



Mesogenic Schiff'S Base Diester with Chloroethyl Tail

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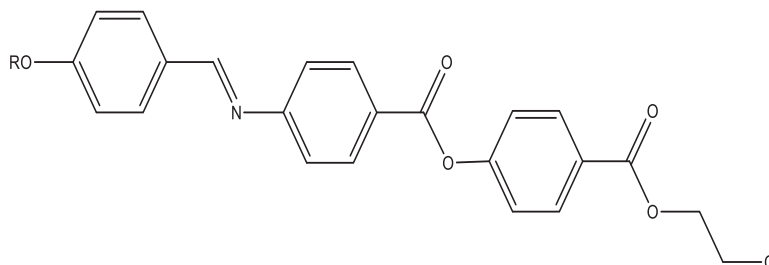
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ABSTRACT

One new mesogenic homologous series of Schiff's base diester with chloroethyl tail having the following general formula.



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



have been synthesized. The molecular structures of the synthesized compounds were characterized by the standard spectroscopic methods and elemental analysis. The mesomorphic behaviour of these new Schiff's base esters was mainly investigated with the help of optical polarizing microscope. For some representative compounds differential scanning calorimetric study was carried out to support the optical observation of transition temperatures and associated enthalpies. In series I, lower members are nematic-mesophase, whereas higher members exhibit smectic mesophase. In series I, methoxy to *n*-hexyloxy derivatives exhibit nematic mesophase, while the smectic A phase commences from *n*-propyloxy derivative and persists up to the last member synthesized. As well as *n*-propyloxy to *n*-hexyloxy derivatives exhibit smectic and nematic mesophase. The mesomorphic properties of these series of compounds are compared with each other and with structurally related systems.

Key words: chloroethyl tail, Schiff's base, smectic A, nematic, mesomorphic properties.

INTRODUCTION

The molecular architecture of liquid crystalline compounds extremely affects the mesophase stability, where the slight change in molecular geometry provides a significant change in their mesomorphic properties [1-2]. Study of several mesogenic homologous series has supported to develop some general rules for the effect of chemical constitution in the smectogenic and nematogenic compounds [3-4]. Schiff base materials are extensively used in several fields, like organometallic chemistry [5], catalytic chemistry [6], photochemistry and biochemistry [7]. Schiff bases have a vital role in the field of liquid crystal researches since Kelker et al. [8] first reported 4-methoxybenzylidene-4'-butylaniline (MBBA) in Schiff base liquid crystal compound. Numerous Schiff bases along low molecular weight have been investigated and synthesized widely toward application of liquid crystal [9-11]. Synthesized a number of 4-*n*-alkoxy-1-naphthylidene Schiff base and cholesteryl naphthoates discovered by Dave et al. As well as he studied their mesomorphism [12-13]. Sie et al. reported heterocyclic benzoxazole liquid crystal according to ester linking group and Schiff base. He studied the compounds displayed enantiotropic smectic A phase [14]. synthesized and studied 1,3, 5-trisubstituted benzene based on star shaped derivatives comprising ester linking group and



Schiff base reported by Yeap et al. [15]. Ha et al. and his helpers have synthesized a series of Schiff base ethers includes a dimethyl amino group at one terminal position and an even number of carbons at the other along the molecular axis [16]. New mesogenic schiff base esters contains polar chloro group tail and two phenyl ring synthesized by Lin et al. [17]. Yeap discovered Schiff base ester based N-[4-(4-*n*-Hexadecanoyloxy benzoyloxy)-Benzylidene]-4-substituted anilines [18]. Schiff base liquid crystal contains (S)-2-octyloxy tail reported by Huang et al. and he was studied the tail effect on formation of antiferroelectric phase and frustrated blue phase [19]. Ha et al. reported the mesomorphic properties of aromatic Schiff base arising from substituents varying in their polarities [20]. Numerous mesogenic homologous series contain two central linkages, one of which may be azomethine and another ester [21–22]. Since 2007 in Yellamaggad et al. reported to synthesized six homologous series based on salicylaldehyde like banana shaped mesogens derived from laterally substituted resorcinol [23]. Doshi et al. discovered homologous series contain vinyl ester and ester linkage group [24–25].

