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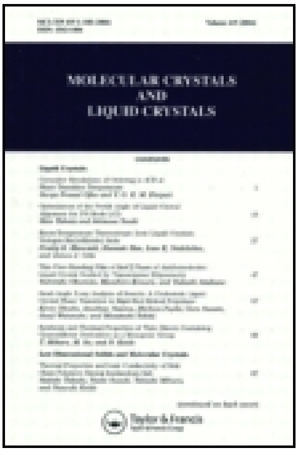

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Synthesis and Characterization of Two Phenyl Ring Core-Based Thiophene Mesogens

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Novel thiophene mesogens built with two phenyl ring core and alkoxy terminal chains are synthesized by multistep route. The phenyl ring core is connected to thiophene by ester unit at (a) 2-position and (b) 3-position to yield 2-series of mesogens. The structural characterization of them is accomplished by using spectroscopy tools and the mesophase characteristics are evaluated by HOPM and DSC. The ^{13}C chemical shifts of representative mesogens calculated from DFT by quantum chemical calculations are compared with experimental ^{13}C chemical shifts and further utilized for structural assignment of core unit carbons. A good agreement between calculated and experimental values is noticed. An enantiotropic nematic phase is confirmed for all the mesogens and accordingly threaded nematic texture in HOPM is observed and is supported by DSC transition enthalpy values. The mesophase as well as thermal stabilities of the mesogens are discussed with reference to terminal chain length and position of the linking unit on thiophene.

Keywords ^{13}C chemical shifts; DFT; mesogen; nematic phase; thiophene

1. Introduction

Designing of thermotropic liquid crystals with heterocyclic units in the core is gaining prominence and an interest in such mesogens is continuously growing [1]. This could be attributed to the presence of hetero atom, which strongly influences the mesophase characteristics by bringing considerable change in polarity, polarizability, and geometry of the molecule [2, 3]. Among the heterocyclic units used for building mesogens, thiophene—a five membered sulfur containing aromatic ring—has attracted prime attention owing to applications in functional organic materials [4, 5]. From molecular structure point of view, insertion of thiophene in the mesogenic core can substantially influence the optical anisotropy and considerably reduces the melting transition temperature [5, 6]. In addition, studies have revealed that thiophene-based mesogens possess a strong lateral dipole, which promotes negative dielectric anisotropy. Further, it eliminates the need for lateral cyano and fluoro substituents in the core, which not only enhances the molecular breadth but also the viscosity [7]. Thus, establishing a relationship between mesogenic structure and the magnitude of the polarizability anisotropy in thiophene mesogens is very crucial both for control

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and optimization of optical properties [8, 9]. Additionally, thiophene mesogens show great promise for use in organic light-emitting devices, as macroscopic alignment of the director in the mesophase favors the generation of anisotropic charge carrier mobility and polarized electroluminescence emission [10]. In this work, we report 2-series of mesogens in which thiophene unit is placed at one end of the molecule. Accordingly, 2-substituted as well as 3-substituted thiophene mesogens are designed in which two phenyl rings connected by ester unit serve as core and alkoxy chains as terminal unit. The main idea in synthesizing and examining the mesophase properties of these mesogens is to explore the influence of thiophene substitution pattern on molecular shape as well as molecular dipole and its impact on mesophase characteristics. For representative mesogens, quantum chemical calculations based on density functional theory (DFT) method are employed for finding the molecular shape as well as ^{13}C chemical shift values.

2. Experimental Details

2.1. Materials

2-thiophene carboxylic acid, 3-thiophene carboxylic acid, 4-benzyloxy phenol, 4-hydroxy methylbenzoate, *n*-bromoalkanes (C4, C8, C10, and C12), and palladium on charcoal (Pd/C, 10%) were purchased from Aldrich, Inc. (St. Louis, MO, USA) and used without further purification. Triethylamine, thionyl chloride ($SOCl_2$), N,N′-dimethylformamide (DMF), tetrahydrofuran (THF), and methanol (SD Fine Chemicals, Ltd., Mumbai, Maharashtra, India) were used as received. Ethyl acetate, diethyl ether, *n*-hexane, acetone, ethyl methyl ketone (EMK), isopropanol, potassium hydroxide (pellets), anhydrous potassium carbonate, anhydrous sodium sulfate, Celite-540, and silica gel (100–200 mesh) were obtained from Merck, Ltd. (Mumbai, Maharashtra, India) and used as received. The 4-alkoxy benzoic acids were synthesized in laboratory except 4-ethoxy benzoic acid, which was procured from Aldrich, Inc.

2.2. Instrumental Details

FT-IR spectra of all the compounds were run on ABB BOMEM MB3000 spectrometer using KBr pellets. ^{1}H and ^{13}C NMR spectra of the compounds in $CDCl_3$ as a solvent were run on a JEOL 500 MHz instrument at room temperature (r.t.) using tetramethylsilane as an internal standard. The resonance frequencies of ^{1}H and ^{13}C were 500.15 and 125.76 MHz, respectively. 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 (Olympus Corp., Tokyo, Japan). 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.

2.3. Computational Details

The gas phase molecular geometries of 2-DCPTC and 3-DCPTC were optimized by using DFT-based Becke's three parameter hybrid exchange functional and Lee−Yang−Parr correlation functional [11] (B3LYP) method employing 6-31G(d) basis set. The NMR chemical shifts were calculated at B3LYP/6-311+G(2d, p) level of theory using the gauge invariant atomic orbitals (GIAO) method to circumvent the gauge problem using B3LYP/6-31G(d) geometry [12]. Cheeseman recommended the 6-311+G(2d, p) basis set for NMR chemical shifts after scrutiny of various basis sets and hence the same was selected for the present study [13]. The scale factor determined for B3LYP/6-311+G(2d, p)//B3LYP/6-31G(d) methodology from the previous study was used for the calculation of ^{13}C NMR chemical shifts [14]. Chemical shifts of tetramethylsilane calculated at the same level of theory were used as reference. All calculations were carried out using Gaussian 03W suite of programs [15].

