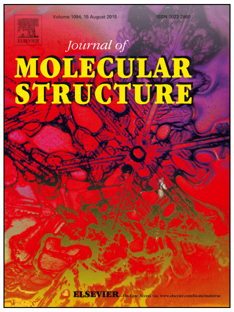

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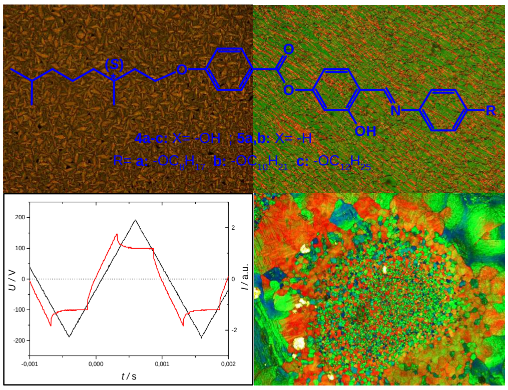
Graphical Abstract



Chiral Polymorphism in New Imine Based Rod-Like Liquid Crystals

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Abstract

New imine based rod-like compounds, composed of three-benzene-ring molecular core linked with azomethine as well as ester groups and terminated with (*S*)-3,7-dimethyloctyloxy chiral unit at one side have been synthesized. The other terminal position has been varied by using *n*-octyloxy/decyloxy/dodecyloxy groups to reveal chain length effect on mesophase behavior. The liquid crystalline properties of the new compounds have been investigated by polarizing optical microscopy, differential scanning calorimetry and electro-optic studies. The novel chiral calamitics derived from Schiff base or salicylaldimine-core show a chiral polymorphism comprising of blue phase and chiral nematic as well as smectics such as chiral tilted smectic and unidentified smectic mesophase.

Keywords: Imine, rod-like liquid crystals, chiral mesophases, polymorphism.

1. Introduction

Liquid crystal state, which is a unique form of matter, have attracted much attention both in the basic sciences and applications, and gives rise to a wide range of advanced technologies such as digital displays, sensors, liquid crystal displays (LCDs), high-performance polymers, transporting of electron, ion or molecule and drug-delivery systems, hybrid composites.[1,2,3,4,5] The wide applicability and commercial success of LCs are based on switching based technologies.[6,7,8,9,10,11,12]

The synthesis of optically active liquid crystals (LCs) especially represents one of the most attractive research area due to their remarkable mesomorphic and electro-optic properties as compared to achiral analogs.[13,14,15] The introduction of asymmetric carbon atom/s into calamitic molecule structure generally leads to the occurrence of a macroscopic twist in the organization of the constituent mesogens which results in the formation of frustrated mesophases such as chiral nematic (N*) phase, blue phases (BPs) as well as complex ordered LC phases such as chiral smectics with unique properties.[16] In recent years, BPs, whose structure is of highly twisted, have attracted a scientific curiosity and developed to emerge unique materials for new applications.[17,18,19,20,21] In general, BPs temperature range is very narrow such as between 0.5-1 °C and it emerges between cholesteric (N*) and isotropic phase.[22,23] Most attractive features of BPs are sub-millisecond response times and optical isotropic behavior[24,25] which make them perfect candidates for a number of applications.[26] The main interest of researches on mesogens with BPs broaden their mesomorphic range in order to make them potential materials for commercial applications such as displays and photonic technology.[27]

The investigation of the structure-property relationships in order to synthesize one-component chiral LCs carrying the desired characteristics for technological applications play a key role for the optimization of important parameters like anisotropy, linearity, polarizability and molecular shape.[28,29] Some modifications on linking units, terminal chains and central aromatic cores of rod-like molecules can induce striking effects on their mesomorphism.[30] An azomethine linking group is generally incorporated to the rod-like structure to increase the length, molecular core polarizability and mesophase stability.[31] These molecules carrying it defined as Schiff bases or imine compounds widely exhibit conventional calamitic LC mesophases[32] such as nematic and/or smectic mesophases. Optically active moieties are widely used in rod-like liquid crystals for the occurrence chiral calamitic mesophases.[31,33,34,35,36,37,38,39] Especially, the studies on three-ring calamitics carrying an

Schiff base linker as well as an ester linking group in the same structure show that the occurrence of chiral mesomophism such as the blue phase-I/II (BPI or BPII) and chiral nematic (N*) and chiral smectic C (SmC*) phases.[40,41,42,43] Additionally, chiral liquid crystals carrying a salicylaldimine core are more stable due to the presence of intramolecular hydrogen bonding between the hydroxy group and the imine group.[31,41,43]

Due to the fact that the introduction of chiral moieties gives rise to the occurence of a rich variety of the polar liquid crystalline mesophases, (*S*)-3,7-dimethyloctyloxy chiral chain has been incorporated into terminal positions in a number of previous studies.[40,44,45,46,47] In this study, the synthesis, structural and mesomorphic characterization of novel chiral calamitics derived from Schiff base or salicylaldimine-core are reported. Aromatic cores in target molecular three-rings architectures are connected with each other by azomethine (-CH=N-) as well as ester (-COO-) linkers which induce lateral polarity. By the aim of understanding the effect of the presence of molecular chirality as well as the variation of chain length on the effect of mesophase behavior, (*S*)-3,7-dimethyloctyloxy chiral moiety at one of the terminals and *n*-octyloxy/decyloxy/dodecyloxy chains at the other were incorporated to the rod-like structure (see Scheme 1). The liquid crystalline properties of the new mesogens were investigated by differential scanning calorimetry, optical polarizing microscopy and electro-optic methods.

2. Experimental

2.1. Materials

2,4-dihydroxybenzaldehyde (Aldrich), 4-hydroxybenzaldehyde (Aldrich), glacial acetic acid (Merck), Ethanol (Merck, 96%), N,N′-dicyclohexylcarbodiimide (Merck) and 4-(dimethylamino)pyridine (Merck) were purchased commercially. For efficient esterification, anhydrous solvent methylene chloride (CH_2Cl_2) was obtained by drying over di-phosphorus pentoxide (Merck) and distilled under a N_2 atmosphere. Solvents used in the purification step such as crystallization and column chromatography (hexane, ethyl acetate, chloroform, acetone, methanol and ethanol) were distilled. Analytical thin-layer chromatography (TLC) was carried out on aluminium plates coated with silica gel 60 F254 (Merck) for aldehyde intermediates and aluminium plates coated with aluminium oxide 60 F254, neutral (Merck) for target imine products. Column chromatography was performed using silica gel 60 (Merck, pore size 60 Å, 230-400 mesh particle size).

