) β-naphthol dissolved in 50 mL methylene chloride, liquid bromine (0.02 mol) add dropwise in to RBF containing β-naphthol with stirring at room temp to produce 1,6-dibromo naphthol. This 1, 6-dibromonaphtaol (0.01 mol) and $NaHSO_3$ (0.01 mol) dissolved in alcohol and reflux the reaction mixture for an hour to obtain BHN. Then, 2-bromo-6-hydroxynaphthol (BHN) (0.01mol) and methyl chloride (0.02mol) dissolved in waler-2-propanol (1:1) mixed solvent and relaxed for 2-3 hours to obtain BMN. This, 2-bromo-6-methoxy naphthol (BMN) (0.01mol) and Grignard reagent Mg, $CH_3C(Br)C$-=OOMgCl (0.01mol) dissolved in alcohol and refluxed the reaction mixture for 2-4hrs, this product was hydrolysed to produce d, l-acid. This d, l-acid was reacted with N-alkyl glucamide in equimolar proportion in alcohol and reflux it for 5 to 6 hrs. The final product was filtered off and washed it by distilled water dried it. The final compound is S-Naproxen with >95 % yield.

Synthetic route:



Synthesis of 4-n-alkoxyaniline

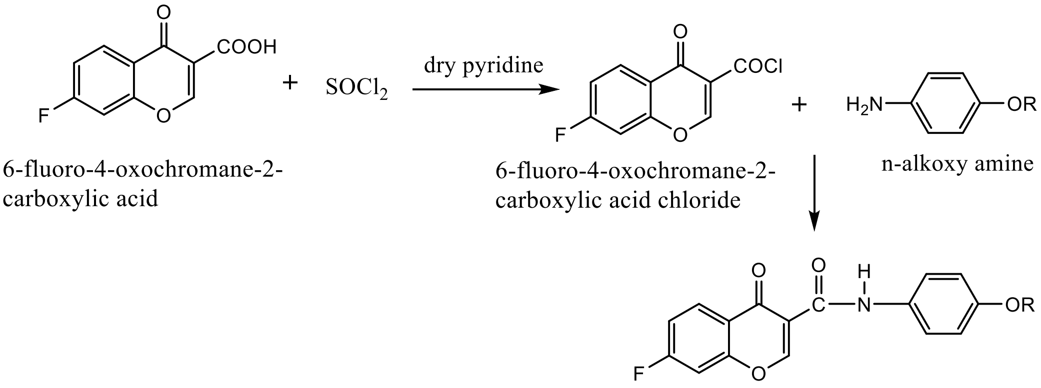
Mixture of appropriate 4-n- alkoxy acetamide (0.146 mol) water (70 mL) and concentrated hydrochloride acid (45 mL) were stirred for 10 to 12 hrs. at 90-95 °C and then cooled to room temperature. The mixture was made alkaline with 50% NaOH at 20°C. The oily product (for the lower member C_1 to C_8) was extracted with ether. The ether extract was dried and concentrated at reduced pressure to give an oil which was purified by distillation. The higher members (10 to 18) separated as solid and were filtered direct without ether extraction. The boiling points and melting points of all the alkoxy anilines agree well with the values reported in the literature.

(a) The 6-fluoro _4_oxo chromane -2- carboxylic acid chlorides were synthesized by methods described in literature [19, 20].
(b) (s) -2-6-methoxy naphthalene -2-yl-propionic acid chlorides were also synthesized by methods described in literature [19, 20].

Synthesis of N-[2-(4-alkoxy phenyl)-2-oxo-ehtyl] -7-fluoro oxo-2-chromane carboxamide [Series-A]
Synthesis of (S) –N-(4-(alkoxy phenyl)-2-(4-methoxy phenyl) carboxamide [series-B]

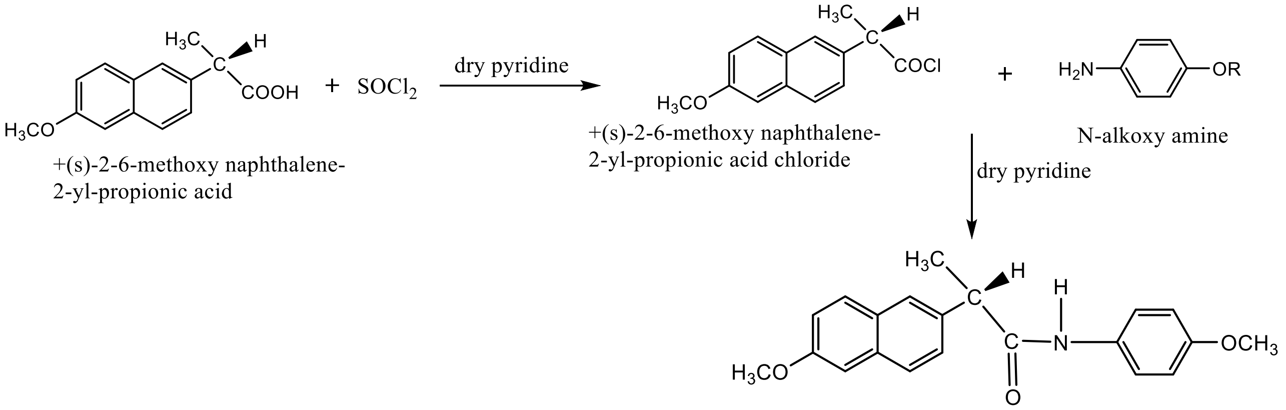
Respective acid chlorides (a) & (b) (0.01mol) were dissolved in 5 mL of dry pyridine. A solution of 4-n- alkoxy aniline (0.01mol) in 10 mL of dry pyridine was added slowly to a cold solution of the above acid chlorides. The reaction mixture was heated on a water bath for about half an hour and was allowed to stand overnight. It was acidified with cold 1:1 hydrochloric acid. Precipitates were filtered and washed with water followed by with diluted sodium hydroxide solution and water. The resulting amide compounds were recrystallized several times from DMF until constant transition temperatures were obtained. The yield of the purified compound between 65 to 70 %. The elemental analysis of all compounds gave satisfactory results.

Synthetic route: Series-A



N-[2-(4-alkoxy phenyl)-2-oxo-ethyl]-7-fluoro oxo-2-chromane carboxamide

Synthetic route: Series-B



(S)-N-[4-(alkoxy phenyl)-2-(4-methoxy phenyl)] carboxamide

Analytical Data:

N–[2—(4- dodecyl phenyl) -2- oxoethyl]-7- fluorooxo-2-chromane carboxamide (Series-A)
Molecular formula: $C_{28}H_{34}O_4NF$ yield :75% clearing point 156°C UV Visible ($CHCl_3$) t max 380-400 nm
Elemental analysis data: C:71.95 %, H: 7.28 5, N: 2.99 % Found: C: 72.05 %, H: 7.35 5, N: 3.01 %
FT-IR (KBr) : ν max/cm^{-1}- 3600-3400 (broad) intermolecular H bonding 3337-3331 (n-H stretching of amide gr) 3040 cm^{-1} (C-H starching aromatic), 3934 and 2868 cm^{-1} (C-H starching aliphatic) 1697, and 1657 cm^{-1} (ring C=O and C=O amide group), 1511 cm^{-1} (C=C starching aromatic) 1621 cm^{-1} (C=NH- bending) 1420 cm^{-1} (C-O stretching) ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87-0.92 (ppm) (t, CH_3 of aliphatic chain), δ 1.28-1.73ppm (m, CH_2 of aliphatic chain), δ 3.92-3.95 ppm (t, O-CH_2 of n alkoxy chain) δ 6.71-7.84 ppm (m, phenyl multiplate), δ 8.2 ppm (s, C=O-N-H- amide group) ^{13}CNMR (400 MHz, $CDCl_3$) δ13.80 ppm (CH_3 of aliphatic chain) δ 21.91-40.15 ppm (CH_2 of aliphatic chain) δ 67.54 ppm (-O-CH_2 carbon of alkoxy attached with phenyl ring) δ 110.71-157.77 ppm (C of substituted phenyl ring), δ 170.47 ppm and 189.07 ppm (due to C=O of amide and C=O of ring, respectively).

