Tetrahedron 65 (2009) 152–157

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis and thermal behavior of chiral oligomers derived from cholesterol

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ARTICLE INFO

Article history:
Received 24 January 2008
Received in revised form 22 October 2008
Accepted 27 October 2008
Available online 5 November 2008

Keywords:
Chirality
TGB phase
Coumarin
Quinolone

ABSTRACT

Synthesis and thermal properties of a series of Schiff base oligomers derived from naturally occurring cholesterol are described. In particular, four of them show smectic A and/or chiral nematic phase/s or an unknown mesophase, while the other is non-mesomorphic. Molecular packing in the SmA phase has been determined by the HRXRD experiment.

1. Introduction

Chirality can be induced in a liquid crystal either by the introduction of an asymmetric carbon in a molecule or chiral moiety as a part of the molecule or spatial conformation of the molecule or in a binary component mixture with a chiral dopant leading to several exotic chiral frustrated phases.[1–5] Cholesterol, a naturally occurring abundant chiral compound, is comprised of fused alicyclic system, possesses rigid long planar shape and chiral molecular structure. The rigid long planar shape of cholesteryl moiety, its non-aromatic nature and its strong ability to interact favorably with the aliphatic chains promote a peculiar localized parallel molecular arrangement. The abundant numbers of chiral centers that are present in the cholesteryl molecule manifest chirality in molecular conformation leading to helical supermolecular structure. Three molecular segments viz. a cholesteryl moiety when elongated with a flexible alkylene spacer to join with a promesogenic aromatic unit joined in a linear fashion form an unsymmetrical liquid crystalline dimer. This unsymmetrical liquid crystal dimer consisting of two structurally different promesogenic groups interlinked through a central spacer belong to a new class of liquid crystals that are under intense investigation by several research groups[6–17] in recent years. A variety of liquid crystalline phases was observed in compounds consisting of cholesteryl moiety linked through a spacer to a two or three ring aromatic system viz. Schiff base, azobenzene, stilbene, aromatic ester, tolane, biphenyl, or terphenyl unit or with out a spacer to one ring aromatic (substituted or unsubstituted) system. However, the compounds with a Schiff base functional group exhibit distinct liquid crystalline phases. Since these dimers/twins exhibit novel liquid crystalline phases as well as interesting thermal phase behavior, they serve as useful models for semi-flexible, main chain liquid crystalline polymers. Moreover, they also exhibit distinctly characteristic properties applicable for new optical materials. Coumarin and quinolone containing materials[18,19] have various applications. The anthracene core is well known for its spectroscopic properties and for being highly photo reactive. In fact, anthracene derivatives are widely used as fluorescent probes. Despite remarkable photophysical and photochemical properties of anthracene insignificant attempts have been made to prepare liquid crystals based on this rigid aromatic moiety.[20,21] The importance of organometallic compound in the field of liquid crystals is well established.[22,23] Liquid crystalline compounds containing a metallic atom in their structure combine properties of the metal with those of mesogen, leading to processable materials with interesting magnetic, electronic, optic, and anisotropic properties. On the other hand, either symmetric or unsymmetric dimers cannot only be regarded as model compounds for liquid crystal polymers, but they also have many interesting liquid crystalline properties.[24,25]

The influence of functional group in the aromatic moiety, the nature of substituents in the end alkyl chain moiety and the nature of end alkyl chain length have remarkable effects on the nature of phase variations. The coumarin and quinolone moieties do not possess any end alkyl group but possess strong dipolar end group. On the other hand, anthracene and ferrocene moieties do not possess any end alkyl group and also any dipolar effect. In