2.2. Instrumentation

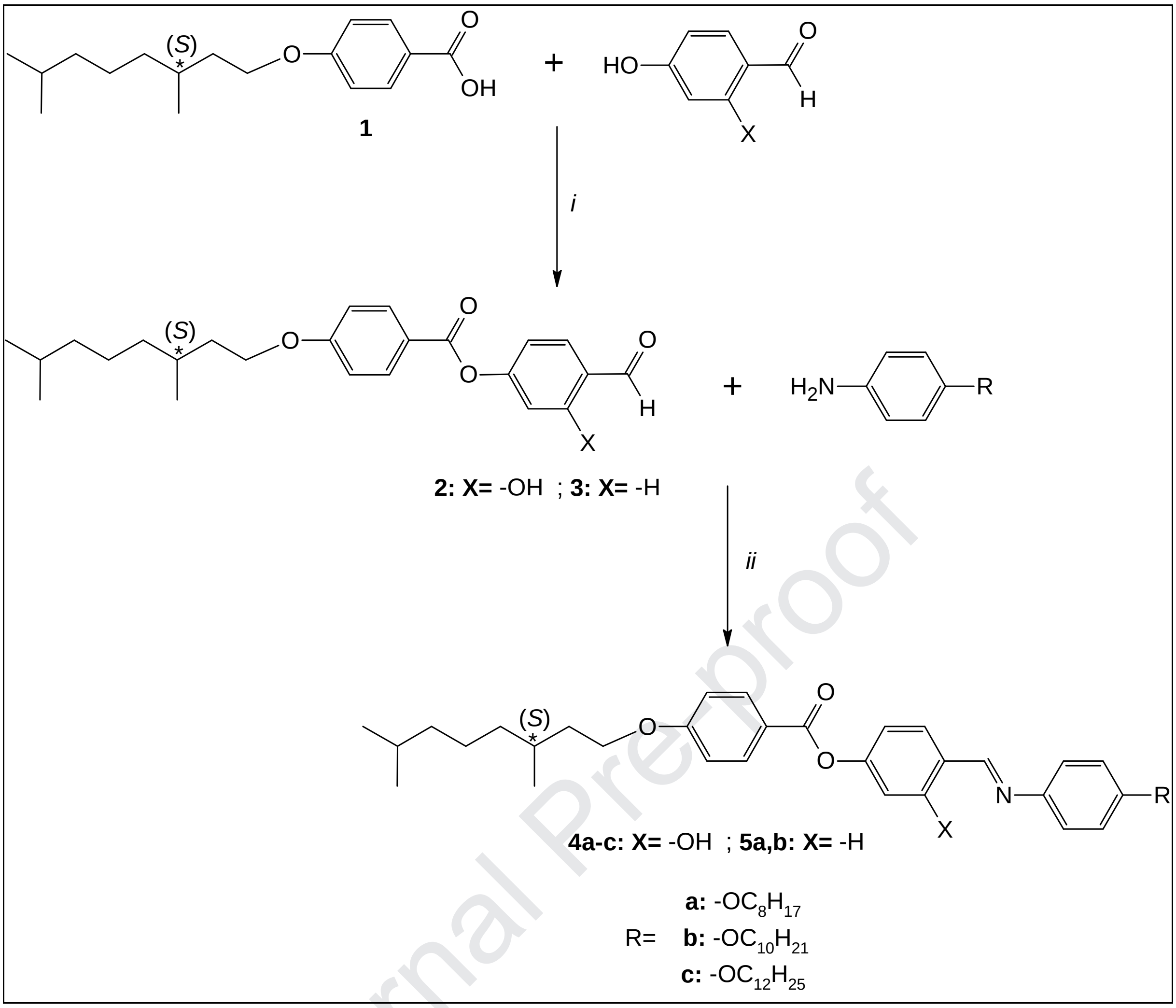
New chiral imine compounds (**4a-c** and **5a**,**b**) were characterized ^{1}H-NMR and ^{13}C-NMR (Bruker Avance III 500 spectrometer, in $CDCl_3$ solution, with tetramethylsilane as internal standard).

The mesomorphic properties of compounds were investigated by using a Mettler FP-82 HT hot stage and control unit in conjunction with a Leica DM2700P polarizing microscope. DSC-thermograms of chiral imine compounds were recorded on a Perkin-Elmer DSC-6, heating and cooling rate: 10 °C min^{-1} in a nitrogen atmosphere. Electro-optical investigation of compound **4a** were performed in a 10 μm polyimide (PI) non-coated ITO cell (EHC, Japan) with a measuring area of 1 cm^2. Switching experiments were carried out with the triangular-wave method[48] using a combination of a function synthesizer (Agilent, model 33220A, load was set to 10 kΩ), an amplifier (Tabor electronics, model 9400), and the current response traces were recorded using an oscilloscope (Agilent, model DSO3202A) across a 5 kΩ resistance.

2.3. Synthesis and characterization

The synthesis of intermediate compounds 2,3 and new imine based rod-like compounds 4a-c and 5a,b

The synthesis of new imine based rod-like compounds **4a-c** and **5a**,**b** which are structurally distinguished by the functionalization of 2-position of the central aromatic ring by one hydroxyl group is presented in Scheme 1. The imine based compounds **4a-c** and **5a**,**b** carrying ester linking unit were prepared with a procedure which is similar to that used for compounds reported earlier.[40] The starting compound (*S*)-4-(3,7-dimethyloctyloxy)benzoic acid[44,49] was synthesized by the alkylation of ethyl 4-hydroxybenzoate with (*S*)-3,7-dimethyloctyl-1-bromide in 2-butanone using K_2CO_3 and then basic hydrolysis of the obtained product with NaOH/H_2O in ethanol. Spectroscopic data and preparation procedures of (*S*)-4-(3,7-Dimethyloctyloxy)benzoic acid was reported in previous studies.[40,49]



Scheme 1. Synthesis of the imine based rod-like compounds **4a-c** and **5a**,**b**. *Reagents and conditions*: (*i*) DCC, DMAP, dry CH_2Cl_2, r.t., overnight; (*ii*) Glacial acetic acid, dry ethanol, reflux at 100 °C, 6h.

The esterification of (*S*)-4-(3,7-dimethyloctyloxy)benzoic acid by treatment with 2,4-hydroxybenzaldehyde or 4-hydroxybenzaldehyde using N,N′-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) as catalyst yield the compounds **2**,**3**. The condensation reaction of compound **2** or **3** and the corresponding aniline compounds *p*-octyloxyaniline / *p*-decyloxyaniline / *p*-dodecyloxyaniline with glacial acetic acid as catalyst in ethanol gives the target imine compounds **4a-c** and **5a**,**b**. The aniline compounds were synthesized as described previously[31] by the reaction of the corresponding alkyl bromide with *p*-nitrophenol in DMF and then the obtained *p*-alkyloxynitrobenzene[50,51,52] were reduced by catalytic hydrogenation (H_2, 10% Pd/C in ethyl acetate) to the corresponding anilines.[53,54,55]

The procedures for the synthesis of intermediate compounds 2,3 and imine based chiral compounds 4a-c and 5a,b

Compounds 2,3:

To a solution of 2.0 mmol of (*S*)-4-(3,7-dimethyloctyloxy)benzoic acid and 2.0 mmol of 2,4-dihydroxybenzaldehyde or 4-hydroxybenzaldehyde in 75 ml of dry dichloromethane, 2.0 mmol of *N,N'*-dicyclohexylcarbodiimide (DCC) and cataytic amount of 4-(dimethylamino)pyridine (DMAP) were added and the reaction mixture was stirred for 24h at room temperature under argon atmosphere. The end of reaction was monitored by TLC (hexane:ethyl acetate/5:1). The reaction mixture was filtered on silica gel with CH_2Cl_2 and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel, eluting with hexane:ethylacetate/10:1.