2.4. Synthesis of Mesogens

2.4.1. Preparation of 4-Dodecyloxy Benzoic Acid.

2.4.1.1. Preparation of 4-Dodecyloxy Methyl Benzoate (1). In a representative experiment, 4-hydroxy methyl benzoate (7.6 g, 0.05 mol) was placed in a 500 ml three-necked round-bottom flask equipped with stirrer and thermometer. To that, N,N′-dimethylformamide (150 ml) and potassium carbonate (10.36 g, 0.075 mol) were added. The resulting mixture was stirred while maintaining the temperature at 90°C, then *n*-bromododecane (12 ml, 0.05 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 down at r.t. poured into a 2-l beaker [16]. The contents were diluted with water (250 ml) and then transferred to a 500 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. The organic layer was dried with anhydrous sodium sulfate. Upon evaporation of ether, 4-dodecyloxy methyl benzoate resulted as a liquid.

2.4.1.2. Hydrolysis of 4-Dodecyloxy Methyl Benzoate (2). 4-dodecyloxy methylbenzoate (13.3 g, 0.04 mol) was placed in a one liter single-necked round-bottom flask equipped with double wall water condenser. Ethanol (250 ml) and potassium hydroxide (6 g, 0.1 mol) dissolved in distilled water (250 ml) were added to the flask. The solution was refluxed for 2 hours and allowed to cool down at r.t. and then neutralized with 10% hydrochloric acid to get a white precipitate. It was purified by recrystallizing from methanol.

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 ($C{-}O{-}C_{asym\ \&\ sym\ str}$ ether); ^{1}H-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.

2.4.2. Synthesis of 4-Hydoxy Phenyl 4-(Dodecyloxy) Benzoate.

2.4.2.1. Synthesis of 4-(Benzyloxy) Phenyl 4-(Dodecyloxy) Benzoate (3a). In an experiment, 4-benzyloxy phenol (5 g, 0.025 mol) was placed in a 500 ml two-necked round-bottom flask with ethyl methyl ketone as solvent, which was kept in an ice bath. Triethylamine (3 ml, 0.03 mol) was added to the reaction solution on stirring. To this, 4-dodecyloxy benzoyl chloride—which was prepared from acid by reacting with thionyl chloride—was slowly added through a pressure equalizing dropping funnel for 30 minutes while maintaining the temperature at 0°C. The stirring was continued for 4 hours and then the precipitated triethylamine salt was filtered and the solvent was removed from the solution under reduced pressure. The solid obtained was washed with 4% potassium hydroxide solution twice to remove unreacted acid, phenol, further washed with water, then dried and recrystallized.

Yield: 67.4%, m.p. 78°C, FT-IR (KBr, cm^{-1}): 2921, 2852 (C—H$_{str}$), 1728 (C=O$_{str}$), 1683, 1606, 1511 (C=C$_{str}$ aromatic), 1464, 1333 (C—H$_{ben}$), 1251, 1200, 1170 (C—O—C$_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-NMR ppm (CDCl$_3$): 8.13 (d, 2H), 7.46 (d, 2H), 7.40 (t, 2H), 7.35 (t, 1H), 7.12 (d, 2H), 7.02 (d, 2H), 6.98 (d, 2H), 5.07 (s, 2H), 4.04 (t, 2H), 1.84 (m, 2H), 1.48 (m, 2H), 1.37 (m, 16H), 0.90 (t, 3H); ^{13}C-NMR ppm (CDCl$_3$): 165.42, 163.57, 156.50, 144.83, 136.98, 132.34, 128.72, 128.13, 127.61, 122.70, 121.69, 115.56, 114.35, 70.51, 68.40, 32.05, 29.79, 29.77, 29.76, 29.73, 29.70, 29.50, 29.22, 26.10, 22.83, and 14.27.

2.4.2.2. Debenzylation of 4-(Benzyloxy) Phenyl 4-(Dodecyloxy) Benzoate (4a). In a typical experiment, 4-(benzyloxy) phenyl 4-(dodecyloxy) benzoate (4 g, 0.0081 mol) was placed in a 250 ml single-necked round-bottom flask and tetrahydrofuran (100 ml) was added. To that, 10% Pd/C (0.4 g) was added while stirring the solution [17]. The hydrogen atmosphere was maintained by purging the hydrogen gas through balloon. The progress of the reaction was monitored through TLC. After the completion of reaction, the solid Pd/C powder was filtered by celite powder. The solution was concentrated to get solid, which was purified by column chromatography on silica gel using a mixture of 20% ethyl acetate in hexane as an eluent.

Yield: 65%, m.p. 112.5°C, FT-IR (KBr, cm^{-1}): 3469 (—OH), 2955, 2918, 2871 (C—H$_{str}$), 1709 (C=O$_{str}$), 1604, 1511 (C=C$_{str}$ aromatic), 1443, 1316 (C—H$_{ben}$), 1257, 1187, 1167,1129 (C—O—C$_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-NMR ppm (CDCl$_3$): 8.13 (d, 2H), 6.96 (m, 4H), 6.75 (d, 2H), 4.03 (t, 2H), 1.81 (m, 2H), 1.46 (m, 2H), 1.35 (m, 16H), 0.88 (t, 3H); ^{13}C-NMR ppm (CDCl$_3$): 166.25, 163.72, 153.85, 144.15, 132.43, 122.62, 121.43, 116.32, 114.41, 68.44, 32.03, 29.77, 29.75, 29.72, 29.71, 29.68, 29.48, 29.18, 26.08, 22.81, and 14.26.