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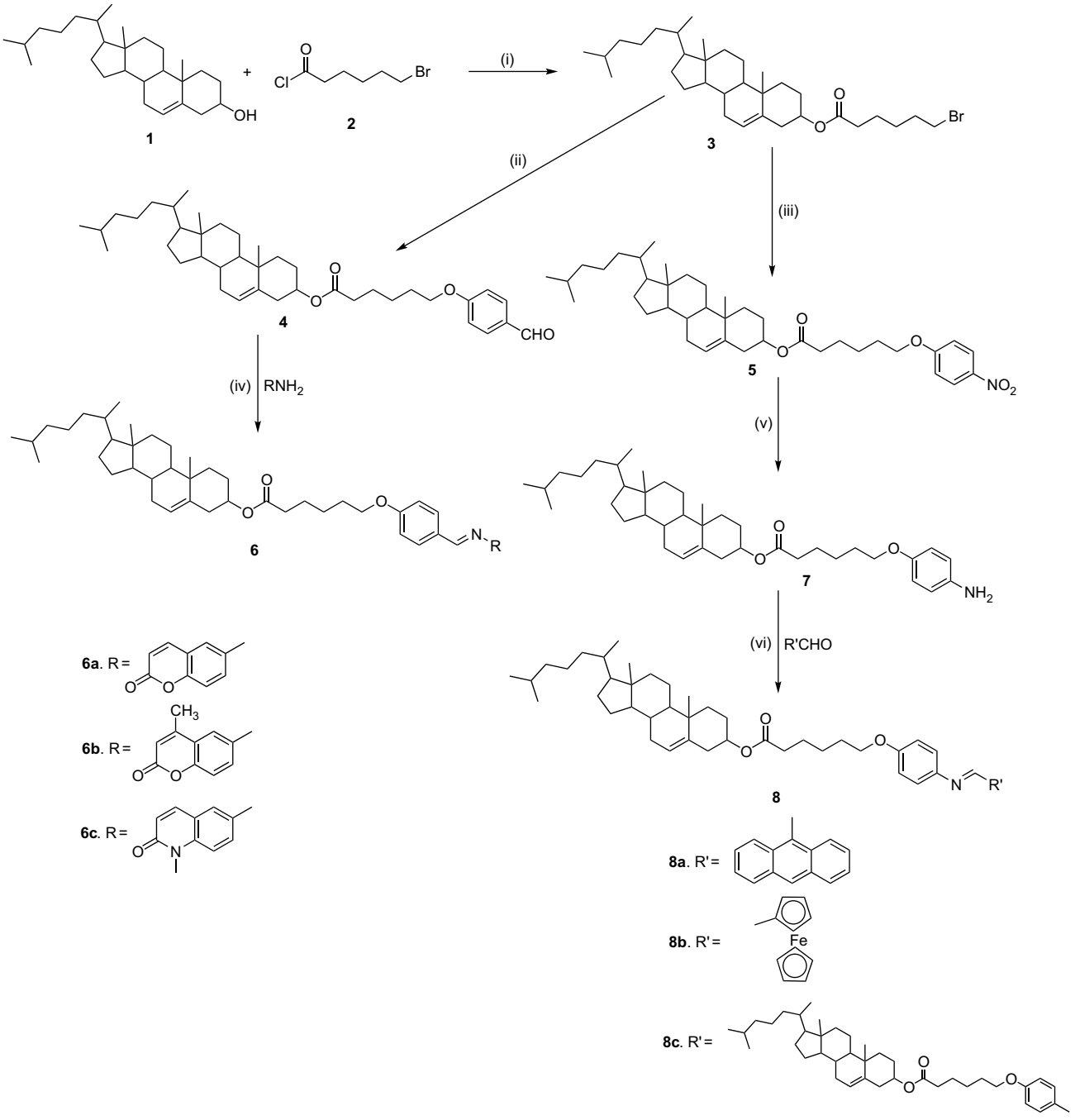
0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.10.085

continuation of our study on liquid crystalline compounds,[26] here we present a series of cholesterol containing compounds and their thermal properties.

The methodology for the synthesis of the materials **6a–c** and **8a–c** is depicted in Scheme 1. Reaction between cholesterol and 6-bromohexanoyl chloride in THF medium at room temperature gave the corresponding ester derivative **3**. The ester derivatives were then subjected to alkylation with *p*-hydroxybenzaldehyde and *p*-nitrophenol, respectively, in refluxing dry acetone in the presence of anhydrous K_2CO_3 to afford corresponding aldehyde[27] **4** and nitro derivative **5**. The nitro derivative on hydrogenation gave the corresponding amine derivative **7**. The aldehyde **4** and amine **7** derivatives on condensation with different amines and aldehydes afford a series of compounds **6a–c** and **8a–c**. All the compounds were characterized from their ^{1}H NMR spectroscopy. A one-proton singlet at about δ=8.40 ppm showed the formation of the Schiff base. In the IR spectroscopy the peak at 1626 cm^{-1} also supported the Schiff base formation.

2. Results and discussion

The transition temperatures and the associated enthalpy values obtained from the DSC for compounds **6a–c**, **8a**, and **8c** are summarized in Table 1. The DSC thermogram of **6a** shows that all the phase transitions are enantiotropic with the exception of SmA–TGB–N* phase transition. The SmA–TGB–N* phase transition could



Scheme 1. Reagents and reaction conditions : (i) THF, pyridine, rt, 12 h; (ii) *p*-Hydroxybenzaldehyde, acetone, reflux, 12 h; (iii) *p*-Nitrophenol, acetone, reflux, 16 h; (iv) EtOH, glacial AcOH (cat), reflux; (v) Pd/C, H_2, EtOAc (solvent); (vi) EtOH, glacial AcOH, reflux.

Table 1
Phase transition temperatures (°C) associated enthalpies (ΔH, KJ mole^{-1}) of the compounds in the heating cycles are summarized below

Compound	Phase transition	Temperature	Enthalpy
6a	Cr–SmA	157.5	27.0
	SmA–TGB	207.1	—
	TGB–N*	208.2	0.7
	N*–I	218.4	3.7
6b	Cr–N*	185.1	0.9
	N*–I	193.5	40.8
6c	Cr–SmA	153.3	19.4
	SmA–TGB	198.0	—
	TGB–N*	198.7	0.8
	N*–I	211.1	3.3
8a	Cr–Lc–I	113.2–121.6	25.2
8c	Cr–N*	163.2	35.4
	N*–unknown mesophase	190.0	0.1
	Unknown mesophase–I	250.5	9.5

Compound **8a** shows a broad peak from the temperature range 113.21–121.06 °C with maxima at 119.5 °C. From POM study liquid crystalline property of this compound was confirmed.
Lc=unknown mesophase, Cr=crystalline phase, SmA=smectic phase, TGB=twisted grainy boundary phase.