Spectroscopic data and preparation procedures of (*S*)-4-(3,7-dimethyloctyloxy)benzoyloxy]benzaldehyde (**3**) was reported in our previous study.[40]

4-Formyl-3-hydroxyphenyl (*S*)-4-(3,7-dimethyloctyloxy)benzoate (2):

Yield: 70 %; colorless crystals. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) = 11.31 (s, 1H, OH), 9.95 (s, 1H, C*H*O), 8.18 (d, $J \approx 8.9$ Hz, 2H, Ar-C*H*), 7.67 (d, $J \approx 8.4$ Hz, 1H, Ar-C*H*), 7.04 (d, $J \approx 8.9$ Hz, 2H Ar-C*H*), 6.98 (dd, $J_1 \approx 8.4$ Hz, $J_2 \approx 2.1$ Hz, 1H, Ar-C*H*), 6.94 (d, $J \approx 2.1$ Hz, 1H, Ar-C*H*), 4.23-4.05 (m; 2H, OCH_2), 2.00-1.86, (m, 1H, C*H*), 1.83-1.50 (m, 3H, C*H*, CH_2), 1.50–1.13 (m, 6H, CH_2), 1.03 (d, $J \approx 6.5$ Hz, 3H, CH_3), 0.94 (d, $J \approx 6.6$ Hz, 6H, CH_3). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ (ppm) = 195.52 (*C*HO), 163.95 (*C*OO), 163.94, 163.25, 157.98, 120.78, 118.64 (Ar-*C*), 134.97, 132.52, 114.51, 114.22, 110.94 (Ar-*C*H), 66.81(O*C*H_2), 39.27, 37.30, 36.02, 24.70 (*C*H_2), 29.87, 28.02 (*C*H), 22.74, 22.65, 19.68 (*C*H_3).

Compounds 4a-c and 5a,b:

In a 100 mL round-bottomed flask, 2.0 mmol of compound **2** or **3** and 2.4 mmol of the corresponding aniline compound were dissolved in 50 mL absolute ethanol. To this solution, a few traces of glacial acetic acid was added as catalyst and the reaction mixture were heated to reflux for 6 h at 100 °C under argon atmosphere. The end of reaction was monitored by TLC (hexane:ethyl acetate/2:1). After cooling, the reaction mixture was kept under cool conditions to allow the precipitation of colorless solid compound for 24 h. The crude product obtained was collected by filtration and repeatedly washed with hot absolute ethanol. It was purified by recrystallization with a mixture of methanol/acetone.

3-Hydroxy-4-{[(4-(Octyloxy)phenylimino]methyl}phenyl (*S*)-4-(3,7-dimethyloctyloxy)benzoate (4a):

Yield: 69 %; colorless crystals. ^{1}**H-NMR** (500 MHz, CDCl$_3$): δ (ppm) = 13.82 (s, broad 1H, Ar-O*H*), 8.63 (s, 1H, *H*C=N), 8.15 (d, *J* ≈ 8.9 Hz, 2H, Ar-C*H*), 7.43 (d, *J* ≈ 8.5 Hz, 1H, Ar-C*H*), 7.29 (d, *J* ≈ 8.9 Hz, 2H, Ar-C*H*), 6.99 (d, *J* ≈ 8.9 Hz, 2H, Ar-C*H*), 6.96 (d, *J* ≈ 8.9 Hz, 2H, Ar-C*H*), 6.91 (d, *J* ≈ 2.2 Hz, 1H, Ar-C*H*), 6.84 (dd, J_1 ≈ 8.4 Hz, J_2≈ 2.2 Hz, 1H, Ar-C*H*), 4.14-4.06 (m, 2H, OCH_2), 4.00 (t, *J* ≈ 6.6 Hz, OCH_2), 1.92-1.79, 1.74-1.45, 1.41-1.16 (3m, 22H, C*H*, CH_2), 0.98 (d, *J* ≈ 6.5 Hz, 3H, CH_3), 0.91-0.89 (m, 9H, CH_3). ^{13}**C-NMR** (125 MHz, CDCl$_3$): δ (ppm) = 164.42 (*C*O), 163.65, 162.45, 158.50, 154.49, 140.87, 121.28, 117.31 (Ar-*C*), 159.40 (H*C*=N), 132.73, 132.37, 122.24, 115.22, 114.36, 112.94, 110.57 (Ar-*C*H), 68.37, 66.70 (O*C*H$_2$), 39.22, 37.26, 36.00, 31.90, 29.83, 29.56, 29.40, 29.32, 29.26, 27.97, 26.03, 24.65 (*C*H, *C*H$_2$), 22.68, 22.60, 19.64, 14.11 (*C*H$_3$). FT-IR: γ (cm^{-1}) = 1719 (C=O), 1622 (C=N).

3-Hydroxy-4-{[(4-(Decyloxy)phenylimino]methyl}phenyl (*S*)-4-(3,7-dimethyloctyloxy)benzoate (4b):

Yield: 65 %; colorless crystals. ^{1}**H-NMR** (500 MHz, CDCl$_3$): δ (ppm) = 13.84 (s, broad 1H, Ar-O*H*), 8.63 (s, 1H, *H*C=N), 8.15 (d, *J* ≈ 8.9 Hz, 2H, Ar-C*H*), 7.42 (d, *J* ≈ 8.5 Hz, 1H, Ar-C*H*), 7.29 (d, *J* ≈ 8.8 Hz, 2H, Ar-C*H*), 6.99 (d, *J* ≈ 8.9 Hz, 2H, Ar-C*H*), 6.96 (d, *J* ≈ 8.9 Hz, 2H, Ar-C*H*), 6.89 (d, *J* ≈ 2.2 Hz, 1H, Ar-C*H*), 6.83 (dd, J_1 ≈ 8.4 Hz, J_2≈ 2.2 Hz, 1H, Ar-C*H*), 4.14-4.06 (m, 2H, OCH_2), 4.00 (t, *J* ≈ 6.6 Hz, 2H, OCH_2), 1.92-1.79, 1.73-1.45, 1.41-1.16 (3m, 26H, C*H*, CH_2), 0.98 (d, *J* ≈ 6.5 Hz, 3H, CH_3), 0.92-0.89 (m, 9H, CH_3). ^{13}**C-NMR** (125 MHz, CDCl$_3$): δ (ppm) = 164.39 (*C*O), 163.66, 162.45, 158.51, 154.49, 140.92, 121.30, 117.32 (Ar-*C*), 159.41, (H*C*=N), 132.73, 132.36, 122.23, 115.23, 114.37, 112.93, 110.52 (Ar-*C*H), 68.38, 66.71 (O*C*H$_2$), 39.22, 37.26, 36.00, 31.81, 29.84, 29.35, 29.26, 29.23, 27.97, 26.04, 24.65 (*C*H, *C*H$_2$), 22.65, 22.59, 19.64, 14.08 (*C*H$_3$). FT-IR: γ (cm^{-1}) = 1720 (C=O), 1618 (C=N).

3-Hydroxy-4-{[(4-(Dodecyloxy)phenylimino]methyl}phenyl (*S*)-4-(3,7-dimethyloctyloxy)benzoate (4c):