2.4.3. Synthesis of 4-{[(4-Dodecyloxyphenyl)carbonyl]oxy} Phenyl Thiophene-2-Carboxylate (2-DDCPTC) (5a).

It was prepared by two-step process. In a typical experiment, 2-thiophene carboxylic acid was placed in a 100 ml single-necked round-bottom flask fitted with a double wall reflux condenser and a calcium chloride guard tube. Thionyl chloride (1.09 ml, 0.0075 mol) and few drops of N,N′-dimethylformamide were added to the flask and refluxed for 1 hour. The excess thionyl chloride was removed by vacuum pump. Then it was dissolved in ethyl methyl ketone (50 ml) and added dropwise through pressure equalizing dropping funnel for 45 minutes at 0°C to the mixture of 4-hydoxy phenyl 4-(dodecyloxy) benzoate (2 g, 0.005 mol) and triethylamine (0.84 ml, 0.006 mol) in ethyl methyl ketone. The reaction mixture was allowed for stirring for 5 hours. Then the flask was taken out, the triethylamine salt was filtered, and the solvent was removed from solution under reduced pressure. The solid obtained was washed twice with 2% potassium hydroxide solution followed by water and then dried, recrystallized from isopropyl alcohol and methanol.

Similar protocols were used for synthesizing other homologues of the series.

Yield: 64.9%, m.p. 102.1°C, FT-IR (KBr, cm^{-1}): 2920, 2852 (C—H$_{str}$), 1728 (C=O$_{str}$), 1608, 1509, (C=C$_{str}$ aromatic), 1416, 1359 (C—H$_{ben}$), 1270, 1185 (C—O—C$_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-NMR ppm (CDCl$_3$): 8.14 (d, 2H), 7.99 (d, 1H), 7.66 (d, 1H), 7.28 (m, 4H), 7.18 (t, 1H), 6.96 (d, 2H), 4.04 (t, 2H), 1.81 (m, 2H), 1.45 (m, 2H), 1.31 (m, 16H), 0.88 (t, 3H), ^{13}C-NMR ppm (CDCl$_3$): 164.92, 163.71, 160.59, 148.71, 147.96, 139.90, 133.72, 132.81, 132.40, 128.16, 122.83, 122.62, 121.39, 114.42, 68.43, 32.02, 29.75, 29.72, 29.69, 29.65, 29.63, 29.45, 26.18, 26.07, 22.79, and 14.23.

2.4.3.1. 4-{[(4-Decyloxyphenyl) Carbonyl] Oxy} Phenyl Thiophene-2-Carboxylate (2-DCPTC) (5b). Yield: 71.5%, m.p. 104°C, FT-IR (KBr, cm^{-1}): 3084 (aromatic C—H$_{str}$), 2922, 2853 (C—H$_{str}$), 1728 (C=O$_{str}$), 1607, 1507 (C=C$_{str}$ aromatic), 1469, 1358 (C—H$_{ben}$), 1266, 1178 (C—O—C$_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-NMR ppm (CDCl$_3$): 8.15 (d, 2H), 7.98 (d, 1H), 7.65 (d, 1H), 7.25 (m, 4H), 7.17 (t, 1H), 6.97 (d, 2H), 4.03 (t, 2H), 1.82 (m, 2H), 1.48 (m, 2H), 1.35 (m, 12H), 0.89 (t, 3H); ^{13}C-NMR ppm (CDCl$_3$): 164.89, 163.72, 160.57, 148.72, 147.98, 139.89, 133.74, 132.81, 132.40, 128.17, 122.83, 122.62, 121.40, 114.43, 68.44, 32.01, 29.67, 29.48, 29.46, 29.44, 29.20, 26.09, 22.79, and 14.25.

2.4.3.2. 4-{[(4-Octyloxyphenyl) Carbonyl] Oxy} Phenyl Thiophene-2-Carboxylate (2-OCPTC) (5c). Yield: 73.4%, m.p. 103°C, FT-IR (KBr, cm^{-1}): 3078 (aromatic C—H$_{str}$), 2924, 2955 (C—H$_{str}$), 1731 (C=O$_{str}$), 1606, 1577, 1502 (C=C$_{str}$ aromatic), 1467, 1359 (C—H$_{ben}$), 1224, 1170 (C—O—C$_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-NMR ppm (CDCl$_3$): 8.13 (d, 2H), 7.99 (d, 1H), 7.67 (d, 1H), 7.26 (m, 4H), 7.17 (t, 1H), 6.98 (d, 2H), 4.03 (t, 2H), 1.82 (m, 2H), 1.47 (m, 2H), 1.34 (m, 8H), 0.89 (t, 3H); ^{13}C-NMR ppm (CDCl$_3$): 164.91, 163.71, 160.59, 148.71, 147.97, 134.90, 133.73, 132.80, 132.41, 128.17, 122.83, 122.62, 121.40, 114.43, 68.44, 31.90, 29.42, 29.33, 29.19, 26.08, 22.75, and 14.2.

2.4.3.3. 4-{[(4-Butoxyphenyl) Carbonyl] Oxy} Phenyl Thiophene-2-Carboxylate (2-BCPTC) (5d). Yield: 72%, m.p. 140°C, FT-IR (KBr, cm^{-1}): 3077 (aromatic C—H$_{str}$), 2853, 2867 (C—H$_{str}$), 1723 (C=O$_{str}$), 1604, 1578, 1505 (C — C$_{str}$ aromatic), 1468, 1386 (C—H$_{ben}$), 1227, 1166 (C—O—C$_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-NMR ppm (CDCl$_3$): 8.12 (d, 2H), 7.97 (d, 1H), 7.67 (d, 1H), 7.25 (m, 4H), 7.18 (t, 1H), 6.96 (d, 2H), 4.05 (t, 2H), 1.82 (m, 2H), 1.49 (m, 2H), 0.99(t, 3H); ^{13}C-NMR ppm (CDCl$_3$): 164.91, 163.72, 160.58, 148.71, 147.98, 134.89, 133.73, 132.81, 132.41, 128.16, 122.82, 122.61, 121.41, 114.43, 68.11, 31.21, 19.29, and 13.92.

