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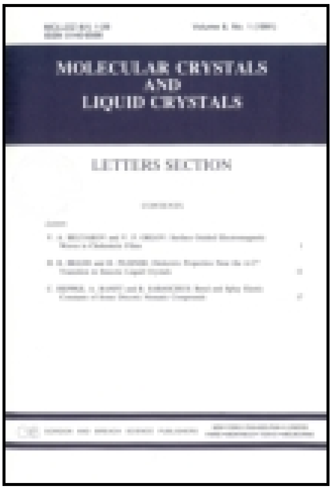

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Synthesis, Structural and Mesophase Characterization of Three Ring Based Thiophene Liquid Crystals

M. Kesava Reddy[a], K. Subramanyam Reddy[a], B. V. N. Phani Kumar[b] & T. Narasimhaswamy[b]

[a] Department of Chemistry, S. V. University, Tirupati 517 502, India
[b] Chemical Physics Lab and Polymer Lab, CSIR-Central Leather Research Institute, Adyar, Chennai 600 020, India

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Synthesis, Structural and Mesophase Characterization of Three Ring Based Thiophene Liquid Crystals

M. KESAVA REDDY,[1] K. SUBRAMANYAM REDDY,[1]
B. V. N. PHANI KUMAR,[2] AND T. NARASIMHASWAMY[2]

[1]Department of Chemistry, S. V. University, Tirupati 517 502, India
[2]Chemical Physics Lab and Polymer Lab, CSIR-Central Leather Research Institute, Adyar, Chennai 600 020, India

Thiophene based calamitic mesogens are receiving paramount importance due to their applications in functional organic materials. The insertion of thiophene in the core unit favours a large change in mesophase characteristics as well as application properties in contrast to those mesogens with phenyl ring core alone. In this work, we report the structural as well as mesophase characterization of six mesogens which are built with a core of three phenyl rings and thiophene ring. The thiophene ring is placed at one end of the core and varied the other end with alkyl/alkoxy chains to investigate the mesophase characteristics. The molecular structures of representative mesogens are confirmed by means of FT-IR and Two-dimensional solution NMR techniques. An enantiotropic nematic phase is observed in all the cases as supported by HOPM and DSC techniques. The mesophase characteristics such as melting and clearing temperatures and phase stability are discussed. A dramatic increase in nematic phase stability for the synthesised mesogens is noticed in contrast to two phenyl ring based thiophene mesogens reported in literature.

Keywords Mesogens; Thiophene; Calamitic; Nematic; NMR; Chemical Shifts

1. Introduction

Calamitic mesogens based on thiophene are increasingly gaining importance owing to their wide range of applications [1–3]. Insertion of thiophene in the mesogenic core not only influences the mesophase transition temperatures considerably but also contributes for interesting properties enabling them to be classified as functional materials [4–6]. The replacement of phenyl ring with thiophene in the core unit of calamitic mesogens results in variation in overall molecular shape [7,8]. The contemporary approach of designing of thermotropic liquid crystals clearly emphasizes the role of molecular shape in varying the mesophase characteristics [9,10]. Usually, the thiophene ring can be introduced in mesogens either at the end or at the center of the core depending upon the position of the linking unit [11–13]. For instance, substitution at 2- or 3-position of thiophene results in calamitic mesogens with thiophene moiety at end of the molecule while 2,5- substitution favours bent-core mesogens [14]. In continuation of our earlier work on thiophene mesogens [15–18], in

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[*]Address correspondence to T. Narasimhaswamy, Chemical Lab & Polymer Lab, CSIR-Central Leather Research Institute, Adyar, Chennai 600020, India. E-mail: tnswamy99@hotmail.com

this paper, 2- and 3-substituted thiophene mesogens built with three phenyl ring core and terminal alkyl/alkoxy chains are studied. For the construction of the core, ester and imines are used as linking units while alkyl/alkoxy chains served as flexible terminal unit [19,20]. Earlier work on two phenyl ring core based thiophene mesogens revealed enantiotropic nematic mesophase with low mesophase stabilities [15, 21, 22]. In order to investigate the influence of additional phenyl ring on mesophase stabilities, in the present work, the core is built with three phenyl rings along with thiophene. Further, the influence of terminal chain on mesophase transition temperatures is studied by varying the length of the terminal group. Since thiophene and its oligomers are finding interesting applications in functional organic materials [23–25], the examination of influence of substitution position and core length of thiophene mesogens is of considerable interest. Further, probing basically simple mesogens proposed in the present work would enable to establish the structure-property correlations which can be extended to structurally complex mesogens that are employed for advanced applications [1,3,4].

2. Experimental Details

2.1 Materials

4-hydroxy benzaldehyde, 2-thiophene carboxylic acid, 3-thiophene carboxylic acid, dodecyl benzoic acid, 4-nitro phenol, N-BOC-4-amino phenol, N,N′-dicyclohexylcarbodiimide (DCC) and 4-dimethylamino pyridine (DMAP) were purchased from Aldrich (USA) and used without further purification. $SnCl_2$, triethylamine, thionyl chloride ($SOCl_2$), N, N′-dimethylformamide (DMF), tetrahydrofuran (THF), ethanol and methanol (SD Fine, Mumbai) were used as received. Trifluoroacetic acid, 4-hydroxy methyl benzoate, dichloromethane, ethyl acetate, diethyl ether, n-hexane, n-heptane, acetone, isopropanol, acetonitrile, ethyl methyl ketone (EMK), potassium hydroxide (pellets), anhydrous potassium carbonate, anhydrous sodium sulphate, sodium chloride, calcium chloride, sodium hydroxide, sodium bicarbonate and hydrochloric acid were obtained from Merck (India) and used as received. 4-hexyloxy benzoic acid and 4-dodecyloxy benzoic acid were synthesized in laboratory.

2.2 Instrumental Details

FT-IR spectra of all the compounds were recorded on ABB BOMEM MB3000 spectrometer using KBr pellets. The nature of the mesophase and the temperature of occurrence were determined with an Olympus BX50 hot-stage optical polarizing microscope (HOPM) equipped with a Linkam THMS 600 stage with a TMS 94 temperature controller. The photographs were taken using an Olympus C7070 digital camera. Differential scanning calorimetry (DSC) traces were recorded using a DSC Q200 instrument with a heating rate of 10°C/minute in nitrogen atmosphere. The data obtained from second heating and cooling is used for discussion. All NMR experiments were run on a JEOL ECA-500 MHz high resolution FT-NMR spectrometer operating at frequencies 500.16MHz (^1H) and 125.77 MHz (^{13}C). An amount of 50 mg of compound was dissolved in 0.6 ml of $CDCl_3$. Tetramethylsilane was used as an internal reference and the spectra were recorded at 25°C. JEOL-Delta software package (version 5.0.2) was used for the purpose of NMR pulse sequences and data processing.

The experimental parameters chosen for 1D $^{1}H/^{13}C$ NMR were, spectral width 15/250 ppm, number of data points 16384/32768, number of scans 8/200, acquisition time 2.18/1.04 s, relaxation delay 5/2 s, and 90° pulse width 13/10.2 μs. Two-dimensional correlation spectra were recorded in order to track ^{1}H-^{1}H and ^{1}H-^{13}C correlations. A relaxation delay of 1.5 s was used in all the 2D experiments.^{1}H-^{1}H COSY spectra were obtained using the gradient version of DQF-COSY (homonuclear double quantum filtered correlation spectroscopy) pulse sequence. The spectra resulted from 1024 (F_2) × 256 (F_1) data matrix size with one scan per t_1 increment. A spectral width of 10 ppm was used in both F_1 and F_2 dimensions. ^{13}C-^{1}H HETCOR (heteronuclear correlation) spectra were recorded using the standard hetcor pulse program. The acquisition parameters were as follow: spectra resulted from 1024 × 128 data matrix size with eight scans per t_1 increment. A spectral width of 200 ppm in F_2 and 10 ppm in F_1 was recorded. The gradient version of ^{1}H-^{13}C HMBC (heteronuclear multiple-bond correlation) experiments was recorded in order to sketch the long-range (two and three bonds) ^{1}H-^{13}C correlations. The long-range coupling constant ($^{n}J_{CH}$) optimized was 8 Hz. The spectra resulted from 2048 × 256 data matrix size with eight scans per t_1 increment. A spectral width of 10 ppm in F_2 and 200 ppm in F_1 was recorded.

2.3 Synthesis of Mesogens

Preparation of 4-hexyloxy benzoic acid

2.3.1. Synthesis of 4-hexyloxybenzoic acid (1a). It was prepared by two step process.

In a representative experiment, 4-hydroxy methylbenzoate (3.8 g, 0.025 mol) was placed in a 250 ml three necked round bottom flask equipped with stirrer and thermometer. To that, DMF (100 ml) and potassium carbonate (5.18 g, 0.0375 mol) were added. The resulting mixture was stirred while maintaining the temperature at 90°C, then n-bromohexane (3.52 ml, 0.025 mol) was added through a pressure equalizing dropping funnel over a period of 30 minutes and the stirring was continued for about 4 hours and then the reaction mixture was allowed to cool to room temperature, poured into a two liter beaker [26]. The contents were diluted with water (75 ml) and then transferred to 250 ml separating funnel and diethyl ether was added. The ether layer collected was washed twice using 10% potassium hydroxide solution and followed by distilled water. Then the organic layer was dried over anhydrous sodium sulphate and upon evaporation of ether, liquid 4-hexyloxy methyl benzoate was collected.

4-hexyloxy methyl benzoate (4.73 g, 0.02 mol) was placed in 250 ml single neck round bottom flask equipped with double wall water condenser. Ethanol (100 ml) and potassium hydroxide (3 g, 0.05mol) dissolved in distilled water (75 ml) were added to the flask. The solution was refluxed for two hours and allowed to cool to room temperature and neutralized with 10% hydrochloric acid to get a white precipitate [26]. The compound was purified by recrystallizing from methanol.

Above procedure was followed for synthesizing other compound namely dodecyloxy benzoic acid.

4-hexyloxy benzoic acid (1a). Yield: 84.7%, m.p-112°C, FT-IR (KBr, cm^{-1}): 2941, 2867 ($C{-}H_{str}$), 2549 (O-$H_{str.}$of carboxylic acid), 1683 ($C{=}O_{str}$ of carboxylic acid), 1604, 1511 ($C{=}C_{str}$ aromatic), 1467, 1426 ($C{-}H_{ben}$) 1297, 1253, 1166, 1121, ($C{-}O{-}C$ $_{asym\&symstr}$ of ether); ^{1}H—NMR ppm ($CDCl_3$): 8.06 (d, 2H), 6.93 (d, 2H), 4.01 (t, 2H), 1.78 (m, 2H), 1.46 (m, 2H), 1.33 (m, 4H), 0.90 (t, 3H); ^{13}C—NMR ppm ($CDCl_3$): 172.38, 163.79, 132.43, 121.48, 114.26, 68.37, 31.64, 29.15, 25.76, 22.69 and 14.13.