Analytical Data:
(S)-N-(4-(alkoxy phenyl)-2-(4-methoxy phenyl) carboxamide [series-B]
Molecular formula: $C_{30}H_{39}O_3N$ yield: 75% clearing point 136 °C UV Visible ($CHCl_3$) t max 380-400 nm
Elemental analysis data: C:78.09 %, H: 8.45, N: 3.03 % Found: C: 78.02 %, H: 8.25, N: 3.06 %

FT-IR (KBr) : ν max/cm^{-1}- 3625-3200 (broad) intermolecular H bonding 3207-3214 (n-H stretching of amide gr) 3005 cm^{-1} (C-H starching aromatic), 2975 and 2869 cm^{-1} (C-H starching aliphatic) 1683 and 1631 cm^{-1} (ring C=O and C=O amide group), 1518 cm^{-1} (C=C starching aromatic) 1395 cm^{-1} (C-O stretching), 1208, 1024 cm^{-1} (-C-O-C, symmetrical, asymmetrical), ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.860-0.890 (ppm) (t, CH_3 of aliphatic chain), δ 1.237 ppm (m, CH_2 of aliphatic chain), δ 1.307-1.714 ppm (t, -CH_2 of n alkoxy chain), 4.018-4.035 ppm (t, -OCH_2, phenyl ring) 3.874-3.845 (s, O-CH_3 of naphthalene) δ 6.76-7.80 ppm (m, phenyl multiplate), δ 10.74 ppm (s, C=O-N-H- amide group) ^{13}CNMR (400 MHz, $CDCl_3$) δ 13.80 ppm (CH_3 of aliphatic chain) δ 27.68-40.14 ppm (CH_2 of aliphatic chain) δ 67.47 ppm (-O-CH_2 carbon of alkoxy attached with phenyl ring) δ 105.00-157.00 ppm (C of substituted phenyl ring), δ 171.88 ppm and 189.00 ppm (due to C=O of amide and C=O of ring respectively).

FT- IR SPECTRAL STUDIES

The FT- IR spectra of the series-A and series –B that exhibit different vibrational modes corresponding to stretching and bending of different functional groups present in the molecule. The FT-IR spectra of representative compound (A6, A14) and (B5, B14) are shown in Figure (1) and Figure (2).

In the present series-A liquid crystal compound exhibit -NH stretching of secondary amide at 3377cm^{-1}, 3331cm^{-1}, as a medium and slightly broad band observed from 3600 cm^{-1} to 3400 cm^{-1} which indicates the intermolecular hydrogen bonding in such compounds. There are two sharp band observed at 1697 cm^{-1} and 1657 cm^{-1} may be due to ring C=O and C=O of the amide group. The -C=NH- bending mode of vibration appears at 1621 cm^{-1}. The band observed at 1406 cm^{-1} corresponding to C-O group.

The asymmetrical and symmetrical stretching of –CH group observed at 2934 cm^{-1} 2868 cm^{-1} respectively. The sharp and medium band observed at 1511 cm due to aromatic V(C=C) stretching.

In the present Series- B liquid crystalline compound broad band start to appear from 3625 cm^{-1} up to 3100 cm^{-1} may be due to H-bonding present in the molecule. The band observed at 3207 cm^{-1} due to –N-H stretching made of amide group. The weak band offer at 3005 cm^{-1}due to aromatic –C-H stretching while band observed between 2975-2938 cm^{-1} and 2851, 2869 cm^{-1} due to aliphatic symmetrical and asymmetrical –C-H stretching bending. The weak band observed at 1630 cm^{-1} may be due to -N-H- banding mode. The –C=O amide group stretching bending observed at 1604 cm^{-1} showing very sharp band. The medium band appear at 1518-1505 cm^{-} due to restricting of aromatic (C=C) group. The sharp band observed at 1395,1391 cm^{-1}may be attributed to –C-O group. Another two bands also observed at 1228-1236 $cm^{-1}$and 1028-1029 cm^{-1} are due to (C-O-C) symmetrical and asymmetrical stretching respectively. The medium band appear at around 825 cm^{-1} is due to rocking vibration of –CH_2- group of alkyl chain. Out of plane deformation of ring hydrogen bond is establishing the position of substituted aromatic nuclei is well known. Although correlation can often be useful in analysis of spectra of the liquid crystalline compound but their performance is variable.

Infrared spectra of the present class of the compounds often shows long wave length regions crowded with many bands of similar intensities, and it is difficult to know which band belongs to this class.

^{1}H NMR study

The ^{1}H-NMR spectra of series A exhibit sharp triplet observed at δ 0.87-0.92 (ppm) is assigned to terminal methyl proton of alkoxy chain. The signals at δ1.28-1.73 in the form of multiplate are observed due to methylene -$(CH_2)_n$-proton of straight alkyl chain of alkoxy group. The large intense singlet at δ 3.83-3.86 ppm). Are observed due to methylene –(-CH_2) n- proton of straight alkyl chain of alkoxy group. The signal around δ 3.92-3.95 (ppm) in triplet is attributed to -O-CH_2-proton of-n-alkoxy group attached to benzene ring. Two doublet signals observed at δ 6.71-6.72, and δ 6.80-6.83 (ppm) appear due to (2H-O and 2H-m) protons of phenyl ring. The signal at δ 7.10-7.12 ppm (d-1H) and other at δ 7.39-7.42 (q-1H) phenyl proton when F atom is present. The signal at 7.82-7.84 (d, 1H) of p-position of phenyl ring near F-atom which is doublet due to ^{19}F (I=1/2). The signal at δ 8.2 ppm (s -1H) may be due to –N-H proton of amide group (-C=O-N-H). The ^{1}H NMR spectra of starting compound (S)- NAPROXEN exhibit a signal at δ 1.461-1.479 ppm as doublet is assigned to the –CH_3 proton attached to chiral carbon. Another signal appeared at δ 3.756-3.809 ppm as quartet is attributed to –C-H proton of chiral carbon. The δ 3.874 ppm signal is observed due to O-CH_3 proton of naphthyl ring. The signal between δ 7.109-7.761 (ppm) due to 6- proton (at o, m, p) of naphthyl ring. The –OH proton of carboxylic acid observed at δ 12.308 ppm as low intense broad band.

The ^{1}H-NMR spectra of amide liquid crystalline compound exhibit a signal at δ 0.862-0.890 as (t, CH_3) of alkoxy chain. The signal observed at δ 1.237 ppm due to –CH_3 proton linked at chiral carbon of NAPROXEN moiety. The multiplate signal observed between δ 1.307-1.714 ppm due to –$(CH_2)_4$- methylene protons of alkoxy chain. The –C-H proton of chiral carbon observed as less intense quartet signal at δ 3.768-3.810 ppm. The O-CH_3 proton of naphthyl ring appeared its intense singlet signal at δ 3.845 ppm whereas –O-CH_2 proton resonate at δ 4.018-4.035 ppm which are attached to phenyl ring. The six- naphthyl ring protons give the signal between δ 6.763-7.804 ppm as a multiple. The carboxylic acid proton converted in to acid chloride and then carbonyl amide –C=O-N-H, this –NH- proton appears as singlet at δ 10.074 ppm, indicating acid chloride converted in to amide.