2.4.3.4. 4-{[(4-Ethoxyphenyl) Carbonyl] Oxy} Phenyl Thiophene-2-Carboxylate (2-ECPTC) (5e). Yield: 75.1%, m.p. 153°C, FT-IR (KBr, cm^{-1}): 3093 (aromatic C—H$_{str}$), 2982 (C—H$_{str}$), 1723 (C=O$_{str}$), 1603, 1504 (C=C$_{str}$ aromatic), 1412, 1359 (C—H$_{ben}$), 1170, 1117 (C—O—C$_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-NMR ppm (CDCl$_3$): 8.14 (d, 2H), 7.99 (d, 1H), 7.67 (d, 1H), 7.26 (m, 4H), 7.18 (t, 1H), 6.97 (d, 2H), 4.11 (t, 2H), 1.46 (t, 3H); ^{13}C-NMR ppm (CDCl$_3$): 164.91, 163.49, 160.61, 148.69, 147.97, 134.89, 133.72, 132.79, 132.42, 128.16, 122.82, 122.62, 121.47, 114.39, 63.91, and 14.76.

2.4.4. Synthesis of 4-{[(4-Dodecyloxyphenyl) Carbonyl] Oxy} Phenyl Thiophene-3-Carboxylate (3-DDCPTC) (6a).

The synthetic approach adopted for synthesizing 2-series is followed for preparing 3-series by using 3-thiophene carboxylic acid as a starting material.

Yield: 67.2%, m.p. 116°C, FT-IR (KBr, cm^{-1}): 3104 (aromatic C—H$_{str}$), 2919, 2951 (C—H$_{str}$), 1728 (C=O$_{str}$), 1609, 1510, (C=C$_{str}$ aromatic), 1471, 1359 (C—H$_{ben}$), 1265, 1194 (C—O—C$_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-NMR ppm (CDCl$_3$): 8.31 (d, 1H), 8.15 (d, 2H), 7.66 (d, 1H), 7.38 (m, 1H), 7.25 (m, 4H), 6.98 (d, 2H), 4.04 (t, 2H), 1.82 (m, 2H), 1.49 (m, 2H), 1.35 (m, 16H), 0.88 (t, 3H); ^{13}C-NMR ppm (CDCl$_3$): 164.93, 163.71, 161.04, 148.63, 148.10, 134.26, 132.81, 132.41, 128.32, 126.53, 122.83, 122.67, 121.41, 114.42, 68.43, 32.02, 29.76, 29.75, 29.73, 29.70, 29.67, 29.47, 29.19, 26.09, 22.80, and 14.25.

2.4.4.1. 4-{[(4-Decyloxyphenyl) Carbonyl] Oxy} Phenyl Thiophene-3-Carboxylate (3-DCPTC) (6b). Yield: 70.1%, m.p. 119°C, FT-IR (KBr, cm^{-1}): 3104 (aromatic C—H$_{str}$), 2921, 2850 (C—H$_{str}$), 1728 (C=O$_{str}$), 1609, 1509, (C=C$_{str}$ aromatic), 1466, 1418 (C—H$_{ben}$), 1262, 1191 (C—O—C$_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-NMR ppm (CDCl$_3$): 8.31 (d, 1H), 8.15 (d, 2H), 7.67 (d, 1H), 7.37 (m, 1H), 7.25 (m, 4H), 6.98 (d, 2H), 4.03 (t, 2H), 1.82 (m, 2H), 1.48 (m, 2H), 1.37 (m, 12H), 0.89 (t, 3H); ^{13}C-NMR ppm (CDCl$_3$): 164.91, 163.71, 161.02, 148.65, 148.10, 134.24, 132.82, 132.27, 128.32, 126.54, 122.83, 122.66, 121.43, 114.43, 68.44, 67.93, 32.01, 29.67, 29.48, 29.44, 29.21, 26.10, 22.80, and 14.25.

2.4.4.2. 4-{[(4-Octyloxyphenyl) Carbonyl] Oxy} Phenyl Thiophene-3-Carboxylate (3-OCPTC) (6c). Yield: 73.8%, m.p. 120.5°C, FT-IR (KBr, cm^{-1}): 3104 (aromatic $\mathrm{C{-}H_{str}}$), 2922, 2853 ($\mathrm{C{-}H_{str}}$), 1730 ($\mathrm{C{=}O_{str}}$), 1610, 1509 ($\mathrm{C{=}C_{str}}$ aromatic), 1468, 1400 ($\mathrm{C{-}H_{ben}}$), 1269, 1192 ($\mathrm{C{-}O{-}C_{asym\ \&\ sym\ str}}$ of ester and ether); ^{1}H-NMR ppm ($\mathrm{CDCl_3}$): 8.31 (d, 1H), 8.14 (d, 2H), 7.67 (d, 1H), 7.38 (m, 1H), 7.25 (m, 4H), 6.97 (d, 2H), 4.04 (t, 2H), 1.82 (m, 2H), 1.47 (m, 2H), 1.35 (m, 8H), 0.90 (t, 3H); ^{13}C-NMR ppm ($\mathrm{CDCl_3}$): 164.92, 163.71, 161.03, 148.64, 148.10, 134.25, 132.82, 132.41, 128.32, 126.54, 122.83, 122.66, 121.42, 114.43, 68.44, 31.91, 29.44, 29.34, 29.19, 26.09, 22.76, and 14.23.

2.4.4.3. 4-{[(4-Butoxyphenyl) Carbonyl] Oxy} Phenyl Thiophene-3-Carboxylate (3-BCPTC) (6d). Yield: 74.1%, m.p. 147.2°C, FT-IR (KBr, cm^{-1}): 3110 (aromatic $\mathrm{C{-}H_{str}}$), 3077, 2953, 2867 ($\mathrm{C{-}H_{str}}$), 1736 ($\mathrm{C{=}O_{str}}$), 1609, 1578, 1504 ($\mathrm{C{=}C_{str}}$ aromatic), 1467, 1384, ($\mathrm{C{-}H_{ben}}$), 1249, 1166 ($\mathrm{C{-}O{-}C_{asym\ \&\ sym\ str}}$ of ester and ether); ^{1}H-NMR ppm ($\mathrm{CDCl_3}$): 8.32 (d, 1H), 8.14 (d, 2H), 7.67 (d, 1H), 7.38 (m, 1H), 7.25 (m, 4H), 6.98 (d, 2H), 4.05 (t, 2H), 1.79 (m, 2H), 1.51 (m, 2H), 0.99 (t, 3H); ^{13}C-NMR ppm ($\mathrm{CDCl_3}$): 164.93, 163.71, 161.04, 148.64, 148.10, 134.25, 132.82, 132.41, 128.32, 126.53, 122.82, 122.66, 121.43, 114.43, 68.11, 31.22, 19.29, and 13.93.

