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Research Article

DESIGN, SYNTHESIS AND STUDY OF CALAMITIC LIQUID CRYSTALS CONTAINING CHALCONE AND SCHIFF BASE LINKAGES ALONG WITH TERMINAL ALKOXY CHAIN

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ABSTRACT

We report here bent shape calamitic thermotropic liquid crystal derivatives of 4-amino acetophenone. Compounds were designed having both chalcone and Schiff base as central linkages with various terminal alkoxy chains. All the compounds were synthesized and well characterized. Compounds were screened for their mesomorphic properties using polarizing optical microscope under heating and cooling cycles. Thermograms of all the compounds were studied using differential scanning calorimetry to get phase transition temperatures and enthalpy. Compounds with chain length of eight to twelve carbons showed nematic mesophase. Compounds with higher chain length showed smectic A mesophase under both heating and cooling cycles.

Keywords: Chalcone linkage, Schiff base linkage, Thermotropic liquid crystal bent shape liquid crystal.

1. INTRODUCTION

Thermotropic liquid crystals are important liquid crystalline materials due to their wide range of applications which include liquid crystal displays, liquid crystal thermometers, optical storage materials, sensing materials [1-3]. The type of mesophase and layer arrangement can be affected by small changes in the molecular shape in thermotropic bent shape liquid crystalline materials [4-5]. At the same time central linkages such as ester, imine, azo, chalcone, etc have major role in formation of mesophase as they maintain the linearity and rigidity within the whole molecular structure along with this they provide thermal stability and wide temperature range to mesophase. Incorporation of one or more such linkages in thermotropic molecules have been found to play major role in mesomorphic properties [6-10].

Chalcone linkage has been used in liquid crystalline compounds due to its geometrical shape, rigidity and thermal stability. Charge transfer property by π-bond conjugation of chalcone linkage also plays important role in fluorescence, dielectric properties of molecules and also in polymerisation process [11-12]. Liquid crystalline properties of molecules containing chalcone linkages can be enhanced by incorporating other central linkages such as imine (Schiff base), ester or azo along with it [13]. Schiff base linkage containing liquid crystalline materials are well explored as it has stepped structure and helps incorporating mesophase property in molecules. Compounds with such linkage are more conducive to the fluorescent and mesogenic behaviour because imine group (-CH=N-) enhances the conjugation of the molecule [14-16].

Cheng et al. have synthesized polycatenar-type organogelators, comprising a cyanochalcone unit and a half disklike phenyl group with two or three long alkoxy chains **1** (Fig. 1) and studied for their supramolecular assembly with respect to their molecular structures. These compounds formed very stable organogels in n-alkanes, cyclohexane, and alcohols. However, compound without cyano group failed to show any gelation ability [17]. Thaker et al. have reported synthesis of bent shape like mesogens **2** with Schiff base and chalcone as central linking group. Compounds with propyl to octyl derivatives have shown nematic phase, while decyl to hexadecyl compounds have shown smectic phase (Fig. 1) [18].

Gallardo et al have studied two new series of bent-shaped compounds derived from chalcones and cyanopyridine for their liquid crystalline behaviour. Both compounds showed hexagonal columnar arrangement at room temperature. Compound **3** showed unstable monotropic liquid crystalline behaviour. While in compound **4**, cyanopyridine bent core stabilized the liquid crystalline behaviour in hexacatenar systems [19].

Sharma et al have reported calamitic liquid crystal compound **5** containing chalcone, Schiff base and ester as central linkages along with various alkoxy chain [20]. Compound **5** with lower alkyl chain have shown SmC mesophase while higher chain length analogues have shown both SmC and nematic mesophase. Jadeja et al have reported Schiff base derivatives of 4-amino-acetophenone **6** and their Cu complexes **7** as thermotropic liquid crystals with SmA fan type mesophase (Fig. 1) [21].