EXPERIMENTAL

Synthesis

For present synthesized homologous sequence required materials: para-Hydroxy benzaldehyde, the appropriate *n*-alkyl halides, anhydrous potassium carbonate, dry acetone, para-Amino benzoic acid, glacial acetic acid, dry ethanol, 2-Chloro ethanol, sulfuric acid, N,N'-Dicyclohexylcarbodiimide (DCC), 4-Dimethylaminopyridine (DMAP) and tetrahydrofuran (THF) were used in present work. The solvent was distilled and dried before use. Fourier transform infrared were collected on shimadzu IR408 spectrometer using KBr pellets. ¹H NMR spectra were carried out by the using of Bruker advanced Neospectrometer (400 MHz) with the help of tetramethyl silane (TMS) and Deuterated chloroform (CDCl₃) solvent. Phase transition shown by polarising optical microscopy along heating stage. Shimadzu DSC-60 (Differential Scanning Calorimeter) through measured enthalpies phase transitions at cooling and heating rates 10°C min⁻¹.



Synthesis of 4-*n*-alkoxy benzaldehyde

4-*n*-Alkoxybenzaldehydes was synthesised from 4-hydroxy benzaldehyde using the method of Vyas and Shah [26]. Overall yield of 4-*n*-Alkoxybenzaldehydes was 62–64%.

Synthesis of 4-((4-*n*-alkoxy benzylidene) amino) benzoic acid

4-((4-*n*-alkoxy benzylidene) amino) benzoic acid was synthesised by Refluxing of 4-*n*-Alkoxybenzaldehydes and 4-amino benzoic acid at 3-4 hours along the presence of ethanol and glacial acetic acid [27]. The yield was filtered and purified by column chromatography and it was confirmed by ¹H NMR and IR analysis.

Synthesis of β-Chloroethyl-4-hydroxybenzoate

The esterification of 4-hydroxybenzoic acid and 2-chloroethanol as described in Scheme. Yielded solid mass of β-Chloroethyl-4-hydroxybenzoate. The ester was distilled under reduced pressure. M.P.: 125°C (reported [28] M.P.: 125°C); Overall yield of β-Chloroethyl-4-hydroxybenzoate was 80%.

Synthesis of 4-((2-chloroethoxy)carbonyl)phenyl(E)-4-((4-*n*-alkoxybenzylidene)amino) benzoate

0.1 Mole of 4-((4-*n*-alkoxy benzylidene) amino) benzoic acid, 0.1 mole of β-Chloroethyl-4-hydroxybenzoate, 0.1 mole of DCC [29] and 0.1 mole of DMAP were dissolved in dry THF and stirred at room temperature for overnight. The insoluble solid was removed through filtration. The crude product was repeatedly crystallized from the ethanol. All the compounds of the present series were synthesized with the same method. Yield in general is 60-65%.

Calorimetric studies:

Calorimetry study is a valuable method for the detection of phase behaviour. It yields quantitative results, therefore, we may lead to conclusions concerning the nature of the different phases which occur during the phase transitions. In present study, enthalpies of derivative of series I (*n*=1) were measured by differential scanning calorimetry study. Readings are recorded in table 3. Thermograms (graph) are given in figure 2.



Optical microscopy studies

The optical microscopic study concluded that the mesophase exhibited by compounds of series **I** as a primary investigation found consistent with the previous results. Microphotograph texture of focal conic texture SmA mesophase (Series **I**; $n=4$) at 200 °C on cooling (Figure 3.) droplet nematic mesophase (Series **I**; $n=1$) at 299 °C on cooling (Figure 4.)