4-dodecyloxy benzoic acid (1b). Yield: 80%, m.p-96.5°C, FT-IR (KBr, cm^{-1}): 2921, 2851 ($C{-}H_{str}$), 2558 ($O{-}H_{str.}$ of carboxylic acid), 1681 ($C{=}O_{str}$ of carboxylic acid), 1605, 1512 ($C{=}C_{str}$ aromatic), 1467, 1427 ($C{-}H_{ben}$), 1255, 1167 ($C{-}O{-}C_{\text{asym \& sym str}}$ ether); $^1H{-}NMR$ ppm ($CDCl_3$): 8.05 (d, 2H), 6.93 (d, 2H), 4.01 (t, 2H), 1.79 (m, 2H), 1.45 (m, 2H), 1.34 (m, 16H), 0.87 (t, 3H); $^{13}C{-}NMR$ ppm ($CDCl_3$): 171.91, 163.86, 132.42, 120.91, 114.27, 68.38, 32.02, 29.76, 29.73, 29.69, 29.65, 29.45, 29.17, 26.06, 22.79 and 14.23.

2.3.2 Synthesis of 4-aminophenyl 4-hexyloxybenzoate (2a, 3a). It was synthesized by two step process

Step.1: Synthesis of 4-nitrophenyl 4-(hexyloxy) benzoate

In a representative experiment, hexyloxy benzoic acid (5g, 0.02 mol) and 4-nitro phenol (2.78 g, 0.02 mol) were placed in a conical flask. To this, dichloromethane (100 ml) was added and the solution was stirred at room temperature with magnetic stirrer. 4-Dimethylamino pyridine (0.24 g, 0.002 mol) was added as a catalyst to the solution. After 10 minutes, dicyclohexylcabodiimide (5.15 g, 0.025 mol) dissolved in dichloromethane was added to the flask and the solution was allowed to stir for 12 hrs [27]. The precipitated N,N'-dicyclohexyl urea was filtered off and washed with excess of dichloromethane (100 ml). The combined organic solution was taken into separating funnel and then washed twice with 5% KOH solution followed by distilled water. The yellow solid obtained was purified by recrystallization from isopropyl alcohol.

For the synthesis of 4-nitrophenyl 4-(dodecyloxy) benzoate, the above procedure was followed.

4-nitrophenyl 4-(hexyloxy) benzoate (2a). Yield: 72.4%, m.p-68°C, FT-IR (KBr, cm^{-1}): 2934, 2865 ($C{-}H_{str}$), 1742 ($C{=}O_{str}$), 1605 and 1516 ($C{=}C_{str}$ aromatic), 1487, 1319 ($C{-}H_{ben}$), 1343 ($-NO_{2str}$), 1255, 1164 ($C{-}O{-}C_{\text{asym\&symstr}}$ of ester and ether respectively); ^1H-NMR ppm ($CDCl_3$): 8.28 (d, 2H), 8.12 (d, 2H), 7.39 (d, 2H), 6.98 (d, 2H), 4.03 (t, 2H), 1.86 (m, 2H), 1.47 (m, 2H), 1.34 (m, 4H), 0.90 (t, 3H); $^{13}C{-}NMR$ ppm ($CDCl_3$): 164.14, 164.03, 156.06, 145.26, 132.59, 125.27, 122.76, 120.40, 114.59, 68.53, 31.63, 29.12, 25.74, 22.69 and 14.13.

4-nitrophenyl 4-(dodecyloxy) benzoate (2b). Yield: 68%, m.p-66.5°C, FT-IR (KBr, cm^{-1}): 3116(aromatic $C{-}H_{str}$), 2916, 2850($C{-}H_{str}$), 1732($C{=}O_{str}$), 1606, 1524($C{=}C_{str}$ aromatic), 1468($C{-}H_{ben}$), 1345($-NO_{2str}$), 1222, 1172, 1110($C{-}O{-}C_{\text{asym\&symstr}}$ of ester and ether respectively);^1H-NMR ppm ($CDCl_3$): 8.30(d, 2H), 8.13(d, 2H), 7.39(d, 2H), 6.99(d, 2H), 4.04(t, 2H), 1.82(m, 2H), 1.47(m, 2H), 1.36(m, 16H), 0.87(t, 3H);^{13}C-NMR ppm ($CDCl_3$): 164.15, 164.04, 156.06, 145.31, 132.61, 125.30, 122.76, 120.45, 114.60, 68.53, 32.02, 29.75, 29.74, 29.69, 29.65, 29.45, 29.15, 26.06, 22.79 and 14.23.

Step.2: Reduction of 4-nitrophenyl 4-(hexyloxy) benzoate

In this experiment, 4-nitrophenyl 4-(hexyloxy) benzoate (3.21 g, 0.00936 mol) and $SnCl_2$ (10.53 g, 0.046 mol) were placed in a single necked round bottom flask along with ethanol and refluxed for two hrs [28]. Then it was cooled to room temperature, neutralized with 10% $NaHCO_3$ solution then filtered and solid obtained was dried in vacuum oven. The solid was treated with 100 ml EMK for 1 hr and the solvent was evaporated to get light brown solid which was recrystallized from heptane.

The above procedure was used to synthesise 4-aminophenyl 4-dodecyloxy benzoate.

4-aminophenyl 4-hexyloxybenzoate (3a). Yield: 76.1%, m.p-91°C, FT-IR (KBr, cm^{-1}): 3407, 3329 (NH_{2str}), 3212 (aromatic $C{-}H_{str}$), 2934, 2861 ($C{-}H_{str}$), 1721 ($C{=}O_{str}$), 1607, 1512 ($C{=}C_{str}$ aromatic), 1467, 1420, 1395 and 1315 ($C{-}H_{ben}$), 1261, 1196, 1166

(C—O—C $_{\text{asym\&symstr}}$ of ester and ether respectively); ^{1}H-NMR ppm (CDCl$_3$): 8.13 (d, 2H), 6.96 (m, 4H), 6.69 (d, 2H), 4.03 (t, 2H), 3.54 (s, 2H), 1.81 (m, 2H), 1.47 (m, 2H), 1.35 (m, 4H), 0.92 (t, 3H); ^{13}C-NMR ppm (CDCl$_3$): 165.68, 163.47, 144.31, 143.21, 132.28, 122.46, 121.88, 115.80, 114.31, 68.38, 31.66, 29.17, 25.77, 22.72 and 14.18.

4-aminophenyl 4-dodecyloxybenzoate (3b). Yield: 71.5%, m.p-96°C, FT-IR (KBr, cm^{-1}): 3460, 3372(NH$_{2\text{str}}$), 2954, 2919, 2850(C—H$_{\text{str}}$), 1715(C=O$_{\text{str}}$), 1629(NH$_{\text{ben}}$), 1605, 1579, 1513(C=C$_{\text{str}}$ aromatic), 1471, 1420(C—H$_{\text{ben}}$), 1258, 1191, 1167, 1120(C—O—C $_{\text{asym\&symstr}}$ of ester and ether respectively);^{1}H-NMR ppm (CDCl$_3$): 8.13(d, 2H), 6.98(m, 4H), 6.70(d, 2H), 4.02(t, 2H), 3.65(s, 2H), 1.81(m, 2H), 1.46(m, 2H), 1.34(m, 16H), 0.89(t, 3H); ^{13}C-NMR ppm (CDCl$_3$): 165.66, 163.46, 144.26, 143.23, 132.27, 122.47, 121.88, 115.78, 114.30, 68.38, 32.01, 29.67, 29.59, 29.54, 29.48, 29.46, 29.44, 29.21, 26.09, 22.81 and 14.26.

2.3.3 Synthesis of 4-aminophenyl 4-dodecylbenzoate (4, 5). It was synthesized by two step process:

Step.1: Synthesis of 4-[(tert-butoxycarbonyl) amino] phenyl 4-dodecylbenzoate **(4)**

In this experiment, 4-dodecyl benzoic acid (5.80 g, 0.02 mol) and N-BOC-4-amino phenol (4.18 g, 0.02 mol) were placed in a 250 ml conical flask. To this, dichloromethane (150 ml) was added and the solution was stirred at room temperature with magnetic stirrer. 4-dimethylamino pyridine (0.24 g, 0.002 mol) was added as a catalyst to the solution. After 10 minutes, dicyclohexylcarbodiimide (5.15 g, 0.025 mol) dissolved in dichloromethane was added to the flask and the solution was allowed to stir for 15 hours. The precipitated N, N'-dicyclohexyl urea was filtered off and washed with excess of dichloromethane (100 ml). The combined organic solution was taken into separating funnel and then washed with 5% KOH solution (2×100 ml), 10% HCl solution(2×100 ml) and followed by distilled water (3×100 ml).The organic layer collected was dried over anhydrous Na$_2$SO$_4$. Upon evaporation of solvent, the white solid resulted was purified by recrystallization from isopropyl alcohol.

4-[(tert-butoxycarbonyl) amino] phenyl 4-dodecylbenzoate (4). Yield: 65.1%, m.p-134°C, FT-IR (KBr, cm^{-1}): 3372(N-H$_{\text{str}}$), 2923, 2851(C—H$_{\text{str}}$), 1727(C=O$_{\text{str}}$), 1704(C=O$_{\text{str}}$), 1609, 1527(C=C$_{\text{str}}$ aromatic), 1465, 1411(C—H$_{\text{ben}}$), 1274, 1241, 1172(C—O—C $_{\text{asym\&symstr}}$ of ester);^{1}H-NMR ppm (CDCl$_3$): 8.08(d, 2H), 7.40(d, 2H), 7.28(d, 2H), 7.11(d, 2H), 6.55(s, 1H), 2.68(t, 2H), 1.64(m, 3H), 1.51(m, 8H), 1.31(m, 18H), 0.87(t, 3H);^{13}C—NMR ppm (CDCl$_3$): 165.55, 152.85, 149.45, 146.40, 136.09, 130.31, 128.73, 127.01, 122.23, 119.51, 36.18, 32.02, 31.24, 29.76, 29.73, 29.70, 29.66, 29.56, 29.45, 29.34, 28.42, 22.79 and 14.23.

Step.2: Synthesis of 4-aminophenyl 4-dodecylbenzoate **(5)**

In a typical experiment, 4-[(tert-butoxycarbonyl)amino]phenyl dodecylbenzoate (4.67 g, 0.0097 mol) was placed in a 250 ml two necked round bottom flask which was kept in an ice bath. Dichloromethane (150 ml) was added to the flask while maintaining 0°C. Then trifluoroacetic acid (13.7 ml, 0.185 mol) was added and the reaction mixture was stirred for two hours [29]. Later it was taken out from the ice bath; saturated sodium bicarbonate solution (50 ml) was added and stirred for 20 minutes. The contents were transferred to a 500 ml separating funnel and dichloromethane was added. The organic layer was washed twice with 1% potassium hydroxide and distilled water respectively. Upon evaporation of dichloromethane, solid 4-aminophenyl 4-dodecylbenzoate was resulted. It was purified by recrystallization from heptane.