^{13}C-NMR study:

The ^{13}C-NMR spectra of Series-A compounds (A6 and A14) exhibit δ 13.80 ppm is assigned to terminal methyl carbon of alkoxy chain. The signals at δ 21.90-40.15 ppm corresponding to different -CH_2- carbon of alkoxy chain. The signal at δ 67.54ppm is attributed –O-CH_2- carbon of n–alkoxy group attached to benzene ring. The signals observed in all compounds between δ 110.71-157.77 ppm are due to substituted phenyl ring carbon. The signals at δ 170.47 ppm and δ189.07 ppm are due to the (-C=O) group of amide linkage and ring C=O respectively.

The ^{13}C- NMR spectra of Series -B compounds (B5 and B14) exhibit δ 13.18 ppm and δ 18.33 ppm corresponding to –CH_3 carbon of alkoxy chain and –CH_3 group attached to chiral carbon atom respectively. The signals observed δ 23.68 ppm is assigned to -C-H carbon known as chiral carbon. The signals observed between δ 27.68-40.14 ppm are due to –$(CH_2)_n$- methylene group of alkoxy chain. The signal appeared at δ 54.93 ppm is assigned to O-CH_3 group attached to naphthyl ring. Whereas O-CH_2 gives the signal at δ 67.47 ppm. The naphthyl carbon give signals between δ 105-157.06 ppm. The carbonyl carbon (C=O) of amide group shows signal at δ 171.88 ppm.

Mass Spectroscopy:

The mass spectrum of the compound A-12 & A-16 of series A are shown in Figure (a, b) which give molecular ion peak at m/z = 466 (m) (4.12) and m/z = 522 $(m-1)^{+}$ (A-16). The mass spectrum of the compound is shown in Figure- (a, b) which gives molecular ion peak at m/z =489 $(m)^{+}$ (B-12) and 517.2 $(m)^{+}$ (B-14). The m/z ratios obtained from the spectra of representative samples are matched with their molecular ion peak.

UV/Visible Spectra study:

The liquid crystalline compounds of series A and B synthesized in present work are slightly colored and therefore, they are subjected for electronic spectral study to know which type of transitions occur in these compounds. Electronic spectra of all compounds were taken in solution state having 10^{-5}M concentration using $CHCl_3$ as solvent.

The band observed in all compounds above 350,370,390 and broad band observed at nearly 400 nm. These may be assigned to $\pi \rightarrow \pi$ * transition having high absorption intensity. The low intense band is not observed, that is due to $n \rightarrow \pi$ * transition which forbidden due to symmetry consideration. The 400 nm broad band may be due to amide linkage showing tail up to visible region.

Thermal and Phase behavior:

The melting points and transition temperature of the compounds of series A given in Table-1 and Table-2 and series B are given in Table-3 and Table-4 respectively. Optical microscopy reveals that series A compound exhibits enantiotropic smectic-A phase (A1, A2, A3, A4, A5, A6, A7, A8, A9, A10) homologous compound. The plot of transition temperature verses the no of carbon atoms in the alkoxy chain Figure (7) exhibits no odd-even effect for any type of transition temperature. The transition temperature of sm-A phase decreased as the series was ascended. This was due to the fact that an increase in number of (-CH_2-) methylene groups in the alkoxy straight chain i.e. called dilution effect.

In this series-B all the ten-compound exhibit enantiotropic smectic-C mesophase. The plot of transition temperature versus the no. of carbon atoms in the alkoxy chain Figure (8) exhibit falling tendency in Cr-Sm-C and SmC-I transition temperature, no odd-even effect could be seen in these types of transition temperatures. DSC is a valuable method for the detection of phase transitions. It gives quantitative results; therefore, we may draw the conclusions concerning the nature of the phases that occurring.

In this study the series-A is completely different than series–B with respect to structure point of view. Only similar is amide linkage and alkoxy –anilide moiety. Inspite of that the thermal stability of both the series is that the thermal stability of both the series is almost same. The isotropic temperature of series–B is slightly higher than that of series–A, this is because of naphthyl moiety is stable than fluoro substituted-2-chromane derivatives.

Table 1: Transition temperature data of N-[2-(4-butoxyphenyl)-2oxoethyl]-7fluoro oxo-2-chromanecarboxamide

Comp. No.	$R=C_nH_{2n+1}$ n =	Sm-A	I
A_1	2	116	156
A_2	4	114	148
A_3	5	112	144
A_4	6	108	140
A_5	8	105	130
A_6	10	101	124
A_7	12	98	120
A_8	14	90	118
A_9	16	86	114
A_{10}	18	83	110

Table 2: The transition temperature (C) of representative compounds from DSC

Code No.	Compound $R=CnH_{2n+1}$ n =	Phase behavior	Remarks
A2	04	$\mathrm{Cr} \xrightarrow{110.0} \mathrm{SmA} \xrightarrow{158.0} \mathrm{I}$ $\mathrm{Cr} \xleftarrow[98.0]{} \mathrm{SmA} \xleftarrow[152.0]{} \mathrm{I}$	Heating Cooling
A6	08	$\mathrm{Cr} \xrightarrow{106.0} \mathrm{SmA} \xrightarrow{116.7} \mathrm{I}$	Heating
A9	16	$\mathrm{Cr} \xrightarrow{88.79} \mathrm{SmA} \xrightarrow{109.6} \mathrm{I}$ $\mathrm{Cr} \xleftarrow[64.11]{} \mathrm{SmA} \xleftarrow[87.19]{} \mathrm{I}$	Heating Cooling

Table 3: Transition temperature data of naproxin 4-alkoxy acid amide (II)

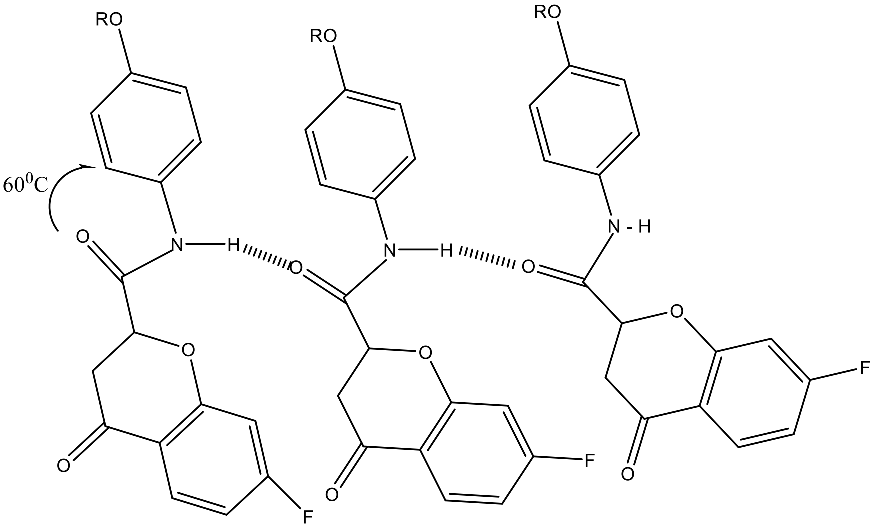
Comp. No.	$R=C_nH_{2n+1}$ n =	Sm-C*	I
B_1	2	119	155
B_2	4	113	153
B_3	5	111	151
B_4	6	112	148
B_5	8	110	140
B_6	10	109	136
B_7	12	107	135
B_8	14	105	138
B_9	16	100	130
B_{10}	18	100	129