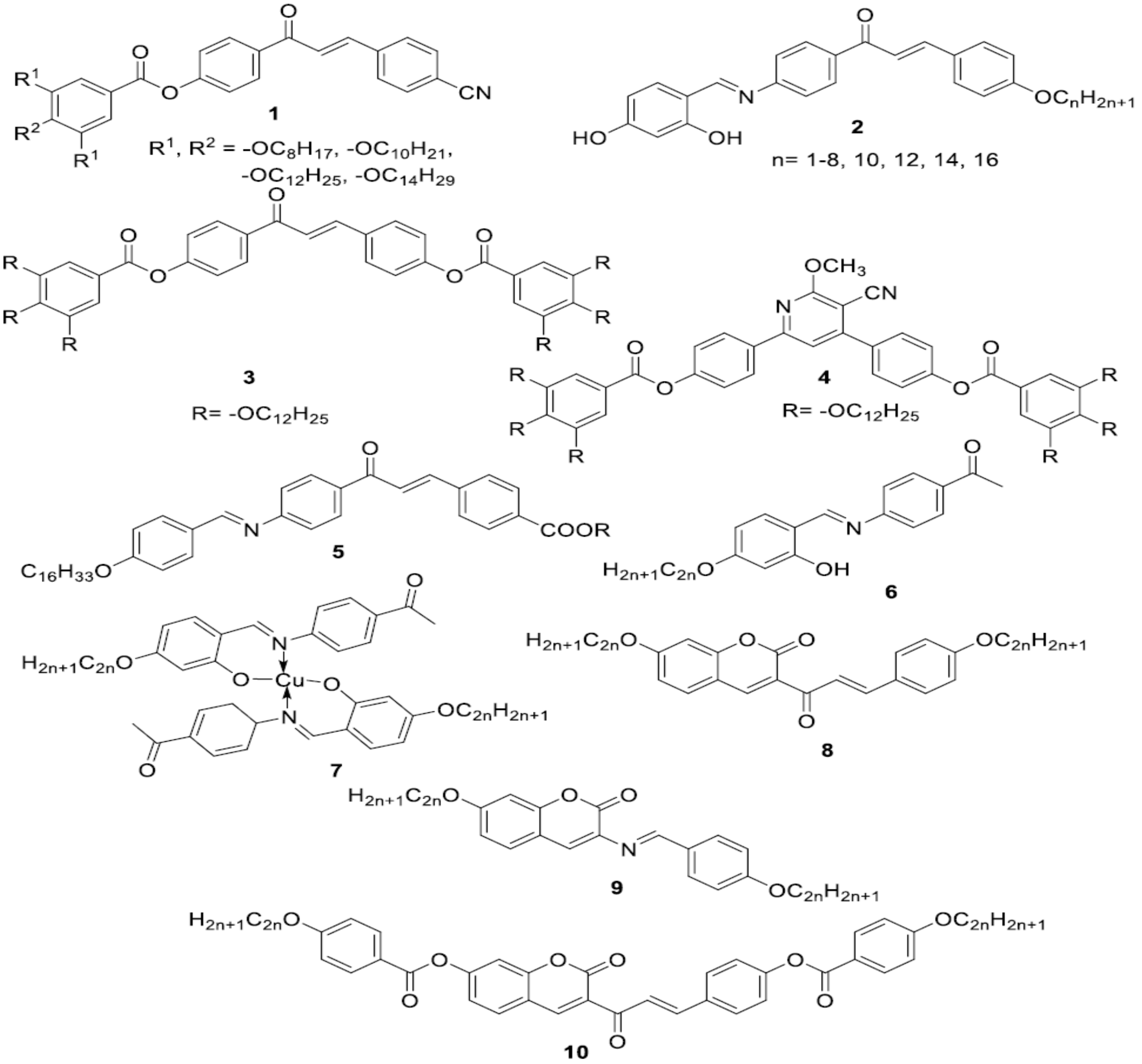


Fig. 1: Chalcone and Schiff base containing derivatives with liquid crystalline properties

Recently our group has also reported design and synthesis of new homologous series of n-alkoxy coumarin derivatives with chalcone as central linkage **8**, Schiff Base as central linkage **9,** bis-ester with chalcone central linkage **10** (Fig. 1) [22-23]. Compounds with lower alkyl chains have shown only nematic phase in homologous series for compounds **8-9**. While all the higher members from the series with alkyl chain length n-decyl and above have shown only SmA phase. Homologous series of compound **10**, lower flexible alkoxy chains showed nematic mesophase uptoheptyloxy chain. Recent literature search on liquid crystal compounds containing both chalcone and Schiff base central linkages, led us to study the effect of sequential increase in alkyl chain length on their mesomorphic behaviour in a molecule containing both chalcone and schiff base linkages. We report herein design and synthesis of bent shape compounds **14a-j** containing chalcone and Schiff base linkages to provide rigidity along with long alkoxy chain to provide flexibility.

2. EXPERIMENTAL

Reagent grade chemicals and solvents were purchased from commercial supplier and used after purification. Thin-layer chromatography was performed on silica gel F254 plates (Merck & Co., Kenilworth, NJ, USA). Acme's silica gel (60-120 mesh) was used for column chromatographic purification. All reactions were carried out in normal atmosphere. Melting points are uncorrected and were measured in open capillary tubes. IR spectra were recorded as KBr pellets on Bruker Spectrometer.^{1}H-NMR spectral data were recorded on Advance Bruker 400 spectrometer (400 MHz) with $CDCl_3$ as solvent and *J* values are in Hz.^{13}C-NMR spectra data were recorded on Bruker Advance NEO 500 spectrometer (500/400 MHz) with $CDCl_3$ as solvent. Liquid crystal properties were studied using Polarizing Optical Microscope -LEICA DM 2500P, CAMERA- LEICA-DFC 295 and Heating Pod-LINKA 19. Thermograms were calculated by DSC (DSC-822, Mettler Toledo having Stare software).

2.1. General method of synthesis of 4-Alkoxy benzaldehyde 12a-j

To a solution of 4-hydroxy benzaldehyde **11** (1.0 g, 8.20mmol, 1.0 eq) in *N*,*N*-dimethylformamide (DMF) (20 mL), anhydrous K_2CO_3 (1.7 g, 12.30mmol, 1.5 eq) was added and stirred for 10-15 min. To the mixture, alkyl bromide (9.02mmol, 1.1 eq) was added followed by catalytic amount of KI. The reaction mixture was stirred for 24-30 hours at room temperature. The completion of reaction was checked by TLC. The reaction mixture was poured in ice-cold water, extracted with dichloromethane (DCM) (3 x 25 mL). The organic layers were combined, washed with water (2 x 25 mL), brine solution (25 mL), dried over anhydrous Na_2SO_4, filtered and concentrated on a rotavapor to give crude compound **12a-j**. The crude compound was purified by column chromatography using pet. Ether: ethyl acetate (95:5) to give pure compound.

2.2. General method of preparation of chalcones 13a-j

To solution of p-aminoacetophenone (0.250 g, 1.85mmol, 1.0 eq) in ethanol (25 mL), 40% aq. solution of NaOH (1.85 mmol, 1.0 eq) was added and stirred at room temperature for 10-15 min. To resulting mixture, 4-alkoxy benzaldehyde **12a-j** (1.85 mmol, 1.0 eq) was added. The reaction mixture was stirred at room temperature for 18-24 h. The completion of reaction was checked by TLC. The reaction mixture was poured into ice-cold water to give solid. The solid was filtered, washed with water, dried and crystallized using ethanol to give compound **13** as light yellow solid. Compound **13** was directly used for next step without any further purification.

2.3. General method of preparation of Schiff base

To a solution of compound **13a-j** (1.0 eq) into absolute ethanol (20 mL), 4-n-alkoxy benzaldehyde **12a-j** (1.0 eq) was added followed by catalytic amount (3-4 drops) of acetic acid. The resulting mixture was refluxed at 76-78°C for 18 h. The reaction mixture was allowed to cool to room temperature, concentrated to half volume under reduced pressure using rotavapor. The resulting solution was allowed to cool in ice bath to give solid. The separated solid was filtered, washed with cold ethanol to give compound **14a-j** as white solid. All the compounds were characterized using IR, ^{1}H-NMR, ^{13}C-NMR, etc.