4-aminophenyl 4-dodecylbenzoate (5). Yield: 68.7%, m.p-94°C, FT-IR (KBr, cm^{-1}): 3400, 3326(NH_{2str}), 2921, 2852(C—H_{str}), 1726(C=O_{str}), 1611(NH_{ben}), 1510(C=Cstr aromatic), 1465(C—H_{ben}), 1278 and 1193(C—O—C $_{asym\&symstr}$ of ester);^{1}H-NMR ppm ($CDCl_3$): 8.12(d, 2H), 7.31(d, 2H), 6.98(d, 2H), 6.70(d, 2H), 3.66(s, 2H), 2.69(t, 2H), 1.66(m, 2H), 1.33(m, 18H), 0.90(t, 3H); ^{13}C-NMR ppm ($CDCl_3$): 165.93, 149.24, 144.41, 143.18, 130.28, 128.71, 127.34, 122.41, 115.77, 36.19, 32.05, 31.29, 29.78, 29.71, 29.65, 29.60, 29.50, 29.38, 22.83 and 14.27.

2.3.4 Synthesis of 2 or 3- thiophene carbonyl chloride (6). 2 (or) 3- thiophene carboxylic acid (3 g, 0.0234 mol) which was placed in a 100 ml single neck round bottomed flask fitted with a double wall reflux condenser and a calcium chloride guard tube. Thionyl chloride (2.13 ml, 0.0292 mol) and a few drops of DMF were added to the flask. The reaction mixture was refluxed for about one hour and the excess $SOCl_2$ was removed by vacuum pump.

2.3.5 Synthesis of 4-formylphenyl thiophene-2-carboxylate or 4-formylphenyl thiophene-3-carboxylate (7, 8). In an experiment, 4-hydroxy benzaldehyde (2.85 g, 0.0234 mol) dissolved in ethyl methyl ketone was placed in a 500 ml two necked round bottomed flask and was kept in an ice bath. Triethylamine (3.3 ml, 0.0234 mol) solution in EMK was added to it. 2 or 3- thiophene carbonyl chloride was added slowly through a pressure equalizing dropping funnel over a period of 30 minutes while maintaining temperature at 0°C and stirring was continued for 4 hours. Then, the precipitated triethylamine salt was filtered off and washed with excess of EMK. The solvent was removed under reduced pressure. The solid so obtained was washed twice with 2% potassium hydroxide solution followed by distilled water, dried and recrystallized from isopropyl alcohol.

4-formylphenyl thiophene-2-carboxylate (7). Yield: 72.5%, m.p-132.7°C, FT-IR (KBr, cm^{-1}): 3100(aromatic C—H_{str}), 2814, 2721, 2069(C—H_{str}), 1725(C=O_{str}), 1692(—HC=O),1593, 1500(C=C_{str} aromatic), 1409, 1356, 1304(C—H_{ben}), 1261, 1206, 1153(C—O—C $_{asym\&symstr}$ of ester), ^{1}H-NMR ppm ($CDCl_3$): 9.99(s, 1H), 7.99(m, 1H), 7.93(d, 2H), 7.69(m, 1H), 7.39(d, 2H), 7.18(m, 1H); ^{13}C-NMR ppm ($CDCl_3$): 191.03, 159.92, 155.33, 135.33, 134.30, 134.18, 132.20, 131.35, 128.33 and 122.53.

4-formylphenyl thiophene-3-carboxylate (8). Yield: 71%, m.p-138°C, FT-IR (KBr, cm^{-1}): 3109(aromatic C—H_{str}), 2928, 2816, 2721(C—H_{str}), 1728(C=O_{str}), 1693(—HC=O), 1593, 1504(C=C_{str} aromatic), 1403, 1304(C—H_{ben}), 1258, 1161(C—O—C $_{asym\&symstr}$ of ester); ^{1}H-NMR ppm ($CDCl_3$): 9.97(s, 1H), 8.32(m, 1H), 7.95(d, 2H), 7.69(d, 1H), 7.38(d, 2H), 7.37(s, 1H);^{13}C—NMR ppm ($CDCl_3$): 191.11, 160.36, 155.49, 134.78, 134.10, 132.23, 131.38, 128.25, 126.83 and 122.62.

2.3.6 Synthesis of (E)-4-((4-(4-(dodecylbenzoyloxy)] phenylimino) methyl) phenyl thiophene-2-carboxylate (or) (E)-4-((4-(4-(dodecyloxy) benzoyloxy)] phenylimino) methyl) phenyl thiophene-2-carboxylate (9a, 9b). In a representative experiment, equimolar 4-formylphenyl thiophene-2-carboxylate (0.75 g, 0.0032 mol) and 4-aminophenyl 4-dodecyl benzoate (1.17 g, 0.0032 mol) (or) 4-aminophenyl 4-dodecyloxy benzoate (1.2 g, 0.0032 mol) were taken in a 100 ml conical flask. A few drops of ethanol were added and the flask was placed in a microwave oven (power: 40 W) for ten minutes. Then it was allowed to cool to room temperature, washed with methanol and recrystallized twice from acetonitrile.

Similarly the synthesis of (E)-4-((4-(4-(hexyloxy) benzoyloxy)] phenylimino) methyl) phenyl thiophene-2-carboxylate was accomplished.

(E)-4-((4-(4-(dodecylbenzoyloxy)] phenylimino) methyl) phenyl thiophene-2-carboxylate (2-DBPPTC) (9a). Yield: 71.3%, m.p-131°C, FT-IR (KBr, cm^{-1}): 2921, 2850($C—H_{str}$), 1729($C=O_{str}$), 1620($-C=N_{str}$), 1505($C=C_{str}$ aromatic), 1469, 1359($C—H_{ben}$), 1256, 1202($C—O—C$ $_{asym\&symstr}$ of ester); ^{1}H-NMR ppm ($CDCl_3$): 8.49(s, 1H), 8.14(d, 2H), 8.01(d, 1H), 7.98(d, 2H), 7.68(d, 1H), 7.39(d, 2H), 7.36(d, 2H), 7.29(d, 2H), 7.26(d, 2H), 7.20(t, 1H), 2.69(t, 2H), 1.63(m, 2H), 1.26(m, 18H), 0.89(t, 3H); ^{13}C-NMR ppm ($CDCl_3$):165.47, 160.74, 159.31, 153.04, 149.57, 149.53, 149.32, 135.09, 134.05, 133.97, 132.61, 130.37, 130.18, 128.78, 128.25, 126.97, 122.53, 122.25, 121.95, 36.20, 32.02, 31.26, 29.75, 29.67, 29.57, 29.47, 29.36, 22.80 and 14.25.

(E)-4-((4-(4-(dodecyloxy) benzoyloxy)] phenylimino) methyl) phenyl thiophene-2-carboxylate (2-DoBPPTC) (9b). Yield: 70.9%, m.p-124°C, FT-IR (KBr, cm^{-1}): 2920, 2850($C—H_{str}$), 1725($C=O_{str}$), 1606, 1509($C=C_{str}$ aromatic), 1468, 1360($C—H_{ben}$), 1269, 1193, 1167($C—O—C$ $_{asym\&symstr}$ of ester and ether respectively);^{1}H-NMR ppm ($CDCl_3$): 8.48(s, 1H), 8.16(d, 2H), 7.99(d, 1H), 7.96(d, 2H) 7.68(d, 1H), 7.34(d, 2H), 7.28(d, 2H), 7.24(d, 2H), 7.19(m,1H), 6.98(d, 2H), 4.04(t, 2H), 1.83(m, 2H), 1.46(m, 2H), 1.31(m, 16H), 0.89(t, 3H); ^{13}C-NMR ppm ($CDCl_3$): 165.14, 163.66, 160.30, 159.22, 153.03, 149.44, 149.39, 135.08, 134.08, 133.96, 132.62, 132.39,130.16, 128.25, 122.57, 122.23, 121.93, 121.55, 114.41, 68.43, 32.01, 29.67, 29.52, 29.48, 29.43, 29.41, 29.20, 26.09, 22.80 and 14.26.

(E)-4-((4-(4-(hexyloxy) benzoyloxy)] phenylimino) methyl) phenyl thiophene-2-carboxylate (2-HoBPPTC) (9c). Yield: 74.1%, m.p-134°C, FT-IR (KBr, cm^{-1}): 2944, 2869 ($C—H_{str}$), 1720 ($C=O_{str}$), 1625 ($—C=N_{str}$), 1606, 1579, 1511 ($C=C_{str}$ aromatic), 1471, 1360 ($C—H_{ben}$), 1220, 1192, 1161, 1100 ($C—O—C$ $_{asym\&symstr}$ of ester and ether respectively); ^{1}H-NMR ppm ($CDCl_3$): 8.47 (s, 1H), 8.15 (d, 2H), 8.0 (d, 1H), 7.97(d, 2H), 7.67 (d, 1H), 7.35 (d, 2H), 7.26 (d, 2H), 7.22 (d, 2H), 7.17 (m, 1H), 6.98 (d, 2H), 4.03 (t, 2H), 1.81 (m, 2H), 1.48 (m, 2H), 1.35 (m, 4H), 0.92 (t, 3H); ^{13}C-NMR ppm ($CDCl_3$): 165.05, 163.61, 160.21, 159.11, 153.0, 149.40, 134.98, 134.04, 133.85, 132.61, 132.31, 130.09, 130.04, 128.15, 122.49, 122.14, 121.84, 121.55, 114.36, 68.43, 31.66, 29.17, 25.78, 22.72 and 14.18.

2.3.7 Synthesis of (E)-4-((4-(4-(dodecylbenzoyloxy)] phenylimino) methyl) phenyl thiophene-3-carboxylate (or) (E)-4-((4-(4-(dodecyloxy) benzoyloxy)] phenylimino) methyl) phenyl thiophene-3-carboxylate (10a, 10b). In a typical experiment, a mixture of 4-formylphenyl thiophene-3-carboxylate (0.5 g, 0.0021mol) and 4-aminophenyl 4-dodecyl benzoate (0.5 g, 0.0021mol) (or) 4-aminophenyl 4-dodecyloxy benzoate (0.82 g, 0.0021mol) in equimolar was taken in a 100 ml conical flask. A few drops of ethanol were added and the flask was placed in a microwave oven (power: 40 W) for ten minutes. Then it was cooled to room temperature, washed with methanol and recrystallized twice from EMK.

Similarly the synthesis of (E)-4-((4-(4-(hexyloxy) benzoyloxy)] phenylimino) methyl) phenyl thiophene-3-carboxylate was carried out.

(E)-4-((4-(4-(dodecylbenzoyloxy)] phenylimino) methyl) phenyl thiophene-3-carboxylate (3-DBPPTC) (10a). Yield: 70.7%, m.p-148.8°C, FT-IR (KBr, cm^{-1}): 3102(aromatic $C—H_{str}$), 2918, 2849($C—H_{str}$), 1730($C=O_{str}$), 1606, 1508 ($C=C_{str}$ aromatic), 1465, 1413($C—H_{ben}$), 1267, 1205($C—O—C$ $_{asym\&symstr}$ of ester);^{1}H-NMR ppm ($CDCl_3$): 8.48(s, 1H), 8.33(d, 1H), 8.13(d, 2H), 7.98(d, 2H), 7.68(d, 1H), 7.39(m, 1H), 7.32(m, 8H), 2.69(t, 2H), 1.63(m, 2H), 1.26(m, 18H), 0.88(t, 3H);^{13}C-NMR ppm (CDCl$_3$): 165.46, 160.74, 159.33, 153.19, 149.55, 149.50, 149.31, 134.46, 133.97, 132.63, 130.37, 130.18, 128.78, 128.31, 126.98, 126.64, 122.53, 122.30, 121.95, 36.21, 32.03, 31.27, 29.75, 29.68, 29.57, 29.47, 29.37, 22.80 and 14.25.