Table 4 : The transition temperature (C) of representative compounds from DSC

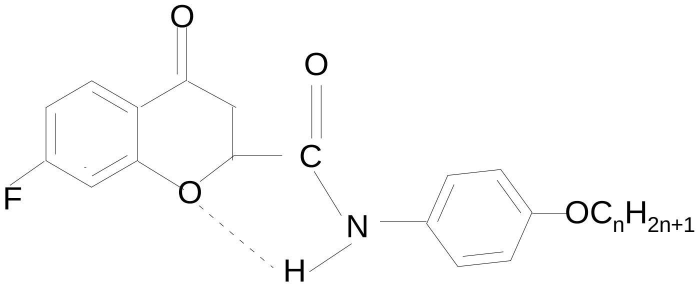
Code No.	Compound $R=C_nH_{2n+1}$ n=	Phase behavior	Remarks
B2	04	$Cr \xrightarrow{110.0} SmC \xrightarrow{160.0} I$ $Cr \xleftarrow[99.0]{} SmC \xleftarrow[140.0]{} I$	Heating Cooling
B5	08	$Cr \xrightarrow{118.0} SmC \xrightarrow{142.0} I$ $Cr \xleftarrow[115.0]{} SmC \xleftarrow[138.0]{} I$	Heating Cooling

Transition temperature data of naproxin 4-alkoxy acid amide (II) Series – II

The melting and clearing temperatures are descending in order as alkyl chain increases. Similarly, all compounds in Series-II (Naproxane series) exhibit mesomorphic properties. The thermal stability of Series-II is little bit higher than Series-I. In each case a Sm-C* (chiral smectic-C) mesomorphase is observed over a similar temperature range (33 °C) The melting and clearing temperature are showing falling tendency as alkyl chain increases. It is known that the most stable conformation of the amide group in benzanilide is the trans form [21]. In this conformation, the angle generated by the molecular axis and the direction of the N-H and C=O bond is about 60°. In the case that the tilt angle is about 30°, the amide groups in the layers are arranged linearly and the lateral intermolecular hydrogen bonding become strongest.



Schematic molecular modeling of benzanilide and the linearly arranged molecules using lateral hydrogen bonding. The formation of intramolecular H-bond could explain the low melting observed for the amide derivatives in Series-I compare to naproxine acid amide Series-II.



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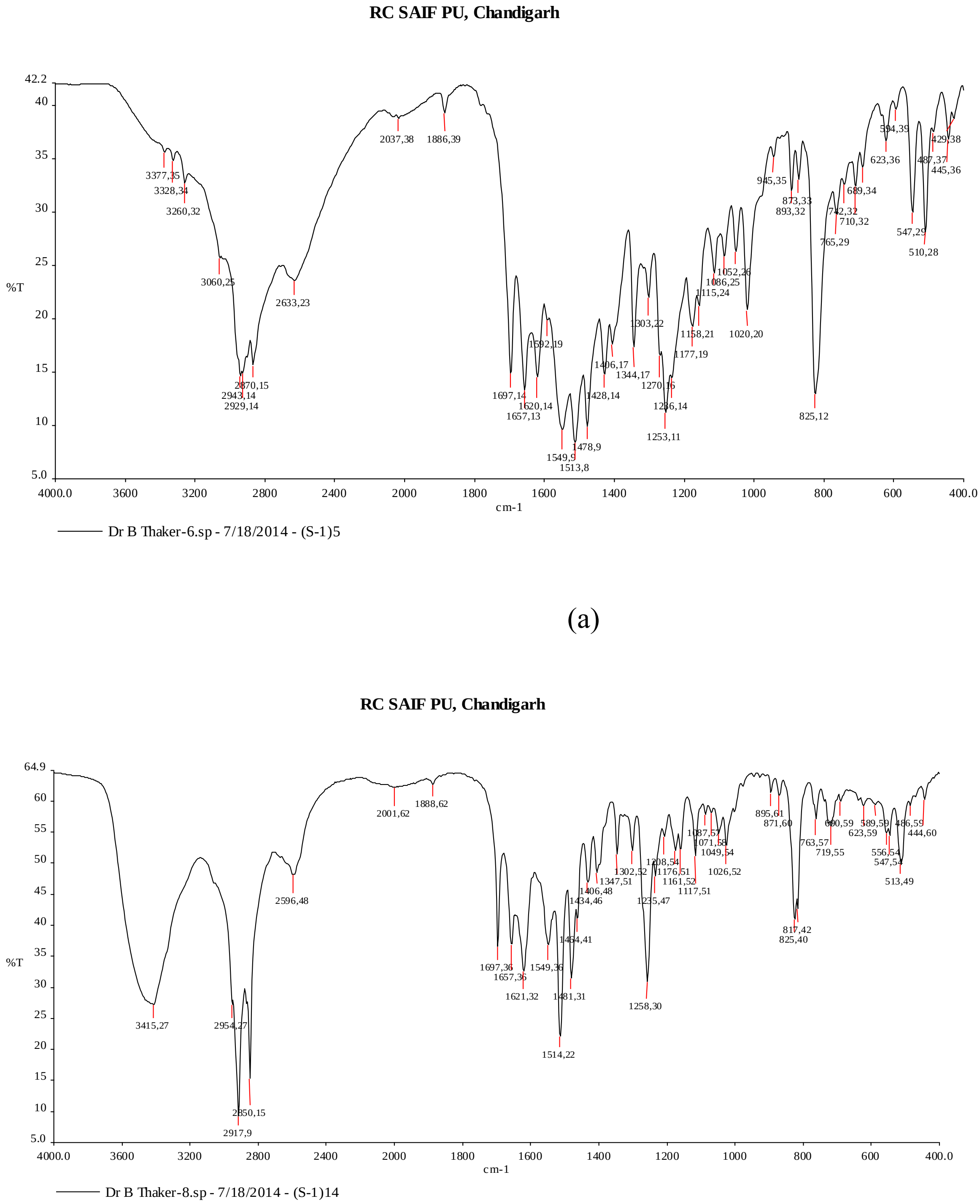
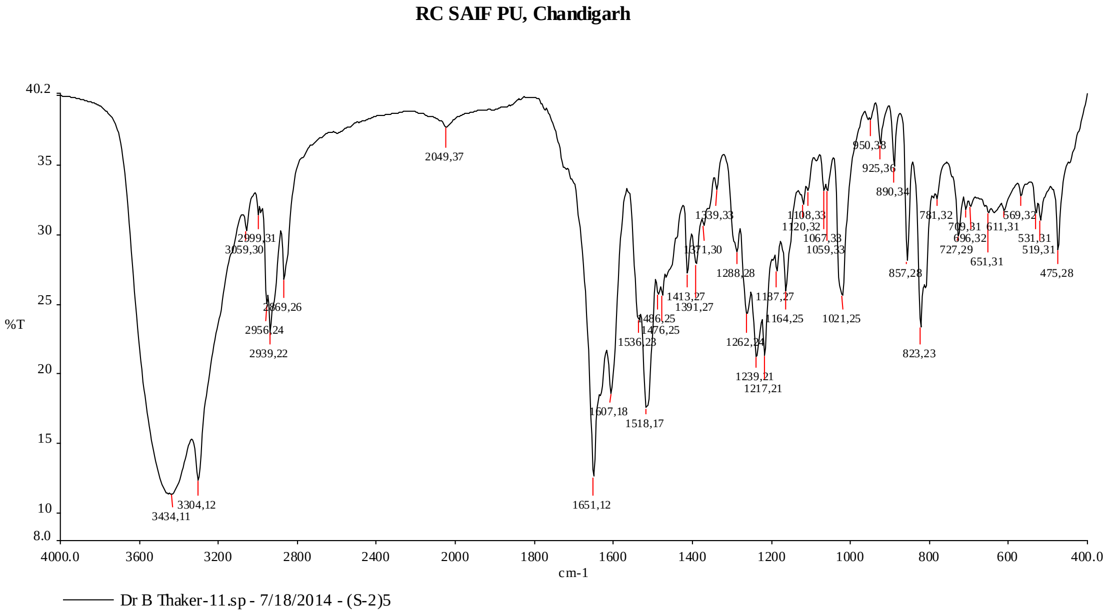