Yield: 68 %; colorless crystals. ^{1}**H-NMR** (500 MHz, CDCl$_3$): δ (ppm) = 13.76 (s, broad 1H, Ar-O*H*), 8.62 (s, 1H, *H*C=N), 8.14 (d, *J* ≈ 8.9 Hz, 2H, Ar-C*H*), 7.41 (d, *J* ≈ 8.5 Hz, 1H, Ar-C*H*), 7.27 (d, *J* ≈ 8.8 Hz, 2H, Ar-C*H*), 6.98 (d, *J* ≈ 8.9 Hz, 2H, Ar-C*H*), 6.95 (d, *J* ≈ 8.9 Hz, 2H, Ar-C*H*), 6.90 (d, $J \approx 2.2$ Hz, 1H, Ar-C*H*), 6.83 (dd, $J_1 \approx 8.4$ Hz, $J_2 \approx 2.2$ Hz, 1H, Ar-C*H*), 4.13-4.06 (m, 2H, OCH_2), 3.99 (t, $J \approx 6.6$ Hz, 2H, OCH_2), 1.91-1.78, 1.74-1.44, 1.38-1.15 (3m, 30H, C*H*, CH_2), 0.98 (d, $J \approx 6.5$ Hz, 3H, CH_3), 0.91-0.88 (m, 9H, CH_3). **^{13}C-NMR** (125 MHz, CDCl$_3$): δ (ppm) = 164.36 (*C*O), 163.66, 162.48, 158.53, 154.60, 140.80, 121.30, 117.24 (Ar-*C*), 159.39, (H*C*=N), 132.74, 132.34, 122.20, 115.25, 114.37, 112.96, 110.53 (Ar-*C*H), 68.39, 66.71 (O*C*H$_2$), 39.21, 37.24, 36.00, 31.89, 29.84, 29.63, 29.60, 29.56, 29.55, 29.36, 29.31, 29.24, 27.95, 26.01, 24.62, (*C*H, *C*H$_2$), 22.65, 22.56, 19.61, 14.06 (*C*H$_3$). FT-IR: γ (cm^{-1}) = 1724 (C=O), 1624 (C=N).

4-{[(4-(Octyloxy)phenylimino]methyl}phenyl (*S*)-4-(3,7-dimethyloctyloxy)benzoate (5a):

Yield: 59 %; colorless crystals. **^{1}H-NMR** (500 MHz, CDCl$_3$): δ (ppm) = 8.56 (s, 1H, *H*C=N), 8.22 (d, $J \approx 8.9$ Hz, 2H, Ar-C*H*), 8.02 (d, $J \approx 8.6$ Hz, 2H, Ar-C*H*), 7.39 (d, $J \approx 8.6$ Hz, 2H, Ar-C*H*), 7.30 (d, $J \approx 8.9$ Hz, 2H, Ar-C*H*), 7.05 (d, $J \approx 8.9$ Hz, 2H, Ar-C*H*), 7.00 (d, $J \approx 8.9$ Hz, 2H, Ar-C*H*), 4.20-4.12 (m, 2H, OCH_2), 4.05 (t, $J \approx 6.6$ Hz, 2H, OCH_2), 1.97-1.83, 1.78-1.51, 1.46-1.20 (3m, 22H, C*H*, CH_2), 1.04 (d, $J \approx 6.5$ Hz; 3H, CH_3), 0.98-0.94 (m, 9H, 3 CH_3). **^{13}C-NMR** (125 MHz, CDCl$_3$): δ (ppm) = 164.67 (*C*O), 163.72, 157.09, 153.28, 144.60, 134.09, 121.34 (Ar-*C*), 158.01 (H*C*=N), 132.40, 129.79, 122.22, 122.25, 115.07, 114.43 (Ar-*C*H), 68.38, 66.76 (O*C*H$_2$), 39.27, 37.31, 36.05, 31.87, 29.89, 29.42, 29.36, 29.29, 28.02, 26.11, 24.70, 22.74 (*C*H, *C*H$_2$), 22.70, 22.64, 19.69, 14.14 (*C*H$_3$). FT-IR: γ (cm^{-1}) = 1730 (C=O), 1625 (C=N).

4-{[(4-(Decyloxy)phenylimino]methyl}phenyl (*S*)-4-(3,7-dimethyloctyloxy)benzoate 5b:

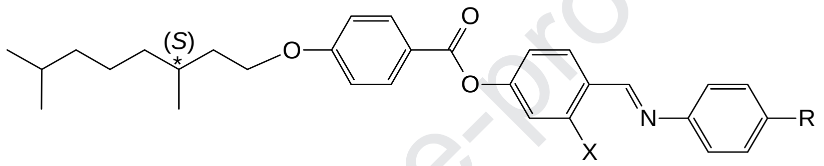
Yield: 71 %; colorless crystals. **^{1}H-NMR** (500MHz, CDCl$_3$): δ (ppm) = 8.56 (s, 1H, *H*C=N), 8.22 (d, $J \approx 8.9$ Hz, 2H, Ar-C*H*), 8.02 (d, $J \approx 8.6$ Hz, 2H, Ar-C*H*), 7.39 (d, $J \approx 8.6$ Hz, 2H, Ar-C*H*), 7.30 (d, $J \approx 8.8$ Hz, 2H, Ar-C*H*), 7.05 (d, $J \approx 8.9$ Hz, 2H, Ar-C*H*), 7.00 (d, $J \approx 8.9$ Hz, 2H, Ar-C*H*), 4.20-4.12 (m, 2H, OCH_2), 4.05 (t, $J \approx 6.6$ Hz, OCH_2), 1.97-1.84, 1.79-1.51, 1.46-1.22 (3m, 26H, C*H*, CH_2), 1.04 (d, $J \approx 6.5$ Hz, 3H, CH_3), 0.97-0.94 (m, 9H, 3 CH_3). **^{13}C-NMR** (125 MHz, CDCl$_3$): δ (ppm) = 164.66 (*C*O), 163.72, 157.08, 153.28, 144.59, 134.11, 121.34 (Ar-*C*), 158.02 (H*C*=N), 132.40, 129.79, 122.25, 122.23, 115.07, 114.43 (Ar-*C*H), 68.37, 66.76 (O*C*H$_2$), 39.28, 37.31, 36.06, 31.95, 29.89, 29.63, 29.61, 29.46, 29.37, 28.02, 26.11, 24.70, (*C*H, *C*H$_2$), 22.73, 22.65, 19.70, 14.16 (*C*H$_3$). FT-IR: γ (cm^{-1}) = 1726 (C=O), 1623 (C=N).

3. Results and discussion

3.1. Liquid Crystal Properties of Compounds 4a-c and 5a,b

The liquid crystal properties of the salicylaldimine and imine-based chiral calamitic molecules **4a-c** and **5a**,**b** were investigated by using optical polarizing microscope (PM) and differential scanning calorimeter (DSC). The mesophase type, transition temperatures (T, in degree Celsius) and the corresponding enthalpies (ΔH, in kJ mol^{-1}) of **4a-c** and **5a**,**b** are presented in Table 1.

Table 1. Mesophase, phase transition temperatures and the corresponding transition enthalpies of the compounds **4a-c** and **5a**,**b**.