Result and Discussion

Table 4 summaries comparison of smectic mesophase range, transition temperature and molecular structure of representative compound **10** ($n=12$) of the present series **I** as well as compare with structurally related other series **A**[30], **B**[31], and **C** [32].

Table 4 also shows that the smectic mesophase range of series-**I** is higher by 11 °C. It can also be noticed that the smectic transition temperatures range of series-**I** are higher by 27 °C, respectively, than those of series **A**. The molecules of series-**I** and **A** differ only at the positions of Central linkage. Series **I** has azomethine (-CH=N-) group on central linkage where as series **A** has ester (-COO-) linkage on same position so due to mesophase range and transition temperatures range series **I** is more polarise than series **A**.

The tendency to stabilize the smectic mesophase and its thermal range in series-**I** is greater than that of series **B**. The molecular structure of compounds of series-**I** differs from series **B** in the number of benzene nuclei and central ester (-COO-) linkages. Compounds of series-**I** are longer than those of series **B** because of the one more additional aromatic ring and the central ester (-COO-) linkage. Gray [33] has explained that an increase in the length of the molecule, and the resulting enhanced anisotropy of polarizability.

Reference to table 4 also indicates that the smectic mesophase range of series-**I** is higher by 15 °C. It can also be noticed that the smectic transition temperatures of Series-**I** are higher by 65 °C, respectively, than those of series **C**. The molecules of Series-**I** and **C** differ only at the terminus. Series-**I** has a chloro (-Cl) terminal group, whereas series **C** has an ethoxy terminal group. The presence of polar terminal chloro(-Cl) group increases the overall polarizability of series-**I** compared to series **C** which is responsible for the higher transition temperature and greater mesophase thermal range of Series-**I**, has azomethine (-CH=N-) group on central



linkage whereas series C has ester (-COO-) linkage on same position so due to mesophase range and transition temperatures range series I is more polarise than series C.

CONCLUSION

A new mesogenic homologous series of diester with chloroethyl tail have been synthesized. Series I is exhibit smectic as well as nematic phase with three-phenyl-ring system, due to the presence of an additional phenyl ring along with an ester linkage.

More polar chloro terminal chain with three phenyl rings having ester and azomethine central linkages exhibit nematic and smectic mesophases. The study indicated that More polar chloro terminal chain affected more adversely on mesophase thermal stabilities as compared to branched chain terminus.



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SPECTRAL DATA

4-((2-chloroethoxy)carbonyl)phenyl (E)-4-((4-(*n*-hexyloxy)benzylidene)amino)benzoate

IR Spectrum (KBr) V_{max}/Cm^{-1} : 3043, 2943, 2875, 1738 (- COO-), 1694 (-CH = N-), 1630 (-CH = CH-), 1595, 1435, 1373, 1282, 1176, 1061, 889, 658.

1H NMR Spectrum (400 MHz, $CDCl_3$) δ in ppm: 0.89 (t, 3H, -CH₃), 1.32-1.47 (m, 6H, 3 X -CH₂-), 1.82 (m, 2 H, -CH₂-C-O-), 4.11 (t, 2H, Ar-O-CH₂-), 4.13-4.56 (t, 4H, 2 X -CH₂-), 7.04 (d, 2H, ArH), 7.42 (d, 2H, ArH), 7.56 (d, 2H, ArH), 7.91 (d, 2H, ArH), 8.19 (d, 2H, ArH), 8.24 (d, 2H, ArH), 8.46 (s, 1H, -CH=N-).

4-((2-chloroethoxy)carbonyl)phenyl (E)-4-((4-(*n*-octyloxy)benzylidene)amino)benzoate

IR Spectrum (KBr) V_{max}/Cm^{-1} : 3049, 2922, 2871, 1724 (- COO-), 1673 (-CH = N-), 1624 (-CH = CH-), 1589, 1423, 1379, 1255, 1162, 1061, 883, 673.