not be detected by DSC even at 1 °C/min rate of heating or cooling and with a sample of 10 mg (the capacity of cup used in DSC pyris1 system). However, the SmA–TGB–N* phase transition is observed on cooling as well as on heating at a very slow rate by thermal microscopy. On cooling the isotropic phase of compound **6a**, elliptical shaped droplets found to appear as shown in Figure 1a, which coalesce (Fig. 1b) to form fan like texture (Fig. 1c) characteristic of cholesteric (N*) phase in accordance with the reported texture for cholesteric phases.[28] On further cooling the sample exhibited homeotropic texture of SmA phase. However, if the transition is maintained over a length of time, a characteristic texture of arcs across fans appeared (Fig. 1d) and either on slow cooling or slow repeated heating and cooling cycles a filament texture (Fig. 1e) appeared very similar to the so called fingerprint texture characteristic of twisted grain boundary phase.[29] On further cooling, the twisted grain boundary phase transforms with a spontaneous development of a homeotropic texture characteristic of uniaxial SmA phase director oriented along the direction of light propagation thus appearing totally dark.

The pitch variation in the cholesteric phase is in general less than 0.2–0.4 μm while it varies rapidly (0.2–1.0 μm, 0.4–1.5 μm) in the twisted grain boundary phase was measured by polarizing microscope with the rotation of analyzer.[30–33] When such phases are confined to sufficiently thin cells with a planar arrangement the helical superstructure may be unwound. Compound **6a** when placed in a thin cell with a cell gap of $d=5\pm0.2$ μm with homogeneous planar boundary conditions, the textures for the cholesteric, TGB, and smectic phases (Fig. 1f) were observed. In this arrangement, the long molecular axes are oriented in the plane of the substrate and the helix axis is perpendicular to the boundary glass plates. X-ray diffraction diagram of compounds **6a** and **6c** exhibit a sharp peak at small angle region with 2θ value 3.18 ($d=27.76$ Å)

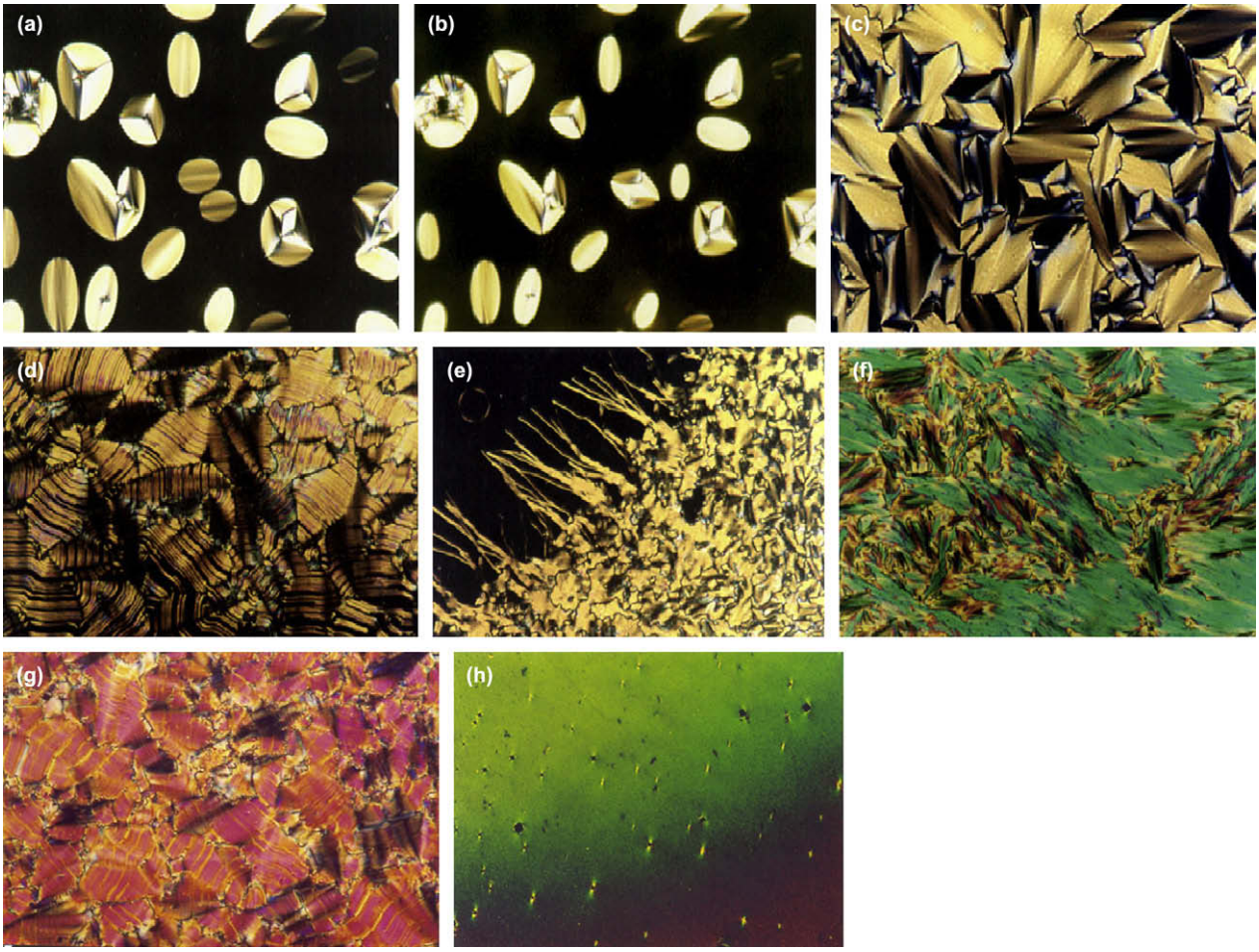


Figure 1. (a) Compound **6a** at 217.3 °C, (b) Compound **6a** at 217.2 °C, (c) Compound **6a** at 216.0 °C, (d) Compound **6a** at 206.8 °C, (e) Compound **6a** at 206.8 °C, (f) Compound **6a** at 181.5 °C, (g) Compound **8c** at 195 °C, (h) Compound **8a** at 94 °C.