2.3.1. *(E)-1-(4-{[(E)-4-Propoxybenzylidene] amino} phenyl)-3-(4-propoxyphenyl)prop-2-en-1-one (14a)*

Off White solid, Yield: 31 %; M.P: 132-134°C; IR (KBr): 3446, 2965, 2937, 2877, 1660, 1628, 1602, 1589, 1572, 1510, 1469, 1420, 1307, 1246, 1169, 1112, 1071, 1022, 978, 857, 834, 819 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05-1.10 (m, 6H), 1.82-1.89 (m, 4H), 3.97-4.03 (m, 4H), 6.95 (d, *J*=8.8Hz, 2H), 7.01 (d, *J*=8.8Hz, 2H), 7.27 (d, *J*=8.4Hz, 2H), 7.48 (d, *J*=15.2Hz, 1H), 7.63 (d, *J*=8.8Hz, 2H), 7.85 (m, 3H), 8.09 (d, *J*=8.4Hz, 2H), 8.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 10.54, 22.52, 69.65, 69.71, 114.78, 114.89, 119.39, 121.01, 127.47, 128.60, 29.88, 130.26, 130.90, 135.49, 144.43, 156.35, 160.99, 161.25, 162.31, 189.41; Anal. Calc. for $C_{28}H_{29}NO_3$; C, 78.66; H, 6.84; N, 3.28; found: C, 78.79; H, 6.91; N, 3.34 %.

2.3.2. (E)-1-(4-{[(E)-4-Butyloxybenzylidene] amino}phenyl)-3-(4-butoxyphenyl)prop-2-en-1-one (14b)

Off White solid, Yield: 28 %; M.P: 120-122°C; IR (KBr): 2955, 2873, 1626, 1597, 1509, 1469 1305, 1250, 1169, 1115, 1072, 1035, 982, 827 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99-1.03(m, 6H), 1.52-1.53(m, 4H), 1.68-1.84(m, 4H), 4.02-4.08(m, 4H), 6.95(d, *J*=8.0 Hz, 2H), 7.01(d, *J*=8.8Hz, 2H), 7.27(d, *J*=6.4Hz, 2H), 7.48(d, *J*=15.6Hz, 1H), 7.63(d, *J*=8.4 Hz, 2H), 7.83(d, *J*=15.6Hz, 1H), 7.87(d, *J*=8.4 Hz, 2H), 8.09(d, *J*=8.0 Hz, 2H), 8.41(s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm 13.87, 19.24, 31.21, 67.88, 67.95, 113.92, 114.81, 119.47, 121.00, 127.65, 128.71, 129.98, 130.93, 132.01, 135.51, 143.05, 144.39, 150.97, 156.36, 160.92, 161.28, 162.35, 164.28, 189.36; Anal. Calc. for $C_{30}H_{33}NO_3$; C, 79.09; H, 7.30; N, 3.07; found: C, 79.18; H, 7.42; N, 3.28 %.

2.3.3. (E)-1-(4-{[(E)-4-Pentyloxybenzylidene] amino}phenyl)-3-(4-pentyloxyphenyl)prop-2-en-1-one (14c)

Off White solid, Yield: 40 %; M.P: 118-120°C; IR (KBr): 2958, 2936, 2868, 1626, 1593, 1570, 1509, 1470, 1419, 1395, 1367, 1307, 1248, 1169, 1112, 1075, 1019, 988, 882, 857, 818 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96-0.98 (m, 6H), 1.43-1.45(m, 8H), 1.83-1.85(m, 4H), 4.00-4.06(m, 4H),6.95(d, *J*=8.4Hz, 2H), 7.01(d, *J*=8.4 Hz, 2H), 7.27(d, *J*=7.2Hz, 2H), 7.48(d, *J*=15.6Hz, 1H), 7.62(d, *J*=8.4Hz, 2H), 7.83(d, *J*=16Hz, 1H), 7.87(d, *J*=8.0Hz, 2H), 8.09 (d, *J*=8.0 Hz, 2H), 8.40(s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm 14.06, 22.48, 28.18, 28.88, 68.18, 68.25, 114.78, 114.91, 119.24, 121.00, 127.50, 128.64, 129.87, 130.24, 130.89, 135.50, 144.39, 156.36, 160.92, 161.27, 162.33, 189.35; Anal. Calc. for $C_{32}H_{37}NO_3$; C, 79.47; H, 7.71; N, 2.90; found: C, 79.53; H, 7.82; N, 2.98 %.

2.3.4. (E)-1-(4-{[(E)-4-Hexyloxybenzylidene] amino}phenyl)-3-(4-hexyloxyphenyl)prop-2-en-1-one (14d)

Off White solid, Yield: 24 %; M.P: 114-116°C; IR (KBr): 3039, 2933, 2866, 1626, 1600, 1571, 1510, 1471, 1420, 1393, 1307, 1250, 1169, 1112, 1076, 1027, 891, 882, 858, 836 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95-0.96 (m, 6H), 1.35-1.40 (m, 8H) 1.48-1.50 (m, 4H), 1.79-1.87 (m, 4H), 4.01-4.07 (m, 4H), 6.95 (d, *J*=8.8Hz, 2H), 7.01 (d, *J*=8.8Hz, 2H), 7.28 (d, *J*=8.4Hz, 2H), 7.48 (d, *J*=15.6Hz, 1H), 7.63 (d, *J*=8.4Hz, 2H), 7.83 (d, *J*=15.6Hz, 1H), 7.87 (d, *J*=8.8Hz, 2H), 8.09 (d, *J*=8.4Hz, 2H), 8.41 (s,1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm 14.07, 22.63, 25.71, 29.15, 31.59, 68.20, 68.27, 114.77, 114.86, 119.42, 121.00, 127.50, 128.64, 129.86, 130.23, 130.89, 135.51, 144.40, 156.37, 160.92, 161.28, 162.33, 189.36; Anal. Calc. for $C_{34}H_{41}NO_3$; C, 79.81; H, 8.08; N, 2.74; found: C, 79.88; H, 8.13; N, 2.81 %.