1H NMR Spectrum (400 MHz, $CDCl_3$) δ in ppm: 0.91 (t, 3H, -CH₃), 1.22-1.52 (m, 10H, 5 X -CH₂-), 1.76 (m, 2 H, -CH₂-C-O-), 4.09 (t, 2H, Ar-O-CH₂-), 4.13-4.56 (t, 4H, 2 X -CH₂-), 7.04 (d, 2H, ArH), 7.42 (d, 2H, ArH), 7.56 (d, 2H, ArH), 7.91 (d, 2H, ArH), 8.19 (d, 2H, ArH), 8.24 (d, 2H, ArH), 8.46 (s, 1H, -CH=N-).

4-((2-chloroethoxy)carbonyl)phenyl (E)-4-((4-(*n*-octyloxy)benzylidene)amino)benzoate

IR Spectrum (KBr) V_{max}/Cm^{-1} : 3043, 2943, 2875, 1738 (- COO-), 1694 (-CH = N-), 1630 (-CH = CH-), 1595, 1435, 1373, 1282, 1176, 1061, 889, 658.



^1H NMR Spectrum (400 MHz, CDCl_3) δ in ppm: 0.91 (t, 3H, -CH₃), 1.23-1.44 (m, 18 H, 9 X -CH₂-), 1.72 (m, 2 H, -CH₂-C-O-), 4.09 (t, 2H, Ar-O-CH₂-), 4.13-4.56 (t, 4H, 2 X -CH₂-), 7.04 (d, 2H, ArH), 7.42 (d, 2H, ArH), 7.56 (d, 2H, ArH), 7.91 (d, 2H, ArH), 8.19 (d, 2H, ArH), 8.24 (d, 2H, ArH), 8.46 (s, 1H, -CH=N-).

Table 1: Transition temperatures ($^{\circ}\text{C}$) of the series I compound

| Compound No. | R= -C _n H _{2n+1} n = | Cr | SmA | N | I | | | |
|--------------|---|----|-----|---|-----|---|-----|---|
| 1 | 1 | • | 171 | • | 301 | • | | |
| 2 | 2 | • | 175 | • | 295 | • | | |
| 3 | 3 | • | 196 | • | 221 | • | 291 | • |
| 4 | 4 | • | 202 | • | 221 | • | 275 | • |
| 5 | 5 | • | 185 | • | 215 | • | 273 | • |
| 6 | 6 | • | 181 | • | 211 | • | 265 | • |
| 7 | 7 | • | 175 | • | | | 258 | • |
| 8 | 8 | • | 169 | • | | | 251 | • |
| 9 | 10 | • | 164 | • | | | 243 | • |
| 10 | 12 | • | 158 | • | | | 238 | • |
| 11 | 14 | • | 154 | • | | | 235 | • |
| 12 | 16 | • | 149 | • | | | 231 | • |

()= monotropic value; Cr=crystalline solid; SmA=smectic A phase; N=nematic phase; I=isotropic liquid phase; •=phase exists.



Table-2 Elemental analysis dodecyloxy derivatives.

| Sr.No. | R= <i>n</i> -alkyl chain | %Theoretically | | | %Observation | | |
|--------|--|----------------|------|------|--------------|------|------|
| | | C | H | N | C | H | N |
| 1 | C ₂₇ H ₂₆ O ₅ NCl | 67.57 | 5.46 | 2.92 | 67.61 | 5.42 | 2.99 |
| 2 | C ₃₁ H ₃₄ O ₅ NCl | 69.46 | 6.39 | 2.61 | 69.49 | 6.34 | 2.67 |
| 3 | C ₃₅ H ₄₂ O ₅ NCl | 70.99 | 7.15 | 2.37 | 71.03 | 7.19 | 2.32 |