and 3.24 (d=27.18 Å), respectively, and a broad diffuse peak in the wide angle region centered at d-spacing of 5.37 Å for both the compounds.[34] The sharp Bragg scattering at small angle region is due to the one-dimensional layering in the condensed SmA phase and diffuse peak in the wide angle region is due to the liquid like co-relation of the molecules. The interlayer distances in SmA for both the compounds were sufficiently larger than the calculated molecular length (L ~22.1 Å for **6a** and **6c**) from molecular modeling. Therefore, we expect a partially bilayered SmA phase for both **6a** and **6c**. A schematic diagram of packing of molecules in smectic phase deduced from X-ray diffraction study is presented in Figure 2.

Compound **6b** on cooling from the isotropic phase, fan like texture characteristic of N* phase appears gradually and fills up the whole field of view. The sample solidifies on further cooling. However, compound **8b** does not show any liquid crystalline property. Monosubstituted ferrocenes are poor candidates for stabilizing liquid crystalline phases. This may be partly attributed to their unfavorable molecular shape (L-shaped geometry) and to the repulsive steric effects of the ferrocene unit reducing the ability of the molecules to be arranged in layers. Compound **8a** when sandwiched between two glass plates and placed in POM, a change of phase occurs at around 115 °C and persists (Fig. 1h) up to room temperature after reappearance of the phase from istropization. On cooling from the isotropic phase, compound **8c** exhibited characteristic texture of N* phase at around 240 °C. On further cooling, phase change occurs at around 194 °C and after that, a texture in which arcs across the fan (Fig. 1g) appears gradually and fills up the whole field of view. The sample solidifies with no change in phase on further cooling. The phase change in both the cases was confirmed from the DSC scan of the sample in heating cycles.

It has been reported earlier that the twisted grain boundary phases are not identical for long and short spacers in such dimeric cholesteryl derivatives.[35] Grandjean planar and columnar textures are observed in cholesteryl dimesogens for short and long spacer molecules, respectively. It was pointed out that the long alkylene spacer has promoted decoupling between the cholesteric and aromatic moieties thereby promoting the columnar phases.

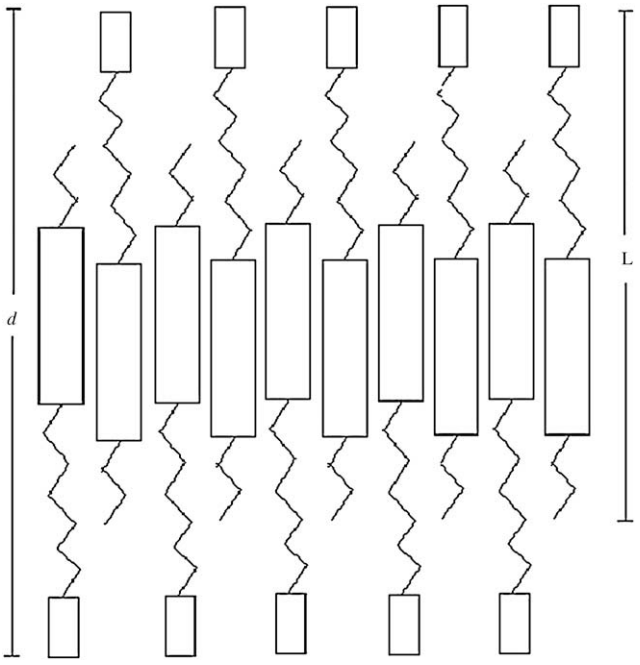


Figure 2. Model of molecules in smectic phase (A_d) deduced from X-ray diffraction study.

The twisted grain boundary phase consists of a helical stack of blocks of smectic liquid crystals separated by grain boundaries made up of an array of screw dislocations. In the Schiff base homologous series, it is reported that the smectic packing depends on the terminal chain length. Further the unusual mesogenic moiety constituted by cholesteryl part, the non-aromatic nature connected with its planar shape and its strong activity to interact favorably with the aliphatic chains probably allow a peculiar arrangement, which supports the coexistence of varying periodicities of incommensurate fluid smectic phases.