Compound	X	R	**T/°C [ΔH kJ/mol]**[a]
4a	OH	-OC$_8$H$_{17}$	**H** →: Cr 84.2 [*26.43*] SmC* 157.1 [*2.97*] N* 174.3 [*1.27*] Iso
			Cr 28.5 [*14.43*] SmX 98.0[b] SmC* 152.1 [*2.66*] N* 169.0[b] BP 169.6 [*1.33*] Iso : ← **C**
4b	OH	-OC$_{10}$H$_{21}$	**H** →: Cr 74.2 [*27.98*] SmC* 153.4 [*2.52*] N* 182.2 [*1.45*] Iso
			Cr 24.7 [*11.87*] SmX 102.0[b] SmC* 144.2 [*2.18*] N* 174.0[b] BP 174.2 [*1.46*][c] Iso : ← **C**
4c	OH	-OC$_{12}$H$_{25}$	**H** →: Cr$_1$ 71.3 [*28.05*] Cr$_2$ 80.4 [*19.70*] SmC* 157.0 [*3.02*] N* 166.7 [*1.12*] Iso
			Cr 37.2 [*26.56*] SmX 96.0[b] SmC* 152.5 [*2.94*] N* 162.1[b] BP 162.7 [*1.10*][c] Iso : ←**C**
5a	H	-OC$_8$H$_{17}$	**H** →: Cr 73.4 [*21.49*] Cr$_2$ 81.2 [*1.33*] SmC* 143.1 [*3.11*] N* 170.4 [*1.19*] Iso
			Cr$_1$ 46.8 [*18.09*] Cr$_2$ 58.7 [0.60] SmX 65.7 [*0.32*] SmC* 139.8 [*3.04*] N* 167.1[b] BP 167.8 [*1.05*] Iso : ← **C**
5b	H	-OC$_{10}$H$_{21}$	**H** →: Cr 70.9 [*22.22*] SmC* 145.4 [*3.69*] N* 164.2 [*1.07*] Iso
			Cr$_1$ 36.3 [*13.04*] Cr$_2$ 57.6 [0.46] SmX 67.2 [*0.76*] SmC* 142.7 [*3.62*] N* 161.3[b] BP 162.2 [*1.47*] Iso : ← **C**
5c[40]	H	-OC$_{12}$H$_{25}$	**H** →: Cr 78.8 [*29.40*] SmC* 145.4 [*3.80*] N* 158.7 [*1.07*] Iso
			Cr 54.3 [*28.14*] SmX 67.3 [*0.63*] SmC* 142.3 [*3.72*] N* 156.0[b] BP 156.5 [*1.39*][c] Iso : ←**C**

[a] Mesophases and phase transition temperatures as observed on heating (H→) and cooling (←C) and corresponding transition enthalpies of the compounds **4a-c** and **5a-c**. [a]Perkin-Elmer DSC-6; enthalpy values in italics in brackets taken from the 2nd heating and cooling scans at a rate of 10 °C min^{-1}; Abbreviations: Cr = crystalline, SmX = unidentified smectic mesophase, SmC* = chiral smectic C phase, N* = chiral nematic phase,

BP = blue phase, Iso = isotropic liquid phase. [b]These transitions were determined by PM. [c]Enthalpy value involves two transitions N*–BP–Iso.

New imine based calamitic molecules **4a-c** and **5a**,**b** with a (*S*)-3,7-Dimethyloctyloxy chiral unit at one of terminal positions show a polymorphism composed of chiral mesophases such as blue phase (BP) and chiral nematic (N*) as well as smectics such as chiral tilted smectic (SmC*) and unidentified smectic mesophase (SmX). Salicylaldimine based compounds **4a-c** carrying (*S*)-3,7-Dimethyloctyloxy chiral group and an *n*-alkyloxy chain with n= 8, 10, 12 at terminals exhibit enantiotropic chiral nematic (cholesteric) N* mesophase which is identified by the characteristic oily-streak texture and chiral tilted smectic (SmC*) with a finger-print texture. Additionally, monotropic mesophases such as blue phase (BP) and unidentified smectic mesophase (SmX) were appeared on cooling. On heating differential thermogram of compound **4a**, three endotherms which corresponds to a phase transition sequence of crystal (Cr)-chiral smectic C* (SmC*)-chiral nematic (N*)-isotropic phase (iso) were detected (see Fig.1a). On cooling from isotropic phase, firstly platelet texture of BP with various colors was appeared in a very narrow temperature range about 0.5 °C and then a rapid transition from BP phase to chiral nematic (N*) mesophase with a characteristic oily streak texture was occured (see Fig. 1b and 1c). The first exotherm on cooling differential thermogram of compound **4a** corresponds to the isotropic phase (Iso) to BP and N* mesophases and enthalpy value involves these two transitions. When temperature arrived at T= 152.1 °C, the oily streak texture of N* phase completely disappeared and a finger-print texture which clearly evidences the presence of a SmC* mesophase starts to appear. The fingerprint texture become more clear by applying direct current voltage (see Fig. 1e which shows the field-induced texture of SmC* mesophase). Below about T= 98.0 °C, an additional monotropic mesophase referred to here as the SmX phase, was observed (see Fig. 2). This transition was not detectable with an exothermic peak on DSC cooling thermogram but a distinct change from dark to in a sequence of red→green→bluish color on texture as well as a textural transformation of finger-print regions point out that a subphase of tilted chiral smectic phase depending on the complexity of the chiral SmC* type structure.[40,56] DSC thermogram and typical textures of a series of chiral mesophases observed for compounds **4a** are shown in Fig. 1 and 2.

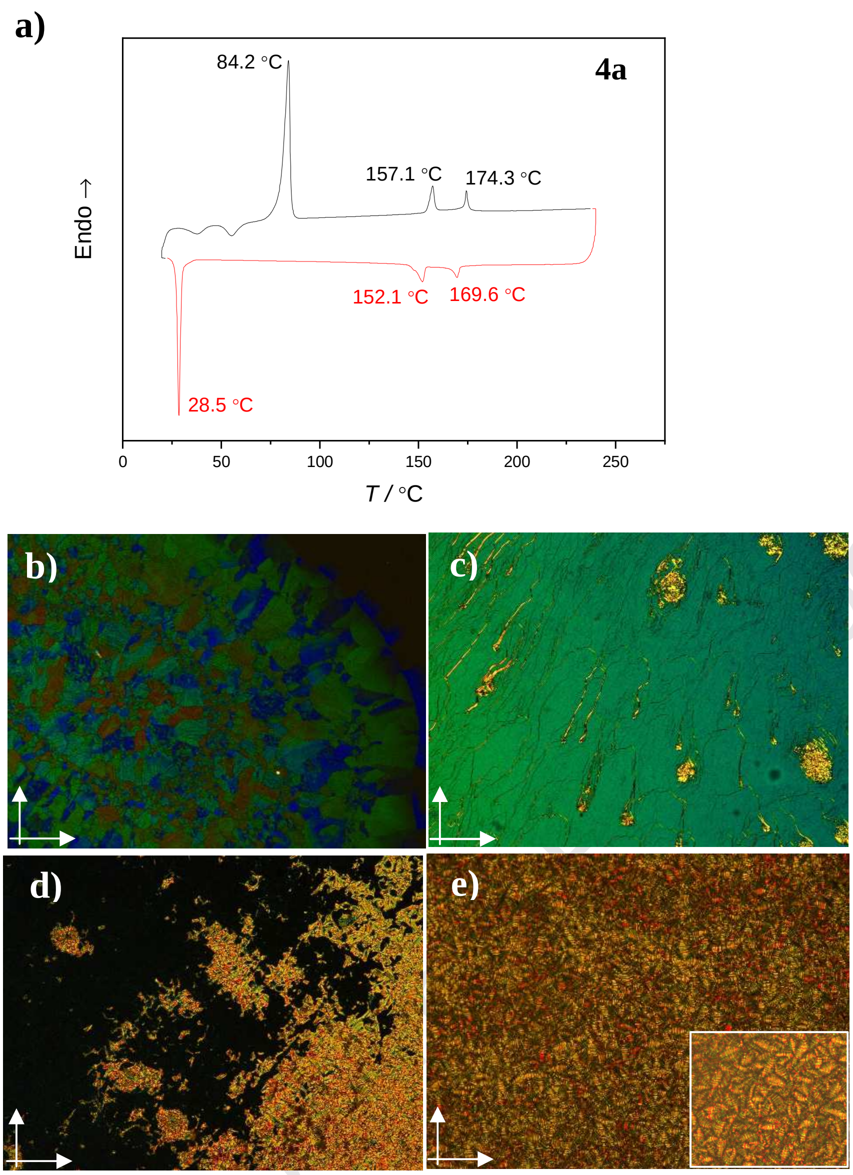


Fig. 1. a) DSC thermogram of compounds **4a** on 2nd heating and cooling (10 °C min^{-1}) and optical textures of mesophases of compound **4a** as observed between crossed polarizers (indicated by arrows) in a ordinary glassplates (magnification ×100); b) platelet texture of BP at T= 169.5 °C ; c) oily-streak texture of N* phase at T= 167.5 °C; d) fingerprint texture of SmC* phase at T= 132.0 °C, e) the fingerprint texture of a SmC* phase obtained under a DC voltage of +3 V at T= 118.4 °C and the inset shows the fingerprint texture at T= 106.0 °C in a 10 µm PI non-coated ITO cell providing planar alignment on cooling.