2.3.5. (E)-1-(4-{[(E)-4-Heptyloxybenzylidene] amino}phenyl)-3-(4-heptyloxyphenyl)prop-2-en-1-one (14e)

Off White solid, Yield: 33 %; M.P: 114-116°C; IR (KBr): 2956, 2930, 2857, 1626, 1594, 1511, 1470, 1420, 1394, 1367, 1308, 1250, 1170, 1112, 1076, 1016, 988, 859, 837, 773 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90-0.94 (m, 6H), 1.34-1.40 (m, 12H), 1.45-1.51 (m, 4H), 1.79-1.87 (m, 4H), 4.00-4.06 (m, 4H), 6.94 (d, *J*=8.8Hz, 2H), 7.00 (d, *J*=8.8Hz, 2H), 7.27 (d, *J*=8.4Hz, 2H), 7.48 (d, *J*=15.6Hz, 1H), 7.62 (d, *J*=8.4Hz, 2H), 7.83 (d, *J*=15.6Hz, 1H), 7.87 (d, *J*=8.8Hz, 2H), 8.09 (d, *J*=8.4Hz, 2H), 8.40 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm 14.12, 22.64, 25.99, 29.07, 29.18, 31.79, 68.20, 68.27, 114.79, 114.91, 119.43, 120.99, 127.50, 128.63, 129.86, 130.23, 130.89, 135.51, 144.40, 156.37, 160.92, 161.28, 162.34, 189.37; Anal. Calc. for $C_{36}H_{45}NO_3$; C, 80.11; H, 8.80; N, 2.60; found: C, 80.22; H, 8.92; N, 2.79 %.

2.3.6. (E)-1-(4-{[(E)-4-Octyloxybenzylidene] amino}phenyl)-3-(4-octyloxyphenyl)prop-2-en-1-one (14f)

Off White solid, Yield: 58 %; M.P: 120-122°C; IR (KBr): 3039, 2955, 2922, 2854, 1626, 1592, 1571, 1510, 1470, 1420, 1392, 1308, 1250, 1169, 1111, 1076, 1025, 994, 858, 835, 820, 723 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89-0.93 (m, 6H), 1.31-1.36 (m, 16H), 1.48-1.49 (m, 4H), 1.79-1.87 (m, 4H), 4.00-4.07 (m, 4H), 6.95 (d, *J*=8.4Hz, 2H), 7.01 (d, *J*=8.8Hz, 2H), 7.28 (d, *J*=8.4Hz, 2H), 7.48 (d, *J*=15.6Hz, 1H), 7.63 (d, *J*=8.8Hz, 2H), 7.83 (d, *J*=15.6Hz, 1H), 7.85 (d, *J*=8.8Hz, 2H), 8.10 (d, *J*=8.4Hz, 2H), 8.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.18, 22.71, 26.04, 29.18, 29.28, 29.39, 31.85, 68.19, 68.26, 114.77, 114.89, 119.35, 121.01, 127.46, 128.60, 129.87, 130.25, 130.90, 135.48, 144.41, 156.36, 160.95, 161.26, 162.32, 189.33; Anal. Calc. for $C_{38}H_{49}NO_3$; C, 80.38; H, 8.70; N, 2.47; found: C, 80.47; H, 8.83; N, 2.56 %.

2.3.7. (E)-1-(4-{[(E)-4-Decyloxybenzylidene] amino}phenyl)-3-(4-decyloxyphenyl)prop-2-en-1-one (14g)

Off White solid, Yield: 22 %; M.P: 108-110°C; IR (KBr): 3449, 2956, 2919, 2851, 1626, 1603, 1590, 1572, 1510, 1471, 1420, 1308, 1251, 1169, 1053, 881, 858, 836, 722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 0.89-0.92 (m, 6H), 1.30-1.49 (m, 24H), 1,79-1.81 (m, 4H), 1.84-1.87 (m, 4H), 4.01-4.07 (m, 4H), 6.95 (d, *J*=8.8Hz, 2H), 7.01 (d, *J*=8.8Hz, 2H), 7.28 (d, *J*=8.4Hz, 2H), 7.48 (d, *J*=15.6Hz, 1H), 7.63 (d, *J*=8.4Hz, 2H) 7.83 (d, *J*=15.6Hz, 1H), 7.87 (d, *J*=8.8Hz, 2H), 8.09 (d, *J*=8.4Hz, 2H), 8.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.15, 22.71, 26.03, 29.18, 29.35, 29.40, 29.59, 31.92, 68.21, 68.28, 114.79, 114.91, 119.43, 120.99, 127.50, 128.64, 129.86, 130.23, 130.89, 135.51, 144.40, 156.37, 160.92, 161.28, 162.34, 189.38; Anal. Calc. for $C_{42}H_{57}NO_3$; C, 80.85; H, 9.21; N, 2.24; found: C, 80.96; H, 9.35; N, 2.38 %.

2.3.8. (E)-1-(4-{[(E)-4-Dodecyloxybenzylidene] amino}phenyl)-3-(4-dodecyloxyphenyl)prop-2-en-1-one (14h)

Off White solid, Yield: 22 %; M.P: 106-108°C; IR (KBr): 2956, 2919, 2851, 1626, 1594, 1511, 1469, 1421, 1396, 1369, 1308, 1253, 1170, 1111, 1025, 987, 837, 821, 774, 724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 0.90 (s, 6H), 1.28-1.48 (brs, 36H), 1.82 (s, 4H), 4.03 (s, 4H), 6.94 (d, *J*=7.2Hz, 2H), 7.00 (d, *J*=6.4Hz, 2H), 7.28 (brs, 2H), 7.48 (d, *J*=15.6Hz, 1H), 7.62 (d, *J*=6.4Hz, 2H), 7.81-7.88 (m, 3H), 8.09 (d, *J*=6.8Hz, 2H), 8.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.16, 22.72, 26.02, 29.18, 29.38, 29.40, 29.59, 29.62, 29.66, 29.68, 31.94, 68.21, 68.28, 114.80, 114.91, 119.44, 121.02, 127.50, 128.63, 129.76, 130.23, 130.95, 135.51, 144.42, 156.37, 160.94, 161.28, 162.34, 189.41; Anal. Calc. for $C_{46}H_{65}NO_3$; C, 81.25; H, 9.63; N, 2.06; found: C, 81.39; H, 9.77; N, 2.16 %.

