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Synthesis and Investigation of Mesomorphic Properties of Ester Linkage containing Compounds

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Abstract: A homologous series consisting –coo- central bridge liquid crystals has been synthesized and investigatedwith a vision to understanding and establishingthe effect of molecular structure in respect of molecular size, geometrical shape and polarizability on liquid crystalline properties.
Unique series consisted of 12 members (C1–C16) of a series. Series consisting nematogenicandsmectogenic properties with respect to their carbon atoms. Novel members of series were selectively characterized and confirmed by elemental analysis, IR spectra, H1NMR spectra, DSC and POM.
Keywords: Liquid crystal, Nematic, Smectic, Mesomorphism

I. INTRODUCTION

The liquid crystalline state of material has maintained its significance in the numerous fields of applications since its discovery in 1888 [1]. The scientific and technological groups are working widely on liquid crystals (LC) [2–12]. The present examination is designed to synthesize novel LC compounds through a homologous series with a sight to understanding and establishing the relationship between mesomorphism and molecular structure [13–15].
Hence, the unique LC materials may be useful for researchers in various branches of science and technology, other than chemistry, mainly for applications. A huge number of homologous series for liquid crystal properties have been reported [16–20]. Novel compounds will be synthesized through homologous series consisting central bridge (–COO-)with dye which consisting (–OH) group at the terminal end side.
The influenceof central and terminal groups on LC properties with reference tomolecular rigidity and flexibility [21–24] will be discussed in a comparative manner with structurally similar LC materials. Present study will include synthesis of novel homologous LCs (thermotropic) containing five phenyl rings in order to provide novel LC materials to various research groups. The novel compounds were characterized by analytical and spectral data. LC properties were examined by using an optical polarizing microscope set up with a heating stage. The proposed investigation will include thermotropic properties and the comparative study of novel homologues with structurally similar series to derive group efficiency order.

II. EXPERIMENTAL AND INSTRUMENTATION

A. Materials

Methanol (MeOH), Potassiumhydroxide(KOH), Potassiumcarbonate (Anhydrous K_2CO_3), Alkyl bromides (R-X) were purchased from S.R.L., Mumbai. Dichloromethane (DCM) and 4-dimethyl amino pyridine (DMAP) were purchased from Sigma Aldrich. Solvents were dried and purified in the usual manner.

B. Instrumentation

The characterization of some selected members of a novel homologousserieswere analyzed by elemental analysis, structure exposition by infrared spectra and 1HNMR spectra. Textures, and Transition temperatures of homologous were identified by visual comparison with known phase standards using aNikon Eclipse LV-100 POL polarizing optical microscope (POM) fitted with a hot stagetemperature-controlled LTSE 420 heating stage (Linkam Scientific Instruments, Tadworth,Surrey, UK) with temperature controlling accuracy of 0.1K. and also confirmed by DSC. Elemental analysis was performed on Perkin-Elemer PE 2400 C, H, Nanalyzer. IR spectra were recorded on Perkin-Elemer GX spectrometer. 1HNMR spectra were determined on a Bruker spectrometer using CDCl3 solvent. Transition temperatures of homologous were determined by DSC(Shimadzu).The FT-IR spectra were recorded as KBr pellet on Shimadzu in the range of 3800-600 cm-1.