(E)-4-((4-(4-(dodecyloxy) benzoyloxy)] phenylimino) methyl) phenyl thiophene-3-carboxylate (3-DoBPPTC) (10b). Yield: 72.8%, m.p-141°C, FT-IR (KBr, cm^{-1}): 3105(aromatic C—H$_{str}$), 2920, 2853(C—H$_{str}$), 1735(C=O$_{str}$), 1608, 1510(C=C$_{str}$ aromatic), 1469, 1408(C—H$_{ben}$), 1280, 1207(C—O—C $_{asym\&symstr}$ of ester and ether respectively);^{1}H-NMR ppm (CDCl$_3$): 8.48(s, 1H), 8.34(d, 1H), 8.15(d, 2H), 7.98(d, 2H), 7.67(d, 1H), 7.40(m, 1H), 7.34(d, 2H), 7.26(d, 2H), 7.24(d, 2H), 6.98(d, 2H), 4.04(t, 2H), 1.82(m, 2H), 1.47(m, 2H), 1.31(m, 16H), 0.89(t, 3H);^{13}C-NMR ppm (CDCl$_3$): 165.17, 163.66, 160.75, 159.30, 153.17, 149.45, 149.38, 134.46, 133.9, 132.62, 132.39,130.17, 128.31, 126.64, 122.58, 122.29, 121.92, 121.53, 114.40, 68.43, 32.02, 29.76, 29.74, 29.70, 29.66, 29.47, 29.20, 26.08, 22.80 and 14.25.

(E)-4-((4-(4-(hexyloxy) benzoyloxy)] phenylimino) methyl) phenyl thiophene-3-carboxylate (3-HoBPPTC) (10c). Yield: 74.3%, m.p-148.3°C, FT-IR (KBr, cm^{-1}): 3106(aromatic C—H$_{str}$), 2929, 2864(C—H$_{str}$), 1729(C=O$_{str}$), 1606, 1508(C=C$_{str}$ aromatic), 1406(C—H$_{ben}$), 1260, 1193(C—O—C $_{asym\&symstr}$ of ester and ether respectively);^{1}H-NMR ppm (CDCl$_3$): 8.48(s, 1H), 8.33(d, 1H), 8.14(d, 2H), 7.98(d, 2H), 7.67(d, 1H), 7.39(d, 1H), 7.34(d, 2H), 7.28(d, 2H), 7.22(d, 2H), 6.98(d, 2H), 4.03(t, 2H), 1.83(m, 2H), 1.48(m, 2H), 1.35(m, 4H), 0.92(t, 3H);^{13}C-NMR ppm (CDCl$_3$): 165.90, 165.14, 163.66, 160.74, 159.28, 153.18, 149.44, 149.38, 134.46, 133.98, 132.39, 130.17, 128.30, 126.65, 122.57, 122.29, 121.93, 121.55, 114.41, 68.42, 31.65, 29.16, 25.77, 22.71 and 14.16.

3. Results and Discussion

The molecular structures of synthesised mesogens are shown in Figures (1 & 2). They are made by varying the substitution position at thiophene with a common core. The core unit is built with three phenyl rings linked by ester and azomethine with a terminal alkyl/alkoxy chain. These are classified into 2-mesogens and 3-mesogens indicating the substitution position at thiophene. Further, the terminal units are varied to have hexyloxy, dodecyloxy, dodecyl chains and accordingly six mesogens are realized. The synthesis is accomplished as outlined in Scheme 1. Consequently, 4-alkoxy benzoic acids are converted to two ring nitro compounds which are reduced to get amino intermediates [28]. Thiophene 2/3-carboxylic acids are converted to aldehyde intermediates using 4-hydroxy benzaldehyde. Upon condensation of thiophene aldehyde with two ring amines, the target three phenyl ring based thiophene mesogens are obtained. The main focus of the work is to find the mesophase characteristics, evaluate the phase and thermal stabilities and compare the data with two phenyl ring based thiophene mesogens reported in literature [12,16]. In the design of the mesogen, the thiophene is placed at one end of the mesogen to investigate its influence on mesophase formation. Further, the molecular structures of representative mesogens are accomplished by solution (1D & 2D) NMR and the nature of the mesophase and transition temperatures are examined by HOPM and DSC.

In FT-IR, 3-DBPPTC shows absorptions at 2918, 2849 cm^{-1} for CH stretching vibrations arising from terminal dodecyl chain, 1730 cm^{-1} and 1615 cm^{-1} for ester carbonyl as well as imine CH stretching of core unit, 1606 and 1508 cm^{-1} for ring skeletal C=C$_{str}$ and 1267 and 1205 cm^{-1} for C—O—C$_{str}$ of ester respectively. The appearance of one ester carbonyl stretching (1730 cm^{-1}) despite the presence of two ester linking units indicates that the absorption frequencies are same. The final structural confirmation of representative

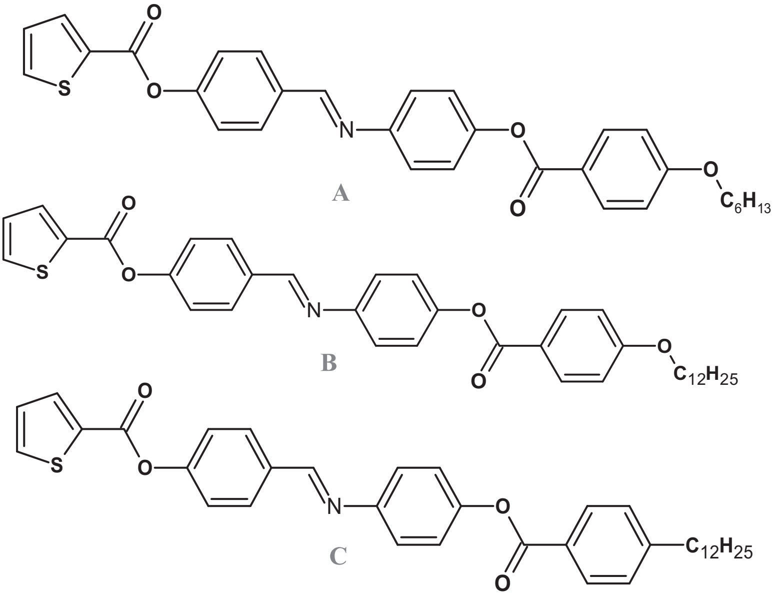


Figure 1. Molecular Structures of 2-HoBPPTC (A), 2-DoBPPTC (B) and 2-DBPPTC (C)

mesogens namely 2-DBPPTC and 3-DBPPTC is carried out using ^{1}H, ^{13}C NMR (Figures 3 & 4) and 2D experiments such as ^{1}H-^{1}H DQF-COSY, ^{13}C—^{1}H HETCOR and ^{1}H-^{13}C HMBC NMR techniques (Figures 5–7). The structural assignment by ^{1}H and ^{13}C NMR in solution is advanced by first identifying the chemical shift values of different units of the mesogen.

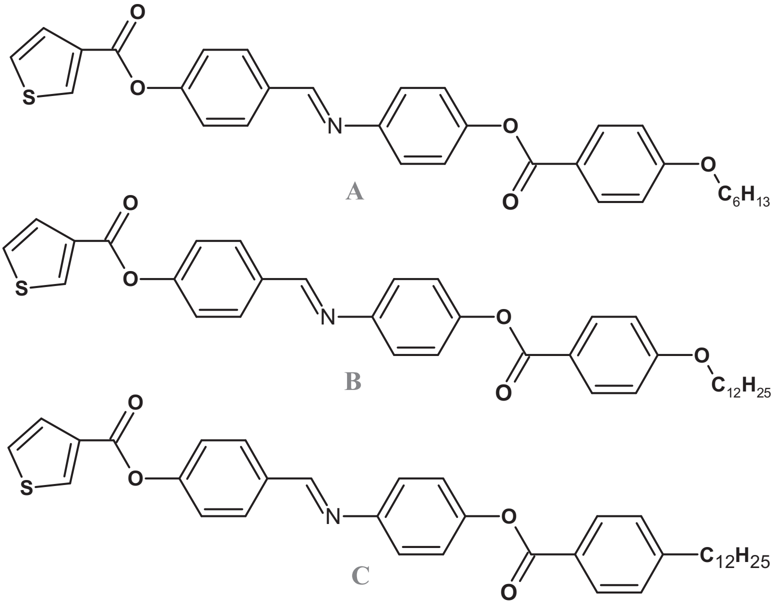
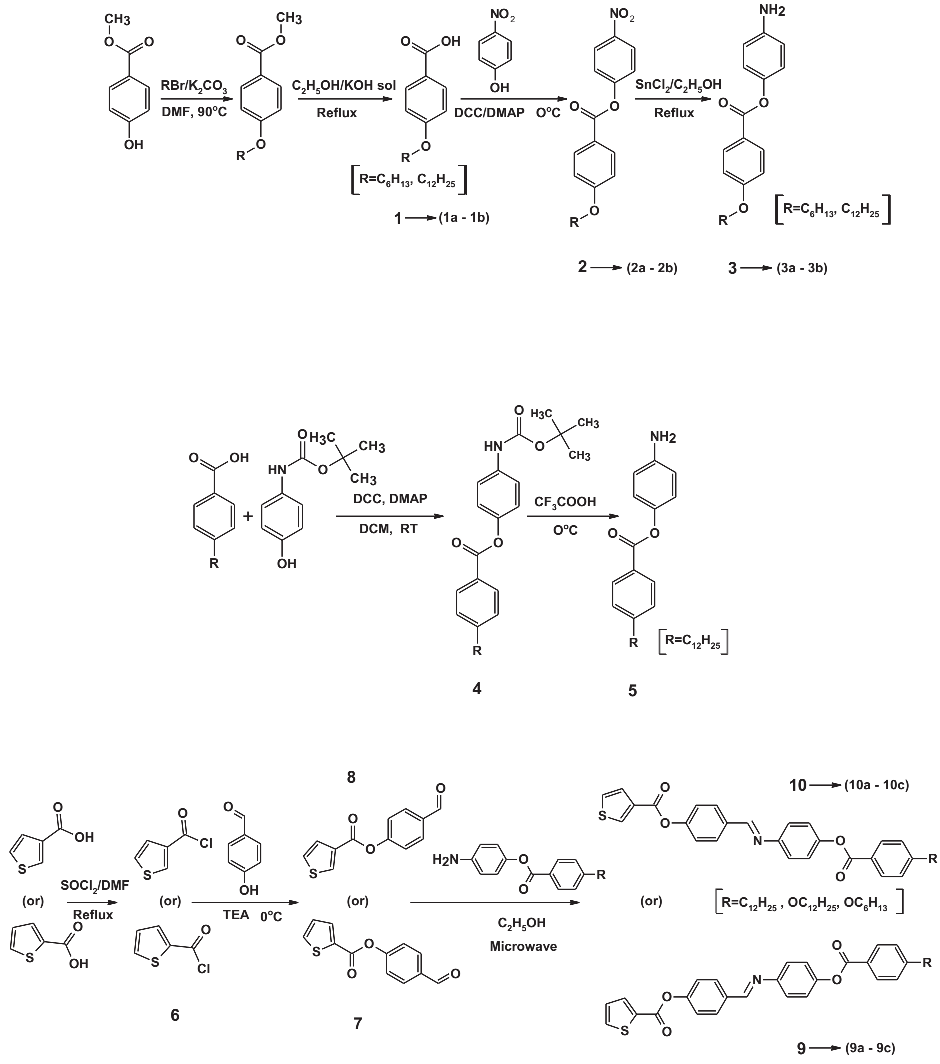