2.4.4.4. 4-{[(4-Ethoxyphenyl) Carbonyl] Oxy} Phenyl Thiophene-3-Carboxylate (3-ECPTC) (6e). Yield: 72.9%, m.p. 162°C, FT-IR (KBr, cm^{-1}): 3106 (aromatic $\mathrm{C{-}H_{str}}$), 2978 ($\mathrm{C{-}H_{str}}$), 1730 ($\mathrm{C{=}O_{str}}$), 1605, 1507 ($\mathrm{C{=}C_{str}}$ aromatic), 1419 ($\mathrm{C{-}H_{ben}}$), 1256, 1167 ($\mathrm{C{-}O{-}C_{asym\ \&\ sym\ str}}$ of ester and ether); ^{1}H-NMR ppm ($\mathrm{CDCl_3}$): 8.31 (d, 1H), 8.13 (d, 2H), 7.66 (d, 1H), 7.38 (m, 1H), 7.25 (m, 4H), 6.97 (d, 2H), 4.11 (t, 2H), 1.45 (t, 3H); ^{13}C-NMR ppm ($\mathrm{CDCl_3}$): 164.93, 163.49, 161.06, 148.63, 148.10, 134.26, 132.79, 132.43, 128.32, 126.54, 122.83, 122.67, 121.48, 114.40, 63.93, and 14.77.

3. Results and Discussion

The molecular structures of representative decyloxy mesogens of both the series along with carbon numbering are shown in Figs. 1 and 2. Scheme 1 depicts the strategy adopted

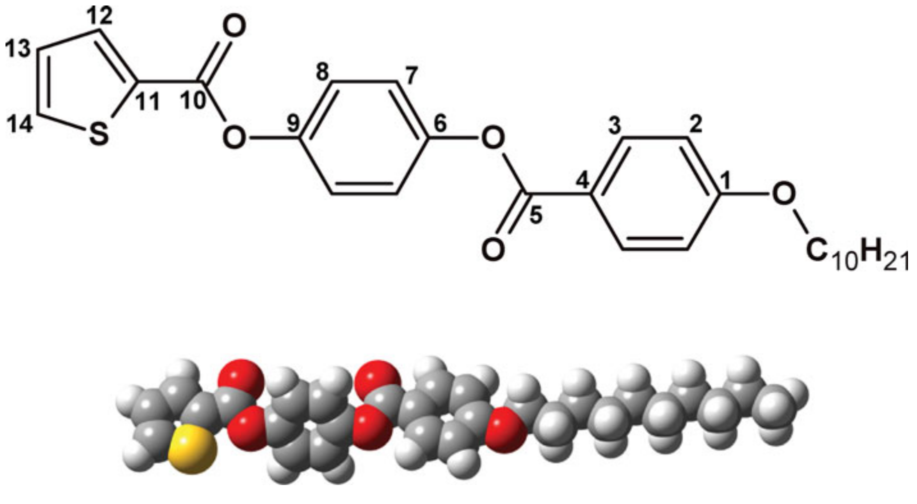


Figure 1. Molecular structure and energy optimized space filled model of 2-DCPTC.

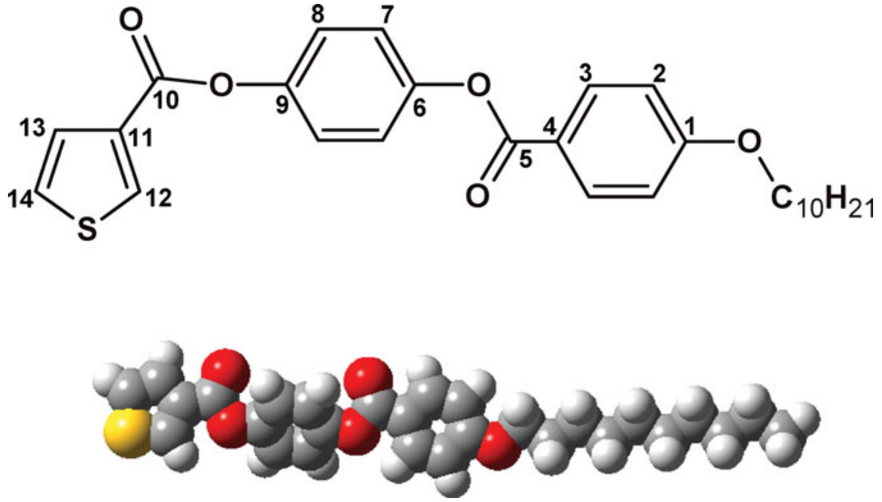
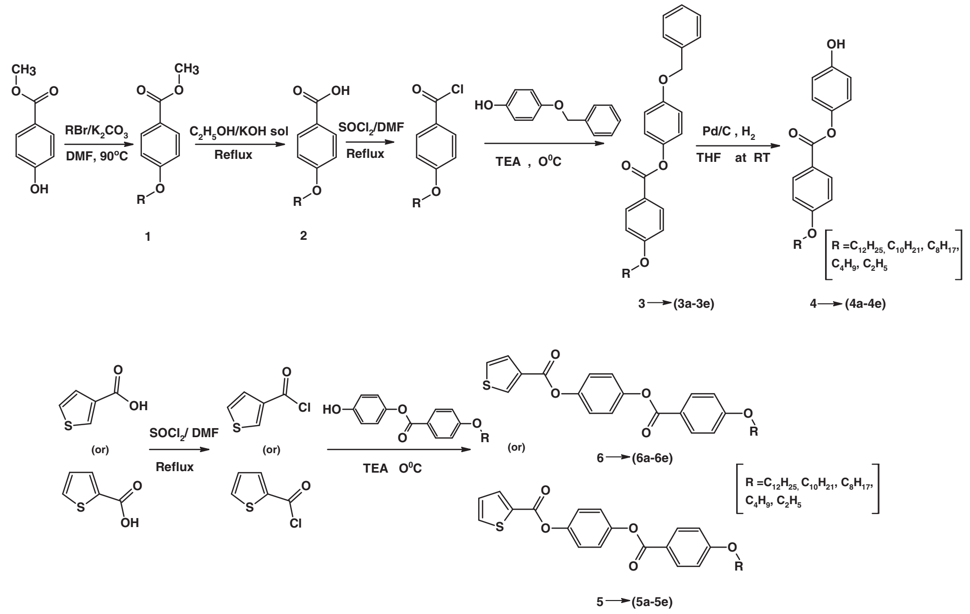