(a)

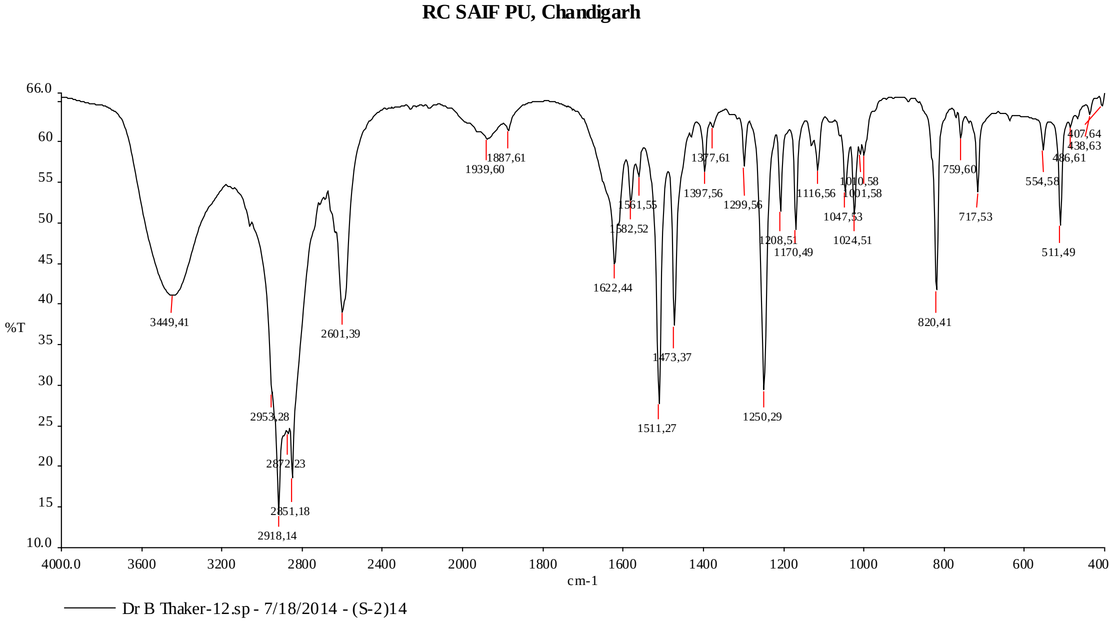
(b)

Figure (1) : (a) FTIR spectra of compound A5, Series : A

(b) FTIR spectra of compound A14, Series : A



(a)



(b)

Figure (2) : (a) FTIR spectra of compound B5, Series : B

(b) FTIR spectra of compound B14, Series : B

DSC Thermogram :