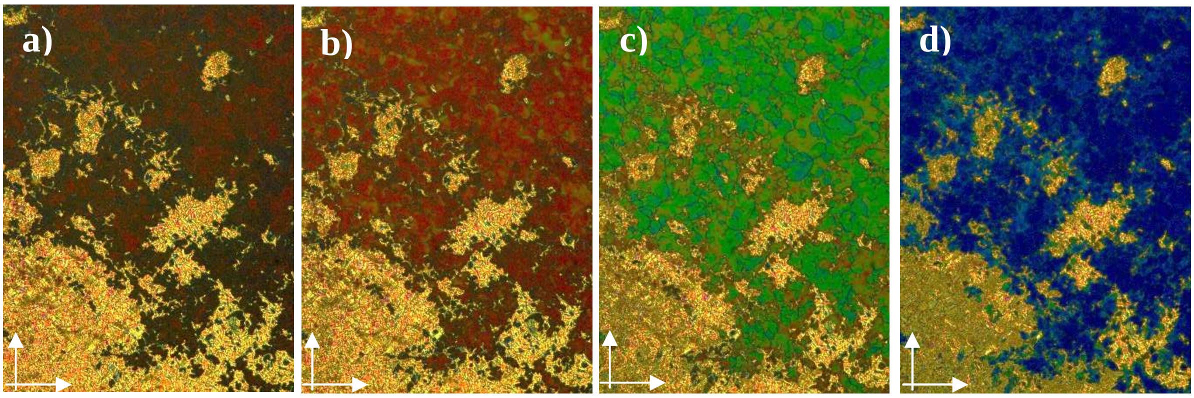


Fig. 2. Optical textures of smectic mesophases of compound **4a** showing a textural transformation until crystallization as observed between crossed polarizers (indicated by arrows) in a ordinary glassplates (magnification ×100); (a) SmC* mesophase at T= 98.0 °C; (b,c,d) SmX mesophase at T= 85.0 °C, 67.0 °C and 46.0 °C, respectively.

Salicylaldimine based compounds **4b** and **4c** with *n*-decyloxy and *n*-dodecyloxy chain, respectively, behave similarly to compound **4a**. Compound **4b** exhibits a phase transition sequence of Cr–SmC*–N*–Iso which are in aggrement with three endotherms in DSC heating curves whereas compound **4c** has an additional endotherm at 71.3 °C which corresponds to $Cr_1 \rightarrow Cr_2$ transition (see Fig. 3). On cooling of both compounds from isotropic phase, the chiral mesophases appeared in a phase transition sequence of blue phase (BP)-chiral nematic (N*)-chiral smectic C* (SmC*)-unidentified smectic mesophase (SmX)-crystal (Cr) as observed during cooling of compound **4a**. For both compounds, the transition temperature of BP→N* phase was determined by PM due to undetectable enthalpy changes by DSC. Additionally, no transition enthalpy could be detected in the DSC cooling scans for SmC*-SmX transition of compounds **4b** and **4c**. The clearing point of compound **4c** is lower about 15 °C than **4b** due on the increase in the length of alkoxy chain at terminal. However, one point we noted here for that **4c** shows a wider SmC* mesophase interval than the salicylaldimine derivative compounds **4a** and **4b** which followed each other with the increase of 2 CH_2 groups in chain. Typical textures of various chiral mesophases observed for compounds **4b** and **4c** are shown in Fig. 4.

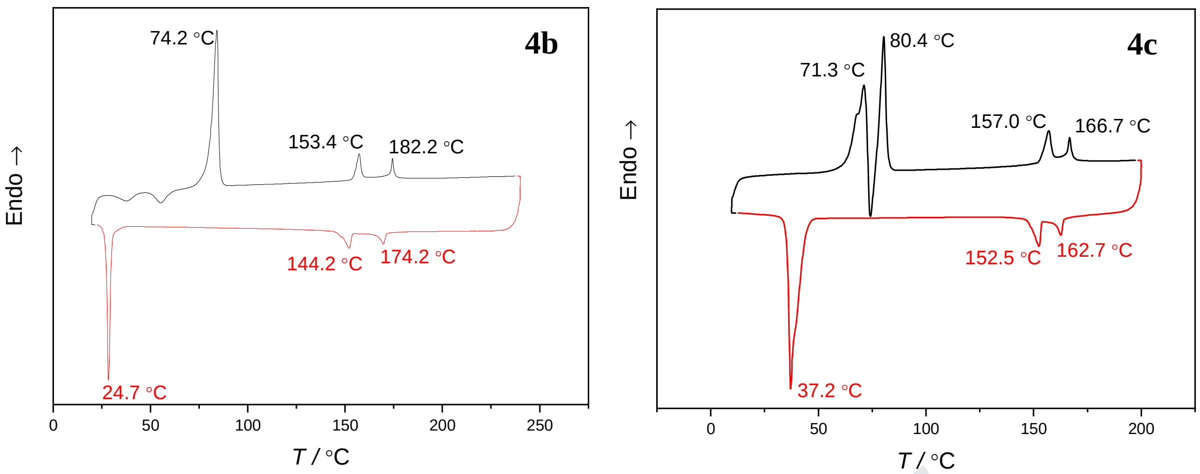


Fig. 3. DSC thermograms of compounds **4b** and **4c** on 2nd heating and cooling (10 °C min^{-1}).