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1) Synthesis Route

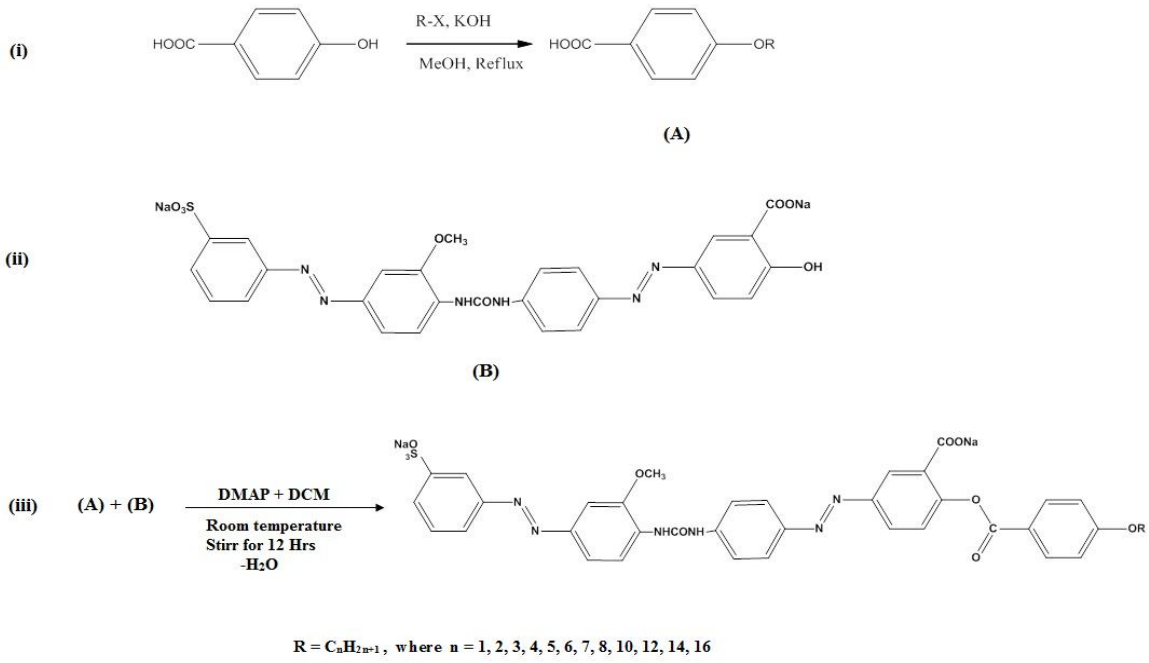
a) n-Alkoxy benzoic acids were prepared by usual established method of Dave andVora[18], by reaction of p- hydroxyl benzoic acid and the corresponding alkyl halides.

b) p-n-Alkoxyacids were carefully treated with dye S(DY-44) in the presence of DMAP and DCM at room temperature for 12 Hrs.

The chemicals 4-Hydroxy benzoic acid, alkyl Halides [R-X], Methanol, Ethanol, KOH, DMAP, DCM and DY-44 required for synthesis and were used as received excepts solvents which were dried and distilled prior to use. The synthetic route to the series is mentioned below in S**cheme-1.**

The transition temperatures of the homologs were determined by hot stage polarizing microscope and also confirmed by DSC. To confirm the structure of the homologs, Infra-red (IR) and nuclear magnetic resonance (NMR) spectra were taken. Analyticaldata support the structure.

Synthesis scheme



Scheme 1. Synthetic route to the series

III. RESULT AND DISCUSSION

A. POM Investigation

The transition temperatures and textures of anewsynthesized compounds were investigated using polarizing optical microscope (POM), when the sample was sandwiched between a clear glass slide and a cover slip. Microphotographs of the texturesobserved for compounds C_6, C_7, C_8 and C_{12} are depicatedin Figure 2.

Here, in existing article, we have synthesized five phenyl ring based homologous serieshaving one ester (-COO-) and two azo (-N=N-) groups and also having one terminal substituent on leftterminalend. The transition temperature of present series-1 is listed in Table 1.

As seen in Table 1, compounds C1 to C3 displays non LCs property, however comp. C4 to C12showingsmecticC(SmC) phase on heating and cooling situation which was further confirmed by DSCanalysis. Mesophase formation was found to be reliant on the location, number and the molecular length of the side alkyl chain which increases the flexibility of molecules attached to the alkoxy side group (-OR).

As shown in Table 1, compound C4 has highermelting type temperature (173.0^{o}C) and high temperature range of solid crystal(Cr) to SmC phase (141.0^{o}C) as compared to other higher group members of compounds in existing series-1.The phase diagram of present

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series-1 is shown in Fig. 1, which indicates the phase behaviour of Cr-SmC and SmC-I transition curve existent in prepared series-1. It is observed that, series increases from lower homologue C4 to higher homologue C12,the transition temperature is decreases from C12 to C4. Cr-SmC phase transition curve exhibit a smooth falling tendency from C1homologue to C7 homologue and earlier increases at C_8 homologue then continue to descend upto last homologue C12. Moreover, decreasing trendfrom C4to C12 homologous in SmC-I transition curve except C8 homologue, this isdue to the presence of odd-even parity of carbon present in methylene group in side alkoxy (-OR) group. The decreasing tendency in melting and clearing temperature couldbe due to the lowering the vanderwaals interactions between aromatic phenyl coresand higher degree of flexibility due to presence of long alkyl chain in alkoxy group at left terminal part [40].