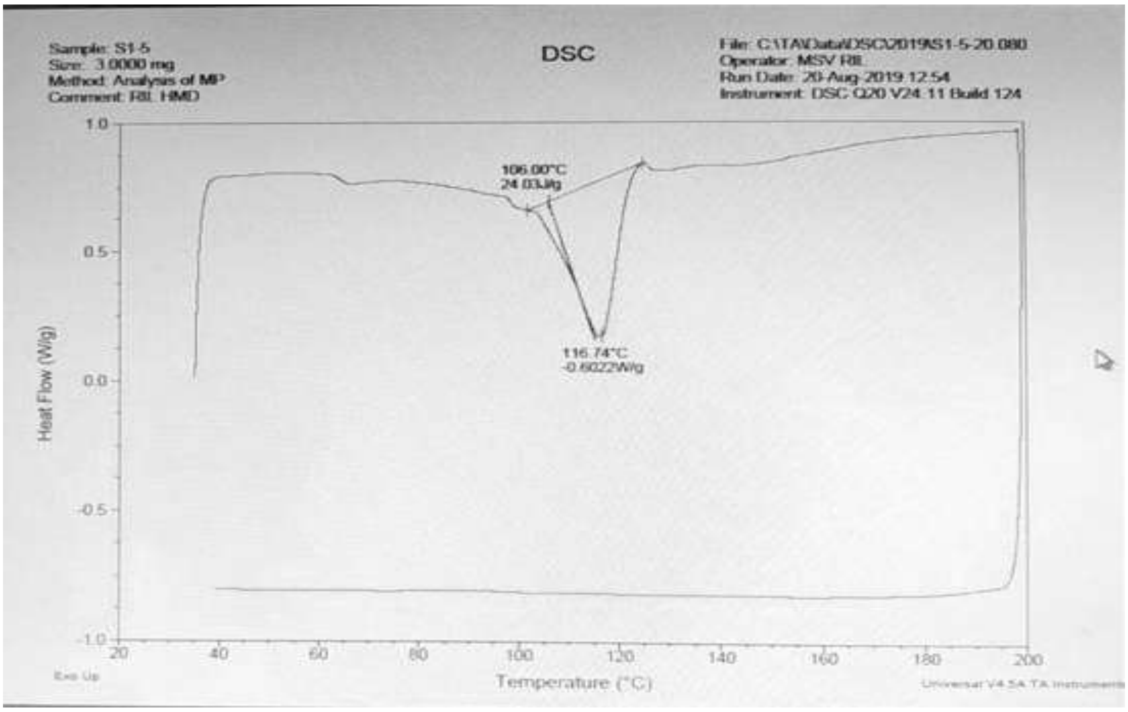


Figure (3) : DSC thermogram of compound A5 Series : A

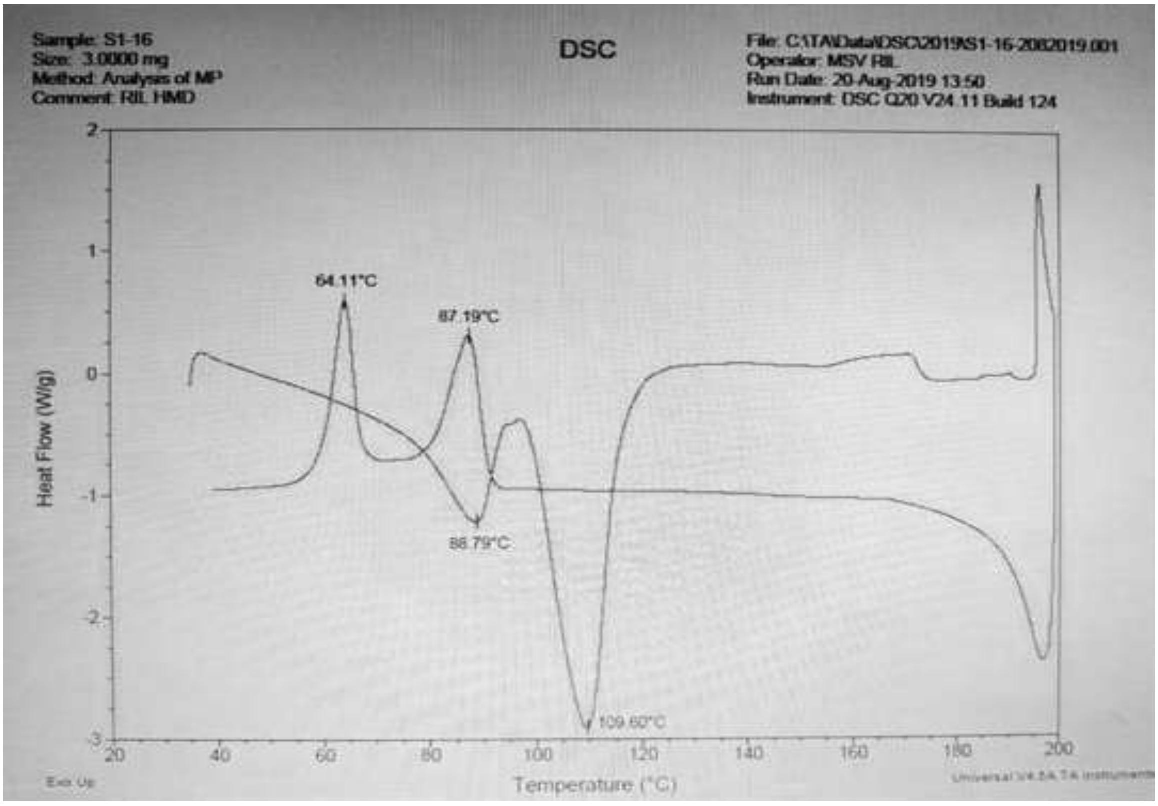


Figure (4) : DSC thermogram of compound A16 Series : A

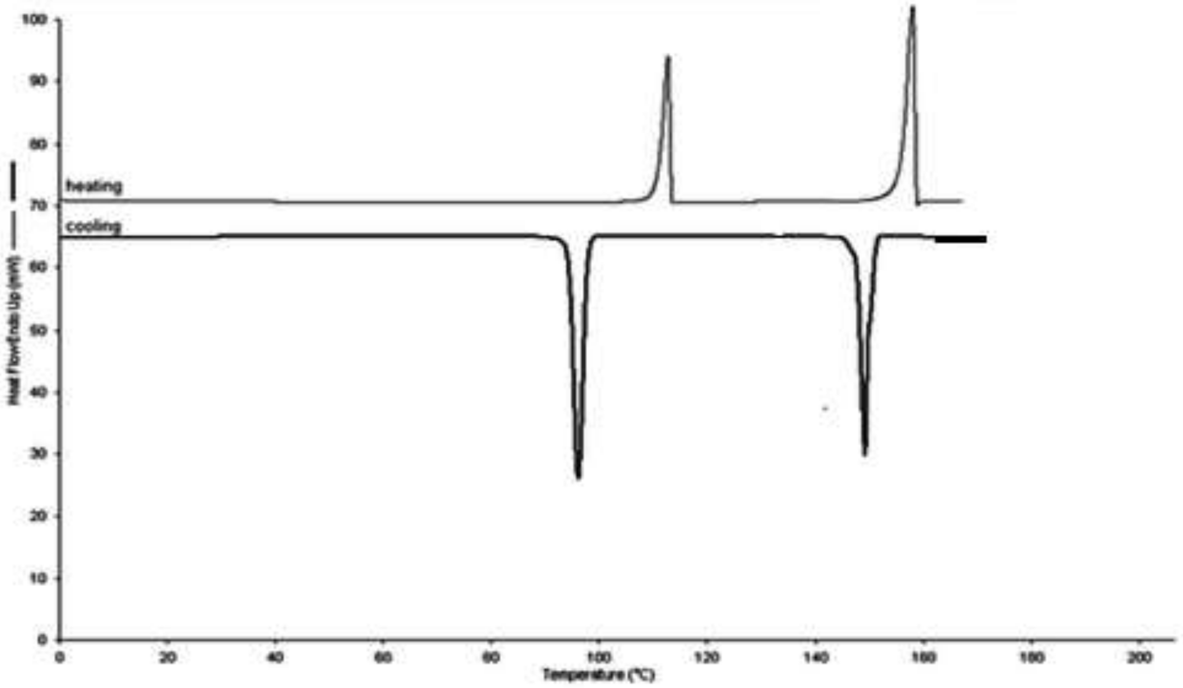


Figure (5) : DSC thermogram of compound B4 Series : B

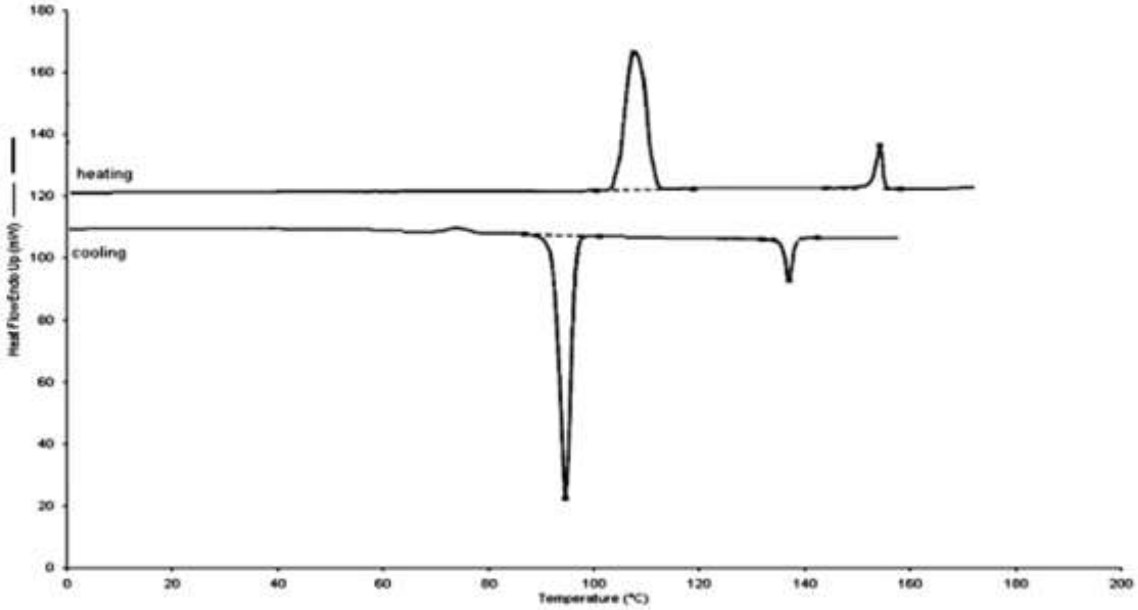