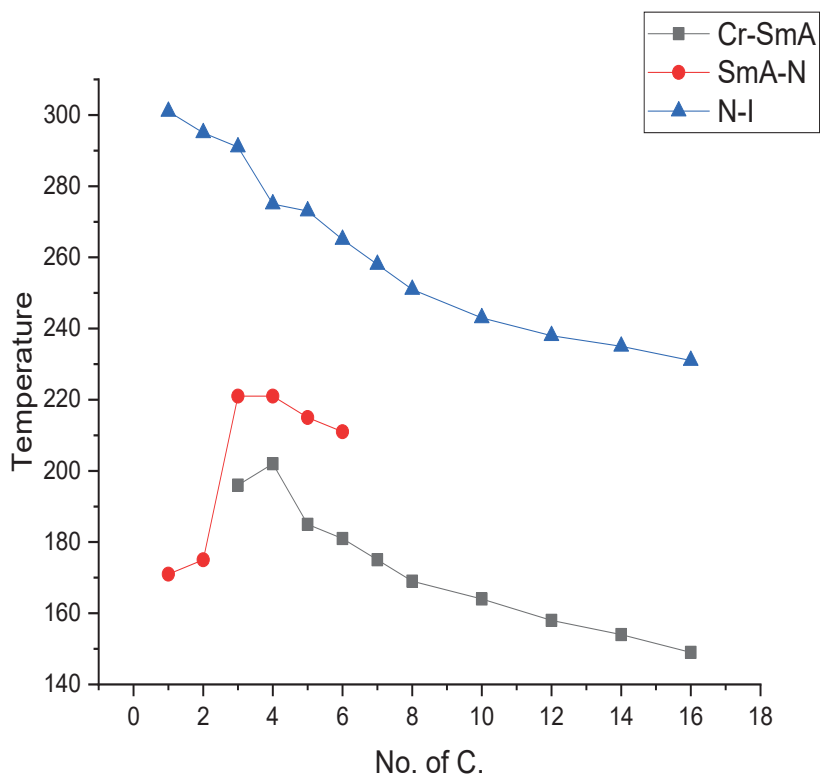


Figure 1: The phase behavior for Series I

Table 3: Enthalpy change, entropy change and normalized entropy of the series II by DSC.

| Compound | Transition | Peak temp./°C | $\Delta H/kJmol^{-1}$ | $\Delta S/Jmol^{-1} K^{-1}$ |
|----------|------------|---------------|-----------------------|-----------------------------|
| II | Cr-SmA | 170.76 | 101.4341 | 0.2286 |
| | SmA-I | 301 | 0.7615 | 0.00133 |