TABLE 1 Transition Temperature in ^oC by POM (Series-1).

Sr. No.	Compounds	Transition temperatures in ^oC			
		Cr-I	Cr-SmC	SmC-N	SmC-I
1	C_1	218.0	.	-	.
2	C_2	195.0	.	-	.
3	C_3	182.0	.	-	.
4	C_4	.	141.0	-	173.0
5	C_5	.	136.0	-	166.0
6	C_6	.	124.0	-	155.0
7	C_7	.	110.0	-	148.0
8	C_8	.	121.0	-	153.0
9	C_{10}	.	106.0	-	133.0
10	C_{12}	.	101.0	-	129.0
11	C_{14}	.	96.0	-	124.0
12	C_{16}	.	93.0	-	119.0

(Cr-I = Crystal to isotropic phase, Cr-SmC = crystal to smectic C phase, SmC-I = Smectic C to isotropic phase).

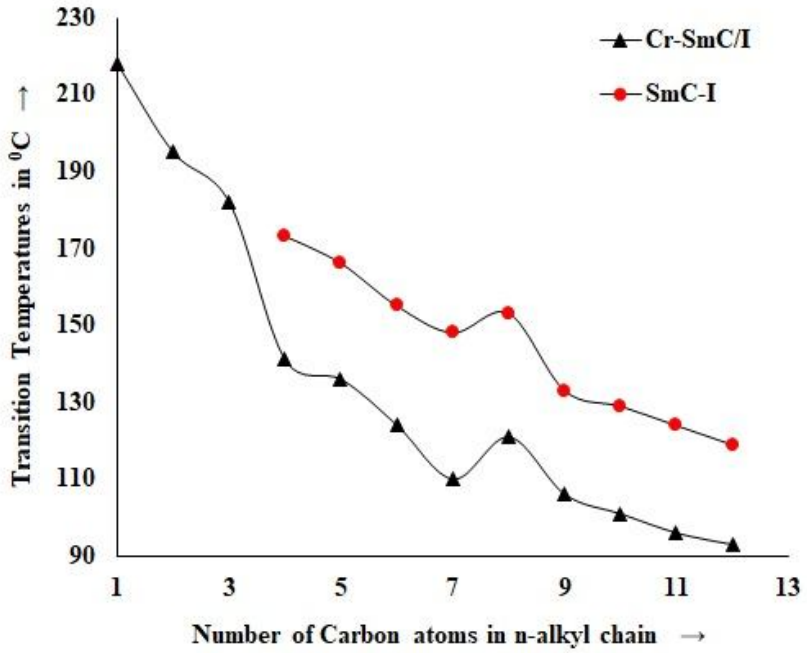


FIGURE 1 Phase diagram of series-1.