Figure 2. Molecular Structures of 3-HoBPPTC (A), 3-DoBPPTC (B) and 3-DBPPTC (C)



Scheme 1. Synthetic strategy for the Target Mesogens

The final assignment, however, is accomplished by making use of 2D spectral data. For 2-DBPPTC, the ^{1}H NMR spectrum showed 10 peaks for the core as well as linking units and four peaks for the terminal chain. The chemical shift values of core unit protons are noticed in the range 7.2-8.49 ppm and based on multiplicity as well as peak integration, the number of protons associated with each peak is arrived. The ^{13}C NMR of 2-DBPPTC showed 19 sharp lines in the range 121-166 ppm for all the core unit carbons. For the terminal chain, 10 peaks are noticed in the range 14-37 ppm. The aromatic CH carbons showed high intensity while quaternary carbons exhibited lowest intensity. The methine carbons of thiophene moiety, on the other hand, showed medium intensity. Table 1 lists the ^{1}H and ^{13}C chemical shifts along with carbon numbering. By using ^{1}H-^{1}H DQF-COSY data, the proton pairs arising from each phenyl ring are identified. For azomethine, no correlation could be found as it is not directly connected to any phenyl ring protons. The ^{13}C—^{1}H HETCOR data

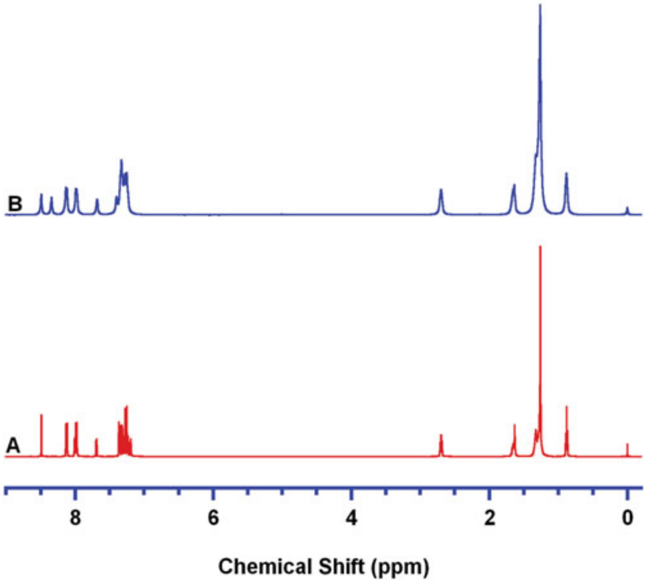


Figure 3. ^{1}H NMR Spectra of 2-DBPPTC (A) and 3-DBPPTC (B)

enabled to identify the ^{13}C chemical shifts of corresponding proton pairs that have been assigned from ^{1}H-^{1}H DQF-COSY. This exercise facilitated the identification of phenyl ring carbons. For thiophene unit, three protons showed 12 signals characteristic of three spin system. By using the scalar coupling constants (J Hz), the individual protons of thiophene ring are assigned. The ^{13}C—^{1}H HETCOR data also provided the assignment of CH carbons of thiophene from proton chemical shifts. The final confirmation, however, is achieved by

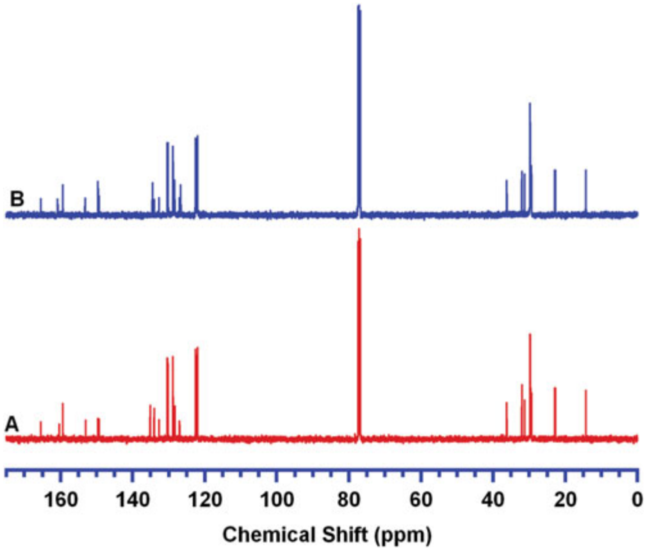
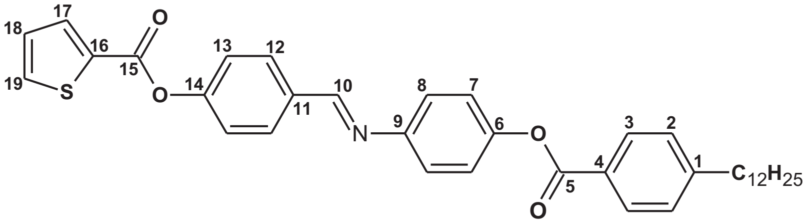


Figure 4. ^{13}C NMR Spectra of 2-DBPPTC (A) and 3-DBPPTC (B)

Table 1. DQF-COSY and HSQC data of 2-DBPPTC



Carbon Number	^{1}H	^{13}C
1	—	149.3
2	7.31	128.8
3	8.13	130.3
4	—	126.9
5	—	165.4
6	—	149.5
7	7.25	122.5
8	7.27	121.9
9	—	149.5
10	8.48	159.3
11	—	134.0
12	7.99	130.1
13	7.36	122.1
14	—	153.0
15	—	160.3
16	—	132.6
17	8.01	135.0
18	7.20	128.1
19	7.69	133.9

making use of ^{1}H—^{13}C HMBC data where proton chemical shifts and the corresponding ^{13}C NMR chemical shift correlations arising from two as well as three bond couplings are noticed. In other words, HMBC provided information about long range couplings of protons with neighbouring carbons. The whole exercise facilitated the complete assignment of core unit of the mesogen. Similar approach is extended to 3-DBPPTC and Tables 1 & 2 list the assigned NMR data from 1D and 2D experiments. A comparison of ^{13}C chemical shifts of 2-DBPPTC and 3-DBPPTC mesogens revealed that except C-17, all other carbons of the core unit showed similar chemical shifts indicating alike chemical environment. A 9 ppm variation in chemical shift values of C-17 carbons, on the other hand, is attributed to effect of position of substitution. In other words, the higher chemical shift value for C-17 carbon of 2-DBPPTC is ascribed to the presence of sulphur as a neighbouring atom.

All the synthesised mesogens are examined by HOPM with a heating rate of 10°C/m. The samples are sandwiched between 12 mm cover slips and are heated to isotropic temperature and the mesophase transitions are noted upon cooling. The HOPM investigations revealed the existence of enantiotropic nematic phase for all the cases (Figure 8) and the appearance of nematic phase is confirmed by observing birefringent droplets on cooling the isotropic liquid [30, 31]. On further cooling, the droplets coalesced to give either threaded

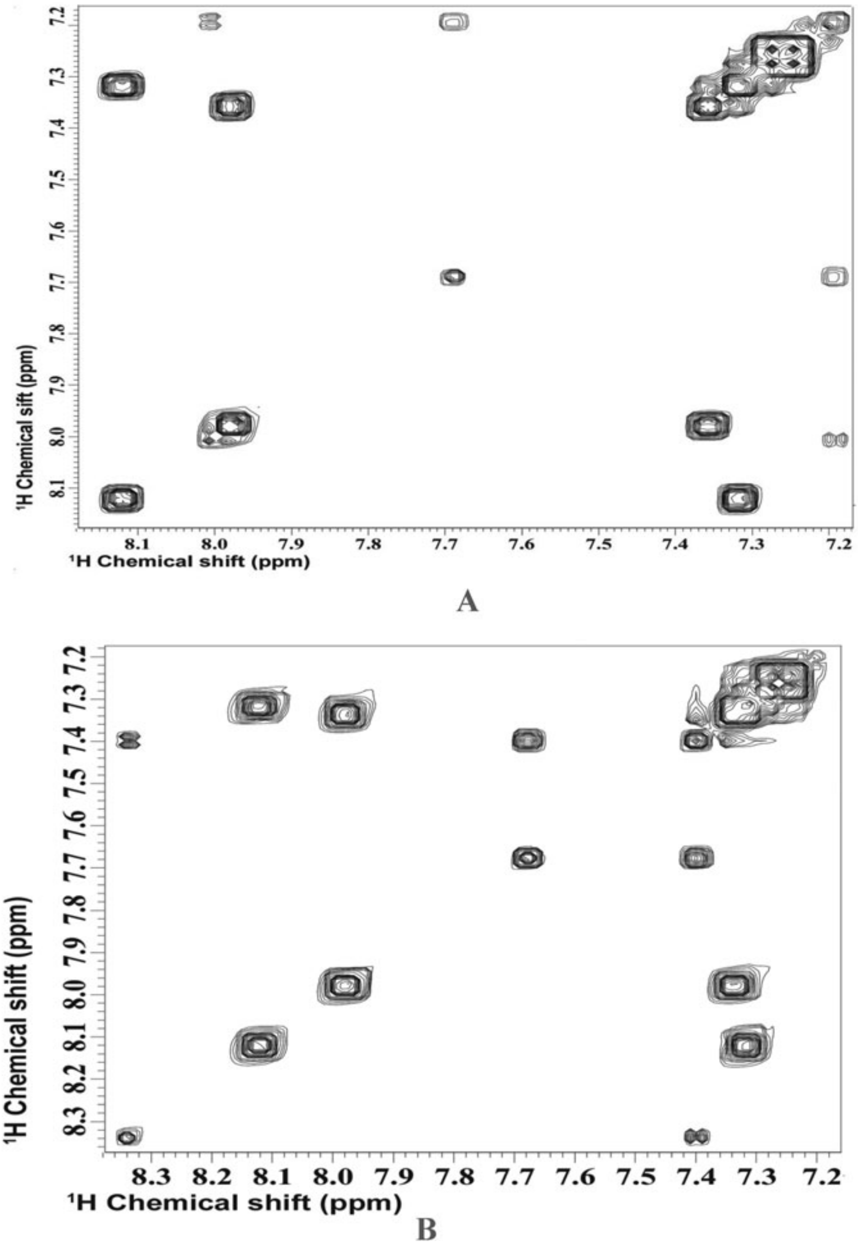
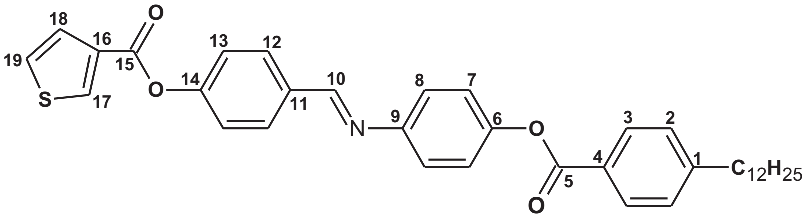