Figure (6) : DSC thermogram of compound B2 Series : B

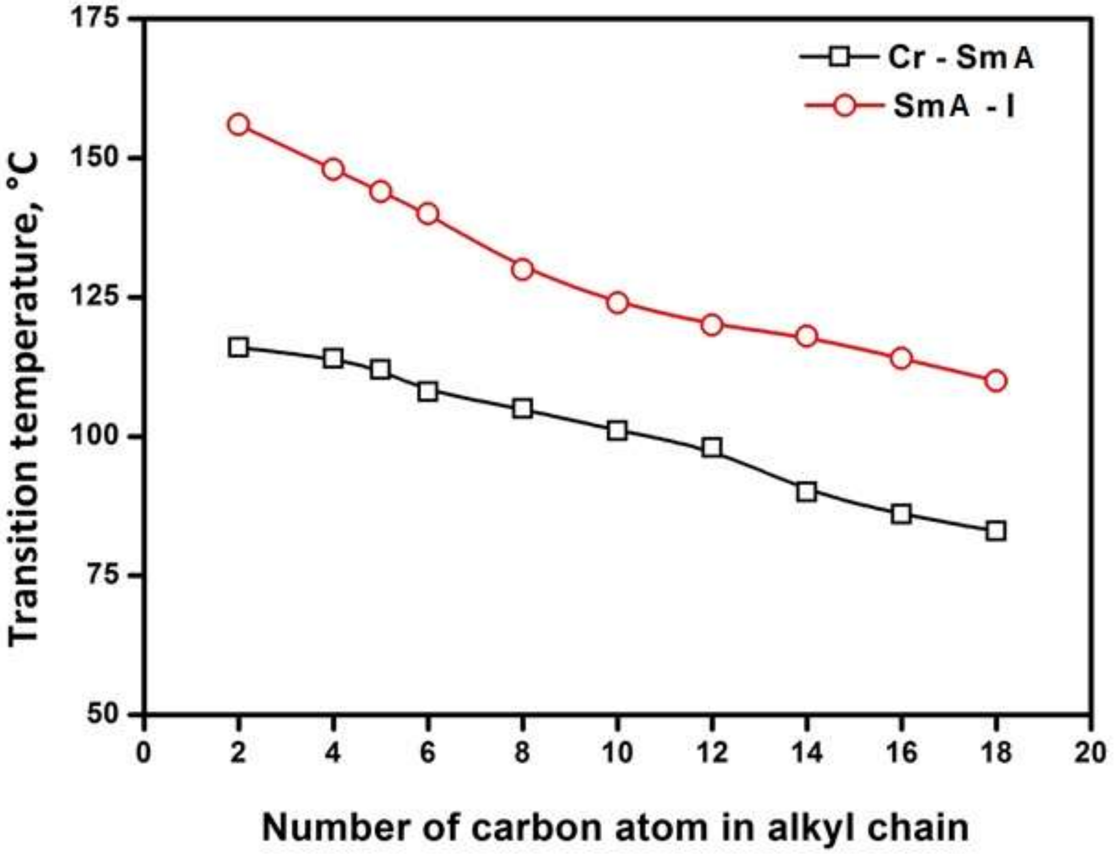


Figure-7 : Transition temperature data of N-[2-(4-butoxyphenyl)-2oxoethyl]-7fluoro oxo-2-chromanecarboxamide (I) Series – A

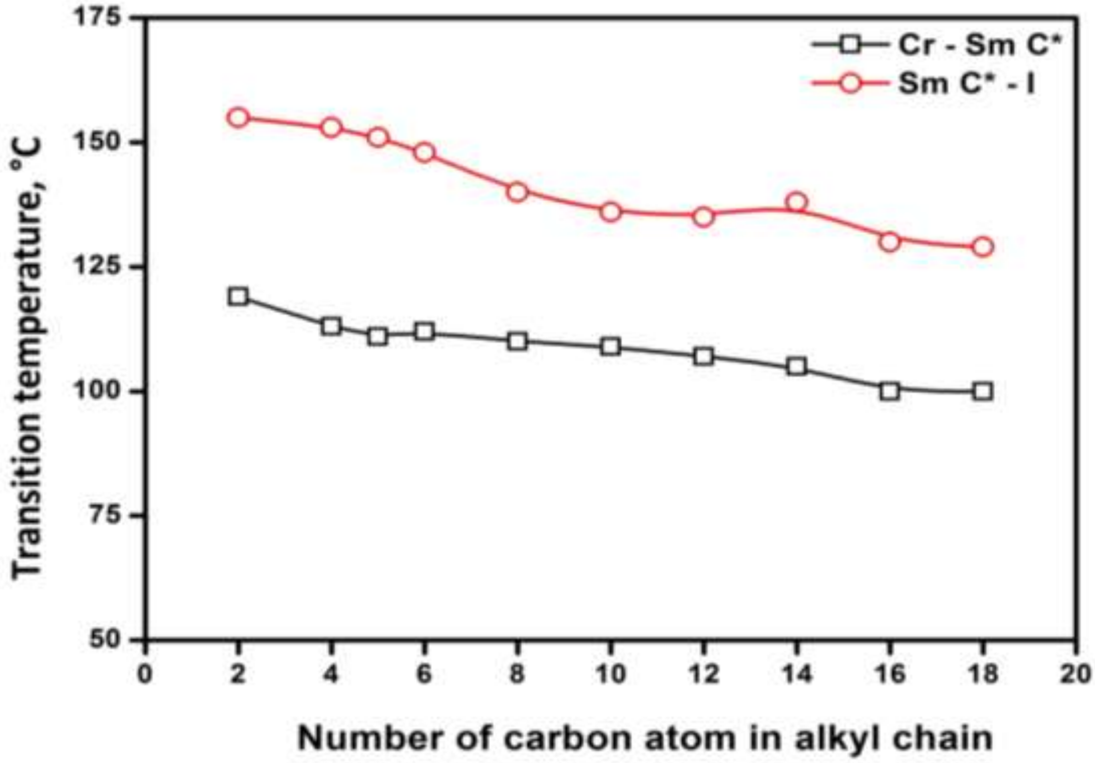
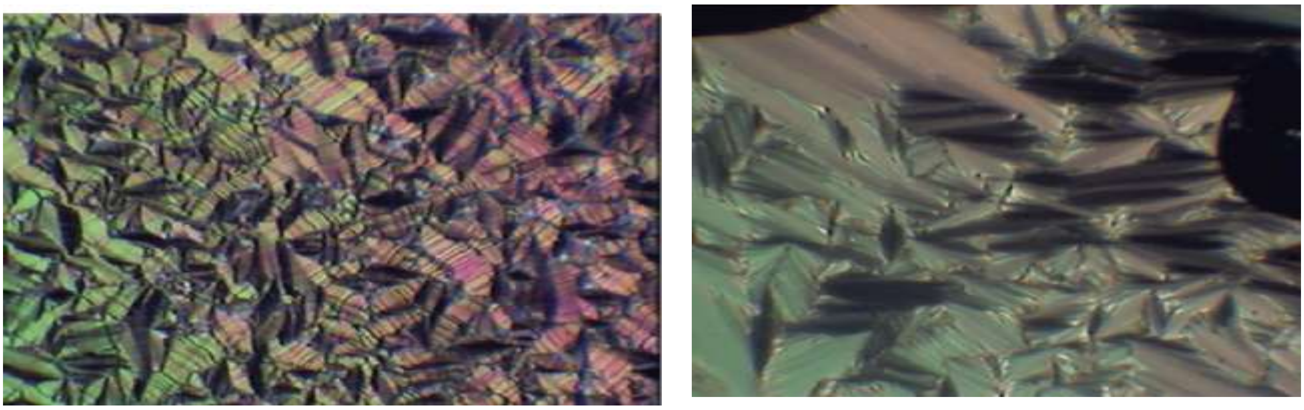
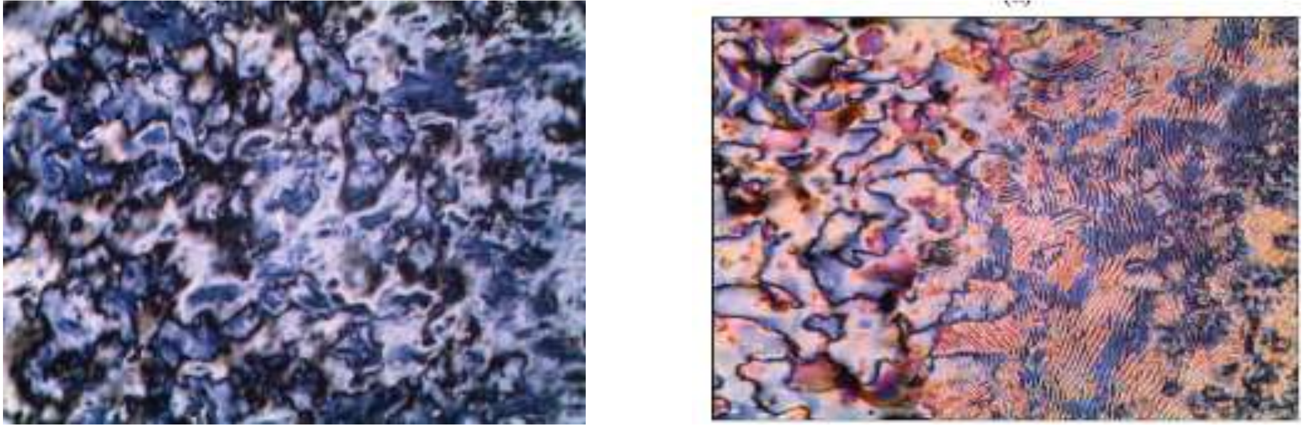