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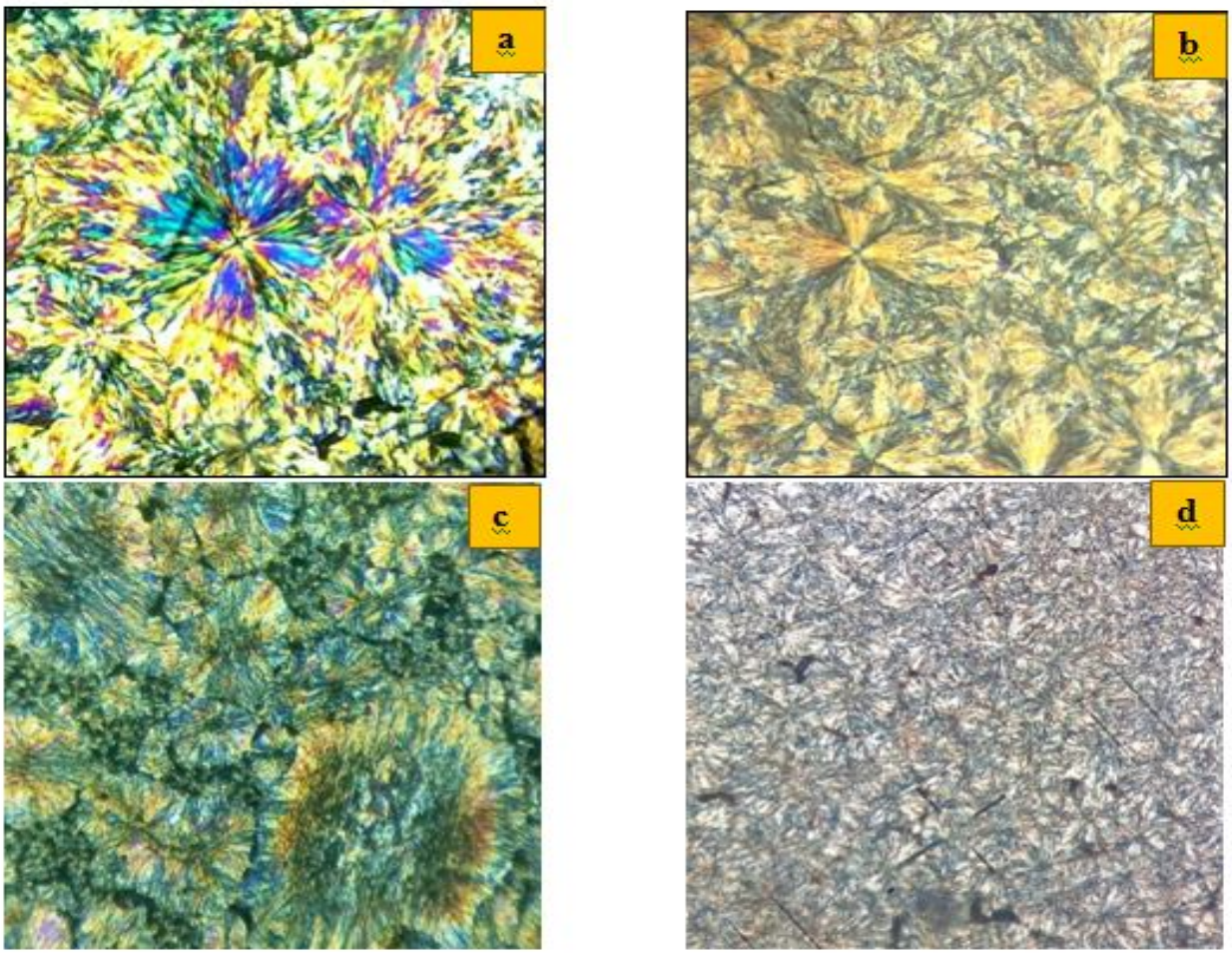


FIGURE 2 MicroPhotographs of the texture obtained for series-1

1) SmC phase at 124 °C for comp. C_6; (b) SmC phase at 110 °C for comp. C_7; (c) texture image of SmC phase at 121°C for comp. C_8;(d) SmC phase at 93 °C for comp. C_{12}.

The synthesised compounds placed on clear glass slide shielded by coverslip were heatedto the isotropic state and heating and cooling rate (2°C/min) respectively and detecting mesophase texture image. Fig. 2 shows microphotographs of the textures for compoundsC_6, C_7, C_8 and C_{12}. Compounds C_6, C_7, C_8 and C_{12}show texture image of SmC phase at 124.0°C, 110.0°C, 121.0°C and 93.0°C on heating condition.

B. DSC Analysis

The thermal behavior of mesogenic compounds was also examined with DSC measurementsat heating and cooling scan rate of 10°C/min.using nitrogen atmosphere.The phase transition temperatures obtained in DSC match splendidly with POM observation.DSC thermographs of compounds $C_6$and $C_{10}$are presented in Fig. 3.The transition temperaturesobtained from the DSC scans of second heating-coolingcycles are shown in Figure3. All compounds are thermally stable as confirmed by the reproducibility of thermogramson several heating and cooling cycles. In Fig. 3, compound C_6exhibits two endothermicpeaks at 124.0°Cand 155.0°C in heating cycle, which correspondenceto the presence of crystal to SmC (Cr-SmC) and SmC-I phase. That was additional confirmed by POM examination. While on cooling condition, againtwo exothermic peaks were traced at 153.0°C and 122.0°C. Compound C_{10}shows two endothermic peaks at 101.0°C and 129.0°C on heating cyclewhich reveals with POM results. On cooling cycle, again this exothermic peak exhibitsat 128.0°C and 102.0°C. The phase transition temperatures are summarized in Table-1.