In unsubstituted cholesteryl-4-*n*-alkoxybenzoates the N*AC* phase variant is reported.[36] Further, the compounds, cholesteryl-2-fluoro-4-*n*-alkoxybenzoates possessing strong lateral dipole moment exhibited enantiotropic BP, N*, TGB, and smectic C* phases.[37] Thus, the occurrence of TGB phase has been attributed to the lateral dipole moment, since this substituent increases the transverse polarity of the system and stabilizes tilted molecular arrangement in smectic phase. It should be pointed out that the occurrence of TGB phase also depends on the length of alkoxy chain.[27,38–42] However, in cholesteryl-4-polyfluoroalkoxy-3-nitrobenzoate, possessing strong lateral dipole moment and rigid perfluoroalkyl end chain, only N* and/or SmA phase(s) are reported.[32] The unsubstituted analogues cholesteryl-4-polyfluoroalkoxybenzoate exhibited SmA and SmE phases,[43] where as in perfluoro homologues of **6a** exhibiting SmA and SmC* phases, large spontaneous polarization is reported.[44,45]

Thus either in a single phenyl ring system having cholesterol as chiral moiety or two phenyl ring system subtle changes in the substitution pattern, the length of spacer, nature of end alkyl groups have strong influence on the occurrence of TGB phase as well as phase variant. Tamaoki et al. studied liquid crystalline properties of dimers consisting of unsubstituted azobenzene core linked to cholesterol segments with varying alkyl chain length.[46] They observed that except for alkyl chain length n=7 all the other compounds (with alkyl chain length n=6, 8–14) showed the fingerprint and single color reflection reflecting Grandjean texture, confirmative of CLC phase. Compound with alkyl chain length n=7 exhibited intercalated smectic phase. They also designed and synthesized compounds having azobenzene and cholesterol moieties connected through an aliphatic chain containing 22 carbons[47] and observed a cholesteric phase showing a Grandjean planar texture with colors in addition to SmA phase for some of the compounds. Therefore, the observation of phase sequence like SmA–TGB–N* in compounds **6a** and **6c** is quite interesting in our case. On the other hand, Tamaoki et al.[48] synthesized dicholesteryl esters of diacetylenedicarboxylic acid with different lengths of methylene linkages. Most of the compounds showed cholestric phase. In our case, we synthesized compound **8c** in which two cholesteric segments are linked through a Schiff base linkage and it shows cholesteric phase in addition to an unknown phase.

In conclusion, we have synthesized some cholesterol-based oligomers with a Schiff base linkage. All the compounds except **8b** showed liquid crystalline properties. Compounds **6a** and **6c** showed SmA–TGB–N* phase transitions. HRXRD suggested a partial bilayered arrangement in SmA phase. Compound **6b** showed a cholesteric phase. Compound **8c** also showed a chlosteric phase with an unknown phase transition.

3. Experimental

3.1. General

All the chemicals were procured from either Sigma Aldrich Chemicals Pvt. Ltd. or Spectrochem, India. Silica gel [(60–120 mesh) was used for chromatographic separation. Silica gel G [E-Merck (India)] was used for TLC. Petroleum ether refers to the fraction

boiling between 60 °C and 80 °C. IR spectra were recorded on a Perkin–Elmer L 120–000A spectrometer (ν_{max} in cm^{-1}) on KBr disks. ^1H NMR (400 MHz) spectra were recorded on a Bruker DPX-500 spectrometer in $CDCl_3$ (chemical shift in δ) with TMS as internal standard. CHN was recorded on 2400 series II CHN analyzer Perkin Elmer from IACS Kolkata. The liquid crystalline properties were established by thermal microscopy (Nikon polarizing microscope LV100POL) attached with Instec hot and cold stage HCS302, with STC200 temperature controller configured for HCS302 and the phase transitions were confirmed by differential scanning calorimetry (Perkin–Elmer DSC Pyris1 system). X-ray diffraction was carried out on a Philips powder diffractometer (PAN analytical model no. pw 3015) operating on X'pert pro software, equipped with a temperature controller permitting low as well as high temperature operation as needed (with Cu Kα radiation of λ=1.5418).

3.2. General procedure for the preparation of nitro 5 and amine 7 derivatives

Ester derivative **3** was prepared by the esterification reaction of cholesterol with 6-bromohexanoyl chloride in THF at room temperature in the presence of pyridine as a base. The ester derivative **3** (500 mg, 0.886 mmol) was then subjected to reaction with *p*-nitrophenol (120 mg, 0.886 mmol) in refluxing acetone (50 mL) in the presence of anhydrous K_2CO_3 (5 equiv) for about 12 h. The reaction mixture was cooled, filtered, and the solvent was removed. The residual mass was extracted with CH_2Cl_2 (3×20 mL). The CH_2Cl_2 extract was washed with water (3×10 mL) and dried (Na_2SO_4). The solvent was removed and the residual mass was purified by column chromatography (5% EtOAc/pet. ether) to afford the desired nitro derivative **5**. Nitro derivative **5** (300 mg, 0.482 mmol) upon hydrogenation in the presence of 10% Pd/C (10 mg) in ethyl acetate at room temperature for about 4 h afforded the desired amine derivative **7** after purification by column chromatography (15% EtOAc/pet. ether). The amine derivative was characterized by IR and NMR spectroscopy. A one-proton doublet at 5.36 ppm region showed that the cholesteric double bond remain intact during the hydrogenation of the nitro derivative to amine. This was further corroborated by two extra peaks in the low field region in the ^{13}C NMR spectrum of all the final Schiff base derivatives derived from the amine derivative **7**.