Figure (8) : Transition temperature data of naproxin 4-alkoxy acid amide (II) Series – B



(a) Smectic-A on cooling.

(b) Smectic-A on cooling.



(c) Smectic –C on cooling

(d) Smectic –C on cooling

\Figure (9) : Polarizing Optical Microscope of A4 compound (a) SmA phase obtained on cooling from the isotropic phase at 152°C, A16 compound (b) SmA phase obtained on cooling from the isotropic phase at 87.0°C, B2 compound (c) SmC phase obtained on cooling at 140°C, B5 compound (d) SmC phase obtained on cooling at 138.0°C.

III. CONCLUSION

We synthesized two series of straight rod-shaped molecules with an amide group and investigated their phase behaviors. Series-I compound exhibited more ordered Smectic-A phase. Series-II compound exhibited chiral Smectic-C* phase. It was assumed that the molecules generated ordered molecular aggregations by introduction of the lateral intermolecular hydrogen bonding.

IV. ACKNOWLEDGEMENT

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V. REFERENCES

[1] M.A. Qaddowra and K.D. Belfied, "Synthesis, Characterization and Texture Observations of Calamitic Liquid Crystalline Compounds," Int.J mol.sci, 2009; 10,4772-4788.

[2] D.Demus, J. Goodby, G W Gray, H.W.spiess and V.Vill, "Low molecular weight liquid crystals. In handbook of liquid crystals ," 1st ed; III Demus Ed; Wiley –VCH: weinheim, Germany 1998 ;vol 2B pp 15-18

[3] P J collings and H Michel, "Introduction to liquid crystals ," 1st ed: Taylors & Francis Ltd .london UK 1997,pp 70-71

[4] B. Bahadur, "Liquid Crystals application and uses," 1st Ed.; 1990; World Scientific Publishing; Singapore, p.11

[5] P.J.collings and J.S Patel, "Handbook of liquid crystal research," 1st ed; Taylor and Francis Ltd London, UK, 1997;P 600.

[6] B.Jones, "Apparent cases of liquid crystal formation in P- alkoxy benzoic acids," J chem..soc,1935; 1,1874.

[7] G.W. Gray and B.Jones, "Mesomorphism and chemical constitution. Part II. The trans-p-n-alkoxycinnamic acids," J chem..soc,1954; 1,2556-2562.

[8] W.Weissflog, P.Moeckel, S.Tschmeg, H.Kresse and Demus, "Synthesis and dielectric properties of liquid crystalline alkyliminomethyl-substituted phenyl benzoates," J.Park.chem, 1981; 323,599-606.

[9] W.Weissflog, D.Demus, S.Diele, P.Nitschke and W.Wedler, " laterally branched mesogens to novel twin molecules," liq.crystal, 1989; 3-5-111-122.

[10] W.Weissflog and D.Demus, "Thermotropic liquid-crystalline compounds with lateral long chain substituents, liquid-crystalline compounds with lateral aromatic branches," Liq .crystal, 1988; 3-275-284.

[11] U.baymeister, Z. Kosturkiewicz, H.Hartung, D.Demus and W.Weissfog, "Thermotropic liquid-crystalline compounds with lateral long chain substituents, crystal and molecular structure of mesogenic 4-ethoxy-3′-(4-ethoxyphenyliminomethyl)-4′-(4-methoxybenzoyloxy) azobenzene," Liq.crystal, 1990; 7, 241-249.

[12] T.Ganicz, W.A.Stanczyk, N.K.Gladkova and I.Sledzinska, "Vinylsilanes as monomers for side chain polymer liquid crystals," Macro molecules, 2000; 33289-293.

[13] N.Yao and A.M.Jamicson, "Transient shear flow behavior of dilute solutions of side-chain liquid-Crystalline polysiloxanes in 4,4′-(n-pentyloxy) cyanobiphenyl," macro molecules, 1998; 31,5399-5406.

[14] C.S.Hsu, P.H.Chu, H.L.Chang and T.H.Hsieh, "Effect of lateral substituents on the mesomorphic properties of side-chain liquid crystalline polysiloxanes containing 4-[(S)-2-methyl-1-butoxy] phenyl 4-(alkenyloxy) benzoate side groups," J polmer science,A,polymer chem. 1997; 35,2793-2800.

[15] A.Inoce,S. Maniwa and V.Ide, "Relation between molecular structure and electrorheological effects in liquid crystalline polymers," J.appli.polym.sci, 1997; 64,303-310.

[16] G.P.C.Jeng, J.F.Kuo and C.Y.chem, "X-ray investigation of terminally carboxyl oligo (ethylene oxide) monomethyl ethers-substituted side-chain liquid-crystalline polysiloxanes," J-appl polym.sci, 1993; 47,781-788.

[17] E.B Florjnczyk, A Orzeszko, I .Sledzinska and E. Gorecka, "Evidence of the smectic antiphase in 4-decyloxybiphenyl ester imide derivatives," J.Mater.chem, 1999; 9, 371.

[18] P.G. Holton, "Process for the resolution of d, 1 2-(6-methoxy-2-napthyl)propionic acid," U.S.4,515,811, 1985; May 7.

[19] V.Prasad, S.W Kang, X. Qi, S.Kumar, "Photo-responsive and electrically switchable mesophases in a novel class of achiral bent-core azo compounds,"J. Mater.Chem., 2004;14,1495.

[20] R. M. Silverstein and F. X. Webster , "Spectroscopic identification of organic compounds," 1997; VI- edition, P. P 91, John Willey & sons, NC; New York

[21] S. Kashino, K. Ito and M. Haisa, Bull, "The Crystal and Molecular Structure of Benzanilide," Chem. Soc. Jpn., 1979;52, 365.