Figure 5. 2D ^{1}H-^{1}H DQF-COSY Spectra of 2-DBPPTC (A) and 3-DBPPTC (B)

texture or marble texture characteristic of nematic phase. The enantiotropic nature of the phase is further confirmed by DSC measurements (Figures 9–11). The DSC scan of 3-DBPPTC (Figure 11 B) shows two peaks in which high intense peak is observed at low temperature whereas the high temperature peak is detected with low intensity. Accordingly, the transition enthalpy values are found to be high for the low temperature peak and lower for high temperature transition. These are assigned to Cr-N and N-I transitions respectively

Table 2. DQF-COSY and HSQC data of 3-DBPPTC



Carbon Number	^{1}H	^{13}C
1	—	149.3
2	7.32	128.7
3	8.13	130.3
4	—	126.9
5	—	165.4
6	—	149.5
7	7.24	122.5
8	7.29	121.9
9	—	149.5
10	8.48	159.3
11	—	133.9
12	7.99	130.1
13	7.31	122.3
14	—	153.1
15	—	160.7
16	—	132.6
17	7.39	126.6
18	7.68	128.4
19	8.34	134.4

[32]. In other words, the high transition enthalpy value indicates the melting temperature (Cr—N) while the second transition is attributed to isotropic transition (N-I). The cooling scan also exhibited two peaks associated with I-N and N-Cr. The appearance of two peaks both in heating as well as cooling cycles is clear signature of enantiotropic nature of the mesophase. For 2-HoBPPTC and 3-HoBPPTC isomers, the isotropic transition temperatures are found to be very high (>300°C) (Figure 9). In order to find the thermal stabilities of these two mesogens, thermogravimetric analysis has been carried out in nitrogen atmosphere. Accordingly, initial degradation is found to be 320°C which suggests that even at 300°C, the mesogens are thermally stable exhibiting nematic phase. Tables 3 & 4 show the transition temperatures, enthalpy values and mesophase stabilities for all the mesogens. The typical enthalpy values for Cr-N transition are found to be ~ 10 k cal/mol whereas for N-I transition, the values are found to be ~ 0.25 k cal/mol [32]. These values are in consistent with literature data of nematogens made up of rod-like core units [32].

The mesophase as well as thermal stability values of all the mesogens are found to be high in contrast to the reported two phenyl ring based thiophene mesogens [12, 16]. For instance, the 2-thiophene based two phenyl ring mesogens with a dodecyloxy terminal chain showed phase stability ~18°C whereas for three phenyl ring mesogen (2-DoBPPTC),

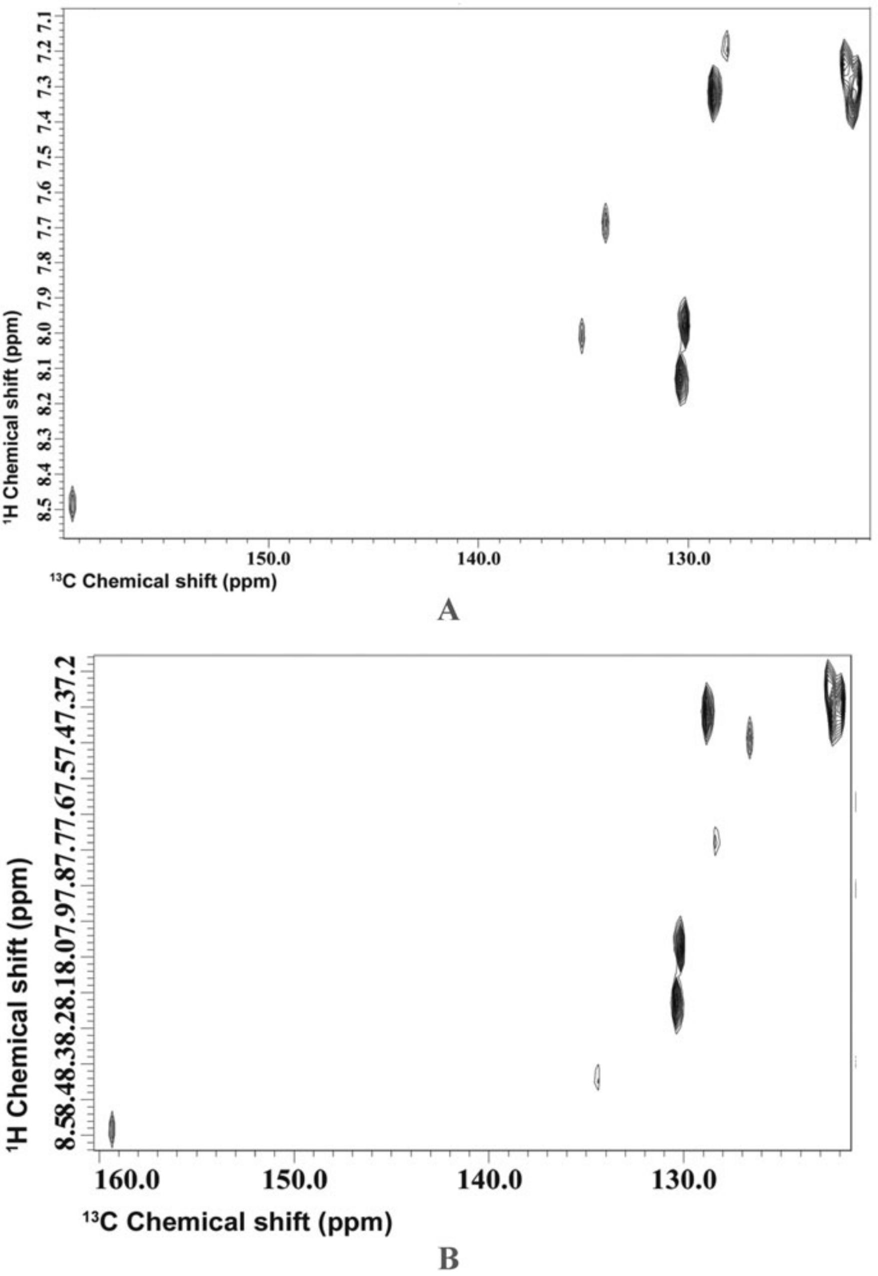


Figure 6. 2D ^{13}C- ^{1}H HETCOR Spectra of 2-DBPPTC (A) and 3-DBPPTC

the value is ∼150°C. Further, the thermal stability of two ring based mesogen is ∼160°C and for 2-DoBPPTC, the value is ∼270°C. Such large mesophase and thermal stabilities for three phenyl ring based mesogens are ascribed to lengthy rod-like core in contrast to two ring based mesogens (Figure 12). Further, the high thermal stabilities indicate that the mesogens possess high molecular anisotropic polarizability. The existence of four rings i.e.

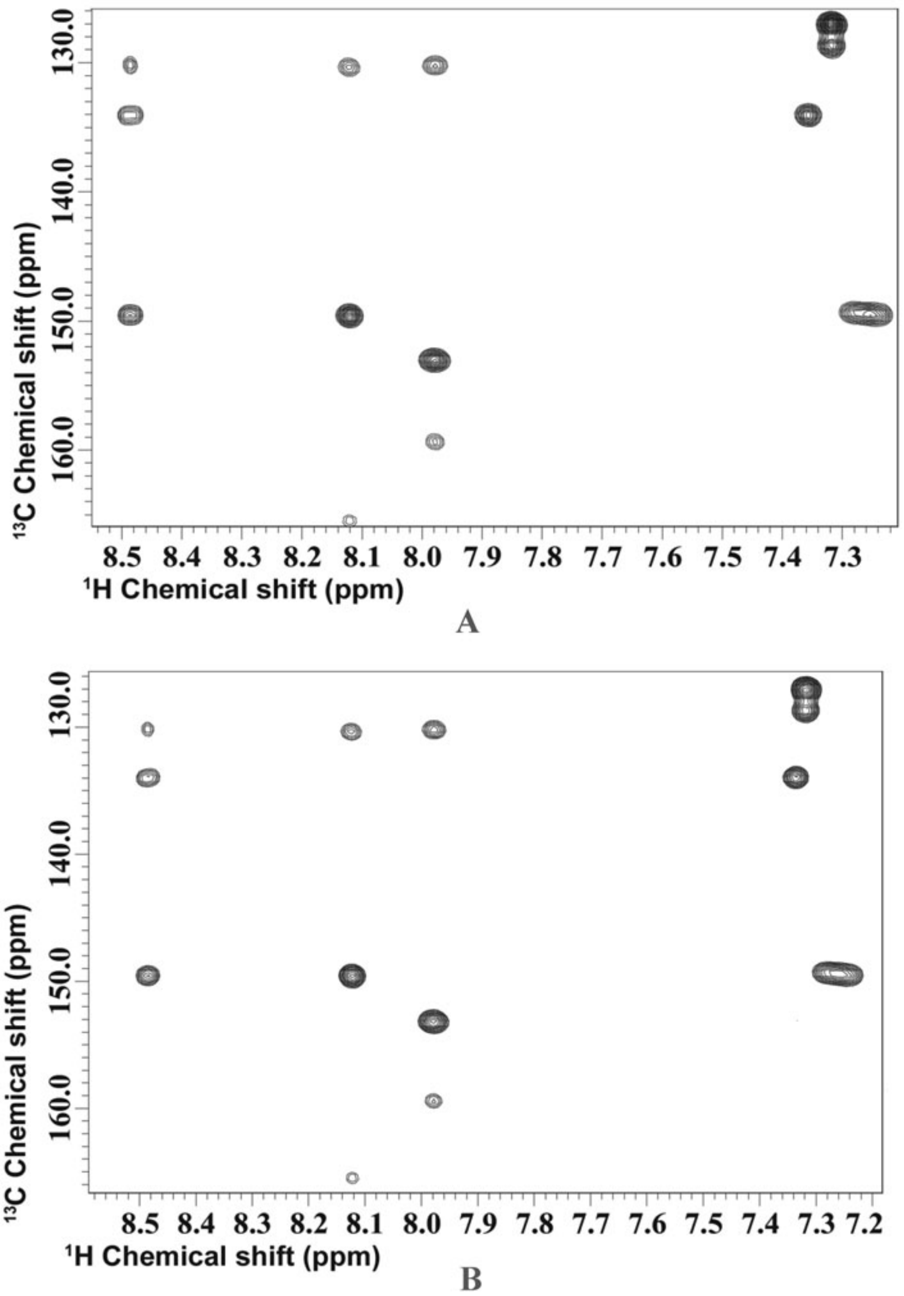


Figure 7. 2D ^{1}H-^{13}C HMBC Spectra of 2-DBPPTC (A) and 3-DBPPTC (B)

three phenyl rings and a thiophene ring besides providing rigidity to the core, enhances the molecular anisotropic polarizability. The thiophene unit in the core further increases the molecular polarizability in view of sulfur atom through the dipole moment. A comparison of mesophase transitions of 2- and 3-series is attempted by taking into account of terminal