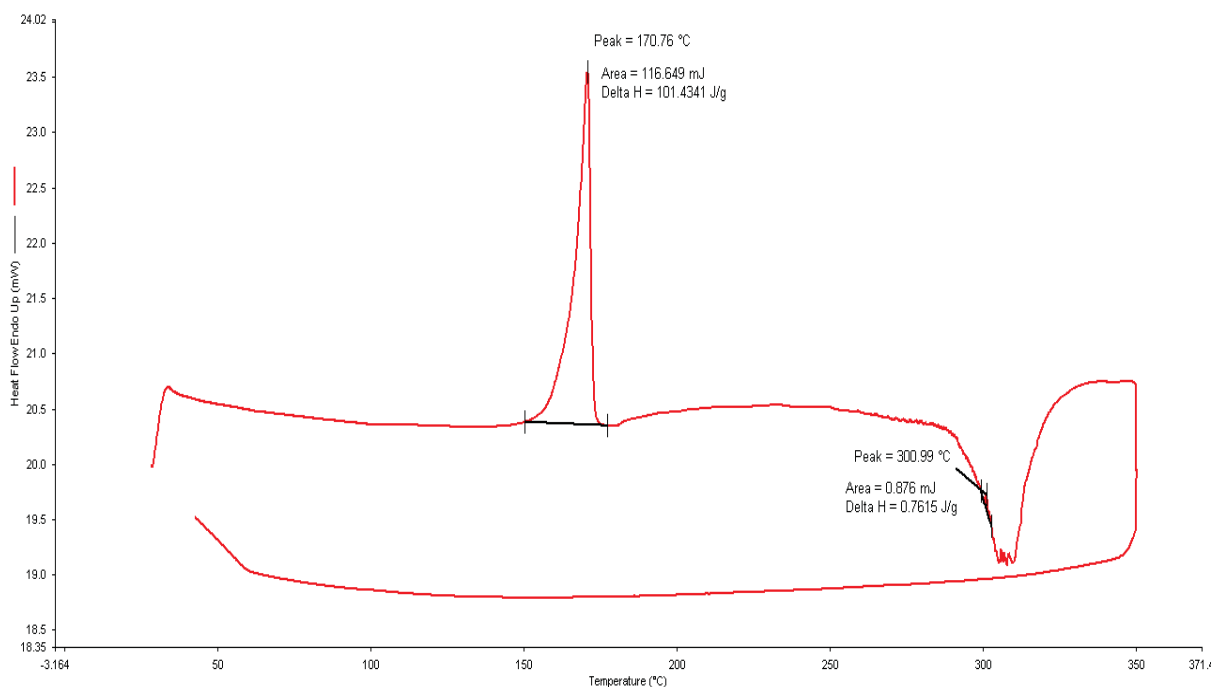


Figure 2: DSC Thermogram of series I ($n=1$)



Figure 3: Microphotograph of focal conic texture SmA mesophase(Series I; $n=4$) at 200 °C on cooling