2.3.9. (E)-1-(4-{[(E)-4-Tetradecyloxybenzylidene] amino}phenyl)-3-(4-tetradecyloxyphenyl) prop-2-en-1-one (14i)

Off White solid, Yield: 23 %; M.P: 108-110°C; IR (KBr): 3449, 2955, 2918, 2849, 1660, 1626, 1603, 1590, 1573, 1511, 1468, 1421, 1394, 1308, 1255, 1221, 1170, 1038, 1022, 878, 858, 831, 723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 0.88-0.90 (m, 6H), 1.28 (br s, 40H), 1.48 (br s, 4H), 1.82-1.83 (m, 4H), 4.01-4.05 (m, 4H), 6.92-6.99 (m, 4H), 7.02-7.28 (m, 2H), 7.48 (d, *J*=15.2Hz, 1H), 7.63 (d, *J*=8.4Hz, 2H), 7.83 (d, *J*=15.2Hz, 1H), 7.87 (d, *J*=8.4Hz, 2H), 8.10 (d, *J*=8.4Hz, 2H), 8.11 (s, 1H); Anal. Calc. for $C_{50}H_{73}NO_3$; C, 81.58; H, 10.00; N, 1.90; found: C, 81.69; H, 10.13; N, 1.98 %.

2.3.10. (E)-1-(4-{[(E)-4-Hexadecyloxybenzylidene] amino}phenyl)-3-(4-hexadecyloxyphenyl) prop-2-en-1-one (14j)

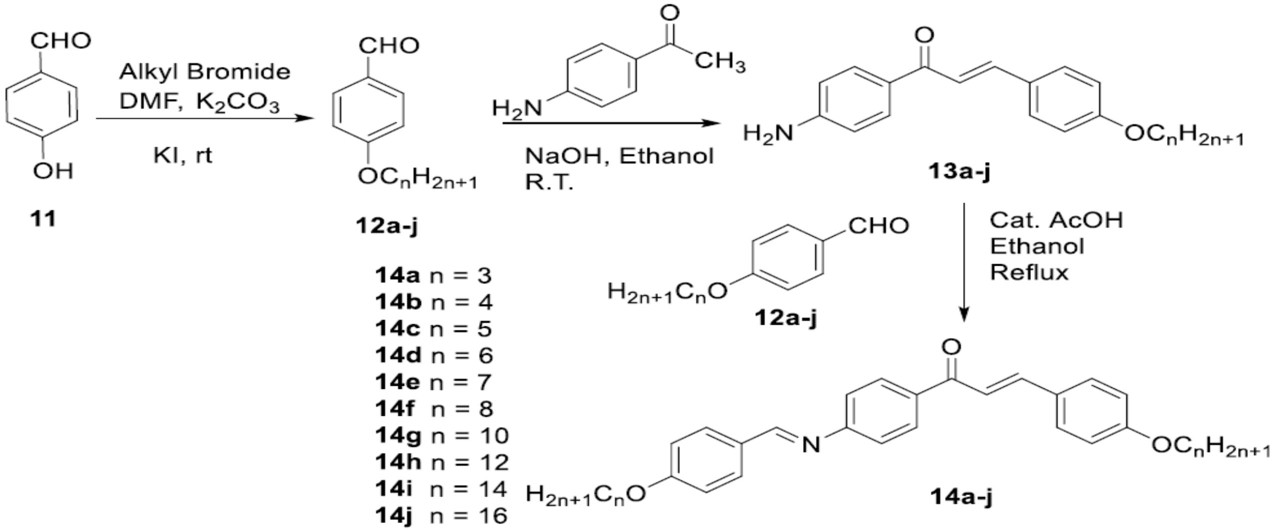
Off White solid, Yield: 20 %; M.P: 104-106°C; IR (KBr): 3447, 2955, 2918, 2850, 1657, 1627, 1593, 1573, 1511, 1469, 1421, 1333, 1308, 1255, 1170, 1075, 857, 836, 821, 723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 0.89 (brs, 6H), 1.28-1.48 (brs, 52H), 1,83 (brs, 4H), 4.04 (brs, 4H), 6.94-6.99 (m, 2H), 7.28-7.37 (m, 2H), 7.48 (d, *J*=15.6Hz, 1H), 7.63 (brs, 2H), 7.81-7.87 (m, 3H), 8.10 (s, 2H), 8.36 (s, 2H), 8.40 (s, 1H); Anal. Calc. for $C_{54}H_{81}NO_3$; C, 81.87; H, 10.31; N, 1.77; found: C, 81.98; H, 1084%.51; N, 1.

3. RESULTS AND DISCUSSION

3.1. Chemistry

Compounds **14a-j** (Scheme-1) were designed, synthesized and analysed for mesophase transition using differential scanning calorimetry (DSC) and polarizing optical microscope (POM). 4-Hydroxybenzaldehyde **11** was alkylated with different alkyl bromides in DMF using anhydrous potassium carbonate and catalytic amount of KI to give 4-alkoxy benzaldehyde **12**. The 4-n-alkoxy benzaldehyde **12a-j** were purified by column chromatography and directly used for reaction with 4-amino acetophenone. 4-Amino acetophenone reacted with different 4-n-alkoxy benzaldehyde **12a-j** under basic conditions using sodium hydroxide in ethanol to give chalcone derivatives **13a-j**. Compounds **13a-j** were reacted with one equivalent of 4-n-alkyloxy benzaldehyde **12** using catalytic amount of acetic acid in ethanol to give the final compounds **14a-j**. All synthesized compounds **11a-j** were characterized by IR, ^1H-NMR and ^{13}C-NMR analyses.