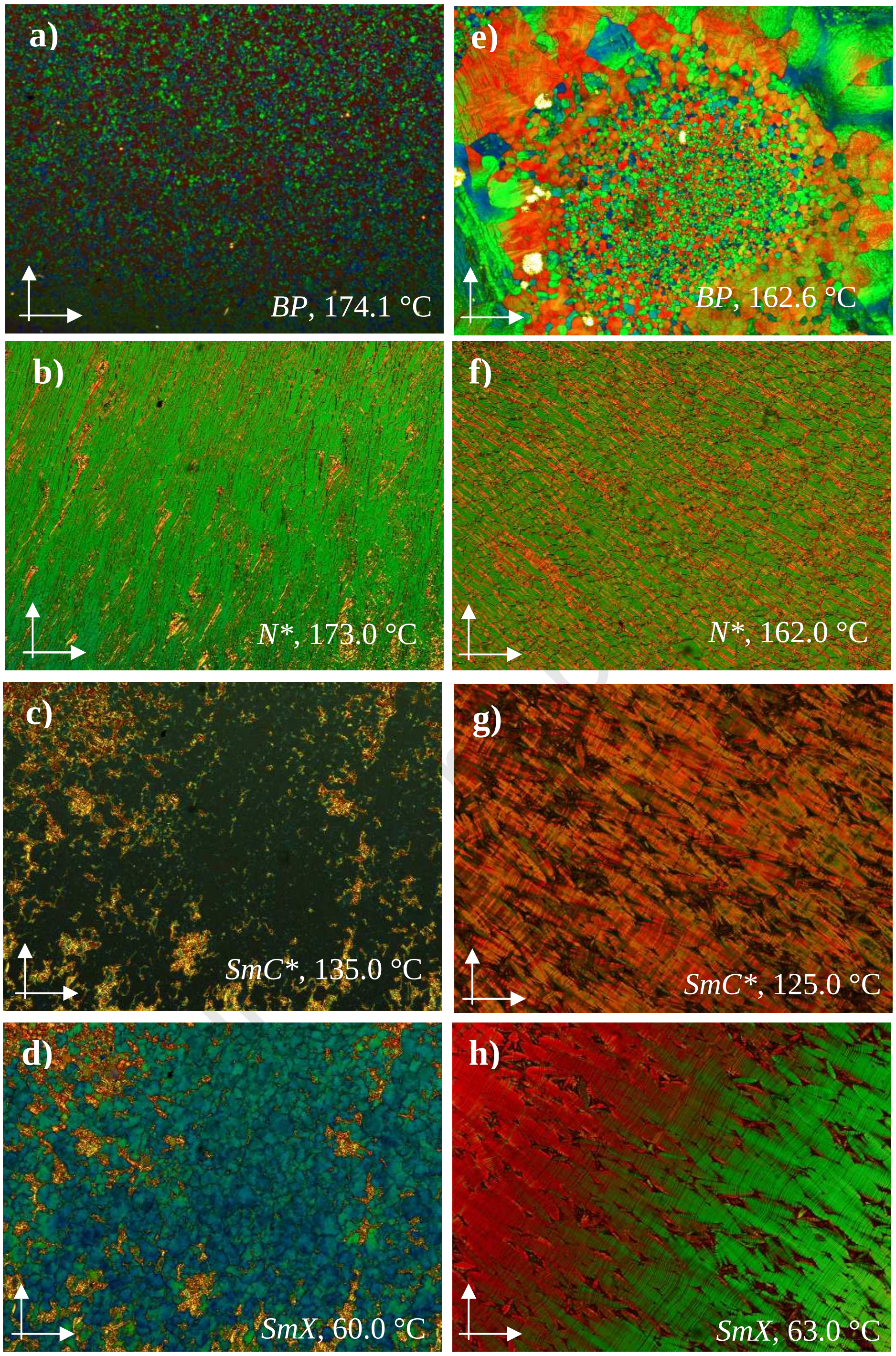


Fig. 4. Optical textures of the chiral mesophases of a-d) compound **4b** and e-h) compound **4c** at the indicated temperatures between crossed polarizers (indicated by arrows) in a ordinary glassplates as observed on cooling from the isotropic liquid (magnification ×100).

The imine compounds **5a** and **5b** which are differentiate from compounds **4a-c** by the absence of OH group in the aromatic ring of salicylaldehyde exhibit similar mesomorphic properties as observed in salicylaldimine analogs **4a-c** in meaning of the occurrence of chiral mesophases. As seen in Fig. 5, compound **5a** exhibits a phase transition sequence of Cr_1→Cr_2→SmC*→N*→Iso which is in agreement with four endotherms on heating curve. On cooling from isotropic phase, blue phase (BP) with a platelet texture firstly appeared at 167.8 °C and then focal conic texture of chiral nematic phase (N*) emerged at 167.1 °C. The oily streaks texture of N* phase was formed after shearing the focal conic pattern of sample (see Fig. 6b). The enthalpy value which corresponds to the first exotherm involves both two transitions. On further cooling, the SmC* mesophase at 139.8 °C appeared by the occurrence of fan-shaped regions with stripe lines which represent the helical order of smectic layers. When the temperature was further decreased, SmC* phase undergoes transformation to a non-specific texture of unknown smectic mesophase (SmX) which was also detected by a calorimetric peak at 65.7 °C in cooling DSC thermogram (see Fig. 5). Below 58.7 °C, crystallization started and an additional transition corresponds to Cr_2→Cr_1 was detected at 46.8 °C in cooling DSC thermogram.

Compound **5b** with a *n*-dodecyloxy terminal chain shows polymorphism which is in agreement with the behaviour observed for analogous imine compound **5a** carrying a *n*-octyloxy terminal chain (see Fig. 5). As compared with **5a**, temperatures which involves Iso→BP and BP→N* transitions decreased about 5-6 °C whereas the occurrence temperatures of SmC* as well as SmX mesophases increased about 2-3 °C. This behavior is not in agreement observed for analogous salicylaldimine compounds **4a** and **4b**. By increasing on terminal chain length, the transition temperatures in a phase sequence of Iso→BP →N* increased about 5 °C whereas transition temperature of SmC* phase decreased about 8 °C. One point we noted here that the change in terminal alkoxy chain length gives rise to more pronounced increase or decrease on transition temperatures of mesophases of salicylaldimines. For example, the comparison of clearing temperatures of salicylaldimine compound **4b** with **4c** and the imine analog **5b** with **5c** depending on the increase of 2 CH_2 groups in terminal shows that the decrease about 6 °C appeared for imine compounds whereas this difference is about 15 °C for salicylaldimine compounds. We would like to mention here that the compound **5c** were previously reported by our group.[40] It is clear from the mesomorphic investigations reported here, mesophase type, the mesophase sequence and changes on transition temperatures depending on chain length are in aggrement with that of the compound **5c** carrying with *n*-dodecyloxy chain. Typical textures of various mesophases observed for compound **5a** are shown in Fig. 6, as representative case for also imine compound **5b**.

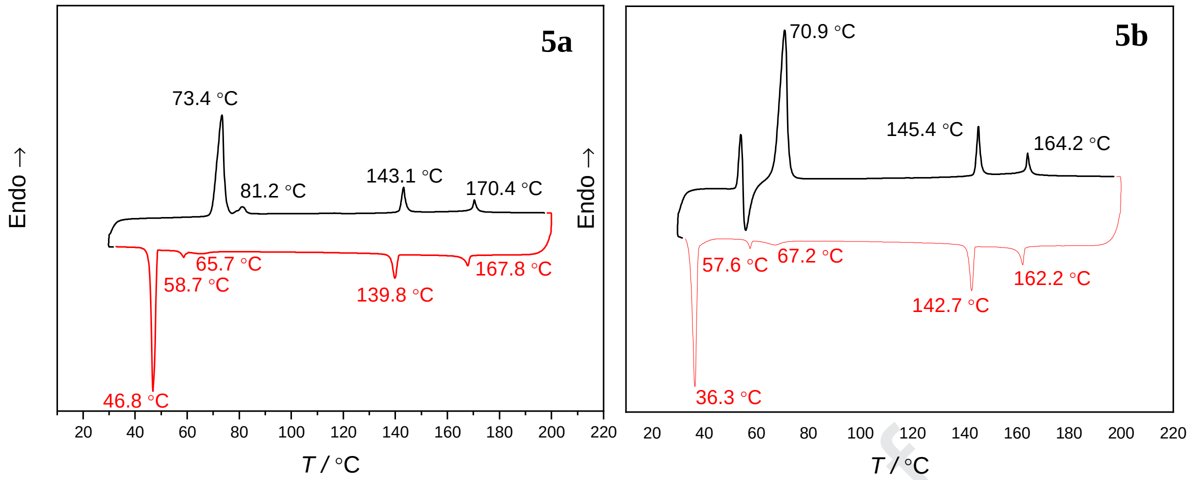


Fig. 5. DSC thermograms of compounds **5a** and **5b** on 2nd heating and cooling (10 °C min^{-1}).