Figure 2. Molecular structure and energy optimized space filled model of 3-DCPTC.

for the synthesis of mesogens. Figs. 1 and 2 also show the energy optimized space filled models of the decyloxy mesogens computed from DFT method of quantum chemical calculations. The ester linking units are employed for the construction of core with alkoxy chain (even carbons except C6 homologue) as terminal unit. The target mesogens as well as the intermediates are well characterized by FT-IR, ^{1}H, and ^{13}C NMR spectroscopy. The FT-IR spectrum of decyloxy mesogen revealed prominent intense vibrations at 2920, 1728, and 1270 cm^{-1}, which are attributed to C—H asymmetric stretching, ester carbonyl stretching, and C—O—C asymmetric stretching vibrations, respectively. In proton NMR, the expected spectral lines with multiplicities are observed accounting for all the protons of the mesogens. For instance, thiophene ring showed characteristic three-spin pattern, while the terminal —OCH_2 is distinctly seen as a triplet at 4.04 ppm, and the other spectral features are in consistent with molecular structure.

3.1. ^{13}CNMR Spectroscopy

Figure 3 shows the proton decoupled ^{13}C NMR spectra of decyloxy mesogens. The chemical shift assignment of the signals of the core unit is carried out using DFT-based quantum chemical calculations. In recent years, DFT-based methods are often employed for structural assignment of mesogens using ^{13}C chemical shifts, as complexity increases with more number of carbons [18–20]. Table 1 lists the ^{13}C chemical shifts of experimentally determined values as well as those computed from DFT method for the core unit of 2-DCPTC and 3-DCPTC. The spectrum shows 14 lines in the region 114–165 ppm for the core unit, while 10 lines are clearly seen in the range 14–69 ppm for the decyloxy chain. A good agreement is noticed between experimental and calculated ^{13}C chemical shifts with exception to ester carbonyl and thiophene carbons. For thiophene ring, the carbon chemical shift assignment is further verified by comparing with the literature data [21]. A close examination of ^{13}C chemical shifts of 2-DCPTC and 3-DCPTC indicates that, except C14, the chemical shifts of core as well as terminal chain are alike in view of structural similarity. A 7 ppm variation noticed for C14 chemical shift between the mesogens is attributed mainly to substitution pattern of the thiophene ring.



Scheme 1. Synthetic strategy for the mesogens.

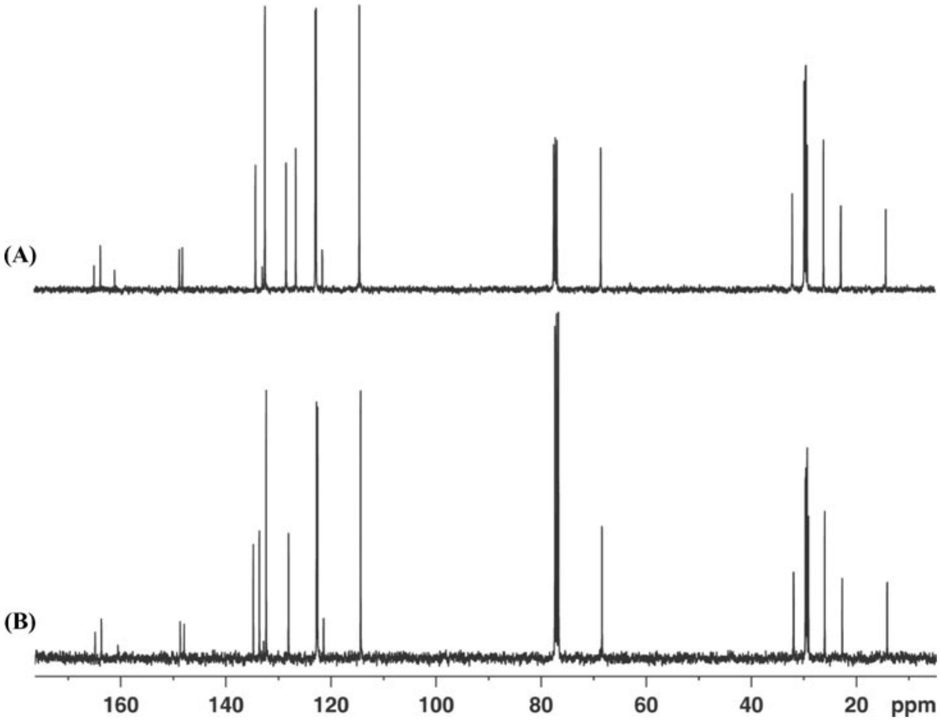


Figure 3. Proton decoupled ^{13}C NMR spectra of (a) 2-DCPTC and (b) 3-DCPTC in solution state.