The IR spectrum of the compound **14f** showed peaks in region of 2954-2854 cm^{-1} corresponding to alkyl chain. Here absence of two peaks around 3300 and 3200 cm^{-1} indicates formation of Schiff base from free amine. It showed peak at 1625 cm^{-1} for carbonyl group of chalcone moiety and peak at 1592 cm^{-1} for imine group. The ^{1}H-NMR of compound **14f** showed methyl and methylene protons of both octyloxy group in the region 0.89-1.87 ppm and methylene protons attached to oxygen were observed as mixed triplet in region of 4.00-4.07 ppm. Aromatic protons were observed in the region of 6.95-8.10 ppm along with chalcone protons at 7.48 and 7.83 ppm with the coupling constant 15.6 Hz indicating trans coupling. The ^{13}C-NMR of compound **14f** showed alkyl chain carbons in the region of 14.14-68.44 ppm, aromatic carbons in region of 113.92-164.28 ppm and carbonyl carbon at 189.36 ppm. We have also attempted to synthesize compound with C18 chain length under same reaction conditions using NaOH, but it gave Schiff base only instead of chalcone product even after prolong heating. Synthesized compounds **14a-j** were studied for their liquid crystalline property using polarizing optical microscope.



Scheme 1: Synthesis of compounds 14a-j

3.2. Mesomorphic properties

The synthesised compounds **14a-j** were studied for thermotropic properties and its melting behaviour was monitored by differential scanning calorimetry (DSC) and polarizing optical microscope analysis (POM) during both heating and cooling scans. Thin film of compound was placed on glass slide, covered with cover slip and heated at the rate of 10°C/min to give isotropic liquid. Changes in textures were observed under microscope during 1st cooling cycle and 2nd heating cycle at the rate of 10°C/min. Clear-cut transition temperatures and textures could be obtained from DSC curves and POM observations for all of the compounds, and they were in good agreement with each other for the multiple heating/cooling cycles. Thermograms were calculated by DSC (DSC-822, Mettler Toledo having Stare software). Phase transitions of all the compounds were measured in both heating and cooling cycle at rate of 10°C/min. The transition temperatures and phase sequences for compounds **14a-j** are summarized in Table 1.

3.2.1. DSC analysis

DSC thermograms for compounds **14a-j** were evaluated for transition temperature and calculating enthalpy of all the synthesized compounds. Compounds **14a-e** exhibited one endotherm from Cr-Iso in heating cycle with no mesogenic property. Compound **14f** and **14g** showed monotropic behaviour by showing two exotherms in cooling cycle for Iso-N and N-Cr transitions during cooling cycle (Fig. 2a).

Compounds **14h** exhibited two endotherms in heating cycle for Cr-N and N-Iso transitions and two exotherms in cooling cycle for Iso-N and N-Cr transitions (Table 1). Compounds **14i-j** exhibited two endotherms in heating cycle for Cr-SmA and SmA-Iso transitions and two exotherms in cooling cycle for Iso-SmA and SmA-Cr transitions (Fig. 2b & Table 1).

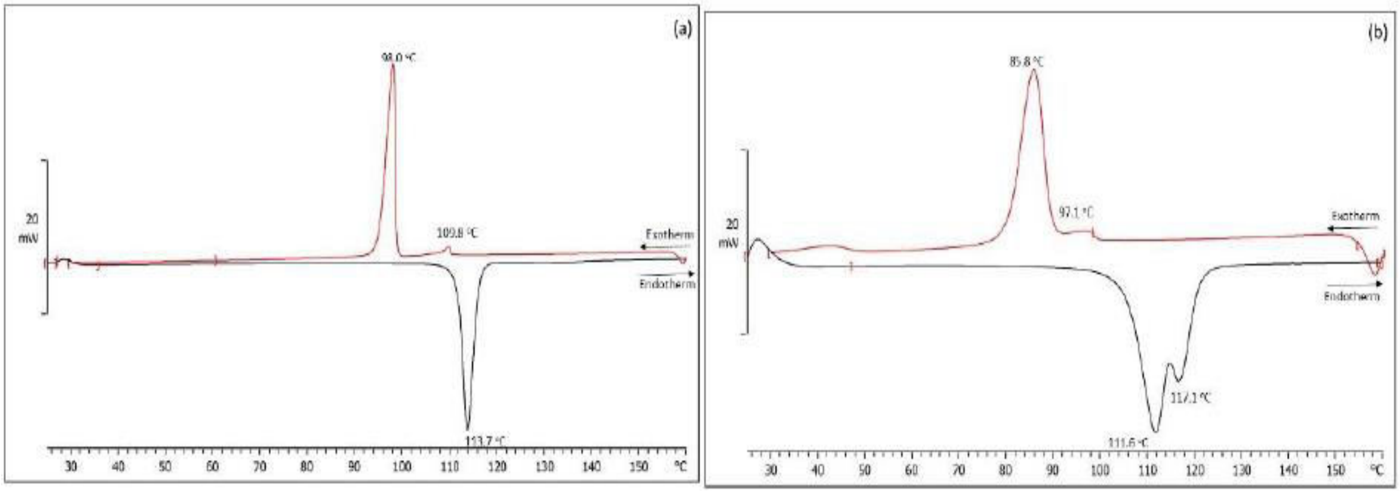
3.2.2. POM analysis

In cooling cycle, compounds **14a-e** were crystallized without any mesophase transition. Similarly in heating cycle, compounds **14a-e** were converted to isotropic liquid without showing any mesophase transition, thus compounds **14a-e** containing alkoxy chains of C4-C7 carbons have not shown any mesophase during cooling and heating cycle.