3.2.1. Compound **5**

Yield 95%; white solid; mp 136–138 °C; R_f=0.75 (5% EtOAc/pet. ether); UV($CHCl_3$) λ_{max}: 307, 222, 204 nm; IR (KBr) ν_{max}: 1365, 1732, 2872, 2950 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 0.84–2.33 (51H, m, aliphatic and cholesteric protons are overlapped), 4.02 (2H, t, *J* 6.3 Hz, OCH_2), 4.59–4.61 (1H, m, OCH), 5.36 (1H, d, *J* 3.7 Hz, =CH), 6.90 (2H, d, *J* 9.1 Hz, ArH), 8.16 (2H, d, *J* 9.1 Hz, ArH), ^{13}C NMR ($CDCl_3$, 75 MHz): 20.9, 22.5, 22.7, 23.8, 24.2, 24.6, 25.4, 27.7, 27.9, 28.1, 28.6, 31.8, 31.8, 34.4, 35.7, 36.1, 36.5, 36.9, 38.1, 39.4, 39.6, 42.2, 49.9, 56.1, 56.6, 68.4, 73.8, 114.3, 122.6, 125.8, 139.5, 141.3, 164.0, 172.8. Anal. Calcd for $C_{39}H_{59}NO_5$: C, 75.32; H, 9.56; N, 2.25%. Found: C, 75.22; H, 9.84; N, 2.26%.

3.2.2. Compound **7**

Yield 90%; white solid; mp 92–94 °C; R_f=0.70 (15% EtOAc/pet. ether); UV ($CHCl_3$) λ_{max}: 283, 233, 207 nm; IR (KBr) ν_{max}: 3425, 2870, 2950, 1731 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 0.66–2.81 (51H, m, aliphatic and cholesteric protons are overlapped), 3.87 (2H, t, *J* 6.1 Hz, OCH_2), 4.57–4.60 (1H, m, OCH), 5.36 (1H, d, *J* 3.7 Hz, =CH), 6.67–6.69 (4H, m, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz): 22.5, 22.7, 23.8, 24.2, 24.7, 25.6, 27.9, 28.1, 29.0, 31.8, 31.8, 34.5, 35.7, 36.1, 36.5, 36.9, 38.1, 39.4, 39.7, 42.2, 50.0, 56.1, 56.6, 68.31, 73.7, 115.6, 116.3, 122.5, 139.6, 139.8, 152.1, 173.0. Anal. Calcd for $C_{39}H_{61}NO_3$: C, 79.14; H, 10.39; N, 2.37%. Found: C, 79.19; H, 10.15; N, 2.11%.

3.2.3. Compound ***6a***

A mixture of aldehyde **4** (100 mg, 0.165 mmol) and 6-aminocoumarin (26 mg, 0.165 mmol) was refluxed in absolute ethanol (10 mL) in the presence of a catalytic amount of glacial acetic acid for 4 h. Pale yellow solid was precipitated out from the reaction mixture. It was collected, washed with ethanol, and dried in vacuum.

Yield 95%; mp 157–159 °C; UV ($CHCl_3$) λ_{max}: 322, 284, 230 nm; IR (KBr) ν_{max}: 1255, 1626, 1731, 2870, 2950 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 0.65–2.31 (51H, m, aliphatic and cholesteric protons are overlapped), 4.01 (2H, t, *J* 6.3 Hz, OCH_2), 4.57–4.62 (1H, m, OCH), 5.35 (1H, d, *J* 3.6 Hz, =CH), 6.43 (1H, d, *J* 9.5 Hz, C_3H of coumarin), 6.95 (2H, d, *J* 8.6 Hz, ArH), 7.27 (1H, d, *J* 2.0 Hz, ArH), 7.33 (1H, d, *J* 8.7 Hz, ArH), 7.37 (1H, dd, *J* 8.7, 2.1 Hz, ArH), 7.70 (1H, d, *J* 9.5 Hz, C_4H of coumarin), 7.81 (2H, d, *J* 8.6 Hz, ArH), 8.39 (1H, s, N=CH). ^{13}C NMR ($CDCl_3$, 125 MHz): 6.8, 13.7, 14.3, 16.0, 17.5, 17.8, 18.8, 19.2, 19.7, 20.5, 22.8, 23.0, 23.2, 23.8, 24.7, 26.8, 26.9, 29.5, 30.7, 31.1, 31.6, 32.0, 33.1, 34.5, 34.7, 37.3, 45.0, 51.1, 51.6, 62.8, 68.8, 109.8, 112.0, 112.5, 114.1, 114.2, 117.6, 119.9, 123.69, 125.6, 134.6, 138.3, 143.8, 147.0, 155.4, 155.7, 157.1, 167.9. $[\alpha]_D$ −19.0 (*c* 0.16, $CHCl_3$). Anal. Calcd for $C_{49}H_{65}NO_5$: C, 78.68; H, 8.76; N, 1.87%. Found: C, 78.18; H, 9.26; N, 1.48%.

3.2.4. Compound ***6b***

A mixture of aldehyde **4** (100 mg, 0.165 mmol) and 4-methyl-7-aminocoumarin (28 mg, 0.165 mmol) was refluxed in absolute ethanol (10 mL) in the presence of a catalytic amount of glacial acetic acid for 12 h. White solid was precipitated out from the reaction mixture. It was collected, washed with ethanol, and dried in vacuum.