Table 1. ^{13}C Chemical shifts of 2-DCPTC and 3-DCPTC

2-DCPTC ^{13}C chemical shift (ppm)			3-DCPTC ^{13}C chemical shift (ppm)	
C. No	Experimental	QCC	Experimental	QCC
1	163.7	162.6	163.7	163.1
2	114.4	116.9	114.4	115.6
3	132.4	133.3	132.4	133.4
4	121.3	121.3	121.4	121.7
5	164.9	161.9	164.9	162.0
6	147.9	147.8	148.1	149.0
7	122.8	122.4	122.8	122.4
8	122.6	120.8	122.6	122.2
9	148.7	147.9	148.6	147.7
10	160.5	157.7	161.0	158.0
11	132.8	138.3	134.2	137.0
12	133.7	134.4	132.8	133.5
13	128.1	125.2	128.3	128.6
14	134.9	136.9	126.5	129.3

3.2. *Mesophase Transitions*

The mesophase characteristics like melting and clearing transitions for both the series are determined by HOPM and DSC techniques. Tables 2 and 3 list the mesophase temperatures and transition enthalpy values. All the mesogens showed enantiotropic nematic phase as confirmed by DSC heating and cooling curves as well microscopy data (Figs. 4 and 5). In HOPM, the samples upon cooling showed characteristic Schlieren or threaded texture typical of nematic phase for all the mesogens. Fig. 6 shows the HOPM photographs of 2-OCPTC (91.2°C) and 3-DDCPTC (120.4°C) mesogen on cooling the isotropic phase. In DSC scan (Figs. 4 and 5), two peaks are typically noticed for all the mesogens among which

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

Code	Transition	Temperature (°C)	ΔH (k.cal/mole)
2-ECPTC	Cr–N	146.8	8.3
	N–I	160.4	0.1
2-BCPTC	Cr–N	137.5	8.0
	N–I	149.1	0.1
2-OCPTC	Cr–N	100.0	5.9
	N–I	120.1	0.1
2-DCPTC	Cr–N	98.2	7.1
	N–I	117.7	0.1
2-DDCPTC	Cr_1–Cr_2	86.8	0.8
	Cr_2–N	99.1	7.5
	N–I	117.1	0.1

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

Code	Transition	Temperature (°C)	ΔH (k.cal/mole)
3-ECPTC	Cr–N	157.8	7.25
	N–I	166.7	0.1
3-BCPTC	Cr–N	140.6	6.3
	N–I	150.0	0.1
3-OCPTC	Cr–N	113.0	7.7
	N–I	131.0	0.1
3-DCPTC	Cr_1–Cr_2	79.6	0.6
	Cr_2–N	113.2	7.7
	N–I	126.3	0.1
3-DDCPTC	Cr_1–Cr_2	86.1	6.5
	Cr_2–N	113.3	10.2
	N–I	122.7	0.3

crystal–nematic transition is associated with higher enthalpy value (~6–8 k.cal/mol), while the nematic–isotropic showed lower values (~0.1–0.3 k.cal/mol). For higher homologues, i.e., 2-DCPTC and 3-DCPTC as well as 2-DDCPTC and 3-DDCPTC, crystal–crystal transitions are observed (Figs. 4 and 5) below crystal–nematic transition. This feature is typical for molecular crystals in which the terminal unit is constructed with lengthy alkyl/alkoxy chain [22]. The transition enthalpy values further substantiate the HOPM

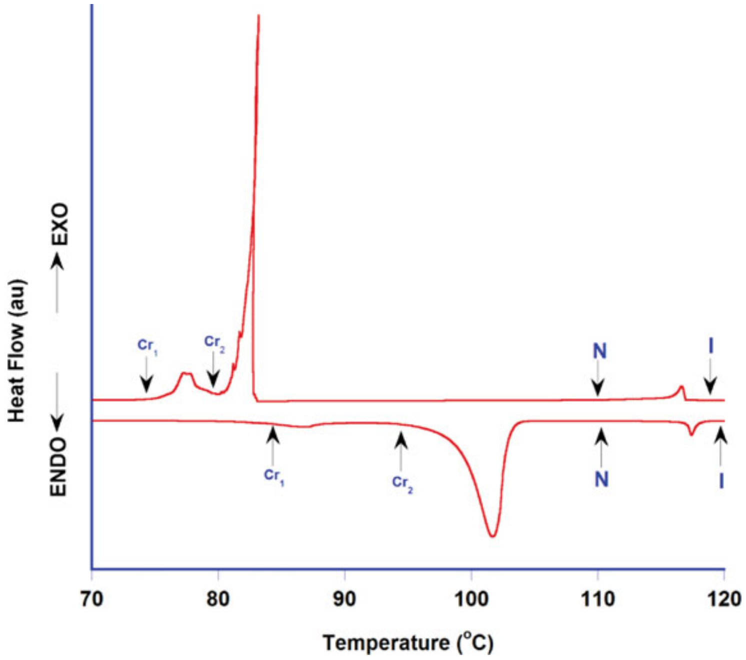


Figure 4. DSC Scan of 2-DDCPTC.

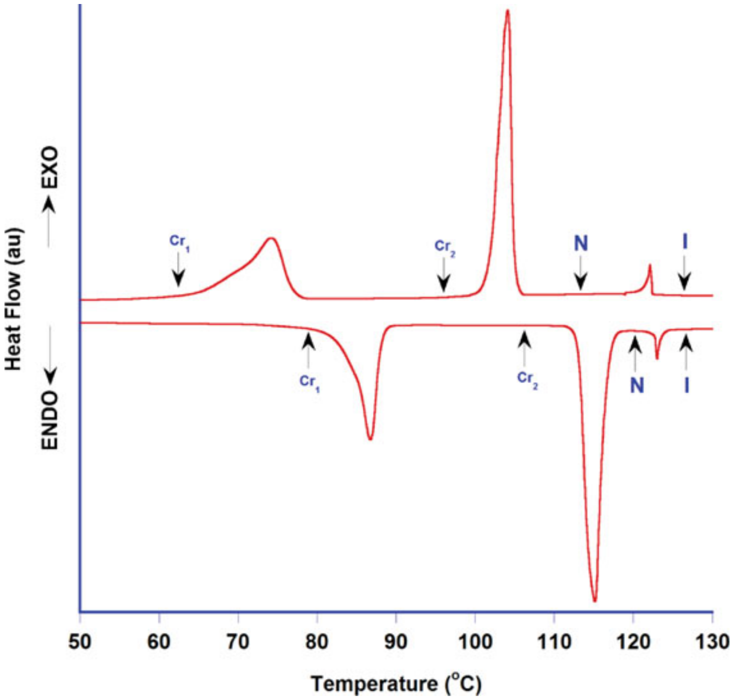


Figure 5. DSC Scan of 3-DDCPTC.

observations. Further, a good agreement is noticed in the transition temperatures measured by HOPM and DSC.