Table 1: Phase assignments, transition temperature °C of compounds 14a-j as determined by POM and DSC

Compd	**Chain length**	**2nd heating process[a] (onset 10°C/min) [°C]/[ΔH KJmol^{-1}]**	**1st cooling process[a] (onset 10°C/min) [°C]/[ΔH KJmol^{-1}]**
14a	3	Cr 141.1(21.89)Iso	Iso 117.2(15.63)Cr
14b	4	Cr 130.3(24.51)Iso	Iso 115.2(12.61)Cr
14c	5	Cr 121.6(39.04)Iso	Iso 103.2(23.18)Cr
14d	6	Cr 119.1(27.12)Iso	Iso 103.0(25.66)Cr
14e	7	Cr 116.9(35.82)Iso	Iso 99.4(30.74)Cr
14f	8	Cr 113.9(64.49)Iso	Iso 104.3(1.61)N 96.6(57.89)Cr
14g	10	Cr 113.7(67.08)Iso	Iso 109.8(2.34)N 98.0(58.72) Cr
14h	12	Cr 100.4(43.51) N 114.7(3.24) Iso	Iso 100.8(2.29) N 87.1(46.14) Cr
14i	14	Cr 111.5(22.60)SmA 117.1(1.66) Iso	Iso 97.1(1.36) SmA85.8 (49.74) Cr
14j	16	Cr 113.7(28.02)SmA119.6(40.74) Iso	Iso 99.6(4.30) SmA92.1(46.37) Cr

[a]Cr: Crystalline state; N: Nematic phase: SmA: Smectic A phase; Iso: Isotropic state



(a) compound 14gwith decyloxy chain (b) compound 14iwith tetradecyloxy chain

Fig. 2: DSC plot in both heating and cooling cycles along with transition temperatures

On changing the chain length from heptyl to octyl group in compound **14f** showed nematic Schlieren texture at 104.3°C (Fig. 3a), Compound **14f** did not show any mesophase transition during heating cycle. Compound **14g** with decyloxy side chain also showed monotropic behaviour and showed nematic droplet turning to Schlieren texture at 109.8°C in cooling cycle (Fig. 3b).

Compound **14h** with dodecyl chain showed nematic Schlieren texture at 100.8°C during cooling cycle, which crystallized on further cooling at 87°C (Fig. 3c-d) and nematic mesophase at 100.4°C during heating cycle. Compounds **14i and 14j** showed smectic A mesophase in in heating and cooling cycle (Fig. 4a-b).

3.2.3. Structure-mesomorphic property relationship

To identify the effects of the terminal chain on the mesomorphic properties, the graph of phase-transition temperatures against the number of carbons side chain in chalcone- Schiff base hybrid with various n-alkoxy chain has been shown in for both cooling and heating cycles.

In 1st cooling cycle, the transition curves Iso-N, Is-SmA N/SmA/Iso-Cr are shown in Fig. 5a. The Iso-N curve started appearing at eight carbon chain length. While Iso-SmA curve appeared from tetradecyloxy carbon chain. Lower members of series up to chain length of seven carbons did not show any mesophase as seen in curve for N/SmA/Iso-Cr transitions. In 2nd heating cycle shown in Fig. 5b, Cr-N/SmA/Iso transition curve exhibited falling tendency without any odd even effect up to n-decyloxy derivative **14g**. Compounds **14h** to **14j** did not show any major change this may be due to the excessive Van der Waals attractive forces between the long alkyl chains.

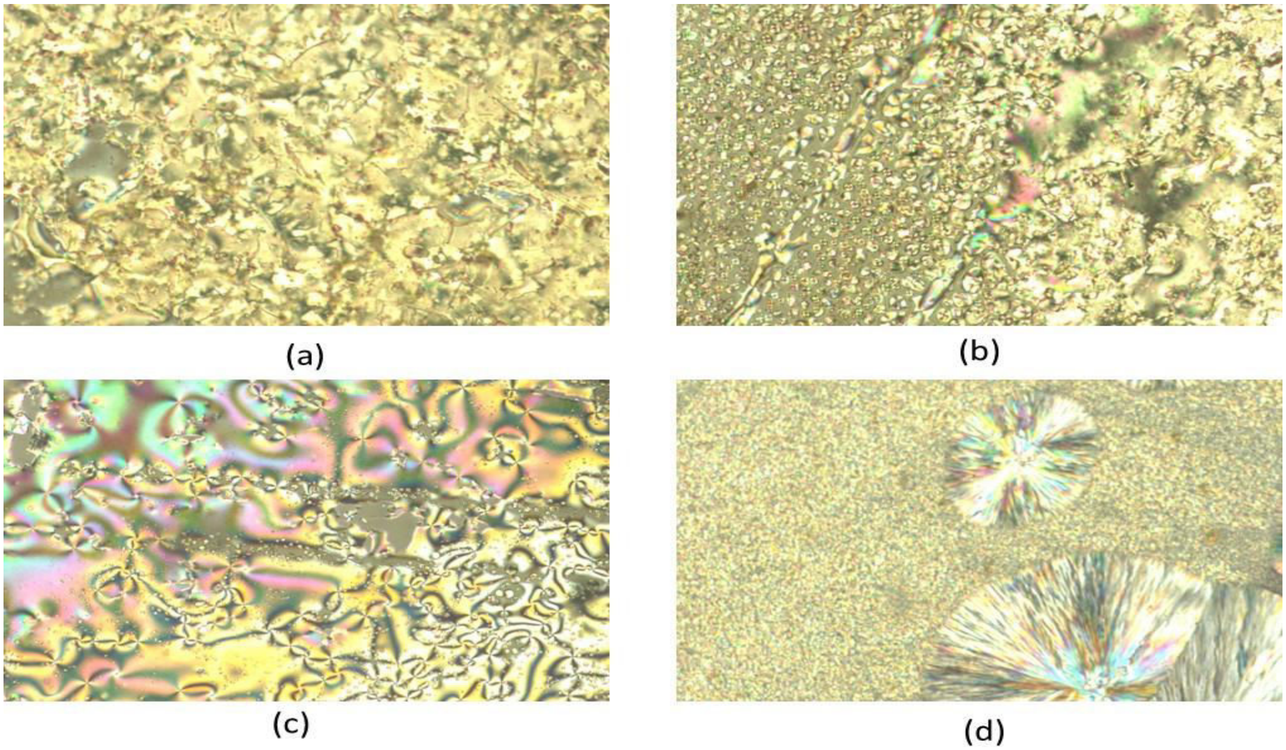


Fig. 3: Liquid crystal phase transition (a) compound 14f nematic Schlieren texture (b) compound 14g nematic droplet to Schlieren texture (c) compound 14h nematic Schlieren texture(d) compound 14h nematic Schlieren to crystallization