Yield 90%; mp 185–187 °C; UV ($CHCl_3$) λ_{max}: 342, 286, 242 nm; IR (KBr) ν_{max}: 1255, 1625, 1730, 2870, 2950 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 0.65–2.31 (51H, m, aliphatic and cholesteric protons are overlapped), 2.43 (3H, s, CH_3), 4.01 (2H, t, *J* 6.4 Hz, OCH_2), 4.57–4.59 (1H, m, OCH), 5.35 (1H, d, *J* 4.0 Hz, =CH), 6.22 (1H, s, C_3H of coumarin), 6.95 (2H, d, *J* 8.6 Hz, ArH), 7.08 (1H, d, *J* 1.9 Hz, ArH), 7.10 (1H, dd, *J* 8.3, 1.9 Hz, ArH), 7.57 (1H, d, *J* 8.3 Hz, ArH), 7.83 (2H, d, *J* 8.6 Hz, ArH), 8.36 (1H, s, N=CH). ^{13}C NMR ($CDCl_3$, 125 MHz): 13.6, 14.2, 15.9, 17.5, 17.8, 18.7, 18.9, 19.7, 20.5, 22.8, 22.8, 23.2, 23.8, 24.6, 26.7, 27.0, 29.6, 30.7, 31.1, 32.0, 33.1, 34.4, 34.6, 37.2, 44.9, 51.1, 51.5, 63.0, 68.7, 109.1, 111.2, 113.2, 115.8, 116.2, 119.2, 122.1, 124.9, 126.2, 137.9, 147.8, 149.4, 149.5, 155.5, 156.4, 157.6, 169.1. $[\alpha]_D$ −17.0 (*c* 0.16, $CHCl_3$). Anal. Calcd for $C_{50}H_{67}NO_5$: C, 78.80; H, 8.86; N, 1.84%. Found: C, 78.45; H, 9.22; N, 2.02%.

3.2.5. Compound ***6c***

A mixture of aldehyde **4** (100 mg, 0.165 mmol) and 1-methyl-6-aminoquinolone (28 mg, 0.165 mmol) was refluxed in absolute ethanol (10 mL) in the presence of a catalytic amount of glacial acetic acid for 8 h. Pale yellow solid was precipitated out from the reaction mixture. It was collected, washed with ethanol, and dried in vacuum.

Yield 94%; mp 153–155 °C; UV ($CHCl_3$) λ_{max}: 331, 284, 232 nm; IR (KBr) ν_{max}: 1255, 1626, 1651, 1734, 2866, 2946 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 0.67–2.32 (51H, m, aliphatic and cholesteric protons are overlapped), 3.74 (3H, s, NCH_3), 4.04 (2H, t, *J* 6.4 Hz, OCH_2), 4.59–4.63 (1H, m, OCH), 5.36 (1H, d, *J* 4.1 Hz, =CH), 6.72 (1H, d, *J* 9.4 Hz, C_3H of quinolone), 6.96 (2H, d, *J* 8.6 Hz, ArH), 7.37–7.39 (2H, m, ArH), 7.48 (1H, dd, *J* 8.9, 2.2 Hz, ArH), 7.67 (1H, d, *J* 9.4 Hz, C_4H of quinolone), 7.84 (2H, d, *J* 8.6 Hz, ArH), 8.45 (1H, s, N=CH). ^{13}C NMR ($CDCl_3$, 125 MHz): 12.2, 19.1, 19.1, 21.4, 22.9, 23.2, 24.2, 25.1, 25.9, 28.2, 28.4, 28.6, 29.2, 29.9, 32.2, 32.3, 34.9, 36.1, 36.5, 36.9, 37.3, 38.5, 39.9, 40.1, 42.7, 50.4, 56.5, 57.0, 68.2, 74.2,

115.1, 115.3, 120.2, 121.6, 122.6, 123.0, 124.7, 129.3, 130.9, 138.5, 139.2, 140.0, 147.0, 160.1, 162.3, 173.3. $[\alpha]_D$ −18.6 (*c* 0.16, $CHCl_3$). Anal. Calcd for $C_{50}H_{68}N_2O_4$: C, 78.91; H, 9.01; N, 3.68%. Found: C, 78.58; H, 9.97; N, 3.52%.

3.2.6. Compound **8a**

A mixture of amine **7** (100 mg, 0.168 mmol) and 9-anthracene aldehyde (34 mg, 0.168 mmol) was refluxed in absolute ethanol (10 mL) in the presence of a catalytic amount of glacial acetic acid for 9 h. Yellow solid was precipitated out from the reaction mixture. It was collected, washed with ethanol, and dried in vacuum.

Yield 85%; mp 113–115 °C; UV ($CHCl_3$) λ_{max}: 254, 204 nm; IR (KBr) ν_{max}: 1255, 1622, 1731, 2866, 2942 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 0.66–2.36 (51H, m, aliphatic and cholesteric protons are overlapped), 4.02 (2H, t, *J* 6.4 Hz, OCH_2), 4.57–4.60 (1H, m, OCH), 5.38 (1H, d, *J* 4.0 Hz, =CH), 7.0 (2H, d, *J* 8.7 Hz, ArH), 7.42 (2H, d, *J* 8.7 Hz, ArH), 7.49–7.52 (2H, m, ArH), 7.54–7.57 (2H, m, ArH), 8.03 (2H, d, *J* 8.3 Hz, ArH), 8.54 (1H, s, ArH), 8.81 (2H, d, *J* 8.8 Hz, ArH), 9.69 (1H, s, CH=N). ^{13}C NMR ($CDCl_3$, 125 MHz): 12.2, 19.1, 19.7, 21.4, 22.9, 23.2, 24.2, 24.6, 25.2, 26.0, 28.2, 28.4, 28.6, 29.3, 32.2, 32.3, 35.0, 36.1, 36.5, 37.0, 37.4, 38.5, 39.9, 40.1, 42.7, 50.4, 56.5, 57.0, 68.4, 74.2, 115.5, 122.7, 123.0, 125.2, 125.7, 127.4, 128.1, 129.3, 130.6, 130.9, 131.7, 140.0, 145.8, 158.0, 158.4, 173.4. $[\alpha]_D$ −20.0 (*c* 0.16, $CHCl_3$). Anal. Calcd for $C_{54}H_{69}NO_3$: C, 83.14; H, 8.91; N, 1.80%. Found: C, 82.92; H, 9.55; N, 1.57%.