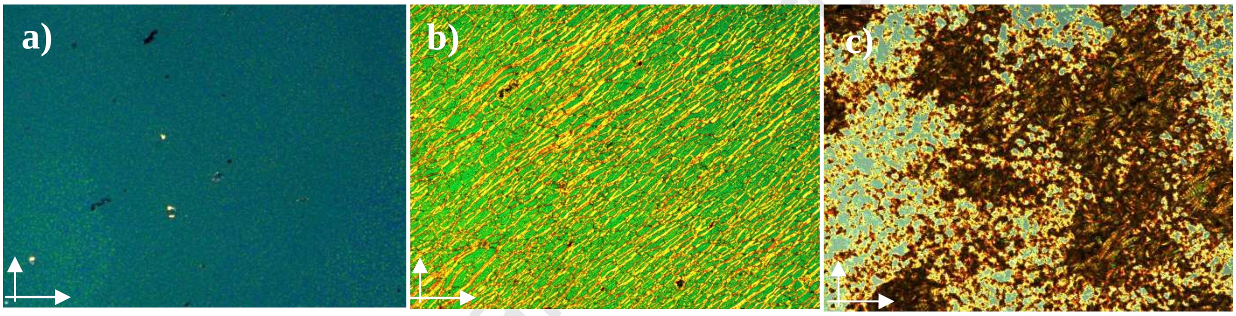


Fig. 6. Optical textures of mesophases of compound **5a** as observed between crossed polarizers (indicated by arrows) in a ordinary glassplates (magnification ×100); a) platelet texture of BP at T= 167.6 °C ; b) oily-streak texture of N* phase at T= 156.0 °C; c) fingerprint texture of SmC* phase at T= 130.0 °C.

3.2. Electro-optical Investigation of Compound 4a

For a representative case, the salicylaldimine based chiral compound **4a** was investigated by triangular wave field experiments. Electro-optic investigations were carried out in 10 µm indium tin oxide (ITO) coated cell without an additional polyimide (PI) alignment layer. The isotropic sample was filled into cell through capillary action. No current response could be observed for the N* phase of **4a** with regardless of the temperature under an applied voltage of up to 38 Vpp µm^{-1}. On further cooling, a very small single polarization current peak in each half period of an applied triangular wave field can be observed below ~152 °C, indicating a ferroelectric like switching. The result of quantitative analysis, obtained by integrating the area under the peak, reveals a polarization value (P_S) of around 230 nC cm^{-2}.

The measured polarization value is in the typical range as known for structurally similar calamitic compounds.[41,42,43] The comparison of polarization value (P_S) shows that the polarization value of salicylaldimine based compound **4a** (P_S= 230 nC cm^{-2}) is slightly higher than that of the imine analog **5c** (P_S= 130 nC cm^{-2}).[40] Similar results were reported for the range of SmC* mesophase of three-ring Schiff bases and salicylaldimines.[43] Triangular wave field experiments show no polar switching in SmX phase of **4a**, even at an applied voltage of 380 V$_{pp}$. As a representative case, switching current responses obtained under a triangular wave field at 122.4 °C and 115.0 °C, respectively are shown in Fig. 7.

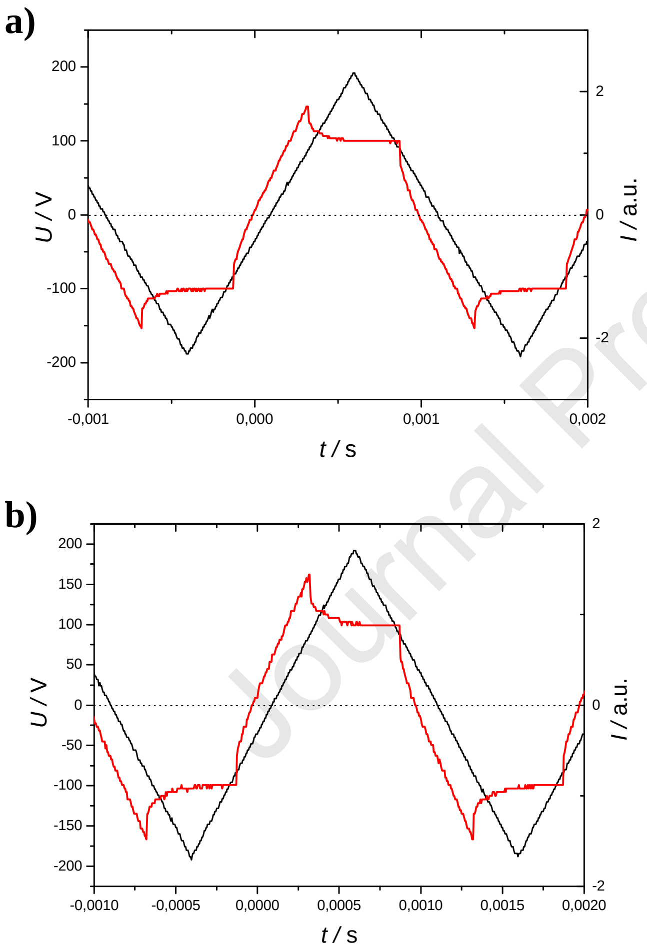


Fig. 7. Switching current response obtained for **4a** in a 10 μm noncoated ITO cell under a triangular wave field; a) at T = 122.4 °C, 380 Vpp, 500 Hz, 5 kΩ and b) at T = 115.0 °C, 380 Vpp, 500 Hz, 5 kΩ.

4. Conclusion

In this study, we have reported the synthesis and characterization of novel mesogens which are composed of three phenyl rings linked with ester and azomethine groups and terminated with (*S*)-3,7-dimethyloctyloxy chiral unit and *n*-octyloxy/decyloxy/dodecyloxy chains. The new azomethine based chiral rod-like molecules show a chiral polymorphism comprising of a chiral mesophases such as blue phase (BP) and chiral nematic (N*) as well as smectics such as chiral tilted smectic (SmC*) and unidentified smectic mesophase (SmX). On cooling, all investigated compounds exhibited blue phases with a very short range of temperatures. Comparison of the mesophase behaviors of salicylaldimine derivative compounds and imine compounds revealed that no change on mesophase type whereas terminal alkoxy chain length gives rise to more pronounced variation on the mesophase intervals of salicylaldimines derivatives. The electro-optical investigations show that the presence of a polar switching in the SmC* mesophase with a relatively small single peak with a low polarization value (P_S= 230 nC cm^{-2}) as reported in structurally similar calamitic compounds. It can be concluded that this type of imine based rod-like compounds terminated with an (*S*)-3,7-dimethyloctyloxy group can generate high chirality which are result in the occurence of a blue phases and switchable smectics which have a significant interest for the development of fast switching displays and new technological applications. LC-Nanoparticle (NP) mixtures prepared by the usage of new materials as a chiral dopant can find a wide applicability in electro-optic, information transfer, memory storage or sensor applications by the improvement in phase transition behavior and stability of blue phases.

Acknowledgement

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Highlights

1. New chiral calamitics based on Schiff base or salicylaldimine-core have been synthesized.

2. The new azomethine based chiral rod-like molecules exhibited a chiral polymorphism.

3. The blue phase and chiral nematic mesophase as well as chiral smectics were observed.

The author(s) declare(s) that there is no conflict of interest for the manuscript titled "**Chiral Polymorphism in New Imine Based Rod-Like Liquid Crystals**".

Yours Sincerely,

Prof. Dr. Belkız Bilgin Eran

Prof. Dr. Hale OCAK

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