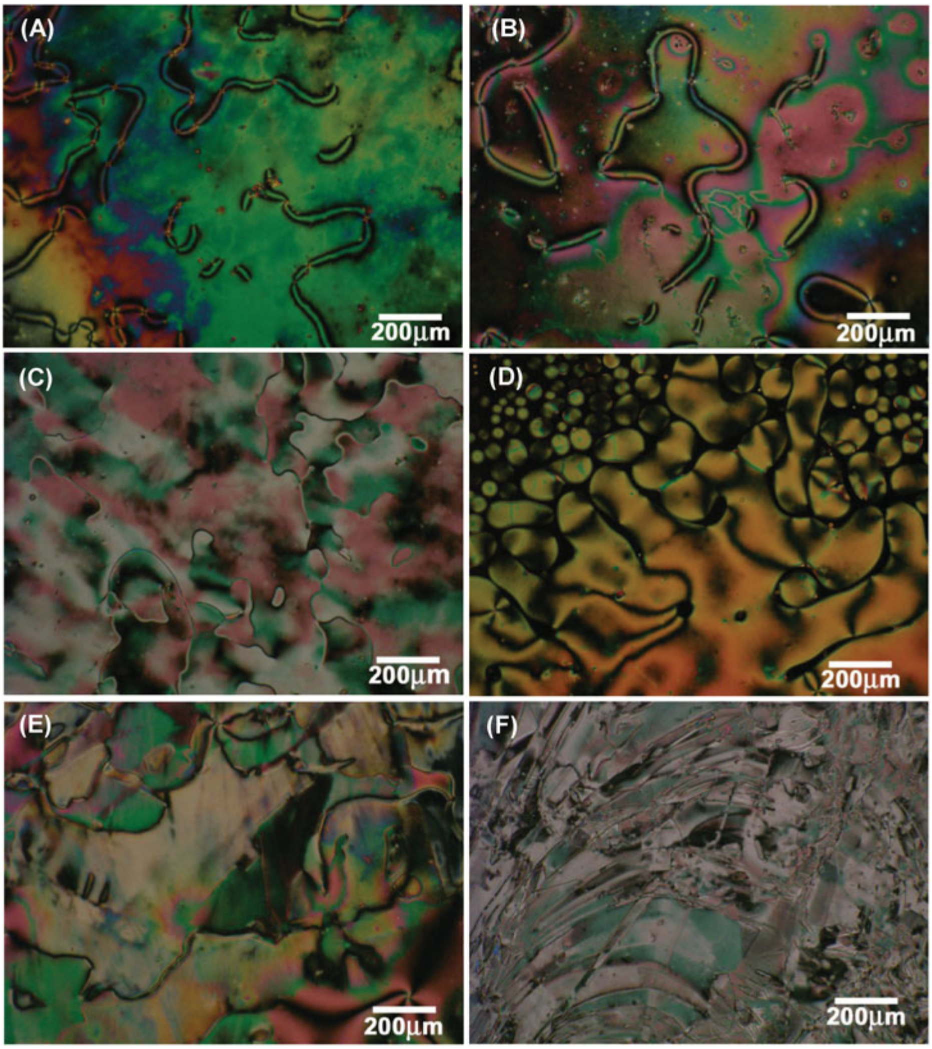


Figure 8. HOPM photographs of mesogens while cooling from isotropic phase (A): 2-DBPPTC nematic phase at 247.6°C, (B): 3-DBPPTC nematic phase at 231°C, (C): 2-DoBPPTC nematic phase at 276°C (D): 3-DoBPPTC nematic phase at 259.5°C, (E): 2-HBPPTC nematic phase at 296.2°C and (F): 3-HBPPTC nematic phase at 155°C

chains. For 2-series of thiophene mesogens, the N-I temperatures decreased with increasing chain length. Among the mesogens with dodecyloxy and dodecyl chains, the mesogen with dodecyl unit (2-DBPPTC) showed lower N-I transition. For 3-series also the decrease of N-I transition with an increase in terminal chain length is observed. As for as the N-I transition values of dodecyloxy and dodecyl mesogens of 3-series, the difference is found to be very less.

The overall comparison of mesophase characteristics of 2- and 3- series of thiophene mesogens discloses that the Cr-N transitions are higher for 3-series than 2-series. The N-I transitions, on the other hand, are found to be higher for 2-series over 3-series. As a result, the 2-series of thiophene mesogens exhibits better mesophase stability. The influence of

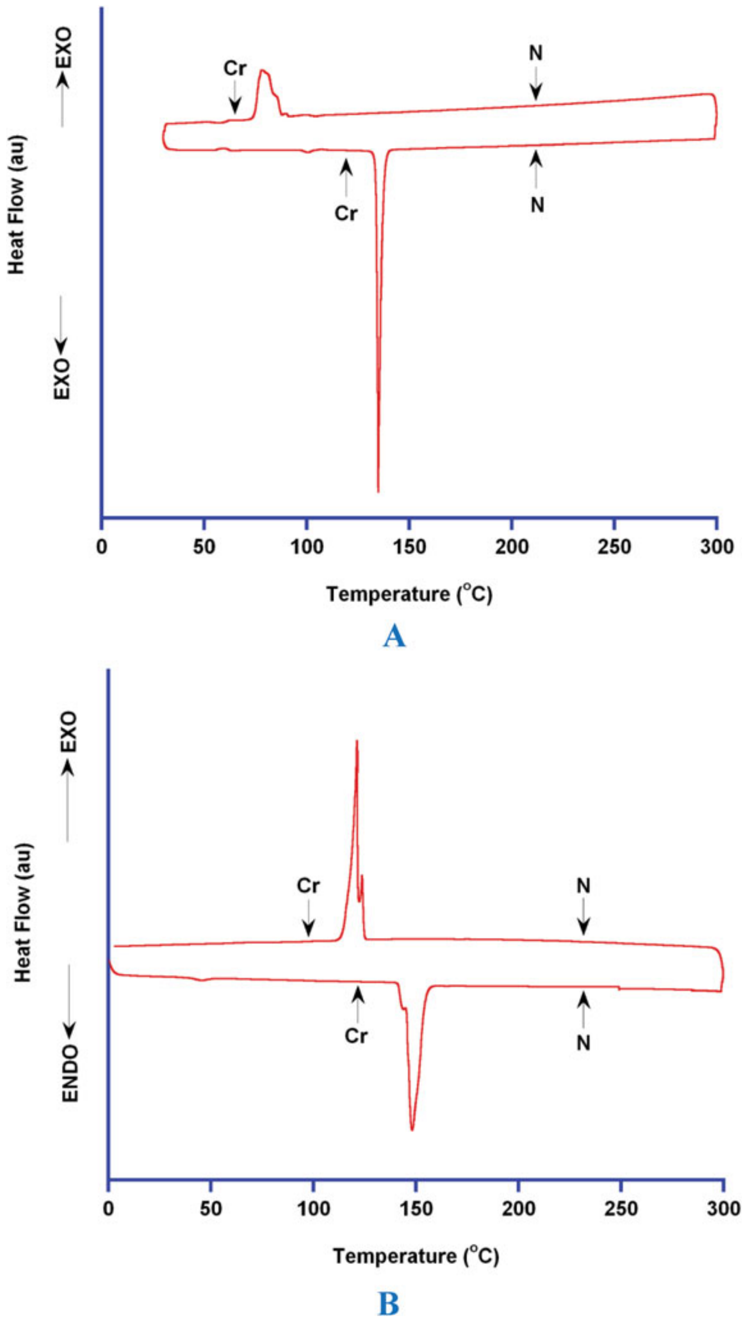


Figure 9. DSC II cycle scans of 2-HoBPPTC (A) and 3-HoBPPTC (B)

terminal chain on mesophase transition temperatures is examined for the both the series. For 3-series, 3-DBPPTC and 3-HoBPPTC mesogens showed very close N-I transitions even though for 2-series, a variation of ~24°C is clearly noticed. The careful examination of mesophase data further reveals that an addition of phenyl ring in the present case, substantial

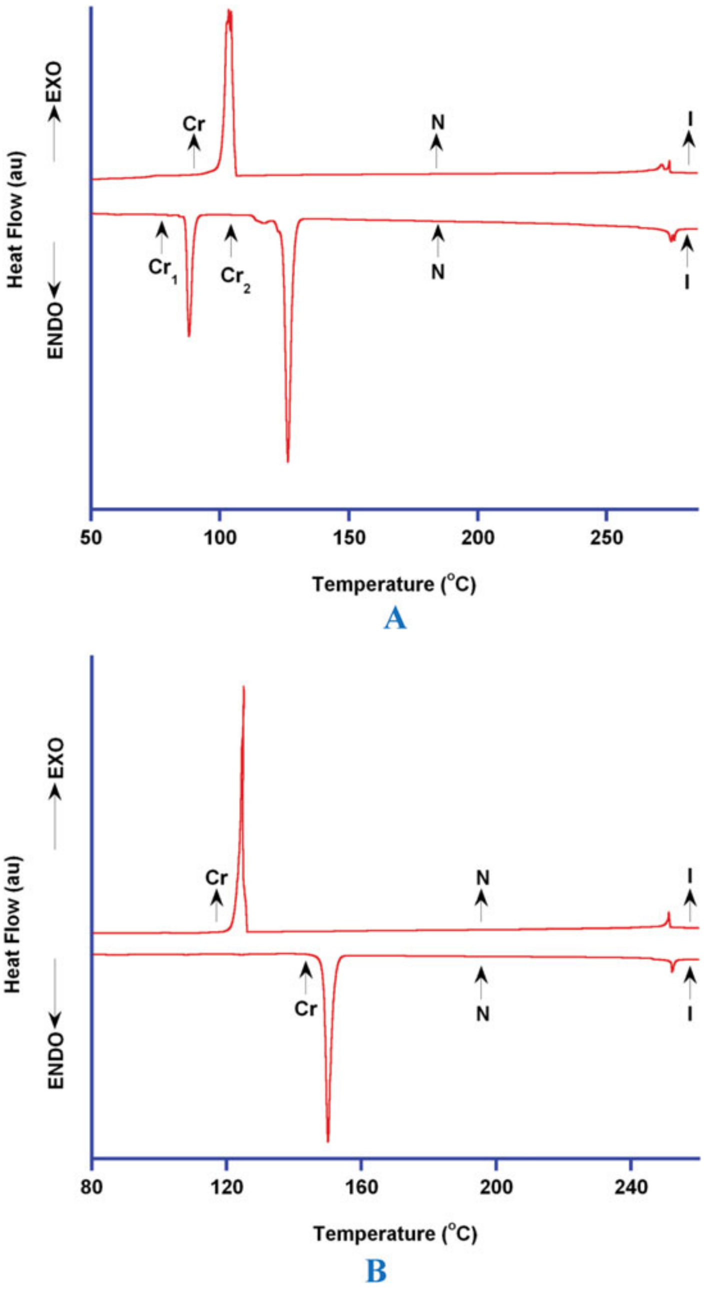


Figure 10. DSC II cycle scans of 2-DoBPPTC (A) and 3-DoBPPTC (B)

increase in Cr-N transition is noticed in contrast to two ring based thiophene mesogens [12, 16]. However, a dramatic increase is observed in N-I transition temperature thus enhancing thermal window of the mesogens. Further, despite the addition of third phenyl ring which boosts the (length) aspect ratio of core unit, the appearance of only nematic phase similar to two phenyl ring based thiophene mesogens advocates that nematic phase dominates if