3.2.7. Compound **8b**

A mixture of amine **7** (100 mg, 0.168 mmol) and ferrocene aldehyde (35 mg, 0.168 mmol) was refluxed in absolute ethanol (10 mL) in the presence of a catalytic amount of glacial acetic acid for 8 h. Ash color solid was precipitated out from the reaction mixture. It was collected, washed with ethanol, and dried in vacuum.

Yield 85%; mp 173–175 °C; UV ($CHCl_3$) λ_{max}: 244, 228, 217 nm; IR ν_{max}: 1255, 1622, 1732, 2866, 2935 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 0.67–2.33 (51H, m, aliphatic and cholesteric protons are overlapped), 3.95 (2H, t, *J* 6.03 Hz, OCH_2), 4.23 (5H, s, ferrocenyl H), 4.45 (2H, s, ferrocenyl H), 4.59–4.61 (1H, m, OCH), 4.77 (2H, s, ferrocenyl H), 5.37 (1H, d, *J* 4.5 Hz, =CH), 6.87 (2H, d, *J* 8.6 Hz, ArH), 7.1 (2H, d, *J* 8.6 Hz, ArH), 8.32 (1H, s, CH=N). ^{13}C NMR ($CDCl_3$, 125 MHz): 12.2, 19.1, 19.7, 21.4, 22.9, 23.2, 24.2, 24.6, 25.2, 26.0, 28.2, 28.4, 28.6, 29.3, 29.4, 30.0, 31.3, 32.2, 32.3, 34.9, 36.1, 36.5, 36.9, 37.3, 38.5, 39.9, 40.1, 42.7, 50.4, 56.5, 57.0, 68.3, 68.7, 69.2, 70.0, 71.4, 73.5, 74.1, 74.2, 115.3, 116.0, 116.8, 122.0, 123.0, 140.0, 146.2, 157.5, 159.9, 173.4, 193.8, 207.3. $[\alpha]_D$ −16.0 (*c* 0.16, $CHCl_3$). Anal. Calcd for $C_{50}H_{69}FeNO_3$: C, 76.38; H, 8.92; N, 1.75%. Found: C, 76.50; H, 9.10; N, 1.90%.

3.2.8. Compound **8c**

A mixture of amine **7** (100 mg, 0.168 mmol) and aldehyde **5** (100 mg, 0.168 mmol) was refluxed in absolute ethanol (10 mL) in the presence of a catalytic amount of glacial acetic acid for 1 h. Pale yellow solid was precipitated out from the reaction mixture. It was collected, washed with ethanol, and dried in vacuum.

Yield 98%; mp 163–165 °C; UV ($CHCl_3$) λ_{max}: 335, 283, 240 nm; IR (KBr) ν_{max}: 1255, 1621, 1731, 2866, 2935 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 0.67–2.33 (102H, m, aliphatic and cholesteric protons are overlapped), 3.94 (2H, t, *J* 6.3 Hz, OCH_2), 3.99 (2H, t, *J* 6.3 Hz, OCH_2), 4.59–4.77 (2H, m, OCH), 5.35 (2H, d, *J* 3.6 Hz, =CH), 6.88 (2H, d, *J* 8.7 Hz, ArH), 6.93 (2H, d, *J* 8.5 Hz, ArH), 7.23 (2H, d, *J* 8.5 Hz, ArH), 7.85 (2H, d, *J* 8.7 Hz, ArH), 8.37 (1H, s, CH=N). ^{13}C NMR ($CDCl_3$, 125 MHz): 12.2, 18.8, 19.7, 21.4, 22.9, 23.2, 24.2, 24.6, 25.1, 25.2, 25.9, 26.0, 28.2, 28.4, 28.6, 29.2, 29.3, 32.2, 32.2, 34.9, 34.9, 36.1, 36.5, 36.9, 37.3, 38.5, 39.9, 40.1, 42.7, 50.4, 56.5, 57.0, 68.6, 68.1, 68.2, 74.2, 74.2, 115.0, 115.3, 122.4, 123.0, 123.0, 129.7, 130.6, 140.0, 145.4, 157.8, 158.2, 161.8, 173.3, 173.4. $[\alpha]_D$ −24.0 (*c* 0.16, $CHCl_3$). Anal. Calcd for $C_{79}H_{119}NO_6$: C, 80.49; H, 10.18; N, 1.19%. Found: C, 80.05; H, 10.12; N, 1.35%.

Acknowledgements

We thank the DST (New Delhi) for financial assistance. Two of us (S.C. and N.P.) are thankful to the CSIR (New Delhi) for their fellowships. We also thank the Material Science Department of the IACS (Kolkata) for HRXRD facilities.

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