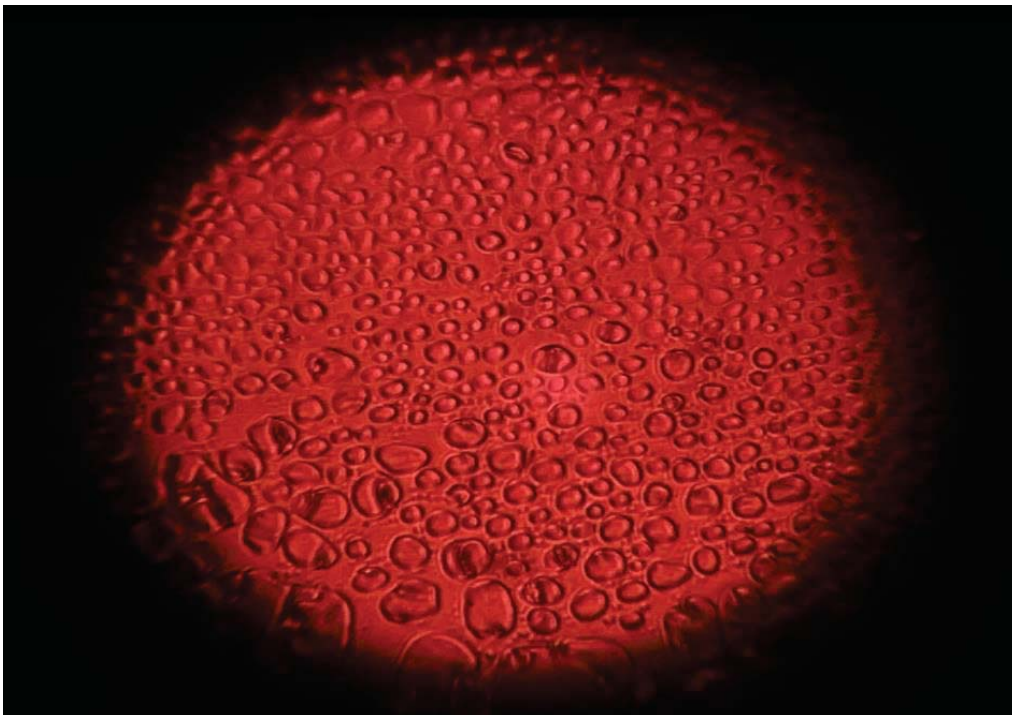
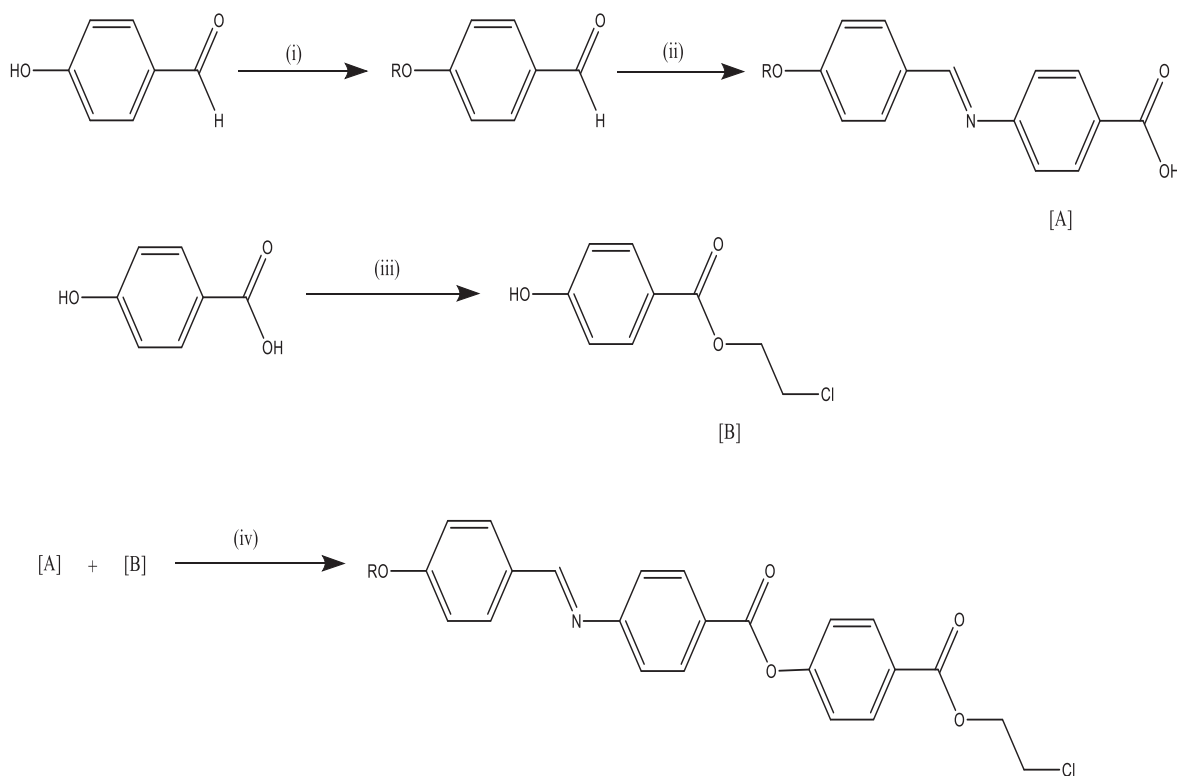


Figure 4: Microphotograph of focal conic texture nematic mesophase (Series I; $n=1$) at 299 °C on cooling

Synthetic route



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

Reagents & conditions: (i) R-Br, Dry K₂CO₃, Dry Acetone, (ii) P-Aminobenzoic acid, Dry ethanol, Acetic acid (iii) 2-Chloro ethanol, Conc.H₂SO₄ (iv) DCC, DMAP, Dry THF.

Table:4 Comparison of the phase transition temperatures, smectic mesophase range and comparative molecular structures of series **I, A, B** and **C**.

| Compound | Cr-SmA | SmA-Iso | Mesophase range/°C | Commencement of smectic A phase |
|----------|--------|---------|--------------------|---------------------------------|
| I | 158 | 238 | 80 | C ₁ |
| A | 142 | 211 | 69 | C ₁ |
| B | 66 | 104 | 38 | C ₁ |
| C | 93 | 158 | 65 | C ₂ |