3.3. Molecular Shape and Mesophase Characteristics

The nematic–isotropic transitions of both the series showed decreasing trend with an increasing terminal chain length. The crystal–nematic transition also exhibited similar

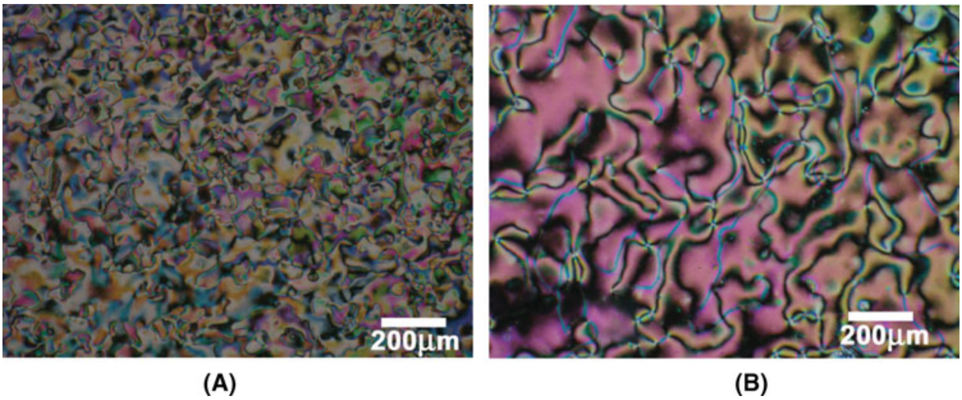


Figure 6. HOPM photographs of mesogens—cooling from isotropic phase (a) 2-OCPTC at 91.2°C nematic Schlieren texture (b) 3-DDCPTC at 120.4°C threaded nematic texture.

trend for 2-series, whereas for 3-series, the value is found to be same for 3-OCPTC and 3-DCPTC. Interestingly, the mesophase stability values for both the series are not high despite two phenyl rings in the core besides thiophene unit. In other words, in contrast to the phase stability values of three ring core [23–25], the thiophene mesogens exhibited lower phase stability. The data also suggest that the mesogens of 2-series showed better phase stability than those of 3-series. A comparison of thermal stability values, on the other hand, suggests that for lower homologues, i.e., C2 and C4, the values are comparable but with an increase in terminal chain length; an increase in thermal stability is clearly noticed for 3-series. These trends can be correlated to the molecular structures of the mesogens and their dipole moments. Figs. 1 and 2 show the energy optimized space filled models of C10 mesogens of 2- as well as 3-series. It can be seen that both 2-DCPTC and 3-DCPTC are rod-like typical of calamitic mesogens. For such mesogens, the crystal–nematic transition is generally found to be high if the core is linear with high polarizability anisotropy [26]. The dipole moments of the 2-DCPTC and 3-DCPTC calculated by DFT method are 2.74 D and 3.50 D, respectively. The relatively high crystal–nematic transition temperature noticed for 3-thiophene mesogens could be ascribed to high dipole moment, which influences the molecular anisotropic polarizability. Any deviation from rod-like shape of the core is known to reduce the mesophase characteristics [27, 28]. Earlier Nugent et al. also observed low mesophase stabilities for thiophene and furan-based mesogens constructed with two phenyl ring core [29]. The thiophene mesogens reported by them too showed enantiotropic nematic mesophase similar to our results. Further, a clear structural similarity between those examined by Nugent et al. and 2- as well as 3-series exists and in both the cases thiophene is positioned at one terminal. The low mesophase stabilities noticed for both the series in contrast to three phenyl ring-based core could be attributed to very high anisotropic polarizability values for three ring mesogens [23–25]. For instance, the mesophase stabilities of **5** (2-series) are ∼12°C–20°C, whereas for **6** (3-series), the values are in the range ∼9°C–18°C. For three phenyl ring core-based mesogens with terminal dimethylamino unit, on the other hand, the values are found to be ∼63°C–108°C [23]. For the case of mesogens with terminal hydroxyhexyloxy chain, the phase stabilities are in the range ∼85°C–113°C [25]. These observations suggest that the replacement of phenyl ring with thiophene in the core unit dramatically reduces the mesophase stability values. Additionally, the high symmetry associated with 1,4-disubstituted phenyl ring is lost by the introduction of irregular pentagon geometry typical for thiophene as reported in literature [30]. As a result, thiophene is rated as a low terminal efficiency group as it brings molecular asymmetry to the mesogen [31].

The investigations on thiophene mesogens indicate that the incorporation of thiophene at terminal position ensures enantiotropic nematic phase and favorably reduces the melting temperature as reported in literature [1–3]. Further, the present study points out that the 3-thiophene series can be used for synthesizing polymeric liquid crystals as 2,5-positions are available for chemical or electrochemical polymerization. Such polymers are anticipated to exhibit polarized emission as reported earlier for structurally similar systems owing to extended conjugation [32]. Furthermore, the solid state ^{13}C NMR experiments are underway, which may provide information about not only the molecular structure in nematic phase but also the orientation of thiophene with respect to orientation axis as demonstrated earlier for similar kind of mesogens [33].

4. Conclusion

The synthesized thiophene-based mesogens with ester connecting units and phenyl ring core showed enantiotropic nematic phase. The phase stabilities for both the series were found to be low, which was attributed to insertion of less symmetrical thiophene at the terminal position. The quantum chemical calculations not only provided the molecular shape for the representative mesogens but also aided the assignment of core unit carbons through ^{13}C chemical shifts. The relatively high crystal–nematic transition temperature noticed for 3-DCPTC was attributed to high dipole moment in contrast to 2-DCPTC. The studies corroborate that the incorporation of thiophene at terminal position not only results in nematic phase but also marginally reduces the melting temperature as observed in earlier investigations [1–3].

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