Table 3. Transition temperatures and enthalpy values of 2-series

Code	Transition	Temperature (°C)	ΔH(k.cal/mole)	Mesophase stability (ΔT) (°C)
2-HoBPPTC#	Cr-N	134.21	8.59	—
	N-I	—	—	—
*2-TMAPH**	Cr-N	123.0	39.2	9
	N-I	132.0	0.8	—
2-DoBPPTC	Cr_1-Cr_2	86.69	3.96	—
	Cr_2-N	124.51	9.89	149.62
	N-I	274.13	0.23	—
*2-DDCPTC**	Cr-N	99.1	7.5	18
	N-I	117.1	0.1	—
2-DBPPTC	Cr-N	131.24	8.99	118.15
	N-I	249.39	0.24	—

2-HoBPPTC (Clearing is above 300°C)
* Thiophene with two phenyl ring mesogens from Refs: [12b &16a]

thiophene ring is placed at terminal position in the core unit [15, 16, 33,34]. If thiophene moiety is placed at the center of the core unit, on the other hand, both nematic and smectic mesophases can be realised [8, 11, 13]. Further, for calamitic mesogens, usually the smectic mesophases are noticed when the linear core is connected with lengthy flexible alkyl/alkoxy chains at both ends [35]. Thus, in a homologous series, for a common core, the nematic phase is often observed when the terminal chain length is short whereas smectic mesophases are seen with increase in terminal chain length [35]. This behaviour is rationalised by taking into account of aspect ratio of the mesogen [35]. For a homologues series, as the core length is constant and length of the chain is variable, the higher homologues are endowed

Table 4. Transition temperatures and enthalpy values of 3-series

Code	Transition	Temperature (°C)	ΔH (k.cal/mole)	Mesophase stability (ΔT)(°C)
3-HoBPPTC#	Cr-N	148.35	9.29	—
	N-I	—	—	—
*3-TMAPH**	Cr-N	113.0	37.4	32
	N-I	145.0	1.1	—
3-DoBPPTC	Cr_1-Cr_2	116.07	6.04	—
	Cr_2-N	141.34	10.09	113.35
	N-I	254.69	0.27	—
*3-DDCPTC**	Cr-N	113.3	10.2	9.4
	N-I	122.7	0.3	—
3-DBPPTC	Cr-N	148.86	9.93	103.13
	N-I	251.99	0.25	—

3-HoBPPTC (Clearing is above 300°C)
* Thiophene with two phenyl ring mesogens from Ref: [12b &16a]

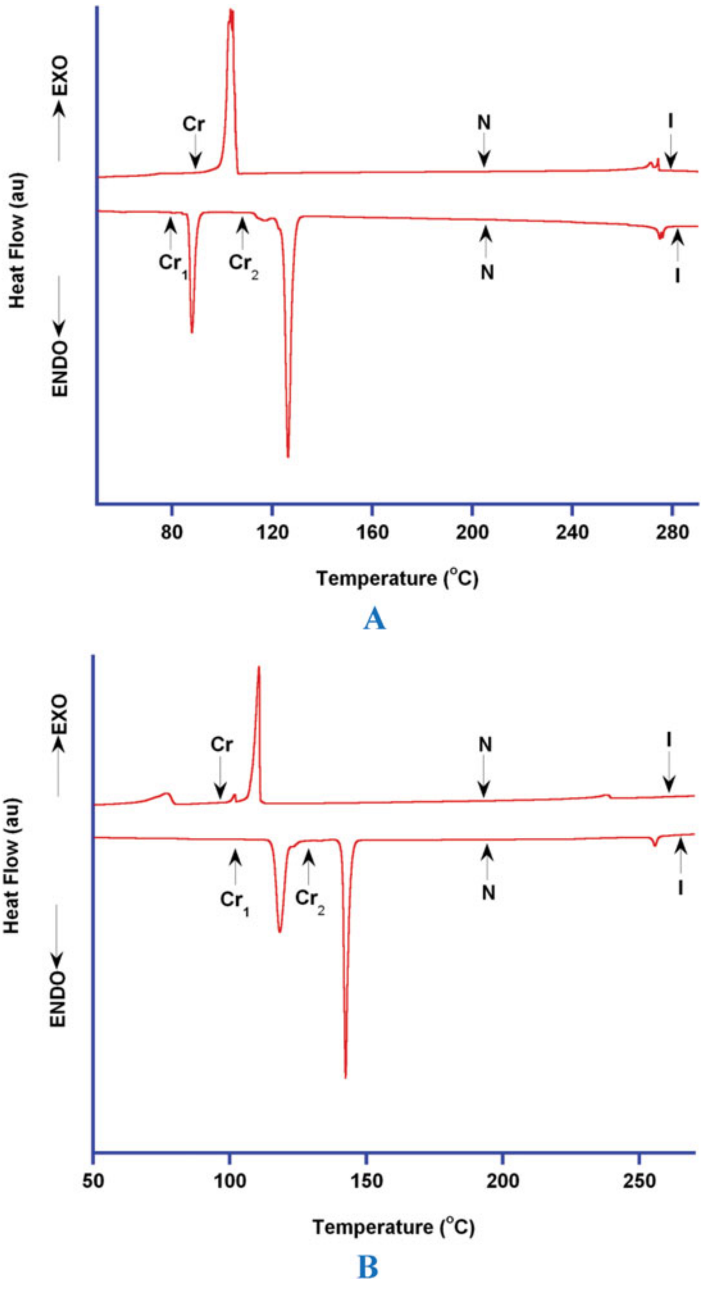


Figure 11. DSC II cycle scans of 2-DBPPTC (A) and 3-DBPPTC (B)

with high aspect ratio. Consequently, the lateral interactions are dominant over terminal interactions; thus favouring smectic mesophase [35]. Yet another way of realising smectic mesophase is to introduce polar terminal groups like nitro, cyano etc. by replacing one of the terminal chains [35]. In the present work, however, all the mesogens showed only nematic mesophase despite lengthy core and terminal chains. As deliberated above, the absence

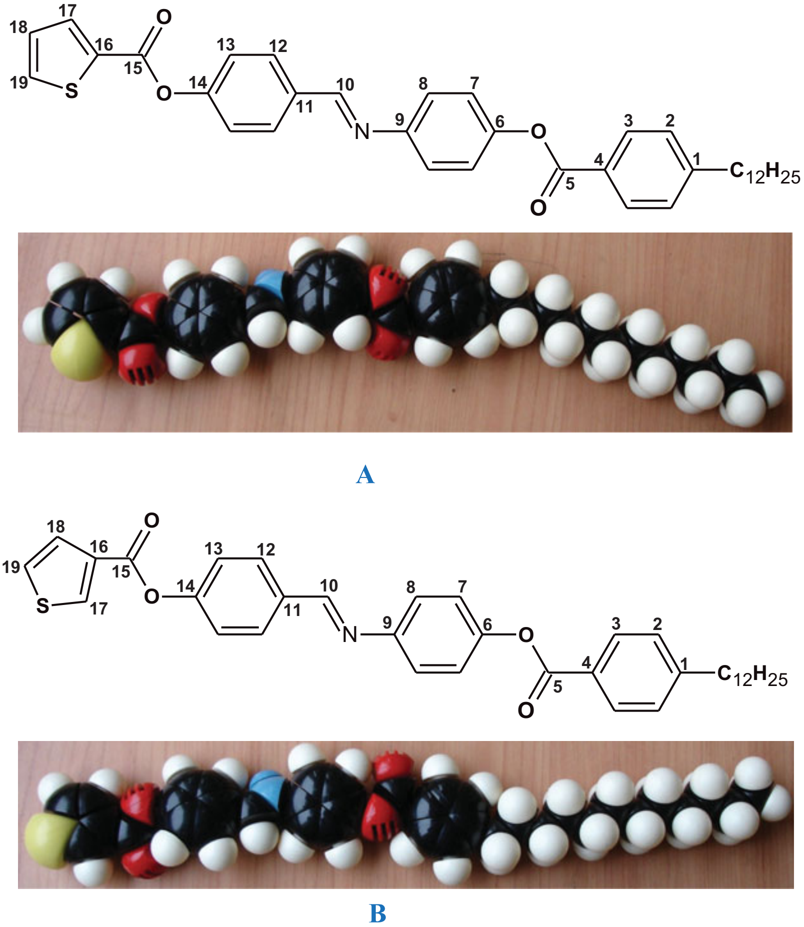


Figure 12. Molecular Structures and space filled models of 2-DBPPTC (A) and 3-DBPPTC (B)

of smectic mesophases in these mesogens can be argued since the mesogens have only one terminal chain as against two terminal chains often required for smectogens. Further, the presence of less symmetric thiophene unit at one end of the mesogen also disfavours layer ordering leading to predominantly nematic mesophase. The influence of lengthy core as well as terminal chain of these mesogens, on the other hand, is very well reflected on nematic phase stability as against to those thiophene mesogens in which only two phenyl rings are present in the core (Tables 3 and 4) [12, 16].

The thiophene mesogens reported in this work are expected to have significant importance as 3-substituted mesogens are susceptible for polymerization and can yield thiophene based polymeric liquid crystals. Such polymers are known to exhibit polarized emission paving the way for their use in organic/polymeric light emitting diodes [15, 36]. The studies can be further extended to incorporate bithiophene, terthiophene at one end of the molecule to examine the mesophase as well as photo-physical properties. Additionally, the solid state ^{13}C NMR experiments of these mesogens in nematic phase are underway which would provide the orientational order for the phenyl rings as well as thiophene moiety and the information can be supportive in understanding the orientational constraints and its impact on material properties.

4. Conclusions

Six thiophene based calamitic mesogens were synthesized by multistep route. The molecular structures were confirmed by FT-IR spectroscopy in solid state and by NMR spectroscopy in solution. The assignment was carried by ^{1}H, ^{13}C, ^{1}H-^{1}H DQF-COSY, ^{13}C—^{1}H HSQC and ^{1}H—^{13}C HMBC techniques. For the assignment of thiophene ring, proton coupling constants (J Hz) were additionally used. The HOPM and DSC measurements confirmed the existence of enantiotropic nematic phase in all the mesogens. The influence of position of substitution on mesophase characteristics reveals that 2-substituted thiophene based mesogens showed low melting. The appearance of only nematic phase was attributed to the presence of thiophene at terminal position. The mesogens based on hexyloxy terminal chains (2-HoBPPTC and 3-HoBPPTC) showed high clearing temperatures and were found to undergo decomposition at 320°C. For all the mesogens, high clearing temperatures (N-I) were attributed to four rings in the core which enhances the molecular anisotropic polarizability. Further, a dramatic increase in mesophase stabilities for three ring mesogens in contrast to two phenyl ring based thiophene mesogens reported in literature demonstrates that core length (aspect ratio) as well as the molecular anisotropic polarizability played major role.

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