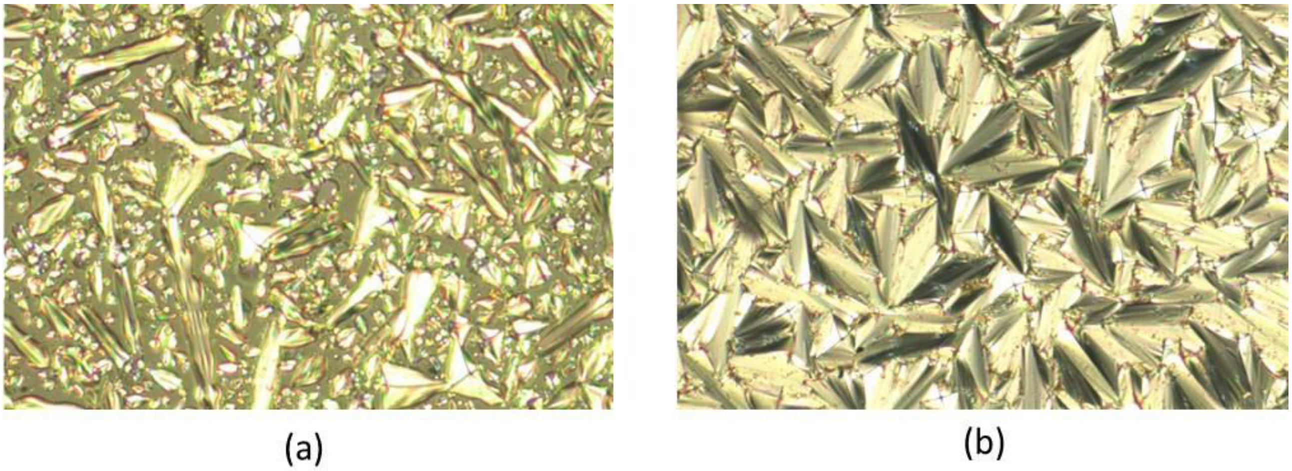


Fig. 4: Liquid crystal phase transition Smectic A mesophase (a) compound 14i (b) compound 14j

The lower members with short chain **14a-f** did not show any mesogenic properties as the isotropic liquid of lower members does not supercool sufficiently for monotropic nematic mesophase to be obtained in 2nd heating cycle. The high melting points of these lower members of series may be partially responsible for the lack of mesophase formation. Although compounds are long, narrow and bent shape with dipolar groups such as chalcone and Schiff base should give strong intermolecular attractions. Intermolecular attractions in compounds **14a-f** are too strong and selective weakening of the cohesive forces may not occur until high temperatures are reached. As the melting process starts, the thermal vibrations may not be allowing an ordered arrangement of the molecules to occur, hence there was no mesophase formation observed in lower members. These intermolecular forces weaken on increasing the alkyl chains in compounds **14h-j**, which has shown N/SmA-Iso transition temperatures in 2nd heating cycle (Fig. 5b).

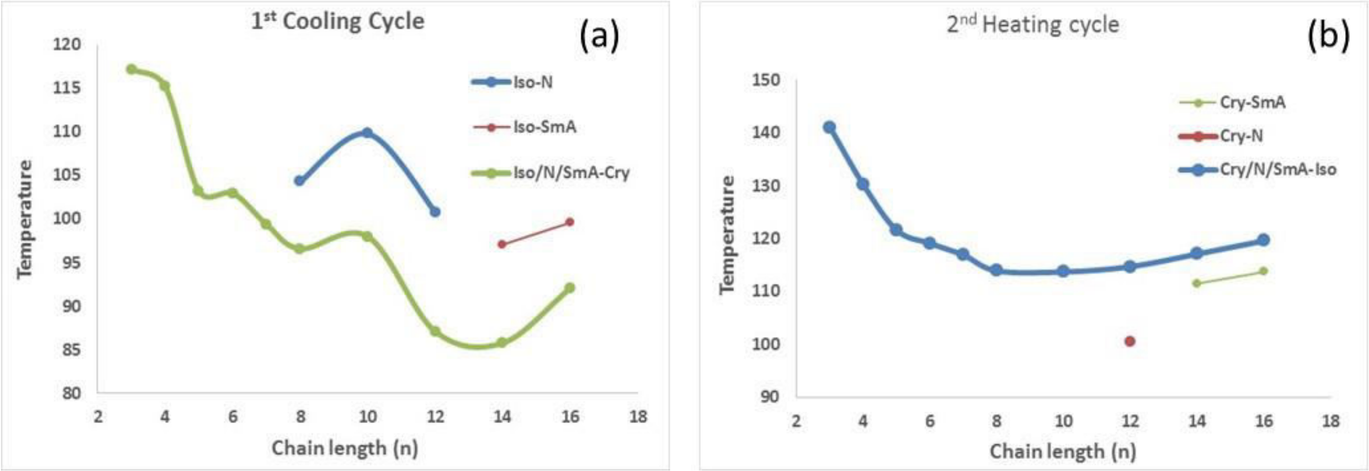


Fig. 5: **Mesomorphic behaviour as a function of the number of carbon atoms (n) in the terminal alkoxy chain in chalcone-Schiff base hybrid derivatives (a) in 1st cooling cycle (b) in 2nd heating cycle**

4. CONCLUSION

Derivatives of 4-amino acetophenone **14a-j** with chalcone and Schiff base as central linkages along with alkoxy side chains were designed and studied for their mesomorphic properties using differential scanning calorimetry (DSC) and polarising optical microscope under both heating and cooling scans. Compounds **14a-e** did not show any mesophase transition, Compounds **14f-g** showed nematic phase during cooling scan only. Compounds **14h** with dodecyloxy chain showed nematic phase during both heating and cooling scans. Compounds **14i** and **14j** with tetradecyloxy and hexadecyloxy chain showed smectic Amesophase during cooling cycle and heating cycle. From these observations we can conclude that change in the linkage from ester group as reported in literature to ether linkage in current molecules, changed the mesomorphic properties drastically. This may be due to change in rigid ester carbonyl to flexible ether linkage, which does not allow intermolecular attractions for lower member of this series to show mesogenic properties.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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