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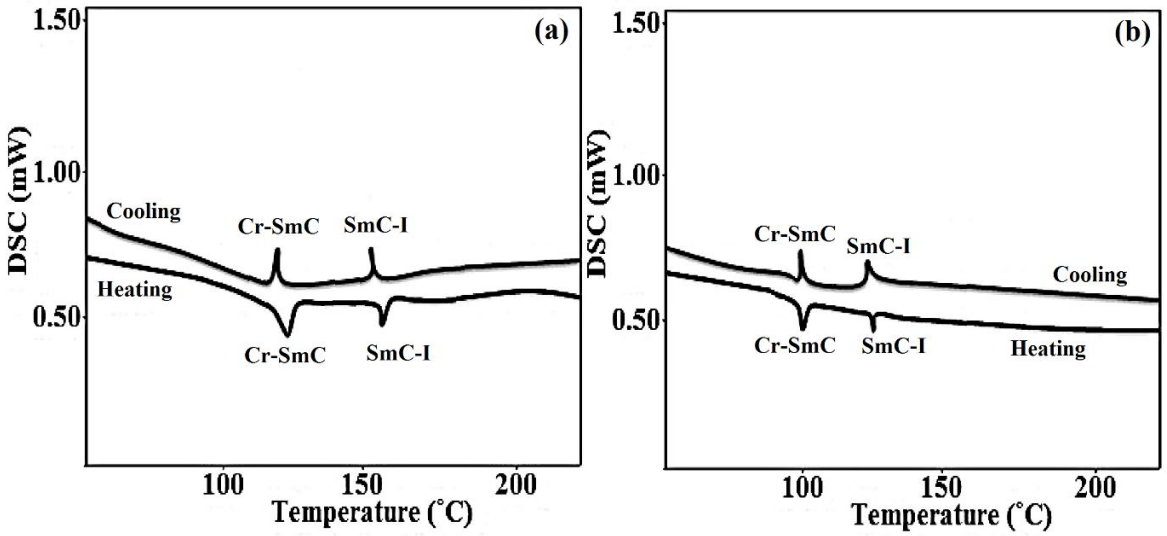
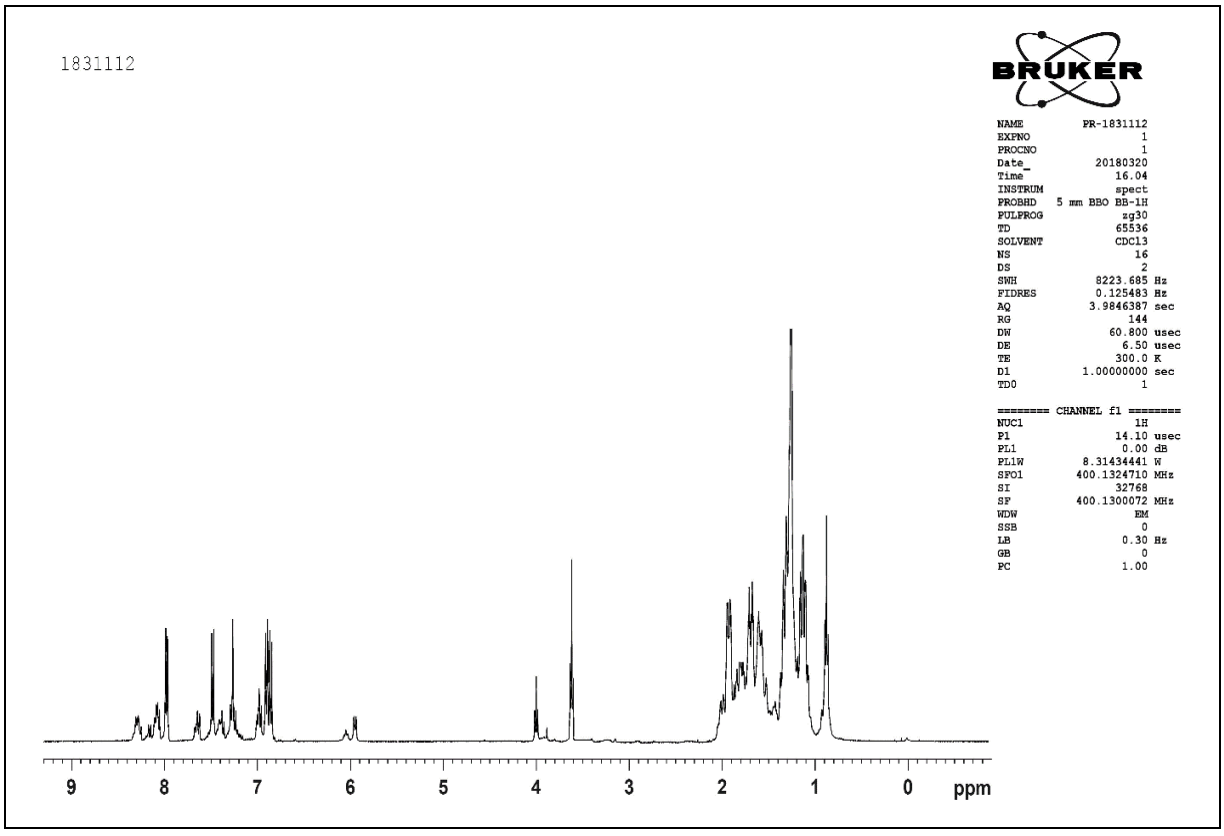


FIGURE 3 The DSC traces of compounds (a) $C_6$and (b) C_{10}.

C. NM Ranalysis

^{1}H NMR spectra in $CDCl_3$ in δ ppm for dodecyloxy derivative

Dodecyloxy: 0.89(t, -CH2-CH3, 4 H), 1.26 (m, n-poly methylene groups of –OC12H25),1.31–p1.76(q, -CH2-CH3, 6 H), 1.76(m, 8Hof poly methylene group), 3.98(t,-OCH2-CH2-,4 H), 7.19 and 7.83(s, ArH, p-disubstitured),8.07–8.19(s, ArH, p-di substituted phenyl ring). Octyloxy: 0.88–0.89(t, -CH2-CH3, 4 H, of –C6H13 and -C8H17), 1.29(m, n-poly methylene groups of -OC8H17), 1.76(m, 8 H of polymethylene), 4.06 (t, 4 H, -OCH2-CH2-of -OC6H13 and -OC8H17), 7.18–7,57 (s, ArH, substituted benzene), 8.07–8.11 (s, ArH, psubstitutedphenyl ring).

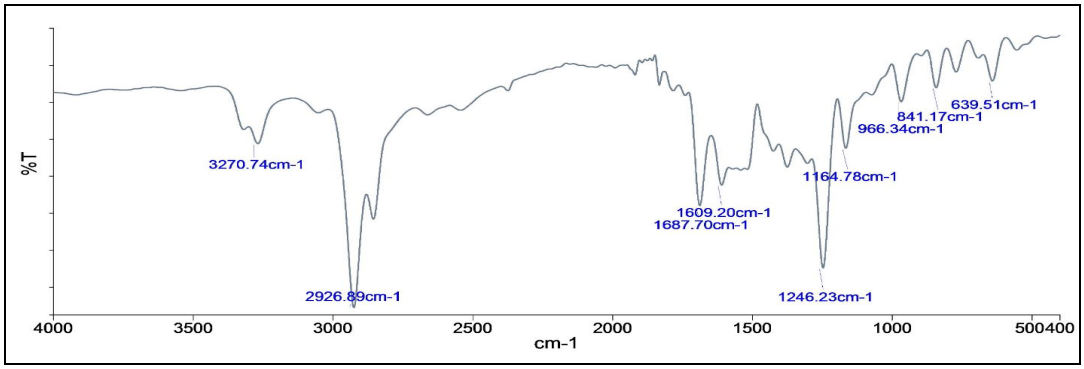


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D. IR Spectra Analysis

IR Spectra (KBr) in cm^{-1} for Propyloxy derivatives

Hexyloxy: 639.51(C-S) of $-SO_3Na$, 841.17(–C-H- def. di-substituted-Para), 966.34 (−C-H- def. hydrocarbon), 1246.23(-C-O str in $-(OCH_3)$), 1609.20 (-N=N-)str, 1687.70 (-C=O group), 1164.78 (-COO- ester group), 2926.89 (-C-H str in CH3), 3270.74(N-H bonding). IR data confirm the structure.



IV. CONCLUSIONS

In summary, we have reported the synthesis and phase behaviour of presently new homologous series containing five aromatic rings. The nature of the mesophase has been established by using POM and DSC studies. Formation of mesophase and the LC properties are very sensitive and liable to the molecular structure.Molecular rigidity and flexibilities of suitable magnitudes as a consequence of molecularstructure are the basis of LC phase formation. The lower member C_1 to C_3 shows non mesogenic behaviour due to presence of short alkyl spacer in n-alkyl chain. Comp. C_4 to C_8, C_{10}, C_{12}, C_{14}, C_{16} shows enantiotropic smecticC phase with good temperature range.

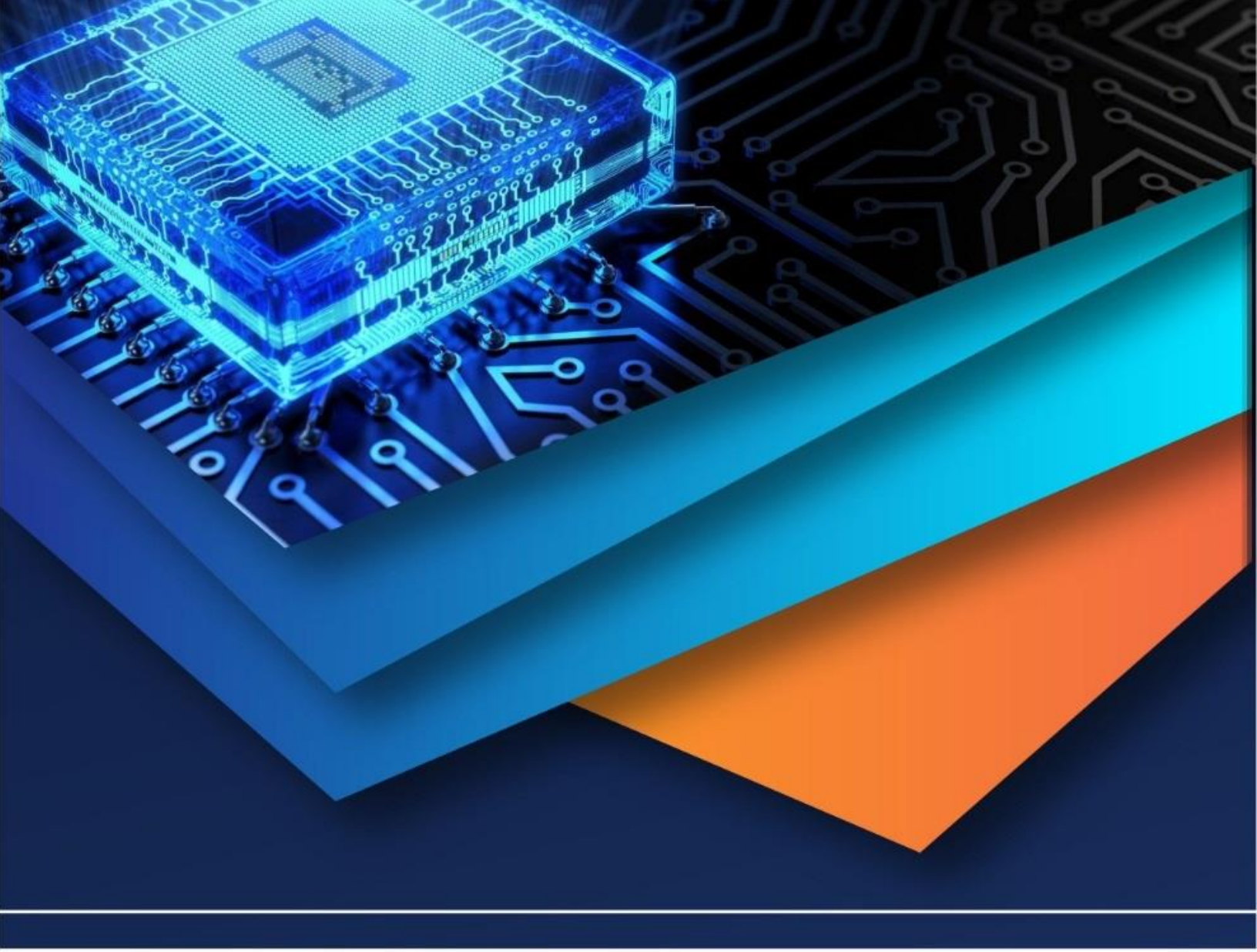
V. ACKNOWLEDGMENT

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